

KAUNO TECHNOLOGIJOS UNIVERSITETAS

AISTĖ JEGOROVĖ

FLUORENILO IR KARBAZOLILO
CHROMOFORŲ TURINČIŲ ORGANINIŲ
PUSLAIDININKIŲ, SKIRTŲ
PEROVSKITINIAMS IR STIBIO SULFIDO
SAULĖS ELEMENTAMS, SINTEZĖ IR
SAVYBĖS

Daktaro disertacija
Gamtos mokslai, chemija (N 003)

2025, Kaunas

Disertacija rengta 2020–2025 metais Kauno technologijos universiteto Cheminės technologijos fakultete, Organinės chemijos katedroje. Mokslinius tyrimus rėmė Lietuvos mokslo taryba.

Mokslinis vadovas:

prof. dr. Vytautas GETAUTIS (Kauno technologijos universitetas, gamtos mokslai, chemija, N 003).

Mokslinis konsultantas:

vyresn. m. d. dr. Marytė DAŠKEVIČIENĖ (Kauno technologijos universitetas, gamtos mokslai, chemija, N 003).

Redagavo: anglų kalbos redaktorius dr. Armandas Rumšas (leidykla „Technologija“), lietuvių kalbos redaktorė Rita Malikėnienė (leidykla „Technologija“).

Chemijos mokslo krypties disertacijos gynimo taryba:

prof. dr. Eglė ARBAČIAUSKIENĖ (Kauno technologijos universitetas, gamtos mokslai, chemija, N 003) – **pirmininkė**;

prof. dr. Saulius GRIGALEVIČIUS (Kauno technologijos universitetas, gamtos mokslai, chemija, N 003);

prof. dr. Vytas MARTYNAITIS (Kauno technologijos universitetas, gamtos mokslai, chemija, N 003);

prof. dr. Edvinas ORENTAS (Vilniaus universitetas, gamtos mokslai, chemija, N 003);

doc. dr. Jolanta ROUSSEAU (Artua universitetas, Prancūzija, technologijos mokslai, cheminė inžinerija, T 005).

Disertacija bus ginama viešame Chemijos mokslo krypties disertacijos gynimo tarybos posėdyje 2025 m. balandžio 25 d. 10.00 val. Kauno technologijos universiteto Rektorato salėje.

Adresas: K. Donelaičio g. 73-402, LT-44249 Kaunas, Lietuva.

Tel. +370 608 28 527; el. paštas doktorantura@ktu.lt

Disertacija išsiųsta 2025 m. kovo 25 d.

Su disertacija galima susipažinti interneto svetainėje <http://ktu.edu> ir Kauno technologijos universiteto bibliotekoje (Gedimino g. 50, LT-44239 Kaunas, Lietuva).

© A. Jegorovė, 2025

KAUNAS UNIVERSITY OF TECHNOLOGY

AISTĖ JEGOROVĖ

SYNTHESIS AND PROPERTIES OF
FLUORENYL- AND
CARBAZOLYLCHROMOPHORES-
CONTAINING ORGANIC SEMICONDUCTORS
FOR PEROVSKITE AND ANTIMONY SULFIDE
SOLAR CELLS

Doctoral dissertation
Natural Sciences, Chemistry (N 003)

2025, Kaunas

The dissertation has been prepared at the Department of Organic Chemistry of the Faculty of Chemical Technology of Kaunas University of Technology in 2020–2025. The research has been sponsored by the Research Council of Lithuania.

Research supervisor:

Prof. Dr. Vytautas GETAUTIS (Kaunas University of Technology, Natural Sciences, Chemistry, N 003).

Research consultant:

Senior Researcher Dr. Marytė DAŠKEVIČIENĖ (Kaunas University of Technology, Natural Sciences, Chemistry, N 003).

Edited by: English language editor Dr. Armandas Rumšas (Publishing House *Technologija*), Lithuanian language editor Rita Malikėnienė (Publishing House *Technologija*).

Dissertation Defence Board of Chemistry Science Field:

Prof. Dr. Eglė ARBAČIAUSKIENĖ (Kaunas University of Technology, Natural Sciences, Chemistry, N 003) – **chairperson**;

Prof. Dr. Saulius GRIGALEVIČIUS (Kaunas University of Technology, Natural Sciences, Chemistry, N 003);

Prof. Dr. Vytas MARTYNAITIS (Kaunas University of Technology, Natural Sciences, Chemistry, N 003);

Prof. Dr. Edvinas ORENTAS (Vilnius University, Natural Sciences, Chemistry, N 003);

Assoc. Prof. Dr. Jolanta ROUSSEAU (Artois University, France, Technological Sciences, Chemical Engineering, T 005).

The dissertation defence will be held on 25 April 2025, at 10.00 a.m. in a public meeting of the Dissertation Defence Board of Chemistry Science Field at the Rectorate Hall of Kaunas University of Technology.

Address: K. Donelaičio 73-402, LT-44249 Kaunas, Lithuania.

Phone: +370 608 28 527; e-mail doktorantura@ktu.lt

The dissertation was sent out on 25 March 2025.

The dissertation is available on <http://ktu.edu> and at the Library of Kaunas University of Technology (Gedimino 50, LT-44239 Kaunas, Lithuania).

TURINYS

LENTELIŲ SĄRAŠAS.....	6
PAVEIKSLŲ SĄRAŠAS.....	7
SCHEMŲ SĄRAŠAS.....	10
SANTRUMPŲ SĄRAŠAS.....	11
1. ĮVADAS.....	13
Autorių indėlis.....	16
Su daktaro disertacijos tema susijusių publikacijų sąrašas.....	17
2. LITERATŪROS APŽVALGA.....	19
2.1. Saulės elementų rūšys.....	19
2.1.1. Pirmos kartos saulės elementai.....	19
2.1.2. Antros kartos saulės elementai.....	20
2.1.3. Trečios kartos saulės elementai.....	22
2.2. Saulės elementų veikimo principas.....	29
2.3. Saulės elementų charakteristikos.....	30
2.4. Organinės skylių transportinės medžiagos naudojamos perovskitiniuose saulės elementuose.....	30
2.5. Skyles transportuojančios medžiagos stibio chalkogenidų saulės elementams.....	38
2.6. Literatūrinės apžvalgos apibendrinimas.....	41
3. PUBLIKACIJŲ APŽVALGA.....	43
3.1. Skyles transportuojančios medžiagos, molekulės centre turinčios fluorenilchromoforus, efektyviems perovskitiniams saulės elementams.....	43
3.2. Bipoliniai krūvius transportuojantys fluoreno dariniai.....	50
3.3. Skyles transportuojantys šakoti fluorenilideno dariniai perovskitiniams saulės elementams.....	55
3.4. Žvaigždės formos karbazolo darinių skylių transportinės medžiagos perovskitiniams saulės elementams.....	61
3.5. Skyles transportuojantys puslaidininkiai, turintys fluoreno bei tiofeno fragmentus, Sb_2S_3 saulės elementams.....	69
3.6. Tiofeno fragmentais sujungtų fluorenų dimerų skyles transportuojančios medžiagos Sb_2S_3 saulės elementams.....	75
4. IŠVADOS IR REZULTATAI.....	81
5. SUMMARY.....	84
6. LITERATŪROS SĄRAŠAS.....	125
7. AUTORĖS PUBLIKACIJOS.....	157
8. CURRICULUM VITAE.....	272
9. PADĖKA.....	277

LENTELIŲ SĄRAŠAS

1 lentelė. Saulės elementų našumo rezultatai naudojant puslaidininkius BTF1–BTF4.....	34
2 lentelė. Terminės, optinės ir fotofizikinės naujų junginių savybės.....	46
3 lentelė. Saulės celių našumo parametrai, gauti iš J – V kreivių.....	49
4 lentelė. Bipolinių fluoreno darinių terminės, optinės ir fotoelektrinės savybės.....	53
5 lentelė. Terminės, optinės ir fotoelektrinės naujų medžiagų savybės.....	58
6 lentelė. Fotovoltiniai saulės elementų parametrai.....	60
7 lentelė. Terminės, optinės ir fotofizikinės susintetintų STM savybės.....	63
8 lentelė. Iš J – V kreivių nustatyti fotovoltiniai saulės elementų parametrai.....	67
9 lentelė. Optiniai, terminiai ir fotoelektriniai naujų STM parametrai.....	73
10 lentelė. Iš J – V kreivių nustatyti fotovoltiniai saulės elementų parametrai.....	75
11 lentelė. Optiniai, terminiai ir fotoelektriniai junginių STM29–STM32 parametrai.....	78
12 lentelė. Iš J – V kreivių nustatyti fotovoltiniai saulės elementų parametrai, kuriuose naudojami STM29–STM32 puslaidininkiai.....	79
Table 13. Thermal, optical and photophysical properties of new materials.....	91
Table 14. Characteristics of solar cells.....	93
Table 15. Thermal, optical and photoelectrical properties of bipolar fluorene derivatives.....	97
Table 16. Thermal, optical, and photoelectrical properties of new materials.....	102
Table 17. Photovoltaic parameters extracted from solar cells based on the various HTMs.....	105
Table 18. Thermal, optical, and photophysical properties of synthesized HTMs.....	108
Table 19. Photovoltaic parameters of solar cells.....	111
Table 20. Optical, thermal and photoelectric parameters of new HTMs.....	115
Table 21. Photovoltaic parameters of solar cells.....	117
Table 22. Optical, thermal, and photoelectric parameters of STM29–STM32.....	121
Table 23. Photovoltaic parameters of conventional solar cells derived from J – V measurements.....	121

PAVEIKSLŲ SĄRAŠAS

1 pav. Monokristalinio silicio saulės elementas	30
2 pav. Polikristalinio silicio saulės elementas	20
3 pav. Amorfinio silicio SE.....	21
4 pav. Kadmio telūrido saulės elementas	20
5 pav. CIGS saulės elementas	20
6 pav. Kvantinių taškų SE.....	21
7 pav. Organinio SE sudėtis	21
8 pav. Polimerinio SE struktūra	22
9 pav. DSSE struktūra.....	24
10 pav. 3D ir 2D perovskitai ir perovskito sudėtis	26
11 pav. Perovskitinių SE struktūra.....	26
12 pav. Stibio sulfido kristalinė struktūra.....	28
13 pav. N-i-p Sb_2S_3 SE	28
14 pav. Hibridinio saulės elemento veikimo principas.....	29
15 pav. Saulės elementų charakteristikos.....	30
16 pav. SC, ST ir spiro-OMeTAD struktūrų palyginimas	31
17 pav. V859 ir V886 struktūrų palyginimas	32
18 pav. STM, kuriose fluorenas naudojamas kaip šoninis fragmentas	33
19 pav. Alkilgrandinėlių ilgio įtaka PCE	33
20 pav. BTF1–BTF4 struktūrinės formulės.....	34
21 pav. TC-36 struktūrinė formulė.....	31
22 pav. 3,6-N struktūrinė formulė.....	36
23 pav. SGT-405(3,6) struktūrinė formulė.....	36
24 pav. MeO-2PACz struktūrinė formulė	38
25 pav. Poli(3-heksiltiofen-2,5-diil) (P3HT).....	38
26 pav. Ftalocianino darinių struktūrinės formulės	40
27 pav. THF tirpalų UV–RŠ absorbcijos spektrai ir normalizuoti fluorescencijos spektrai: a) STM1 ir STM3–STM5; b) STM2 ir STM6–STM8.....	45
28 pav. STM1, STM2 ir spiro-OMeTAD THF tirpalų UV–RŠ absorbcijos spektrai ir normalizuoti fluorescencijos spektrai	45
29 pav. Geriausių saulės elementų $J-V$ kreivės ir stabilumo tyrimas, kaip STM naudojant: a), d) spiro-OMeTAD, STM1 ir STM2; b), e) STM3–STM5; c), f) STM6–STM8	48
30 pav. Bipolinių fluoreno darinių TGA kreivės.....	51
31 pav. Naujų bipolinių junginių DSK kreivės: a) turinčių karbonilgrupes (STM9–STM12); b) turinčių cianopakaitus (STM13 ir STM14).....	52
32 pav. Bipolinių fluoreno darinių UV–RŠ spektrai: a) THF tirpalų ($c= 10^{-4}$ mol/l); b) sluoksnių.....	52
33 pav. Elektronų fotoemisijos ore spektrai: a) junginių, turinčių karbonilgrupes (STM9–STM12); b) junginių, turinčių cianopakaitus (STM13 ir STM14).....	54
34 pav. Krūvininkų dreifinio judrio priklausomybė nuo elektrinio lauko stiprio	54
35 pav. Tikslinių junginių TGA kreivės.....	57
36 pav. Tikslinių medžiagų DSK antrojo kaitinimo kreivės.....	57

37 pav. Tikslinių medžiagų UV–RŠ spektrai iš: a) THF tirpalų ($c = 10^{-4}$ mol/l); b) plonų plėvelių.....	58
38 pav. Šakotos struktūros fluorenilideno fragmentą turinčių junginių jonizacijos potencialai	59
39 pav. Junginių STM15–STM20 krūvininkų dreifinio judrio priklausomybė nuo elektrinio lauko stiprio.....	59
40 pav. Saulės elementų struktūra (a); prietaiso skerspjūvio vaizdas (b).....	60
41 pav. Saulės elementų su STM16 ir spiro-OMeTAD stabilumas.....	61
42 pav. Terminės žvaigždės formos karbazolo darinių savybės: a) TGA rezultatai; b) antrojo kaitinimo DSK kreivės	63
43 pav. Tikslinių junginių UV–RŠ ir fluorescencijos spektrai: a) THF tirpalų (atitinkamai $c = 10^{-4}$ g/mol ir $c = 10^{-5}$ g/mol); b) plėvelių.....	57
44 pav. Tikslinių junginių STM21–STM25 jonizacijos potencialai	65
45 pav. Molekulių STM21–STM25 fragmentų išsidėstymas erdvėje.....	65
46 pav. Naujų junginių STM21–STM25 krūvininkų dreifinio judrio priklausomybės nuo elektrinio lauko stiprio: a) grynų medžiagų; b) kompozicijoje su PC-Z (1:1)...	66
47 pav. Geriausių saulės elementų $J-V$ kreivės.....	67
48 pav. Neįkapsuliuotų prietaisų stabilumo tyrimas.....	68
49 pav. Saulės elementų našumas, veikiant juos skirtingomis temperatūromis	68
50 pav. SE sluoksniai prieš terminio atsparumo tyrimą (kaireje) ir po terminio atsparumo tyrimo (dešinėje)	69
51 pav. STM28 ^1H BMR spektro fragmentas.....	71
52 pav. Junginio STM28 H,H COSY spektro fragmentas.....	71
53 pav. Junginio STM28 NOESY spektro fragmentas.....	72
54 pav. STM26–STM28 TGA kreivės.....	67
55 pav. STM26–STM28 ir P3HT UV–RŠ spektrai.....	73
56 pav. Sb_2S_3 saulės elemento konstrukcija (a); $J-V$ kreivės: b) STM26; c) STM27; d) STM28, esant skirtingoms STM koncentracijoms.....	74
57 pav. Geriausių prietaisų $J-V$ kreivės.....	75
58 pav. Tikslinių junginių STM29–STM32 TGA kreivės.....	77
59 pav. DSK antrojo kaitinimo kreivės.....	78
Figure 60. UV–vis absorption (solid lines) and normalized fluorescence (dashed lines) spectra from THF solutions: a) STM1 and STM3–STM5; b) STM2 and STM6–STM8.....	89
Figure 61. UV–vis absorption (solid lines) and normalized fluorescence (dashed lines) spectra from THF solutions of STM1, STM2 and Spiro-OMeTAD	89
Figure 62. The $J-V$ curves of best-performing SC and the results of the stability test of HTMs: a), d) Spiro-OMeTAD, STM1 and STM2; b), e) STM3–STM5; c), f) STM6–STM8.....	93
Figure 63. TGA curves of bipolar fluorene derivatives.....	96
Figure 64. DSC curves of new bipolar materials: a) containing carbonyl groups (STM9–STM12); b) with cyano substituents (STM13 and STM14)	96
Figure 65. UV–vis spectra of bipolar fluorene derivatives in: a) THF solutions ($c = 10^{-4}$ mol/l); b) thin layers.....	98

Figure 66. Electron photoemission in air spectra of new compounds: a) containing carbonyl groups (STM9–STM12); b) with cyano fragments (STM13 and STM14)...	98
Figure 67. Charge carrier drift mobility dependence on electric field.....	99
Figure 68. TGA curves of the target compounds.....	101
Figure 69. DSC second heating cycle of the target materials.....	102
Figure 70. UV–vis spectra of target materials from: a) THF solutions ($c = 10^{-4}$ mol/l); b) thin layers.....	103
Figure 71. Ionization potentials of branched compounds containing fluorenylidene fragments.....	103
Figure 72. Dependence of charge drift mobilities on electric field.....	104
Figure 73. Structure of SC (a); Cross-sectional view of the device (b).....	104
Figure 74. Stability of solar cells containing STM16 and Spiro-OMeTAD.....	105
Figure 75. Thermal properties of starburst carbazole derivatives: a) TGA results; b) DSC curves of second heating.....	107
Figure 76. UV–vis and FL spectra of: a) THF solutions ($c = 10^{-4}$ g/mol and $c = 10^{-5}$ g/mol, respectively); b) thin films.....	109
Figure 77. The ionization potentials of target compounds STM21–STM25.....	109
Figure 78. Hole drift mobility dependencies on electric field: a) pure materials; b) in composition with PC-Z (1:1)	110
Figure 79. J – V curves of the best devices.....	111
Figure 80. The stability study of encapsulated devices.....	112
Figure 81. The efficiency of solar cells under different temperatures.....	112
Figure 82. Solar cells' layers before (left) and after (right) thermal stability test.....	113
Figure 83. TGA curves of STM26–STM28.....	114
Figure 84. UV–vis spectra of STM26–STM28 and P3HT.....	115
Figure 85. Construction of the Sb_2S_3 solar cell (a); J – V curves of: b) STM26, c) STM27, d) STM28, using different concentrations.....	116
Figure 86. J – V curves of the best-performing devices.....	117
Figure 87. The TGA curves of target compounds STM29–STM32.....	119
Figure 88. Second heating curves of DSC.....	120

SCHEMŲ SĄRAŠAS

1 schema. Spirobifluorenų darinio DM sintezės schema.....	31
2 schema. KR216 ir 2,7 BCz-OMeTAD sintezės schema.....	32
3 schema. FH27 sintezės schema.....	33
4 schema. BTTI darinių sintezės schema.....	35
5 schema. SFXDAnCBZ sintezės schema.....	36
6 schema. TBPC junginių sintezės schema.....	37
7 schema. DTPThMe-ThTPA sintezės schema.....	39
8 schema. T-BDT ir F-BDT sintezės schema.....	39
9 schema. Chinolino darinių sintezės schema.....	40
10 schema. V1235 ir V1236 sintezės schema.....	41
11 schema. 9-etil-N-(4-metoksifenil)-9H-karbazol-3-amino (1) bei bis(9-etil-9H-karbazol-3-il)amino (2) sintezė.....	43
12 schema. Spiro-OMeTAD analogų STM1 ir STM2 sintezė.....	44
13 schema. „Pusinių“ spiro-OMeTAD analogų SMT3–STM8 sintezė.....	44
14 schema. Tarpinių šoninių fragmentų 3 ir 4 sintezė.....	50
15 schema. Bipolinių fluoreno darinių STM9–STM14 sintezė.....	51
16 schema. Tarpinio junginio 10 sintezė.....	55
17 schema. Šakotos struktūros fluorenilideno darinių STM15–STM20 sintezė.....	56
18 schema. Naujų žvaigždės formos junginių STM21–STM25 sintezė.....	62
19 schema. Tikslinių junginių STM26–STM28 sintezė.....	70
20 schema. Tarpinių junginių 14 ir 15 sintezė.....	76
21 schema. Tikslinių junginių STM29–STM32 sintezė.....	77
Scheme 22. Synthesis of 9-ethyl-N-(4-methoxyphenyl)-9H-carbazol-3-amine (1) and bis(9-ethyl-9H-carbazol-3-yl)amine (2).....	88
Scheme 23. Synthesis of Spiro-OMeTAD analogues STM1 and STM2.....	88
Scheme 24. Synthesis of „half“ Spiro-OMeTAD analogues SMT3–STM8.....	89
Scheme 25. Synthesis of intermediates 3 and 4.....	95
Scheme 26. Synthesis of fluorene derivatives STM9–STM14.....	95
Scheme 27. Synthesis of intermediate 10.....	100
Scheme 28. Synthesis of branched structure fluorenylidene derivatives STM15–STM20.....	101
Scheme 29. Synthesis of new starburst materials STM21–STM25.....	106
Scheme 30. Synthesis of target compounds STM26–STM28.....	114
Scheme 31. Synthesis of intermediates 14 and 15.....	118
Scheme 32. Synthesis of target compounds STM29–STM32.....	119

SANTRUMPŲ SĄRAŠAS

2D – dvimatis;
3D – trimatis;
AZO – aliuminiu legiruotas cinko oksidas;
BMR – branduolių magnetinis rezonansas;
c – koncentracija, mol/l;
CIGS – vario galio indžio disulfidas;
COSY – koreliacinė spektroskopija;
c-TiO₂ – kompaktiškas titano dioksidas;
DMF – *N,N*-dimetilformamidas;
DMSO – dimetilsulfoksidas;
DSK – diferencinė skenuojamoji kalorimetrija;
DSSE – dažikliais sujautrintas saulės elementas;
E – elektrinio lauko stiprumas;
 E_{ea} – elektronų giminingumas;
 E_g – draustinė energijos juosta;
Egzo – egzoterminis procesas;
ES – Europos Sąjunga;
ETM – elektronus transportuojanti medžiaga;
ETS – elektronus transportuojantis sluoksnis;
eV – elektronvoltai;
FA⁺ – formamidžio organinis katijonas;
FF – užpildymo koeficientas;
FK209 CoTFSI – tris[2-(1*H*-pirazol-1-il)-4-*tret*-butilpiridin]kobalto (III) tris[bis(trifluormetilsulfonil)]imidais;
FL – fluorescencija;
FTO – fluoru legiruotas alavo oksidas;
hν – krintančios spinduliuotės kvanto energija;
HOMO – aukščiausia užimta molekulinė orbitalė;
I – fotosrovės stipris;
 I_p – jonizacijos potencialas;
IR – infraraudonoji spinduliuotė;
 I_{sc} – trumpojo jungimo srovės stipris;
ITO – indžiu legiruotas alavo oksidas;
IZO – indžiu legiruotas cinko oksidas;
 J_{sc} – trumpojo jungimo srovės stiprio tankis;
J-V – fotosrovės ir įtampos kreivės;
KOtBu – kalio *tret*-butoksidas;
KT – kvantiniai taškai;
LiTFSI – ličio bis(trifluormetansulfonil)imido druska;
LUMO – žemiausia neužpildyta molekulinė orbitalė;
nm – nanometrai;
MA⁺ – metilamonio organinis katijonas;
MGT – maksimalios galios taškas;
m-TiO₂ – mezoporinis titano dioksidas;

NaOtBu – natrio *tret*-butoksidas;
 NOESY – branduolių Overhauserio efekto spektroskopija;
 $(n\text{-Bu})_4\text{N}^+\text{Br}^-$ – tetrabutilamonio bromidas;
 OLED – organiniai šviestukai;
 OSE – organiniai saulės elementai;
 PCE – fotovoltinio elemento efektyvumas;
 PC-Z – bisfenolio-Z polikarbonatas;
 $\text{Pd}_2(\text{dba})_3$ – tris(dibenzilidenacetono)dipaladis (0);
 $\text{Pd}(\text{OAc})_2$ – paladžio (II) acetatas;
 $\text{Pd}(\text{PPh}_3)_4$ – tetrakis(trifenilfosfino)paladis (0);
 PEDOT:PSS – poli(3,4-etilendioksitiofenas):poli(stireno sulfonatas);
 PESA – fotoelektronų spektroskopija ore;
 PPV – poli(p-fenilenvinilenas);
 PSE – perovskitinis saulės elementas;
 PTAA – poli-[bis(4-fenil)(2,4,6-trimetilfenil)aminas];
 PTB7 – poli({4,8-bis[(2-ethylheksil)oksi]benz[1,2-*b*:4,5-*b'*]ditiofen-2,6-diil}{3-fluor-2-[(2-ethylheksil)karbonil]tieno[3,4-*b*]tiofenediilas});
 P3HT – poli-3-heksiltiofeno polimeras;
 sant. vnt. – santykiniai vienetai;
 Sb_2S_3 – stibio trisulfidas;
 SE – saulės elementas;
 spiro-OMeTAD – 2,2',7,7'-tetrakis[*N,N*-di(4-metoksifenil)amino]-9,9'-spirobifluorenas;
 STM – skyles transportuojanti medžiaga;
 STS – skyles transportuojantis sluoksnis;
*t*BP – 4-*tret*-butilpiridinas;
 TCO – skaidrus, elektrai laidus oksidas;
 TGA – termogravimetrinė analizė;
 THF – tetrahidrofuranas;
 $T_{\text{kr.}}$ – kristalizacijos temperatūra;
 $T_{\text{lyd.}}$ – lydymosi temperatūra;
 $T_{\text{sk.}}$ – 5 % bandinio masės nuostolių temperatūra;
 $T_{\text{st.}}$ – stiklėjimo temperatūra;
 $[(t\text{-Bu})_3\text{PH}]\text{BF}_4$ – tri-*tret*-butilfosfonio tetrafluoroboratas;
 UV-RŠ – ultravioletinės ir regimosios šviesos spinduliuotė;
 val. – valanda;
 V_{OC} – atvirosios grandinės įtampa;
 XPhos – 2-dicikloheksilfosfino-2',4',6'-triizopropilbifenilas;
 XTOF – kserografinio laiko lėkio metodas;
 Δ – virimo temperatūra;
 ε – ekstinkcijos koeficientas;
 λ_{abs} – absorbcijos maksimumas;
 λ_{FL} – emisijos maksimumas;
 μ_0 – dreifinis judris esant nuliniam elektrinio lauko stipriui;
 μM – mikrometrai.

1. ĮVADAS

Šiuo metu Žemėje gyvena daugiau nei 8 milijardai žmonių [1]. Kasmet šis skaičius didėja šimtais milijonų. Toks populiacijos augimas skatina daugiau naudoti Žemės išteklius: naftą, anglį, dujas. Per metus jis siekia daugiau nei 100 milijonų tonų [2]. Šie energijos šaltiniai nėra atsinaujinantys, todėl ilginiui jų mažės ir nebeužteks žmonijos poreikiui patenkinti. Taip pat tokio didelio masto iškastinio kuro naudojimas neatsiejamas nuo aplinkos taršos, kuri sukelia šiltnamio efektą. 2023 m. fiksuota vidutinė paviršiaus temperatūra yra pati didžiausia per 174 metų laikotarpį [3]. Manoma, jog 2025 m. vidutinė paviršiaus temperatūra bus dar didesnė [4]. Šylant klimatui didėja sausra, kuri sukelia maisto ir vandens stygių. Todėl atsiranda poreikis šį efektą minimizuoti. ES įsipareigojo iki 2030 m. stipriai sumažinti iškastinio kuro naudojimą, teikti pirmenybę atsinaujinantiems energijos šaltiniams, o iki 2050 m. pasiekti nulinę klimato taršą [5]. Norint pasiekti tokius rezultatus, iškastinį kurą galima keisti atsinaujinančiais energijos šaltiniais: vėjo, saulės, geotermine, hidroenergija, biomase.

Saulė – galingiausias, nemokamas ir neišsenkantis žmoniui prieinamas energijos šaltinis. Kasmet Žemę pasiekia dideli saulės energijos kiekiai. Manoma, kad per vieną dieną Saulė išspinduliuoja tokį energijos kiekį, kurio užtektų 27 metams žmonijos poreikiams patenkinti [6]. Jau daugiau nei 70 metų tobulinama saulės elementų (SE) technologija suteikė galimybių paprastam vartotojui elektros energiją išgauti tvariais būdais [7]. Svarbiausia, kad energija gaminama neteršiant aplinkos. Gaminant energiją nevyksta jokių garsų sukeliančių procesų (kitais žodžiais tariant, nei su vėjo jėgavėmis) ir prietaisai neturi judančių konstrukcijų, kurios ilginiui nusidėvėtų. Tokio tipo energija gali būti išgaunama ir mažai apgyvendintose, nutolusiose vietovėse, kur energijos tiekimo instaliacija elektros laidais būtų apsunkinta. SE galima montuoti tiesiog ant pastatų, taip neužimant žemės ploto. Tačiau ši technologija turi ir minusų – išgaunamos energijos kiekis tiesiogiai priklauso nuo oro sąlygų ir paros laiko, didelė įrangos kaina. Dar nėra išrasto būdo, kaip žmonija galėtų valdyti meteorologines sąlygas, tačiau elemento kainą galima reguliuoti keičiant žaliavas, tobulinant jų gryninimo procesus, parenkant tinkamus metodus elemento gamybai. Šiuo metu populiariausi ir komerciškai prieinami yra silicio SE, tačiau jų gamyba yra gana sudėtinga, reikalaujanti brangių žaliavų ir didelių energijos sąnaudų [8]. Todėl ieškoma kitų alternatyvų, kurios taip pat efektyviai generuotų saulės energiją į elektros energiją. Taip buvo išrasti hibridiniai prietaisai, sudaryti iš neorganinių ir organinių medžiagų. Jie yra pigūs ir lengvai modifikuojami. Perovskitiniai saulės elementai (PSE) yra daug žadanti inovatyvi technologija, galinti sumažinti iš saulės išgaunamos energijos kainą. Jie tobulinami jau nuo 2009 m. ir pasiekė didesnę nei 26 % našumą [9, 10]. Tačiau ši technologija turi trūkumų, trukdančių jos komercializavimui. Vienas jų – šviesą absorbuojančio komponento – perovskito stabilumas. Šiuo metu bandoma šią kliūtį pašalinti modifikuojant perovskitinio sluoksnio sudėtį įvairiais halogenais ir priedais [11]. Šio tipo efektyviausiuose elementuose naudojamų organinių puslaidininkų kaina yra ganėtinai didelė. Siekdami sumažinti prietaiso kainą, mokslininkai ieško pigesnių

krūvininkus pernešančių alternatyvų, gaunamų paprastais sintezės metodais. Įvykdžius šias sąlygas būtų galima PSE komercializuoti.

Šalia PSE yra tobulinami ir kiti naujos kartos saulės elementai, pavyzdžiui, kvantinių taškų, organiniai, vario-indžio-galio-diselenido (CIGS) ir kt. prietaisai. Nuo 2014 m. sparčiai vystomos Sb_2S_3 saulės elementų technologijos efektyvumas jau siekia 8 % [12]. Šie prietaisai gali būti iš dalies skaidrūs, todėl matoma perspektyva juos integruoti į pastatų langus. Šviesą sugeriantis sluoksnis sudarytas iš pigių žaliavų, šį sluoksnį galima padengti daugeliu būdų [13]. Tačiau šią technologiją riboja tam tikri veiksniai, trukdantys pasiekti aukštą efektyvumą. Vienas iš jų – ne itin efektyvus skylių transportinių medžiagų naudojimas, tokių kaip 2,2',7,7'-tetrakis[*N,N*-di(4-metoksifenil)amino]9,9'-spirobifluoreno (spiro-OMeTAD) ar poli(3-heksiltiofen-2,5-diilo) P3HT. Spiro-OMeTAD sintezė yra gana sudėtinga [14], gauti aukšto regioselektyvumo P3HT nėra paprasta [15], o komerciškai prieinami šie junginiai yra gana brangūs [16, 17]. Todėl siekiama rasti pigesnes šiuo metu naudojamų STM alternatyvas, pasiekiant panašų arba geresnį prietaisų efektyvumą.

Darbo tikslas – susintetinti skyles transportuojančius fluorenilo ir karbazolilo chromoforus turinčius mažamolekulinius junginius, ištirti jų savybes ir pritaikomumą naujos kartos saulės elementams.

Disertacijos tikslui įgyvendinti suformuluoti šie uždaviniai:

1. Susintetinti STM, molekulės centre turinčias fluorenilchromoforus, efektyviems perovskitiniais saulės elementams. Ištirti jų termines, optines ir fotoelektrines savybes bei pritaikymą perovskitiniuose saulės elementuose.

2. Susintetinti abiejų ženklų krūvininkus transportuojančius puslaidininkius, periferijoje turinčius akceptorinius ir donorinius fragmentus, juos charakterizuoti ir ištirti jų pritaikomumą perovskitiniuose saulės elementuose.

3. Susintetinti aromatiniais fragmentais sujungtus fluorenilpakaitus turinčias STM, ištirti jų termines, optines ir fotoelektrines savybes, jų įtaką perovskitinių saulės elementų našumui.

4. Iš karbazolildarinių susintetinti naujus žvaigždės formos p-puslaidininkius, ištirti jų termines, optines ir fotoelektrines savybes bei veikimą perovskitiniuose saulės elementuose.

5. Susintetinti tiofeno ir fluorenilideno fragmentus turinčius skyles pernešančius darinius; ištirti jų optines, termines ir fotoelektrines savybes bei pritaikymą Sb_2S_3 saulės elementuose.

6. Susintetinti tiofeno tilteliais sujungtus fluorenilideno fragmentus turinčius organinius puslaidininkius ir ištirti jų optines, termines, fotoelektrines savybes bei pritaikymo galimybes Sb_2S_3 saulės elementuose.

Daktaro disertacijos naujumas ir sąryšis tarp publikacijų

Jau kelerius metus perovskitinius SE stengiamasi paleisti į rinką, tačiau tai riboja jų modulių efektyvumas ir stabilumas [18]. Šias problemas galima suvaldyti parenkant tinkamas puslaidininkines medžiagas. Gaila, bet standartais laikomi krūvininkus pernešantys sluoksniai neatitinka pramoninei tokių elementų gamybai keliamų reikalavimų, t. y. tam skirti puslaidininkiai nėra pakankamai pigūs bei lengvai

sintetiniami. Dažniausiai kaip teigiamuosius krūvininkus pernešanti medžiaga naudojamas spiro-OMeTAD. Naudojant šią medžiagą fiksuojami rekordiniai prietaisų našumai. Tačiau ji turi keletą minusų, tokių kaip nepakankamas stabilumas prietaise, sluoksnių kristalizacijos rizika ir sudėtinga sintezė, reikalaujanti agresyvių reagentų [14]. Todėl svarbu ieškoti naujų STM, kurios būtų paprastai sintetintos, o saulės elemente išliktų stabilios morfologinės būsenos. Keturiuose autorės pristatomose publikacijose nagrinėjamos tikslingai sumodeliuotos ir susintetintos molekulinės struktūros, skirtos perovskitiniais saulės elementams, pasižyminčios pageidaujamomis morfologinėmis savybėmis, o kai kuriais atvejais ir gerokai paprastesne sinteze nei spiro-OMeTAD.

Pirmoje publikacijoje nagrinėjami spiro-OMeTAD analogai, kuriuose 4-metoksifenilchromoforai keičiami 9-etilkarbazolilais, tikintis, kad jie pagerins morfologines ir fotoelektrines tikslinių junginių savybes. Taip pat buvo pasiūlyti lengvai sintetiniami jų „pusiniai“ analogai, siekiant išsiaiškinti, ar fluorenilo centrinį fragmentą turintys junginiai perovskitiniuose SE veiks taip pat efektyviai kaip ir spirobifluorenų klasės medžiagos. Gautus puslaidininkius testuojant PSE fiksuotas 15,7–18,3 % našumas, kuris šiek tiek nusileido gerai ištirtam standartui spiro-OMeTAD, tačiau dėl geresnių naujų puslaidininkių morfologinių savybių pasiektas geresnis PSE stabilumas.

Kitoje publikacijoje aprašoma naujos koncepcijos fluoreno darinių, turinčių tiek donorines, tiek akceptorines grupes, sintezė ir gautų tikslinių medžiagų savybės. Visi susintetinti bipoliniai fluoreno dariniai pasižymi puikiais terminėmis savybėmis. 5 % masės jie praranda aukštesnėje nei 400 °C temperatūroje bei pasižymi stabilia amorfine būsena. Stiklėjimo temperatūros atitinka STM keliamus reikalavimus. Jonizacijos potencialai taip pat yra tinkami, norint šiuos bipolinius fluoreno darinius panaudoti SE gamybai. Daugelis šių darinių pasižymi abiejų ženklų krūvininkų pernaša. Tačiau fiksuotas skylių dreifinis judris siekia tik 10^{-7} cm²/Vs silpnuose elektriniuose laukuose, todėl šios medžiagos nebuvo išbandytos perovskitinių saulės elementų konstrukcijoje.

Šakotos struktūros fluorenilideno fragmentus turinčių naujų organinių puslaidininkių sintezė aprašyta trečioje publikacijoje. Čia pateikti išsamūs naujų junginių optinių savybių, morfologinio stabilumo ir fotoelektriniai tyrimai. Visi susintetinti tiksliniai puslaidininkiai pasižymi puikiais terminėmis savybėmis. 5 % masės jie praranda aukštesnėje nei 450 °C temperatūroje ir pasižymi stabilia amorfine būsena. Naujus puslaidininkius kaip STM pritaikius PSE buvo fiksuotas 19,61–22,13 % našumas. Prietaisas su skylių transportuojančiu organiniu puslaidininkiu **STM16**, kurio fluorenilideno fragmentai sujungti fenilenžiedo *meta*- padėtimis, pasižymi panašiu efektyvumu kaip ir elementas su spiro-OMeTAD, tačiau gan nemažai jį lenkia prietaiso stabilumu.

Ketvirtoje publikacijoje aprašyti žvaigždės formos skylių transportuojantys puslaidininkiai, kuriuose centrinis karbazolilchromoforas sujungtas su fragmentais, turinčiais 2- ir 3- padėtyje pakeistus karbazolilpakaitus. Iki šio straipsnio publikavimo karbazolilchromoforas nebuvo pritaikytas kartu kaip centrinis ir šoninis fragmentas tokio tipo dariniuose. Tikslinės medžiagos buvo gautos vienos stadijos sinteze. Nauji junginiai pasižymėjo geromis morfologinėmis savybėmis ir stabilia amorfine būsena.

Prietaisų, kuriuose kaip STM panaudoti šie žvaigždės formos dariniai, efektyvumas siekė 19 %, nežymiai nusileidžiant saulės elementui su spiro-OMeTAD standartu. Tačiau prietaisų stabilumo testas įrodė naujų organinių puslaidininkių pranašumą. Ypač šis pranašumas išryškėjo naudojant junginį **STM21**, tiriant PSE stabilumą keliant temperatūrą.

Šalia perovskitinių saulės elementų taip pat tyrinėjami ir kiti naujos kartos saulės elementų prietaisai. Sb_2S_3 saulės elementų efektyvumas nusileidžia perovskitiniams SE, tačiau absorbuojančio sluoksnio stabilumas yra didesnis ir jam pagaminti nenaudojamos toksiškos medžiagos [19]. Jų našumą galima padidinti kaip STM naudojant spiro-OMeTAD arba P3HT. Tačiau tai nėra pačios tinkamiausios medžiagos Sb_2S_3 saulės elementams dėl kainos, sintezės sudėtingumo ir „parazitinės“ absorbcijos. Remiantis perovskitinių SE tyrimų patirtimi, akivaizdu, kad, tinkamai parinkus teigiamuosius krūvininkus pernešančias medžiagas, galima pasiekti aukštą prietaisų našumą. Penktojoje publikacijoje aprašomi lengvai sintetinami, prie centrinio fluoreno fragmento įvairius tiofeno chromoforų kiekius turintys organiniai puslaidininkiai. Nauji junginiai pasižymi geromis morfologinėmis savybėmis. Saulės elementų, kuriuose kaip SMT panaudotos tiofeno pakaitus turinčios medžiagos, našumas pasiekė 4,94 %, kuris yra didesnis nei prietaisų su standartu P3HT. Taip pat visi tiksliniai junginiai yra palyginti pigūs, lyginant jų sintezės kainą su komerciškai prieinamu P3HT [16].

Šeštoje publikacijoje aprašytos skyles transportuojančios medžiagos, kurių centre esantis difenilaminais arba trifenilaminais pakeistas fluorenų dimeras yra sujungtas skirtingą tiofeno fragmentų skaičių turinčiais tilteliais. Šios molekulės yra pirmiau aptartų STM dimeriniai analogai. Dauguma šių STM pasižymi tinkamomis terminėmis, optinėmis ir fotoelektrinėmis savybėmis, todėl šie puslaidininkiai panaudoti Sb_2S_3 saulės elementų konstravime. SE, kuriame kaip STM panaudotas puslaidininkis **STM30**, turintis tris tiofeno ir keturis difenilamino fragmentus, našumas (4,5 %) buvo aukščiausias ir nedaug nusileido SE su standartu P3HT (4,7 %), tačiau dėl gauto prietaiso didesnio pralaidumo regimosios šviesos spinduliuotei yra perspektyvus skaidriems SE konstruoti.

Autorių indėlis

Disertacijos autorė sumodeliavo, susintetino ir išgrynino šešias organinių junginių grupes, aprašytas 3.1–3.6 poskyriuose. Taip pat užfiksavo ir analizavo ultravioletinės ir regimosios šviesos ir fluorescencijos spektrus, tikslinių ir tarpinių junginių lydymosi temperatūras, apskaičiavo 3.5 poskyryje aprašytų tikslinių medžiagų kainas. Autorė analizavo magnetinio branduolių rezonanso, masės spektrus, cheminės analizės, terminių ir fotoelektrinių charakteristikų duomenis, rengė publikacijas. Publikacijų bendra autoriai iš Lozanos politechnikos instituto (*École Polytechnique Fédérale de Lausanne*) Chemijos ir chemijos inžinerijos institutas dr. Cristina Momblona, dr. Hiroyuki Kanda, dr. Keith Brooks, Nadja Klipfel ir dr. Jianxing Xia konstravo ir testavo prietaisus, bendradarbiavo rengiant rankraštį. Dr. Albertus Adrian Sutanto analizavo saulės elementus, prof. dr. Mohammad Khaja Nazeeruddin bendradarbiavo rašant ir peržiūrint publikacijos rankraštį.

Publikacijų bendraautoriai iš Kauno technologijos universiteto (KTU) Organinės chemijos katedros, dr. Marytė Daškevičienė konsultavo sintezės ir medžiagų gryninimo klausimais, dr. Artiom Magomedov bendradarbiavo atliekant sintezės darbus ir padėjo rengti publikacijos rankraštį, dr. Rimgailė Degutytė, dr. Kristina Kantminienė, prof. dr. Tadas Malinauskas ir dr. Kasparas Rakšys konsultavo rengiant publikacijos juodraščių ir rankraštį, prof. dr. Vytautas Getautis konsultavo molekulių dizaino klausimais, vadovavo tyrimams ir teikė konsultacijas rašant juodraščių, bendradarbiavo peržiūrint publikacijos rankraštį.

Publikacijos bendraautoriai iš Karaliaus Abdulaziz universiteto Pažangių medžiagų tyrimų kompetencijų centro prof. dr. Abdullah M. ir dr. Khalid A. Alamry analizavo tyrimų rezultatus ir bendradarbiavo rengiant rankraštį.

Publikacijų bendraautoriai iš Vilniaus universiteto (VU) Cheminės fizikos instituto prof. dr. Vyginas Jankauskas atliko krūvininkų dreifinio judrio matavimus ir padėjo aprašyti tyrimus. Romualdas Jonas Čepas ir dr. Kristijonas Genevičius atliko fotofizikinius tyrimus, bendradarbiavo rengiant ir formatuojant rankraštį. Dr. Alytis Gruodis atliko molekulinis skaičiavimus, dr. Eligijus Kamarauskas – jonizacijos potencialo matavimus.

Publikacijos bendraautoriai iš Kyoto universiteto Cheminių tyrimų instituto doc. dr. Minh Anh Troung atliko saulės elementų konstravimą ir tyrimus. Dr. Richard Murdey ir prof. dr. Atsushi Wakamiya konsultavo rengiant publikacijos rankraštį.

Publikacijų bendraautoriai iš Talino technologijos universiteto Medžiagų ir aplinkosaugos technologijų katedros dr. Sreekanth Mandati ir Nimish Juneja bendradarbiavo rašant rankraštį, atliko saulės celių konstravimą ir tyrimus. Dr. Atanas Katerski, doc. dr. Nicolae Spalatu, dr. Tatjana Dedova, prof. dr. Malle Krunkis ir prof. dr. Ilona Oja Acik padėjo analizuoti duomenis, bendradarbiavo rengiant publikacijos rankraštį.

Publikacijų bendraautoriai iš Latvijos universiteto Kietųjų kūnų fizikos instituto dr. Raitis Grzibovskis ir dr. Aivars Vembris atliko jonizacijos potencialo ir krūvininkų dreifinio judrio matavimus, bendradarbiavo rengiant ir tikrinant rankraštį.

Publikacijos bendraautoris iš Energijos technologijos instituto prof. dr. Smagul Karazhanov bendradarbiavo rengiant rankraštį.

Su daktaro disertacijos tema susijusių publikacijų sąrašas

1. **Jegorovė, Aistė**; Truong, Minh Anh; Murdey, Richard; Daskeviciene, Maryte; Malinauskas, Tadas; Kantminiene, Kristina; Jankauskas, Vyginas; Getautis, Vytautas; Wakamiya, Atsushi. Starburst carbazole derivatives as efficient hole transporting materials for perovskite solar cells // Solar RRL. Weinheim : Wiley VCH. ISSN 2367-198X. 2022, vol. 6, iss. 1, art. no. 2100877, p. 1–7. (Web of Science). DOI: 10.1002/solr.202100877. [IF: 7,900; Q1].
2. **Jegorovė, Aistė**; Momblona, Cristina; Daškevičienė, Marytė; Magomedov, Artiom; Degutytė, Rimgailė; Asiri, Abdullah M.; Jankauskas, Vyginas; Sutanto, Albertus Adrian; Kanda, Hiroyuki; Brooks, Keith; Klipfel, Nadja; Nazeeruddin, Mohammad Khaja; Getautis, Vytautas. Molecular engineering of fluorene-based hole-transporting materials for efficient

- perovskite solar cells // Solar RRL. Weinheim : Wiley VCH. ISSN 2367-198X. 2022, vol. 6, iss. 6, art. no. 2100990, p. 1–9. (Web of Science). DOI: 10.1002/solr.202100990. [IF: 7,900; Q1].
3. Mandati, Sreekanth; Juneja, Nimish; Katerski, Atanas; **Jegorovė, Aistė**; Grzibovskis, Raitis; Vembris, Aivars; Dedova, Tatjana; Spalatu, Nicolae; Magomedov, Artiom; Karazhanov, Smagul; Getautis, Vytautas; Krunks, Malle; Oja Acik, Ilona. 4.9% efficient Sb₂S₃ solar cells from semitransparent absorbers with fluorene-based thiophene-terminated hole conductors // ACS applied energy materials. Washington, DC : American chemical society. ISSN 2574-0962. 2023, vol. 6, iss. 7, p. 3822–3833. (Web of Science). DOI: 10.1021/acsaem.2c04097. [IF: 5,500; Q2].
 4. **Jegorovė, Aistė**; Xia, Jianxing; Steponaitis, Matas; Daskeviciene, Maryte; Jankauskas, Vyngintas; Gruodis, Alytis; Kamarauskas, Egidijus; Malinauskas, Tadas; Rakstys, Kasparas; Alamry, Khalid A.; Getautis, Vytautas; Nazeeruddin, Mohammad Khaja. Branched fluorenylidene derivatives with low ionization potentials as hole-transporting materials for perovskite solar cells // Chemistry of materials. Washington DC : American Chemical Society. ISSN 0897-4756. eISSN 1520-5002. 2023, vol. 35, iss. 15, p. 5914–5923. (Web of Science). DOI: 10.1021/acs.chemmater.3c00708. [IF: 7,200; Q1].
 5. **Jegorovė, Aistė**; Daškevičienė, Marytė; Kantminienė, Kristina; Jankauskas, Vyngintas; Čepas, Romualdas Jonas; Gruodis, Alytis; Getautis, Vytautas; Genevičius, Kristijonas. New fluorene-based bipolar charge transporting materials // RSC Advances. Cambridge : Royal Society of Chemistry. ISSN 2046-2069. 2024, vol. 14, iss. 5, p. 2975–2982. (Web of Science). DOI: 10.1039/d3ra07583d. [IF: 3,900; Q2].
 6. Juneja, Nimish; **Jegorovė, Aistė**; Grzibovskis, Raitis; Katerski, Atanas; Daskeviciene, Maryte; Malinauskas, Tadas; Vembris, Aivars; Karazhanov, Smagul; Spalatu, Nicolae; Getautis, Vytautas; Krunks, Malle; Oja Acik, Ilona. Dopant-free Fluorene Based Dimers linked with Thiophene Units as Prospective Hole Transport Materials for Sb₂S₃ solar cells // Sustainable Energy Fuels. Washington, DC : American chemical society. ISSN 2398-4902. 2024, vol. 8, 4324–4334. (Web of Science). DOI: 10.1039/D4SE00472H. [IF: 5,0; Q2].

2. LITERATŪROS APŽVALGA

Prieš daugiau nei dešimtmetį įvairių elektroninių prietaisų gamybos procesuose dominavo neorganinės medžiagos. Tačiau jos turėjo keletą trūkumų, tokių kaip sudėtinga medžiagų modifikacija ar grynimasis. Todėl mokslininkai pradėjo domėtis organinės kilmės mažamolekulinėmis medžiagomis remdamiesi tuo, kad jų optinės, terminės ir fotoelektrinės savybės gali būti lengvai modifikuojamos, o gautos medžiagos pritaikytos įvairių optoelektrinių prietaisų gamyboje. Nuo tada iki dabar buvo ištirta daugybė organinių puslaidininkių, kuriuos galima suskirstyti į tris tipus:

- elektronus transportuojančius;
- skyles transportuojančius;
- skyles ir elektronus transportuojančius junginius.

Nagrinėjant literatūrą galima rasti daugybę įvairių skyles transportuojančių medžiagų, kurios turi karbazolo, fluoreno, tiofeno, pirazolo, benzotriazolo ir kt. fragmentus, lemiančius greitą krūvininkų transportą ir sluoksnio stabilumą. Tokios medžiagos pritaikomos elektroniniuose prietaisuose, tokiuose kaip organiniai šviesą emituojantys diodai. Taip pat sparčiai vystomas organinių puslaidininkių naudojimas hibridiniams saulės elementams. Šiai sričiai taikomų medžiagų tyrimai plėtojami iki šiol, siekiant padidinti jų atsparumą išoriniams veiksniams ir pagerinti termines bei fotoelektrines savybes.

2.1. Saulės elementų rūšys

Saulės celė (SC) – prietaisas, kuris elektrocheminių procesų metu sugeriamus saulės spindulius paverčia elektros energija. Pirmasis toks įtaisas buvo sukonstruotas 1954 m., jo našumas siekė 6 % [7]. Tokias SC sujungus gauti saulės elementai (SE), kurie naudoti energijai tiekti kosmose esančioms stotims. 1973 m. brangstant naftai visuomenės susidomėjimas SE didėjo, todėl prietaisai buvo rekonstruoti ir pritaikyti naudoti Žemės paviršiuje [20]. Šie patobulinimai taip pat sumažino SE kainą ir padidino jų našumą iki 10 % [20]. Šiuo metu didžiausias komercializuoto saulės elemento efektyvumas yra 24,3 % [21], celės – 47,6 % [10]. Silicio SE vis dar dominuoja saulės energetikos rinkoje, tačiau atsiranda ir kitų alternatyvų, tokių kaip kadmio telūrido (CdTe), CIGS, perovskitiniai, Sb₂S₃ ir kt. SE, kuriems mokslininkai skiria daug dėmesio, nes gamybos požiūriu jie yra pigesni [22].

Saulės elementai gali būti sukonstruoti iš įvairių organinės arba neorganinės prigimties medžiagų. Todėl yra sukurta klasifikavimo sistema, kuri SE skirsto į:

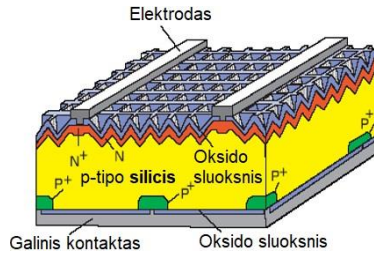
1. pirmos kartos SE;
2. antros kartos SE;
3. trečios kartos SE.

Šie prietaisai skiriasi veikliosios medžiagos (šviesą absorbuojančios medžiagos) prigimtimi ir naudojamo sluoksnio storiu.

2.1.1. Pirmos kartos saulės elementai

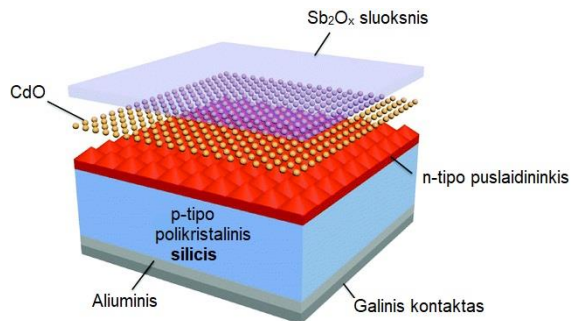
Kaip minėta anksčiau, pirmosios saulės celės efektyvumas siekė 6 %. Per kelerius metus jis padidėjo iki 15 %. Tuo metu tai buvo labai aukštas SC efektyvumas, todėl atsirado potencialas pastaruosius prietaisus plėsti taip gaunant didesnius

modulius ir sugeneruojant didesnę energijos kiekį. Bėgant metams ši technologija išstobulėjo ir dabar saulės celių našumas siekia 27,6 % [23], o elementų – 24,3 % [21]. Tokius rezultatus pasiekė monokristalinio silicio (Si) prietaisai (1 pav.). Monokristaliniuose silicio saulės elementuose aktyvusis sluoksnis gaminamas iš pavienių silicio kristalų. Gamybos metu silicio kristalai išpjunami iš didelių dydžių kristalų luitų [24]. Tačiau šią technologiją vis tiek riboja rekombinacijos procesai tarp kontakto ir skylių transportinės medžiagos [25].



1 pav. Monokristalinio silicio saulės elementas [26]

Norint pagaminti didelio efektyvumo elementą, naudojamas labai aukšto grynumo silicis, kurio gamyba užima daug laiko ir sunaudoja didelį kiekį energijos. Todėl buvo išvystyta šios technologijos atšaka, kurioje naudojamas polikristalinis silicis, t. y. silicis, sudarytas iš skirtingų kristalų. Tokiam Si gauti naudojamos paprastesnės technikos. Tačiau SC ir elementų efektyvumas yra mažesnis (~20 %) [26, 27]. Taip pat naudojamas ganėtinai storas Si aktyvusis sluoksnis (~350 μm) [24].



2 pav. Polikristalinio silicio saulės elementas [28]

Gamybos metu, kietėjant išlydytam Si, susidaro įvairios kristalinės struktūros. Polikristalinio Si SE yra pigesni už monokristalinio Si prietaisus, tačiau šiuo atveju kartu su kaina mažėja ir efektyvumas [24].

Pirmos kartos saulės elementai susideda iš dviejų skirtingų puslaidininkių medžiagų sluoksnių, legiruotų skirtingais p ir n priedais [29]. n-Si gaunamas tada, kuomet Si legiruojamas fluoru. p-Si sluoksnis legiruojamas boru. Elektronų pernaša vyksta dėl glaudžios p-silicio ir n-silicio sluoksnių jungties [30].

2.1.2. Antros kartos saulės elementai

Į antros kartos SE įeina amorfinio silicio ($\alpha\text{-Si}$) ir plonų sluoksnių prietaisai (kadmio telūrido (CdTe), vario galio indžio diselenido (CIGS) ir kt. SE). Šie įtaisai

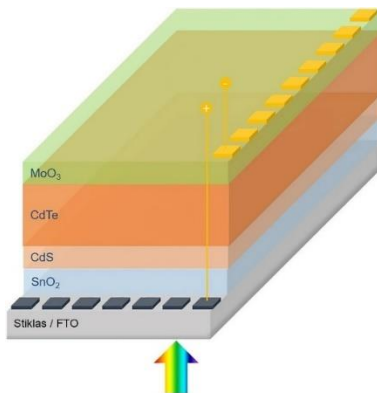
yra ekonomiškesni nei pirmos kartos SE, nes jų aktyvaus sluoksnio storis siekia ~ 1 μm [24].

1975 m. atliekant amorfinių puslaidininkių tyrimus, pastebėta, kad α :Si-H lydinį galima legiruoti priedais. Amorfinio silicio naudojimas sumažino SE konstravimo metu susidariusių defektų skaičių [22, 31]. Amorfinio silicio SE konstrukcija yra paprasta, jie gali būti gaminami žemose temperatūrose, substratams naudojamos pigios polimerinės ir kitos lanksčios medžiagos [24]. Šie SE turi pranašumų – iš jų galima lengvai gaminti didelius ir skaidrius modulius. Ši technologija naudojama ir kišeniniuose skaičiuotuose, aprūpinti energija namus, pastatus ar nuotolinius prietaisus [32].



3 pav. Amorfinio silicio SE

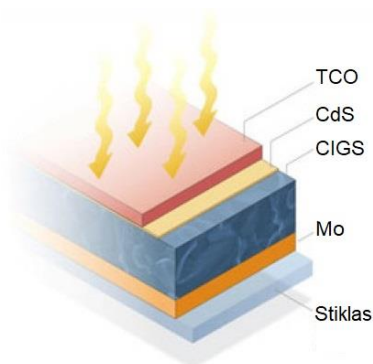
CdTe SE gamyba yra pigesnė, palyginti su pirmos kartos prietaisais. CdTe pasižymi gera absorbcija ir cheminiu stabilumu. CdTe sluoksnis dažniausiai yra prie kadmio sulfido sluoksnio, susidarant p-n sandūrai. Tačiau kadmio yra sunkus metalas, kuris yra toksiškas aplinkai, kaupiasi žmonių, gyvūnų organizmuose ir augaluose. Tai viena iš priežasčių, ribojanti CdTe elementų pramoninę gamybą [24, 33].



4 pav. Kadmio telūrido saulės elementas [34]

Cu(In,Ga)Se_2 (CIGS) SE pasižymi didele absorbcija ir ilgalaikiu stabilumu. Tačiau absorbuojančios plėvelės yra ganėtinai brangios, nes In ir Ga laikomi retaisiais metalais. CIGS pasižymi didesniu efektyvumu (23,6 %) nei CdTe SC (23,1 %) [23].

CIGS sluoksnį galima padengti įvairiais metodais, tokiais kaip purškimas, garinimas, spausdinimas, nusodinimas ir kt.



5 pav. CIGS saulės elementas [35]

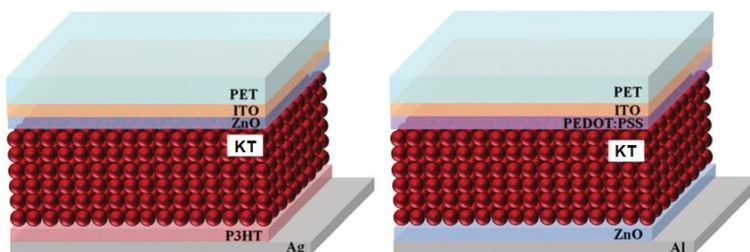
Prietaisų substratai gali būti sudaryti iš polimerinių medžiagų, stiklo, plieno, aliuminio ir kt. CIGS veikimo laikas ilgas [36].

2.1.3. Trečios kartos saulės elementai

Trečios kartos SE pasižymi gana aukštu našumu, jų gamyba pigi. Jiems yra priskiriami šie prietaisai:

- 1) kvantinių taškų SE;
- 2) organiniai SE;
- 3) polimeriniai SE;
- 4) dažais sujautrinti SE;
- 5) perovskitiniai SE;
- 6) stibio sulfido SE.

Kvantiniai taškai (KT) yra puslaidininkinių nanokristalai, pasižymintys fluorescencija, todėl dažnu atveju naudojami biologijoje ląstelių vaizdinimui ar OLED technologijose [37].

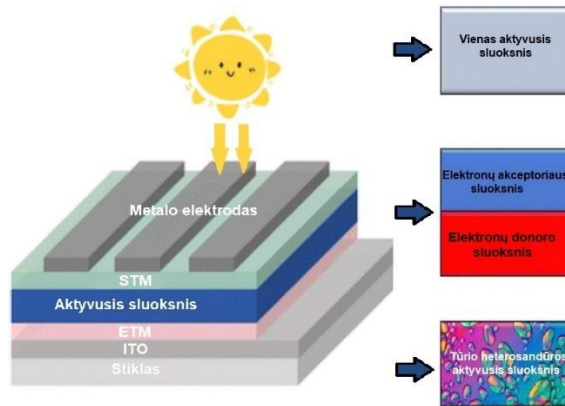


6 pav. Kvantinių taškų SE [38]

Dalelių dydis siekia 2–12 nm, jis ganėtinai paprastai reguliuojamas, taip lengvai keičiant optines savybes ir elektrinį laidumą [39]. Dažniausiai formuojant KT naudojamas kadmio selenidas, sulfidas ar telūridas (CdSe [40, 41], CdS [40, 42] ar CdTe [40, 43]) ir švino selenidas, sulfidas (PbSe [44–46], PbS [47, 48]). Yra žinoma, kad vykstant vieno fotono sugėrimui, sužadinas vienas elektronas susidarant vienai

elektrono ir skylės porai. Kvantinių taškų atveju, fotono sugėrimo metu susidaro dvi arba trys elektronų ir skylių poros [24]. KT prietaisai gali būti konstruojami n-i-p ir p-i-n architektūros. Kvantinių taškų SE sudaryti iš penkių sluoksnių: SMT ir ETM, kvantinių taškų sluoksnio, metalo elektrodo (Au, Ag, Al) ir skaidraus elektrodo (ITO, PET) [39, 49, 50].

Organinės SC pirmą kartą sukonstruotos 1960 m. ir siekė 0,1 % našumą [51]. Bėgant metams ši technologija tobulėjo. Šiuo metu ją galima suskirstyti į tris tipus: vieno sluoksnio, dviejų sluoksnių ir heterosandūros OSE [39].

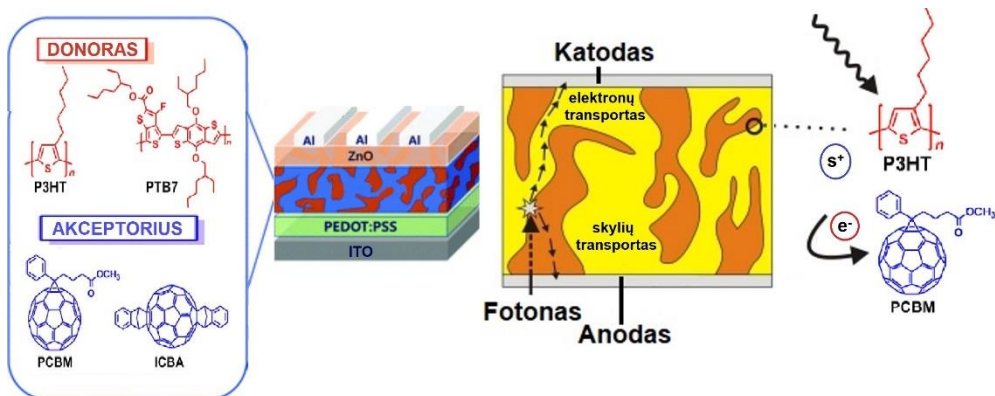


7 pav. Organinio SE sudėtis [37, 52]

OSE susideda iš STM, ETM, aktyvaus sluoksnio ir elektrodų [39, 51, 52]. Tačiau vieno aktyviojo sluoksnio prietaiso efektyvumas yra gana mažas dėl eksitonų rekombinacijos [40]. Dvisluoksnyje SE struktūroje akceptorinis ir donorinis sluoksniai gali būti atskiri, tačiau prietaisai nėra efektyvūs dėl neefektyvaus krūvininkų atskyrimo [53]. Tūrio heterosandūros SE absorbcinis sluoksnis yra donoro ir akceptoriaus molekulių mišinys. Tūrio heterosandūra palengvina eksitonų difuziją link paviršių sandūros taip pasiekiant didesnę efektyvumą [36, 54].

Aktyviajam sluoksniui gali būti naudojami įvairūs porfirino [55, 56], benziofeno [57, 58] ir kt. [52] dariniai, kurie atlieka elektronų donoro funkciją. Kaip elektronų akceptoriai gali būti naudojami perilenų [59, 60], naftalenų [61, 62] ir kt. dariniai [36, 52]. Didžiausias pasiekto SE našumas yra 19,2 % [23].

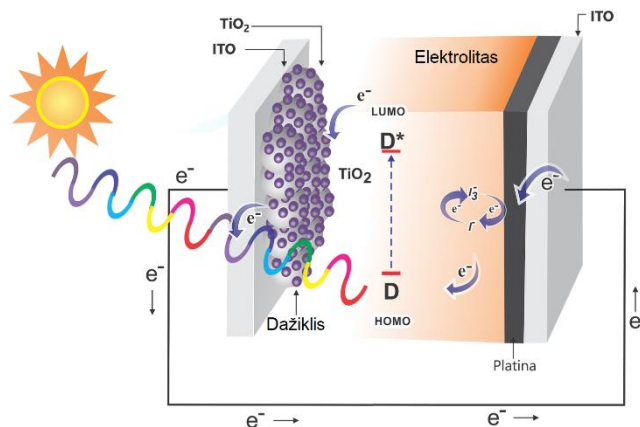
Į organinių SE sudėtį galima įtraukti polimerus, kurie puikiai pakeičia mažas organines molekules ir suteikia galimybę sukonstruoti didesnio paviršiaus ploto SE. Šios molekulės naudojamos siekiant pagerinti krūvininkų transportą ir saulės šviesos sugertį [39]. Kai kurios polimerinės medžiagos pasižymi lankstumu, lengvu apdirbimu, maža kaina, gera absorbcija, jų savybės galima lengvai keisti modifikuojant molekulinę struktūrą. Dėl šių priežasčių mokslininkai pradėjo naudoti polimerines medžiagas saulės celėms konstruoti. Polimerinio SE aktyvusis sluoksnis sudarytas iš donoro (polimero) ir akceptoriaus (fulereno ar kt.) mišinio. Prietaisą sudaro STM, ETM, aktyvusis sluoksnis, metalo elektrodas (Ca, Mg ar Al) ir laidus oksidas (ITO) [63, 64].



8 pav. Polimerinio SE struktūra [64-66]

Kaip akseptoriai tokio tipo prietaisuose naudoti perileno dariniai, tačiau nebuvo pasiekiamas aukštas našumas [59, 67]. Juos pakeitus fulerenų dariniais, efektyvumas padidėjo [64]. Fulerenų dariniai pasižymi dideliu elektronų judriu [68]. Taip pat galima naudoti ir kitas medžiagas, pavyzdžiui, poli(*p*-fenilenvinileno) (PPV) [69], benzotiazolo [70-72] ir kt. [73-75] darinius. Donorinei aktyvaus sluoksnio daliai gali būti naudojami šie polimerai: PPV dariniai [69], P3HT ir jo dariniai [76-78], pasižymintys geru skylių mobilumu ir kt. [64, 74, 79] medžiagos.

Dažais sujautrintų SE (DSSE) pradininkas yra M. Gracelis [80]. Šie prietaisai sudaryti iš šviesą sugeriančio dažiklio, ETM, elektrolito ir elektrodų [81]. Pradinis DSSE efektyvumas siekė tik kelis procentus [80], o šiuo metu siekia 13 % [10]. Tačiau tam tikri iššūkiai riboja šią technologiją, pvz., dažiklio molekulių nestabilumas. Dažniausiai pastarosios suyra esant UV ar IR spinduliuočių apšvitai [24, 82].



9 pav. DSSE struktūra [81]

Elektronams transportuoti naudojami metalų oksidai, pvz., TiO_2 [83, 84]. Tai stabili, netoksiška medžiaga, naudojama kaip baltas pigmentas dažams, dantų pastoms, kremams nuo saulės ir kt. Galima naudoti ir ZnO [85, 86], kuris pasižymi didesniu elektronų judriu, bet mažesniu stabilumu nei TiO_2 . SnO_2 gali būti naudojamas su dažikliais, kurie turi žemą LUMO, pvz., perilenois [87, 88].

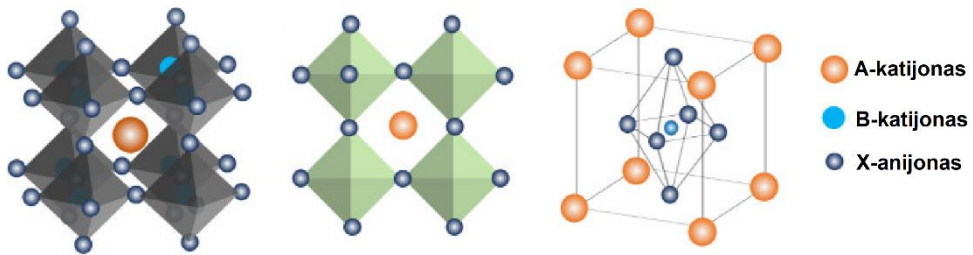
Vienas svarbiausių DSSE komponentų yra dažiklis. Jis turi pasižymėti šiomis charakteristikomis [89]:

- 1) gera regimosios šviesos ir infraraudonosios spinduliuotės absorbcija;
- 2) turi turėti inkarines grupes: $-\text{COOH}$, $-\text{H}_2\text{PO}_3$, $-\text{SO}_3\text{H}$ ir kt., kad galėtų „prisikabinti“ prie elektronų pernešančio oksido paviršiaus;
- 3) dažiklis turi būti optiškai, termiškai ir elektrochemiškai stabilus.

Remiantis šiomis taisyklėmis DSSE naudojami metalų kompleksų [90-92], porfirinų [93, 94], ftalocianinų [95, 96] ir bemetaliai organiniai dažikliai [89]. Organiniai dažikliai, palyginti su metalų kompleksais, turi pranašumų, tokių kaip lengvai keičiama molekulinė struktūra ir mažesnė kaina [89]. Į šių elementų sudėtį taip pat dažnai įeina kumarino [97], indolino [98, 99], triarilamino [96, 100], karbazolo [101-103] ir kt. [97, 98, 104, 105] grupių dažikliai.

Perovskitas yra junginys, sudarytas iš kalcio titano oksido mineralo. Tačiau šiai grupei medžiagų priskiriami ir kiti junginiai, turintys analogišką kristalografinę struktūrą ir bendrą ABX_3 formą. A – organinis / neorganinis katijonas, pvz., cezis (Cs^+), metilamonis (MA^+ , CH_3NH_3^+) ir formamidis (FA^+ , $\text{CH}_3\text{CH}_2\text{NH}_3^+$). B – metalo katijonas, pvz., Sn^{2+} ar Pb^{2+} . X yra halogeno anijonas, pvz., jodidas, bromidas ar chloridas [39]. Metalų halogenidų perovskitai, sudaryti iš švino (Pb^{2+}), metilamonio (CH_3NH_3^+) ir halogenido anijono, pvz., jodido (I^-) arba bromido (Br^-), sulaukė daug mokslininkų dėmesio, siekiant pastaruosius pritaikyti SE. Parenkant skirtingus halogenus galima lengvai keisti draustinės juostos tarpą, pvz., MAPbI_3 1,58 eV, MAPbBr_3 2,28 eV ir MAPbCl_3 2,88 eV. Perovskitai, turintys jodido fragmentų, pagal draustinės juostos tarpą yra tinkamiausi SE, tačiau jie yra mažiausiai stabilūs ir sudaro silpną ryšį su Pb^+ katijonais. Todėl dalis I^- jonų keičiami Br^- ar Cl^- anijonais. Tokiu atveju padidėja draustinės juostos tarpas ir sluoksnio stabilumas [106]. Jeigu papildomų anijonų yra daugiau, sumažėja SE efektyvumas [107]. MA pagrindu pagaminti perovskitai SE testuoti pirmieji [9]. Tačiau MA perovskitai pasižymėjo mažu krūvininkų judriu ir dideliu draustinės juostos tarpu, o 85 °C temperatūroje tokie perovskitai yra lakūs [107]. Tada buvo išbandyti FAPbI_3 perovskitai, kurių savybės, tokios kaip krūvininkų gyvavimo trukmė ir difuzijos ilgis, buvo geresnės nei MAPbI_3 , tačiau stabilumas nebuvo didelis [108]. Manoma, kad FAPbI_3 mažą stabilumą lemia didelis FA^+ jonas [107]. CsPbI_3 taip pat testuotas SE [109], tačiau prietaisai nebuvo stabilūs. Perovskitas iš aktyvios juodos formos gali pereiti į geltoną, kai tampa neaktyvus. Siekiant sulėtinti geltonos fazės atsiradimą, sukurti dviejų katijonų (MAFA) perovskitai. Tačiau juose vis tiek fiksuota geltonos fazės priemaiša. Cs^+ katijonus panaudojus MAFA sistemoje, pagerėjo plėvelių stabilumas ir prietaiso našumas, o juose esančios geltonosios fazės priemaišos kiekis buvo itin mažas [110]. Šviną perovskite galima pakeisti divalentiu stronciu (Sr) [111, 112] alavu (Sn) [113, 114] ir kt. [115-117]. Tačiau perovskito sluoksniai nepasiekia tokio gero stabilumo, kaip silicio saulės elementuose naudojamas silicis. Įrenginiuose aptinkami paviršių defektai, sukuriantys rekombinacinius procesus. Todėl mokslininkai toliau ieško junginių ar priedų, kuriais būtų galima šiuos defektus pasyvuoti [11].

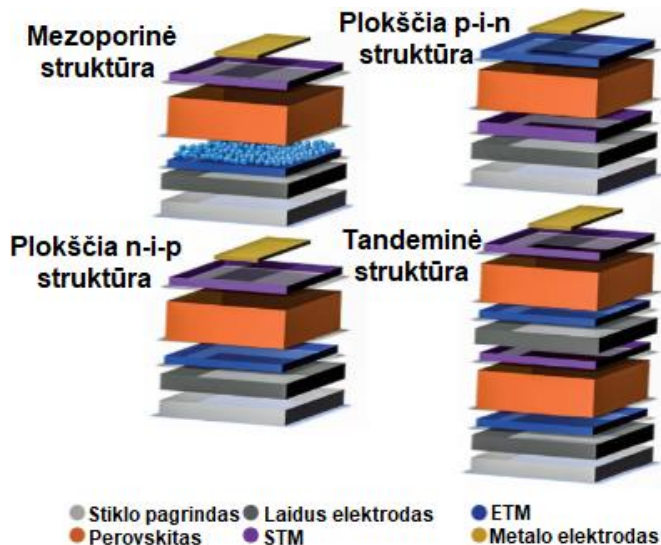
Šiuo metu naudojamos 2D arba 3D perovskitų struktūros (10 pav.). $(\text{R-NH}_3)_2\text{MX}_4$ (R – organinis katijonas, M – metalas) yra dažniausiai sutinkama 2D struktūrų formulė, o 3D sudarytos iš RNH_3PbX_3 .



10 pav. 3D ir 2D perovskitai ir perovskito sudėtis [36]

Tokie perovskitai gerai absorbuoja spindulius regimojoje srityje, pasižymi dideliu eksitonų difuzijos ilgiu, didele defektų tolerancija, dideliu krūvininkų mobilumu ir kt. [36]. Tobulinant šiuos prietaisus jau pasiektas 27,0 % našumas [10]. Perovskitiniai SE konstruojami įvairiais sluoksnių dengimo būdais: vakuuminio užgarinimo [118, 119], purškimo [120, 121] ir kt. metodais [122-124]. Sukamojo liejimo būdas taip pat taikomas formuojant perovskitines plėveles [39, 125]. Net ir plonos perovskito plėvelės pasižymi gera absorbcija [11]. Tai yra privalumas, nes, esant ploniems sluoksniams, efektyviau pasiskirsto krūvininkai, todėl padidėja SE našumas. Perovskito krūvininkų dreifinis judris yra 1–10 cm²/Vs [11].

Yra kelios galimos šių elementų architektūros: mezoporinė, plokščia n-i-p, invertuota p-i-n ir tandeminė. Perovskitinis SE dažniausiai sudarytas iš perovskitinio sluoksnio, STM, ETM ir dviejų elektrodų (Au, Ag, Al, ITO, FTO). Siekiant optimizuoti prietaisus, visi sluoksniai modifikuojami keičiant skaidrumą, morfologiją ar storį [11].



11 pav. Perovskitinių SE struktūra [110]

Elektronus transportuojanti medžiaga (ETM) reikalinga krūvininkams pernešti link elektrodo ir skylėms blokuoti. Elektronus pernešančias medžiagas galima suskirstyti į organines ir neorganines. n-i-p architektūroje dažniausiai naudojamos

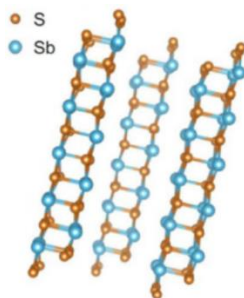
neorganinės ETM, o p-i-n struktūroje – organinės [126]. Mezoporinis TiO_2 yra neorganinės kilmės ir naudojamas mezoporinėse perovskitinėse SC [127, 128]. Plokščios struktūros perovskitiniuose SE dažniausiai naudojami ZnO [129, 130], TiO_2 [131, 132], SnO_2 [133, 134]. Kaip ETM naudojamos organinės kilmės medžiagos, tokios kaip fulerenų [135, 136] ar naftalenų [137, 138] dariniai. SE su šiomis medžiagomis pasižymi aukštu našumu, tačiau pastarųjų kaina yra gana didelė, o tirpumas nėra labai geras. Taip pat galima konstruoti perovskitinius SE be ETM, tačiau tokiu atveju aktyvusis sluoksnis turėtų būti labai homogeniškas ir su kuo mažiau defektų [139].

STM paskirtis – pernešti po elektronų sužadinimo likusias skyles link atitinkamo elektrodo. Šiam tikslui yra naudojamos organinės ir neorganinės medžiagos. CuI pasižymi geromis skylių pernašos savybėmis, tačiau naudojant jį kaip STM fiksuoti gana nedideli našumai dėl rekombinacijos nuostolių [126, 140]. CuSCN pasižymi geru krūvininkų judriu ir terminiu stabilumu, dideliu skaidrumu, geru tirpumu ir gali būti naudojamas tiek n-i-p, tiek p-i-n architektūrose [107, 141]. Tačiau tirpikliai, naudojami neorganinėms medžiagoms padengti gali ištirpinti arba pažeisti perovskitinį sluoksnį [126]. Organiniai skyles pernešantys junginiai gali būti suskirstyti į du tipus: polimerines ir mažamolekulinės skyles pernešančias medžiagas. Polimerinės medžiagos: PEDOT, polikarbazolai, polianilinai, politiofenai. Dažniausiai p-i-n prietaisuose kaip STM naudojamas organinės prigimties PEDOT:PSS [142, 143]. Ši medžiaga pasižymi tinkamu HOMO energetiniu lygmeniu, geru laidumu, tačiau yra gana nestabili. PTAA pasižymi gana aukštu skylių judriu ($\sim 10^{-2} \text{ cm}^2/\text{Vs}$) bei geresniu stabilumu, lyginant su daugeliu organinių molekulių. PTAA galima naudoti ir n-i-p ir p-i-n architektūros SC [144-146]. Mažamolekuliniams junginiams gali būti priskiriamas spiro-OMeTAD, dažnai sutinkamas n-i-p struktūros perovskitiniuose SE. Spiro-OMeTAD oksidacijos laipsnis nėra pakankamas, todėl SC našumai yra nedideli [147, 148]. Kobalto kompleksai (Co60) ir geležies trichloridas (FeCl_3) yra priedai, kurie gali efektyviai oksiduoti spiro-OMeTAD, taip padidėjant laidumui [149, 150]. Taip pat rūgštiniai priedai, tokie kaip benzilkarboksirūgštis, gali sustiprinti oksidacijos procesą ir sutrumpinti PSE senėjimo laiką [150, 151]. Naudojami ir kiti priedai, tokie kaip ličio bis(trifluormetansulfonil)imidas LiTFSI ir 4-*tret*-butilpiridinas [152, 153].

Elektrodams naudojamos medžiagos gali būti suskirstytos į metalus, anglies darinius ir laidžius oksidus [150]. Metalai pasižymi dideliu laidumu ir geba atspindėti šviesą. Dažniausiai SE konstruojami su auksu (Au) [154, 155], sidabru (Ag) [156, 157], variu (Cu) [158] ir kt. [159, 160]. Naudojant Ag ir Au galima gauti labai aukštą prietaisų našumą, tačiau laikui bėgant perovskitas reaguoja su pastaraisiais metalais ir aktyvusis sluoksnis yra iš dalies suardomas [161]. Kiti naudojami metalai yra pigesni ir stabilesni, tačiau juos naudojant prietaisuose dar nebuvo pasiekta rekordinio efektyvumo. Anglies elektrodai yra pigūs, pasižymi geru laidumu ir cheminiu stabilumu [161, 162]. Anglies elektrodai gali būti sudaryti iš laidaus grafito [163, 164], grafeno [165, 166] ar anglies nanovamzdelių [167, 166]. Indžiu legiruotas alavo oksidas (ITO) [168, 169], fluoru legiruotas alavo oksidas (FTO) [170, 171], aliuminiu legiruotas cinko oksidas (AZO) [172], indžiu legiruotas cinko oksidas (IZO) [173]

naudojami kaip skaidrūs elektrodai. Laidžius oksidus naudojant kaip abu elektrodus galima gauti skaidrius prietaisus arba tandemų sandarai tinkamas celes [161, 174].

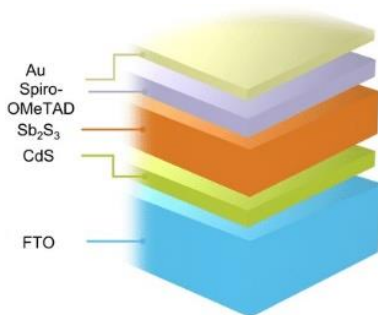
Siekiant patobulinti DSSE, buvo taikytos įvairios prietaiso modifikacijos. Viena iš jų – Sb_2S_3 aktyviojo sluoksnio naudojimas SE konstrukcijoje. Sb_2S_3 pasižymi dideliu absorbcijos koeficientu (prie 450 nm – $1,8 \times 10^5 \text{ cm}^{-1}$) [175]. Sb_2S_3 kristalizuojasi kambario temperatūroje. Ryšiai, kuriais jungiasi stibis ir siera dažniausiai yra kovalentinės kilmės [176].



12 pav. Stibio sulfido kristalinė struktūra [176]

Sb_2S_3 sluoksniai dažniausiai formuojami cheminio nusodinimo vonioje (angl. *the chemical bath deposition*) metodu, cheminės reakcijos metu iš stibio trietanolamino ir tioacetamido [19]. Gautos amorfinės plėvelės kaitinamos maždaug 300 °C temperatūroje tam, kad padidėtų kristališkumas ir sumažėtų draustinės juostos tarpas [177].

Pirmosios Sb_2S_3 SC našumas siekė 5,19 %. Pagal prietaiso architektūrą Sb_2S_3 SE skirstomi į mezoporinius, n-i-p ir p-i-n struktūros [178].



13 pav. n-i-p Sb_2S_3 SE [179]

Mezoporiniai prietaisai sudaryti iš laidaus oksido (TCO), mezoporinio ETM, aktyvaus, STM ir metalo elektrodo sluoksnių. Plokščios architektūros prietaisai sudaryti iš analogiškų sluoksnių, tik kaip ETM naudojami kompaktiški oksidų sluoksniai [180]. Elektrodams naudojami Au, Ni, Al arba Ag [176, 181, 182]. Šie SE išlieka gana stabilūs net po kelių mėnesių. Mokslininkai išsiaiškino, kad galima pasiekti tokį aukštą stabilumą, jog po 90 dienų neįkapsuliuotos SC praranda tik 0,2 % našumo [183].

Norint sukonstruoti efektyvų prietaisą, reikia tinkamai parinkti jį sudarančias medžiagas. Sb_2S_3 SE atveju ETM turi pasižymėti šiomis savybėmis:

- 1) dideliu elektronų mobilumu ir skylių blokavimu;
- 2) skaidrumu, kad saulės spinduliai pasiektų absorbuojantį sluoksnį;
- 3) su aktyviuoju sluoksniu suderinamu energetiniu lygmeniu;
- 4) vientisų sluoksnių sudarymu.

Šiuos kriterijus atitinka TiO_2 , ZnO , CdS ir SnO_2 sluoksniai [182]. p-i-n prietaisuose kaip elektronus transportuojantis sluoksnis (ETS) naudojamas CdS . Tačiau šiuose SE atsiranda daug paviršiaus defektų, kurie mažina prietaisų našumą [182, 184, 185].

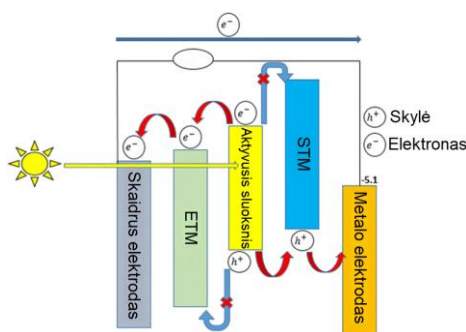
Skyles transportuojančio sluoksnio (STS) reikalavimai [182]:

- 1) turi blokuoti elektronus ir būti tinkamo energetinio lygmens;
- 2) turi gerai pernešti teigiamuosius krūvininkus;
- 3) turi būti atsparus karščiui, deguonies poveikiui, drėgmei, UV spinduliuotei ir kt.;
- 4) padengus STM aktyvūs sluoksnis turi išlikti nepažeistas.

Siekiant pasiekti aukštesnį SE našumą, STM sluoksniai yra apdorojami legiravimu [186, 187]. Taip pat didesnę efektyvumą galima gauti liejant tarp sluoksnius [188, 189]. Konstruojant prietaisą svarbu parinkti tinkamą skyles transportuojančio sluoksnio storį. Mokslininkai įrodė, kad SE didesniu našumu pasižymi tada, kai STM sluoksnis yra plonesnis [13, 190]. Įprastai skylėms transportuoti liejami CuSCN [186], P3HT [191, 192], spiro-OMeTAD [193, 194] sluoksniai.

2.2. Saulės elementų veikimo principas

Vykstant fotonų sugerčiai, aktyvaus sluoksnio elektronai, peršoka į laidumo juostą, paliekdami tarpelius (skylutes arba teigiamuosius krūvininkus) (14 pav.). Elektronai juda link ETM, skylės link SMT, galiausiai krūvininkai difunduoja link atitinkamų elektrodų [64].



14 pav. Hibridinio saulės elemento veikimo principas [130]

Jei prie elektrodų prijungiama išorinė grandinė, krūvininkai iš ETM keliauja grandine nuo vieno elektrodo link kito, taip gaunant elektros energiją. Kai elektronai prateka išorine grandine, susijungia su skylėmis elektrodo ir STM sandūroje [39].

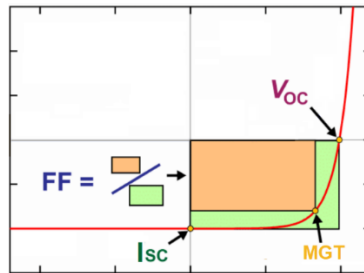
2.3. Saulės elementų charakteristikos

Trumpojo jungimo srovė (I_{sc}) – srovė prietaise, fiksuota esant nulinei varžai, įtampai ir SE apšvitai. Tai reiškia maksimalią elektros srovę, kurią gali sugeneruoti įrenginys [36, 195].

Didžiausia galima įtampa, kurią gali generuoti fotovoltinis elementas, vadinama atvirosios grandinės įtampa (V_{oc}). Matuojama tada, kai SE srovė lygi 0 [196].

Srovės ir įtampos kreivės taškas, nurodantis didžiausią įmanomą stačiakampio plotą (žr. 15 pav.) vadinamas maksimaliu galios tašku (MGT) [36]. MGT fiksuojamas V_{oc} ir I_{sc} statinių sankirtoje [195].

Užpildymo koeficientas (FF) rodo santykį tarp teoriškai ir praktiškai gautos didžiausios prietaiso galios [195].



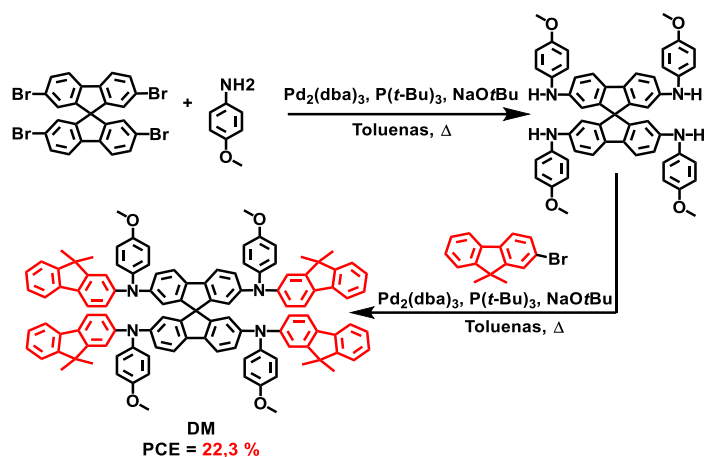
15 pav. Saulės elementų charakteristikos [196]

Fotovoltinio elemento efektyvumas (PCE) – tai matmuo, rodantis santykį tarp sugertų saulės spindulių ir pagamintos elektros energijos. Efektyvumas priklauso nuo prietaiso architektūros, naudojamų medžiagų, pastarųjų jautrumo įvairių bangos ilgių šviesos spinduliams, krintančios šviesos intensyvumo, darbinės temperatūros, paviršiaus tekstūros ir atspindžio ir kt. [195].

2.4. Organinės skylių transportinės medžiagos naudojamos perovskitiniuose saulės elementuose

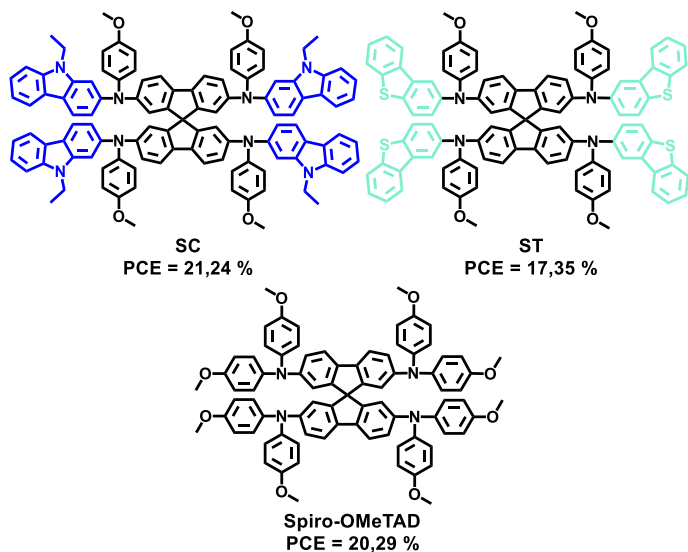
Perovskitinių saulės elementų istorija prasideda 2009 m., kai T. Miyasaka su kolegomis sukonstravo prietaisą perovskito pagrindu, kurio našumas siekė beveik 4 % [9]. Tačiau tokiame elemente, skylių pernašai naudoti skysti elektrolitai. Vėliau mokslininkai pasekė DSSC pavyzdžiu ir perovskitinių saulės elementų konstrukcijoje išbandė spiro-OMeTAD [197]. Tuomet pasiektas 10,9 % našumas. Tačiau norint susintetinti spiro-OMeTAD reikalinga kelių žingsnių sintezė ir agresyvūs reagentai [14]. Nepaisant ilgos 2,2',7,7'-tetrabrom-9,9'-spirobifluoreno fragmento sintezės, pastarasis taikomas naujų STM gamybai, nes SE našumo rezultatai būna labai aukšti.

Dažniausiai keturios arba aštuonios metoksifenilgrupės keičiamos įvairiais fragmentais. Buchwaldo–Hartwigo reakcijos sąlygomis keturias minėtas grupes pakeitus fluoreno pakaitais gautas didesnis SE našumas (22,3 %) ir stabilumas nei su spiro-OMeTAD (21,3 %) [198].



1 schema. Spirobifluorenų darinio DM sintezės schema [198]

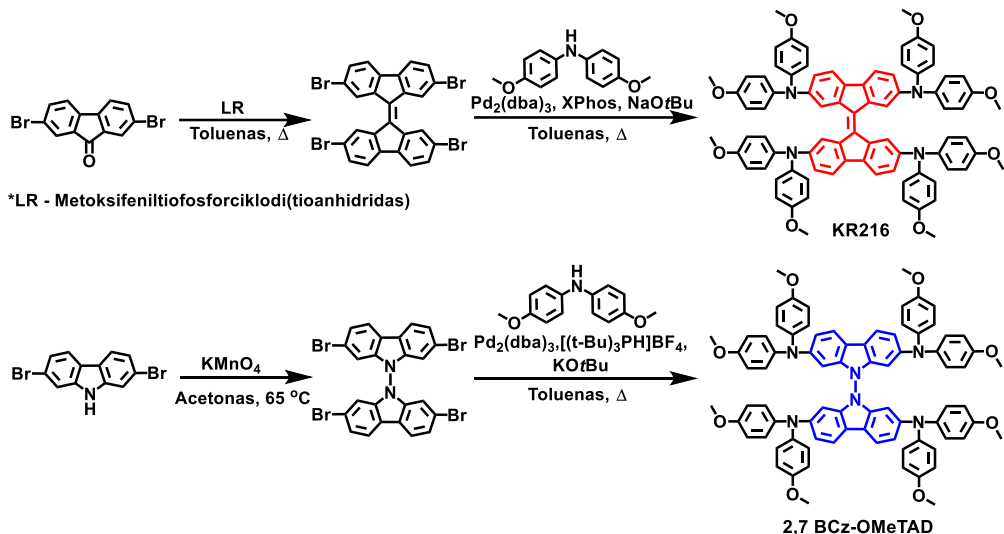
Taip pat galima metoksifenilgrupės keisti donorinių atomų turinčiais fragmentais. Prijungus karbazolilpakaitus didėja SE našumas [199-201], o dibenzotiofeno chromoforai šiuo atveju efektyvumą sumažina [200]. ST yra kristališkesnis, todėl, formuojantis sluoksniui, ilgainiui susiformuoja kristalai. Šio proceso metu sluoksnyje atsiranda tarpelių, todėl yra tikimybė susiformuoti sidabro jodidui (susijungiant jonams iš elektrodo ir perovskito), taip sumažėjant prietaiso stabilumui.



16 pav. SC, ST ir spiro-OMeTAD struktūrų palyginimas [200]

Metoksifenilgrupės taip pat galima keisti dibenzofurano [202], metoksinaftaleno [203], dimetilamino benzonitrilo [204], fentiazino [205] fragmentais gaunant didesnius SE efektyvumus.

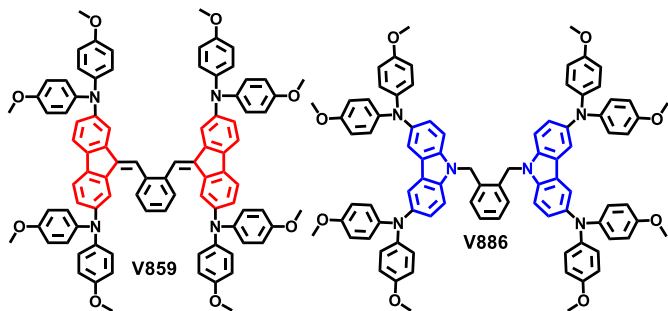
Taip pat gerą SE našumą ir / ar stabilumą galima gauti modifikavus spirobifluoreno centrinių fragmentų donoriniais heteroatomais, tokiais kaip azotas [206-208], deguonis [209, 210] ir sierą [211, 212]. Mokslininkai naudoja ir kitą strategiją – vietoje spirobifluoreno centrinio fragmento renka jam artimus darinius. Dažniausiai tai yra bifluorenilidenilo [213-215] ir bikarbazolilo [216-218] chromoforai.



2 schema. KR216 ir 2,7 BCz-OMeTAD sintezės schema [219, 220]

Paprastai tokios medžiagos sintetamos dviejų pakopų sinteze. Pirmiausia gaunami centriniai fragmentai. KR216 atveju 2,2',7,7'-tetrabrom-9,9'-bifluorenilidenas buvo gautas 2,7-dibrom-9H-fluorenonui reaguojant su Lawessono reagentu susidarant 9,9'-ilideno (C=C) dvigubajam ryšiui. Norint gauti karbazolilo darinį tetrabrom-*N,N'*-bikarbazolą, 2,7-dibromkarbazolas veikiamas kalio permanganatu. Tiksliniai puslaidininkiai KR216 ir 2,7BCz-OMeTAD gaunami Buchwaldo–Hartwigo reakcijos sąlygomis sujungiant pirmame etape susintetintus centrinius fragmentus su 4,4'-dimetoksifenilaminu.

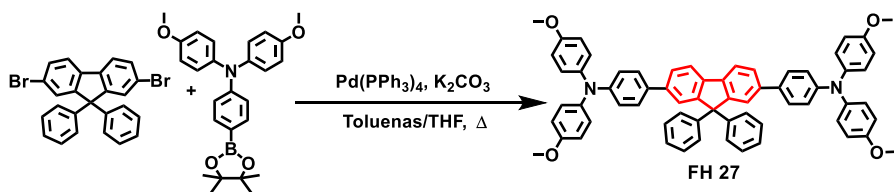
Sintetunami ir panašūs dariniai, kai fluoreno ar karbazolo fragmentai yra atskiriami fenilenžiedais ar heterocikliniais junginiais [221-223].



17 pav. V859 ir V886 struktūrų palyginimas [222, 224]

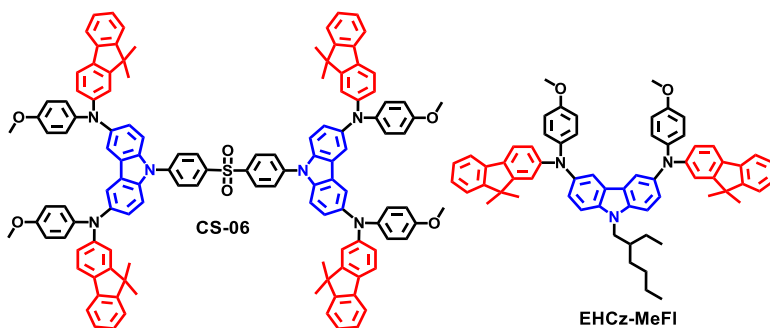
Su šiomis medžiagomis sukonstruotų SE našumas ir stabilumas yra gana aukštas.

Galima sintetinti ir mažesnes, paprasčiau gaunamas molekules, kuriose yra fluoreno fragmentų. Gautus tikslinius junginius įdėjus į SE, gaunamas aukštas efektyvumas ir geras stabilumas. Pavyzdžiui, naudojant fluoreną kaip centrinį fragmentą Suzuki reakcijos sąlygomis susintetinta medžiaga FH27, kurią panaudojus saulės elemente pasiektas 22,96 % efektyvumas. Nors prietaisai su spiro-OMeTAD pasižymėjo šiek tiek aukštesniu našumu (23,33 %), tačiau pastarųjų stabilumas buvo mažesnis [225].



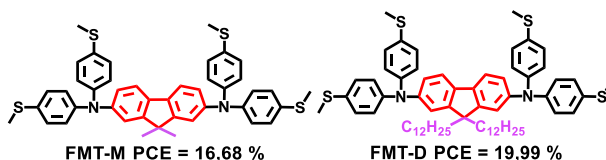
3 schema. FH27 sintezės schema [225]

Dažnu atveju medžiagų, kuriose fluorenas naudojamas kaip centrinis fragmentas, našumas yra gana aukštas [225-227]. Fluorenų pakaitus taip pat galima naudoti sintetinant STM, kurios gali polimerizuotis [228, 229]. Tokios medžiagos dažnai naudojamos invertuotose struktūrose ir joms nereikalingas legiravimas priedais. Su šiais junginiais sukonstravus SC fiksuojamas aukštas jų efektyvumas.



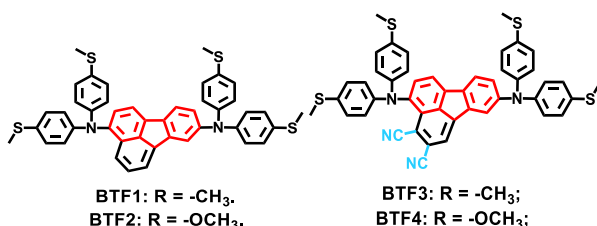
18 pav. STM, kuriose fluorenas naudojamas kaip šoninis fragmentas [230, 231]

Galima fluoreno fragmentus, kaip ir minėtų spirobifluorenų atveju, panaudoti kaip šoninius chromoforus [230, 232, 233]. Tikėtina, kad tokiu atveju padidės junginio stiklėjimo temperatūra. Tokias medžiagas naudojant SC, galima gauti didesnį našumą, nei naudojant standartu laikomą spiro-OMeTAD [231, 234, 235].



19 pav. Alkilgrandinės ilgio įtaka PCE [236]

Nagrinėjant alkilgrandinėlių įtaką medžiagų savybėms, matoma, jog ilgėjant alkilgrandinėlei didėja SC našumas, kurį lemia padidėjęs krūvininkų dreifinis judris [236]. Taip pat žinoma, kad elektronus atitraukiančios grupės gali sustiprinti sluoksnių sąveiką, prisijungti laisvus perovskito paviršiuje esančius švino jonus ir padidinti krūvininkų transportą [237-239]. Šiam tikslui galima pritaikyti karbonil- [240-242] ir cianogrupes [243, 244]. Naudojant fluoreną kaip centrinį fragmentą, buvo susintetinti junginiai, turintys cianogrupes. Juos panaudojus SE gauti aukšti našumai [226]. Taip pat buvo atliktas tyrimas, analizuojant cianogrupių įtaką medžiagų savybėms. Junginiai be ciano fragmentų BTF1 ir BTF2 pasižymi mažesniu jonizacijos potencialu, krūvininkų dreifiniais judriais, kurie lemia prietaiso našumą, nei jų analogai su cianogrupėmis [245].



20 pav. BTF1–BTF4 struktūrinės formulės [245]

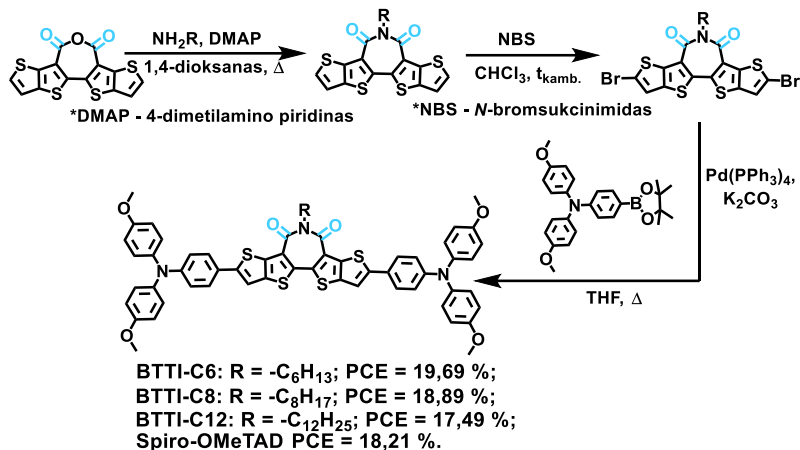
Šias medžiagas (be legiravimo) įterpus į n-i-p tipo prietaisus, buvo pasiektas aukštesnis našumas, nei naudojant spiro-OMeTAD. p-i-n prietaisuose tik SE su BTF4 pasižymėjo didesniu našumu nei prietaisas su standartu PEDOT:PSS.

1 lentelė. Saulės elementų našumo rezultatai naudojant puslaidininkius BTF1–BTF4

Junginio Nr.	Našumas, %
n-i-p	
BTF1	9,97
BTF2	10,45
BTF3	16,34
BTF4	18,03
Spiro-OMeTAD	9,33
p-i-n	
BTF1	11,19
BTF2	11,96
BTF3	15,09
BTF4	17,01
PEDOT:PSS	16,42

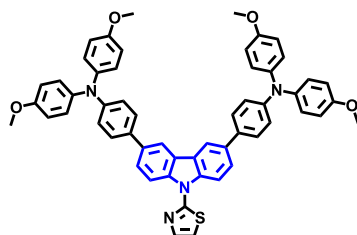
Taip pat buvo sukonstruoti n-i-p prietaisai su karbonilgrupės turinčiais junginiais, kurie pasižymi didesniu efektyvumu ir stabilumu nei SE su legiruotu spiro-OMeTAD [246]. Minėtos naujos medžiagos gautos trijų žingsnių sinteze ir naudotos prietaisuose be priedų. Tyrinėti puslaidininkiai skiriasi alkilgrandinėlių ilgiu. Tiek jonizacijos potencialai, tiek skylių judriai yra labai panašūs. Terminės savybės taip pat yra beveik vienodos. Tačiau didžiausiu našumu pasižymėjo SE, kurioje yra

trumpiausią alkilgrandinėlę turintis junginys BTTI-C6. Tokie rezultatai gaunami dėl geresnės sluoksnio morfologinės būsenos.



4 schema. BTTI darinių sintezės schema [246]

Karbazolo fragmentai taip pat dažnai taikomi STM sintezei. Įprastai karbazolų klasės junginių sintezė būna ganėtinai pigi ir paprasta, o patį karbazolą galima įvairiai modifikuoti, taip keičiant tikslinių produktų savybes. Karbazolą ar jo darinius galima naudoti kaip centrinį fragmentą, o tikslinius junginius naudojant SE fiksuojamas aukštas jų efektyvumas [247, 248]. Pavyzdžiui, panaudojus medžiagą TC-36, turinčią karbazolo centrinį fragmentą buvo pasiektas aukštesnis SC našumas ir didesnis stabilumas, nei naudojant spiro-OMeTAD [249].

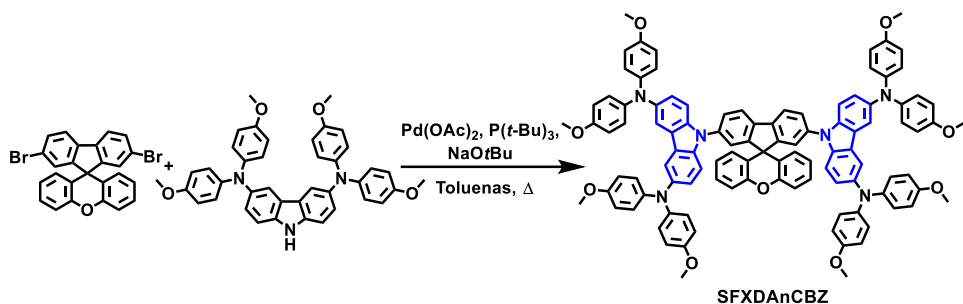


TC-36 PCE = 22,86 %;
Spiro-OMeTAD PCE = 21,77 %;

21 pav. TC-36 struktūrinė formulė [249]

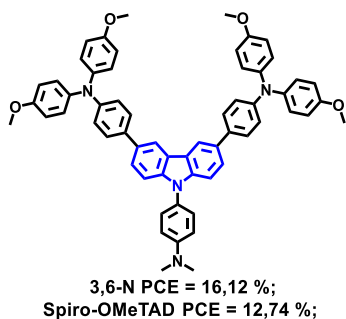
Taip pat aukštų SE našumo rezultatų galima pasiekti naudojant medžiagas, kuriose karbazolilai yra molekulės periferinėje dalyje [199, 250, 251]. Kai kuriais atvejais nepavyksta pasiekti prietaisų, kuriuose naudojamas spiro-OMeTAD, efektyvumo. Tačiau optimizuojant tirpalų, naudojamų STS liejimui, koncentracijas galima pasiekti labai panašių rezultatų. Pavyzdžiui, naudojant vieno žingsnio sinteze gautą medžiagą SFXDAnCBZ SE struktūroje pasiektas 20,87 % našumas. Sluoksniui lieti naudoto tirpalo koncentracija – 28,57 mg/ml. Didinant arba mažinant koncentraciją, SE našumas mažėja. Prietaisai su spiro-OMeTAD pasiekia 21,13 % efektyvumą, tačiau naudojama minėto junginio tirpalo koncentracija yra 85,8 mg/ml.

Nors prietaisų efektyvumai skiriasi mažiau nei 1 %, SE konstruoti sunaudotų STM kiekis skiriasi maždaug tris kartus [210].



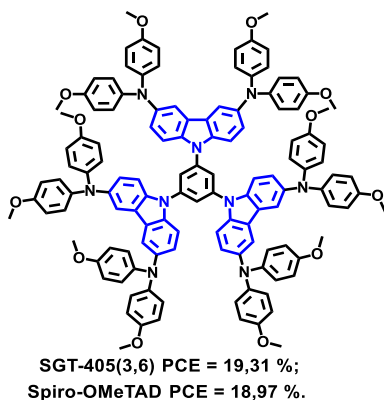
5 schema. SFXDAnCBZ sintezės schema [210]

Karbazolų fragmentus turinčius junginius galima naudoti ir be priedų [220, 252]. Dažniausiai tokiu atveju SC našumas sumažėja, tačiau jis būna didesnis nei prietaisų su nelegiruotu spiro-OMeTAD [220, 253].



22 pav. 3,6-N struktūrinė formulė [253]

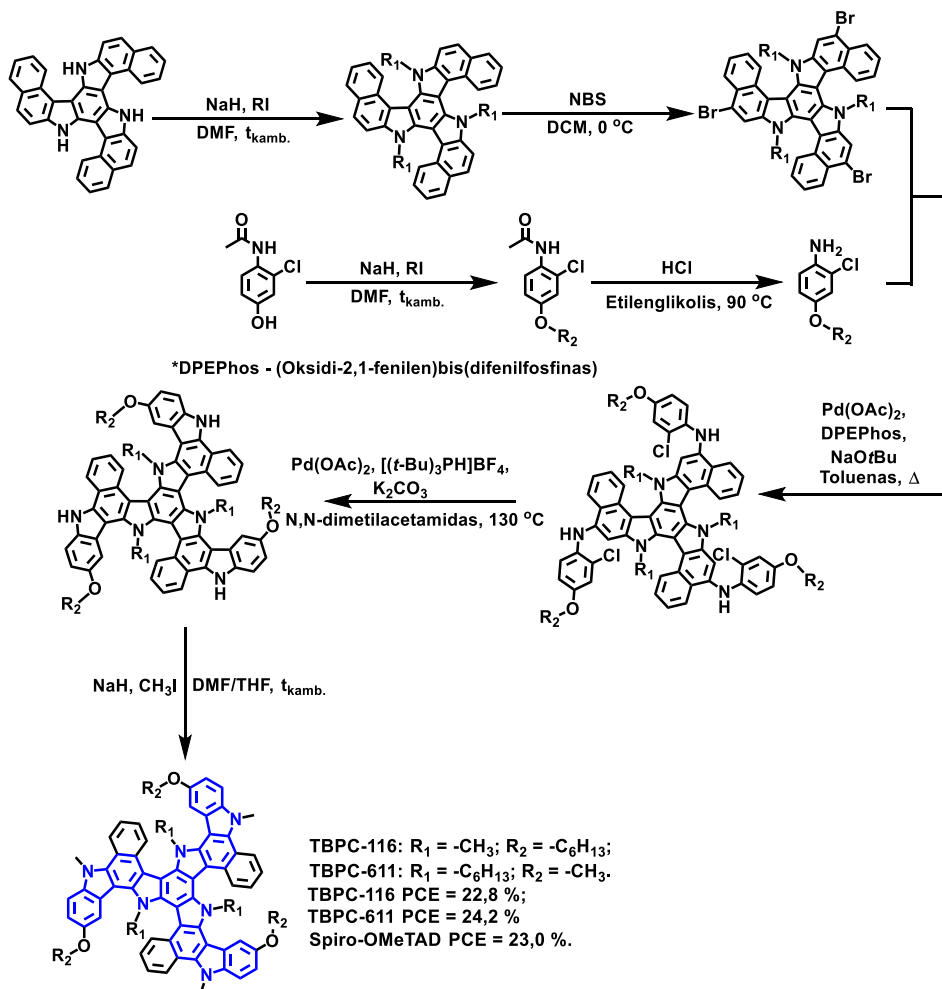
Karbazolilpakaitai dažnai naudojami žvaigždės formos dariniams sintetinti. Karbazolo fragmentas ar jo dariniai gali būti molekulės centre [254-256] arba šonuose [257, 258].



23 pav. SGT-405(3,6) struktūrinė formulė [259]

Dažnu atveju šias medžiagas naudojant SC, gaunamas aukštas našumas ir geras stabilumas. Pavyzdžiui, karbazolilus naudojant kaip šoninius pakaitus, fiksuotas didesnis prietaiso našumas, nei naudojant spiro-OMeTAD [259].

24 % SE efektyvumas fiksuotas panaudojus karbazolo darinį kaip centrinį fragmentą. Tiksliniai junginiai gauti 7 pakopų sinteze. Taip pat publikacijoje apžvelgiama alkilgrandinėls padėties įtaka tiek medžiagų, tiek prietaisų savybėms. Krūvininkų dreifinis judris padidėja tiesiogiai prie karbazolo azoto jungiantis ilgai alkilgrandinėlei. Tikėtina, kad dėl šios priežasties fiksuojamas ir didesnis SE efektyvumas. Taip pat TBPC-611 pasižymi aukštesne stiklėjimo temperatūra [260].



6 schema. TBPC junginių sintezės schema [260]

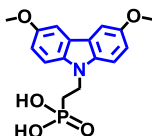
Yra žinoma, jog perovskitas taip pat gali pernešti skyles, todėl galima konstruoti prietaisus be STM [261-263]. Tačiau SC našumai yra mažesni. Tikėtina, kad šiuo atveju geresnių rezultatų būtų galima pasiekti optimizuojant perovskitinio sluoksnio kokybę ir ETM/perovskito paviršių sąsają [126].

2.5. Skyles transportuojančios medžiagos stibio chalkogenidų saulės elementams

Kita intensyviai tiriama naujos kartos saulės elementų rūšis yra stibio chalkogenidų saulės elementai. Pritaikius puslaidininkines medžiagas, tokias kaip PbS, CdS, CdSe, CdTe, In₂S₃, Cu_{2-x}S ir CuInS₂ šviesą absorbuojančiam sluoksniui saulės elementuose, stibio chalkogenidai išsiskyrė pasiekdami bemaž geriausius rezultatus. Vienoje iš pirmųjų publikacijų aprašyto Sb₂S₃ saulės elemento, kuriame kaip skylių transportinė medžiaga panaudotas neorganinis junginys CuSCN, efektyvumas buvo 3,37 % [264]. Naudojant įvairius priedus su šia STM pavyko pasiekti 5,66 % prietaisų efektyvumą [265]. Tačiau stibio chalkogenidų saulės elementų su neorganinėmis STM trūkumas – mažas prietaisų užpildymo koeficientas.

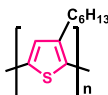
Vienas pirmųjų bandymų padidinti FF, naudojant alternatyvius organinius STM, buvo atliktas Moon su kolegomis [266]. Jie pasiūlė perovskitiniuose saulės elementuose gerai žinomą spiro-OMeTAD, kuris su priedais pasižymi gana aukštu krūvininkų dreifiniu judriu, taip pat šios molekulės energetiniai lygmenys yra palankūs teigiamiesiems krūvininkams sėkmingai keliauti link elektrodo. Naudojant šią medžiagą kaip STM pasiektas mažamolekuliniams junginiams priskiriamas Sb₂S₃ saulės elemento rekordas – 8,0 % [267], o Sb₂(S, Se)₃ SE efektyvumas su šia medžiaga siekia 10,7 % [268].

Junginiai, gebantys suformuoti monosluoksnius, gali būti taikomi ne tik perovskitinių, bet ir stibio sulfido saulės elementų konstrukcijoje [269]. Sb₂S₃ prietaisuose skyles transportuojančio spiro-OMeTAD sluoksnis buvo apdorotas sluoksnį formuojančiu MeO-2PACz. Tokiu būdu pasiektas 8,06 % efektyvumas, o be papildomo apdoravimo – 7,13 %.



24 pav. MeO-2PACz struktūrinė formulė

Manoma, kad monosluoksnis geriau padengia Sb₂S₃ paviršių, taip sumažėjant efektyvumo nuostoliams. Tačiau tolesni tyrimai parodė, kad priedai, naudojami spiro-OMeTAD krūvininkų judriui pagerinti, labai kenkia prietaisų stabilumui. Dėl šios priežasties pradėtos tyrinėti polimerinės medžiagos. Polimerinė skyles transportuojanti medžiaga, kodiniu pavadinimu P3HT, pasižymi aukštu skylių dreifiniu judriu, siekiančiu 0,1 cm²/Vs.

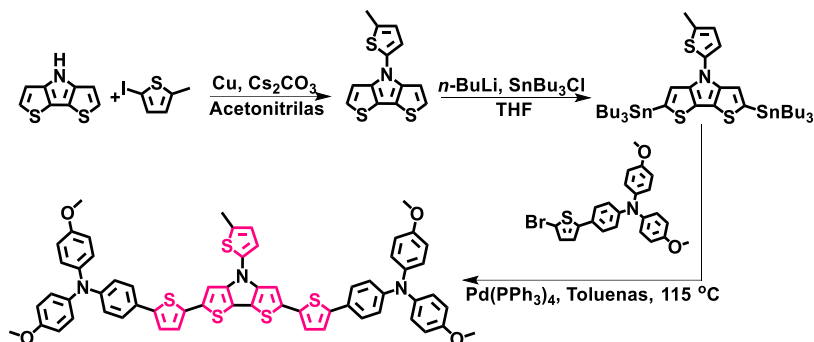


25 pav. Poli(3-heksiltiofen-2,5-diilas) (P3HT)

Šis polimeras gerai tirpsta ir yra termiškai atsparus. P3HT savo struktūroje turi heteroatomą, kuris gali sąveikauti su stibiu, gerėjant skyles transportuojančio ir elektromagnetinę spinduliuotę absorbuojančio stibio chalkogenido paviršių sąveikai.

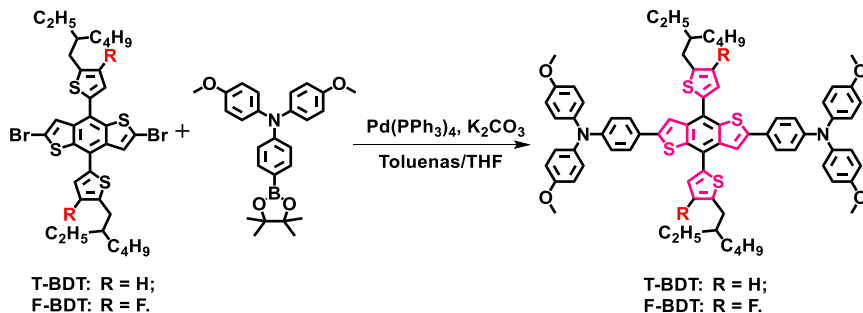
Tačiau jo absorbcijos spektras regimojoje srityje iš dalies sutampa su aktyviojo sluoksni absorbcijos spektru, sumažėjant stibio chalkogenido sugeriamų šviesos fotonų skaičiui. Iki šiol naudojant šią medžiagą kaip STM Sb_2Se_3 saulės elementuose buvo pasiektas 7,44 % efektyvumas [270].

Taip pat stibio chalkogenidų prietaisuose naudojami ir kiti polimerai, turintys tiofeno fragmentus, tokie kaip PCPDTBT, su kuriuo saulės elementų našumas buvo beveik 8,6 % [271], PTB7-th – 5,7 % [272], PCDTBT – 5,11 % [273]. Šios medžiagos gaunamos kelių pakopų sinteze [274-276], kai kuriais atvejais žemose temperatūrose [277], o komerciškai prieinamų junginių kaina didelė [278-281]. Todėl vyksta pigesnių, stabilios amorfinės būsenos ir „parazitine“ absorbcija nepasižyminčių medžiagų paieška, kurios efektyviai veiktų kaip STS ir galėtų būti pritaikytos stibio chalkogenidų SE. Remiantis minėtų polimerų pavyzdžiu, trijų žingsnių sinteze buvo susintetintas ditienpirolo centrinį fragmentą turintis darinys DTPThMe-ThTPA su spiro-OMeTAD molekulėje sutinkamais metoksifenilpakaitais [282].



7 schema. DTPThMe-ThTPA sintezės schema [282]

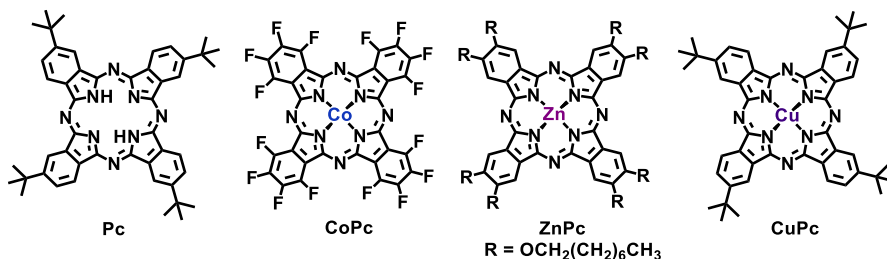
Gauto tikslinio junginio stiklėjimo temperatūra buvo beveik 120 °C, terminio stabilumo temperatūra didesnė nei 400 °C, o skylių dreifinis judris siekė $1,67 \times 10^{-3} \text{ cm}^2/\text{Vs}$. Šią medžiagą panaudojus kaip STM $\text{Sb}_2(\text{S},\text{Se})_3$ saulės elementuose pasiektas 9,69 % efektyvumas, kuris yra didesnis nei prietaiso su spiro-OMeTAD (8,9 %). Tikėtina, kad didesnis efektyvumas buvo gautas dėl didesnio skylių judrio ir sieros atomų sąveikos su stibiu, sumažėjant nuostoliams.



8 schema. T-BDT ir F-BDT sintezės schema [283]

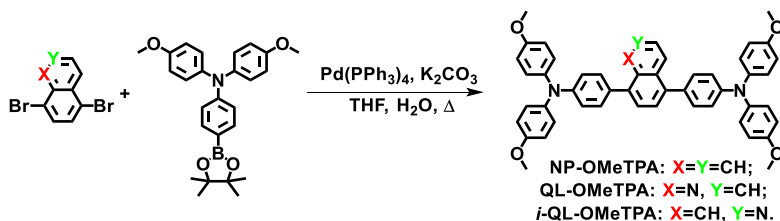
Pasitelkiant panašų struktūrinį molekulės modelį, Suzuki reakcijos sąlygomis susintetinti junginiai T-BDT ir F-BDT, molekulės centre turintys benzoditiofeno fragmentus [283]. Ištyrus gautų medžiagų savybes nustatyta, kad jos yra amorfinės būsenos, o krūvininkų dreifiniai judriai yra didesni nei spiro-OMeTAD (F-BDT – $1,32 \times 10^{-3} \text{ cm}^2/\text{Vs}$, T-BDT – $9,40 \times 10^{-4} \text{ cm}^2/\text{Vs}$, spiro-OMeTAD – $7,84 \times 10^{-4} \text{ cm}^2/\text{Vs}$). Elementas su medžiaga, turinčia elektronų akceptorinę grupę, pasižymėjo didžiausiu našumu – 9,13 %, o prietaisas su junginiu T-BDT pasiekė 8,24 %. Manoma, kad didesnis našumas buvo pasiektas dėl fluoro atomo, kuris, kaip ir tiofenai, sąveikauja su nekoordinuotais Sb^{3+} jonais, gerėjant paviršių sukibimui.

Gerai rezultatai, pasiekti su spiro-OMeTAD, paskatino mokslininkus tyrinėti ir kitas molekules, turinčias standų centrinį fragmentą. Ftalocianinų dariniai pasižymi aukštu skylių judriu [284], geru terminiu ir cheminiu stabilumu, todėl jie yra tinkami testuoti stibio chalkogenidų saulės elementuose. H. Guo ir kt. paskelbė keturių paprastai sintetinamų ftalocianinų darinių [284, 285] naudojimą kaip STM $\text{Sb}_2(\text{S}, \text{Se})_3$ prietaisuose [286]. Naudojant bemetalį ftalocianiną buvo pasiektas aukščiausias SE našumas (8,42 %) ir didesnis stabilumas nei su standartu spiro-OMeTAD (8,28 %).



26 pav. Ftalocianino darinių struktūrinės formulės [286]

Pasitelkiant Suzuki reakcijos sąlygas, naudojant {4-[bis(4-metoksifenil)amino]fenil}borono rūgštį, 1,4-dibromnaftaleną / 5,8-dibromchinoliną / 5,8-dibromizochinoliną ir paladžio katalizatorių, susintetinti trys nauji chinolino dariniai, molekulės periferijoje turintys 4,4'-dimetoksitrifenilamino chromoforus [287].

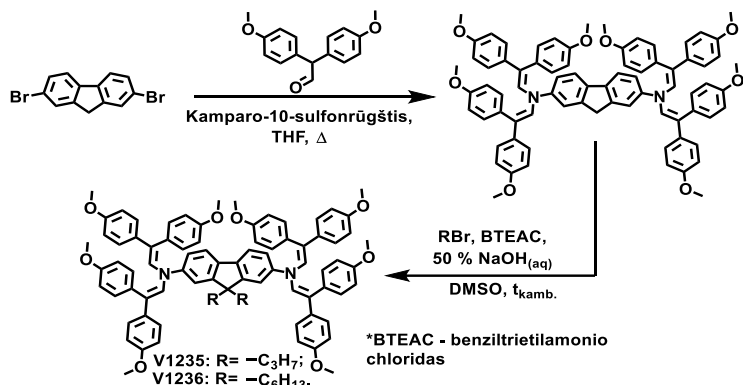


9 schema. Chinolino darinių sintezės schema [287]

Šias medžiagas panaudojus kaip STM saulės elementuose pasiektas didesnis našumas nei su etalonu spiro-OMeTAD (NP-OMeTPA – 5,35 %, QL-OMeTPA – 5,61 %, *i*-QL-OMeTPA – 4,35 %, spiro-OMeTAD – 5,26 %). Lyginant NP-OMeTPA ir QL-OMeTPA matoma, kad SE su medžiaga, turinčia piridino fragmentą, pasižymi didesniu efektyvumu. Tikėtina, kad heteroatomas sąveikauja su nekoordinuotu Sb^{3+}

jonu, taip atsirandant geresniam paviršių sukibimui. Tačiau prietaisų su *i*-QL-OMeTPA našumas yra mažesnis, galbūt dėl mažesnio krūvininkų dreifinio judrio. Taip pat saulės elementai, į kurių sudėtį įeina medžiagos su piridino fragmentu, pasižymi didesniu ilgalaikiu stabilumu.

KTU Organinės chemijos katedroje buvo susintetintos enaminų klasės medžiagos, gautos kondensacijos metodu iš 2,7-diamino fluoreno ir 2,2-bis(4-metoksifenil)acetaldehido. Nors SE su naujomis medžiagomis ir nepasiekė rekordinio našumo, tačiau prietaiso su enaminu V1236 našumas buvo didesnis (3,9 %) nei su gerai ištirtu P3HT (3,7 %) [13]. Šis rezultatas buvo pagerintas (4,3 %) tikslinio STM centriniame fluoreno fragmente esant trumpesnėms alkilgrupėms (V1235) [288].



10 schema. V1235 ir V1236 sintezės schema [13, 288]

Svarbu paminėti, kad STM, skirtų stibio chalkogenidų saulės elementams, nėra labai daug. Matoma, jog tinkamai parinkus junginius skylių transportiniams sluoksniams formuoti galima padidinti prietaiso efektyvumą. Kaip minėta anksčiau, Sb chalkogenido sluoksniis pasižymi dideliu stabilumu, todėl šios medžiagos pagrindu pagaminti prietaisai yra labai perspektyvūs ir jų tyrinėjimas bei tobulinimas yra labai aktualus.

2.6. Literatūrinės apžvalgos apibendrinimas

Atsinaujinantys energijos šaltiniai kasmet vis labiau populiarėja. 2024 m. daugiau nei trečdalis Lietuvoje suvartotos energijos pagaminta saulės ir vėjo elektrinėmis [289]. Yra žinoma, jog komerciškai prieinamų saulės elementų efektyvumas siekia maždaug 21–22 % efektyvumu. Mokslininkai siekia našumą padidinti keisdami SE konstrukcijas arba naudodami naujas medžiagas jau žinomiems prietaisams. Stibio sulfido saulės celės pasižymi geru aktyviojo sluoksnio patvarumu. Tikėtina, kad tinkamai parinktos medžiagos ir jų liejimo metodai galėtų padidinti SE našumą. Perovskitiniai saulės elementai laikomi vienais perspektyviausių prietaisų, kurie galėtų dideliu našumu generuoti elektros energiją. Tačiau šiuo metu pastarieji elementai nėra labai stabilūs. Taip nutinka dėl paties perovskito defektų. Dar viena stabilumo mažėjimo priežasčių yra kristalizuotis galinčios spiro-OMeTAD medžiagos naudojimas, kuriai kristalizuojantis STM sluoksnyje susidaro tarpeliai, todėl perovskitas ir elektrodas kontaktuoja tiesiogiai, reaguojant laisvai

migruojantiems jonams ir užteršiant elektrodo paviršių. Taip pat spiro-OMeTAD krūvininkų dreifinis judris nėra didelis, todėl reikalingi legirantai, laidumui pagerinti ir skylių dreifiniam judriui paspartinti. Dėl šių priežasčių mokslininkai ieško spiro-OMeTAD alternatyvų, kurios ne tik pasižymėtų dideliu krūvininkų judriu, bet ir būtų morfologiškai stabilios. Prieš tai aptartos medžiagos, turinčios fluorenil-, karbazolil-, akceptorinių pakaitų, pasižymi geromis fotoelektrinėmis ir terminėmis savybėmis, todėl šių medžiagų tyrimai yra aktualūs. Tikėtina, jog naudojant šiuos fragmentus kartu ar atskirai galima susintetinti labai perspektyvius puslaidininkius, kurie gali būti panaudoti kaip STM hibridiniams saulės elementams.

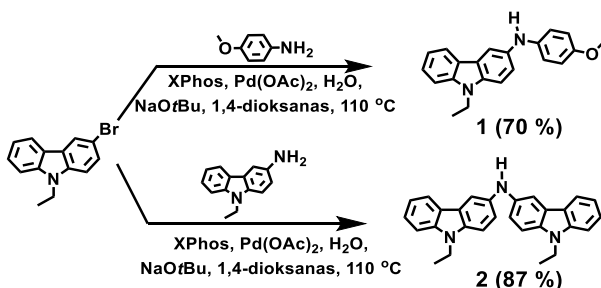
3. PUBLIKACIJŲ APŽVALGA

Norint, kad naujos kartos saulės elementai būtų tinkami ilgalaikiam paprasto vartotojo naudojimui ir konkuruotų su komerciniais silicio saulės elementais, reikia užtikrinti jų ilgaamžiškumą, aukštą našumą ir konkurencingą kainą. Tai galima padaryti parinkus tinkamas medžiagas celėms konstruoti. Žinoma, kad STM yra labai svarbi saulės elemento sudėtinė dalis, galinti pagerinti jo savybes. Keičiant STM molekulės struktūrą, varijuojant įvairiomis funkcinėmis grupėmis galima labai padidinti prietaiso našumą ir (ar) ilgaamžiškumą. Šiuo metu geriausias perovskitinių saulės elementų efektyvumas fiksuojami kaip STM naudojant spiro-OMeTAD. Tačiau šio junginio sintezė yra gana sudėtinga, išeiga nėra didelė ir pasitaiko atvejų, kuomet šis junginys susikristalizuoja saulės elemente, atsirandant tarpeliams, dėl kurių nevyksta efektyvi krūvininkų pernaša. Todėl mokslininkai ieško stabilesnių ir pigesnių šios medžiagos alternatyvų, išlaikant panašų prietaisų efektyvumą.

3.1. Skyles transportuojančios medžiagos, molekulės centre turinčios fluorenilchromoforus, efektyviems perovskitiniams saulės elementams

Šiame skyriuje nagrinėjami nauji fluoreno klasės junginiai, remiantis publikuotu straipsniu: *Solar RRL*, **2022**, 6, 2100990, A. Jegorovė, C. Momblona, M. Daskeviciene, A. Magomedov, R. Degutyte, A. M. Asiri, V. Jankauskas, A. A. Sutanto, H. Kanda, K. Brooks, N. Klipfel, M. N. Nazeerudin, V. Getautis [290]; cituota 11 kartų.

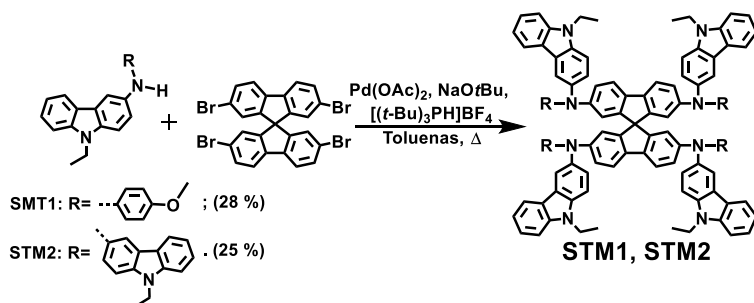
Kaip minėta anksčiau, spiro-OMeTAD sintezė yra gana sudėtinga, tikslinis junginys yra kristalinės būsenos, todėl atsiranda rizika pastarojo sluoksniui susikristalizuoti saulės elemente, atsirandant efektyvumo nuostoliams. Todėl manyta, kad medžiagos kristališkumą galima sumažinti didinant puslaidininkio molekulę ir modifikuojant ją alkilfunkcinėmis grupėmis. Kadangi karbazolo dariniai yra vieni populiariausių bei pigiausių STM sintezei naudojamų fragmentų, buvo nuspręsta susintetinti spiro-OMeTAD analogus, kuriuose 4-metoksifenilchromoforai keičiami 9-etilkarbazolilais, tikintis, kad jie pagerins morfologines ir fotoelektrines tikslinių junginių savybes. Taip pat buvo sintetinami jų „pusiniai“ analogai, siekiant išsiaiškinti, ar fluorenilo centrinių fragmentų turintys junginiai perovskitiniuose SE veiks taip pat efektyviai kaip ir spirobifluorenų klasės junginiai.



11 schema. 9-etil-*N*-(4-metoksifenil)-9*H*-karbazol-3-amino (1) ir bis(9-etil-9*H*-karbazol-3-il)amino (2) sintezė

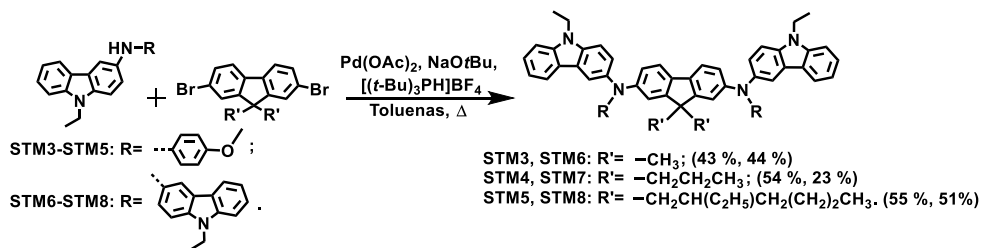
Šioje publikacijoje nagrinėjama aštuonių naujų fluoreno darinių sintezė, savybės ir jų pritaikymas perovskitiniuose saulės elementuose. Pirmiausia, Buchwaldo–Hartwigo amininimo reakcijos sąlygomis, naudojant Pd katalizatorių, buvo susintetinti aminai **1** ir **2**, turintys 9-etilkarbazolilchromoforus (11 schema).

Naujas spiro-OMeTAD analogas **STM1**, turintis spirobifluoreno centrinį fragmentą, šonines 4-metoksifenil- ir alkilkarbazolilgrupes, buvo susintetintas Buchwaldo–Hartwigo kopuliavimo reakcijos sąlygomis, sujungiant 2,2',7,7'-tetrabrom-9,9'-spirobi-(9H-fluoreną) su antriniu aminu **1**, naudojant paladžio acetatą ($\text{Pd}(\text{OAc})_2$) kaip katalizatorių (4 schema). Vietoj amino **1** panaudojus bis(9-etil-9H-karbazol-3-il)aminą (**2**), buvo susintetintas spiro-OMeTAD analogas **STM2**, turintis tik 9-etilkarbazolilchromoforus periferinėje STM molekulės dalyje (12 schema).



12 schema. Spiro-OMeTAD analogų **STM1** ir **STM2** sintezė

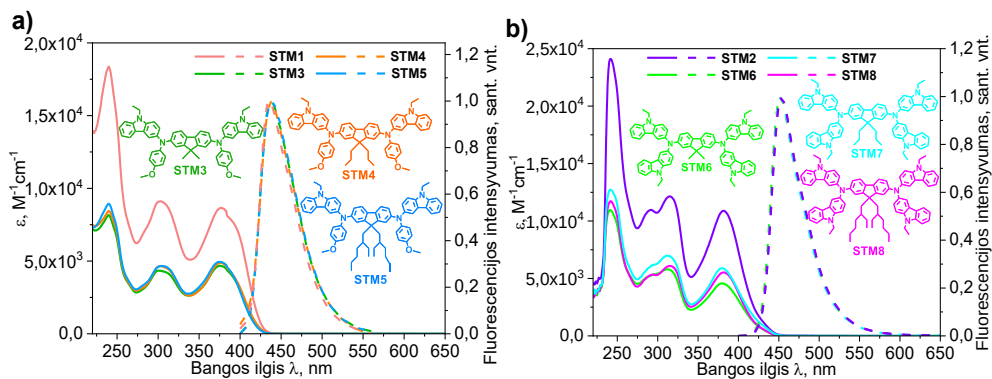
Buchwaldo–Hartwigo reakcijos sąlygomis 9-alkil-2,7-dibromfluoreną veikiant pirmiau minėtais antriniais aminais **1** ir **2** buvo susintetinti „pusiniai“ spiro-OMeTAD analogai **STM3–STM8**, turintys du ir keturis karbazolilchromoforus periferinėje STM molekulės dalyje, o centre – 9-padėtyje įvairius alkilpakeitimus turintį fluorenilchromoforą (13 schema).



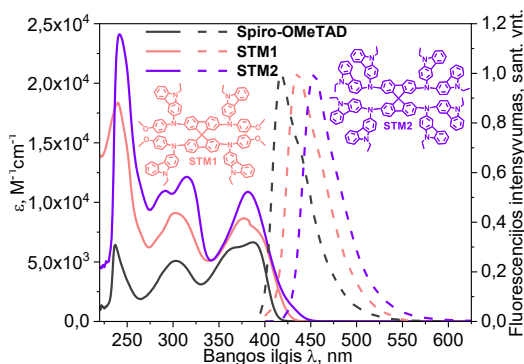
13 schema. „Pusinių“ spiro-OMeTAD analogų **SMT3–STM8** sintezė

Norint įvertinti, kaip/ar keičiasi konjuguotos π -elektronų sistemos susintetintuose STM, buvo užrašyti ultravioletinės–regimosios šviesos (UV–RŠ) ir fluorescencijos (FL) spektrai. Gauti rezultatai pateikiami 2 lentelėje ir 27, 28 pav. Iš gautų rezultatų matoma, kad mažesnės medžiagos – „pusiniai“ spiro-OMeTAD analogai pasižymi mažesnio intensyvumo absorbcijos smailėmis nei jų spirobifluorenų klasės analogai. Taip pat lyginant **STM1** bei **STM3–STM5** ir analogiškai **STM2** bei **STM6–STM8** nėra matomų ryškių absorbcijos maksimumų

verčių poslinkių. Tai įrodo, kad skirtingas skaičius 4-metoksifenil- ir (ar) karbazolilchromoforų nepaveikia naujų skylių transportinių medžiagų konjugacijos.



27 pav. THF tirpalų UV–RŠ absorbcijos spektrai (linijos) ir normalizuoti fluorescencijos spektrai (punkttyrinės linijos): a) **STM1** ir **STM3–STM5**; b) **STM2** ir **STM6–STM8** (UV–RŠ $c = 10^{-4}$ mol/l, FL $c = 10^{-5}$ mol/l)



28 pav. **STM1**, **STM2** ir spiro-OMeTAD THF tirpalų UV–RŠ absorbcijos spektrai (linijos) ir normalizuoti fluorescencijos spektrai (punkttyrinės linijos) (UV–RŠ $c = 10^{-4}$ mol/l, FL $c = 10^{-5}$ mol/l)

Lyginant spirobifluorenų klasės junginius tarpusavyje, matoma, kad **STM1** ir **STM2** absorbcijos spektrai vizualiai panašūs į spiro-OMeTAD. Pastebimi tik maži pakitimai, kuriuos lemia metoksifenilpakaitų pakeitimas karbazolilchromoforais. Didėjant karbazolilpakaitų skaičiui molekulėje intensyvėja absorbcijos maksimumai (hiperchrominis efektas). Nagrinėjant fluorescencijos spektrus, pastebimas bathochrominis poslinkis (**spiro-OMeTAD** – 417 nm, **STM1** – 435 nm, **STM2** – 453 nm) galimai sukeltas didelio energijų skirtumo tarp nesužadintos ir sužadintos molekulių būsenų.

Gauti tiksliniai junginiai saulės elementuose naudojami plonų plėvelių pavidalu. Vienas pigiausių ir paprasčiausių būdų suformuoti medžiagos plėvelę yra sukamojo liejimo metodas. Tačiau ne visada pavyksta gauti vientisas plėveles. Tam, kad medžiagų plėvelės būtų homogeniškos, tiksliniai junginiai turi būti termiškai patvarūs ir turėti aukštą stiklėjimo temperatūrą.

Naujų STM masės nuostoliai, esant aukštomis temperatūroms, nustatyti termogravimetrinės analizės metodu (TGA). Tikslinių puslaidininkių stiklėjimo temperatūros nustatytos diferencinės skenuojamosios kalorimetrijos metodu (DSK). Gauti duomenys pateikti 2 lentelėje.

2 lentelė. Terminės, optinės ir fotofizikinės naujų junginių savybės

Junginys	T_{st} , °C ^a	T_{sk} , °C	λ_{abs} , nm ^b	I_p , eV	μ_0 , cm ² /Vs, ($E_0 = 0$ V/cm)
9,9'-spirobifluoreno fragmentą turinčios medžiagos					
Spiro-OMeTAD [291]	124	449	237, 303, 367, 387	5,0	$4,1 \times 10^{-5}$
STM1	169	438	240, 303, 377	5,28	$5,6 \times 10^{-6c}$
STM2	139	512	242, 291, 315, 382	4,90	$3,6 \times 10^{-4c}$
Fluoreno fragmentą turinčios medžiagos su 4-metoksifenil- ir karbazolilchromoforais					
STM3	147	452	240, 301, 376	4,93	$3,9 \times 10^{-4}$
STM4	133	441	240, 303, 377	4,95	$3,9 \times 10^{-4}$
STM5	77	401	240, 305, 375	5,02	$2,9 \times 10^{-5}$
Fluoreno fragmentą turinčios medžiagos su karbazolilchromoforais					
STM6	196	490	241, 292, 312, 380	4,85	$3,6 \times 10^{-5c}$
STM7	183	461	242, 297, 312, 380	4,85	$1,2 \times 10^{-5c}$
STM8	127	515	242, 295, 315, 382	4,96	3×10^{-5c}

^aStiklėjimo temperatūros fiksuotos diferencinės skenuojamosios kalorimetrijos antrojo kaitinimo metu; ^bUV–RŠ spektruose fiksuoti absorbcijos maksimumų poslinkiai (THF, $c = 10^{-4}$ mol/l); ^cmedžiagų krūvininkų dreifinis judris, apskaičiuotas ekstrapoliuojant matavimų kompozicijose (1:1) su polikarbonatu Z (PC-Z), rezultatus.

Visi nauji junginiai 5 % masės praranda juos kaitinant aukštesnėje nei 400 °C temperatūroje. Toks atsparumas aukštomis temperatūroms yra didelis privalumas, nes veikdamas saulės elementas gali įkaisti iki ~60 °C [292]. Lyginant šiame darbe susintetintų spirobifluorenų klasės junginių ir literatūroje pateiktus spiro-OMeTAD TGA tyrimo rezultatus, galima teigti, kad keturių 4-metoksifenilgrupių pakeitimas karbazolo fragmentais šiek tiek sumažina T_{sk} . (spiro-OMeTAD – 449 °C [291], **STM1** – 438 °C). Įdomu, jog visų 4-metoksifenilchromoforų pakeitimas karbazolilpakaitais, labai didina junginių terminį atsparumą (**STM2** – 512 °C).

Naujos fluorenų klasės medžiagos, turinčios du karbazolo fragmentus molekulėje, 5 % masės praranda 401–452 °C diapazone. Mažiausia terminio atsparumo temperatūra užfiksuota junginio **STM5**, turinčio dvi šakotas alkilgrandinėles centriniame fluoreno fragmente.

STM, turinčios keturis karbazolilchromoforus molekulėje, 5 % masės praranda aukštesnių temperatūrų diapazone (461–515 °C). Šių medžiagų atveju pastebimas ir kitas įdomus efektas – medžiaga **STM8**, turinti šakotus alkilpakaitus, pasižymi

aukščiausia terminio atsparumo temperatūra. Galbūt, esant didesnei molekulinei masei, vyksta stipresnė sąveika tarp junginio molekulių, susidarant ganėtinai tvarkingam erdviniam išsidėstymui, lemiančiam padidėjusią 5 % masės nuostolių temperatūrą.

Lyginant spirobifluorenų klasės medžiagų ir spiro-OMeTAD stiklėjimo temperatūras matomas T_{st} padidėjimas, didėjant molekulinei masei (spiro-OMeTAD – 124 °C [291], **STM1** – 169 °C), tačiau iki tam tikros ribos (**STM2** – 139 °C). Nagrinėjant „pusinius“ spiro-OMeTAD analogus matoma, jog, ilgėjant alkilgrandinėlei centriniame molekulės fragmente, stiklėjimo temperatūrų skaitinė vertė mažėja (**STM3** – 147 °C, **STM4** – 133 °C, **STM5** – 77 °C ir **STM6** – 196 °C, **STM7** – 183 °C, **STM8** – 127 °C). Lyginant junginių, turinčių 4-metoksifenil- ir karbazolilchromoforus (**STM3–STM5**), ir medžiagų, turinčių tik karbazolilpakaitus (**STM6–STM8**) T_{st} duomenis matoma, kad mažesnės molekulės pasižymi ~50 °C mažesne stiklėjimo temperatūra. Toks efektas pastebimas dėl mažesnio molekulės simetriškumo, kuris lemia netvarkingą erdvinį struktūrų išsidėstymą. Mažiausia T_{st} užfiksuota junginio **STM5** (T_{st} – 77 °C). Tikėtina, kad tokia stiklėjimo temperatūra yra per žema norint panaudoti šią medžiagą saulės elementuose. Visų kitų naujų STM stiklėjimo temperatūros yra aukštesnės nei 100 °C, todėl jos tinkamos naudoti saulės elementuose, nes T_{st} yra gerokai didesnė už prietaiso darbinę temperatūrą.

Svarbu paminėti, kad visų naujų junginių DSK tyrimo metu kristalų išsilydymo procesą reiškiantys endoterminiai virsmai neužfiksuoti. Iš gautų rezultatų galima spręsti, jog medžiagos yra tik amorfinės būsenos. Tokiu atveju, formuojant junginių plėveles, galima gauti homogeniškus sluoksnius, kurie ilgainiui nekeis morfologinės būsenos.

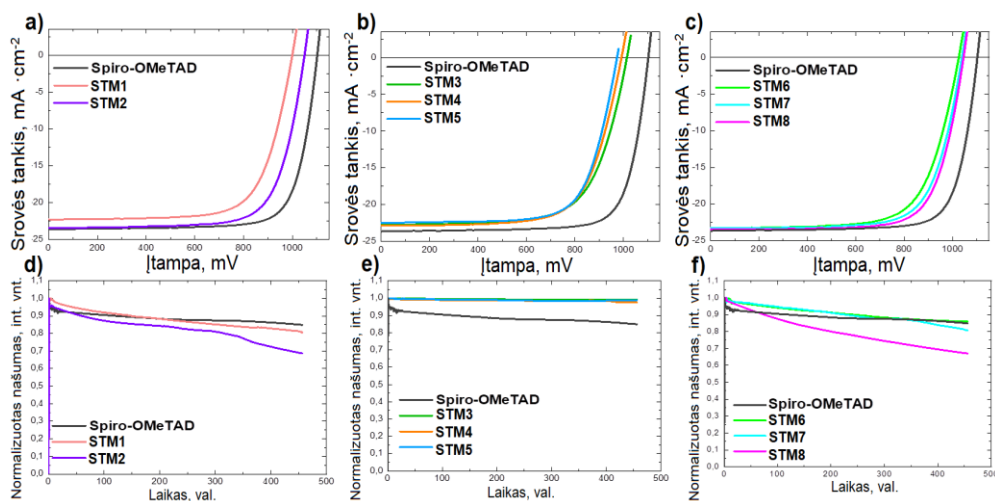
Norint išsiaiškinti, ar gauti tiksliniai junginiai yra energetiškai suderinami su perovskito ir elektrodo sluoksniais, buvo atlikti elektronų fotoemisijos ore matavimai, nustatant jonizacijos potencialų (I_p) vertes. Gauti rezultatai pateikiami 2 lentelėje. Lyginant spirobifluorenų klasės medžiagų I_p skaitines vertes, matoma, kad karbazolo fragmentai molekulėje sumažina jonizacijos potencialą (spiro-OMeTAD – 5,0 eV, **STM1** – 4,83 eV). Manoma, jog vertės pokytis vyksta dėl to, kad karbazolo fragmentai lengviau oksiduojasi. Tačiau molekulėje esant daugiau karbazolilchromoforų, pastebimas priešingas efektas – jonizacijos potencialas šiek tiek padidėja (**STM2** – 4,9 eV). Šiuo atveju dėl didelių pakaitų gausos galbūt plėvelėje molekulės yra labai suvaržytos ir karbazolilpakaitų išsidėstymas yra netvarkingas, kas lemia nežymų I_p padidėjimą.

Sugretinus fluorenų klasės junginių rezultatus akivaizdu, kad alkilgrandinės ilgis didina jonizacijos potencialus (**STM3** – 4,93 eV, **STM4** – 4,95 eV, **STM5** – 5,02 eV ir **STM6** – 4,85 eV, **STM7** – 4,85 eV, **STM8** – 4,96 eV). Tikėtina, kad toks efektas vyksta dėl tam tikro molekulių erdvinio išsidėstymo. Didesnis karbazolilchromoforų kiekis molekulėje sumažina I_p dėl lengvesnės jų oksidacijos. Visgi visų susintetintų STM oksidacijos potencialai yra suderinami su SC naudojamu perovskito energiniais lygmenimis.

Krūvininkų dreifinis judris μ taip pat labai svarbus saulės elementų veikimui. Manoma, kad egzistuoja koreliacija tarp krūvininkų kryptingo judėjimo greičio ir saulės elemento efektyvumo, t. y. kuo didesnis greitis, tuo daugiau elementas

sugeneruoja elektros energijos. Dalies grynų medžiagų nepavyko pamatuoti, todėl jos maišytos su PC-Z. Gautos skaitinės vertės perskaičiuotos ekstrapoliuojant duomenis, taip apskaičiuojant junginių krūvininkų dreifinio judrio rezultatus (2 lentelė). Akivaizdu, kad ilgesnės alkilgrandinės centriniame fluoreno fragmente sumažina krūvininkų judrį. Galbūt judrumas mažėja dėl didesnių atstumų tarp molekulių ilgėjant alkilgrandinėms ir (ar) dėl nepalankaus išsidėstymo erdvėje. Tikėtina, jog dėl analogiškos priežasties krūvininkų dreifinį judrį mažina ir karbazolilchromoforai STM struktūroje. Tačiau spirobifluorenų klasės junginiams stebimas atvirkštinis efektas – visus šoninius fragmentus pakeitus karbazolilchromoforais, kryptingas krūvininkų judris padidėja. Remiantis gautais rezultatais galima teigti, kad naujų STM krūvininkų dreifinis judris yra tinkamas, norint šias medžiagas panaudoti perovskitiniuose SE.

Atlikus terminius ir fotoelektrinius tyrimus bei įsitikinus, kad susintetinti nauji junginiai gali būti panaudoti perovskitiniuose saulės elementuose, buvo sukonstruoti n-i-p struktūros SE. Geriausių prietaisų rezultatai pateikiami 29 paveiksle ir 3 lentelėje. Buvo sukonstruoti šios struktūros saulės elementai: FTO / c-TiO₂ / m-TiO₂ / SnO₂ / perovskitas [(FAPbI₃)_{0,87}(MAPbBr₃)_{0,13}]_{0,92}(CsPbI₃)_{0,08} / STM / Au. Teigiamuosius krūvininkus pernešanti medžiaga naudota kartu su 4-*tret*-butilpiridinu (tBP), ličio bis(trifluormetansulfonil)imidu (LiTFSI) ir tri[2-(1*H*-pirazol-1-il)-4-*tret*-(butilpiridin)]kobalto tris[bis(trifluormetilsulfonil)]imidas (CoTFSI, FK209).



29 pav. Geriausių saulės elementų J - V kreivės ir stabilumo tyrimas, kaip STM naudojant: a), d) spiro-OMeTAD, STM1 ir STM2; b), e) STM3–STM5; c), f) STM6–STM8. Stabilumo tyrimas atliktas neįkapsuliuojant prietaisų, N₂ aplinkoje, 25 °C

Lyginant spirobifluorenų klasės junginius (spiro-OMeTAD analogus) matoma, kad keičiant 4-metoksifenilpakaitus karbazolilchromoforais, saulės elementų efektyvumas mažėja. Tikėtina, kad atvirosios grandinės įtampos (V_{oc}) nuosmukį sukelia didesnė rekombinacija, dėl perovskito/STM paviršių sandūroje esančių tarpelių ar netolygumų. Nepaisant to, sukonstruoti SE siekia 17,6 % (STM1) ir 18,3 %

(STM2) efektyvumus, nedaug atsiliekančius nuo kontrolinio prietaiso su spiro-OMeTAD (20,1 %). Saulės elementai, kuriuose kaip STM naudoti susintetinti „pusiniai“ spiro-OMeTAD analogai, pasižymi šiek tiek mažesniu našumu. Didesnis efektyvumas pasiektas naudojant medžiagas, turinčias keturis karbazolilchromoforus. Pagal 3 lentelėje pateiktus duomenis galima teigti, kad, prietaisuose naudojant STM, turinčias karbazolil- ir 4-metoksifenilpakaitus, elementų efektyvumas siekia 16 %. Manoma, kad mažesnę našumą lemia blogesnė perovskito/STM paviršių sąveika. Kaip minėta anksčiau, 4-metoksifenil- ir karbazolilchromoforus turinčios STM (STM3–STM5) pasižymi mažesniu simetriškumu nei jų analogai, turintys tik karbazolilpakaitus (STM6–STM8).

3 lentelė. Saulės celių našumo parametrai, gauti iš J – V kreivių

Junginio Nr.	V_{oc} , mV	J_{sc} , mA · cm ⁻²	FF	PCE , %
9,9'-spirobifluoreno fragmentą turinčios STM				
Spiro-OMeTAD	1108	23,60	0,77	20,1
STM1	1000	22,32	0,79	17,6
STM2	1059	23,41	0,74	18,3
Fluoreno fragmentą turinčios STM su 4-metoksifenil- ir karbazolilchromoforais				
STM3	1014	22,80	0,68	15,7
STM4	992	22,89	0,69	15,7
STM5	987	22,35	0,73	16,1
Fluoreno fragmentą turinčios STM su karbazolilchromoforais				
STM6	1034	23,37	0,71	17,2
STM7	1045	23,32	0,73	17,8
STM8	1048	23,35	0,74	18,1

Galbūt, liejant sluoksnius, metoksibenzono ir karbazolo fragmentus turinčios STM molekulės išsidėsto erdvėje toli viena nuo kitos, taip veikiant perovskito/STM sandūros paviršiaus morfologiją, sumažinant krūvininkų dreifinį judrį ir suaktyvinant paviršių sandūroje vykstančius rekombinacijos procesus [293]. Alkilgrandinėlių ilgis beveik nepaveikia trumpojo jungimo srovės tankio, kurio skaitinės vertės yra bemaž vienodos 22,4–22,8 mA cm⁻², elementuose naudojant **STM3–STM5** ir 22,3 mA cm⁻², naudojant **STM6–STM8** kaip STM.

Neįkapsuliuotų sukonstruotų prietaisų stabilumas tirtas N₂ aplinkoje, 25 °C temperatūroje (29 pav., d–f). Lyginant spiro-OMeTAD ir jo analogų rezultatus galima teigti, kad saulės elemento stabilumas mažėja didėjant STM molekulei. Per 450 prietaiso veikimo valandų maksimalus spiro-OMeTAD našumas iš 100 % nukrenta iki 85 %, **STM1** – 81 % ir **STM2** – 69 %. Panaši tendencija stebima „pusinių“ spiro-OMeTAD analogų, turinčių tik karbazolilchromoforus, atveju – ilgėjant alkilgrandinėlei SE efektyvumas mažėja (**STM6** – 86 %, **STM7** – 81 % ir **STM8** – 67 %). Nurodytomis sąlygomis testuojant SE, kurių sudėtyje yra STM, turinčių 4-metoksifenil- ir karbazolilpakaitus (**STM3–STM5**), efektyvumas beveik nekito.

Taigi perovskitiniai SE, kuriuose panaudoti nauji organiniai puslaidininkiai, efektyvumu šiek tiek nusileidžia prietaisams, kuriuose naudojamas etalonas spiro-OMeTAD. Tačiau akivaizdu, jog fluorenil- centrinį fragmentą bei 4-metoksifenil- ir

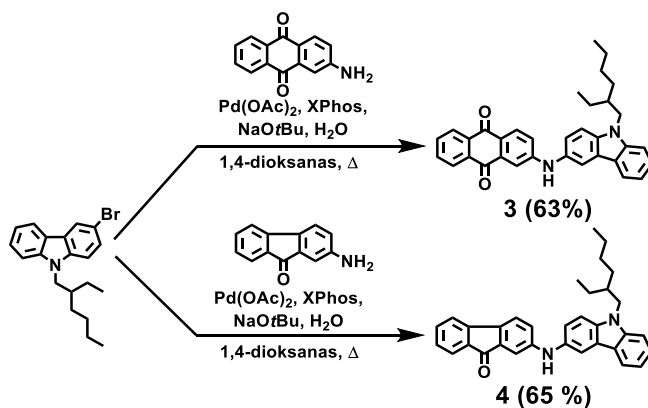
karbazolilpakaitus molekules periferinėje dalyje turinčios medžiagos (**STM3–STM5**) užtikrina puikų sukonstruotų prietaisų stabilumą.

3.2. Bipoliniai krūvių transportuojantys fluoreno dariniai

Remiantis publikuotu straipsniu *RSC Adv.*, **2024**, 14, 2975, *A. Jegorovė, M. Daskeviciene, K. Kantminiene, V. Jankauskas, R. J. Čepas, A. Gruodis, V. Getautis ir K. Genevičius* [294] (*cituota 1 kartą*) šiame skyriuje aprašomi donorinius ir akceptorinius fragmentus turintys bei abiejų ženklų krūvininkus transportuojantys fluoreno dariniai.

Žinant, kad bipolinės medžiagos gali sąveikauti su perovskito sluoksniu, taip sumažinant rekombinacijos procesus šių sluoksnių sandūroje ir gerinant saulės elementų našumą bei stabilumą [241, 242], buvo nuspręsta pirmiau pristatytus fluoreno fragmentą molekules centre turinčius junginius modifikuoti, susintetinant krūvininkus transportuojančias medžiagas, turinčias tiek donorinius, tiek akceptorinius chromoforus molekules periferinėje dalyje. Publikacijoje aprašomi šeši bipoliniai krūvių transportuojantys fluoreno dariniai.

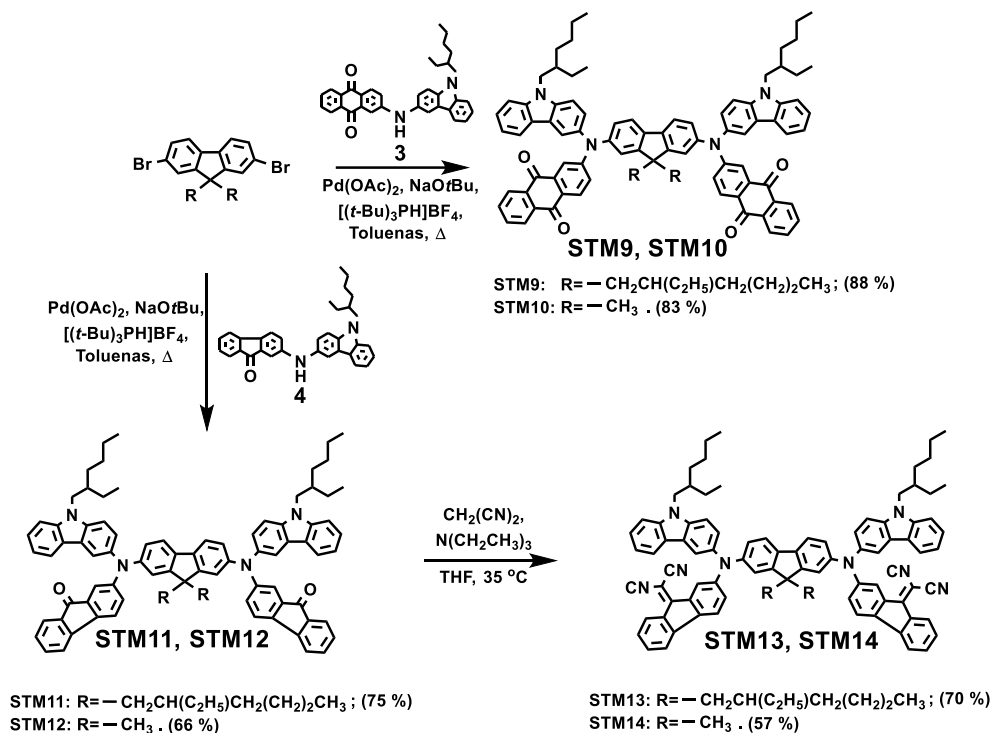
Pirmiausia susintetinti tikslių junginių šoniniai fragmentai, turintys karbazolil- ir antrachinono-/9*H*-fluorenono chromoforus (14 schema).



14 schema. Tarpinių šoninių fragmentų **3** ir **4** sintezė

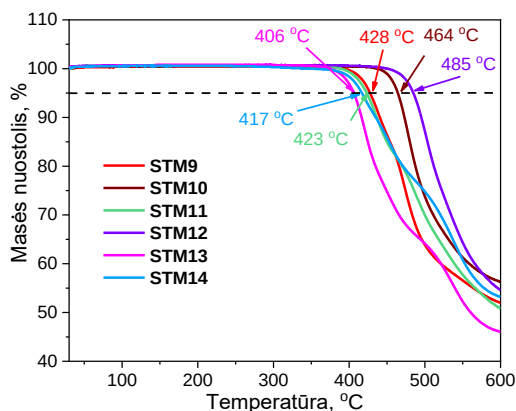
3-brom-9-(2-etilheksil)karbazolui Buchwaldo–Hartwigo metodikos sąlygomis reaguojant su 2-aminoantrachinonu bei 2-amino-9*H*-fluorenonu, buvo gauti aminai **3** ir **4**, turintys tiek elektrondonorinių, tiek elektronakceptorinių savybių chromoforų. Bipoliniai fluoreno dariniai **STM9** ir **STM10**, turintys 9,9-dialkil-9*H*-fluoreno centrinį fragmentą bei šonines alkilkarbazolilo / antrachinono grupes, buvo susintetinti Buchwaldo–Hartwigo kopuliavimo reakcijos sąlygomis, sujungiant 2,7-dibrom-9,9-dimetil-9*H*-fluoreną ir 2,7-dibrom-9,9-di(2-etilheksil)-9*H*-fluoreną su aminu **3**, naudojant Pd(OAc)₂ kaip katalizatorių (15 schema). Vietoj amino **3** panaudojus 2-[[9-(2-etilheksil)-9*H*-karbazol-3-il]amino}-9*H*-fluoren-9-oną (**4**), buvo susintetinti fluoreno dariniai **STM11** ir **STM12**, turintys tiek donorinius 9-alkilkarbazolil-, tiek akceptorinius 9*H*-fluorenilchromoforus periferinėje STM molekules dalyje. Siekiant sustiprinti šių junginių akceptorines savybes, jie

Knoevenagelio kondensacijos reakcijos sąlygomis buvo veikiami malono nitrilu, išskiriant atitinkamus bipolinius fluoreno darinius **STM13** ir **STM14** (15 schema).



15 schema. Bipolinių fluoreno darinių **STM9–STM14** sintezė

Tolėsniame šio darbo etape buvo ištirtos tikslinių bipolinių junginių terminės savybės. Iš gautų duomenų matoma, kad bipoliniai junginiai 5 % savo masės praranda esant aukštesnei nei 400 °C temperatūrai (4 lentelė ir 30 pav.).

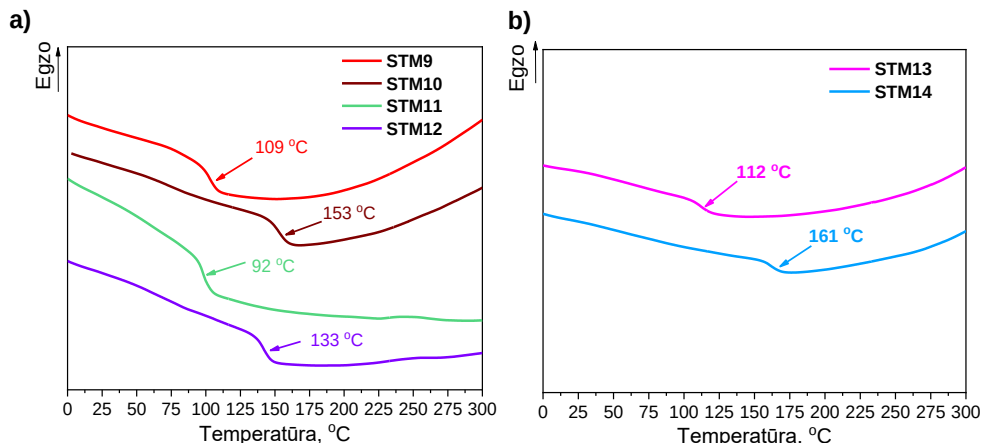


30 pav. Bipolinių fluoreno darinių TGA kreivės

Kaip ir tikėtasi, ilgas ir šakotas alkilgrandinės keičiant metilgrupėmis medžiagos masės nuostoliai vyksta aukštesnėse temperatūrose (**STM9** – 428 °C,

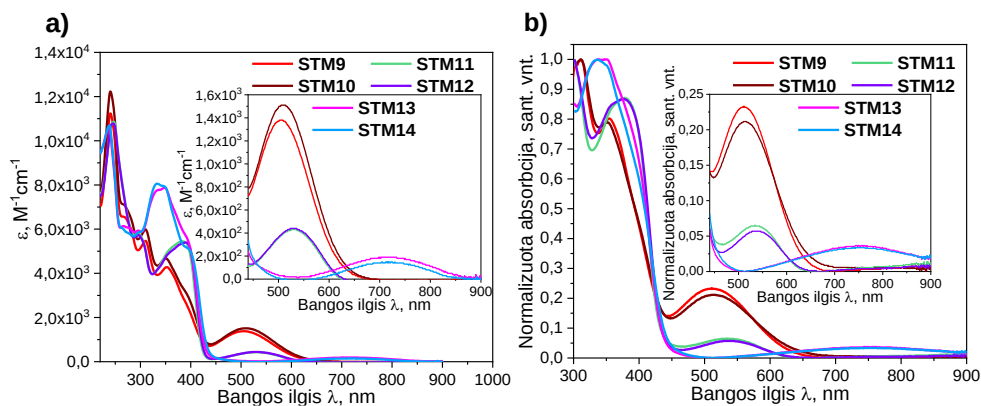
STM10 – 464 °C). Karbonilgrupės keičiant nitrilgrupėmis, vyksta atvirkštinis efektas (**STM11** – 423 °C, **STM13** – 406 °C).

Taip pat buvo užfiksuotos naujų bipolinių medžiagų stiklėjimo temperatūros (4 lentelė ir 31 pav., a, b). Analizuojant gautas DSK kreives matoma, kad daugelio junginių stiklėjimo temperatūros yra didesnės nei 100 °C.



31 pav. Naujų bipolinių junginių DSK kreivės: a) turinčių karbonilgrupes (**STM9**–**STM12**); b) turinčių cianopakaitus (**STM13** ir **STM14**)

Junginiai, turintys metilpakaitus molekulėse, pasižymi aukštesnėmis stiklėjimo temperatūromis nei jų analogai, turintys ilgus ir šakotus alkilfragmentus (**STM10** – 153 °C, **STM12** – 133 °C, **STM14** – 161 °C ir **STM9** – 109 °C, **STM11** – 92 °C, **STM13** – 112 °C). Taip pat pastebėta, jog fluorenono fragmentai mažina T_{st} . Tačiau atvirkštinis efektas fiksuojamas ketogrupes keičiant nitrilgrupėmis. Jokie endoterminiai virsmai DSK kreivėse nebuvo užfiksuoti, todėl galima teigti, jog visos tikslinės bipolinės medžiagos yra tik amorfinės būsenos. Dėl šios savybės tikėtina, jog pavyks gauti geros kokybės puslaidininkių sluoksnius.



32 pav. Bipolinių fluoreno darinių UV–RŠ spektrai: a) THF tirpalų ($c = 10^{-4}$ mol/l); b) sluoksnių

Norint įvertinti junginių optines savybes, atlikti medžiagų tirpalų (THF, $c = 10^{-4}$ mol/l) ir plonų sluoksnių UV–RŠ matavimai (4 lentelė ir 32 pav.). Tiriant tirpalų absorbciją fiksuojamos mažiausiai trys absorbcijos smailės. Taip pat galima pastebėti, kad medžiagų, kurios skiriasi alkilgrandinėlių ilgiu, spektrų forma yra labai panaši. Tai lemia, jog sočiosios alkilgrandinės beveik nepaveikia molekulių π -elektronų konjugacijos. Visų naujų junginių tirpalai pasižymi intensyviais $\pi \rightarrow \pi^*$ absorbcijos maksimumais intervale 270–450 nm, kurie perdengia mažo intensyvumo $n \rightarrow \pi^*$ elektronų perėjimo smailes, įprastai fiksuojamas ties 400 nm. Regimojoje srityje fiksuojamos karbonilgrupės turinčių **STM9–STM12** (450–650 nm) ir nitrilinius pakaitus turinčių **STM13** ir **STM14** (550–900 nm) puslaidininkių absorbcijos maksimumai, priskiriami donoro-akceptoriaus krūvio pernašai [295].

4 lentelė. Bipolinių fluoreno darinių terminės, optinės ir fotoelektrinės savybės

Junginys	$T_{st.}^a, ^\circ\text{C}$	$T_{sk.}, ^\circ\text{C}$	$\lambda_{abs}^b, \text{nm}$	I_p, eV	$\mu_{skyl.}^c, \text{cm}^2/\text{Vs}$	$\mu_{elek.}^d, \text{cm}^2/\text{Vs}$
STM9	109	428	311, 355, 512	5,18	$2,6 \times 10^{-7}$	$4,6 \times 10^{-9}$
STM10	153	464	311, 352, 514	5,21	$1,4 \times 10^{-7}$	$1,1 \times 10^{-9}$
STM11	92	423	378, 534	5,02	$3,9 \times 10^{-7}$	–
STM12	133	485	377, 537	5,02	$9,2 \times 10^{-8}$	–
STM13	112	406	337, 346, 760	5,18	$1,2 \times 10^{-7}$	$1,0 \times 10^{-8}$
STM14	161	417	337, 750	5,16	$2,8 \times 10^{-8}$	$3,5 \times 10^{-9}$

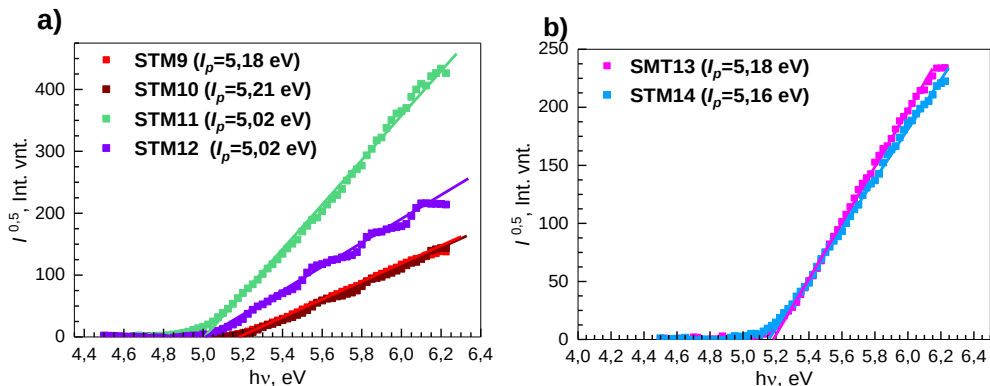
^aStiklėjimo temperatūros, fiksuotos diferencinės skenuojamosios kalorimetrijos antrojo kaitinimo metu; ^bUV–RŠ spektruose fiksuoti absorbcijos maksimumų poslinkiai iš sluoksnių; ^cteigiamųjų krūvininkų dreifinis judris silpnuose laukuose; ^delektronų dreifinis judris silpnuose laukuose.

Lyginant medžiagas, turinčias dvi (**STM11**, **STM12**) ir keturias (**STM9**, **STM10**) karbonilgrupes, akivaizdu, kad papildoma elektronų donorinė grupė paveikia konjuguotą sistemą, paslinkdama absorbcijos smailes hipsochromiškai, tačiau stebima intensyvesnė sugertis ties 510 nm. Dėl stipresnių cianogrupių akceptorinių savybių regimojoje srityje fiksuojamos absorbcijos smailės slenkasi į ilgesnių bangų pusę.

Lyginant tirpalų ir plėvelių spektrus matomas nežymus absorbcijos smailių poslinkis į ilgesnių bangų pusę (~ 3 nm) (32 pav.), tačiau alkilgrandinėlių ilgio ir akceptorinių grupių tendencijos išlieka panašios. Junginiai su daugiau karbonilgrupių (**STM9** ir **STM10**) pasižymi intensyvesne absorbcija ties 510 nm, o junginiams su cianopakaitais regimojoje srityje fiksuojamas batochrominis absorbcijos maksimumų poslinkis. Taip pat buvo tirta ir tikslinių junginių tirpalų ($c = 10^{-5}$ mol/l) bei jų sluoksnių fluorescencija (FL), tačiau emisija nefiksuota.

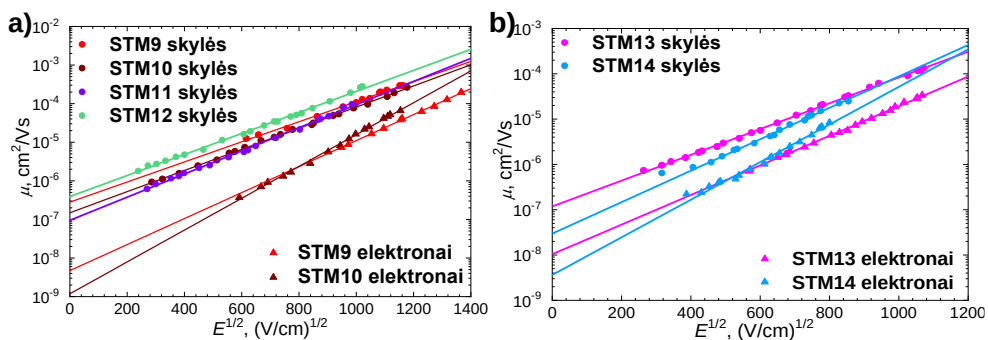
Siekiant išsiaiškinti naujų medžiagų HOMO energetinius lygmenis, elektronų fotoemisijos ore (PESA) metodu nustatytos jonizacijos potencialo (I_p) vertės iš plonų plėvelių (4 lentelė ir 33 pav.). Medžiagos, turinčios antrachinono fragmentus molekulėje pasižymi didžiausiomis I_p vertėmis (**STM9** – 5,18 eV, **STM10** – 5,21 eV). Kaip ir tikėtasi, ilgesni ir šakoti alkilpakaitai 9-oje fluoreno padėtyje jonizacijos potencialui įtakos beveik neturi. Lyginant tarpusavyje bipolinius fluoreno junginius, turinčius karbonilgrupes, fiksuojamas I_p vertės sumažėjimas, molekulėje esant mažiau

elektronų akceptorinių grupių (**STM9** – 5,18 eV, **STM10** – 5,21 eV ir **STM11** – 5,02 eV, **STM12** – 5,02 eV). Tačiau ketogrupes keičiant stipresniais elektronų akceptoriais – nitrilgrupėmis, jonizacijos potencialai padidėja (**STM11** – 5,02 eV, **STM12** – 5,02 eV ir **STM13** – 5,18 eV, **STM14** – 5,16 eV). Taigi galima teigti, kad akceptorinių grupių skaičiaus didinimas ir šių savybių stiprinimas didina I_p .



33 pav. Elektronų fotoemisijos ore spektrai: a) junginių, turinčių karbonilgrupes (**STM9**–**STM12**); b) junginių, turinčių cianopakaitus (**STM13** ir **STM14**)

Žinant, kad susintetinti fluoreno dariniai turi tiek elektronų donorinių, tiek akceptorinių grupių, galima tikėtis, jog jos gali transportuoti abiejų ženklų krūvininkus. Dėl šios priežasties kserografinio laiko lėkio (XTOF) metodu buvo įvertinti šių junginių krūvininkų judriai (4 lentelė ir 34 pav.). Junginiuose, turinčiuose 9-fluorenono chromoforus (**STM11** ir **STM12**), elektronų judėjimas nebuvo užfiksuotas, fiksuota tik teigiamųjų krūvininkų pernaša. Ketogrupę keičiant stipresnėmis akceptorinėmis savybėmis pasižyminčiu ciano fragmentu ir didinant akceptorinių pakaitų skaičių molekulėje, fiksuojama ir elektronų pernaša. Iš gautų rezultatų matoma, kad medžiagos, turinčios antrachinono (**STM9** ir **STM10**) bei dicianofluorenilideno (**STM13** ir **STM14**) fragmentus, pasižymi tiek teigiamųjų, tiek neigiamųjų krūvininkų pernaša.



34 pav. Krūvininkų dreifinio judrio priklausomybė nuo elektrinio lauko stiprio

Lyginant rezultatus tarpusavyje matoma, kad skylių judris yra maždaug viena eile didesnis nei elektronų kryptingas judėjimas (**STM9** – $\mu_{0 \text{ skyl.}} = 2,6 \times 10^{-7} \text{ cm}^2/\text{Vs}$ ir

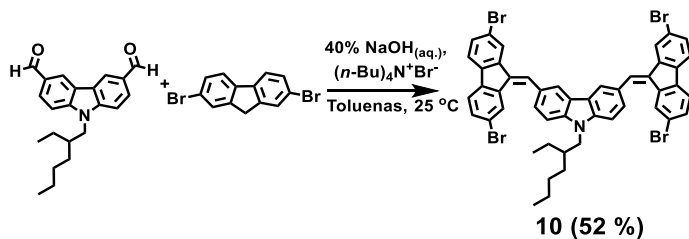
STM9 – $\mu_0 \text{elek.} = 4,6 \times 10^{-9} \text{ cm}^2/\text{Vs}$, **STM10** – $\mu_0 \text{skyl.} = 1,4 \times 10^{-7} \text{ cm}^2/\text{Vs}$ ir **STM10** – $\mu_0 \text{elek.} = 1,1 \times 10^{-9} \text{ cm}^2/\text{Vs}$, **STM13** – $\mu_0 \text{skyl.} = 1,2 \times 10^{-7} \text{ cm}^2/\text{Vs}$ ir **STM13** – $\mu_0 \text{elek.} = 1,0 \times 10^{-8} \text{ cm}^2/\text{Vs}$, **STM14** – $\mu_0 \text{skyl.} = 2,8 \times 10^{-8} \text{ cm}^2/\text{Vs}$ ir **STM14** – $\mu_0 \text{elek.} = 3,5 \times 10^{-9} \text{ cm}^2/\text{Vs}$). Ilgesnės ir šakotos sočiosios alkilgrandinės nežymiai padidina teigiamųjų krūvininkų dreifinį judrį, bet mažina neigiamųjų krūvininkų pernešą. Atvirkštinė tendencija stebima ketogrupę keičiant cianogrupę – elektronų dreifinis judris padidėja, tačiau kryptingas skylių judėjimas yra lėtesnis.

Visi susintetinti bipoliniai fluoreno dariniai pasižymi puikiais terminėmis savybėmis. 5 % masės jie praranda aukštesnėje nei 400 °C temperatūroje. Stiklėjimo temperatūros atitinka STM keliamus reikalavimus. Jonizacijos potencialai taip pat yra tinkami, norint šiuos bipolinius fluoreno darinius panaudoti SE gamybai. Daugelis šių darinių pasižymi abiejų ženklų krūvininkų pernaša. Tačiau fiksuotas skylių dreifinis judris siekia tik $10^{-7} \text{ cm}^2/\text{Vs}$ silpnuose elektriniuose laukuose, todėl šios medžiagos nebuvo pritaikytos perovskitiniais saulės elementams konstruoti.

3.3. Skyles transportuojantys šakoti fluorenilideno dariniai perovskitiniais saulės elementams

Remiantis publikuotu straipsniu *Chem. Mater.*, **2023**, 35, 5914–5923, A. Jegorovė, J. Xia, M. Steponaitis, M. Daskeviciene, V. Jankauskas, A. Gruodis, E. Kamarauskas, T. Malinauskas, K. Rakstys, K. A. Alamry, V. Getautis ir M. K. Nazeeruddin [296]; (cituota 7 kartus) šiame skyriuje aprašytos fluorenilideno fragmentus turinčios skyles transportuojančios medžiagos.

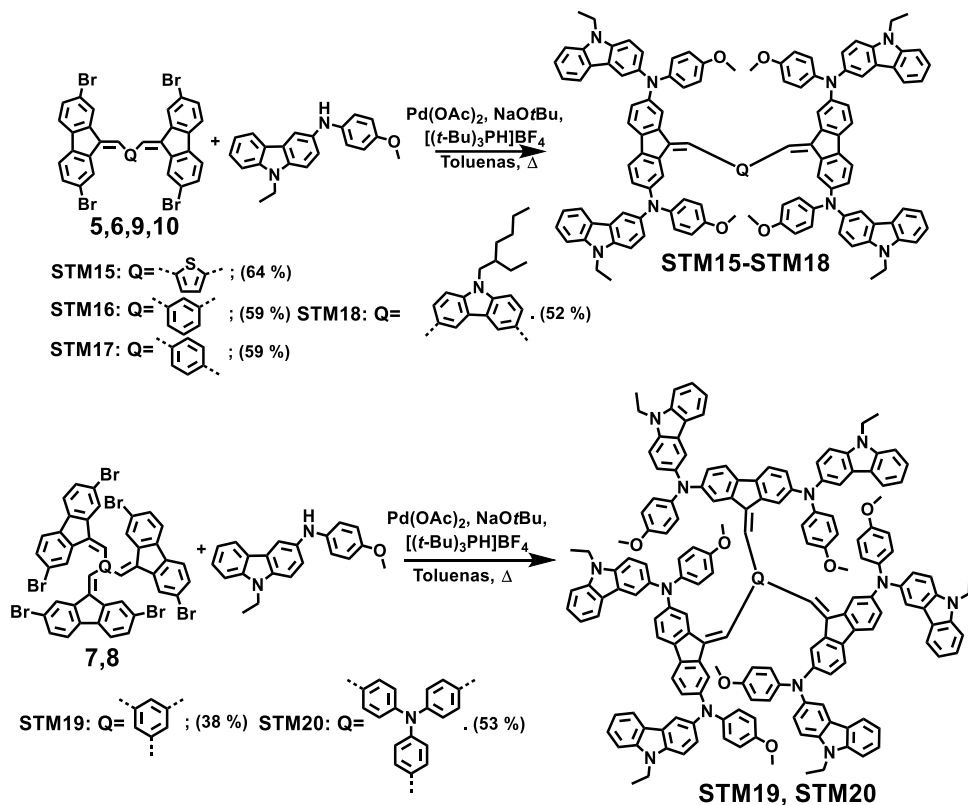
Perovskitiniai saulės elementai tobulinami jau daugiau nei dešimtmetį, tačiau kaip minėta anksčiau, STM etalonu vis dar naudojamas ne itin stabilus ir brangus spiro-OMeTAD. Pastebėta, jog, pritaikant panašų molekulės dizainą galima pasiekti gana gerų rezultatų tiek našumo, tiek stabilumo srityje [297, 298]. Yra dvi pagrindinės strategijos, kaip gauti panašius junginius į spiro-OMeTAD: 1) kaip centrinį fragmentą naudoti spirobifluoreną, pakeičiant šoninius 4-metoksifenilchromoforus (pirmoji aptarta publikacija) [198, 203]; 2) pakeisti centrinį spirobifluoreno fragmentą kitais chromoforais, paliekant 4,4'-dimetoksifenilaminus molekulės periferijoje arba tinkamai parenkant kitus šoninius fragmentus [219, 247].



16 schema. Tarpinio junginio **10** sintezė

Pirmoji strategija atrodė patikimesnė, paprastesnė ir sėkmingesnė, norint pasiekti aukštą prietaisų našumą. Tačiau antrasis metodas taip pat tapo populiarus, nes taip galima gauti pigesnius ir stabilesnius tikslinius junginius. Iš pirmoje publikacijoje aptartų tyrimų galima matyti, kad tinkamas skaičius karbazolilchromoforų kai kuriais

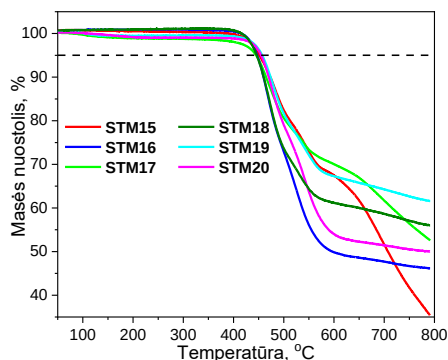
atvejais padidina prietaisų stabilumą, todėl kaip šoninius fragmentus nuspręsta naudoti 9-etil-*N*-(4-metoksifenil)-9*H*-karbazol-3-aminą. Norint, jog medžiaga būtų panaši į spiro-OMeTAD, į molekulės „centrinę dalį“ yra įterpti fluorenilidenilchromoforai, sujungti įvairiais aromatiniais pakaitais.



17 schema. Šakotos struktūros fluorenilideno darinių **STM15–STM20** sintezė

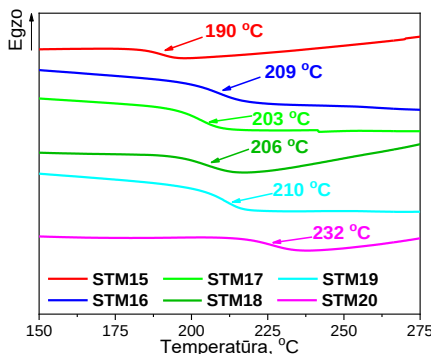
Visos susintetintos tikslinės medžiagos gali būti padalintos į dvi grupes: molekulės, turinčios du fluorenilideno fragmentus, ir junginiai, kurių struktūrose yra po tris fluorenilidenilchromoforus (16 schema). Tarpinės medžiagos **5–10** buvo susintetintos Knoevenagelio kondensacijos reakcijos toluene metu, naudojant 40 % NaOH tirpalą ir tarpfazinį katalizatorių tetrabutilamonio bromidą. Kadangi junginius **5–9** kiti tyrėjai jau yra aprašę savo moksliniuose darbuose, 16 schemoje pateikiama tik naujo karbazolo darinio sintezė: 9-(2-etilheksil)karbazol-3,6-dikarboksialdehidus minėtomis sąlygomis reaguoja su dviem 2,7-dibrom-9*H*-fluoreno ekvivalentais, išskiriant tarpinį junginį **10**. Tiksliniai produktai **STM15–STM20** gauti tarpinius junginius **5–10**, paladžio katalizuojamos kryžminio jungimosi reakcijos metu sujungiant su 9-etil-*N*-(4-metoksifenil)-9*H*-karbazol-3-aminu (17 schema).

Siekiant nustatyti tikslinių šakotos struktūros junginių terminį ir morfologinį stabilumą, buvo atlikti medžiagų TGA ir DSK tyrimai (5 lentelė ir 35 pav.).



35 pav. Tikslinių junginių TGA kreivės

Iš gautų TGA duomenų matoma, kad visi junginiai 5 % masės praranda esant aukštesnei nei 440 °C temperatūrai. Taip pat pastebima, kad, molekulėje esant daugiau fluorenilidenilpakaitų, T_{sk} nežymiai padidėja.

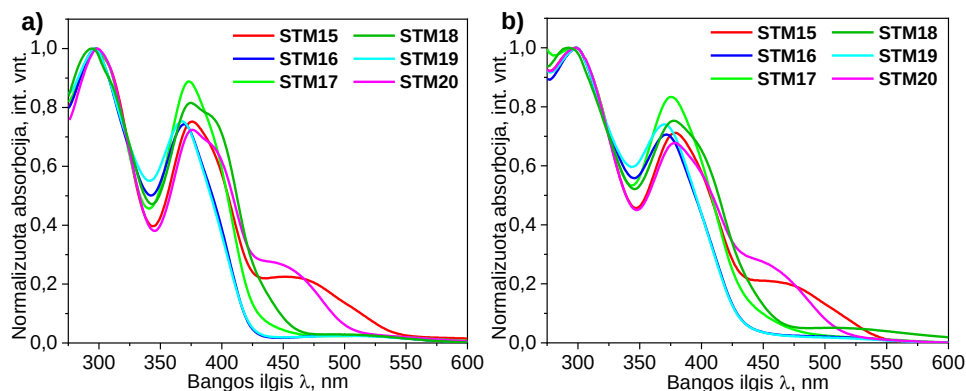


36 pav. Tikslinių medžiagų DSK antrojo kaitinimo kreivės

Naujų medžiagų stiklėjimo temperatūros išsidėsčiusios 190–232 °C intervale ir yra aukštesnės nei etalono spiro-OMeTAD [291]. Lyginant visus junginius tarpusavyje, galima įžvelgti tam tikrus dėsningumus. Tiofeno centrinių fragmentų pakeitus fenil- ar karbazolilchromoforais, T_{st} padidėja (5 lentelė ir 36 pav.). Šiems chromoforams susijungus per fenilenžiedo *meta*- padėtis, T_{st} nežymiai padidėja. Tikslinių organinių puslaidininkinių stiklėjimo temperatūros padidėjimas taip pat fiksuojamas ir molekulėje esant po tris fluorenilideno fragmentus (**STM19** – 210 °C ir **STM20** – 231 °C). Šio terminio tyrimo metu taip pat nebuvo fiksuoti ir jokie kiti faziniai virsmai, įrodant, kad medžiagos yra amorfinės būsenos. Todėl tikėtina, jog iš šių medžiagų liejami sluoksniai bus kokybiški.

Siekiant išsiaiškinti naujų tikslinių junginių optines savybes, užfiksuoti jų THF tirpalų ($c = 10^{-4}$ mol/l) ir plonų plėvelių UV–RŠ spektrai (5 lentelė ir 37 pav., a, b). Matoma, kad visų medžiagų absorbcijos spektruose fiksuojami du intensyvūs elektronų $\pi \rightarrow \pi^*$ perėjimai ties ~300 nm ir ~375 nm. Fluorenilideno fragmentų sujungimą keičiant iš *meta*- į *para*- padėtį, absorbcijos smailės slenkasi šiek tiek bathochromiškai, sukeliant konjugacinės sistemos padidėjimą molekulėje. Analogiškas

maksimumų polinkis matomas ir molekulės sudėtyje esant tiofeno (**STM15**) ir trifenilamino (**STM20**) centriniais fragmentams.



37 pav. Tikslinių medžiagų UV–RŠ spektrai iš: a) THF tirpalų ($c = 10^{-4}$ mol/l); b) plonų plėvelių

Taip pat šių puslaidininkių sugerties spektruose pastebima papildoma absorbcijos smailė ties $\sim 450\text{--}470$ nm, kuri gali būti priskirta elektronų $\pi \rightarrow \pi^*$ perėjimams. Lyginant tirpalų ir plėvelių absorbcijos spektrus, matomas labai minimalus absorbcijos maksimumų batochrominis poslinkis.

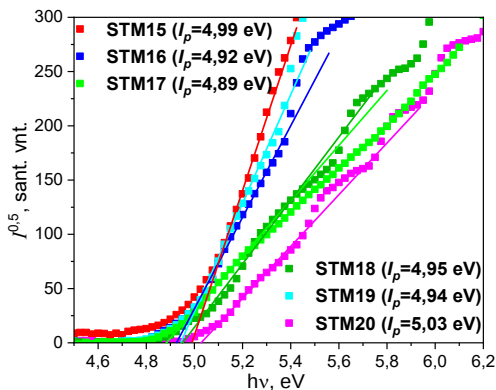
5 lentelė. Terminės, optinės ir fotoelektrinės naujų medžiagų savybės

Junginys	$T_{st.}^a, ^\circ\text{C}$	$T_{sk.}, ^\circ\text{C}$	$\lambda_{abs.}^b, \text{nm}$	$\lambda_{abs.}^c, \text{nm}$	I_p, eV	$\mu_0^d, \text{cm}^2/\text{Vs}$
STM15	190	451	298, 376, 461	299, 379, 466	4,99	$5,4 \times 10^{-7}$
STM16	209	452	297, 369	299, 372	4,92	$8,5 \times 10^{-7}$
STM17	203	445	298, 373	298, 375	4,89	$1,9 \times 10^{-6}$
STM18	206	446	295, 375	293, 378	4,95	$4,3 \times 10^{-7}$
STM19	210	457	297, 367	299, 370	4,94	$4,9 \times 10^{-7}$
STM20	232	455	299, 376, 451	298, 379, 454	5,03	$1,3 \times 10^{-6}$

^aStiklėjimo temperatūros fiksuotos diferencinės skenuojamosios kalorimetrijos antrojo kaitinimo metu; ^bUV–RŠ spektruose fiksuoti absorbcijos maksimumų poslinkiai (THF, $c = 10^{-4}$ mol/l); ^cplonų sluoksnių UV–RŠ spektruose fiksuoti absorbcijos maksimumų poslinkiai; ^dskylių dreifinio judrio vertės kompozicijoje su PC-Z (1:1), kai elektrinio lauko stipris lygus 0.

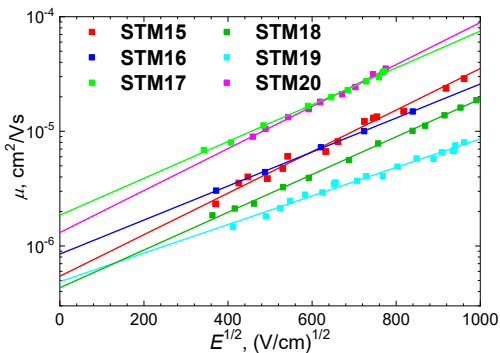
Norinti išsiaiškinti, ar naujų medžiagų HOMO lygmuo atitinka STM skirtus reikalavimus, PESA metodu buvo užfiksuoti jų I_p (5 lentelė ir 38 pav.). Iš gautų rezultatų matoma, kad junginių jonizacijos potencialai išsidėstę $4,92\text{--}5,03$ eV diapazone. Medžiagos, kurių fluorenilideno fragmentai sujungti fenilenžiedais, pasižymi mažesniais jonizacijos potencialais (**STM16** – 4,92 eV, **STM17** – 4,89 eV, **STM19** – 4,94 eV). Galima konstatuoti, jog šiuo atveju papildomų fluorenilideno ir 9-etil-*N*-(4-metoksifenil)-9*H*-karbazol-3-amino fragmentų įterpimas į molekulę

nedaro didelės įtakos HOMO skaitinėms vertėms. Medžiagos, molekulės centre turinčios pakaitus su heteroatomais, pasižymi šiek tiek didesniais I_p (**STM15** – 4,99 eV, **STM18** – 4,95 eV, **STM20** – 5,03 eV).



38 pav. Šakotos struktūros fluorenilideno fragmentą turinčių junginių jonizacijos potencialai

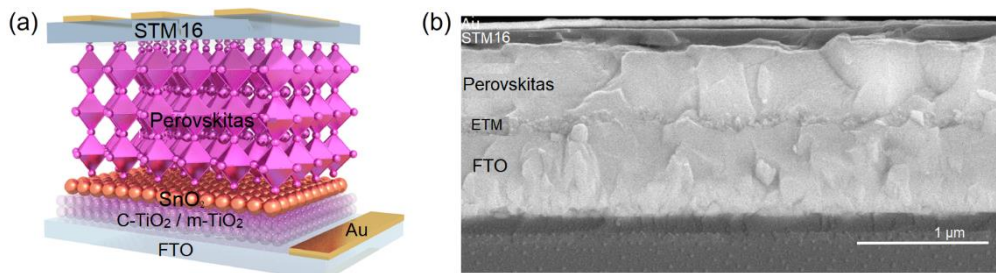
Krūvininkų dreifinis judris nustatytas kserografinio laiko lėkio metodu (5 lentelė ir 39 pav.). Išliejus plonus susintetintų puslaidininkių plėvelių sluoksnius pastebėta, kad jie trūkinėja taip prarasdami homogeniškumą. Todėl jų krūvininkų judris buvo įvertintas kompozicijoje (1:1) su PC-Z. Matoma, jog medžiaga **STM17** pasižymi didžiausiu krūvininkų dreifiniu judriu silpnuose laukuose (**STM17** $\mu_0 = 1,9 \times 10^{-6} \text{ cm}^2/\text{Vs}$). Galima pastebėti, jog krūvininkų dreifinis judris pagerėja, kai fluorenilideno fragmentai yra sujungti per fenilenziedo *para*- padėtis (**STM16** – $8,5 \times 10^{-7} \text{ cm}^2/\text{Vs}$, **STM17** – $1,9 \times 10^{-6} \text{ cm}^2/\text{Vs}$ ir **STM20** – $1,3 \times 10^{-6} \text{ cm}^2/\text{Vs}$). Lyginant gautų medžiagų dreifinius judrius su spiro-OMeTAD, matoma, jog jie šiek tiek nusileidžia etalonui (spiro-OMeTAD – $2,81 \times 10^{-6} \text{ cm}^2/\text{Vs}$ [290]).



39 pav. Junginių **STM15–STM20** krūvininkų dreifinio judrio priklausomybė nuo elektrinio lauko stiprio

Šakotos struktūros fluorenilideno fragmentą turintys junginiai buvo panaudoti n-i-p architektūros PSE kaip skyles transportuojantys sluoksniai (40 pav., a). SE konstrukcija: FTO / SnO_2 / TiO_2 (m- TiO_2 ir c- TiO_2) / $\text{Cs}_{0,03}\text{MA}_{0,048}\text{FA}_{0,922}\text{PbI}_3$ / STM / Au. Norint pagerinti STM krūvininkų pernašą, visi junginiai legiruoti pirmiau

paminėtais priedais. 40 pav., b, pateiktame elektroniniame saulės elemento skerspjūvio vaizde matoma, kad junginys **STM16** tolygiai padengia perovskito paviršių. Todėl tikėtina, jog prietaisas pasižymės geru stabilumu.



40 pav. Saulės elementų struktūra (a); prietaiso skerspjūvio vaizdas (b)

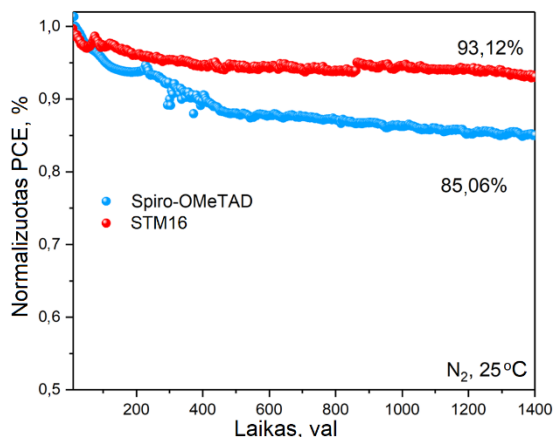
Gautos saulės elementų charakteristikos pateiktos 6 lentelėje. PSE, kuriuose STM fluorenilideno fragmentai sujungti fenilenžiedu, efektyvumas yra geriausias (**STM16** – 22,13 % ir **STM17** – 21,26 %) ir labai mažai nusileidžia lyginamajam prietaisui su etalonu laikomu spiro-OMeTAD (22,83 %).

6 lentelė. Fotovoltiniai saulės elementų parametrai

Junginys	J_{sc} , mA cm ⁻²	V_{oc} , V	FF	PCE , %
STM15	24,54	1,065	0,793	20,72
STM16	24,57	1,112	0,810	22,13
STM17	24,50	1,082	0,802	21,26
STM18	24,45	1,061	0,788	20,44
STM19	24,43	1,06	0,796	20,61
STM20	24,38	1,03	0,781	19,61
Spiro-OMeTAD	24,79	1,133	0,813	22,83

Efektyvumas beveik nepriklauso nuo centrinio molekulės chromoforo substitucijos. Iš gautų duomenų matoma, kad saulės celių efektyvumas mažėja, kuomet kaip STM naudojamos medžiagos, centriniuose fragmentuose turinčios didesnę chromoforą: prietaisai, kuriuose yra puslaidininkiai **STM18** ir **STM20**, turintys karbazolil- arba trifenilamino chromoforą, pasižymėjo mažiausiu našumu (**STM18** – 20,44 % ir **STM20** – 19,61 %).

Prietaisų stabilumas yra labai svarbi saulės elemento charakteristika. Norint išsiaiškinti, kiek laiko saulės elementas gali efektyviai veikti fiksuojamas jo efektyvumas esant maksimaliai prietaiso apkrovai (41 pav.). Akivaizdu, kad prietaisas, kuriame kaip STM naudojamas junginys **STM16**, praranda tik kelis našumo procentus net praėjus 1400 val. PSE, kuriame yra Spiro-OMeTAD tyrimo pabaigoje yra praradęs beveik 15 % efektyvumo.



41 pav. Saulės elementų su STM16 ir spiro-OMeTAD stabilumas

Atliktų terminių, optinių ir fotoelektrinių naujų STM tyrimų rezultatai atitinka teigiamuosius krūvininkus pernešančioms medžiagoms keliamus reikalavimus. Testuojant medžiagas saulės elementuose nustatyta, kad pastarųjų našumas yra artimas prietaisams, kuriuose naudojamas spiro-OMeTAD. Ištyrus SE stabilumą konstatuota, jog puslaidininkis **STM16** padidina prietaiso ilgaamžiškumą.

3.4. Žvaigždės formos karbazolo darinių skylių transportinės medžiagos perovskitiniais saulės elementams

Šiame skyriuje nagrinėjami nauji žvaigždės formos karbazolo dariniai, remiantis publikuotu straipsniu *Solar RRL*, **2022**, 6, 2100877, *A. Jegorovė, M. A. Truong, R. Murdey, M. Daskeviciene, T. Malinauskas, K. Kantminiene, V. Jankauskas, V. Getautis, A. Wakamiya* [299]; cituota 14 kartų.

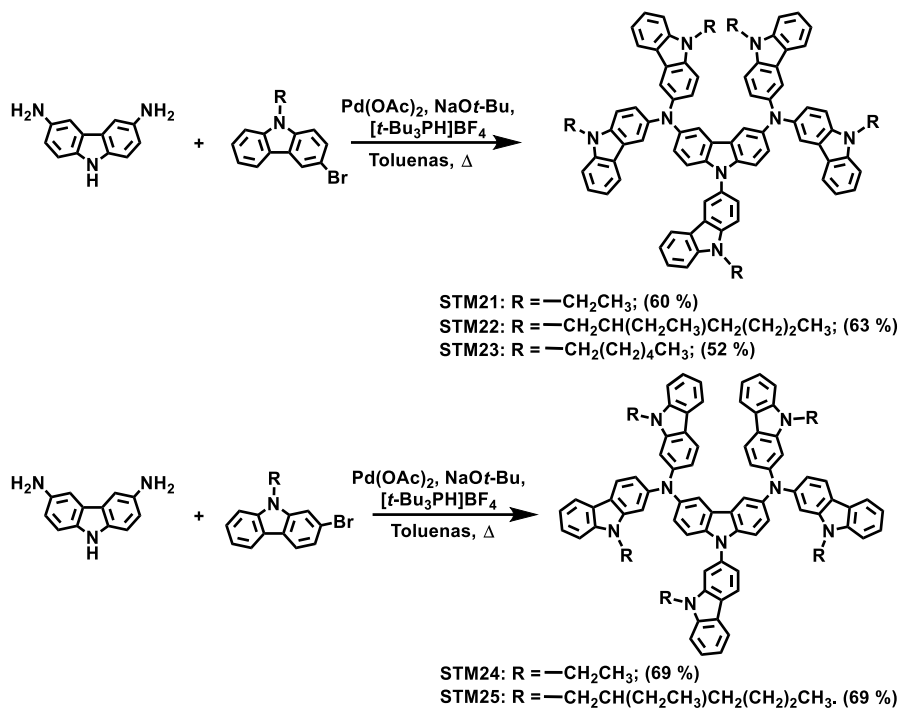
Morfologinis STM stabilumas prietaiso veikimo temperatūroje yra labai svarbus, kad saulės elementai būtų stabilūs. Žinoma, jog žvaigždės formos struktūros molekulės dažniausiai yra amorfinės būsenos. Paprastai šių molekulių pakaitai būna dideli ir standūs, taip gaunant dideles molekules, kurios yra termiškai stabilios [300]. Žvaigždės formos STM gerai veikia perovskitinėse saulės celėse, todėl ši medžiagų klasė sulaukia nemažai mokslininkų dėmesio [301, 302].

Jau minėta, kad karbazolilchromoforai yra plačiai naudojami kaip pagrindiniai statybiniai fragmentai skylių transportinėms medžiagoms dėl privalumų, tokių kaip maža jų kaina, geras kryptingas krūvininkų judėjimas, cheminis stabilumas bei lengvas fragmentų modifikavimas įvairiomis funkcinėmis grupėmis [303, 304]. Karbazolilpakaitai organiniuose puslaidininkiuose gali būti naudojami kaip plokšti centriniai [230, 305] arba kaip šoniniai chromoforai [306, 307], pasižymintys skylių pernaša. Daugelio karbazolilchromoforų turinčių žvaigždės formos molekulių stiklėjimo temperatūros yra aukštesnės nei spiro-OMeTAD. Kol kas, iki šios publikacijos, žvaigždės formos struktūros STM, turinčios centriniam ir šoniniuose fragmentuose karbazolilchromoforus nebuvo žinomos.

Daugelyje publikacijų teigiama, jog alkilgrandinėlių ilgis ir šakotumas turi didžiulę įtaką medžiagų morfologinėms, terminėms, krūvininkų pernašos savybėms

bei fotovoltinio prietaiso efektyvumui [308, 309]. Todėl tiksliniams junginiams sintetinti buvo pasirinkti karbazolilfragmentai, turintys skirtingus alkilpakaitus, norint išsiaiškinti, kokią įtaką pastarieji padarys aptartoms savybėms.

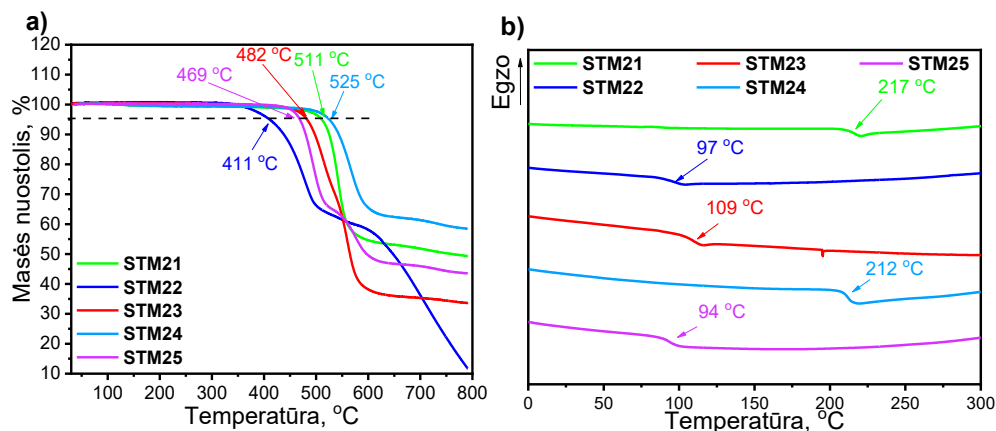
Publikacijoje aptartos penkios naujos žvaigždės formos junginių klasės medžiagos. Naujos medžiagos gautos iš komerciškai prieinamo 3,6-diamino-9H-karbazolo, kuris sintetinamose molekulėse buvo panaudotas kaip centrinis fragmentas (18 schema).



18 schema. Naujų žvaigždės formos junginių STM21–STM25 sintezė

Taikant paladžio katalizuojamos C-N ryšio sudarymo reakcijos metodiką, prie 3,6-diamino-9H-karbazolo jungiant 2- arba 3-brom-9-alkilkarbazolus, buvo susintetinti tiksliniai junginiai **STM21–STM25** su 2- ar 3-ioje padėtyje pakeistais 9-alkilkarbazolais fotolaidžių molekulių periferijoje. Visos reakcijos įvyko per 5 val., jų išeigos siekia 52–69 %, o išskirtos tikslinės medžiagos gerai tirpsta organiniuose tirpikliuose.

Naujų puslaidininkinių terminės savybės įvertintos TGA ir DSK metodais. Gauti rezultatai pavaizduoti 42 pav., a, ir pateikti 7 lentelėje. Visos susintetintos medžiagos 5 % masės praranda aukštesnėje nei 400 °C temperatūroje, kuri yra gerokai aukštesnė nei perovskitinio saulės elemento veikimo temperatūra. Lyginant tikslinius junginius tarpusavyje matoma, kad ilginant alkilgrandinę medžiagos 5 % masės praranda žemesnėse temperatūrose (**STM21** – 511 °C, **STM22** – 411 °C, **STM23** – 482 °C, **STM24** – 525 °C, **STM25** – 469 °C). Įdomu, kad puslaidininkinių su 2-padėtyje pakeistais karbazolo fragmentais T_{sk} yra didesnė nei 3-padėtyje pakeistų analogų (**STM21** – 511 °C, **STM24** – 525 °C).



42 pav. Terminės žvaigždės formos karbazolo darinių savybės: a) TGA rezultatai; b) antrojo kaitinimo DSK kreivės

Pirmojo ir antrojo kaitinimo metu, atliekant DSK tyrimą, nepastebėta jokių endoterminių smailių, reiškiančių kristalų išsilydymą, vadinasi, gauti tiksliniai junginiai yra tik amorfinės būsenos (42 pav., b).

7 lentelė. Terminės, optinės ir fotofizikinės susintetintų STM savybės

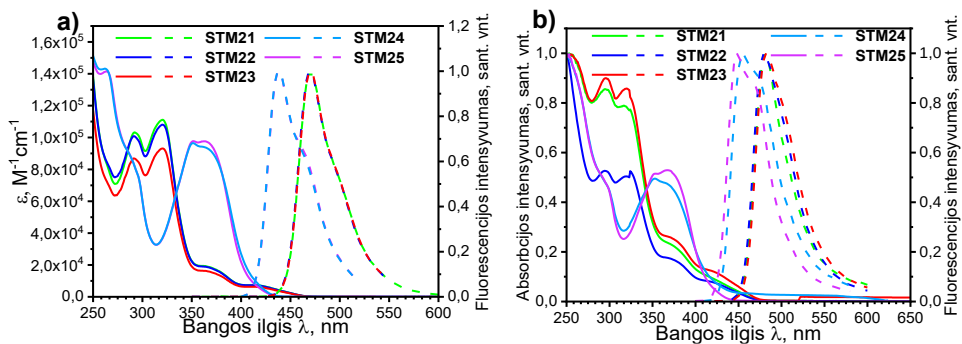
STM	T_{st} , °C ^{a)}	$T_{sk..}$, °C	λ_{abs}^b , nm	λ_{PL}^b , nm	I_p , eV	E_g^c , eV	μ_0^d , cm ² V ⁻¹ s ⁻¹	μ_0^e , cm ² V ⁻¹ s ⁻¹
STM21	217	511	292, 321, 365, 413	471	4,86	2,75	–	$3,1 \times 10^{-6}$
STM22	97	411	291, 320, 365, 413	471	4,99	2,76	$3,7 \times 10^{-6}$	$4,1 \times 10^{-7}$
STM23	109	482	291, 321, 365, 413	471	4,87	2,73	$3,5 \times 10^{-6}$	$5,0 \times 10^{-7}$
STM24	212	525	262, 359	438	5,16	2,90	$6,1 \times 10^{-6}$	$5,1 \times 10^{-7}$
STM25	94	469	264, 359	438	5,24	2,93	$1,0 \times 10^{-5}$	$5,8 \times 10^{-7}$
spiro- OMeTAD [311]	126	449	387	–	5,01 [305]	3,01	$1,2 \times 10^{-4}$	$2,9 \times 10^{-6}$

^aStiklėjimo temperatūros, fiksuotos DSK antrojo kaitinimo metu; ^bUV–RŠ spektruose fiksuoti absorbcijos maksimumų poslinkiai FL spektruose fiksuoti emisijos maksimumai (atitinkamai 10^{-4} mol/l ir 10^{-5} mol/l); ^c E_g apskaičiuotas iš UV–RŠ ir FL plėvelių spektrų sankirtos; ^dkrūvininkų judrio vertė silpnuose laukuose; ^ekrūvininkų judrio vertė kompozicijoje su PC-Z (1:1) silpnuose laukuose.

Iš 7 lentelėje pateiktų rezultatų galima matyti, kad ilginant alkilgradinėle ar didinant jos šakotumą, stiklėjimo temperatūra sumažėja (**STM21** – 217 °C, **STM23** – 109 °C ir **STM22** – 97 °C). Karbazolilchromoforų prisijungimo prie centrinio fragmento padėtis didelės įtakos stiklėjimo temperatūrai neturi (**STM21** – 217 °C ir **STM24** – 212 °C, **STM22** – 97 °C ir **STM25** – 94 °C), tačiau galima stebėti šiek tiek didesnes medžiagų T_{st} , kuriose karbazolai prijungti per 3-padėtį. Junginių, kurie turi trumpiausias alkilgrandinėles (**STM21** ir **STM24**), T_{st} yra didesnė nei etalono spiro-OMeTAD (126 °C), tikėtina, dėl sumažėjusios molekulinės netvarkos [310]. Todėl galima tikėtis, jog prietaisai su šiomis medžiagomis bus termiškai stabilesni, nes šios medžiagos nesikristalizuos saulės elemente, priešingai nei spiro-OMeTAD.

Iš UV–RŠ spektrų matoma, kad alkilgrandinėlės ilgis beveik neturi įtakos absorbcijos smailių poslinkiams. Junginių, turinčių 3-padėtyje pakeistus karbazolilchromoforus, (**STM21–STM23**) spektruose prie 270–340 nm, matomos intensyvios $\pi \rightarrow \pi^*$ absorbcijos smailės, o prie >350 nm, maksimumai, priklausantys $n \rightarrow \pi^*$ elektronų šuoliukams, yra mažesnio intensyvumo (43 pav., a). Žvaigždės formos medžiagų, turinčių 2-padėtyje pakeistus karbazolilchromoforus, absorbcijos maksimumai pasislinkę batochromiškai ir hiperchromiškai, matyt, dėl didesnės konjuguotos dvigubųjų ryšių sistemos šiose molekulėse, lyginant su 3-padėtyje pakeistais analogais. FL spektre matomas junginių, turinčių per 3-padėtį prisijungusius karbazolilchromoforus, emisijos maksimumas ties 471 nm. Pakeitus karbazolilpakaitų prijungimo padėtį iš 3-C į 2-C, fiksuojamas hipsochrominis emisijos smailės poslinkis (440 nm).

Lyginant susintetintų naujų STM tirpalų UV–RŠ ir FL spektrus (43 pav., a) su atitinkamais spektrais, užfiksuotais iš plėvelių (43 pav., b), matomas smailių poslinkių panašumas – spektrai beveik identiški. Taip pat buvo apskaičiuotas Stokso poslinkis, kuris padeda įvertinti krūvių pernašai svarbias struktūrines junginių deformacijas, vykstant elektronų sužadinimui.

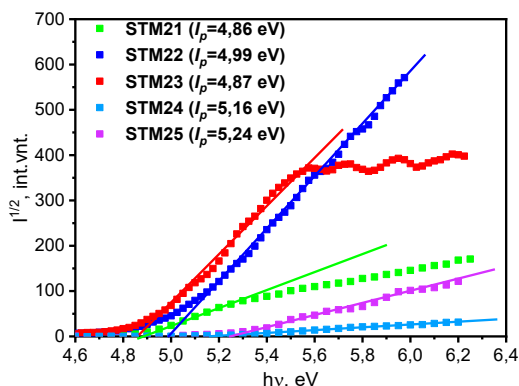


43 pav. Tikslinių junginių UV–RŠ ir fluorescencijos spektrai: a) THF tirpalų (atitinkamai $c = 10^{-4}$ g/mol ir $c = 10^{-5}$ g/mol); b) plėvelių

Visos medžiagos pasižymi dideliais Stokso poslinkiais (apie 100 nm), kurie apibūdina reikšmingas struktūrines deformacijas elektronų sužadinimo metu. Yra žinoma, kad dideliais Stokso poslinkiais pasižyminčios medžiagos lengviau sąveikauja su perovskito paviršiumi [312], todėl galima tikėtis, jog tikslinės STM turi potencialą efektyviems PSE gauti.

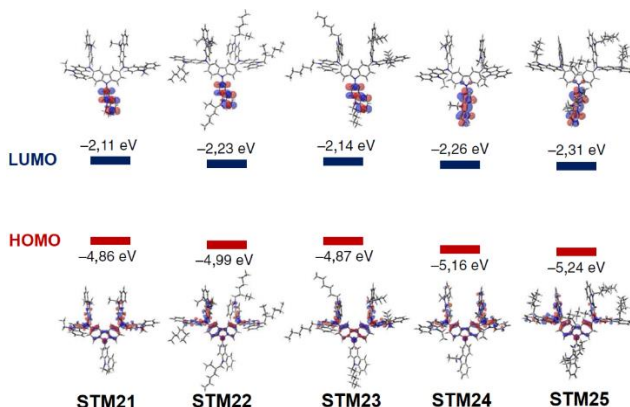
Tikslinių junginių draustinės juostos energija (E_g) buvo apskaičiuota iš plėvelių UV–RŠ ir FL spektrų sankirtos. Junginiai, turintys 3-padėtyje pakeistų karbazolilchromoforų, pasižymi maždaug 2,8 eV draustinės juostos energija, o 2-padėtyje pakeisti karbazolai šiek tiek padidina E_g (apie 0,1 eV).

Žvaigždės formos STM jonizacijos potencialai buvo išmatuoti PESA metodu (44 pav.). Iš gautų rezultatų matoma, jog žemesniais potencialais pasižymi medžiagos, kurių šoniniai 9-alkilkarbazolų fragmentai prijungti per 3-C padėtį (**STM21** – 4,86 eV ir **STM24** – 5,16 eV, **STM22** – 4,99 eV ir **STM25** – 5,24 eV). Alkilgrandinėlės ilgis ir šakotumas labai didelės įtakos jonizacijos potencialo pokyčiui neturi, tačiau tam tikra tendencija gali būti pastebėta, t. y. prijungus ilgas ir (ar) šakotas alkilgradinėles, I_p nežymiai padidėja.



44 pav. Tikslinių junginių STM21–STM25 jonizacijos potencialai

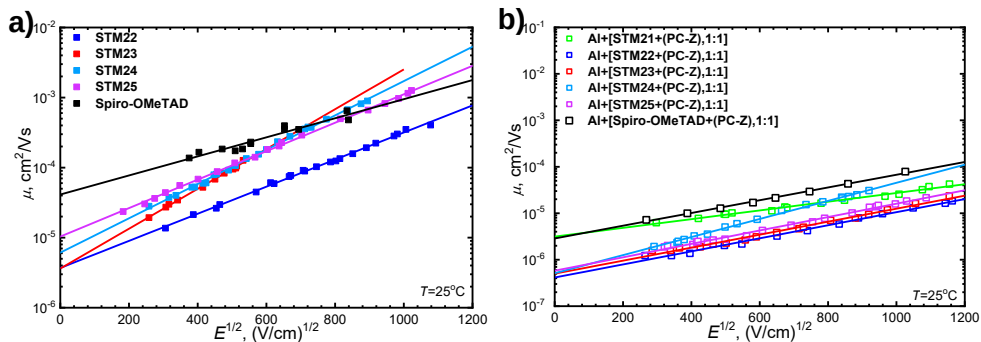
Norint tinkamai parinkti medžiagas SE, labai svarbu žinoti ne tik I_p vertes, bet ir žemiausios neužimtos molekulinės orbitalės (LUMO) skaitines vertes. Taip galima užkirsti kelią galimam nekryptingam krūvininkų judėjimui, dėl ko SE našumas sumažėja. LUMO vertės apskaičiuotos prie neigiamos HOMO (I_p) skaitinės vertės pridėjus E_g , gautą iš plėvelių absorbcijos spektrų.



45 pav. Molekulių STM21–STM25 fragmentų išsidėstymas erdvėje

Junginiai, turintys 3-padėtimi prijungtus karbazolilchromoforus, pasižymi didesne LUMO verte (žr. 45 pav.). Atsižvelgus į gautus rezultatus, galima teigti, kad HOMO ir LUMO vertės yra palankios, norint medžiagas panaudoti PSE.

Krūvininkų dreifinis judris buvo nustatytas atliekant XTOF matavimus (7 lentelė ir 46 pav., a, b).



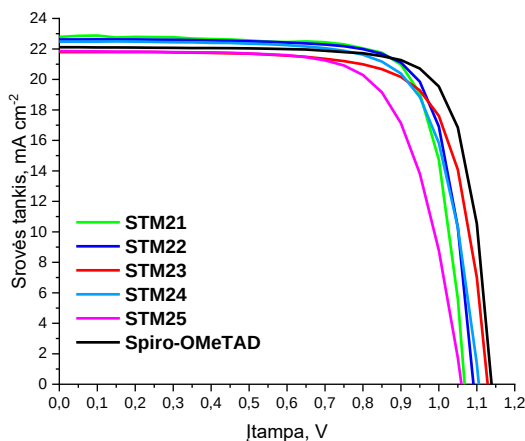
46 pav. Naujų junginių STM21–STM25 krūvininkų dreifinio judrio priklausomybės nuo elektrinio lauko stiprio: a) gryną medžiagų; b) kompozicijoje su PC-Z (1:1)

Grynų medžiagų kryptingas krūvininkų judėjimas yra tarp $3,5 \times 10^{-6}$ cm²/Vs ir $1,0 \times 10^{-5}$ cm²/Vs (7 lentelė ir 46 pav. a). Gauti μ_0 rezultatai yra šiek tiek žemesni nei spiro-OMeTAD, tačiau tokio skylių judrio visiškai pakanka norint šias medžiagas panaudoti PSE [313]. Ruošiant medžiagų sluoksnius tyrimui pastebėta, kad **STM21** tirpalas nesuformuoja homogeniško sluoksnio, todėl šio junginio krūvininkų dreifinio judrio nepavyko nustatyti. Norint sulygtinti visų tikslinių junginių krūvininkų dreifinius judrius, visos STM tirtos ir kompozicijoje su PC-Z (7 lentelė ir 46 pav., b). Lyginant gautus rezultatus matoma, jog **STM21** ir spiro-OMeTAD skylių judriai yra panašūs, tačiau visų kitų tikslinių medžiagų skylių pernaša yra viena eile žemesnė.

Tikslinės medžiagos testuotos n-i-p plokščios architektūros prietaisuose: ITO / SnO₂ / perovskitas / STM / Au. Perovskito, panaudoto šiuose fotovoltiniuose prietaisuose, sudėtis yra: Cs_{0,05}FA_{0,08}MA_{0,15}PbI_{2,75}Br_{0,25} [314]. Konstruojant SE, optimizuotos STM tirpalų koncentracijos (**STM21** c = 0,03 mol/l, **STM22** – 0,02 mol/l, **STM23** – 0,03 mol/l, **STM24** – 0,02 mol/l, **STM25** – 0,02 mol/l), o STM, panaudotos kartu su jas legiruojančiais priedais – FK209, CoTFSI (0,03 ekv.), LiTFSI (0,54 ekv.) ir TBP (3,3 ekv.). Yra žinoma, kad spiro-OMeTAD sluoksnis prietaise turi būti didesnis nei 200 nm, norint gauti efektyviausius PSE [315, 316]. PSE su susintetintais žvaigždės formos karbazolilchromoforus turinčiais junginiais panašų efektyvumą gali pasiekti liejant kur kas plonesnius STM sluoksnius. Be to, karbazolilfragmentus turintys žvaigždės formos dariniai pasižymi geresnėmis morfologinėmis savybėmis, o tai užtikrina kokybiškus STM sluoksnius naudojant mažesnius medžiagų kiekius: **STM21** – 140 nm, **STM22** – 115 nm, **STM23** – 130 nm, **STM24** – 140 nm, **STM25** – 120 nm, spiroOMeTAD – 240 nm.

Geriausių PSE srovės tankio ir įtampos (*J–V*) kreivės pavaizduotos 47 paveiksle, o fotovoltiniai parametrai apibendrinti 8 lentelėje. Lyginant rezultatus matoma, kad SE, į kurių sudėtį įeina STM, turinčios trumpesnes alkilgrandinėles, pasižymi didesniu efektyvumu (**STM21** – 18,9 % ir **STM24** – 18,4 %) nei prietaisai,

kurių analogiškos krūvininkus pernešančios medžiagos turi ilgus ar šakotus alkilpakaitus (**STM23** – 18,3 % ir **STM25** – 16,3 %). Taip pat pastebima, jog prietaisai, kuriuose STM turi 2-padėtyje pakeistus karbazolilchromoforus, pasižymi žemesniu efektyvumu.



47 pav. Geriausių saulės elementų J – V kreivės

Kaip STM naudojant **STM22**, buvo pasiektas didžiausias efektyvumas (19,0 %), tačiau, lyginant SE rezultatų vidurkius matoma, kad geriausiai veikė žvaigždės formos junginys **STM21** (18,6 %). Nors prietaisų efektyvumas kiek nusileidžia SE su spiro-OMeTAD, daugeliu atvejų jie geresni už literatūroje pateikiamus PSE rezultatus, į kurių sudėtį įeina žvaigždės formos junginiai [317, 318].

PSE stabilumas tirtas 10 val. bedeguonėje aplinkoje. Nors visų saulės elementų pradinis našumas yra gana panašus, veikiant juos spinduliuote po tam tikro laiko pastebimi prietaisų našumo pokyčiai (48 pav.).

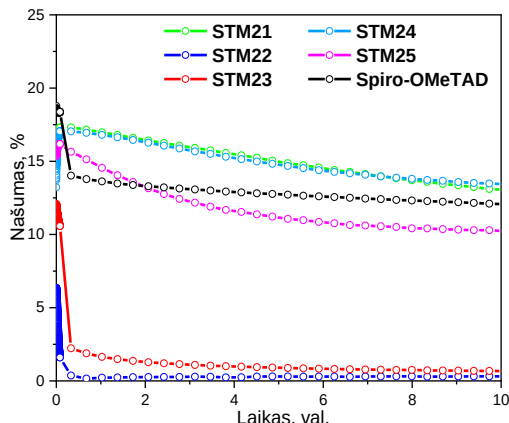
8 lentelė. Iš J – V kreivių nustatyti fotovoltiniai saulės elementų parametrai

STM ^a	J_{sc} ^b , mA cm ⁻²	V_{oc} ^b , V	FF ^b	PCE ^b , %
STM21	22,8 (22,4±0,5)	1,07 (1,09±0,02)	0,78 (0,76±0,01)	18,9 (18,6±0,3)
STM22	22,6 (22,5±0,2)	1,09 (1,06±0,02)	0,77 (0,76±0,01)	19,0 (18,0±0,6)
STM23	21,8 (21,6±0,3)	1,13 (1,11±0,01)	0,74 (0,72±0,01)	18,3 (17,4±0,5)
STM24	22,5 (22,3±0,2)	1,11 (1,12±0,01)	0,74 (0,73±0,01)	18,4 (18,2±0,2)
STM25	21,9 (21,6±0,4)	1,06 (1,07±0,02)	0,70 (0,67±0,02)	16,3 (15,5±0,5)
spiro-OMeTAD	22,1 (22,5±0,3)	1,14 (1,12±0,02)	0,78 (0,78±0,01)	19,7 (19,5±0,3)

^aSTM koncentracija: **STM21**, **STM23** ir **STM24** $c = 0,03$ mol/l, **STM22** ir **STM25** $c = 0,06$ mol/l. Sluoksnių storis: **STM21** – 140 nm, **STM22** – 115 nm, **STM23** –

130 nm, **STM24** – 140 nm, **STM25** – 120 nm ir spiro-OMeTAD – 240 nm; ^bvidutinės vertės apskaičiuotos remiantis 9 prietaisų matavimų duomenimis.

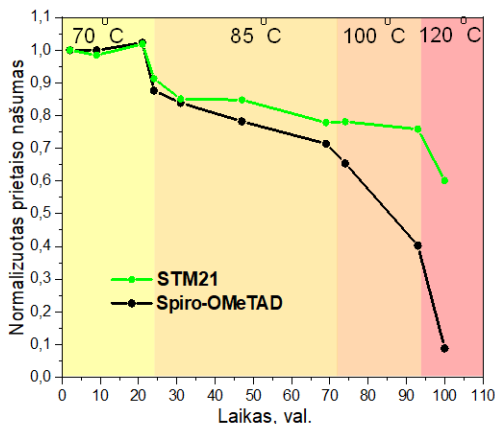
Iš gautų rezultatų matoma, kad saulės celių, kuriose kaip STM naudojami **STM22** ir **STM23**, didelis našumo sumažėjimas fiksuojamas dar nepraėjus nė 1 valandai nuo tyrimo pradžios.



48 pav. Neįkapsuliuotų prietaisų stabilumo tyrimas

Prietaisas, kuriame naudojamas spiro-OMeTAD, taip pat praranda apie 5 % našumo per pirmąją tyrimo valandą, o po 10 valandų siekia tik 12 %. Elementuose naudojant **STM25**, po 10 valandų fiksuojamas 10 % našumas. Savo stabilumu visus lenkė PSE su puslaidininkiais **STM21** ir **STM24**.

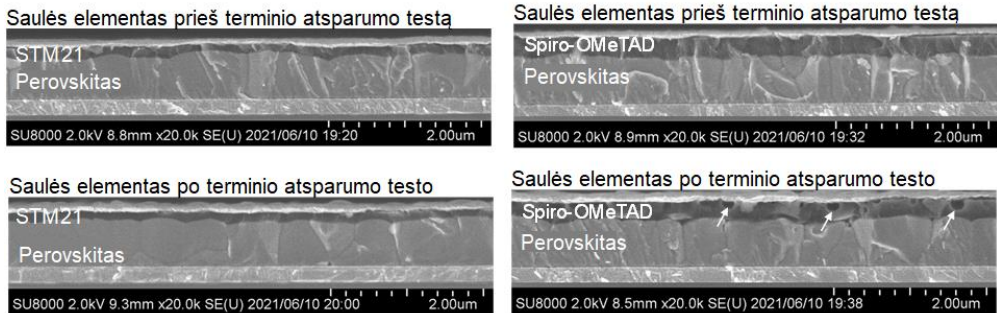
Taip pat buvo tirtas PSE stabilumas su junginiu **STM21**, kintant temperatūrai (49 pav.). Prietaisų su **STM21** terminis stabilumas yra didesnis nei SE su spiro-OMeTAD.



49 pav. Saulės elementų našumas, veikiant juos skirtingomis temperatūromis

Iš gautų rezultatų matoma, kad prietaisų, kuriuose kaip SMT naudojamas **STM21**, našumas šiek tiek sumažėja kaitinant juos 100 °C 24 valandas. Tomis

pačiomis sąlygomis tirtų elementų, kuriuose naudojamas spiro-OMeTAD, našumo sumažėjimas yra didesnis. Kaitinant prietaisus 120 °C, efektyvumas taip pat sumažėja, tačiau prietaiso, į kurio sudėtį įeina **STM21**, efektyvumas vis tiek išlieka didesnis. Po šio tyrimo **STM21** sluoksnis saulės elemente išliko lygus ir vientisas, o spiro-OMeTAD sluoksnyje atsivėrė ertmės (50 pav.).



50 pav. SE sluoksniai prieš terminio atsparumo tyrimą (kairėje) ir po terminio atsparumo tyrimo (dešinėje)

Manoma, jog didesnę PSE terminį stabilumą sąlygoja didesnės stiklėjimo temperatūrų vertės (**STM21** – 217 °C, **STM22** – 97 °C, **STM23** – 109 °C, **STM24** – 212 °C, **STM25** – 94 °C ir spiro-OMeTAD – 126 °C [311]).

Apibendrinus gautus rezultatus galima teigti, kad tiksliniai žvaigždės formos junginiai pasižymi geresnėmis morfologinėmis savybėmis. Kaip ir tikėtasi, prietaisai su **STM21** pasižymėjo aukščiausiu našumu, kuris yra kiek mažesnis nei PSE su spiro-OMeTAD, tačiau pastarąjį ženkliai lenkia stabilumu.

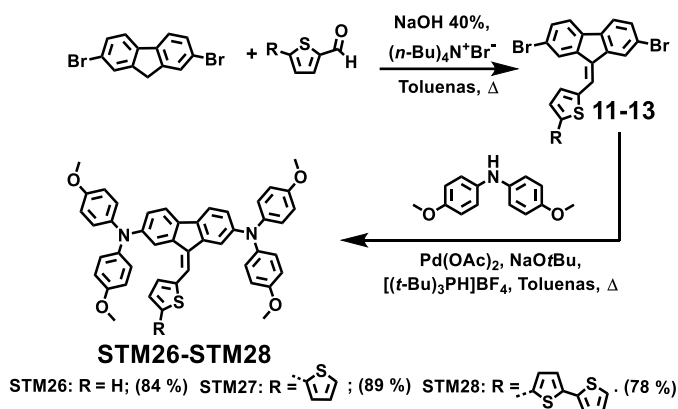
3.5. Skyles transportuojantys puslaidininkiai, turintys fluoreno bei tiofeno fragmentus, Sb_2S_3 saulės elementams

Šioje publikacijoje aprašomi nauji fluorenilidenilo ir tiofeno chromoforus turintys junginiai, remiantis publikuotu straipsniu *ACS Appl. Energy Mater.*, **2023**, 6, 3822–3833, S. Mandati, N. Juneja, A. Katerski, A. Jegorovė, R. Grzibovskis, A. Vembris, T. Dedova, N. Spalatu, A. Magomedov, S. Karazhanov, V. Getautis, M. Krunks, I. O. Acik [319]; cituota 14 kartų.

Perovskitiniai saulės elementai pasižymi aukštu našumu, tačiau jų stabilumas dar nėra pakankamas. Todėl šalia pastarųjų SE tobulinimo yra išbandomi ir kiti fotovoltiniai prietaisai, kuriuose naudojamos stabilesnės šviesą absorbuojančios medžiagos [320]. Viena iš šių medžiagų yra stibio sulfidas (Sb_2S_3). Jis pasižymi dideliu absorbcijos koeficientu ($\sim 10^5 \text{ cm}^{-1}$) ir stabilumu [177]. Taip pat net ir esant ploniems ($\sim 100 \text{ nm}$) Sb_2S_3 sluoksniams, pasiekiamas gan geras saulės elementų efektyvumas [321]. Sb_2S_3 prietaisų sudėtis labai panaši į perovskitinių: FTO / TiO_2 / Sb_2S_3 / STM / Au. Dažniausiai kaip STM šiuose elementuose naudojami poli(3-heksiltiofenas) (P3HT) [322, 323] ar priedais legiruotas spiro-OMeTAD [324, 325]. Tačiau šių medžiagų sintezė yra gana sudėtinga, sąlygojanti didesnę jų kainą. Dar viena labai pageidaujama STM charakteristika – ji neturi sugerti regimosios šviesos, jos sluoksniai turi būti skaidrūs. Taip yra todėl, kad ji liejama ant šviesą sugeriančio

sluoksniu viršaus. P3HT pasižymi „parazitine“ absorbcija regimojoje srityje, taip sumažėjant saulės elementų našumui [13, 322]. Dėl šios priežasties mokslininkai ieško alternatyvų pirmiau paminėtiems STM, tikslingai mažindami saulės elementų kainą ir didindami jų našumą.

Šioje publikacijoje aprašomi trys tiksliniai junginiai, kuriuose prie centrinio fluoreno fragmento 9-padėtyje prijungtas įvairus skaičius tiofeno chromoforų, o puslaidininkio periferinėje dalyje prijungti 4,4'-dimetoksidifenilaminų pakaitai. Yra žinoma, kad tiofeno S atomas gali sudaryti koordinacinę ryšį su Sb atomais, taip pagerinant STM ir Sb₂(S, Se)₃ paviršių sandūrą [326]. Manoma, jog šis ryšys veikia kaip „tunelis“ krūvininkams, taip padidėjant atviros grandinės įtampai ir užpildymo faktoriui.

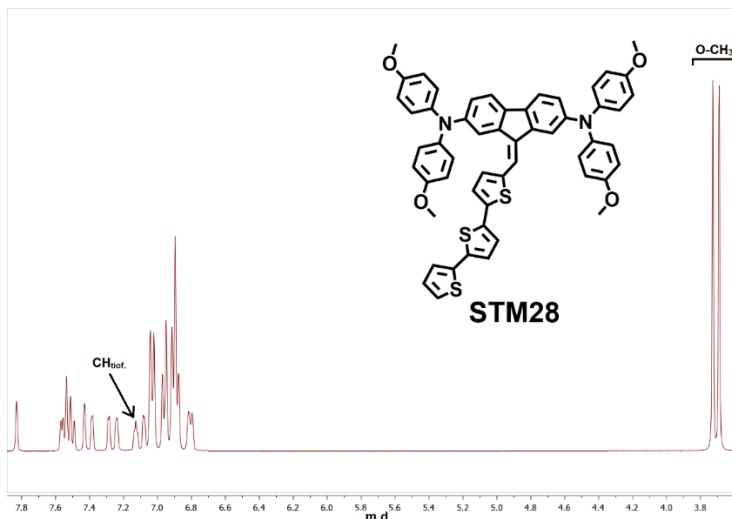


19 schema. Tikslinių junginių STM26–STM28 sintezė

Norint gauti tikslines medžiagas Knoevenagelio kondensacijos reakcijos metodu buvo susintetinti skyles transportuojančių organinių puslaidininkinių centrinių fragmentai **11–13**, turintys 1–3 tiofeno chromoforus. Šioje reakcijoje NaOH 40 % tirpalas naudotas kaip bazinis komponentas, o tetrabutilamonio bromidas – kaip tarpfazinis katalizatorius. Kitame etape tarpiniai produktai **11–13** paladžio katalizuojamos reakcijos metu buvo sujungti su 4,4'-dimetoksidifenilaminais, taip gaunant tikslinius junginius **STM26–STM28** (19 schema).

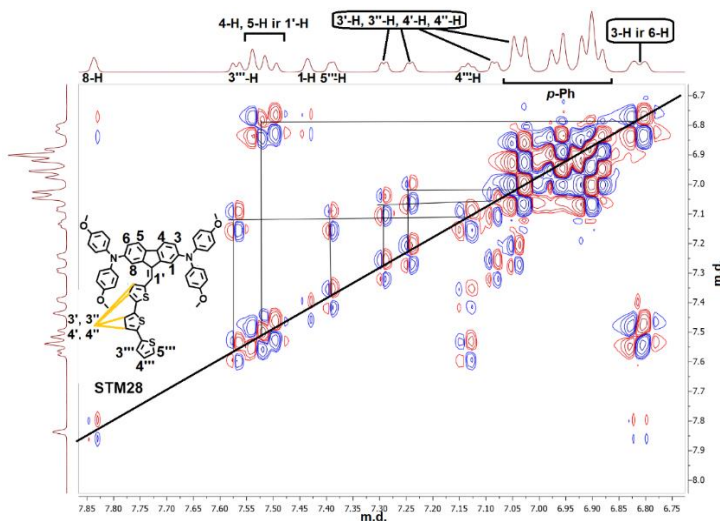
Junginių struktūra patvirtinta ¹H ir ¹³C BMR spektrais ir elementinės analizės metodu. **STM28** ¹H BMR spektro fragmentas pateiktas 51 pav. Ties 3,69 ir 3,73 m.d. stebimi du singletai, priskiriami OCH₃ grupėje esantiems protonų signalams. Tienilžiedo protono 4'''-H tripletas yra prie 7,13 m.d. (*J* = 4,4 Hz). Kitos silpnuose laukuose (6,80–7,83 m.d.) esančios smailės priskiriamos aromatiniams protonams. Siekiant išsiaiškinti, kuriuos aromatinių žiedų protonus atitinka gauti signalai, užrašytas H,H-COSY spektras (52 pav.). Du multipletai ties 6,93–6,86 m.d. ir 7,06–7,00 m.d. bei vienas dubletas ties 6,96 m.d. (*J* = 8,6 Hz) priklauso *p*-metoksifenilų protonams. Nagrinėjant H,H COSY spektro rezultatus matoma, kad terminalinio tienilžiedo protonas (t, *J* = 4,4 Hz) 4'''-H prie 7,13 m.d. sąveikauja su to paties tienilžiedo protonu 5'''-H, esančiu prie 7,38 m.d. (d, *J* = 3,6 Hz) (52 pav.). 4'''-H taip pat sąveikauja ir su ties 7,56 m.d. esančiu terminalinio tienilžiedo protonu 3'''-H (d, *J*

= 5,1 Hz). Kitų tienilžiedų protonai stebimi prie 7,28 (d, $J = 3,7$ Hz), 7,23 (d, $J = 3,9$ Hz), 7,08 (d, $J = 3,9$ Hz), 7,06–7,00 (m) m.d. Matoma, jog protonas, kurio signalas fiksuojamas esant 7,28 m.d. (d, $J = 3,7$ Hz), sąveikauja su protonu, esančiu ties 7,08 (d, $J = 3,9$ Hz) m.d., o protonas ties 7,23 m.d. (d, $J = 3,9$ Hz) – su protonu, kurio signalas persidengęs su *p*-metoksifenilo protonų signalais (7,06 – 7,00 m.d.).



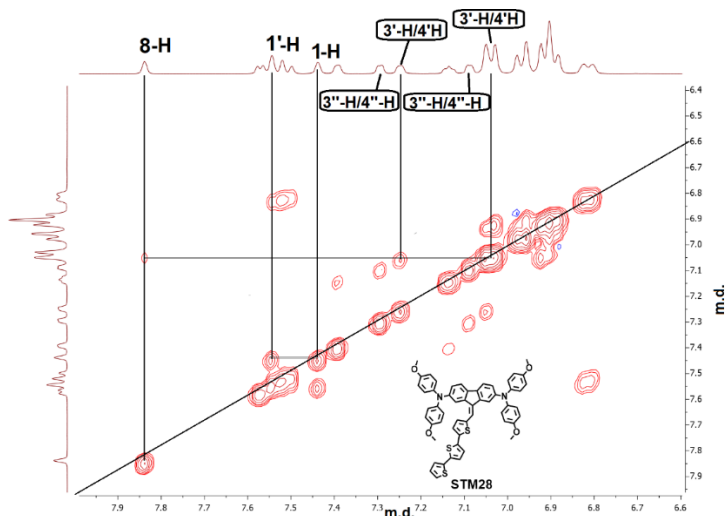
51 pav. STM28 ^1H BMR spektro fragmentas

Fluoreno 3-H ir 6-H protonų dubletas ($J = 8,3$ Hz) yra ties 6,80 m.d. Pastarieji sąveikauja su fluoreno 4-H ir 5-H protonais, kurių signalai fiksuoti ties 7,55–7,46 m.d. Šis multipletas rodo 3 protonų signalus, todėl manoma, kad šiame multiplete yra ir =CH– protono signalas. Spektre stebimi du ekvivalentūs singletai, esantys ties 7,83 ir 7,43 m.d., priskiriami fluoreno 1-H ir 8-H protonams.



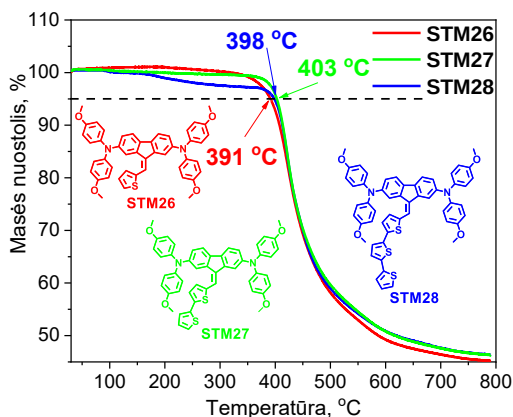
52 pav. Junginio STM28 H,H COSY spektro fragmentas

Norint išsiaiškinti, kurio tienilžiedo protonams priklauso atitinkami signalai ties 7,28 (d, $J = 3,7$ Hz), 7,23 (d, $J = 3,9$ Hz), 7,08 (d, $J = 3,9$ Hz), 7,06–7,00 (m) m.d., užrašytas NOESY spektras (53 pav.).



53 pav. Junginio STM28 NOESY spektro fragmentas

Nagrinėjant NOESY spektrą pastebima, jog 8-H protonas (7,83 m.d.) sąveikauja su tienilžiedo 3'-H ir 4'-H protonais (7,23 m.d. ir 7,06–7,00 m.d.). Likusios tienilžiedo protonų (7,28 m.d. ir 7,08 m.d.) smailės priskiriamos 3''-H ir 4''-H protonų signalams. =CH– protonas, kurio signalas fiksuojamas anksčiau minėtame multiplete ties 7,55–7,46 m.d., sąveikauja su fluoreno 1-H protonu (7,43 m.d.).



54 pav. STM26–STM28 TGA kreivės

Norint nustatyti tikslinių medžiagų termines savybes, buvo atlikti TGA ir DSK tyrimai. Iš gautų rezultatų matoma (54 pav. ir 9 lentelė), kad visos medžiagos 5 % masės praranda esant didesnei nei 390 °C temperatūrai. Lyginant **STM26** ir daugiau tiofeno fragmentų turinčius **STM27** ir **STM28** pastebima, jog padidėjusi molekulinė

masė sąlygoja masės nuostolius aukštesnėse temperatūrose (**STM26** – 391 °C, **STM27** – 403 °C, **STM28** – 398 °C).

Nagrinėjant DSK rezultatus akivaizdu, kad visų medžiagų stiklėjimo temperatūros yra šiek tiek mažesnės nei 100 °C (**STM26** – 92 °C, **STM27** – 97 °C, **STM28** – 99 °C). Lyginant visus naujus junginius tarpusavyje, matoma, kad didėjant tiofeno fragmentų skaičiui molekulėje, stiklėjimo temperatūra padidėja. Taip pat tiek pirmojo, tiek antrojo kaitinimo metu nefiksuoti jokie kiti faziniai virsmi, išskyrus **STM26** atveju ($T_{lyd.}$ – 202 °C). Tai reiškia, jog medžiagos **STM27** ir **STM28** yra tik amorfinės būsenos, todėl tikėtina, jog šių medžiagų plėvelės ilgainiui išliks homogeniškos.

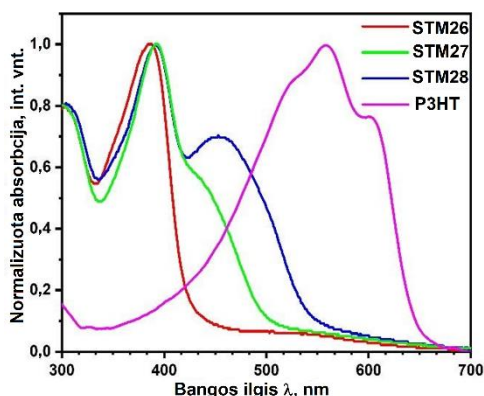
Medžiagų konjugacijai išsiaiškinti užrašyti UV–RŠ spektrai iš plėvelių. Anot absorbcijos spektrų rezultatų, naujų junginių $\pi \rightarrow \pi^*$ elektroninių perėjimų smailės, kurias galima priskirti 4,4'-dimetoksifenilaminų apsuptiems fluoreno fragmentams, yra išsidėsčiusios 270–430 nm diapazone.

9 lentelė. Optiniai, terminiai ir fotoelektriniai naujų STM parametrai

STM	$T_{st.}^a, ^\circ\text{C}$	$T_{sk.}^c, ^\circ\text{C}$	$\lambda_{abs}^b, \text{nm}$	I_p^c, eV	$\mu_0^d, \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$
STM26	92	391	303, 386	4,95	$7,07 \times 10^{-7}$
STM27	97	403	299, 393, 438	4,95	$2,15 \times 10^{-7}$
STM28	99	398	293, 392, 449	5,0	$3,68 \times 10^{-6}$

^aStiklėjimo ($T_{st.}$) temperatūros fiksuotos DSK antrojo kaitinimo metu; ^bplėvelių UV–RŠ spektruose fiksuoti absorbcijos maksimumų poslinkiai; ^cjonizacijos potencialai pamatuoti fotoelektronų emisijos (PES) metodu; ^dkrūvininkų judrio vertė silpnuose laukuose.

Didėjant tiofenų pakaitų skaičiui molekulėse, tikslinių junginių UV–RŠ spektrų absorbcijos juostos, priskiriamos $\pi \rightarrow \pi^*$ perėjimams, slenkasi batochromiškai (55 pav. ir 9 lentelė).



55 pav. STM26–STM28 ir P3HT UV–RŠ spektrai

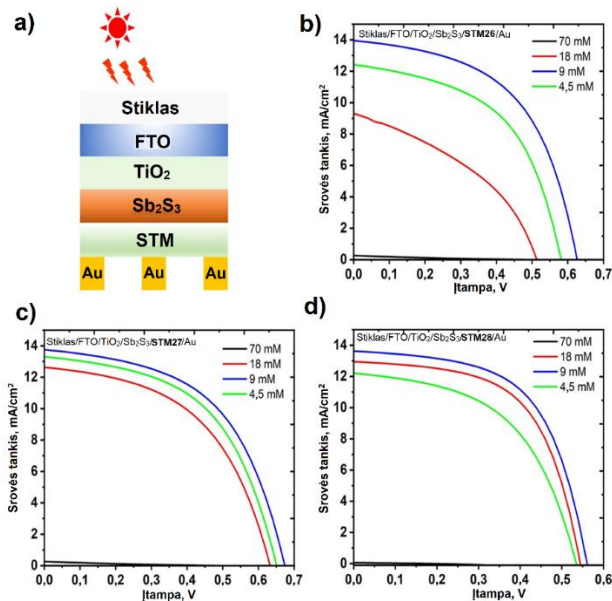
Lyginant naujų tiofeno fragmentus turinčių junginių spektrus su P3HT, galima teigti, kad intensyviausia jo absorbcija stebima 400–650 nm srityje, o **STM26**–

STM28 tame pačiame diapazone pasižymi gerokai mažesnėmis sugerties smailėmis. Todėl galima tikėtis, kad naujos medžiagos geriau atliks STM funkciją sukonstruotuose saulės elementuose.

Naujų STM jonizacijos potencialai nustatyti fotoelektronų emisijos metodu (PES). Iš gautų rezultatų matoma, jog junginių I_p vertės yra 4,95–5,0 eV intervale. Beveik vienodas HOMO vertes galima lemti tiofenų fragmentų išsidėstymas erdvėje. Didžiausiu I_p pasižymi junginys, turintis daugiausiai tiofenų fragmentų molekulėje **STM28** ($I_p = 5,0$ eV) (9 lentelė).

Norint išsiaiškinti, kaip greitai medžiaga gali judėti krūvininkai, laiko lėkio metodu ištirtas kryptingas skylių judėjimas. Lyginant medžiagas tarpusavyje, matoma, kad krūvininkų dreifinis judris šiek tiek sumažėja, prijungiant du tiofeno fragmentus į molekulę (**STM26** – $7,07 \times 10^{-7}$ cm²/Vs, **STM27** – $2,15 \times 10^{-7}$ cm²/Vs). Esant didžiausiam tienilpakaitų skaičiui, skylių dreifinis judris padidėja (**STM28** – $3,68 \times 10^{-6}$ cm²/Vs).

Iš gautų optinių, terminių ir fotoelektinių savybių rezultatų galima teigti, kad šios medžiagos gali būti panaudotos kaip STM saulės elementuose, todėl buvo sukonstruoti prietaisai, kuriuose Sb₂S₃ naudojamas kaip absorbuojantis sluoksnis (56 pav., a). Prietaiso konstrukcija: stiklas / FTO / TiO₂ / Sb₂S₃ / STM / Au. 56 pav., b–d, pateiktas saulės elementų optimizavimas, keičiant STM koncentraciją.

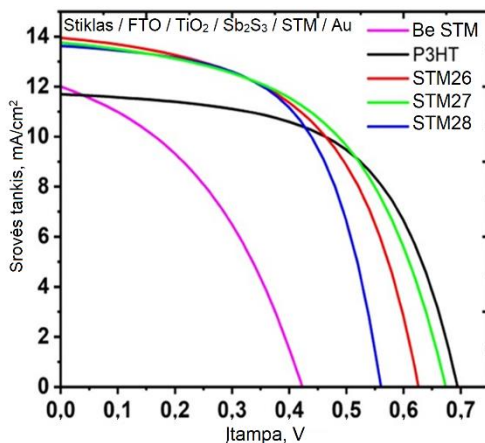


56 pav. Sb₂S₃ saulės elemento konstrukcija (a); J – V kreivės: b) **STM26**; c) **STM27**; d) **STM28**, esant skirtingoms STM koncentracijoms

Iš gautų rezultatų matoma, jog STM sluoksniui formuoti panaudojus 70 mmol koncentracijos **STM26** tirpalą, fiksuojamas itin mažas saulės elemento efektyvumas. Didinant tirpalo praskiedimą, padidėja ir prietaiso našumas (70 mmol – 0,1 %, 18 mmol – 2 %, 9 mmol – 4,7 %), tačiau iki tam tikros ribos (4,5 mmol – 3,8 %). Tokia pati tendencija matoma ir liejant sluoksnius iš **STM27** ir **STM28** tirpalų (**STM27**: 70

mmol – 0,2 %, 18 mmol – 4,0 %, 9 mmol – 4,9 % ir 4,5 mmol – 4,5 %; **STM28**: 70 mmol – 0,15 %, 18 mmol – 4,1 %, 9 mmol – 4,5 % ir 4,5 mmol – 3,4 %). Akivaizdu, kad norint sukonstruoti efektyviausius prietaisus, turėtų būti naudojami 9 mmol koncentracijos STM tirpalai.

Gauti rezultataiulyginti su prietaisų, kuriuose kaip STM naudojamas P3HT (10 lentelė ir 57 pav.), rezultatais.



57 pav. Geriausių prietaisų J – V kreivės

Lyginant rezultatus tarpusavyje akivaizdu, jog geresni rezultatai yra pasiekiami, kai prietaisuose naudojamas STM sluoksnis – efektyvumas be STM yra tik 2,12 %. Taip pat matoma, kad saulės elementai, kuriuose yra naujos tiofeno fragmentus turinčios medžiagos, našumu pralenkia ir prietaisus su P3HT sluoksniu. Todėl galima teigti, jog šioje publikacijoje aptartos tikslinės medžiagos gali padidinti Sb_2S_3 SC efektyvumą.

10 lentelė. Iš J – V kreivių nustatyti fotovoltiniai saulės elementų parametrai

STM	J_{sc} , mA cm^{-2}	V_{oc} , V	FF	PCE , %
Be STM	12,0	0,43	0,41	2,12
P3HT	11,7	0,69	0,58	4,68
STM26	13,9	0,63	0,54	4,73
STM27	13,7	0,68	0,53	4,94
STM28	13,6	0,56	0,59	4,50

Apžvelgus naujų medžiagų termines, optines ir fotoelektrines savybes, matoma, kad jos tenkina sąlygas, keliamas STM, naudojamoms Sb_2S_3 saulės elementuose. Testuojant tikslinius junginius, šiuose SE fiksuojamas prietaisų efektyvumo padidėjimas. Saulės elementas, į kurio sudėtį įeina **STM27** pasižymi aukščiausiu našumu, kuris yra didesnis nei prietaiso su standartu P3HT.

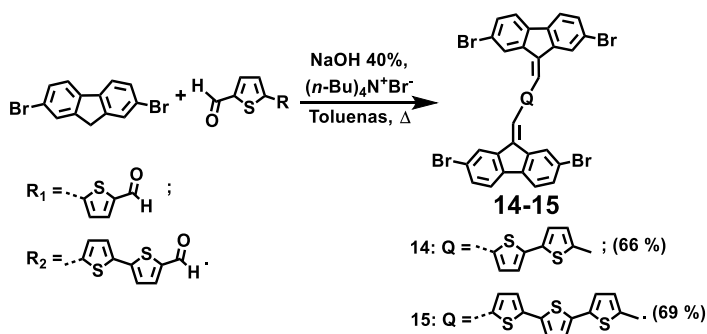
3.6. Tiofeno fragmentais sujungtų fluorenų dimerų skylos transportuojančios medžiagos Sb_2S_3 saulės elementams

Šiame poskyryje nagrinėjami skylos transportuojantys tiofeno fragmentais sujungti fluorenų dimerai, remiantis publikuotu straipsniu *Sustainable Energy Fuels*,

2024, 8, 4324–4334, N. Juneja, A. Jegorovė, R. Grzibovskis, A. Katerski, M. Daskeviciene, T. Malinauskas, A. Vembris, S. Karazhanov, N. Spalatu, V. Getautis, M. Krunks, I. O. Acik [327]; (cituota 2 kartus).

Ankstesnėje publikacijoje aprašyti organiniai puslaidininkiai **STM26–STM28** gerai veikia Sb₂S₃ saulės elementuose, tačiau jų stiklėjimo temperatūros nėra optimalios (jos artimos 100 °C) ir tai gali neigiamai paveikti prietaiso stabilumą. Remiantis pirmosios publikacijos patirtimi buvo nuspręsta susintetinti **STM26–STM28** dimerinius analogus, siekiant pagerinti termines savybes. Šioje publikacijoje aprašoma keturių tikslinių medžiagų, kuriuose molekulės centre esantis fluorenų dimeras pakeistas 4,4'-dimetoksidifenilaminais, yra sujungtas skirtingu tiofeno fragmentų tilteliu (**STM29** ir **STM30**). Taip pat, siekiant padidinti molekulės konjuguotų dvigubų ryšių sistemą, kuri gali turėti įtakos krūvininkų dreifiniam judriui, prie minėto centrinio fragmento buvo prijungti ir trifenilaminų dariniai, gaunant molekules **STM31** ir **STM32**, turinčias šoninius 4,4'-dimetoksitrifenilamino chromoforus.

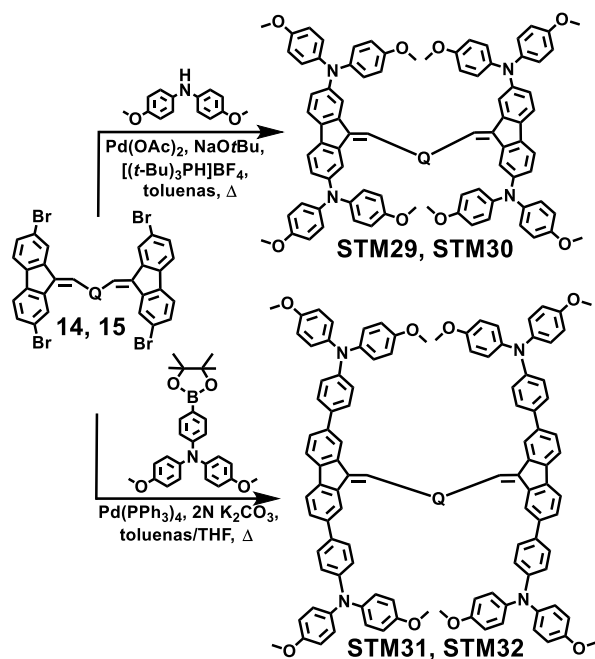
Šių dviejų grupių medžiagų sintezė yra skirtinga, nors abiem atvejais yra katalizuojama paladžio dariniais.



20 schema. Tarpinių junginių **14** ir **15** sintezė

Pirmiausia, taikant Knoevenagelio kondensacijos sąlygas, buvo susintetinti centriniai fragmentai **14** ir **15**, turintys du ir tris tiofeno chromoforus (20 schema). Reakcijos vykdytos 4 val. tolueno virimo temperatūroje, gaunant 66–69 % išeigas.

Sintetinant tikslinius organinius puslaidininkius **STM29** ir **STM30**, turinčius 4,4'-dimetoksidifenilamino pakaitus, buvo taikyta Buchwaldo–Hartwigo reakcijos metodika (21 schema), reakcijoje naudojant katalizatorių paladžio acetatą. Gauti tiksliniai produktai gryninti chromatografiškai, o gautos išeigos siekia 70 %. 4,4'-dimetoksitrifenilamino šoniniai chromoforai prie centrinių fragmentų **14** ir **15** buvo prijungti Suzuki reakcijos sąlygomis (21 schema). Reakcijos vykdytos 24 valandas, katalizuojant tetrakis(trifenilfosfino)paladžiui, gaunant tikslinius produktus **STM31** ir **STM32**, išgrynintus chromatografiškai, atitinkamai su 48 % ir 42 % išeigomis.

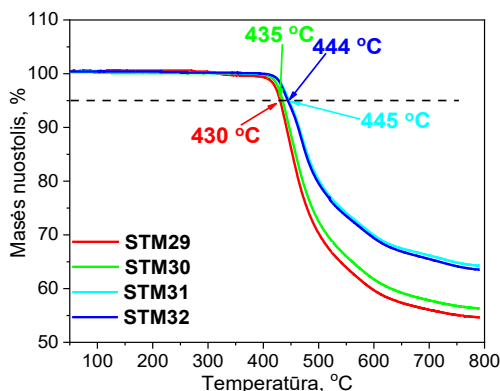


14, STM29, STM31: $Q = \text{---} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{---} \end{array} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{---} \end{array} \text{---}$; (70 %, 64 %)

15, STM30, STM32: $Q = \text{---} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{---} \end{array} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{---} \end{array} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{---} \end{array} \text{---}$.(48 %, 42 %)

21 schema. Tikslinių junginių STM29–STM32 sintezė

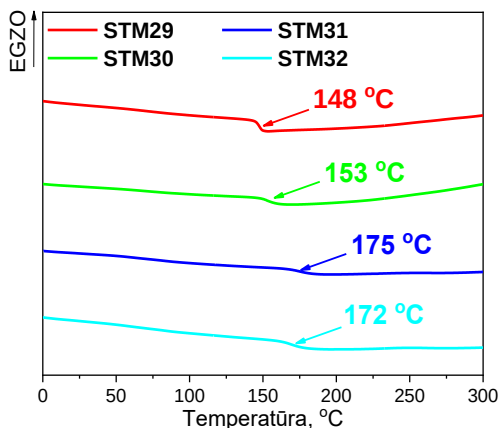
Terminės naujų tikslinių junginių savybės tirtos DSK ir TGA metodais. Iš gautų rezultatų matoma, kad nauji junginiai 5 % masės praranda 430–445 °C temperatūrų intervale (58 pav.). Sulyginus junginių, turinčių difenilaminų fragmentus, duomenis galima teigti, jog šiuo atveju ilgesnis tiofenų tiltelis šiek tiek padidina terminį patvarumą. Taip pat galima pastebėti, kad medžiagos, turinčios trifenilaminų fragmentus, pasižymi didesne T_{sk} .



58 pav. Tikslinių junginių STM29–STM32 TGA kreivės

Lyginant šias medžiagas su puslaidininkių analogais, aptartais ankstesniame skyrelyje (**STM26–STM28**), galima teigti, jog padidinus junginių molekulinę masę, T_{sk} taip pat padidėja.

Nagrinėjant DSK rezultatus matoma, kad visi junginiai yra molekuliniai stiklai, kurių stiklėjimo temperatūros fiksuojamos 148–175 °C ribose ir yra didesnės nei anksčiau aptartų analogų **STM26–STM28** (11 lentelė ir 59 pav.).



59 pav. DSK antrojo kaitinimo kreivės

Organinis puslaidininkis **STM32**, molekulės centre turintis tris tiofeno ir du šoninius 4,4'-dimetoksitriphenilamino pakaitus, yra tik amorfinės būsenos, nes DSK tyrimo metu, be virsmo „stiklas–skystis“, nevyksta jokių kitų fazinių virsmų. Kaip minėta anksčiau, tokios medžiagos labai pageidautinos saulės elementuose, nes jų sluoksniai išlieka homogeniški, o tai labai svarbu prietaiso našumui ir stabilumui.

Tikslinių produktų THF tirpalų UV–RŠ spektruose (11 lentelė) fiksuojamos absorbcijos juostos ties 300 nm ir 375 nm priskiriamos puslaidininkių molekulių šoninių chromoforų $\pi \rightarrow \pi^*$ elektronų perėjimams.

11 lentelė. Optiniai, terminiai ir fotoelektriniai naujų junginių **STM29–STM32** parametrai

STM	T_{st} ^a , °C	T_{lyd} ^b , °C	T_{sk} , °C	λ_{abs} ^c , nm	I_p ^d , eV	μ_0 ^e , cm ² V ⁻¹ s ⁻¹
STM29	148	276	430	293, 383, 468	4,94	$9,86 \times 10^{-7}$
STM30	153	157	435	300, 383, 479	4,94	$1,29 \times 10^{-6}$
STM31	175	175, 307	445	285, 377, 467	5,05	$3,38 \times 10^{-6}$
STM32	172	–	444	286, 377, 480	5,08	$1,85 \times 10^{-6}$

^aStiklėjimo (T_{st}) temperatūros fiksuotos DSK antrojo kaitinimo metu; ^blydymosi (T_{lyd}) temperatūros fiksuotos DSK pirmojo kaitinimo metu; ^cUV–RŠ spektruose fiksuoti

absorbcijos maksimumų poslinkiai (THF, $c = 10^{-4}$ mol/l); ^djonizacijos potencialai pamatuoti PES metodu; ^ekrūvininkų judrio vertė silpnuose laukuose.

Mažesnio intensyvumo smailės, esančios ties $\sim 425\text{--}500$ nm, priskiriamos centrinių tiofeno fragmentų analogiškiems valentinių elektronų $\pi \rightarrow \pi^*$ šuoliukams. Esant daugiau tiofeno pakaitų, pastariesiems priskiriamos smailės slenkasi batochromiškai. Lyginant tikslinių junginių UV–RŠ spektrus tarpusavyje, matoma, kad šoninius 4,4'-dimetoksitrifenilamino pakaitus turinčios medžiagos pasižymi intensyvesne absorbcija, tikėtina, dėl papildomo fenilenžiedo. Sugretinus gautų dimerų ir jų analogų, aprašytų 2.5 poskyryje, absorbcijos spektrų rezultatus, galima pastebėti, jog sugerties smailės yra labai panašios, todėl galima teigti, jog dimerų dvigubų ryšių konjugacija beveik nekinta.

Puslaidininkių **STM29–STM32** krūvininkų dreifinio judrio skaitinės vertės, nustatytos ToF metodu yra $9,86 \times 10^{-7} - 3,38 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ intervale (11 lentelė). Galima teigti, kad papildomi fenilenžiedai šoniniuose molekulių fragmentuose krūvininkų dreifinį judrį šiek tiek padidina.

Norint įsitinkinti, kad šių medžiagų energiniai lygmenys yra tinkami Sb_2S_3 saulės elementams, buvo nustatyti jų jonizacijos potencialai (11 lentelė). Matoma, jog visų šių STM I_p skaitinės vertės yra $\sim 5,0$ eV (**STM29** – 4,94 eV, **STM30** – 4,94 eV, **STM31** – 5,05 eV ir **STM32** – 5,08 eV). Papildomi tiofenų fragmentai molekulių centre beveik nekeičia jonizacijos potencialo, o papildomi fenilpakaitai šoniniuose molekulės chromoforuose I_p vertę kiek padidina.

Sukonstruotų SE (stiklas / FTO / TiO_2 / Sb_2S_3 / STM / Au) charakteristikos pateiktos 12 lentelėje. Prietaisas be STM siekė vos 1,9 % efektyvumą. Naudojant P3HT ir 4,4'-dimetoksidifenilamino pakaitus turinčius puslaidininkius **STM29** ir **STM30**, fiksuojami J_{sc} ir V_{oc} padidėjimai, lemiantys ir didesnį prietaisų našumą (P3HT – 4,7 %, **STM29** – 3,9 % ir **STM30** – 4,5 %). Tačiau kaip STM naudojant 4,4'-dimetoksitrifenilamino pakaitus turinčius darinius **STM31** ir **STM32** saulės elementai beveik neveikia (**STM31** – 0,8 % ir **STM32** – 0,7 %). Galbūt **STM31** ir **STM32** HOMO energiniai lygmenys yra per daug artimi Sb_2S_3 HOMO lygmeniui (Sb_2S_3 – –5,1 eV).

12 lentelė. Iš J – V kreivių nustatyti fotovoltiniai saulės elementų parametrai, kuriuose naudojami **STM29–STM32** puslaidininkiai

STM	$J_{sc}, \text{mA cm}^{-2}$	V_{oc}, mV	$FF, \%$	$PCE, \%$
Be STM	8,7	478	46	1,9
P3HT	12,2	689	55	4,7
STM29	9,7	656	43	3,9
STM30	12,1	673	56	4,5
STM31	5,7	439	35	0,8
STM32	6,1	437	33	0,7

Nors SC su tiksliniais junginiais ir neaplenkė prietaiso našumo su standartu P3HT, tačiau optimaliausių prietaisų sluoksniams lieti sunaudota mažiau šių tikslinių medžiagų, todėl ir pastarųjų sluoksniai yra plonesni ($\sim 20\text{--}25$ nm, P3HT $\sim 80\text{--}100$ nm). Dėl šios priežasties saulės elementų su tiksliniais junginiais **STM29–STM32**

pralaidumas yra didesnis nei standarto (**STM29** – 24 %, **STM30** – 26 %, **STM31** – 23 %, **STM32** – 23 % ir P3HT – 21 %), sąlygojantis šių organinių puslaidininkių naudojimą skaidrioms SE konstrukcijoms.

Apibendrinant visas apžvelgtas publikacijas, galima teigti, kad susintetintų skylių transportuojančių fluorenil- ir karbazolilchromoforus turinčių organinių puslaidininkių terminės, optinės bei fotoelektrinės savybės yra tinkamos, norint šiuos tikslinius junginius panaudoti naujos kartos saulės elementuose. Tai buvo įtikinamai pademonstruota sukonstruojant ir charakterizuojant efektyvius perovskitinius ir Sb_2S_3 saulės elementus.

4. IŠVADOS IR REZULTATAI

Disertacijoje pristatyti perspektyvūs fluorenilo ir karbazolilo chromoforų turintys *p*-organiniai puslaidininkiai naujos kartos saulės elementams. Darbo metu suformuluotos išvados:

1. Taikant Buchwaldo–Hartwigo reakcijos metodiką susintetinti spiro-OMeTAD bei „pusiniai“ analogai, kuriuose 4-metoksifenilchromoforai pakeisti 9-etilkarbazolilchromoforais. Atlikus šių skyles transportuojančių organinių puslaidininkių savybių tyrimus nustatyta, kad:
 - 1.1. visų tikslinių junginių T_{sk} yra aukštesnė nei 400 °C. 4-metoksifenilchromoforus keičiant didesniais 9-etilkarbazolilchromoforais, terminis molekulių patvarumas didėja. Daugumos tikslinių junginių T_{st} yra didesnė nei 100 °C. Ilgesni ir šakoti alkilpakaitai mažina molekulinio stiklo susidarymo temperatūrą;
 - 1.2. spiro-OMeTAD bei „pusiniuose“ analoguose 4-metoksifenilchromoforų keitimas 9-etilkarbazolilchromoforais mažina I_p skaitines vertes (**STM3** – 4,93 eV, **STM6** – 4,85 eV), o ilgesni alkilpakaitai jas kiek didina (**STM3** – 4,93 eV, **STM4** – 4,95 eV, **STM5** – 5,02 eV);
 - 1.3. didžiausiu teigiamųjų krūvininkų judriu iš spiro-OMeTAD analogų pasižymėjo molekulė **STM2** ($3,6 \times 10^{-4}$ cm²/Vs), kurioje visi 4-metoksifenilchromoforai pakeisti 9-etilkarbazolilchromoforais. Iš „pusinių“ analogų – molekulės **STM3** bei **STM4**, turinčios abu minėtus chromoforus ($3,9 \times 10^{-4}$ cm²/Vs);
 - 1.4. „pusinis“ spiro-OMeTAD analogas **STM2**, turintis 4-metoksifenil- ir karbazolilpakaitus periferinėje molekulės dalyje, demonstruoja saulės elementų galios efektyvumą artimą etaloniniam, tačiau jį gerokai lenkia stabilumu.
2. Paladžio katalizuojamos ir Knoevenagelio kondensacijos reakcijų sąlygomis buvo susintetinti akceptorinius ir donorinius chromoforus turintys bipoliniai fluoreno dariniai. Atlikus šių junginių savybių tyrimus nustatyta, kad:
 - 2.1. susintetinti fluoreno dariniai yra termiškai stabilūs – 5 % masės svorio praranda aukštesnėje nei 400 °C temperatūroje;
 - 2.2. visi tiksliniai junginiai yra stabilios amorfinės būsenos. Jų T_{st} yra aukštesnė nei 100 °C, išskyrus junginio **STM11** ($T_{st} = 92$ °C);
 - 2.3. šių organinių puslaidininkių jonizacijos potencialo (5,02–5,21 eV) vertės priklauso nuo akceptorinių fragmentų kiekio ir jų savybių stiprumo: I_p didėja, didėjant ketogrupių skaičiui molekulėse bei šias grupes keičiant nitrilogrupėmis;
 - 2.4. susintetinti fluoreno dariniai, turintys 9-alkilkarbazolilo bei 9*H*-fluorenono chromoforus, pasižymi teigiamųjų krūvininkų pernaša, siekiančia $3,9 \times 10^{-7}$ cm²/Vs silpnuose elektriniuose laukuose. Dariniai su 9-alkilkarbazolilo ir dicianofluorenilidenilo arba antrachinono chromoforais pasižymi abiejų ženklų krūvininkų pernaša siekiančia $3,9 \times 10^{-7}$ cm²/Vs (skylių) bei $1,0 \times 10^{-8}$ cm²/Vs (elektronų) silpnuose elektriniuose laukuose.

3. Dviejų pakopų reakcijos metu buvo susintetinti šakotos struktūros fluorenilidenilo ir karbazolilo pakaitus turintys junginiai, centre turintys įvairius aromatinius fragmentus. Tiriant jų savybes nustatyta, kad:
 - 3.1. tikslinės medžiagos pasižymi aukštu terminiu stabilumu. Visi tiksliniai produktai 5 % masės praranda didesnėje nei 440 °C temperatūroje;
 - 3.2. didesnę konjuguotą dvigubų ryšių sistemą turi molekulės, kuriose substituoti fluorenilidenilo fragmentai sujungti benzeno centriniu fragmentu *p*-padėtimi, 1,4-pakeistu tiofenu bei trifenilaminu;
 - 3.3. visi tiksliniai junginiai turi stabilią amorfinę būseną. Jų T_{st} yra 190–231 °C intervale;
 - 3.4. tikslinių medžiagų jonizacijos potencialai yra 4,92–5,03 eV diapazone. Geriausiu krūvininkų dreifiniu judriu pasižymi organinis puslaidininkis **STM17** ($\mu_0 = 1,9 \times 10^{-6} \text{ cm}^2/\text{Vs}$);
 - 3.5. sukonstravus prietaisus, kuriuose kaip STM naudojami tiksliniai junginiai, gauti aukšti PSE našumai. Saulės elementų, kuriuose STM fluorenilidenilo fragmentai sujungti fenilenžiedu, efektyvumas yra geriausias (**STM16** – 22,13 % ir **STM17** – 21,26 %) ir labai mažai nusileidžia palyginamajam prietaisui su etalonu spiro-OMeTAD (22,83 %), tačiau jį lenkia stabilumu.
4. Kryžminio kopuliavimo reakcijos metu susintetinti skirtingomis padėtimis prijungtus karbazolilchromoforus turintys žvaigždės formos skyles transportuojantys puslaidininkiai. Ištyrus jų savybes, buvo nustatyta, kad:
 - 4.1. tiksliniai junginiai demonstruoja aukštą terminį stabilumą: T_{sk} fiksuojamos 411–525 °C diapazone, o stiklėjimo temperatūros yra 190–231 °C intervale. Visi junginiai pasižymi stabilia amorfine būsena. Šie rodikliai gerokai lenkia spiro-OMeTAD standartą;
 - 4.2. keičiant šoninių karbazolilchromoforų prisijungimo padėtį iš 3-C į 2-C, absorbcijos maksimumai ties 360 nm padidėja, o alkilgrandinės ilgis beveik nepaveikia sugerties smailių intensyvumo ir poslinkių. Taip pat matomas hipsochrominis emisijos maksimumo poslinkis, karbazolilpakaitų prisijungimo padėtį keičiant iš 3-C į 2-C;
 - 4.3. tikslinių medžiagų HOMO vertės yra nuo –4,86 iki –4,99 eV, o LUMO – nuo –2,11 iki –2,26 eV. Gautų energinių lygmenų skaitinės vertės puikiai dera su saulės elemente naudojamu perovskitu. Krūvininkų dreifinis judris fiksuotas nuo $3,5 \times 10^{-6}$ iki $1,0 \times 10^{-5} \text{ cm}^2/\text{Vs}$;
 - 4.4. geriausiu prietaiso galios efektyvumu (19 %) pasižymėjo saulės elementas su puslaidininkiu **STM22**.
5. Naudojant Knoevenagelio kondensacijos ir Buchwaldo–Hartwigo reakcijų sąlygas, susintetinti tiofeno ir 4,4'-dimetoksifenilamino chromoforus turintys skyles transportuojantys junginiai, kurių savybių tyrimais nustatyta, kad:
 - 5.1. visi tiksliniai junginiai 5 % masės praranda ~400 °C, o aukščiausia T_{sk} pasižymi medžiaga **STM27** ($T_{sk} = 403 \text{ °C}$), turinti didžiausią tiofeno chromoforų skaičių. Didėjant tiofeno fragmentų skaičiui molekulėse, jų T_{st} didėja (**STM26** – 92 °C, **STM27** – 97 °C, **STM28** – 99 °C);

- 5.2. keičiant tiofeno fragmentų skaičių, I_p vertės beveik nekinta ir yra išsidėsčiusios 4,95–5,0 eV intervale. Geriausiu krūvininkų dreifiniu judriu pasižymi organinis puslaidininkis **STM28** ($\mu_0 = 3,68 \times 10^{-6} \text{ cm}^2/\text{Vs}$);
- 5.3. didžiausias efektyvumas būdingas SE (stiklas / FTO / TiO_2 / Sb_2S_3 / STM / Au), kuriame kaip STM naudota **STM27** (4,94 %), taip pralenkiant prietaiso su etalonu P3HT našumą (4,68 %). Našumu nedaug atsiliko SE su **STM26** (4,73 %), o jos 1 g sintezės kaina yra tik 13 €, t. y. keliolika kartų mažesnė už P3HT kainą.
6. Taikant skirtingas paladžio katalizuojamų reakcijų metodikas, susintetintos tikslinės skyles transportuojančios medžiagos, kurių centre esantis difenilaminais arba trifenilaminais pakeistas fluorenų dimeras, yra sujungtas skirtingą tiofeno fragmentų skaičių turinčiais tilteliais. Įvertinus šių junginių savybes nustatyta, kad:
 - 6.1. didėjant dimerinių puslaidininkių molekulinei masei tiek $T_{sk.}$, tiek $T_{st.}$ didėja. Visų tikslinių junginių $T_{sk.}$ siekia daugiau nei 400 °C, o $T_{st.}$ yra 148–175 °C intervale;
 - 6.2. didinant tiofeno fragmentų skaičių dimerų centre, I_p beveik nekinta, tačiau papildomas fenilenžiedas šoniniuose fragmentuose I_p padidina (**STM29** – 4,95 eV ir **STM31** – 5,05 eV, **STM30** – 4,95 eV ir **STM32** – 5,08 eV). Analogiška tendencija būdinga ir krūvininkų dreifiniam judriui (**STM29** – $9,86 \times 10^{-7} \text{ cm}^2/\text{Vs}$ ir **STM31** – $3,38 \times 10^{-6} \text{ cm}^2/\text{Vs}$, **STM30** – $1,29 \times 10^{-6} \text{ cm}^2/\text{Vs}$ ir **STM32** – $1,85 \times 10^{-6} \text{ cm}^2/\text{Vs}$);
 - 6.3. geriausiu galios našumu pasižymėjo sukonstruoti saulės elementai (stiklas / FTO / TiO_2 / Sb_2S_3 / STM / Au) su puslaidininkiu **STM30**, kuris siekė 4,5 %. Dėl gauto prietaiso didesnio pralaidumo regimajai spinduliutei, jis perspektyvus skaidriems Sb_2S_3 saulės elementams konstruoti.

5. SUMMARY

5.1. Introduction

There are more than 8 billion people on Earth [1], and each year, the population grows by tens of millions, leading to greater consumption of Earth's natural resources, such as oil, coal, gas, of which, over 100 million tons are consumed annually [2]. These energy resources are non-renewable, which means that their supply will eventually get exhausted and become insufficient to meet humanity's needs. Furthermore, this large-scale consumption is closely linked to pollution, which contributes to global warming and triggers droughts, along with food and water shortages. To reduce the consumption of Earth's resources, renewable energy sources, such as wind, solar, and geothermal power should be utilized.

The Sun is the most powerful, unlimited, and free-of-charge energy source available to humankind, and, every year, large amounts of solar energy reach the Earth. For over 70 years, the solar cells technology has enabled consumers to produce energy in sustainable ways. Additionally, this method of energy extraction is ideal for scarcely populated, remote areas where it would be challenging to install a full-scale wired energy infrastructure. However, the solar technology has its drawbacks: the produced energy depends on the weather conditions and daytime hours, and the equipment is costly. Although there is no way to control the weather conditions, the cost of solar devices can be reduced by using more affordable raw materials and selecting suitable methods for solar cells fabrication.

Currently, Silicon solar cells are the most popular and most readily commercially available option. Nevertheless, their production is difficult due to the need for expensive raw materials and high energy consumption [8]. To address these issues, scientists are exploring alternative options including hybrid solar cells made from organic and inorganic materials. One promising technology is *perovskite solar cells* (PSC) which have the potential to reduce the cost of solar energy. PSC development began in 2009, and this technology has already achieved more than 26 % efficiency [9, 10]. Regardless, challenges remain, particularly with the stability of perovskite, which hinders commercialization. Currently, many extensive are being made to improve stability, e. g., utilizing various halogens or additives [11]. Additionally, the most efficient solar cells require expensive organic semiconductors. Scientists are working on developing cheaper alternatives which could be synthesized through simpler methods so that to reduce the cost of solar cells.

Similarly with PSC, other types of solar cells have been developed, such as *quantum dots* (QD), organic, or *copper-indium-gallium-selenide* (CIGS) devices. Since 2014, the Sb_2S_3 solar cell technology has seen rapid development, reaching 8 % efficiency [12]. These devices can be partially transparent, making them a promising option for integration into window construction. The light absorbing layer is made from inexpensive raw materials and can be produced by using various methods [13]. Nonetheless, this technology is limited by certain factors indicating low efficiency. The inefficient use of *hole transporting materials* (HTM), such as 2,2',7,7'-tetrakis[*N,N*-di(4-methoxyphenyl)amino]9,9'-spirobifluorene Spiro-OMeTAD or poly(3-heksylthiophene-2,5-diyl) P3HT may be one of the reasons why this

technology still fails to achieve high efficiency. The synthesis of Spiro-OMeTAD is complex [14], and achieving high regioselectivity of P3HT is difficult [15]. Although both semiconductors are commercially available, they are expensive [16, 17]. Therefore, it is crucial to develop cheaper alternative materials that can be used as efficient hole transporting materials and achieve similar or superior device performance.

The **aim of this work** is to synthesize hole-transporting semiconductors with fluorenyl- and carbazolyl- chromophores and investigate the properties of target compounds and their applicability to hybrid solar cells.

To accomplish the aim of the dissertation, the following tasks have been established:

1. To synthesize and investigate thermal, optical and photoelectrical properties of HTMs with fluorenyl chromophores, and their application in perovskite solar cells;
2. To synthesize bipolar semiconductors containing donor and acceptor fragments at their periphery; to characterize these materials and investigate their application in perovskite solar cells;
3. To synthesize HTMs with fluorenyl chromophores linked by aromatic fragments, and investigate the influence of these fragments on their optical, thermal, and photoelectrical properties, as well as their efficiency in perovskite solar cells;
4. To synthesize starburst p-type semiconductors using carbazole derivatives as raw materials, and examine their optical, thermal, and photoelectrical properties, along with their performance in perovskite solar cells;
5. To synthesize hole-transporting materials composed of thiophene and fluorenylidene fragments; to study their optical, thermal, and photoelectrical properties, and their application in Sb_2S_3 solar cells;
6. To synthesize organic semiconductors with fluorenylidene fragments connected by thiophene bridges, and evaluate their optical, thermal, and photoelectrical properties, as well as their potential application in Sb_2S_3 solar cells.

Novelty of the doctoral dissertation and its Connection to the Publications

In recent years, perovskite solar cells have been developed for commercialization, but their efficiency and stability remain limited [18]. These challenges can be controlled by selecting suitable semiconductor materials. Unfortunately, the standard HTMs in use today do not meet the requirements for industrial-scale production of perovskite solar cells, such as easy and low-cost synthesis. Spiro-OMeTAD is the commonly used HTM as it led to the development of devices with the highest efficiencies. In spite of that, it suffers from several disadvantages, including insufficient stability in devices, a risk of crystallization within the layer, and a challenging synthesis process which requires aggressive reagents [14]. Therefore, developing new HTMs that can be synthesized by using simpler methods while maintaining high stability in solar cells construction is crucial. In four of the author's publications, purposefully designed and synthesized molecular structures intended for use in perovskite solar cells are examined. These structures are

characterized by suitable morphological properties and, in some cases, offer simpler synthesis routes than Spiro-OMeTAD.

In the first publication, Spiro-OMeTAD analogues were developed by replacing 4-methoxyphenyl chromophores with 9-ethylcarbazolyl fragments, with the expectation of improving the morphological and photoelectric properties of the target compounds. Additionally, more easily synthesized ‘half’ analogues were proposed to determine whether solar cells containing materials with the fluorenyl central core could perform as efficiently as those with spirobifluorene-based compounds. The devices tested with target semiconductors showed an efficiency of 15.7–18.3 %, which was slightly lower than that of Spiro-OMeTAD. Even so, the improved morphological properties lead to superior stability in solar cells compared to those employing Spiro-OMeTAD.

In another publication, the synthesis and properties of new fluorene derivatives containing donor and acceptor chromophores were described. All new bipolar materials exhibited excellent thermal properties and a stable amorphous state. The decomposition temperatures (where the materials lose 5 % of their mass) were above 400 °C. The glass transition temperatures meet the requirements for HTMs. Additionally, the ionization potentials were suitable for applying the target materials in perovskite solar cells. Most of the new derivatives can transport both holes and electrons. However, the measured hole mobilities are too low (10^{-7} cm²/Vs), and therefore these compounds were not tested in perovskite solar cells.

The synthesis of branched HTMs containing fluorenylidene fragments was presented in the third publication. Detailed results of optical, morphological and photoelectrical properties were provided. All the target semiconductors exhibited good thermal properties with decomposition temperatures exceeding 450 °C and a stable amorphous state. The new compounds were tested in solar cells, and were found to achieve efficiencies of 19.61–22.13 %. A device containing the hole-transporting organic semiconductor **STM16** performed similarly to a solar cell with Spiro-OMeTAD, while demonstrating better stability.

In the fourth publication, starburst compounds with carbazole fragments in both the molecule core and periphery were developed. Prior to this article getting published, carbazole fragments had not been used as either central or side chromophores in this kind of derivatives. The target materials were synthesized by utilizing a one-step process. The new compounds demonstrated favorable morphological properties and a stable amorphous state. Devices containing the new HTMs reached 19 % efficiency, which is slightly inferior to the benchmark Spiro-OMeTAD, whereas, for all of them, the stability test revealed the superiority of the new organic semiconductors. This advantage was especially evident in case of **STM21**, which demonstrated an improved SC stability under specific thermal conditions.

Along with perovskite solar cells, other types of devices have also been developed. The efficiencies of Sb₂S₃ SC are lower than those of perovskite devices; nevertheless, the stability of the absorbing layer is higher, and no toxic materials are used in the process of its manufacturing [19]. The efficiency of these cells could be increased by using Spiro-OMeTAD or P3HT as HTM. Nevertheless, these materials

are not highly suitable for Sb_2S_3 SC due to their high cost, complicated synthesis, and ‘parasitic’ absorption. Based on the experience with perovskite solar cells, it is evident that a properly chosen HTM can enhance the solar cell efficiency. In the fifth publication, easily synthesized organic semiconductors with various thiophene chromophores were defined. The new compounds exhibit good morphological properties. Solar cells with the target HTMs attained 4.94 % efficiency, thus outperforming a device with standard P3HT. Additionally, all the target materials are relatively cheap compared to the commercially available alternative P3HT [16].

In the sixth publication, hole transporting materials containing fluorenyl dimers linked by thiophene bridges and diphenyl or triphenyl chromophores were developed. These molecules are dimer analogues of the HTMs discussed above. Most of these materials demonstrate suitable thermal, optical and photoelectric properties; therefore, these semiconductors were used in the construction of Sb_2S_3 solar cells. A device with compound **STM30**, containing three thiophene and four diphenylamine fragments, achieved the highest efficiency of 4.5 %, which is slightly lower than that of the benchmark P3HT (4.7 %). Nevertheless, due to its better transparency to visible light, this material is promising for the manufacturing of transparent devices.

5.2. Overview of Publications

In order for new-generation solar cells to be suitable for long-term use by similar customers and remain competitive with commercially available Si SC, longevity, high efficiency and low cost must be ensured. This can be achieved by selecting the appropriate materials for solar cell construction. It is well-known that HTM is a crucial component of SC, as it can significantly enhance the properties of devices. By modifying the molecular structure of the hole-transporting material and incorporating various functional groups, both the efficiency and stability of the device can be improved. Currently, the best efficiencies are achieved when Spiro-OMeTAD is used as the hole-transporting material. In spite of that, the synthesis of this compound is complex with yields that are not particularly impressive. In some cases, the Spiro-OMeTAD layer can crystallize within the device, leading to gaps and a reduced performance. Therefore, scientists are actively seeking more stable and cost-effective alternative materials that could reach similar device efficiencies.

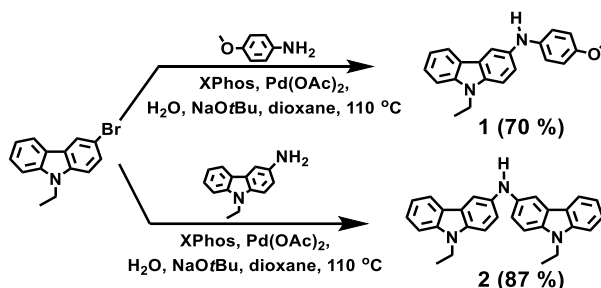
5.2.1. Molecular engineering of fluorene-based hole-transporting materials for efficient perovskite solar cells

In this chapter, new fluorene-class materials, are explored based on the published article: *Solar RRL*, **2022**, 6, 2100990, by A. Jegorovė, C. Momblona, M. Daskeviciene, A. Magomedov, R. Degutyte, A. M. Asiri, V. Jankauskas, A. A. Sutanto, H. Kanda, K. Brooks, N. Klipfel, M. N. Nazeeruddin, V. Getautis [290]; which has been cited 11 times.

As mentioned above, the synthesis of Spiro-OMeTAD is complex, and the target material is in a crystalline state. Therefore, there is a risk that the layer made from this material can crystallize, thereby causing efficiency losses. It is believed that the crystallinity of such compounds can be reduced by enlarging the semiconductor molecule and modifying it with alkyl functional groups. Since carbazole derivatives

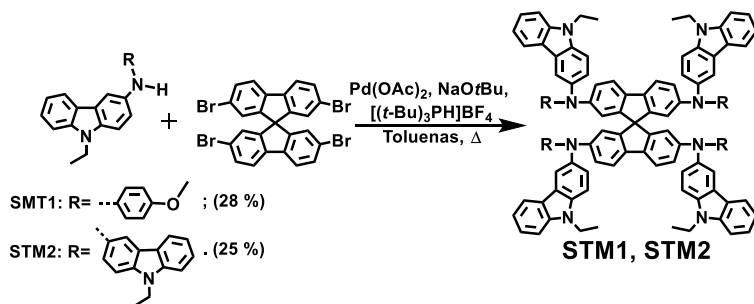
are among the most popular and cost-effective fragments used for HTM synthesis, it was decided to synthesize Spiro-OMeTAD analogues, where 4-methoxyphenyl chromophores are replaced with 9-ethylcarbazolyl fragments, hoping that the latter will improve the morphological and photoelectrical properties. Additionally, their ‘half’ analogues were synthesized to determine whether compounds with the fluorenyl central core could perform as efficiently as spirobifluorene-class materials in perovskite SCs.

This publication focuses on the synthesis, properties, and application of eight new fluorene derivatives. First, by using the Hartwig-Buchwald amination conditions with a Pd catalyst, amines **1** and **2**, which contain 9-ethylcarbazolyl chromophores, were synthesized (Scheme 22).



Scheme 22. Synthesis of 9-ethyl-*N*-(4-methoxyphenyl)-9*H*-carbazol-3-amine (**1**) and bis(9-ethyl-9*H*-carbazol-3-yl)amine (**2**)

The new Spiro-OMeTAD analogue **STM1**, with the spirobifluorene central core and 4-methoxyphenyl and alkyl carbazolyl groups, was synthesized by utilizing the Buchwald-Hartwig reaction conditions. In this process, 2,2',7,7'-tetrabromo-9,9'-spirobifluorene was coupled with secondary amine **1**, while employing palladium acetate (Pd(OAc)₂) as the catalyst (Scheme 23).

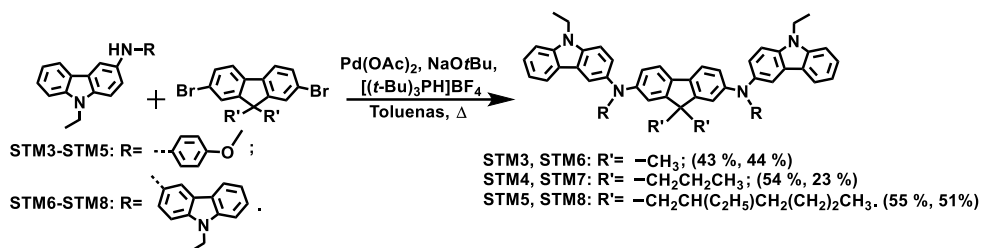


Scheme 23. Synthesis of Spiro-OMeTAD analogues **STM1** and **STM2**

By using amine **2** instead of amine **1**, Spiro-OMeTAD analogue **STM2**, which contains only 9-ethylcarbazolyl chromophores at its periphery, was synthesized (Scheme 23).

By using the Buchwald-Hartwig reaction conditions, 9-alkyl-2,7-dibromofluorene was linked with the previously mentioned secondary amines **1** and **2**. ‘Half’ Spiro-OMeTAD analogues **STM3–STM8**, featuring two and four carbazolyl

chromophores at their periphery and a central core of fluorene with various alkyl chains, were obtained (Scheme 24).



Scheme 24. Synthesis of ‘half’ Spiro-OMeTAD analogues SMT3–STM8

To evaluate the changes in the conjugated π -electron systems of new HTMs, ultraviolet-visible (UV-vis) and fluorescence (PL) spectra were recorded. The obtained results are presented in Table 13 and Figures 60 and 61.

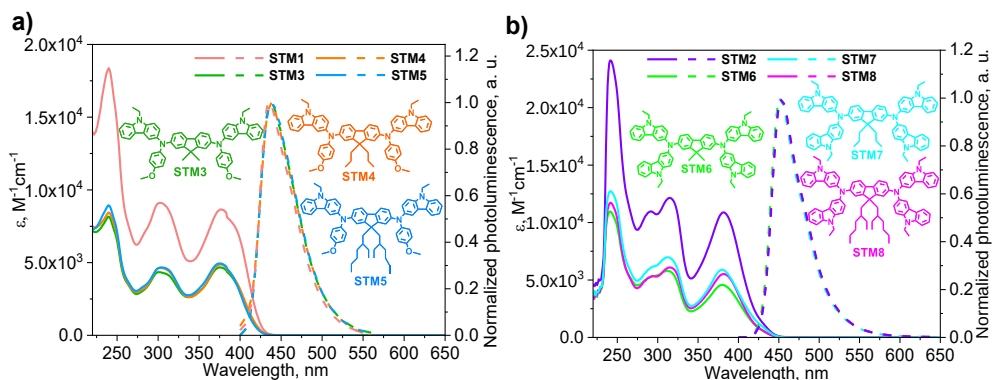


Figure 60. UV-vis absorption (solid lines) and normalized fluorescence (dashed lines) spectra from THF solutions: a) STM1 and STM3–STM5; b) STM2 and STM6–STM8 (UV-vis $c = 10^{-4}$ mol/l, FL $c = 10^{-5}$ mol/l)

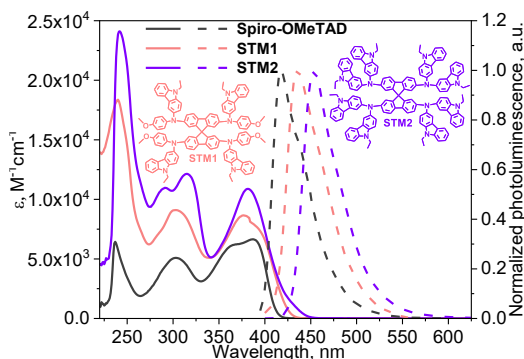


Figure 61. UV-vis absorption (solid lines) and normalized fluorescence (dashed lines) spectra from THF solutions of STM1, STM2 and Spiro-OMeTAD (UV-vis $c = 10^{-4}$ mol/l, FL $c = 10^{-5}$ mol/l)

From the obtained results, it can be seen that the smaller materials ('half' analogues of Spiro-OMeTAD) show lower absorption intensity peaks compared to their spirobifluorene-class analogues. Additionally, when comparing **STM1** and **STM3–STM5** and, similarly, **STM2** and **STM6–STM8**, no significant shift in the absorption maximum values was observed. This indicates that the different numbers of 4-methoxyphenyl and carbazolyl chromophores do not significantly influence the conjugation of new HTMs.

In comparison with spirobifluorene-class compounds, it is evident that the absorption spectra of **STM1** and **STM2** are visually similar to that of Spiro-OMeTAD. Only minor differences can be observed which may be attributed to the replacement of 4-methoxyphenyl chromophores with carbazolyl fragments. As the number of carbazolyl substituents in the molecule increases, the absorption maximum shifts bathochromically. This effect is particularly noticeable in the UV region (~250 nm), where transitions in the heterocyclic electrons systems dominate.

In the fluorescence spectra, a bathochromic shift is also observed (**Spiro-OMeTAD** – 417 nm, **STM1** – 435 nm, **STM2** – 453 nm), which may be caused by the significant energy difference between the ground and the excited states.

The obtained target materials are used in SC for thin-layer formation. One of the cheapest and simplest methods to form a material film is spin-coating. However, it is not always successful in creating homogenous layers. To achieve uniform films, the target compounds should be thermally stable and have a high glass transition temperature (T_g).

The new HTM mass losses at high temperatures were examined by using *thermogravimetric analysis* (TGA). The glass transition temperatures were determined by *differential scanning calorimetry* (DSC). The obtained data are presented in Table 13. All new compounds lose 5 % of their mass (T_d) at temperatures higher than 400 °C. This level of thermal resistance is a significant advantage, as operating solar cells can heat up to ~60 °C [292]. When comparing spirobifluorene-class materials in this work with the properties of Spiro-OMeTAD reported in the literature, it is evident that replacing four 4-methoxyphenyl groups with carbazolyl fragments leads to lower T_g (Spiro-OMeTAD – 449 °C [291], **STM1** – 438 °C). Interestingly, exchanging 4-methoxyphenyl chromophores with carbazolyl substituents notably improves the compound's thermal resistance (**STM2** – 512 °C).

New fluorene-class materials containing two carbazolyl fragments lose 5 % of their mass at 401–452 °C. The material with the lowest thermal resistance temperature is semiconductor **STM5**, which contains two branched alkyl chains in the central fluorene fragment. HTMs with four carbazolyl chromophores in the molecule demonstrates higher T_d temperatures (461–515 °C). In the case of the latter materials, another interesting effect can be observed, specifically, material **STM8**, containing branched alkyl chains, exhibits the highest thermal resistance. It is possible that a higher molecular mass leads to stronger interactions between molecules, which may result in a more orderly spatial arrangement, thereby improving T_d .

When comparing the glass transition temperatures of spirobifluorene-class materials and Spiro-OMeTAD, an increase in T_g due to a higher molecular mass can be observed (Spiro-OMeTAD – 124 °C [291], **STM1** – 169 °C), but only up to a

certain limit (**STM2** – 139 °C). When examining ‘half’ Spiro-OMeTAD analogues, it can be seen that longer alkyl chains in the central core result in lower T_g (**STM3** – 147 °C, **STM4** – 133 °C, **STM5** – 77 °C, and **STM6** – 196 °C, **STM7** – 183 °C, **STM8** – 127 °C). When comparing the T_g of materials with 4-methoxyphenyl and carbazolyl chromophores (**STM3–STM5**) to compounds containing only carbazolyl substituents (**STM6–STM8**), it is evident that smaller molecules exhibit ~50 °C lower glass transition temperatures. This effect could be attributed to the lower symmetry of the molecule, which leads to disordered spatial arrangement. The lowest T_g was noted for **STM5** (T_g – 77 °C), which is likely too low for practical use in SCs. However, all other new HTMs have T_g higher than 100 °C, making them suitable for use in solar cell construction, as these T_g values are well above the typical device operating temperatures.

Table 13. Thermal, optical and photophysical properties of new materials

Compound	T_g^a , °C	T_d , °C	λ_{abs}^b , nm	I_p , eV	μ_0 , cm ² /Vs ($E_0 = 0$ V/cm),
Materials with a 9,9'-Spirobifluorene central core					
Spiro-OMeTAD [291]	124	449	237, 303, 367, 387	5.0	4.1×10^{-5}
STM1	169	438	240, 303, 377	5.28	5.6×10^{-6c}
STM2	139	512	242, 291, 315, 382	4.90	3.6×10^{-4c}
Materials containing a fluorene core with 4-methoxyphenyl and carbazolyl chromophores					
STM3	147	452	240, 301, 376	4.93	3.9×10^{-4}
STM4	133	441	240, 303, 377	4.95	3.9×10^{-4}
STM5	77	401	240, 305, 375	5.02	2.9×10^{-5}
Materials containing a fluorene core with carbazolyl chromophores					
STM6	196	490	241, 292, 312, 380	4.85	3.6×10^{-5c}
STM7	183	461	242, 297, 312, 380	4.85	1.2×10^{-5c}
STM8	127	515	242, 295, 315, 382	4.96	3.0×10^{-5c}

^aGlass transition temperatures from DSC the second heating; ^bUV–vis spectra (THF, $c = 10^{-4}$ mol/l); ^ccharge carrier mobility of pure materials, calculated by extrapolating measurement results from compounds with polycarbonate Z (PC-Z) in a 1:1 composition.

It is of importance to note that, during the DSC investigation of all new materials, no endothermic transformation (indicative of the melting process) was

observed. This suggests that the materials exist only in the amorphous state. As a result, there is potential to achieve a homogeneous layer when forming films.

To determine whether the target materials are energetically compatible with perovskite and electrode layers, measurements of electron photoemission in air (PESA) were performed. That is how the ionization potential (I_p) values were obtained. The results are presented in Table 13. When comparing the I_p values of spirobifluorene-class materials, it is evident that carbazolyl fragments in the molecule result in a lower ionization potential (Spiro-OMeTAD – 5.0 eV, **STM1** – 4.83 eV). It can be suggested that this change occurs due to the easier oxidation of the carbazolyl fragments. However, the inclusion of a higher number of carbazolyl chromophores leads to the opposite effect as the ionization potential slightly increases (**STM2** – 4.9 eV). In this case, because of the abundance of moieties, the molecules are likely very constrained in the film, and carbazolyl side groups get positioned in a more disordered manner, which causes a slight increase in the I_p values.

In contrast to fluorene-class derivatives, it is evident that the length of the alkyl chain increases the ionization potentials (**STM3** – 4.93 eV, **STM4** – 4.95 eV, **STM5** – 5.02 eV, and **STM6** – 4.85 eV, **STM7** – 4.85 eV, **STM8** – 4.96 eV). This effect is likely due to a specific spatial arrangement of the molecules. The larger number of carbazolyl chromophores in the molecule decreases I_p , caused by an easier oxidation of the latter. Nevertheless, all the synthesized HTMs have oxidation potentials comparable to the energy levels of perovskite.

Charge drift mobility (μ) is also highly important for the solar cell operation. It is believed that a correlation exists between the charge mobility and the solar cell efficiency, i. e., the higher is the mobility, the higher is the efficiency of the solar cell. Not all materials could be measured in their pure form; therefore, those that could not be measured pure were mixed with polycarbonate Z (PC-Z). The numerical values of the results were recalculated by extrapolation, thus obtaining the hole drift mobility results for the new semiconductors (Table 13). It is evident that longer alkyl chains attached to the fluorene central core decrease the hole drift mobility. This effect may be due to the increased distance between molecules, or because of unfavorable spatial arrangements. Similarly, for the same reason, carbazolyl chromophores result in lower μ . However, spirobifluorene-class materials exhibit the opposite effect – i. e., replacing all the side fragments with carbazolyl chromophores increases the hole transport. Based on these results, it is clear that the hole drift mobility of new compounds is suitable for use in perovskite SCs.

Upon examining the thermal and photoelectrical measurement results, and being convinced that the synthesized new compounds can be used in perovskite SCs, n-i-p structure devices were constructed. The best results for solar cells are given in Figure 62 and Table 14. The construction of solar cells was as follows: FTO / *c*-TiO₂ / *m*-TiO₂ / SnO₂ / perovskite [(FAPbI₃)_{0.87}(MAPbBr₃)_{0.13}]_{0.92}(CsPbI₃)_{0.08} / STM / Au. HTMs were used in conjunction with 4-*tert*-butylpyridine (*t*BP), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and tris(2-(1*H*-pyrazol-1-yl)-4-*tert*-(butylpyridine)cobalt(III)tris(bis(trifluoromethylsulfonyl)imide (CoTFSI, FK209).

In comparing spirobifluorene-class compounds (Spiro-OMeTAD analogues), it can be seen that replacing 4-methoxyphenyl moieties with carbazolyl chromophores

results in lower SC efficiencies. It is likely that the decline in the open circuit voltage (V_{oc}) is caused by higher recombination due to either holes or unevenness at the perovskite/HTM surface junction. Nevertheless, the SC achieves efficiencies of 17.6 % and 18.3 % with materials **STM1** and **STM2**, respectively, which is not far behind the control device containing Spiro-OMeTAD (20.1 %).

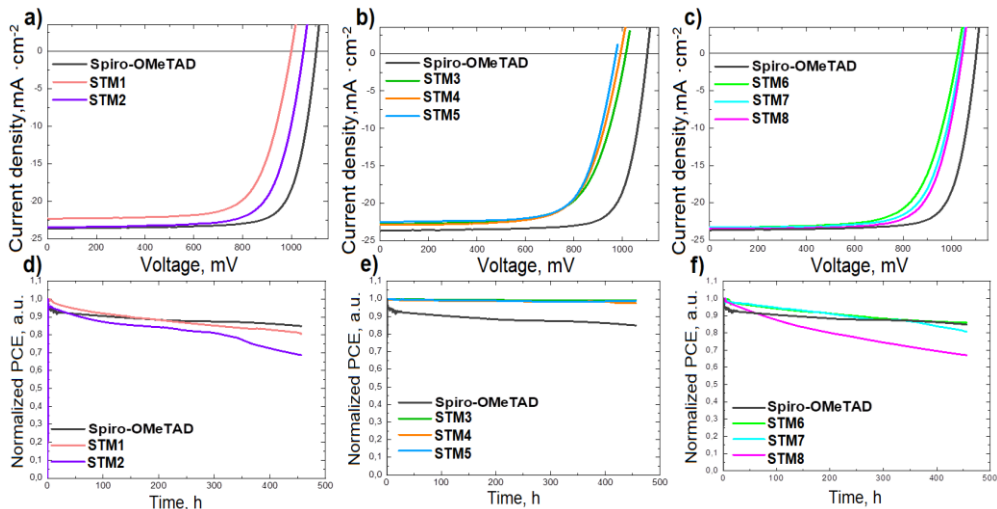


Figure 62. The J - V curves of best-performing SCs and the results of the stability test of HTMs: a), d) Spiro-OMeTAD, **STM1** and **STM2**; b), e) **STM3**–**STM5**; c), f) **STM6**–**STM8**. The stability tests were performed without encapsulating the devices, under N_2 atmosphere, at 25 °C

The solar cells that utilize ‘half’ Spiro-OMeTAD analogues as HTMs achieve slightly lower efficiencies. A higher performance is observed in materials containing four carbazolyl chromophores.

Table 14. Characteristics of solar cells

Compound	V_{oc} , mV	J_{sc} , $\text{mA} \cdot \text{cm}^{-2}$	FF	PCE , %
Materials with a 9,9'-Spirobifluorene central core				
Spiro-OMeTAD	1108	23.60	0.77	20.1
STM1	1000	22.32	0.79	17.6
STM2	1059	23.41	0.74	18.3
Materials containing a fluorene core with 4-methoxyphenyl and carbazolyl chromophores				
STM3	1014	22.80	0.68	15.7
STM4	992	22.89	0.69	15.7
STM5	987	22.35	0.73	16.1
Materials containing a fluorene core with carbazolyl chromophores				
STM6	1034	23.37	0.71	17.2
STM7	1045	23.32	0.73	17.8
STM8	1048	23.35	0.74	18.1

According to the data presented in Table 14, devices with HTMs containing carbazolyl and 4-methoxyphenyl substituents achieve ~16 % efficiency. It is believed that the lower performance is caused by poor interaction between the perovskite and HTM interfaces.

As mentioned above, materials containing 4-methoxyphenyl and carbazolyl moieties (**STM3–STM5**) have a lower symmetry than their counterparts with only carbazolyl substituents (**STM6–STM8**). In thin layer, the molecules of the derivatives with 4-methoxyphenyl and carbazolyl fragments may be spaced farther apart, thereby affecting the morphology of the perovskite/HTM junction surface, which results in a lower hole drift mobility and a higher recombination [293]. The length of the alkyl chain has practically no influence on the short-circuit current density, with values of 22.4–22.8 mA cm⁻² for devices with **STM3–STM5** and 22.3 mA cm⁻² for those containing **STM6–STM8**.

The stability of non-encapsulated devices was investigated under N₂ atmosphere at 25 °C (Figure 62, d–f). When comparing Spiro-OMeTAD and its analogues, it is evident that the solar cell stability decreases as the HTM molecule size increases. After 450 hours of operation, the maximum device efficiency decreased from 100 % to 85 % for Spiro-OMeTAD, to 81 % for **STM1** and to 69 % for **STM2**. A similar trend is observed for ‘half’ Spiro-OMeTAD analogues including carbazolyl chromophores – i. e., their efficiency decreases with an increasing alkyl chain length (**STM6** – 86 %, **STM7** – 81 % and **STM8** – 67 %). In contrast, devices containing HTM with both 4-methoxyphenyl and carbazolyl moieties (**STM3–STM5**) exhibit almost no change in performance under the specified conditions.

In summary, perovskite solar cells using new HTMs experience a slight decrease in efficiency compared to that with Spiro-OMeTAD. However, materials with the fluorenyl central core and 4-methoxyphenyl and carbazolyl fragments at their periphery ensure excellent device stability.

5.2.2. New fluorene-based bipolar charge transporting materials

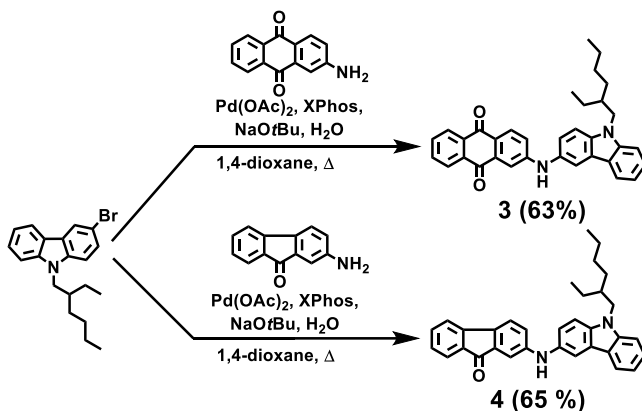
With reference to the published article *RSC Adv.*, **2024**, 14, 2975, *A. Jegorovė, M. Daskeviciene, K. Kantminiene, V. Jankauskas, R. J. Čepas, A. Gruodis, V. Getautis and K. Genevičius* [294], which has been cited 1 time; this chapter describes fluorene derivatives with both acceptor and donor groups that can transport electrons and holes.

It is believed that bipolar materials can interact with the perovskite layer, which may decrease the process of recombination, resulting in an improved efficiency and stability [241, 242]. Because of this, it was decided to modify the previously reported molecules with the fluorene central core, by synthesizing charge-transporting materials containing donor and acceptor chromophores at the molecular periphery. In the publication, six bipolar derivatives were developed.

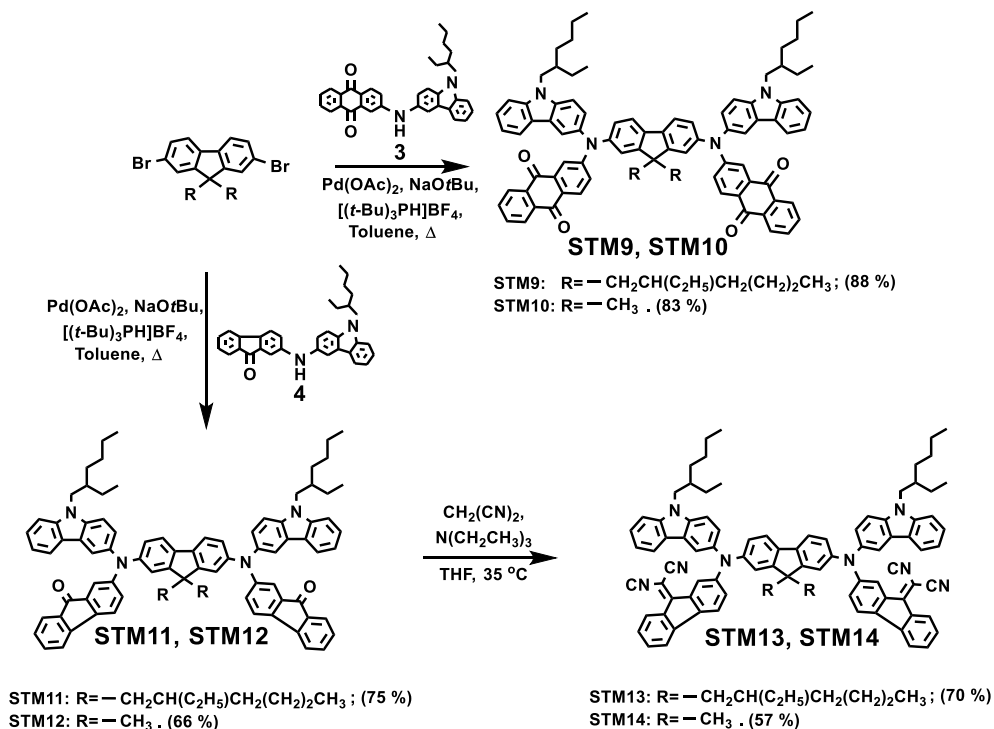
Firstly, the side fragments were utilized by using the Buchwald-Hartwig synthesis conditions. 3-bromo-9-(2-ethyl)hexylcarbazole was linked with 2-aminoanthraquinone or 2-amino-9*H*-fluorenone, and amines **3** and **4** were obtained (Scheme 25), containing electron-donor and electron-acceptor chromophores.

Bipolar fluorene derivatives **STM9** and **STM10**, containing a 9,9-dialkyl-9*H*-fluorene central fragment and side groups of alkylcarbazole/anthraquinone, were

synthesized by using the Buchwald-Hartwig cross-coupling reaction conditions by connecting 2,7-dibromo-9,9-dimethyl-9*H*-fluorene and 2,7-dibromo-9,9-di(2-ethylhexyl)-9*H*-fluorene with amine **3**, using Pd(OAc)₂ as the reaction catalyst (Scheme 26).



Scheme 25. Synthesis of intermediates **3** and **4**



Scheme 26. Synthesis of fluorene derivatives **STM9–STM14**

By replacing amine **3** with 2-((9-(2-ethylhexyl)-9*H*-carbazol-3-yl)amino)-9*H*-fluoren-9-one (**4**), fluorene derivatives **STM11** and **STM12**, containing both donor

(9-alkylcarbazolyl) and acceptor chromophores (9*H*-fluorenone) at the peripheral positions, were synthesized.

To further enhance the acceptor properties of these compounds, they were modified by incorporating malononitrile while using the Knoevenagel condensation reaction conditions, yielding fluorene derivatives **STM13** and **STM14**, respectively (Scheme 26).

In the next step, the thermal properties of the target bipolar materials were investigated. The obtained data showed that these bipolar compounds lose 5 % of their mass at temperatures higher than 400 °C (Table 15 and Figure 63).

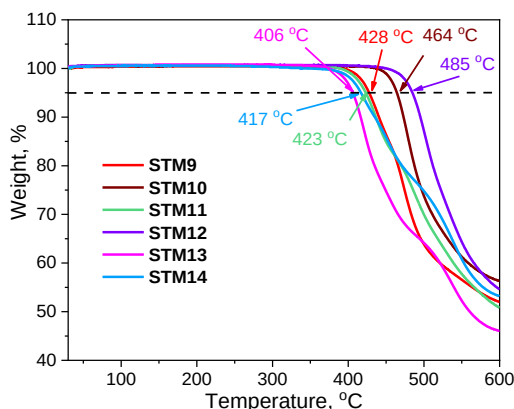


Figure 63. TGA curves of bipolar fluorene derivatives

As expected, replacing long and branched alkyl chains with methyl groups led to a higher thermal stability, as evidenced by the decomposition temperatures (**STM9** – 428 °C, **STM10** – 464 °C).

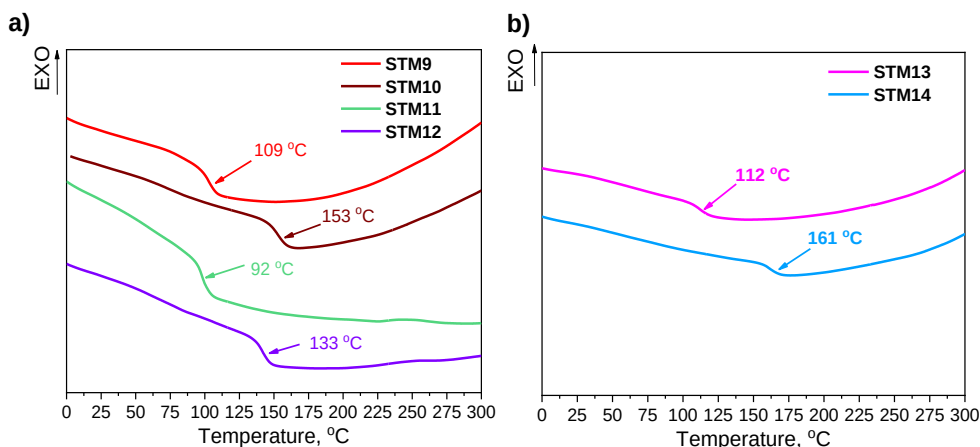


Figure 64. DSC curves of new bipolar materials: **a)** containing carbonyl groups (**STM9–STM12**); **b)** with cyano substituents (**STM13** and **STM14**)

Conversely, substituting carbonyl groups with nitrile fragments had the opposite effect (**STM11** – 423 °C, **STM13** – 406 °C). Additionally, the glass transition

temperatures of new bipolar materials were determined (Table 15 and Figures 64, a, b). Analysis of the DSC curves revealed that the glass transition temperatures of most compounds are greater than 100 °C. Compounds containing methyl substituents are characterized by higher T_g values than their analogues with long and branched alkyl fragments (**STM10** – 153 °C, **STM12** – 133 °C, **STM14** – 161 °C vs. **STM9** – 109 °C, **STM11** – 92 °C, **STM13** – 112 °C). Furthermore, it can be observed that the presence of fluorenone fragments decreases T_g , while the substitution of keto groups with nitrile groups leads to the opposite effect. No endothermic peaks were observed in the DSC curves, thus indicating that all new bipolar materials exist in an amorphous state. Therefore, it is likely that these materials can form high-quality layers.

In order to evaluate the optical properties of the compounds, the UV–vis spectra of the solutions and thin layers were recorded (Table 15 and Figure 65).

Table 15. Thermal, optical and photoelectrical properties of bipolar fluorene derivatives

Compound	T_g , ^a °C	T_d , °C	λ_{abs} ^b , nm	I_p , eV	μ_{hole}^c , cm ² /Vs	$\mu_{elec.}^d$, cm ² /Vs
STM9	109	428	311, 355, 512	5.18	2.6×10^{-7}	4.6×10^{-9}
STM10	153	464	311, 352, 514	5.21	1.4×10^{-7}	1.1×10^{-9}
STM11	92	423	378, 534	5.02	3.9×10^{-7}	–
STM12	133	485	377, 537	5.02	9.2×10^{-8}	–
STM13	112	406	337, 346, 760	5.18	1.2×10^{-7}	1.0×10^{-8}
STM14	161	417	337, 750	5.16	2.8×10^{-8}	3.5×10^{-9}

^aGlass transition temperatures were determined from DSC (second heating cycle);

^bUV–vis spectra of thin layers; ^chole drift mobility at zero field strength; ^delectrons drift mobility at zero field strength.

When investigating the absorption spectra of the solutions, at least three absorbance peaks were observed. Additionally, it was found that the spectral shapes for materials differing by the alkyl chain length were almost identical. This indicates that saturated alkyl chains do not significantly influence the molecular π -electron conjugation. All solutions of new materials can be characterized by intense $\pi \rightarrow \pi^*$ absorption peaks in the range of 270–450 nm, which overlap with low-intensity $n \rightarrow \pi^*$ peaks. The absorption maxima in the visible region can be attributed to the donor-acceptor charge transfer [295].

When comparing materials with two (**STM11**, **STM12**) and four (**STM9**, **STM10**) carbonyl groups, it is evident that the additional electron donor groups influence the conjugated system, resulting in a hypsochromic shift. However, more intense absorption at 510 nm was also observed. Due to the stronger acceptor properties of the cyano group, the absorption peaks shift to longer wavelengths in the visible region.

When contrasting the UV–vis spectra of solutions and thin layers, a small shift of approximately 3 nm towards the longer wavelengths was observed (Figure 65). However, the trends related to the alkyl chain length and the acceptor group remained consistent. Compounds with more carbonyl groups (**STM9** and **STM10**) showed absorption maxima at 510 nm, while the absorption peaks of materials with cyano

substituents were bathochromically-shifted in the visible region. Additionally, the FL spectra were recorded; however, no emission was detected.

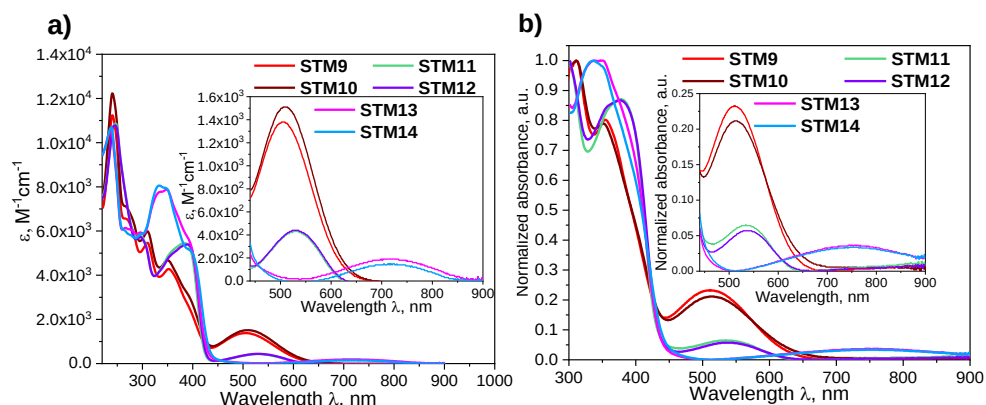


Figure 65. UV-vis spectra of bipolar fluorene derivatives in: **a)** THF solutions ($c = 10^{-4}$ mol/l); **b)** thin layers

To evaluate the HOMO levels of the new materials, the PESA method was used to determine the ionization potential values (Table 15 and Figure 66). Materials containing anthraquinone fragments are characterized by the highest values of I_p (**STM9** – 5.18 eV, **STM10** – 5.21 eV). As expected, longer and branched alkyl chains at the 9th position of fluorene do not influence the ionization potential. When comparing the bipolar fluorene materials, a decrease in the I_p values is observed when fewer electron acceptor groups are present (**STM9** – 5.18 eV, **STM10** – 5.21 eV and **STM11** – 5.02 eV, **STM12** – 5.02 eV). However, the replacement of keto groups with stronger electron acceptors, such as nitrile fragments, results in an increase in the ionization potentials (**STM11** – 5.02 eV, **STM12** – 5.02 eV and **STM13** – 5.18 eV, **STM14** – 5.16 eV). This suggests that a higher number of acceptor groups and stronger electron-accepting properties can elevate the value of I_p .

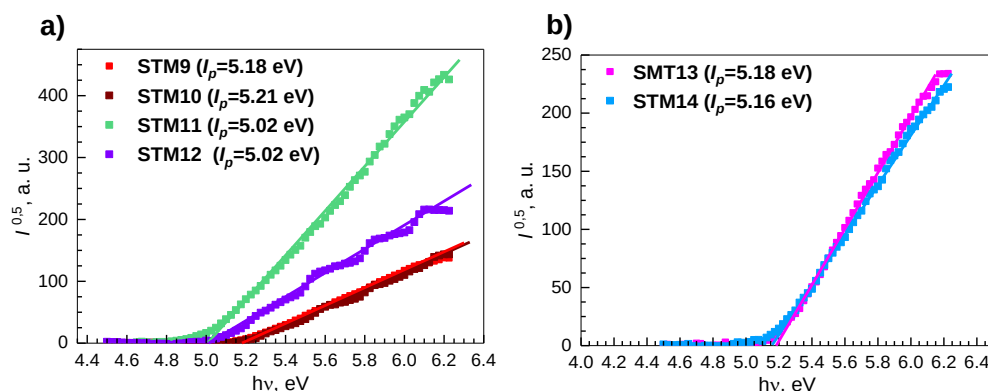


Figure 66. Electron photoemission in air spectra of new compounds: **a)** containing carbonyl groups (**STM9**–**STM12**); **b)** with cyano fragments (**STM13** and **STM14**)

Since the new fluorene derivatives contain both electron donor and acceptor groups, it is expected that they can transport both charge carriers. To confirm this, *time-of-flight* measurements (XTOF) were performed with the objective to evaluate charge mobility (Table 15 and Figure 67). For materials with 9-fluorenone chromophores (**STM11** and **STM12**), electron mobility was not observed, while hole mobility was detected. Substitution of the keto group with a dicyanofluorenylidene fragment, which has stronger acceptor properties, and an increase of the number of acceptor substituents in the molecule resulted in the appearance of electron mobility.

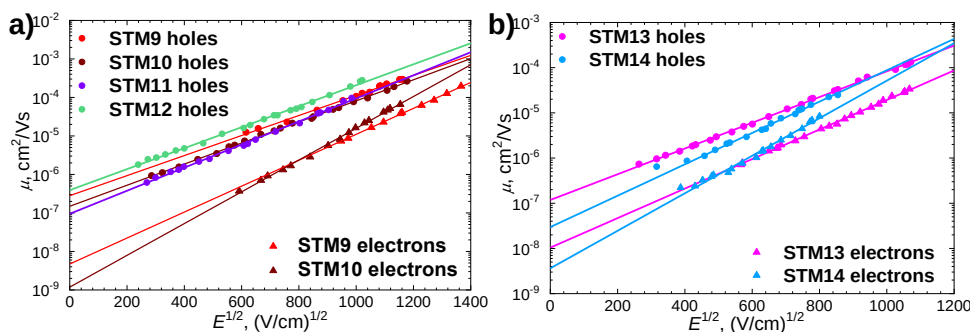


Figure 67. Charge carrier drift mobility dependence on electric field

The results show that materials containing anthraquinone (**STM9** and **STM10**) and dicyanofluorenylidene (**STM13** and **STM14**) fragments exhibit both positive and negative charge mobility. When comparing the results, it is evident that hole mobility is approximately an order of magnitude higher than electron drift mobility (**STM9** – $\mu_{0 \text{ hole}} = 2.6 \times 10^{-7} \text{ cm}^2/\text{Vs}$ and **STM9** – $\mu_{0 \text{ elec.}} = 4.6 \times 10^{-9} \text{ cm}^2/\text{Vs}$, **STM10** – $\mu_{0 \text{ hole}} = 1.4 \times 10^{-7} \text{ cm}^2/\text{Vs}$ and **STM10** – $\mu_{0 \text{ elec.}} = 1.1 \times 10^{-9} \text{ cm}^2/\text{Vs}$, **STM13** – $\mu_{0 \text{ hole}} = 1.2 \times 10^{-7} \text{ cm}^2/\text{Vs}$ and **STM13** – $\mu_{0 \text{ elec.}} = 1.0 \times 10^{-8} \text{ cm}^2/\text{Vs}$, **STM14** – $\mu_{0 \text{ hole}} = 2.8 \times 10^{-8} \text{ cm}^2/\text{Vs}$ and **STM14** – $\mu_{0 \text{ elec.}} = 3.5 \times 10^{-9} \text{ cm}^2/\text{Vs}$). The presence of longer and branched alkyl chains slightly improves the hole drift mobility, while the electron mobility decreases. Conversely, the replacement of the keto group with a cyano fragment increases the electron drift mobility, although the hole transport becomes slower.

All the synthesized bipolar fluorene derivatives exhibit excellent thermal properties. They lose 5 % of their mass at temperatures exceeding 400 °C. The glass transition temperatures meet the requirements for HTMs. The ionization potentials of these fluorene derivatives are also suitable for use in SC manufacturing. Most of these materials show both holes and electrons mobility, although the hole drift mobility reaches only $10^{-7} \text{ cm}^2/\text{Vs}$ in weak fields. Therefore, these materials were not applied for the construction of perovskite solar cells.

5.2.3. Branched fluorenylidene derivatives with low ionization potentials as hole-transporting materials for perovskite solar cells

Based on the published article *Chem. Mater.*, **2023**, 35, 5914–5923, A. Jegorovė, J. Xia, M. Steponaitis, M. Daskeviciene, V. Jankauskas, A. Gruodis, E. Kamarauskas, T. Malinauskas, K. Rakstys, K. A. Alamry, V. Getautis and M. K. Nazeeruddin [296];

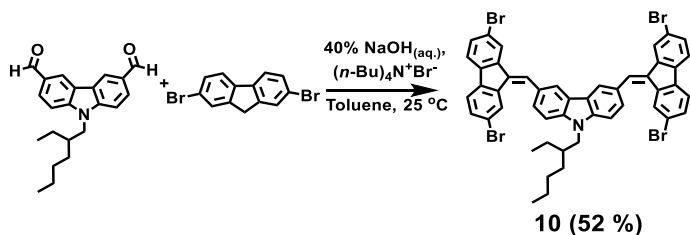
the article has been cited 7 times, this chapter reports on hole-transporting materials with fluorenylidene fragments.

The evaluation of perovskite solar cells began more than a decade ago; however, as mentioned above, Spiro-OMeTAD is still used as a benchmark for HTM. It has been observed that the use of a similar molecular design can lead to good results in terms of both efficiency and stability [297, 298].

There are two main strategies to obtain structurally similar materials to Spiro-OMeTAD: (1) by using spirobifluorene as a central fragment, substituting 4-methoxyphenyl chromophores (as in the first publication) [198, 203], or (2) imitating the spatial arrangement of Spiro-OMeTAD by carefully selecting the central and side fragments [219, 247].

The first strategy is generally considered more reliable, simpler, and more successful for achieving high performance of the device under development. However, the second strategy has also gained popularity due to its potential to produce cheaper and more stable target compounds. From the data described in the first publication, it can be inferred that the proper number of carbazolyl fragments can, in some cases, increase the stability of the device. Therefore, 9-ethyl-*N*-(4-methoxyphenyl)-9*H*-carbazol-3-amine was chosen as a side chromophore. In order to ensure that the materials were structurally similar to Spiro-OMeTAD, fluorenylidene fragments were introduced into the molecular ‘central part’ and linked through various aromatic moieties.

All the synthesized target materials can be divided into two groups: molecules containing two fluorenylidene fragments and compounds with three fluorenylidene moieties. Intermediates **5–10** were synthesized by using the Knoevenagel condensation reaction conditions in toluene, while utilizing 40 % NaOH solution and phase-transfer catalyst tetrabutylammonium bromide. Since compounds **5–9** have been reported in other scientific works, only the new carbazolyl derivative synthesis is presented here: 9-(2-ethylhexyl)carbazol-3,6-dicarboxy-aldehyde reacted under the above-mentioned conditions with two equivalents of 2,7-dibromo-9*H*-fluorene, thus yielding intermediate **10** (Scheme 27).



Scheme 27. Synthesis of intermediate **10**

The target materials **STM15–STM20** were obtained through a palladium cross-coupling reaction, linking intermediates **5–10** with 9-ethyl-*N*-(4-methoxyphenyl)-9*H*-carbazol-3-amine (Scheme 28).



Temperature (°C)	STM15 (%)	STM16 (%)	STM17 (%)	STM18 (%)	STM20 (%)
100	100	100	100	100	100
200	100	100	100	100	100
300	100	100	100	100	100
400	100	100	100	100	100
500	85	75	90	90	90
600	65	50	70	65	65
700	45	48	60	55	55
800	35	45	55	50	50

101

The glass transition temperatures of all the materials are in the 190–232 °C range, which is higher than the benchmark Spiro-OMeTAD [291]. When comparing all the materials, certain trends are apparent. The replacement of the thiophene central core with phenyl or carbazolyl chromophores results in improved T_g values (Table 16 and Figure 69).

Table 16. Thermal, optical, and photoelectrical properties of new materials

Compound	T_g , ^a , °C	T_d , °C	λ_{abs} , ^b , nm	λ_{abs} , ^c , nm	I_p , eV	μ_0^d , cm ² /Vs
STM15	190	451	298, 376, 461	299, 379, 466	4.99	5.4×10^{-7}
STM16	209	452	297, 369	299, 372	4.92	8.5×10^{-7}
STM17	203	445	298, 373	298, 375	4.89	1.9×10^{-6}
STM18	206	446	295, 375	293, 378	4.95	4.3×10^{-7}
STM19	210	457	297, 367	299, 370	4.94	4.9×10^{-7}
STM20	232	455	299, 376, 451	298, 379, 454	5.03	1.3×10^{-6}

^aGlass transition temperatures were recorded during the second heating cycle of DSC measurement; ^bUV-vis (THF, $c = 10^{-4}$ mol/l); ^cUV-vis spectra of thin films; ^dhole drift mobility in combination with PC-Z (1:1) at zero field strength.

Fluorenylidene chromophores are linked through the phenyl ring in the meta position, and T_g increases slightly. The glass transition temperatures also increase for molecules with three fluorenylidene fragments (STM19 – 210 °C and STM20 – 231 °C).

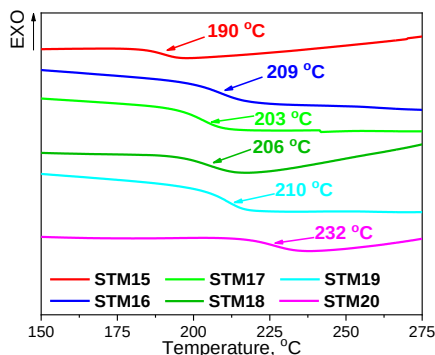


Figure 69. DSC second heating cycle of the target materials

In this study, no other phase transitions were observed, thus confirming that materials are completely amorphous. Therefore, it is likely that high-quality layers can be obtained from these materials.

In order to evaluate the optical properties of the new compounds, the UV-vis spectra of THF solutions ($c = 10^{-4}$ mol/l) and thin films were recorded (Table 16 and Figure 70). It can be observed that two cases of intense $\pi \rightarrow \pi^*$ electron transition occur at approximately 300 nm and 375 nm in all the absorption spectra. Replacing the linkage of fluorenylidene fragments from the meta to the para position results in a slight bathochromic shift due to an increased conjugation. A corresponding shift in

the absorption maxima is also noted with the inclusion of thiophene (**STM15**) and triphenylamine (**STM20**) in the central core of the molecular structure. Additionally, an extra peak appears at $\sim 450\text{--}470\text{ nm}$ in the absorption spectra of these semiconductors, which can be attributed to $\pi \rightarrow \pi^*$ electron transitions. When comparing the absorption spectra of solutions and thin films, a minimal bathochromic shift is observed.

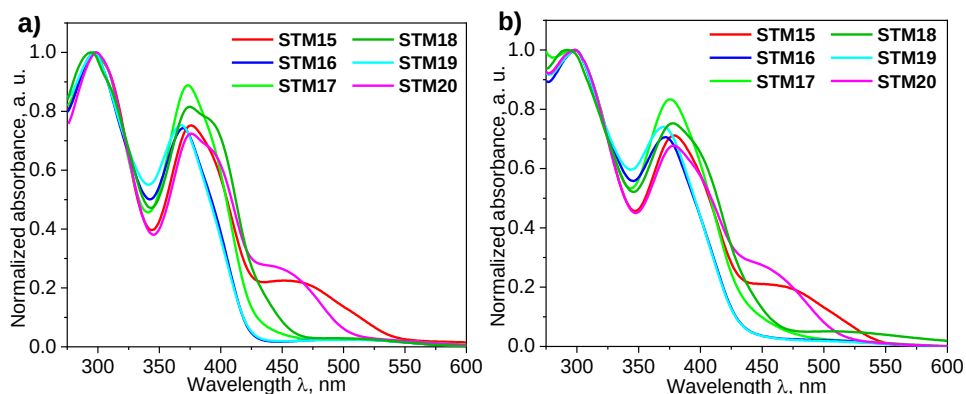


Figure 70. UV-vis spectra of target materials from: a) THF solutions ($c = 10^{-4}$ mol/l); b) thin layers

In order to ascertain whether the HOMO levels of the new materials meet the requirements for HTMs, the I_p values were recorded by using the PESA method (Table 16 and Figure 71). From the obtained results, it is evident that the ionization potentials range from 4.92 eV to 5.03 eV. Materials with fluorenylidene fragments linked by phenyl rings exhibit lower ionization potentials (**STM16** – 4.92 eV, **STM17** – 4.89 eV, **STM19** – 4.94 eV). It can be noted that the additional fluorenylidene and 9-ethyl-*N*-(4-methoxyphenyl)-9*H*-carbazol-3-amine fragments do not significantly influence the HOMO values. Materials containing central cores with heteroatoms have slightly higher I_p values (**STM15** – 4.99 eV, **STM18** – 4.95 eV, **STM20** – 5.03 eV).

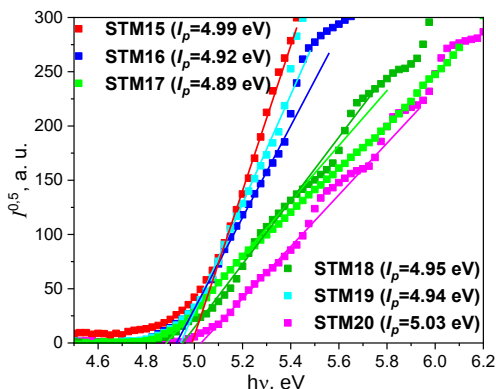


Figure 71. Ionization potentials of branched compounds containing fluorenylidene fragments

Charge drift mobility was determined by using XTOF data (Table 16 and Figure 72). After casting the layers of the synthesized semiconductors, cracking was observed, leading to a loss of homogeneity. Therefore, their drift mobility was evaluated in a composition with PC-Z (1:1). It is evident that **STM17** exhibits the highest hole transport in weak fields (**STM17** $\mu_0 = 1.9 \times 10^{-6} \text{ cm}^2/\text{Vs}$). Hole drift mobility improves when fluorenylidene fragments are linked through the phenyl ring para positions (**STM16** – $8.5 \times 10^{-7} \text{ cm}^2/\text{Vs}$, **STM17** – $1.9 \times 10^{-6} \text{ cm}^2/\text{Vs}$ and **STM20** – $1.3 \times 10^{-6} \text{ cm}^2/\text{Vs}$). Upon comparing the hole drift mobilities with Spiro-OMeTAD, it can be seen that they are slightly lower than the benchmark (Spiro-OMeTAD – $2.81 \times 10^{-6} \text{ cm}^2/\text{Vs}$ [290]).

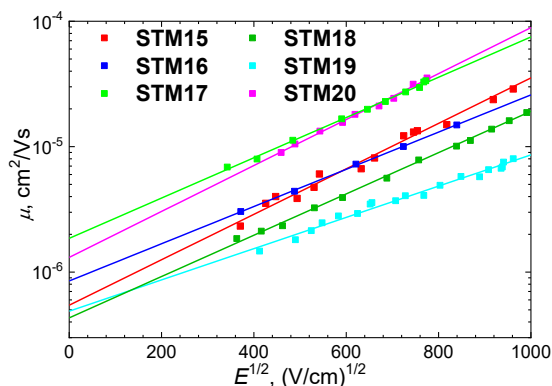


Figure 72. Dependence of charge drift mobilities on electric field

The branched structure compounds were used as an HTM layer in the n-i-p architecture solar cells (Figure 73, a). The construction of the device was FTO / SnO_2 / TiO_2 / $\text{Cs}_{0.045}\text{MA}_{0.045}\text{FA}_{0.91}\text{PbI}_3$ / HTM / Au. To improve the hole mobility of HTM, all the materials were doped with the above-mentioned additives. In Figure 73, b, the cross-sectional view of the device shows that material **STM16** evenly covers the surface of the perovskite layer. Therefore, it is likely that the device will demonstrate good stability. The solar cell performance data are given in Table 17.

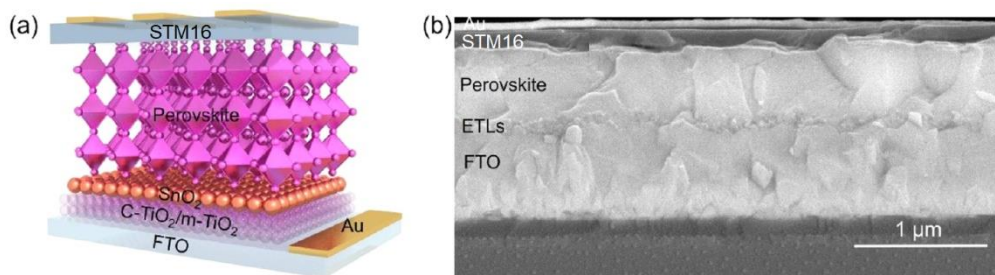


Figure 73. Structure of SC (a); Cross-sectional view of the device (b)

The devices that contains HTMs where fluorenylidene fragments are linked by phenyl rings achieves the highest efficiencies (**STM16** – 22.13 % and **STM17** – 21.26 %), which are slightly lower than SC with Spiro-OMeTAD (22.83 %). Efficiency is

almost independent of the substitution at the central fragment of the molecule that links the fluorenylidene chromophores. From the data, it can be seen that the performance of the solar cells decreases when HTMs with larger chromophores in their central parts are used: devices with semiconductors **STM18** and **STM20**, containing carbazoyl or triphenylamine chromophores, have the lowest efficiencies (**STM18** – 20.44 % and **STM20** – 19.61 %).

Table 17. Photovoltaic parameters extracted from solar cells based on various HTMs

Compound	J_{sc} , mA cm^{-2}	V_{oc} , V	FF	PCE , %
STM15	24.54	1.065	0.793	20.72
STM16	24.57	1.112	0.810	22.13
STM17	24.50	1.082	0.802	21.26
STM18	24.45	1.061	0.788	20.44
STM19	24.43	1.06	0.796	20.61
STM20	24.38	1.03	0.781	19.61
Spiro-OMeTAD	24.79	1.133	0.813	22.83

The stability of the device is also an emphatically important characteristic of SC. To evaluate how long a solar cell can function efficiently, these efficiencies were monitored under maximum load (Figure 74). It is evident that the device with **STM16** loses only a few percent of efficiency even after 1400 hours. On the other hand, the solar cell containing Spiro-OMeTAD lost approximately 15 % of its efficiency by the end of the testing.

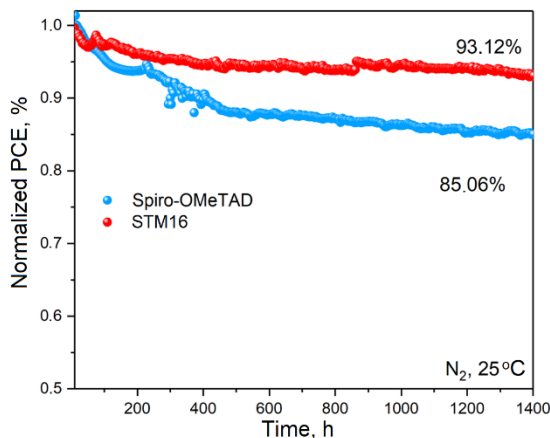


Figure 74. Stability of solar cells containing **STM16** and Spiro-OMeTAD

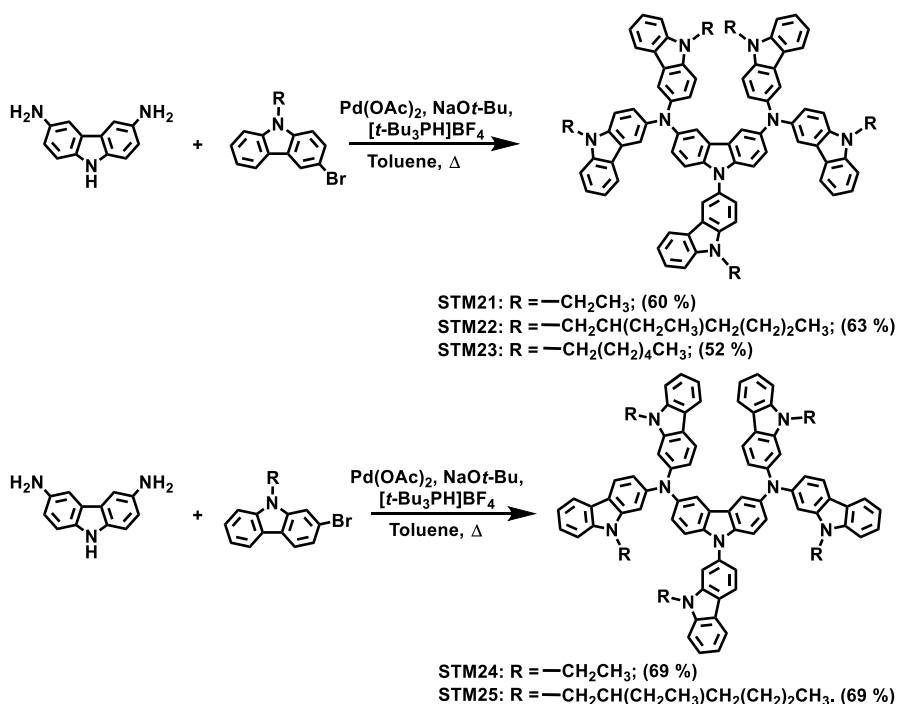
The thermal, optical, and photoelectrical properties of the target compounds meet the requirements for hole-transporting materials. The testing of these materials in solar cells established that the efficiency values of these devices are close to that of Spiro-OMeTAD. The stability results clearly indicate that semiconductor **STM16** enhances the longevity of SCs.

5.2.4. Starburst carbazole derivatives as efficient hole transporting materials for perovskite solar cells

In this chapter, star-shaped carbazole derivatives are described, based on article published in *Solar RRL*, (2022, 6, 2100877) by A. Jegorovė, M. A. Truong, R. Murdey, M. Daskeviciene, T. Malinauskas, K. Kantminiene, V. Jankauskas, V. Getautis, and A. Wakamiya [299]; the article has been cited 14 times.

The morphological stability of HTM under the device's operating temperature is crucial for ensuring good stability of solar cells. It is known that star-shaped molecules are usually in an amorphous state. The moieties of these molecules are generally large and rigid, resulting in massive molecules that exhibit high thermal stability [300]. Starburst HTMs perform well in perovskite solar cells, which is why this class of materials has gained significant attention from scientists [301, 302].

As mentioned above, carbazolyl chromophores are widely used as key fragments in the construction of HTMs, owing to their advantages, such as low cost, good hole transport, chemical stability, and ease of modification with various functional groups [303, 304]. Carbazolyl moieties can be utilized as central [230, 305] or peripheral [306, 307] fragments, capable of hole transport. Most starburst molecules containing carbazolyl chromophores have higher glass transition temperatures compared to Spiro-OMeTAD. Prior to this publication, no starburst HTM, with carbazolyl moieties in both central and peripheral positions had been reported.



Scheme 29. Synthesis of new starburst materials STM21–STM25

Many publications suggest that the length and branching of alkyl chains significantly affect the morphological, thermal, and charge-transporting properties of materials, as well as their overall impact on the efficiency of photovoltaic devices [308]. Therefore, carbazolyl fragments with alkyl chains were chosen for the synthesis of the target compounds to determine whether they would influence the properties mentioned before.

This publication describes five new starburst compounds. These new semiconductors were synthesized from commercially available 3,6-diamino-9H-carbazole, which was used as a central core for the new molecules (Scheme 29).

By using the methodology of palladium-catalyzed C-N bond formation, 3,6-diamino-9H-carbazole was linked with 2- or 3-bromo-9-alkylcarbazoles to synthesize materials **STM21–STM25**, while incorporating 2nd or 3rd position substituted 9-alkylcarbazoles in the periphery of photoconductive molecules. All reactions occurred over approximately five hours, yielding 52–69 %. The target compounds exhibit good solubility in organic solvents.

The thermal properties of the new semiconductors were evaluated by using the TGA and DSC methods. The results are presented in Figure 75, a and Table 18.

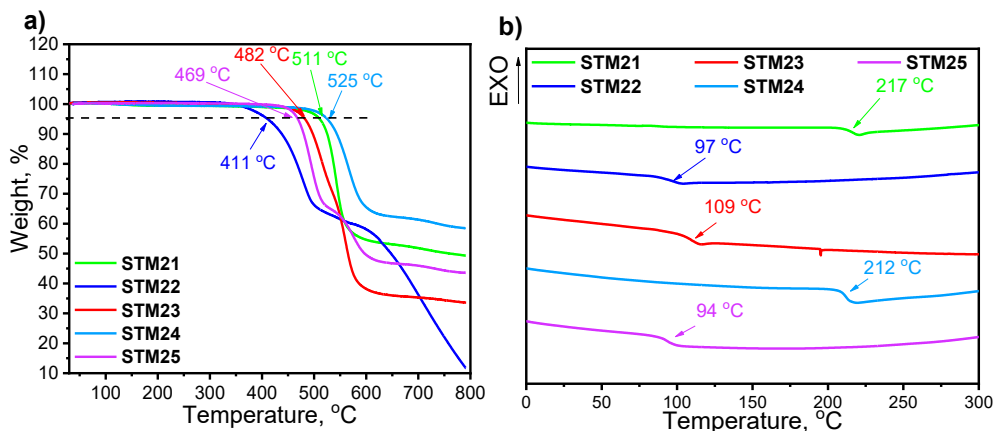


Figure 75. Thermal properties of starburst carbazole derivatives: a) TGA results; b) DSC curves of second heating

All the synthesized materials demonstrate a 5 % mass loss at temperatures above 400 °C, which is substantially higher than the operational temperatures of perovskite solar cells. When comparing the target materials, it is evident that longer alkyl chains result in a reduced thermal stability (T_d for: **STM21** – 511 °C, **STM22** – 411 °C, **STM23** – 482 °C, **STM24** – 525 °C, **STM25** – 469 °C). Interestingly, the decomposition temperature of materials with the 2nd position substituted carbazolyl fragments is higher than for the 3rd position substituted analogues (**STM21** – 511 °C, **STM24** – 525 °C).

During both the first and the second heating cycles, no endothermal peaks were observed, which indicates no crystal melting. Thus, the target compounds exist only in an amorphous state (Figure 75, b). Based on the data given in Table 18, it can be assumed that an increase of the alkyl chain length or its branching leads to a decreased

glass transition temperature (**STM21** – 217 °C, **STM23** – 109 °C and **STM22** – 97 °C).

The position of the carbazoyl chromophores linked to the central core does not significantly influence the T_g values (**STM21** – 217 °C and **STM24** – 212 °C, **STM22** – 97 °C and **STM25** – 94 °C). However, higher glass transition temperatures are observed for materials where carbazoyl chromophores are linked via the 3rd position. Compounds with shorter alkyl chains exhibit higher T_g than the benchmark Spiro-OMeTAD (126 °C), likely due to reduced molecular disorder [310]. As a result, it can be expected that devices using these materials will be more thermally stable since they will not crystallize in solar cells, unlike Spiro-OMeTAD.

Table 18. Thermal, optical, and photophysical properties of synthesized HTMs

HTM	T_g , °C ^{a)}	T_d , °C	λ_{abs}^b , nm	λ_{PL}^b , nm	I_p , eV	μ_0^c , cm ² V ⁻¹ s ⁻¹	μ_0^d , cm ² V ⁻¹ s ⁻¹
STM21	217	511	292, 321, 365, 413	471	4.86	–	3.1×10^{-6}
STM22	97	411	291, 320, 365, 413	471	4.99	3.7×10^{-6}	4.1×10^{-7}
STM23	109	482	291, 321, 365, 413	471	4.87	3.5×10^{-6}	5.0×10^{-7}
STM24	212	525	262, 359	438	5.16	6.1×10^{-6}	5.1×10^{-7}
STM25	94	469	264, 359	438	5.24	1.0×10^{-5}	5.8×10^{-7}
Spiro-OMeTAD [311]	126	449	387	–	5.01 [305]	1.2×10^{-4}	2.9×10^{-6}

^aGlass transition temperatures were recorded from the second DSC heating cycle;

^bUV–vis and FL spectra (10^{-4} mol/l and 10^{-5} mol/l, respectively) in THF solution;

^chole drift mobility in weak fields; ^dhole drift mobility in composition with PC-Z (1:1) at zero field strength.

From the UV–vis spectra, it can be seen that the alkyl chain has a minimal impact on the shifts of the absorption peaks. For compounds containing 3rd position substituted carbazoyl chromophores (**STM21–STM23**), intense $\pi \rightarrow \pi^*$ absorption peaks are observed at 270–340 nm, while the maxima at wavelengths of >350 nm can be attributed to $n \rightarrow \pi^*$ transitions, which have a lower intensity (Figure 76, a). In the structures of star-shaped molecules containing 2nd position substituted carbazoyl chromophores, the absorption maxima exhibit both bathochromic and hypsochromic shifts, perhaps due to the longer conjugation compared to their 3rd position substituted counterparts. In the FL spectra, it is observed that materials with 3rd position

substituted carbazoyl chromophores demonstrate emission maxima at 471 nm. Replacing the linking position from 3-C to 2-C results in a bathochromic shift of the emission peak (to 440 nm).

When comparing the UV-vis and FL spectra in solution (Figure 76, a) with spectra from thin films (Figure 76, b), it is evident that the peaks' shifts are nearly identical. Additionally, the Stokes shift was calculated, which helps to evaluate the structural deformation of materials, as this is important for charge transport. All the materials under investigation show a large Stokes shift (approximately 100 nm), indicating a significant structural deformation during electron excitation. It is known that materials with large Stokes shifts can more easily interact with the perovskite surface [312], suggesting that the target HTMs have potential for manufacturing efficient SCs.

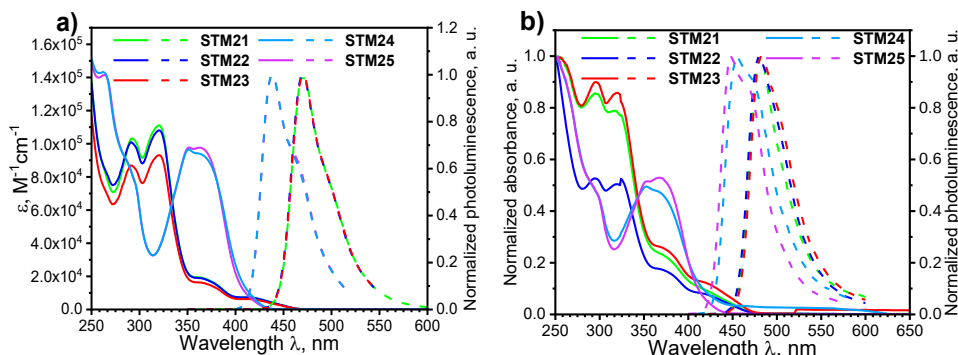


Figure 76. UV-vis and FL spectra of: a) THF solutions ($c = 10^{-4}$ g/mol and $c = 10^{-5}$ g/mol, respectively); b) thin films

The ionization potentials of starburst structure HTMs were measured by using the PESA method (Figure 77).

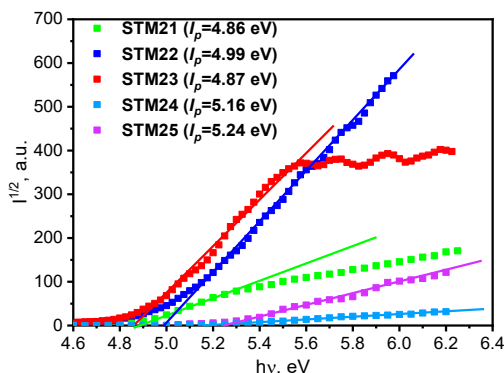


Figure 77. The ionization potentials of target compounds STM21–STM25

From the obtained results, it is evident that materials with 9-alkylcarbazoles connected through the 3-C position have lower ionization potentials (STM21 – 4.86 eV and STM24 – 5.16 eV, STM22 – 4.99 eV and STM25 – 5.24 eV). The length and branching of the alkyl chain do not significantly influence the change of I_p , however,

certain tendencies can still be observed, such as longer and branched alkyl chains, resulting in an increase in I_p .

The hole drift mobilities were determined by using XTOF measurements (Table 18 and Figure 78). The hole drift mobilities of pure materials range between $3.5 \times 10^{-6} \text{ cm}^2/\text{Vs}$ and $1.0 \times 10^{-5} \text{ cm}^2/\text{Vs}$. The obtained results show slightly lower μ_0 values compared to Spiro-OMeTAD. However, this level of hole mobility is sufficient for the use of these materials in SCs [313].

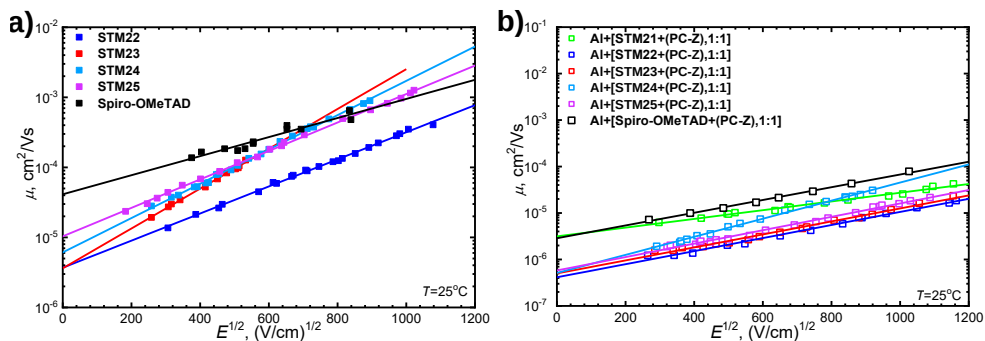


Figure 78. Hole drift mobility dependencies on electric field: a) pure materials; b) in composition with PC-Z (1:1)

During the preparation of materials' layers for the investigation, it was observed that pure **STM21** does not form a homogenous thin film; therefore, hole drift mobility in this compound was not detected. To compare all the materials' μ_0 , all HTMs were evaluated in combination with PC-Z. Contrasting the results, it is evident that the hole mobility values of **STM21** and Spiro-OMeTAD are similar, while μ_0 values for all other target materials are about one order lower.

The target compounds were tested in n-i-p planar architecture devices: ITO / SnO_2 / perovskite / STM / Au. The perovskite composition was used in the following SC: $\text{Cs}_{0.05}\text{FA}_{0.08}\text{MA}_{0.15}\text{PbI}_{2.75}\text{Br}_{0.25}$ [314]. During the construction of solar cells, the concentrations of the solutions were optimized (**STM21** c = 0.03 mol/l, **STM22** – 0.02 mol/l, **STM23** – 0.03 mol/l, **STM24** – 0.02 mol/l, **STM25** – 0.02 mol/l). Doping additives were also used: FK209, CoTFSI – 0.04 eq., LiTFSI – 0.54 eq., TBP – 3.3 eq. It is known that, for Spiro-OMeTAD, the layer must be thicker than 200 nm to obtain the most effective devices [315, 316]. In contrast, SCs with the newly synthesized semiconductors containing carbazoyl chromophores can achieve a similar efficiency with thinner layers: **STM21** – 140 nm, **STM22** – 115 nm, **STM23** – 130 nm, **STM24** – 140 nm, **STM25** – 120 nm, Spiro-OMeTAD – 240 nm.

The best current density–voltage (J – V) curves are given in **Figure 79**, while the photovoltaic parameters are summarized in **Table 19**. Comparing the results, it can be seen that solar cells containing HTMs with shorter alkyl chains reach higher efficiencies (**STM21** – 18.9 % and **STM24** – 18.4 %) than devices with semiconductors possessing long and branched alkyl chains (**STM23** – 18.3 % and **STM25** – 16.3 %). Additionally, it is observed that devices with materials containing carbazoyl groups linked through the 2nd position exhibit lower efficiencies. Using **STM22** as the HTM results in a higher efficiency (19.0 %), though a comparison of

the averages of solar cell performances shows that the highest efficiency was achieved by the device with **STM21** (18.6 %). Although the performance of these devices is slightly lower than that of Spiro-OMeTAD, in most cases, they outperform SC values reported in the literature, which include starburst materials [301, 317, 318].

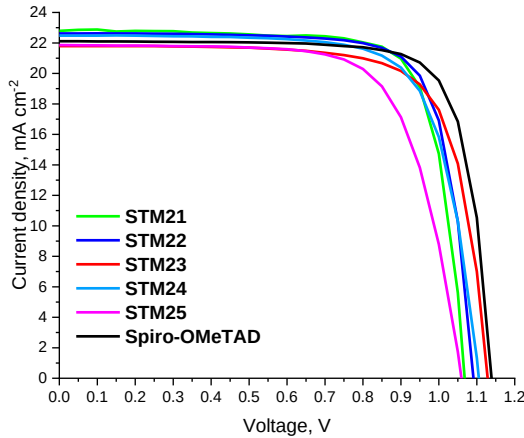


Figure 79. J – V curves of the best devices

Table 19. Photovoltaic parameters of solar cells

HTM ^a	J_{sc} ^b , mA cm ⁻²	V_{oc} ^b , V	FF ^b	PCE ^b , %
STM21	22.8 (22.4±0.5)	1.07 (1.09±0.02)	0.78 (0.76±0.01)	18.9 (18.6±0.3)
STM22	22.6 (22.5±0.2)	1.09 (1.06±0.02)	0.77 (0.76±0.01)	19.0 (18.0±0.6)
STM23	21.8 (21.6±0.3)	1.13 (1.11±0.01)	0.74 (0.72±0.01)	18.3 (17.4±0.5)
STM24	22.5 (22.3±0.2)	1.11 (1.12±0.01)	0.74 (0.73±0.01)	18.4 (18.2±0.2)
STM25	21.9 (21.6±0.4)	1.06 (1.07±0.02)	0.70 (0.67±0.02)	16.3 (15.5±0.5)
Spiro-OMeTAD	22.1 (22.5±0.3)	1.14 (1.12±0.02)	0.78 (0.78±0.01)	19.7 (19.5±0.3)

^aConcentration of HTMs: **STM21**, **STM23** and **STM24** $c = 0.03$ mol/l, **STM22** and **STM25** $c = 0.06$ mol/l. Thickness of the films: **STM21** – 140 nm, **STM22** – 115 nm, **STM23** – 130 nm, **STM24** – 140 nm, **STM25** – 120 nm and Spiro-OMeTAD – 240 nm; ^bthe average values were calculated with reference to data of 9 device measurements.

The stability of the devices was studied over 10 hours in a non-oxygen environment. While the initial efficiencies of all solar cells are similar, exposure to solar radiation over time reveals differences in performance (Figure 80). From the obtained data, it is evident that the efficiency of solar cells with **STM22** and **STM23** decreases within the first hour of investigation. The device containing Spiro-OMeTAD also loses 5 % of its primary efficiency during the first hour, and, after 10

hours, the performance drops to about 12 %. Solar cells with **STM25** exhibit 10 % efficiency after 10 hours. The best stability of the devices was obtained when using **STM21** and **STM24** as HTMs.

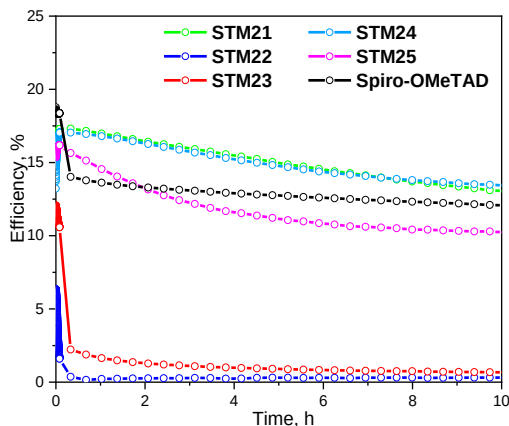


Figure 80. The stability study of encapsulated devices

Additionally, the stability of SC containing **STM21** was investigated by altering the temperature (Figure 81).

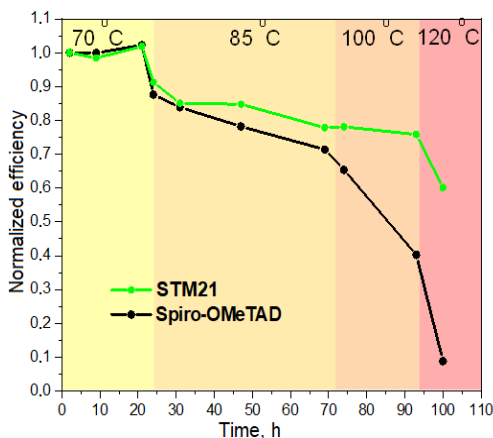


Figure 81. The efficiency of solar cells under different temperatures

The stability of the device with **STM21** is better than that with Spiro-OMeTAD. The data show that the efficiency of devices with **STM21** decreases after exposure to 100 °C for 24 hours. Under the same conditions, SCs with Spiro-OMeTAD show a greater drop in efficiency. At 120 °C, the efficiency decreases further; however, the performance of the solar cell with **STM21** remains higher. After these tests, the **STM21** layer retained its smoothness and solidity, while the Spiro-OMeTAD film developed cavities (Figure 82). The superior stability of the SC was attributed to the higher glass transition temperatures of the materials (**STM21** – 217 °C, **STM22** – 97 °C, **STM23** – 109 °C, **STM24** – 212 °C, **STM25** – 94 °C and Spiro-OMeTAD – 126 °C [311]).

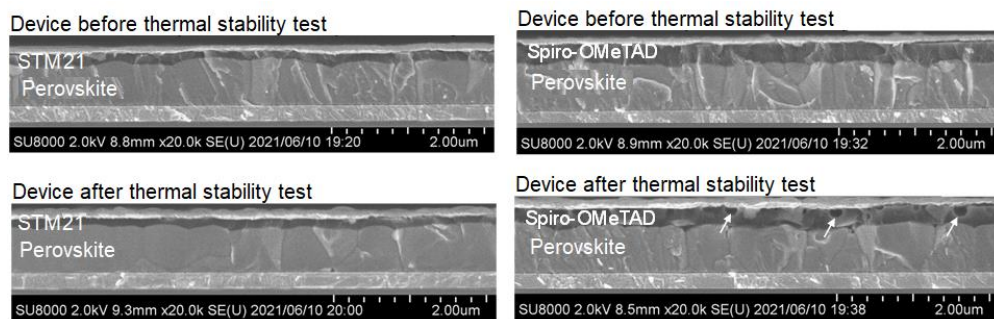


Figure 82. Solar cells' layers before (left) and after (right) the thermal stability test

In conclusion, the new starburst materials exhibit better morphological properties than Spiro-OMeTAD. As expected, devices with **STM21** achieved the highest performance, which is slightly lower than that of Spiro-OMeTAD. However, SC with **STM21** demonstrated greater stability than that achieved with Spiro-OMeTAD.

5.2.5. 4.9 % efficient Sb_2S_3 solar cells from semitransparent absorbers with fluorene-based thiophene-terminated hole conductors

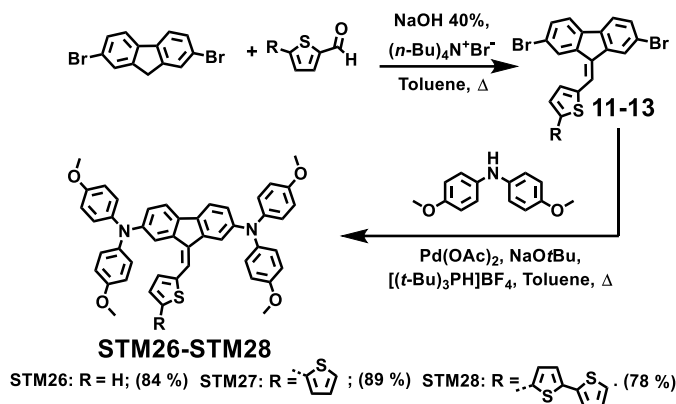
The new materials containing fluorenylidene and thiophene chromophores are reported based on the published article *ACS Appl. Energy Mater.*, **2023**, 6, 3822–3833, by S. Mandati, N. Juneja, A. Katerski, A. Jegorovè, R. Grzibovskis, A. Vembris, T. Dedova, N. Spalatu, A. Magomedov, S. Karazhanov, V. Getautis, M. Krunk, I. O. Acik [319]; cited 14 times.

Perovskite solar cells exhibit high efficiencies; however, their stability is limited. Therefore, other species of photovoltaic devices have been developed, by using more stable light-absorbing materials [320]. Antimony sulfide (Sb_2S_3) is one of these materials which demonstrate a high absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$) and great stability [177]. Additionally, a good solar cell efficiency can be achieved by using thin layers ($\sim 100 \text{ nm}$) [321]. The construction of Sb_2S_3 devices is similar to perovskite SC: $\text{FTO} / \text{TiO}_2 / \text{Sb}_2\text{S}_3 / \text{HTM} / \text{Au}$. In these devices, poly(3-hexylthiophene) (P3HT) [322, 323] or doped Spiro-OMeTAD [324, 325] is used as the hole-transporting material. However, the synthesis of these materials is complex, leading to high costs for the latter. One desirable characteristic of HTMs is that they must not absorb visible light, and their layers should be transparent, as HTM is cast on the surface of the light-absorbing layer. P3HT exhibits 'parasitic' absorption in the visible region, thus decreasing the performance of the device [13, 322]. Furthermore, in order to obtain efficient P3HT layers, they must be heated to 170°C . Due to these limitations, researchers are exploring alternative derivatives for HTMs to develop cheaper and more efficient devices.

In this publication, three target compounds were developed, containing varying numbers of thiophene chromophores linked to the 9th position of the fluorene fragment. 4,4'-Dimethoxydiphenylamine moieties were incorporated at the periphery of the molecules. It is known that the sulfur atom in thiophene can form a coordination

bond with antimony atoms, thereby improving the interface between HTM and $\text{Sb}_2(\text{S}, \text{Se})_3$ [326]. This bond is hypothesized to act as a ‘tunnel’ for charge, resulting in a higher open-circuit voltage and superior fill factor values.

To obtain the target materials, the central fragments (**11–13**) of hole transporting organic semiconductors were synthesized by utilizing the Knoevenagel condensation reaction conditions. NaOH (40%) solution was used as the base, while tetrabutylammonium bromide served as a phase-transfer catalyst. In the next step, intermediates **11–13** were linked with 4,4'-dimethoxydiphenylamine by using a palladium catalyst to produce the target materials **STM26–STM28** (Scheme 30).



Scheme 30. Synthesis of target compounds **STM26–STM28**

To evaluate the thermal properties of the target materials, TGA and DSC studies were performed. From the results, it is evident that all semiconductors lose 5 % of their mass at temperatures higher than 390 °C (Figure 83 and Table 20).

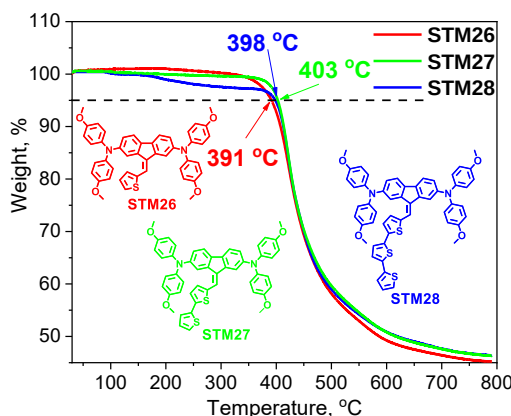


Figure 83. TGA curves of **STM26–STM28**

Comparing **STM26** with the more thiophene-rich **STM27** and **STM28**, it is clear that a higher molecular mass leads to higher decomposition temperatures (**STM26** – 391 °C, **STM27** – 403 °C, **STM28** – 398 °C).

DSC results reveal that the glass transition temperatures of all materials are below 100 °C (**STM26** – 92 °C, **STM27** – 97 °C, **STM28** – 99 °C). The T_g increases with the number of thiophene substituents in the molecule (Table 20). Moreover, no other phase transitions were observed during the first and second heating, except for **STM26** (T_m – 202 °C). This indicates that materials **STM27** and **STM28** are entirely amorphous, making it likely that their layers will remain homogenous over time.

To evaluate the conjugation of the materials, the UV–vis spectra from thin layers were recorded. It can be observed that the $\pi \rightarrow \pi^*$ transition peaks, found in the region of 230–430 nm, can be attributed to fluorene fragments.

Table 20. Optical, thermal and photoelectric parameters of new HTMs

HTM	T_g^a , °C	T_d , °C	λ_{abs}^b , nm	I_p^c , eV	μ_0^d , cm ² /Vs
STM26	92	391	303, 386	4.95	7.07×10^{-7}
STM27	97	403	299, 393, 438	4.95	2.15×10^{-7}
STM28	99	398	293, 392, 449	5.0	3.68×10^{-6}

^aGlass transition temperatures detected during second heating; ^bUV–vis spectra from thin layers; ^cionization potential determined by the photoemission (PES) method; ^dcharge drift mobility at zero field strength.

An increase in the number of thiophene moieties in the molecule results in a bathochromic shift of the absorption bands in the UV–vis spectra, attributed to $\pi \rightarrow \pi^*$ transitions (Figure 84 and Table 20). When comparing the spectra of the new materials with that of P3HT, it is evident that the latter absorbs more intensely in the range of 400–650 nm, while **STM26–STM28** exhibit much smaller absorption peaks in the same region. Therefore, it can be expected that the new materials will function better as HTMs in the constructed solar cells.

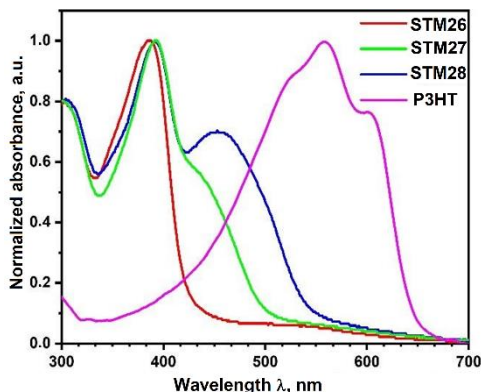


Figure 84. UV–vis spectra of **STM26–STM28** and P3HT

The ionization potentials of new HTMs were studied by using the *photoemission method* (PES). From the obtained results, it can be seen that I_p values are in the range of 4.95–5.0 eV. Likely, the near-identical HOMO values are fixed due to the specific arrangement of the thiophene fragments in space. The highest ionization potential is

exhibited by material **STM28** which contains the largest number of thiophene fragments ($I_p = 5.0$ eV) (Table 20).

To assess how quickly the materials can transport charge, the XTOF method was used to measure hole drift mobility. Upon comparing the results, it can be seen that charge drift mobility decreases when two thiophene fragments are linked to the molecule (**STM26** – 7.07×10^{-7} cm²/Vs, **STM27** – 2.15×10^{-7} cm²/Vs). Materials with the larger number of thiophene moieties exhibit the highest μ_0 (**STM28** – 3.68×10^{-6} cm²/Vs).

From the obtained optical and photoelectrical data, it can be confirmed that these materials can be used as HTMs in Sb₂S₃ solar cells. Therefore, devices were constructed with the following configuration: Glass / FTO / TiO₂ / Sb₂S₃ / HTM / Au (Figure 85, a). In Figures 85, b–d, the optimization of SC can be observed by changing the concentration of the HTM used.

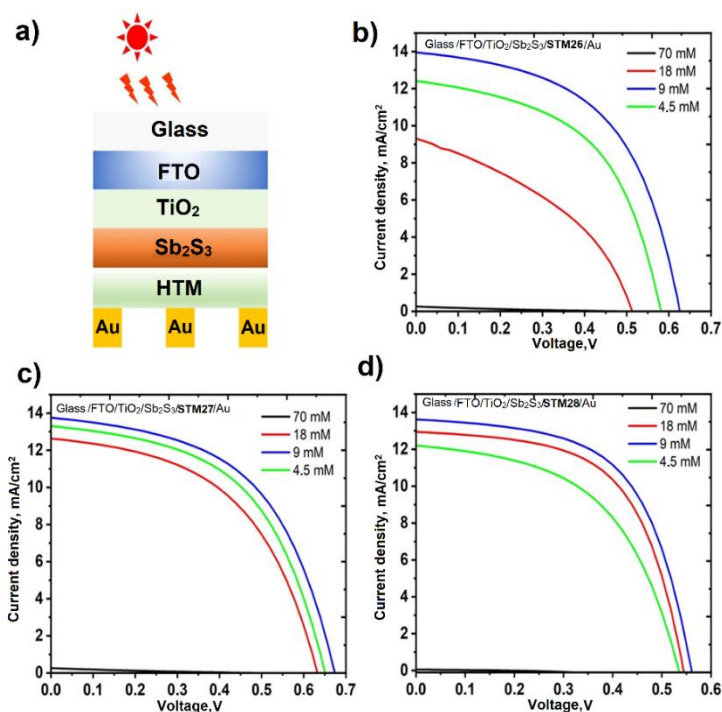


Figure 85. a) Construction of the Sb₂S₃ solar cell; J - V curves of: b) STM26, c) STM27, d) STM28, using different concentrations

From the accrued data, it is evident that the lowest efficiency is achieved when 70 mmol concentration of **STM26** solution is used for the HTM layer formation. When the solution is diluted, the performance improves (70 mmol – 0.1 %, 18 mmol – 2 %, 9 mmol – 4.7 %), however , the improvement only advances up to a certain limit (4.5 mmol – 3.8 %). A similar trend is observed for **STM27** and **STM28** (**STM27**: 70 mmol – 0.2 %, 18 mmol – 4.0 %, 9 mmol – 4.9 % and 4.5 mmol – 4.5 %; **STM28**: 70 mmol – 0.15 %, 18 mmol – 4.1 %, 9 mmol – 4.5 % and 4.5 mmol –

3.4 %). It is clear that the 9 mmol concentration is the optimal choice for achieving the most efficient devices.

The obtained data are compared with the performance of devices using P3HT (Table 21 and Figure 86).

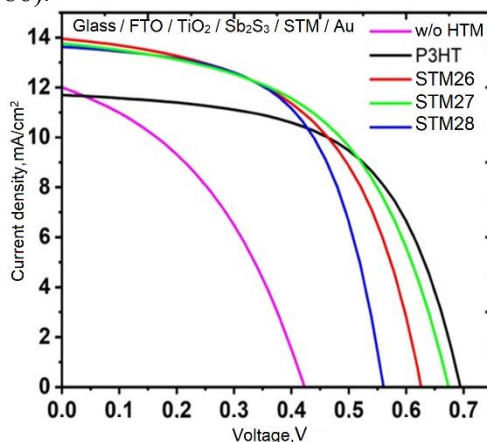


Figure 86. J - V curves of the best-performing devices

When comparing the results, it is evident that better performance is achieved when HTM is used – as the device without HTM shows only 2.12 % efficiency. It can also be noticed that solar cells containing new HTMs perform better than that with P3HT. Thus, it can be concluded that the target materials developed in this publication can increase the efficiency of Sb_2S_3 SCs.

Table 21. Photovoltaic parameters of solar cells

HTM	J_{sc} , mA cm^{-2}	V_{oc} , V	FF	PCE , %
no HTM	12.0	0.43	0.41	2.12
P3HT	11.7	0.69	0.58	4.68
STM26	13.9	0,63	0.54	4.73
STM27	13.7	0.68	0.53	4.94
STM28	13.6	0.56	0.59	4.50

After reviewing the thermal, optical and photoelectrical properties of new compounds, it is clear that they meet the criteria required for HTMs, used in Sb_2S_3 solar cells. Testing these target semiconductors in devices shows an increase in the efficiency of solar cells, which is even higher than that of the standard P3HT.

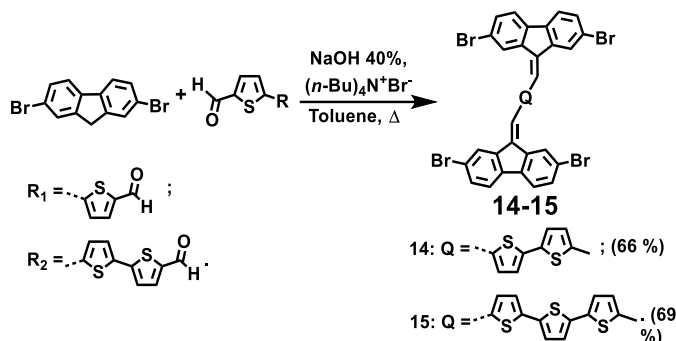
5.2.6. Dopant-free fluorene-based dimers linked with thiophene units as prospective hole transport materials for Sb_2S_3 solar cells

In this chapter, hole-transporting materials with fluorene fragments linked by thiophene bridges are reviewed, based on an article published in *Sustainable Energy Fuels*, **2024**, 8, 4324–4334, by N. Juneja, A. Jegorovė, R. Grzibovskis, A. Katerski, M. Daskeviciene, T. Malinauskas, A. Vembris, S. Karazhanov, N. Spalatu, V. Getautis, M. Krunks, I. O. Acik [327]; cited 2 times.

In a previous publication, organic semiconductors **STM26–STM28** were shown to perform well in Sb_2S_3 solar cells, however, their glass transition temperatures (around 100 °C) were not optimal, which could slightly affect the device's stability. Based on the findings of an earlier study, it was decided to synthesize dimeric analogues of **STM26–STM28** to improve their thermal properties. In this article, four target materials are reported, where fluorene dimers at the molecular center, linked by thiophene bridges, are substituted with 4,4'-dimethoxydiphenylamine (**STM29** and **STM30**). Moreover, in order to extend the molecule's conjugated system, triphenylamine derivatives were attached to the central fragment, resulting in **STM31** and **STM32**, which contain 4,4'-dimethoxytriphenylamine chromophores.

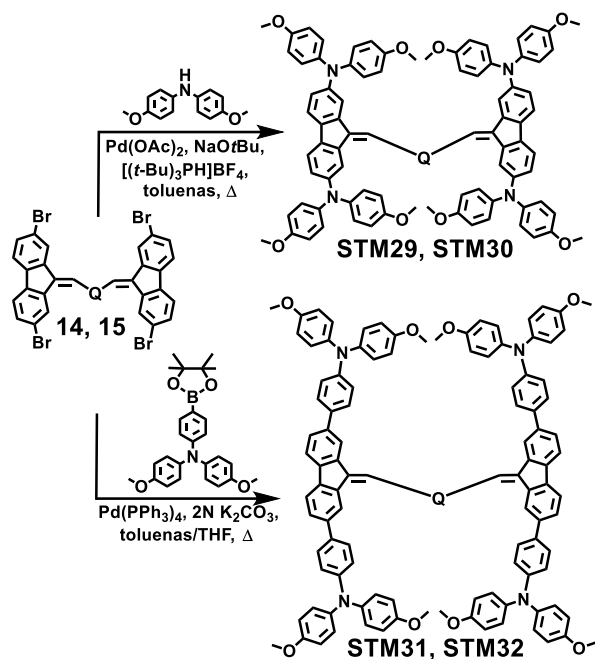
The synthesis of these two groups of materials differs, though both are catalyzed by palladium derivatives. Initially, under the Knoevenagel condensation conditions, central fragments **14** and **15**, with two and three thiophene chromophores, respectively, were synthesized (Scheme 31). The reactions were carried out for four hours at the boiling point of toluene, yielding 66–69 %.

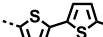
For the synthesis of **STM29** and **STM30**, containing 4,4'-dimethoxydiphenyl moieties, the Buchwald-Hartwig reaction conditions were utilized with $\text{Pd}(\text{OAc})_2$ as a catalyst (Scheme 32). The target materials were purified by column chromatography, achieving yields of 70 %.

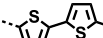


Scheme 31. Synthesis of intermediates **14** and **15**

4,4'-dimethoxydiphenylamine side chromophores were linked to central fragments **14** and **15** via Suzuki coupling (Scheme 32). The reaction proceeded for 24 hours by using tetrakis(triphenylphosphine)palladium as a catalyst. The target materials **STM31** and **STM32** were purified by using column chromatography, with yields of 48 % and 42 %, respectively.



14, STM29, STM31: Q =  ; (70 %, 64 %)

15, STM30, STM32: Q =  .(48 %, 42 %)

Scheme 32. Synthesis of target compounds **STM29–STM32**

Thermal analysis of the new derivatives was performed by using DSC and TGA methods. The data show that the compounds lose 5 % of their mass in the temperature range of 430–445 °C (Figure 87).

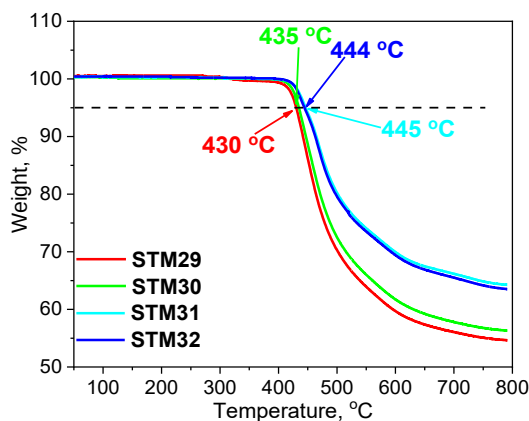


Figure 87. TGA curves of target compounds **STM29–STM32**

A Comparison of materials with diphenylamine fragments reveals that the longer thiophene bridge increases the decomposition temperature. Additionally, glass

transition temperatures are higher when the triphenylamine fragment is attached. When compared with their analogues in the previous article (**STM26–STM28**), an increase in the molecular mass leads to higher T_g values.

From the DSC results, it is evident that all materials are molecular glasses, with glass transition temperatures in the range of 148–175 °C, which is higher than their previously reported analogues **STM26–STM28** (Table 22 and Figure 88).

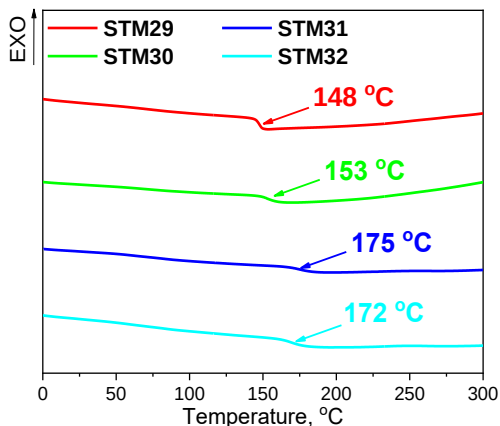


Figure 88. Second heating curves of DSC

Organic semiconductor **STM32**, which has three thiophene fragments in the molecule's center and 4,4'-dimethoxytriphenylamine moieties at its periphery, is fully amorphous, as no other endothermal peaks were observed during the DSC studies. Such materials are highly desirable for solar cells due to their ability to form homogenous layers, which is crucial for the stability and efficiency of the device.

The UV–vis spectra of the target materials show absorbance bands at 300 nm and 375 nm, attributed to $\pi \rightarrow \pi^*$ transitions of the side chromophores of the semiconductor's molecules (Table 22). Lower intensity peaks, at around 425–500 nm, correspond to $\pi \rightarrow \pi^*$ transitions of the thiophene fragments. A bathochromic shift can be observed as more thiophene units are introduced. When comparing the UV–vis spectra, materials with 4,4'-dimethoxytriphenylamine fragments exhibit stronger absorption, likely due to the additional phenyl ring. However, the absorption peaks of the dimers and their analogues described in Section 5.2.5 are very similar, indicating that the conjugation of the dimers remains almost unchanged.

The hole drift mobilities of semiconductors **STM29–STM32**, measured by using the ToF method, range from 9.86×10^{-7} to 3.38×10^{-6} cm²/Vs (Table 22). It can be noted that additional phenyl rings at the periphery of the molecules slightly increase the charge drift mobility.

To assess whether the energy levels of these materials are suitable for Sb₂S₃ solar cells, the ionization potentials were measured (Table 22). The I_p values for all the new HTMs are approximately 5.0 eV (**STM29** – 4.94 eV, **STM30** – 4.94 eV, **STM31** – 5.05 eV and **STM32** – 5.08 eV). Additional thiophene moieties at the center of the molecule do not significantly affect the ionization potential, while the attachment of extra phenyl rings leads to a slight increase of the potential.

Table 22. Optical, thermal, and photoelectrical parameters of **STM29–STM32**

HTM	T_g^a , °C	T_m^b , °C	T_g , °C	λ_{abs}^c , nm	I_p^d , eV	μ_0^e , cm ² V ⁻¹ s ⁻¹
STM29	148	276	430	293, 383, 468	4.94	9.86×10^{-7}
STM30	153	157	435	300, 383, 479	4.94	1.29×10^{-6}
STM31	175	175, 307	445	285, 377, 467	5.05	3.38×10^{-6}
STM32	172	-	444	286, 377, 480	5.08	1.85×10^{-6}

^aGlass transition temperatures determined from the second DSC heating; ^bmelting points determined from the first DSC heating; ^cUV–vis spectra (THF, $c = 10^{-4}$ mol/l); ^dionization potentials measured by using the PES method; ^ehole drift mobility values at zero field strength.

The characteristics of SC made from glass / FTO / TiO₂ / Sb₂S₃ / HTM / Au are given in Table 23. A device without HTM achieved 1.9 % efficiency. When P3HT or semiconductors **STM29** and **STM30** containing 4,4'-dimethoxydiphenylamine fragments, were used, both J_{sc} and V_{oc} increased, thus improving the solar cell's performance (P3HT – 4.7 %, **STM29** – 3.9 % and **STM30** – 4.5 %). However, when materials **STM31** and **STM32** with 4,4'-dimethoxytriphenylamine chromophores were utilized, the device efficiency decreased significantly (**STM31** – 0.8 % and **STM32** – 0.7 %), likely due to the HOMO levels of **STM31** and **STM32** being too close to that of Sb₂S₃ (Sb₂S₃ – -5.1 eV).

Table 23. Photovoltaic parameters of conventional solar cells derived from J – V measurements

HTM	J_{sc} , mA cm ⁻²	V_{oc} , mV	FF , %	PCE , %
no HTM	8.7	478	46	1.9
P3HT	12.2	689	55	4.7
STM29	9.7	656	43	3.9
STM30	12.1	673	56	4.5
STM31	5.7	439	35	0.8
STM32	6.1	437	33	0.7

Although SCs with the target materials did not outperform the device with the benchmark P3HT, the photovoltaic cell with the new compounds used thinner layers (~ 20–25 nm compared to P3HT's ~ 80–100 nm). Consequently, the solar cells with **STM29–STM32** showed a higher transparency (**STM29** – 24 %, **STM30** – 26 %, **STM31** – 23 %, **STM32** – 23 % and P3HT – 21 %). This suggests that the new derivatives could be used in the construction of transparent SCs.

After evaluating the thermal, optical, and photoelectrical properties, it was established that the target semiconductors are suitable for Sb₂S₃ SCs. Among the new compounds, devices with **STM30** demonstrated the best performance with 26 % transparency.

In conclusion, hole-transporting materials containing fluorenyl and carbazolyl fragments exhibit suitable thermal, optical, and photoelectrical properties for use in next-generation solar cells. This was convincingly demonstrated by constructing and characterizing efficient perovskite and Sb₂S₃ solar cells.

5.3. Conclusions

This dissertation presents promising *p*-organic semiconductors containing fluorenyl and carbazolyl chromophores. The following conclusions were formed on the grounds of the study:

1. Spirobifluorene derivatives and their ‘half’ analogues, containing 4-methoxyphenyl and 9-ethylcarbazolyl chromophores, have been synthesized by using the Buchwald-Hartwig reaction conditions. After investigating the properties of hole-transporting organic semiconductors, it has been found that:
 - 1.1. All compounds showed decomposition temperatures above 400 °C. The replacement of 4-methoxyphenyl chromophores with 9-ethylcarbazolyl moieties increased the thermal stability. Most target compounds have a glass transition temperature above 100 °C, although longer and branched alkyl fragments reduced the values of T_g ;
 - 1.2. I_p values decrease when 4-methoxyphenylchromophore is replaced by 9-ethylcarbazolyl (**STM3** – 4.93 eV, **STM6** – 4.85 eV), while longer alkyl chains slightly elevate the ionization potential values (**STM3** – 4.93 eV, **STM4** – 4.95 eV, **STM5** – 5.02 eV);
 - 1.3. The highest hole drift mobility (3.6×10^{-4} cm²/Vs) was observed for **STM2**, which has only 9-ethylcarbazolyl fragments. Among the ‘half’ analogues, **STM3** and **STM4** exhibited the highest μ_0 (3.9×10^{-4} cm²/Vs);
 - 1.4. A solar cell containing the ‘half’ Spiro-OMeTAD analogue **STM2** demonstrated an efficiency which is close to the benchmark, while providing significantly better stability levels.
2. Fluorene derivatives with both donor and acceptor chromophores were synthesized by using palladium-catalyzed and Knoevenagel condensation reactions. Analysis of their properties established that:
 - 2.1. These fluorene derivatives exhibit high thermal stability, by virtue of losing 5 % of their mass only above 400 °C;
 - 2.2. All the target compounds have a stable amorphous state, with T_g values higher than 100 °C, except for semiconductor **STM11** (T_g = 92 °C);
 - 2.3. Ionization potential values (5.02–5.21 eV) are influenced by the number and type of the acceptor fragments. I_p increases with the addition of more carbonyl groups in the molecules, or by replacing them with nitrile groups;
 - 2.4. Fluorene derivatives containing 9-alkylcarbazole and 9*H*-fluorenone chromophores transport only holes, with a mobility of up to 3.9×10^{-7} cm²/Vs. In contrast, materials with 9-alkylcarbazole and nitrile or anthraquinone fragments can transport both electrons and holes, while

achieving hole mobility of $3.9 \times 10^{-7} \text{ cm}^2/\text{Vs}$ and electron mobility of $1.0 \times 10^{-8} \text{ cm}^2/\text{Vs}$ at zero field strength.

3. By using a two-step synthesis route, materials of a branched structure containing fluorenylidene and carbazolyl moieties, along with various aromatic fragments at the molecular core, were obtained. Investigation of these materials revealed that:
 - 3.1. The target materials demonstrated thermal stability higher than 400 °C;
 - 3.2. Materials containing fluorenylidene fragments linked *via* the para position of the phenyl ring, 1,4-substituted thiophene or triphenylamine, showed greater conjugation;
 - 3.3. All the target materials have a stable amorphous state and exhibit T_g in the range of 190–231 °C;
 - 3.4. The ionization potentials of the new semiconductors are in the range of 4.92–5.03 eV. The best hole drift mobility was exhibited by material **STM17** ($\mu_0 = 1.9 \times 10^{-6} \text{ cm}^2/\text{Vs}$);
 - 3.5. Devices with **STM16** and **STM17** showed the highest efficiency, 22.14 % and 21.26 % respectively, thereby outperforming a solar cell with Spiro-OMeTAD in terms of stability.
4. By conducting the cross-coupling reaction, starburst hole-transporting semiconductors containing carbazolyl chromophores linked by different positions have been synthesized. The study of their properties revealed that:
 - 4.1. The target compounds demonstrated high thermal resistance, with T_d ranging from 411 to 525 °C and glass transition temperatures between 190–231 °C. All the new materials exhibit a stable amorphous state, and these values are significantly higher than that of Spiro-OMeTAD;
 - 4.2. Replacement of the linking position of carbazolyl moieties from 3-C to 2-C increases the absorption maximum at 360 nm, while the alkyl chain does not notably affect the intensity or shifts of the absorption peaks. Additionally, a hypsochromic shift in the emission maximum is observed when the linking position of carbazolyl substituents changes from 3-C to 2-C;
 - 4.3. The HOMO values of the target compounds range from -4.86 to -4.99 eV, which aligns well with the perovskite used in solar cells. The hole drift mobilities are arranged in the range of 3.5×10^{-6} to $1.0 \times 10^{-5} \text{ cm}^2/\text{Vs}$;
 - 4.4. The device containing semiconductor **STM22** showed the highest power conversion efficiency of 19 %.
5. By utilizing the Knoevenagel condensation and Buchwald-Hartwig reaction conditions, hole-transporting materials with thiophene and 4,4'-dimethoxyphenylamine chromophores were synthesized. The examination of their properties revealed the following:
 - 5.1. All the target compounds lost 5 % of their mass at approximately 400 °C, with **STM27** showing the highest decomposition temperature ($T_d = 403$ °C). An increase in the number of thiophene moieties improved the T_g values (**STM26** – 92 °C, **STM27** – 97 °C, **STM28** – 99 °C);

- 5.2. The ionization potential values do not significantly depend on the number of thiophene fragments (4.95–5.0 eV). Organic semiconductor **STM28** demonstrated the best carrier mobility ($\mu_0 = 3.68 \times 10^{-6} \text{ cm}^2/\text{Vs}$);
- 5.3. The device with **STM27** showed the highest efficiency (4.94 %), thus outperforming the solar cell containing the reference material P3HT (4.68 %).
6. By using different methods of palladium-catalyzed reactions, target hole-transporting materials containing diphenylamine or triphenylamine chromophores along with fluorenyl and thiophene fragments have been synthesized. After evaluating the properties of these materials, it has been determined that:
 - 6.1. An increase in the molecular mass of dimeric semiconductors leads to higher both T_d and T_g values. All the target materials exhibited decomposition temperatures above 400 °C, with T_g values varying between 148 and 175 °C;
 - 6.2. An increase of the number of thiophene fragments in the dimer's center does not significantly affect the I_p values. However, adding a phenyl ring to the side fragments increases the ionization potential (**STM29** – 4.95 eV and **STM31** – 5.05 eV, **STM30** – 4.95 eV and **STM32** – 5.08 eV). A similar trend can be observed for charge drift mobilities (**STM29** – $9.86 \times 10^{-7} \text{ cm}^2/\text{Vs}$ and **STM31** – $3.38 \times 10^{-6} \text{ cm}^2/\text{Vs}$, **STM30** – $1.29 \times 10^{-6} \text{ cm}^2/\text{Vs}$ and **STM32** – $1.85 \times 10^{-6} \text{ cm}^2/\text{Vs}$);
 - 6.3. A device with semiconductor **STM30** achieved the highest efficiency (4.5 %). However, due to its higher transparency to visible light, compared to the benchmark P3HT, the latter holds a future potential for use in the construction of transparent Sb_2S_3 solar cells.

6. LITERATŪROS SĄRAŠAS

1. Population Matters. Interneto Puslapis. Prieiga per: https://populationmatters.org/?gad_source=1&gclid=Cj0KCQjwxeyxBhC7ARIsAC7dS3_PXiclfbpUf3Nu6bWNAzYyDSg6Dhzkf7oLYGFwvsYFMmP9_UOoWuQaAvkAEALw_wcB. [žiūrėta 2024-11-06].
2. Yale Environment 360. Interneto Puslapis. Prieiga per: <https://e360.yale.edu/digest/world-consumes-100-billion-tons-of-materials-every-year-report-finds>. [žiūrėta 2024-05-08].
3. World Meteorological Organization. Interneto Puslapis. Prieiga per: <https://www.ncei.noaa.gov/news/global-climate-202413>. [žiūrėta 2025-02-26].
4. National Centers of Environmental Information. Interneto Puslapis. Prieiga per: <https://www.ncei.noaa.gov/news/global-climate-202501>. [žiūrėta 2025-02-026].
5. European Environment Agency. *EU Action*. Interneto Puslapis. Prieiga per: <https://www.eea.europa.eu/en/topics/in-depth/climate-change-mitigation-reducing-emissions?activeTab=e3e6b879-fef4-4a88-9436-5f0064698270>. [žiūrėta 2024-05-08].
6. GÜNES, S. ir N. S. SARICIFTCI. Hybrid solar cells. *Inorganica Chim. Acta*, 361, 2008, 3, 581–588. Interaktyvus. ISSN 0020-1693. Prieiga per ScienceDirect, <https://doi.org/10.1016/j.ica.2007.06.042>. [žiūrėta 2024-05-08].
7. CHAPIN, D. M.; FULLER, C. S. ir PEARSON, G. L. A New Silicon p-n Junction Photocell for Converting Solar Radiation into Electrical Power. *Journal of Applied Physics*, 25, 1954, 676–677. Interaktyvus. ISSN 0021-8979. Prieiga per: AIP Publishing, <https://doi.org/10.1063/1.1721711>. [žiūrėta 2024-05-08].
8. DI SABATINO, Marisa; HENDAWI, Rania ir GARCIA, Alfredo S. Silicon Solar Cells: Trends, Manufacturing Challenges, and AI Perspectives. *Crystals*, 14, 2024, 2. Interaktyvus. ISSN 2073-4352. Prieiga per: MDPI, <https://doi.org/10.3390/cryst14020167>. [žiūrėta 2024-05-08].
9. KOJIMA, Akihiro; TESHIMA, Kenjiro; SHIRAI, Yasuo ir MIYASAKA, Tsutomu. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *Journal of the American Chemical Society*, 131, 2009, 17, 6050–6051. Interaktyvus. ISSN 0002-7863. Prieiga per: ACS Publications, <https://doi.org/10.1021/ja809598r>. [žiūrėta 2024-05-08].
10. NREL. *Emerging PV*. Interneto Puslapis. Prieiga per: <https://www.nrel.gov/pv/assets/images/cell-pv-eff-emergingpv.jpg>. [žiūrėta 2024-05-08].
11. NOMAN, Muhammad; KHAN, Zeeshan ir JAN, Shayan Tariq. A comprehensive review on the advancements and challenges in perovskite solar cell technology. *RSC Advances*, 14, 2024, 8, 5085–5131. Interaktyvus. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D3RA07518D>. [žiūrėta 2024-05-08].
12. EENSALU, Jako S.; MANDATI, Sreekanth; DON, Christopher H.; FINCH, Harry; DHANAK, Vinod R. ir kt. Sb2S3 Thin-Film Solar Cells Fabricated from an Antimony Ethyl Xanthate Based Precursor in Air. *ACS Applied Materials & Interfaces*, 15, 2023, 36, 42622–42636. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsami.3c08547>. [žiūrėta 2024-05-08].
13. JUNEJA, Nimish; MANDATI, Sreekanth; KATERSKI, Atanas; SPALATU, Nicolae; DASKEVICIUTE-GEGUZIENE, Sarune ir kt. Sb2S3 solar cells with a cost-effective and dopant-free fluorene-based enamine as a hole transport material. *Sustainable Energy Fuels*, 6, 2022, 13, 3220–3229. Interaktyvus. ISSN 2398-4902. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D2SE00356B>. [žiūrėta 2024-05-08].

14. MATTIELLO, Sara; LUCARELLI, Giulia; CALASCIBETTA, Adiel; POLASTRI, Lorenzo; GHIGLIETTI, Erika ir kt. Sustainable, Efficient, and Scalable Preparation of Pure and Performing Spiro-OMeTAD for Perovskite Solar Cells. *ACS Sustainable Chemistry & Engineering*, 10, 2022, 14, 4750–4757. Interaktyvus. ISSN 2168-0485. Prieiga per: ACS Publications, <https://doi.org/10.1021/acssuschemeng.2c00493>. [žiūrėta 2024-05-08].
15. ANSARI, Muhammad Azhar; MOHIUDDIN, Shaikh; KANDEMIRLI, Fatma ir MALIK, Muhammad Imran. Synthesis and characterization of poly(3-hexylthiophene): improvement of regioregularity and energy band gap. *RSC Advances*, 8, 2018, 15, 8319–8328. Interaktyvus. ISSN 2046-2069. Prieiga per: Royal Society of Chemistry, <http://dx.doi.org/10.1039/C8RA00555A>. [žiūrėta 2024-05-08].
16. TCI Chemicals. Interneto Puslapis. Prieiga per: <https://www.tcichemicals.com/LT/en/p/P2513>. [žiūrėta 2024-05-08].
17. TCI Chemicals. Interneto Puslapis. Prieiga per: <https://www.tcichemicals.com/LT/en/p/T3672>. [žiūrėta 2024-05-07].
18. Saule Technologies. Products. Interneto Puslapis. Prieiga per: <https://sauletech.com/product/>. [žiūrėta 2024-05-09].
19. WANG, Xiaomin; TANG, Rongfeng; WU, Chunyan; ZHU, Changfei ir CHEN, Tao. Development of antimony sulfide–selenide Sb₂(S, Se)₃-based solar cells. *Journal of Energy Chemistry*, 27, 2018, 3, 713–721. Interaktyvus. ISSN 2095-4956. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.jchem.2017.09.031>. [žiūrėta 2024-05-09].
20. FRAAS, Lewis i. L. P. *Solar Cells and their Applications*. Second ed. New Jersey: John Wiley & Sons, Inc., Hoboken, 2010. ISBN 978-0-470-44633-1.
21. Clean Energy Reviews. Interneto Puslapis. Prieiga per: <https://www.cleanenergyreviews.info/blog/most-efficient-solar-panels>. [žiūrėta 2024-10-15].
22. BOSIO, Alessio; PASINI, Stefano ir ROMEO, Nicola. The History of Photovoltaics with Emphasis on CdTe Solar Cells and Modules. *Coatings*, 10, 2020, 4. Interaktyvus. ISSN 2079-6412. Prieiga per: Multidisciplinary Digital Publishing Institute, <https://doi.org/10.3390/coatings10040344>. [žiūrėta 2024-07-01].
23. NREL. *Best Research-Cell Efficiency Chart*. Interneto Puslapis. Prieiga per: <https://www.nrel.gov/pv/cell-efficiency.html>. [žiūrėta 2024-10-23].
24. SHARMA, Shruti ir SHARMA, Ashutosh. Solar Cells: In Research and Applications—A Review. *Materials Sciences and Applications*, 6, 2015, 1145–1155. Interaktyvus. ISSN 2153-1188. Prieiga per: Scientific Research An Academic Publisher, <https://doi.org/10.4236/msa.2015.612113>. [žiūrėta 2024-10-23].
25. RAZZAQ, Arsalan; ALLEN, Thomas; LIU, Wenzhu; LIU, Zhengxin ir DE WOLF, Stefaan. Silicon heterojunction solar cells: Techno-economic assessment and opportunities. *Joule*, 6, 2022, 514–542. Interaktyvus. ISSN 2542-4351. Prieiga per: Cell Press, <https://doi.org/10.1016/j.joule.2022.02.009>. [žiūrėta 2024-10-23].
26. PV-Manufacturing. *Perc Solar Cells*. Interneto Puslapis. Prieiga per: <https://pv-manufacturing.org/perc-solar-cells/>. [žiūrėta 2024-10-23].
27. Jingsun Power. Interneto Puslapis. Prieiga per: <https://lt.jingsun-power.com/solar-panel/poly-solar-panel/330w-poly-solar-panel.html>. [žiūrėta 2024-10-23].
28. XU, Yichen; LIU, Jie; CUI, Yonghua; YIN, Rui; WANG, Xishu ir kt. Efficient polycrystalline silicon solar cells with double metal oxide layers. *Dalton Transactions*, 48, 2019, 11, 3687–3694. Interaktyvus. ISSN 1477-9226. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C8DT04233K>. [žiūrėta 2024-10-23].

29. KHATIBI, Ali; RAZI ASTARAEI, Fatemeh ir AHMADI, Mohammad. Generation and combination of the solar cells: A current model review. *Energy Science & Engineering*, 7, 2019, 305–322. Interaktyvus. ISSN 2050-0505. Prieiga per: Online Wiley Library, <https://doi.org/10.1002/ese3.292>. [žiūrėta 2024-10-23].
30. RATHORE, Neelam; PANWAR, N. L.; YETTOU, Fatiha ir GAMA, Amor. A Comprehensive review on different types of solar photovoltaic cells and their applications. *International Journal of Ambient Energy*, 42, 2019, 10, 1200–1217. Interaktyvus. ISSN 2162-8246. Prieiga per: Taylor and Francis Online, <https://doi.org/10.1080/01430750.2019.1592774>. [žiūrėta 2024-10-23].
31. TAWALARE, P. K. Optimizing photovoltaic conversion of solar energy. *AIP Advances*, 11, 2021, 10, 100701. Interaktyvus. ISSN 2158-3226. Prieiga per: AIP Publishing, <https://doi.org/10.1063/5.0064202>. [žiūrėta 2024-10-23].
32. DAMBHARE, Mugdha; BUTEY, Bhavana ir MOHARIL, Sanjiv. Solar photovoltaic technology: A review of different types of solar cells and its future trends. *Journal of Physics: Conference Series*, 1913, 2021, 012053. Interaktyvus. ISSN 1742-6596. Prieiga per: IOP Publishing, <https://doi.org/10.1088/1742-6596/1913/1/012053>. [žiūrėta 2024-10-23].
33. ABERLE, Armin G. Thin-film solar cells. *Thin Solid Films*, 517, 2009, 17, 4706–4710. Interaktyvus. ISSN 0040-6090. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.tsf.2009.03.056>. [žiūrėta 2024-10-23].
34. CETINKAYA, Caglar; ÇOKDUYGULULAR, Erman; KINACI, Barış; GÜZELÇİMEN, Feyza; ÖZEN, Yunus ir kt. Highly improved light harvesting and photovoltaic performance in CdTe solar cell with functional designed 1D-phonic crystal via light management engineering. *Scientific Reports*, 12, 2022, 11245. Interaktyvus. ISSN 2045-2322. Prieiga per: Nature, <https://doi.org/10.1038/s41598-022-15078-w>. [žiūrėta 2024-10-23].
35. ENERGY EFFICIENCY & RENEWABLE ENERGY. *Copper Indium Gallium Diselenide*. Interneto Puslapis. Prieiga per: <https://www.energy.gov/eere/solar/copper-indium-gallium-diselenide>. [žiūrėta 2024-10-23].
36. SOONMIN, Ho; Hardani; NANDI, Pronoy; MWANKEMWA, Benard S.; MALEVU, Thembinkosi D. ir kt. Overview on Different Types of Solar Cells: An Update. *Applied Sciences*, 13, 2023, 4, 2051. Interaktyvus. ISSN 2076-3417. Prieiga per: Multidisciplinary Digital Publishing Institute, <https://doi.org/10.3390/app13042051>. [žiūrėta 2024-05-08].
37. COTTA, Mônica. Quantum Dots and Their Applications: What Lies Ahead?. *ACS Applied Nano Materials*, 3, 2020, 4920–4924. Interaktyvus. ISSN 2574-0970. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsanm.0c01386>. [žiūrėta 2024-10-23].
38. ZHANG, Xiaoliang; ZHANG, Jindan; LIU, Jianhua ir JOHANSSON, Erik M. J. Solution processed flexible and bending durable heterojunction colloidal quantum dot solar cell. *Nanoscale*, 7, 2015, 27, 11520–11524. Interaktyvus. ISSN 2040-3364. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C5NR02617B>. [žiūrėta 2024-10-24].
39. REHMAN, Fatima; SYED, Iqar Hussain; KHANAM, Saira; IJAZ, Sumbel; MEHMOOD, Haris ir kt. Fourth-generation solar cells: a review. *Energy Advances*, 2, 2023, 9, 1239–1262. Interaktyvus. ISSN 2753-1457. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D3YA00179B>. [žiūrėta 2024-10-23].
40. NIDEEP, T. K.; MANIKANDAN, Ramya ir KAILASNATH, M. An Investigation on the Photovoltaic Performance of Quantum Dot Solar Cells Sensitized by CdTe, CdSe and CdS having Comparable Size. *Superlattices and Microstructures*, 141, 2020, 106477. Interaktyvus. ISSN 0749-6036. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.spmi.2020.106477>. [žiūrėta 2024-10-23].

41. RAHMAN, Mohammad Mominur; KARIM, Mohammad Rezaul; ALHARBI, Hamad F.; ALDOKHAYEL, Belal; UZZAMAN, Tauriq ir kt. Cadmium Selenide Quantum Dots for Solar Cell Applications: A Review. *Chemistry – An Asian Journal*, 16, 2021, 8, 902–921. Interaktyvus. ISSN 1861-471X. Prieiga per: Wiley Online Library, <https://doi-org.ezproxy.ktu.edu/10.1002/asia.202001369>. [žiūrėta 2024-10-23].
42. JUNG, Eun Sun; BASIT, Muhammad Abdul; ABBAS, Muhammad Awais; ALI, Ijaz; KIM, Dae Woong ir kt. Improved CdS quantum dot distribution on a TiO₂ photoanode by an atomic-layer-deposited ZnS passivation layer for quantum dot-sensitized solar cells. *Solar Energy Materials and Solar Cells*, 218, 2020, 110753. 110753. Interaktyvus. ISSN 0927-0248. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.solmat.2020.110753>. [žiūrėta 2024-10-23].
43. VENKATACHALAM, Vijayaraj; GANAPATHY, Sasikala; PERUMAL, Ilaiyaraja ir ANANDHAN, Manikandan. Crystal shape and size of CdTe colloidal quantum dots controlled by silver doping for enhanced quantum dots sensitized solar cells performance. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 656, 2023, 130296. Interaktyvus. ISSN 0927-7757. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.colsurfa.2022.130296>. [žiūrėta 2024-10-23].
44. BASHIR, Rabia; KASHIF BILAL, Muhammad; BASHIR, Amna ir ALI, Awais. Fabrication of PbSe colloidal quantum dot solar cells using low-temperature Li-doped ZnO electron transport layer. *Solar Energy*, 256, 2023, 67–75. Interaktyvus. ISSN 0038-092X. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.solener.2023.03.060>. [žiūrėta 2024-10-23].
45. LIU, Sisi; WANG, Meng; YU, Xiong; LI, Hao; LU, Haifei ir kt. Efficient PbSe Quantum Dot Infrared Photovoltaic Applying MXene Modified ZnO Electron Transport Layer. *Advanced Optical Materials*, 12, 2023, 2301252. Interaktyvus. ISSN 2195-1071. Prieiga per: Wiley Online Library, <https://doi-org.ezproxy.ktu.edu/10.1002/adom.202301252>. [žiūrėta 2024-10-23].
46. LIU, Yang; LI, Fei; SHI, Guozheng; LIU, Zeke; LIN, Xiaofang ir kt. PbSe Quantum Dot Solar Cells Based on Directly Synthesized Semiconductive Inks. *ACS Energy Letters*, 5, 2020, 12, 3797–3803. Interaktyvus. ISSN 2380-8195. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsenergylett.0c02011>. [žiūrėta 2024-10-23].
47. HUANG, Tengzuo; WU, Chunyan; CHEN, Zuyan; SHEN, Shuang; YANG, Jinpeng ir kt. Optimizing Surface Passivation of n-Type Quantum Dots for Efficient PbS Quantum Dot Solar Cells. *Solar RRL*, 8, 2024, 2400073. Interaktyvus. ISSN 2367-198X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/solr.202400073>. [žiūrėta 2024-10-24].
48. HUANG, Tengzuo; WU, Chunyan; YANG, Jinpeng; HU, Pengyu; QIAN, Lei ir kt. Reducing the Open-Circuit Voltage Loss of PbS Quantum Dot Solar Cells via Hybrid Ligand Exchange Treatment. *ACS Applied Materials & Interfaces*, 16, 2024, 1, 915–923. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsami.3c16599>. [žiūrėta 2024-10-24].
49. WEI, Yuyao; NAKAMURA, Mako; DING, Chao; LIU, Dong; LI, Hua ir kt. Unraveling the Organic and Inorganic Passivation Mechanism of ZnO Nanowires for Construction of Efficient Bulk Heterojunction Quantum Dot Solar Cells. *ACS Applied Materials & Interfaces*, 14, 2022, 31, 36268–36276. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsami.2c10508>. [žiūrėta 2024-10-24].
50. HE, Yunfei; REN, Yin; LI, Sisi; LI, Jiahua; WANG, Yahong ir kt. Construction and photovoltaic performances of transport layer/quantum dot/transport layer sandwich nanowire

arrays. *Materials Science in Semiconductor Processing*, 170, 2024, 107946. Interaktyvus. ISSN 1369-8001. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.mssp.2023.107946>. [žiūrėta 2024-10-24].

51. LIU, Yahui; LI, Bowen; MA, Chang-Qi; HUANG, Fei; FENG, Guitao ir kt. Recent progress in organic solar cells (Part I material science). *Science China Chemistry*, 65, 2022, 224–268. Interaktyvus. ISSN 1674-7291. Prieiga per: Springer Nature Link, <https://doi.org/10.1007/s11426-021-1180-6>. [žiūrėta 2024-10-25].

52. DING, Pengfei; YANG, Daobin; YANG, Shuncheng ir GE, Ziyi. Stability of organic solar cells: toward commercial applications. *Chemical Society Reviews*, 53, 2024, 2350–2387. Interaktyvus. ISSN 1460-4744. Prieiga per: Royal Society of Chemistry, <https://doi.org.ezproxy.ktu.edu/10.1039/D3CS00492A>. [žiūrėta 2024-10-25].

53. LI, Yang; HUANG, Wei; ZHAO, Dejiang; WANG, Lu; JIAO, Zhiqiang ir kt. Recent Progress in Organic Solar Cells: A Review on Materials from Acceptor to Donor. *Molecules*, 27, 2022, 6, 1800, 1–31. Interaktyvus. ISSN 1420-3049. Prieiga per: Multidisciplinary Digital Publishing Institute, <https://doi.org/10.3390/molecules27061800>. [žiūrėta 2024-10-25].

54. NAYAK, Pabitra K. ir CAHEN, David. Updated Assessment of Possibilities and Limits for Solar Cells. *Advanced Materials*, 26, 2014, 10, 1622–1628. Interaktyvus. ISSN 0935-9648. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adma.201304620>. [žiūrėta 2024-10-25].

55. PIRADI, Venkatesh; YAN, Feng; ZHU, Xunjin ir WONG, Wai-Yeung. A recent overview of porphyrin-based π -extended small molecules as donors and acceptors for high-performance organic solar cells. *Materials Chemistry Frontiers*, 5, 2021, 19, 7119–7133. Interaktyvus. ISSN 2052-1537. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D1QM00952D>. [žiūrėta 2024-10-25].

56. SHEN, Haojiang; REN, Yi; LI, Jianfeng; XU, Yixuan; HAN, Chenyang ir kt. Enhanced Performance via π -Bridge Alteration of Porphyrin-Based Donors for All-Small-Molecule Organic Solar Cells. *Chinese Journal of Chemistry*, 41, 2022, 644–650. Interaktyvus. ISSN 1001-604X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/cjoc.202200652>. [žiūrėta 2024-10-25].

57. TAN, Hua; TAN, Hongyi; ZHENG, Xiangjun; YANG, Jia; YU, Junting ir kt. Significant influence of the benzothiophene ring substitution position on the photovoltaic performance of benzodithiophene-based donor polymers. *Journal of Materials Chemistry C*, 8, 2020, 9, 3183–3191. Interaktyvus. ISSN 2050-7526. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C9TC06594F>. [žiūrėta 2024-10-26].

58. HU, Dingqin; YANG, Qianguang; CHEN, Haiyan; WOBEN, Friso; LE CORRE, Vincent M. ir kt. 15.34% efficiency all-small-molecule organic solar cells with an improved fill factor enabled by a fullerene additive. *Energy & Environmental Science*, 13, 2020, 7, 2134–2141. Interaktyvus. ISSN 1754-5692. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D0EE00714E>. [žiūrėta 2024-10-26].

59. CAO, Jin ir YANG, Shaopeng. Progress in perylene diimides for organic solar cell applications. *RSC Advances*, 12, 2022, 12, 6966–6973. Interaktyvus. ISSN 2046-2069. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D1RA08484D>. [žiūrėta 2024-10-26].

60. Akash ir TIWARI, J. P. Recent advancements in perylene diimide as an electron acceptor in organic solar cells. *Journal of Materials Chemistry C*, 12, 2024, 3, 838–853. Interaktyvus. ISSN 2050-7526. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D3TC04054B>. [žiūrėta 2024-10-26].

61. RUNDEL, Kira; MANIAM, Subashani; DESHMUKH, Kedar; GANN, Eliot; PRASAD, Shyamal K. K. ir kt. Naphthalene diimide-based small molecule acceptors for organic solar cells. *Journal of Materials Chemistry A*, 5, 2017, 24, 12266–12277. Interaktyvus. ISSN 2050-7488. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C7TA02749D>. [žiūrėta 2024-10-26].
62. ALI, Usman; JAVED, Ayesha; RAMZAN, Hina; SHOAIB, Muhammad; RAZA, Ali ir kt. Molecular designing of naphthalene diimide based fullerene-free small organic solar cell - Acceptors with high photovoltaic performance by density functional theory. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 228, 2020, 117685. Interaktyvus. ISSN 1386-1425. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.saa.2019.117685>. [žiūrėta 2024-10-26].
63. YIN, Zhihong; WANG, Yang; GUO, Qing; ZHU, Lei; LIU, Haiqin ir kt. Efficient all-polymer solar cells based on a narrow-bandgap polymer acceptor. *Journal of Materials Chemistry C*, 8, 2020, 45, 16180–16187. Interaktyvus. ISSN 2050-7526. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D0TC03303K>. [žiūrėta 2024-10-26].
64. MURAD, Ary,R.; IRAQI, Ahmed; AZIZ, Shujahadeen B.; ABDULLAH, Sozan,N. ir BRZA, Mohamad A. Conducting Polymers for Optoelectronic Devices and Organic Solar Cells: A Review. *Polymers*, 12, 2020, 11, 2627. Interaktyvus. ISSN 2073-4360. Prieiga per: Multidisciplinary Digital Publishing Institute, <https://doi.org/10.3390/polym12112627>. [žiūrėta 2024-10-26].
65. Karlsruher Institut Für Technologie. *Drying Process of Polymer Solar Cells: Phase Separation and Morphology Formation*. Interneto Puslapis. Prieiga per: https://www.tft.kit.edu/21_152.php. [žiūrėta 2024-11-06].
66. TCI. *Organic Solar Cell (OPV) Materials*. Interneto Puslapis. Prieiga per: <https://www.tcichemicals.com/CA/en/c/12802>. [žiūrėta 2024-11-04].
67. SHI, Qinqin; JIANFEI, Wu; WU, Xiaoxi; PENG, Aidong ir HUANG, Hui. Perylene Diimide-Based Conjugated Polymers for All-Polymer Solar Cells. *Chemistry - A European Journal*, 26, 2020, 12510–12522. Interaktyvus. ISSN 0947-6539. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/chem.202001011>. [žiūrėta 2024-11-04].
68. SPELLER, Emily; CLARKE, Andrew; LUKE, Joel; LEE, Harrison Ka Hin; DURRANT, James ir kt. From Fullerene Acceptors to Non-Fullerene Acceptors: Prospects and Challenges in the Stability of Organic Solar Cells. *Journal of Materials Chemistry A*, 7, 2019, 23361–23377. Interaktyvus. ISSN 2050-7496. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C9TA05235F>. [žiūrėta 2024-11-04].
69. XIE, Xiaohua; LIU, Xu; ZENG, Dan ir ZHAO, Longfeng. The Potentials in Solar Cells for MEH-PPV Derivatives: Molecular Design and Performance Prediction: The Potentials in Solar Cells for MEH-PPV Derivatives. *Bulletin of the Korean Chemical Society*, 41, 2020, 719–726. Interaktyvus. ISSN 1229-5949. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/bkcs.12059>. [žiūrėta 2024-11-04].
70. ZHOU, Kangkang; XIAN, Kaihu ir YE, Long. Morphology control in high-efficiency all-polymer solar cells. *InfoMat*, 4, 2022, e12270. Interaktyvus. ISSN 2567-3165. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/inf2.12270>. [žiūrėta 2024-11-04].
71. WANG, Wei; WU, Qiang; SUN, Rui; GUO, Jing; WU, Yao ir kt. Controlling Molecular Mass of Low-Band-Gap Polymer Acceptors for High-Performance All-Polymer Solar Cells. *Joule*, 4, 2020, 5, 1070–1086. Interaktyvus. ISSN 2542-4351. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.joule.2020.03.019>. [žiūrėta 2024-11-04].

72. FENG, Kui; GUO, Han; SUN, Hl ir GUO, Xugang. n-Type Organic and Polymeric Semiconductors Based on Bithiophene Imide Derivatives. *Accounts of Chemical Research*, 54 2021, 20, 3804–3817. Interaktyvus. ISSN 0001-4842. Prieiga per: ACS Publications, <https://doi.org/10.1021/acs.accounts.1c00381>. [žiūrėta 2024-11-04].
73. YUXIANG, Li; JIA, Zhiyan; ZHANG, Qilin; WU, Ziang; QIN, Hongmei ir kt. Towards Efficient All-Polymer Solar Cells via Halogenation on Polymer Acceptor. *ACS Applied Materials & Interfaces*, 12, 2020, 29, 33028–33038. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsami.0c08442>. [žiūrėta 2024-11-04].
74. ZHANG, Lu; DING, Zicheng; ZHAO, Ruyan; JIRUI, Feng; MA, Wei ir kt. Effect of polymer donor aggregation on the active layer morphology of amorphous polymer acceptor-based all-polymer solar cells. *Journal of Materials Chemistry C*, 8, 2020, 16, 5613–5619. Interaktyvus. ISSN 2050-7526. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C9TC06668C>. [žiūrėta 2024-11-04].
75. WANG, Ning; YU, Yingjian; ZHAO, Ruyan; DING, Zicheng; LIU, Jun ir kt. Improving Active Layer Morphology of All-Polymer Solar Cells by Solution Temperature. *Macromolecules*, 53, 2020, 9, 3325–3331. Interaktyvus. ISSN 1520-5835. Prieiga per: ACS Publications, <https://doi.org/10.1021/acs.macromol.0c00633>. [žiūrėta 2024-11-04].
76. CHATTERJEE, Shreyam; JINNAI, Seihou ir IE, Yutaka. Nonfullerene acceptors for P3HT-based organic solar cells. *Journal of Materials Chemistry A*, 9, 2021, 35, 18857–18886. Interaktyvus. ISSN 2050-7488. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D1TA03219D>. [žiūrėta 2024-11-04].
77. LI, Youle; ZHANG, Yue; WU, Baoqi; PANG, Shuting; YUAN, Xiyue ir kt. High-Efficiency P3HT-Based All-Polymer Solar Cells with a Thermodynamically Miscible Polymer Acceptor. *Solar RRL*, 6, 2022, 7, 2200073. Interaktyvus. ISSN 2367-198X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/solr.202200073>. [žiūrėta 2024-11-04].
78. LIANG, Ziqi; HE, Jiangting; ZHAO, Bin; GAO, Mengyuan; CHEN, Yu ir kt. 8.30% Efficiency P3HT-based all-polymer solar cells enabled by a miscible polymer acceptor with high energy levels and efficient electron transport. *Science China Chemistry*, 66, 2022, 216–227. Interaktyvus. ISSN 1674-7291. Prieiga per: Springer Nature Link, <https://doi.org/10.1007/s11426-022-1386-1>. [žiūrėta 2024-11-04].
79. ZHANG, Zhi-Guo ir LI, Yongfang. Polymerized Small-Molecule Acceptors for High-Performance All-Polymer Solar Cells. *Angewandte Chemie*, 60, 2020, 4422–4433. Interaktyvus. ISSN 1433-7851. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/anie.202009666>. [žiūrėta 2024-11-04].
80. O'REGAN, Brian ir GRÄTZEL, Michael. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature*, 353, 1991, 6346, 737–740. Interaktyvus. ISSN 1476-4687. Prieiga per: Nature, <https://doi.org/10.1038/353737a0>. [žiūrėta 2024-11-04].
81. PNG EGG. Interneto Puslapis. Prieiga per: <https://www.pngegg.com/en/png-efdw>. [žiūrėta 2024-11-05].
82. PARASURAMAN, Dhanasekaran. An Extensive Analysis of Dye-Sensitized Solar Cell (DSSC). *Brazilian Journal of Physics*, 54, 2024, 28. Interaktyvus. ISSN 1678-4448. Prieiga per: Springer Nature Link, <https://doi.org/10.1007/s13538-023-01375-w>. [žiūrėta 2024-11-05].
83. RAJARAMANAN, Tharmakularasa; HEIDARI GOURJI, Fatemeh; YOGENTHIRAN, Elilan; SHIVATHARSINY, Yohi; SENTHILNANTHANAN, Meena ir kt. Natural sensitizer extracted from *Mussaenda erythrophylla* for dye-sensitized solar cell. *Scientific Reports*, 13,

- 2023, 13844. Interaktyvus. ISSN 2045-2322. Prieiga per: Nature, <https://doi.org/10.1038/s41598-023-40437-6>. [žiūrėta 2024-11-05].
84. Sharma; DAWO, Chandan; MULCHANDANI, Komal; KUMAWAT, Uttam; SINGHAL, R. ir kt. Revealing the photophysics of N719 dye based dye-sensitized solar cell. *Optical Materials*, 142, 2023, 114113. Interaktyvus. ISSN 0925-3467. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.optmat.2023.114113>. [žiūrėta 2024-11-05].
85. ALI, Jamshed; BIBI, Safia; JATOI, Wahid; TUZEN, Mustafa; JAKHRANI, Mushtaque ir kt. Green synthesized zinc oxide nanostructures and their applications in dye-sensitized solar cells and photocatalysis: A review. *Materials Today Communications*, 36, 2023, 106840. Interaktyvus. ISSN 2352-4928. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.mtcomm.2023.106840>. [žiūrėta 2024-11-05].
86. S, Selva Esakki,E.; VIVEK, P. ir SUNDAR, S. M. Influence on the efficiency of Dye-Sensitized Solar Cell using Cd doped ZnO via solvothermal method. *Inorganic Chemistry Communications*, 147, 2022, 110213. Interaktyvus. ISSN 1387-7003. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.inoche.2022.110213>. [žiūrėta 2024-11-05].
87. AROTE, Sandeep; GAPALE, Dipak; PALVE, Balasaheb ir BAVISKAR, Prashant. Influence of surface passivation by MgO on photovoltaic performance of SnO₂ based dye-sensitized solar cells. *Next Energy*, 4, 2024, 100140. Interaktyvus. ISSN 2949-821X. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.nxener.2024.100140>. [žiūrėta 2024-11-05].
88. WANG, Dongting; LI, Yuchen; DING, Yimin; JIA, Xiangchen; ZHONG, Daopeng ir kt. Facile Synthesis of a Multifunctional SnO₂ Nanoparticles/Nanosheets Composite for Dye-Sensitized Solar Cells. *ACS Omega*, 8, 2023, 47, 44578–44585. Interaktyvus. ISSN 2470-1343. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsomega.3c04472>. [žiūrėta 2024-11-05].
89. SEN, Anik; PUTRA, Miftahussurur; BISWAS, Abul; BEHERA, Anil Kumar ir GROSS, Axel. Insight on the choice of sensitizers/dyes for dye sensitized solar cells: A review. *Dyes and Pigments*, 213, 2023, 111087. Interaktyvus. ISSN 0143-7208. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.dyepig.2023.111087>. [žiūrėta 2024-11-05].
90. WAHYUONO, Ruri; BRAUMÜLLER, Markus; BOLD, Sebastian; AMTHOR, Sebastian; NAUROOZI, Djawed ir kt. Localizing the initial excitation – A case study on NiO photocathodes using Ruthenium dipyrrophenazine complexes as sensitizers. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 252, 2021, 119507. Interaktyvus. ISSN 1386-1425. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.saa.2021.119507>. [žiūrėta 2024-11-05].
91. GIANNOUDIS, Emmanouil; BOLD, Sebastian; MÜLLER, Carolin; SCHWAB, Alexander; BRUHNKE, Jakob ir kt. Hydrogen Production at a NiO Photocathode Based on a Ruthenium Dye–Cobalt Diimine Dioxime Catalyst Assembly: Insights from Advanced Spectroscopy and Post-operando Characterization. *ACS Applied Materials & Interfaces*, 13, 2021, 42, 49802–49815. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsaami.1c12138>. [žiūrėta 2024-11-05].
92. AMTHOR, Sebastian; BRAUN, Hanna; GRÖNE, Julius; NAUROOZI, Djawed; JACOB, Timo ir kt. Tailored protective groups for surface immobilization of ruthenium dyes. *Dalton Transactions*, vol. 49, 2020, 12, 3735–3742. Interaktyvus. ISSN 1477-9226. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C9DT03591E>. [žiūrėta 2024-11-06].
93. GANGADHAR, Palivela Siva; GONUGUNTLA, Spandana; MADANABOINA, Sruthi; ISLAVATH, Nanaji; PAL, Ujjwal ir kt. Unravelling the impact of thiophene auxiliary in new porphyrin sensitizers for high solar energy conversion. *Journal of Photochemistry and*

Photobiology A: Chemistry, 392, 2020, 112408. Interaktyvus. ISSN 1010-6030. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.jphotochem.2020.112408>. [žiūrėta 2024-11-06].

94. KURUMISAWA, Yuma; HIGASHINO, Tomohiro; NIMURA, Shimpei; TSUJI, Yukihiro; IYAMA, Hitomi ir kt. Renaissance of Fused Porphyrins: Substituted Methylene-Bridged Thiophene-Fused Strategy for High-Performance Dye-Sensitized Solar Cells. *Journal of the American Chemical Society*, 141, 2019, 25, 9910–9919. Interaktyvus. ISSN 0002-7863. Prieiga per: ACS Publications, <https://doi.org/10.1021/jacs.9b03302>. [žiūrėta 2024-11-06].

95. ILGÜN, Cidal; SEVİM, Altuğ Mert; ÇAKAR, Soner; ÖZACAR, Mahmut ir GÜL, Ahmet. Novel Co and Zn-Phthalocyanine dyes with octa-carboxylic acid substituents for DSSCs. *Solar Energy*, 218, 2021, 169–179. Interaktyvus. ISSN 0038-092X. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.solener.2021.02.042>. [žiūrėta 2024-11-06].

96. URBANI, Maxence; RAGOUSI, Maria-Eleni; NAZEERUDDIN, Mohammad ir TORRES, Tomas. Phthalocyanines for dye-sensitized solar cells. *Coordination Chemistry Reviews*, 381, 2019, 1–64. Interaktyvus. ISSN 0010-8545. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.ccr.2018.10.007>. [žiūrėta 2024-11-06].

97. AHMED, Shahnaz; BORA, Smiti Rani; CHUTIA, Tridip ir KALITA, Dhruva Jyoti. Structural modulation of phenothiazine and coumarin based derivatives for high performance dye sensitized solar cells: a theoretical study. *Physical Chemistry Chemical Physics*, 23, 2021, 23, 13190–13203. Interaktyvus. ISSN 1463-9076. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D1CP00036E>. [žiūrėta 2024-11-06].

98. TIAN, Lu; WANG, Yajun; ZHANG, Yushuang; LI, Xiaoyan; WU, Wenjun ir kt. Molecular Engineering of Indoline Dyes and Their Application in Dye-Sensitized Solar Cells: Effect of Planarity and Side Chain on Interfacial Charge-Transfer Processes. *ACS Applied Energy Materials*, 4, 2021, 1, 242–248. Interaktyvus. ISSN 2574-0962. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsam.0c02199>. [žiūrėta 2024-11-06].

99. TANAKA, Ellie; MIKHAILOV, Maxim S.; GUDIM, Nikita S.; KNYAZEVA, Ekaterina A.; MIKHALCHENKO, Ludmila V. ir kt. Structural features of indoline donors in D–A– π –A type organic sensitizers for dye-sensitized solar cells. *Molecular Systems Design & Engineering*, 6, 2021, 9, 730–738. Interaktyvus. ISSN 2058-9689. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D1ME00054C>. [žiūrėta 2024-11-06].

100. WAN, Zhongquan; YANG, Jinyu; XIA, Jianxing; SHU, Hongyu; YAO, Xiaojun ir kt. Simple molecular structure but high efficiency: Achieving over 9% efficiency in dye-sensitized solar cells using simple triphenylamine sensitizer. *Journal of Power Sources*, 506, 2021, 230214. Interaktyvus. ISSN 0378-7753. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.jpowsour.2021.230214>. [žiūrėta 2024-11-06].

101. CHEN, Hao; COLE, Jacqueline M.; STENNING, Gavin B. G.; YANGUAS-GIL, Angel; ELAM, Jeffrey W. ir kt. Imaging Dye Aggregation in MK-2, N3, N749, and SQ-2 dye···TiO₂ Interfaces That Represent Dye-Sensitized Solar Cell Working Electrodes. *ACS Applied Energy Materials*, 3, 2020, 4, 3230–3241. Interaktyvus. ISSN 2574-0962. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsam.9b02001>. [žiūrėta 2024-11-06].

102. BISWAL, Dharmendra; JHA, Anjali ir SEN, Anik. Screening donor and acceptor groups for organic azo-based dyes for dye sensitized solar cells. *Journal of Molecular Structure*, 1228, 2021, 129776. Interaktyvus. ISSN 0022-2860. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.molstruc.2020.129776>. [žiūrėta 2024-11-06].

103. HAN, Liang; LIU, Jie; LIU, Yang ir CUI, Yanhong. Novel D–A– π –A type benzocarbazole sensitizers for dye sensitized solar cells. *Journal of Molecular Structure*, 1180, 2019, 651–

658. Interaktyvus. ISSN 0022-2860. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.molstruc.2018.12.052>. [žiūrėta 2024-11-06].
104. DING, Haoran; CHU, Yanmeng; XU, Mengyu; ZHANG, Shicong; YE, Haoran ir kt. Effect of π -bridge groups based on indeno[1,2-b]thiophene D–A– π –A sensitizers on the performance of dye-sensitized solar cells and photocatalytic hydrogen evolution. *Journal of Materials Chemistry C*, 8, 2020, 42, 14864–14872. Interaktyvus. ISSN 2050-7526. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D0TC03302B>. [žiūrėta 2024-11-06].
105. HEMAVATHI, B.; V., Jayadev; RAMAMURTHY, Praveen C.; PAI, Ranjith Krishna; NARAYANAN UNNI, K. N. ir kt. Variation of the donor and acceptor in D–A– π –A based cyanopyridine dyes and its effect on dye sensitized solar cells. *New Journal of Chemistry*, 43, 2019, 39, 15673–15680. Interaktyvus. ISSN 1144-0546. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C9NJ03460A>. [žiūrėta 2024-11-06].
106. BUSH, Kevin A.; FROHNA, Kyle; PRASANNA, Rohit; BEAL, Rachel E.; LEIJTENS, Tomas ir kt. Compositional Engineering for Efficient Wide Band Gap Perovskites with Improved Stability to Photoinduced Phase Segregation. *ACS Energy Letters*, 3, 2018, 2, 428–435. Interaktyvus. ISSN 2380-8195. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsenerylett.7b01255>. [žiūrėta 2024-11-06].
107. KIM, Jin Young; LEE, Jin-Wook; JUNG, Hyun; SHIN, Hyunjung ir PARK, Nam-Gyu. High-Efficiency Perovskite Solar Cells. *Chemical reviews*, 120, 2020, 15, 7867–7918. Interaktyvus. ISSN 1520-6890. Prieiga per: ACS Publications, <https://doi.org/10.1021/acs.chemrev.0c00107>. [žiūrėta 2024-11-06].
108. LEE, Jin-Wook; SEOL, Dong-Jin; CHO, An-Na ir PARK, Nam-Gyu. High-Efficiency Perovskite Solar Cells Based on the Black Polymorph of HC(NH₂)₂PbI₃. *Advanced materials*, 26, 2014, 4991–4998. Interaktyvus. ISSN 0935-9648. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adma.201401137>. [žiūrėta 2024-11-07].
109. EPERON, Giles E.; PATERNO, Giuseppe M.; SUTTON, Rebecca J.; ZAMPETTI, Andrea; HAGHIGHIRAD, Amir Abbas ir kt. Inorganic caesium lead iodide perovskite solar cells. *Journal of Materials Chemistry A*, 3, 2015, 39, 19688–19695. Interaktyvus. ISSN 2050-7488. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C5TA06398A>. [žiūrėta 2024-11-07].
110. CORREA-BAENA, Juan; SALIBA, Michael; BUONASSISI, Tonio; GRAETZEL, Michael; ABATE, Antonio ir kt. Promises and challenges of perovskite solar cells. *Science*, 358, 2017, 739–744. Interaktyvus. ISSN 1095-9203. Prieiga per: Science, <https://doi.org/10.1126/science.aam6323>. [žiūrėta 2024-11-07].
111. PATIL, Jyoti V.; MALI, Sawanta S. ir HONG, Chang Kook. Fully-inorganic strontium incorporated CsPbI₂Br perovskite solar cells with promoted efficiency and stability. *Journal of Energy Chemistry*, 62, 2021, 451–458. Interaktyvus. ISSN 2095-4956. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.jechem.2021.04.003>. [žiūrėta 2024-11-07].
112. LI, Rui; ZHANG, Huanyu; HAN, Xing; HUO, Xiangtao; ZHANG, Mei ir kt. Efficient Nanorod Array Perovskite Solar Cells: A Suitable Structure for High Strontium Substitution in Nature. *ACS Applied Materials & Interfaces*, 12, 2020, 9, 10515–10526. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsami.9b22556>. [žiūrėta 2024-11-07].
113. LIU, Xinghua; YAN, Kang; TAN, Dawei; LIANG, Xiao; ZHANG, Hongmei ir kt. Solvent Engineering Improves Efficiency of Lead-Free Tin-Based Hybrid Perovskite Solar Cells beyond 9%. *ACS Energy Letters*, 3, 2018, 11, 2701–2707. Interaktyvus. ISSN 2380-

8195. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsenergylett.8b01588>. [žiūrėta 2024-11-07].

114. GUPTA, Satyajit; CAHEN, David ir HODES, Gary. How SnF₂ Impacts the Material Properties of Lead-Free Tin Perovskites. *The Journal of Physical Chemistry C*, 122, 2018, 25, 13926–13936. Interaktyvus. ISSN 1932-7447. Prieiga per: ACS Publications, <https://doi.org/10.1021/acs.jpcc.8b01045>. [žiūrėta 2024-11-07].

115. DAI, W. B.; XU, S.; ZHOU, J.; HU, J.; HUANG, K. ir kt. Lead-free, stable, and effective double FA₄GeIISbIIICl₁₂ perovskite for photovoltaic applications. *Solar Energy Materials and Solar Cells*, 192, 2019, 140–146. Interaktyvus. ISSN 0927-0248. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.solmat.2018.12.031>. [žiūrėta 2024-11-07].

116. LI, Xiaolei; LI, Bochao; CHANG, Jianhui; DING, Bin; ZHENG, Shuaizhi ir kt. (C₆H₅CH₂NH₃)₂CuBr₄: A Lead-Free, Highly Stable Two-Dimensional Perovskite for Solar Cell Applications. *ACS Applied Energy Materials*, 1, 2018, 6, 2709–2716. Interaktyvus. ISSN 2574-0962. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsaem.8b00372>. [žiūrėta 2024-11-07].

117. LI, Tianyang; WANG, Xiaoming; YAN, Yanfa ir MITZI, David B. Phase Stability and Electronic Structure of Prospective Sb-Based Mixed Sulfide and Iodide 3D Perovskite (CH₃NH₃)SbSI₂. *The Journal of Physical Chemistry Letters*, 9, 2018, 14, 3829–3833. Interaktyvus. ISSN 1948-7185. Prieiga per: ACS Publications, <https://doi.org/10.1021/acs.jpcclett.8b01641>. [žiūrėta 2024-11-07].

118. FENG, Jiangshan; JIAO, Yuxiao; WANG, Hui; ZHU, Xuejie; SUN, Youming ir kt. High-throughput large-area vacuum deposition for high-performance formamidine-based perovskite solar cells. *Energy & Environmental Science*, 14, 2021, 5, 3035–3043. Interaktyvus. ISSN 1754-5692. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D1EE00634G>. [žiūrėta 2024-11-07].

119. LEE, Joo-Hong; KIM, Byung Soon; PARK, Jinkyun; LEE, Jin-Wook ir KIM, Kyungkon. Opportunities and Challenges for Perovskite Solar Cells Based on Vacuum Thermal Evaporation. *Advanced Materials Technologies*, 8, 2023, 20, 2200928. Interaktyvus. ISSN 2365-709X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/admt.202200928>. [žiūrėta 2024-11-07].

120. ALANAZI, Tarek I. Current spray-coating approaches to manufacture perovskite solar cells. *Results in Physics*, 44, 2023, 106144. Interaktyvus. ISSN 2211-3797. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.rinp.2022.106144>. [žiūrėta 2024-11-07].

121. BISHOP, James E.; SMITH, Joel A. ir LIDZEY, David G. Development of Spray-Coated Perovskite Solar Cells. *ACS Applied Materials & Interfaces*, 12, 2020, 43, 48237–48245. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsaami.0c14540>. [žiūrėta 2024-11-07].

122. LEI, Yusheng; CHEN, Yimu; ZHANG, Ruiqi; LI, Yuheng; YAN, Qizhang ir kt. A fabrication process for flexible single-crystal perovskite devices. *Nature*, 583, 2020, 7818, 790–795. Interaktyvus. ISSN 1476-4687. Prieiga per: Nature, <https://doi.org/10.1038/s41586-020-2526-z>. [žiūrėta 2024-11-07].

123. ZHANG, Kai; WANG, Zheng; WANG, Gaopeng; WANG, Jian; LI, Yu ir kt. A prenucleation strategy for ambient fabrication of perovskite solar cells with high device performance uniformity. *Nature Communications*, 11, 2020, 1, 1006. Interaktyvus. ISSN 2041-1723. Prieiga per: Nature, <https://doi.org/10.1038/s41467-020-14715-0>. [žiūrėta 2024-11-07].

124. LI, Hengyue; ZUO, Chuantian; SCULLY, Andrew; ANGMO, Dechan; YANG, Junliang ir kt. Recent progress towards roll-to-roll manufacturing of perovskite solar cells using slot-die processing. *Flexible and Printed Electronics*, 5, 2019, 014006. Interaktyvus. ISSN 2058-8585. Prieiga per: iop science, <https://doi.org/10.1088/2058-8585/ab639e>. [žiūrėta 2024-11-07].
125. LIU, Xingyue; TAN, Xianhua; LIU, Zhiyong; YE, Haibo; SUN, Bo ir kt. Boosting the efficiency of carbon-based planar CsPbBr₃ perovskite solar cells by a modified multistep spin-coating technique and interface engineering. *Nano Energy*, 56, 2019, 184–195. Interaktyvus. ISSN 2211-2855. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.nanoen.2018.11.053>. [žiūrėta 2024-11-07].
126. HUSSAIN, Istiak; TRAN, Hoang Phong; JAKSIK, Jared; MOORE, Justin; ISLAM, Nazmul ir kt. Functional materials, device architecture, and flexibility of perovskite solar cell. *Emergent Materials*, 1, 2018, 3, 133–154. Interaktyvus. ISSN 2522-574X. Prieiga per: Springer Nature Link, <https://doi.org/10.1007/s42247-018-0013-1>. <https://doi.org/10.1016/j.nanoen.2018.11.053>. [žiūrėta 2024-11-07].
127. HSU, Chou-Yi; AL-SALMAN, H.; HUSSEIN, Hussein H.; JURAEV, Nizomiddin; MAHMOUD, Zaid H. ir kt. Experimental and theoretical study of improved mesoporous titanium dioxide perovskite solar cell: The impact of modification with graphene oxide. *Heliyon*, 10, 2024. Interaktyvus. ISSN 2405-8440. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.heliyon.2024.e26633>. [žiūrėta 2024-11-07].
128. LIU, Jiale; LI, Sheng; QIU, Zexiong; LIU, Yang; QIU, Cheng ir kt. Stratified Oxygen Vacancies Enhance the Performance of Mesoporous TiO₂ Electron Transport Layer in Printable Perovskite Solar Cells. *Small*, 19, 2023, 32, 2300737. Interaktyvus. ISSN 1613-6810. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/sml.202300737>. [žiūrėta 2024-11-07].
129. GANTUMUR, Munkhtuul; HOSSAIN, Mohammad Ismail; SHAHIDUZZAMAN, Md; TAMANG, Asman; RAFIJ, Junayed Hossain ir kt. Tungsten-Doped ZnO as an Electron Transport Layer for Perovskite Solar Cells: Enhancing Efficiency and Stability. *ACS Applied Materials & Interfaces*, 16, 2024, 28, 36255–36271. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publication, <https://doi.org/10.1021/acsami.4c03591>. [žiūrėta 2024-11-07].
130. ZAINAL ABIDIN, Nurul Aliyah; ARITH, Faiz; NOORASID, N. S.; SARKAWI, Hafez; MUSTAFA, A. N. ir kt. Dopant engineering for ZnO electron transport layer towards efficient perovskite solar cells. *RSC Advances*, 13, 2023, 48, 33797–33819. Interaktyvus. ISSN 2046-2069. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D3RA04823C>. [žiūrėta 2024-11-07].
131. MEHRABIAN, Masood; AFSHAR, Elham Norouzi ir AKHAVAN, Omid. TiO₂ and C60 transport nanolayers in optimized Pb-free CH₃NH₃SnI₃-based perovskite solar cells. *Materials Science and Engineering: B*, 287, 2023, 116146. Interaktyvus. ISSN 0921-5107. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.mseb.2022.116146>. [žiūrėta 2024-11-07].
132. TAKAHASHI, Saemi; UCHIDA, Satoshi; JAYAWEERA, Piyankarage V. V.; KANEKO, Shoji ir SEGAWA, Hiroshi. Impact of compact TiO₂ interface modification on the crystallinity of perovskite solar cells. *Scientific Reports*, 13, 2023, 1, 16068. Interaktyvus. ISSN 2045-2322. Prieiga per: Nature, <https://doi.org/10.1038/s41598-023-43395-1>. [žiūrėta 2024-11-07].
133. GONG, Jue; CUI, Yupeng; LI, Faming ir LIU, Mingzhen. Progress in Surface Modification of SnO₂ Electron Transport Layers for Stable Perovskite Solar Cells. *Small*

Science, 3, 2023, 6, 2200108. Interaktyvus. ISSN 2688-4046. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/smsc.202200108>. [žiūrėta 2024-11-07].

134. DU, Bin; HE, Kun; TIAN, Gangqi; CHE, Xiang ir SONG, Lin. Robust electron transport layers of SnO₂ for efficient perovskite solar cells: recent advances and perspectives. *Journal of Materials Chemistry C*, 11, 2023, 40, 13625–13646. Interaktyvus. ISSN 2050-7526. Prieiga per: ACS Publications, <https://doi.org/10.1039/D3TC02445H>. [žiūrėta 2024-11-07].

135. SUN, Chao; YANG, Panpan; NAN, Ziang; TIAN, Chengbo; CAI, Yuanting ir kt. Well-Defined Fullerene Bisadducts Enable High-Performance Tin-Based Perovskite Solar Cells. *Advanced Materials*, 35, 2023, 9, 2205603. Interaktyvus. ISSN 0935-9648. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adma.202205603>. [žiūrėta 2024-11-07].

136. SHUI, Qing-Jun; SHAN, Shiqi; ZHAI, Yong-Chang; AOYAGI, Shinobu; IZAWA, Seiichiro ir kt. Evaporable Fullerene Indanones with Controlled Amorphous Morphology as Electron Transport Layers for Inverted Perovskite Solar Cells. *Journal of the American Chemical Society*, 145, 2023, 50, 27307–27315. Interaktyvus. ISSN 0002-7863. Prieiga per: ACS Publications, <https://doi.org/10.1021/jacs.3c07192>. [žiūrėta 2024-11-07].

137. FÜRER, Sebastian O.; RIETWYK, Kevin J.; PULVIRENTI, Federico; MCMEEKIN, David P.; SURMIAK, Maciej Adam ir kt. Naphthalene-imide Self-assembled Monolayers as a Surface Modification of ITO for Improved Thermal Stability of Perovskite Solar Cells. *ACS Applied Energy Materials*, 6, 2023, 2, 667–677. Interaktyvus. ISSN 2574-0962. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsaem.2c02735>. [žiūrėta 2024-11-07].

138. SHI, Yangwei; MCCARTHY, Declan P.; LUNGWITZ, Dominique; JIANG, Fangyuan; TADDEI, Margherita ir kt. Photo-Crosslinkable Naphthalene Diimide Polymer for Solution-Processed n–i–p Perovskite Solar Cells. *Chemistry of Materials*, 36, 2024, 2, 795–802. Interaktyvus. ISSN 0897-4756. Prieiga per: ACS Publications, <https://doi.org/10.1021/acs.chemmater.3c02295>. [žiūrėta 2024-11-07].

139. GU, Ningxia; SONG, Lixin; ZHANG, Pengyun; FENG, Ye; DU, Pingfan ir kt. ETL-Free Perovskite Solar Cells with an Efficiency of 19.81% in Open Air. *ACS Sustainable Chemistry & Engineering*, 11, 2023, 37, 13646–13655. Interaktyvus. ISSN 2168-0485. Prieiga per: <https://doi.org/10.1021/acssuschemeng.3c03514>. [žiūrėta 2024-11-07].

140. JAN, Shayan Tariq ir NOMAN, Muhammad. Exploring the potential of MAgel₃ perovskite cells with novel charge transport material optimization. *Optik*, 301, 2024, 171684. Interaktyvus. ISSN 0030-4026. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.ijleo.2024.171684>. [žiūrėta 2024-11-07].

141. TANG, Ziqi; YAO, Disheng; LI, Ying; LI, Chao; XIA, Tian ir kt. Efficient and Stable CuSCN-based Perovskite Solar Cells Achieved by Interfacial Engineering with Amidinothiourea. *ACS Applied Materials & Interfaces*, 16, 2024, 18, 23973–23984. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsaami.3c18974>. [žiūrėta 2024-11-07].

142. REYES-MOLINA, Rosa; CARRILLO-SENDEJAS, Julio C.; MANSUROVA, Svetlana ir COSME, Ismael. Effect of PEDOT:PSS optical properties at the frontal interface on electrical performance in MAPbI₃ perovskite solar cells. *Optical Materials*, 150, 2024, 115299. Interaktyvus. ISSN 0925-3467. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.optmat.2024.115299>. [žiūrėta 2024-11-07].

143. KIM, Kyoungtae; KIM, Minhee; LEE, Hyeonseok; CHUNG, Dae-won ir KIM, Jinhyun. Multi-Functional PEDOT:PSS as the Efficient Perovskite Solar Cells. *Small*, 20, 2024, 38, 2402341. Interaktyvus. ISSN 1613-6810. Prieiga per: ACS Publications, <https://doi.org/10.1002/sml.202402341>. [žiūrėta 2024-11-07].

144. MURUGAN, Santhosh; LIU, Xuewen ir LEE, Eun-Cheol. Improved current density of inverted perovskite solar cells via hole transport layer doping. *Journal of Materials Chemistry C*, 12, 2024, 20, 7278–7285. Interaktyvus. ISSN 2050-7526. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D4TC00053F>. [žiūrėta 2024-11-07].
145. TSAREV, Sergey; YAKUSHCHENKO, Igor K.; LUCHKIN, Sergey Yu; KUZNETSOV, Petr M.; TIMERBULATOV, Ruslan S. ir kt. A new polytriarylamine derivative for dopant-free high-efficiency perovskite solar cells. *Sustainable Energy Fuels*, 3, 2019, 10, 2627–2632. Interaktyvus. ISSN 2398-4902. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C9SE00448C>. [žiūrėta 2024-11-07].
146. WANG, Yihao; DUAN, Leiping; ZHANG, Meng; HAMEIRI, Ziv; LIU, Xu ir kt. PTAA as Efficient Hole Transport Materials in Perovskite Solar Cells: A Review. *Solar RRL*, 6, 2022, 8, 2200234. Interaktyvus. ISSN 2367-198X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/solr.202200234>. [žiūrėta 2024-11-07].
147. KUMAR, Vinay; KUMAR, Deepak; CHAVAN, Rohit D.; KUMAR, Kodali Phani; YADAGIRI, Bommaramoni ir kt. Molecular modification of spiro[fluorene-9,9'-xanthene]-based dopant-free hole transporting materials for perovskite solar cells. *Journal of Materials Chemistry A*, 12, 2024, 14, 8370–8380. Interaktyvus. ISSN 2050-7488. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D3TA07851E>. [žiūrėta 2024-11-07].
148. HATAMVAND, Mohammad; VIVO, Paola; LIU, Maning; TAYYAB, Muhammad; DASTAN, Davoud ir kt. The role of different dopants of Spiro-OMeTAD hole transport material on the stability of perovskite solar cells: A mini review. *Vacuum*, 214, 2023, 112076. Interaktyvus. ISSN 0042-207X. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.vacuum.2023.112076>. [žiūrėta 2024-11-07].
149. GU, Xiaoyu; LI, Yang; MU, Yanfei; ZHANG, Min; LU, Tongbu ir kt. FeCl₃ as a low-cost and efficient p-type dopant of Spiro-OMeTAD for high performance perovskite solar cells. *RSC Advances*, 8, 2018, 17, 9409–9413. Interaktyvus. ISSN 2046-2069. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C8RA00243F>. [žiūrėta 2024-11-07].
150. SURESH KUMAR, N. ir CHANDRA BABU NAIDU, K. A review on perovskite solar cells (PSCs), materials and applications. *Journal of Materiomics*, 7, 2021, 5, 940–956. Interaktyvus. ISSN 2352-8478. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.jmat.2021.04.002>. [žiūrėta 2024-11-07].
151. GUAN, Lin; ZHENG, Zhipeng ir GUO, Yiping. Enhanced hole transport in benzoic acid doped spiro-OMeTAD composite layer with intergrowing benzoate phase for perovskite solar cells. *Journal of Alloys and Compounds*, 832, 2020, 154991. Interaktyvus, ISSN 0925-8388. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.jallcom.2020.154991>. [žiūrėta 2024-11-07].
152. WU, Tai; ZHUANG, Rongshan; ZHAO, Rongjun; ZHAO, Rongmei; ZHU, Lizhong ir kt. Understanding the Effects of Fluorine Substitution in Lithium Salt on Photovoltaic Properties and Stability of Perovskite Solar Cells. *ACS Energy Letters*, 6, 2021, 6, 2218–2228. Interaktyvus. ISSN 2380-8195. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsenenergylett.1c00685>. [žiūrėta 2024-11-07].
153. WAN, Zhongquan; JIANG, Shaoliang; LU, Hui; ZHU, Jinqing; WANG, Yuanxi ir kt. Replacing Li⁺ in Li-TFSI with a benzene ring: constructing non-ionic p-dopants for stable and efficient perovskite solar cells. *Journal of Materials Chemistry C*, 12, 2024, 22, 8078–8086. Interaktyvus. ISSN 2050-7526. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D4TC00595C>. [žiūrėta 2024-11-07].

154. LEE, Jaehwi; SHIN, Yun Seop; OLEIKI, Elham; SEO, Jongdeuk; ROE, Jina ir kt. Constructing orderly crystal orientation with a bidirectional coordinator for high efficiency and stable perovskite solar cells. *Energy & Environmental Science*, 17, 2024, 16, 6003–6012. Interaktyvus. ISSN 1754-5692. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D4EE02017K>. [žiūrėta 2024-11-07].
155. WANG, Renjie; LI, Yiming; ZHU, Jingwei; ZHENG, Qiao; DENG, Hui ir kt. A comparative study of alkylammonium halide interface modification for high efficiency and ion migration stability perovskite solar cells. *Materials Today Physics*, 45, 2024, 101472. Interaktyvus. ISSN 2542-5293. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.mtphys.2024.101472>. [žiūrėta 2024-11-07].
156. LIANG, Zheng; ZHANG, Yong; XU, Huifen; CHEN, Wenjing; LIU, Boyuan ir kt. Homogenizing out-of-plane cation composition in perovskite solar cells. *Nature*, 624, 2023, 7992, 557–563. Interaktyvus. ISSN 1476-4687. Prieiga per: Nature, <https://doi.org/10.1038/s41586-023-06784-0>. [žiūrėta 2024-11-07].
157. AZMI, Randi; ZHUMAGALI, Shynggys; BRISTOW, Helen; ZHANG, Shanshan; YAZMACIYAN, Aren ir kt. Moisture-Resilient Perovskite Solar Cells for Enhanced Stability. *Advanced Materials*, 36, 2024, 12, 2211317. Interaktyvus. ISSN 0935-9648. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adma.202211317>. [žiūrėta 2024-11-07].
158. CHENG, Fangwen; ZHAN, Shaoqi; CAI, Yuanting; CAO, Fang; DAI, Xinfeng ir kt. Interfacial Property Tuning Enables Copper Electrodes in High-Performance n–i–p Perovskite Solar Cells. *Journal of the American Chemical Society*, 145, 2023, 36, 20081–20087. Interaktyvus. ISSN 0002-7863. Prieiga per: ACS Publications, <https://doi.org/10.1021/jacs.3c07222>. [žiūrėta 2024-11-07].
159. NJEMA, George G.; KIBET, Joshua K.; NGARI, Silas M. ir RONO, Nicholas. Numerical optimization of interface engineering parameters for a highly efficient HTL-free perovskite solar cell. *Materials Today Communications*, 39, 2024, 108957. ISSN 2352-4928. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.mtcomm.2024.108957>. [žiūrėta 2024-11-07].
160. KUMAR, Arun; RANI, Sonia ir SUNDAR GHOSH, Dhriti. Kitchen-grade aluminium foil as dual-purpose substrate-cum-electrode for ultrathin, ultralight, and bendable perovskite solar cells. *Solar Energy Materials and Solar Cells*, 268, 2024, 112737. Interaktyvus. ISSN 0927-0248. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.solmat.2024.112737>. [žiūrėta 2024-11-07].
161. CHEN, Rui; ZHANG, Wenjun; GUAN, Xinyu; RAZA, Hasan; ZHANG, Shasha ir kt. Rear Electrode Materials for Perovskite Solar Cells. *Advanced Functional Materials*, 32, 2022, 26, 2200651. Interaktyvus. ISSN 1616-301X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adfm.202200651>. [žiūrėta 2024-11-07].
162. QUE, Meidan; ZHANG, Boyue; CHEN, Jin; YIN, Xingtian ir YUN, Sining. Carbon-based electrodes for perovskite solar cells. *Materials Advances*, 2, 2021, 17, 5560–5579. Interaktyvus. ISSN 2633-5409. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D1MA00352F>. [žiūrėta 2024-11-07].
163. YADAV, Surendra K. Hydrophobic compressed carbon/graphite based long-term stable perovskite solar cells. *Materials Chemistry and Physics*, 268, 2021, 124709. Interaktyvus. ISSN 0254-0584. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.matchemphys.2021.124709>. [žiūrėta 2024-11-07].
164. MATHIAZHAGAN, Gayathri; WAGNER, Lukas; BOGATI, Shankar; ÜNAL, Kübra Yasaroglu; BOGACHUK, Dmitry ir kt. Double-Mesosopic Hole-Transport-Material-Free Perovskite Solar Cells: Overcoming Charge-Transport Limitation by Sputtered Ultrathin

- Al₂O₃ Isolating Layer. *ACS Applied Nano Materials*, 3, 2020, 3, 2463–2471. Interaktyvus. ISSN 2574-0970. Prieiga per: <https://doi.org/10.1021/acsanm.9b02563>. [žiūrėta 2024-11-07].
165. ABDELLATIF, Sameh O.; GHANNAM, Rami ir KHALIFA, Ziad. Optoelectronic and Morphological Surface Resistance Evaluation of Laser-Induced Graphene Counter Electrodes for Potential Applications in Cesium Lead Halide Perovskite Solar Cells. *ACS Applied Electronic Materials*, 6, 2024, 8, 5745–5758. Interaktyvus. ISSN 2637-6113. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsaem.4c00786>. [žiūrėta 2024-11-07].
166. CHOI, Jin-Myung; HAN, Jiye; YOON, Jonghyuk; KIM, Soyeon; JEON, Il ir kt. Overview and Outlook on Graphene and Carbon Nanotubes in Perovskite Photovoltaics from Single-Junction to Tandem Applications. *Advanced Functional Materials*, 32, 2022, 42, 2204594. Interaktyvus. ISSN 1616-301X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adfm.202204594>. [žiūrėta 2024-11-07].
167. LUO, Qiang; WU, Ronggen; MA, Lantian; WANG, Chaojun; LIU, Hu ir kt. Recent Advances in Carbon Nanotube Utilizations in Perovskite Solar Cells. *Advanced Functional Materials*, 31, 2021, 6, 2004765. Interaktyvus. ISSN 1616-301X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adfm.202004765>. [žiūrėta 2024-11-07].
168. HASNAIN, Syed M.; QASIM, Irfan; IQBAL, Abid; AMIN. MIR, M. ir ABU-LIBDEH, N. Novel dual absorber configuration for eco-friendly perovskite solar cells: design, numerical investigations and performance of ITO-C60-MASnI₃-RbGeI₃-Cu₂O-Au. *Solar Energy*, 278, 2024, 112788. Interaktyvus. ISSN 0038-092X. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.solener.2024.112788>. [žiūrėta 2024-11-07].
169. ZHAN, Changling; LUO, Chao; GAO, Feng; WANG, Xianjin; LI, Yang ir kt. Indium Tin Oxide Induced Internal Positive Feedback and Indium Ion Transport in Perovskite Solar Cells. *Angewandte Chemie International Edition*, 63, 2024, 30, e202403824. Interaktyvus. ISSN 1433-7851. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/anie.202403824>. [žiūrėta 2024-11-07].
170. JU, Sucheol; CHOI, Seung Ju; SUNG, Hansang; KIM, Minjin; SONG, Ji Won ir kt. High-performance and selective semi-transparent perovskite solar cells using 3D-structured FTO. *Renewable Energy*, 222, 2024, 119817. Interaktyvus. ISSN 0960-1481. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.renene.2023.119817>. [žiūrėta 2024-11-07].
171. DENG, Jidong; HUANG, Xiaofeng; CHE, Yuliang; WANG, Xiao; ZHANG, Xiaoli ir kt. Salt-Based Catalyzer to Aid Heterogeneous Nucleation Enabling >23% Efficient Electron-Transport-Layer-Free Perovskite Solar Cells. *Advanced Functional Materials*, 2024, 2408392. Interaktyvus. ISSN 1616-301X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adfm.202408392>. [žiūrėta 2024-11-07].
172. LI, Nan; MENG, Fanping; HUANG, Feng; YU, Gang; WANG, Zenggui ir kt. Room-Temperature Sputtered Aluminum-Doped Zinc Oxide for Semitransparent Perovskite Solar Cells. *ACS Applied Energy Materials*, 3, 2020, 10, 9610–9617. Interaktyvus. ISSN 2574-0962. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsaem.0c01081>. [žiūrėta 2024-11-07].
173. YING, Zhiqin; YANG, Xi; ZHENG, Jingming; ZHU, Yudong; XIU, Jingwei ir kt. Charge-transfer induced multifunctional BCP:Ag complexes for semi-transparent perovskite solar cells with a record fill factor of 80.1%. *Journal of Materials Chemistry A*, 9, 2021, 20, 12009–12018. Interaktyvus. ISSN 2050-7488. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D1TA01180D>. [žiūrėta 2024-11-07].
174. XU, Yumeng; LIN, Zhenhua; WEI, Wei; HAO, Yue; LIU, Shengzhong ir kt. Recent Progress of Electrode Materials for Flexible Perovskite Solar Cells. *Nano-Micro Letters*, 14,

- 2022, 1, 117. Interaktyvus. ISSN 2150-5551. Prieiga per: Springer Nature Link, <https://doi.org/10.1007/s40820-022-00859-9>. [žiūrėta 2024-11-07].
175. VERSAVEL, Matthieu Y. ir HABER, Joel A. Structural and optical properties of amorphous and crystalline antimony sulfide thin-films. *Thin Solid Films*, 515, 2007, 18, 7171–7176. Interaktyvus. ISSN 0040-6090. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.tsf.2007.03.043>. [žiūrėta 2024-11-07].
176. FARHANA, Mohaiyadeen Aliyar; MANJCEEVAN, Arumukham ir BANDARA, Jayasundera. Recent advances and new research trends in Sb₂S₃ thin film based solar cells. *Journal of Science: Advanced Materials and Devices*, 8, 2023, 1, 100533. Interaktyvus. ISSN 2468-2179. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.jsamd.2023.100533>. [žiūrėta 2024-11-07].
177. KONDRITAS, Rokas; CHEN, Chao ir TANG, Jiang. Sb₂S₃ Solar Cells. *Joule*, 2, 2018, 5, 857–878. Interaktyvus. ISSN 2542-4351. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.joule.2018.04.003>. [žiūrėta 2024-11-07].
178. WANG, Qian; CHEN, Zhu; WANG, Jianyue; XU, Yinyan; WEI, Yaping ir kt. Sb₂S₃ solar cells: functional layer preparation and device performance. *Inorganic Chemistry Frontiers*, 6, 2019, 12, 3381–3397. Interaktyvus. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C9QI00800D>. [žiūrėta 2024-11-07].
179. LIAN, Wei Tao; CHENHUI, Jiang; YIN, Yiwei; TANG, Rongfeng; LI, Gang ir kt. Revealing composition and structure dependent deep-level defect in antimony trisulfide photovoltaics. *Nature Communications*, 12, 2021, 3260. Interaktyvus. ISSN 2041-1723. Interaktyvus. Prieiga per: Nature communications, <https://doi.org/10.1038/s41467-021-23592-0>. [žiūrėta 2024-11-08].
180. MYAGMARSEEREJID, Purevlkham; INGRAM, Malaika; BATMUNKH, Munkhbayar ir ZHONG, Yu Lin. Doping Strategies in Sb₂S₃ Thin Films for Solar Cells. *Small*, 17, 2021, 39, 2100241. Interaktyvus. ISSN 1613-6810. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/smll.202100241>. [žiūrėta 2024-11-08].
181. GUO, Huafei; ZHAO, Cong; XING, Yelei; TIAN, Huijun; YAN, Dacheng ir kt. High-Efficiency Sb₂Se₃ Solar Cells Modified by Potassium Hydroxide. *The Journal of Physical Chemistry Letters*, 2, 2021, 51, 12352–12359. Interaktyvus. ISSN 1948-7185. Prieiga per: ACS Publications, <https://doi.org/10.1021/acs.jpclett.1c03802>. [žiūrėta 2024-11-08].
182. SHAH, Usman Ali; CHEN, Shiwu; KHALAF, Gomaa Mohamed Gomaa; JIN, Zhixin ir SONG, Haisheng. Wide Bandgap Sb₂S₃ Solar Cells. *Advanced Functional Materials*, 31, 2021, 27, 2100265. Interaktyvus. ISSN 1616-301X. Prieiga per: Wiley Online Library, <https://doi-org.ezproxy.ktu.edu/10.1002/adfm.202100265>. [žiūrėta 2024-11-08].
183. CHEN, Xu; LI, Zhiqiang; ZHU, Hongbing; WANG, Ying; LIANG, Baolai ir kt. CdS/Sb₂S₃ heterojunction thin film solar cells with a thermally evaporated absorber. *Journal of Materials Chemistry C*, 5, 2017, 36, 9421–9428. Interaktyvus. ISSN 2050-7526. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C7TC02460F>. [žiūrėta 2024-11-08].
184. GAO, Chunhui; HUANG, Jialiang; LI, Huangxu; SUN, Kaiwen; LAI, Yanqing ir kt. Fabrication of Sb₂S₃ thin films by sputtering and post-annealing for solar cells. *Ceramics International*, 45, 2019, 3, 3044–3051. Interaktyvus. ISSN 0272-8842. Prieiga per: Science Direct, <https://doi.org/10.1016/j.ceramint.2018.10.155>. [žiūrėta 2024-11-08].
185. LIU, Lu; ZHANG, Shengli; WU, Jian-Yu; WANG, Wei-Huang; LIU, Wei ir kt. Current improvement of substrate structured Sb₂S₃ solar cells with MoSb₂ interlayer. *Chinese Physics B*, 29, 2020, 5, 058801. Interaktyvus. ISSN 2058-3834. Prieiga per: IOPScience, <https://doi.org/10.1088/1674-1056/ab8220>. [žiūrėta 2024-11-08].

186. ALIYAR FARHANA, Mohaiyadeen ir BANDARA, Jayasundera. Enhancement of the photoconversion efficiency of Sb₂S₃ based solar cell by overall optimization of electron transport, light harvesting and hole transport layers. *Solar Energy*, 247, 2022, 32–40. Interaktyvus. ISSN 0038-092X. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.solener.2022.10.025>. [žiūrėta 2024-11-08].
187. LIU, Rong; ZHU, Liangxin; GE, Chengfeng; CAO, Wenbo; KUANG, Jiajin ir kt. Improved Sb₂S₃/TiO₂ Nanorray Heterojunction Solar Cells by an Insulating Hole-Selective Tunneling Layer. *ACS Applied Energy Materials*, 6, 2023, 3, 1926–1932. Interaktyvus. ISSN 2574-0962. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsaem.2c03863>. [žiūrėta 2024-11-08].
188. ZHU, Liangxin; LIU, Rong; WAN, Zhiyang; CAO, Wenbo; DONG, Chao ir kt. Parallel Planar Heterojunction Strategy Enables Sb₂S₃ Solar Cells with Efficiency Exceeding 8 %. *Angewandte Chemie International Edition*, 62, 2023, 50, e202312951. Interaktyvus. ISSN 1433-7851. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/anie.202312951>. [žiūrėta 2024-11-08].
189. CHEN, Junwei; LI, Gaoyang; XU, Zhiheng; XU, Chenchen; NAVEED, Faisal ir kt. Recent Advances and Prospects of Solution-Processed Efficient Sb₂S₃ Solar Cells. *Advanced Functional Materials*, 34, 2024, 18, 2313676. Interaktyvus. ISSN 1616-301X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adfm.202313676>. [žiūrėta 2024-11-08].
190. LIU, C. P.; WANG, H. E.; NG, T. W.; CHEN, Z. H.; ZHANG, W. F. ir kt. Hybrid photovoltaic cells based on ZnO/Sb₂S₃/P3HT heterojunctions. *physica status solidi (b)*, 249, 2012, 3, 627–633. Interaktyvus. ISSN 0370-1972. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/pssb.201147393>. [žiūrėta 2024-11-08].
191. XU, Yafeng; CHEN, Wenyong; HU, Linhua; PAN, Xu; YANG, Shangfeng ir kt. Template deposition of Sb₂S₃ for solid-state sensitized solar cells. *Journal of Alloys and Compounds*, 784, 2019, 947–953. Interaktyvus. ISSN 0925-8388. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.jallcom.2019.01.131>. [žiūrėta 2024-11-08].
192. MA, Guochen; WANG, Chongchong; ZHENG, Qiao; JIN, Mengjia; CHENG, Shuying ir kt. Ti doped Sb₂S₃ thin film for improved performance of inorganic-organic hybrid solar cells. *Materials Letters*, 260, 2020, 126879. Interaktyvus. ISSN 0167-577X. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.matlet.2019.126879>. [žiūrėta 2024-11-08].
193. NING, Huan; GUO, Huafei; ZHANG, Jiayi; WANG, Xin; JIA, Xuguang ir kt. Enhancing the efficiency of Sb₂S₃ solar cells using dual-functional potassium doping. *Solar Energy Materials and Solar Cells*, 221, 2021, 110816. Interaktyvus. ISSN 0927-0248. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.solmat.2020.110816>. [žiūrėta 2024-11-08].
194. HAN, Jian; PU, Xingyu; ZHOU, Hui; CAO, Qi; WANG, Shuangjie ir kt. Synergistic Effect through the Introduction of Inorganic Zinc Halides at the Interface of TiO₂ and Sb₂S₃ for High-Performance Sb₂S₃ Planar Thin-Film Solar Cells. *ACS Applied Materials & Interfaces*, 12, 2020, 39, 44297–44306. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsaami.0c11550>. [žiūrėta 2024-11-08].
195. RIGHINI, Giancarlo C. ir ENRICHI, Francesco. Chapter One - Solar cells' evolution and perspectives: a short review. In: *Solar Cells and Light Management*, 1–32. Interaktyvus. Elsevier, 2020. ISBN 9780081027622. Prieiga per: <https://doi.org/10.1016/B978-0-08-102762-2.00001-X>. [žiūrėta 2024-11-08].
196. JEAN, Joel; BROWN, Patrick; JAFFE, Robert; BUONASSISI, Tonio ir BULOVIĆ, Vladimir. Pathways for Solar Photovoltaics. *Energy Environ.Sci.*, 8, 2015, 1200–1219.

Interaktyvus. ISSN 1754-5692. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C4EE04073B>. [žiūrėta 2024-11-08].

197. LEE, Lee; TEUSCHER, Teuscher; MIYASAKA, Miyasaka; MURAKAMI, Murakami ir SNAITH, Snaith. Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites. *Science*, 338, 2012, 6107, 643–647. Interaktyvus. ISSN 0036-8075. Prieiga per: Science, <https://doi.org/10.1126/science.1228604>. [žiūrėta 2024-11-08].

198. JEON, Nam Joong; NA, Hyejin; JUNG, Eui Hyuk; YANG, Tae-Youl; LEE, Yong Guk ir kt. A fluorene-terminated hole-transporting material for highly efficient and stable perovskite solar cells. *Nature Energy*, 3, 2018, 8, 682–689. Interaktyvus. ISSN 2058-7546. Prieiga per: Nature, <https://doi.org/10.1038/s41560-018-0200-6>. [žiūrėta 2024-11-08].

199. WANG, Wang; WANG, Wang; ZHANG, Zhang; WEI, Wei; CAI, Cai ir kt. De Novo Design of Spiro-Type Hole-Transporting Material: Anisotropic Regulation Toward Efficient and Stable Perovskite Solar Cells. *Research*, 7, 2024, 0332. Prieiga per: Science Partner Journal, <https://doi.org/10.34133/research.0332>. [žiūrėta 2024-11-08].

200. DENG, Zihao; HE, Maosheng; ZHANG, Yi; ULLAH, Fateh; DING, Kui ir kt. Design of Low Crystallinity Spiro-Typed Hole Transporting Material for Planar Perovskite Solar Cells to Achieve 21.76% Efficiency. *Chemistry of Materials*, 33, 2021, 1, 285–297. Interaktyvus. ISSN 0897-4756. Prieiga per: ACS Publications, <https://doi.org/10.1021/acs.chemmater.0c03772>. [žiūrėta 2024-11-08].

201. HAN, Mingyuan; LIANG, Yongpeng; CHEN, Jianlin; ZHANG, Xianfu; GHADARI, Rahim ir kt. A N-Ethylcarbazole-Terminated Spiro-Type Hole-Transporting Material for Efficient and Stable Perovskite Solar Cells. *ChemSusChem*, 15, 2022, 20, e202201485. Interaktyvus. ISSN 1864-5631. Prieiga per: European Chemical Societies Publishing, <https://doi.org/10.1002/cssc.202201485>. [žiūrėta 2024-11-08].

202. LIANG, Yongpeng; CHEN, Jianlin; ZHANG, Xianfu; HAN, Mingyuan; GHADARI, Rahim ir kt. Dibenzo heterocyclic-terminated spiro-type hole transporting materials for perovskite solar cells. *Journal of Materials Chemistry C*, 10, 2022, 30, 10988–10994. Interaktyvus. ISSN 2050-7526. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D2TC02564G>. [žiūrėta 2024-11-08].

203. JEONG, Mingyu; CHOI, In Woo; YIM, Kanghoon; JEONG, Seonghun; KIM, Minjin ir kt. Large-area perovskite solar cells employing spiro-Naph hole transport material. *Nature Photonics*, 16, 2022, 2, 119–125. Interaktyvus. ISSN 1749-4893. Prieiga per: Nature, <https://doi.org/10.1038/s41566-021-00931-7>. [žiūrėta 2024-11-08].

204. ONOZAWA-KOMATSUZAKI, Nobuko; TSUCHIYA, Daisuke; INOUE, Shinichi; KOGO, Atsushi; FUNAKI, Takashi ir kt. Highly Efficient Dopant-Free Cyano-Substituted Spiro-Type Hole-Transporting Materials for Perovskite Solar Cells. *ACS Applied Energy Materials*, 5, 2022, 6, 6633–6641. Interaktyvus. ISSN 2574-0962. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsaem.2c00078>. [žiūrėta 2024-11-08].

205. LIU, You; LIU, Fang; WANG, Jungan; HUANG, Hongyan; YAN, Suhao ir kt. Tetrakis (N-phenothiazine) spirobifluorene-based hole-transporting material towards high photovoltage perovskite photovoltaics for driving electrochromic devices. *Dyes and Pigments*, 188, 2021, 109164. Interaktyvus. ISSN 0143-7208. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.dyepig.2021.109164>. [žiūrėta 2024-11-08].

206. WANG, Ya-Kun; YUAN, Zhong-Cheng; SHI, Guo-Zheng; LI, Yong-Xi; LI, Qian ir kt. Dopant-Free Spiro-Triphenylamine/Fluorene as Hole-Transporting Material for Perovskite Solar Cells with Enhanced Efficiency and Stability. *Advanced Functional Materials*, 26, 2016,

- 9, 1375–1381. Interaktyvus. ISSN 1616-301X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adfm.201504245>. [žiūrėta 2024-11-08].
207. LI, Ming-Hsien; HSU, Che-Wei; SHEN, Po-Shen; CHENG, Hsin-Min; CHI, Yun ir kt. Novel spiro-based hole transporting materials for efficient perovskite solar cells. *Chemical Communications*, 51, 2015, 85, 15518–15521. Interaktyvus. ISSN 1359-7345. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C5CC04405G>. [žiūrėta 2024-11-08].
208. ZHU, Xiang-Dong; MA, Xing-Juan; WANG, Ya-Kun; LI, Yun; GAO, Chun-Hong ir kt. Hole-Transporting Materials Incorporating Carbazole into Spiro-Core for Highly Efficient Perovskite Solar Cells. *Advanced Functional Materials*, 29, 2018. Interaktyvus. ISSN 1616-301X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adfm.201807094>. [žiūrėta 2024-11-08].
209. CHEN, Yan; WANG, Yanqing; WU, Di; WU, Wenfei; WU, Yu ir kt. Fluorene-terminated hole transporting materials with a spiro[fluorene-9,9'-xanthene] core for perovskite solar cells. *New Journal of Chemistry*, 45, 2021, 12, 5497–5502. Interaktyvus. ISSN 1144-0546. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D0NJ06262F>. [žiūrėta 2024-11-08].
210. LEE, Do Yoon; SIVAKUMAR, Gangala; Manju; MISRA, Rajneesh ir SEOK, Sang Il. Carbazole-Based Spiro[fluorene-9,9'-xanthene] as an Efficient Hole-Transporting Material for Perovskite Solar Cells. *ACS Applied Materials & Interfaces*, 12, 2020, 25, 28246–28252. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsami.0c06318>. [žiūrėta 2024-11-08].
211. NAKAR, Rana; RAMOS, F. J.; DALINOT, Clément; MARQUES, Pablo Simon; CABANETOS, Clément ir kt. Cyclopentadithiophene and Fluorene Spiro-Core-Based Hole-Transporting Materials for Perovskite Solar Cells. *The Journal of Physical Chemistry C*, 123, 2019, 37, 22767–22774. Interaktyvus. ISSN 1932-7447. Prieiga per: ACS Publications, <https://doi.org/10.1021/acs.jpcc.9b05931>. [žiūrėta 2024-11-08].
212. RAKSTYS, Kasparas; PAEK, Sanghyun; SOHAIL, Muhammad; GAO, Peng; CHO, Kyung Taek ir kt. A highly hindered bithiophene-functionalized dispiro-oxepine derivative as an efficient hole transporting material for perovskite solar cells. *Journal of Materials Chemistry A*, 4, 2016, 47, 18259–18264. Interaktyvus. ISSN 2050-7488. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C6TA09028A>. [žiūrėta 2024-11-08].
213. KULA, Slawomir; PAJĄK, Agnieszka; SZLAPA-KULA, Agata; MIESZCZANIN, Angelika; GNIDA, Paweł ir kt. 9,9'-bifluorenylidene derivatives as novel hole-transporting materials for potential photovoltaic applications. *Dyes and Pigments*, 174, 2020, 108031. Interaktyvus. ISSN 0143-7208. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.dyepig.2019.108031>. [žiūrėta 2024-11-08].
214. ZHANG, Xianfu; LIU, Xuepeng; GHADARI, Rahim; LI, Maohui; ZHOU, Zi'an ir kt. Tetraphenylethylene-Arylamine Derivatives as Hole Transporting Materials for Perovskite Solar Cells. *ACS Applied Materials & Interfaces*, 13, 2021, 10, 12322–12330. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsami.1c01606>. [žiūrėta 2024-11-08].
215. CHEN, Yung-Chung; YEN, Jui-Hua; CHUNG, Chung-Lin ir CHEN, Chih-Ping. Methoxy groups on bifluorenylidene-based hole transporting materials result in highly efficient and stable dopant-free inverted perovskite solar cells. *Solar Energy*, 179, 2019, 371–379. Interaktyvus. ISSN 0038-092X. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.solener.2019.01.008>. [žiūrėta 2024-11-08].

216. XIAO, Jing; YU, Hui-Juan; WANG, Dian; GAO, Wei-Jie; SHINOHARA, Akira ir kt. An Acetylene-Linked 9,9'-Bicarbazole-Based Hole-Transporting Material for Efficient Perovskite Solar Cells. *Energy Fuels*, 36, 2022, 4, 2086–2094. Interaktyvus. ISSN 0887-0624. Prieiga per: ACS Publications, <https://doi.org/10.1021/acs.energyfuels.1c03692>. [žiūrėta 2024-11-08].
217. MAQSOOD, Nimra; ASIF, Areeba; ANS, Muhammad; HAMEED, Qudsia Sehar; ELMUSHYAKHI, Abraham ir kt. Molecular engineering of bicarbazole-based donor molecules with remarkable photovoltaic parameters for organic solar cells. *Optik*, 281, 2023, 170818. Interaktyvus. ISSN 0030-4026. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.ijleo.2023.170818>. [žiūrėta 2024-11-08].
218. LI, Bin; CAI, Yuan; TIAN, Xia; LIANG, Xiaozhong; LI, Da ir kt. Decorating hole transport material with –CF₃ groups for highly efficient and stable perovskite solar cells. *Journal of Energy Chemistry*, 62, 2021, 523–531. Interaktyvus. ISSN 2095-4956. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.jechem.2021.04.017>. [žiūrėta 2024-11-08].
219. RAKSTYS, Kasparas; SALIBA, Michael; GAO, Peng; GRATIA, Paul; KAMARAUSKAS, Egidijus ir kt. Highly Efficient Perovskite Solar Cells Employing an Easily Attainable Bifluorenylidene-Based Hole-Transporting Material. *Angewandte Chemie International Edition*, 55, 2016, 26, 7464–7468. Interaktyvus. ISSN 1433-7851. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/anie.201602545>. [žiūrėta 2024-11-08].
220. YIN, Chengrong; LU, Jianfeng; XU, Yachao; YUN, Yikai; WANG, Kai ir kt. Low-Cost N,N'-Bicarbazole-Based Dopant-Free Hole-Transporting Materials for Large-Area Perovskite Solar Cells. *Advanced Energy Materials*, 8, 2018, 21, 1800538. Interaktyvus. ISSN 1614-6832. Prieiga per: Wiley Online Library, <https://doi.org.ezproxy.ktu.edu/10.1002/aenm.201800538>. [žiūrėta 2024-11-08].
221. LU, Chunyuan; CHOI, In Taek; KIM, Jeongho ir KIM, Hwan Kyu. Simple synthesis and molecular engineering of low-cost and star-shaped carbazole-based hole transporting materials for highly efficient perovskite solar cells. *Journal of Materials Chemistry A*, 5, 2017, 38, 20263–20276. Interaktyvus. ISSN 2050-7488. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C7TA04762B>. [žiūrėta 2024-11-08].
222. MAGOMEDOV, Artiom; PAEK, Sanghyun; GRATIA, Paul; KASPARAVICIUS, Ernestas; DASKEVICIENE, Maryte ir kt. Diphenylamine-Substituted Carbazole-Based Hole Transporting Materials for Perovskite Solar Cells: Influence of Isomeric Derivatives. *Advanced Functional Materials*, 28, 2018, 9, 1704351. Interaktyvus. ISSN 1616-301X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adfm.201704351>. [žiūrėta 2024-11-08].
223. ZONG, Xueping; QIAO, Wenhua; CHEN, Yu; SUN, Zhe; LIANG, Mao ir kt. A new binaphthol based hole-transporting materials for perovskite solar cells. *Tetrahedron*, 73, 2017, 24, 3398–3405. Interaktyvus. ISSN 0040-4020. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.tet.2017.05.020>. [žiūrėta 2024-11-08].
224. MALINAUSKAS, Tadas; SALIBA, Michael; MATSUI, Taisuke; DASKEVICIENE, Maryte; URNIKAITE, Simona ir kt. Branched methoxydiphenylamine-substituted fluorene derivatives as hole transporting materials for high-performance perovskite solar cells. *Energy & Environmental Science*, 9, 2016, 5, 1681–1686. Interaktyvus. ISSN 1754-5692. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C5EE03911H>. [žiūrėta 2024-11-08].
225. CHEN, Wangchao; ZHANG, Zhi; WANG, Ming; CHEN, Xuan; LI, Haitao ir kt. Conformation Tailoring of Diphenylfluorene-Cored Isomers as Hole-Transport Materials for Perovskite Solar Cells. *Solar RRL*, 8, 2024, 4, 2300954. Interaktyvus. ISSN 2367-198X.

Prieiga per: Wiley Online Library, <https://doi.org/10.1002/solr.202300954>. [žiūrėta 2024-11-08].

226. LI, Rui; LIU, Maning; MATTA, Sri Kasi; ALMASRI, Alaa; TIAN, Jingshu ir kt. Twisted or Planar? Side-Chain Tailoring of Fluorene-Based Hole-Transport Materials for Efficient and Stable Perovskite Solar Cells. *Solar RRL*, 7, 2023, 18, 2300367. Interaktyvus. ISSN 2367-198X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/solr.202300367>. [žiūrėta 2024-11-08].

227. LI, Maohui; MA, Shuang; MATEEN, Muhammad; LIU, Xuepeng; DING, Yong ir kt. Facile donor (D)- π -D triphenylamine-based hole transporting materials with different π -linker for perovskite solar cells. *Solar Energy*, 195, 2020, 618–625. Interaktyvus. ISSN 0038-092X. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.solener.2019.11.071>. [žiūrėta 2024-11-08].

228. ZHANG, Yun; KOU, Chun; ZHANG, Junjie; LIU, Yahui; LI, Wenhua ir kt. Crosslinked and dopant free hole transport materials for efficient and stable planar perovskite solar cells. *Journal of Materials Chemistry A*, 7, 2019, 10, 5522–5529. Interaktyvus. ISSN 2050-7488. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C8TA12060A>. [žiūrėta 2024-11-08].

229. WAN, Li; ZHANG, Wenxiao; FU, Sheng; CHEN, Lijun; WANG, Yueming ir kt. Achieving over 21% efficiency in inverted perovskite solar cells by fluorinating a dopant-free hole transporting material. *Journal of Materials Chemistry A*, 8, 2020, 14, 6517–6523. Interaktyvus. ISSN 2050-7488. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D0TA00522C>. [žiūrėta 2024-11-08].

230. SCHLOEMER, Tracy H.; GEHAN, Timothy S.; CHRISTIANS, Jeffrey A.; MITCHELL, Deborah G.; DIXON, Alex ir kt. Thermally Stable Perovskite Solar Cells by Systematic Molecular Design of the Hole-Transport Layer. *ACS Energy Letters*, 4, 2019, 2, 473–482. Interaktyvus. ISSN 2380-8195. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsenenergylett.8b02431>. [žiūrėta 2024-11-08].

231. QIN, Tian; WU, Fei; ZHU, Linna; CHI, Weijie; ZHANG, Yi ir kt. A hole-transporting material with substituted fluorene as end groups for high-performance perovskite solar cells. *Organic Electronics*, 100, 2022, 106325. Interaktyvus. ISSN 1566-1199. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.orgel.2021.106325>. [žiūrėta 2024-11-08].

232. WANG, Yu-Duan; SHAO, Jiang-Yang; LAN, Zhong-Rui ir ZHONG, Yu-Wu. Fluorene-Modified Zinc Porphyrin as Low-Cost Hole-Transporting Material for Efficient Perovskite Solar Cells. *Organic Materials*, 4, 2022, 2, 28–35. Interaktyvus. ISSN 2625-1825. Prieiga per: Thieme, <https://doi.org/10.1055/a-1873-5360>. [žiūrėta 2024-11-08].

233. LI, Haoyu; WANG, Zhangyan; SUN, Yuanqing; SU, Yangyang; ZHAO, Zhenxiao ir kt. Peripheral substituent regulation of bias structured azulene-based hole transport materials for perovskite solar cells. *New Journal of Chemistry*, 47, 2023, 41, 19057–19062. Interaktyvus. ISSN 1144-0546. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D3NJ04110G>. [žiūrėta 2024-11-08].

234. ZHAI, Mengde; MIAO, Yawei; WANG, Haoxin; WANG, Linqin; DING, Xingdong ir kt. Rational design of phenothiazine-based hole transport material with fluorene-containing asymmetric peripheral donor group for perovskite solar cells. *Dyes and Pigments*, 202, 2022, 110279. Interaktyvus. ISSN 0143-7208. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.dyepig.2022.110279>. [žiūrėta 2024-11-08].

235. HAO, Cen-rong; ZONG, Xueping; CHENG, Yang; ZHAO, Mei; LUO, Ming ir kt. Facile fluorene-based hole-transporting materials and their dual application toward inverted and

regular perovskite solar cells. *Sustainable Energy Fuels*, 5, 2021, 21, 5548–5556. ISSN 2398-4902. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D1SE01122G>. [žiūrėta 2024-11-08].

236. SUN, Zhe; LIU, Zhengxu; ZHANG, Jiajia; ZHOU, Chuanyu; CHEN, Ziyin ir kt. Impact of Alkyl Chain Length on the Properties of Fluorenyl-Based Linear Hole-Transport Materials in p-i-n Perovskites Solar Cells. *ACS Applied Energy Materials*, 5, 2022, 7, 7988–7996. ISSN 2574-0962. Interaktyvus. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsaem.2c00197>. [žiūrėta 2024-11-08].

237. ZHU, Linna; XU, Jing; SHAN, Yahan; ZHONG, Cheng; TANG, Xiaosheng ir kt. Diaryl ketone-based hole-transporting materials for efficient perovskite solar cells. *Journal of Materials Chemistry C*, 7, 2019, 11, 3226–3230. Interaktyvus. ISSN 2050-7526. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C9TC00331B>. [žiūrėta 2024-11-08].

238. IGCI, Cansu; PAEK, Sanghyun; RAKSTYS, Kasparas; KANDA, Hiroyuki; SHIBAYAMA, Naoyuki ir kt. D- π -A-Type Triazatruxene-Based Dopant-Free Hole Transporting Materials for Efficient and Stable Perovskite Solar Cells. *Solar RRL*, 4, 2020, 9, 2000173. Interaktyvus. ISSN 2367-198X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/solr.202000173>. [žiūrėta 2024-11-08].

239. SI, Shenglin; YIN, Tianzhou; GUO, Yixuan; ZHANG, Zimin; WEN, Haoxin ir kt. An Acceptor–Donor–Acceptor Molecule Tailored Versatile Buffer Enabling Efficient and Stable Perovskite Solar Cells. *Advanced Functional Materials*, 34, 2024, 36, 2401951. Interaktyvus. ISSN 1616-301X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adfm.202401951>. [žiūrėta 2024-11-08].

240. LIU, Wenjun; PENG, Yaole; KONG, Fantai; GHADARI, Rahim; ZHAO, Chundie ir kt. Two birds with one stone: dopant-free squaraine hole-transporting material for perovskite solar cell. *Materials Today Energy*, 37, 2023, 101411. Interaktyvus. ISSN 2468-6069. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.mtener.2023.101411>. [žiūrėta 2024-11-08].

241. DASKEVICIUTE-GEGUZIENE, Sarune; ZHANG, Yi; RAKSTYS, Kasparas; XIAO, Chuanxiao; XIA, Jianxing ir kt. Passivating Defects of Perovskite Solar Cells with Functional Donor-Acceptor–Donor Type Hole Transporting Materials. *Advanced Functional Materials*, 33, 2023, 1, 2208317. Interaktyvus. ISSN 1616-301X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adfm.202208317>. [žiūrėta 2024-11-09].

242. SUN, Yuan; ZHAO, Chundie; ZHANG, Jinxue; PENG, Yaole; GHADARI, Rahim ir kt. Multifunctional organic semiconductor for dopant-free perovskite solar cells. *Synthetic Metals*, 285, 2022, 117027. Interaktyvus. ISSN 0379-6779. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.synthmet.2022.117027>. [žiūrėta 2024-11-09].

243. LATYPOVA, Alina F.; EMELIANOV, Nikita A.; BALAKIREV, Dmitry O.; SUKHORUKOVA, Polina K.; KALINICHENKO, Nadezhda K. ir kt. Design Principles for Organic Small Molecule Hole-Transport Materials for Perovskite Solar Cells: Film Morphology Matters. *ACS Applied Energy Materials*, 5, 2022, 5, 5395–5403. Interaktyvus. ISSN 2574-0962. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsaem.1c03119>. [žiūrėta 2024-11-09].

244. JI, Xiaofei; ZHOU, Tong; FU, Qiang; WANG, Wenxuan; WU, Ziang ir kt. Dopant-Free Two-Dimensional Hole Transport Small Molecules Enable Efficient Perovskite Solar Cells. *Advanced Energy Materials*, 13, 2023, 11, 2203756. Interaktyvus. ISSN 1614-6832. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/aenm.202203756>. [žiūrėta 2024-11-09].

245. SUN, Xianglang; XUE, Qifan; ZHU, Zonglong; XIAO, Qi; JIANG, Kui ir kt. Fluoranthene-based dopant-free hole transporting materials for efficient perovskite solar cells.

- Chemical Science*, 9, 2018, 10, 2698–2704. Interaktyvus. ISSN 2041-6520. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C7SC05484J>. [žiūrėta 2024-11-09].
246. TU, Bao; WANG, Yang; CHEN, Wei; LIU, Bin; FENG, Xiyuan ir kt. Side-Chain Engineering of Donor–Acceptor Conjugated Small Molecules As Dopant-Free Hole-Transport Materials for Efficient Normal Planar Perovskite Solar Cells. *ACS Applied Materials & Interfaces*, 11, 2019, 51, 48556–48563. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsami.9b17386>. [žiūrėta 2024-11-09].
247. RAKSTYS, Kasparas; PAEK, Sanghyun; DREVILKAUSKAITE, Aida; KANDA, Hiroyuki; DASKEVICIUTE, Sarune ir kt. Carbazole-Terminated Isomeric Hole-Transporting Materials for Perovskite Solar Cells. *ACS Applied Materials & Interfaces*, 12, 2020, 17, 19710–19717. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsami.9b23495>. [žiūrėta 2024-11-09].
248. LIU, Xuepeng; MA, Shuang; DING, Yong; GAO, Jing; LIU, Xiaolong ir kt. Molecular Engineering of Simple Carbazole-Triphenylamine Hole Transporting Materials by Replacing Benzene with Pyridine Unit for Perovskite Solar Cells. *Solar RRL*, 3, 2019, 5, 1800337. Interaktyvus. ISSN 2367-198X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/solr.201800337>. [žiūrėta 2024-11-09].
249. CHEN, Wangchao; SUN, Jianjun; ZHANG, Zhi; WU, Miaomiao; LI, Zhaoqian ir kt. Thiazole Functionalized Hole Transport Material Featuring Defect Passivation Effects for High-Performance Perovskite Solar Cells. *ACS Materials Letters*, 5, 2023, 6, 1772–1780. Interaktyvus. ISSN 2639-4979. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsmaterialslett.3c00225>. [žiūrėta 2024-11-09].
250. PETRULEVICIUS, Julius; YANG, Yi; LIU, Cheng; STEPONAITIS, Matas; KAMARAUSKAS, Egidijus ir kt. Asymmetric Triphenylethylene-Based Hole Transporting Materials for Highly Efficient Perovskite Solar Cells. *ACS Applied Materials & Interfaces*, 16, 2024, 6, 7310–7316. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsami.3c17811>. [žiūrėta 2024-11-09].
251. LIU, Licheng; MIAO, Yawei; ZHAI, Mengde; WU, Tai; DING, Xingdong ir kt. Symmetric acridine bridging hole transport material for perovskite solar cell. *Dyes and Pigments*, 213, 2023, 111158. Interaktyvus. ISSN 0143-7208. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.dyepig.2023.111158>. [žiūrėta 2024-11-09].
252. XU, Linjun; HUANG, Peng; ZHANG, Jing; JIA, Xuguang; MA, Zhijie ir kt. N,N-Di-para-methylthiophenylamine-Substituted (2-Ethylhexyl)-9H-Carbazole: A Simple, Dopant-Free Hole-Transporting Material for Planar Perovskite Solar Cells. *The Journal of Physical Chemistry C*, 121, 2017, 40, 21821–21826. Interaktyvus. ISSN 1932-7447. Prieiga per: ACS Publications, <https://doi.org/10.1021/acs.jpcc.7b04469>. [žiūrėta 2024-11-09].
253. LIU, Xuepeng; MA, Shuang; MATEEN, Muhammad; SHI, Pengju; LIU, Cheng ir kt. Molecular engineering of simple carbazole-arylamine hole-transport materials for perovskite solar cells. *Sustainable Energy Fuels*, 4, 2020, 4, 1875–1882. Interaktyvus. ISSN 2398-4902. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C9SE01242G>. [žiūrėta 2024-11-09].
254. LI, Wenhui; ZHAO, Wenning; LI, Kairui ir HAN, Xiuxun. A review on conventional perovskite solar cells with organic dopant-free hole-transport materials: roles of chemical structures and interfacial materials in efficient devices. *Journal of Materials Chemistry C*, 12, 2024, 4, 1147–1176. Interaktyvus. ISSN 2050-7526. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D3TC03472K>. [žiūrėta 2024-11-09].

255. ZHOU, Suer; DASKEVICIENE, Maryte; STEPONAITIS, Matas; BUBNIENE, Giedre; JANKAUSKAS, Vygtas ir kt. Low-Cost Dopant-Free Carbazole Enamine Hole-Transporting Materials for Thermally Stable Perovskite Solar Cells. *Solar RRL*, 6, 2022, 1, 2100984. Interaktyvus. ISSN 2367-198X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/solr.202100984>. [žiūrėta 2024-11-09].
256. CHEN, Jui-Heng; LEE, Kun-Mu; TING, Chang-Chieh ir LIU, Ching-Yuan. Step-saving synthesis of star-shaped hole-transporting materials with carbazole or phenothiazine cores via optimized C–H/C–Br coupling reactions. *RSC Advances*, 11, 2021, 15, 8879–8885. Interaktyvus. ISSN 2046-2069. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D0RA10190G>. [žiūrėta 2024-11-10].
257. ILLICACHI, Luis A.; URIETA-MORA, Javier; CALBO, Joaquín; ARAGÓ, Juan; IGCI, Cansu ir kt. Azatruxene-Based, Dumbbell-Shaped, Donor– π -Bridge–Donor Hole-Transporting Materials for Perovskite Solar Cells. *Chemistry – A European Journal*, 26, 2020, 48, 11039–11047. Interaktyvus. ISSN 0947-6539. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/chem.202002115>. [žiūrėta 2024-11-10].
258. XIA, Ziyang; ZHANG, Wei; CHEN, Cheng; MIAO, Yawei; DING, Xingdong ir kt. Low-cost star-shaped hole-transporting materials with isotropic properties and its application in perovskite solar cells. *Dyes and Pigments*, 207, 2022, 110695. Interaktyvus. ISSN 0143-7208. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.dyepig.2022.110695>. [žiūrėta 2024-11-10].
259. LU, Chunyuan; AFTABUZZAMAN, M.; HOON KIM, Chul ir KYU KIM, Hwan. Novel trifluoropropoxy-substituted asymmetric carbazole derivatives as efficient and hydrophobic hole transporting materials for high-performance and stable perovskite solar cells. *Chemical Engineering Journal*, 428, 2022, 131108. Interaktyvus. ISSN 1385-8947. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.cej.2021.131108>. [žiūrėta 2024-11-10].
260. FANG, Lingyi; ZHANG, Yuyan; LI, Tianyu; WEI, Yuefang; YUAN, Yi ir kt. Helical Polycyclic Heteroaromatic as Hole Transport Material for Perovskite Solar Cell: Remarkable Impact of Alkyl Substitution Position. *Advanced Energy Materials*, 13, 2023, 34, 2301455. Interaktyvus. ISSN 1614-6832. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/aenm.202301455>. [žiūrėta 2024-11-10].
261. SAJID, Sajid; ALZAHMI, Salem; SALEM, Imen B.; PARK, Jongee ir OBAIDAT, Ihab M. Lead-Free Perovskite Homo Junction-Based HTM-Free Perovskite Solar Cells: Theoretical and Experimental Viewpoints. *Nanomaterials*, 13, 2023, 6, 983. Interaktyvus. ISSN 2079-4991. Prieiga per: Multidisciplinary Digital Publishing Institute, <https://doi.org/10.3390/nano13060983>. [žiūrėta 2024-11-10].
262. SOVA, Rimbi Rodiyana; Shobih; BUDIAWAN, Widhya; SEPTINA, Wilman; YULIANTINI, Lia ir kt. Enhanced performance of HTM-free perovskite solar cells with free-standing carbon electrode via surface treatment and conductive support. *Synthetic Metals*, 306, 2024, 117646. Interaktyvus. ISSN 0379-6779. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.synthmet.2024.117646>. [žiūrėta 2024-11-10].
263. ALMALKI, Masaud; ALOTAIBI, Mohammad Hayal; ALANAZI, Anwar Q.; EICKEMEYER, Felix T.; ALENZI, Sultan M. ir kt. Interfacial Modulation through Mixed-Dimensional Heterostructures for Efficient and Hole Conductor-Free Perovskite Solar Cells. *Advanced Functional Materials*, 34, 2024, 6, 2309789. Interaktyvus. ISSN 1616-301X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adfm.202309789>. [žiūrėta 2024-11-10].
264. ITZHAİK, Yafit; NIITSOO, Olivia; PAGE, Miles ir HODES, Gary. Sb2S3-Sensitized Nanoporous TiO2 Solar Cells. *The Journal of Physical Chemistry C*, 113, 2009, 11, 4254–

4256. Interaktyvus. ISSN 1932-7447. Prieiga per: ACS Publications, <https://doi.org/10.1021/jp900302b>. [žiūrėta 2024-11-10].
265. ITO, Seigo; TSUJIMOTO, Kazuki; NGUYEN, Duy-Cuong; MANABE, Kyohei ir NISHINO, Hitoshi. Doping effects in Sb₂S₃ absorber for full-inorganic printed solar cells with 5.7% conversion efficiency. *International Journal of Hydrogen Energy*, 38, 2013, 36, 16749–16754. Interaktyvus. ISSN 0360-3199. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.ijhydene.2013.02.069>. [žiūrėta 2024-11-10].
266. MOON, Soo-Jin; ITZHAİK, Yafit; YUM, Jun-Ho; ZAKEERUDDIN, Shaik M.; HODES, Gary ir kt. Sb₂S₃-Based Mesoscopic Solar Cell using an Organic Hole Conductor. *The Journal of Physical Chemistry Letters*, 1, 2010, 10, 1524–1527. Interaktyvus. ISSN 1948-7185. Prieiga per: ACS Publications, <https://doi.org/10.1021/jz100308q>. [žiūrėta 2024-11-10].
267. WANG, Shaoying; ZHAO, Yuqi; CHE, Bo; LI, Chuang; CHEN, Xueling ir kt. A Novel Multi-Sulfur Source Collaborative Chemical Bath Deposition Technology Enables 8%-Efficiency Sb₂S₃ Planar Solar Cells. *Advanced Materials*, 34, 2022, 41, 2206242. Interaktyvus. ISSN 0935-9648. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adma.202206242>. [žiūrėta 2024-11-10].
268. ZHAO, Yuqi; WANG, Shaoying; JIANG, Chenhui; LI, Chuang; XIAO, Peng ir kt. Regulating Energy Band Alignment via Alkaline Metal Fluoride Assisted Solution Post-Treatment Enabling Sb₂(S,Se)₃ Solar Cells with 10.7% Efficiency. *Advanced Energy Materials*, 12, 2022, 1, 2103015. Interaktyvus. ISSN 1614-6832. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/aenm.202103015>. [žiūrėta 2024-11-10].
269. CHEN, Xueling; ZHAO, Yuqi; LI, Chuang; WANG, Xiaomin; XIAO, Peng ir kt. Interfacial Engineering by Self-Assembled Monolayer for High-Performance Sb₂S₃ Solar Cells. *Advanced Energy Materials*, 14, 2024, 33, 2400441. Interaktyvus. ISSN 1614-6832. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/aenm.202400441>. [žiūrėta 2024-11-10].
270. SHALVEY, Thomas P.; DON, Christopher H.; BOWEN, Leon; VEAL, Tim D. ir MAJOR, Jonathan D. Understanding the Role of Organic Hole Transport Layers on Pinhole Blocking and Performance Improvement in Sb₂Se₃ Solar Cells. *Advanced Materials Interfaces*, 2024, 2400394. Interaktyvus. ISSN 2196-7350. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/admi.202400394>. [žiūrėta 2024-11-10].
271. JACOB OLASOJI, Abimbola; HYUCK HEO, Jin ir HYUK IM, Sang. Facile fabrication of crack-free TiO₂ inverse opal thin-film and its application as electron transporting scaffold for efficient Sb₂S₃-sensitized solar cells. *Journal of colloid and interface science*, 678, 2025, 842–853. Interaktyvus. ISSN 0021-9797. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.jcis.2024.08.259>. [žiūrėta 2024-11-10].
272. LIU, Rong; SHEN, Zhitao; WAN, Zhiyang; ZHU, Liangxin; CHEN, Junwei ir kt. Nanoarray heterojunction and its efficient solar cells without negative impact of photogenerated electric field. *Communications Physics*, 4, 2021, 1, 177. ISSN 2399-3650. Prieiga per: Nature, <https://doi.org/10.1038/s42005-021-00678-1>. [žiūrėta 2024-11-10].
273. MKAWI, Elmoiz Merghni ir AL-HADEETHI, Yas. Enhanced Antimony Sulfide Sb₂S₃ Nanobars Solar Cell Performance with Doped PCDTBT Polymer. *International Journal of Energy Research*, 2023, 2023, 1, 2636957. Interaktyvus. ISSN 0363-907X. Prieiga per: Wiley Online Library, <https://doi.org/10.1155/2023/2636957>. [žiūrėta 2024-11-10].
274. KETTLE, J.; HORIE, M.; MAJEWSKI, L. A.; SAUNDERS, B. R.; TULADHAR, S. ir kt. Optimisation of PCPDTBT solar cells using polymer synthesis with Suzuki coupling. *Solar Energy Materials and Solar Cells*, 95, 2011, 8, 2186–2193. Interaktyvus. ISSN 0927-0248.

Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.solmat.2011.03.022>. [žiūrėta 2024-11-10].

275. LOMBECK, Florian; MATSIDIK, Rukiya; KOMBER, Hartmut ir SOMMER, Michael. Simple Synthesis of P(Cbz-alt-TBT) and PCDTBT by Combining Direct Arylation with Suzuki Polycondensation of Heteroaryl Chlorides. *Macromolecular Rapid Communications*, 36, 2015, 2, 231–237. Interaktyvus. ISSN 1022-1336. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/marc.201400437>. [žiūrėta 2024-11-10].

276. TETREAULT, Adam R.; DANG, Minh-Trung ir BENDER, Timothy P. PTB7 and PTB7-Th as universal polymers to evaluate materials development aspects of organic solar cells including interfacial layers, new fullerenes, and non-fullerene electron acceptors. *Synthetic Metals*, 287, 2022, 117088. Interaktyvus. ISSN 0379-6779. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.synthmet.2022.117088>. [žiūrėta 2024-11-10].

277. OSAKA, Itaru ir MCCULLOUGH, Richard D. Advances in Molecular Design and Synthesis of Regioregular Polythiophenes. *Accounts of Chemical Research*, 41, 2008, 9, 1202–1214. Interaktyvus. ISSN 0001-4842. Prieiga per: ACS Publications, <https://doi.org/10.1021/ar800130s>. [žiūrėta 2024-11-10].

278. Sigma Aldrich. *Poly(3-hexylthiophene-2,5-diyl)*. Interneto puslapis. Prieiga per: <https://www.sigmaaldrich.com/LT/en/substance/poly3hexylthiophene25diyl1234510493450> 1. [žiūrėta 2024-10-23].

279. Sigma Aldrich. *PCPDTBT*. Interneto puslapis. Prieiga per: <https://www.sigmaaldrich.com/LT/en/product/aldrich/754005>. [žiūrėta 2024-10-23].

280. Ossila enabling science. *PCDTBT*. Interneto puslapis. Prieiga per: https://www.ossila.com/products/pcdtbt?_pos=1&_sid=a85a3acc6&_ss=r. [žiūrėta 2024-10-23].

281. BLD Pharm. *Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2-6-diyl]*. Interneto puslapis. Prieiga per: <https://www.bldpharm.com/products/1469791-66-9.html?BD=BD01122809>. [žiūrėta 2024-10-23].

282. JIANG, Chenhui; ZHOU, Jie; TANG, Rongfeng; LIAN, Weitao; WANG, Xiaomin ir kt. 9.7%-efficient Sb₂(S,Se)₃ solar cells with a dithieno[3,2-b: 2',3'-d]pyrrole-cored hole transporting material. *Energy & Environmental Science*, 14, 2021, 1, 359–364. Interaktyvus. ISSN 1754-5692. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D0EE02239J>. [žiūrėta 2024-11-11].

283. CHEN, Wangchao; WU, Miaomiao; CHEN, Xuan; ZHANG, Zhi; GUO, Fuling ir kt. Superior Intermolecular Noncovalent Interactions Empowered Dopant-Free Hole Transport Materials for Efficient and Stable Sb₂(S,Se)₃ Solar Cells. *Advanced Functional Materials*, 34, 2024, 22, 2313403. Interaktyvus. ISSN 1616-301X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/adfm.202313403>. [žiūrėta 2024-11-11].

284. HU, Qikun; REZAEI, Ehsan; DONG, Qingshun; SHAN, Haiquan; CHEN, Qian ir kt. P3HT/Phthalocyanine Nanocomposites as Efficient Hole-Transporting Materials for Perovskite Solar Cells. *Solar RRL*, 3, 2019, 1, 1800264. Interaktyvus. ISSN 2367-198X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/solr.201800264>. [žiūrėta 2024-11-11].

285. KHARISOV, B. I.; ORTIZ MENDEZ, U. ir RIVERA DE LA ROSA, J. Low-temperature synthesis of phthalocyanine and its metal complexes. *Russian Journal of Coordination*

Chemistry, 32, 2006, 9, 617–631. Interaktyvus. ISSN 1608-3318. Prieiga per: Springer Nature Link, <https://doi.org/10.1134/S1070328406090016>. [žiūrėta 2024-11-11].

286. GUO, Huafei; HUANG, Shan; NI, Xiaomeng; ZHU, Hongcheng; SU, Jian ir kt. High-efficiency and stable Sb₂(S,Se)₃ thin film solar cells with phthalocyanine as a hole transport layer. *Journal of Materials Chemistry C*, 11, 2023, 37, 12707–12713. Interaktyvus. ISSN 2050-7526. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D3TC01980B>. [žiūrėta 2024-11-11].

287. XU, Shuangting; WU, Jing; GUO, Fuling; WU, Miaomiao; CHEN, Sijian ir kt. Self-passivation hole-transporting materials with pyridine-containing cores for antimony chalcogenide solar cells studied under dopant-free conditions. *Sustainable Energy Fuels*, 7, 2023, 1, 61–65. Interaktyvus. ISSN 2398-4902. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D2SE01448C>. [žiūrėta 2024-11-11].

288. JUNEJA, Nimish; DASKEVICIUTE-GEGUZIENE, Sarune; SPALATU, Nicolae; MANDATI, Sreekanth; KATERSKI, Atanas ir kt. Employment of dopant-free fluorene-based enamines as innovative hole transport materials to boost the transparency and performance of Sb₂S₃ based solar cells. *Materials Science in Semiconductor Processing*, 169, 2024, 107934. Interaktyvus. ISSN 1369-8001. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.mssp.2023.107934>. [žiūrėta 2024-11-11].

289. *Lietuvos Energetikos Agentūra. Interneto Puslapis*. Prieiga per: <https://www.ena.lt/uploads/2024-men-data/2024-metin%C4%97-energetikos-duomenu-apzvalga-20241219.pdf>. [žiūrėta 2025-02-28].

290. JEGOROVĖ, Aistė; MOMBLONA, Cristina; DAŠKEVIČIENĖ, Marytė; MAGOMEDOV, Artiom; DEGUTYTE, Rimgaile ir kt. Molecular Engineering of Fluorene-Based Hole-Transporting Materials for Efficient Perovskite Solar Cells. *Solar RRL*, 6, 2022, 6, 2100990. Interaktyvus. ISSN 2367-198X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/solr.202100990>. [žiūrėta 2024-11-12].

291. MALINAUSKAS, Tadas; TOMKUTE-LUKSIENE, Daiva; SENS, Rüdiger; DASKEVICIENE, Maryte; SEND, Robert ir kt. Enhancing Thermal Stability and Lifetime of Solid-State Dye-Sensitized Solar Cells via Molecular Engineering of the Hole-Transporting Material Spiro-OMeTAD. *ACS Applied Materials & Interfaces*, 7, 2015, 21, 11107–11116. Interaktyvus. ISSN 1944-8244. Prieiga per: ACS Publication, <https://doi.org/10.1021/am5090385>. [žiūrėta 2024-11-12].

292. GEHLHAAR, Robert; MERCKX, Tamara; QIU, Weiming ir AERNOUTS, Tom. Outdoor Measurement and Modeling of Perovskite Module Temperatures. *Global Challenges*, 2, 2018, 7, 1800008. Interaktyvus. ISSN 2056-6646. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/gch2.201800008>. [žiūrėta 2024-11-12].

293. DRIGO, Nikita; ROLDAN-CARMONA, Cristina; FRANCKEVIČIUS, Marius; LIN, Kun-Han; GEGEVIČIUS, Rokas ir kt. Doped but Stable: Spirobisacridine Hole Transporting Materials for Hysteresis-Free and Stable Perovskite Solar Cells. *Journal of the American Chemical Society*, 142, 2020, 4, 1792–1800. Interaktyvus. ISSN 0002-7863. Prieiga per: ACS Publications, <https://doi.org/10.1021/jacs.9b07166>. [žiūrėta 2024-11-12].

294. JEGOROVĖ, Aistė; DAŠKEVIČIENĖ, Marytė; KANTMINIENĖ, Kristina; JANKAUSKAS, Vygtintas; ČEPAS, Romualdas Jonas ir kt. New fluorene-based bipolar charge transporting materials. *RSC Advances*, 14, 2024, 5, 2975–2982. Interaktyvus. ISSN Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D3RA07583D>. [žiūrėta 2024-11-12].

295. BUIKA, G.; V. GETAUTIS ir V. MARTYNAITIS IR K. RUTKAUSKAS. *Organinių junginių spektroskopija: vadovėlis*. Kaunas: Vitae litera, 2007. ISBN 9789955686316.
296. JEGOROVĖ, Aistė; XIA, Jianxing; STEPONAITIS, Matas; DASKEVICIENE, Maryte; JANKAUSKAS, Vygintas ir kt. Branched Fluorenylidene Derivatives with Low Ionization Potentials as Hole-Transporting Materials for Perovskite Solar Cells. *Chemistry of Materials*, 35, 2023, 15, 5914–5923. Interaktyvus. ISSN 0897-4756. Prieiga per: ACS Publications, <https://doi.org/10.1021/acs.chemmater.3c00708>. [žiūrėta 2024-11-12].
297. XU, Bo; ZHU, Zonglong; ZHANG, Jinbao; LIU, Hongbin; CHUEH, Chu-Chen ir kt. 4-Tert-butylpyridine Free Organic Hole Transporting Materials for Stable and Efficient Planar Perovskite Solar Cells. *Advanced Energy Materials*, 7, 2017, 19, 1700683. Interaktyvus. ISSN 1614-6832. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/aenm.201700683>. [žiūrėta 2024-11-12].
298. SALIBA, Michael; ORLANDI, Simonetta; MATSUI, Taisuke; AGHAZADA, Sadig; CAVAZZINI, Marco ir kt. A molecularly engineered hole-transporting material for efficient perovskite solar cells. *Nature Energy*, 1, 2016, 2, 15017. Interaktyvus. ISSN 2058-7546. Prieiga per: Nature, <https://doi.org/10.1038/nenergy.2015.17>. [žiūrėta 2024-11-12].
299. JEGOROVĖ, Aistė; TRUONG, Minh Anh; MURDEY, Richard; DASKEVICIENE, Maryte; MALINAUSKAS, Tadas ir kt. Starburst Carbazole Derivatives as Efficient Hole Transporting Materials for Perovskite Solar Cells. *Solar RRL*, 6, 2022, 1, 2100877. Interaktyvus. ISSN 2367-198X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/solr.202100877>. [žiūrėta 2024-11-12].
300. SHIROTA, Yasuhiko ir KAGEYAMA, Hiroshi. Charge Carrier Transporting Molecular Materials and Their Applications in Devices. *Chemical reviews*, 107, 2007, 4, 953–1010. Interaktyvus. ISSN 0009-2665. Prieiga per: ACS Publications, <https://doi.org/10.1021/cr050143+>. [žiūrėta 2024-11-13].
301. RAKSTYS, Kasparas; IGCI, Cansu ir NAZEERUDDIN, Mohammad Khaja. Efficiency vs. stability: dopant-free hole transporting materials towards stabilized perovskite solar cells. *Chemical Science*, 10, 2019, 28, 6748–6769. Interaktyvus. ISSN 2041-6520. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C9SC01184F>. [žiūrėta 2024-11-13].
302. YIN, Xinxing; SONG, Zhaoning; LI, Zaifang ir TANG, Weihua. Toward ideal hole transport materials: a review on recent progress in dopant-free hole transport materials for fabricating efficient and stable perovskite solar cells. *Energy & Environmental Science*, 13, 2020, 11, 4057–4086. Interaktyvus. ISSN 1754-5692. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D0EE02337J>. [žiūrėta 2024-11-13].
303. GAO, Ligu; SCHLOEMER, Tracy H.; ZHANG, Fei; CHEN, Xihan; XIAO, Chuanxiao ir kt. Carbazole-Based Hole-Transport Materials for High-Efficiency and Stable Perovskite Solar Cells. *ACS Applied Energy Materials*, 3, 2020, 5, 4492–4498. Interaktyvus. ISSN 2574-0962. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsaem.0c00179>. [žiūrėta 2024-11-13].
304. LI, Mengyuan; WANG, Zhihui; LIANG, Mao; LIU, Liyuan; WANG, Xuda ir kt. Low-Cost Carbazole-Based Hole-Transporting Materials for Perovskite Solar Cells: Influence of S,N-Heterocycle. *The Journal of Physical Chemistry C*, 122, 2018, 42, 24014–24024. Interaktyvus. ISSN 1932-7447. Prieiga per: ACS Publications, <https://doi.org/10.1021/acs.jpcc.8b09482>. [žiūrėta 2024-11-13].
305. DASKEVICIENE, Maryte; PAEK, Sanghyun; MAGOMEDOV, Artiom; CHO, Kyoung Taek; SALIBA, Michael ir kt. Molecular engineering of enamine-based small organic compounds as hole-transporting materials for perovskite solar cells. *Journal of Materials*

Chemistry C, 7, 2019, 9, 2717–2724. Interaktyvus. ISSN 2050-7526. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C8TC06297H>. [žiūrėta 2024-11-13].

306. XUE, Yuyuan; WU, Ying ir LI, Yuan. Readily synthesized dopant-free hole transport materials with phenol core for stabilized mixed perovskite solar cells. *Journal of Power Sources*, 344, 2017, 160–169. Interaktyvus. ISSN 0378-7753. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.jpowsour.2017.01.121>. [žiūrėta 2024-11-13].

307. ZHU, Linna; SHAN, Yahan; WANG, Rui; LIU, Debei; ZHONG, Cheng ir kt. High-Efficiency Perovskite Solar Cells Based on New TPE Compounds as Hole Transport Materials: The Role of 2,7- and 3,6-Substituted Carbazole Derivatives. *Chemistry – A European Journal*, 23, 2017, 18, 4373–4379. Interaktyvus. ISSN 0947-6539. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/chem.201605187>. [žiūrėta 2024-11-13].

308. FUENTES PINEDA, Rosinda; TROUGHTON, Joel; PLANELLS, Miquel; SANCHEZ-MOLINA SANTOS, Irene; MUHITH, Farmin ir kt. Effect of alkyl chain length on the properties of triphenylamine-based hole transport materials and their performance in perovskite solar cells. *Physical Chemistry Chemical Physics*, 20, 2018, 2, 1252–1260. Interaktyvus. ISSN 1463-9076. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C7CP07682G>. [žiūrėta 2024-11-13].

309. LIN, Kun-Han; PRLJ, Antonio ir CORMINBOEUF, Clémence. How does alkyl chain length modify the properties of triphenylamine-based hole transport materials?. *Journal of Materials Chemistry C*, 6, 2018, 5, 960–965. Interaktyvus. ISSN 2050-7526. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C7TC05318E>. [žiūrėta 2024-11-13].

310. TRUONG, Minh Anh; LEE, Jaehyun; NAKAMURA, Tomoya; SEO, Ji-Youn; JUNG, Mina ir kt. Influence of Alkoxy Chain Length on the Properties of Two-Dimensionally Expanded Azulene-Core-Based Hole-Transporting Materials for Efficient Perovskite Solar Cells. *Chemistry – A European Journal*, 25, 2019, 27, 6741–6752. Interaktyvus. ISSN 0947-6539. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/chem.201806317>. [žiūrėta 2024-11-14].

311. BRAUKYLA, Titas; XIA, Rui; DASKEVICIENE, Maryte; MALINAUSKAS, Tadas; GRUODIS, Alytis ir kt. Inexpensive Hole-Transporting Materials Derived from Tröger's Base Afford Efficient and Stable Perovskite Solar Cells. *Angewandte Chemie International Edition*, 58, 2019, 33, 11266–11272. Interaktyvus. ISSN 1433-7851. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/anie.201903705>. [žiūrėta 2024-11-14].

312. LI, Hairong; FU, Kunwu; HAGFELDT, Anders; GRÄTZEL, Michael; MHAISALKAR, Subodh G. ir kt. A Simple 3,4-Ethylenedioxythiophene Based Hole-Transporting Material for Perovskite Solar Cells. *Angewandte Chemie International Edition*, 53, 2014, 16, 4085–4088. Interaktyvus. ISSN 1433-7851. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/anie.201310877>. [žiūrėta 2024-11-14].

313. SHEIBANI, Esmaeil; YANG, Li ir ZHANG, Jinbao. Recent Advances in Organic Hole Transporting Materials for Perovskite Solar Cells. *Solar RRL*, 4, 2020, 12, 2000461. Interaktyvus. ISSN 2367-198X. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/solr.202000461>. [žiūrėta 2024-11-14].

314. OZAKI, Masashi; ISHIKURA, Yasuhisa; TRUONG, Minh Anh; LIU, Jiewei; OKADA, Iku ir kt. Iodine-rich mixed composition perovskites optimised for tin(IV) oxide transport layers: the influence of halide ion ratio, annealing time, and ambient air aging on solar cell performance. *Journal of Materials Chemistry A*, 7, 2019, 28, 16947–16953. Interaktyvus. ISSN 2050-7488. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/C9TA02142F>. [žiūrėta 2024-11-14].

315. JEONG, Jeong; CHOI, Choi; GO, Go; CHO, Cho; KIM, Kim ir kt. Stable perovskite solar cells with efficiency exceeding 24.8% and 0.3-V voltage loss. *Science*, 369, 2020, 6511, 1615–1620. Interaktyvus. ISSN 0036-8075. Prieiga per: Science, <https://doi.org/10.1126/science.abb7167>. [žiūrėta 2024-11-14].
316. SALIBA, Michael; CORREA-BAENA, Juan; WOLFF, Christian M.; STOLTERFOHT, Martin; PHUNG, Nga ir kt. How to Make over 20% Efficient Perovskite Solar Cells in Regular (n–i–p) and Inverted (p–i–n) Architectures. *Chemistry of Materials*, 30, 2018, 13, 4193–4201. Interaktyvus. ISSN 0897-4756. Prieiga per: ACS Publications, <https://doi.org/10.1021/acs.chemmater.8b00136>. [žiūrėta 2024-11-14].
317. MOLINA-ONTORIA, Agust; ZIMMERMANN, Iwan; GARCIA-BENITO, In; GRATIA, Paul; ROLDÁN-CARMONA, Cristina ir kt. Benzotrithiophene-Based Hole-Transporting Materials for 18.2 % Perovskite Solar Cells. *Angewandte Chemie International Edition*, 55, 2016, 21, 6270–6274. Interaktyvus. ISSN 1433-7851. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/anie.201511877>. [žiūrėta 2024-11-14].
318. BERTON, Nicolas; NAKAR, Rana ir SCHMALTZ, Bruno. DMPA-containing carbazole-based hole transporting materials for perovskite solar cells: Recent advances and perspectives. *Synthetic Metals*, 252, 2019, 91–106. Interaktyvus. ISSN 0379-6779. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.synthmet.2019.04.004>. [žiūrėta 2024-11-14].
319. MANDATI, Sreekanth; JUNEJA, Nimish; KATERSKI, Atanas; JEGOROVĚ, Aistė; GRZIBOVSKIS, Raitis ir kt. 4.9% Efficient Sb₂S₃ Solar Cells from Semitransparent Absorbers with Fluorene-Based Thiophene-Terminated Hole Conductors. *ACS Applied Energy Materials*, 6, 2023, 7, 3822–3833. Interaktyvus. ISSN 2574-0962. Prieiga per: ACS Publications, <https://doi.org/10.1021/acsaem.2c04097>. [žiūrėta 2024-11-14].
320. MAVLONOV, Abdurashid; RAZYKOV, Takhir; RAZIQ, Fazal; GAN, Jiantuo; CHANTANA, Jakapan ir kt. A review of Sb₂Se₃ photovoltaic absorber materials and thin-film solar cells. *Solar Energy*, 201, 2020, 227–246. Interaktyvus. ISSN 0038-092X. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.solener.2020.03.009>. [žiūrėta 2024-11-14].
321. BÜTTNER, Pascal; SCHELER, Florian; DÖHLER, Dirk; BARR, Maïssa K. S.; BOSCH, Michael ir kt. Continuous, crystalline Sb₂S₃ ultrathin light absorber coatings in solar cells based on photonic concentric p–i–n heterojunctions. *Nano Energy*, 103, 2022, 107820. Interaktyvus. ISSN 2211-2855. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.nanoen.2022.107820>. [žiūrėta 2024-11-15].
322. ZIMMERMANN, Eugen; PFADLER, Thomas; KALB, Julian; DORMAN, James A.; SOMMER, Daniel ir kt. Toward High-Efficiency Solution-Processed Planar Heterojunction Sb₂S₃ Solar Cells. *Advanced Science*, 2, 2015, 5, 1500059. Interaktyvus. ISSN 2198-3844. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/advs.201500059>. [žiūrėta 2024-11-15].
323. YOU, Myoung Sang; LIM, Choong-Sun; KWON, Do Hyeong; HEO, Jin Hyuck; IM, Sang Hyuk ir kt. Oxide-free Sb₂S₃ sensitized solar cells fabricated by spin and heat-treatment of Sb(III)(thioacetamide)₂Cl₃. *Organic Electronics*, 21, 2015, 155–159. Interaktyvus. ISSN 1566-1199. Prieiga per: ScienceDirect, <https://doi.org/10.1016/j.orgel.2015.02.015>. [žiūrėta 2024-11-15].
324. CHEN, Junwei; QI, Juanjuan; LIU, Rong; ZHU, Xiaoguang; WAN, Zhiyang ir kt. Preferentially oriented large antimony trisulfide single-crystalline cuboids grown on polycrystalline titania film for solar cells. *Communications Chemistry*, 2, 2019, 1, 121. Interaktyvus. ISSN 2399-3669. Prieiga per: Nature, <https://doi.org/10.1038/s42004-019-0225-1>. [žiūrėta 2024-11-15].

325. ZHANG, Yan; LI, Shi'ang; TANG, Rongfeng; WANG, Xiaomin; CHEN, Chao ir kt. Phosphotungstic Acid Regulated Chemical Bath Deposition of Sb₂S₃ for High-Efficiency Planar Heterojunction Solar Cell. *Energy Technology*, 6, 2018, 11, 2126–2131. Interaktyvus. ISSN 2194-4288. Prieiga per: Wiley Online Library, <https://doi.org/10.1002/ente.201800238>. [žiūrėta 2024-11-15].
326. XIANG, Yinan; GUO, Huanxin; CAI, Zhiyuan; JIANG, Chenhui; ZHU, Changfei ir kt. Dopant-free hole-transporting materials for stable Sb₂(S,Se)₃ solar cells. *Chemical Communications*, 58, 2022, 30, 4787–4790. Interaktyvus. ISSN 1359-7345. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D1CC07041J>. [žiūrėta 2024-11-15].
327. JUNEJA, Nimish; JEGOROVĖ, Aistė; GRZIBOVSKIS, Raitis; KATERSKI, Atanas; DASKEVICIENE, Maryte ir kt. Dopant-free fluorene based dimers linked with thiophene units as prospective hole transport materials for Sb₂S₃ solar cells. *Sustainable Energy Fuels*, 8, 2024, 18, 4324–4334. Interaktyvus. ISSN 2398-4902. Prieiga per: Royal Society of Chemistry, <https://doi.org/10.1039/D4SE00472H>. [žiūrėta 2024-11-15].

Molecular Engineering of Fluorene-Based Hole-Transporting Materials for Efficient Perovskite Solar Cells

Aistė Jegorovė, Cristina Momblona, Marytė Daškevičienė, Artiom Magomedov, Rimgaile Degutyte, Abdullah M. Asiri, Vygintas Jankauskas, Albertus Adrian Sutanto, Hiroyuki Kanda, Keith Brooks, Nadja Klipfel, Mohammad Khaja Nazeeruddin,* and Vytautas Getautis*

New Spiro-OMeTAD analogues and the simpler “half” structures with the terminated methoxyphenyl and/or carbazolyl chromophores are successfully synthesized under Hartwig–Buchwald amination conditions using commercially available starting materials. New fluorene-based hole-transporting materials combined with suitable ionization energies properly align with the valence band of the perovskite absorber. Additionally, these compounds are amorphous, which is an advantage for the formation of homogenous films, as well as eliminate the possibility for films to crystallize during operation of the devices. The most efficient perovskite solar cells devices contain carbazolyl-terminated Spiro-OMeTAD analogue V1267 and reach a power conversion efficiency of 18.3%, along with a short-circuit current density, open-circuit voltage, and fill factor of 23.41 mA cm⁻², 1.06 V, and 74.0%, respectively. Moreover, “half” structures with methoxyphenyl/carbazolyl fragments show excellent long-term stability and outperform Spiro-OMeTAD and, therefore, hold a great prospect for practical wide-scale applications in optoelectronic devices.

variety of the available deposition techniques, such as solution-processing (e.g., inject printing,^[4] slot die,^[5] blade coating,^[6] etc.) and vapor deposition.^[7–9] Moreover, over the years, several different architectures of the devices have been investigated (e.g., n–i–p or “regular,” p–i–n or “inverted,” mesoscopic),^[10,11] which further increases attractiveness of this technology.

The main reason behind the rapid progress of the PSCs mostly comes from the optimization of the perovskite absorber layer, starting from the deposition methods,^[12] advancing to the composition optimization,^[13] and finally shifting the focus to the interfaces.^[14] However, the progress also strongly depends on the other components of the PSCs, such as electron and hole-selective contacts.^[15–19] In particular, use of the modern synthetic methods

opens a way for a huge variety of the organic hole-transporting materials (HTMs), while systematic study of variations could lead to the innovations in the field of molecular electronics.^[20–24]

Carbazole and fluorene chromophores are among the most popular structural building blocks, used for the construction of the organic HTMs.^[25–30] In a recent work, it was shown that the replacement of the methoxyphenyl fragment of the popular HTM Spiro-OMeTAD with the 9,9-dimethylfluorenyl chromophore led to the superior performance.^[31] Such an increase in

1. Introduction

Perovskite solar cells (PSCs) have recently emerged as a promising technology for the further cost reduction of the energy production from the sunlight. Starting from the first publication by A. Kojima et al. back in 2009,^[1] PSCs have reached 25.5% efficiency of the single-junction devices,^[2] and over 29% efficiency of the silicon/perovskite tandem devices.^[3] The advantage of the PSCs over traditional solar cell technologies lays in the vast

A. Jegorovė, M. Daškevičienė, A. Magomedov, V. Getautis
Department of Organic Chemistry
Kaunas University of Technology
LT-50254 Kaunas, Lithuania
E-mail: vytautas.getautis@ktu.lt

C. Momblona, A. A. Sutanto, H. Kanda, K. Brooks, N. Klipfel,
M. K. Nazeeruddin
Group for Molecular Engineering of Functional Material
Institute of Chemical Sciences and Engineering
Ecole Polytechnique Fédérale de Lausanne
CH-1951 Sion, Switzerland
E-mail: mdkhaja.nazeeruddin@epfl.ch

R. Degutyte
Department of Food Science and Technology
Kaunas University of Technology
Kaunas LT-50254, Lithuania

A. M. Asiri
Center of Excellence for Advanced Materials Research (CEAMR)
King Abdulaziz University
Jeddah 21589, Saudi Arabia

V. Jankauskas
Institute of Chemical Physics
Vilnius University
Vilnius LT-10257, Lithuania

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/solr.202100990>.

DOI: 10.1002/solr.202100990

the efficiency and stability was attributed to the optimized thermal properties, as well as beneficial alignment of the energy levels. Moreover, the advantage of carbazole-based HTMs could be the absence of methoxy substituents, such as the ones found on Spiro-OMeTAD. In this case, the hydrophobicity of HTM layer is expected to increase, thus positively affecting the device stability.^[32]

In this work, we have investigated Spiro-OMeTAD analogues, in which the methoxyphenyl groups were replaced by carbazolyl chromophores. Thermal, optical, and electrical properties of these compounds are compared to those of the Spiro-OMeTAD. In addition, materials with simpler, "half" structures were investigated, where 9,9-positions of the central fluorene fragment are occupied by different alkyl chains. Finally, new compounds were investigated in the *n-i-p* PSCs. The new Spiro-OMeTAD analogues present high efficiencies exceeding 17%. The devices fabricated with methoxyphenyl and carbazolyl or only carbazolyl groups achieve high efficiencies of 15%–16% and 17%–18% power conversion efficiency (PCE), respectively. The methoxyphenyl-/carbazolyl-based devices demonstrate excellent stability.

2. Results and Discussion

2.1. Synthesis

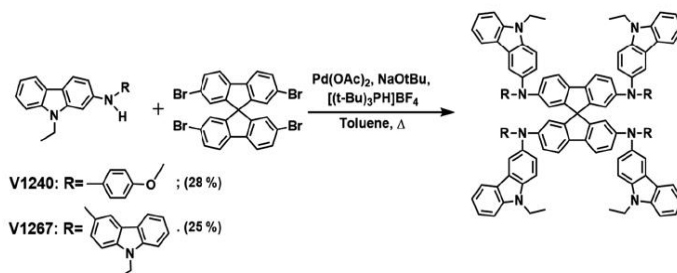
For the synthesis of new HTMs, used in this study, Hartwig–Buchwald amination reaction conditions were utilized. Spirobifluorene derivatives were synthesized using commercially available 2,2',7,7'-tetrabromo-9,9'-spirobifluorene as a precursor (Scheme 1), while for the "half" compounds,

2,7-dibromofluorene, alkylated with various aliphatic chains, was used (Scheme 2). These starting materials were coupled with 9-ethyl-*N*-(4-methoxyphenyl)-9*H*-carbazol-3-yl-amine to give target compounds V1222, V1226, V1238, V1240, and bis(9-ethyl-9*H*-carbazol-3-yl)amine, to give V1257, V1258, V1267, and V1269. Overall, this relatively simple synthetic strategy gives an opportunity to obtain series of compounds that can be evaluated for their possible application in the PSCs. Detailed synthetic procedures and methods, used to get target and precursor compounds, as well as their detailed structural characterizations, are given in Supporting Information.

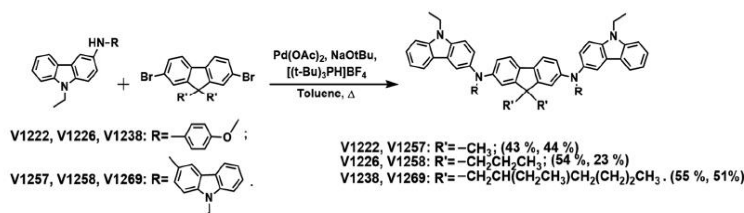
2.2. Optical Properties

To investigate optical properties of the synthesized compounds, ultraviolet–visible (UV–vis) and photoluminescence (PL) spectra of the respective solutions in tetrahydrofuran (THF) were recorded. In Figure 1, comparison between Spiro-OMeTAD, V1240, and V1267 are presented.

As it can be seen, the overall shape of the spectra of the new materials is similar to that of the Spiro-OMeTAD, inclining that only minor changes are induced by the change of the methoxyphenyl moieties for carbazolyl chromophores. With the growing number of carbazole units, an increase of absorption intensity (hyperchromic effect) can be observed, especially in the region around 250 nm, where absorption is dominant by that of the transitions in the heterocyclic systems. In contrast, in the PL spectra, a significant redshift is observed (Spiro-OMeTAD–417 nm, V1240–435 nm, V1267–453 nm), suggesting larger energy differences between ground state and excited state.



Scheme 1. Synthesis of the spirobifluorene derivatives V1240 and V1267.



Scheme 2. Synthesis of the "half" compounds V1222, V1226, V1238, V1257, V1258, and V1269.

Table 1. Thermal and photophysical properties of the synthesized compounds.

Compound	$T_g^{a)}$ [°C]	$T_d^{b)}$ [°C]	E_{ox} [eV]	I_p [eV]	μ_0 , [cm ² (V · s) ⁻¹] ($E_0 = 0$ V cm ⁻¹)	μ , [cm ² (V · s) ⁻¹] ($E = 6.4 \times 10^5$ V cm ⁻¹)	σ , [S cm ⁻¹]
9,9'-Spirobifluorene-based compounds							
Spiro-OMeTAD	124 ($T_m = 245$ °C) ^{c)}	449	5.19	5.0	4.1×10^{-5}	5.0×10^{-4}	3.01×10^{-4}
V1240	169	438	5.15	4.83	$5.6 \times 10^{-6d)}$	$8.8 \times 10^{-4d)}$	2.60×10^{-4}
V1267	139	512	5.07	4.90	$3.6 \times 10^{-4d)}$	$1.6 \times 10^{-3d)}$	6.96×10^{-4}
Fluorene-based "half" molecules with methoxyphenyl and carbazolyl chromophores							
V1222	147	452	5.16	4.93	$3.9 \times 10^{-4d)}$	$3.1 \times 10^{-2d)}$	4.63×10^{-4}
V1226	133	441	5.16	4.95	$3.8 \times 10^{-5d)}$	$1.9 \times 10^{-3d)}$	3.51×10^{-4}
V1238	77	401	5.16	5.02	1.8×10^{-5}	5.3×10^{-4}	3.28×10^{-5}
Fluorene-based "half" molecules with carbazolyl chromophores							
V1257	196	490	5.08	4.85	$3.6 \times 10^{-5d)}$	$1.6 \times 10^{-3d)}$	1.94×10^{-4}
V1258	183	461	5.08	4.85	$1.2 \times 10^{-5d)}$	$1.2 \times 10^{-3d)}$	2.68×10^{-4}
V1269	127	515	5.08	4.96	$3 \times 10^{-5d)}$	$2.9 \times 10^{-4d)}$	1.98×10^{-4}

^{a)}Glass transition temperature, extracted from the second differential scanning calorimetry (DSC) heating cycle; ^{b)}decomposition temperature, corresponding to the 5% weight loss; ^{c)}melting point (T_m) was not detected for all of the new compounds; ^{d)}the values of the hole drift mobility were evaluated by extrapolation of the results, obtained from the measurements of the mixture of the hole-transporting materials (HTMs) with Z-polycarbonate (PC-Z) polymer binder.

T_d (Spiro-OMeTAD $T_d = 449$ °C,^[34] **V1240** $T_d = 438$ °C), while T_d increases by 63 °C when all methoxyphenyl fragments are substituted by carbazolyl moieties (**V1267** $T_d = 512$ °C).

For the "half" compounds with two carbazolyl moieties, T_d values are in the range of 401–452 °C with lower value observed for the material **V1238** possessing longest aliphatic chain. HTMs with four carbazolyl fragments in general have shown higher T_d values in the range of 461–515 °C. Interestingly, in this case, compound **V1269** with 2-ethylhexyl aliphatic chains has shown the highest T_d , suggesting that there are significant differences in the packing of the molecules. Comparing these "half" compounds groups with each other, it is evident that incorporation of carbazolyl fragments into molecule increases T_d .

The glass transition temperatures (T_g) of all new compounds are given in Table 1 and Figures S4 and S5, Supporting Information. Both new spirobifluorene-based compounds **V1240** and **V1267** have shown higher T_g (169 and 139 °C, respectively) in comparison with Spiro-OMeTAD (124 °C), what can be explained by increased molecular weight.

Comparison of T_g of the "half" compounds revealed that materials with longer side chains showed lower T_g values. Overall, T_g of the compounds with both methoxyphenyl and carbazolyl chromophores (**V1222**, **V1226**, and **V1238**) was lowered by ≈ 50 °C compared to that of the respective analogues with only carbazolyl chromophores (**V1257**, **V1258**, and **V1269**). The reason behind this could be lower symmetry of the first group of compounds. The lowest T_g of 77 °C in case of compound **V1238** could negatively affect the long-term stability of the devices,^[34] but all the other HTMs showed T_g significantly exceeding 100 °C.

In addition, it is important to note that melting process was not observed for all of new synthesized compounds, indicating that they have only an amorphous state, what is an advantage for the formation of homogenous films, thus eliminating possibility for films to crystallize during operation of the devices.

2.4. Electrical Properties

To evaluate energy levels of new HTMs, their oxidation potential (E_{ox}) in the solution and solid-state ionization potential (I_p) values were measured by means of cyclic voltammetry (CV) and photoelectron spectroscopy in air (PESA) techniques, respectively. The results are presented in Table 1 and Figures S6–S8, Supporting Information. It is evident from the CV measurements that upon the introduction of carbazole, moiety material can be more readily oxidized, and therefore compounds, in which all methoxyphenyl fragments have been substituted by carbazolyl, exhibit lower E_{ox} values. Other changes in the structures have almost no impact on E_{ox} values. Similar trend is observed for I_p values; however, in this case, the variation in values for the compounds with the same chromophores is larger, suggesting some influence of packing in the bulk. In both cases, the values obtained for spirocompounds are somewhat larger than that of the corresponding "half" molecules. Overall, all synthesized HTMs are compatible with perovskite absorber materials values of the energy levels.

The ability of new HTMs to transport charges was evaluated by the xerographic time-of-flight (XTOF) technique, and measured hole drift mobility (μ_0 and μ) values are presented in Table 1 and Figures S9 and S10, Supporting Information. Some of materials cannot be measured from pure layers and, therefore, the charge transfer in layers of blends with bisphenol Z-polycarbonate (PC-Z), in weight ratios of 1:1, 1:2, 1:3, or 1:4, which were of suitable quality, was studied in detail. Based on the exponential dependence of the charge carrier mobility on the average distance between the charge-transporting molecules,^[35] interpolated mobility values were found for the case when the material is pure. The validity of such interpolation has been confirmed in several cases where hole mobility in samples of pure material has been measured. The hole transport properties of Spiro-OMeTAD were evaluated for comparison and presented in Table 1, and Figure S11, Supporting Information.

As a general trend, it can be seen that introduction of longer aliphatic chains has a negative impact for the ability to transport charges, which can be attributed to increased influence of the insulating fragments. “Half” compounds have higher mobility values for the series of compounds with both, methoxyphenyl and carbazolyl chromophores. However, different situation is observed for spiro compounds, where HTM **V1240** has demonstrated lower values, in comparison to that of **V1267**. Such difference might be attributed to the differences in the packing, occurring due to presence of the spiro core in the structure. Interestingly, all “half” HTM molecules have similar charge drift mobility compared to Spiro-OMeTAD, and such a molecule with both methoxyphenyl and carbazolyl chromophores (**V1222**) exhibits even better drift mobility. Only the spiro analogue of the latter (**V1240**) is inferior to the Spiro-OMeTAD compound in weak fields. Nevertheless, all synthesized compounds are showing transporting abilities sufficient for their application in PSCs.

Thin-film photoluminescence measurements were performed to analyze the hole extraction capability of different HTMs. The perovskite and perovskite/HTM layers were prepared on glass and excited at a wavelength of 625 nm from the perovskite or HTM side, respectively. The corresponding spectra are presented in Figure 3, and the quenching effect provoked by the HTM was compared with the bare perovskite emission (Table S1, Supporting Information). A significantly quenched emission is observed upon deposition of the HTMs on top of the bare perovskite layer, suggesting an efficient hole extraction. The samples (Figure 3c) containing fluorene-based “half” (Figure 3b) molecules with carbazolyl or methoxyphenyl and carbazolyl units present (Figure 3a) a higher quenched emission than for spirobifluorene-based HTMs, suggesting a better hole-extracting capability. The lateral conductivity of the different HTMs was measured with organic field-effect transistor (OFET) substrates (Figure S12, Supporting Information) and the values are presented in Table 1. All HTMs present similar conductivity values with that of the Spiro-OMeTAD ($\approx 10^{-4} \text{ S cm}^{-1}$) except of the **V1238**, which show the lowest value of studied HTMs with a conductivity of $3.28 \times 10^{-5} \text{ S cm}^{-1}$.

Time-resolved photoluminescence (TRPL) measurements were carried out to further evaluate the HTMs (see Figure S13, Supporting Information). The decays were measured with an

excitation wavelength of 640 nm and the samples were illuminated from the perovskite or HTM side, respectively. The decays were fitted to a double exponential equation, where τ_1 and τ_2 correspond to the fast and slow components, respectively. The corresponding fitting parameters are listed in Table S2, Supporting Information. As observed, the perovskite thin film exhibits τ_1 and τ_2 values of 100.6 and 336.4 ns, respectively, and these values decrease significantly after the HTM deposition. The new synthesized HTMs present slower decays than the reference Spiro-OMeTAD, indicating slower charge recombination processes for the reported HTMs than for Spiro-OMeTAD.^[36]

2.5. Performance in Solar Cells

Solution-processed n-i-p PSCs were fabricated to investigate new compounds in comparison to the widely employed Spiro-OMeTAD. The device structure is fluorine doped tin oxide (FTO)/c-TiO₂/m-TiO₂/SnO₂/(FAPbI₃)_{0.87}(MAPbBr₃)_{0.13}/0.92 (CsPbI₃)_{0.08}/HTM/Au, where the HTM (20 mM in chlorobenzene) was doped with *tert*-butylpyridine (tBP), lithium tris(bis(trifluoromethylsulfonyl)imide) (LiTFSI) and tris(2-(1*H*-pyrazol-1-yl)-4-*tert*-(butylpyridine)cobalt(III) (CoTFSI, FK209). Further details on the device fabrication can be found in Supporting Information.

The top-view and cross-sectional scanning electron microscopy (SEM) images (Figures S14–S16, Supporting Information) demonstrate that the surface coverage of perovskite layer by the HTMs is complete and without presence of pin holes or aggregation.^[37,38] The best-performing solar cells employing new HTMs are presented in Figure 4a–c and the corresponding photovoltaic (PV) parameters are listed in Table 2.

The replacement of methoxyphenyl for carbazolyl in spirobifluorene-based HTMs leads to solar cells with lower performance than the devices containing the widely used Spiro-OMeTAD. A strong decrease in open-circuit voltage (V_{OC}) values indicates higher recombination in the device presumably due to issues at the perovskite–HTM interface. Despite the low V_{OC} values, the devices still lead to high PCEs of 17.6% and 18.3% for **V1240** and **V1267**, respectively.

For the devices fabricated with “half” fluorene-based HTMs, the solar cells containing carbazolyl chromophores present higher device performance than their equivalent one formed with methoxyphenyl and carbazolyl units. The lower PV performance

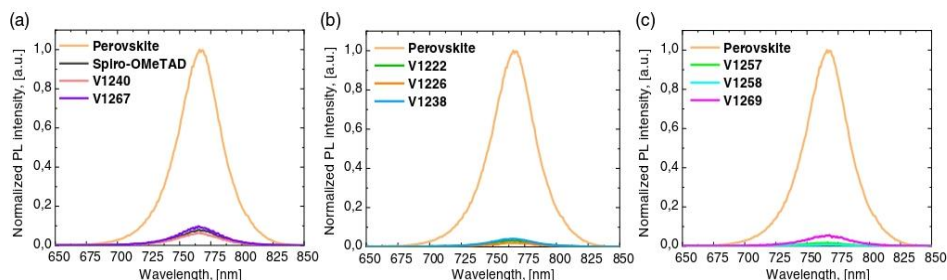


Figure 3. PL spectra of perovskite and perovskite/HTM layers deposited on glass ($\lambda_{exc} = 625 \text{ nm}$). a) 9,9'-Spirobifluorene-based HTMs: Spiro-OMeTAD, **V1240** and **V1267**. b) Fluorene-based “half” molecules with methoxyphenyl and carbazolyl moieties: **V1222**, **V1226**, **V1238** and c) fluorene-based “half” molecules with carbazolyl moieties: **V1257**, **V1258**, and **V1269**.

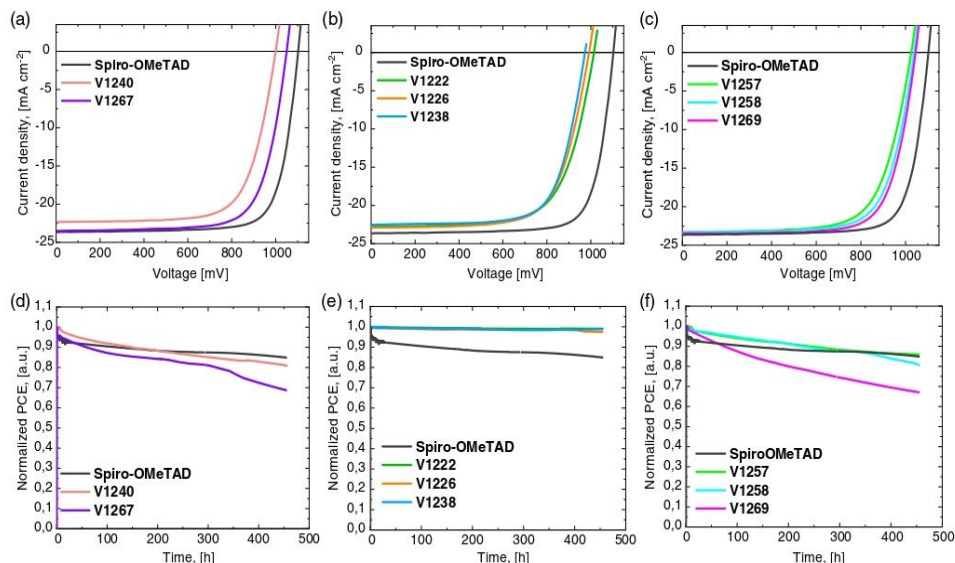


Figure 4. J - V curves and long-term stability of the most efficient solar cells containing a,d) Spiro-OMeTAD, V1240 and V1267 HTMs; b,e) V1222, V1226, and V1238 HTMs; and c,f) V1257, V1258, and V1269 HTMs. The stability test was performed in unencapsulated devices kept in N_2 atmosphere at 25 °C.

Table 2. PV parameters extracted from the corresponding J - V curves of the champion devices.

Compound	V_{oc} [mV]	J_{sc} [$mA\ cm^{-2}$]	FF	PCE, [%]
9,9'-Spirobifluorene-based materials				
Spiro-OMeTAD	1108	23.60	0.77	20.1
V1240	1000	22.32	0.79	17.6
V1267	1059	23.41	0.74	18.3
Fluorene-based "half" molecules with methoxyphenyl and carbazoyl chromophores				
V1222	1014	22.80	0.68	15.7
V1226	992	22.89	0.69	15.7
V1238	987	22.35	0.73	16.1
Fluorene-based "half" molecules with carbazoyl chromophores				
V1257	1034	23.37	0.71	17.2
V1258	1045	23.32	0.73	17.8
V1269	1048	23.35	0.74	18.1

FF: fill factor; PCE: power conversion efficiencies

of the devices with methoxyphenyl- and carbazoyl-based HTMs cannot be attributed to issues in the electronic properties of the molecules (see Table 1).

Therefore, the lower performance in methoxyphenyl and carbazoyl devices might be originated by a poorer perovskite/HTM interface than by perovskite/carbazoyl-HTM one. As mentioned earlier, the HTMs containing both methoxyphenyl and carbazoyl equivalents (V1222, V1226, V1238) present lower symmetry than

the compounds with only carbazoyl chromophores (V1222, V1226, V1238). This suggest that methoxyphenyl- and carbazoyl-based HTMs present lower ordered packing of the molecules in the film affecting also the perovskite-HTM morphology and therefore reducing the carrier transport and enhancing the interfacial recombination through the perovskite-HTM interface.^[39] As previously observed,^[30] the increasing alkyl chain length does not influence on the short-circuit current density values of the devices as the values are almost identical (22.4 – $22.8\ mA\ cm^{-2}$ for methoxyphenyl- and carbazoyl-HTM and $22.3\ mA\ cm^{-2}$ for carbazoyl-HTMs). The device performance is enhanced at increasing alkyl chain length due to higher fill factor (FF) values. The corresponding external quantum efficiency (EQE) of the devices is presented in Figure S17, Supporting Information.

The long-term stability of the devices was evaluated in unencapsulated device under continuous 1 sun illumination in N_2 atmosphere at 25 °C (see Figure 4d–f). The devices containing spirobifluorene-based materials present a continuous decrease of PCE, in accordance with other reported long-term stability of devices containing Spiro-OMeTAD, achieving 85% (Spiro-OMeTAD), 81% (V1240), or 69% (V1267) of its maximum efficiency under 450 h operation. Similar behaviors are observed for devices containing fluorene-based "half" molecules with carbazoyl chromophores with efficiency decays of 86%, 81%, or 67% for V1257, V1258, and V1269, respectively, after 450 h illumination. On the contrary, devices containing HTM with methoxyphenyl and carbazoyl units (V1222, V1226, V1238) presents with almost no degradation after 450 h under continuous illumination.

Water contact angles of the HTMs film coated on glass substrate were measured to better understand their stability upon humidity (Figure S18, Supporting Information). The water contact angle increase with the extension of alkyl chains at the 9,9-positions of the central fluorene fragment in the “half” structures, from 81°, 80° (V1222, V1257) and 86°, 87° (V1226, V1258) to 90° (V1238, V1269), while the smallest contact angle of 72° was obtained in case of Spiro-OMeTAD analogue V1267 possessing the carbazoyl chromophores. In addition, the increased hydrophobicity is observed for the other Spiro-OMeTAD analogue V1240 possessing the methoxyphenyl and carbazoyl moieties. The water contact angle (82°) in this case is higher than that of Spiro-OMeTAD (77°). The trend of the contact angle is broadly in line with the results of the stability measurements.

In addition, we conducted the stability test at a maximum power point (MPP) under continuous light soaking at AM 1.5G illumination of 750 s (Figure S19, Supporting Information). The devices were unencapsulated and the measurements were carried out in air (25 °C, HR < 40%). All the devices present light soaking effect in which the PV response is enhanced in the first 5 s except for Spiro-OMeTAD and V1238. After this rise, the efficiency of all the devices starts to slightly decrease. The increase of the initial efficiency and its stabilization for stability test has been reported in the literature for organic small molecules. Although the exact reason of this rise still remains unclear, one possible origin of the observed fluctuation might be associated with slow relaxation processes in the thin organic film.^[26,39–41]

3. Conclusion

In summary, we present the synthesis of the series of novel Spiro-OMeTAD analogues with the simple “half” structures and a systematic study of the impact of a terminated photoconductive chromophore on thermal, optical, photophysical, and photovoltaic properties. Molecular engineering of new HTMs was realized under Hartwig–Buchwald amination conditions using commercially available starting materials. New compounds bear alkylated fluorene and spirobifluorene fragments as molecule core, while 9-ethyl-*N*-(4-methoxyphenyl)-9*H*-carbazol-3-amine and bis(9-ethyl-9*H*-carbazol-3-yl)amine were used to build side chromophores. All synthesized HTMs exhibit excellent thermal stability, which depends on alkyl chain length and the number of carbazoyl moieties, at up to 400 °C. Moreover, the new synthesized HTMs, with the exception of the “half” compound with branched aliphatic chains at 9-positions of fluorene core and possessing both methoxyphenyl and carbazoyl chromophores (V1238), exhibited higher glass transition temperatures resulting in superior thermal stability compared to that of Spiro-OMeTAD. Additionally, these fluorene compounds are amorphous, which has the advantage of being able to form homogeneous films and further of reducing the possibility for the films to crystallize during device operation. All “half” HTM molecules have similar charge drift mobility compared to Spiro-OMeTAD, and such a molecule with both methoxyphenyl and carbazoyl chromophores (V1222) exhibits even better drift mobility. Only the spiro analogue V1240 is inferior to the Spiro-OMeTAD compound in weak fields. The PCE of the most efficient n–i–p PSCs perovskite devices containing

carbazoyl-terminated Spiro-OMeTAD analogue V1267 has reached 18.3%, and thus has outperformed the devices fabricated using the other HTMs: V1269 (18.1%), V1258 (17.8%), V1240 (17.6%), V1257 (17.21%), V1238 (16.1%), V1226 (15.7%), and V1222 (15.7%). Furthermore, “half” structures with methoxyphenyl/carbazoyl fragments show excellent long-term stability and outperform Spiro-OMeTAD. The devices employing newly synthesized “half” compounds with methoxyphenyl/carbazoyl fragments maintained their efficiency with almost no performance decrease, while the efficiency of the devices using Spiro-OMeTAD dropped to 85% after 450 h under continuous illumination in N₂ atmosphere. We believe that this study offers a facile approach for developing new HTMs that can influence the PSC performance via molecular engineering of the side chromophores of the fluorene-based HTMs.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

A.J. and C.M. contributed equally to this work. The research leading to these results had received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 763977 of the PerTPV project. M.D. acknowledges the funding from the Research Council of Lithuania (grant no. MIP-19-14). Prof. Raffaella Buonsanti is acknowledged for the use of the Fluorolog system. Dr. E. Kamarauskas is acknowledged for ionization potential measurements.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

carbazoyl chromophores, fluorene, hole-transporting materials, perovskite solar cells, spiro-OMeTAD analogues

Received: November 22, 2021

Revised: February 9, 2022

Published online: February 24, 2022

- [1] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, 131, 6050.
- [2] <https://www.nrel.gov/pv/cell-efficiency.html> (accessed: September 2021).
- [3] A. Al-Ashouri, E. Köhnen, B. Li, A. Magomedov, H. Hempel, P. Caprioglio, J. A. Márquez, A. B. Morales Vilches, E. Kasparavicius, J. A. Smith, N. Phung, D. Menzel, M. Grischek, L. Kegelmann, D. Skroblin, C. Gollwitzer, T. Malinauskas, M. Jošt,

- G. Matič, B. Rech, R. Schlattmann, M. Topić, L. Korte, A. Abate, B. Stannowski, D. Neher, M. Stollerfoht, T. Unold, V. Getautis, S. Albrecht, *Science* **2020**, 370, 1300.
- [4] F. Mathies, E. J. W. List-Kratochvil, E. L. Unger, *Energy Technol.* **2020**, 8, 1900991.
- [5] J. Li, J. Dagar, O. Shargaieva, M. A. Flatken, H. Köbler, M. Fenske, C. Schultz, B. Stegemann, J. Just, D. M. Többsen, A. Abate, R. Munir, E. Unger, *Adv. Energy Mater.* **2021**, 11, 2003460.
- [6] M. Ernst, J. P. Herterich, C. Margenfeld, M. Kohlstädt, U. Würfel, *Sol. RRL* **2021**, 26, 2100535.
- [7] J. Ávila, C. Momblona, P. P. Boix, M. Sessolo, H. J. Bolink, *Joule* **2017**, 1, 431.
- [8] M. Roß, L. Gil-Escrig, A. Al-Ashouri, P. Tockhorn, M. Joß, B. Rech, S. Albrecht, *ACS Appl. Mater. Interfaces* **2020**, 12, 39261.
- [9] Z. Li, J. Li, H. Cao, Y. Qian, J. Zhai, Y. Qiu, L. Yang, S. Yin, *ACS Appl. Mater. Interfaces* **2021**, 13, 45496.
- [10] P. Roy, N. K. Sinha, S. Tiwari, A. Khare, *Sol. Energy* **2020**, 198, 665.
- [11] M. Saliba, J. P. Correa-Baena, C. M. Wolff, M. Stollerfoht, N. Phung, S. Albrecht, D. Neher, A. Abate, *Chem. Mater.* **2018**, 30, 4193.
- [12] N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu, S. I. Seok, *Nat. Mater.* **2014**, 13, 897.
- [13] M. Saliba, T. Matsui, J. Y. Seo, K. Domanski, J. P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, M. Grätzel, *Energy Environ. Sci.* **2016**, 9, 1989.
- [14] M. Stollerfoht, C. M. Wolff, J. A. Márquez, S. Zhang, C. J. Hages, D. Rothhardt, S. Albrecht, P. L. Burn, P. Meredith, T. Unold, D. Neher, *Nat. Energy* **2018**, 3, 847.
- [15] L. Calió, S. Kazim, M. Grätzel, S. Ahmad, *Angew. Chem. Int. Ed.* **2016**, 55, 14522.
- [16] Z. Shariatinia, *Renewable Sustainable Energy Rev.* **2020**, 119, 109608.
- [17] C. H. Teh, R. Daik, E. L. Lim, C. C. Yap, M. A. Ibrahim, N. A. Ludin, K. Sopian, M. A. M. Teridi, *J. Mater. Chem. A* **2016**, 4, 15788.
- [18] J. Li, B. Lu, F. Niu, P. Zeng, X. Zhan, *Small Methods* **2018**, 2, 1800082.
- [19] X. Tong, F. Lin, J. Wu, Z. M. Wang, *Adv. Sci.* **2016**, 3, 1500201.
- [20] B. Li, Y. Cai, X. Tian, X. Liang, D. Li, Z. Zhang, S. Wang, K. Guo, Z. Liu, *J. Energy Chem.* **2021**, 62, 523.
- [21] S. Yang, H. Zhao, M. Wu, S. Yuan, Y. Han, Z. Liu, K. Guo, S. F. Liu, S. Yang, H. Zhao, S. Yuan, Y. Han, Z. Liu, S. Liu, M. Wu, K. Guo, *Sol. Energy Mater. Sol. Cells* **2019**, 201, 110052.
- [22] M. Wu, J. Li, R. Zhang, X. Tian, Z. Han, X. Lu, K. Guo, Z. Liu, Z. Wang, *Org. Lett.* **2018**, 20, 780.
- [23] K. Guo, M. Wu, S. Yang, Z. Wang, J. Li, X. Liang, F. Zhang, Z. Liu, Z. Wang, *Sol. RRL* **2019**, 3, 1800352.
- [24] T. Braukyla, R. Xia, M. Daskeviciene, T. Malinauskas, A. Gruodis, V. Jankauskas, Z. Fei, C. Momblona, C. Roldán-Carmona, P. J. Dyson, V. Getautis, M. K. Nazeeruddin, *Angew. Chem. Int. Ed.* **2019**, 58, 11266.
- [25] X. Liu, S. Ma, M. Mateen, P. Shi, C. Liu, Y. Ding, M. Cai, M. Guli, M. K. Nazeeruddin, S. Dai, *Sustainable Energy Fuels* **2020**, 4, 1875.
- [26] K. Rakstys, S. Paek, A. Drevilkauskaitė, H. Kanda, S. Daskeviciute, N. Shibayama, M. Daskeviciene, A. Gruodis, E. Kamarauskas, V. Jankauskas, V. Getautis, M. K. Nazeeruddin, *ACS Appl. Mater. Interfaces* **2020**, 12, 19710.
- [27] C. Hao, X. Zong, Y. Cheng, M. Zhao, M. Luo, Y. Zhang, S. Xue, *Sustainable Energy Fuels* **2021**, 5, 5548.
- [28] T. Qin, F. Wu, L. Zhu, W. Chi, Y. Zhang, Z. Yang, J. Zhao, Z. Chi, *Organic Electronics* **2022**, 100, 106325.
- [29] D. Y. Lee, G. Sivakumar, Manju, R. Misra, S. I. Seok, *ACS Appl. Mater. Interfaces* **2020**, 12, 28246.
- [30] S. Daskeviciute, C. Momblona, K. Rakstys, A. A. Sutanto, M. Daskeviciene, V. Jankauskas, A. Gruodis, G. Bubniene, V. Getautis, M. K. Nazeeruddin, *J. Mater. Chem. A* **2021**, 9, 301.
- [31] N. J. Jeon, H. Na, E. H. Jung, T. Y. Yang, Y. G. Lee, G. Kim, H. W. Shin, S. I. Seok, J. Lee, J. Seo, *Nat. Energy* **2018**, 3, 682.
- [32] J. Wang, H. Zhang, B. Wu, Z. Wang, Z. Sun, S. Xue, Y. Wu, A. Hagfeldt, M. Liang, *Angew. Chem., Int. Ed.* **2019**, 58, 15721.
- [33] E. Aydin, T. G. Allen, M. De Bastiani, L. Xu, J. Ávila, M. Salvador, E. Van Kerschaver, S. De Wolf, *Nat. Energy* **2020**, 5, 851.
- [34] T. Malinauskas, D. Tomkute-Luksiene, R. R. Sens, M. Daskeviciene, R. Send, H. Wonneberger, V. Jankauskas, I. Bruder, V. Getautis, *ACS Appl. Mater. Interfaces* **2015**, 7, 11107.
- [35] A. Matoliukstyte, E. Burbulis, J. V. Gražulevičius, V. Gaidelis, V. Jankauskas, *Synth. Met.* **2008**, 158, 462.
- [36] C. Igci, S. Paek, K. Rakstys, H. Kanda, N. Shibayama, V. Jankauskas, C. Roldán-Carmona, H. Kim, A. M. Asiri, M. K. Nazeeruddin, *Sol. RRL* **2020**, 4, 1.
- [37] J. Y. Feng, K. W. Lai, Y. S. Shue, A. Singh, C. H. P. Kumar, C. T. Li, W. T. Wu, J. T. Lin, C. W. Chu, C. C. Chang, C. Su, *J. Mater. Chem. A* **2019**, 7, 14209.
- [38] X. C. Li, Y. G. Tu, C. Meng, W. Song, T. Cheng, Y. T. Gong, J. Min, R. Zhu, W. Y. Lai, W. Huang, *ACS Appl. Mater. Interfaces* **2019**, 11, 45717.
- [39] N. Drigo, C. Roldán-Carmona, M. Franckevičius, K. H. Lin, R. Gegevičius, H. Kim, P. A. Schouwink, A. A. Sutanto, S. Olthof, M. Sohail, K. Meerholz, V. Gulbinas, C. Corminboeuf, S. Paek, M. K. Nazeeruddin, *J. Am. Chem. Soc.* **2020**, 142, 1792.
- [40] M. Daskeviciene, S. Paek, A. Magomedov, K. T. Cho, M. Saliba, A. Kizeleviciute, T. Malinauskas, A. Gruodis, V. Jankauskas, E. Kamarauskas, M. K. Nazeeruddin, V. Getautis, *J. Mater. Chem. C*, **2019**, 7, 2717.
- [41] D. Vaitukaityte, Z. Wang, T. Malinauskas, A. Magomedov, G. Bubniene, V. Jankauskas, V. Getautis, H. J. Snaith, *Adv. Mater.* **2018**, 30, 1803735.

Supporting Information

Molecular Engineering of Fluorene-Based Hole Transporting Materials for Efficient Perovskite Solar Cells

Aistė Jegorovė^{†,1}, Cristina Momblona^{‡,2}, Maryte Daskeviciene,¹ Artiom Magomedov,¹ Rimgailė Degutyte,³ Abdullah M. Asiri,⁴ Vyintas Jankauskas,⁵ Albertus Adrian Sutanto,² Hiroyuki Kanda,² Keith Brooks,² Nadja Klipfel,² Mohammad Khaja Nazeeruddin,^{2*} and Vytautas Getautis^{1*}

¹Department of Organic Chemistry, Kaunas University of Technology, Kaunas LT-50254, Lithuania.

²Group for Molecular Engineering of Functional Material, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1951 Sion, Switzerland.

³Department of Food Science and Technology, Kaunas University of Technology, Kaunas LT-50254, Lithuania.

⁴Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, P.O. Box 80203, 21589 Jeddah, Saudi Arabia.

⁵Institute of Chemical Physics, Vilnius University, Vilnius LT-10257, Lithuania.

[†]A.J. and [‡]C.M. contributed equally to this work.

*Corresponding authors: mdkhaja.nazeeruddin@epfl.ch; vytautas.getautis@ktu.lt.

General methods

Chemicals required for the synthesis were purchased from Sigma-Aldrich and TCI Europe and used as received without additional purification. 2,7-dibromo(9,9'-dialkyl) fluorenes was synthesized as previously reported ^[1-3]. New spirobifluorene and fluorene class compounds were synthesized following previously described procedures. ¹H NMR spectra were recorded at 400 MHz on a Bruker Avance III spectrometer, ¹³C NMR spectra were collected using the same instrument at 101 MHz. The chemical shifts, expressed in ppm, were relative to tetramethylsilane (TMS). All the experiments were performed at 25 °C. Mass spectra (MS) were recorded using the Waters SQ Detector 2 mass spectrometer. The samples were prepared by dissolving compound in the mixture of methanol/acetonitrile (ratio 1:1). Reactions were monitored by thin-layer chromatography on ALUGRAM SIL G/UV254 plates and developed with UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was used for column chromatography. Elemental analysis was performed with an Exeter Analytical CE-440 elemental analyzer, Model 440 C/H/N/.

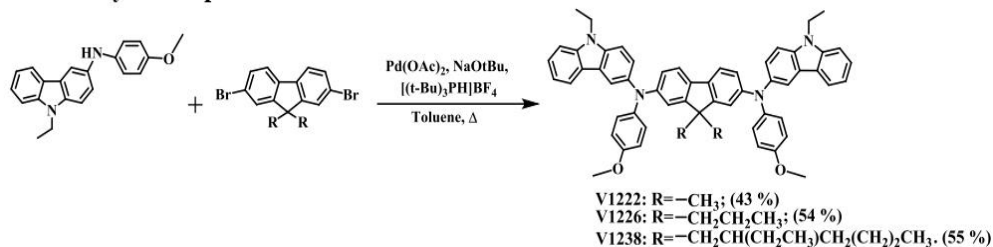
UV/VIS spectral analysis of the samples solutions (THF, 10⁻⁴ mol/l) was performed on a Perkin Elmer Lambda 35 UV / VIS spectrophotometer. The layer thickness of the solution is d = 10 mm. Diffraction grating crack width 2 nm. Spectral recording speed 2 nm / s. The wavelength λ is given in nm. The time-resolved fluorescence spectra of the samples solutions (THF, 10⁻⁵ mol/l) were recorded on a Edinburgh Instruments FLS920 light emission intensity spectrophotometer. Solutions of new compounds exposed to different wavelengths: materials **V1222** - 310 nm, **V1226** - 255 nm, **V1238** - 260 nm, **V1240** - 260 nm, compounds **V1257** - 310 nm, **V1258** - 255 nm, **V1267** - 260 nm, **V1269** - 260 nm. The layer thickness of the solution is d = 1 cm. The crack width of the diffraction grating is 2.5 nm. The wavelength λ is given in nm. Films of new compounds were exposed at 380 nm wavelength.

The transformations of thermal changes of target materials were recorded with a TA Instruments Q2000 differential scanning calorimeter in a nitrogen atmosphere. From the obtained thermal curves, the glass transition temperature of the materials is determined. Heating and cooling mode reaches 10 ° C / min. The destruction temperatures of the new compounds were recorded by TA Instruments Q50 by thermogravimetric analysis in a nitrogen atmosphere. The decomposition temperature of a compound is recorded when the weight loss is 5%. Heating mode 20 ° C / min.

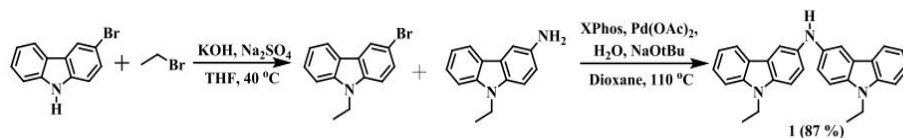
2,7-dibromo(9,9'-dialkyl)fluorenes were synthesized using KO^tBu as a base (15 eq), DMSO as a solvent (15 mL/eq) at 0°C for 12 h. Spectral data is in agreement with the values reported in the literature.^[4–6]

9-ethyl-N-(4-methoxyphenyl)-9*H*-carbazol-3-amine and compound **1** was synthesized by Buchwald-Hartwig amination using Pd catalyst. Spectral data is in agreement with the values reported in the literature^[7].

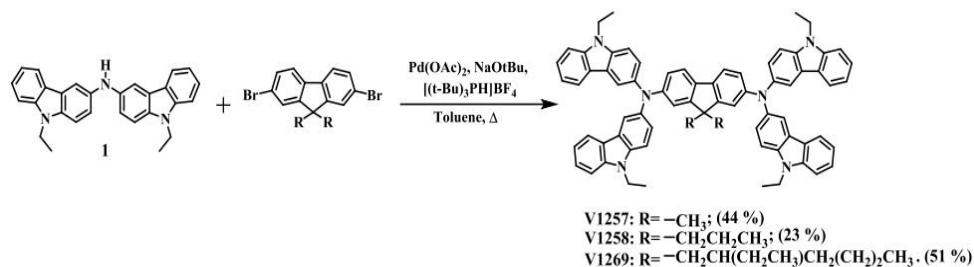
Detailed synthetic procedures



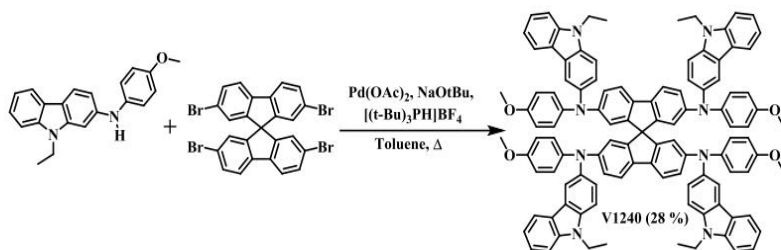
Scheme S1. Synthesis of fluorene derivatives with carbazolyl and methoxyphenyl fragments.



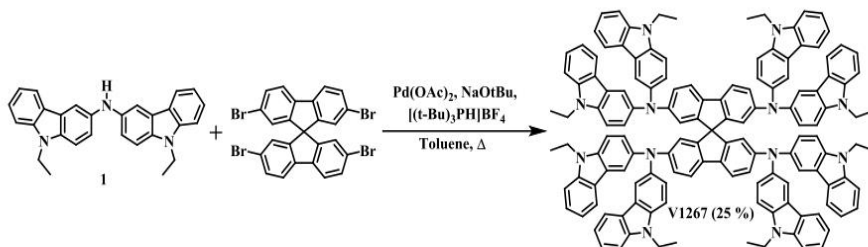
Scheme S2. Synthesis of bis(9-ethyl-9*H*-carbazol-3-yl)amine (**1**).



Scheme S3. Synthesis of fluorene derivatives with carbazolyl chromophores.

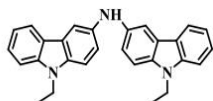


Scheme S4. Synthesis of Spiro-OMeTAD analogue **V1240**.



Scheme S5. Synthesis of Spiro-OMeTAD analogue **V1267**.

Bis(9-ethyl-9H-carbazol-3-yl)amine (**1**)



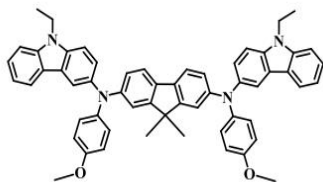
Anhydrous dioxane (44 mL) with few drops of distilled water (0.5 mmol) was purged with Argon for 20 minutes. After that, the temperature was raised to 80 °C, Pd acetate (0.06 g, 0.2 mmol) and XPhos (0.64 g, 1 mmol) were added. The mixture was stirred for 1.5 minute and temperature was raised to 110 °C. Once the temperature reached 110 °C, 3-amino-9-ethylcarbazole (11.8 g, 59 mmol), 3-bromo-9-ethylcarbazole (**2**) (11.99 g, 43 mmol) and sodium *tert*-butoxide (5.91 g, 61 mmol) were added and stirred for 45 minutes (TLC control, acetone/hexane 1:4). After that, reaction mixture was extracted with ethyl acetate, organic layer dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The crude product was purified by column chromatography (THF/hexane 3:22 v:v), R_f=0.15 and light orange brown solid was collected as a final product. Yield 14.24 g, 87 %.

¹H NMR (400 MHz, THF-*d*₈) δ: 7.94 (d, *J* = 7.75 Hz, 2H), 7.81 (s, 2H), 7.42–7.30 (m, 6H), 7.24 (d, *J* = 8.62 Hz, 2H), 7.06 (t, *J* = 7.35 Hz, 2H), 6.89 (s, 1H), 4.37 (q, *J* = 7.12 Hz, 4H), 1.38 (t, *J* = 7.12 Hz, 6H).

¹³C NMR (101 MHz, THF-*d*₈) δ: 141.6, 139.7, 136.4, 126.1, 124.8, 124.0, 121.1, 119.4, 118.9, 109.9, 109.3, 38.18, 14.27.

Anal. Calcd. For: C₂₈H₂₅N₃: C 83.34; H 6.24; N 10.41; found: C 83.29; H 6.31; N 10.24.

***N,N*-bis(9-ethyl-9*H*-carbazol-3-yl)-*N,N*-bis(4-methoxyphenyl)-9,9-dimethyl-9*H*-fluorene-2,7-yl-diamine (V1222)**



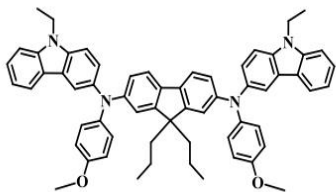
Reaction mixture of 2,7-dibromo-9,9-dimethyl-9*H*-fluorene (0.77 g, 2 mmol, 1 eq.), 9-ethyl-*N*-(4-methoxyphenyl)-9*H*-carbazol-3-amine (2.08 g, 6 mmol, 3 eq.) and anhydrous toluene (22.4 mL) was purged with Argon for 30 minutes. Afterwards, palladium (II) acetate (0.05 g, 0.2 mmol, 0.055 eq.) and tri-*tert*-butylphosphonium tetrafluoroborate (0.14 g, 0.4 mmol, 0.11 eq) was added and stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (0.63 g, 6 mmol, 3 eq.) were added and the mixture was heated at reflux for 5 hours (TLC control, acetone/hexane 1:4). After cooling to room temperature, reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried by Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: CHCl₃/*n*-hexane 8:17 v:v) R_f=0.64. Final product was dissolved in THF and precipitated from methanol to collect the final product as a light greenish yellow solid powder. Yield 0.79 g, 43 %.

¹H NMR (400 MHz, THF-*d*₈) δ: 7.94 (d, *J* = 7.74 Hz, 2H), 7.89 (s, 2H), 7.46–7.32 (m, 8H), 7.25 (d, *J* = 8.07 Hz, 2H), 7.13–7.03 (m, 8H), 6.85 (d, *J* = 8.26 Hz, 2H), 6.80 (d, *J* = 8.88 Hz, 4H), 4.39 (q, *J* = 7.05 Hz, 4H), 3.73 (s, 6H), 1.41 (t, *J* = 7.05 Hz, 6H), 1.26 (s, 6H).

^{13}C NMR (101 MHz, THF- d_8) δ : 155.6, 141.7, 138.0, 126.5, 125.0, 124.0, 121.3, 121.1, 120.3, 119.5, 116.3, 115.4, 110.2, 109.5, 55.7, 47.5, 38.3, 27.6, 14.3.

Anal. Calcd. For $\text{C}_{57}\text{H}_{50}\text{N}_4\text{O}_2$: C 83.18; H 6.12; N 6.81; O 3.89; found: C 83.25; H 6.08; N 6.79. $\text{C}_{57}\text{H}_{50}\text{N}_4\text{O}_2[\text{M}^+]$ exact mass = 822.39, MS (ESI) = 822.77.

***N,N*-bis(9-ethyl-9*H*-carbazol-3-yl)-*N,N*-bis(4-methoxyphenyl)-9,9-dipropyl-9*H*-fluorene-2,7-yl-diamine (V1226)**



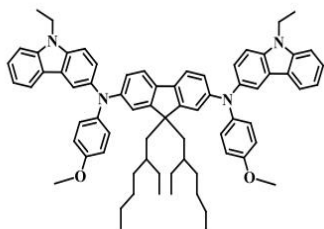
Reaction mixture of 2,7-dibromo-9,9-dipropyl-9*H*-fluorene (0.72 g, 1 mmol), 9-ethyl-*N*-(4-methoxyphenyl)-9*H*-carbazol-3-amine (1.53 g, 4 mmol) and anhydrous toluene (12 mL) was purged with Argon for 30 minutes. Afterwards, palladium (II) acetate (0.05 g, 0.2 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.1 g, 0.3 mmol) was added and stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (0.46 g, 4 mmol) were added and the mixture was heated at reflux for 5 hours (TLC control, acetone/hexane 1:4). After cooling to room temperature, reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried by Na_2SO_4 , filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: CHCl_3/n -hexane 8:17 v:v) R_f =0.70. Final product was dissolved in THF and precipitated from ethanol to collect the final product as a light greenish yellow solid powder. Yield 0.84 g, 54 %.

^1H NMR (400 MHz, Acetone- d_6) δ : 7.96 (d, J = 7.76 Hz, 2H), 7.90 (s, 2H), 7.54–7.40 (m, 8H), 7.23 (m, 2H), 7.15–7.02 (m, 8H), 6.94–6.75 (m, 6H), 4.44 (q, J = 6.96 Hz, 4H), 3.77 (s, 6H), 1.70–1.60 (m, 4H), 1.40 (t, J = 6.96 Hz, 6H), 0.85–0.70 (m, 4H), 0.64 (t, J = 7.14 Hz, 6H).

^{13}C NMR (101 MHz, Acetone- d_6) δ : 156.5, 152.3, 149.1, 141.4, 137.6, 135.4, 126.7, 125.3, 124.5, 123.4, 121.2, 120.1, 119.5, 117.8, 116.9, 115.4, 110.4, 109.7, 55.7, 55.6, 43.4, 38.1, 18.2, 14.9, 14.2.

Anal. Calcd. For $C_{61}H_{58}N_4O_2$: C 83.34; H 6.65; N 6.37; O 3.64; found: C 83.4; H 6.61; N 6.21.
 $C_{61}H_{58}N_4O_2[M^+]$ exact mass = 878.46, MS (ESI) = 878.83.

***N,N*-bis(9-ethyl-9*H*-carbazol-3-yl)-*N,N*-bis(4-methoxyphenyl)-9,9-bis(2-ethylhexyl)-9*H*-fluorene-2,7-yl-diamine (V1238)**



Reaction mixture of 2,7-dibromo-9,9-bis(2-ethylhexyl)-9*H*-fluorene (0.97 g, 1 mmol), 9-ethyl-*N*-(4-methoxyphenyl)-9*H*-carbazol-3-amine (1.69 g, 5 mmol) and anhydrous toluene (17 mL) was purged with Ar for 30 minutes. Afterwards, palladium (II) acetate (0.05 g, 0.2 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.12 g, 0.4 mmol) was added and stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (0.51 g, 5 mmol) were added and the mixture was heated at reflux for 5 hours (TLC control, acetone/hexane 1:4). After cooling to room temperature, reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried by Na_2SO_4 , filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: acetone/*n*-hexane 4:21 v:v) R_f =0.52. Final product was dissolved in THF and precipitated from methanol to collect the final product as a light greenish yellow solid powder. Yield 1.01 g, 55 %.

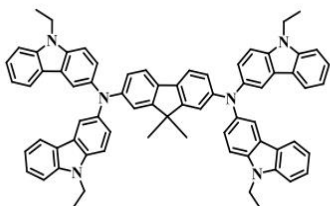
1H NMR (400 MHz, Acetone- d_6) δ : 7.96 (d, J = 7.76 Hz, 2H); 7.90–7.83 (m, 2H); 7.57–7.49 (m, 6H); 7.43 (t, J = 7.65 Hz, 2H); 7.30–7.21 (m, 2H); 7.17–6.80 (m, 14H); 4.46 (q, J = 6.94 Hz, 4H); 3.78 (s, 6H); 1.81–1.67 (m, 4H); 1.41 (t, J = 6.94 Hz, 6H); 1.13–0.82 (m, 16H); 0.78 (t, J = 6.38 Hz, 6H); 0.74–0.64 (m, 2H); 0.58 (t, J = 7.03 Hz, 6H).

^{13}C NMR (101 MHz, Acetone- d_6) δ : 156.4; 156.3; 156.2; 152.3; 152.2; 148.6; 141.6; 137.8; 137.7; 135.9; 135.6; 126.7; 126.5; 126.3; 126.0; 125.6; 125.5; 125.4; 124.6; 124.5; 123.4; 122.6;

121.9; 121.5; 121.1; 120.1; 119.5; 119.2; 118.6; 118.4; 118.3; 118.13; 118.08; 115.4; 110.5; 109.8; 55.7; 55.5; 45.4; 38.1; 35.48; 35.46; 34.7; 34.6; 23.7; 14.6; 14.5; 14.3; 14.2; 10.9; 10.8.

Anal. Calcd. For $C_{71}H_{78}N_4O_2$: C 83.65; H 7.71; N 5.50; O 3.14; found: C 83.61; H 7.58; N 5.36. $C_{71}H_{78}N_4O_2[M^+]$ exact mass = 1018.61, MS (ESI) = 1019.15.

***N,N,N,N*-tetra(9-ethyl-9*H*-carbazol-3-yl)-9,9-dimethyl-9*H*-fluoren-2,7-yl-diamine (V1257)**



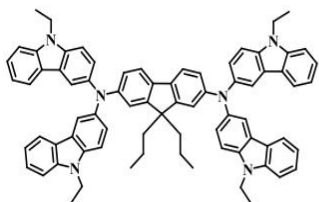
Reaction mixture of 2,7-dibromo-9,9-dimethyl-9*H*-fluorene (0.9 g, 2 mmol), bis(9-ethyl-9*H*-carbazol-3-yl) amine (3.09 g, 7 mmol) and anhydrous toluene (20 mL) was purged with Argon for 30 minutes. Afterwards, palladium (II) acetate (0.06 g, 0.2 mmol) and tri-tert-butylphosphonium tetrafluoroborate (0.16 g, 0.5 mmol) was added and stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (0.73 g, 7 mmol) were added and the mixture was heated at reflux for 5 hours (TLC control, acetone/hexane 1:4). After cooling to room temperature, reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried by Na_2SO_4 , filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 3:22 v:v) R_f =0.41. Final product was dissolved in THF and precipitated from methanol to collect the final product as a light greenish yellow solid powder. Yield 1.12 g, 44 %.

1H NMR (400 MHz, THF- d_8) δ : 7.99 (s, 4H), 7.93 (d, J = 7.8 Hz, 4H), 7.48–7.29 (m, 18H), 7.18 (s, 2H), 7.06 (t, J = 7.4 Hz, 4H), 6.92 (d, J = 8.42 Hz, 2H), 4.39 (q, J = 7.15 Hz, 8H), 1.41 (t, J = 7.15 Hz, 12H), 1.26 (s, 6H).

^{13}C NMR (101 MHz, THF- d_8) δ : 155.4, 149.8, 142.1, 141.5, 137.7, 133.0, 126.3, 125.6, 124.9, 123.9, 121.3, 120.7, 120.1, 119.3, 118.9, 115.9, 110.1, 109.3, 47.36, 38.14, 27.5, 14.1.

Anal. Calcd. For $C_{71}H_{60}N_6$: C 85.51; H 6.06; N 8.43; found: C 85.41; H 6.03; N 8.26. $C_{71}H_{60}N_6[M^+]$ exact mass = 996.49, MS (ESI) = 996.99.

***N,N,N,N*-Tetra(9-ethyl-9*H*-carbazol-3-yl)-9,9-dipropyl-9*H*-fluorene-2,7-yl-diamine
(V1258)**



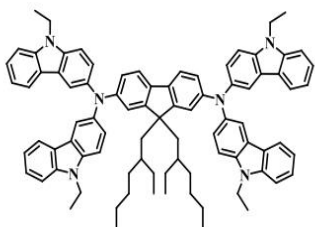
Reaction mixture of 2,7-dibromo-9,9-dipropyl-9*H*-fluorene (0.9 g, 2 mmol), bis(9-ethyl-9*H*-carbazol-3-yl)amine (2.66 g, 6 mmol) and anhydrous toluene (18 mL) was purged with Argon for 30 minutes. Afterwards, palladium (II) acetate (0.05 g, 0.2 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.13 g, 0.4 mmol) was added and stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (0.63 g, 6 mmol) were added and the mixture was heated at reflux for 5 hours (TLC control, acetone/hexane 1:4). After cooling to room temperature, reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried by Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: acetone/*n*-hexane 1:4 v:v) *R*_f=0.48. Final product was dissolved in THF and precipitated from methanol to collect the final product as a light greenish yellow solid powder. Yield 0.61 g, 23 %.

¹H NMR (400 MHz, Acetone-*d*₆) δ: 8.00 (s, 4H); 7.94 (d, *J* = 7.78 Hz, 4H); 7.52 (d, *J* = 8.25 Hz, 4H); 7.48–7.37 (m, 10H); 7.30 (d, *J* = 8.62 Hz, 4H); 7.16 (s, 2H); 7.09 (t, *J* = 7.50 Hz, 4H); 6.87 (d, *J* = 7.97 Hz, 2H); 4.43 (q, *J* = 7.08 Hz, 8H); 1.61–1.51 (m, 4H); 1.40 (t, *J* = 7.08 Hz, 12H); 0.87–0.77 (m, 4H); 0.63 (t, *J* = 7.22 Hz, 6H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ: 152.2, 141.4, 137.5, 126.6, 125.5, 124.5, 123.5, 121.2, 120.8, 120.0, 119.4, 117.7, 116.5, 110.4, 109.7, 55.6, 43.4, 38.1, 18.2, 15.0, 14.2.

Anal. Calcd. For $C_{75}H_{68}N_6$: C 85.52; H 6.51; N 7.98; found: C 85.48; H 6.47; N 7.85.
 $C_{75}H_{68}N_6[M^+]$ exact mass = 1052.55, MS (ESI) = 878.83.

***N,N,N,N*-tetra(9-ethyl-9*H*-carbazol-3-yl)-9,9-bis(2-ethylhexyl)-9*H*-fluoren-2,7-yl-diamine
(V1269)**



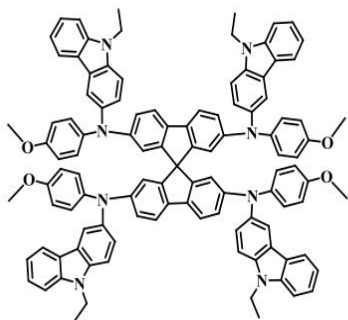
Reaction mixture of 2,7-dibromo-9,9-bis(2-ethylhexyl)-9*H*-fluorene (0.75 g, 1 mmol), bis(9-ethyl-9*H*-carbazol-3-yl) amine (1.65 g, 4 mmol) and anhydrous toluene (14 mL) was purged with Argon for 30 minutes. Afterwards, palladium (II) acetate (0.05 g, 0.2 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.12 g, 0.4 mmol) was added and stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (0.4 g, 4 mmol) were added and the mixture was heated at reflux for 5 hours (TLC control, acetone/hexane 1:4). After cooling to room temperature, reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried by Na_2SO_4 , filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 2:23 v:v) R_f =0.53. Final product was dissolved in THF and precipitated from methanol to collect the final product as a light greenish yellow solid powder. Yield 0.85 g, 51 %.

1H NMR (400 MHz, Acetone- d_6) δ : 8.01–7.89 (m, 8H); 7.57–7.47 (m, 10H); 7.45–7.31 (m, 8H); 7.15–7.05 (m, 6H); 6.99 (d, J = 7.79 Hz, 2H); 4.46 (q, J = 6.91 Hz, 8H); 1.75–1.63 (m, 4H); 1.42 (t, J = 6.91 Hz, 12H); 1.14–0.89 (m, 16H); 0.83–0.71 (m, 8H); 0.61 (t, J = 7.32 Hz, 6H).

^{13}C NMR (101 MHz, Acetone- d_6) δ : 152.37; 152.31; 149.4; 142.3; 141.6; 137.7; 137.6; 136.0; 135.7; 126.7; 125.7; 125.6; 125.4; 124.68; 124.66; 124.6; 123.6; 122.4; 121.7; 121.3; 120.2; 119.56; 119.53; 119.50; 118.9; 118.3; 118.1; 118.0; 117.7; 110.5; 109.9; 55.6; 45.6; 38.2; 35.67; 34.8; 27.9; 27.7; 23.8; 14.7; 14.3; 11.1.

Anal. Calcd. For $\text{C}_{85}\text{H}_{88}\text{N}_6$: C 85.53; H 7.43; N 7.04; found: C 85.50; H 7.39; N 6.91.
 $\text{C}_{85}\text{H}_{88}\text{N}_6[\text{M}^+]$ exact mass = 1193.42, MS (ESI) = 1192.71.

***N,N,N,N*-tetrakis(9-ethyl-9*H*-carbazol-3-yl)-*N,N,N,N*-tetrakis(4-methoxyphenyl)-9,9-spirobi[fluorene]-2,2',7,7'-yl-tetraamine (V1240)**



Reaction mixture of 2,2',7,7'-tetrabromo-9,9'-spirobi-[9*H*-fluorene] (0.99 g, 1 mmol), 9-ethyl-*N*-(4-methoxyphenyl)-9*H*-carbazol-3-amine (2.98 g, 9 mmol) and anhydrous toluene (21 mL) was purged with Argon for 30 minutes. Afterwards, palladium (II) acetate (0.05 g, 0.2 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.12 g, 0.4 mmol) was added and stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (0.9 g, 9 mmol) were added and the mixture was heated at reflux for 24 hours (TLC control, acetone/hexane 1:4). After cooling to room temperature, reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried by Na_2SO_4 , filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/toluene/*n*-hexane 1:1:3 v:v:v) $R_f=0.21$. Final product was dissolved in THF and precipitated from ethanol to collect the final product as a light greenish yellow solid powder. Yield 0.9 g, 28 %.

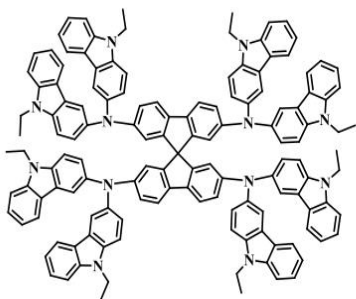
^1H NMR (400 MHz, THF- d_8) δ : 7.97 (d, $J = 7.76$ Hz, 4H); 7.83 (s, 4H); 7.46 (d, $J = 8.21$ Hz, 4H); 7.43–7.35 (m, 8H); 7.33 (d, $J = 8.27$ Hz, 4H); 7.21 (d, $J = 8.63$ Hz, 4H); 7.10 (t, $J = 7.42$

Hz, 4H); 7.03 (d, $J = 8.91$ Hz, 8H); 6.84–6.76 (m, 12H); 6.68 (s, 4H); 4.42 (q, $J = 7.05$ Hz, 8H); 3.76 (s, 12H); 1.43 (t, $J = 7.05$ Hz, 12H).

^{13}C NMR (101 MHz, THF- d_8) δ : 155.5; 150.4; 148.1; 142.4; 140.7; 140.4; 137.0; 135.0; 125.6; 125.0; 124.7; 124.0; 123.0; 121.5; 120.6; 119.6; 118.6; 117.6; 116.7; 114.4; 109.3; 108.5; 54.8; 37.4; 13.4.

Anal. Calcd. For $\text{C}_{109}\text{H}_{88}\text{N}_8\text{O}_4$: C 83.18; H 5.64; N 7.12; O 4.07; found: C 83.14; H 5.57; N 7.08. $\text{C}_{109}\text{H}_{88}\text{N}_8\text{O}_4[\text{M}^+]$ exact mass = 1572.69, MS (ESI) = 1573.69.

***N,N,N,N,N,N,N,N*-octakis(9-ethyl-9*H*-carbazol-3-yl)-*N,N,N,N*-9,9-spirobi[fluorene]-2,2',7,7'-yl-tetraamine (V1267)**



Reaction mixture of 2,2',7,7'-tetrabromo-9,9'-spirobi-[9*H*-fluorene] (0.85 g, 1 mmol), bis(9-ethyl-9*H*-carbazol-3-yl)amine (4.33 g, 10 mmol) and anhydrous toluene (21 mL) was purged with Argon for 30 minutes. Afterwards, palladium (II) acetate (0.05 g, 0.2 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.12 g, 0.4 mmol) was added and stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (0.96 g, 10 mmol) were added and the mixture was heated at reflux for 24 hours (TLC control, acetone/hexane 1:4). After cooling to room temperature, reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried by Na_2SO_4 , filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/toluene/*n*-hexane 5:8:12 v:v:v) R_f =0.62. Final product was dissolved in THF and precipitated from ethanol to collect the final product as a light greenish yellow solid powder. Yield 0.66 g, 25 %.

^1H NMR (400 MHz, Toluene- d_8) δ : 8.28–8.23 (m, 8H); 7.85–7.79 (m, 8H); 7.68 – 7.59 (m, 8H); 7.44 (d, $J = 8.3$ Hz, 4H); 7.38–7.27 (m, 16H); 7.17–7.12 (m, 4H); 7.08–7.04 (m, 6H); 6.99–6.96 (m, 6H); 3.74 (q, $J = 7.0$ Hz, 16H); 0.97 (t, $J = 7.0$ Hz, 24H).

^{13}C NMR (101 MHz, Toluene- d_8) δ : 152.0; 148.8; 142.3; 142.1; 140.9; 137.0; 125.9; 124.6; 123.4; 121.6; 121.01; 119.9; 119.0; 118.0; 117.9; 117.8; 117.6; 109.4; 108.6; 37.3; 11.0.

Anal. Calcd. For $\text{C}_{137}\text{H}_{108}\text{N}_{12}$: C 85.59; H 5.66; N 8.64; found: C 85.53; H 5.51; N 8.56.
 $\text{C}_{137}\text{H}_{108}\text{N}_{12}[\text{M}^+]$ exact mass = 1920.88, MS (ESI) = 1920.78.

Cite this: *RSC Adv.*, 2024, 14, 2975

New fluorene-based bipolar charge transporting materials†

Aistė Jegorovė,^{*a} Marytė Daškevičienė,^a Kristina Kantminienė,^b
Vy gintas Jankauskas,^c Romualdas Jonas Čepas,^{b,c} Alytis Gruodis,^c
Vytautas Getautis^{b,a} and Kristijonas Genevičius^c

Air-stable and solution-processable fluorene-based bipolar charge transporting materials (CTMs) were designed, synthesized, and analyzed. These CTMs feature anthraquinone, 9-fluorenone, and 9-dicyanofluorenylidine groups and exhibit good film formation properties for solvent processing. Quantum chemistry simulations and optical absorption measurements proved that several stable conformers and charge transfer complexes form inside the molecules. Hole mobilities in CTMs were around 10^{-4} to 10^{-5} cm² V⁻¹ s⁻¹, while electron mobility in compounds with anthraquinone and 9-dicyanofluorenylidine groups was approximately one order of magnitude lower.

Received 6th November 2023
Accepted 10th January 2024

DOI: 10.1039/d3ra07583d

rsc.li/rsc-advances

Introduction

The innovative design of organic compounds and the tuning of their practical properties has become an important tool of materials science used to address major contemporary global issues, including the energy crisis and environmental impact. Therefore, the synthesis of new organic functional molecules and their adjustment for high performance materials has been gaining considerable attention in recent years. In the last few decades, the development of organic compounds as active components of electronic and optoelectronic devices, such as organic solar cells (OSCs),^{1,2} dye-sensitized solar cells (DSCs),³ organic field-effect transistors (OFET),^{4–6} organic light-emitting diodes (OLEDs),^{7,8} and organic photorefractive devices⁹ has contributed to a significant breakthrough in their technological applications and expanded fundamental research knowledge that could be used for future scientific and technological advancement.

Electronic or optoelectronic devices that employ organic materials as active elements benefit from the important advantages of organic materials, such as their potentially low cost and light mass as well as the ability to form thin-film large-surface-area flexible devices. The first industrial-scale application of organic semiconductors was xerography.¹⁰ Since then, charge transporting materials have played a significant role in

many of the technologies that have evolved from xerography.¹¹ Although an extensive data on hole- or electron-transporting materials have been reported in scientific literature, molecules capable of transporting both holes and electrons have received much less attention.¹²

Different strategies have been implemented to achieve bipolar behaviour of organic materials for electronic and optoelectronic applications. Methods used to ensure bipolarity include layered heterostructure, interpenetrating network, and charge transfer complex creation.^{13–16} Several disadvantages are associated with the first two of these methods, such as the increased complexity of the manufactured device; the higher probability of occurrence of defect points or nonuniformity of the layer owing to formed defective charge transfer complexes, and the possible long-term instability. In addition, it is well known that the formation of charge transfer complexes significantly reduces the charge mobility of one of the components used,^{11,17} so achieving balance between the mobility of electrons and holes in the layer becomes a challenging issue. Therefore, a more reasonable approach toward bipolarity of organic materials is to design the bipolar charge transporting material (CTM) as a single compound. Thus, utilization of a bipolar material reduces both the number of mixed materials and helps maintain device stability. Additionally, it is technologically advantageous for such materials to be air-operable and soluble in common organic solvents since low-cost organic electronic or optoelectronic devices require material deposition *via* solution processes instead of expensive vacuum thermal deposition.

However, the reported number of single-component air-stable and soluble bipolar CTMs capable of transporting both carrier types is limited despite the obvious advantages of such molecules. Aso *et al.* achieved bipolar transport by attaching a hole-transporting oligothiophene unit to the fullerene core.¹⁸

^aDepartment of Organic Chemistry, Kaunas University of Technology, Radvilėnų pl. 19, Kaunas, 50254, Lithuania

^bDepartment of Physical and Inorganic Chemistry, Kaunas University of Technology, Radvilėnų pl. 19, Kaunas, 50254, Lithuania

^cInstitute of Chemical Physics, Vilnius University, Saulėtekio al. 3, Vilnius 10257, Lithuania. E-mail: romualdas.cepas@ff.vu.lt

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3ra07583d>

Several other fullerene derivatives bearing, for example, dendritic oligothiophene side chains,¹⁹ oligophenyleneethynyls,²⁰ thioxanthenes,²¹ hydrazones,^{22,23} or hexa-*peri*-hexabenzocoronene²⁴ have also been shown to exhibit bipolar behaviour, though with moderate charge-carrier mobilities. These compounds have quite complex structures and require expensive starting materials and/or elaborate multistep syntheses. Fullerene derivatives widely used as acceptors in OSCs are associated with poor absorption, high cost, and insufficient stability. As an alternative, bipolar small molecule acceptors based on the fused terthieno[3,2-*b*]thiophene or benzodithiophene donor core and various electron-withdrawing end groups have been tested in OSCs.^{25,26}

Various small molecule donor materials incorporating diketopyrrolopyrrole fragment in their structure have been designed and synthesized for solution-processed optoelectronic devices.^{27–33} Imide derivatives are another successful class of materials used for bipolar CTMs.^{34,35} The carbazole moiety, because of its electron donating ability, is a convenient donor component of bipolar CTMs, while triazine, cyano, pyridine, phosphine oxide, *etc.* are used as acceptor fragments.³⁶ Velasco *et al.* investigated stable long-lived organic carbazole-based radical adducts as an electron donor-acceptor system with bipolar charge transport behaviour. High electron and hole mobilities up to 10^{-2} and 10^{-3} cm² V⁻¹ s⁻¹, respectively, were achieved.^{37,38} Kim *et al.* reported the synthesis of the bipolar hosts bearing 9,9-bis(9-alkylcarbazole)thioxanthene-*S,S*-dioxide moiety for application in white organic light emitting diodes. The thioxanthene-*S,S*-dioxide moiety possesses good electron-transporting ability, while the bis-ethylhexyl-, octyl-, dodecyl- or heptadecanycarbazole moieties have good hole-transporting ability.³⁹

Recently, we designed and synthesized air-stable and solution-processable tetracarboxydiimide-based bipolar CTMs, bearing electron-transporting 1,4,5,8-naphthalene- or 3,4,9,10-perylenetetracarboxydiimide cores with attached 1-phenyl-1,2,3,4-tetrahydroquinoline moieties as end-capping hole-

transporting groups in a straightforward and simple manner without the need for advanced synthetic procedures, expensive catalysts or sensitive reagents.⁴⁰

Generally, soluble and air-stable bipolar CTMs have quite complex structures and require expensive starting materials and/or elaborate multistep synthesis. In this work, we have designed and synthesized air-stable and solution-processable fluorine-based bipolar materials **V1393**, **V1421**, **V1457**, **V1458**, **V1484**, and **V1485** (Fig. 1). These CTMs were obtained from inexpensive starting materials through simple reactions and possess electron transporting anthraquinone, 9-fluorenone, or 9-dicyanofluorenylidine with attached carbazolyl electron-donating moieties. The optical, thermal, and charge carrier transport properties of the synthesized CTMs were studied. The existence of possible conformers and excitation energies were calculated by the means of quantum chemistry simulations.

Results and discussion

Target bipolar molecules were synthesized *via* the synthetic route depicted in Scheme 1. The precursors (side-amines) were synthesized by coupling 3-bromo-9-ethylcarbazole with 2-aminoanthraquinone and 2-amino-9*H*-fluorenone. The target compounds **V1393**, **V1421**, **V1457**, and **V1458** were synthesized under Buchwald–Hartwig amination reaction conditions using a central fluorene-based core as the starting material. The dicyanofluorenylidine derivatives **V1484** and **V1485** were synthesized by modifying the keto group to malononitrile by Knoevenagel condensation in basic medium.

The chemical structures of the synthesized compounds were verified by NMR spectroscopy, mass spectrometry, elemental analysis, and infrared spectroscopy data. A detailed description of the synthetic procedures and analysis is presented in the ESI†

Thermal stability of new bipolar molecules was evaluated by thermogravimetric analysis (TGA) in nitrogen atmosphere (Fig. 2). As seen from the data presented in Table 1 and Fig. 2, all

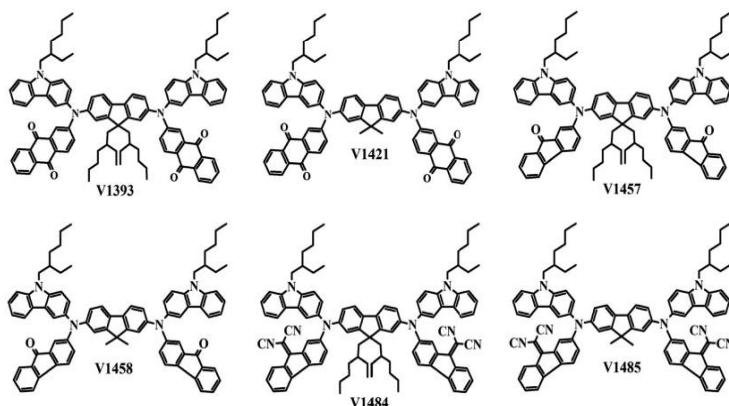
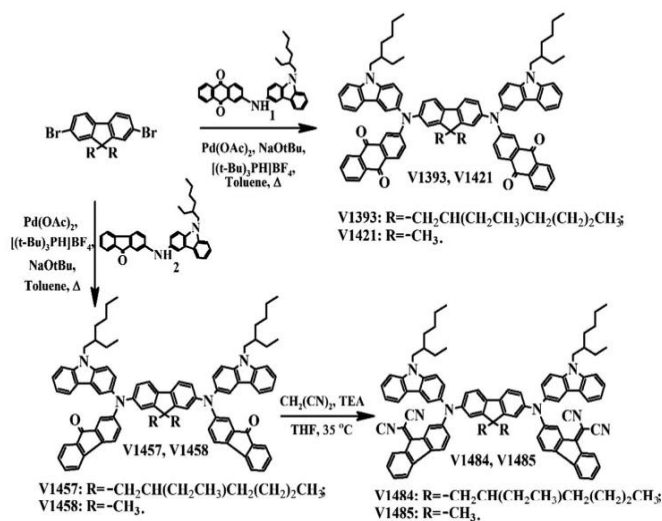


Fig. 1 Chemical structures of the synthesized bipolar compounds bearing different structural units.



Scheme 1 Synthesis of new fluorene-based bipolar compounds V1393, V1421, V1457, V1458, V1484, and V1485.

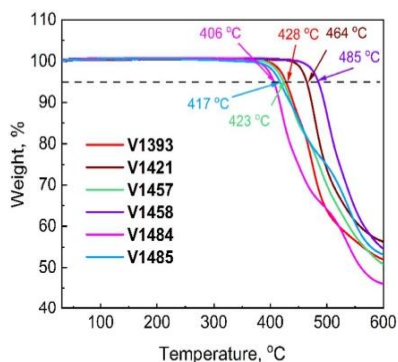


Fig. 2 TGA curves of new bipolar molecules.

bipolar compounds are thermally stable at temperatures higher than 400°C that is well above operating temperatures of most electronic devices.

The results of differential scanning calorimetry (DSC) measurements are shown in Fig. 3. According to the DSC scans, the glass transition temperatures (T_g) were observed at 109 and 153°C for V1393 and V1421, respectively. Notably, the T_g of V1457 and V1458 are lower than those of their analogues with anthraquinone moieties (92°C for V1457 and 133°C for V1458). The glass transition temperatures increased when the cyano groups were incorporated into the molecules (112°C for V1484 and 161°C for V1485). Furthermore, as expected, all materials with longer alkyl side chains demonstrated lower glass transition temperatures than those of the ones with shorter alkyl

chains. No endothermic peaks were observed during two heating cycles, what proves that all new materials are amorphous. It is preferable that new bipolar molecules would have an amorphous state in order to obtain good quality films.

For obtaining more information about electronic structure, quantum chemistry simulations of the molecular structure and several most probable conformers as well as dimers were performed using Gaussian 16 software.⁴¹ The density functional (DFT) Cam-B3LYP method and the 6-31G (d) basis set supplemented with polarization functions (d,p) were used for ground state optimization. Solvation effects were not considered in all cases. The list of two most probable molecular conformations is presented in the ESI, Table S1† and xy projections are in Fig. S2–S4.† Generally, total molecular symmetry is absent in the analyzed structures, but in several cases partial symmetry (or quasi-symmetry according to central fluorene unit) could be established (for example, V1421b, V1458b, and V1485b). Substituents are oriented in a chaotic manner, and large number of different conformers could be obtained. The population of low-lying excited molecular states S_1 and S_2 could be realized using the partially allowed transitions $S_0 \rightarrow S_n$, $n = 1, 2$ (Table S2†). The parameters of transition between MO (which are related to the population of “spectroscopic” states S_n , $n = 1, 2$) are presented in the ESI, Table S3.† In all cases, the dominant and most significant electron jump is provided between HOMO and LUMO. Spatial distributions of electron density (for the HOMO-1, HOMO, LUMO and LUMO+1 of each compound) are presented in the ESI, Tables S4–S6.† Generally, electron transition between HOMO and LUMO corresponds to the charge redistribution between the core (fluorene) and substituents (for example, anthraquinone). In case of both conformers of V1421 and V1393, by population of the lowest excited state, charge

Table 1 Thermal, optical, and photophysical properties of the bipolar compounds

Compound	T_g^a [°C]	T_{d5}^a [°C]	λ_{abs}^b [nm]	I_p^c [eV]	HOMO ^d [eV]	LUMO ^e [eV]	μ_{hole}^f [cm ² V ⁻¹ s ⁻¹]	μ_{elec}^g [cm ² V ⁻¹ s ⁻¹]
V1393	109	428	311, 355, 512	5.18	5.38	3.85	2.6×10^{-7}	4.6×10^{-9}
V1421	153	464	311, 352, 514	5.21	5.51	4.0	1.4×10^{-7}	1.1×10^{-9}
V1457	92	423	378, 534	5.02	5.34	3.97	3.9×10^{-7}	—
V1458	133	485	377, 537	5.02	5.46	4.09	9.2×10^{-8}	—
V1484	112	406	337, 346, 760	5.18	5.54	4.16	1.2×10^{-7}	1.0×10^{-8}
V1485	161	417	337, 750	5.16	5.42	4.09	2.8×10^{-8}	3.5×10^{-9}

^a Glass transition (T_g) and 5% weight loss (T_{d5}) temperatures recorded from DSC and TGA, respectively (10 °C min⁻¹, N₂ atmosphere). ^b UV-vis spectra were measured from thin layers. ^c Ionization energies of the films were measured using PESA. ^d HOMO energy levels were estimated from the CV measurements. ^e LUMO energy levels were estimated from the CV measurements. ^f Hole mobility value at zero field strength. ^g Electron mobility value at zero field strength.

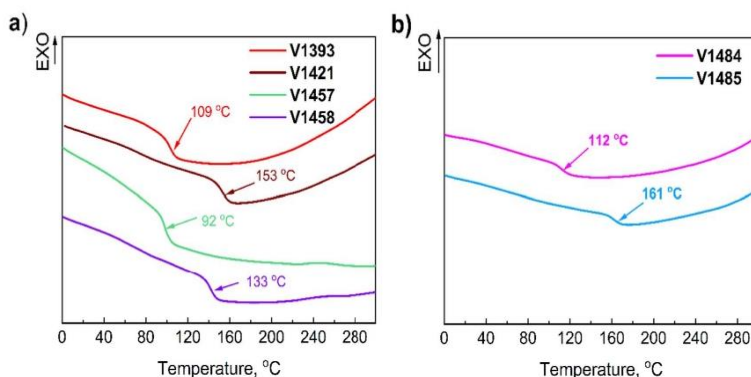


Fig. 3 DSC curves for the second run of the bipolar molecules bearing (a) carbonyl groups (V1393, V1421, V1457 and V1458) and (b) cyanoilidene moieties (V1484 and V1485) (heating rate of 10 °C min, N₂ atmosphere).

redistribution could be named as the closest to that of pure CT. Substituents are present in the role of electron acceptor (charge donor) (Table S4†). The tendencies for both conformers of V1458 and V1457 are the same. The HOMO orbital is localized in the central fluorene unit and in well-oriented substituents (Table S5†). Small changes occur for both conformers of V1485 and V1484. The chaotic orientation of the 2-ethylhexyl- fragment related to the central fluorene unit predetermines the strong non-symmetric displacement of the substituents (Table S6†). Due to that, only the left part of V1484a is involved in significant charge redistribution by excitation.

To understand the nature of electronic excitations, we decided to provide the natural transition orbitals (NTO) analysis using Gaussian16 routine: Density=(Check, Transition=1,2) Pop=(NTO, SaveNTO) for first and second transitions. HOMO and LUMO NTO (which correspond the electronic densities of hole and electron NTO pairs) for allowed first transition are presented in ESI, Tables S7–S9.†

List of several most probable molecular dimers is presented in ESI, Table S10.† Two typical structures in most informative projections are presented in Fig. S23.† First structure of open V-shaped type (dimmer Eh0, V1421b + V1421b) presents amorphous behaviour of low density condensed phase.

Intermolecular structure could be organized using weak van-der Waals forces, which relates two molecules through substituents. Second structure of core-to-core type (dimmer Eh2, V1458b + V1458b) represents amorphous behaviour of high density condensed phase. Intermolecular structure could be organized overlap of central core unit of different molecules. Additional relations of two molecules are organized through the substituents. Orientation of two core units is not parallel, but closed to perpendicular (dihedral angle –20 deg).

A comparison of the UV-visible absorption spectra of the new HTMs recorded in THF solution and from solid films is shown in Fig. 4, and the corresponding data are listed in Table 1.

In general, the spectra of all target compounds display not less than three absorption bands. As expected, the same group molecules, which structures differ in the length of the alkyl chains, present similar absorption profiles from 250 to 900 nm. The spectra of all new compounds display an intensive π - π^* absorption bands at 270–450 nm, while the weak absorption band with maximum in the visible region has n - π^* nature. While comparing spectra of V1393, V1421, and V1457, V1458 the red shifted absorption peaks can be detected. Stronger absorption for V1393, V1421 around 510 nm is attributed to the presence of additional oxygen atoms. The same phenomenon

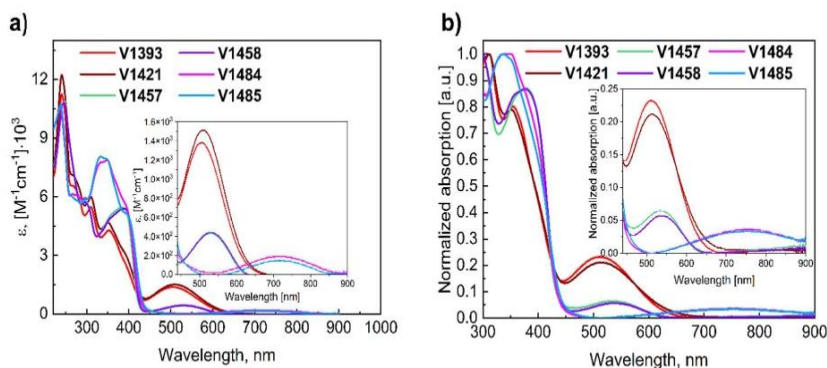


Fig. 4 UV-vis spectra of the target compounds from (a) THF solutions ($c = 10^{-4} \text{ mol l}^{-1}$); (b) solid films.

was observed when dicyanoylide groups were added to the molecule.

When compared to the solution samples, the absorption of film samples exhibits a minimal red shift ($\sim 3 \text{ nm}$) (Fig. 4b), suggesting a significant degree of intermolecular interactions in the solid state. Additionally, this shift supports the presence of aggregates even in low-concentration solutions. Quantum chemistry calculations further validated these findings, indicating that such intermolecular transitions were only feasible in dimer structures. The photoluminescence (PL) measurements were conducted on the solutions and solid layers of materials, but no observable emission was detected.

To assess the energy levels of novel bipolar molecules, their oxidation (E_{ox}) and reduction (E_{red}) potentials in solution and ionization potential (I_p) values in the solid-state were determined using cyclic voltammetry (CV) and photoelectron spectroscopy in air (PESA) techniques, respectively. The experimental results are depicted in Fig. 5, S19,† and Table 1. Materials with anthraquinone moieties have the highest I_p

values (5.18 and 5.21 eV for **V1393** and **V1421**, respectively). As expected, the alkyl chain attached to the 9-fluorenyl core practically does not affect I_p . The comparison between molecules containing anthraquinone fragment and molecules containing fluorene-9-one chromophores has revealed compelling evidence that a decrease in the number of electron-withdrawing keto groups within the molecule leads to a reduction in the ionization potential. The opposite effect, *i.e.* increase of the I_p values, was recorded when cyanoylide fragments were present in the molecule instead of the keto groups. The inclusion of additional electron-acceptor fragments or strengthening them in this concept resulted in an increase in the ionization potential values.

The CV measurements (Fig. S19†) have clearly indicated that materials containing anthraquinone exhibit two oxidation peaks and two reduction peaks in a positive region, while compounds incorporating the fluorene-9-one and cyanoylide groups display three peaks corresponding to oxidation and reduction processes. Comparison of **V1393**, **V1421** with **V1457**,

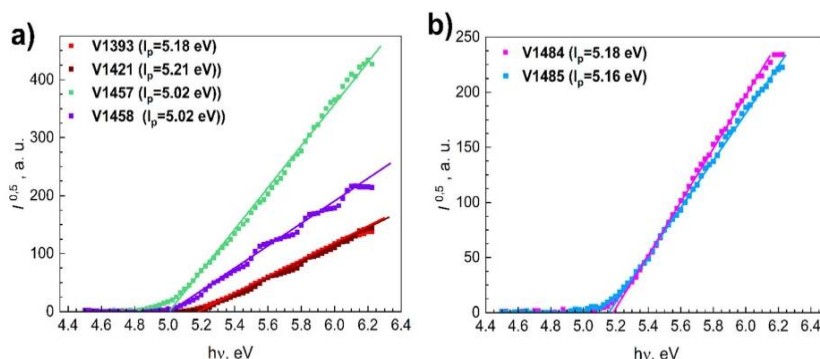


Fig. 5 Photoemission in air spectra of new compounds with (a) carbonyl groups (**V1393**, **V1421**, **V1457**, and **V1458**) and (b) cyanoylide substituents (**V1484** and **V1485**).

V1458 has apparently revealed that reducing the number of oxygen atoms in the molecule results in a slight decrease in the oxidation potential (E_{ox}) value. Other modifications in the structures have a minimal effect on the E_{ox} values.

The CV of the analyzed compounds has demonstrated reversible reduction during the scanning process in a negative region, indicating the electrochemical stability of the synthesized materials. It is important to note that these values do not represent absolute electron affinity or ionization energies in the solid state, but they can be utilized to compare different compounds relative to each other. The estimated ranges for the LUMO and HOMO energy levels of the novel compounds were found to be between -3.85 eV and -4.16 eV, and between -5.02 eV and -5.21 eV, respectively.

The hole and electron mobility is a fundamental parameter when bipolar molecules are evaluated. To analyze the charge transport properties of novel compounds, time-of-flight measurements (XTOF) were employed; the transient signals are presented in the ESI, Fig. S24–S29.† These measurements were conducted in films of the pure compounds, and the obtained mobility dependencies on electrical field are presented in Fig. 6.

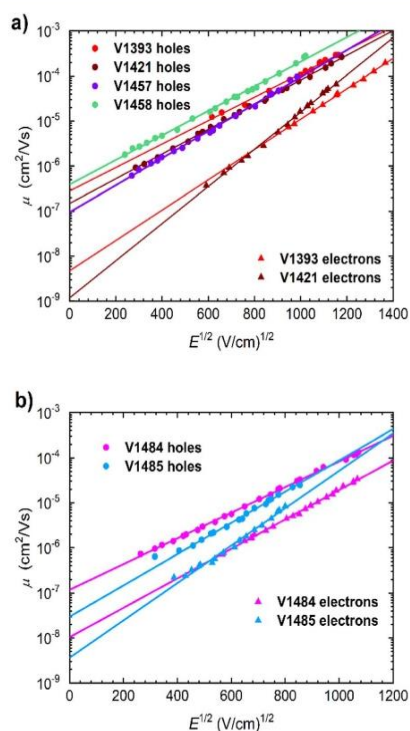


Fig. 6 Electric field dependencies of the new materials containing (a) anthraquinone and fluorenone functional groups (V1393, V1421, V1457, and V1458) and (b) cyanoylidene group (V1484 and V1485).

The results have clearly indicated that molecules containing anthraquinone fragments (**V1393**, **V1421**) and cyanoylidene substituents (**V1484**, **V1485**) exhibit both negative and positive charge transport capabilities with hole mobility reaching values of one order of magnitude higher than those of electrons. However, no electron-clear transients were obtained in compounds **V1457** and **V1458** bearing 9-fluorenone chromophores as electron acceptors. The only noticeable effect of longer alkyl chains (**V1393**, **V1457**, and **V1484**) was a slight improvement of hole mobilities at low electric fields, thus a case could be made that longer alkyl chains may be beneficial for more optimal molecular arrangement for charge transport. Replacement of the keto groups with cyanoylidene groups resulted in decreased hole drift mobility and increased electron mobility. The most balanced charge mobility has been recorded in the bipolar molecules **V1484** and **V1485**, where the hole mobility is $1.2 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and the electron mobility is $1.0 \times 10^{-8} \text{ V}^{-1} \text{ s}^{-1}$ at near zero electric fields.

Photocurrent decay measurements were conducted to gain deeper insights into charge transport within the layers. The applied electrical field was insufficient to facilitate the extraction of charge carriers from the layer, causing photocurrent decay to be predominantly influenced by

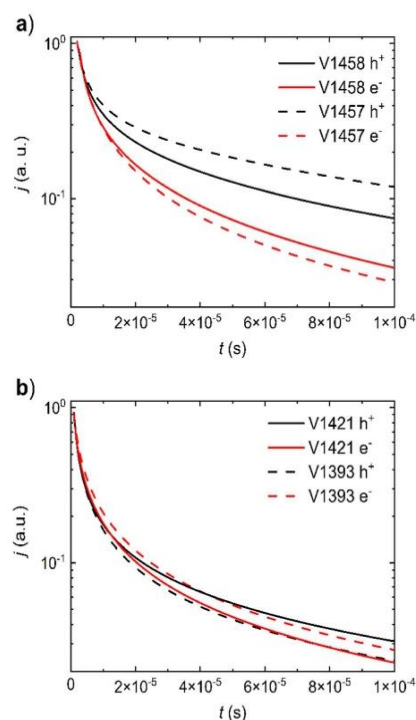


Fig. 7 Photocurrent decay profiles of compound films containing (a) fluorenone functional groups (V1457 and V1458) and (b) anthraquinone groups (V1393 and V1421).

charge carrier trapping, detrapping, and recombination processes.^{42,43}

The resulting profiles were normalized to compare the photocurrent tail regions of decay (ranging from 2×10^{-5} to 1×10^{-4} s), which primarily were attributed to deep traps and recombination mechanisms. In layers featuring anthraquinone fragments (Fig. 7b), the photocurrent decay profiles for both holes and electrons exhibit similar kinetics with minimal observable impact from additional alkyl groups. On the contrary, the most significant alterations in the slower decay region were observed when altering the length of the alkyl chains in compounds containing fluorenone groups (V1458, V1457) (Fig. 7a). The lengthening of the alkyl chains resulted in a reduced influence of trapping and detrapping on hole transport and increased recombination, as evidenced by the significantly lower hole mobilities observed in V1458. However, electron photocurrent decay seemed to exhibit only marginal sensitivity to the same alkyl chain modifications. Compounds featuring cyanoylidine fragments (V1484, V1485) (Fig. S30†) displayed a similar improvement when additional alkyl chains were introduced. This led to slower electron photocurrent decay alongside higher electron mobilities. These findings underscore the importance of additional alkyl groups in optimizing the molecular arrangement within the layer, subsequently enhancing charge carrier transport. Notably, the discernible differences in hole and electron current decays corroborate the discrepancies found in charge carrier mobilities.

Conclusions

New amorphous bipolar fluorine-based materials featuring anthraquinone, 9-fluorenone, or 9-dicyanofluorenylidine groups along with attached carbazolyl electron-donating moieties have been developed and synthesized via a straightforward synthesis. These amorphous materials exhibit homogeneous, cohesive, and continuous film-formation properties for solvent processing. Optical absorption and quantum chemistry simulations have confirmed the formation of a CT complex within the molecule, along with the emergence of a few of the most probable dimer structures, specifically V-type and core-to-core type structures. According to quantum chemistry calculations, several stable conformers are possible due to a complex geometry of the molecules.

The hole mobility in all materials is around 10^{-4} – 10^{-5} cm² V⁻¹ s⁻¹, while the electron mobility in compounds with anthraquinone and 9-dicyanofluorenylidine groups is approximately one order of magnitude lower. Electron transport in compounds with 9-fluorenone was highly dispersive and clear kink in photocurrent was not observed.

Author contributions

Aistė Jegorovė: writing – original draft, synthesis and characterization of materials; Marytė Daškevičienė: conceptualization, synthesis and characterization of materials; Kristina Katminienė: writing – original draft; Vygtas Jankauskas: project administration, supervision, investigation; Romualdas

Jonas Čepas: investigation, formal analysis, visualization, writing – original draft; Alytis Gruodis: formal analysis, investigation; Vytautas Getautis: conceptualization, supervision; Kristijonas Genevičius: investigation, formal analysis, writing – review & editing.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

This research was funded by a grant (No. S-MIP-22-8) from the Research Council of Lithuania. Computations were performed on resources at the High Performance Computing Center “HPC Saulėtekis” (Faculty of Physics, Vilnius University, Lithuania). Dr E. Kamarauskas is acknowledged for ionisation potential measurements.

References

- 1 A. Bessette and G. S. Hanan, *Chem. Soc. Rev.*, 2014, **43**, 3342–3405.
- 2 A. Wadsworth, M. Moser, A. Marks, M. S. Little, N. Gasparini, C. J. Brabec, D. Baran and I. McCulloch, *Chem. Soc. Rev.*, 2019, **48**, 1596–1625.
- 3 A. B. Muñoz-García, I. Benesperi, G. Boschloo, J. J. Concepcion, J. H. Delcamp, E. A. Gibson, G. J. Meyer, M. Pavone, H. Pettersson, A. Hagfeldt and M. Freitag, *Chem. Soc. Rev.*, 2021, **50**, 12450–12550.
- 4 M. Chen, L. Yan, Y. Zhao, I. Murtaza, H. Meng and W. Huang, *J. Mater. Chem. C*, 2018, **6**, 7416–7444.
- 5 H. Jiang, S. Zhu, Z. Cui, Z. Li, Y. Liang, J. Zhu, P. Hu, H.-L. Zhang and W. Hu, *Chem. Soc. Rev.*, 2022, **51**, 3071–3122.
- 6 Y. Weng, Z. Yu, T. Wu, L. Liang and S. Liu, *New J. Chem.*, 2023, **47**, 5086–5109.
- 7 A. J. Shah Nawaz, S. S. Swayamprabha, M. R. Nagar, R. A. K. Yadav, S. Gull, D. K. Dubey and J.-H. Jou, *J. Mater. Chem. C*, 2019, **7**, 7144–7158.
- 8 M. Sheokand, Y. Rout and R. Misra, *J. Mater. Chem. C*, 2022, **10**, 6992–7017.
- 9 K.-L. Wang, J.-C. Jiang, C.-H. Jhu, S. Wada, T. Sassa and M. Horie, *J. Mater. Chem. C*, 2020, **8**, 13357–13367.
- 10 D. S. Weiss, *J. Imaging Sci. Technol.*, 2016, **60**, 1–24.
- 11 D. S. Weiss and M. Abkowitz, *Chem. Rev.*, 2010, **110**, 479–526.
- 12 Y. Zhang, Y. Wang, C. Gao, Z. Ni, X. Zhang, W. Hu and H. Dong, *Chem. Soc. Rev.*, 2023, **52**, 1331–1381.
- 13 E. J. Meijer, D. M. de Leeuw, S. Setayesh, E. van Veenendaal, B.-H. Huisman, P. W. M. Blom, J. C. Hummelen, U. Scherf and T. M. Klapwijk, *Nat. Mater.*, 2003, **2**, 678–682.
- 14 C. Rost, D. J. Gundlach, S. Karg and W. Riefl, *J. Appl. Phys.*, 2004, **95**, 5782–5787.
- 15 T. D. Anthopoulos, D. M. de Leeuw, E. Cantatore, S. Setayesh, E. J. Meijer, C. Tanase, J. C. Hummelen and P. W. M. Blom, *Appl. Phys. Lett.*, 2004, **85**, 4205–4207.
- 16 A. Dodabalapur, H. E. Katz, L. Torsi and R. C. Haddon, *Science*, 1995, **269**, 1560–1562.

- 17 Y. Yamaguchi, T. Fujiyama, H. Tanaka and M. Yokoyama, *Denshi Shashin Gakkaishi*, 1991, **30**, 274–281.
- 18 Y. Kunugi, K. Takimiya, N. Negishi, T. Otsubo and Y. Aso, *J. Mater. Chem.*, 2004, **14**, 2840–2841.
- 19 N. Negishi, Y. Ie, H. Tada, T. Kaneda and Y. Aso, *Chem. Lett.*, 2007, **36**, 544–545.
- 20 J.-F. Nierengarten, T. Gu, T. Aernouts, W. Geens, J. Poortmans, G. Hadzioannou and D. Tsamouras, *Appl. Phys. A*, 2004, **79**, 47–49.
- 21 S. Amriou, A. Mehta and M. R. Bryce, *J. Mater. Chem.*, 2005, **15**, 1232–1234.
- 22 S. Urnikaite, T. Malinauskas, V. Gaidelis, V. Jankauskas and V. Getautis, *Chem.-Asian J.*, 2012, **7**, 614–620.
- 23 S. Urnikaite, T. Malinauskas, V. Gaidelis, R. Maldzius, V. Jankauskas and V. Getautis, *Carbon*, 2011, **49**, 320–325.
- 24 W. W. H. Wong, D. Vak, Th. B. Singh, S. Ren, C. Yan, D. J. Jones, I. I. Liaw, R. N. Lamb and A. B. Holmes, *Org. Lett.*, 2010, **12**, 5000–5003.
- 25 Y. Chen, T. Liu, H. Hu, T. Ma, J. Y. L. Lai, J. Zhang, H. Ade and H. Yan, *Adv. Energy Mater.*, 2018, **8**, 1801203.
- 26 L. Gao, Z.-G. Zhang, H. Bin, L. Xue, Y. Yang, C. Wang, F. Liu, T. P. Russell and Y. Li, *Adv. Mater.*, 2016, **28**, 8288–8295.
- 27 Y. Zhang, C. Kim, J. Lin and T.-Q. Nguyen, *Adv. Funct. Mater.*, 2012, **22**, 97–105.
- 28 L. Wang, X. Zhang, H. Tian, Y. Lu, Y. Geng and F. Wang, *Chem. Commun.*, 2013, **49**, 11272–11274.
- 29 A. Riaño, P. M. Burrezo, M. J. Mancheño, A. Timalsina, J. Smith, A. Facchetti, T. J. Marks, J. T. L. Navarrete, J. L. Segura, J. Casado and R. P. Ortiz, *J. Mater. Chem. C*, 2014, **2**, 6376–6386.
- 30 T. Bura, N. Leclerc, R. Bechara, P. Lévêque, T. Heiser and R. Ziessel, *Adv. Energy Mater.*, 2013, **3**, 1118–1124.
- 31 Y. Lin, L. Ma, Y. Li, Y. Liu, D. Zhu and X. Zhan, *Adv. Energy Mater.*, 2013, **3**, 1166–1170.
- 32 H. Bai, P. Cheng, Y. Wang, L. Ma, Y. Li, D. Zhu and X. Zhan, *J. Mater. Chem. A*, 2013, **2**, 778–784.
- 33 H. Shi, W. Fu, M. Shi, J. Ling and H. Chen, *J. Mater. Chem. A*, 2015, **3**, 1902–1905.
- 34 Q. Wu, L. Li, J. Hai, X. Zhang, Z. Lu, J. Yang, Y. Liu, L. Zhang and C. Zhan, *Dyes Pigm.*, 2016, **132**, 41–47.
- 35 G. Balaji, T. S. Kale, A. Keerthi, A. M. Della Pelle, S. Thayumanavan and S. Valiyaveetil, *Org. Lett.*, 2011, **13**, 18–21.
- 36 Y. Wang, J. H. Yun, L. Wang and J. Y. Lee, *Adv. Funct. Mater.*, 2021, **31**, 2008332.
- 37 M. Reig, C. Gozálvéz, V. Jankauskas, V. Gaidelis, J. V. Grazulevicius, L. Fajari, L. Juliá and D. Velasco, *Chem.-Eur. J.*, 2016, **22**, 18551–18558.
- 38 A. Bobet, A. Cuadrado, L. Fajari, I. Sirés, E. Brillas, M. P. Almajano, V. Jankauskas, D. Velasco and L. Juliá, *J. Phys. Org. Chem.*, 2019, **32**, e3974.
- 39 K. S. Kim, D. U. Kim, K. S. Joung and J.-W. Yu, *Thin Solid Films*, 2020, **696**, 137781.
- 40 M. Daskeviciene, S. Urnikaite, G. Planciunaite, T. Malinauskas, A. Gruodis, M. Viliunas, E. Kamarauskas, V. Gaidelis, V. Jankauskas and V. Getautis, *Dyes Pigm.*, 2018, **158**, 157–164.
- 41 Citation | Gaussian.com, <https://gaussian.com/citation/>, (accessed October 26, 2023).
- 42 S. Valouch, M. Nintz, S. W. Kettlitz, N. S. Christ and U. Lemmer, *IEEE Photonics Technol. Lett.*, 2012, **24**, 596–598.
- 43 C. R. McNeill, I. Hwang and N. C. Greenham, *J. Appl. Phys.*, 2009, **106**, 024507.

Supporting Information

*Aistė Jegorovė,^a Maryte Daskeviciene,^a Kristina Kantminienė,^b Vygintas Jankauskas,^c
Romualdas Jonas Čepas,^c Alytis Gruodis,^c Vytautas Getautis^a and Kristijonas Genevičius^{c*}*

^a Department of Organic Chemistry, Kaunas University of Technology, Radvilėnų pl. 19, Kaunas, 50254 Lithuania

^b Department of Physical and Inorganic Chemistry, Kaunas University of Technology, Radvilėnų pl. 19, Kaunas, 50254 Lithuania

^c Institute of Chemical Physics, Vilnius University, Saulėtekio al. 3, Vilnius 10257, Lithuania

Materials

2-Ethylhexylbromide, Silicagel (230–400 mesh, 60 Å), palladium (II) acetate, 2-(dicyclohexylphosphino)-2',4',6'-triisopropyl-1,1'-biphenyl (XPhos), *tri-tert*-butylphosphonium tetrafluoroborate, 3-bromo-9*H*-carbazole, malononitrile, and triethylamine were supplied from Sigma-Aldrich. Potassium *tert*-butoxide (k-OtBu), 2-aminoanthracene-9,10-dione, sodium *tert*-butoxide (Na-OtBu), and 2-aminofluorenone were purchased from TCI Europe N. V.. *n*-Hexane, dioxane, ethylacetate, tetrahydrofuran (THF), acetone, toluene, methanol (MeOH), potassium hydroxide (KOH), sodium sulphate (Na₂SO₄), and acetic acid were purchased from Eurochemicals. Ethanol (EtOH) was purchased from “Vilniaus degtinė”. All commercial chemicals were used as received without further purification.

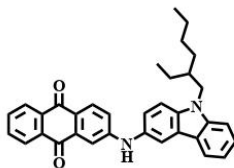
General methods

3-Bromo-9-(2-ethylhexyl)-9*H*-carbazole was synthesized as previously reported. ^[1] Its spectral data were in agreement with the reported values.

¹H NMR spectra were recorded at 400 MHz on a Bruker Avance III spectrometer, ¹³C NMR spectra were collected using the same instrument at 101 MHz. The chemical shifts, expressed in ppm, were relative to tetramethylsilane (TMS). All the experiments were performed at 25 °C. Reactions were monitored by thin-layer chromatography on ALUGRAM SIL G/UV254 plates and developed under UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å) was used for column chromatography.

Elemental analysis was performed on an Exeter Analytical CE-440 elemental analyzer, Model 440 C/H/N.

The transformations of thermal changes of target compounds were recorded with a TA Instruments Q2000 differential scanning calorimeter in a nitrogen atmosphere. From the obtained thermal curves, the glass transition temperatures of the materials were determined.



Anhydrous dioxane (15 mL) with a few drops of distilled water (0.5 mmol) added was purged with argon at room temperature for 20 minutes. Then, the temperature was raised to 80 °C, palladium(II) acetate (0.017 g, 0.08 mmol) and XPhos (0.11 g, 0.23 mmol) were added. The mixture was stirred for 1.5 min and temperature was raised to 110 °C. Once the temperature reached 110 °C, 2-aminoanthraquinone (4.1 g, 18 mmol), 3-bromo-9-(2-ethylhexyl)-9H-carbazole (5.48 g, 15.3 mmol), and sodium *tert*-butoxide (2.06 g, 21 mmol) were added and the reaction mixture was stirred for 60 minutes (TLC control, THF/*n*-hexane 1:4). Afterwards, the reaction mixture was extracted with ethyl acetate, organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The crude product was purified by column chromatography (THF/*n*-hexane 3:22 v:v), and pearl ruby red residue was collected as a final product. Yield 4.8 g, 63 %.

¹H NMR (400 MHz, THF-*d*₈) δ: 8.36 (s, 1H), 8.24 (d, *J* = 7.4 Hz, 1H), 8.19 (d, *J* = 7.5 Hz, 1H), 8.13–7.99 (m, 3H), 7.80–7.65 (m, 3H), 7.56–7.34 (m, 4H), 7.26 (d, *J* = 8.7 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 4.27 (d, *J* = 7.4 Hz, 2H), 1.55–1.19 (m, 9H), 0.96 (m, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H).

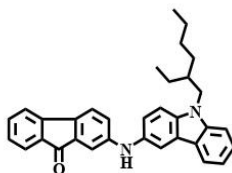
¹³C NMR (101 MHz, THF-*d*₈) δ: 183.9, 181.0, 153.3, 142.6, 139.5, 136.4, 135.4, 134.8, 134.6, 133.7, 133.0, 130.4, 127.5, 127.4, 126.7, 124.7, 124.6, 123.5, 122.9, 121.2, 119.6, 118.2, 115.9, 111.0, 110.7, 110.1, 48.1, 40.5, 31.9, 29.7, 24.0, 14.4, 11.3.

FTIR ν (cm⁻¹): 3334 (NH), 3054 (CH_{arom.}); 2955, 2926, 2857 (CH_{alif.}); 1668 (C=O).

Anal. Calcd. For C₃₄H₃₂N₂O₂: C 81.57; H 6.44; N 5.60; O 6.39; found: C 81.61; H 6.42; N 5.57.

C₃₄H₃₂N₂O₂ [M⁺] exact mass = 500.25, MS (ESI) = 499.01.

2-((9-(2-Ethylhexyl)-9H-carbazol-3-yl)amino)-9H-fluoren-9-one (2)



Anhydrous dioxane (17 mL) with a few drops of distilled water (0.5 mmol) added was purged with argon at room temperature for 20 minutes. Then, the temperature was raised to 80 °C, palladium(II) acetate (0.019 g, 0.09 mmol) and XPhos (0.12 g, 0.25 mmol) were added. The mixture was stirred for 1.5 min and temperature was raised to 110 °C. Once the temperature reached 110 °C, 2-amino-9H-fluorenone (3.9 g, 20 mmol), 3-bromo-9-(2-ethylhexyl)-9H-carbazole (6 g, 17 mmol), and sodium *tert*-butoxide (2.25 g, 23 mmol) were added and the reaction mixture was stirred for 20 minutes (TLC control, THF/*n*-hexane 1:4). Afterwards, the reaction mixture was extracted with ethyl acetate, organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The crude product was purified by column chromatography (acetone/*n*-hexane 3:22 v:v), and purple residue was collected as a final product. Yield 5.14 g, 65 %.

¹H NMR (400 MHz, THF-*d*₈) δ: 8.03 (d, *J* = 7.8 Hz, 1H), 7.91 (s, 1H), 7.60 (s, 1H), 7.51–7.34 (m, 7H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.19 (s, 1H), 7.12 (t, *J* = 7.2 Hz, 2H), 7.04 (d, *J* = 8.1, 2.3 Hz, 1H), 4.24 (d, *J* = 7.5 Hz, 2H), 1.55–1.18 (m, 9H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, THF-*d*₈) δ: 193.9, 149.5, 146.8, 142.5, 138.7, 136.9, 135.4, 135.2, 134.9, 134.5, 127.7, 126.4, 124.6, 124.4, 123.6, 122.3, 122.2, 121.1, 119.8, 119.3, 119.2, 114.6, 110.8, 110.5, 109.9, 48.0, 40.5, 31.9, 29.7, 24.0, 14.4, 11.3.

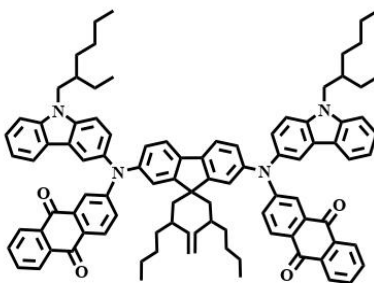
FTIR ν (cm⁻¹): 3372 (NH), 3050 (CH_{arom}); 2956, 2927, 2870, 2857 (CH_{alif}); 1705 (C=O).

Anal. Calcd. For C₃₃H₃₂N₂O: C 83.86; H 6.82; N 5.93; O 3.39; found: C 83.89; H 6.75; N

5.96.

$C_{33}H_{32}N_2O$ $[M^+]$ exact mass = 472.25, MS (ESI) = 473.57.

2,7-Bis(*N,N*-bis[anthracene-9,10-dione-2-yl]-*N,N'*-bis[9-(2-ethylhexyl)-9*H*-carbazol-3-yl]amine)-9,9-bis(2-ethylhexyl)-9*H*-fluorene (V1393)



A mixture of 2,7-dibromo-9,9-bis(2-ethylhexyl)-9*H*-fluorene (0.57 g, 1 mmol), 2-((9-(2-ethylhexyl)-9*H*-carbazol-3-yl)amino)anthracene-9,10-dione (**1**) (1.5 g, 3 mmol), and anhydrous toluene (12 mL) was purged with argon for 30 minutes. Afterwards, palladium(II) acetate (0.012 g, 0.05 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.032 g, 0.1 mmol) were added and the reaction mixture was stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (0.29 g, 3 mmol) was added and the mixture was heated at reflux for 6 h (TLC control, toluene/acetone/hexane 5:3:17). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 , filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: toluene/acetone/*n*-hexane 5:1:19 v:v:v). The final product was dissolved in THF and precipitated from ethanol to collect the final product as a pearl ruby red powder. Yield 1.22 g, 88 %.

1H NMR (400 MHz, Acetone- d_6) δ : 8.25–8.17 (m, 4H), 8.14 (d, $J = 7.5$ Hz, 2H), 8.10–8.04 (m, 4H), 7.91–7.77 (m, 6H), 7.69–7.63 (m, 4H), 7.58 (d, $J = 8.3$ Hz, 2H), 7.54–7.40 (m, 8H), 7.29–7.21 (m, 2H), 7.18 (t, $J = 7.4$ Hz, 2H), 4.35 (d, $J = 7.4$ Hz, 4H), 2.19–2.09 (m, 2H), 2.02–

1.83 (m, 4H) 1.49–1.18 (m, 16H), 1.00–0.73 (m, 28H), 0.70–0.54 (m, 8H), 0.46 (q, $J = 7.2$ Hz, 6H).

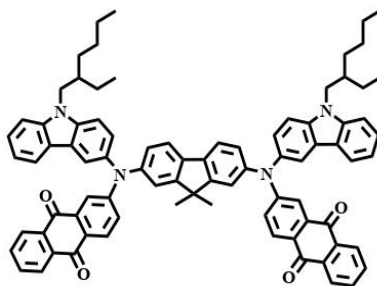
^{13}C NMR (101 MHz, Acetone- d_6) δ : 183.7, 181.5, 155.2, 153.8, 145.8, 142.5, 140.2, 139.4, 138.0, 135.8, 135.02, 134.95, 134.5, 134.3, 129.7, 127.5, 127.4, 127.1, 126.8, 126.5, 125.34, 125.27, 124.9, 123.7, 123.3, 122.4, 121.9, 121.4, 120.4, 119.9, 114.8, 111.7, 110.5, 56.2, 48.0, 45.2, 40.3, 35.6, 34.8, 31.6, 27.4, 27.3, 25.1, 23.8, 23.5, 14.4, 14.3, 11.3, 10.62, 10.60.

FTIR ν (cm^{-1}): 3050 ($\text{CH}_{\text{arom.}}$); 2956, 2925, 2857 ($\text{CH}_{\text{alif.}}$); 1672 (C=O).

Anal. Calcd. For $\text{C}_{97}\text{H}_{102}\text{N}_4\text{O}_4$: C 83.94; H 7.41; N 4.04; O 4.61; found: C 83.89; H 7.45; N 4.07.

$\text{C}_{97}\text{H}_{102}\text{N}_4\text{O}_4$ [M^+] exact mass = 1386.79, MS (ESI) = 1387.68.

2,7-Bis(*N,N*-bis[anthracene-9,10-dione-2-yl]-*N,N'*-bis[9-(2-ethylhexyl)-9*H*-carbazol-3-yl]amine-9,9-dimethyl-9*H*-fluorene (V1421)



A mixture of 2,7-dibromo-9,9-dimethyl-9*H*-fluorene (0.55 g, 1.6 mmol), 2-((9-(2-ethylhexyl)-9*H*-carbazol-3-yl)amino)anthracene-9,10-dione (**1**) (2.4 g, 4.8 mmol), and anhydrous toluene (15 mL) was purged with argon for 30 minutes. Afterwards, palladium(II) acetate (0.02 g, 0.09 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.052 g, 0.18 mmol) were added and the reaction mixture was stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (0.46 g, 4.8 mmol) was added and the mixture was heated at reflux for 5 h (TLC control, toluene/acetone/hexane 5:3:17). After cooling to room temperature, the

190

reaction mixture was filtered through celite and extracted with ethyl acetate. The organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: toluene/acetone/*n*-hexane 6:1:18 v:v:v). The final product was dissolved in THF and precipitated from methanol to collect the final product as a pearl ruby red powder. Yield 1.58 g, 83 %.

¹H NMR (400 MHz, THF-*d*₈) δ: 8.24 (d, *J* = 7.5 Hz, 2H), 8.16 (d, *J* = 7.5 Hz, 2H), 8.13–8.00 (m, 6H), 7.84–7.69 (m, 8H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.53–7.47 (m, 4H), 7.46–7.37 (m, 4H), 7.31 (dd, *J* = 8.8, 2.6 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 2H), 4.30 (d, *J* = 7.4 Hz, 4H), 2.20 – 2.05 (m, 2H), 1.55–1.22 (m, 22H), 0.97 (t, *J* = 7.4 Hz, 6H), 0.88 (t, *J* = 7.1 Hz, 6H).

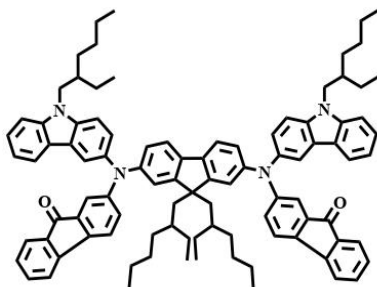
¹³C NMR (101 MHz, THF) δ: 187.9, 185.8, 161.1, 159.4, 151.1, 147.2, 144.7, 142.9, 141.2, 140.4, 139.7, 139.2, 139.1, 138.4, 134.2, 132.0, 131.4, 130.8, 130.6, 130.3, 129.7, 128.1, 126.3, 125.9, 125.4, 124.7, 124.3, 120.4, 115.9, 114.7, 52.6, 52.4, 45.0, 36.4, 34.2, 31.6, 28.5, 18.9, 15.8.

FTIR ν (cm⁻¹): 3321, 3064 (CH_{arom.}); 2959, 2927, 2858, (CH_{alif.}); 1671 (C=O).

Anal. Calcd. For C₈₃H₇₄N₄O₄: C 83.67; H 6.26; N 4.70; O 5.37; found: C 83.71; H 6.23; N 4.72.

C₈₃H₇₄N₄O₄ [M⁺] exact mass = 1190.57, MS (ESI) = 1191.56.

2,7-*N,N'*-bis[9-(2-ethylhexyl)-9*H*-carbazol-3-yl]-*N,N*-bis[9*H*-fluoren-9-one]amine-9,9-bis(2-ethylhexyl)-9*H*-fluorene (V1457)



A mixture of 2,7-dibromo-9,9-bis(2-ethylhexyl)-9H-fluorene (0.45 g, 0.8 mmol), 2-((9-(2-ethylhexyl)-9H-carbazol-3-yl)amino)-9H-fluoren-9-one (**2**) (1.1 g, 2.4 mmol), and anhydrous toluene (8 mL) was purged with argon for 30 minutes. Afterwards, palladium(II) acetate (0.01 g, 0.04 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.026 g, 0.09 mmol) were added and the reaction mixture was stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (0.23 g, 2.4 mmol) was added and the mixture was heated at reflux for 15 h (TLC control, acetone/hexane 1:24). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. The organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: acetone/*n*-hexane 1:24 v:v). The final product was dissolved in THF and precipitated from ethanol to collect the final product as a cherish red powder. Yield 0.8 g, 75 %.

¹H NMR (400 MHz, THF-*d*₈) δ: 8.02–7.89 (m, 4H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.55–7.35 (m, 14H), 7.33–7.06 (m, 14H), 4.26 (d, *J* = 7.4 Hz, 4H), 2.23–2.06 (m, 2H), 1.92–1.77 (m, 4H), 1.51–1.21 (m, 16H), 1.11 – 0.82 (m, 28H), 0.80 – 0.62 (m, 8H), 0.62 – 0.49 (m, 6H).

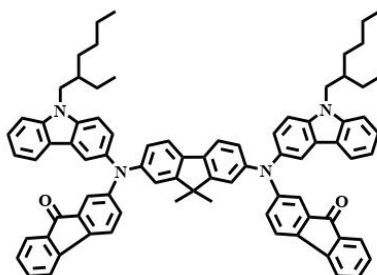
¹³C NMR (101 MHz, THF) δ: 193.2, 153.1, 151.6, 147.4, 147.3, 146.0, 142.7, 139.9, 139.5, 137.8, 137.0, 136.6, 135.5, 135.4, 128.4, 126.7, 126.0, 125.0, 124.7, 124.5, 123.6, 122.0, 121.4, 121.2, 121.0, 120.4, 119.6, 119.4, 117.4, 111.0, 110.1, 55.9, 48.1, 45.6, 40.6, 35.70, 35.67, 34.9, 31.9, 29.8, 29.6, 27.8, 27.7, 24.0, 23.9, 14.6, 14.4, 11.3, 10.9, 10.8.

FTIR ν (cm⁻¹): 3414, 3051 (CH_{arom.}); 2956, 2925, 2857 (CH_{alif.}); 1714 (C=O).

Anal. Calcd. For C₉₅H₁₀₂N₄O₂: C 85.67; H 7.72; N 4.21; O 2.40; found: C 85.70; H 7.69; N 4.23.

C₉₅H₁₀₂N₄O₄ [M⁺] exact mass = 1330.80, MS (ESI) = 1331.88.

2,7-*N,N'*-bis[9-(2-ethylhexyl)-9*H*-carbazol-3-yl]-*N,N*-bis[9*H*-fluoren-9-one]amine-9,9-dimethyl-9*H*-fluorene (V1458)



A mixture of 2,7-dibromo-9,9-dimethyl-9*H*-fluorene (0.35 g, 1 mmol), 2-((9-(2-ethylhexyl)-9*H*-carbazol-3-yl)amino)-9*H*-fluoren-9-one (**2**) (1.4 g, 3 mmol), and anhydrous toluene (9 mL) was purged with argon for 30 minutes. Afterwards, palladium(II) acetate (0.013 g, 0.06 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.032 g, 0.1 mmol) were added and the reaction mixture was stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (0.29 g, 3 mmol) was added and the mixture was heated at reflux for 8 h (TLC control, toluene/acetone/hexane 5:3:17). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. The organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: toluene/acetone/*n*-hexane 4:1:20 v:v:v). The final product was dissolved in THF and precipitated from methanol to collect the final product as a cherish red powder. Yield 0.75 g, 66 %.

^1H NMR (400 MHz, THF- d_8) δ : 8.03–7.95 (m, 4H), 7.58 (d, J = 8.2 Hz, 2H), 7.54–7.36 (m, 14H), 7.36–7.24 (m, 6H), 7.24–7.14 (m, 4H), 7.14–7.03 (m, 4H), 4.26 (d, J = 7.4 Hz, 4H), 2.21–2.03 (m, 2H), 1.58–1.13 (m, 22H), 0.96 (t, J = 7.4 Hz, 6H), 0.87 (t, J = 7.0 Hz, 6H).

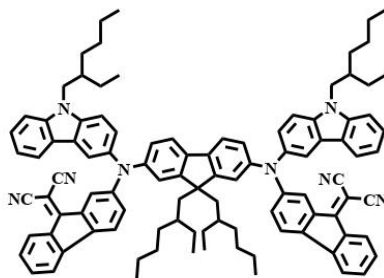
^{13}C NMR (101 MHz, THF) δ : 193.2, 156.2, 151.5, 147.8, 146.0, 142.6, 139.8, 139.6, 137.2, 136.5, 135.5, 135.4, 135.2, 128.5, 127.2, 126.7, 126.0, 125.0, 124.5, 123.9, 123.6, 122.1, 121.3, 121.1, 120.4, 119.6, 119.5, 119.1, 117.7, 111.1, 110.0, 48.1, 47.7, 40.6, 31.9, 29.7, 27.7, 24.0, 14.4, 11.3.

FTIR ν (cm^{-1}): 3050 (CH_{arom}); 2956, 2926, 2858 (CH_{alif}); 1714 (C=O).

Anal. Calcd. For $\text{C}_{81}\text{H}_{74}\text{N}_4\text{O}_2$: C 85.68; H 6.57; N 4.93; O 2.82; found: C 85.72; H 6.54; N 4.90.

$\text{C}_{81}\text{H}_{74}\text{N}_4\text{O}_2$ [M^+] exact mass = 1134.58, MS (ESI) = 1135.30.

2,7-*N,N'*-bis[9-(2-ethylhexyl)-9*H*-carbazol-3-yl]-*N,N*-bis[dicyano-9-ylidene-9*H*-fluorene-2-yl]amine-9,9-bis(2-ethylhexyl)-9*H*-fluorene (V1484)



A mixture of 2,2'-((9,9-bis(2-ethylhexyl)-9*H*-fluorene-2,7-diyl)bis((9-(2-ethylhexyl)-9*H*-carbazol-3-yl)azanediyl))bis(9*H*-fluoren-9-one) (**V1457**) (0.65 g, 0.5 mmol), malononitrile (0.07 g, 1.1 mmol), and THF (6.5 mL) was stirred for a few minutes. Afterwards, triethylamine (0.45 mL, 3 mmol) was added slowly drop-by-drop, and the reaction mixture was stirred at 35°C for 16 h (TLC control, acetone/hexane 1:4). After cooling to room temperature, the reaction mixture was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 , filtered and the solvent was removed by vacuum rotary evaporation. The product was purified

by column chromatography (eluent: acetone/*n*-hexane 2:23 v:v). The final product was dissolved in acetone and precipitated from ethanol to collect the final product as a moss green powder. Yield 0.5 g, 70 %.

^1H NMR (400 MHz, THF- d_8) δ : 8.25 (d, $J = 7.8$ Hz, 2H), 8.15 (t, $J = 5.5$ Hz, 2H), 7.97–7.92 (m, 4H), 7.65 (d, $J = 8.2$ Hz, 2H), 7.56–7.36 (m, 12H), 7.35–7.29 (m, 2H), 7.26–7.06 (m, 10H), 4.26 (d, $J = 7.5$ Hz, 4H), 2.16–2.05 (m, 2H), 1.88–1.76 (m, 4H), 1.51–1.31 (m, 16H), 1.09–0.79 (m, 28H) 0.76–0.62 (m, 8H), 0.51 (t, $J = 7.4$ Hz, 6H).

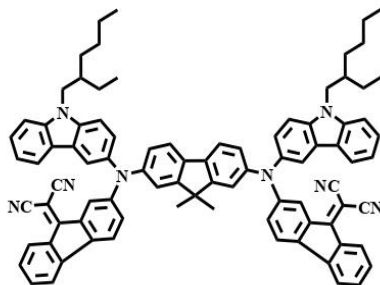
^{13}C NMR (101 MHz, THF) δ : 161.7, 153.2, 151.8, 147.0, 142.6, 139.7, 139.4, 136.5, 135.6, 135.2, 128.4, 127.3, 126.6, 126.4, 126.0, 125.1, 124.5, 123.6, 122.2, 121.4, 121.2, 121.1, 120.8, 120.4, 119.6, 119.5, 114.3, 113.7, 111.2, 110.1, 77.0, 55.9, 48.1, 45.4, 40.5, 35.5, 34.9, 31.9, 29.8, 29.4, 27.7, 27.6, 24.0, 23.9, 14.8, 14.7, 14.5, 11.3, 10.7.

FTIR ν (cm^{-1}): 3054 (CH_{arom}); 2956, 2925, 2870, 2857 (CH_{alif}); 2224 (CN).

Anal. Calcd. For $\text{C}_{101}\text{H}_{102}\text{N}_8$: C 84.95; H 7.20; N 7.85; found: C 84.93; H 7.22; N 7.85.

$\text{C}_{101}\text{H}_{102}\text{N}_8$ $[\text{M}^+]$ exact mass = 1426.82, MS (ESI) = 1427.269

2,7-*N,N'*-bis[9-(2-ethylhexyl)-9*H*-carbazol-3-yl]-*N,N*-bis[diciano-9-ylidene-9*H*-fluorene-2-yl]amine-9,9-dimethyl-9*H*-fluorene (V1485)



A mixture of 2,2'-((9,9-dimethyl-9*H*-fluorene-2,7-diyl)bis((9-(2-ethylhexyl)-9*H*-carbazol-3-yl)azanediyl))bis(9*H*-fluoren-9-one) (**V1458**) (0.74 g, 0.7 mmol), malononitrile (0.1 g, 1.5 mmol), and THF (7 mL) was stirred for a few minutes. Afterwards, triethylamine (0.6 mL, 4.2

mmol) was slowly added drop-by-drop and the reaction mixture was stirred at 35°C for 16 h (TLC control, acetone/hexane 1:4). After cooling to room temperature, the reaction mixture was extracted with ethyl acetate. The organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: acetone/*n*-hexane 1:4 v:v). The final product was dissolved in THF and precipitated from methanol to collect the final product as a moss green powder. Yield 0.49 g, 57 %.

¹H NMR (400 MHz, THF-*d*₈) δ: 8.28–8.20 (m, 4H), 8.02–7.95 (m, 4H), 7.60–7.30 (m, 18H), 7.25–7.16 (m, 4H), 7.14–7.03 (m, 4H), 4.26 (d, *J* = 7.4 Hz, 4H), 2.18 – 2.04 (m, 2H), 1.51–1.17 (m, 22H), 0.95 (t, *J* = 7.4 Hz, 6H), 0.88 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, THF) δ: 161.7, 156.2, 151.6, 147.4, 144.2, 142.6, 139.8, 139.5, 136.4, 135.6, 135.4, 135.2, 135.0, 128.4, 127.3, 126.9, 126.7, 126.1, 125.1, 124.1, 123.6, 122.4, 121.3, 121.3, 120.8, 120.4, 119.7, 119.6, 119.0, 114.3, 113.7, 111.3, 110.1, 76.9, 48.1, 47.8, 40.5, 31.9, 29.7, 27.4, 24.0, 14.4, 11.3.

FTIR ν (cm⁻¹): 3052 (CH_{arom.}); 2956, 2926, 2858 (CH_{alif.}); 2224 (CN).

Anal. Calcd. For C₈₇H₇₄N₈: C 84.85; H 6.06; N 9.10; found: C 84.90; H 6.01; N 9.09.

C₈₇H₇₄N₈ [M⁺] exact mass = 1230.60, MS (ESI) = 1231.40.

Branched Fluorenylidene Derivatives with Low Ionization Potentials as Hole-Transporting Materials for Perovskite Solar Cells

Aistė Jegorovė,[†] Jianxing Xia,[‡] Matas Steponaitis, Maryte Daskeviciene, Vyngintas Jankauskas, Alytis Gruodis, Egidijus Kamarauskas, Tadas Malinauskas, Kasparas Rakstys, Khalid A. Alamry, Vytautas Getautis,^{*} and Mohammad Khaja Nazeeruddin^{*}

Cite This: *Chem. Mater.* 2023, 35, 5914–5923

Read Online

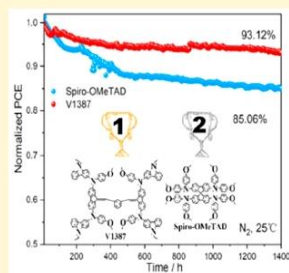
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: A group of small-molecule hole-transporting materials (HTMs) that are based on fluorenylidene fragments were synthesized and tested in perovskite solar cells (PSCs). The investigated compounds were synthesized by a facile two-step synthesis, and their properties were measured using thermoanalytical, optoelectronic, and photovoltaic methods. The champion PSC device that was doped with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) reached a power conversion efficiency of 22.83%. The longevity of the PSC device with the best performing HTM, V1387, was evaluated in different conditions and compared to that of 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD), showing improved stability. This work provides an alternative HTM strategy for fabricating efficient and stable PSCs.



1. INTRODUCTION

Since the naming of the first perovskite in the 19th century,¹ various materials have been discovered and described as perovskites.^{2–4} These materials can be organic,⁵ inorganic,⁶ or hybrid.⁷ With a few exceptions, perovskites are generalized with the formula ABX_3 , where A and B are cations of different charges (mono- and dications) and X is an anion that coordinates B. The recent attention of perovskite materials for use in optoelectronics should come as no surprise, as they have large absorption coefficients, tunable compositions and absorption edges, long charge carrier diffusion lengths, high defect tolerances, and efficient charge transport properties.^{8,9} Furthermore, perovskites can be processed in a variety of different ways,^{10–13} making them attractive not only for research but also for potential commercial applications.^{14,15}

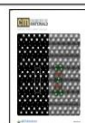
One of the most researched topics in science is the study of perovskite solar cells (PSCs). Since the first article published in 2009, the efficiency of PSCs has skyrocketed from 3.8% to over 26%.¹⁶ However, the rapid emergence of PSCs does not mean the technology has no flaws. Unsolved fabrication issues, unstable charge-transporting materials, and the long-term stability of perovskite compositions and devices must be addressed before this technology can reach the market. Additionally, using a quality hole-transporting material (HTM) is crucial for creating efficient and stable PSC devices.^{17,18} The function of an HTM is to efficiently transport photogenerated positive carriers from the absorber to the electrode. To achieve this, the HTM has to be chemically and morphologically stable, have the appropriate energy levels, and

have a relatively high carrier mobility.¹⁹ Over the years, efficiency records have mostly been broken by devices using either 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD) or poly[bis(4-phenyl)-(2,4,6-trimethylphenyl)amine] (PTAA) as an HTM. However, these materials are expensive and relatively difficult to synthesize, and spiro-MeOTAD is known to have stability issues.^{20–23} In order to replace spiro-MeOTAD, researchers have synthesized many new molecules with the same “award winning” structural design,^{24–26,26} hoping to achieve higher power conversion efficiencies (PCEs). Various polymers have also been developed in an attempt to replace PTAA as an HTM.^{27–30} To mimic spiro-MeOTAD, there are two commonly used strategies: (1) keep the central spiro core and only change the substituents around it^{31–33} or (2) build a molecule by carefully choosing substituents around a chosen central core in order to imitate the spatial arrangement of spiro-MeOTAD.^{34–36} Early on in the research of PSCs, the first strategy proved more fruitful, successfully creating PSCs with higher PCEs. The second strategy then became more

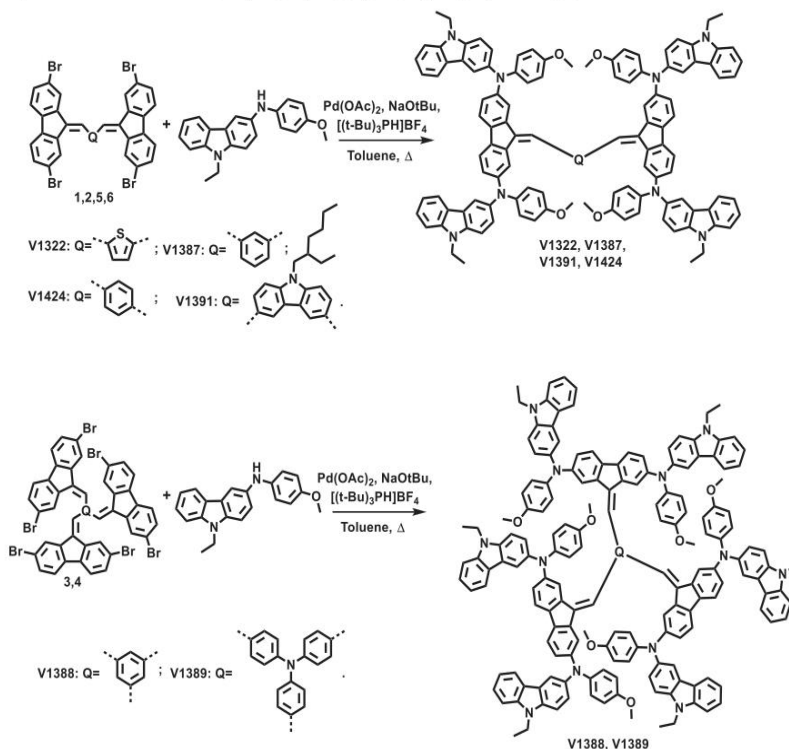
Received: March 29, 2023

Revised: July 11, 2023

Published: July 29, 2023



Scheme 1. Synthesis of the HTMs V1322, V1387, V1391, V1424, V1388, and V1389



popular later on, when the cost and stability of PSC devices became factors that needed to be addressed.

In one of our previous works, we demonstrated that using HTMs based on methoxydiphenylamine-substituted fluorene derivatives with a small central core is a good strategy for fabricating highly efficient PSCs.³⁷ To expand on our aforementioned study, we decided to employ carbazole-containing substituents as electron donating units, as this is known to tune the highest occupied molecular orbital (HOMO) level and help reach a high PCE.^{38–40} Furthermore, carbazole is a suitable building block for HTMs due to the possibility of having numerous substitutions of the carbazole unit. Various carbazole-containing scaffolds as electron donating units were used in order to tune the energy levels of HTMs, showing a good photovoltaic performance. For example, SGT series,^{41,42} benzodithiazole,⁴³ bipyridine,⁴⁴ and pyrene-based⁴⁵ electron donating units were used to fabricate highly efficient devices.

In this work, we describe the synthesis and application of new HTMs comprised of various central core units and substituted carbazole derivatives. These materials can be obtained in a facile two-step synthesis procedure. Their thermal, optical, and photoelectrical properties were also thoroughly investigated. All of the tested novel HTMs were successfully applied in PSCs, reaching an efficiency of up to 22%. Furthermore, the device employing the best performing HTM, V1387, demonstrated improved long-term stability

compared to PSCs that use spiro-MeOTAD as a *p*-type charge carrier.

2. RESULTS AND DISCUSSION

All of the newly synthesized HTMs can be divided into two groups: molecules with two fluorene units in their central core structure and molecules with three fluorene units. Compounds 1–6 were synthesized by a base-catalyzed condensation reaction; an example of said reaction can be seen in Scheme S1. All HTMs were obtained by palladium cross-coupling reactions between the respective central core unit and 9-ethyl-N-(4-methoxyphenyl)-9H-carbazol-3-amine (Scheme 1). Detailed synthetic protocols of said materials are described in the Supporting Information.

To determine the thermal and morphological stability of the HTMs, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used. Analysis of the TGA data suggests that all HTMs decompose around 450 °C (Figure 1), far above the temperature required for conventional device operation.¹⁴ DSC measurements reveal that the new organic semiconductors are molecular glasses having glass transition temperatures (T_g) between 190 and 232 °C (Figure S1), surpassing the T_g of spiro-MeOTAD (124 °C).⁴⁶ This suggests that our new materials are more morphologically stable.

Quantum chemistry simulations of the ground state molecular structures for several of the most probable

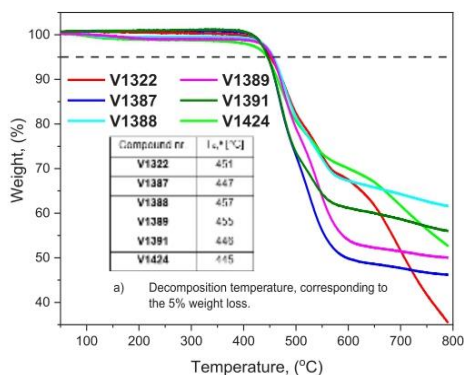


Figure 1. TGA curves of the synthesized HTMs.

conformers were provided using Gaussian 16⁴⁷ software by means of density functional theory (DFT) via the B3LYP method and a 6-31G(d) basis set, supplemented with polarization functions (d). Solvation effects were not considered in all cases. A list of several of the most probable molecular conformations is presented in Table S2. Two projections (xy and xz) of each of the mentioned conformations are presented in Figures S5–S10. In all cases, it is necessary to point out that the molecular structures are presented in a chaotic manner due to the absence of total or partial symmetry and the existence of a very large number of different conformers. All presented structures in Table S2 were obtained using a gradient optimization technique (convergence of the maximum force, root mean square (RMS) force, maximum displacement, and RMS displacement parameters has been achieved). Electronic excitations were simulated using a semi-empirical temporal difference (TD) method (for singlets). The parameters of the electronic excitations (transition energies ΔE_1 ($S_0 \rightarrow S_1$) and ΔE_2 ($S_0 \rightarrow S_2$) and corresponding oscillator strengths f_1 and f_2) are presented in Table S7. The populations of the low lying excited molecular states S_1 and S_2 could be realized using forbidden transitions: $S_0 \rightarrow S_n$, where $n = 1$ and 2 (oscillator strengths $f_n \rightarrow 0$). In a condensed phase, due to close intermolecular contacts, this

prohibition is partially removed. The parameters of the transition between the molecular orbitals (MOs), which are related to the population of the “spectroscopic” states S_n ($n = 1$ and 2) are presented in Table S3. In all cases, the dominant and most significant electron jump exists between the HOMO and the lowest unoccupied molecular orbital (LUMO). The spatial distributions of electron density (for the HOMO–1, HOMO, LUMO, and LUMO+1 of each compound) are presented in Tables S4–S6. For V1322, the thiophene core plays an important role in establishing the charge redistribution between the center core (and partially the left substituent) and the right substituent (see Table S4). For V1387, the phenyl core (linked in positions 1 and 3 to two fluorene substituents) forms a unit that has a similar role: to establish the charge redistribution between the left and right substituents and the central core (see Table S4). For V1391, a central core is formed using carbazole with two linked fluorines, and a core fragment takes part in the charge redistribution between the left and right substituents and the central core (see Table S5). For V1424, the phenyl core (linked in positions 1 and 4 to two fluorene substituents) forms a unit that has a similar role: to establish the charge redistribution between the left and right substituents and the central core (see Table S5). The formation of a central unit is more effective for V1424 than in the case of V1387, due to the different link conditions. For V1388, the phenyl core (linked in positions 1, 3, and 5 to three fluorene substituents) forms a unit for establishing the charge redistribution between the left and right substituents and the central core (see Table S6). For V1389, a central unit is formed from triphenylamine (TPA), and the charge redistribution between the left and right substituents and the central core is established (see Table S6).

The ultraviolet–visible (UV–vis) absorption spectra of the V series HTMs were measured in a tetrahydrofuran (THF) solution and on glass substrates (Figure 2a,b). All of the compounds have two major absorption peaks at around 300 and 375 nm, which represent the π – π^* transitions. The materials V1322 and V1389 both have an extra peak in the 450–470 nm range, which most likely corresponds to the π – π^* transitions with some charge transfer character, owing to the electron-rich nature of triarylamine and thiophene π systems. When comparing the spectra of the same compounds

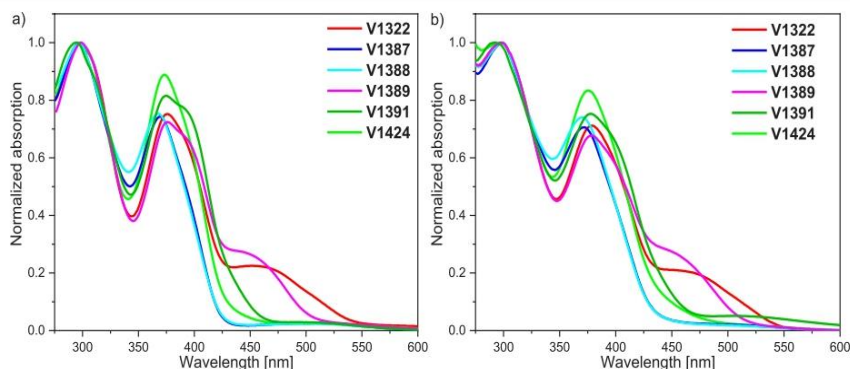


Figure 2. UV–vis absorption spectra of the V series HTMs (a) in a THF solution and (b) as thin films on glass substrates.

in solution to those acting as thin films, practically no shift in absorption is observed.

To evaluate the energy levels of the synthesized materials in the solid state, the ionization potential (I_p) was measured by photoelectron spectroscopy in air (PESA), where the measurement error was evaluated to be 0.03 eV. The I_p values of the synthesized HTMs can be seen in Figure 3. All of the tested

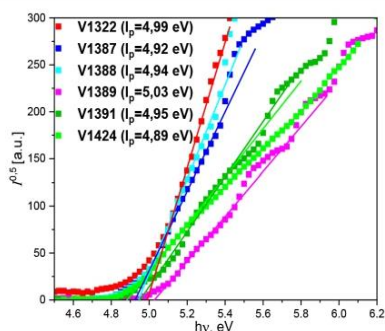


Figure 3. Ionization potential of the compounds V1322, V1387, V1388, V1389, V1391, and V1424.

materials have a relatively high HOMO energy level at ~ 5.0 eV. After analyzing the data, it seems that the biggest influence on I_p is the central core rather than the number of substitutions around it. The HTMs that contain single phenyl rings in their core (V1387, V1388, and V1424) have the highest HOMO levels, while the HTMs that have carbazole, thiophene, and TPA central fragments have slightly lower energy levels. This minor difference in I_p could be the cause of slightly bulkier cores, which in turn causes more steric hindrance in the solid state.

Hole mobility was measured from thin films via the xerographic time-of-flight (XTOF) method, with the electric field dependencies of the hole drift mobilities shown in Figure 4. Due to poor layer formation, the investigated materials had to be mixed with bisphenol Z polycarbonate (PC-Z, weight ratio 1:1) in order to form uniform thin films, which are necessary for accurate drift carrier mobility evaluation. V1424 had the highest zero-field hole mobility ($\mu_0 = 1.9 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), while the mobility values for the other semi-

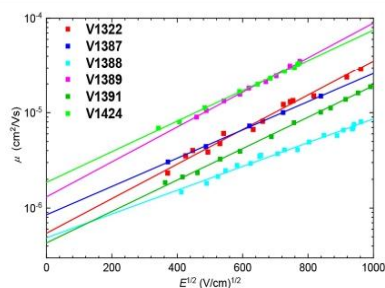


Figure 4. Charge carrier mobility of the V series HTMs, measured with PC-Z.

conductors were slightly lower. In comparison to spiro-MeOTAD ($\mu_0 = 1.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),⁴⁸ these values are significantly lower. However, it is worth noting that results acquired from HTM mixtures with PC-Z are generally at least one order of magnitude lower than those of the pristine material. The thermal, optical, and photoelectrical properties of the new *p*-type semiconductors are summarized in Table 1.

Next, PSCs were prepared with the synthesized materials in a regular configuration (*n-i-p*). For each PSC, fluorinated tin oxide (FTO) was used as a front contact, SnO_2 and compact and mesoporous TiO_2 (*c*- TiO_2 and *m*- TiO_2 , respectively) were used as the electron-transporting layers (ETLs), a triple cation perovskite was used as the light absorber, and the synthesized HTM was responsible for transporting positive charges toward the back contact, which in this case was gold (Figure 5a). Cross-sectional scanning electron microscopy (SEM) images of one of the devices can be seen in Figure 5b. Surface SEM was also used to study V1387 on the perovskite layer. As compared with the bare perovskite film, the additional layer of V1387 fully covered the perovskite crystal (Figure S2). The energy level illustration of various HTMs depicted in Figure 5c shows that all of the HTMs that were created in this study have around the same energy as spiro-OMeTAD; thus, they are suitable for hole transportation in PSCs.^{49,50} Time-resolved photoluminescence (TRPL, Figure 5d) was performed on the glass/perovskite/V1387 and glass/perovskite/spiro-OMeTAD films. The TRPL decay time was fitted by a bi-exponential model with fast (τ_1) and slow (τ_2) components, which indicate the interfacial transportation and recombination, respectively. The average decay time (τ_{ave}) is calculated using the equation $\tau_{\text{ave}} = \sum A_i \tau_i^2 / \sum A_i \tau_i$, where A_i and τ_i represent the decay amplitude and the decay time component, respectively (Table 2). For interfacial transport, the fast (τ_1) component was considered. When the spiro-OMeTAD was employed for the thin film, the decay time was 68.7 ns, with an average decay time of 143.4 ns. In comparison, for the perovskite/V1387 interface, a slightly slower decay time with $\tau_1 = 82.8$ ns and an average decay time of $\tau = 227.5$ ns were obtained. These results imply that V1387-based PSCs would exhibit a slightly lower or similar photovoltaic performance compared to that of spiro-OMeTAD-based PSCs.

Next, the solar cells were characterized under simulated solar illumination by measuring the current density as a function of the applied voltage (*J*-*V* curves; see Figure 6a). The characteristic photovoltaic parameters of the PSCs with different HTMs were extracted from the *J*-*V* scans and are reported in Table 3, where the results of the devices are arranged in order from lowest to highest PCE. All of the HTMs were doped with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in order to improve hole mobility. An analysis of the results suggests that the efficiency of the PSC decreases as the central core size of the HTM increases, since the PSCs with the HTMs that had bulkier TPA and carbazole core units (V1389 and V1391, respectively) demonstrated the lowest PCE values. Conversely, out of all the new HTMs tested in PSCs, the best results were achieved with compounds that possessed the highest HOMO levels, V1387 and V1424, which differ from one another only in the positions of the substitutions on the phenyl ring. However, this small structural variation between V1387 and V1424 results in an almost 1% difference in PCE, with V1387 reaching a significantly high efficiency of 22.13%. In comparison, the benchmark HTM spiro-MeOTAD slightly outperformed the V1387 devices

Table 1. Thermal, Optical, and Photophysical Properties of the Synthesized Materials

ID	T_g ($^{\circ}\text{C}$) ^a	T_{dec} ($^{\circ}\text{C}$) ^a	λ_{abs} (nm) ^b	λ_{em} (nm) ^c	I_p (eV) ^d	E_g (eV) ^e	μ_0 ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) ^f
V1322	190	451	298, 376, 461	299, 379, 466	4.99	2.25	5.4×10^{-7}
V1387	209	452	297, 369	299, 372	4.92	2.82	8.5×10^{-7}
V1388	210	457	297, 367	299, 370	4.94	2.82	4.9×10^{-7}
V1389	231	455	299, 376, 451	298, 379, 454	5.03	2.38	1.3×10^{-6}
V1391	206	446	295, 375	293, 378	4.95	2.59	4.3×10^{-7}
V1424	203	445	298, 373	298, 375	4.89	2.64	1.9×10^{-6}

^aThe glass transition (T_g) and decomposition (T_{dec}) temperatures were determined by DSC and TGA, respectively ($10^{\circ}\text{C}/\text{min}$, N_2 atmosphere).

^bThe absorption spectra were measured in a THF solution (10^{-4} M). ^cThe absorption spectra were measured from thin films on glass substrates.

^dThe HOMO energy levels of the thin films were measured using PESA. ^eThe optical band gaps E_g were estimated from the edges of the electronic absorption spectra in the solid state. ^fThe mobility values at zero field strength.

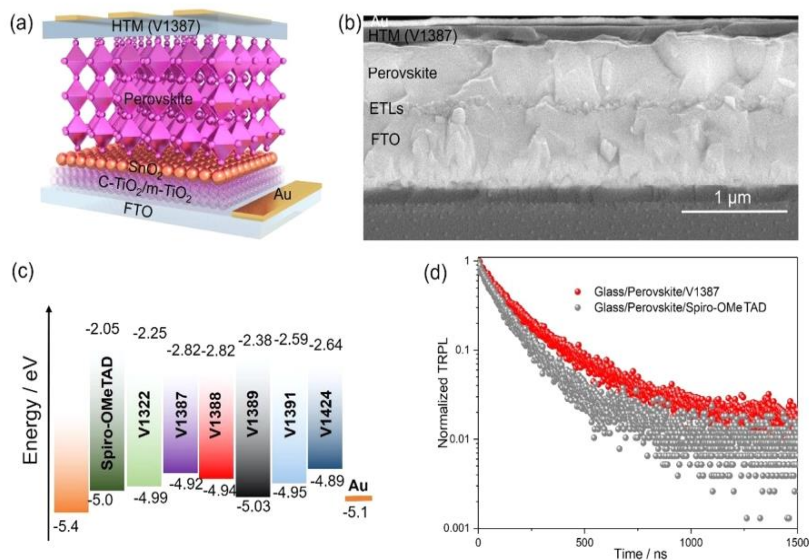


Figure 5. (a) A representative illustration of the structure of the fabricated PSCs. (b) A cross-sectional SEM image of the solar cell that used V1387 as its HTM. (c) The energy levels of the various HTMs created in this study compared against spiro-OMeTAD and gold. (d) The TRPL measurements of a sample based on glass/perovskite/V1387 (red) and of a sample based on glass/perovskite/spiro-OMeTAD (gray).

Table 2. Fitting Parameters of the Bi-Exponential Decay Function for TRPL Analysis of Glass/Perovskite Samples with Spiro-OMeTAD and V1387

films	fraction A_1 (%)	τ_1 (ns)	fraction A_2 (%)	τ_2 (ns)	average decay time, τ_{ave} (ns) ^a
FTO/perovskite/spiro-OMeTAD	61.1	68.7	38.9	186.7	143.4
FTO/perovskite/V1387	59.1	82.8	40.9	287.6	227.5

^aThe average decay time is calculated according to the equation $\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

(22.83%), delivering a PCE of 23.42% (Table S1, Figures 6b,c and S3). The $J-V$ hysteresis of the champion PSCs can be observed in Figures 6b,c and S3. Low hysteresis indexes of 1.04 for V1387-based solar cells and 1.03 for spiro-OMeTAD-based solar cells were determined, which demonstrate the high quality of the fabricated PSCs. The steady state efficiencies were measured under AM1.5G illumination and are shown in Figure 6d. The devices based on spiro-OMeTAD and on V1387 exhibit stable performances after 120 s output and show PCE values of 23.31% and 22.75%, respectively. It is clear that these values are extremely close to those obtained from

the $J-V$ curves. In addition, the incident photon to current efficiency (IPCE) of the devices based on V1387 was determined to be 24.17 mA cm^{-2} (Figure S4), which is consistent with the short-circuit current (J_{sc}) values.

Maximum power point (MPP) tracking of the devices employing V1387 and spiro-OMeTAD was compared under N_2 conditions (Figure 7a). Remarkably, the device with V1387 retained 93.12% of its initial efficiency after a 1400 h output, whereas the device with spiro-OMeTAD maintained only 85.06% of the initial PCE under the same conditions. Figure 7b shows the T_{90} values of the stability of the devices. It can be

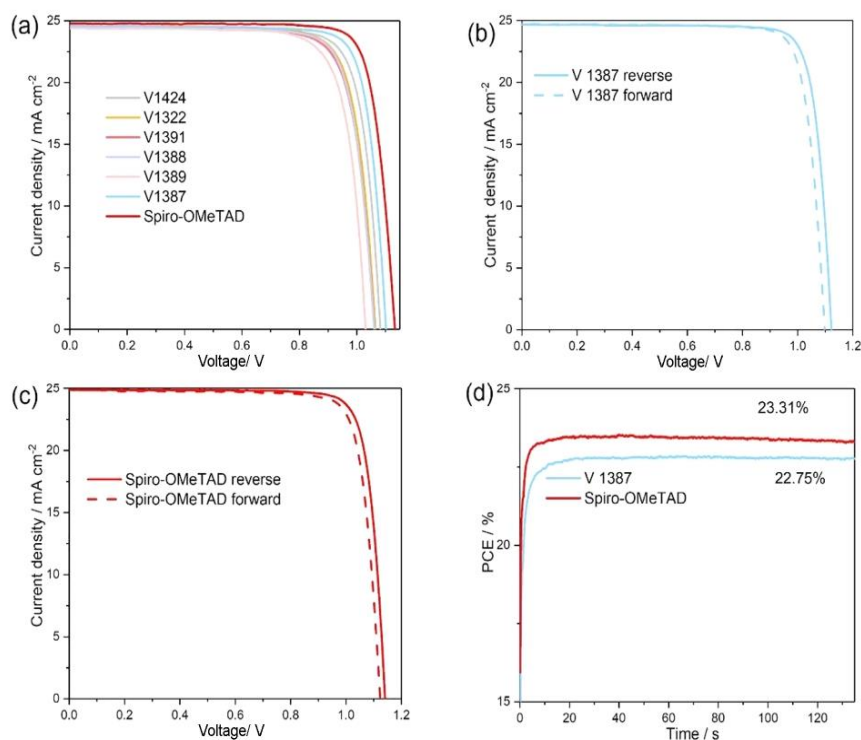


Figure 6. (a) J - V curves of the PSCs based on the various HTMs. (b) Reverse and forward J - V curves of the PSCs based on V1387. (c) Reverse and forward J - V curves of the PSCs based on spiro-OMeTAD. (d) The steady state efficiencies of the champion PSCs based on spiro-OMeTAD (red) and V1387 (blue).

Table 3. Photovoltaic Parameters Extracted from PSCs Based on the Various HTMs

HTMs	J_{sc} (mA cm ⁻²)	V_{oc} (V)	fill factor, FF	PCE (%)
V1389	24.38	1.03	0.781	19.61
V1391	24.45	1.061	0.788	20.44
V1388	24.43	1.06	0.796	20.61
V1322	24.54	1.065	0.793	20.72
V1424	24.50	1.082	0.802	21.26
V1387	24.57	1.112	0.810	22.13
spiro-OMeTAD	24.79	1.133	0.813	22.83

seen that the device based on spiro-OMeTAD is less stable and reaches the T_{90} line quickly, in only 373 h. In addition, the V1387-based PSCs exhibit better ambient stability than devices based on spiro-OMeTAD (Figure 7c). Water contact angle (WCA) measurements reveal that the V1387 film doped with LiTFSI exhibits a higher WCA (73°) than the spiro-OMeTAD-based films under the same conditions (68°). Hence, the greater hydrophobicity of V1387 partially explains the high stability of the device that contains this HTM.

3. CONCLUSIONS

In this study, the synthesis and application of new HTMs that are composed of various central core units and substituted

carbazole derivatives were developed in a facile two-step synthesis procedure. Their thermal, optical, and photoelectrical properties, as well as the PSC devices and interfacial transportation performances, were thoroughly investigated. All of the novel tested HTMs were successfully applied in PSCs, reaching an efficiency of up to 22.83%. Furthermore, the device employing the best performing HTM, V1387, demonstrated improved long-term stability compared to PSCs that used spiro-MeOTAD as a p -type organic charge carrier.

4. EXPERIMENTAL SECTION

4.1. Materials. Titanium diisopropoxide bis(acetylacetonate) (TAA), 4-*tert*-butylpyridine (*t*-BP), tin(IV) chloride pentahydrate (SnCl₄), bis(trifluoromethane) sulfonamide lithium salt (LiTFSI), FK209 [tris(2-(1H-pyrazol-1-yl)-4-*tert*-butylpyridine)-cobalt(III)-tris(bis(trifluoromethylsulfonyl)imide)], chlorobenzene, dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) were supplied from Sigma-Aldrich. Mesoporous TiO₂ (30-NRT), FAI, MAI, and MACl were purchased from GreatCell Solar. HAT6 and PbI₂ were purchased from TCI. Spiro-OMeTAD was purchased from Merck. All of the purchased chemicals were used as received without further purification.

4.2. Device Fabrication. For each device that was created, chemically etched FTO glass (Nippon Sheet Glass) was first cleaned with a detergent solution, deionized water, acetone, and isopropanol.

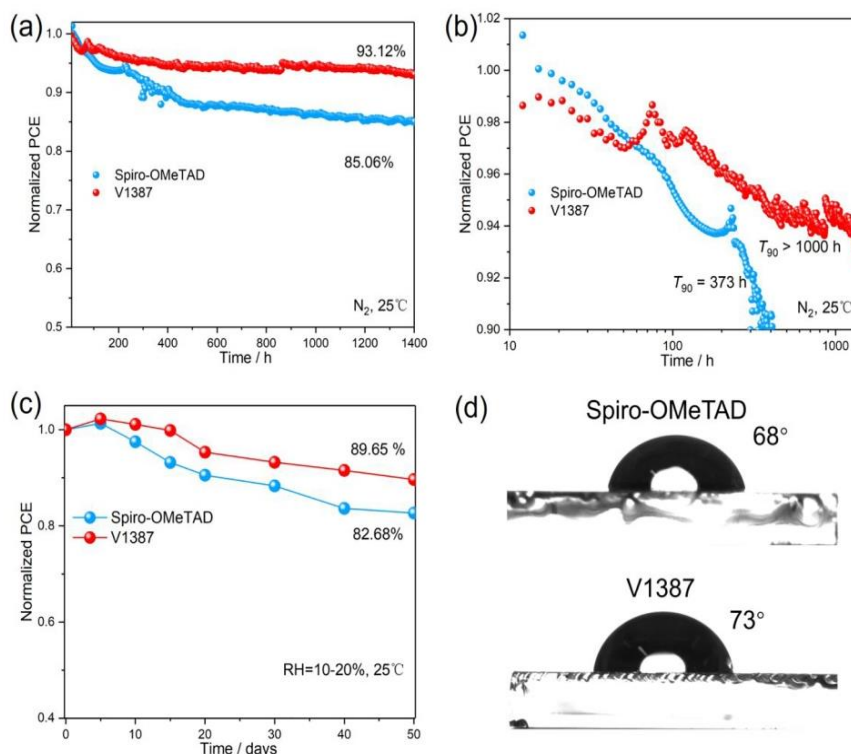


Figure 7. (a) MPP stability of the PSCs based on spiro-OMeTAD and V1387 under the N₂ storage condition (25 °C). (b) T_{90} stability of the PSCs based on spiro-OMeTAD and V1387. (c) Ambient stability of the PSCs based on spiro-OMeTAD and V1387. (d) The contact angles of the spiro-OMeTAD and V1387 films.

To create the compact TiO₂ (c-TiO₂) layer, a TAA solution in ethanol (1.2 mL of TAA in 20 mL of anhydrous isopropanol) was sprayed at 450 °C and was further heated for 1 h at 450 °C. Then, mesoporous TiO₂ (m-TiO₂) paste was diluted with ethanol with a ratio of 1:10, coated on top of the c-TiO₂ substrate at a speed of 3000 rpm for 20 s, and finally heated at 500 °C for 20 min. The tin oxide layer was formed by dissolving SnCl₄ in deionized water at a concentration of 12 μ L/mL, spin-coating that solution on the mesoporous TiO₂ layer at a speed of 3000 rpm for 20 s, and heating the substrate at 190 °C for 60 min. Next, perovskite precursor solutions in DMSO/DMF 1:4 v/v (CsI = 11.78 mg; MAI = 11.12 mg; FAI = 228.72 mg; PbI₂ = 709.95 mg; MACl = 18.90 mg) were successively spin-coated onto the substrate at 1000 rpm for 10 s and 5000 rpm for 30 s, consecutively. Then, 200 μ L of chlorobenzene was dropped on the substrate for 10 s at 5000 rpm, and the perovskite films were annealed at 150 °C for 10 min. The spiro-OMeTAD HTM solution was prepared by dissolving 80 mg of spiro-OMeTAD (Merck) in 1 mL of chlorobenzene. The novel HTMs of this study were prepared by dissolving 50 mg of each compound in 1 mL of chlorobenzene. The following additives were added: 18 μ L of LiTFSI from the stock solution (520 mg in 1 mL of acetonitrile), 13 μ L of FK209 [tris(2-(1*H*-pyrazol-1-yl)-4-*tert*-butylpyridine)-cobalt(III)-tris(bis(trifluoromethylsulfonyl)imide)] (375 mg in 1 mL of acetonitrile), and 30 μ L of 4-*tert*-butylpyridine. The HTM layer was formed by spin-coating the desired HTM solution at 4000 rpm for 20 s in order to achieve a thickness of 70 nm. Finally, deposition of the Au electrode completed the device. All of the preparative work done to

deposit the perovskite and spiro-OMeTAD was carried out in a N₂-filled glovebox.

4.3. Device Characterization. The samples were prepared by spin-coating the HTM solution in chlorobenzene onto a FTO film (2000 rpm, 20 s); they were then irradiated by a 450 W Xe lamp filtered through a double monochromator (5 nm bandpass). The film morphology was investigated by using a high-resolution scanning electron microscope (SEM) (Merlin, Zeiss) that was equipped with a GEMINI II column and a Schottky field emission gun. Images were acquired with an in-lens secondary electron detector. For the PL lifetime measurements, samples were excited with a 408 nm pulsed laser (MDL 300, PicoQuant) with a 40 μ m cm² pulse energy density. Current–voltage characteristics were recorded by applying an external potential bias to the cell while recording the generated photocurrent with a digital source meter (Keithley Model 2400). The light source was a 450 W Xe lamp (Oriel), equipped with a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH) in order to match the emission spectrum of the lamp to the AM1.5G standard. Before each measurement, the exact light intensity was determined by using a calibrated Si reference diode that was equipped with an infrared cutoff filter (KG3, Schott). The cells were masked with an active area of 0.09 cm². Contact angle measurements were done with the help of a DSA30 drop shape analyzer instrument and analyzed with the help of the Krüss ADVANCE software.

4.4. Ionization Potential Measurements. The ionization potential was investigated by using the electron photoemission method, and the study was performed in air. The sample solutions

(THF) were poured onto an aluminum-coated polyester film that was coated with an adhesive layer of a methyl methacrylate and methacrylic acid copolymer. A diffraction grating monochromator with a deuterium lamp was used for the experiment. The power of the falling light was $\sim 5 \times 10^{-8}$ W. A negative voltage (~ 100 V) was connected to the test sample. The electron photoemission current was measured with an open Geiger–Müller counter. The measurement method error was evaluated to be 0.03 eV.

4.5. Hole Drift Mobility Measurements. Carrier drift mobility was determined by the time-of-flight (XTOF) method. The material solution (THF) was poured onto aluminum-coated glass plates. The sample was poured from a solution of a pure substance, and the layers were dried for 1 h at 60 °C. The thickness of the transport layer was measured with an optical microscope-interferometer. The drift mobility of the holes (μ) was determined by using the electrophotographic mode with an electric field of $(0.1/1) \times 10^6$ V/cm. Charge carriers were generated at the layer surface by illumination with a nitrogen laser using nanosecond pulses ($\lambda = 337$ nm). In most cases, the layers of pure material produced for the hole transport studies were of poor quality due to cracking and were not suitable for XTOF measurements due to rapid discharging. Therefore, charge transfer in layers of blends with bisphenol Z-polycarbonate (PC-Z), in weight ratios of 1:1, was used.

4.6. Study of Quantum Chemistry. Simulations of the ground state molecular structures for several of the most probable conformers were provided using Gaussian 16 software by means of density functional theory (DFT) via the B3LYP method and a 6-31G(d) basis set, supplemented with polarization functions (d). A list of several of the most probable molecular conformations is presented in Table S2. Two projections (xy and xz) of the mentioned conformations are presented in Figures S5–S10.

Electronic excitations were simulated using the semi-empirical TD method (for singlets). The parameters of the transition between MOs, which are related to the population of “spectroscopic” states, are presented in Table S3. Spatial distributions of the electron density for the HOMO–1, HOMO, LUMO, and LUMO+1 are presented in Tables S4–S6.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.3c00708>.

Detailed synthetic procedures, DSC and SEM data, detailed photovoltaic parameters, J – V curves, and results of the performed quantum chemistry studies (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Vytautas Getautis – Department of Organic Chemistry, Kaunas University of Technology, Kaunas S02S4, Lithuania;
 orcid.org/0000-0001-7695-4677;
 Email: vytautas.getautis@ktu.lt

Mohammad Khaja Nazeeruddin – Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne 1015, Switzerland;
 orcid.org/0000-0001-5955-4786;
 Email: mdkhaja.nazeeruddin@epfl.ch

Authors

Aistė Jegorovė – Department of Organic Chemistry, Kaunas University of Technology, Kaunas S02S4, Lithuania

Jianxing Xia – Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne 1015, Switzerland

Matas Steponaitis – Department of Organic Chemistry, Kaunas University of Technology, Kaunas S02S4, Lithuania

Maryte Daskeviciene – Department of Organic Chemistry, Kaunas University of Technology, Kaunas S02S4, Lithuania
 Vyngintas Jankauskas – Institute of Chemical Physics, Vilnius University, Vilnius 10257, Lithuania

Alytis Gruodis – Institute of Chemical Physics, Vilnius University, Vilnius 10257, Lithuania

Egidijus Kamarauskas – Institute of Chemical Physics, Vilnius University, Vilnius 10257, Lithuania

Tadas Malinauskas – Department of Organic Chemistry, Kaunas University of Technology, Kaunas S02S4, Lithuania;
 orcid.org/0000-0002-5478-6550

Kasparas Rakstys – Department of Organic Chemistry, Kaunas University of Technology, Kaunas S02S4, Lithuania;
 orcid.org/0000-0001-8016-9567

Khalid A. Alamry – Chemistry Department, Faculty of Science, King Abdulaziz University, 21589 Jeddah, Saudi Arabia

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.chemmater.3c00708>

Author Contributions

[†]A.J. and J.X. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work has received funding from the European Regional Development Fund (Project 01.2.2-LMT-K-718-03-0040) under grant agreement with the Research Council of Lithuania (LMTLT) and from the Deputyship for Research & Innovation, Ministry of Education in Saudi Arabia, Project S26. Computations were performed on resources at the High Performance Computing Center, “HPC Saulėtekis” (Faculty of Physics, Vilnius University, Lithuania).

■ REFERENCES

- (1) Rose, G. In *De novis quibusdam fossilibus quae in montibus Uralis inveniuntur*; AG Schade, 1839; Chapters 3–5.
- (2) Li, W.; Wang, Z.; Deschler, F.; Gao, S.; Friend, R. H.; Cheetham, A. K.; et al. Chemically diverse and multifunctional hybrid organic–inorganic perovskites. *Nat. Rev. Mater.* **2017**, *2*, 16099.
- (3) Zhang, F.; Lu, H.; Tong, J.; Berry, J.; Beard, M. C.; Zhu, K. Advances in two-dimensional organic–inorganic hybrid perovskites. *Energy Environ. Sci.* **2020**, *13*, 1154.
- (4) Gao, Y.; Pan, Y.; Zhou, F.; Niu, G.; Yan, C. Lead-free halide perovskites: a review of the structure–property relationship and applications in light emitting devices and radiation detectors. *J. Mater. Chem. A* **2021**, *9*, 11931.
- (5) Ye, H. Y.; et al. Metal-free three-dimensional perovskite ferroelectrics. *Science* **2018**, *361*, 151.
- (6) Xiang, W.; Tress, W. Review on Recent Progress of All-Inorganic Metal Halide Perovskites and Solar Cells. *Adv. Mater.* **2019**, *31*, 1902851.
- (7) Grancini, G.; Nazeeruddin, M. K. Dimensional tailoring of hybrid perovskites for photovoltaics. *Nat. Rev. Mater.* **2019**, *4*, 4.
- (8) Yin, W. J.; Shi, T.; Yan, Y. Unique Properties of Halide Perovskites as Possible Origins of the Superior Solar Cell Performance. *Adv. Mater.* **2014**, *26*, 4653.
- (9) Chen, Q.; De Marco, N.; Yang, Y.; Song, T.-B.; Chen, C.-C.; Zhao, H.; Hong, Z.; Zhou, H.; Yang, Y. Under the spotlight: The organic–inorganic hybrid halide perovskite for optoelectronic applications. *Nano Today* **2015**, *10*, 355.
- (10) Li, H.; Zuo, C.; Scully, A. D.; Angmo, D.; Yang, J.; Gao, M. Recent progress towards roll-to-roll manufacturing of perovskite solar cells using slot-die processing. *Flex. Print. Electron.* **2020**, *5*, 014006.

- (11) Taylor, A. D.; Sun, Q.; Goetz, K. P.; An, Q.; Schramm, T.; Hofstetter, Y.; Litterst, M.; Paulus, F.; Vaynzof, Y.; et al. A general approach to high-efficiency perovskite solar cells by any antisolvent. *Nat. Commun.* **2021**, *12*, 1878.
- (12) Schackmar, F.; Eggers, H.; Frericks, M.; Richards, B. S.; Lemmer, U.; Hernandez-Sosa, G.; Paetzold, U. W. Perovskite Solar Cells with All-Inkjet-Printed Absorber and Charge Transport Layers. *Adv. Mater. Technol.* **2021**, *6*, 2000271.
- (13) Babaei, A.; Zanon, K. P. S.; Gil-Escrig, L.; Pérez-del-Rey, D.; Boix, P. P.; Sessolo, M.; Bolink, H. J. Efficient Vacuum Deposited P-I-N Perovskite Solar Cells by Front Contact Optimization. *Frontiers in Chemistry*. **2020**, *7*, 936.
- (14) Khenkin, M. V.; Katz, E. A.; Abate, A.; et al. Consensus statement for stability assessment and reporting for perovskite photovoltaics based on ISOS procedures. *Nat. Energy*. **2020**, *5*, 35.
- (15) Xu, K.; Al-Ashouri, A.; Peng, Z. W.; et al. Slot-Die Coated Triple-Halide Perovskites for Efficient and Scalable Perovskite/Silicon Tandem Solar Cells. *ACS Energy Lett.* **2022**, *7*, 3600.
- (16) Yoo, J. J.; Seo, G.; Chua, M. R.; et al. Efficient perovskite solar cells via improved carrier management. *Nature*. **2021**, *590*, 587.
- (17) Pham, H. D.; Yang, T. C. J.; Jain, S. M.; Wilson, G. J.; Sonar, P. Development of Dopant-Free Organic Hole Transporting Materials for Perovskite Solar Cells. *Adv. Energy Mater.* **2020**, *10*, 1903326.
- (18) Yin, X.; He, Y.; Wang, X.; Wu, Z.; Pang, E.; Xu, J.; Wang, J. Recent Advances in Thermally Activated Delayed Fluorescent Polymer—Molecular Designing Strategies. *Front. Chem.* **2020**, *8*, 1.
- (19) Kasparavičius, E.; Magomedov, A.; Malinauskas, T.; Getautis, V. Long-Term Stability of the Oxidized Hole-Transporting Materials used in Perovskite Solar Cells. *Chem. Eur. J.* **2018**, *24*, 9910.
- (20) Magomedov, A.; Kasparavičius, E.; Rakstys, K.; Paek, S.; Gasilova, N.; Genevičius, K.; Juska, G.; Malinauskas, T.; Nazeeruddin, M. K.; Getautis, V. Pyridination of hole transporting material in perovskite solar cells questions the long-term stability. *J. Mater. Chem. C* **2018**, *6*, 8874.
- (21) Meng, L.; You, J.; Yang, Y. Addressing the stability issue of perovskite solar cells for commercial applications. *Nat. Commun.* **2018**, *9*, 5265.
- (22) Kasparavičius, E.; Franckevičius, M.; Malinauskienė, V.; Genevičius, K.; Getautis, V.; Malinauskas, T. Oxidized Spiro-OMeTAD: Investigation of Stability in Contact with Various Perovskite Compositions. *ACS Appl. Energy Mater.* **2021**, *4*, 13696.
- (23) Bi, D.; Sun, L.; Grätzel, M.; Hagfeldt, A.; Gao, P.; Xu, B. Facile synthesized organic hole transporting material for perovskite solar cell with efficiency of 19.8%. *Nano Energy*. **2016**, *23*, 138.
- (24) Xu, B.; Zhu, Z.; Zhang, J.; Liu, H.; Chueh, C. C.; Li, X.; Jen, A. K. Y. 4-Tert-butylpyridine Free Organic Hole Transporting Materials for Stable and Efficient Planar Perovskite Solar Cells. *Adv. Energy Mater.* **2017**, *7*, 1700683.
- (25) Saliba, M.; Orlandi, S.; Matsui, T.; et al. A molecularly engineered hole-transporting material for efficient perovskite solar cells. *Nat. Energy*. **2016**, *1*, 15017.
- (26) Kranthiraja, K.; Park, S. H.; Kim, H.; Gunasekar, K.; Han, G.; Kim, B. J.; Kim, C. S.; Kim, S.; Lee, H.; Nishikubo, R.; Saeki, A.; Jin, S. H.; Song, M. Accomplishment of Multifunctional π -Conjugated Polymers by Regulating the Degree of Side-Chain Fluorination for Efficient Dopant-Free Ambient-Stable Perovskite Solar Cells and Organic Solar Cells. *ACS Appl. Mater. Interfaces*. **2017**, *9*, 36053.
- (27) Matsui, T.; Petriktye, I.; Malinauskas, T.; Domanski, K.; Daskeviciene, M.; Steponaitis, M.; Gratia, P.; Tress, W.; Correa-Baena, J. P.; Abate, A.; Hagfeldt, A.; Grätzel, M.; Nazeeruddin, M. K.; Getautis, V.; Saliba, M. Additive-Free Transparent Triarylamine-Based Polymeric Hole-Transport Materials for Stable Perovskite Solar Cells. *ChemSusChem*. **2016**, *9*, 2567.
- (28) Valero, S.; Collavini, S.; Völker, S. F.; Saliba, M.; Tress, W. R.; Zakeeruddin, S. M.; Grätzel, M.; Delgado, J. L. Dopant-Free Hole-Transporting Polymers for Efficient and Stable Perovskite Solar Cells. *Macromolecules*. **2019**, *52*, 2243.
- (29) Xu, Y.; Bu, T.; Li, M.; Qin, T.; Yin, C.; Wang, N.; Li, R.; Zhong, J.; Li, H.; Peng, Y.; Wang, J.; Xie, L.; Huang, W. Non-Conjugated Polymer as an Efficient Dopant-Free Hole-Transporting Material for Perovskite Solar Cells. *ChemSusChem* **2017**, *10*, 2578.
- (30) Jeong, M.; Choi, I. W.; Yim, K.; et al. Large-area perovskite solar cells employing spiro-Naph hole transport material. *Nat. Photonics* **2022**, *16*, 119.
- (31) Jeon, N. J.; Na, H.; Jung, E. H.; et al. A fluorene-terminated hole-transporting material for highly efficient and stable perovskite solar cells. *Nat. Energy* **2018**, *3*, 682.
- (32) Hu, Z.; Fu, W.; Yan, L.; Miao, J.; Yu, H.; He, Y.; Goto, O.; Meng, H.; Chen, H.; Huang, W. Effects of heteroatom substitution in spiro-bifluorene hole transport materials. *Chem. Sci.* **2016**, *7*, 5007.
- (33) Zhu, H.; Zhang, F.; Liu, X.; Sun, M.; Han, J.; You, J.; Wang, S.; Xiao, Y.; Li, X. Dopant-free hole-transport material with a tetraphenylethene core for efficient perovskite solar cells. *Energy Technol.* **2017**, *5*, 1257.
- (34) Gratia, P.; Magomedov, A.; Malinauskas, T.; Daskeviciene, M.; Abate, A.; Ahmad, S.; Grätzel, M.; Getautis, V.; Nazeeruddin, M. K. A Methoxydiphenylamine-Substituted Carbazole Twin Derivative: An Efficient Hole-Transporting Material for Perovskite Solar Cells. *Angew. Chem.* **2015**, *54*, 11409.
- (35) Rakstys, K.; Paek, S.; Drevilkauskaitė, A.; Kanda, H.; Daskeviciute, S.; Shibayama, N.; Daskeviciene, M.; Gruodis, A.; Kamarasus, E.; Jankauskas, V.; Getautis, V.; Nazeeruddin, M. K. Carbazole-Terminated Isomeric Hole-Transporting Materials for Perovskite Solar Cells. *ACS Appl. Mater. Interfaces*. **2020**, *12*, 19710.
- (36) Malinauskas, T.; Saliba, M.; Matsui, T.; Daskeviciene, M.; Urnikaitė, S.; Gratia, P.; Send, R.; Wonneberger, H.; Bruder, I.; Grätzel, M.; Getautis, V.; Nazeeruddin, M. K. Branched methoxydiphenylamine-substituted fluorene derivatives as hole transporting materials for high-performance perovskite solar cells. *Energy Environ. Sci.* **2016**, *9*, 1681.
- (37) Chen, Z.; Li, H.; Zheng, X.; Zhang, Q.; Li, Z.; Hao, Y.; Fang, G. Low-Cost Carbazole-Based Hole-Transport Material for Highly Efficient Perovskite Solar Cells. *ChemSusChem*. **2017**, *10*, 3111.
- (38) Liu, X. X.; Ding, X.; Ren, Y.; Yang, Y.; Ding, Y.; Liu, X. X.; Alsaedi, A.; Hayat, T.; Yao, J.; Dai, S. A star-shaped carbazole-based hole-transporting material with triphenylamine side arms for perovskite solar cells. *J. Mater. Chem. C* **2018**, *6*, 12912.
- (39) Yu, W.; Yang, Q.; Zhang, J.; Tu, D.; Wang, X.; Liu, X.; Li, G.; Guo, X.; Li, C. Simple Is Best: A p-Phenylene Bridging Methoxydiphenylamine-Substituted Carbazole Hole Transporter for High-Performance Perovskite Solar Cells. *ACS Appl. Mater. Interfaces*. **2019**, *11*, 30065.
- (40) Kang, M. S.; Sung, S. D.; Choi, I. T.; Kim, H.; Hong, M.; Kim, J.; Lee, W. I.; Kim, H. K. Novel Carbazole-Based Hole-Transporting Materials with Star-Shaped Chemical Structures for Perovskite-Sensitized Solar Cells. *ACS Appl. Mater. Interfaces*. **2015**, *7*, 22213.
- (41) Lu, C.; Choi, I. T.; Kim, J.; Kim, H. K. Simple synthesis and molecular engineering of low-cost and star-shaped carbazole-based hole transporting materials for highly efficient perovskite solar cells. *J. Mater. Chem. A* **2017**, *5*, 20263.
- (42) Wu, F.; Ji, Y.; Zhong, C.; Liu, Y.; Tan, L.; Zhu, L. Fluorine-substituted benzothiadiazole-based hole transport materials for highly efficient planar perovskite solar cells with a FF exceeding 80%. *Chem. Commun.* **2017**, *53*, 8719.
- (43) Wu, F.; Shan, Y.; Qiao, J.; Zhong, C.; Wang, R.; Song, Q.; Zhu, L. Replacement of Biphenyl by Bipyridine Enabling Powerful Hole Transport Materials for Efficient Perovskite Solar Cells. *ChemSusChem*. **2017**, *10*, 3833.
- (44) Li, D.; Shao, J. Y.; Li, Y. Y.; Li, Y. Y.; Deng, L. Y.; Zhong, Y. W.; Meng, Q. New hole transporting materials for planar perovskite solar cells. *Chem. Commun.* **2018**, *54*, 1651.
- (45) Leijtens, T.; Ding, I. K.; Giovenzana, T.; Bloking, J. T.; McGehee, M. D.; Sellinger, A. Hole Transport Materials with Low

Glass Transition Temperatures and High Solubility for Application in Solid-State Dye-Sensitized Solar Cells. *ACS Nano* **2012**, *6*, 1455.

(47) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16*, rev. C.01; Gaussian, Inc., Wallingford, CT, 2019.

(48) Rakstys, K.; Saliba, M.; Gao, P.; Gratia, P.; Kamarauskas, E.; Paek, S.; Jankauskas, V.; Nazeeruddin, M. K. Highly Efficient Perovskite Solar Cells Employing an Easily Attainable Bifluorenylidene-Based Hole-Transporting Material. *Angew. Chem., Int. Ed.* **2016**, *55*, 7464.

(49) Daskeviciute-Geguziene, S.; Zhang, Y.; Rakstys, K.; Kreiza, G.; Khan, S. B.; Kanda, H.; Paek, S.; Daskeviciene, M.; Kamarauskas, E.; Jankauskas, V.; Asiri, A. M.; Getautis, V.; Nazeeruddin, M. K. Green-Chemistry-Inspired Synthesis of Cyclobutane-Based Hole-Selective Materials for Highly Efficient Perovskite Solar Cells and Modules. *Angew. Chem., Int. Ed.* **2022**, *61*, 61.

(50) Jeong, M.; Choi, I. W.; Go, E. M.; Cho, Y.; Kim, M.; Lee, B.; Jeong, S.; Jo, Y.; Choi, H. W.; Lee, J.; Bae, J. H.; Kwak, S. K.; Kim, D. S.; Yang, C. Stable perovskite solar cells with efficiency exceeding 24.8% and 0.3-V voltage loss. *Science*. **2020**, *369*, 1615.

Branched fluorenylidene derivatives with low ionization potentials as hole-transporting materials for perovskite solar cells

Supporting Information

Aistė Jegorovė,^{a†} Jianxing Xia,^{b†} Matas Steponaitis,^a Maryte Daskeviciene,^a Vyginas Jankauskas,^c Alytis Gruodis,^c Egidijus Kamarauskas,^c Tadas Malinauskas,^a Kasparas Rakstys,^a Khalid A Alamry,^d Vytautas Getautis^{a} and Mohammad Khaja Nazeeruddin^{b*}*

^a Department of Organic Chemistry, Kaunas University of Technology, Radvilenu pl. 19, Kaunas, 50254 Lithuania

^b Institute of Chemical Sciences and Engineering, École Polytechnique Federale de Lausanne (EPFL), Lausanne, 1015 Switzerland

^c Institute of Chemical Physics Vilnius University, Sauletekio al. 3, Vilnius 10257, Lithuania

^d Chemistry Department, Faculty of Science, King Abdulaziz University, P. O. Box 80203, Jeddah, 21589, Saudi Arabia

† A. J. and X. J. contributed equally to this work.

*Corresponding authors:

vytautas.getautis@ktu.lt; mdkhaja.nazeeruddin@epfl.ch

General methods

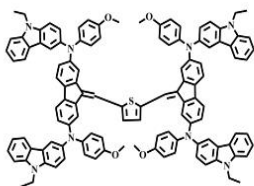
Chemicals required for the synthesis were purchased from Sigma-Aldrich and TCI Europe and used as received without additional purification. New fluorene class compounds were synthesized following previously described procedures. ^1H NMR spectra were recorded at 400 MHz on a Bruker Avance III spectrometer, ^{13}C NMR spectra were collected using the same instrument at 101 MHz. The chemical shifts, expressed in ppm, were relative to tetramethylsilane (TMS). All the experiments were performed at 25 °C. Reactions were monitored by thin-layer chromatography on ALUGRAM SIL G/UV254 plates and developed with UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was used for column chromatography.

UV/VIS spectral analysis of the sample solutions (THF, 10^{-4} mol/l) and thin films was performed on a Perkin Elmer Lambda 35 UV / VIS spectrophotometer. The layer thickness of the solution is $d = 1$ mm. Diffraction grating crack width 2 nm. Spectral recording speed 2 nm / s. The wavelength λ is given in nm. Elemental analysis was performed with an Exeter Analytical CE-440 elemental analyzer, Model 440 C/H/N/.

The transformations of thermal changes of target materials were recorded with a TA Instruments Q2000 differential scanning calorimeter in a nitrogen atmosphere. From the obtained thermal curves, the glass transition temperature of the materials is determined. Heating and cooling mode reaches 10 ° C / min. The destruction temperatures of the new compounds were recorded by TA Instruments Q50 by thermogravimetric analysis in a nitrogen atmosphere. The decomposition temperature of a compound is recorded when the weight loss is 5%. Heating mode 20 ° C / min.

Compounds **1-5** were synthesized following procedures reported in the literature.^[1] 9-ethyl-*N*-(4-methoxyphenyl)-9*H*-carbazol-3-amine was synthesized by Buchwald-Hartwig amination using Pd catalyst. Spectral data is in agreement with the values reported in the literature ^[2].

Synthesis



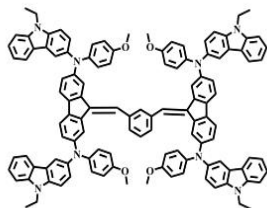
9,9'-(thiophene-2,5-diylbis(methanylylidene))bis(*N*²,*N*⁷-bis(9-ethyl-9*H*-carbazol-3-yl)-*N*²,*N*⁷-bis(4-methoxyphenyl)-9*H*-fluorene-2,7-diamine (V1322)

Reaction mixture of 2,5-bis((2,7-dibromo-9*H*-fluoren-9-ylidene)methyl)thiophene (**1**) (0.45 g, 0.6 mmol), 9-ethyl-*N*-(4-methoxyphenyl)-9*H*-carbazol-3-amine (1.13 g, 3.6 mmol) and anhydrous toluene (8 mL) was purged with Argon for 30 minutes. Afterwards, palladium (II) acetate (0.008 g, 0.03 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.02 g, 0.06 mmol) was added and stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (0.35 g, 3.6 mmol) was added and the mixture was heated at reflux for 5 hours (TLC control, THF/hexane 1:1.5). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. The organic layer was dried by Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 8:17 v:v). The final product was dissolved in THF and precipitated from ethanol to collect the final product as a brown solid powder. Yield 0.65 g, 64 %.

¹H NMR (400 MHz, THF-*d*₈) δ: 8.01 – 7.88 (m, 6H), 7.84 (s, 2H), 7.64 (s, 2H), 7.49 – 6.90 (m, 38H), 6.89 – 6.74 (m, 6H), 6.73 – 6.63 (m, 4H), 6.08 (s, 2H), 4.34 (q, *J* = 7.14 Hz, 4H), 4.16 (q, *J* = 7.14 Hz, 4H), 3.71 (s, 6H), 3.55 (s, 6H), 1.35 (t, *J* = 7.14 Hz, 6H), 1.25 (t, *J* = 7.14 Hz, 6H).

¹³C NMR (101 MHz, THF-*d*₈) δ: 156.8, 156.5, 149.3, 148.9, 143.4, 142.4, 141.9, 141.60, 141.56, 141.5, 141.4, 140.8, 138.0, 137.9, 137.8, 136.9, 134.7, 134.1, 131.3, 127.2, 126.6, 126.5, 126.1, 125.9, 125.4, 125.0, 124.9, 123.8, 123.7, 121.3, 121.23, 121.16, 119.9, 119.4, 119.03, 118.96, 118.3, 118.0, 115.5, 115.3, 110.3, 110.2, 109.4, 55.6, 55.5, 38.14, 38.05, 14.3, 14.2.

Anal. Calcd. For C₁₁₆H₉₂N₈O₄S: C 82.24; H 5.47; N 6.61; O 3.78; S 1.89; found: C 82.31; H 5.42; N 6.59.



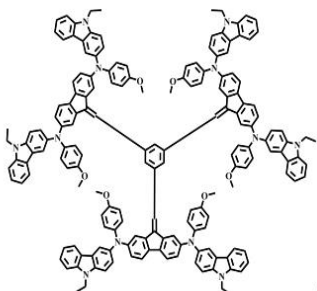
9,9'-(1,3-phenylenebis(methanylylidene))bis(*N*²,*N*⁷-bis(9-ethyl-9*H*-carbazol-3-yl)-*N*²,*N*⁷-bis(4-methoxyphenyl)-9*H*-fluorene-2,7-diamine (V1387)

Reaction mixture of 1,3-bis((2,7-dibromo-9*H*-fluoren-9-ylidene)methyl)benzene (**2**) (0.55 g, 0.7 mmol), 9-ethyl-*N*-(4-methoxyphenyl)-9*H*-carbazol-3-amine (1.33 g, 4.2 mmol) and anhydrous toluene (9.5 mL) was purged with Argon for 30 minutes. Afterwards, palladium (II) acetate (0.009 g, 0.04 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.023 g, 0.08 mmol) was added and stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (0.4 g, 4.2 mmol) was added and the mixture was heated at reflux for 8 hours (TLC control, THF/hexane 1:1.5). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. The organic layer was dried by Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 8:17 v:v). The final product was dissolved in toluene and precipitated from *n*-hexane to collect the final product as a light terracotta solid powder. Yield 0.7 g, 59 %.

¹H NMR (400 MHz, CDCl₃) δ: 7.96 (d, *J* = 7.8 Hz, 2H), 7.91 (s, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.64 (s, 2H), 7.46 – 7.29 (m, 14H), 7.29 – 7.24 (m, 4H); 7.21 – 6.94 (m, 16H), 6.94 – 6.70 (m, 14H), 6.56 (d, *J* = 8.7 Hz, 4H), 6.29 (d, *J* = 7.7 Hz, 2H), 4.30 – 4.11 (m, 8H), 3.71 (s, 6H), 3.62 (s, 6H), 1.43 – 1.26 (m, 12H).

^{13}C NMR (101 MHz, CDCl_3) δ : 155.3, 155.1, 147.8, 147.6, 142.3, 140.5, 140.3, 139.4, 137.4, 136.9, 136.8, 136.3, 135.7, 133.4, 126.9, 126.2, 125.7, 125.4, 125.2, 124.7, 123.8, 123.6, 122.7, 122.6, 122.3, 120.62, 120.55, 118.7, 118.4, 117.7, 115.5, 114.7, 114.4, 114.0, 109.2, 109.0, 108.5, 108.4, 55.5, 55.3, 37.6, 37.4, 13.93, 13.86.

Anal. Calcd. For $\text{C}_{118}\text{H}_{94}\text{N}_8\text{O}_4$: C 83.96; H 5.61; N 6.64; O 3.79; found: C 83.89; H 5.63; N 6.69.



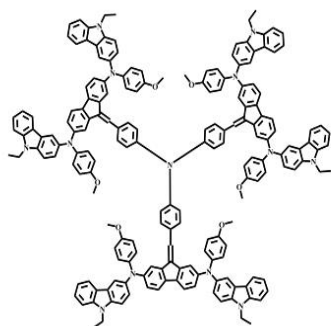
9,9',9''-(benzene-1,3,5-triyltris(methanylylidene))tris(N^2,N^7 -bis(9-ethyl-9H-carbazol-3-yl)- N^2,N^7 -bis(4-methoxyphenyl)-9H-fluorene-2,7-diamine (V1388)

Reaction mixture of 1,3,5-tris((2,7-dibromo-9H-fluorene-9-ylidene)methyl)benzene (**3**) (0.65 g, 0.6 mmol), 9-ethyl- N -(4-methoxyphenyl)-9H-carbazol-3-amine (1.7 g, 5.4 mmol) and anhydrous toluene (12 mL) was purged with Argon for 30 minutes. Afterwards, palladium (II) acetate (0.07 g, 0.03 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.020 g, 0.07 mmol) was added and stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (0.52 g, 5.4 mmol) was added and the mixture was heated at reflux for 8 hours (TLC control, THF/hexane 1:1.5). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. The organic layer was dried by Na_2SO_4 , filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 1:1.5 v:v). The final product was dissolved in toluene and precipitated from *n*-hexane to collect the final product as a light terracotta solid powder. Yield 0.57 g, 38 %.

¹H NMR (400 MHz, CDCl₃) δ: 8.00 – 7.89 (m, 6H), 7.59 (d, *J* = 7.7 Hz, 3H), 7.51 (s, 3H), 7.46 – 7.25 (m, 22H), 7.22 – 7.02 (m, 21H), 6.88 (t, *J* = 7.4 Hz, 3H), 6.85 – 6.76 (m, 8H), 6.74 – 7.62 (m, 12H), 6.50 (s, 3H), 6.43 (d, *J* = 8.6 Hz, 6H), 6.38 (s, 3H), 4.19 (q, *J* = 7.1 Hz, 6H), 3.94 (q, *J* = 7.1 Hz, 6H), 3.63 (s, 9H), 3.51 (s, 9H), 1.31 (t, *J* = 7.1 Hz, 9H), 1.18 (t, *J* = 7.1 Hz, 9H).

¹³C NMR (101 MHz, CDCl₃) δ: 155.2, 155.1, 147.9, 147.3, 142.4, 141.4, 141.0, 140.4, 140.1, 139.4, 137.7, 136.8, 136.7, 136.3, 135.6, 133.0, 129.1, 128.3, 128.0, 126.6, 125.9, 125.8, 125.5, 125.3, 125.1, 124.8, 123.8, 123.3, 122.61, 122.57, 122.0, 120.6, 120.5, 119.0, 118.7, 118.6, 117.8, 114.8, 114.3, 114.1, 109.3, 109.0, 108.6, 108.3, 55.5, 55.2, 37.5, 37.3, 13.9, 13.8.

Anal. Calcd. For C₁₇₄H₁₃₈N₁₂O₆: C 83.83; H 5.58; N 6.74; O 3.85; found: C 83.87; H 5.55; N 6.73.



9-(4-bis(4-((2,7-bis((9-9-ethyl-9H-carbazol-3-yl)(4-methoxyphenyl)amino)-9H-fluoren-9-ylidene)methyl)phenyl)amino)benzylidene-*N*²,*N*⁷-bis(4-methoxyphenyl)-9H-fluorene-2,7-diamine (V1389)

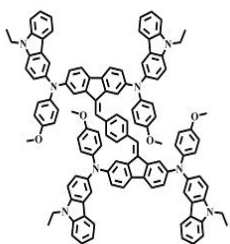
Reaction mixture of tris(4-((2,7-dibromo-9H-fluoren-9-ylidene)phenyl)amine (**4**) (0.6 g, 0.5 mmol), 9-ethyl-*N*-(4-methoxyphenyl)-9H-carbazol-3-amine (1.42 g, 4.5 mmol) and anhydrous toluene (10 mL) was purged with Argon for 30 minutes. Afterwards, palladium (II) acetate (0.07 g, 0.03 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.017 g, 0.06 mmol) was added and

stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (0.43 g, 4.5 mmol) was added and the mixture was heated at reflux for 5 hours (TLC control, THF/hexane 1.5:1). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. The organic layer was dried by Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 11:14 v:v). The final product was dissolved in toluene and precipitated from *n*-hexane to collect the final product as a brown solid powder. Yield 0.7 g, 53 %.

¹H NMR (400 MHz, CDCl₃) δ: 8.00 – 7.88 (m, 6H), 7.84 – 7.62 (m, 9H), 7.50 – 7.31 (m, 20H), 7.26 – 6.94 (m, 46H), 6.87 (d, *J* = 8.5 Hz, 6H), 6.67 (d, *J* = 8.4 Hz, 6H), 6.13 (d, *J* = 8.2 Hz, 6H), 4.35 (q, *J* = 7.2 Hz, 6H), 4.02 (q, *J* = 7.2 Hz, 6H), 3.81 (s, 9H), 3.51 (s, 9H), 1.45 (t, *J* = 7.2 Hz, 9H), 1.20 (t, *J* = 7.2 Hz, 9H).

¹³C NMR (101 MHz, CDCl₃) δ: 145.8, 141.1, 140.4, 140.3, 130.5, 130.4, 125.8, 125.6, 123.3, 122.6, 122.4, 120.6, 120.4, 118.7, 118.6, 113.7, 109.2, 108.6, 55.5, 55.3, 37.7, 37.4, 14.0, 13.8.

Anal. Calcd. For C₁₈₆H₁₄₇N₁₃O₆: C 83.98; H 5.57; N 6.84; O 3.61; found: C 83.96; H 5.59; N 6.84.



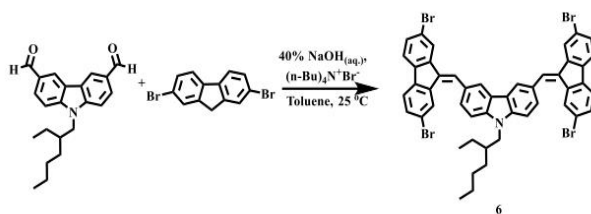
9,9'-(1,4-phenylenebis(methanylylidene))bis(*N*²,*N*⁷-bis(9-ethyl-9H-carbazol-3-yl)-*N*²,*N*⁷-bis(4-methoxyphenyl)-9H-fluorene-2,7-diamine (V1424)

Reaction mixture of 1,4-bis((2,7-dibromo-9H-fluorene-9-ylidene)methyl)benzene (**5**) (0.75 g, 1 mmol), 9-ethyl-*N*-(4-methoxyphenyl)-9H-carbazol-3-amine (1.9 g, 6 mmol) and anhydrous

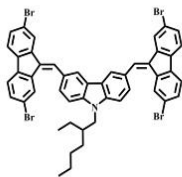
toluene (13 mL) was purged with Argon for 30 minutes. Afterwards, palladium (II) acetate (0.013 g, 0.06 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.032 g, 0.1 mmol) was added and stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (0.58 g, 6 mmol) was added and the mixture was heated at reflux for 5 hours (TLC control, THF/hexane 1:1.5). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. The organic layer was dried by Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 8:17 v:v). The final product was dissolved in THF and precipitated from ethanol to collect the final product as a light brown solid powder. Yield 1 g, 59 %.

¹H NMR (400 MHz, CDCl₃) δ: 8.02 – 7.86 (m, 4H), 7.85 – 7.60 (m, 4H), 7.52 – 7.11 (m, 25H), 7.11 – 6.80 (m, 19H), 6.74 (s, 2H), 6.61 (d, *J* = 8.1 Hz, 4H), 6.34 (s, 4H), 4.35 (q, *J* = 7.3 Hz, 4H), 3.93 (q, *J* = 7.3 Hz, 4H), 3.81 (s, 6H), 3.58 (s, 6H), 1.44 (t, *J* = 7.3 Hz, 6H), 1.21 (t, *J* = 7.3 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ: 155.1, 148.1, 147.8, 140.5, 140.2, 135.1, 128.2, 125.8, 125.6, 122.6, 122.5, 120.6, 120.3, 118.7, 118.6, 109.3, 108.6, 55.6, 55.2, 37.7, 37.3, 14.0.



Scheme S1. Synthesis of fluorene derivative **6**.



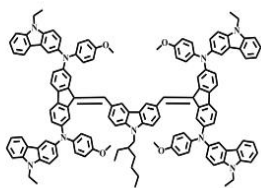
3,6-bis((2,7-dibromo-9H-fluoren-9-ylidene)methyl)-9-(2-ethylhexyl)-9H-carbazole (6)

A mixture of 2,7-dibromofluorene (1.86 g, 5.7 mmol), 9-(2-ethylhexyl)carbazole-3,6-dicarboxaldehyde (0.55 g, 1.6 mmol) and toluene (14.5 mL) was stirred for 10 minutes. Afterwards, NaOH solution (14.5 mL, 40% w/w) and tetrabutylammonium bromide (0.28 g, 0.88 mmol) were added and the reaction mixture was stirred at room temperature for 50 minutes (TLC control, acetone/*n*-hexane 1:4). After cooling to room temperature, the reaction mixture was extracted with ethyl acetate. The organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The crude product was crystallized from THF/acetone mixture (1:1, v:v) to obtain orange crystals which were used without any further purification in the next step. Yield 0.8 g (52%).

¹H NMR (400 MHz, THF-*d*₈) δ 8.46 (s, 2H), 8.15 (d, *J* = 14.9 Hz, 4H), 8.05 (s, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 6H), 7.48 (dd, *J* = 20.2, 8.1 Hz, 4H), 4.43 (d, *J* = 7.4 Hz, 2H), 1.60 – 1.39 (m, 6H), 1.37 – 1.28 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.88 (m, 4H).

¹³C NMR (101 MHz, THF) δ 140.05, 139.94, 137.12, 136.45, 135.48, 134.77, 130.72, 130.57, 129.10, 128.59, 126.02, 125.16, 124.70, 121.69, 121.30, 120.51, 120.01, 119.39, 119.17, 119.11, 118.50, 107.76, 65.14, 37.56, 29.04, 26.80, 23.01, 21.17, 11.58, 8.39.

Anal. Calcd. For C₁₁₈H₉₄N₈O₄: C 83.96; H 5.61; N 6.64; O 3.79; found: C 83.89; H 5.63; N 6.69.



9,9'-((9-(2-ethylhexyl)-9H-carbazole-3,6-diyl)bis(methanylylidene))bis(*N*²,*N*⁷-bis(9-ethyl-9H-carbazol-3-yl)-*N*²,*N*⁷-bis(4-methoxyphenyl)-9H-fluorene-2,7-diamine (V1391)

Reaction mixture of 3,6-bis((2,7-dibromo-9H-fluoren-9-ylidene)methyl)-9-(2-ethylhexyl)-9H-carbazole (**6**) (0.55 g, 0.6 mmol), 9-ethyl-*N*-(4-methoxyphenyl)-9H-carbazol-3-amine (1.14 g, 3.6 mmol) and anhydrous toluene (9 mL) was purged with Argon for 30 minutes. Afterwards, palladium (II) acetate (0.07 g, 0.03 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.02 g, 0.07 mmol) was added and stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (0.35 g, 3.6 mmol) was added and the mixture was heated at reflux for 5 hours (TLC control, THF/hexane 1:1.5). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. The organic layer was dried by Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 8:17 v:v). The final product was dissolved in THF and precipitated from ethanol to collect the final product as an orange solid powder. Yield 0.55 g, 49%.

¹H NMR (400 MHz, CDCl₃) δ: 7.96 (d, *J* = 7.8 Hz, 2H), 7.93 – 7.83 (m, 6H), 7.70 (d, *J* = 11.8 Hz, 4H), 7.56 – 7.49 (m, 4H), 7.48 – 7.26 (m, 20H), 7.19 – 6.97 (m, 12H), 6.92 (d, *J* = 8.4 Hz, 6H), 6.84 (d, *J* = 8.8 Hz, 4H), 6.63 (d, *J* = 8.8 Hz, 6H), 4.34 (q, *J* = 7.2 Hz, 4H), 4.11 (q, *J* = 7.2 Hz, 4H), 3.80 (s, 6H), 3.59 (s, 6H), 3.36 – 3.26 (m, 2H), 1.64 (s, 1H), 1.44 (t, *J* = 7.2 Hz, 6H), 1.27 (t, *J* = 7.2 Hz, 6H), 1.20 – 0.88 (m, 6H), 0.79 (t, *J* = 6.7 Hz, 3H), 0.69 (t, *J* = 6.7 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ: 154.8, 141.3, 140.5, 140.5, 140.3, 137.7, 136.8, 136.4, 134.5, 128.8, 127.1, 126.9, 125.7, 125.6, 123.8, 123.5, 122.7, 122.6, 121.7, 120.7, 120.6, 119.3, 118.7,

118.6, 118.4, 114.6, 114.3, 113.9, 109.2, 108.9, 108.5, 77.4, 77.1, 76.7, 55.6, 55.4, 37.7, 37.5, 30.6, 28.5, 24.0, 23.0, 14.04, 13.98, 13.8, 10.8.

Anal. Calcd. For $C_{132}H_{113}N_9O_4$: C 83.91; H 6.03; N 6.67; O 3.39; found: C 83.87; H 6.06; N 6.68.

Starburst Carbazole Derivatives as Efficient Hole Transporting Materials for Perovskite Solar Cells

Aistė Jegorovė, Minh Anh Truong, Richard Murdey, Maryte Daskeviciene, Tadas Malinauskas, Kristina Kantminiene, Vygintas Jankauskas, Vytautas Getautis,* and Atsushi Wakamiya*

Five new star-shaped carbazole-based molecules are successfully synthesized from low-cost, commercially available reagents via a simple one-step synthesis route. All carbazole derivatives comprise a 3,6-diaminocarbazole core with carbazole peripheral groups substituted at the 2- or 3-positions and various aliphatic side chains. These molecules are evaluated as hole transporting materials to replace 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) in perovskite solar cells. Power conversion efficiencies of the devices with these carbazole hole transporting layers reach 19.0%, comparable with 19.7% obtained with the spiro-OMeTAD-based device. The thermal and operational stability of the candidate molecules are found to depend on the side chain substituents. Two candidate molecules with ethyl side chains show superior thermal stability compared with that of the reference solar cells prepared with spiro-OMeTAD.

1. Introduction

Organic–inorganic hybrid perovskite solar cells (PSCs) have been attracting increasing worldwide attention as competitive alternatives to conventional silicon-based solar cells^[1] owing to their low-cost constituent materials, solution processing,^[2,3] and high power conversion efficiencies (PCEs).^[4–6] In recent years,

significant progress has been made in PSCs,^[7–9] leading to a dramatic increase in PCEs from an initial value of 3.8% reported by Miyasaka and co-workers in 2009 to over 25% recently.^[4,10]

In a typical PSC device, a perovskite absorber is located between the organic hole transporting material (HTM) and electron transporting material (ETM). HTMs, owing to their effective hole extraction/collection ability and interfacial modification to block the electron transfer from perovskite to the metal anode, are essential components for efficient PSCs.^[11–13] So far, the state-of-the-art 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) is the most recognized and widely used HTM in PSCs due to its amorphous nature, high

solubility, and outstanding performance.^[14] However, high cost for synthesis and purification of spiro-OMeTAD is a drawback for the commercialized application of PSCs.^[15,16] In addition, because of its moderate glass transition temperature (T_g), most of the spiro-OMeTAD-based PSC devices are associated with serious thermal degradation.^[17] Consequently, the development of low-cost, efficient, and thermally durable HTMs remains a crucial challenge for large-scale applications. Up to now, various types of HTMs have been developed and some of them have been reported to show comparable performance in comparison with that of spiro-OMeTAD; however, most of them still require multistep synthetic procedures.^[12,18–25]

Carbazole (Cbz) moiety has been widely used as a building block in HTMs for PSCs due to its low cost, good charge transporting ability, chemical stability, and facile modification with a wide variety of functional groups.^[26–39] In addition, the carbazole-based HTMs have the advantage in that they do not contain methoxy substituents, such as those found on spiro-OMeTAD, and could increase the hydrophilicity of the HTM layer, thus affecting the device stability.^[40] Carbazole moiety can act as the core unit with a planar structure^[26–33] and/or periphery moiety with the hole transporting function.^[34–41]

Morphological stability of the HTMs is an important factor to consider, especially at elevated temperatures at which real-world devices have to operate. Among the many HTMs developed to date, starburst molecules are known as a group of compounds that readily form amorphous glasses. Their nonplanar molecular structure, bulky and rigid substituents, presence of different

A. Jegorovė, M. Daskeviciene, T. Malinauskas, V. Getautis
Department of Organic Chemistry
Kaunas University of Technology
Kaunas 50254, Lithuania
E-mail: vytautas.getautis@ktu.lt

M. A. Truong, R. Murdey, A. Wakamiya
Institute for Chemical Research
Kyoto University
Gokasho, Uji, Kyoto 611-0011, Japan
E-mail: wakamiya@scl.kyoto-u.ac.jp

K. Kantminiene
Department of Physical and Inorganic Chemistry
Kaunas University of Technology
Kaunas 50254, Lithuania

V. Jankauskas
Institute of Chemical Physics
Vilnius University
Vilnius 10257, Lithuania

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/solr.202100877>.

DOI: 10.1002/solr.202100877

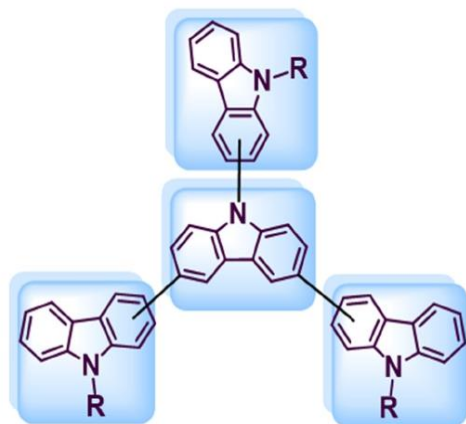


Figure 1. Carbazole-containing π -electron starburst molecules.

conformers, and relatively large molecular size are attributed to the enhanced stability of the amorphous glassy state as well as higher T_g .^[42] Furthermore, starburst HTMs have demonstrated good performance in PSCs,^[23,25,43] indicating good prospects for the development of efficiently performing HTMs.

In this context, Cbz-containing π -electron starburst molecules with more than four peripheral groups stretching in different directions were found to exhibit significantly higher T_g compared with spiro-OMeTAD.^[33–36,38,39] To the best of our knowledge, until now, HTMs in which the Cbz chromophore is used as both the central core and the peripheral branch have not been reported.

It has been shown on numerous instances that the length and branching of aliphatic chains can significantly influence the morphology, thermal and charge transport properties, as well as photovoltaic performance in PSCs.^[44,45] Therefore, another important factor that we wanted to evaluate was the effect of aliphatic substituents on the properties and performances of these carbazole-based starburst molecules (Figure 1).

In this work, we report the synthesis of a series of π -electron starburst molecules, bearing Cbz moiety as a central core and peripheral branches. We also investigated their structure–property relationship. The electrical and photovoltaic properties of the synthesized compounds in PSCs have been evaluated in respect of the linking position of the Cbz chromophores, as well as the length and branching of the aliphatic chain at the nitrogen atom.

2. Results and Discussion

2.1. Thermal Properties

Thermal behavior of the new HTMs was evaluated by thermogravimetric analysis (TGA) in nitrogen atmosphere. The thermal characteristics are presented in Figure S1a, Supporting Information, and summarized in Table 1. All the synthesized compounds are thermally stable at temperatures higher than 400 °C, which is sufficiently high to withstand the typical processing conditions of PSCs.

The results of differential scanning calorimetry (DSC) measurements are shown in Figure 2. The corresponding glass transition temperatures (T_g) are listed in Table 1.

No endothermic peaks corresponding to the melting of the crystals were observed over two heating cycles, revealing that all synthesized carbazole derivatives are amorphous (Figure S1b, Supporting Information). It is clear that increasing the length and branching of the aliphatic chains on the peripheral Cbz chromophores decreased the T_g values significantly (217 °C for V1310, 109 °C for V1332, and 97 °C for V1323). Whether peripheral Cbz chromophores are attached to the diaminocarbazole core at the 3- or 2-positions has comparatively little effect (97 °C for V1323 vs 94 °C for V1381 and 212 °C for V1377 vs 217 °C for V1310), although T_g values can be seen to be slightly higher in the case of 3-substitution. The T_g values for HTMs bearing the shortest aliphatic chains (217 °C for V1310, 212 °C for V1377) are significantly higher than that of spiro-OMeTAD (126 °C). This trend can be explained in terms of the reduced molecular disorder in the compounds with shorter alkyl chains.^[46] It can be anticipated that these molecules should outperform spiro-OMeTAD in terms of thermal stability in general and resistance to crystallization in particular.

Table 1. Thermal, optical, and photophysical properties of the synthesized HTMs.

HTM	T_g [°C] ^{a)}	T_{d5} [°C] ^{a)}	λ_{abs} [nm] ^{b)}	λ_{PL} [nm] ^{b)}	I_p [eV] ^{c)}	E_g [eV] ^{d)}	E_{on} [eV] ^{e)}	μ_0 [cm ² V ⁻¹ s ⁻¹] ^{f)}	μ_0 [cm ² V ⁻¹ s ⁻¹] ^{g)}
V1310	217	511	292, 321, 365, 413	471	4.86	2.75	−2.11	—	3.1×10^{-6}
V1323	97	411	291, 320, 365, 413	471	4.99	2.76	−2.23	3.7×10^{-6}	4.1×10^{-7}
V1332	109	482	291, 321, 365, 413	471	4.87	2.73	−2.14	3.5×10^{-6}	5.0×10^{-7}
V1377	212	525	262, 359	438	5.16	2.90	−2.26	6.1×10^{-6}	5.1×10^{-7}
V1381	94	469	264, 359	438	5.24	2.93	−2.31	1.0×10^{-5}	5.8×10^{-7}
spiro-OMeTAD ^[48]	126	449	387	—	5.01 ²⁸	3.01	−2.11	1.2×10^{-4}	2.9×10^{-6}

^{a)}Glass transition (T_g) and 5% weight loss (T_{d5}) temperatures observed from DSC and TGA, respectively (10 °C min⁻¹, N₂ atmosphere); ^{b)}UV–vis and PL spectra were measured in tetrahydrofuran (THF) solutions (10⁻⁴ M and 10⁻⁵ M, respectively); ^{c)}Ionization energies of the films measured using photoelectron spectroscopy in air (PESA); ^{d)} E_g estimated from the intersection of absorption and emission spectra of solid films; ^{e)} $E_{on} = I_p - E_g$; ^{f)}Mobility value at zero field strength^[38–60]; ^{g)}Mobility value at zero field strength with bisphenol-Z polycarbonate (PC-Z) (1:1) added.^[58–60]

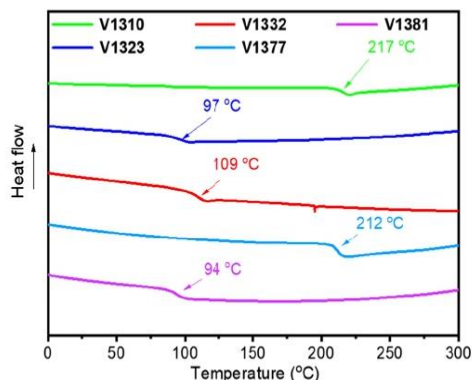


Figure 2. DSC curves for the second run of the HTMs (heating rate of $10^{\circ}\text{C min}^{-1}$, N_2 atmosphere).

2.2. Optical Properties

Ultraviolet–visible (UV–vis) spectra of the molecules in THF solution have shown negligible differences among the compounds bearing various aliphatic chains. The spectra of the compounds with peripheral 3-substituted Cbz chromophores (V1310, V1323, and V1332) display intensive π – π^* absorption bands at 270–340 nm and a series of less intensive absorption bands at >350 nm (Figure 3a). An intense absorption band in the spectra of the molecules containing peripheral 2-substituted Cbz chromophores (V1377 and V1381) can be observed at 360 nm. To gain understanding of the features of the absorption spectra, time-dependent density functional theory (TD-DFT) calculations of the lowest-energy singlet-excited electronic states (S_n) were carried out at the CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory (see Table S1–S5, Supporting Information). For molecules with 3-substituted Cbz in peripheral groups (V1310, V1323, and V1332), the weak and broad absorption band centered at around 420 nm has been ascribed to the combination of two

weak electronic transitions $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_3$. In contrast, for molecules with 2-substituted Cbz in peripheral groups (V1377 and V1381), the absorption bands in the long wavelength region, which are ascribed to the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions, cannot be observed due to their low oscillator strength. However, the $S_0 \rightarrow S_3$ transition results in a strong absorption band centered at around 370 nm.

In the photoluminescence (PL) spectra, the compounds bearing peripheral 3-substituted Cbz chromophores gave the maximum emission peaks centered at 471 nm in the PL spectra, compared with 440 nm for the derivatives bearing peripheral 2-substituted Cbz chromophores. The redshift of the PL peaks indicates that the conjugation in the 3-substituted Cbz derivatives is more extended than that in the 2-substituted ones.

The features and trends were maintained after the compounds were spin coated on glass substrates (Figure 3b). Stokes shift can be used to probe the structural deformation between the ground- and excited-state geometries during the electron excitation process, which can give beneficial information on molecular flexibility. Large Stokes shifts of ≈ 100 nm have been observed for all compounds, indicating significant structural deformation of the photoconductors during the electron excitation process. Previously, it has been demonstrated that a large Stokes shift is also favorable for the infiltration of the HTMs into the top of the perovskite layer^[47] and from this perspective, the synthesized HTMs have the potential to improve the performance of PSCs.

The optical gap (E_g) was determined from the intersection of the thin-film absorption and PL spectra of the thin films. The optical gap for the derivatives bearing peripheral 3-substituted Cbz chromophores is around 2.8 eV, while the corresponding value for the derivatives bearing peripheral 2-substituted Cbz chromophores is estimated to be slightly higher, at ≈ 2.9 eV (Table 1).

2.3. Photoelectrical Properties

The surface ionization potentials (I_p) of the thin films were measured by photoelectron spectroscopy in air (PESA) (Figure 4).

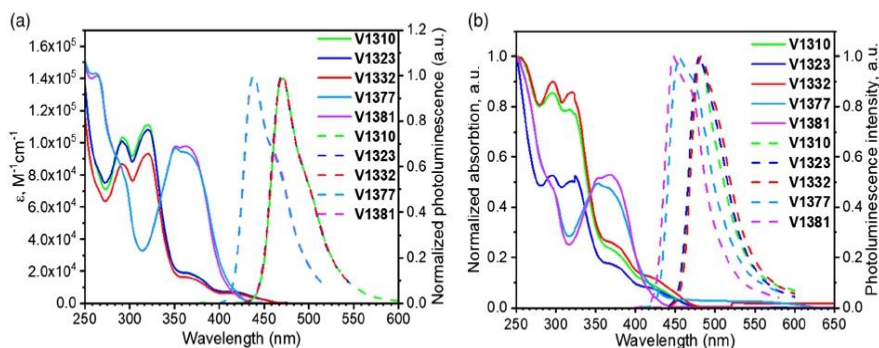


Figure 3. a) UV–vis absorption (solid line) and PL (dashed line) spectra of the investigated HTMs in THF solution (UV–vis: 10^{-4} M; PL: 10^{-5} M). b) UV–vis absorption (solid line) and PL (dashed line) spectra of HTMs thin films.

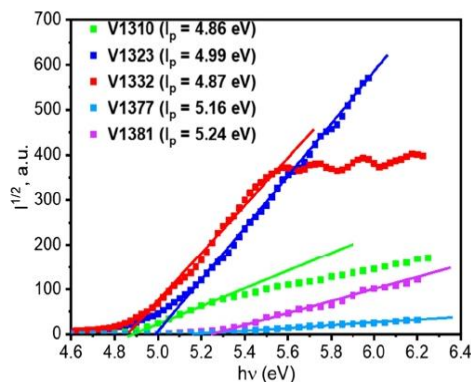


Figure 4. Photoemission in air spectra of the new HTMs.

As expected, given the shared core structure of the five carbazole molecules, only small variations in the ionization potentials are observed, ranging from 4.86 eV for **V1310** to 5.24 eV for **V1381**, and all are closely comparable with spiro-OMeTAD (5.01 eV).^[48] 3-substituted HTMs show shallower I_p than those of 2-substituted HTMs, attributed to the more effective conjugation length, as will be mentioned in theoretical calculations part. The lowest unoccupied molecular orbital (LUMO) energy level was assessed by adding the highest occupied molecular orbital (HOMO) energy level to the optical bandgap obtained from the absorption edge of the thin-film absorption spectra. The energy-level data are compiled in Table 1. Both the HOMO and LUMO energy levels are higher than the

corresponding valance bands (VBs) and conduction bands (CBs) of typical perovskite materials such as MAPbI₃ (MA: methylammonium, VB = −5.45 eV, CB = −3.90 eV)^[49] or Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.75}Br_{0.25} (FA: formamidinium, VB = −5.56 eV, CB = −3.99 eV).^[50] Therefore, efficient hole extraction and electron blocking should be expected.

The frontier molecular orbitals are shown in Figure 5 (also see Figure S2–S5, Supporting Information). Neither HOMO nor LUMO extend to the alkyl substituents, confirming that the electronic properties should be independent of the choice of the aliphatic chain. The HOMOs of the molecules with 2-substituted Cbz (**V1377** and **V1381**) do not extend to the nitrogen atoms of the Cbz peripheral groups, while those of the 3-substituted Cbz (**V1310**, **V1332**, and **V1323**) do. The more extended conjugation in the 3-substituted Cbz results in a smaller observed bandgap and shallower HOMO energy level.

The hole mobility of the carbazole compounds was estimated from xerographic time of flight (XTOF) measurements (Table 1, Figure S6, Supporting Information). The charge mobility of the pure materials ranges from 3.5×10^{-6} to $1.0 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is somewhat lower than that of spiro-OMeTAD, and nonetheless, it is sufficient for the application of these materials as hole transport materials in PSCs. However, **V1310** layers were one noticeable exception as their quality was insufficient for XTOF measurements. To evaluate the charge mobility in **V1310**, a mixture of HTM and polymeric film forming material polycarbonate (PC-Z) was used. Addition of the polymer dilutes the charge transporting material and reduces the overall hole mobility approximately to one order of magnitude; however, it allows comparing **V1310** with other investigated materials. The XTOF data have shown that **V1310** demonstrates very similar results to spiro-OMeTAD, measured

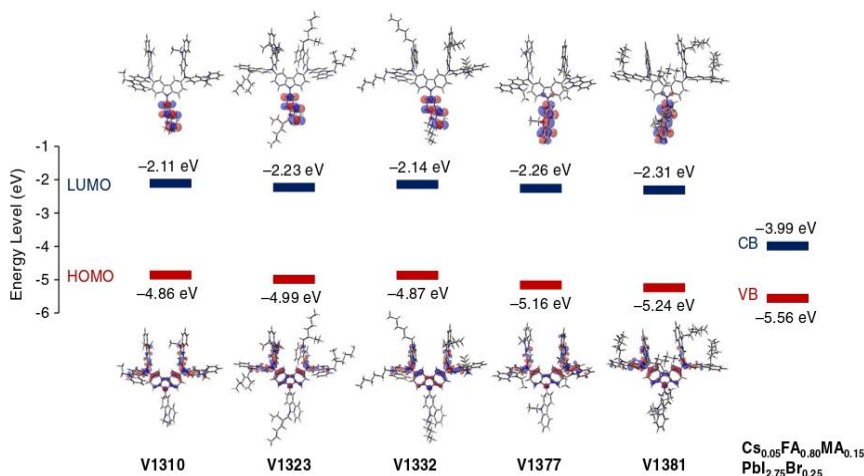


Figure 5. The frontier molecular orbitals (isovalue: 0.03) performed at B3LYP/6-31G(d) together with the HOMO and LUMO levels of the star-shaped Cbz derivatives in the thin film, determined by PESA and optical bandgap analysis measurements. The VB and CB of Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.75}Br_{0.25} are included as reference levels.

under identical conditions. The detailed XTOF measurement procedures are provided in Supporting Information.

The reorganization energies (λ_{reorg}) of the star-shaped Cbz derivatives and spiro-OMeTAD, which represent their relaxation after the formation of radical cations (Figure S7, Supporting Information), were also calculated according to the B3LYP/6-31G(d) level of theory and are summarized in Table S6, Supporting Information. To simplify the calculations, V1310 and V1377 with ethyl chains were chosen as representatives of molecules bearing 3- and 2-substituted carbazole peripheral groups, respectively. In general, according to Marcus theory, the small λ_{reorg} indicates fast transfer rate for holes.^[51] As shown in Table S6, Supporting Information, the λ_{reorg} value estimated for spiro-OMeTAD is 145 meV, which is close to the previously reported value.^[52] λ_{reorg} for V1310 and V1377 are 148 and 166 meV, respectively, suggesting that V1310 may show improved hole transporting ability compared with V1377.

2.4. Fabrication and Performance of PSCs

Performance of the new star-shaped HTMs was evaluated in the photovoltaic PSCs utilizing a conventional n–i–p planar architecture fabricated with the following layers: an indium tin oxide (ITO)-coated glass substrate, SnO₂, perovskite, HTM, and a gold electrode. For comparison, spiro-OMeTAD reference devices were also prepared with the same device architecture. The details of the device fabrication are provided in the Supporting Information. A mixed-composition Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.75}Br_{0.25} perovskite material was used, with cesium, formamidinium (FA), and methylammonium (MA) cations and a I/Br ratio of 11:1.^[50] The HTMs were dissolved in chlorobenzene with different concentrations (V1310: 0.03 M, V1323: 0.02 M, V1332: 0.03 M, V1377: 0.02 M, V1381: 0.02 M, or spiro-OMeTAD: 0.06 M). The different concentrations were selected to give the optimal film thickness for each material. Although spiro-OMeTAD layer must generally exceed 200 nm to achieve reproducible high-performance PSCs,^[53,54] it was found that with the carbazole-based HTMs, comparable performance could be realized using much thinner HTM layers. The implication is that while spiro-OMeTAD has superior hole transport properties, the new molecules have better morphology, such that they better cover the perovskite layer at lower thickness. Co^{III}-based oxidizing agent tris(2-(1*H*-pyrazol-1-yl)-4-*tert*-butylpyridine)cobalt(III) tris(bis(trifluoromethanesulfonyl)imide) (FK209 Co^{III} TFSI, 0.03 equiv.), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 0.54 equiv.), and 4-*tert*-butylpyridine (TBP, 3.3 equiv.) were mixed with all HTM solutions.

The thickness, coverage, and morphology of the HTM layers were characterized with the aid of cross-sectional SEM (Figure S8, Supporting Information), top-view SEM (Figure S9, Supporting Information), and atomic force microscopy (AFM) (Figure S10, Supporting Information) imaging. All the spin-coated HTM films uniformly coat the perovskite layer, reducing the root-mean-square (RMS) surface roughness from 33 nm for the perovskite substrate, to 13, 10, 6.5, 7.7, 9.3, and 11 nm, for V1310, V1323, V1332, V1377, V1381, and spiro-OMeTAD, respectively. The average film thickness was 140, 115, 130,

140, 120, and 240 nm for V1310, V1323, V1332, V1377, V1381, and spiro-OMeTAD, respectively.

The performance of the solar cells was evaluated under AM 1.5G simulated sunlight. The forward current density–voltage (*J*–*V*) curves of the best devices for each HTM are shown in Figure 6, and the photovoltaic parameters are summarized in Table 2.

Regardless of the HTM used, functional and efficient cells could be readily prepared and they were competitive with the spiro-OMeTAD reference. Overall, the HTMs bearing short, linear alkyl chains (V1310, V1377) give better performance than those with longer, branched alkyl chains (V1323, V1332, and V1381).

Of the devices based on HTMs with 3-substituted Cbz in the peripheral groups, the best forward scan PCE for V1310, V1323, and V1332 was 18.9%, 19.0%, and 18.3%, respectively, with an average forward scan PCE of 18.6%, 18.0%, and 17.4%. Showing the same trend, the best (average) forward scan PCE for the devices based on HTMs with 2-substituted Cbz in peripheral groups was 18.4% (18.2%) for V1377 and only 16.3% (15.5%) for V1381. The obtained results are similar or better than those demonstrated by other starburst HTMs investigated by other research groups.^[23,34,55–57] The performance drop is largely the result of the loss of fill factor with some additional contribution from the falling *J*_{SC} values. The forward–reverse scan hysteresis broadly increases as the performance decreases, with V1310 having the smallest hysteresis and V1332 having the largest (Table 2, Figure S11, Supporting Information). The *J*_{SC} values attained from the *J*–*V* curves are in good agreement with the integrated current densities estimated from the incident photon-to-current efficiency (IPCE) measurements (Figure S12, Supporting Information).

Impedance measurements were made on the solar cell devices under AM 1.5G and short-circuit conditions. It should be noted that it was not possible to maintain stable operation of the V1323- and V1332-based devices over the 10 min measurement interval required to record the impedance data. For all devices, the photoinduced capacitance (Figure S13, Supporting Information) increased at low frequencies as a result of the photogenerated charge density filling the deep trap levels in the device. V1310- and V1377-based devices showed the lowest increase

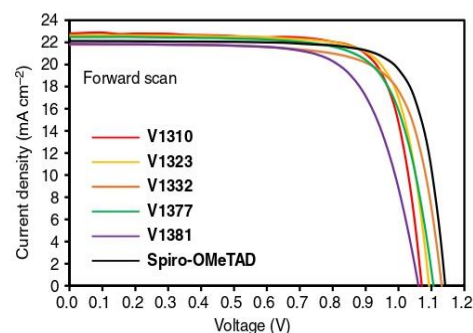


Figure 6. Champion forward scan *J*–*V* characteristics of PSCs using the synthesized HTMs and spiro-OMeTAD.

Table 2. Photovoltaic parameters of conventional PSCs derived from *J*–*V* measurements.

HTM ^{a)}	Scan ^{b)}	J_{sc} [mA cm ⁻²] ^{c)}	V_{oc} [V] ^{d)}	FF ^{d)}	PCE [%] ^{d)}	HI ^{d)}
V1310	Forward	22.8 (22.4 ± 0.5)	1.07 (1.09 ± 0.02)	0.78 (0.76 ± 0.01)	18.9 (18.6 ± 0.3)	–0.044
	Reverse	22.8 (22.3 ± 0.6)	1.07 (1.08 ± 0.01)	0.74 (0.72 ± 0.03)	18.1 (17.4 ± 1.0)	
V1323	Forward	22.6 (22.5 ± 0.2)	1.09 (1.06 ± 0.02)	0.77 (0.76 ± 0.01)	19.0 (18.0 ± 0.6)	–0.056
	Reverse	22.7 (22.4 ± 0.2)	1.08 (1.05 ± 0.02)	0.73 (0.72 ± 0.02)	18.0 (16.9 ± 0.6)	
V1332	Forward	21.8 (21.6 ± 0.3)	1.13 (1.11 ± 0.01)	0.74 (0.72 ± 0.01)	18.3 (17.4 ± 0.5)	–0.109
	Reverse	21.6 (21.3 ± 0.4)	1.12 (1.10 ± 0.01)	0.68 (0.65 ± 0.04)	16.5 (15.4 ± 1.2)	
V1377	Forward	22.5 (22.3 ± 0.2)	1.11 (1.12 ± 0.01)	0.74 (0.73 ± 0.01)	18.4 (18.2 ± 0.2)	–0.034
	Reverse	22.5 (22.3 ± 0.2)	1.10 (1.11 ± 0.01)	0.72 (0.72 ± 0.01)	17.8 (17.7 ± 0.2)	
V1381	Forward	21.9 (21.6 ± 0.4)	1.06 (1.07 ± 0.02)	0.70 (0.67 ± 0.02)	16.3 (15.5 ± 0.5)	–0.094
	Reverse	21.8 (21.5 ± 0.3)	1.05 (1.06 ± 0.02)	0.65 (0.60 ± 0.04)	14.9 (13.6 ± 1.0)	
Spiro-OMeTAD	Forward	22.1 (22.5 ± 0.3)	1.14 (1.12 ± 0.02)	0.78 (0.78 ± 0.01)	19.7 (19.5 ± 0.3)	–0.065
	Reverse	22.0 (22.3 ± 0.3)	1.12 (1.10 ± 0.02)	0.75 (0.74 ± 0.01)	18.5 (18.2 ± 0.3)	

^{a)}HTM concentration: 0.03 m for **V1310**, **V1332**, and **V1377**, 0.02 m for **V1323** and **V1381**, 0.06 m for spiro-OMeTAD. The corresponding thickness is 140, 115, 130, 140, 120, and 240 nm for **V1310**, **V1323**, **V1332**, **V1377**, **V1381**, and spiro-OMeTAD, respectively; ^{b)}Forward and reverse indicate the scan directions from J_{sc} to V_{oc} and from V_{oc} to J_{sc} , respectively; ^{c)}The average values (average value ± one standard deviation) were calculated from nine devices; ^{d)}Hysteresis index (HI) = (PCE_{Reverse} – PCE_{Forward})/PCE_{Reverse}.

in low-frequency capacitance, the **V1381**-based device performed similarly to the spiro-OMeTAD reference, and the values for **V1323** and **V1332**, which had already degraded substantially from their initial PCEs at the time of the impedance measurements, were significantly higher. A lower low-frequency capacitance signal is desirable, as it indicates that fewer of the photogenerated charge carriers are trapped, that is, the charge is more efficiently extracted by the HTM. The capacitance results are also reflected by the hysteresis in the *J*–*V* curves, with less charge or ion accumulation at the perovskite/HTM interface in the case of **V1310** and **V1377** resulting in smaller hysteresis. The complex impedance plot (Figure S14, Supporting Information) shows that the parallel resistance follows a similar trend to the low-frequency capacitance signal. As the quality of the perovskite films can be taken to be consistent across different devices, the difference in the recombination resistance may be attributed to the relative hole extraction ability of the different HTMs. **V1310** and **V1377** have shown superior performance in this respect, with modeled parallel resistance values of 90

and 80 Ω cm², respectively. **V1381** is similar to the spiro-OMeTAD reference, at around 50 Ω cm², while the values for **V1323** and **V1332**, which already degraded substantially from their initial PCE at the time of the impedance measurements, were much lower. Although the series resistance, as indicated by the high-frequency intercept of the complex impedance curve with the real axis, was similar for all the devices, at 1 Ω cm², devices based on **V1377** and **V1381** had a noteworthy additional shift of the main loop away from this intercept by additional 1 Ω cm² (Figure S15, Supporting Information). This additional series resistance, which is bypassed at high frequencies, can be attributed to the significant electrical resistance of the HTM layers with 2-substituted Cbz in the peripheral groups. The difference in HTM conductivity is in good agreement with the estimated hole mobilities and calculated reorganization energies discussed above.

Although the initial PCE of all devices was comparatively high, very large differences became readily apparent after even short periods of operation under AM 1.5G. For the stability tests, the devices were placed in a N₂-filled measurement chamber and the device performance under AM 1.5G was monitored with a maximum power point tracking (MPPT) algorithm. First, the devices were subjected to a short 300 s MPPT prior to the impedance measurements presented above. After the impedance tests were complete, the MPPT algorithm was run for 10 h. The results, shown in Figure 7, confirm that although all devices initially gave PCE above 15%, the performance of the **V1323** and **V1332** devices degraded rapidly during the initial 300 s stabilization test. The PCE of the spiro-OMeTAD device dropped rapidly to 14% after the impedance measurements, after which the losses stabilized, reaching 12% after 10 h. The output of the **V1381** device fell from an initial value of 16% to 10% after 10 h. **V1310** and **V1377** devices had the best operational stability, with similar MPPT curves falling from a maximum of ≈18% to ≈13% after 10 h.

To investigate the interfacial charge separation, steady-state PL quenching and time-resolved PL (TRPL) decay were explored for the pristine perovskite and perovskite/HTM films. After

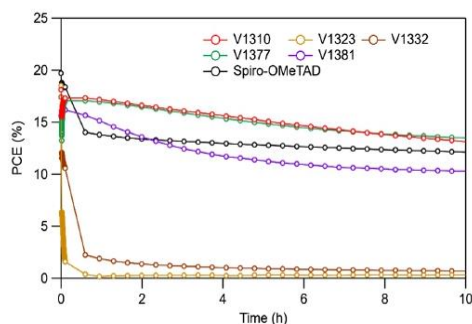


Figure 7. Normalized MPPT data for the unencapsulated PSCs constructed with investigated HTMs and spiro-OMeTAD under AM 1.5G in inert atmosphere. An initial 300 s MPPT test was followed by the impedance measurements, after which the devices were subjected to the second MPPT test, this time for 10 h.

fabricating HTMs on perovskite layers, the PL peak intensity was reduced, falling to 32%, 20%, 37%, 77%, 39%, and 22% for V1310, V1323, V1332, V1377, V1381, and spiro-OMeTAD, respectively (Figure S16, Supporting Information). The TRPL lifetime for the pristine perovskite film was found to be 100.9 ns, and the TRPL lifetime for the perovskite/HTM films decreased to 52.2, 14.3, 20.6, 78.2, 21.5, and 10.9 nm for V1310, V1323, V1332, V1377, V1381, and spiro-OMeTAD, respectively (Figure S17, Supporting Information). PL quenching of compounds with peripheral 3-substituted Cbz chromophores (V1310, V1323, and V1332) is faster and more efficient than compounds with peripheral 2-substituted Cbz chromophores (V1377 and V1381), while quenching for the molecules with the more bulky alkyl chain substituents (V1323, V1332, and V1381) is faster and more efficient than for the molecules with shorter chains (V1310 and V1377).

Shelf stability tests were also performed on the unencapsulated devices to examine their thermal durability under ambient atmosphere (Figure S18, Supporting Information). After heating the device up to 120 °C, the efficiencies of devices using V1310, V1377 remained superior to those of spiro-OMeTAD based devices, while the efficiencies of devices using V1323, V1332, and V1381 were substantially lower. In fact, the output from the cells using these three HTMs all dropped dramatically after heating at 80 °C for 1 h. To ensure that the degradation was not caused by oxygen or moisture, the thermal stability of V1310 and spiro-OMeTAD-based devices was evaluated in a N₂-filled glovebox (O₂, H₂O < 0.1 ppm) (Figure 8 and Figure S19, Supporting Information).

As shown in Figure 8, the efficiency of the V1310-based device remained at 76% of the initial efficiency after heating at up to 100 °C for 24 h. In contrast, under the same conditions, the device efficiency using spiro-OMeTAD fell to 40% of the initial value. After further heating at 120 °C for 7 h, the efficiency of spiro-OMeTAD containing PSCs dropped to 9% of the initial value, while that of V1310-based device still retained 60% of the initial efficiency. After this test, the V1310 layer remained smooth and uniform, while the spiro-OMeTAD layer developed cavities (Figure S20, Supporting Information). The higher thermal stability of devices using V1310 and V1377 as HTMs is a direct result of their higher *T_g* values compared with V1323, V1332, V1381, and spiro-OMeTAD.

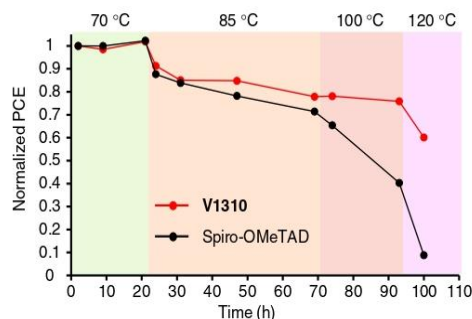


Figure 8. PCE evolution of the PSC devices under N₂ without encapsulation, under 100 mW cm⁻² photon flux (AM 1.5G).

3. Conclusion

New π -electron starburst molecules, bearing the carbazole moiety as a central core as well as peripheral groups, were synthesized and evaluated as HTMs to replace spiro-OMeTAD in PSCs. Amorphous, uniform thin films of these materials are readily fabricated by spin coating. Molecules with 3-substituted carbazole peripheral groups have more extended π -conjugations, leading to higher charge carrier mobility compared with the 2-substituted derivatives. All synthesized compounds performed well as efficient HTMs for PSCs, with PCEs ranging from 16.3% to 19.0%. Moreover, the carbazole compounds with short aliphatic chains showed exceptionally high glass transition temperatures over 200 °C, resulting in superior thermal stability compared with that of spiro-OMeTAD. After heating at 120 °C in N₂ atmosphere, the efficiency of devices using spiro-OMeTAD dropped to 9%, while the efficiency of the devices using the carbazole-based HTMs still remained at 60% of the initial value. Given their high efficiency, ease of fabrication, good stability, and favorable electronic properties, these simple and low-cost carbazole hole transport materials promise to be effective alternatives to spiro-OMeTAD in commercial PSCs.

4. Experimental Section

The facile synthesis procedure is outlined in **Scheme 1** with the detailed synthetic procedures and full chemical characterization provided in Supporting Information. New π -electron starburst molecules bearing Cbz moiety as a central core as well as peripheral groups were synthesized by the one-step palladium-catalyzed Buchwald–Hartwig C–N cross-coupling reaction. Reactions of commercially available 3,6-diaminocarbazole with 3-bromo- and 2-bromo-*N*-alkylcarbazoles provided target compounds V1310, V1323, V1332, V1377, and V1381 in 52–69% yields.

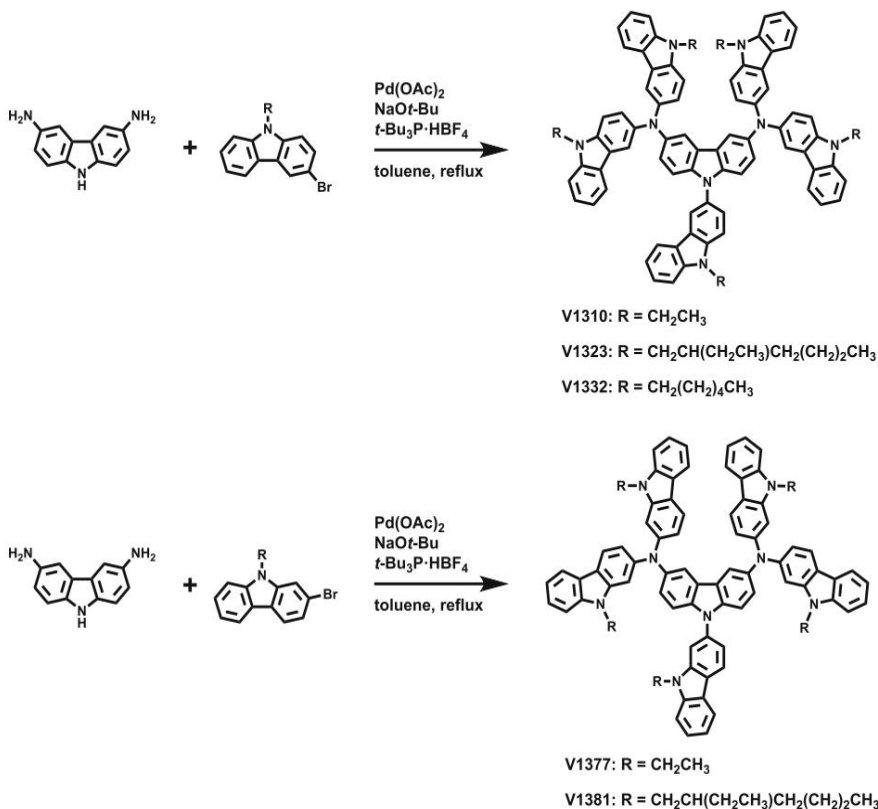
The synthesized compounds were purified by column chromatography; however, all attempts to crystallize them were unsuccessful. The chemical structures of the synthesized compounds were verified by ¹H, ¹³C NMR spectroscopy and elemental analysis. The obtained molecules were soluble in common organic solvents typically used for the deposition of the hole transporting layer in perovskite devices (chlorobenzene, chloroform, tetrahydrofuran, etc.).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

A.J. and M.A.T. contributed equally to this work. This work was supported by the Research Council of Lithuania under grant agreement no. 01.2.2-LMT-K-718-03-0040 (SMARTMOLECULES) and by the Japan Society for the Promotion of Science (JSPS) under the KAKENHI JP19K05666, JP20K22531, and JP21H04699 research grants. Additional support from the JST-COI (JPMJC1307) and NEDO programs is gratefully acknowledged. Further research funding was provided from the International Collaborative Research Program of ICR, Kyoto University, and the ICR Grants for Promoting Integrated Research, Kyoto University.



Scheme 1. Synthesis of new star-shaped Cbz derivatives V1310, V1323, V1332, V1377, and V1381.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

Keywords

amorphous thin films, carbazole, hole transporting materials, perovskite solar cells, thermal stabilities

Received: October 20, 2021
Revised: November 7, 2021
Published online: November 21, 2021

[1] G. Hodes, *Science* **2013**, 342, 317.

- [2] W. Nie, H. Tsai, R. Asadpour, J. C. Blancon, A. J. Neukirch, G. Gupta, J. J. Crochet, M. Chhowalla, S. Tretiak, M. A. Alam, H. Wang, A. D. Mohite, *Science* **2015**, 347, 522.
- [3] Y. Rong, Y. Hu, A. Mei, H. Tan, M. I. Saidaminov, S. Il Seok, M. D. McGehee, E. H. Sargent, H. Han, *Science* **2018**, 361, 1214.
- [4] <https://www.nrel.gov/pv/cell-efficiency.html> (accessed: June 2021).
- [5] F. Li, X. Deng, F. Qi, Z. Li, D. Liu, D. Shen, M. Qin, S. Wu, F. Lin, S. H. Jang, J. Zhang, X. Lu, D. Lei, C. S. Lee, Z. Zhu, A. K. Y. Jen, *J. Am. Chem. Soc.* **2020**, 142, 20134.
- [6] J. Jeong, M. Kim, J. Seo, H. Lu, P. Ahlawat, A. Mishra, Y. Yang, M. A. Hope, F. T. Eickemeyer, M. Kim, Y. J. Yoon, I. W. Choi, B. P. Darwich, S. J. Choi, Y. Jo, J. H. Lee, B. Walker, S. M. Zakeeruddin, L. Emsley, U. Rothlisberger, A. Hagfeldt, D. S. Kim, M. Grätzel, J. Y. Kim, *Nature* **2021**, 592, 381.
- [7] A. N. Cho, N. G. Park, *ChemSusChem* **2017**, 10, 3687.
- [8] B. Chen, P. N. Rudd, S. Yang, Y. Yuan, J. Huang, *Chem. Soc. Rev.* **2019**, 48, 3842.
- [9] A. K. Jena, A. Kulkarni, T. Miyasaka, *Chem. Rev.* **2019**, 119, 3036.
- [10] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, 131, 6050.
- [11] A. Krishna, A. C. Grimsdale, *J. Mater. Chem. A* **2017**, 5, 16446.

- [12] L. Calió, S. Kazim, M. Grätzel, S. Ahmad, *Angew. Chem., Int. Ed.* **2016**, *55*, 14522.
- [13] J. Seo, J. H. Noh, S. Il Seok, *Acc. Chem. Res.* **2016**, *49*, 562.
- [14] Z. Hawash, L. K. Ono, Y. Qi, *Adv. Mater. Interfaces* **2018**, *5*, 1700623.
- [15] P. Gratia, A. Magomedov, T. Malinauskas, M. Daskeviciene, A. Abate, S. Ahmad, M. Grätzel, V. Getautis, M. K. Nazeeruddin, *Angew. Chem., Int. Ed.* **2015**, *54*, 11409.
- [16] D. Vaitukaityte, Z. Wang, T. Malinauskas, A. Magomedov, G. Bubniene, V. Jankauskas, V. Getautis, H. J. Snaith, *Adv. Mater.* **2018**, *30*, 1803735.
- [17] N. J. Jeon, H. Na, E. H. Jung, T. Y. Yang, Y. G. Lee, G. Kim, H. W. Shin, S. Il Seok, J. Lee, J. Seo, *Nat. Energy* **2018**, *3*, 682.
- [18] Z. Yu, L. Sun, *Adv. Energy Mater.* **2015**, *5*, 1500213.
- [19] C. H. Teh, R. Daik, E. L. Lim, C. C. Yap, M. A. Ibrahim, N. A. Ludin, K. Sopian, M. A. Mat Teridi, *J. Mater. Chem. A* **2016**, *4*, 15788.
- [20] S. Ameen, M. A. Rub, S. A. Kosa, K. A. Alamry, M. S. Akhtar, H. S. Shin, H. K. Seo, A. M. Asiri, M. K. Nazeeruddin, *ChemSusChem* **2016**, *9*, 10.
- [21] J. Urieta-Mora, I. García-Benito, A. Molina-Ontoria, N. Martín, *Chem. Soc. Rev.* **2018**, *47*, 8541.
- [22] W. Zhou, Z. Wen, P. Gao, *Adv. Energy Mater.* **2018**, *8*, 1702512.
- [23] K. Rakstys, C. Igci, M. K. Nazeeruddin, *Chem. Sci.* **2019**, *10*, 6748.
- [24] E. Sheibani, L. Yang, J. Zhang, *Sol. RRL* **2020**, *4*, 202000461.
- [25] X. Yin, Z. Song, Z. Li, W. Tang, *Energy Environ. Sci.* **2020**, *13*, 4057.
- [26] M. Daskeviciene, S. Paek, Z. Wang, T. Malinauskas, G. Jokubauskaite, K. Rakstys, K. T. Cho, A. Magomedov, V. Jankauskas, S. Ahmad, H. J. Snaith, V. Getautis, M. K. Nazeeruddin, *Nano Energy* **2017**, *32*, 551.
- [27] M. Li, Z. Wang, M. Liang, L. Liu, X. Wang, Z. Sun, S. Xue, *J. Phys. Chem. C* **2018**, *122*, 24014.
- [28] M. Daskeviciene, S. Paek, A. Magomedov, K. T. Cho, M. Saliba, A. Kizeleviciute, T. Malinauskas, A. Gruodis, V. Jankauskas, E. Kamarauskas, M. K. Nazeeruddin, V. Getautis, *J. Mater. Chem. C* **2019**, *7*, 2717.
- [29] L. Gao, T. H. Schloemer, F. Zhang, X. Chen, C. Xiao, K. Zhu, A. Sellinger, K. Zhu, *ACS Appl. Energy Mater.* **2020**, *3*, 4492.
- [30] F. Liu, F. Wu, W. Ling, L. Zhu, Q. Li, Z. Li, *Sol. RRL* **2021**, *5*, 2100070.
- [31] C. Yin, J. Lu, Y. Xu, Y. Yun, K. Wang, J. Li, L. Jiang, J. Sun, A. D. Scully, F. Huang, J. Zhong, J. Wang, Y. B. Cheng, T. Qin, W. Huang, *Adv. Energy Mater.* **2018**, *8*, 1800538.
- [32] T. H. Schloemer, T. S. Gehan, J. A. Christians, D. G. Mitchell, A. Dixon, Z. Li, K. Zhu, J. J. Berry, J. M. Luther, A. Sellinger, *ACS Energy Lett.* **2019**, *4*, 473.
- [33] X. Yin, L. Guan, J. Yu, D. Zhao, C. Wang, N. Shrestha, Y. Han, Q. An, J. Zhou, B. Zhou, Y. Yu, C. R. Grice, R. A. Awni, F. Zhang, J. Wang, R. J. Ellingson, Y. Yan, W. Tang, *Nano Energy* **2017**, *40*, 163.
- [34] N. Berton, R. Nakar, B. Schmaltz, *Synth. Met.* **2019**, *252*, 91.
- [35] K. Rakstys, S. Paek, A. Drevilkauskaitė, H. Kanda, S. Daskeviciute, N. Shibayama, M. Daskeviciene, A. Gruodis, E. Kamarauskas, V. Jankauskas, V. Getautis, M. K. Nazeeruddin, *ACS Appl. Mater. Interfaces* **2020**, *12*, 19710.
- [36] A. Magomedov, S. Paek, P. Gratia, E. Kasparavicius, M. Daskeviciene, E. Kamarauskas, A. Gruodis, V. Jankauskas, K. Kantminiene, K. T. Cho, K. Rakstys, T. Malinauskas, V. Getautis, M. K. Nazeeruddin, *Adv. Funct. Mater.* **2018**, *28*, 1704351.
- [37] L. Zhu, Y. Shan, R. Wang, D. Liu, C. Zhong, Q. Song, F. Wu, *Chem. Eur. J.* **2017**, *23*, 4373.
- [38] L. Zhu, J. Xu, Y. Shan, C. Zhong, X. Tang, D. Long, Y. Zhang, F. Wu, *J. Mater. Chem. C* **2019**, *7*, 3226.
- [39] C. Lu, I. T. Choi, J. Kim, H. K. Kim, *J. Mater. Chem. A* **2017**, *5*, 20263.
- [40] J. Wang, H. Zhang, B. Wu, Z. Wang, Z. Sun, S. Xue, Y. Wu, A. Hagfeldt, M. Liang, *Angew. Chem., Int. Ed.* **2019**, *58*, 15721.
- [41] Y. Xue, Y. Wu, Y. Li, *J. Power Sources* **2017**, *344*, 160.
- [42] Y. Shiota, H. Kageyama, *Chem. Rev.* **2007**, *107*, 953.
- [43] Y. K. Wang, Z. Q. Jiang, L. S. Liao, *Chinese Chem. Lett.* **2016**, *27*, 1293.
- [44] R. Fuentes Pineda, J. Troughton, M. Planells, I. Sanchez-Molina Santos, F. Muhiith, G. S. Nichol, S. Haque, T. Watson, N. Robertson, *Phys. Chem. Chem. Phys.* **2018**, *20*, 1252.
- [45] K. H. Lin, A. Prlj, C. Corminboeuf, *J. Mater. Chem. C* **2018**, *6*, 960.
- [46] M. A. Truong, J. Lee, T. Nakamura, J. Y. Seo, M. Jung, M. Ozaki, A. Shimazaki, N. Shioya, T. Hasegawa, Y. Murata, S. M. Zakeeruddin, M. Grätzel, R. Murdey, A. Wakamiya, *Chem. Eur. J.* **2019**, *25*, 6741.
- [47] H. R. Li, K. W. Fu, A. Hagfeldt, M. Grätzel, S. G. Mhaisalkar, A. C. Grimsdale, *Angew. Chem., Int. Ed.* **2014**, *53*, 4085.
- [48] T. Brauklyla, R. Xia, M. Daskeviciene, T. Malinauskas, A. Gruodis, V. Jankauskas, Z. Fei, C. Momblona, C. Roldán-Carmona, P. J. Dyson, V. Getautis, M. K. Nazeeruddin, *Angew. Chem., Int. Ed.* **2019**, *58*, 11266.
- [49] M. Ozaki, Y. Nakaike, A. Shimazaki, M. Jung, N. Maruyama, S. Yakumaru, A. I. Rafieh, P. Ekanayake, T. Saito, Y. Shimakawa, T. Sasamori, Y. Murata, R. Murdey, A. Wakamiya, *Bull. Chem. Soc. Jpn.* **2019**, *92*, 1972.
- [50] M. Ozaki, Y. Ishikura, M. A. Truong, J. Liu, I. Okada, T. Tanabe, S. Sekimoto, T. Ohtsuki, Y. Murata, R. Murdey, A. Wakamiya, *J. Mater. Chem. A* **2019**, *7*, 16947.
- [51] B. Xu, H. Tian, L. Lin, D. Qian, H. Chen, J. Zhang, N. Vlachopoulos, G. Boschloo, Y. Luo, F. Zhang, A. Hagfeldt, L. Sun, *Adv. Energy Mater.* **2015**, *5*, 1401185.
- [52] W.-J. Chi, Q.-S. Li, Z.-S. Li, *Nanoscale* **2016**, *8*, 6146.
- [53] M. Saliba, J. P. Correa-Baena, C. M. Wolff, M. Stollerfoht, N. Phung, S. Albrecht, D. Neher, A. Abate, *Chem. Mater.* **2018**, *30*, 4193.
- [54] M. Jeong, I. W. Choi, E. M. Go, Y. Cho, M. Kim, B. Lee, S. Jeong, Y. Jo, H. W. Choi, J. Lee, J. H. Bae, S. K. Kwak, D. S. Kim, C. Yang, *Science* **2020**, *369*, 1615.
- [55] H. Choi, J. W. Cho, M. S. Kang, J. Ko, *Chem. Commun.* **2015**, *51*, 9305.
- [56] M. S. Kang, S. Do Sung, I. T. Choi, H. Kim, M. Hong, J. Kim, W. I. Lee, H. K. Kim, *ACS Appl. Mater. Interfaces* **2015**, *7*, 22213.
- [57] A. Molina-Ontoria, I. Zimmermann, I. Garcia-Benito, P. Gratia, C. Roldán-Carmona, S. Aghazada, M. Graetzel, M. K. Nazeeruddin, N. Martín, *Angew. Chem., Int. Ed.* **2016**, *55*, 6270.
- [58] E. Montrimas, V. Gaidelis, A. Pazera, *Lith. J. Phys.* **1966**, *6*, 569.
- [59] A. Y. C. Chan, C. Juhasz, *Int. J. Electron.* **1987**, *62*, 625.
- [60] S. M. Vaezi-Nejad, *Int. J. Electron.* **1987**, *62*, 361.

Supporting Information

Starburst Carbazole Derivatives as Efficient Hole Transporting Materials for Perovskite Solar Cells

Aistė Jegorovė,^{†,1} Minh Anh Truong,^{†,2} Richard Murdey,² Maryte Daskeviciene,¹ Tadas Malinauskas,¹ Kristina Kantminiene,³ Vygintas Jankauskas,⁴ Vytautas Getautis,^{*,1} and Atsushi Wakamiya^{*,2}

¹Department of Organic Chemistry, Kaunas University of Technology, Kaunas 50254, Lithuania.

²Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan.

³Department of Physical and Inorganic Chemistry, Kaunas University of Technology, Kaunas 50254, Lithuania.

⁴Institute of Chemical Physics, Vilnius University, Vilnius 10257, Lithuania.

[†]A.J. and M.A.T. contributed equally to this work.

*Corresponding authors: vytautas.getautis@ktu.lt; wakamiya@scl.kyoto-u.ac.jp

General

Chemicals required for the synthesis were purchased from Sigma-Aldrich and TCI Europe and used as received without additional purification. Spectral data of intermediate compounds is in agreement with the values reported in the literature. ^1H NMR and ^{13}C NMR spectra were collected at 400 and 101 MHz, respectively on a Bruker Avance III spectrometer. The chemical shifts, expressed in ppm, were relative to tetramethylsilane (TMS). All the experiments were performed at 25 °C. Reactions were monitored by thin-layer chromatography on ALUGRAM SIL G/UV254 plates and developed with UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was used for column chromatography. Elemental analysis was performed with an Exeter Analytical CE-440 elemental analyser, Model 440 C/H/N/.

Thermogravimetric analysis (TGA) was performed on a Q50 thermogravimetric analyzer (TA Instruments) at a scan rate of 10 °C min⁻¹ under nitrogen atmosphere. The values are given for a weight-loss of 5% (T_{d5}). Differential scanning calorimetry (DSC) was performed on a TA Instruments Q2000 differential scanning calorimeter under nitrogen atmosphere. Heating and cooling rate is 10 °C min⁻¹.

UV–vis spectral analysis of the sample in solution (THF, 10⁻⁴ mol L⁻¹) was performed on a Perkin Elmer Lambda 35 UV/VIS spectrophotometer. The layer thickness of the solution is $d = 1$ mm. Diffraction grating crack width is 2 nm. Spectral recording speed is 2 nm s⁻¹. The wavelength λ is given in nm. The time-resolved fluorescence spectra of the sample in solution (THF, 10⁻⁵ mol L⁻¹) were recorded on an Edinburgh Instruments FLS920 light emission intensity spectrophotometer. Solutions of new compounds were exposed to different wavelengths: **V1310** - 330 nm, **V1323** - 330 nm, **V1332** - 330 nm, **V1377** - 380 nm, **V1381** - 380 nm. The layer thickness of the solution is $d = 1$ cm. The crack width of the diffraction grating is 1.5 nm. The wavelength λ is given in nm.

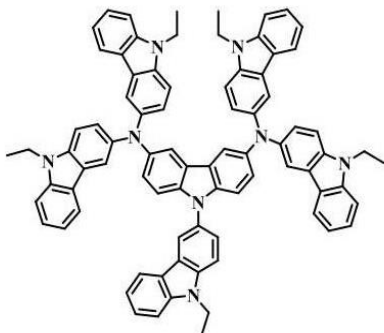
Scanning electron microscopy (SEM) was performed with an S8010 (Hitachi HighTechnologies Co.).

For the time-resolved photoluminescence (TRPL) measurements, the samples were excited by picosecond pulsed light at a wavelength of 688 nm (Advanced Laser Diode System). The excitation fluence was set at 100 nJ cm⁻². The PL signals were recorded using an avalanche photodiode (ID Quantique) and a time-correlated single photon counting board (PicoQuant). PL lifetimes were obtained by fitting the PL decay curve with a double exponential function and calculating the average lifetime. PL spectra were recorded using a N₂ cooled charge-coupled-device array equipped with a monochromator (Princeton Instruments). To avoid oxygen contamination and degradation, the samples were kept in an Ar-filled metallic box for the whole process.

Photocurrent—voltage measurements for perovskite solar cells were measured in air with an OTENTO-SUNIII (BUNKOUKEIKI co., Ltd.) and a Keithley 2400. The light intensity of the illumination source was adjusted by using standard silicon photodiodes: BS520 for J—V characteristics and SiPD S 1337-1010BQ for IPCE measurements.

Detailed synthetic procedures

1. 9-Ethyl-N^{3'},N^{3''},N^{6'},N^{6''}-tetrakis(9-ethyl-9*H*-carbazol-3-yl)-9*H*-[3,9'-bicarbazole]-3',6'-diamine (**V1310**)



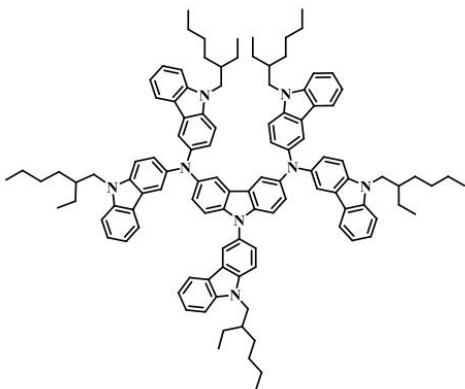
A mixture of 3,6-diaminocarbazole (0.8 g, 4 mmol), 3-bromo-9-ethylcarbazole (8.22 g, 30 mmol), and anhydrous toluene (46 mL) was purged with Ar for 30 minutes. Afterwards, palladium(II) acetate (0.1 g, 0.4 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.26 g, 0.8 mmol) were added and the reaction mixture was stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (2.92 g, 30 mmol) was added and the mixture was heated at reflux for 8 hours (TLC control, acetone/*n*-hexane 1:4). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 8:17, v:v). 20% solution of the final product in THF was poured with intensive stirring into a 15-fold excess of ethanol. The precipitate as a light yellow powder was filtered off, washed with ethanol, and dried. Yield 3.2 g (60%).

¹H NMR (400 MHz, THF-*d*₈) δ: 8.36 (d, *J* = 2.0 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.85–7.78 (m, 9H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.66 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.15 (m, 22H), 6.98 (t, *J* = 7.4 Hz, 4H), 4.50 (q, *J* = 7.2 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 8H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 12H).

¹³C NMR (101 MHz, THF-*d*₈) δ: 143.0, 142.6, 140.7, 140.4, 139.1, 138.7, 135.9, 126.0, 125.1, 124.9, 124.0, 124.0, 123.7, 123.3, 122.9, 122.7, 120.5, 120.2, 119.3, 118.9, 118.0, 116.1, 115.3, 110.2, 109.5, 108.8, 108.7, 108.1, 37.3, 37.0, 13.2.

Anal. Calcd. For: C₈₂H₆₆N₈: C 84.65; H 5.72; N 9.63; found: C 84.67; H 5.73; N 9.60.

2. 9-(2-Ethylhexyl)-*N*^{3'},*N*^{3'},*N*^{6'},*N*^{6'}-tetrakis(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)-9*H*-[3,9'-bicarbazole]-3',6'-diamine (**V1323**)



A mixture of 3,6-diaminocarbazole (0.4 g, 2 mmol), 3-bromo-9-(2-ethylhexyl)-9H-carbazole (5.08 g, 14 mmol), and anhydrous toluene (28 mL) was purged with Ar for 30 minutes. Afterwards, palladium (II) acetate (0.024 g, 0.11 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.064 g, 0.22 mmol) was added and the reaction mixture was stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (1.35 g, 14 mmol) was added and the mixture was heated at reflux for 5 hours (TLC control, acetone/*n*-hexane 1:4). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 3:22, v:v). 20% solution of the final product in THF was poured with intensive stirring into a 15-fold excess of ethanol. The precipitate as a light yellow powder was filtered off, washed with ethanol, and dried. Yield 2 g (63%).

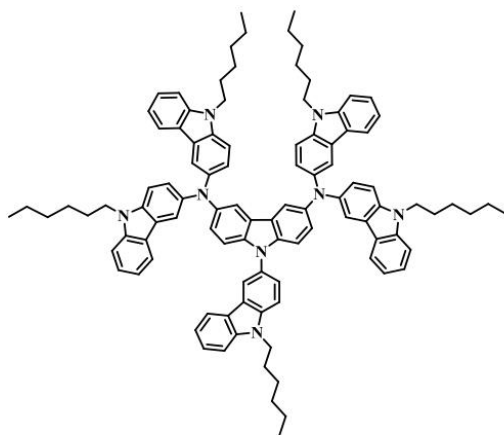
¹H NMR (400 MHz, Acetone-*d*₆) δ: 8.33 (s, 1H), 8.05 (s, 1H), 7.88 – 7.70 (m, 10H), 7.68–7.44 (m, 8H), 7.39 (t, *J* = 7.6 Hz, 4H), 7.34 – 7.06 (m, 13H), 7.02 (t, *J* = 7.5 Hz, 4H), 4.34 (d, *J* = 7.6 Hz, 2H), 4.17 (d, *J* = 7.3 Hz, 8H), 2.05 (p, *J* = 6.3 Hz, 4H), 1.51–1.14 (m, 41H), 1.01–0.75 (m, 30H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ: 143.1, 142.4, 141.5, 141.4, 139.9, 138.5, 136.8, 129.0, 126.2, 125.3, 125.0, 123.8, 123.6, 123.4, 122.5, 122.4, 120.7, 120.2, 119.1, 118.2, 115.3,

110.5, 110.3, 109.8, 109.5, 109.0, 47.1, 46.9, 39.3, 30.7, 28.5, 24.1, 22.8, 13.4, 13.4, 10.34, 10.3.

Anal. Calcd. For: C₁₁₂H₁₂₆N₈: C 84.91; H 8.02; N 7.07; found: C 84.87; H 8.26; N 6.87.

3. 9-Hexyl-*N*^{3'},*N*^{3'},*N*^{6'},*N*^{6'}-tetrakis(9-hexyl-9*H*-carbazol-3-yl)-9*H*-[3,9'-bicarbazole]-3',6'-diamine (**V1332**)



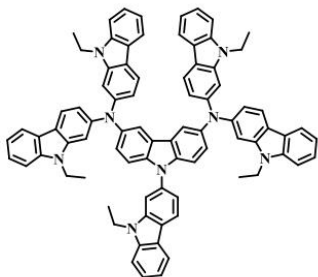
A mixture of 3,6-diaminocarbazole (0.12 g, 0.06 mmol), 3-bromo-9-hexyl-9*H*-carbazole (1.19 g, 3.6 mmol), and anhydrous toluene (6.6 mL) was purged with Ar for 30 minutes. Afterwards, palladium (II) acetate (0.015 g, 0.06 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.03 g, 0.1 mmol) were added and stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (0.35 g, 3.6 mmol) was added and the reaction mixture was heated at reflux for 5 hours (TLC control, acetone/*n*-hexane 1:4). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: acetone/*n*-hexane 1:24, v:v). 20% solution of the final product in THF was poured with intensive stirring into a 15-fold excess of ethanol. The precipitate as a light yellow powder was filtered off, washed with ethanol, and dried. Yield 0.45 g (52%).

^1H NMR (400 MHz, Acetone- d_6) δ : 8.29 (s, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.86–7.68 (m, 10H), 7.65–7.38 (m, 8H), 7.34 (t, J = 7.5 Hz, 4H), 7.23 (d, J = 8.1 Hz, 4H), 7.20–7.03 (m, 9H), 6.96 (t, J = 7.6 Hz, 4H), 4.39 (t, J = 7.2 Hz, 2H), 4.23 (t, J = 7.3 Hz, 8H), 1.94–1.68 (m, 10H), 1.43–1.11 (m, 30H), 0.94–0.61 (m, 15H).

^{13}C NMR (101 MHz, Acetone- d_6) δ : 142.4, 140.9, 139.4, 138.5, 136.4, 134.0, 125.4, 123.5, 123.4, 122.5, 120.2, 118.2, 115.9, 115.4, 110.5, 109.5, 108.8, 104.1, 100.9, 99.4, 42.6, 31.4, 31.4, 26.7, 26.6, 22.3, 13.4.

Anal. Calcd. For: $\text{C}_{102}\text{H}_{106}\text{N}_8$: C 84.84; H 7.40; N 7.76; found: C 84.89; H 7.65; N 7.46.

4. 9-Ethyl- $N^{3'},N^{3'},N^{6'},N^{6'}$ -tetrakis(9-ethyl-9H-carbazol-2-yl)-9H-[2,9'-bicarbazole]-3',6'-diamine (**V1377**)



A mixture of 3,6-diaminocarbazole (0.37 g, 1.8 mmol), 2-bromo-9-ethylcarbazole (3.02 g, 11 mmol), and anhydrous toluene (17.1 mL) was purged with Ar for 30 minutes. Afterwards, palladium (II) acetate (0.23 g, 0.1 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.06 g, 0.2 mmol) were added and stirred for 10 minutes under Argon. After that, sodium *tert*-butoxide (1.06 g, 11 mmol) was added and the reaction mixture was heated at reflux for 5 hours (TLC control, acetone/*n*-hexane 1:4). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried over Na_2SO_4 , filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 7:18, v:v). 20%

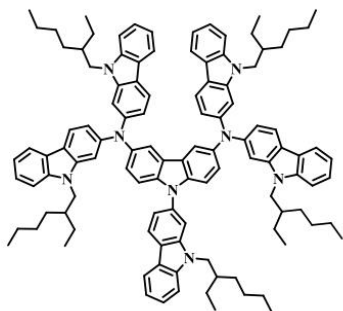
solution of the final product in THF was poured with intensive stirring into a 15-fold excess of methanol. The precipitate as a light yellow powder was filtered off, washed with methanol, and dried. Yield 1.5 g (69%).

^1H NMR (400 MHz, Acetone- d_6) δ : 8.38 (d, J = 8.1 Hz, 1H), 8.21 (d, J = 7.7 Hz, 1H), 8.02 (m, 2H), 7.94 (d, J = 7.7 Hz, 4H), 7.92–7.84 (m, 5H), 7.62 (d, J = 8.1 Hz, 1H), 7.55–7.45 (m, 4H), 7.42–7.22 (m, 15H), 7.11 (t, J = 7.4 Hz, 4H), 6.94 (d, J = 8.1 Hz, 4H), 4.52 (q, J = 7.1 Hz, 2H), 4.17 (q, J = 7.1 Hz, 8H), 1.42 (t, J = 7.1 Hz, 3H), 1.18 (t, J = 7.0 Hz, 12H).

^{13}C NMR (101 MHz, Acetone- d_6) δ : 147.8, 141.9, 141.1, 140.84, 140.75, 140.3, 138.6, 135.2, 126.1, 125.4, 124.6, 124.1, 123.1, 122.5, 122.2, 121.5, 120.7, 120.4, 119.4, 119.3, 118.8, 117.9, 117.5, 115.9, 110.9, 109.0, 108.4, 107.3, 103.2, 37.4, 36.9, 13.3, 13.1.

Anal. Calcd. For: $\text{C}_{82}\text{H}_{66}\text{N}_8$: C 84.65; H 5.72; N 9.63; found: C 84.68; H 5.96; N 9.36.

5. 9-(2-Ethylhexyl)- $N^{3'},N^{3'},N^{6'},N^{6}'$ -tetrakis(9-(2-ethylhexyl)-9*H*-carbazol-2-yl)-9*H*-[2,9'-bicarbazole]-3',6'-diamine (**V1381**)



A mixture of 3,6-diaminocarbazole (0.25 g, 1.3 mmol), 2-bromo-9-(2-ethylhexyl)-9*H*-carbazole (3.15 g, 8.8 mmol), and anhydrous toluene (17 mL) was purged with Ar for 30 minutes. Afterwards, palladium (II) acetate (0.016 g, 0.07 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.03 g, 0.1 mmol) were added and the reaction mixture was stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (0.85 g, 8.8 mmol) was added and the reaction mixture was heated at reflux for 5 hours (TLC control, acetone/*n*-

hexane 1:4). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: acetone/*n*-hexane 1:24, v:v). 20% solution of the final product in THF was poured with intensive stirring into a 15-fold excess of ethanol. The precipitate as a light yellow powder was filtered off, washed with ethanol, and dried. Yield 1.1 g (69%).

¹H NMR (400 MHz, THF-*d*₈) δ: 8.36 (d, *J* = 8.6 Hz, 1H), 8.18 (d, *J* = 7.4 Hz, 1H), 7.97 (s, 2H), 7.92 (d, *J* = 7.7 Hz, 4H), 7.87 (d, *J* = 8.4 Hz, 4H), 7.79 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.51–7.42 (m, 4H), 7.38–7.15 (m, 15H), 7.08 (t, *J* = 7.4 Hz, 4H), 6.99 (d, *J* = 7.9 Hz, 4H), 4.33 (d, *J* = 7.7 Hz, 2H), 4.12–3.87 (m, 8H), 2.20–.11 (m, 1H), 1.88 (p, *J* = 6.3 Hz, 4H), 1.51–1.01 (m, 40H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.80 (t, *J* = 7.0 Hz, 3H), 0.73 (t, *J* = 7.4 Hz, 12H), 0.66 (t, *J* = 7.1 Hz, 12H).

¹³C NMR (101 MHz, THF-*d*₈) δ: 145.8, 140.1, 139.9, 139.4, 136.9, 123.9, 123.4, 122.4, 122.3, 121.3, 119.3, 118.4, 118.2, 117.2, 116.6, 116.04, 115.95, 115.6, 113.8, 108.6, 107.3, 106.6, 105.7, 101.8, 65.1, 65.0, 64.8, 64.6, 64.4, 64.1, 45.3, 44.6, 37.6, 37.5, 29.2, 29.0, 23.0, 22.9, 22.8, 22.7, 22.5, 22.3, 22.1, 21.12, 20.96, 11.5, 11.4, 8.5, 8.4.

Anal. Calcd. For: C₁₂₂H₁₂₆N₈: C 84.91; H 8.02; N 7.07; found: C 84.75; H 8.22; N 7.03.

4.9% Efficient Sb_2S_3 Solar Cells from Semitransparent Absorbers with Fluorene-Based Thiophene-Terminated Hole Conductors

Sreekanth Mandati,* Nimish Juneja, Atanas Katerski, Aistė Jegorovė, Raitis Grzibovskis, Aivars Vembris, Tatjana Dedova, Nicolae Spalatu, Artiom Magomedov, Smagul Karazhanov, Vytautas Getautis, Malle Krunks, and Ilona Oja Acik*



Cite This: *ACS Appl. Energy Mater.* 2023, 6, 3822–3833



Read Online

ACCESS |



Metrics & More



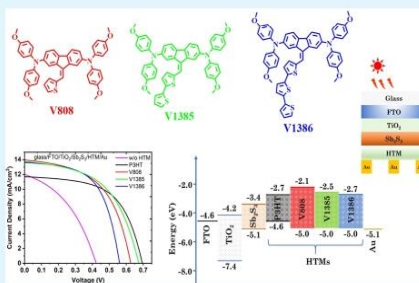
Article Recommendations



Supporting Information

ABSTRACT: Fluorene-based hole transport materials (HTMs) with terminating thiophene units are explored, for the first time, for antimony sulfide (Sb_2S_3) solar cells. These HTMs possess largely simplified synthesis processes and high yields compared to the conventional expensive hole conductors making them reasonably economical. The thiophene unit-linked HTMs have been successfully demonstrated in ultrasonic spray-deposited Sb_2S_3 solar cells resulting in efficiencies in the range of 4.7–4.9% with an average visible transmittance (AVT) of 30–33% (400–800 nm) for the cell stack without metal contact, while the cells fabricated using conventional P3HT have yielded an efficiency of 4.7% with an AVT of 26%. The study puts forward cost-effective and transparent HTMs that avoid a post-coating activation at elevated temperatures like P3HT, devoid of parasitic absorption losses in the visible region and are demonstrated to be well aligned for the band edges of Sb_2S_3 thereby ascertaining their suitability for Sb_2S_3 solar cells and are potential candidates for semitransparent applications.

KEYWORDS: antimony sulfide, solar cells, thiophene, hole transport material, semitransparent



1. INTRODUCTION

The energy crisis is among the major problems of the present day's growing world with digitalization and the internet of things. In addition, the limited availability of fossil fuels, the dominant sources of current days' energy and the associated problems of pollutant emissions by burning fossil fuels is a bigger concern. Considering the UNO's policies of net-zero emissions by 2050 coupled with the goals set by many countries worldwide to produce clean energy necessitates the requirement of alternative energy sources that are clean, abundant, and easy to harvest. Renewable energy technologies are the need of the hour to meet these demands and among them, solar photovoltaics (PV) is a technology that has tremendous potential to be a major yet important energy harvesting source. Solar energy is abundantly available and PV is a green technology that facilitates the conversion of sunlight to electricity in a clean manner once the solar panels are in fully operational condition. Furthermore, building-integrated photovoltaics (BIPV) is an emerging technology in PV wherein solar panels could be integrated into buildings that produce energy to meet some portion of energy demand within. Energy-efficient buildings are going to be the future with the growing smart city infrastructure and contribute effectively toward net-zero emissions. Semitransparent solar cells could play an important role in BIPV and could be integrated into

windows. Intense investigations are underway to explore novel materials and device architectures that are suitable for semitransparent solar cells.

Among various emerging materials, antimony sulfide (Sb_2S_3) is the promising candidate for the photovoltaic community owing to the earth-abundant and environmentally friendly constituent elements alongside appropriate optoelectronic properties such as a desirable band gap of ≈ 1.7 eV, large absorption coefficient ($\approx 10^5 \text{ cm}^{-1}$) and long-term stability.^{1–3} The Shockley–Queisser limit of the power conversion efficiency (PCE) of the single junction Sb_2S_3 solar cells is 28.64%.¹ Sb_2S_3 absorbers are potential contenders for semitransparent solar cells due to their relatively wide band gap and the possibility to yield higher PCEs even with very thin absorber layers ($\approx 100 \text{ nm}$).⁴ Further, the wide band gap of Sb_2S_3 also makes them a wiser choice for tandem cell applications.^{5–7} The highest reported PCE of Sb_2S_3 solar cells

Received: December 21, 2022

Accepted: March 14, 2023

Published: March 23, 2023



Table 1. Reported Device Parameters of Sb₂S₃ Solar Cells with Different HTMs, Device Configurations, Methods of Preparation, and Thicknesses^a

HTM	device configuration	Sb ₂ S ₃ (deposition technique)	Sb ₂ S ₃ thickness (nm)	solar cell parameters				reference
				V _{OC} (mV)	J _{SC} (mA/cm ²)	FF (%)	PCE (%)	
P3HT	ITO/ZnO/Sb ₂ S ₃ /P3HT/Ag	TE	210	450	12.6	42	2.4	21
	ITO/TiO ₂ /Sb ₂ S ₃ /P3HT/Au	CBD	200	630	6.1	35	1.4	22
	ITO/TiO ₂ /Sb ₂ S ₃ /P3HT/Ag	ALD	155	732	9.3	62	4.3	2
	FTO/TiO ₂ /Sb ₂ S ₃ /P3HT/Au	SC		616	8.1	46	2.3	16
	ITO/TiO ₂ /Sb ₂ S ₃ /P3HT/Au	USP	150	618	6.0	51	1.9	23
	ITO/TiO ₂ /Sb ₂ S ₃ /P3HT/Au	USP	100	693	13.8	58	5.5	6
Spiro-OMeTAD	FTO/TiO ₂ /Sb ₂ S ₃ /Spiro-OMeTAD/Au	CBD	84	690	13.4	50	4.6	17
	FTO/TiO ₂ /Sb ₂ S ₃ /Spiro-OMeTAD/Au	SC	400	660	13.1	59	5.2	18
	FTO/TiO ₂ /Sb ₂ S ₃ /Spiro-OMeTAD/Au	SC	140	632	12.9	52	4.3	24
	FTO/TiO ₂ /Sb ₂ S ₃ /Spiro-OMeTAD/Ag	TE	300	620	10.7	56	3.8	25
	FTO/TiO ₂ /Sb ₂ S ₃ /Spiro-OMeTAD/Au	SC	162	650	17.7	62	7.1	26
	FTO/TiO ₂ /Sb ₂ S ₃ /Spiro-OMeTAD/Au	SC	146	720	17.2	57	7.1	27
	FTO/CdS/Sb ₂ S ₃ /Spiro-OMeTAD/Au	HT	300	707	15.2	56	6.0	28
	FTO/CdS/Sb ₂ S ₃ /Spiro-OMeTAD/Au	TE	200	720	15.9	54	6.2	29
	FTO/TiO ₂ /CdS/Sb ₂ S ₃ /Spiro-OMeTAD/Au	HT	1000	748	15.3	57	6.5	30
	FTO/CdS/Sb ₂ S ₃ /Spiro-OMeTAD/Au	CBD	214	757	17.4	60.5	8.0	8
	FTO/TiO ₂ /ZnS/Sb ₂ S ₃ /P3HT/PEDOT:PSS/Au	ALD	75	626	15.7	52	5.1	31
	FTO/TiO ₂ /Sb ₂ S ₃ /P3HT/PEDOT:PSS/Au	ALD	90	667	14.9	58	5.8	32
V1236	FTO/TiO ₂ /Sb ₂ S ₃ /HTM/Au	USP	90	612	13.8	46	3.9	33

^aHTM: hole transport material; TE: thermal evaporation; CBD: chemical bath deposition; SC: spin coating; USP: ultrasonic spray pyrolysis; HT: hydrothermal; ALD: atomic layer deposition, V1236: (N²,N²,N²,N²-tetrakis[2,2-bis(4-methoxyphenyl)vinyl]-9,9-dihexyl-9H-fluorene-2,7-diamine).

is 8%, achieved recently through a multi-sulfur source approach using the chemical bath deposition method (CBD).⁸ The overall efficiencies are rather limited by the deficiencies in open circuit voltage (V_{OC}) that are attributed to the self-trapping of carriers due to lattice deformation and/or to the intrinsic defects, which sets the maximum attainable V_{OC} to 0.8 V.^{9,10} Antimony selenide (Sb₂Se₃), another class of antimony chalcogenide, is also a potential candidate for PV applications and is explored extensively.^{11–13}

In addition to the considerable challenges in improving the PCEs, the method of Sb₂S₃ absorber fabrication is critical for upscaling. The high-efficiency Sb₂S₃ solar cells so far are mostly prepared by spin coating and CBD.^{8–15} While the spin coating technique demonstrates excellent control of parameters and reproducibility but is limited to laboratory scale and also has high material wastage (>90%). CBD, on the other hand, has promise for large-scale demonstration but needs longer deposition time at relatively low temperatures (<10 °C) to obtain the desired thickness of the absorbers. Our group has previously demonstrated the fabrication of Sb₂S₃ solar cells by the ultrasonic spray pyrolysis method, which offers large-area uniformity and is an industrially scalable technique with low capital.⁶ Further, the Sb₂S₃ solar cells are often fabricated in planar superstrate configuration wherein TiO₂ is the most commonly used electron transport layer (ETL) deposited on a transparent conducting oxide followed by the Sb₂S₃ absorber, hole transport material (HTM), and finally, the back contact, often Au. HTMs are the vital component of planar or mesoscopic Sb₂S₃ solar cells that drive the transport of photogenerated holes to the back contact and reduce recombination losses.² In general, conventional HTMs like poly(3-hexylthiophene) (P3HT),^{2,16} 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMe-

TAD),^{17,18} poly[4,4-dialkyl-4H-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene-2,6-diyl-*alt*-2,1,3-benzothiadiazole-4,7-diyl} (PCPDTBT),^{19,20} etc. are the most commonly employed in the fabrication of Sb₂S₃ solar cells. The use of these different HTMs in Sb₂S₃ solar cells where the Sb₂S₃ absorbers are prepared by different techniques and device architectures are summarized in Table 1 alongside the power conversion efficiencies achieved. It may be noted that only organic HTMs and planar configuration devices are considered for summary.

It may be noted that except for V1236, an economic and transparent hole conductor previously reported by our group,³³ other studies have majorly used conventional P3HT and Spiro-OMeTAD. These hole conductors are very expensive mainly due to their complex, expensive, and time-consuming synthesis processes³⁴ and are also moisture sensitive, and thereby could be significant barriers to the potential upscale for commercial applications. Further, tailoring HTMs with suitable thickness is also important to obtain high-efficiency solar cells but may hinder the overall transparency of the solar cell stack, an important parameter in semitransparent solar cells. For instance, the commonly employed P3HT exhibits parasitic absorption in the visible spectral region, which induces a loss in the total transmittance of the solar cell.^{2,33} In addition, P3HT also requires additional post-coating activation at temperatures around 170 °C either in a vacuum or inert atmosphere.³⁵ Therefore, it becomes imperative to explore low-cost novel HTMs, which could be easily synthesized using available commercial starting materials while possessing suitable properties like good thermal stability, desired solubility, and hole mobility.

In view of the above, the study herein proposes to fabricate Sb₂S₃ solar cells by a scalable and industrially benign ultrasonic

spray pyrolysis (USP) method by employing novel, low-cost, and transparent hole conductors from fluorene-based molecules with terminated thiophene units. The 4,4'-dimethoxydiphenylamine-substituted fluorene fragment is used due to its wider application in the organic HTMs, in particular, Spiro-OMeTAD, while thiophene units are added mimicking P3HT HTM. The new materials follow simple synthesis processes with high yields thereby having considerably lower costs than conventional HTMs. Sb_2S_3 solar cells with new HTMs are fabricated in the standard superstrate configuration wherein ETL and absorber are deposited by USP while HTMs are spin coated followed by the thermal evaporation of Au. Comprehensive characterization of solar cells through different techniques clearly demonstrates that the cells with new HTMs yield similar or better PCEs compared to the conventional P3HT-based devices and have exhibited enhanced average visible transmittance in the 400–800 nm range. Further, the band energetics show that the new HTMs possess favorable band alignment with the Sb_2S_3 absorber thereby validating their efficacy toward semitransparent solar cells.

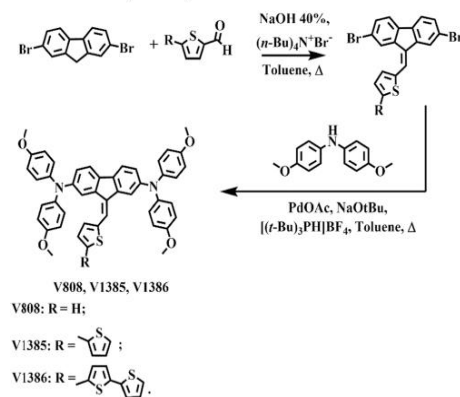
2. EXPERIMENTAL SECTION

2.1. Materials. The following materials were used: FTO substrate ($7 \Omega \text{ sq}^{-1}$), titanium(IV) tetraisopropoxide (TTIP)—99 wt % (Acros Organics), acetylacetone—99 wt % (Acros Organics), ethanol—96.6 vol % (Estonian Spirit), methanol—99.9 vol % (Sigma-Aldrich), antimony trichloride—99.99 wt % (Sigma-Aldrich), thiourea—99 wt % (Sigma-Aldrich), chlorobenzene—99.5 vol % (Sigma-Aldrich), poly(3-hexylthiophene-2,5-diyl) (P3HT)—100 kDa, >90% regioregular (Sigma-Aldrich), and materials related to HTM synthesis as mentioned in the S1. The materials were used as received.

2.2. Solar Cell Fabrication. Antimony sulfide (Sb_2S_3) solar cells were fabricated in superstrate configuration (glass/FTO/ $\text{TiO}_2/\text{Sb}_2\text{S}_3$ /HTM/Au). The fabrication process started with thorough cleaning of the glass/FTO substrate with DI water, acetone, and IPA in an ultrasonic bath for 10 min each followed by boiling the substrates in DI water and purging with N_2 gas. The TiO_2 electron transport layer (ETL) and Sb_2S_3 absorbers were deposited by an indigenously made ultrasonic spray deposition system. TiO_2 was sprayed from a solution mixture of 0.2 M TTIP with 0.2 M acetylacetone in ethanol by using a spray rate of $\approx 2.5 \text{ mL/min}$ for 30 min on a hot plate maintained at around 340°C . The sprayed TiO_2 samples were then annealed at 450°C for 30 min in air. Sb_2S_3 thin films were spray-deposited from a solution mixture of 60 mM SbCl_3 and 180 mM thiourea in methanol. The films were deposited at a spray rate of 2 mL/min while maintaining a substrate temperature of $\approx 200^\circ\text{C}$. The as-deposited Sb_2S_3 films were annealed at around $250\text{--}260^\circ\text{C}$ for 5 min under nitrogen. The hole transport materials (HTM) explored in this study are the fluorene-based molecules with linked thiophene units $\text{N}^2, \text{N}^2, \text{N}^7, \text{N}^7$ -tetrakis(4-methoxyphenyl)-9-(thiophen-2-ylmethylene)-9H-fluorene-2,7-diamine (**V808**), 9-([2,2':5',2''-terthiophen]-5-ylmethylene)- $\text{N}^2, \text{N}^2, \text{N}^7, \text{N}^7$ -tetrakis(4-methoxyphenyl)-9H-fluorene-2,7-diamine (**V1385**), and 9-([2,2':5',5'-bithiophen]-5-ylmethylene)- $\text{N}^2, \text{N}^2, \text{N}^7, \text{N}^7$ -tetrakis(4-methoxyphenyl)-9H-fluorene-2,7-diamine (**V1386**). The detailed synthesis procedure of **V808**, **V1385**, and **V1386** is described in Section S1 while the synthesis process is presented in Scheme 1. The HTM layers were spin coated on glass/FTO/ $\text{TiO}_2/\text{Sb}_2\text{S}_3$ samples followed by the thermal evaporation of Au contacts. The active area of solar cells was 7.06 mm^2 .

2.3. Characterization. The crystal structure and phase constitution of the as-deposited and annealed Sb_2S_3 thin films were examined using a Rigaku Ultima IV X-ray diffractometer with a $\text{Cu K}\alpha$ source ($\lambda = 1.5406 \text{ \AA}$). In addition, micro-Raman spectroscopy was further used to ascertain the crystalline purity while also detecting the possible presence of the minute antimony oxide phase and micro-Raman spectra were recorded at room temperature using a Horiba Labram HR 800 in backscattering mode with a He Ne laser of 532

Scheme 1. Synthetic Route to the Novel Hole Transporting Materials V808, V1385, and V1386



nm. A Zeiss HR FESEM was used to analyze the cross-sectional morphologies of the layers. The optical absorption and transmittance measurements were made using a Jasco V-670 ultraviolet–visible spectrophotometer (UV–VIS) in the range of 300–1000 nm. For the band diagram construction, photoelectron emission spectroscopy (PES) and photoconductivity methods were used. For these methods, the measurement system consisted of an ENERGETIQ Laser-Driven Light Source (LDLS EQ-99) as a light source, a Spectral Products DK240 1/4m monochromator, and a Keithley 617 electrometer. The measurements were performed in vacuum at a pressure of $\sim 10^{-5}$ mbar. Both methods are described in detail in S2. The hole transport materials were characterized comprehensively using thermogravimetric analysis (TGA), differential scanning calorimetric (DSC) analysis, and absorption spectroscopy. The work function of Au contacts was measured using a Kelvin probe. The current–voltage (I – V) characteristics of the fabricated solar cells were measured using Wavelabs LS-2 LED solar simulator with an AM1.5G (100 mW cm^{-2}) light source. A Newport 69911 system with a 300 W Xenon lamp was used to measure the external quantum efficiency (EQE) of the fabricated solar cells.

3. RESULTS AND DISCUSSION

The fluorene-based thiophene-linked hole transport materials (HTMs) are explored in this study for the fabrication of Sb_2S_3 solar cells. The design of these p-type photoconductors has been inspired by recently published findings that thiophene can coordinate with Sb atoms in $\text{Sb}_2(\text{S}_2\text{Se})_3$ leading to the improvement of the interfacial properties between $\text{Sb}_2(\text{S}_2\text{Se})_3$ and HTM.^{36,37} This interaction provides desirable channels for carrier transport, which significantly enhances the open circuit voltage and fill factor. In a single thiophene unit-linked molecule (**V808**), 4,4'-dimethoxydiphenylamine chromophores are symmetrically connected on both sides of the fluorene core, which was easily modified chemically by the thiophene end-group. **V808** is synthesized through a simple two-step process (Scheme 1) devoid of expensive/complex materials/steps with considerably good yields thereby resulting in low synthesis costs. On a similar note, to further investigate the possibility of better interaction, the molecules are synthesized by adding 2 and 3 thiophene units to the fluorene core, which are thus named **V1385** and **V1386**, respectively. The detailed synthesis procedure of **V808**, **V1385**, and **V1386** is described in Section S1 and the cost estimation is given in Tables S1–S3, respectively. It may be observed that the synthesis cost of a

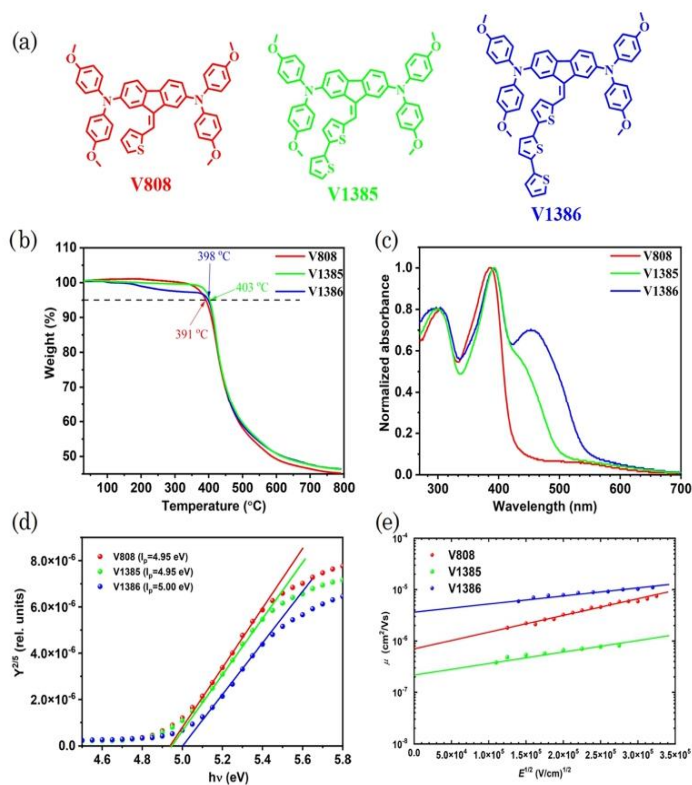


Figure 1. (a) Chemical structures of new fluorene-based hole transport materials with terminating thiophene units (V808, V1385, and V1386), (b) thermogravimetric analysis (TGA) data, (c) normalized absorbance spectra of the HTMs deposited on glass, (d) photoemission spectra in air for determining the ionization potential, and (e) electric field dependencies of the hole mobility of V808, V1385, and V1386.

single thiophene linking molecule (V808) is ≈ 13 € per gram while those of the ones with 2 and 3 thiophene units are 32 and 177 € per gram, respectively, indicating the increase in cost is majorly owing to the increased price of the starting thiophenecarbaldehyde. However, the cost of single and double thiophene unit-linked molecules (V808 and V1385) is considerably cheaper in comparison to the conventional hole conductors like P3HT and Spiro-OMeTAD. Irrespective of the cost, all three materials are comprehensively characterized and are explored as HTMs in Sb_2S_3 solar cells. The typical chemical structures of V808, V1385, and V1386 with 1, 2, and 3 linked thiophene units, respectively, are shown in Figure 1a. Figure 1b shows the thermogravimetric analysis (TGA) curves of V808, V1385, and V1386, and as the plots reveal all three materials start to decompose at temperatures >390 °C, which is far above the temperature for conventional device operation. The differential scanning calorimetric (DSC) curves of new HTMs are shown in Figure S1. All compounds have shown T_g slightly less than 100 °C (92, 97, and 99 °C for V808, V1385, and V1386, respectively). Comparison of T_g of new materials reveals that an increase in thiophene fragments in the molecule leads to slightly increased T_g and could be attributed to the increased molecular weight. In addition, it is important to note that the melting process is observed just for V808, while other

new synthesized compounds (V1385 and V1386) have shown no endothermic peaks, indicating that they have only an amorphous state, which is an advantage for the formation of homogenous films as it eliminates the possibility of crystallization of films during preparation/operation of devices. The normalized absorbance spectra of the films, deposited on glass, are shown in Figure 1c. As can be seen, the spectra of new compounds display intensive $\pi-\pi^*$ absorption bands at 270–430 nm, which might be attributed to the 4,4'-dimethoxydiphenylamine-substituted fluorene fragment. In addition, with the increase in the number of thiophene units, the ($\pi-\pi^*$) transition associated with this conjugated part exhibits a strong bathochromic shift. For compound V1386, this results in a band with the absorption maximum at 453 nm, for V1385 it appears as a shoulder to the main peak, while for V808 it overlaps with the main peak. The normalized absorbance spectra of new HTMs are also compared with the conventional P3HT as presented in Figure S2, which shows that P3HT absorbs significantly in the 400–650 nm region while the new HTMs possess much less absorption in the same region thereby demonstrating better visible light transparency.

The solid-state ionization potential (I_p) of HTMs is determined using photoelectron emission spectroscopy

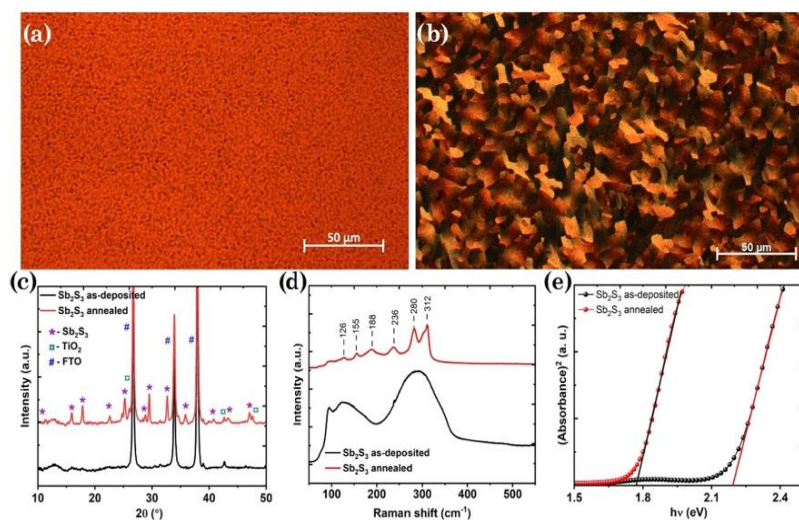


Figure 2. Morphological, structural, and optical characteristics of Sb_2S_3 thin films deposited by ultrasonic spray pyrolysis: Optical microscopy images of (a) as-deposited and (b) annealed Sb_2S_3 , (c) XRD patterns, (d) Raman spectra, and (e) (absorbance)² vs $h\nu$ plots of as-deposited and annealed Sb_2S_3 .

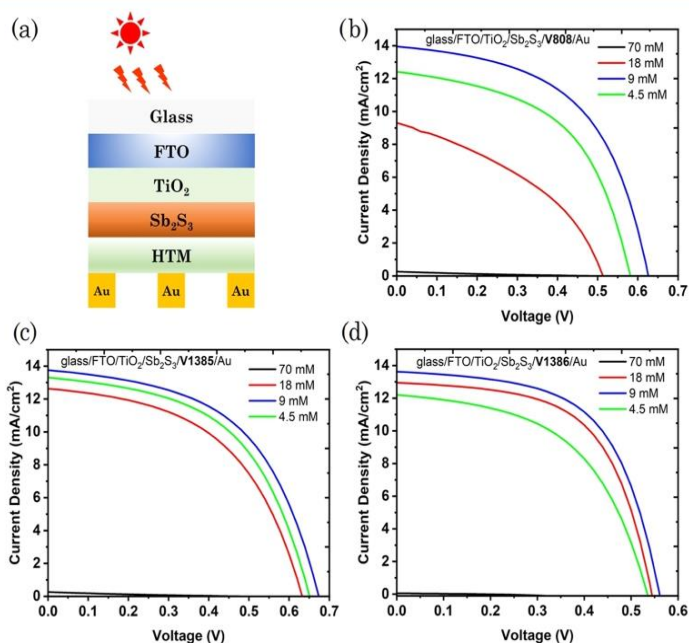


Figure 3. (a) Schematic illustration of device configuration (glass/FTO/ TiO_2 / Sb_2S_3 /HTM/Au) of Sb_2S_3 solar cells (Note: Not to scale), J – V characteristics of solar cells with (b) V808, (c) V1385, and (d) V1386 as HTMs with the variation in precursor concentrations from 4.5 to 70 mM in each case.

(PES) of the thin films (Figure 1d), which clearly reveals that the I_p levels of V808, V1385, and V1386 are determined to be -4.95 eV, -4.95 , and -5.00 eV, respectively. Almost similar I_p

values can be explained by the unfavorable arrangement of thiophene fragments. As can be seen from absorbance spectra, the increase of the conjugated system is very slight with the

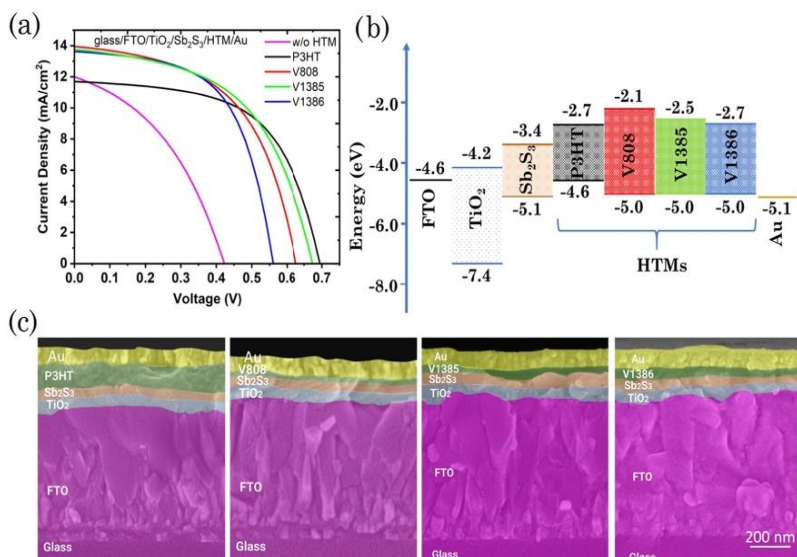


Figure 4. (a) *J*–*V* characteristics of champion cells, (b) band energy diagram and (c) cross-sectional images of Sb₂S₃ solar cells with P3HT, V808, V1385, and V1386 as HTMs, respectively.

increasing number of thiophene moieties in the molecule, therefore the highest occupied molecular orbital (HOMO) levels can be very similar. Further, hole drift-mobility of HTMs is estimated using the time of flight (ToF) method with Ekspla PL kHz ps tunable laser as a light source and a Tektronix MDO3024 oscilloscope for signal registration. As shown in Figure 1e, the inferred zero-field hole mobilities are 7.07×10^{-7} , 2.15×10^{-7} , and 3.68×10^{-6} cm²/(V·s), for V808, V1385, and V1386, respectively.

Sb₂S₃ thin films are deposited by the USP process on glass/FTO/TiO₂ samples. Optical microscopic images are recorded to ascertain the conformal coverage of Sb₂S₃ films on TiO₂ as shown in Figure 2a and as the image, which is recorded for a considerably larger area, unveils that the films are conformally covered devoid of any pin holes or crystallization during the deposition. The crystallization of Sb₂S₃ thin films during deposition in the USP process is a commonly observed feature, which is a detrimental process that reduces the quality of films for solar cell applications as this crystallization during deposition is an uncontrollable process and the resulting crystallinity is not the desired form too, which is absent in the present study. Further, the as-deposited films are characterized by XRD and Raman as shown in Figure 2c,d. The XRD pattern shows the sharp peaks pertaining to FTO and TiO₂ layers while the Raman spectra reveal broad characteristic peaks of Sb₂S₃, confirming that the as-deposited films are amorphous in nature. Upon annealing under a nitrogen atmosphere at 250 °C, the Sb₂S₃ films exhibit crystallinity. Optical microscopy images of annealed Sb₂S₃ films show a large grain structure as shown in Figure 2b without any voids or pin holes. The XRD patterns of annealed Sb₂S₃ show several sharp peaks in addition to the existing FTO and TiO₂ peaks, which correspond to the orthorhombic stibnite Sb₂S₃ phase (ICDD PDF 01-075-4013). On a similar note, the Raman spectra of annealed Sb₂S₃ show sharp peaks characteristic of Sb₂S₃

thereby corroborating the XRD analysis and confirming the formation of the crystalline stibnite Sb₂S₃ phase. Further, the band gap of Sb₂S₃ absorbers is inferred from (absorbance)² vs *hν* plots as shown in Figure 2e. The band gap of amorphous Sb₂S₃ is determined to be around 2.2 eV while that of crystallized one is 1.7 eV, which agree well with the values reported previously.³³ Therefore, it may be inferred that the crystalline Sb₂S₃ absorbers with the desired band gap are successfully fabricated by the area-scalable USP process followed by annealing.

In the next step, the Sb₂S₃ solar cells are fabricated in the planar configuration, as shown in Figure 3a, using conventional P3HT and new V808, V1385, and V1386 as HTMs, which are spin coated onto glass/FTO/TiO₂/Sb₂S₃ samples and Au is thermally evaporated. While the concentration of P3HT has been previously optimized for the best efficient Sb₂S₃ solar cells,³³ the new HTMs require a similar process. Therefore, prior to comparison with P3HT-based solar cells, the concentration of the precursors in spin coating has been optimized for new HTMs. Figure 3b–d shows the current density–voltage (*J*–*V*) characteristics of solar cells with concentration variation in each case for V808, V1385, and V1386, respectively. The variation in the associated device parameters with concentration is shown in Figure S3. For an initial concentration of 70 mM V808, the solar cells exhibit very low PCEs, essentially due to the negligible photocurrent. The concentration of V808 is therefore diluted considerably in steps of ca. 4× resulting in 18, 9, and 4.5 mM. As shown in the *J*–*V* curves in Figure 3b, the efficiencies of solar cells for V808 concentrations of 70, 18, 9, and 4.5 mM are 0.1, 2.0, 4.7, and 3.8%, respectively. The device parameters, *V*_{OC}, *J*_{SC}, and FF have followed an identical trend that the respective values are maximum for 9 mM V808 and are lower on either side (see Figure S3a,b). To identify the plausible reasons, the series resistance (*R*_s) of the devices is determined from the *J*–*V* data

that a very large R_s ($>200 \Omega\text{-cm}^2$) is observed for the 70 mM V808 device, which decreased significantly with a decrease in the concentration resulting in considerable improvement in J_{SC} . The large R_s may be attributed to the larger thickness of V808 arising from the large concentration. It may therefore be concluded that 9 mM V808 is considered optimal resulting in the highest PCE among all. On a similar note, the power conversion efficiencies of the solar cells with 70, 18, 9, and 4.5 mM concentrations of V1385 are obtained to be 0.2, 4.0, 4.9, and 4.5%, respectively. For the case of V1386, the obtained efficiencies are 0.15, 4.1, 4.5, and 3.4% for concentrations of 70, 18, 9, and 4.5 mM. The variation trends in the associated device parameters are also similar as shown in Figure S3c–f. It may therefore be inferred that the 9 mM concentration in each case has resulted in the best device efficiencies of 4.7, 4.9, and 4.5% for solar cells with V808, V1385, and V1386 as HTMs, respectively.

While the new molecules V808, V1385, and V1386 have demonstrated reasonable efficiencies, it is important to compare them with existing conventional proven HTMs. Therefore, to further validate the efficacy of new molecules as the HTM layer in Sb_2S_3 solar cells, they are compared with conventional P3HT-based devices. The J – V characteristics of champion Sb_2S_3 solar cells with P3HT, V808, V1385, and V1386 are shown in Figure 4a. In addition, to understand the need for an HTM in devices, solar cells fabricated without the HTM layer are also shown. The device parameters are listed in Table 2. The solar cells without HTM have exhibited a PCE of

Table 2. Device Parameters of Champion Sb_2S_3 Solar Cells with P3HT, V808, V1385, and V1386 HTMs

HTM	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)	R_s ($\Omega\text{-cm}^2$)	R_{SH} ($\Omega\text{-cm}^2$)
no HTM	0.43	12.0	0.41	2.12	1.33	167
P3HT	0.69	11.7	0.58	4.68	2.1	1190
V808	0.63	13.9	0.54	4.73	1.01	586
V1385	0.68	13.7	0.53	4.94	2.3	569
V1386	0.56	13.6	0.59	4.50	0.89	844

2.12% with a reasonably low V_{OC} of 0.43 V, a J_{SC} of 12.0 mA/cm^2 , and an FF of 0.41. Such characteristics are often classically observed for bare Sb_2S_3 -based solar cells devoid of HTM. The band energy positions of different device layers explored in the present study are determined using photoelectron emission spectroscopy and the band energy diagram is presented in Figure 4b. The Sb_2S_3 absorber possesses the valence (VBE) and conduction band edges (CBE) at -5.1 and -3.4 eV, respectively, and with Au and TiO_2 on either side of the absorber in solar cells without HTM, the transport of photogenerated electrons and holes is reasonably smooth owing to the favorable band edge positions. However, with Au being the back contact there is no barrier for electrons from the conduction band of Sb_2S_3 at the Sb_2S_3 /Au interface thereby leading to recombination often resulting in low V_{OC} and FF. The devices also exhibit a very low shunt resistance (R_{SH}) of $\approx 167 \Omega\text{-cm}^2$. On the other hand, the solar cells with conventional P3HT have demonstrated a PCE of 4.68% with a V_{OC} of 0.69 V, a J_{SC} of 11.7 mA/cm^2 , and an FF of 0.58. It can be observed that the device parameters are considerably increased, particularly the V_{OC} and FF. The presence of an HTM contributes in various ways to enhance the conversion efficiency of solar cells as they improve band energetics of the

device for improved transport of photogenerated carriers while reducing recombination losses as they block the electrons by passivating the interface across Sb_2S_3 -HTM. As seen from Figure 4b, P3HT possesses the VBE and CBE at -4.6 and -2.7 eV, respectively, that its presence could provide a barrier at the Sb_2S_3 -HTM interface for the electrons to travel back and therefore, reduce the recombination losses. The devices have shown a significantly enhanced $R_{SH} \approx 1.2 \text{ k}\Omega\text{-cm}^2$, an almost 7-fold increment compared to the bare cells. It may also be observed that the series resistance (R_s) of the P3HT-based devices has slightly increased compared to the bare cells and could be due to the additional P3HT layer, which is a reasonably resistive material. However, due to the enhanced charge transport and reduced recombination losses owing to the favorable band alignment, the V_{OC} is significantly increased and J_{SC} has not changed hugely despite the higher R_s .

The solar cells with new HTMs have demonstrated efficiencies of 4.73, 4.94, and 4.50% for V808, V1385, and V1386, respectively. Primarily, it is important to note that the new HTMs have exhibited efficiencies either on par or slightly higher than the conventional P3HT, which clearly demonstrates their validation. Another major observation from Figure 4a and Table 2 is that the solar cells with V808, V1385, and V1386 have yielded considerably higher J_{SC} almost close to 14 mA/cm^2 over the P3HT devices (11.7 mA/cm^2). However, the V_{OC} values of the devices with new HTMs are relatively lower than that of P3HT devices. As can be seen, the V_{OC} of solar cells with V808, V1385, and V1386 are 0.63, 0.68, and 0.56, respectively, while the V_{OC} of P3HT-based solar cells is 0.69 V. The band edge positions of new HTMs are compared with P3HT alongside other device layers as shown in Figure 4b and it can be observed that all the new HTMs possess the same VBE at -5.0 eV while that of P3HT is -4.6 eV. For the transport of photogenerated holes, the VBE of P3HT is in a favorable position with respect to the Sb_2S_3 absorber compared to the new HTMs, however, with the back contact (Au) energy level being -5.1 eV, the relatively smoother transport of holes is feasible in solar cells with new HTMs compared to P3HT. In addition, the CBE positions of new HTMs are -2.1 , -2.5 , and -2.7 eV for V808, V1385, and V1386, respectively, compared to P3HT (-2.7 eV). As may be observed, the interface barrier at the Sb_2S_3 -HTM interface is larger for new HTMs over P3HT, which is responsible for electron blocking at the interface and leads to reduced recombination losses. While the higher J_{SC} may be ascribed to the favorable band alignment of new HTMs, the lower V_{OC} values compared to P3HT are not as expected especially considering the larger band gap of new HTMs than P3HT. Particularly, considerably lower V_{OC} (0.56 V) in solar cells with V1386 with a deficiency of almost 100 mV or more compared to other solar cells despite its reasonably higher mobility is still a question, although it may be speculated that this is owing to the increase in the number of thiophene units, the coverage might not be as uniform as compared to other layers leading to agglomerated conducting paths that may act as trap centers for photogenerated carriers. On that note, the wettability of new HTMs alongside P3HT in their precursor form is explored on the Sb_2S_3 surface. It is observed that all the HTMs including P3HT have shown excellent wettability with close to 0° contact angle for new HTMs and 2° for P3HT. The visual appearance of the samples upon dropping the precursor droplet onto Sb_2S_3 indicates that the P3HT drop remains as it is while the new HTM precursor drop spreads quickly in no time, which shows the relatively

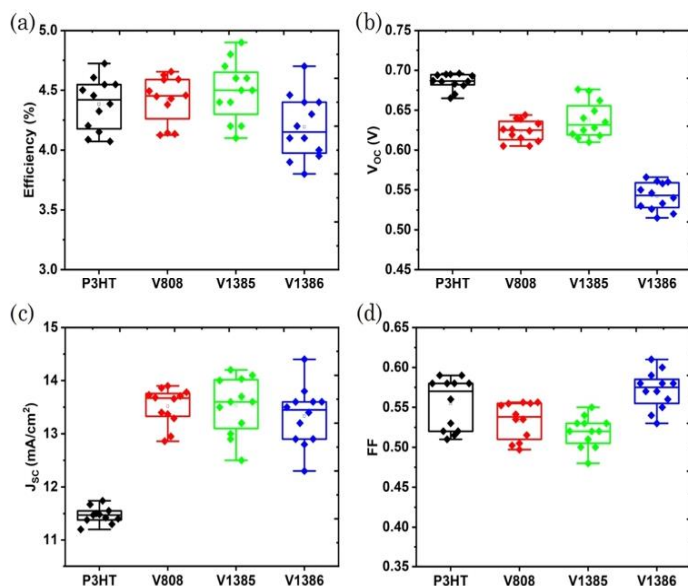


Figure 5. Reproducibility box plots of Sb_2S_3 solar cells with P3HT, V808, V1385, and V1386 as HTMs: (a) Efficiency, (b) V_{OC} , (c) J_{SC} , and (d) fill factor (FF).

better wettability of new HTMs on the Sb_2S_3 surface. Therefore, despite possessing better interaction capability and favorable band edge positions, the solar cells with new HTMs have either marginally achieved similar V_{OC} as that of the conventional P3HT or have yielded lower values. In addition, it is known that mobility plays a crucial role in the performance of solar cells, but in this study, other factors that influence the PV parameters might be dominant. One of the important PV parameters is V_{OC} and its variation is generally ascribed to the energy levels, however, as they are quite similar, the other main aspect could be the interfacial recombination at Sb_2S_3 -HTM. Now, there might be two sources of recombination—one is direct contact between the electrode and absorber layer (microshunts), due to the thinner films (which could explain lower V_{OC} than P3HT), second—the quality of the interface between the absorber and HTM. Thiophenes, in principle, are introduced for the better interface, for e.g., surface passivation, however, then one would expect the best performance for V1386. So, a further inspection of the Sb_2S_3 -HTM interface through advanced characterization techniques like deep-level transient spectroscopy may be needed to understand the role of interfacial defects on the performance of solar cells, and can be explored in future studies.

The cross-sectional images of solar cells with P3HT and new HTMs are shown in Figure 4c. While TiO_2 and Sb_2S_3 have an almost similar thickness in each case, P3HT is reasonably thicker (≈ 100 nm) compared to the new HTMs (≈ 25 – 30 nm). It may be noted that each individual HTM herein is optimized by its precursor concentration in spin coating to obtain the best efficient solar cells. Apparently, a thick P3HT is needed in order to get an efficiency of $\approx 4.7\%$ whereas a considerably thinner layer of each of the new HTMs is sufficient to obtain similar or slightly higher efficiencies (4.5–

4.9%). This proves the fact that the new HTMs, particularly V808 and V1385, are not only considerably cheaper but also the required materials consumption is significantly lower, which warrants the plausible fabrication of Sb_2S_3 solar cells with efficiencies close to 5% at a much cheaper cost. In addition, for the reproducibility of devices, the statistical box plots of efficiency, and the associated device parameters are shown in Figure 5. As Figure 5a unveils, the efficiency spread is almost identical in each case with P3HT and new HTMs. Further, the average efficiencies are also in a similar range in each of the optimized cases, except for the case of V1386, which shows a slightly lower efficiency owing to the low V_{OC} . Similarly, the trend in V_{OC} , J_{SC} , and FF is almost the same as that for the champion numbers with reasonably identical spreads. The V_{OC} in V1386-based solar cells is considerably lower while the J_{SC} in P3HT-solar cells is the lowest and the FFs range from 0.5 to 0.6 in all the cases. As the statistics indicate, the high reproducibility of the results is obtained in the present study.

The normalized external quantum efficiency (EQE) curves of solar cells with P3HT and new HTM layers are shown in Figure 6a. In addition, the integrated photocurrent density ($J_{integrated}$) calculated using EQE spectra is also shown and it can be noted that almost identical J_{SC} values are obtained from EQE data to the values extracted from J – V curves. A pertinent aspect to be noted is the dip in EQE for solar cells with P3HT in the range of 500–650 nm, which may be attributed to the parasitic absorption losses.² When an absorber is thinner or comparable to the thickness of HTM, the light that gets transmitted through the absorber gets reflected back from the back contact and often, the reflected light could be reabsorbed in the absorber to result in photogenerated carriers. However, if the HTM is sufficiently thick, then the reflected light gets

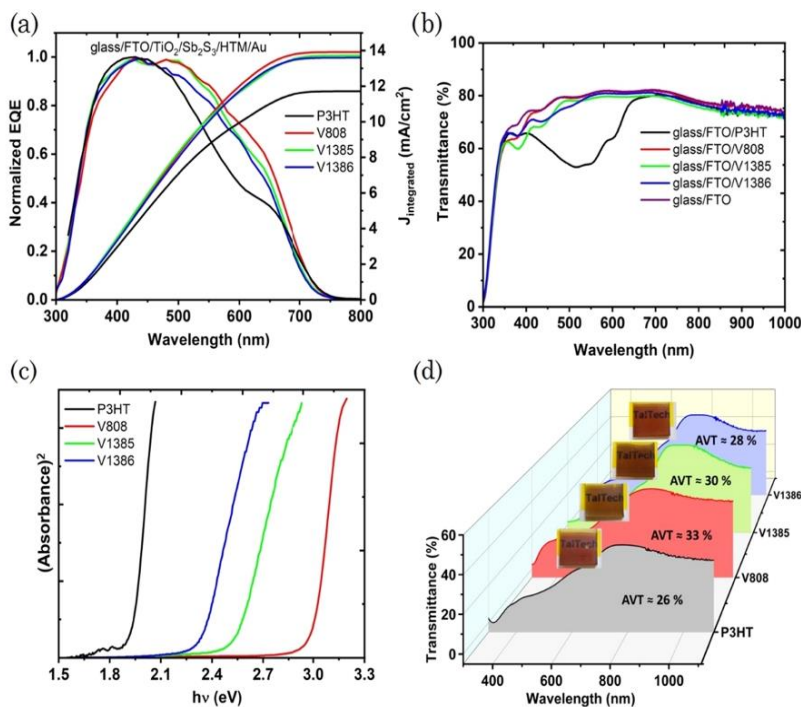


Figure 6. (a) Normalized external quantum efficiency (EQE) curves and the integrated J_{SC} of Sb_2S_3 solar cells with P3HT, V808, V1385, and V1386 as HTMs, (b) transmittance curves of glass/FTO/P3HT, glass/FTO/V808, glass/FTO/V1385 and glass/FTO/V1386, (c) $(\text{absorbance})^2$ vs $h\nu$ plots of P3HT, V808, V1385, and V1386 for band gap determination, and (d) transmittance curves of the device stack with P3HT, V808, V1385, and V1386 as HTMs without Au (inset: Respective sample photographs captured with a background showing semi-transparency).

absorbed in the HTM layer leading to parasitic absorption. In this study, P3HT is considerably thick and thus exhibits parasitic absorption while the considerably thinner new HTMs (V808, V1385, and V1386) does not show any similar dip in EQE, which could further explain the enhanced J_{SC} values in the respective solar cells. Optical transmittance studies are performed for bare P3HT and new V808, V1385, and V1386 HTM layers on glass/FTO substrates, as shown in Figure 6b, where the absorption by P3HT is corroborated with EQE results as observed from the dip in transmittance in 400–650 nm region. Further, it may also be observed that the new HTMs exhibit considerable transparency similar to that of the glass/FTO substrate. The band gaps of P3HT, V808, V1385, and V1386 are inferred to be ≈ 1.9 , 2.9, 2.5, and 2.3 eV, respectively, from the plots shown in Figure 6c and the absorption coefficient-based Tauc's plots in Figure S4, which ascertains the fact that new HTMs are optically more transparent in the visible region compared to P3HT. Finally, the overall transparency of device stacks without top metal contact is analyzed (see Figure 6d) and the solar weighted average visible transmittance (AVT) (400–800 nm) of devices with P3HT, V808, V1385, and V1386 HTMs are determined to be ≈ 26 , 33, 30, and 28%, respectively. In the case of new HTMs, as the thiophene units increased the band gap decreased resulting in slightly reduced transparency as

witnessed from the overall device transmittance. The sample pictures of glass/FTO/ TiO_2 / Sb_2S_3 /HTM where HTM is P3HT, V808, V1385, and V1386 are shown with a background and it may be observed that all the samples exhibit decent transparency with visibility being the highest for V808. While all device stacks exhibit reasonably good AVT values as required for semitransparent applications, the devices with new HTMs exhibit enhanced transparency, which is due to their increased transmittance over P3HT. The cost-effective fluorene-based thiophene-terminated (V808, V1385, V1386) HTMs are successfully demonstrated in Sb_2S_3 solar cells as potentially suitable candidates for semitransparent applications and efforts are underway to increase the PCE of solar cells and upscaling the devices.

4. CONCLUSIONS

Novel cost-effective and transparent fluorene-based thiophene-terminated hole transport materials (V808, V1385, and V1386) are demonstrated, for the first time, in semitransparent Sb_2S_3 solar cells exhibiting a power conversion efficiency of 4.5–4.9% and an average visible transmittance of 30–33% (without the metal) in the 400–800 nm range. Solar cells with the conventional P3HT as HTM have yielded 4.7% efficiency, however, they have exhibited lower transparency (26%) owing to parasitic absorption losses in P3HT. The band diagram of

solar cells with new HTMs and P3HT are compared, which unveils that new HTMs have exhibited favorable band offset validating them as effective HTMs for Sb_2S_3 solar cells. The new HTMs with terminated thiophene units have demonstrated reasonably improved wettability over conventional P3HT that could provide better interaction channels for charge carrier transport thus leading to enhanced current density. However, a closer inspection of Sb_2S_3 -HTM needs to be further explored to unravel the interfacial effects as the solar cells with new HTMs have exhibited reasonably lower V_{OC} values, particularly in the case of V808 and V1386.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.2c04097>.

Synthesis procedure, DSC, J - V characteristics of solar cells, and absorption spectra related data of V808, V1385, and V1386 (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Sreekanth Mandati – Department of Materials and Environmental Technology, Laboratory of Thin Film Chemical Technologies, Tallinn University of Technology, 19086 Tallinn, Estonia; orcid.org/0000-0002-3317-271X; Email: sreekanth.mandati@taltech.ee

Ilona Oja Acik – Department of Materials and Environmental Technology, Laboratory of Thin Film Chemical Technologies, Tallinn University of Technology, 19086 Tallinn, Estonia; Email: ilona.oja@taltech.ee

Authors

Nimish Juneja – Department of Materials and Environmental Technology, Laboratory of Thin Film Chemical Technologies, Tallinn University of Technology, 19086 Tallinn, Estonia

Atanas Katerski – Department of Materials and Environmental Technology, Laboratory of Thin Film Chemical Technologies, Tallinn University of Technology, 19086 Tallinn, Estonia

Aistē Jēgorovē – Department of Organic Chemistry, Kaunas University of Technology, Kaunas LT-50254, Lithuania

Raitis Grizbovskis – Institute of Solid State Physics, University of Latvia, Riga LV 1063, Latvia

Aivars Vembris – Institute of Solid State Physics, University of Latvia, Riga LV 1063, Latvia

Tatjana Dedova – Department of Materials and Environmental Technology, Laboratory of Thin Film Chemical Technologies, Tallinn University of Technology, 19086 Tallinn, Estonia

Nicolae Spalatu – Department of Materials and Environmental Technology, Laboratory of Thin Film Chemical Technologies, Tallinn University of Technology, 19086 Tallinn, Estonia; orcid.org/0000-0003-0234-2170

Artiom Magomedov – Department of Organic Chemistry, Kaunas University of Technology, Kaunas LT-50254, Lithuania; orcid.org/0000-0003-3159-1870

Smagul Karazhanov – Institute for Energy Technology (IFE), NO 2027 Kjeller, Norway

Vytautas Getautis – Department of Organic Chemistry, Kaunas University of Technology, Kaunas LT-50254, Lithuania; orcid.org/0000-0001-7695-4677

Malle Krunk – Department of Materials and Environmental Technology, Laboratory of Thin Film Chemical Technologies, Tallinn University of Technology, 19086 Tallinn, Estonia; orcid.org/0000-0003-4658-4403

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsaem.2c04097>

Author Contributions

S.M. conceptualization, design of experiments, analysis of the results, and manuscript writing; N.J. experiments and contribution to manuscript writing; A.K. and T.D. support in experiments and data acquisition; N.S. and S.K. supported in analysis; A.J., A.M., and V.G. synthesized and characterized new HTMs; R.G. and A.V. performed ionization potential and hole mobility measurements, M.K. and I.O.A. provided support for analysis and finalizing the manuscript draft. All authors have given approval to the final version of the manuscript.

Funding

EEA Grants—S-BMT-21-1 (LT08-2-LMT-K-01-003). Estonian Research Council—PRG627 and PSG689. Archimedes Foundation—TK141 (TAR16016EK). European Union Horizon2020—952509 and 739508.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The “Development of Semitransparent Bifacial Thin-Film Solar Cells for Innovative Applications” benefits from a 999372 € grant from Iceland, Liechtenstein, and Norway through the EEA Grants. The aim of the project is to develop a new approach based on novel materials and structures and production technologies, which are the key to further increase the share and range of applications of PV in areas with sub-average sunlight, including Baltic and Nordic countries. Therefore, the development of resource saving, cost-effective, and efficient PV devices is a primary challenge of this project. Project contract with the Research Council of Lithuania (LMTLT) number is S-BMT-21-1 (LT08-2-LMT-K-01-003). Department of Materials and Environmental Technology, Tallinn University of Technology has received funding from the Estonian Research Council projects PRG627 “Antimony chalcogenide thin films for next-generation semitransparent solar cells applicable in electricity producing windows” and PSG689 “Bismuth Chalcogenide Thin-Film Disruptive Green Solar Technology for Next-Generation Photovoltaics”, and the Estonian Centre of Excellence project TK141 (TAR16016EK) “Advanced materials and high-technology devices for energy recuperation systems”, the European Union’s Horizon2020 program under the ERA Chair project SGSOLAR grant agreement No 952509. Institute of Solid-State Physics, University of Latvia has received funding from the European Union’s Horizon2020 Framework Programme H2020-WIDE-SPREAD-01-2016-2017-TeamingPhase2 under grant agreement no. 739508, project CAMART². The authors thank Dr. Tadas Malinauskas and Dr. Valdek Mikli for their support in the preparation and characterization of the samples.

■ ABBREVIATIONS

HTM, hole transport material
V808, N^2,N^2,N^7,N^7 -tetrakis(4-methoxyphenyl)-9-(thiophen-2-ylmethylene)-9H-fluorene-2,7-diamine
V1385, 9-([2,2':5',2"-terthiophen]-5-ylmethylene)- N^2,N^2,N^7,N^7 -tetrakis(4-methoxyphenyl)-9H-fluorene-2,7-diamine
V1386, 9-([2,2'-bithiophen]-5-ylmethylene)- N^2,N^2,N^7,N^7 -tetrakis(4-methoxyphenyl)-9H-fluorene-2,7-diamine
P3HT, poly(3-hexylthiophene)
Spiro-OMeTAD, 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene
PCPDTBT, poly{4,4'-dialkyl-4H-cyclopenta[2,1-b;3,4-b']-dithiophene-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl}
AVT, average visible transmittance
DSC, differential scanning calorimetry
TGA, thermal gravimetric analysis
EQE, external quantum efficiency

■ REFERENCES

- (1) Kondrotas, R.; Chen, C.; Tang, J. Sb2S3 Solar Cells. *Joule* **2018**, 2, 857–878.
- (2) Zimmermann, E.; Pfadler, T.; Kalb, J.; Dorman, J. A.; Sommer, D.; Hahn, G.; Weickert, J.; Schmidt-Mende, L. Toward High-Efficiency Solution-Processed Planar Heterojunction Sb2S3 Solar Cells. *Adv. Sci.* **2015**, 2, No. 1500059.
- (3) Castro, J. R.; Dale, P.; Mahon, M. F.; Molloy, K. C.; Peter, L. M. Deposition of Antimony Sulfide Thin Films from Single-Source Antimony Thiolate Precursors. *Chem. Mater.* **2007**, 19, 3219–3226.
- (4) Büttner, P.; Scheler, F.; Döhler, D.; Barr, M. K. S.; Bosch, M.; Rey, M.; Yokosawa, T.; Hinz, S.; Maultzsch, J.; Spieker, E.; Vogel, N.; Mínguez-Bacho, I.; Bachmann, J. Continuous, Crystalline Sb2S3 Ultrathin Light Absorber Coatings in Solar Cells Based on Photonic Concentric p-i-n Heterojunctions. *Nano Energy* **2022**, 103, No. 107820.
- (5) Shah, U. A.; Chen, S.; Khalaf, G. M. G.; Jin, Z.; Song, H. Wide Bandgap Sb2S3 Solar Cells. *Adv. Funct. Mater.* **2021**, 31, No. 2100265.
- (6) Eensalu, J. S.; Katerski, A.; Kärber, E.; Weinhardt, L.; Blum, M.; Heske, C.; Yang, W.; Acik, I. O.; Krunk, M. Semitransparent Sb2S3 Thin Film Solar Cells by Ultrasonic Spray Pyrolysis for Use in Solar Windows. *Beilstein J. Nanotechnol.* **2019**, 10, 2396–2409.
- (7) Lee, S.-J.; Sung, S.-J.; Yang, K.-J.; Kang, J.-K.; Kim, J. Y.; Do, Y. S.; Kim, D.-H. Approach to Transparent Photovoltaics Based on Wide Band Gap Sb2S3 Absorber Layers and Optics-Based Device Optimization. *ACS Appl. Energy Mater.* **2020**, 3, 12644–12651.
- (8) Wang, S.; Zhao, Y.; Che, B.; Li, C.; Chen, X.; Tang, R.; Gong, J.; Wang, X.; Chen, G.; Chen, T.; Li, J.; Xiao, X. A Novel Multi-Sulfur Source Collaborative Chemical Bath Deposition Technology Enables 8%-Efficiency Sb2S3 Planar Solar Cells. *Adv. Mater.* **2022**, 34, No. 2206242.
- (9) Yang, Z.; Wang, X.; Chen, Y.; Zheng, Z.; Chen, Z.; Xu, W.; Liu, W.; Yang, Michael, Y.; Zhao, J.; Chen, T.; Zhu, H. Ultrafast Self-Trapping of Photoexcited Carriers Sets the Upper Limit on Antimony Trisulfide Photovoltaic Devices. *Nat. Commun.* **2019**, 10, No. 4540.
- (10) Dong, J.; Liu, Y.; Wang, Z.; Zhang, Y. Boosting VOC of Antimony Chalcogenide Solar Cells: A Review on Interfaces and Defects. *Nano Sel.* **2021**, 2, 1818–1848.
- (11) Krautmann, R.; Spalatu, N.; Gunter, R.; Abou-Ras, D.; Unold, T.; Schorr, S.; Krunk, M.; Oja Acik, I. Analysis of Grain Orientation and Defects in Sb2Se3 Solar Cells Fabricated by Close-Spaced Sublimation. *Sol. Energy* **2021**, 225, 494–500.
- (12) Vidal-Fuentes, P.; Placidi, M.; Sánchez, Y.; Becerril-Romero, I.; Andrade-Arzuva, J.; Jehl, Z.; Pérez-Rodríguez, A.; Izquierdo-Roca, V.; Saucedo, E. Efficient Se-Rich Sb2Se3/CdS Planar Heterojunction Solar Cells by Sequential Processing: Control and Influence of Se Content. *Sol. RRL* **2020**, 4, No. 2000141.
- (13) Hobson, T. D. C.; Phillips, L. J.; Hutter, O. S.; Shiel, H.; Swallow, J. E. N.; Savory, C. N.; Nayak, P. K.; Mariotti, S.; Das, B.; Bowen, L.; Jones, L. A. H.; Featherstone, T. J.; Smiles, M. J.; Farnworth, M. A.; Zoppi, G.; Thakur, P. K.; Lee, T.-L.; Snaith, H. J.; Leighton, C.; Scanlon, D. O.; Dhanak, V. R.; Durose, K.; Veal, T. D.; Major, J. D. Isotype Heterojunction Solar Cells Using N-Type Sb2Se3 Thin Films. *Chem. Mater.* **2020**, 32, 2621–2630.
- (14) Zhu, L.; Chen, J.; Liu, R.; Dong, C.; Yang, S.; Chen, T.; Chen, C.; Qiao, Q.; Wang, M. Solution-Processed Compact Sb2S3 Thin Films by a Facile One-Step Deposition Method for Efficient Solar Cells. *Sol. RRL* **2021**, 5, No. 2100666.
- (15) Choi, Y. C.; Lee, D. U.; Noh, J. H.; Kim, E. K.; Seok, S. I. Highly Improved Sb2S3 Sensitized-Inorganic–Organic Heterojunction Solar Cells and Quantification of Traps by Deep-Level Transient Spectroscopy. *Adv. Funct. Mater.* **2014**, 24, 3587–3592.
- (16) You, M. S.; Lim, C.-S.; Kwon, D. H.; Heo, J. H.; Im, S. H.; Chae, K. J. Oxide-Free Sb2S3 Sensitized Solar Cells Fabricated by Spin and Heat-Treatment of Sb(III)(Thioacetamide)2Cl3. *Org. Electron.* **2015**, 21, 155–159.
- (17) Zhang, Y.; Li, S.; Tang, R.; Wang, X.; Chen, C.; Lian, W.; Zhu, C.; Chen, T. Phosphotungstic Acid Regulated Chemical Bath Deposition of Sb2S3 for High-Efficiency Planar Heterojunction Solar Cell. *Energy Technol.* **2018**, 6, 2126–2131.
- (18) Chen, J.; Qi, J.; Liu, R.; Zhu, X.; Wan, Z.; Zhao, Q.; Tao, S.; Dong, C.; Ashebir, G. Y.; Chen, W.; Peng, R.; Zhang, F.; Yang, S.; Tian, X.; Wang, M. Preferentially Oriented Large Antimony Trisulfide Single-Crystalline Cuboids Grown on Polycrystalline Titania Film for Solar Cells. *Commun. Chem.* **2019**, 2, No. 121.
- (19) Nie, R.; Seok, S. I. Efficient Antimony-Based Solar Cells by Enhanced Charge Transfer. *Small Methods* **2020**, 4, No. 1900698.
- (20) Nie, R.; Yun, H.; Paik, M.-J.; Mehta, A.; Park, B.; Choi, Y. C.; Seok, S. I. Efficient Solar Cells Based on Light-Harvesting Antimony Sulfide. *Adv. Energy Mater.* **2018**, 8, No. 1701901.
- (21) Liu, C. P.; Wang, H. E.; Ng, T. W.; Chen, Z. H.; Zhang, W. F.; Yan, C.; Tang, Y. B.; Bello, I.; Martinu, L.; Zhang, W. J.; Jha, S. K. Hybrid Photovoltaic Cells Based on ZnO/Sb2S3/P3HT Heterojunctions. *Phys. Status Solidi B* **2012**, 249, 627–633.
- (22) Reja-Jayan, B.; Manthiram, A. Effects of Bifunctional Metal Sulfide Interlayers on Photovoltaic Properties of Organic–Inorganic Hybrid Solar Cells. *RSC Adv.* **2013**, 3, 5412–5421.
- (23) Kärber, E.; Katerski, A.; Acik, I. O.; Mere, A.; Mikli, V.; Krunk, M. Sb2S3 Grown by Ultrasonic Spray Pyrolysis and Its Application in a Hybrid Solar Cell. *Beilstein J. Nanotechnol.* **2016**, 7, 1662–1673.
- (24) Wang, X.; Li, J.; Liu, W.; Yang, S.; Zhu, C.; Chen, T. A Fast Chemical Approach towards Sb2S3 Film with a Large Grain Size for High-Performance Planar Heterojunction Solar Cells. *Nanoscale* **2017**, 9, 3386–3390.
- (25) Lan, C.; Liang, G.; Lan, H.; Peng, H.; Su, Z.; Zhang, D.; Sun, H.; Luo, J.; Fan, P. Microstructural and Optical Properties of Sb2S3 Film Thermally Evaporated from Antimony Pentasulfide and Efficient Planar Solar Cells. *Phys. Status Solidi RRL* **2018**, 12, No. 1800025.
- (26) Han, J.; Pu, X.; Zhou, H.; Cao, Q.; Wang, S.; He, Z.; Gao, B.; Li, T.; Zhao, J.; Li, X. Synergistic Effect through the Introduction of Inorganic Zinc Halides at the Interface of TiO2 and Sb2S3 for High-Performance Sb2S3 Planar Thin-Film Solar Cells. *ACS Appl. Mater. Interfaces* **2020**, 12, 44297–44306.
- (27) Han, J.; Wang, S.; Yang, J.; Guo, S.; Cao, Q.; Tang, H.; Pu, X.; Gao, B.; Li, X. Solution-Processed Sb2S3 Planar Thin Film Solar Cells with a Conversion Efficiency of 6.9% at an Open Circuit Voltage of 0.7 V Achieved via Surface Passivation by a SbCl3 Interface Layer. *ACS Appl. Mater. Interfaces* **2020**, 12, 4970–4979.
- (28) Tang, R.; Wang, X.; Lian, W.; Huang, J.; Wei, Q.; Huang, M.; Yin, Y.; Jiang, C.; Yang, S.; Xing, G.; Chen, S.; Zhu, C.; Hao, X.; Green, M. A.; Chen, T. Hydrothermal Deposition of Antimony Selenosulfide Thin Films Enables Solar Cells with 10% Efficiency. *Nat. Energy* **2020**, 5, 587–595.
- (29) Lian, W.; Jiang, C.; Yin, Y.; Tang, R.; Li, G.; Zhang, L.; Che, B.; Chen, T. Revealing Composition and Structure Dependent Deep-

Level Defect in Antimony Trisulfide Photovoltaics. *Nat. Commun.* **2021**, *12*, No. 3260.

(30) Ning, H.; Guo, H.; Zhang, J.; Wang, X.; Jia, X.; Qiu, J.; Yuan, N.; Ding, J. Enhancing the Efficiency of Sb₂S₃ Solar Cells Using Dual-Functional Potassium Doping. *Sol. Energy Mater. Sol. Cells* **2021**, *221*, No. 110816.

(31) Büttner, P.; Scheler, F.; Pointer, C.; Döhler, D.; Yokosawa, T.; Spiecker, E.; Boix, P. P.; Young, E. R.; Mínguez-Bacho, I.; Bachmann, J. ZnS Ultrathin Interfacial Layers for Optimizing Carrier Management in Sb₂S₃-Based Photovoltaics. *ACS Appl. Mater. Interfaces* **2021**, *13*, 11861–11868.

(32) Kim, D.-H.; Lee, S.-J.; Park, M. S.; Kang, J.-K.; Heo, J. H.; Im, S. H.; Sung, S.-J. Highly Reproducible Planar Sb₂S₃-Sensitized Solar Cells Based on Atomic Layer Deposition. *Nanoscale* **2014**, *6*, 14549–14554.

(33) Juneja, N.; Mandati, S.; Katerski, A.; Spalatu, N.; Daskeviciute-Geguziene, S.; Vembris, A.; Karazhanov, S.; Getautis, V.; Krunk, M.; Oja Acik, I. Sb₂S₃ Solar Cells with a Cost-Effective and Dopant-Free Fluorene-Based Enamine as a Hole Transport Material. *Sustainable Energy Fuels* **2022**, *6*, 3220–3229.

(34) Petrus, M. L.; Bein, T.; Dingemans, T. J.; Docampo, P. A Low Cost Azomethine-Based Hole Transporting Material for Perovskite Photovoltaics. *J. Mater. Chem. A* **2015**, *3*, 12159–12162.

(35) Eensalu, J. S.; Katerski, A.; Kärber, E.; Acik, I. O.; Mere, A.; Krunk, M. Uniform Sb₂S₃ Optical Coatings by Chemical Spray Method. *Beilstein J. Nanotechnol.* **2019**, *10*, 198–210.

(36) Jiang, C.; Zhou, J.; Tang, R.; Lian, W.; Wang, X.; Lei, X.; Zeng, H.; Zhu, C.; Tang, W.; Chen, T. 9.7%-Efficient Sb₂(S,Se)₃ Solar Cells with a Dithieno[3,2-b:2',3'-d']Pyrrole-Cored Hole Transporting Material. *Energy Environ. Sci.* **2021**, *14*, 359–364.

(37) Xiang, Y.; Guo, H.; Cai, Z.; Jiang, C.; Zhu, C.; Wu, Y.; Zhu, W.-H.; Chen, T. Dopant-Free Hole-Transporting Materials for Stable Sb₂(S,Se)₃ Solar Cells. *Chem. Commun.* **2022**, *58*, 4787–4790.

Recommended by ACS

Combining ZnO and Organosilica Nanodots as a Thick Cathode Interlayer for Highly Efficient and Stable Inverted Polymer Solar Cells

Mengqi Cui, Li Nian, *et al.*

MARCH 21, 2023

ACS APPLIED ENERGY MATERIALS

READ 

Exploration of the Effect of Fluorination on the Doping-Free Linear Dibenzothiophene-Based Hole-Transport Material Applied for Inverted Perovskite Solar Cells

Zhengxu Liu, Ningyi Yuan, *et al.*

JANUARY 25, 2023

ACS APPLIED ENERGY MATERIALS

READ 

Modulation of the TCO/MoO_x Front Contact Enables >21% High-Efficiency Dopant-Free Silicon Solar Cells

Junjun Li, Jian Yu, *et al.*

DECEMBER 16, 2022

ACS APPLIED ENERGY MATERIALS

READ 

Fill Factor Loss in a Recombination Junction for Monolithic Tandem Solar Cells

Johan Lauwaert.

APRIL 06, 2023

ACS APPLIED ENERGY MATERIALS

READ 

Get More Suggestions >

Supporting Information

4.9 % efficient Sb₂S₃ solar cells from semi-transparent absorbers with fluorene-based thiophene terminated hole conductors

Sreekanth Mandati^{1,*}, *Nimish Juneja*¹, *Atanas Katerski*¹, *Aistė Jegorovė*², *Raitis Grībovskis*³, *Aivars Vembris*³, *Tatjana Dedova*¹, *Nicolae Spalatu*¹, *Artiom Magomedov*², *Smagul Karazhanov*⁴, *Vytautas Getautis*², *Malle Krums*¹, and *Ilona Oja Acik*^{1,#}

¹Laboratory of Thin Film Chemical Technologies, Department of Materials and Environmental Technology, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia.

²Department of Organic Chemistry, Kaunas University of Technology, Kaunas LT-50254, Lithuania.

³Institute of Solid State Physics, University of Latvia,

via, Kengaraga Str. 8, Riga, Latvia.

⁴Institute for Energy Technology (IFE), P.O Box 40, NO 2027, Kjeller, Norway.

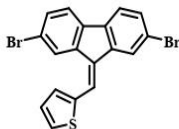
*Corresponding author: sreekanth.mandati@taltech.ee

#co-corresponding author: ilona.oja@taltech.ee

S1: Detailed synthesis procedure of V808, V1385 and V1386

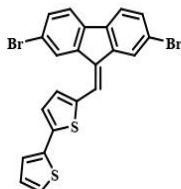
Chemicals required for the synthesis were purchased from Sigma-Aldrich and TCI Europe and used as received without additional purification. ¹H NMR and ¹³C NMR spectra were collected at 400 and 101 MHz, respectively on a Bruker Avance III spectrometer. The chemical shifts, expressed in ppm, were relative to tetramethylsilane (TMS). All the experiments were performed at 25 °C. Reactions were monitored by thin-layer chromatography on ALUGRAM SIL G/UV254 plates and developed with UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was

used for column chromatography. Elemental analysis was performed with an Exeter Analytical CE-440 elemental analyzer, Model 440 C/H/N.



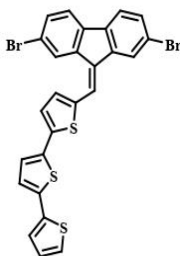
2-((2,7-dibromo-9H-fluoren-9-ylidene)methyl)thiophene (1)

A mixture of thiophene-2-carbaldehyde (1 g, 9 mmol), 2,7-dibromofluorene (4.37 g, 13.5 mmol), and toluene (19 mL) was stirred for 10 minutes. Afterwards, NaOH solution (19 mL, 40% W/W) and tetrabutylammonium bromide (0.67 g, 2 mmol) were added and the reaction mixture was heated at reflux for 2 hours (TLC control, acetone/*n*-hexane 1:4). After cooling to room temperature, the reaction mixture was filtered off and crude crystals were used without any further purification in the next step. T_m = 185–186 °C. Yield 2.9 g (77%).



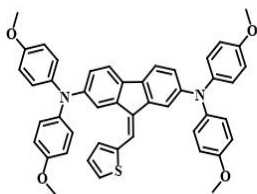
5-((2,7-dibromo-9H-fluoren-9-ylidene)methyl)-2,2'-bithiophene (2)

A mixture of [2,2'-bithiophene]-5-carbaldehyde (1 g, 5 mmol), 2,7-dibromofluorene (2.46 g, 7 mmol), and toluene (12 mL) was stirred for 10 minutes. Afterwards, NaOH solution (12 mL, 40% W/W) and tetrabutylammonium bromide (0.38 g, 1 mmol) were added and the reaction mixture was heated at reflux for 2 hours (TLC control, acetone/*n*-hexane 1:4). After cooling to room temperature, the reaction mixture was filtered off and crude crystals were used without any further purification in the next step. T_m = 197–199 °C. Yield 2 g (80%).



5-((2,7-dibromo-9H-fluoren-9-ylidene)methyl)-2,2':5,2''-terthiophene (3)

A mixture of [2,2':5,2''-terthiophene]-5-carbaldehyde (1 g, 3.6 mmol), 2,7-dibromofluorene (1.75 g, 5.4 mmol), and toluene (10 mL) was stirred for 10 minutes. Afterwards, NaOH solution (10 mL, 40% W/W) and tetrabutylammonium bromide (0.26 g, 0.08 mmol) were added and the reaction mixture was heated at reflux for 2 hours (TLC control, acetone/*n*-hexane 1:4). After cooling to room temperature, the reaction mixture was filtered off and crude crystals were used without any further purification in the next step. T_m = 212.5–214.5 °C . Yield 1.5 g (72%).



N²,N²,N⁷,N⁷-tetrakis(4-methoxyphenyl)-9-(thiophen-2-ylmethylene)-9H-fluorene-2,7-diamine (V808)

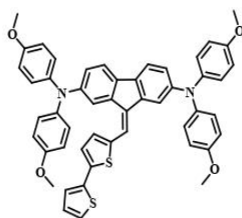
A mixture of 2-((2,7-dibromo-9H-fluoren-9-ylidene)methyl)thiophene (1) (0.37 g, 0.9 mmol), bis(4-methoxyphenyl)amine (0.69 g, 3 mmol), and anhydrous toluene (6 mL) was purged with Ar for 30 minutes. Afterwards, palladium (II) acetate (0.011 g, 0.05 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.03 g, 0.1 mmol) was added and the reaction mixture was stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (0.29 g, 3 mmol) was added and the mixture was heated at reflux for 8 hours (TLC control, acetone/*n*-hexane 1:24). After cooling

to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. The organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The crude product was crystallized from THF/ethanol mixture (1:1, v:v) to obtain purple crystals. T_m = 192–193 °C (acetone/ethanol, 1:1). Yield 0.55 g (84%).

¹H NMR (400 MHz, THF-*d*₈) δ: 7.69 (s, 1H), 7.44 – 7.31 (m, 4H), 7.26 (d, *J* = 5.2 Hz, 1H), 7.09 – 6.95 (m, 9H), 6.94 – 6.77 (m, 10H), 6.72 (t, *J* = 4.0 Hz, 1H), 3.77 (s, 6H), 3.74 (s, 6H).

¹³C NMR (101 MHz, THF-*d*₈) δ: 156.0, 155.7, 147.6, 147.4, 141.6, 141.2, 140.8, 138.8, 137.1, 136.0, 134.4, 133.2, 129.1, 127.0, 126.7, 126.2, 125.5, 122.8, 121.2, 119.02, 119.0, 118.6, 117.8, 114.5, 114.4, 114.3, 54.7, 54.6.

Anal. Calcd. For: C₄₆H₃₈N₂O₄S: C 77.29; H 5.36; N 3.92; O 8.95; S 4.48; found: C 77.39; H 5.31; N 3.88.



9-([2,2'-bithiophen]-5-ylmethylene)-N², N², N⁷, N⁷-tetraakis(4-methoxyphenyl)-9H-fluorene-2,7-diamine (V1385)

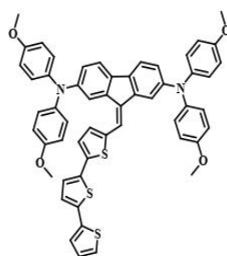
A mixture of 5-((2,7-dibromo-9H-fluorene-9-ylidene)methyl)-2,2'-bithiophene (**2**) (0.35 g, 0.7 mmol), bis(4-methoxyphenyl)amine (0.48 g, 2.1 mmol), and anhydrous toluene (5 mL) was purged with Ar for 30 minutes. Afterwards, palladium (II) acetate (0.09 g, 0.04 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.02 g, 0.08 mmol) was added and the reaction mixture was stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (0.2 g, 2.1 mmol) was added and the mixture was heated at reflux for 5 hours (TLC control, acetone/*n*-hexane 1:4). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate.

The organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 4:21, v:v). 20% solution of the final product in acetone was poured with intensive stirring into a 20-fold excess of ethanol. The precipitate as a brown powder was filtered off and dried. Yield 0.56 g (89%).

¹H NMR (400 MHz, Acetone-*d*₆) δ: 7.92 (s, 1H), 7.51 – 7.37 (m, 5H), 7.15 – 6.98 (m, 11H), 6.93 (d, *J* = 3.8 Hz, 1H), 6.91 – 6.82 (m, 10H), 3.77 (s, 6H), 3.75 (s, 6H).

¹³C NMR (101 MHz, Acetone-*d*₆) δ: 156.1, 155.8, 147.8, 147.5, 141.4, 141.1, 141.0, 139.1, 137.6, 136.8, 136.5, 135.2, 134.2, 132.8, 131.9, 128.2, 126.5, 125.8, 125.4, 124.4, 123.9, 122.7, 121.2, 119.6, 119.4, 118.7, 117.3, 114.8, 114.7, 114.1, 54.84, 54.82.

Anal. Calcd. For: C₅₀H₄₀N₂O₄S₂: C 75.35; H 5.06; N 3.51; O 8.03; S 8.05; found: C 75.29; H 5.09; N 3.53.



9-([2,2':5',2''-terthiophen]-5-ylmethylene)-N², N², N⁷, N⁷-tetrakis(4-methoxyphenyl)-9H-fluorene-2,7-diamine (V1386)

A mixture of 5-((2,7-dibromo-9H-fluoren-9-ylidene)methyl)-2,2':5,2''-terthiophene (**3**) (0.29 g, 0.05 mmol), bis(4-methoxyphenyl)amine (0.46 g, 2 mmol), and anhydrous toluene (4 mL) was purged with Ar for 30 minutes. Afterwards, palladium (II) acetate (0.007 g, 0.03 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.03 g, 0.1 mmol) was added and the reaction mixture was stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (0.19 g, 2 mmol) was added and the mixture was heated at reflux for 8 hours (TLC control, acetone/*n*-hexane 1:4). After

cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 , filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 3:21, v:v). 20% solution of the final product in acetone was poured with intensive stirring into a 40-fold excess of ethanol. The precipitate as a brown powder was filtered off and dried. Yield 0.35 g (78%).

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.83 (s, 1H), 7.58 – 7.46 (m, 4H), 7.45 – 7.41 (m, 1H), 7.38 (d, $J = 3.8$ Hz, 1H), 7.28 (d, $J = 3.8$ Hz, 1H), 7.23 (d, $J = 3.9$ Hz, 1H), 7.15 – 7.10 (m, 1H), 7.07 (d, $J = 3.8$ Hz, 1H), 7.06 – 7.00 (m, 5H), 7.99 – 7.93 (m, 4H), 6.93 – 6.86 (m, 8H), 6.80 – 6.77 (m, 2H), 3.73 (s, 6H), 3.69 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ : 156.1, 155.5, 147.8, 147.3, 141.5, 141.0, 140.8, 138.5, 137.6, 136.71, 136.7, 136.3, 134.9, 134.4, 133.7, 133.5, 132.9, 129.0, 127.0, 126.5, 126.0, 125.7, 125.5, 125.0, 124.8, 123.5, 120.4, 120.2, 116.5, 115.4, 115.3, 115.1, 67.5, 55.7, 55.6.

Anal. Calcd. For: $\text{C}_{54}\text{H}_{42}\text{N}_2\text{O}_4\text{S}_3$: C 73.78; H 4.82; N 3.19; O 7.28; S 10.94; found: C 73.68; H 4.86; N 3.24.



Cite this: *Sustainable Energy Fuels*,
2024, 8, 4324

Dopant-free fluorene based dimers linked with thiophene units as prospective hole transport materials for Sb_2S_3 solar cells†

Nimish Juneja,^a Aistē Jegorovė,^b Raitis Grzibovskis,^c Atanas Katerski,^a Maryte Daskeviciene,^b Tadas Malinauskas,^b Aivars Vembris,^c Smagul Karazhanov,^d Nicolae Spalatu,^a Vytautas Getautis,^b Malle Krunks^{*a} and Ilona Oja Acik^a

Novel dopant-free dimers comprising methoxydiphenylamine substituted fluorene derivatives and connected by central cores consisting of different numbers of thiophene moieties were synthesized and explored as hole transport materials (HTMs) in Sb_2S_3 absorber solar cells. Energy level diagrams show agreeable band offsets validating the compatibility of novel HTMs for the $\text{FTO}/\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{HTM}/\text{Au}$ solar cell with TiO_2 and Sb_2S_3 layers deposited by ultrasonic spray. X-ray photoelectron spectroscopy (XPS) study reveals the Sb 3d core level peak shift upon applying any of the HTMs on Sb_2S_3 indicating an increased electron density surrounding Sb atoms which refers to the interaction of S from electron-rich thiophene units with Sb in the absorber at the $\text{Sb}_2\text{S}_3/\text{HTM}$ interface. It is demonstrated that application of HTMs containing diphenylamine units in their side fragments increases the cell open circuit voltage from 478 mV to 673 mV, fill factor from 46% to 56% and conversion efficiency from 1.9% to 4.5% as compared to the device without any HTM and the observed improvement can be explained by the passivation of the interfacial states. In contrast, no enhancement in device performance has been observed when applying HTMs containing triphenylamine units although strong Sb–S interaction has been detected at the $\text{Sb}_2\text{S}_3/\text{HTM}$ interface. Quantum chemical simulation results suggest that to achieve enhanced charge selectivity by the organic HTM layer, the HOMO of the HTMs should be formed by the thiophene groups. Possible phenomena occurring at the $\text{Sb}_2\text{S}_3/\text{HTM}$ interface are discussed providing new insights towards understanding the charge transfer at the $\text{Sb}_2\text{S}_3/\text{HTM}$ interface.

Received 8th April 2024
Accepted 16th July 2024

DOI: 10.1039/d4se00472h

rsc.li/sustainable-energy

1. Introduction

The need for resource saving energy applications in society requires accelerated development and design of materials and solar cell devices with a wide set of properties which would allow an extended application range beyond Si photovoltaics (PVs). At this scale, for a new PV technology, it is insufficient to be only competitive with the current established c-Si or CdTe thin film technologies regarding the performance and stability but it should also be environmentally friendly and comprise earth abundant chemical elements. An emerging family of

promising cost-efficient PV materials, such as antimony and bismuth-based chalcogenides^{1–3} and lead-free chalcogenide perovskites⁴ are currently under investigation in the PV community. Among these materials, antimony chalcogenides such as Sb_2S_3 , Sb_2Se_3 and $\text{Sb}_2(\text{S}_2\text{Se})_3$ showed a nascent track record of rapid performance development, reaching power conversion efficiencies (PCEs) of 8.0%, 10.57% and 10.75%, respectively.^{3–7} These materials have garnered substantial R&D efforts within the PV community due to their compelling attributes such as their abundance in nature, environmentally benign elemental constituents, as well as commendable optoelectronic characteristics and stability.^{2,8,9} In particular, the utility of Sb_2S_3 absorbers makes them viable for employment in semi-transparent solar cells, owing to their band gap of 1.7 eV, and a high absorption coefficient (10^5 cm^{-1} at 450 nm). These advantageous attributes make them particularly well-suited for integration within tandem cell device configurations and as solar windows.

In many solar cells, including antimony chalcogenide-based solar cells, a hole transporting layer (HTL) is utilized to extract and transport photogenerated charge carriers from the

^aDepartment of Materials and Environmental Technology, Tallinn University of Technology, Ehitajate tee 5, Tallinn, 19086, Estonia. E-mail: malle.krunks@ttu.ee

^bDepartment of Organic Chemistry, Kaunas University of Technology, Kaunas, LT-50254, Lithuania

^cInstitute of Solid State Physics, University of Latvia, Kengaraga Str. 8, Rīga, LV-1063, Latvia

^dInstitute for Energy Technology (IFE), P.O. Box 40, Kjeller, NO 2027, Norway

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4se00472h>

absorber layer to the electrode. The HTL also serves as a barrier layer for electron leakage and as a protective layer to screen the active layer from oxygen and moisture. The HTL can be made of inorganic and organic materials. An ideal material for the HTL should have an excess of holes, high hole mobility, good thermal stability, low density of defects, high solubility in a suitable solvent, simple synthesis process and appropriate band energy alignment with the absorber.^{10,11} In general, organic hole transporting materials (HTMs) like poly(3-hexylthiophene) (P3HT)^{11–13} and 2,2',7,7'-tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD)^{5,14,15} or a combination of them¹⁶ are the most commonly employed to fabricate efficient Sb chalcogenide solar cells, although Spiro-OMeTAD is the most efficient one to date delivering a PCE of around 10%.^{7,17,18} However, both these HTMs possess serious drawbacks for large-scale applications. P3HT and Spiro-OMeTAD are expensive due to their complex and time-consuming synthesis processes.¹⁹ In addition, P3HT exhibits parasitic absorption of light in the visible spectral region, leading to a decrease in the overall optical transmittance of the solar cell^{13,20–22} while Spiro-OMeTAD exhibits low values of conductivity and hole mobility.²³ Common additives such as lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 4-*tert*-butylpyridine (TBP) are used to improve the electrical properties of Spiro-OMeTAD films,²⁴ which, in turn, seriously worsen the stability of the devices. Therefore, the exploration and advancement of easily synthesizable and dopant-free HTMs is a challenging task.

It has been demonstrated that fluorene-based enamines synthesized by a facile condensation reaction are efficient dopant-free HTMs for high performance perovskite solar cells yielding a PCE of 17.1% that outperforms the device with undoped Spiro-OMeTAD exhibiting a PCE of 10.4%.²⁵ Fluorene-based enamines were recently explored as dopant-free HTMs in Sb₂S₃ solar cells.^{20,21} The devices with new transparent HTMs exhibited higher PCEs, up to 4.3% compared to 3.8% by the reference device with P3HT, and *ca.* 20% higher optical transparency.²¹

Novel transparent HTM molecules comprising 4,4'-dime-thoxydiphenylamine-substituted fluorene fragments, widely used in organic HTMs, including Spiro-OMeTAD,²⁶ and thiophene units mimicking P3HT, were synthesized by a simple and high yield synthesis process.²² Thiophene units were added into the molecule targeting application in antimony chalcogenide active layer solar cells, as the thiophene could interact with Sb atoms at the absorber/HTM interface and an improvement in interfacial properties is expected.^{27–29} In our previous study, HTMs from fluorene-based molecules with terminated thiophene units proved their applicability in Sb₂S₃ solar cells, the devices demonstrate PCEs of 4.7–4.9% and an average optical transparency in the visible spectral range of *ca.* 30%, outperforming the parameters of the P3HT-based device.²²

In this study four new dopant-free HTMs (V1422, V1423, V1454 and V1455) were synthesized, characterized and explored in Sb₂S₃ solar cells. The novelty of the study lies in development and optimization of new HTMs and their evaluation as prospective charge transport materials in Sb₂S₃ thin film

devices. The synthesized molecules are dimers containing diphenylamine units (V1422 and V1423) and triphenylamine units (V1454 and V1455) in their side fragments. The common structural feature of all molecules is that the central core consists of different numbers of thiophene moieties. The properties of the novel HTMs are thoroughly studied; quantum chemical calculations are employed to analyze HTM molecular geometry and determine the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) positions. The suitability of the synthesized materials as HTMs in planar Sb₂S₃-based solar cells is examined. The solar cell stack comprises glass/FTO/TiO₂/Sb₂S₃/HTM/Au, with TiO₂ and the absorber layer deposited through ultrasonic spray deposition and the HTM layer *via* spin coating. Various characterization methods applied to the materials, interfaces and devices provide insights on the functionality of this new family of dopant-free HTMs for Sb-chalcogenide-based solar cells.

2. Experimental

2.1. Materials

Chemicals required for the synthesis of the HTMs were purchased from Sigma-Aldrich and TCI Europe and used without any additional purification. Comprehensive information on the synthetic procedures of HTMs is detailed in the ESI.† For the fabrication of solar cells, the following substances were used as received: FTO substrate (10 Ω sq^{−1}), titanium(IV) tetraisopropoxide (TTIP) from Acros Organics (99 wt%), acetylacetone from Acros Organics (99 wt%), ethanol from Estonian Spirit (96.6 vol%), methanol from Sigma-Aldrich (99.9 vol%), antimony trichloride from Sigma-Aldrich (99.99 wt%), thiourea from Sigma-Aldrich (99 wt%), chlorobenzene from Sigma-Aldrich (99.5 vol%), and poly(3-hexylthiophene-2,5-diyl) (P3HT) from Sigma-Aldrich (regio regular, >90%).

2.2. Methods

2.2.1. Fabrication of the solar cell. Solar cell devices are fabricated in superstrate configuration (glass/FTO/TiO₂/Sb₂S₃/HTM/Au) using a similar experimental procedure to that outlined in our previous investigations.^{20–22} A fluorine-doped tin oxide (FTO)-coated glass substrate with a sheet resistivity of 10 Ω sq^{−1} is subjected to a cleaning process, with steps involving rinsing and boiling in deionized water, followed by drying with N₂. TiO₂ is deposited using ultrasonic spray pyrolysis (USP) with substrate temperature maintained at 340 °C and then annealed (450 °C, 30 min) on a hot plate in air. Similarly, the absorber Sb₂S₃ is deposited using USP (198 °C) and annealed (250 °C, 5 min) in a N₂ environment. The HTM powders were dissolved in chlorobenzene. The V-series HTM solutions in concentrations of 4, 2, 1 and 0.6 mM were spin-coated (3000 rpm, 30 s) on the absorber at room temperature. For P3HT, 1% wt concentration is utilized, followed by spin coating (3000 rpm, 30 s). The P3HT samples undergo an additional activation step at 170 °C for 5 minutes in a nitrogen environment after spin coating. Subsequently, a thermal evaporation process is employed to deposit

an 80–100 nm thick gold (Au) back contact using a shadow mask (contact area = 7.06 mm²).

2.2.2. Characterization of synthesized HTMs and fabricated solar cells. Chemical compositions of the synthesised HTMs were studied by NMR and MS spectroscopy. ¹H NMR and ¹³C NMR spectra were collected at 400 and 101 MHz, respectively on a Bruker Avance III spectrometer. The chemical shifts, expressed in ppm, were relative to tetramethylsilane (TMS). All the experiments were performed at 25 °C. Reactions were monitored by thin-layer chromatography on ALUGRAM SIL G/UV254 plates and developed with UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was used for column chromatography. Elemental analysis was performed with an Exeter Analytical CE-440 elemental analyser, Model 440 C/H/N. Thermogravimetric analysis (TGA) was performed on a Q50 thermogravimetric analyser (TA Instruments) at a scan rate of 10 °C min⁻¹ under a nitrogen atmosphere. The values are given for a weight-loss of 5% (*T*_{d5}). Differential scanning calorimetry (DSC) was performed on a TA Instruments Q2000 differential scanning calorimeter under a nitrogen atmosphere. The heating and cooling rate was 10 °C min⁻¹. The UV-vis spectral analysis of the sample in solution (THF, 10⁻⁴ mol L⁻¹) was performed on a PerkinElmer Lambda 35 UV/VIS spectrophotometer. The layer thickness of the solution is *d* = 1 mm and the diffraction grating crack width is 2 nm.

The ionization potential (*I*_p) values of all the functional layers were measured by the photoelectron yield spectroscopy (PYS) method. The optical band gap values (*E*_g) of the absorber and HTM films were calculated from the absorption spectra using Tauc plots. Additionally, the work function of the Au metal contacts was measured through a Kelvin probe. The hole drift mobility of the HTMs was measured utilizing the time-of-flight (ToF) method. The X-ray diffraction (XRD) pattern of the glass/FTO/TiO₂/Sb₂S₃ stack was measured using a Rigaku Ultima-IV with a Cu K_α source (λ = 1.5406 Å) in the 2 θ range of 10–80°. Micro-Raman spectra were measured at room temperature using a Horiba Labram HR 800 instrument. The He-Ne laser intensity was attenuated to 143 mW mm⁻² with a focal area of $\varnothing$ 5 mm. Scanning electron microscopy (SEM) was used to measure the thickness of the absorber and HTM layers. The instrument used was a Zeiss HR FESEM Ultra 55 with an electron beam accelerating voltage of 4 kV.

X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Fisher ESCALAB Xi system with a monochromatic Al K α (1486.7 eV) X-ray source, and the studied area had a diameter of 650 μ m. The total transmittance and total reflectance spectra of the two cell stacks – glass/HTM and glass/FTO/TiO₂/Sb₂S₃/HTM were recorded on an ultraviolet-visible (UV-VIS) spectrophotometer in the range of 300–1100 nm. The Average Visible Transmittance (AVT) values for the glass/HTM and glass/FTO/TiO₂/Sb₂S₃/HTM samples were calculated from the total transmittance spectra in the range of 400–800 nm. The current-voltage (*J*–*V*) characteristics were acquired from a Wavelabs LS-2 LED solar simulator under standard AM1.5G conditions at an irradiance of 100 mW cm⁻². The measurements were performed at room temperature. The external quantum efficiency (EQE) spectra were measured using a Newport 69911 system.

Density Functional Theory (DFT) calculations were performed using B3LYP functional and the 6-31G(d,p) basis set. The highest occupied and lowest unoccupied molecular orbitals of the molecules were calculated for the optimized molecule geometry of the ground state. All calculations were carried out with the Gaussian 09W program and graphical representation was done using the Avogadro program.³⁰

3. Results and discussion

The investigated HTMs can be classified into two distinct groups, as depicted in Fig. 1a: molecules featuring diphenylamine units in their side fragments (V1422 and V1423) and molecules containing triphenylamine units (V1454 and V1455). The common structural feature of both groups is that the central core consists of different numbers of thiophene moieties. The thermal stability of the HTMs was investigated with the help of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The data from TGA suggest that the HTMs decompose in the range of 430–445 °C (Fig. S1, in the ESI[†]), exceeding the temperature necessary for both the device preparation and operation.³¹ Consequently, thiophene linked fluorene-based dimers with a higher molecular mass and therefore stronger intramolecular interaction possess higher decomposition temperatures compared to their monomeric analogues (391–403 °C).²²

DSC measurements indicate that thiophene linked fluorene-based dimers are molecular glasses, exhibiting glass transition temperatures (*T*_g) ranging from 148 °C to 175 °C (Fig. S2[†]), exceeding that of Spiro-OMeTAD (124 °C)³⁶ as well as of their monomeric analogues.²² The thermal characteristics of the analysed HTMs are presented in Table 1. Comparing the *T*_g of new HTMs has revealed that the inclusion of triphenylamine units in HTMs' side fragments (V1454 and V1455) results in an elevated *T*_g. This increase could be attributed to the higher molecular mass associated with the additional triphenylamine units. It is noteworthy that V1455, with a central trithiophene-based unit and triphenylamine as side fragments, exhibits no endothermic peaks, suggesting an entirely amorphous state (Fig. S2[†]). This property is advantageous for the formation of homogeneous films, eliminating the potential for film crystallization during either device preparation or operation. The ultraviolet-visible (UV-Vis) absorption spectra of the HTMs (Fig. S3[†]) present two prominent absorption peaks at wavelengths of 300 and 375 nm, corresponding to the π – π^* transitions of the side chromophores. Notably, the spectra exhibit an additional peak in the 425–550 nm range, which corresponds to π – π^* transitions, and is attributed to the electron-rich thiophene π systems. Comparison of the absorption curves of molecules featuring diphenylamine units in their side fragments (V1422 and V1423) and molecules containing triphenylamine units (V1454 and V1455) has revealed that the latter show higher absorption. It can be assumed that this is due to the presence of an additional phenyl fragment in these compounds. Moreover, comparison of the absorption spectra presented in Fig. S3[†] with those reported for monomeric analogues in the previous study²² revealed that the number and positions of

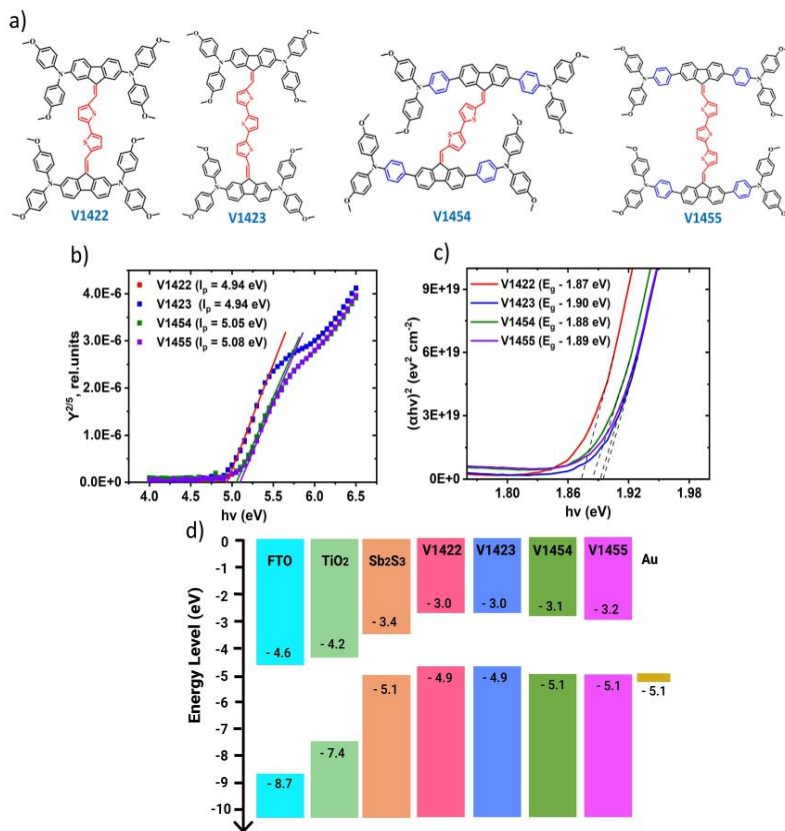


Fig. 1 (a) Chemical structures of synthesised HTMs – V1422, V1423, V1454 and V1455, (b) ionization potential (I_p), and (c) band gap (E_g) values calculated from the absorption spectra using Tauc plots for V1422, V1423, V1454 and V1455 thin films deposited on glass substrates, and (d) energy band diagram of constituent layers of the solar cell.

absorption peaks remain nearly unchanged, indicating that the conjugated system of the thiophene linked fluorene-based dimers is basically unaffected. As presented in Table 1, the inferred zero-field hole mobilities are 9.86×10^{-7} , 1.29×10^{-6} , 3.38×10^{-6} , and 1.85×10^{-6} cm² V⁻¹ s⁻¹ for V1422, V1423, V1454, and V1455, respectively. Therefore, it can be concluded that the presence of the additional phenyl ring in the side diphenyl units of V1454 and V1455 slightly increased the hole drift mobility.

To understand the energy level alignment of the synthesized HTMs with that of Sb₂S₃ and the metal back contact, a Photoelectron Yield Spectroscopy (PYS) technique was employed for measuring the ionization potential (I_p) (see Fig. 1b). The HOMO levels of V1422, V1423, V1454 and V1455 are found to be at -4.94 , -4.94 , -5.05 and -5.08 eV relative to the vacuum level, respectively. Thus, HTMs bearing triphenylamine units (instead of diphenylamine units) exhibit slightly lower HOMO levels. The calculated band gap (E_g) values for HTMs V1422, V1423,

Table 1 Properties of the synthesized HTMs – V1422, V1423, V1454 and V1455: glass transition temperature (T_g), melting temperature (T_m), 5% weight loss temperature (T_{d5}), optical absorption peak position (λ_{abs}), hole drift mobility (μ_0), band gap energy (E_g) and ionization potential (I_p)

HTM	T_g (°C)	T_m (°C)	T_{d5} (°C)	λ_{abs} (nm)	μ_0 (cm ² V ⁻¹ s ⁻¹)	E_g (eV)	I_p (eV)
V1422	148	276	430	293, 383, 468	9.86×10^{-7}	1.87	4.94
V1423	153	—	435	300, 383, 479	1.29×10^{-6}	1.90	4.94
V1454	175	307	445	285, 377, 467	3.38×10^{-6}	1.88	5.05
V1455	172	—	444	286, 377, 480	1.85×10^{-6}	1.89	5.08

V1454 and V1455 thin films are 1.87, 1.90, 1.88 and 1.89 eV, respectively (see Fig. 1c). The energy band diagram is presented in Fig. 1d and reveals agreeable band offsets conducive to the photogenerated carrier transport from the absorber to the metal back contact.

The Sb_2S_3 absorber layer was characterized using XRD and Raman spectroscopy. Data are presented in Fig. S4, in the ESI.† The XRD results confirmed the presence of a single phase of orthorhombic Sb_2S_3 (ICDD PDF 01-075-4013) without any secondary phase.^{9,13,20,22} The Raman spectrum shows sharp peaks at 128, 155, 188, 236, 280, 302, and 312 cm^{-1} , which are characteristic of the crystalline Sb_2S_3 layer. The band gap of the Sb_2S_3 film was 1.78 eV, as calculated from the absorption spectra using the Tauc plot (Fig. S4†), which is in line with the values previously reported for sprayed Sb_2S_3 films.^{9,13,20,21} The SEM cross-sectional images of solar cells with two HTMs, V1423 and V1454, both deposited from 2 mM solutions, are presented in Fig. S5, in the ESI.† The thickness of the Sb_2S_3 absorber layer was approximately 80 nm.

To study a possible chemical interaction at the Sb_2S_3 /HTM interface, XPS studies were performed for HTMs on a glass substrate and Sb_2S_3 solar cell stacks without and with an HTM. The XPS spectra of Sb_2S_3 /HTM (V1422, V1423, V1454 and V1455) samples in the Sb 3d region and S 2p region are shown in the ESI, in Fig. S6 and S7,† respectively. The Sb 3d spectra for Sb_2S_3 films and Sb_2S_3 covered with a thin layer of V1423 and V1454, are shown in Fig. 2a and b, respectively. The binding energies (BEs) of Sb 3d core level peaks in the Sb_2S_3 sample are located at 539.7 eV for $\text{Sb } 3d_{3/2}$ and 530.3 eV for $\text{Sb } 3d_{5/2}$. For the samples

of Sb_2S_3 with V1423, the BE peak positions are shifted to lower energy values, to 539.2 eV for $\text{Sb } 3d_{3/2}$ and to 529.9 eV for $\text{Sb } 3d_{5/2}$.

A similar shift in Sb 3d core level peak positions to lower BE values is also observed for the sample with V1454 as the HTM (Fig. 2b). The noted shift towards lower binding energy values, in comparison to pristine Sb_2S_3 , indicates an increased electron density around the Sb atoms in the absorber. A similar shift in the Sb 3d core level peak was observed when a dithieno[3,2-*b*:2',0'-*b'*]pyrrole-cored small molecule (DTPThMe-ThTPA)³² and thiophene-modified quinoxaline core small molecules²⁷ were applied onto the $\text{Sb}_2(\text{S,Se})_3$ film.

S 2p core level spectra for Sb_2S_3 films, HTMs (V1423, V1454) and Sb_2S_3 /HTM samples are shown in Fig. 2c and d. S $2p_{3/2}$ peaks for Sb_2S_3 and Sb_2S_3 /V1423 samples are positioned at BEs of 162.0 and 161.5 eV, respectively (see Fig. 2c). A similar shift of the S $2p_{3/2}$ peak towards the lower BE region is observed when V1454 is applied onto Sb_2S_3 (Fig. 2d). V1454 deposited onto a glass substrate shows the S $2p_{3/2}$ peak at 162.4 eV, but after deposition of V1454 onto Sb_2S_3 the S 2p peak of V1454 shifted to a higher energy region and peaked at a BE of 164.2 eV (see Fig. 2d and Fig. S7 in the ESI†).

A similar shift of the S 2p peak of thiophene-modified quinoxaline core small molecules to higher energies has been detected when applied to the $\text{Sb}_2(\text{S,Se})_3$ layer.²⁷ Interestingly, we did not detect S 2p peaks characteristic of V1423 in the spectrum of the Sb_2S_3 /V1423 stack (Fig. 2c), although the shifts in the positions of S 2p peak and Sb 3d peak of the Sb_2S_3 were clearly detected upon application of V1423 onto Sb_2S_3 . The

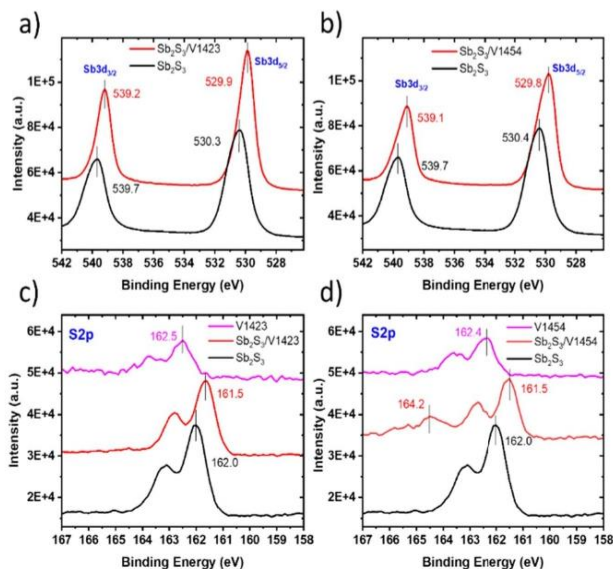


Fig. 2 XPS core level spectra (a) Sb 3d for Sb_2S_3 and $\text{Sb}_2\text{S}_3/\text{V1423}$, (b) Sb 3d for Sb_2S_3 and $\text{Sb}_2\text{S}_3/\text{V1454}$, (c) S 2p for Sb_2S_3 , V1423 and $\text{Sb}_2\text{S}_3/\text{V1423}$, and (d) S 2p for Sb_2S_3 , V1454 and $\text{Sb}_2\text{S}_3/\text{V1454}$.

shifts observed in Sb 3d and S 2p peak positions of Sb_2S_3 as well as in S 2p peak positions of HTMS refer to the interaction between S atoms from electron-rich thiophene units and Sb atoms from the Sb-chalcogenide compound which is expected to improve the interfacial carrier extraction ability.

Solar cells based on Sb_2S_3 were prepared in the superstrate configuration glass/FTO/ TiO_2 / Sb_2S_3 /HTM/Au (see the sketch in Fig. 3a and SEM images in Fig. S5, in the ESI†). The systematic change in the concentration of V-series HTM solutions (4, 2, 1, 0.6 mM) was studied. The resulting output parameters are presented in Table S1, in the ESI.† Solar cells fabricated with 2 mM solutions showed the highest performance, independent of the HTM used. The current-voltage (J - V) characteristics of the best performing devices using 2 mM HTM solutions are presented in Fig. 3b, and the cell output parameters are summarized in Table 2. The reference device, lacking an HTM, yielded a V_{OC} of 478 mV, J_{SC} of 8.7 mA cm^{-2} , FF of 0.46, and a PCE of 1.9%. Introduction of V1422 and V1423 as HTMs resulted in open circuit voltages of 656 and 673 mV, respectively. On application of HTMs, also other solar cell parameters improved

as compared to the cells without an HTM. In the case of the cell with V1423, J_{SC} improved from 9.0 to 12.1 mA cm^{-2} , FF from 0.46 to 0.56 and PCE from 1.9 to 4.5%. Therefore, the utilization of HTMs – V1422 and V1423 substantially mitigates carrier recombination at the back interface, leading to improved carrier collection. Notably, the device with the HTM – V1423 yielded device output characteristics comparable to those employing P3HT. In contrast, solar cell devices with V1454 and V1455, having triphenylamine side fragments, yielded V_{OC} values of 439 and 437 mV, respectively. As compared to the solar cell without any HTM, there was no improvement in V_{OC} values. In addition, an increase in series resistance (R_s) values and a decrease in J_{SC} , FF and overall PCE was recorded (Fig. 3b and Table 2). High R_s values up to ca. $5 \Omega \text{ cm}^2$ in solar cells could result from an excessively thick layer. For the purpose of reducing the HTM layer thickness, solar cells were fabricated with diluted HTM solutions. The concentration of HTM solutions was decreased from 2 mM to 0.6 mM. However, no notable improvement in solar cell parameters was observed, as detailed in the ESI, Table S1.† The external quantum efficiency (EQE)

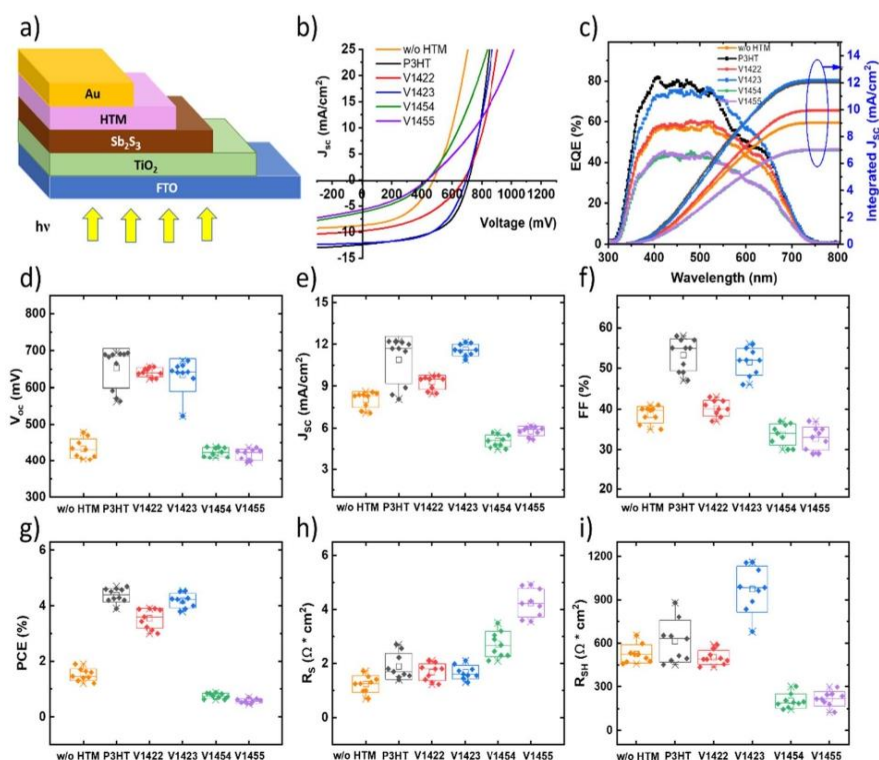


Fig. 3 (a) Schematic of the Sb_2S_3 absorber solar cell (glass/FTO/ TiO_2 / Sb_2S_3 /HTM/Au) fabricated in the superstrate configuration, (b) J - V characteristics, (c) external quantum efficiency (EQE) curves with the calculated integrated J_{SC} curves of the champion solar cells without (w/o) the HTM and with different HTMs (P3HT, V1422, V1423, V1454 and V1455). Box plots of Sb_2S_3 solar cells without any HTM (Sb_2S_3 /Au) and with P3HT, V1422, V1423, V1454 and V1455 as HTMs: (d) V_{OC} , (e) J_{SC} , (f) fill factor (FF), (g) PCE, (h) series resistance (R_s), and (i) shunt resistance (R_{SH}).

Table 2 Key performance metrics of champion Sb_2S_3 solar cells without (w/o) any HTM and with HTMs (V1422, V1423, V1454, V1455 and P3HT)

HTM	HTM conc. (mg mL ⁻¹)	V_{OC} (mV)	J_{SC} (mA cm ⁻²)	Integrated J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)	R_{s} (Ω cm ²)	R_{SH} (Ω cm ²)
w/o	—	478	8.7	9.0	46	1.9	1.1	514
V1422	2 mM	656	9.7	9.9	43	3.9	1.7	436
V1423	2 mM	673	12.1	12.0	56	4.5	1.3	1005
V1454	2 mM	439	5.7	6.8	35	0.8	2.7	192
V1455	2 mM	437	6.1	7.1	33	0.7	4.9	198
P3HT	1 wt%	689	12.2	12.2	55	4.7	1.8	526

graphs of the champion devices without any HTM and with different HTM layers are presented in Fig. 3c. It should be noted that the integrated J_{SC} , calculated based on EQE spectra, closely correspond to the values obtained from the J - V curves (see Table 2). A dip in the spectral response in the case of the device with P3HT can be seen in the range of 550–650 nm, which is attributed to its parasitic absorption losses.^{20,22} Normalized EQE curves of the devices with investigated HTMs are presented in the ESI, in Fig. S9.† The concavity in the EQE curve is less pronounced in the case of samples with V-series HTMs. All investigated HTMs have a similar band gap, within the range of 1.8–1.9 eV. However, the V-series HTM layers were considerably thinner, approximately 20–25 nm, in contrast to P3HT, with a thickness of about 80–100 nm. Thus, devices with V-series HTMs show an average visible transmittance (AVT) of 24–26% compared to 21% by the P3HT-based device (see Fig. S10 in the ESI†). A statistical representation (*i.e.*, box plots) of solar cell parameters of the fabricated cells without any HTM and with investigated HTMs (Fig. 3d–i) refers to high reproducibility of the results.

Although the interaction between the S atom from the thiophene unit and Sb from Sb_2S_3 has been noted in all interfaces with V-series HTMs, only the use of V1422 and V1423 as HTMs led to an increase in the open-circuit voltage (V_{OC}) of up to 650–670 mV. Furthermore, only the application of V1423 in the solar cell structure resulted in fill factor values of up to 56%, leading to conversion efficiencies exceeding 4% (see box-plot, in Fig. 3), which is very close to that obtained using P3HT as the HTM. Our results show that V1423, a dimer molecule with three thiophene units in its structure is the most efficient one in this family of novel HTMs. The application of V1454 and V1455 as HTM layers did not reduce the interface recombination or improve the carrier collection. V_{OC} remains on the level of 400 mV comparable to the cells without the HTM, fill factor values are low and vary in the region 30–35%. The current density is *ca.* two times lower as compared to the cell with V1423 and the solar cell exhibits a high R_{s} value of *ca.* 5 Ω cm² (Fig. 3d–i). Consequently, the solar cell conversion efficiencies are below 1%, that is two times lower than that recorded for the cells without any HTM.

As stated above, the interaction of S from the thiophene unit with Sb from Sb_2S_3 at the absorber surface may explain the improvement of the V_{OC} and overall solar cell parameters *via* passivation of the interfacial states. Although such a mechanism is validated by the enhanced V_{OC} in V1422 and V1423-

based devices, the abrupt decrease in the V_{OC} and overall performance of V1454 and V1455-based cells indicate that there might be another concomitant phenomenon which prevails or compensates the benefit of thiophene-based interactions. A possible explanation for the low V_{OC} and PCE of V1454 and V1455-based cells, can be linked to the dipole effects at the absorber/HTM interface. As demonstrated in organic solar cells, insertion of organic materials between the photoactive absorber layer and electrodes can be an efficient approach for manipulation of the electric potential distribution by dipole moments at the electrode surface.^{33–35} Several experimental and numerical simulation studies reported that the dipoles at the back/front interfaces have to be aligned in such a way that it allows accumulation of high hole concentration at the vicinity of hole contact and high electron density at the vicinity of electron contact.^{33,36} The efficiency of photogenerated charge carrier separation (and thus, improved charge selectivity) is influenced by the specific arrangement of the molecules and the orientation of the permanent dipole moment. Thus, in some cases, depending on the angular configuration and molecular arrangement, the organic molecules can act as hole or electron selective layers. For example, Kippelen *et al.*, demonstrated that the HTM – PEDOT:PSS can be easily altered to a well-functionalized electron transport layer by complexation with polyethylenimine ethoxylated (PEIE) molecules.³⁷

Considering these approaches, it can be assumed that in V1454 and V1455 based solar cell devices, the additional phenyl fragment in the HTMs reconfigured the angular and molecular arrangement resulting in unsuitable alignment in the orientation of the dipoles at the back interface. As a consequence, this imposes an increase of an “incorrect” type of charge carrier concentration in the vicinity of the metal back contact (*i.e.*, electron proximity of the Hall contact), decreasing the V_{OC} and deteriorating the overall device performance. Validation of this hypothesis can be assured by in-depth analysis of the changes in the work function of the contact electrode in proximity of the HTM. This approach would imply complex correlative measurements of Kelvin-probe AFM and UPS combined with numerical simulations which has been applied in organic solar cells³³ and remains a great challenge for the emerging Sb_2S_3 /HTM interface.

The anomalous low performance of V1454 and V1455-based cells can be approached from a different angle – by analysing the molecular geometry and orbitals and correspondingly, the positions of the Highest Occupied Molecular Orbital (HOMO)

and Lowest Unoccupied Molecular Orbital (LUMO) of V1422 (a representative of molecules with diphenylamine units in their structures) and V1454 (a representative of molecules with triphenylamine units in their structures) from quantum chemical simulation. Fig. 4 presents the optimized geometry of HTM compound molecules of V1422 and V1454, and their HOMO and LUMO.

The result of the simulation shows that HOMO levels of both V1454 and V1422 are formed by fluorene and benzene rings, while LUMO is primarily located on the thiophene groups. In addition to this HOMO–LUMO configuration, compared to V1422 (having a nonplanar orientation of fluorene in relation to the thiophene groups), V1454 exhibits more planar

arrangement of fluorene groups relative to the thiophene groups. The latter effect allows a greater accessibility of the thiophene moieties in V1454 and consequently, a stronger interaction between S atoms in the thiophene group and Sb from Sb_2S_3 . This strong interaction is highlighted by the observed shift of the V1454 S $2p_{3/2}$ peak towards the higher BE region when applied onto Sb_2S_3 (Fig. 2d, XPS analysis). However, this strong interaction does not result in an improved charge carrier transport through the interface since the HOMO level is not located on thiophene moieties and thus the condition for the accumulation of the “right” type of charge carrier (*i.e.*, holes) at the back interface is not satisfied. Thus, the quantum chemical simulation results suggest that to achieve

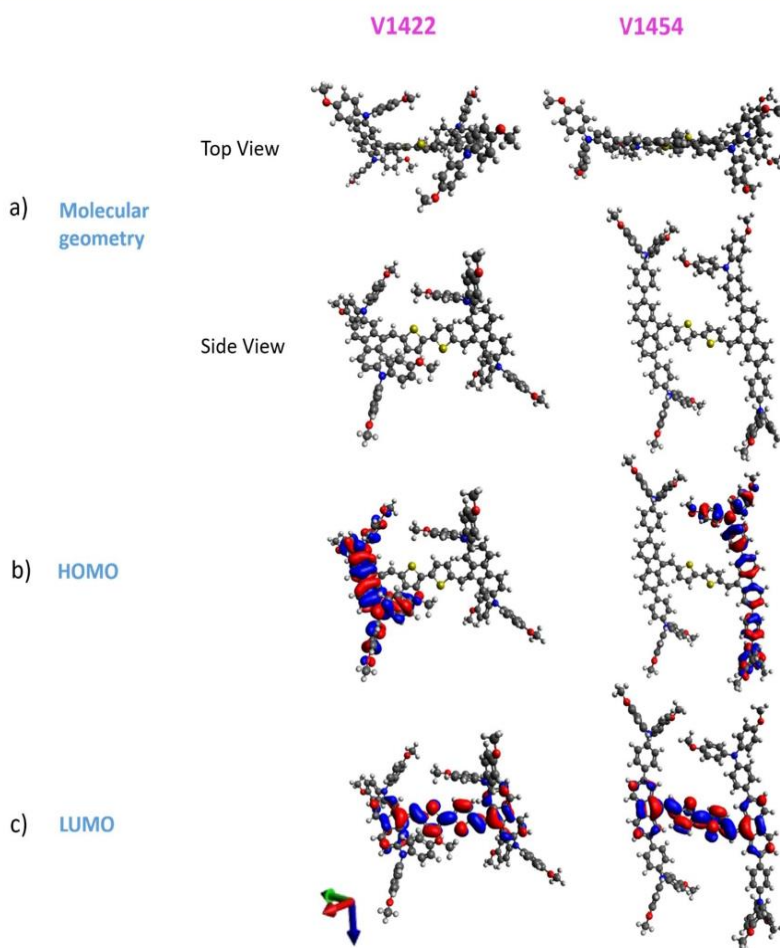


Fig. 4 (a) Optimized geometry of HTM molecules – V1422 and V1454 in top and side views, (b) highest occupied molecular orbital (HOMO) in HTMs – V1422 (left) and V1454 (right), (c) lowest unoccupied molecular orbital (LUMO) in HTMs – V1422 (left) and V1454 (right). Colors used for atoms: gray – C, white – H, yellow – S, red – O and blue – N.

higher efficiency of photogenerated charge carrier separation and improved charge selectivity by an organic HTM layer, the HOMO of the HTMs should be formed by the thiophene groups. Although this hypothesis may interfere with other requirements for the alignment of the electronic states at the organic/inorganic interfaces, these results lay a solid foundation for further investigations and understanding the charge transfer kinetics at the $\text{Sb}_2\text{S}_3/\text{HTM}$ interface.

4. Conclusion

Four dopant-free dimers (V1422, V1423, V1454, V1455) comprising methoxydiphenylamine substituted fluorene derivatives and connected by central cores consisting of different numbers of thiophene moieties were synthesized by a solution chemical route. Synthesized organic semiconductors are molecular glasses, exhibiting glass transition and thermal decomposition temperatures of 148–175 °C and 430–445 °C, respectively and having an energy band gap of 1.9 eV and ionization potential of 4.9–5.1 eV. Synthesized organic semiconductors were explored, for the first time, as HTMs in superstrate configuration $\text{FTO}/\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{HTM}/\text{Au}$ solar cells in which the Sb_2S_3 absorber and TiO_2 layers were deposited by the ultrasonic spray method while HTM layers were obtained by spin-coating. Energy level diagrams demonstrate agreeable band offsets validating the applicability of the synthesized materials as efficient HTMs in an $\text{FTO}/\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{HTM}/\text{Au}$ device. It has been shown that application of the HTM layer on top of the Sb_2S_3 layer induces a shift in the Sb 3d core level peak to lower binding energies, indicating increased electron density surrounding the Sb atoms. Such a shift confirms the interaction between S atoms from thiophene units and Sb atoms from the absorber occurring at the $\text{Sb}_2\text{S}_3/\text{HTM}$ interface. By introducing HTMs comprising diphenylamine units in their structures (V1422, V1423) into the solar cell structure, an increase in the device output characteristics compared to the device without an HTM layer was observed. The highest boost in device performance was observed for V1423-based cells, exhibiting an increase of the V_{OC} from 478 mV to 673 mV, fill factor from 46% to 56%, and PCE from 1.9% to 4.5%.

Thus, it can be concluded that this type of HTM effectively mitigates carrier recombination at the back interface, and contributes to better collection of carriers. The application of V1454 and V1455 (molecules with triphenylamine units in their structures) as HTM layers did not improve the device parameters as the V_{OC} remained on the level of 430 mV (comparable to the cells without HTMs) while the fill factor values reached the lowest level of 30–35%. For the same cells, the J_{SC} values were two times lower compared to the cells with V1423 and the PCEs of solar cells were below 1% – two times lower than those recorded for the cells without any HTM. The abrupt decrease in the V_{OC} , J_{SC} and overall performance of V1454 and V1455-based cells indicates the presence of a concomitant phenomenon which prevails or compensates the benefit of thiophene-based interactions. Possible phenomena occurring at the $\text{Sb}_2\text{S}_3/\text{HTM}$ interface were discussed through the prism of correlation between the efficiency of the charge transfer/charge selectivity

and final device performance, including possible impacts of the dipole effect as well as a prospective analysis from the quantum chemical simulation side. The results of quantum chemical simulation suggest that to achieve higher efficiency of photogenerated charge carrier separation and improved charge selectivity by the organic HTM layer, the HOMO of the HTMs should be configured by the thiophene groups. So far, the results of this study provide new perspectives on the chemical and physical understanding of $\text{Sb}_2\text{S}_3/\text{HTM}$ organic/inorganic interfaces towards the identification of suitable innovative HTMs which would allow a significant boost in the efficiency of the emerging Sb-chalcogenide thin film PV technology.

Data availability

The data that support the findings of this study will be made available by the corresponding author upon request.

Author contributions

Nimish Juneja – conceptualization, methodology, validation, data curation, writing – original draft. Aistė Jegorovė – conceptualization, methodology, validation, writing – review & editing. Raitis Grzibovskis – methodology, validation, writing – review & editing. Atanas Katerski – methodology, validation. Maryte Daskeviciene – writing – review & editing. Tadas Malinauskas – writing – review & editing. Aivars Vembris – conceptualization, methodology, validation, writing – review & editing. Smagul Karazhanov – writing – review & editing. Nicolae Spalatu – methodology, formal analysis, visualization, supervision, writing – review & editing. Vytautas Getautis – conceptualization, methodology, validation, writing – review & editing. Malle Krunk – conceptualization, methodology, validation, supervision, writing – review & editing. Ilona Oja Acik – conceptualization, funding acquisition, project administration, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The “Development of Semi-Transparent Bifacial Thin Film Solar Cells for Innovative Applications” benefits from a 999372 € grant from Iceland, Liechtenstein and Norway through the EEA Grants. The aim of the project is to develop a new approach based on novel materials and structures and production technologies, which are the key to further increasing the share, and range of application of PV in areas with sub-average sunlight, including Baltic and Nordic countries. Therefore, development of resource saving, cost-effective and efficient PV devices is a primary challenge of this project. The project contract no. with the Research Council of Lithuania (LMTLT) is S-BMT-21-1 (LT08-2-LMT-K-01-003). Department of Materials and Environmental Technology, Tallinn University of Technology has received funding from the Estonian Research Council, projects

PRG627 "Antimony Chalcogenide Thin films for Next-Generation Semi-transparent Solar Cells Applicable in Electricity Producing Windows" and PSG689 "Bismuth Chalcogenide Thin-Film Disruptive Green Solar Technology for Next Generation Photovoltaics". The research was partially funded by the European Union's Horizon 2020 ERA Chair project 5GSOLAR (grant agreement no. 952509). The research was supported by the European Cooperation in Science and Technology (COST) project RENEW-PV (CA21148) and by the Estonian Ministry of Education and Research (project TK210; TK210U8 "Center of Excellence in Sustainable Green Hydrogen and Energy Technologies"). Institute of Solid-State Physics, University of Latvia has received funding from the European Union's Horizon 2020 Framework Programme H2020-WIDESPREAD-01-2016-2017-TeamingPhase2 under grant agreement no. 739508, project CAMART².

Notes and references

- N. Cates and M. Bernechea, *APL Mater.*, 2018, **6**, 084503.
- S. Barthwal, R. Kumar and S. Pathak, *ACS Appl. Energy Mater.*, 2022, **5**, 6545–6585.
- M. Koltsov, S. V. Gopi, T. Raadik, J. Krustok, R. Josepson, R. Grzibovskis, A. Vembris and N. Spalatu, *Sol. Energy Mater. Sol. Cells*, 2023, **254**, 112292.
- C. Comparotto, P. Ström, O. Donzel-Gargand, T. Kubart and J. J. S. Scragg, *ACS Appl. Energy Mater.*, 2022, **5**, 6335–6343.
- S. Wang, Y. Zhao, B. Che, C. Li, X. Chen, R. Tang, J. Gong, X. Wang, G. Chen, T. Chen, J. Li and X. Xiao, *Adv. Mater.*, 2022, **34**, 2206242.
- Y. Zhao, S. Wang, C. Li, B. Che, X. Chen, H. Chen, R. Tang, X. Wang, G. Chen, T. Wang, J. Gong, T. Chen, X. Xiao and J. Li, *Energy Environ. Sci.*, 2022, **15**, 5118–5128.
- Y. Zhao, S. Wang, C. Jiang, C. Li, P. Xiao, R. Tang, J. Gong, G. Chen, T. Chen, J. Li and X. Xiao, *Adv. Energy Mater.*, 2022, **12**, 2103015.
- A. A. F. Husain, W. Z. W. Hasan, S. Shafie, M. N. Hamidon and S. S. Pandey, *Renewable Sustainable Energy Rev.*, 2018, **94**, 779–791.
- J. S. Ensalu, A. Katerski, E. Kärber, L. Weinhardt, M. Blum, C. Heske, W. Yang, I. Oja Acik and M. Krunk, *Beilstein J. Nanotechnol.*, 2019, **10**, 2396–2409.
- V. K. H. Bui and T. P. Nguyen, *Polymers*, 2023, **15**, 4443.
- E. Zimmermann, T. Pfadler, J. Kalb, J. A. Dorman, D. Sommer, G. Hahn, J. Weickert and L. Schmidt-Mende, *Adv. Sci.*, 2015, **2**, 1500059.
- M. S. You, C.-S. Lim, D. H. Kwon, J. H. Heo, S. H. Im and K. J. Chae, *Org. Electron.*, 2015, **21**, 155–159.
- J. S. Ensalu, A. Katerski, E. Kärber, I. Oja Acik, A. Mere and M. Krunk, *Beilstein J. Nanotechnol.*, 2019, **10**, 198–210.
- J. Chen, J. Qi, R. Liu, X. Zhu, Z. Wan, Q. Zhao, S. Tao, C. Dong, G. Y. Ashebir, W. Chen, R. Peng, F. Zhang, S. Yang, X. Tian and M. Wang, *Commun. Chem.*, 2019, **2**, 121.
- Y. Zhang, S. Li, R. Tang, X. Wang, C. Chen, W. Lian, C. Zhu and T. Chen, *Energy Technol.*, 2018, **6**, 2126–2131.
- Y. Yang, C. Shi, K. Lv, Q. Wang, X. Sun and W. Chen, *New J. Chem.*, 2021, **45**, 10357–10361.
- X. Jin, Y. Fang, T. Salim, M. Feng, Z. Yuan, S. Hadke, T. C. Sum and L. H. Wong, *Adv. Mater.*, 2021, **33**, 2104346.
- R. Tang, X. Wang, W. Lian, J. Huang, Q. Wei, M. Huang, Y. Yin, C. Jiang, S. Yang, G. Xing, S. Chen, C. Zhu, X. Hao, M. A. Green and T. Chen, *Nat. Energy*, 2020, **5**, 587–595.
- M. L. Petrus, T. Bein, T. J. Dingemans and P. Docampo, *J. Mater. Chem. A*, 2015, **3**, 12159–12162.
- N. Juneja, S. Mandati, A. Katerski, N. Spalatu, S. Daskeviciute-Geguziene, A. Vembris, S. Karazhanov, V. Getautis, M. Krunk and I. Oja Acik, *Sustainable Energy Fuels*, 2022, **6**, 3220–3229.
- N. Juneja, S. Daskeviciute-Geguziene, N. Spalatu, S. Mandati, A. Katerski, R. Grzibovskis, A. Vembris, S. Karazhanov, V. Getautis, M. Krunk and I. Oja Acik, *Mater. Sci. Semicond. Process.*, 2024, **169**, 107934.
- S. Mandati, N. Juneja, A. Katerski, A. Jegorov, R. Grzibovskis, A. Vembris, T. Dedova, N. Spalatu, A. Magomedov, S. Karazhanov, V. Getautis, M. Krunk and I. Oja Acik, *ACS Appl. Energy Mater.*, 2023, **6**, 3822–3833.
- D. Poplavskyy and J. Nelson, *J. Appl. Phys.*, 2003, **93**, 341–346.
- S.-J. Moon, Y. Itzhak, J.-H. Yum, S. M. Zakeeruddin, G. Hodes and M. Grätzel, *J. Phys. Chem. Lett.*, 2010, **1**, 1524–1527.
- S. Daskeviciute, C. Momblona, K. Rakstys, A. A. Sutanto, M. Daskeviciene, V. Jankauskas, A. Gruodis, G. Bubniene, V. Getautis and M. K. Nazeeruddin, *J. Mater. Chem. A*, 2021, **9**, 301–309.
- T. Malinauskas, D. Tomkute-Luksiene, R. Sens, M. Daskeviciene, R. Send, H. Wonneberger, V. Jankauskas, I. Bruder and V. Getautis, *ACS Appl. Mater. Interfaces*, 2015, **7**, 11107–11116.
- Y. Xiang, H. Guo, Z. Cai, C. Jiang, C. Zhu, Y. Wu, W.-H. Zhu and T. Chen, *Chem. Commun.*, 2022, **58**, 4787–4790.
- S. Xu, J. Wu, F. Guo, M. Wu, S. Chen, W. Chen and C. Shi, *Sustainable Energy Fuels*, 2023, **7**, 61–65.
- S. H. Im, C.-S. Lim, J. A. Chang, Y. H. Lee, N. Maiti, H.-J. Kim, M. K. Nazeeruddin, M. Grätzel and S. Il Seok, *Nano Lett.*, 2011, **11**, 4789–4793.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson and H. Nakatsuji, *Gaussian 09, Revision A.02*, Gaussian Inc., Wallingford CT, 2016.
- M. V. Khenkin, E. A. Katz, A. Abate, G. Bardizza, J. J. Berry, C. Brabec, F. Brunetti, V. Bulović, Q. Burlingame, A. Di Carlo, R. Cheacharoen, Y.-B. Cheng, A. Colmann, S. Cros, K. Domanski, M. Dusza, C. J. Fell, S. R. Forrest, Y. Galagan, D. Di Girolamo, M. Grätzel, A. Hagfeldt, E. von Hauff, H. Hoppe, J. Kettle, H. Köbler, M. S. Leite, S. Liu, Y.-L. Loo, J. M. Luther, C.-Q. Ma, M. Madsen, M. Manceau, M. Matheron, M. McGehee, R. Meitzner, M. K. Nazeeruddin, A. F. Nogueira, Ç. Odabaşı, A. Osherov, N.-G. Park, M. O. Reese, F. De Rossi, M. Saliba, U. S. Schubert, H. J. Snaith, S. D. Stranks, W. Tress, P. A. Troshin, V. Turkevich, S. Veenstra, I. Visoly-Fisher, A. Walsh, T. Watson, H. Xie, R. Yıldırım, S. M. Zakeeruddin, K. Zhu and M. Lira-Cantu, *Nat. Energy*, 2020, **5**, 35–49.

- 32 C. Jiang, J. Zhou, R. Tang, W. Lian, X. Wang, X. Lei, H. Zeng, C. Zhu, W. Tang and T. Chen, *Energy Environ. Sci.*, 2021, **14**, 359–364.
- 33 U. Würfel, M. Sefler, M. Unmüssig, N. Hofmann, M. List, E. Mankel, T. Mayer, G. Reiter, J. Bubendorff, L. Simon and M. Kohlstädt, *Adv. Energy Mater.*, 2016, 1600594.
- 34 J. Kesters, T. Ghooos, H. Penxten, J. Drijkoningen, T. Vangerven, D. M. Lyons, B. Verreet, T. Aernouts, L. Lutsen, D. Vanderzande, J. Manca and W. Maes, *Adv. Energy Mater.*, 2013, **3**, 1180–1185.
- 35 F. A. Nüesch, *Chimia*, 2013, **67**, 388–392.
- 36 C. F. N. Marchiori and M. Koehler, *J. Phys. D Appl. Phys.*, 2014, **47**, 215104.
- 37 Y. Zhou, C. Fuentes-Hernandez, J. Shim, J. Meyer, A. J. Giordano, H. Li, P. Winget, T. Papadopoulos, H. Cheun, J. Kim, M. Fenoll, A. Dindar, W. Haske, E. Najafabadi, T. M. Khan, H. Sojoudi, S. Barlow, S. Graham, J.-L. Brédas, S. R. Marder, A. Kahn and B. Kippelen, *Science*, 2012, **336**, 327–332.

Supplementary Data

Dopant-free Fluorene Based Dimers linked with Thiophene Units as Prospective Hole Transport Materials for Sb₂S₃ Solar Cells

Nimish Juneja, ^a Aistė Jegorovė, ^b Raitis Grzibovskis, ^c Atanas Katerski, ^a Maryte Daskeviciene, ^b Tadas Malinauskas, ^b Aivars Vembris, ^c Smagul Karazhanov, ^d Nicolae Spalatu, ^a Vytautas Getautis, ^b Malle Krunks^a and Ilona Oja Acik ^a

- ^a Department of Materials and Environmental Technology, Tallinn University of Technology, Ehitajate tee 5, Tallinn, 19086, Estonia.
- ^b Department of Organic Chemistry, Kaunas University of Technology, Kaunas, LT-50254, Lithuania.
- ^c Institute of Solid State Physics, University of Latvia, Kengaraga Str. 8, Riga, LV-1063, Latvia.
- ^d Institute for Energy Technology (IFE), P.O Box 40, Kjeller, NO 2027, Norway.

E-mail: malle.krunks@taltech.ee
nicolae.spalatu@taltech.ee

General

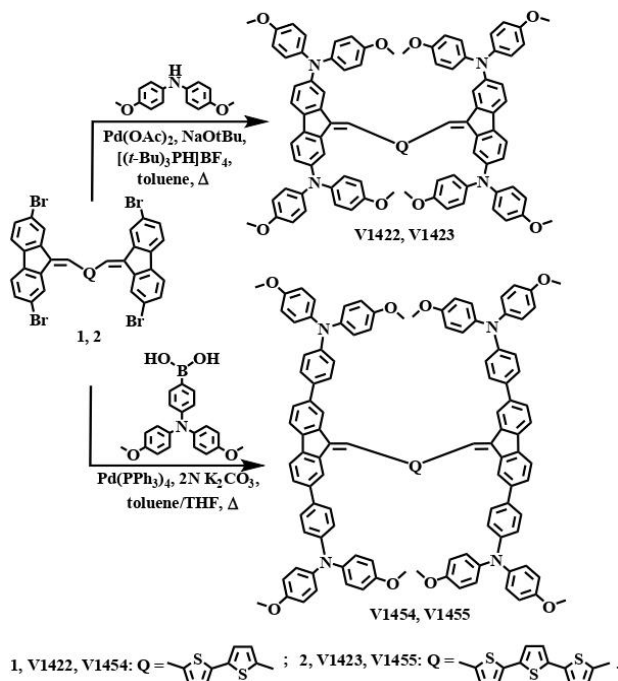
Chemicals required for the synthesis were purchased from Sigma-Aldrich and TCI Europe and used as received without additional purification. ¹H NMR and ¹³C NMR spectra were collected at 400 and 101 MHz, respectively on a Bruker Avance III spectrometer. The chemical shifts, expressed in ppm, were relative to tetramethylsilane (TMS). All the experiments were performed at 25 °C. Reactions were monitored by thin-layer chromatography on ALUGRAM SIL G/UV254 plates and developed with UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was used for column chromatography. Elemental analysis was performed with an Exeter Analytical CE-440 elemental analyzer, Model 440 C/H/N.

Thermogravimetric analysis (TGA) was performed on a Q50 thermogravimetric analyser (TA Instruments) at a scan rate of 10 °C min⁻¹ under nitrogen atmosphere. The values are given for a weight-loss of 5% (*T*₀₅). Differential scanning calorimetry (DSC) was performed on a TA Instruments Q2000 differential scanning calorimeter under nitrogen atmosphere. Heating and cooling rate is 10 °C min⁻¹.

UV–vis spectral analysis of the sample in solution (THF, 10⁻⁴ mol L⁻¹) was performed on a Perkin Elmer Lambda 35 UV/VIS spectrophotometer. The layer thickness of the solution is *d* = 1 mm. Diffraction grating crack width is 2 nm. Spectral recording speed is 2 nm s⁻¹. The wavelength *λ* is given in nm.

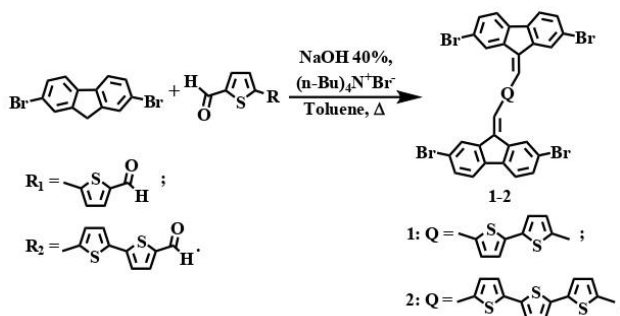
V1422 and V1423 containing diphenylamine chromophores were obtained through palladium cross-coupling reactions connecting the central dithiophene or trithiophene-based fluorenylidene-

terminated unit with 4,4'-dimethoxydiphenylamine (**Scheme 1**). New p-type photoconductors - V1454 and V1455 with triphenylamine side fragments were obtained under Suzuki coupling reaction conditions (**Scheme 1**). The starting compounds 1 and 2 were synthesized by a condensation reaction of 2,7-dibromofluorene with corresponding thiophene dicarbaldehyde catalyzed by a base.



Scheme 1. Synthesis route to the HTMs **V1422**, **V1423**, **V1454**, and **V1455**.

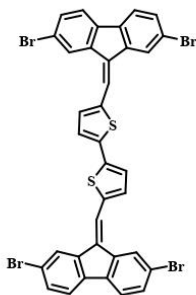
Detailed synthetic procedures



Scheme S1. Synthesis of the intermediates **1**, **2**.

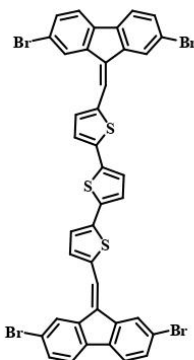
Detailed synthetic procedures

5,5'-Bis[(2,7-dibromo-9H-fluoren-9-ylidene)methyl]-2,2'-bithiophene (1)



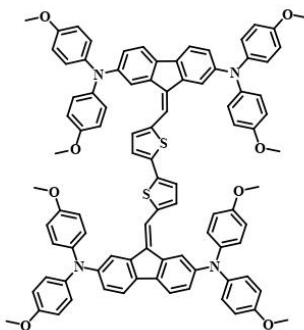
A mixture of [2,2'-bithiophene]-5,5'-dicarbaldehyde (0.5 g, 2 mmol), 2,7-dibromofluorene (1.62 g, 5 mmol), and toluene (10 mL) was stirred for 10 minutes. Afterwards, NaOH solution (10 mL, 40% W/W) and tetrabutylammonium bromide (0.25 g, 0.76 mmol) were added and the reaction mixture was heated at reflux for 4 hours (TLC control, acetone/*n*-hexane 1:1.5). After cooling to room temperature, the reaction mixture was filtered off and crude crystals were washed with water, ethanol and ethyl acetate to obtain terracotta crystals ($M_p = 326\text{--}327\text{ }^{\circ}\text{C}$). Yield 1.1 g (66%). In the next step crude crystals were used without any further purification.

5,5''-Bis[(2,7-dibromo-9H-fluoren-9-ylidene)methyl]-2,2':5,2''-terthiophene (2)



A mixture of [2,2':5,2''-terthiophene]-5,5''-dicarbaldehyde (0.5 g, 1.6 mmol), 2,7-dibromofluorene (1.3 g, 4 mmol), and toluene (9 mL) was stirred for 10 minutes. Afterwards, NaOH solution (9 mL, 40% W/W) and tetrabutylammonium bromide (0.2 g, 0.06 mmol) were added and the reaction mixture was heated at reflux for 4 hours (TLC control, acetone/*n*-hexane 1:1.5). After cooling to room temperature, the reaction mixture was filtered off and crude crystals were washed with water, ethanol and ethyl acetate to obtain dark red crystals. Yield 1 g (69%). In the next step crude crystals were used without any further purification.

9,9'-[(2,2'-Bithiophene)-5,5'-diylbis(methanylylidene)]bis[*N*²,*N*²,*N*⁷,*N*⁷-tetrakis(4-methoxyphenyl)-9H-fluorene-2,7-diamine] (V1422)



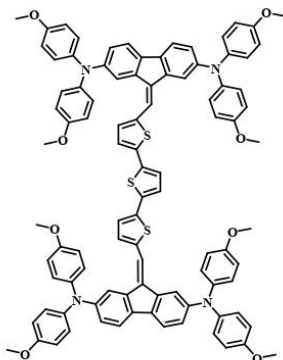
A mixture of 5,5'-bis((2,7-dibromo-9H-fluorene-9-ylidene)methyl)-2,2'-bithiophene (**1**) (0.45 g, 0.5 mmol), bis(4-methoxyphenyl)amine (0.69 g, 3 mmol), and anhydrous toluene (6 mL) was purged with Ar for 30 minutes. Afterwards, palladium (II) acetate (0.007 g, 0.03 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.017 g, 0.06 mmol) was added and the reaction mixture was stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (0.29 g, 3 mmol) was added and the mixture was heated at reflux for 5 hours (TLC control, acetone/*n*-hexane 1:4). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 7:18, v:v). The crude product was recrystallized from toluene to obtain brown crystals. Yield 0.5 g (70%). *M*_p = 273–274 °C.

¹H NMR (400 MHz, CDCl₃) δ: 7.85 (s, 2H), 7.57 – 6.52 (m, 48H), 3.79 (s, 12H), 3.70 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ: 138.6, 138.3, 136.9, 135.1, 132.8, 132.2, 131.2, 130.7, 130.3, 129.7, 129.1, 128.3, 125.8, 124.3, 124.0, 123.8, 123.5, 119.6, 119.4, 118.6, 118.4, 118.3, 115.3, 114.9, 114.6, 114.4, 114.2, 114.0, 55.52, 55.5.

Anal. Calcd. For: C₉₂H₇₄N₄O₈S₂: C 77.40; H 5.22; N 3.92; O 8.96; S 4.49; found: C 77.35; H 5.26; N 3.89.

9,9'-[(2,2':5',2''-Terthiophene)-5,5'-diylbis(methanylylidene)]bis[*N*²,*N*²,*N*⁷,*N*⁷-tetrakis(4-methoxyphenyl)-9H-fluorene-2,7-diamine] (V1423)

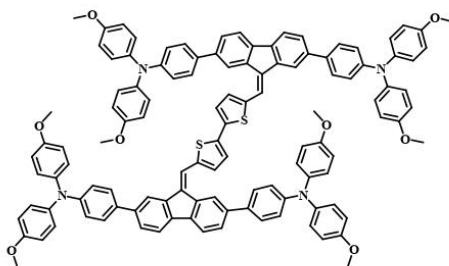


A mixture of 5,5''-bis((2,7-dibromo-9H-fluorene-9-ylidene)methyl)-2,2':5,2''-terthiophene (**2**) (0.45 g, 0.5 mmol), bis(4-methoxyphenyl)amine (0.69 g, 3 mmol), and anhydrous toluene (6 mL) was purged with Ar for 30 minutes. Afterwards, palladium (II) acetate (0.007 g, 0.03 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.017 g, 0.06 mmol) was added and the reaction mixture was stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (0.29 g, 3 mmol) was added and the mixture was heated at reflux for 5 hours (TLC control, acetone/*n*-hexane 1:4). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 9:16, v:v). 20% solution of the final product in THF was poured with intensive stirring into a 15-fold excess of ethanol. The precipitate as a red powder was filtered off, washed with ethanol, and dried. Yield 0.48 g (64%).

¹H NMR (400 MHz, CDCl₃) δ: 7.83 (s, 2H), 7.59 – 6.32 (m, 50H), 3.79 (s, 12H), 3.75 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ: 151.1, 141.0, 140.8, 138.6, 138.1, 137.0, 136.2, 135.6, 134.9, 131.0, 125.0, 123.9, 119.2, 118.4, 118.3, 118.2, 114.8, 114.7, 114.6, 114.2, 113.8, 103.6, 77.4, 77.0, 76.7, 55.5, 55.48. Anal. Calcd. For: C₉₆H₇₆N₄O₈S₃: C 76.37; H 5.07; N 3.71; O 8.48; S 6.37; found: C 76.29; H 5.09; N 3.75.

4,4',4'',4'''-(((2,2'-bithiophene)-5,5'-diylbis(methanylylidene))bis(9H-fluorene-2,7-diyl-9-ylidene))tetrakis(*N*, *N*-bis(4-methoxyphenyl)aniline) (V1454)



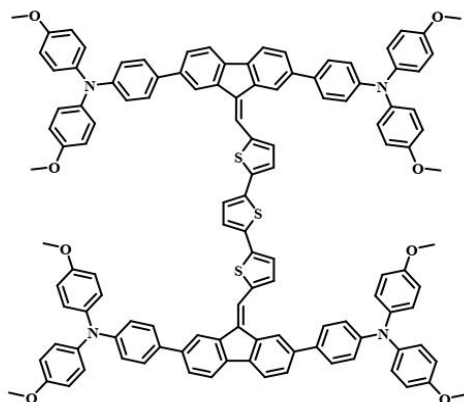
A mixture of 5,5'-bis((2,7-dibromo-9H-fluoren-9-ylidene)methyl)-2,2'-bithiophene (**1**) (0.5 g, 0.6 mmol), 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (2.6 g, 6 mmol), and anhydrous toluene/THF (16.6 mL/33.4 mL) was purged with Ar for 20 minutes. Afterwards, tetrakis(triphenylphosphine)palladium (0.8 g, 0.7 mmol) and 2M K₂CO₃ solution (20 mL) was added, and the reaction mixture was heated at 90 °C for 24 hours (TLC control, THF/*n*-hexane 1:1). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 11:14, v:v). The crude product was recrystallized from toluene to obtain wine red crystals. Yield 0.5 g (48%). M_p = 295–296 °C.

¹H NMR (400 MHz, CDCl₃) δ: 8.50 (s, 2H), 7.80 (s, 2H), 7.62 (t, *J* = 9.0 Hz, 4H), 7.55 – 7.41 (m, 10H), 7.40 – 7.28 (m, 6H), 7.19 – 6.76 (m, 34H), 6.69 (d, *J* = 8.2 Hz, 8H), 3.78 (s, 12H), 3.61 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ: 155.9, 141.0, 140.7, 140.6, 139.6, 139.4, 139.2, 139.0, 138.9, 137.3, 136.9, 136.2, 131.4, 127.5, 127.3, 126.6, 124.5, 122.7, 120.9, 120.4, 120.0, 119.8, 118.4, 118.2, 114.7, 114.6, 55.5, 55.4.

Anal. Calcd. For: C₁₁₆H₉₀N₄O₈S₂: C 80.44; H 5.24; N 3.23; O 7.39; S 3.70; found: C 80.40; H 5.26; N 3.24.

4,4',4'',4'''-(((2,2':5',2''-terthiophene]-5,5''-diylbis(methanylylidene))bis(9H-fluorene-2,7-diyl-9-ylidene))tetrakis(N, N-bis(4-methoxyphenyl)aniline) (V1455)



A mixture of 5,5''-bis((2,7-dibromo-9H-fluoren-9-ylidene)methyl)-2,2':5',2''-terthiophene (**2**) (0.5 g, 0.5 mmol), 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (2.2 g, 5 mmol), and anhydrous toluene/THF (16.6 mL/33.4 mL) was purged with Ar for 20 minutes. Afterwards, tetrakis(triphenylphosphine)palladium (0.7 g, 0.6 mmol) and 2M K₂CO₃ solution (20 mL) was added, and the reaction mixture was heated at 90 °C for 24 hours (TLC control, THF/*n*-hexane 11:14). After cooling to room temperature, the reaction mixture was filtered through

celite and extracted with ethyl acetate. Organic layer was dried over Na_2SO_4 , filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 11:14, v:v). 20% solution of the final product in THF was poured with intensive stirring into a 15-fold excess of ethanol. The precipitate as a dark red powder was filtered off, washed with ethanol, and dried. Yield 0.4 g (42%).

^1H NMR (400 MHz, CDCl_3) δ : 8.57 (s, 2H), 7.79 (s, 2H), 7.63 (dd, $J = 13.4, 13.5$ Hz, 4H), 7.54 – 7.37 (m, 14H), 7.35 (d, $J = 3.7$ Hz, 2H), 7.12 – 6.91 (m, 28H), 6.83 (d, $J = 8.5$ Hz, 8H), 6.76 (d, $J = 8.5$ Hz, 8H), 3.78 (s, 12H), 3.69 (s, 12H).

^{13}C NMR (101 MHz, CDCl_3) δ : 156.0, 148.1, 140.9, 140.7, 139.6, 139.5, 139.2, 139.0, 138.5, 137.2, 136.9, 136.4, 135.7, 133.4, 133.0, 131.6, 127.5, 127.3, 126.9, 126.8, 126.6, 125.0, 124.1, 122.6, 120.9, 120.8, 120.0, 119.8, 118.5, 118.2, 114.7, 55.5, 55.45.

Anal. Calcd. For: $\text{C}_{120}\text{H}_{92}\text{N}_4\text{O}_8\text{S}_3$: C 79.44; H 5.11; N 3.09; O 7.05; S 5.30; found: C 79.40; H 5.16; N 3.06.

8. CURRICULUM VITAE

Aistė Jegorovė

aiste.ilciukaite@ktu.lt

Išsilavinimas:

2002–2012	Anykščių Antano Vienuolio gimnazija
2012–2014	Anykščių Jono Biliūno gimnazija
2014–2018	Kauno Technologijos Universitetas (Bakalauro studijos)
2018–2020	Kauno Technologijos Universitetas (Magistro studijos)
2020–2025	Kauno Technologijos Universitetas (Doktorantūros studijos)

Profesinė patirtis:

2020-05-04–2020-08-31	Kauno technologijos universitetas, projektas „Funkcinės molekulės naujos kartos saulės elementams: nuo sintezės link komercializavimo“, projekto inžinierė.
2020-04-24–2023-04-30	Kauno technologijos universitetas, projektas „Funkcinės molekulės naujos kartos saulės elementams: nuo sintezės link komercializavimo“, jaunesnioji mokslo darbuotoja.
2020-07-20–2023-08-31	Kauno technologijos universitetas, projektas „Efektyvios bei tvarios krūvius transportuojančios molekulės energiją taupančioms technologijoms (SMARTMOLECULES)“, jaunesnioji mokslo darbuotoja.
2022-11-01–2023-10-30	Kauno technologijos universitetas, projektas „Tandeminių perovskito-silicio modulių gamybos pramoniniu mastu bandomoji linija (PEPPERONI)“, jaunesnioji mokslo darbuotoja.
2023-01-01–dabar	Kauno technologijos universitetas, projektas „Padidinto stabilumo bei taikomumo perovskitiniai saulės elementai (VALHALLA)“, jaunesnioji mokslo darbuotoja.
2023-11-01–dabar	Kauno technologijos universitetas, projektas „Racionaliai sukurti ploni kontaktiniai sluoksniai, įgalinantys didelio ploto perovskitų/silicio tandeminių saulės elementų gamybą (RADICALS)“, jaunesnioji mokslo darbuotoja.
2024-01-06–dabar	Kauno technologijos universitetas, projektas „Misijomis grįstų mokslo ir inovacijų programų įgyvendinimas“, jaunesnioji mokslo darbuotoja.

2024-09-02–dabar	Kauno technologijos universitetas, projektas „Technologinių ir fizinių mokslų ekselencijos centras (TiFEC)“, jaunesnioji mokslo darbuotoja.
------------------	---

Mokslinis darbas:

2019	Lietuvos mokslo tarybos remiami studentų vasaros praktikos tyrimai.
2019–2020	Lietuvos mokslo tarybos remiama studentų mokslinė praktika.
2017–dabar	Tiriamasis darbas prof. dr. Vytauto Getaučio mokslinėje grupėje: organinių puslaidininkų, kurie gali būti panaudoti hibridinėms saulės celėms, sintezė ir tyrimų analizė.

Visuomeninė veikla:

2025	Vilkaviškio Aušros gimnazijoje skaitytas pranešimas „Nuo mokyklos suolo iki mokslinių atradimų: kelias į saulės elementų tyrimus“ ir demonstruoti saulės elementų konstravimo eksperimentai.
2024	Kauno Santaros gimnazijoje vesta pamoka „Saulės energija – kova su klimato kaita“ ir demonstruoti saulės elementų konstravimo eksperimentai.
2024	Kauno r. Karmėlavos Balio Buračo gimnazijos Ramučių skyriuje vesta pamoka „Saulės energija – kova su klimato kaita“ ir demonstruoti saulės elementų konstravimo eksperimentai.
2024	Kauno r. Karmėlavos Balio Buračo gimnazijoje vesta pamoka „Saulės energija – kova su klimato kaita“ ir demonstruoti saulės elementų konstravimo eksperimentai.
2024	Prienų r. Jiezno gimnazijoje vesta pamoka „Saulės energija – kova su klimato kaita“ ir demonstruoti saulės elementų konstravimo eksperimentai.
2024	Prezidentūroje Žaliųjų idėjų mugėje pristatyti hibridiniai saulės elementai ir demonstruoti saulės elementų konstravimo eksperimentai.
2023	Šalčininkų mokyklų mokiniams vestos paskaitos ir demonstruoti saulės elementų konstravimo eksperimentai.
2022	Vaškų miestelio mokyklų mokiniams vestos paskaitos ir demonstruoti saulės elementų konstravimo eksperimentai.

Apdovanojimai:

2020	10-osios jaunųjų mokslininkų konferencijos „Fizikinių ir technologijos mokslų tarpdalykiniai tyrimai“ 3 vietos laureatė.
------	--

Stipendijos:

2020

INFOBALT vardinė stipendija.

2024

Lietuvos mokslo tarybos finansuojama parama doktorantams už studijų rezultatus.

Publikacijos recenzuojamuose mokslo leidiniuose:

1. Solovjova, Joana; Malinauskas, Tadas; Daskeviciene, Maryte; Kasparavicius, Ernestas; **Iliciukaite, Aistė**; Sackus, Algirdas; Paulauskas, Valdas; Getautis, Vytautas. Triphenylamine-based phenylhydrazone indolium cationic dyes for solid-state DSSC applications // Materials letters. Amsterdam : Elsevier. ISSN 0167-577X. eISSN 1873-4979. 2020, vol. 274, art. no. 128001, p. 1-5. (Web of Science). DOI: 10.1016/j.matlet.2020.128001. [IF: 3,423; Q2].
2. **Jegorovė, Aistė**; Truong, Minh Anh; Murdey, Richard; Daskeviciene, Maryte; Malinauskas, Tadas; Kantminiene, Kristina; Jankauskas, Vygintas; Getautis, Vytautas; Wakamiya, Atsushi. Starburst carbazole derivatives as efficient hole transporting materials for perovskite solar cells // Solar RRL. Weinheim : Wiley VCH. ISSN 2367-198X. 2022, vol. 6, iss. 1, art. no. 2100877, p. 1–7. (Web of Science). DOI: 10.1002/solr.202100877. [IF: 7,9; Q1].
3. **Jegorovė, Aistė**; Momblona, Cristina; Daškevičienė, Marytė; Magomedov, Artiom; Degutyte, Rimgaile; Asiri, Abdullah M.; Jankauskas, Vygintas; Sutanto, Albertus Adrian; Kanda, Hiroyuki; Brooks, Keith; Klipfel, Nadja; Nazeeruddin, Mohammad Khaja; Getautis, Vytautas. Molecular engineering of fluorene-based hole-transporting materials for efficient perovskite solar cells // Solar RRL. Weinheim : Wiley VCH. ISSN 2367-198X. 2022, vol. 6, iss. 6, art. no. 2100990, p. 1–9. (Web of Science). DOI: 10.1002/solr.202100990. [IF: 7,9; Q1].
4. Mandati, Sreekanth; Juneja, Nimish; Katerski, Atanas; **Jegorovė, Aistė**; Grzibovskis, Raitis; Vembris, Aivars; Dedova, Tatjana; Spalatu, Nicolae; Magomedov, Artiom; Karazhanov, Smagul; Getautis, Vytautas; Krunks, Malle; Oja Acik, Ilona. 4.9% efficient Sb2S3 solar cells from semitransparent absorbers with fluorene-based thiophene-terminated hole conductors // ACS applied energy materials. Washington, DC : American chemical society. ISSN 2574-0962. 2023, vol. 6, iss. 7, p. 3822–3833. (Web of Science). DOI: 10.1021/acsaem.2c04097. [IF: 5,5; Q2].
5. **Jegorovė, Aistė**; Xia, Jianxing; Steponaitis, Matas; Daskeviciene, Maryte; Jankauskas, Vygintas; Gruodis, Alytis; Kamarauskas, Egidijus; Malinauskas, Tadas; Rakstys, Kasparas; Alamry, Khalid A.; Getautis, Vytautas; Nazeeruddin, Mohammad Khaja. Branched fluorenylidene derivatives with low ionization potentials as hole-transporting materials for perovskite solar cells // Chemistry of materials. Washington DC : American Chemical Society. ISSN 0897-4756. eISSN 1520-5002. 2023, vol. 35, iss. 15, p. 5914–5923. (Web of Science). DOI: 10.1021/acs.chemmater.3c00708. [IF: 7,2; Q1].

6. Kamarauskas, Egidijus; **Jegorove, Aiste**; Čepas, Romualdas J.; Daskeviciute-Geguziene, Sarune; Genevicius, Kristijonas; Franckevicius, Marius; Talaikis, Martynas; Dobuzinskas, Rokas; Scheler, Florian; Sveinbjornsson, Kari; Jankauskas, Vygintas; Getautis, Vytautas. Cross-linkable fluorene-based hole transporting materials for perovskite solar cells // Chemical physics. Amsterdam : Elsevier. ISSN 0301-0104. eISSN 1873-4421. 2024, vol. 579, art. no. 112183, p. 1–7. (Web of Science). DOI: 10.1016/j.chemphys.2024.112183. [IF: 2,0; Q3].
7. **Jegorovė, Aistė**; Daškevičienė, Marytė; Kantminienė, Kristina; Jankauskas, Vygintas; Čepas, Romualdas Jonas; Gruodis, Alytis; Getautis, Vytautas; Genevicius, Kristijonas. New fluorene-based bipolar charge transporting materials // RSC Advances. Cambridge : Royal Society of Chemistry. ISSN 2046-2069. 2024, vol. 14, iss. 5, p. 2975–2982. (Web of Science). DOI: 10.1039/d3ra07583d. [IF: 3,9; Q2].
8. Juneja, Nimish; **Jegorovė, Aistė**; Grzibovskis, Raitis; Katerski, Atanas; Daskeviciene, Maryte; Malinauskas, Tadas; Vembris, Aivars; Karazhanov, Smagul; Spalatu, Nicolae; Getautis, Vytautas; Krunks, Malle; Oja Acik, Ilona. Dopant-free Fluorene Based Dimers linked with Thiophene Units as Prospective Hole Transport Materials for Sb₂S₃ solar cells // Sustainable Energy Fuels. Washington, DC : American chemical society. ISSN 2398-4902. 2024, **2024**, 8, 4324–4334. (Web of Science). DOI: 10.1039/D4SE00472H. [IF: 5,0; Q2].

Mokslinės konferencijos:

1. Synthesis and properties of enamine based hole transporting materials containing oxygroups : stendinis pranešimas // Open readings 2019: 62nd international conference for students of physics and natural sciences, Kovo 19-22, 2019 Vilnius, Lietuva.
2. Oksi- ir metoksigrupes turinčių enaminų sintezė ir savybės: žodinis pranešimas // Respublikinės studentų mokslinės konferencijos „Chemija ir cheminė technologija 2019“, Gegužės 17, 2019, Vilnius, Lietuva.
3. New fluorene-based hole transporting organic semiconductors for efficient hybrid solar cells: stendinis pranešimas // Lithuania-Poland workshop on physics and technology, Rugsėjo 26-27, 2019, Vilnius, Lietuva.
4. New fluorene derivatives as positive charge carriers for efficient perovskite solar cells: stendinis pranešimas // Open readings 2020: 63rd international conference for students of physics and natural sciences, Kovo 17-20, Vilnius, Lietuva.
5. Teigiamus krūvininkus transportuojantys keturis karbazolilchromoforus turintys fluoreno dariniai efektyviems perovskitiniais saulės elementams: žodinis pranešimas // Studentų moksliniai tyrimai 2019/2020, Rugsėjo 29, 2020, Vilnius, Lietuva.
6. New fluorene derivatives as hole transporting materials for efficient perovskite solar cells: stendinis pranešimas // Functional materials and

- nanotechnologies: [13th international conference], FM&NT-2020: virtualus renginys. Lapkričio 23-26, 2020, Vilnius, Lietuva.
7. Fluoreno klasės puslaidininkiai efektyviems hibridiniams saulės elementams: žodinis pranešimas // Fizinių ir technologijos mokslų tarpdalykiniai tyrimai: 10-oji jaunųjų mokslininkų konferencija. Rugsėjo 23, 2020, Vilnius, Lietuva.
 8. New fluorene class semiconductors as hole transporting materials for perovskite solar cells: standinis pranešimas // Open readings 2021: 64th international conference for students of physics and natural sciences, Kovo 16-19, 2021, Vilnius, Lietuva.
 9. Carbazole derivatives as hole transporting materials for efficient solar cells: standinis pranešimas // Chemistry and chemical technology: 16th international conference of Lithuanian Chemical Society, Rugsėjo 24, 2021, Vilnius, Lietuva.
 10. Starburst carbazole derivatives as efficient hole transporting materials for perovskite solar cells: standinis pranešimas // Proceedings of nanoGe Spring meeting 2022: AdvMatSyn22: Advanced materials synthesis, characterization, and theory: for the green energy leap: virtualus renginys. Kovo 7-11, 2022, Valensija, Ispanija.
 11. Molecular engineering of the fluorene-based hole transporting materials for efficient perovskite solar cells: standinis pranešimas // Open readings 2022: 65th international conference for students of physics and natural sciences, Kovo 15-18, 2022, Vilnius, Lietuva.
 12. Inexpensive fluorene-based hole transporting material with terminated thiophene unit for efficient semi-transparent Sb_2S_3 solar cells: standinis pranešimas // Proceedings of international conference on hybrid and organic photovoltaics (HOPV22), Gegužės 19-25, 2022, Valensija, Ispanija.
 13. Fluorene - terminated materials for efficient perovskite solar cells: standinis pranešimas // Balticum organicum syntheticum [BOS] 2022: in memory of prof. Victor Sniečkus. Liepos 3-6, 2022, Vilnius, Lietuva.
 14. Star-shaped compounds for efficient perovskite solar cells: standinis pranešimas // 28th PhotoIUPAC, Liepos 17-22, 2022, Amsterdamas, Olandija.
 15. Fluorene-based hole transporting material with terminated thiophene unit for efficient semitransparent Sb_2S_3 solar cells: standinis pranešimas // Chemistry and chemical technology: proceedings of international scientific conference. Spalio 14, 2022, Kaunas, Lietuva.

9. PADĖKA

Nuoširdžiai dėkoju vadovui prof. dr. Vytautui Getaučiui už suteiktą galimybę tapti jo vadovaujamos mokslinės grupės dalimi, už patarimus, pamokymus, rūpestį ir pasitikėjimą bei paskatinimą siekti daugiau.

Dėkoju dr. Marytei Daškevičienei, kuri supažindino su sintezės darbais, įvairiomis gryninimo procedūromis. Pirmaisiais mūsų pažinties metais ji pasakė: „Jūs visi (studentai) man kaip vaikai.“ Šiuos žodžius patvirtino jos rūpestis, pagalba ir palaikymas. Per šiuos septynerius pažinties metus ji kartu džiaugėsi sėkme ir krintosi, kai nesisekdavo. Džiaugiuosi, kad šis žmogus vedė mane moksliniu keliu.

Atskirą padėką norėčiau išreikšti ir laboratorijos kompanionei bei draugei dr. Šarūnei Daškevičiūtei. Smagu buvo augti ir tobulėti kartu su Tavimi.

Ačiū visiems prof. dr. Vytauto Getaučio grupės nariams už pagalbą, patarimus, draugystę ir geros atmosferos palaikymą laboratorijoje.

Esu be galo dėkinga savo šeimai už rūpestį ir palaikymą.

UDK 549.641+621.383.51](043.3)

SL344. 20xx-xx-xx, xx leidyb. apsk. I. Tiražas 14 egz. Užsakymas xxx.

Išleido Kauno technologijos universitetas, K. Donelaičio g. 73, 44249 Kaunas
Spausdino leidyklos „Technologija“ spaustuvė, Studentų g. 54, 51424 Kaunas