

KAUNAS UNIVERSITY OF TECHNOLOGY

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SYNTHESIS AND INVESTIGATION OF
ELECTROACTIVE TRIPHENYLETHENE,
CARBAZOLE AND TRIPHENYLAMINE
DERIVATIVES FOR ORGANIC LIGHT
EMITTING DEVICES

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KAUNO TECHNOLOGIJOS UNIVERSITETAS

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CONTENTS

LIST OF ABBREVIATIONS	6
INTRODUCTION	8
1. LITERATURE REVIEW.....	12
1.1. Overview of OLEDs.....	12
1.1.1. Structure of OLEDs.....	13
1.1.2. Fabrication methods of OLEDs.....	13
1.2. Organic electroactive materials.....	15
1.2.1. Synthesis methods of organic electroactive materials.....	15
1.2.2. Organic light emitting materials.....	18
1.2.3. Organic host materials.....	29
1.2.4. Charge transporting materials.....	33
1.3. Conclusion of the literature review.....	37
2. EXPERIMENTAL.....	39
2.1. Instrumentation.	39
2.2. Device fabrication.....	40
2.3. Materials.....	40
2.3.1. Synthesis of compounds 1–4.....	40
2.3.2. Synthesis of compounds 5–8.....	43
2.3.3. Synthesis of compounds 9–12.....	46
2.3.4. Synthesis of compounds 13–17.....	48
3. RESULTS AND DISCUSSION.....	52
3.1. Triphenylethene-based derivatives for blue non-doped organic light emitting diodes.....	52
3.2. Bis(trifluoromethyl)phenyl disubstituted aromatic diamines.....	60
3.3. Methoxy-substituted carbazole-based polymers for solution-processable organic light emitting diodes.....	67
3.4. Derivatives containing three donor fragments for organic light emitting diodes.....	75
4. CONCLUSIONS	83
5. SANTRAUKA.....	85
LITERATURE.....	111
CURRICULUM VITAE.....	128
LIST OF PUBLICATIONS RELATED TO THISIS.....	128
LIST OF CONFERENCES RELATED TO THISIS.....	129
ACKNOWLEDGEMENTS.....	131

LIST OF ABBREVIATIONS

Abbreviations:

ACQ	aggregation-caused quenching
A-D-A	acceptor-donor-acceptor
AIE/E	aggregation induced enhanced emission/enhancements
CE	current efficiency
CF ₃	non-conjugated trifluoromethyl
CIE	chromaticity coordinate
COSY	correlation spectroscopy
CT	charge transfer
CV	cyclic voltammetry
Cz	carbazole
D-A-D'	donor-acceptor-donor
DCM	dichloromethane
DSC	differential scanning calorimetry
ΔE_{ST}	difference between (E_S-E_T)
EA ^{PE}	electron affinity of PE
EBL	electron blocking
EML	emission layer
E _S	singlet state
E _T	triplet state
EL	electroluminescent spectra
ET	triplet energy
EQE	external quantum efficiency
F	fluorene
HBL	hole blocking
HOMO	highest occupied molecular orbital
HSQC	heteronuclear single quantum coherence spectroscopy
HTM	hole transporting layer
IP ^{PE}	ionization potentials of PE
ISC	intersystem crossing
IQE	internal quantum efficiency
ITO	indium tin oxide
LEB	lowest energy band
LUMO	lowest unoccupied molecular orbitals
N	nitrogen
NMR	nuclear magnetic resonance
OFET	organic field effect transistor
OLED	organic light emitting diode
PE	photoelectron emission
PL	photoluminescence
PhOLED	phosphorescent OLED
PLEDs	polymeric light-emitting diodes

PLQY	photoluminescence quantum yields
RAFT	reversible addition–fragmentation chain-transfer
RDRP	reversible deactivation radical polymerization
RIM	restriction of Intramolecular Motions
RIR	restriction intramolecular rotation
RISC	reverse intersystem crossing
TADF	thermally activated delayed fluorescence
TD-DFT/DFT	time dependent-/density functional theory
TGA	thermogravimetric analysis
THF	tetrahydrofuran
ToF	time of flight
TOL	toluene
XRD	single crystal X-ray diffraction

INTRODUCTION

Civilization is driven towards improving the quality of life. Technological advancements help humans to achieve this goal [1]. In this context, an important objective is the effective and reliable lighting technology. This led to the development and discovery of such emitting devices as the torch with blazing fire in the ancient civilization which gradually progressed towards the *light emitting diode* (LED) in the modern era [2]. Research on these emitting devices evolved into mainstream commercial products, such as displays for televisions, monitors, or mobile devices. In the spirit of saving the planet and commercializing more environmentally safe technologies, scientists and governments started researching the field of organic electronics. This field deals with such technologies as organic thin film transistors, organic solar cells, *organic light emitting diodes* (OLEDs), etc. Interestingly, OLED is a relatively new concept that has been gaining attention among researchers for the past two decades. This approach of the device design architecture significantly influenced the cost of manufacturing, thus in turn reducing the carbon footprint of the display technology [3,4,5].

The first time when organic compounds were used in OLEDs was in 1987 by Tang and co-workers. Because of their low molecular weight, flexibility, and processing cost, organic electroactive materials have been attracting a great deal of attention due to their unique electrical and photophysical properties [6,7]. Organic electroactive compounds are considered as suitable candidates for optoelectronic devices (3, 4, 5). The versatility of organic molecules provides the possibility to design π -conjugated low-molar-mass and polymeric semiconductors [8,9]. Organic emitters are a key component of OLEDs and are a predeterminant factor for the efficiencies of OLEDs. Host materials with appropriate energy levels and triplet energies, along with balanced charge carrier transport and the high thermal stability as well as morphological stability of their layers can enable to obtain excellent performance of OLEDs [10].

The fundamental design of OLEDs involves an organic layer sandwiched between the negatively charged anode and the positively ionized cathode. The organic layer is designed with π -conjugated compounds with electroluminescent properties to achieve a balanced/efficient recombination of holes and electrons. Additionally, optical and photophysical, thermal and morphological properties, along with the appropriate energy levels, are the main requirements for organic electroactive materials [11,12,13]. The combination of electron-donating (D) and electron withdrawing (A) groups and/or linkers (L) in the design of organic semiconductors is used to achieve a wide range of beneficial characteristics [14].

Although the progress of organic electronics has improved, there are several problems that still need to be solved. Such problems as the high production cost, high roll-off, short lifetime, and the low efficiency of OLEDs are the most important ones to be addressed [15]. Materials with a certain combination of features can deliver the desired device properties. This can be a challenging task, and therefore, profound understanding of the impact of the structure of the electroactive

compounds on their characteristics is essential. The efficient materials with a high *photoluminescence quantum yield* (PLQY), the required energy levels, as well as high hole and electron transporting ability can be synthesized by the proper selection of D/A and/or L moieties. Simple organic fluorescence or phosphorescence materials are of great interest. Multifunctional simple organic compounds are favorable competitors for the enhanced performance of organic electroluminescent devices.

The aim of this work is the design, synthesis, and investigation of new organic electroactive compounds based on triphenylethene, carbazole and triphenylamine moieties for potential application in OLEDs.

To achieve the aim of the dissertation, the following tasks were formulated:

- Synthesis of new triphenylethene-based compounds, bis(trifluoromethyl)phenyl disubstituted aromatic diamines, methoxysubstituted carbazole-based polymers and V-shape carbazole-based derivatives with various donor moieties.
- Investigation and analysis of the properties of the synthesized compounds.
- Study of the compounds as hole transporting materials, emitters, or hosts in organic fluorescent and phosphorescent OLEDs.

The key statements of the doctoral dissertation:

- Design of triphenylethene-based derivatives is an effective strategy to obtain highly emissive compounds possessing aggregation induced emission.
- F atoms in electroactive compounds form intermolecular and intramolecular interactions resulting in a decrease of ionization potential and an improvement of charge mobility properties.
- Polymers are appropriate for effective solution processed OLEDs because of their ability to form amorphous, morphologically stable materials.
- The low-energy bands of compounds which originated from the intramolecular charge transfer allow achieving thermally activated fluorescence.

Novelty of the work:

- For the first time, aggregation induced enhanced emission for triphenylethene-based derivatives containing 2,6-di-*tert*-butylcarbazole or 9,9-dimethyl-9,10-dihydroacridine as donor moieties has been observed, and their application as emitters in OLEDs has been demonstrated.
- New aromatic diamines with bis(trifluoromethyl)phenyl substituents have been synthesized, and the mesomeric effect has been detected for compounds with 2,5-bis(trifluoromethyl)benzene moieties.

- New 3,6-dimethoxycarbazole-based polymers obtained by RAFT polymerization have been tested as hole transporting materials and hosts in solution-processed OLEDs. The best phosphorescent device exhibited an external quantum efficiency of 10.6%.
- Four new derivatives of carbazole and various donor fragments such as 9,9-dimethyl-9,10-dihydroacridine, 10*H*-phenothiazine, 10*H*-phenoxazine, 5*H*-dibenzo[*b,f*]azepine, have been synthesized, and their applicability for the fabrication of phosphorescent OLEDs has been demonstrated. The device contained 10,10'-(9-(2-ethylhexyl)-9*H*-carbazole-3,6-diyl)bis(9,9-dimethyl-9,10-dihydroacridine), exhibiting thermally activated delayed fluorescence, and demonstrated the highest external quantum efficiency reaching 12.6%.

Personal input of the author

Chapters. 3.1–3.4. Bernard Ronit Sebastine (Department of Polymer Chemistry and Technology, Kaunas University of Technology), the author, has designed, synthesized, and purified organic electroactive compounds. The author performed and analyzed the results of theoretical calculations, conducted structure analysis, performed UV-VIS absorption, and *photoluminescence* (PL), including quantum yield and excited-state lifetime and *cyclic voltammetry* (CV) measurements. Dr. Viktorija Andrulevičienė and Prof. Juozas Vidas Gražulevičius (Department of Polymer Chemistry and Technology, Kaunas University of Technology) advised on the modeling and synthesis of molecules, and contributed to analyzing the properties of the synthesized compounds, and to preparing scientific publications. Dr. Juratė Simokaitienė (Department of Polymer Chemistry and Technology, Kaunas University of Technology) performed the thermal measurements DSC and TGA. The measurements of the mass spectra were performed by Dr. Eigirdas Skuodis (Department of Polymer Chemistry and Technology, Kaunas University of Technology); the results were further analyzed by the author. Electron photoemission measurements, and charge mobility measurements, fabrication and characterization of OLEDs were done by Dr. Dmytro Volyniuk and Dr. Oleksandr Bezikonnyi (Department of Polymer Chemistry and Technology, Kaunas University of Technology); the results were further analyzed by the author. The measurements of *single crystal X-ray diffraction* (XRD) analysis were performed by Associate Professor Dr. Audrius Bučinskas (Department of Polymer Chemistry and Technology, Kaunas University of Technology). Dr. Galyna Sych (Department of Polymer Chemistry and Technology, Kaunas University of Technology) advised on molecular design, synthesis, and structural confirmation; Prof. Dr. Azhar Ariffin (Department of Chemistry, Faculty of Science, University of Malaya) advised on NMR analysis and explanations of the cyclopalladation reaction mechanisms. Dr. Sohrab Nasiri (Department of Polymer Chemistry and Technology, Kaunas University of Technology) assisted in the measurements of photophysical properties. Dr. Dalius Gudeika (Department of Polymer Chemistry and Technology, Kaunas University of Technology) assisted in manuscript editing and relevant corrections. Dr. Rimantas Henrikas Kublickas (Department of Food Science and

Technology, Kaunas University of Technology) assisted in manuscript editing and relevant corrections. Mr. George Belousov, Dr. Aliaksei Vaitusionak, and Dr. Sergei Kostjuk (Research Institute for Physical Chemical Problems of the Belarusian State University) performed the polymerization of monomers and conducted polymer kinetics experiments. Dr. Uliana Tsiko (Department of Polymer Chemistry and Technology, Kaunas University of Technology) assisted in manuscript editing and relevant corrections. Dr. Bo-Yen Lin (Department of Electrical Engineering, Yuan Ze University), Chia-Hsun Chen (Graduate Institute of Photonics and Optoelectronics and Department of Electrical Engineering, National Taiwan University), Jing-Xiang Huang (Graduate Institute of Photonics and Optoelectronics and Department of Electrical Engineering, National Taiwan University) and Chi-Feng Lin (Department of Electro-Optical Engineering, National United University) fabricated and characterized phosphorescent OLEDs. Tien-Lung Chiu (Department of Electrical Engineering, Yuan Ze University) and Jiun-Haw Lee (Graduate Institute of Photonics and Optoelectronics and Department of Electrical Engineering, National Taiwan University) analyzed the electroluminescent characteristics of the phosphorescent OLEDs.

1. LITERATURE REVIEW

1.1. Overview of OLEDs

For the two most recent decades, OLEDs have been intensively studied as a new class of display technology due to their flexible nature, environmental friendliness, and the low cost of production [16,17]. The first OLED was reported by Ching Wan Tang and Steven Van Slyke at Eastman Kodak company in 1987 [18]. This led to extensive studies over the years with the objective to improve the efficiency of OLEDs [19].

The evolution of OLEDs started from the 1st generation emitters, also known as fluorescent OLEDs, where organic dyes were used as fluorescent emitters [20]. In a device, the injected holes and electrons are combined in an emissive layer to generate excitons in an applied electric field. In the 1st generation OLEDs, only 25% of the generated excitons can be harvested through the transition from *first singlet* (S_1) to *ground state* (S_0) ($S_1 \rightarrow S_0$) **Fig. 1**. Therefore, the maximum EQE of OLEDs using fluorescent emitters is limited to 5% [21].

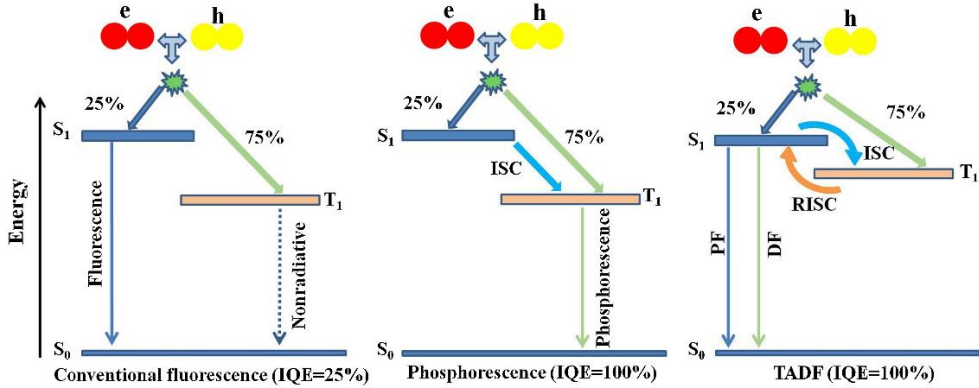


Fig. 1. Emission mechanisms of 1st, 2nd and 3rd generation OLEDs [22].

In the 2nd generation of devices, named PHOLEDs, heavy metals were used to accelerate radiative decay through phosphorescence. Thus, *intersystem crossing* (ISC) from S_1 to the excited *triplet state* (T_1) was successfully achieved in the 2nd generation OLEDs [23]. The phosphorescence mechanism in PHOLEDs is presented in **Fig. 1**. Due to the allowed ISC from the S_1 to the T_1 state, and by cultivating excitons from both states, theoretically, emitters could reach the *internal quantum efficiency* (IQE) of up to 100% [24].

The 3rd generation OLEDs are currently being used in commercial devices and are composed of highly promising *thermally activated delayed fluorescent* (TADF) materials [25]. TADF materials demonstrate a small *energy gap* (ΔE_{ST}) between S_1 and T_1 . This allows to occur the spin-forbidden *reverse intersystem crossing* (RISC)

process in a number of materials **Fig. 1**. Through RISC, triplet excitons can upconvert into the S_1 state and radiatively relax to the S_0 , which would lead to the theoretical IQE of 100% [26].

1.1.1. Structure of OLEDs

OLEDs are composed of organic *hole-transporting* (HTL), *emissive* (EML) and *electron-transporting* (ETL) layers introduced between two electrodes to improve the efficiency and lifetime of the devices [27]. The multilayer structure of OLEDs is presented in **Fig. 2**. The organic materials used in OLEDs are known as organic semiconductors with electrical conductivity via delocalization of π electrons through conjugation within the molecules [28]. Based on the type of emission, organic materials are classified as fluorescent or phosphorescent materials [29]. *Indium tin oxide* (ITO) is commonly used as the anode in OLEDs due to its high conductivity and transparency [30]. Meanwhile, barium, calcium, and aluminum are often used as cathodes [31]. Holes from the anode and electrons from the cathode are injected into the HTL and ETL, respectively, and transported to the EML when the current flows through the OLED.

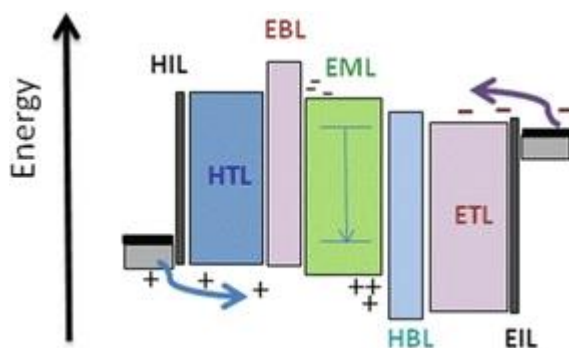


Fig. 2. Scheme of the energy levels of the materials in a multilayer OLED [32].

The construction of effective OLEDs requires the alignment of the energy levels of materials to ensure balanced charge carrier-injection into the EML [33]. In some cases, additional layers, such as the *hole blocking* (HBL) and *electron blocking* (EBL) layers, are used to prevent the reverse transfer of charge carriers from the EML. This helps to increase the probability of recombination of charge carriers in the EML [34].

1.1.2. Fabrication methods of OLEDs

OLEDs can be fabricated by using dry or wet processes. The most widely used dry process is the vacuum deposition technique, in which, thermal evaporation of the materials is used to produce thin films of the materials in OLEDs [35], **Fig. 3**.

Vacuum deposition makes it easy to fabricate ideal multilayer structured devices denoted by very high purity and a high degree of horizontal molecular orientation [36]. It was established that extremely small amounts of impurities at the EML deteriorates the lifetime of the OLEDs [37], therefore, the vacuum deposition process is prominently attractive for the fabrication of highly efficient OLEDs [38]. We note that only small molecules featuring high thermal stability can be used for the fabrication of organic optoelectronic devices by vacuum deposition [39].

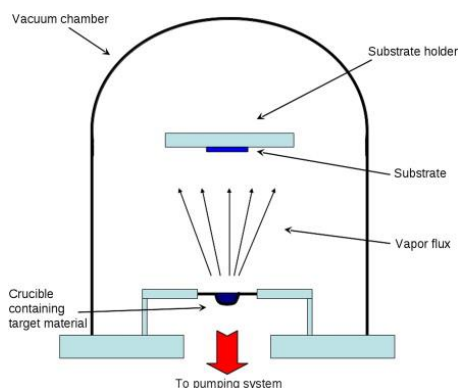


Fig. 3. Illustration of a typical thermal evaporation system [40].

In the case of wet processes, spin-coating is a common technique for the production of thin films in OLEDs [41]. In this method, organic emissive materials are dissolved in a solvent and dropped onto a flat substrate. The substrate rotates at a high speed to spread the materials smoothly on the flat surface, and then dries until the solvent has evaporated. The schematic process of the spin-coating is shown in **Fig. 4**. Thus, an organic layer on a flat substrate is formed. The thickness of the film is directly proportional to the concentration, the speed of rotation, and the composition of the solution [42]. The main advantages of the solution processing method are the low cost of the production process and the easy fabrication of large-area devices [43]. In contrast to vacuum deposition, optoelectronic devices can be fabricated by spin-coating while using small molecules and polymers [44,45].

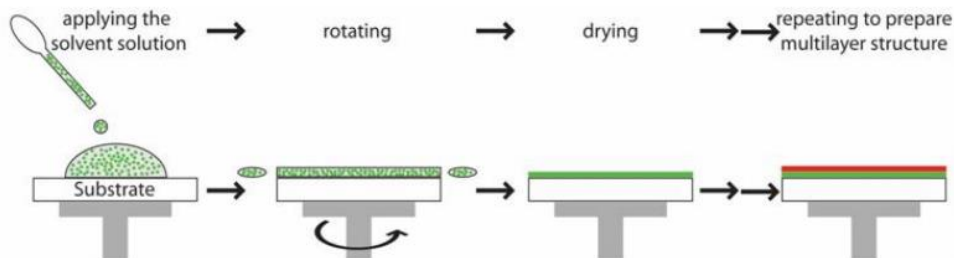


Fig. 4. Scheme of the spin-coating process [46].

1.2. ORGANIC ELECTROACTIVE MATERIALS

To achieve high efficiencies in OLEDs it is essential to design and synthesize organic electroactive materials that can be used as organic emitters, hosts, and charge transporting materials. The investigation of these materials has become an important field of the OLED technology. The investigation of the materials revealed the impact of their structure on the photophysical, electrochemical, thermal, and photoelectrical properties [47,48,49].

1.2.1. Synthesis methods of organic electroactive materials

Organic optoelectronics requires commercially attractive materials with simple and low-cost synthesis [50]. Synthesis of new organic electroactive materials involves procedures for making compounds from commercially available starting materials and their purification. In this chapter, the well-known organic synthetic methods used for the synthesis of the electroactive compounds presented in the dissertation are described.

Palladium catalyzed Heck coupling

Heck coupling is a chemical reaction between aryl halides and alkenes to form the C-C bond in the presence of a base and a *Palladium* (Pd) catalyst [51,52].

The steps of the reaction mechanism are as follows:

- a. Palladium inserts itself in the aryl to the bromide bond during oxidative addition. The alkene and palladium then combine to produce a π -complex (3)
- b. In the syn addition step, the alkene introduces itself into the palladium-carbon bond.
- c. The beta-hydride elimination step takes place with the production of a new palladium-alkene complex (here, the arrows point in the opposite direction) (5), and the complex gets broken in the next step.
- d. In the final step, D, the palladium(II) molecule is reductively eliminated by potassium carbonate, thus generating the palladium(0) compound.

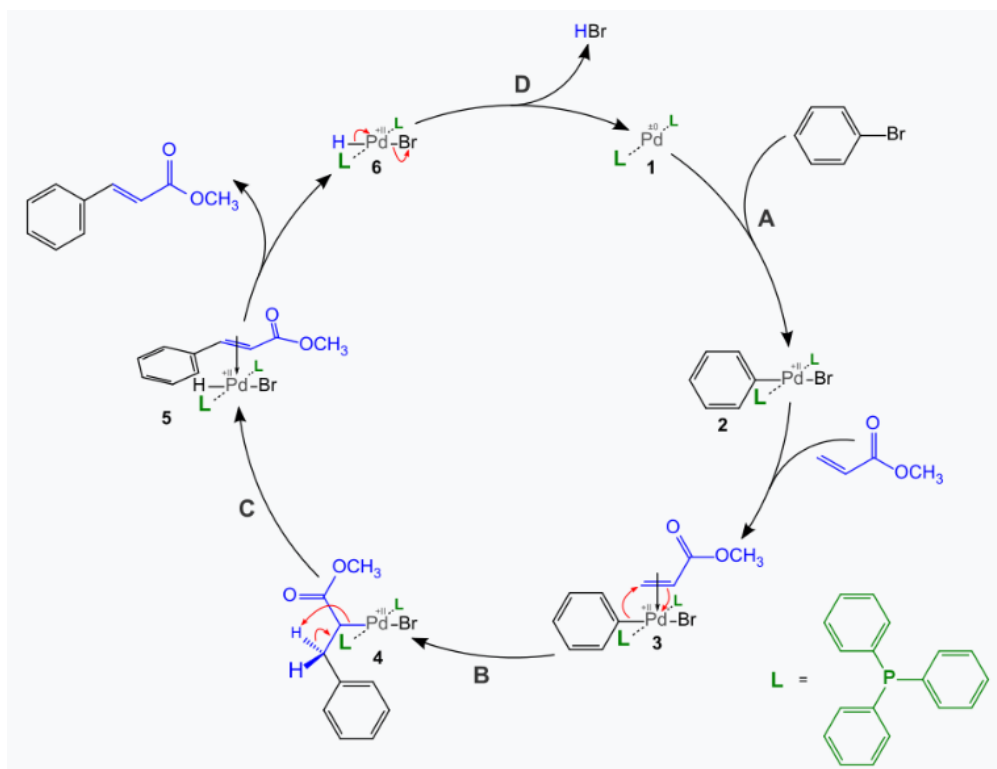


Fig. 5. Reaction mechanism of Heck Coupling [53].

In the Heck coupling reaction, there is the possibility of the unusual rearrangement of the complex during the syn addition step. This leads to a phenomenon known as **cyclopalladation**. In this process, Pd forms a π -complex by bonding with the halogen atom to form alkene bonds in the next step with Pd and thus producing a carbon-Pd bond. Here, the intermediate is stable enough as a coordinative ligand. This provides sufficient time for the intermediates to proceed toward cyclopalladation with the neighboring carbon atom [54,55].

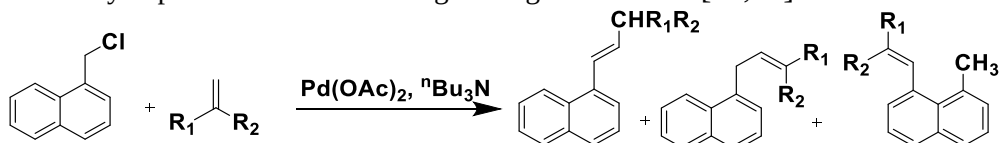


Fig. 6. Reaction to cyclopalladation [55].

Palladium catalyzed Buchwald–Hartwig amination

In organic chemistry, this method is used to couple aromatic amines with aromatic halides. The reaction mechanism is like that of the Heck coupling reaction, and it results in the C-N bond formation in the presence of Pd and a base [56].

The steps of the reaction mechanism are as follows:

- A. Pd (II) is reduced to Pd (0) by the oxidative addition of the aromatic halide to Pd.
- B. The coordination of the aromatic amine to Pd yields a new complex.
- C. The coordination of the amine via ligand exchange takes place.
- D. The separation of dimeric complexes forms (C) in the presence of monomeric species with phosphine and an amine ligand.
- E. The base added to the mixture separates hydrogen and halide from the Pd complex and allows nitrogen to bond with Pd. In reductive elimination, Pd is eliminated, which results in the final product.

However, a side reaction may occur wherein β -hydride elimination followed by reductive elimination produces hydro-de-halogenated arenes and the corresponding imine (a functional group with the carbon-nitrogen double bond).

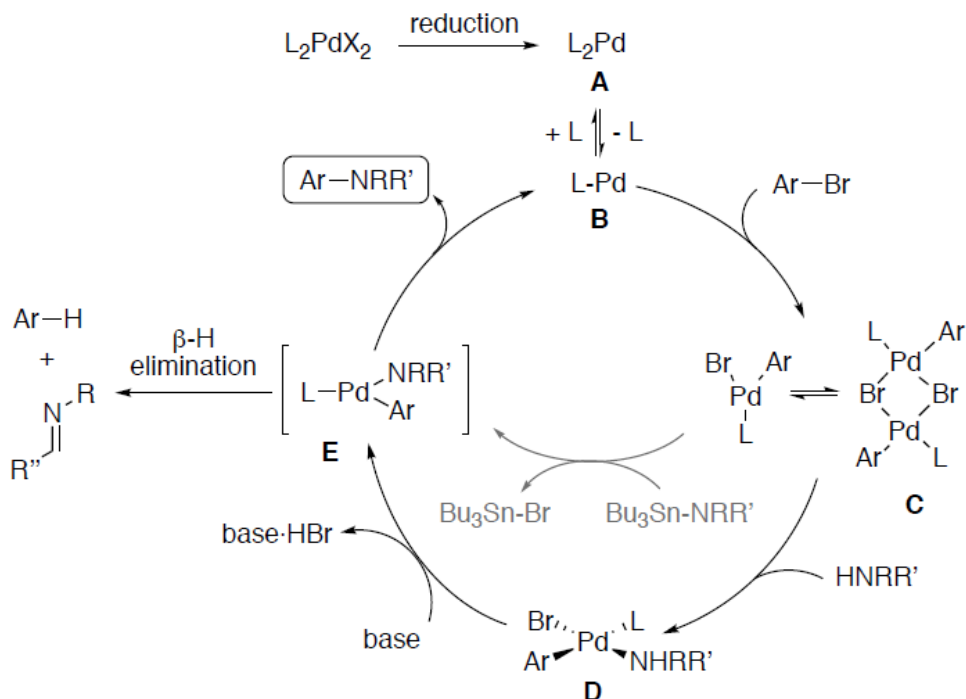


Fig. 7. Reaction mechanism of Buchwald-Hartwig reaction [57].

Reversible addition-fragmentation chain transfer (RAFT) polymerization

RAFT polymerization is the type of reversible deactivation radical polymerization. The procedure was developed to control the distribution of molecular weights, copolymerization, and macromolecular architecture in radical polymerization [58].

The steps of the reaction mechanism are as follows [59]:

- I. During the initiation step, the radical initiator decomposes into free radicals which react with the monomer.
- II. The monomeric radical reacts with the monomer and propagates the growth of the polymeric chain.
- III. During the RAFT pre-equilibrium, the polymeric radical reacts with the RAFT agent and results in the fragmentation process which may cause the loss of the radical.
- IV. The radical bonds with the monomer and forms a new polymeric chain.
- V. During the main RAFT equilibrium, the radicals are shared with all the remaining species that have not been terminated, which leads to the narrow polydispersity index.
- VI. Active polymeric chains react to prevent further reactions through the process called biradical termination.

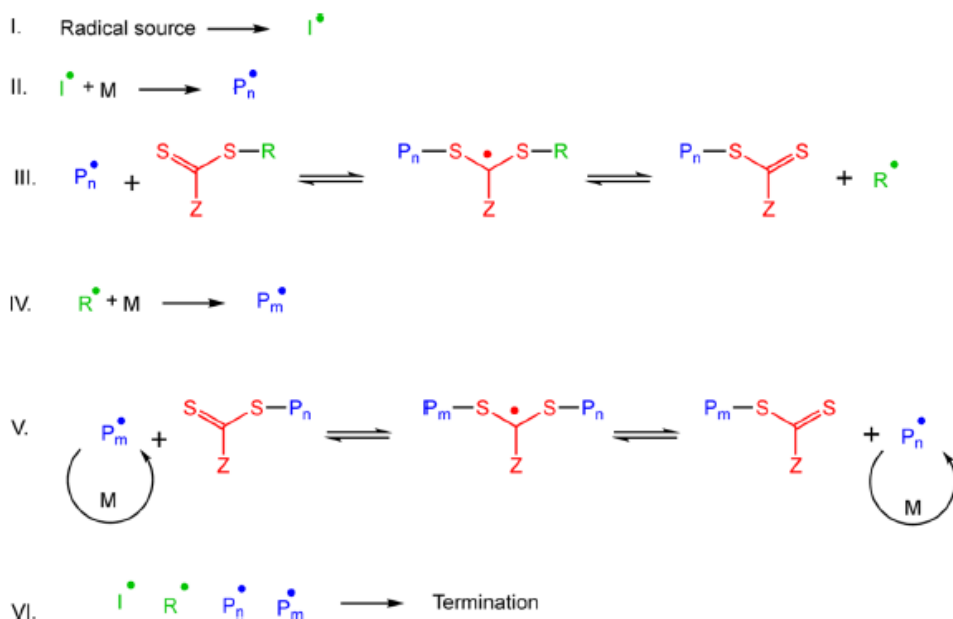


Fig. 8. Reaction mechanism of RAFT polymerization [59].

1.2.2. Organic light emitting materials

One of the major drawbacks of fluorescent materials is the emission quenching in the solid state; any procedure that reduces a substance's fluorescence intensity is referred to as quenching. Aggregate formation results in *aggregation-caused quenching* (ACQ), which results in a decrease of the fluorescence intensity which was discovered by Förster in 1954 [60]. Planar or close to planar compounds are experiencing intense intermolecular π - π stacking interactions which result in the emission quenching of luminophores [61,62]. ACQ prevents the application of

organic light emitting materials in OLEDs as it dramatically decreases the efficiency of the devices. To overcome the ACQ effect, several approaches have been developed and investigated [63]. The phenomenon where compounds are non-emissive in a solvent but begin to emit light in the aggregate solid state is known as *aggregation induced emission / enhancement* AIE / AIEE, and it was first observed by the group of Ben Zhong Tang in 2001 [64]. AIE/AIEE is composed of the mechanism of *restriction of intramolecular motions* (RIM) which, in turn, includes such phenomena as the *restriction intramolecular rotation* (RIR) and *restriction of intramolecular vibrations* (RIV) **Fig. 9** [65]. The information gained through AIE/AIEE gives deeper insights into the light emission of optoelectronic materials. The research of this phenomenon indicates that the intramolecular rotation or the vibration of moieties effectively dissipates the exciton energy, but RIM and RIV can activate radiative transition [65].

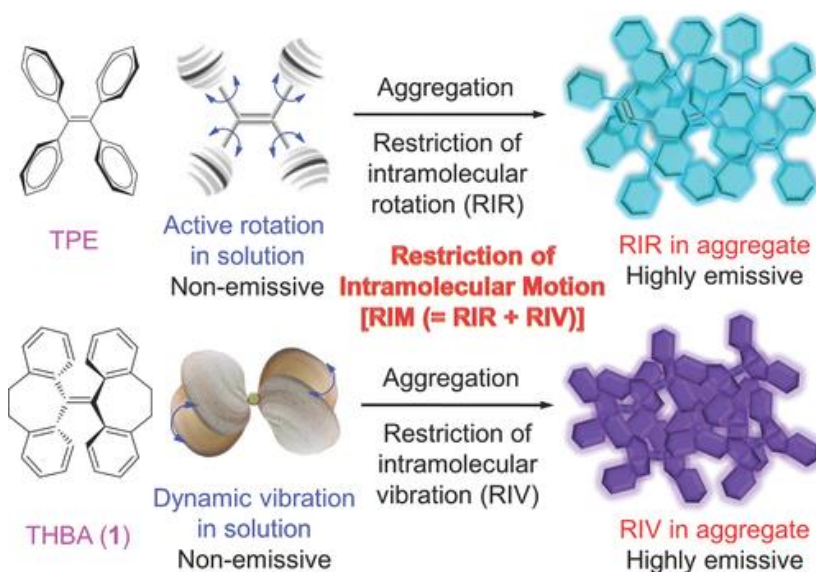


Fig. 9. Schematic presentation how non-emissive materials become emissive in the solid states due to RIR and RIV effects [65].

The development of AIE/AIEE organic materials with a low molar mass opens up a wide range of applications. Some of the highly emissive materials are used as fluorescent emitters in OLEDs and sensors [66]. One of the well-studied AIE/AIEE examples is *tetra-phenylethane* (TPE), in which, four phenyl rings are connected to the central ethylene core through single bonds [67]. The materials in a dilute solution are non-emissive because of the active intramolecular rotations, which leads to a low emission or the absence of emission in the solution. However, in the solid state, because of aggregation, the intramolecular rotations are highly restricted due to the physical constraints, which leads to the increase of the emission [68].

Two AIE materials, PPBC and DPPBC, shown in **Fig. 10** [69], with phenylethene-carbazole moieties were used as emitters for the non-doped blue and blue-green OLEDs, respectively. The PL properties of compounds were studied in the mixtures of tetrahydrofuran and water (THF/H₂O). A remarkable fluorescence enhancement was recorded in the THF/H₂O solutions of PPBC and DPPBC when the volume of water reached 90%. The synthesized compounds are insoluble in water, therefore, aggregates form in the mixture as we get THF/H₂O with a high water content. The best OLED with DPPBC in the emission layer demonstrated the maximum luminance, current efficiency, and power efficiency of 10290 cd m⁻², 4.075 cd A⁻¹ and 2.559 lm/w, respectively.

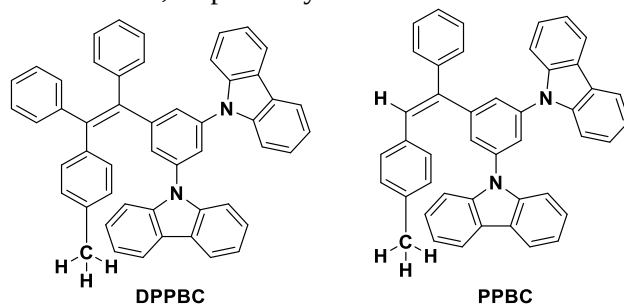


Fig. 10. Structure of DPPBC and PPBC [69].

Two AIE derivatives TPE-TPAPBI and TPE-DPBI [70] with triphenylamine and/or 1,2-diphenyl-1*H*-benzimidazole moieties showed excellent PLQY approaching 100% in solid films. TPE-TPAPBI **Fig. 11**, due to having hole- and electron-transporting fragments on both sides of the TPE linker, demonstrated balanced mobility of charge carriers. The non-doped OLED with TPE-TPAPBI as the emitter demonstrated exclusive characteristics. The device showed ultra-high luminance of 125 300 cdm⁻² and the EQE, power, and current efficiencies of 5.8%, 14.6 lmW⁻¹ and 16.8 cdA⁻¹, respectively. The fluorescent OLED exceeded the limit of EQE of 5% apparently because of the horizontal orientation of the TPE-TPAPBI molecules.

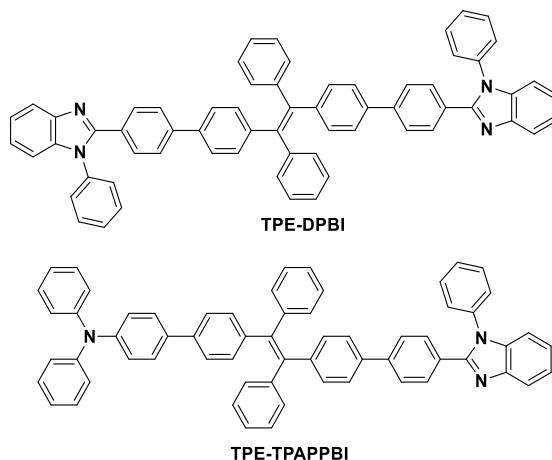


Fig. 11. Structure of TPE-DPBI and TPE-TPAPPBI [70].

TADF emitters are highly desired for applications in OLEDs because of the harvesting of both singlet and triplet excitons. These emitters with the AIE characteristics are a promising strategy to achieve highly efficient non-doped OLEDs.

A new luminogen *dibenzothiophene-benzoyl-9,9-dimethyl-9,10-dihydroacridine* (DBT-BZ-DMAC) with an asymmetrical structure was synthesized and investigated by various methods. A robust AIEgen, DBT-BZ-DMAC, was designed and synthesized with the asymmetrical *donor-acceptor-donor* (D-A-D') structure **Fig. 12**. DBT-BZ-DMAC exhibited intriguing AIE, TADF and *mechanoluminescence* (ML) properties. The AIE nature of DBT-BZ-DMAC allows it to display strong solid-state PL, as well as prominent ML. DBT-BZ-DMAC's neat film was more stable than the doped DBT-BZ-DMAC in CBP. DBTBZ-DMAC was used as an emitter to produce doped and non-doped OLEDs.

Doped OLEDs with low doping concentrations are denoted by excellent peak EL efficiencies. However, the efficiency roll-off is large, as it generally is with most OLEDs using TADF emitters. The peak efficiency values decrease, but the efficiency roll off seems to be smaller as the doping concentration increases. The OLED non-doped offers excellent peak EL efficiencies at 43.3 cd A^{-1} , 35.7 Lm W^{-1} and 14.2%. The external current efficiency roll off is very low at 0.46%. The peak values at 1000 cd/m^2 are close to the non-doped OLEDs, which allows it to outperform OLEDs doped at high luminance. This is the most efficient non-doped OLED ever made by using TADF. It features a very low efficiency roll-off. Combining AIE and TADF merits could be a promising molecular design concept for developing ideal light emitters with stable and efficient OLEDs [71].

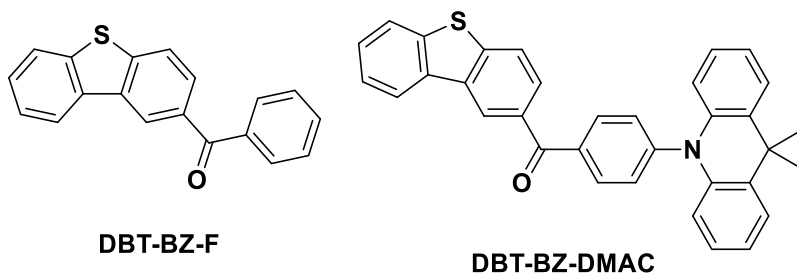


Fig. 12. Structure of DBT-BZ-DMAC [71].

Combining TADF and AIE is a promising strategy for designing new luminescent materials. The authors of [72] modified 2,3,4,5,6-penta(9*H*-carbazol-9-yl) benzonitrile (5CzBN) from an ACQ molecule into an AIEgen by the addition of the 5CzBN core with alkyl chain-linked spiro-bi-fluorene dendrons. These materials have the potential to display AIE-TADF properties.

Three AIE-TADF molecules, specifically, 5CzBN-SSP, 5CzBN-DSP, and 5CzBN-PSP, were designed and synthesized **Fig. 13**. These materials are suitable for solution processes due to their higher molecular weights and alkyl chains. It is interesting to note that core-dendron materials showed the AIE phenomenon, whereas the core 5CzBN or dendron spirobiuorene had ACQ properties. These AIE-TADF materials (5CzBN-SSP, 5CzBN-DSP and 5CzBNPSP) were used as emitters. Fully solution-processed OLEDs with these AIE-TADF materials achieved EQE at 7.3%, 13.9%, and 20.1%, respectively. This is much higher than the OLEDs that are fully solution processed and based on 5CzBN. Core-dendron systems are a great candidate for high-efficiency solution-processed OLEDs. This research opens new avenues for designing new AIE-TADF emitters that are efficient in optoelectronic applications [72].

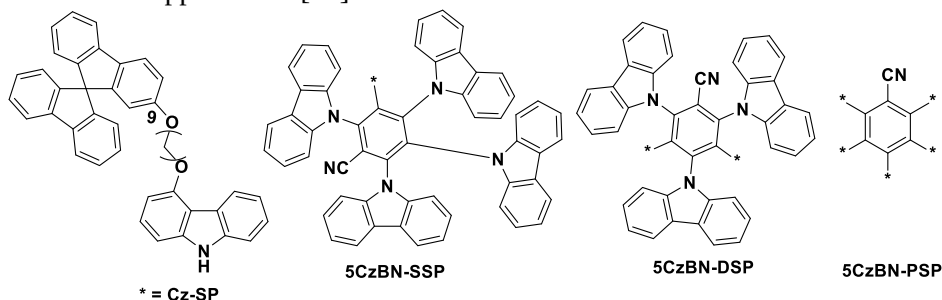


Fig. 13. Structures of 5CzBN-SSP, 5CzBN-DSP and 5CzBN-PSP [72].

Polymeric light-emitting Diodes (PLEDs), as the congener, of organic light emitting diodes, have several advantages, such as a low-cost, along with the wet fabrication process that makes them suitable for large-area flexible displays and lighting fields. Most emissive polymers in PLEDs are subject to ACQ, which results in a large efficiency roll-off. Two polymers, pTPE-DPA-Cz and pTPE-DPA-Flu,

with AIE, were synthesized by using the Suzuki-Miyaura Polycoupling reaction **Fig. 14**.

Fully solution-processed OLEDs with these AIE-TADF materials achieved EQE at 7.3%, 13.9%, and 20.1%, respectively. This is far higher than the OLEDs that are fully solution processed and based on 5CzBN. Core-dendron systems will be a great candidate for high-efficiency solution-processed OLEDs. The devices demonstrated a low-efficiency roll-off, which was a significant achievement for AIE polymer-based PLEDs [73].

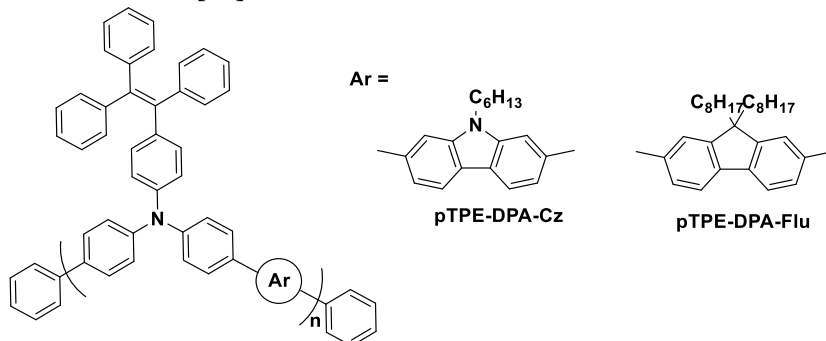
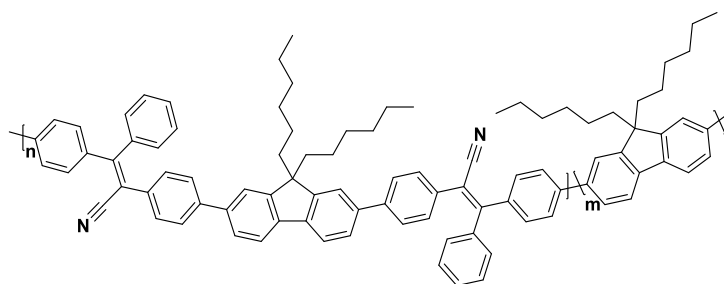


Fig. 14. Structure of pTPE-DPA-Cz and pTPE-DPA-Flu [73].

The white light emitting devices and materials have attracted a lot of attention and will play an important part in the next generation of solid-state lighting applications. The AIE route offers a straightforward solution to the problem of solid state ACQ. Hence, in order to explore the influence of the AIE moiety on the solid state emission of a polymer, the author designed and synthesized a new and simple architecture of the yellow light emitting 2Z,2'Z-3,3'-((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(3,1-phenylene))bis(2-(4-bromophenyl)-3-phenylacrylonitrile (FBPAN) AIEE moiety **Fig. 15**. White light emission is demonstrated by using a derivative from tetraphenylethene, FBPAN building blocks that alternate with the 9,9'-dihexylfluorene center. Due to the FBPAN monomer's twisted conformation, the absolute quantum yield of PL in the solid state was 63.4%. The AIEE active FBPAN endowed the copolymers with an improved AIEE performance, and the copolymers exhibited enhanced emission even at very low feed ratios (0.5%) of the AIEgen compared to the reported tetraphenylethylenefluorene copolymers with 10% feed ratios. These materials showed a *chromaticity coordinate* (CIE) (0.32, 0.31) which is very similar to the standard white light emission (0.33, 0.33). The maximum luminance, current, and power efficiency were 13 455 cd/m², 7.56 cd A⁻¹ and 5.32 lm W⁻¹, respectively. These copolymers offer significant advantages for device fabrication due to the balanced charge transport, as well as a lower energy offset. Based on our findings, it is possible to develop new light emitting materials by using this rational molecular strategy [74].



COPOLYMERS

m = 0.50	n = 0.50	FBPAN 50,
m = 0.75	n = 0.25	FBPAN 25,
m = 0.90	n = 0.10	FBPAN 10,
m = 0.95	n = 0.05	FBPAN 5,
m = 0.99	n = 0.01	FBPAN 1,
m = 0.995	n = 0.005	FBPAN 0.5

Fig. 15. Structure of FBPAN [74].

The synthesis and photophysical properties of the star-shaped *fluoranthene-tetraphenylethylene* (TFPE) conjugated luminogen, **Fig. 16**, with *aggregation-induced, blue-shifted emission* (AIBSE) properties, was reported. The authors designed and synthesized a star-shaped material by using TPE as the propeller unit, in combination with the bulky TFPE as an ensemble. The phenomenon of AIBSE was studied by solvatochromic and temperature-dependent emission methods. *Scanning electron microscopy* (SEM) and *tunneling electron microscopy* (TEM) were used to investigate nanoaggregates of TFPE that had been formed by varying water/THF ratios and correlated with optical property. The luminogen displayed unusual AIBSE both in the solid and the aggregate states. Blue-shifted emission with higher quantum yields was possible due to the fluoranthene unit excited-state planarization and the twisted *intramolecular rotation* (IMR) of the phenyl rings. The nanoaggregates formed of TFPE at 30% and 70% water in THF had unique sensitivity with detection limits of 0.8 ppb and 0.5 ppb, respectively. The nanoaggregates that formed in the water fractions of 30% and 70% showed high Stern-Volmer constants ($K_{sv}=79998, 51120 \text{ m}^3/\text{mol}$), respectively. These results show that photoinduced electron transfer is dominant in static quenching [75].

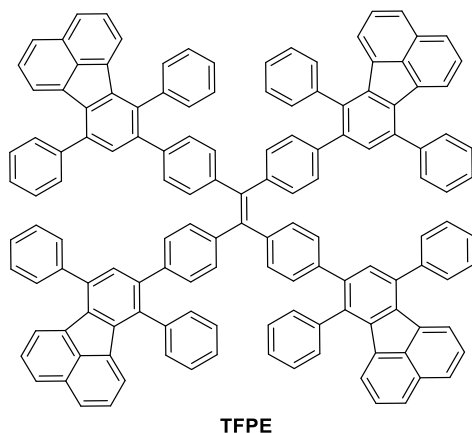


Fig. 16. Structure of TFPE [75].

Two *phenothiazine* (PTZ)-based tetraphenylethylene derivatives of phenothiazine were developed and synthesized. The main goal was to achieve high solid-state emission as well as a good *mechano-fluorochromism* (MFC) behavior. The strong electron donating capability of PTZ could also affect TPE's electron donating capacity, which resulted in the dipolar nature in the molecules. PTZ moieties attached with TPE are expected to alter the twisting of the molecules, which could further impact the mechanochromic properties. The synthesized materials PTZTPE-1 and PTZTPE-4 are highly emissive in the solid state, which is crucial for a molecule to show MFC, **Fig. 17**. PTZ's strong donor capability could impact the donor capacity of TPE, and thus cause changes in the electronic and photophysical properties. The spectral shifts in response to the mechanical stimuli are nearly identical for both mono- and tetra substituted tetraphenylethylene (PTZTPE-1, and PTZTPE-4). PTZTPE-4 does not have significant D-A characters, while PTZTPE-1 has D-A characteristics. This was confirmed by the solvatochromic behavior and TD-DFT research. These compounds could be used as smart materials to change their color in response to a mechanical stimulus and will help in the development of mechanoresponsive organic materials [76].

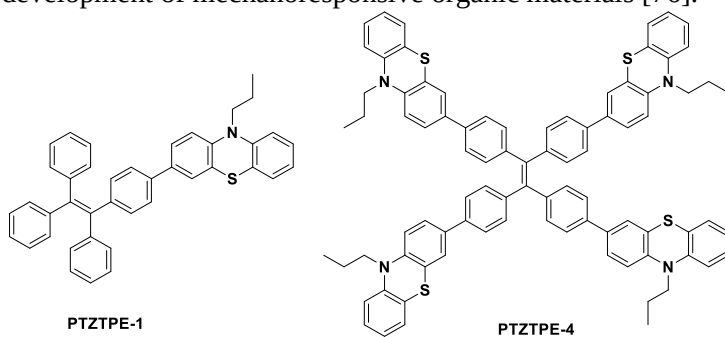


Fig. 17. Chemical structures of **PTZTPE-1** and **PTZTPE-4** [76].

Various modifications can be made to improve the characteristics of fluorescent materials. One of the common methods is the addition of various substituents to the emissive molecules. The substitution of F or CF₃ containing moieties to the emitters is a well-established practice among researchers [77]. This slight modification influences the properties of the materials and enables them to act as π conjugated electron transporting materials. The balanced bipolar *charge transfer* (CT) in emitters can improve the characteristics of the OLEDs.

9,9'-((6-(4-Fluorophenyl)-1,3,5-triazine-2,4-diyl))bis(2,1-phenylene))bis(3,6-di-tert-butyl-9H-carbazole) (FTrzTCz), **Fig. 18.**, was synthesized as a TADF emitter and an assistant dopant for green fluorescent OLEDs. A fluorine substituted triazine was developed as an acceptor moiety to control the acceptor strength, and 3,6-di-tert-butylcarbazole was introduced as a donor moiety for blue emission energy and suppressing the Dexter energy transfer. F atoms in the triazine acceptors induce strong CT character through the increased acceptor strength, a short delayed fluorescent lifetime, and a fast RISC. The EQE for the FTrzTCz was 18.5%, and the efficiency roll-off was increased. FTrzTCz was an assistant dopant and provided high EQE in hyperfluorescent devices, at 17.9%. The F functionalized triazine accepting agent could be used to design TADF materials or assistant dopants for hyperfluorescent OLEDs [77].

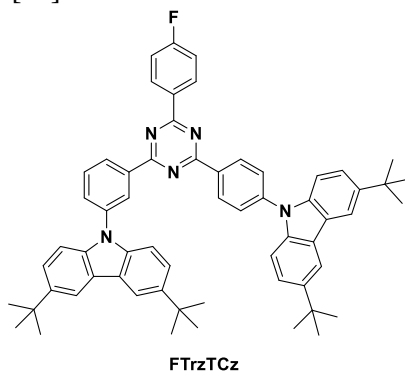


Fig. 18. Structure of FTrzTCz [77].

The authors of [78] discuss their previous reports that combined tetra- and penta-carbazole electronic donors with conjugated electron acceptors, such as benzophenone or cyanopyridine for green-to-orange TADF emission. They realized that simply inserting a phenyl bridge between the multi-carbazole donor and non-conjugated CF₃-electron acceptors could be a promising strategy to explore deep blue TADF materials-based light-performed TADF emitters. It is generally difficult to realize deep blue TADF emission, especially when there are more electron-donors, such as penta- or tetra-carbazoles, in p-conjugated acceptors.

A blue TADF emitter 4'-(trifluoromethyl)-[1,1'-biphenyl]-2,3,4,5,6-pentayl-pentakis(9H-carbazole) (5CzDPhCF₃), **Fig. 19.**, was designed by involving the non-conjugated CF₃ moiety as an electron-withdrawing unit which dominates the acceptor properties by the electron inductive effect instead of other widely reported

conjugated effects in TADF materials. By the variation on the number of the carbazole donors (from tetra- to penta-) in trifluoromethylbenzene, 4CzPhCF₃ and 5CzPhCF₃ presented tunable optoelectronic properties; the PL peak was achieved at 445 and 495 nm, and the maximum EQE of 0.62 and 5.2% with CIE of (0.17,0.18) and (0.21,0.33) was observed, respectively, in 1,3-bis(N-carbazolyl) benzene (mCP) hosted solution-processed OLEDs. Blue TADF OLEDs were vacuum deposited with the maximum EQE at 9.5 and 2.0%, respectively, with CIE values of (0.157, 0.66) and (0.75, 0.327), for 5CzPhCF₃; 5CzDPhCF₃ [78].

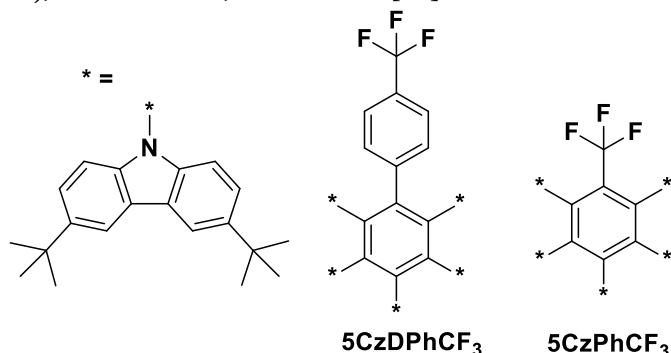


Fig. 19. Structure of 5CzDPhCF₃ and 5CzPhCF₃ [78].

Recently, Jonathan S. W., et al. [79] discussed the possibility of using *trifluoromethyl* (CF₃) for fast delayed fluorescence in TADFs with conjugated organic structures, see **Fig. 20**. The study discussed fast blue/green TADF emission along with the importance of the photophysical and molecular design characteristics for fluorescent emitters. Their work demonstrated how altering the S₁ and T₁ states can lead to a significant improvement in the delayed fluorescence. The authors demonstrated the synthesis and detailed photophysical characterization of four new functionalized D-A-D compounds using CF₃-substitutedthioxanthene-S, S-dioxide and dimethyl acridine units. The CF₃-substituted TADF acceptor in b-d has been a valuable structural tool to probe the effects of the orbital/exciton characteristics on the rates of TADF emissions. This helped better understand the TADF mechanism, and aid in the future molecular design. Tuning with trifluoromethyl substitutes enhances the rate of TADF emission with rapid delayed components. Meanwhile, TADF in conjugated organic molecules can be maximized by tuning the excitonic characteristics of the E_s or E_T excited states of CF₃ substitutes.

TD-DFT calculations support the orbital change. These results provide important insights for designing TADF emitters. The order of excited states can have an impact on the delayed fluorescence rates. It is important to understand how orbital distribution and singlet state characteristics affect the emission rates to increase delayed fluorescence and reduce triplet interactions that can cause annihilation. Many compounds have been reported to show rapid blue/green, thermally activated delayed fluorescence with major delayed fluorescence lifetime components sized $\approx 1\text{--}2$ ms [79].

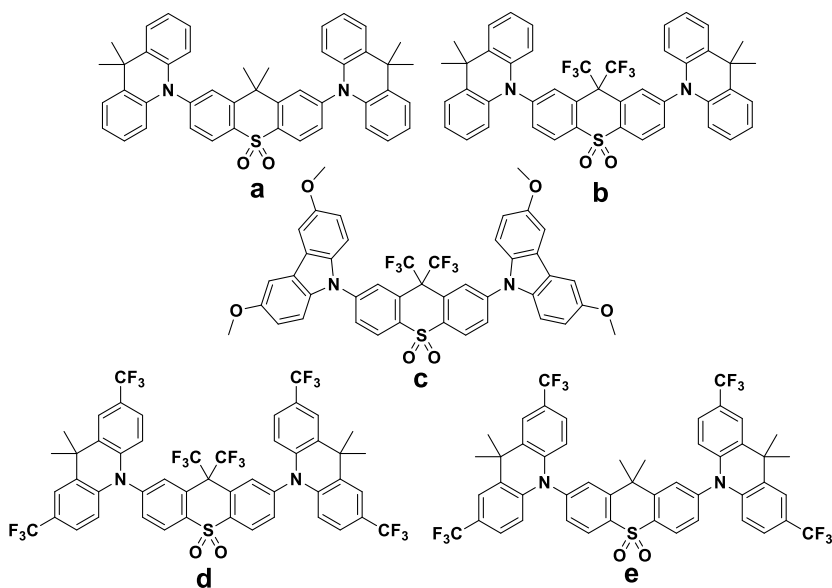


Fig. 20. Chemical structures of materials **a-e** [79].

PF-1 polymer displayed excellent properties reported in [80], including the intense and broad emission bands, solubility in high concentrations, and easy processing into thin solid films, good quality. PF-1 was structurally modified to include the fluorine group CF_3 . The new polymer was used to make OLEDs. This new polymer Poly[(benzo[*c*][1,2,5]thiadiazole-4,7-diylbis(9,9-dimethyl-9H-fluorene-7,2-diyl))-3,3-diyl(1-(3-(trifluoromethyl)phenyl)-2-oxindole)], **Fig. 21**, was used as EML.

The new polymer, PF-2F, showed a high EQE for fluorescent materials up to 2.6% and an excellent current efficiency of 35.3 cd/A even under a simple architecture: Anode/HIL/EML/EIL/Cathode. This is a significant improvement over the 2.1% efficiency achieved with PF-1. The PF-2F polymer was the only one to include the trifluoromethyl groups. Spin coating was used to obtain very high-quality solid state thin films with a film roughness of only 1–2 nm. OLED luminance was also enhanced using the PF-2F Polymer. The OLEDs performance was also evaluated when PFN or LiF was used as EIL. PF-2F could also be used as an emissive layer for flexible devices [80].

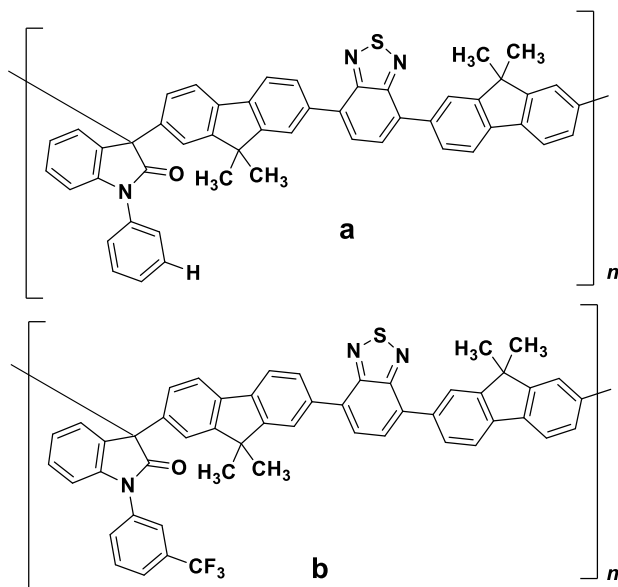


Fig. 21. Synthesis of (a) **PF-1** and (b) **PF-2F** [80].

1.2.3. Organic host materials

The idea of energy transfer from a host material to a guest material to generate electro phosphorescence is a widely used methodology amongst researchers (81, 82) [81,82]. Although it is possible to find hosts with small energy gaps, it is necessary that there is a transfer of energy between the transport layer and HOMO & LUMO. To solve this difficulty, a trick was used to employ the host material as an inert matrix (83) [83]. With these effects in mind, several methods were investigated to analyze a major component of OLEDs, that is, the exciton formation of the devices, i.e., the host-guest energy transfer exciton formation [84].

The authors reported zigzag-shaped, *meta*- and *para*-linked D-p-A-p-D blue emitters [85], m-BTPAPy, **Fig. 22**, and pBTPAPy, which were based on a nonsymmetrical connection strategy which uses the identical π -conjugated group. The phenanthrimidazole moiety was linked to pyridine via a naphthyl spacer through *para*- and *meta*-linking modes. Due to the intermolecular stacking suppression, the highly twisted mBTPAPy has a higher PLQY (0.98/0.85) than p-BTPAPy (0.95/0.80). Non-doped blue devices, with multifunctional m-BTPAPy/p-BTPAPy, have an EQE of 7.12/5.12%, a PE of 5.92/5.42 lm/W, and a luminance of 58675/76234cd/m² and a CE of 6.12/5.86 cd/A [85].

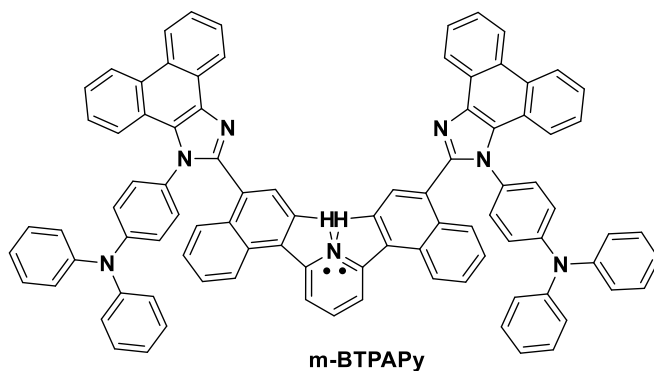


Fig. 22. Structure of m-BTPAPy [85].

Many organic emitters are emissive in a highly concentrated solution or in a solid-state neat film. Notably, Tang et al. [86] suggested an innovative phenomenon of AIE whose intensity is lower in a solution but increases as aggregates are formed. The molecule of bis(3,5-di(9H-carbazol-9-yl)phenyl)amine (CzPA) and a TPE hybrid was designed as AIE fluorophore, CzPATPE, **Fig. 23**, as a solution processed host material in hybrid white OLED.

Solution processable CzPATPE was designed as a sky-blue emissive host material for white OLED. It displays white EL with a color chromaticity CIE x,y (0.36, 0.43). The maximum EL efficiency of the white OLED is 3.4 cd/A, or 1.8 lm/W [86].

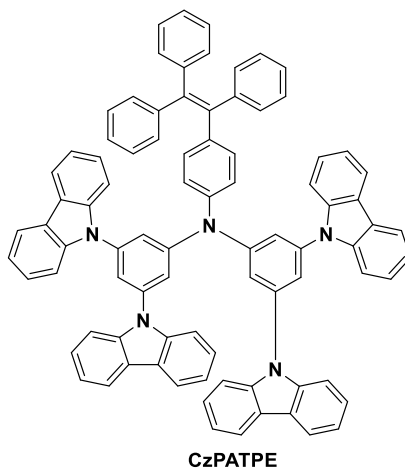


Fig. 23. Structure of CzPATPE [86].

The traditional radical polymerization can be a simple, metal-ion-free method of polymerization. This method is great for electronic materials as metal ion contamination can be reduced in polymers [87]. The author has been looking into *polystyrene* (PS-based) hosts which would include charge transporting groups in their side chains [87]. Free radical polymerization produced bipolar homopolymers

PCBZOXD, and PCBZTAZ, see **Fig. 24**. In these PS-based polymeric materials, *ortho*-carbazolyl-1,3,4-oxadiazolyl and *ortho*-carbazolyl-1,2,4-triazolyl substituted benzenes behave as the CT side units. PCBZOXD, and PCBZTAZ host materials were developed for high-efficiency sky-blue and EL devices. The design of the molecules was based upon the *ortho*-connection concept of bipolar moieties. This can effectively interrupt their conjugation length. These materials were used as the host materials for TADF-OLED and blue/green PhOLEDs. The solution processed PhOLEDs show a good device performance with the current efficiency of 11 cd/A for sky-blue emission, and 23.7 cd/A for green emission. 4CzIPN is a TADF green emitter that achieved a high current efficiency (27.3 cd/A) [87].

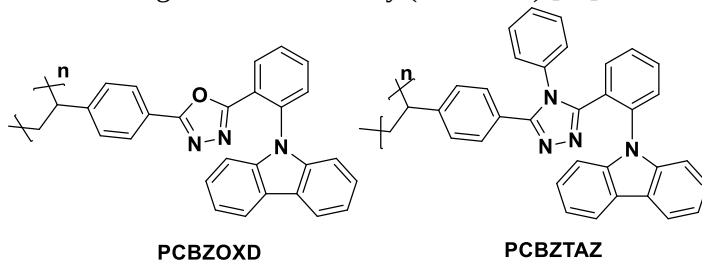


Fig. 24. Structures of PCBZOXD, and PCBZTAZ [87].

Phenanthrimidazole (PPI) derivatives have been described as multifunctional materials with excellent stability [88]. However, a new strategy for designing PPIs is needed to create an efficient ETM denoted by high electron mobility. The efficient ETM with an increased electron mobility can be achieved by combining heteroaromatics with a π -conjugated system. A new design strategy for PPIs is required to achieve a higher efficiency. Researchers have described the derivatives of pyridine styrylphenanthroimidazole, SPPI- (C_2Py , N_1Py and $C2N_1Py$), **Fig. 25** [88], as ETMs and host materials for blue *OLEDs* and *PHOLEDs*, respectively. The investigation of the optical and carrier transport capabilities of pyridine styrylphenanthroimidazoles were determined with respect to the linkage position in conjunction with the number of pyridine fragments.

Devices with SPPI- (C_2Py , N_1Py and $C2N_1Py$) have a maximum CE value of 14.28, 9.63, and 16.93 cd, respectively. They also have a maximum PE value of 9.32, 4.74, and 11.23 lmW^{-1} and a maximum EQE value of 7.93, 5.50, and 8.68%, respectively. This is in comparison with the widely used ETM BPhen. A simple multifunctional design strategy could be a way to create low-cost and high-quality luminogens for *OLEDs* [88].

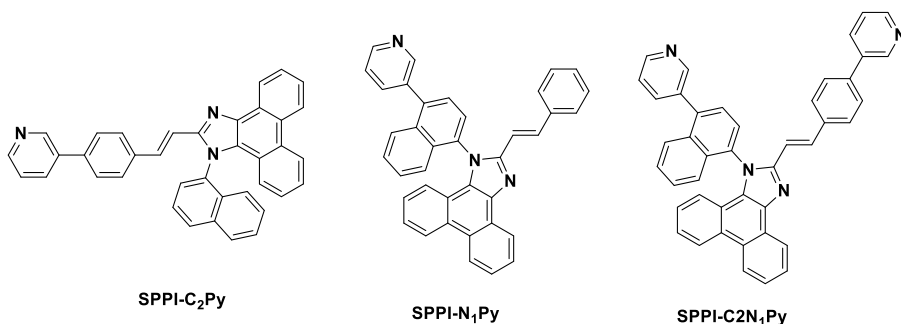


Fig. 25. Structure of SPPI- (C₂Py, N₁Py and C₂N₁Py) [88].

It has been a challenging task to design high-efficiency universal host materials for red, blue, and green (RGB) phosphors in the field of PhOLEDs. The introduction of different heterocycles may lead to instability in the device performance and increase the design complexity [89]. The first-ever pure hydrocarbon materials (PHC) were investigated and used as hosts for RGB PhOLEDs [89]. By combining the simplest PHC units, the hosts were synthesized, see **Fig. 26**. The authors of [89] depict how electronic and physical properties can be modified in accordance with the substitution pattern and the nature of the substitutes.

Particularly, mSTPh demonstrated the highest EQEs (27.3%, 26.0% and 27.1%, respectively, for RGB PhOLEDs). This performance of RGB PhOLEDs is the best for a universal host, and it shows that PHCs can behave as universal hosts, without intentionally introducing heteroatoms. PHCs are also easy to synthesize, and they are cost-effective for large-scale OLED production. This concept could open new avenues for the design of optoelectronic materials [89].

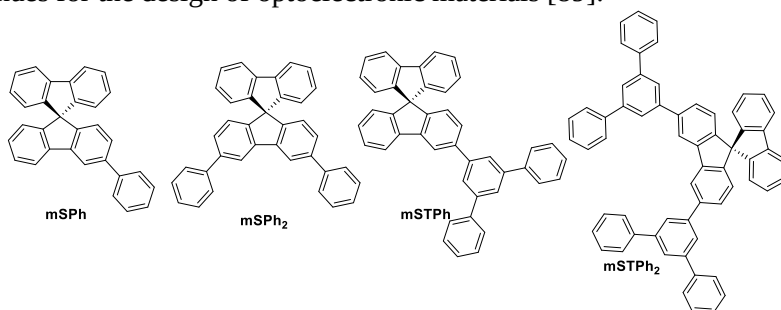


Fig. 26. Synthesis of PHC host materials [89].

All PhOLEDs that have been tested for their efficiency are made with heteroatoms. One of the major drawbacks of PhOLEDs is they are complex, and instability is present in the materials due to the heteroatoms they contain. The author of [90] discusses PHC materials composed of homoatoms. The C1 position of 9,9'-spirobifluorene (SBF) can be used to create a steric-inhibited environment

which affords desirable photophysical properties with a broad HOMO/LUMO gap and a high ET_1 [90].

The *meta*-terphenyl derivative 1-mtp-SBF, **Fig. 27**, achieves a high ES_1/ET_1 energy of 3.96/ 2.88 eV, and an EQE of 27.7% in white PhOLEDs by using a simple EML constructed with sky-blue and yellow emitters. This shows that the PHC strategy must be considered when developing new host materials. It also opens the door to simpler, large-scale electronics [90].

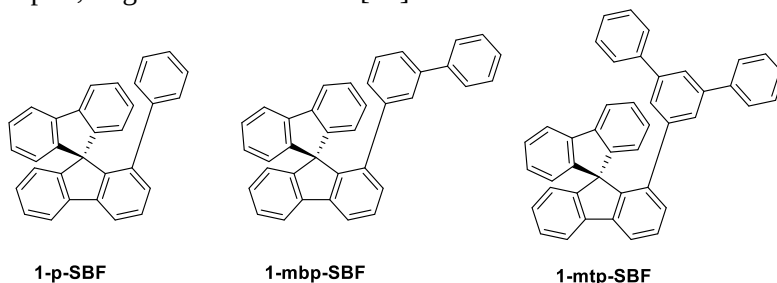


Fig. 27. Structures of 1-p-SBF, 1-mbp-SBF, 1-mtp-SBF [90].

1.2.4. Charge transporting materials

Carbazole (Cz) contains an electron donating nitrogen (N) atom, and also exhibits interesting photophysical characteristics, such as high fluorescence, excellent hole transporting capability, and a high triplet energy. Scholars managed to synthesize and present new Cz derivatives with AIE luminogens (triPE and tetraPE) at either the C-2, C-3, or N-9 positions of the Cz moiety, **Fig. 28** [91]. Electrochemical stability was found for Cz derivatives substituting at the C-3 position. The maximum PL wavelengths of these compounds are between 472–498 nm. The highest PLQY of 43.9% was observed for the solid sample of ECz-Tetr-Ortho. The PE spectrum of the compounds' solid films revealed similar IP for the C-2 substituted Cz compounds and C-3 substituted Cz compound (5.49–5.65 eV), but a slightly higher value for N-9 substituted Cz derivatives at 5.74 eV was determined. In the solid films of C-9 substituted Cz compound, the holes drift mobilities reached $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [91].

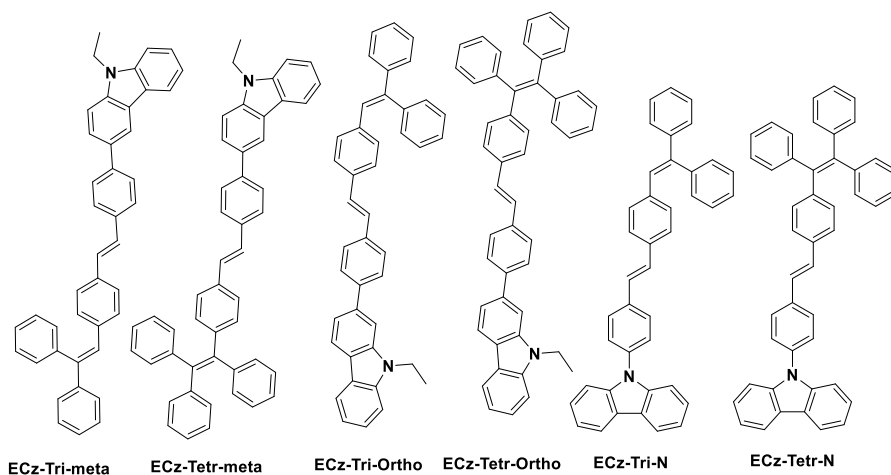
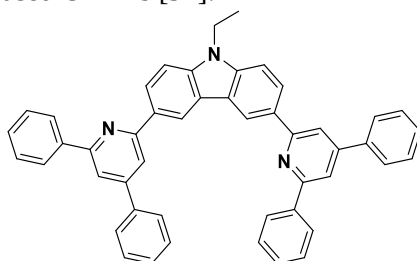


Fig. 28. Structures of tri- or tetraphenylethylene-substituted phenyl [91].

The author described an integrated HTM, 3,6-bis(4,6-diphenylpyridin-2-yl)-9-ethyl-9H-carbazole (CDP), **Fig. 29** [92], by functionalizing the carbazole moiety with pyridine substituents. CDP had a moderately high triplet energy, good thermal stability, and excellent hole transportability. CDP was chosen as an HTM based on electrochemical and optical investigations. As an emissive material, the OLED device with a green phosphorescent OLED was tested.

Solution-processed CDP-based OLEDs were fabricated containing phosphorescent green emitter ($\text{Ir}(\text{PPy})_3$) and compared with conventional N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) based OLEDs. The CDP-based OLEDs displayed a superior performance with its decreased layer thickness of 25–5 nm, and a maximum EQE, PE, and brightness of 17.2%, 66.8 lm/W, 64.0 cd/A and 18,740 cd/m², respectively. This material clearly demonstrated an enhancement in the device performance due to a reduced thickness of the hole transport layer in CDP based OLEDs [92].



CDP

Fig. 29. Structure of CDP [92].

Solution-processed OLEDs using a TADF material as the emitter have garnered considerable interest. A novel high triplet energy and crosslinkable HTM grafted with oxetane groups, N,N-bis(4-(6-((3-ethyloxetan-3-yl)

methoxy)hexyloxy)phenyl)-3,5-di(9H-carbazol-9-yl)benzenamine (Oxe-DCDPA)), **Fig. 30** (93), was proposed as double HTLs, composed of N,N'-bis(4-(6-(3-ethyloxetan-3-yl)methoxy)-N,N'-diphenyl-4,4'-diamine with high hole mobility and Oxe-DCDPA with a high triplet energy.

For solution-processed TADF OLED, X-DCDPA was used as HTL for the first time to insert between HIL and EML via the additional step for promoting hole injection while preventing exciton quench by PEDOT: PSS layer and energy transfer from EML to HTL, and providing electron and exciton blocking ability. This resulted in a high EQE/L of 26.1%/94.8 cd A⁻¹ for the green emission and 24.0%/74.0 cd A⁻¹ for the bluish-green emission. In addition, the researchers employed the twin HTLs, X-OTPD/ X-DCDPA, for the green and bluish-green devices, thereby boosting their EQE/L to 30.8%/111.9 cd A⁻¹ and 27.2%/83.8 cd A⁻¹, respectively. Both figures are additional records for the highest TADF OLEDs handled by a solution [93].

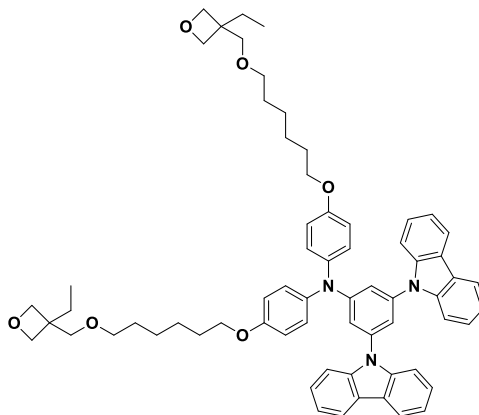


Fig. 30. Structures of Oxe-DCDPA [93].

New Cz-based emitters including tetra-/triphenylethene, **Fig. 31**, units have been created to increase the efficiency of non-doped OLEDs. Depending on the replacement pattern, the emitters displayed an intense blue or green emission which was augmented by aggregation. The authors synthesized Cz derivatives containing one or two tri/tetraphenylethenyl moieties as OLED emitters exhibiting PLQY in the solid-state due to AIE amplification. At high electric fields, the *time-of-flight* (ToF) hole drift mobilities of compounds with two substituents reached 10⁻³ cm²/V. OLEDs based on a Cz derivative with two tetraphenylethenyl substituents linked through the nitrogen atom in the C-3 position of the carbazole moiety exhibited the highest maximum brightness exceeding 50000 cd/m² along with a high maximum current, power, and EQE of 17 cd/A, 9.2 lm/W, and 5.32% respectively. Both their hole-injecting and hole-transporting characteristics were exceptional [94].

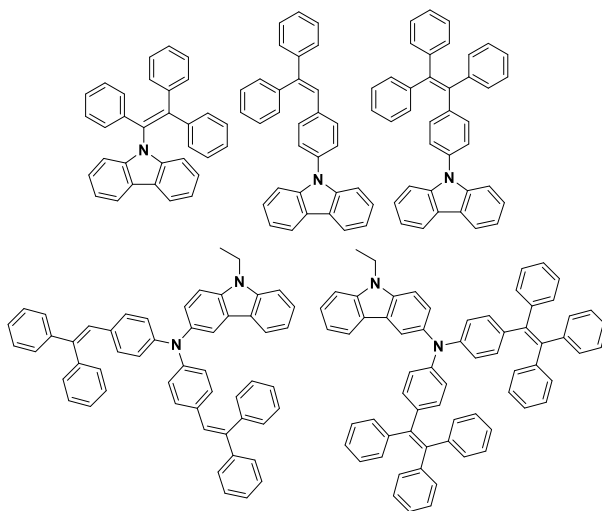


Fig. 31. Cz-based HTMs with tetra-/triphenylethene moieties [94].

In the current study [95], a variety of fluorinated phenylpyridine-based ETMs were synthesized based on 3,5,3',5'-tetra-3-pyridyl-[1,1';3',1'']terphenyl (B3PyPB). The effect of the F atom(s) in the core skeleton on their physical characteristics, such as the molecule orientation, electron transport, and electron injection, were studied. The monofluorinated ETM possessed a relatively large orientation order parameter of 0.23 and an electron mobility of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which was 10 times greater than that of its nonfluorinated counterpart due to concerted intermolecular interactions involving not only the hydrogen bonds but also the aromatic fluorine atoms, in addition to π - π stacking.

In order to improve the molecular orientation of these ETMs, the substitution position(s) of the F atom(s) is/are of utmost importance. Notably, a FIrpic-based blue PhOLED constructed with B3PyMFB as an ETM displayed a low operating voltage of 3.5 V at 1000 cd/m^2 brightness. Therefore, the authors suggested that fluorinated ETMs will aid in the decrease of the OLEDs' operating voltage. In addition, this study should shed light on the evolution of ETMs of the future generation [95].

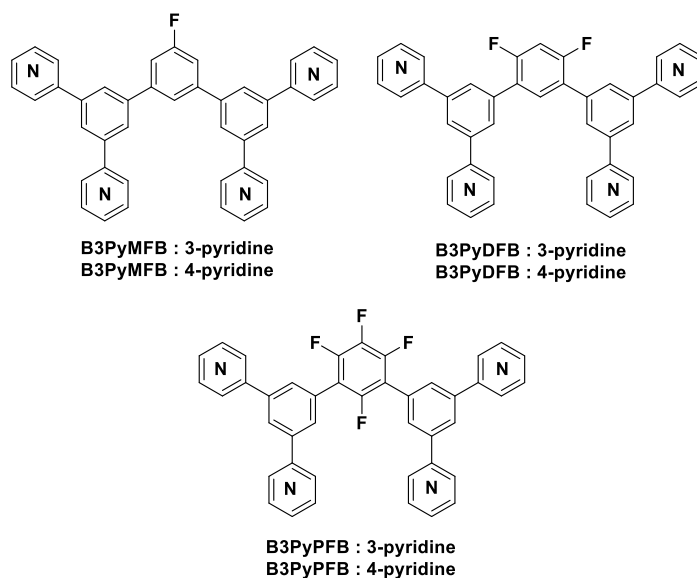


Fig. 32. Structures of fluorinated ETMs [95].

1.3. Conclusion of the literature review

Although the OLED technology has substantially developed during recent years, it still suffers from such drawbacks as short lifetimes and color purities, and commercially available OLEDs' efficiencies are limited to 25–30% EQE. Even with these drawbacks, OLEDs offer possibilities including thin, bright, and flexible displays. The ideal way to increase the efficiency of OLEDs is to harvest the high radiative constant and delayed fluorescence properties from electrochemically and thermally stable D-A type emitter materials.

The architecture of the 3rd generation materials increases the PLQY of the materials. These materials suffer from ACQ, which results in a decreased PLQY; yet, this drawback can be fixed with host materials which are used as dopants. To break free of this dopant strategy, materials with bipolar charge transport, solid-state luminescence, and AIE/AIEE materials are being studied and investigated. The luminescence intensity and color of the emission can be influenced via the manipulation of the conformational arrangements or molecular packing. Polymeric materials displayed promising characteristics, such as efficient solution processable devices with strong EQE. The charge transporting properties play an important role in organic devices. In the literature, the design strategy for materials with strong charge transporting properties has been discussed, and it has been revealed that Cz and TPE based materials exhibited better performance in real-life devices. One of

the hardest difficulties to overcome is to design a multifunctional delayed fluorescence material with tunable color emission, which would be an ideal candidate to improve the EQE of OLEDs.

Based on the literature review, in our work, we have investigated and presented the possibilities of applying organic electroactive materials in various aspects of organic electronics, such as addressing the problems of ACQ, discussing steric hindrance properties and their impact on the donor and acceptor moieties, and the approach towards polymeric materials in pursuit to improve the charge mobilities of the devices and tri-donor materials so that to enhance the hole transporting properties of the devices.

2. EXPERIMENTAL

2.1. Instrumentation

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded by using *Bruker DRX 400 P* (400 MHz (^1H), 100 MHz (^{13}C)) and *Bruker AVN III 600* MHz. Heteronuclear single quantum coherence spectroscopy (HSQC) and correlation spectroscopy (COSY) measurements were performed with *Bruker AVN III* (600 MHz (^1H), 151 MHz (^{13}C)) in deuterated chloroform (CDCl_3). Chemical shifts (δ) are reported in ppm referenced to tetramethyl silane (TMS). UV/Vis spectra of 10^{-4} M solutions and thin films of the compounds were recorded by using quartz cells with a *Perkin Elmer Lambda 35* spectrometer. The PL spectra of 10^{-5} M solutions and thin films were recorded by using *Edinburgh Instruments FLS980 Fluorescence Spectrometer*. Thin solid films were prepared by the drop casting technique from 1 mg/ml solution of a compound in THF. Differential scanning calorimetry (DSC) measurements were made with *TA Instruments DSC Q2000*. The samples were heated at a scan rate of 10 $^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere. Thermal gravimetric analysis (TGA) measurements were performed with *TA_TGA Q50* at a heating rate of 20 $^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere. Electrochemical analysis was performed with a *micro-Autolab III* instrument equipped with the standard three-electron configuration. The CV three-electrode cell contained a glassy carbon working electrode, an Ag/Ag reference electrode, and a platinum wire counter electrode. Measurements were made for anhydrous THF with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The measurements were calibrated by using a ferrocene/ferrocenium (Fc) system, as an internal standard. Single crystals for X-ray diffraction analysis of the target compounds were obtained by the slow evaporation technique while using mixtures of various solvents (acetonitrile, methanol, and dichloromethane). Crystallographic analysis was performed by employing XtaLAB mini diffractometer (*Rigaku*) with a monochromated graphite Mo K α ($\lambda = 0.71075$ Å) X-ray source. The measurements were performed at room temperature. The crystallographic data for the structures reported in this paper have been deposited in the *Cambridge Crystallographic Data Centre* with CCDCs Nos. 2004089, 2004090 and 2004091, respectively. The copies of the data can be obtained free of charge on application to CCDC (*The Cambridge Structural Database* (CSD), *The Cambridge Crystallographic Data Centre* (CCDC), (<http://www.ccdc.cam.ac.uk/solutions/csd-system/components/csd/>)). The calculations and visualization of the structures were performed by using the *OLEX2* [96] crystallographic software package except for refinement which was performed with *SHELXL* [97]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were included in the structure factor at idealized positions by using a riding model and were refined isotropically.

The ionization potentials (IP^{PE}) of the layers of the synthesized compounds were measured by the electron photoemission in air method [98]. The hole drift mobility of the materials was estimated by using the *time-of-flight* (ToF) method.

The samples were fabricated with the structures ITO/compound/Al. Commercial *indium tin oxide* (ITO) coated glass was used as a substrate which was initially chemically cleaned by using a bath of distilled water and acetone. Al films were sequentially vacuum deposited onto precleaned ITO-coated glass substrates under a vacuum of $2\text{--}5\times 10^{-6}$ mBar by using vacuum equipment developed by *Kurt J. Lesker*; the vacuum equipment was built in an *MB EcoVap4G* glovebox. In the ToF experiments, charges were generated by a pulsed third-harmonic Nd:YAG laser *EKSPLA NL300* working at a pulse duration of 3–6 ns and the wavelength of 355 nm. Electric fields were applied by using a *Keithley 6517B* electrometer. A digital storage oscilloscope *Tektronix TDS 3032C* was used to record ToF transients. The drift mobility was calculated by using the formula $\mu=d^2/U\cdot t_t$, where d is the layer thickness, and U is the surface potential at the moment of illumination, t_t is the transit time which was estimated from the intersection point of two slopes on the ToF transient plots built on a log-log scale. *Density Functional Theory* (DFT) and *Time Dependent-DFT* (TD-DFT) calculations employing the B3LYP functional and 6-31G(d,p) basis set were performed with *Gaussian 16* software.

2.2. Device Fabrication

A *SPIN150-v³* spin-coater developed by *Semiconductor Production Systems* was used for the deposition of TFB layers and EML. P1 ($M_n=16100$) and P2 ($M_n=5500$) were utilized for EML deposition. 200 and 150 μl of solutions of TFB and EML, respectively, with 4 mg/ml concentration were poured onto 2×1.5 cm ITO substrate and spin-coated with 4000 rpm, 375 rpm/s for 30 s. The ITO substrate was then placed on a heating plate with a temperature of 180 °C for 40 min for thermal annealing and securing the HTL layer and 50 °C for 30 min after EML deposition (when EML was made by spin-coating), respectively. The other layers were deposited by using the method of thermal vacuum evaporation, and *Kurt J. Lesker* equipment was in-built in an *MB EcoVap4G* glove box with a rate of deposition of few Å/sec under the pressure of 2×10^{-6} mBar. The current density-voltage and brightness-voltage correlations were measured simultaneously by using a *6517B* electrometer, a *Keithley 2400C* sourcemeter, a calibrated *PH100-Si-HA-D0* photodiode, and a *11S-LINK* Power and Energy Monitor. *AvaSpec-2048XL* was used for the measurement of *electroluminescent spectra* (EL) of OLEDs. An *Edinburgh Instruments FLS980* microsecond lamp was additionally used for TREL measurements along with the equipment for EL characterization.

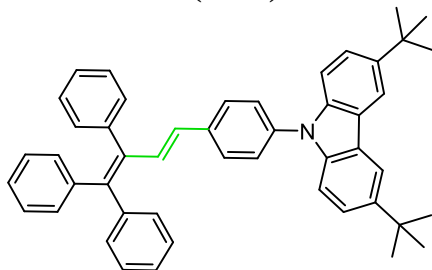
2.3. Materials

2.3.1. Synthesis of compounds 1–4

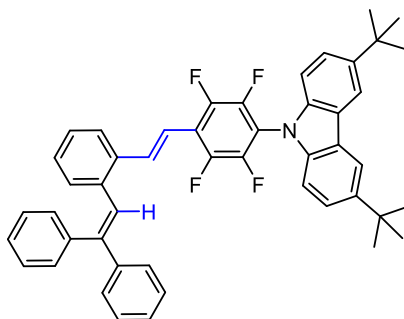
9,9-Dimethyl-9,10-dihydroacridine, palladium (II) acetate ($\text{Pd}(\text{OAc})_2$), tris(*o*-tolyl) phosphine ($\text{P}(\text{o-tol})_3$), dimethylformamide (DMF), triethylamine (TEA), 1-bromo-1,2,2-Triphenylethene, 2,3,4,5,6-pentafluoro-styrene, 4-bromo-styrene were purchased from *Aldrich* and used as received.

3,6-Di-*tert*-butyl-9H-carbazole was synthesized according to the procedure reported in [99]. 3,6-Di-*tert*-butyl-9-(4-vinylphenyl)-9H-carbazole (**CzS**) and 10-(4-vinylphenyl)-9,9-dimethyl-9,10-dihydroacridine (**AcS**) were synthesized by the Buchwald-Hartwig coupling reaction [100]. 3,6-Di-*tert*-butyl-9-(2,3,5,6-tetrafluoro-4-vinylphenyl)-9H-carbazole (**CzS-F**) and 10-(2,3,5,6-tetrafluoro-4-vinylphenyl)-9,9-dimethyl-9,10-dihydroacridine (**AcS-F**) were prepared by the previously reported procedure [101].

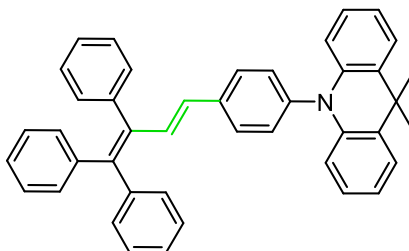
General procedure for the synthesis of compounds 1–4. Compound **CzS**, **CzS-F**, **AcS** or **AcS-F** (1 eq), 1-bromo-1,2,2-Triphenylethene (1.5 eq), Pd(OAc)₂ (0.01 eq), P(*o*-tol)₃ (0.045 eq) were added to a pre-dried Schlenk flask and degassed. Then, an inert atmosphere was introduced, dry DMF and TEA were added at the end, and the mixture was heated at 110 °C for 14 h. The reaction was monitored by thin layer chromatography. The mixture was poured into cold water and extracted with ethyl acetate, concentrated under vacuum, and the crude product was purified by column chromatography by using hexane: dichloromethane (5:1) as eluent. The target product was recrystallized from isopropanol, acetonitrile, methanol (MeOH) or dichloromethane (DCM).



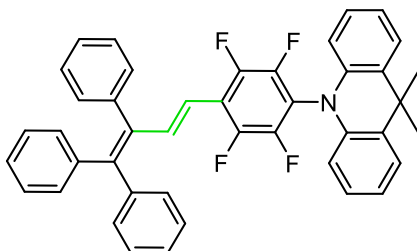
3,6-Di-*tert*-butyl-9-(4-((*E*)-3,4,4-triphenylbuta-1,3-dienyl)phenyl)-9H-carbazole (1) was prepared according to the general procedure using **CzS** (0.50 g, 1.31 mmol), 1-bromo-1,2,2-Triphenylethene (0.65 g, 1.96 mmol), Pd(OAc)₂ (0.003 g, 0.013 mmol), P(*o*-tol)₃ (0.017 g, 0.058 mmol), TEA (3 ml) and DMF (10 ml) to acquire white crystals with 42% yield (0.42 g). *M*_p = 240–243 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.04 (d, *J* = 1.7 Hz, 2H), 7.56–7.23 (m, 19H), 7.13–7.05 (m, 3H), 7.01–6.95 (m, 2H), 6.27 (d, *J* = 16.0 Hz, 1H), 1.50 (s, 18H). ¹³C NMR (151 MHz, CDCl₃) δ 143.25, 142.89, 142.85, 142.50, 140.48, 139.12, 138.93, 137.11, 136.42, 131.75, 131.54, 131.33, 131.16, 128.08, 128.01, 127.69, 127.53, 127.40, 126.82, 126.66, 126.37, 123.60, 123.40, 116.23, 109.28, 34.75, 32.04. Elemental analysis calcd (%) for C₄₈H₄₅N: C, 90.66; H, 7.13; N, 2.20; Found: C, 90.71; H, 7.16; N, 2.25.



3,6-Di-*tert*-butyl-9-(2,3,5,6-tetrafluoro-4-((*E*)-3,4,4-triphenylbuta-1,3dienyl)phenyl)-9H-carbazole (2) was prepared according to the general procedure using **CzS-F** (0.2 g, 0.44 mmol), 1-bromo-1,2,2-Triphenylethene (0.22 g, 0.66 mmol), Pd(OAc)₂ (0.001 g, 0.0044 mmol), P(*o*-tol)₃ (0.006 g, 0.019 mmol), TEA (3 ml) and DMF (10 ml). The target product was crystallized from the mixture of MeOH and DCM to acquire yellow crystals with 50% yield (0.155 g). *M_p* (DSC) = 166 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 1.5 Hz, 2H), 7.59 (d, *J* = 16.4 Hz, 1H), 7.41–7.27 (m, 6H), 7.22–7.13 (m, 6H), 7.01–6.93 (m, 5H), 6.87 (dd, *J* = 6.5, 3.0 Hz, 2H), 6.27 (d, *J* = 16.4 Hz, 1H), 1.38 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 146.58, 143.94, 142.33, 141.79, 139.28, 138.79, 138.41, 131.45, 131.12, 131.06, 128.22, 128.11, 128.00, 127.45, 127.17, 126.82, 123.99, 123.95, 116.48, 109.31, 34.76, 31.97. Elemental analysis calcd (%) for C₄₈H₄₁F₄N: C, 81.45; H, 5.84; F, 10.74; N, 1.98; Found: C, 81.49; H, 5.79; N, 2.02.



10-(4-((*E*)-3,4,4-triphenylbuta-1,3-dienyl)phenyl)-9,9-dimethyl-9,10-dihydro-acridine (3) was prepared according to the general procedure using **AcS** (0.44 g, 1.41 mmol), 1-bromo-1,2,2-Triphenylethene (0.71 g, 2.11 mmol), Pd(OAc)₂ (0.0031g, 0.0141 mmol), P(*o*-tol)₃ (0.0193g, 0.063 mmol), TEA (3 ml) and DMF (10 ml). The target product was crystallized from the mixture of MeOH and DCM to acquire yellow crystals with 43% yield (0.338 g). *M_p* = 253–255 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.50–7.16 (m, 18H), 7.12–7.01 (m, 3H), 6.99–6.86 (m, 5H), 6.28 (d, *J* = 16.0 Hz, 1H), 6.20 (dd, *J* = 7.9, 1.1 Hz, 2H), 1.67 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 143.52, 142.77, 142.41, 140.87, 140.40, 140.07, 138.85, 137.69, 132.21, 131.61, 131.50, 131.39, 131.28, 131.12, 129.99, 128.74, 128.07, 128.01, 127.55, 127.38, 126.82, 126.39, 126.32, 125.18, 120.51, 114.03, 35.95, 31.22. Elemental analysis calcd (%) for C₄₃H₃₅N: C, 91.29; H, 6.24; N, 2.48; Found: C, 91.24; H, 6.28; N, 2.51.

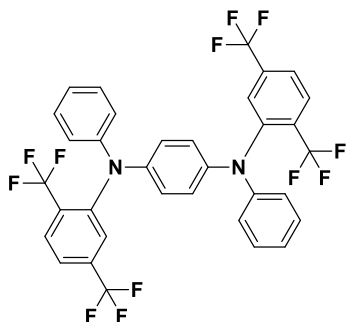


10-(2,3,5,6-tetrafluoro-4-((E)-3,4,4-triphenylbuta-1,3-dienyl)phenyl)-9,9-dimethyl-9,10-dihydro-9,9-dimethyl acridine (4) was prepared according to the general procedure using **AcS-F** (0.2 g, 0.521 mmol), 1-bromo-1,2,2-Triphenylethene (0.26 g, 0.78 mmol), $\text{Pd}(\text{OAc})_2$ (0.001g, 0.00521 mmol), tris(*o*-tolyl)phosphine (0.00714g, 0.0234 mmol), TEA (3 ml) and DMF (10 ml). The target product was crystallized from the mixture of acetonitrile and DCM to acquire yellow crystals with 14% yield (0.049 g). $M_p = 234\text{--}236\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 16.4$, 1H), 7.40 (dd, $J = 7.5$, 1.6 Hz, 2H), 7.45–7.19 (m, 11H), 7.10–6.90 (m, 8H), 6.40–6.29 (m, 3H), 1.67 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.78, 142.28, 141.75, 139.24, 138.77, 131.42, 131.21, 131.11, 131.05, 128.22, 128.11, 128.03, 127.45, 127.18, 126.84, 125.38, 122.03, 117.14, 112.94, 36.09, 30.49. Elemental analysis calcd (%) for $\text{C}_{43}\text{H}_{31}\text{F}_4\text{N}$: C, 80.99; H, 4.90; F, 11.92; N, 2.20; Found: C, 81.02; H, 4.94; N, 2.25.

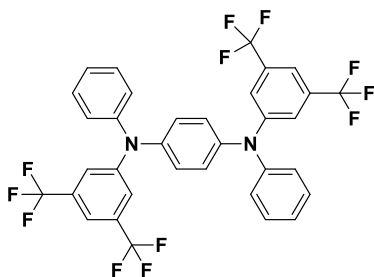
2.3.2. Synthesis of compounds 5–8

*N*1,*N*1,*N*4-diphenylbenzene-1,4-diamine, *N*1,*N*4-di(naphthalen-2-yl)benzene-1,4-diamine, 1-bromo-3,5-bis(trifluoromethyl)benzene and 2-bromo-1,4-bis(trifluoromethyl)benzene were purchased from *Fluorochem*. $\text{Pd}(\text{OAc})_2$, tris(dibenzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$), sodium *tert*-butoxide (*t*-BuONa), tri-*tert*-butylphosphine ($\text{P}(\text{t-Bu})_3$) solution 1.0 M in toluene, and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (X-phos) were purchased from *Aldrich*. All commercial materials were used as received.

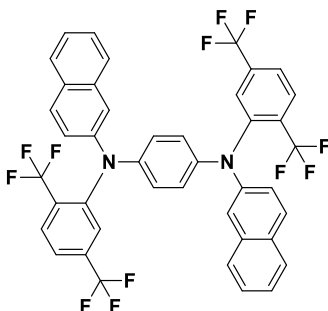
General procedure for the synthesis of compounds 5-8. To a Schlenk tube, diamines (1 eq.), bromo-trifluoromethyl benzene (2.2 eq.), *t*-BuONa (3 eq.) and 15 ml of anhydrous *Toluene* (TOL) were added. The reaction mixture was degassed by bubbling with argon for 15 min under stirring. Then, $\text{Pd}(\text{OAc})_2$ (0.15 eq.), $\text{P}(\text{t-Bu})_3$ (0.05) or $\text{Pd}_2(\text{dba})_3$ 0.08 eq.) and X-Phos (0.32 eq.) were added, and the reaction mixture was degassed for another 10 min. The reaction mixture was stirred at 110 $^\circ\text{C}$ under an argon atmosphere. After 14 h, the reaction mixture was cooled down to room temperature and extracted with ethyl acetate. The organic phase was dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The product was purified by column chromatography by using *dichloromethane* (DCM) and hexane in a volume ratio of 1:5 as an eluent. The product was crystallized from the eluent giving the target materials.



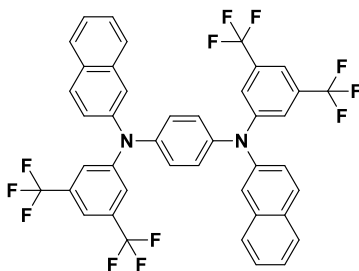
N1,N4-bis(2,5-bis(trifluoromethyl)phenyl)-N1,N4-diphenylbenzene-1,4-diamine (5) was prepared by the general procedure using N1,N4-diphenylbenzene-1,4-diamine (0.2 g, 0.76 mmol), 2-bromo-1,4-bis(trifluoromethyl)benzene (0.28 ml, 1.67 mmol), *t*-BuONa (0.21 g, 2.28 mmol), Pd₂(dba)₃ (0.054 g, 0.06 mmol) and X-Phos (0.114 g, 0.24 mmol). The product was crystallized from the eluent, giving yellowish crystals with a yield of 45% (0.23 g). ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.53–7.56 (m, 4H), 7.21–7.26 (m, 4H), 6.99 (t, *J* = 7.3 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 4H), 6.83 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 147.74, 146.29, 142.93, 135.70, 135.37, 132.04, 131.73, 129.36, 129.31, 129.19, 129.06, 129.02, 124.28, 124.08, 122.64, 122.32, 122.28, 122.10, 121.60, 121.31, 121.35. MS (APCI⁺), *m/z* = 684 [M⁺].



N1,N4-bis(3,5-bis(trifluoromethyl)phenyl)-N1,N4-diphenylbenzene-1,4-diamine (6) was prepared by general procedure using N1,N4-diphenylbenzene-1,4-diamine (0.5 g, 1.9 mmol), 1-bromo-3,5-bis(trifluoromethyl)benzene (0.74 ml, 2.97 mmol), *t*-BuONa (0.6 g, 6.65 mmol) and 15 mL of anhydrous TOL. Pd(OAc)₂ (0.034 g, 0.285 mmol) and P(*t*-Bu)₃ (0.036 ml, 0.108 mmol) yield of white crystals 45% (0.55 g). ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.39 (m, 10H), 7.21–7.26 (m, 6H), 7.07 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 149.09, 145.80, 142.66, 133.04, 132.71, 132.38, 132.06, 130.09, 126.36, 125.53, 125.28, 124.57, 121.86, 120.46, 114.30. MS (APCI⁺), *m/z* = 684 [M⁺].



N1,N4-bis(2,5-bis(trifluoromethyl)phenyl)-N1,N4-di(naphthalen-2-yl)benzene-1,4-diamine (7) was synthesized by general procedure using N1,N4-di(naphthalen-2-yl)benzene-1,4-diamine (0.5 g, 1.35 mmol), 2-bromo-1,4-bis(trifluoromethyl)benzene (0.51 ml, 2.97 mmol), *t*-BuONa (0.385 g, 4.05 mmol), Pd(OAc)₂ (0.024 g, 0.108 mmol) and P(*t*-Bu)₃ (0.025 ml, 0.108 mmol). The resin-like product was precipitated into isopropanol. The yield of a yellowish solid was 46% (0.50 g). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.72–7.77 (m, 4H), 7.61–7.60 (m, 6H), 7.43–7.35 (m, 4H), 7.17–7.22 (m, 4H), 6.90 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 146.24, 145.37, 143.11, 135.78, 135.48, 134.14, 131.98, 131.73, 129.91, 129.42, 129.10, 129.05, 129.02, 127.64, 127.00, 126.56, 124.73, 124.54, 124.47, 124.31, 124.12, 122.66, 122.51, 121.55, 121.31, 118.54. MS (APCI⁺), *m/z* = 784 [M⁺].



N1,N4-bis(3,5-bis(trifluoromethyl)phenyl)-N1,N4-di(naphthalen-2-yl)benzene-1,4-diamine (8) was synthesized by the general procedure using N1,N4-di(naphthalen-2-yl)benzene-1,4-diamine (0.5 g, 1.35 mmol), 1-bromo-3,5-bis(trifluoromethyl)benzene (0.51 ml, 2.97 mmol), *t*-BuONa (0.385 g, 4.05 mmol), Pd(OAc)₂ (0.024 g, 0.108 mmol) and P(*t*-Bu)₃ (0.025 ml, 0.108 mmol). The resin-like product was precipitated into isopropanol. The yield of a yellowish solid was 71% (0.78 g). ¹H NMR (400 MHz, CDCl₃) δ 7.83–7.88 (m, 4H), 7.75–7.67 (m, 2H), 7.58 (s, 2H), 7.45–7.51 (m, 8H), 7.42 (s, 2H), 7.32 (dd, *J* = 8.8, 2.2 Hz, 2H), 7.14 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 149.07, 143.32, 142.78, 134.36, 133.17, 132.84, 132.51, 132.18, 131.14, 130.12, 127.80, 127.35, 126.86, 126.45, 125.81, 124.55, 124.43, 122.79, 121.84, 120.89, 114.68. MS (APCI⁺), *m/z* = 784 [M⁺].

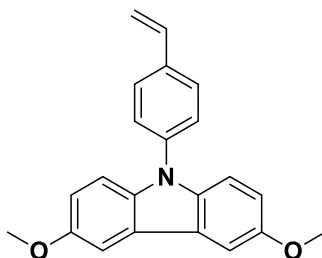
2.3.3. Synthesis of compounds 9–12

3,6-Dimethoxy-9H-carbazole, 1-bromo-4-vinylbenzene, 1-bromo-3-vinylbenzene, $\text{Pd}_2(\text{dba})_3$ (*Sigma-Aldrich*, 97%), X-Phos, *t*-BuONa, deuterated chloroform (CDCl_3), chloroform (CHCl_3), DCM, hexane, ethyl acetate, MeOH and ethanol were purchased from *Sigma-Aldrich* and used as received.

2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) was synthesized according to the procedure published in [102]. 2,2'-Azobisisobutyronitrile (AIBN) (2,2') (*Sigma-Aldrich*, >98%) was recrystallized from ethanol.

Cyclohexanone (*Sigma-Aldrich*, $\geq 99\%$) was dried overnight with CaH_2 and then distilled from CaH_2 under reduced pressure. THF (*Sigma-Aldrich*, >99%) was treated with sodium and distilled twice in an inert atmosphere. TOL (*Eurochemicals*) was dried by heating under reflux over sodium in the presence of benzophenone as an indicator and then distilled under an inert atmosphere.

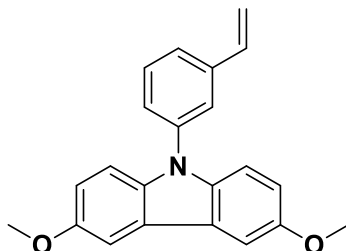
General procedure for the synthesis of monomers 9–10. In a Schlenk tube with a magnetic stirrer, dimethoxy-9H-carbazole (1 eq), 1-bromo-4-vinylbenzene (1.1 eq) or 1-bromo-3-vinylbenzene (1.1 eq), *t*-BuONa (2 eq) and anhydrous TOL were added. The reaction mixture was degassed and purged with argon for 15 min under stirring. Then, $\text{Pd}_2(\text{dba})_3$ (0.02 eq) as a catalyst and X-Phos (0.04 eq) as a ligand were added. The reaction mixture was repeatedly degassed and purged with argon for another 10 min and stirred at 110 °C under an argon atmosphere. After 14 h, the reaction mixture was cooled down to room temperature and extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The product was purified by column chromatography while using DCM and hexane at a volume ratio of 1:5 as mobile phase.



3,6-Dimethoxy-9-(4-vinylphenyl)-9H-carbazole (9)

Dimethoxy-9H-carbazole (3 g, 13.2 mmol), 1-bromo-4-vinylbenzene (1.9 ml, 14.5 mmol), *t*-BuONa (2.54 g, 26.4 mmol), $\text{Pd}_2(\text{dba})_3$ (0.24 g, 0.26 mmol), X-Phos (0.25 g, 0.53 mmol) and 16 ml of anhydrous TOL were used. The product was crystallized from the eluent giving the target monomer. The yield of yellow crystals was 41% (1.8 g). ^1H NMR (400 MHz, CDCl_3) δ : 7.61 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 2.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.9 Hz, 2H), 7.04 (dd, J = 8.9 Hz, J = 2.5 Hz, 2H), 6.82 (dd, J = 17.6 Hz, J = 10.9 Hz, 1H), 5.84 (d, J = 17.6 Hz, 1H), 5.35 (d, J = 11.0 Hz, 1H), 3.95 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ : 154.07,

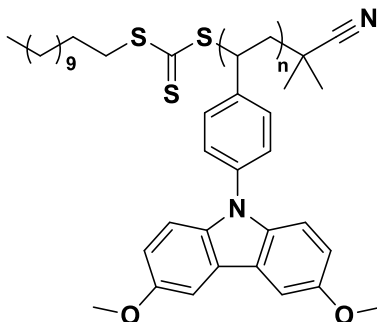
137.60, 136.19, 136.02, 127.54, 126.60, 123.68, 115.20, 114.47, 110.76, 102.92, 56.13. IR, cm^{-1} : 3059 (ar. C-H), 2941, 2931, (aliph. C-H), 2836 (O-CH₃), 1606, 1581 (ar. C=C), 1297, 1283 (C-N). MS (APCI⁺), m/z = 329 [M]⁺.



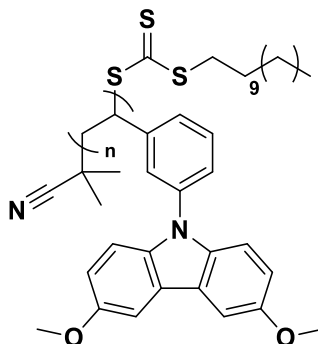
3,6-Dimethoxy-9-(3-vinylphenyl)-9H-carbazole (10)

Dimethoxy-9H-carbazole (1.7 g, 7.5 mmol), 1-bromo-3-vinylbenzene (1.07 ml, 8.2 mmol), *t*-BuONa (1.44 g, 15.0 mmol), Pd₂(dba)₃ (0.14 g, 0.15 mmol), X-Phos (0.14 g, 0.30 mmol) and 16 ml of anhydrous TOL were used. The brown resin was yielded at 85% (2.1 g). ¹H NMR (400 MHz, CDCl₃) δ : 7.58-7.51 (m, 4H), 7.44-7.33 (m, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.04 (dd, J = 11.8 Hz, J = 4.6 Hz 2H), 6.79 (dd, J = 17.6, 10.8 Hz, 1H), 5.81 (d, J = 17.6 Hz, 1H), 5.34 (d, J = 10.8 Hz, 1H), 3.95 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 154.04, 136.29, 136.10, 129.95, 126.01, 124.85, 123.61, 115.22, 110.72, 102.90, 56.15. IR, cm^{-1} : 3062 (ar. C-H), 2933, 2901, (aliph. C-H), 2830 (O-CH₃), 1604, 1573, 1488 (ar. C=C), 1290 (C-N). MS (APCI⁺), m/z = 330 [M⁺H]⁺.

General procedure for the synthesis of polymers 11–12. Polymerization was carried out under dry argon atmosphere in a Schlenk tube. Liquid reagents were transferred to the reactor via dry syringes against a continuous argon flow. In a typical polymerization experiment, 91.1 μL solution of DDMAT in cyclohexanone (0.05 M) and 151.8 μL solution of AIBN in cyclohexanone (0.01 M) were sequentially added to a solution containing **9** or **10** (100 mg) in cyclohexanone (60.7 μL). After three freeze-pump-thaw cycles, the reaction was started by immersing a Schlenk tube in an oil bath preheated to 70 °C. After a predetermined time, ca. 75 μL aliquots were withdrawn and poured into excess ethanol. The precipitated polymers were separated from the solution by centrifugation and then dried in vacuum at 50 °C. Before analysis, polymers were re-precipitated twice from chloroform to methanol. Monomer conversions were determined gravimetrically.



9-(4-(sec-butyl)phenyl)-3,6-dimethoxy-9H-carbazole (11) A precipitated polymer with 90% yield was acquired. ^1H NMR (400 MHz, CDCl_3) δ : 6.20–7.50 (m, 10H), 3.50–3.90 (m, 10H), 2.00–2.50 (m, 1H), 1.50–2.00 (m, 2H), 0.8–0.9 (m, 9H), 1.10–1.30 (m, 18H).

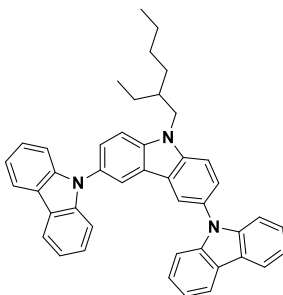


9-(3-(sec-butyl)phenyl)-3,6-dimethoxy-9H-carbazole (12) A precipitated polymer with 61% yield was acquired. ^1H NMR (400 MHz, CDCl_3) δ : 6.00–7.60 (m, 10H), 3.30–4.00 (m, 10H), 1.80–2.60 (m, 1H), 1.50–2.00 (m, 2H), 0.8–0.9 (m, 9H), 1.10–1.30 (m, 18H).

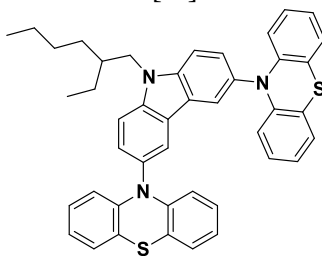
2.3.4. Synthesis of compounds 13–17

9H-Carbazole, *N*-Bromosuccinimide (NBS), 10H-phenothiazine, 10H-phenoxazine, 9,10-dihydro-9,9-dimethylacridine), *t*-BuONa and $\text{Pd}(\text{dba})_3$ were purchased from *Aldrich*. 2-Ethylhexyl bromide and dibenz[b,f]azepine were received from *TCI Chemicals*. X-phos was purchased from *Fluorochem*. Na_2SO_4 and KOH were received from *Eurochemicals*. 2,7-Dibromocarbazole and 2,7-dibromo-9-(2-ethylhexyl)carbazoleethylhexyl carbazole were synthesized according to the procedures published in [103].

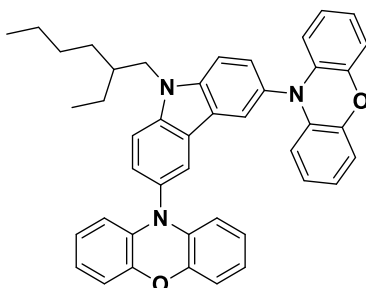
General procedure for the synthesis of compounds 13–17. 2,7-Dibromo-9-carbazole (1 eq.), arylamine (arylamine (2.2 eq.), $\text{Pd}(\text{dba})_3$ (0.08 eq.), X-Phos (0.32 eq.) and *t*-BuONa (3 eq.) were dissolved in anhydrous TOL. The solution was degassed and purged with argon for 15 min. The reaction mixture was then stirred at 110 °C under argon atmosphere. The completeness of the reaction was monitored by thin layer chromatography. After being cooled to room temperature, the reaction mixture was diluted with water and extracted with chloroform. The organic phase was dried over anhydrous Na_2SO_4 , filtered, and distilled. The products were purified by column chromatography.



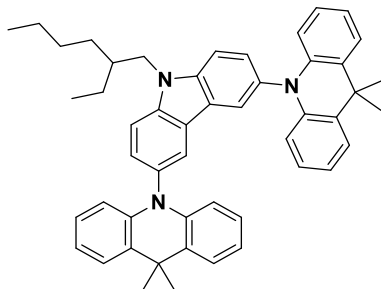
9'-(2-Ethylhexyl)-9'H-9,3':6',9''-tercarbazole (13) 1.3 g (2.97 mmol) of 3,6-dibromo-9-(2-ethylhexyl)carbazole, 1.09 g (6.54 mmol) of 9H-carbazole, 0.86 g (8.91 mmol) of *t*-BuONa, 0.22 g (0.24 mmol) of Pd(dba)₃, 0.45 g (0.95 mmol) of X-Phos, and 20 ml of anhydrous TOL were used. A mixture of hexane and dichloromethane at volume ratio 5:1 was used as an eluent. The yield of the product was 1.19 g with 66% efficiency. ¹H NMR (400 MHz, DMSO) δ : 8.57 (s, 2H), 8.25 (d, *J* = 7.7 Hz, 4H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 4H), 7.34 (d, *J* = 8.1 Hz, 4H), 7.27 (t, *J* = 7.3 Hz, 4H), 4.49 (d, *J* = 7.2 Hz, 2H), 2.17 (m, 1H), 1.53–1.20 (m, 8H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.85 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ : 141.52, 140.70, 128.89, 126.57, 125.86, 123.46, 122.55, 120.90, 120.52, 120.12, 111.60, 110.14, 47.63, 30.76, 28.60, 24.30, 23.06, 14.33, 11.27. MS (APCI⁺), *m/z* = 609.18 [M]⁺.



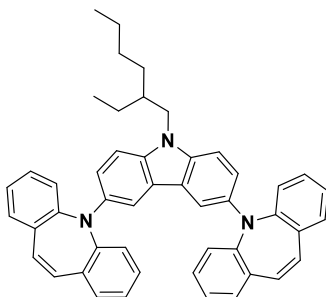
10,10'-(9-(2-Ethylhexyl)-9H-carbazole-3,6-diyl)bis(10H-phenothiazine) (14) 1.3 g (2.97 mmol) of 3,6-dibromo-9-(2-ethylhexyl)carbazole, 1.30 g (6.54 mmol) of 10H-phenothiazine, 0.86 g (8.91 mmol) of *t*-BuONa, 0.22 g (0.24 mmol) of Pd(dba)₃, 0.45 g (0.95 mmol) of X-Phos, and 20 ml of anhydrous TOL were used. A mixture of hexane and dichloromethane at volume ratio 5:1 was used as an eluent. The yield of the product was 1.1 g with 55% efficiency. ¹H NMR (400 MHz, DMSO) δ : 8.39 (s, 2H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 7.3 Hz, 4H), 6.87–6.79 (m, 8H), 6.15 (d, *J* = 8.0 Hz, 4H), 4.44 (d, *J* = 7.3 Hz, 2H), 2.12 (m, 1H), 1.45–1.21 (m, 8H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.81 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ : 144.82, 140.82, 131.99, 129.28, 127.64, 126.91, 124.21, 123.76, 119.01, 116.23, 112.63, 47.45, 30.70, 28.49, 24.39, 23.02, 14.25, 11.28. MS (APCI⁺), *m/z* = 673.54 [M]⁺.



10,10'-(9-(2-Ethylhexyl)-9H-carbazole-3,6-diyl)bis(10H-phenoxazine) (15) 1.3 g (2.97 mmol) of 3,6-dibromo-9-(2-ethylhexyl)carbazole, 1.20 g (6.54 mmol) of 10H-phenoxazine, 0.86 g (8.91 mmol) of *t*-BuONa, 0.22 g (0.24 mmol) of Pd(dba)₃, 0.45 g (0.95 mmol) of X-Phos, and 20 ml of anhydrous TOL were used. A mixture of hexane and dichloromethane at volume ratio 5:1 was used as an eluent. The yield of the product was 0.53 g with 27.8% efficiency. ¹H NMR (400 MHz, THF) δ: 8.06 (s, 2H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 6.51 (d, *J* = 7.7 Hz, 4H), 6.45 (t, *J* = 7.5 Hz, 4H), 6.39 (t, *J* = 7.6 Hz, 4H), 5.80 (d, *J* = 7.8 Hz, 4H), 4.29 (d, *J* = 7.6 Hz, 2H), 2.12 (m, 1H), 1.47–1.14 (m, 8H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.78 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, THF) δ: 144.00, 140.94, 135.20, 130.66, 128.27, 124.59, 123.13, 122.97, 120.80, 114.91, 113.41, 111.87, 47.51, 39.60, 30.87, 28.65, 23.06, 13.39, 10.26. MS (APCl⁺), *m/z* = 641.46 [M]⁺.



10,10'-(9-(2-Ethylhexyl)-9H-carbazole-3,6-diyl)bis(9,9-dimethyl-9,10-dihydroacridine) (16) 1.3 g (2.97 mmol) of 3,6-dibromo-9-(2-ethylhexyl)carbazole, 1.37 g (6.54 mmol) of 9,9-dimethyl-9,10-dihydroacridine, 0.86 g (8.91 mmol) of *t*-BuONa, 0.22 g (0.24 mmol) of Pd(dba)₃, 0.45 g (0.95 mmol) of X-Phos, and 20 ml of anhydrous TOL were used. A mixture of hexane and dichloromethane at volume ratio 5:1 was used as an eluent. The yield of the product was 1.16 g with 56.41% efficiency. ¹H NMR (400 MHz, CDCl₃) δ: 8.01 (s, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.46–7.41 (m, 6H), 6.95–6.88 (m, 8H), 6.33 (d, *J* = 7.7 Hz, 4H), 4.33 (d, *J* = 7.6 Hz, 2H), 2.22 (m, 1H), 1.70 (s, 12H), 1.56–1.32 (m, 8H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ: 141.66, 140.77, 132.68, 130.02, 129.06, 126.28, 125.09, 124.35, 123.27, 120.35, 114.27, 111.41, 48.10, 39.72, 36.01, 31.23, 28.87, 24.69, 23.14, 14.08, 11.11. MS (*m/z*): MS (APCl⁺), *m/z* = 694.32 [M+H]⁺.



5,5'-(9-(2-Ethylhexyl)-9H-carbazole-3,6-diyl)bis(5H-dibenzo[b,f]azepine)

(17) 1.3 g (2.97 mmol) of 3,6-dibromo-9-(2-ethylhexyl)carbazole, 1.83 g (6.54 mmol) of 5H-dibenzo[b,f]azepine, 0.86 g (8.91 mmol) of *t*-BuONa, 0.22 g (0.24 mmol) of Pd(dba)₃, 0.45 g (0.95 mmol) of X-Phos, and 20 ml of anhydrous TOL were used. A mixture of hexane and dichloromethane at volume ratio 5:1 was used as an eluent. The yield of the product was 0.56 g with 28.7% efficiency. ¹H NMR (400 MHz, DMSO) δ: 7.58–7.50 (m, 12H), 7.43 (t, *J* = 7.3 Hz, 4H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.85 (s, 4H), 6.25–6.23 (m, 4H), 3.91 (d, *J* = 7.2 Hz, 2H), 1.77 (m, 1H), 1.25–1.07 (m, 8H), 0.78–0.73 (m, 6H). ¹³C NMR (101 MHz, DMSO) δ: 144.11, 142.18, 136.86, 135.54, 131.22, 131.13, 130.87, 130.32, 127.41, 121.75, 112.28, 109.58, 101.46, 46.72, 30.51, 28.42, 23.99, 23.05, 14.23, 11.04. MS (*m/z*): MS (APCI⁺), *m/z* = 661.56 [*M*+H]⁺.

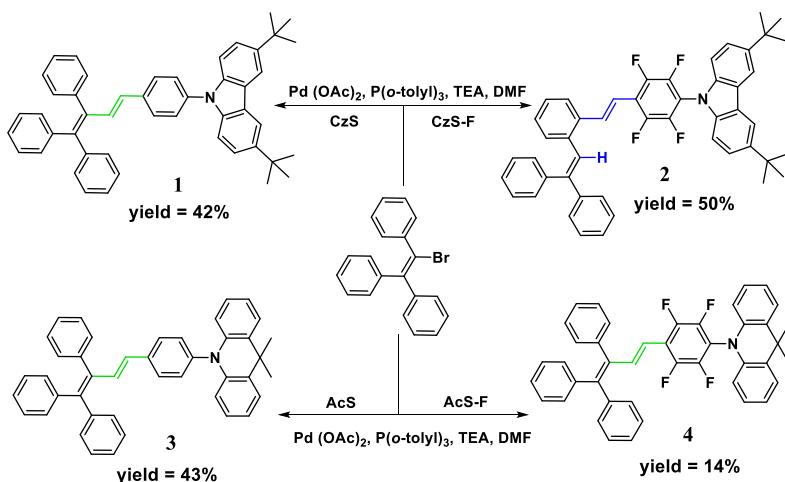
3. RESULTS AND DISCUSSION

3.1. Triphenylethene-based derivatives for blue non-doped organic light emitting diodes

This chapter is based on the work published by Ronit Sebastine Bernard, Galyna Sych, Sohrab Nasiri, Oleksandr Bezikonnyi, Dmytro Volyniuk, Jūratė Simokaitienė, Audrius Bučinskas, Dalius Gudeika, Azhar Ariffin, Juozas V. Gražulevičius. *Triphenylethene-based emitters exhibiting aggregation induced emission enhancement and balanced bipolar charge transport for blue non-doped organic light-emitting diodes* // Synthetic Metals 271 (2021) 116641. JIF: 3.266. DOI:10.1016/j.synthmet.2020.116641

Fluorescent materials displaying AIE/E gained a great deal of attention amongst researchers in the recent years due to their vast possibilities in applications of organic electronics [104]. *Triphenylethene* (TPE) and *tetraphenylethylene* (TEPE) derivatives have been widely studied due to their AIE and AIEE properties [105,106,107]. AIE and AIEE materials with heterocyclic compounds exhibit strong enhanced emission in the aggregate state [108]. These materials play a major role in solving the problem of *aggregation caused quenching* (ACQ) [109].

AIEE compounds **1–4** were synthesized by using the Heck coupling reaction, and the rare phenomenon of cyclopalladation (54,55) was observed for compound **2**. The structures of the compounds **1–4** and their yields are presented in **Scheme 1**.



Scheme 1. Synthetic routes for compounds **1–4**

The 5% weight loss temperatures of the synthesized compounds **1–4** in the range of 307–355 °C were estimated by TGA measurements. In the TGA curves, the substantial residue of carbonization was not observed, which suggests that

compounds **1–4** experienced sublimation during the experiment. Non-fluorinated compounds **1** and **3** exhibited higher 5% weight loss temperatures in comparison to their fluorinated analogues **2** and **4**. The DSC measurements revealed that all compounds were obtained as crystalline substances. During the 1st heating scan, compounds **1**, **2**, **3**, and **4** showed endothermic melting signals at the temperatures of 224, 166, 260 and 242 °C, respectively. Compounds **2** and **4** containing tetrafluorophenylene moieties showed lower melting points compared to non-fluorinated derivatives **1** and **3**. Apparently, this observation can be explained by the weaker intramolecular interactions between molecules in the crystals of compounds **2** and **4**. Although fluorine is ordinarily a stronger hydrogen bond donor, when attached to carbon in aromatic compounds, its ability to form a strong interaction with hydrogen is limited [110].

Table 1. Thermal characteristics of compounds **1–4**

Compound	T _d , °C	T _g , °C	T _m , °C	T _c , °C
1	355	123	244	-
2	343	104	166	-
3	326	100	260/257*	167
4	307	89	242	-
T _d : 5% weight loss temperature; T _g : glass transition temperature; T _m : melting point; T _c : crystallization temperature; * second heating scan				

CV was employed to investigate the reduction and oxidation processes of the synthesized compounds. The *IP of CV* (IP_{CV}) and the *electron affinity of CV* (EA_{CV}) values given in **Table 2** were determined from the onset of the oxidation and reduction waves of the CV curves. The values of IP_{CV} of compounds **2** and **4** containing tetrafluorophenylene moieties were found to be higher than for the corresponding compounds containing non-fluorinated phenylene units. Compounds **2** and **4** also showed higher EA_{CV} values than compounds **1** and **3**. The reversible oxidation of compounds **1** and **2** can be explained by the presence of *tert*-butyl groups at **C-3** and **C-6** positions of the carbazole moiety. They prevent electropolymerization, which is typical for carbazole derivatives having no substituents at positions **C-3** and **C-6**.

Photoelectron emission (PE) spectrometry was used for the estimation of the solid-state IP_{PE} of the compounds, see **Table 2**. They were found to be in the range of 5.88–6.37 eV. The results of PE measurements revealed the same trend as CV measurements. The values of IP_{PE} were found to be by 0.24–0.68 eV higher than those of IP_{CV}. This discrepancy can be explained by the different extent of aggregation of the molecules in the solution and the solid state.

The *highest occupied molecular orbitals* (HOMOs) of compounds **1** and **2** appear to be present throughout the molecules, while the HOMOs of compounds **3** and **4** are located on the electron-donating acridan fragment. The *lowest unoccupied molecular orbitals* (LUMOs) are localized in the phenyl, tetrafluorophenylene and TPE moieties. The absolute values of HOMO and LUMO energies (**Table 2**) are

considerably lower than the corresponding values of ionization potentials and electron affinities estimated by CV and PE measurements. This observation can be explained by the fact that the performed theoretical calculations did not consider the factor of the environment.

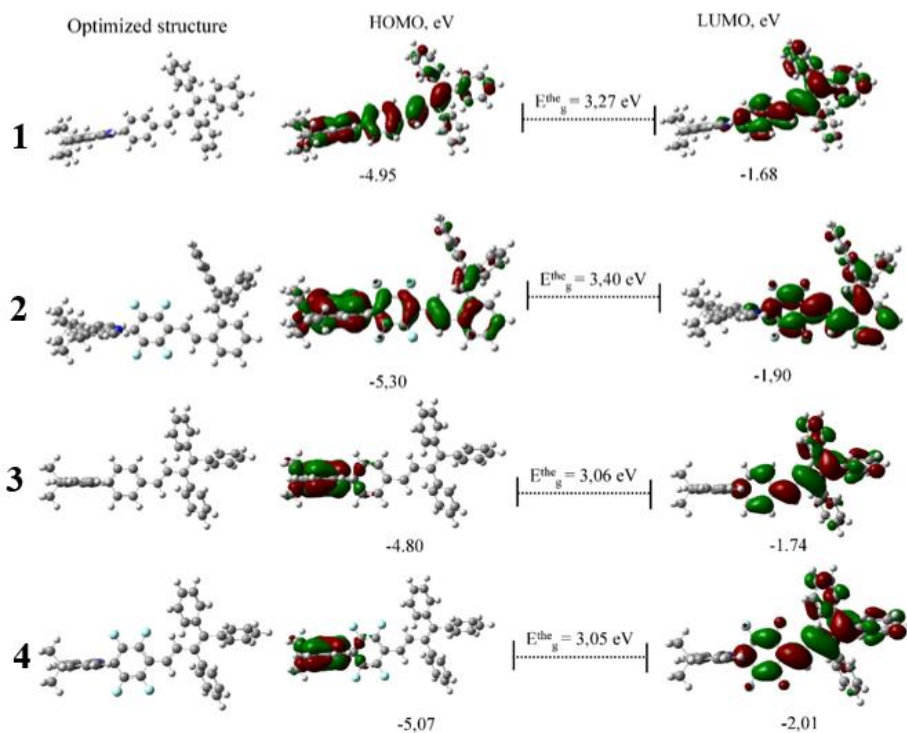


Fig. 33. Optimised structures and HOMO/LUMO energy levels calculated by using B3LYP/6-31G (d, p) basis set. Energy gap $E_g^{\text{theo}} = \text{HOMO} - \text{LUMO}$.

Table 2. Electrochemical and photoelectrical characteristics of materials

Compound	CV (DCM)				Theoretical values, eV		Solid films, eV		
	E_{ox}^a , V	E_{red}^a , V	IP_{cv}^b , eV	EA_{cv}^c , eV	HOMO ^d	LUMO ^d	IP_{PE}^e	EA^f	E_g^{opt} ^g
1	0.91	-2.00	5.71	2.80	-4.95	-1.68	6.02	2.72	2.83
2	1.14	-1.71	5.94	3.09	-5.30	-1.90	6.18	2.78	2.9
3	0.82	-2.26	5.62	2.54	-4.80	-1.74	5.88	3.08	2.84
4	0.89	-1.74	5.69	3.06	-5.07	-2.01	6.37	2.63	2.81

^aOnset of oxidation/reduction waves; ^b IP_{cv} – ionization potential (E_{ox} BS+4.8); ^c EA_{cv} – electron affinity (E_{red} +4.8); ^dTheoretically calculated energies (HOMO, LUMO); ^eIonization potential; ^fElectron affinity ($\text{IP}_{\text{PE}} - E_g$); ^gOptical bandgap ($1239.84 / \lambda_{\text{abs}}^{\text{film}}$).

PL and absorption spectra of dilute TOL, THF solutions (10^{-4} M) and neat films of the compounds were measured, and the corresponding data is collected in **Table 3**. The absorption spectra of the neat films of compounds **1–4** displayed a slight red shift of the *lowest energy band* (LEB) by 10–30 nm in comparison with the spectra of their solutions. This effect could be associated with the formation of aggregates and the intramolecular interactions of the compounds in the solid state. The PL spectra of compounds **2** and **4** showed positive solvatochromism due to the presence of electron-accepting tetrafluorophenylene moieties. The spectra of the films of the compounds contain peaks in the sky-blue region of 484–487 nm. The red shift of the maxima of the PL spectra of polar THF solutions with respect to those of TOL solutions of the donor-acceptor compounds **2** and **4** may be related to the *intramolecular charge transfer* (ICT). Consequently, the presence of electron donors and the tetrafluorophenylene moiety determines the ICT [111,112].

The THF solutions of compounds **1–4** exhibited lower PLQY than their films (**Table 3**). This observation can be attributed to AIEE. Due to the strong donation ability of acridine, compounds **3** and **4** have higher PLQY values in the solid state than the carbazole-based derivatives.

Fluorescence lifetimes (PL-decay) of the dilute THF solutions and neat films of target compounds were examined by recording the fluorescence decay curves with the corresponding exponential fits. The films showed prompt fluorescence. The PL-decays were adequately represented by double exponential fits with the lifetimes (τ_1 and τ_2) of several nanoseconds with the media-dependent fractional amount of intensity (**Table 3**). The fast component (τ_1) can be related to fast nonradiative annihilation of the excited states, while the slow component (τ_2) can be related to slow radiative relaxation of the excited states. In the solid state, compound **4** showed the highest fractional amount of intensity (66%) of the slow component with τ_2 of 9 ns (**Table 3**). This observation can be explained by efficient radiative relaxation of the excited states of compound **4**. As a result, OLED containing compound **4** as an emitter was characterized by the lowest roll-off efficiency as it shown below.

Table 3. Photophysical characteristics of materials

Compounds	$\lambda_{\text{abs}}/\lambda_{\text{em}}$ (nm)			η_{PL} (%) THF/Film	τ_1/τ_2 (χ^2) (ns)	
	THF	TOL	Film		THF	Film
1	361/452	363/448	372/484	0.1/17	0.71/3.16 (1.078)	0.85/3.80 (1.012)
2	348/463	357/432	362/487	11/16	0.53/4.27 (1.031)	0.53/2.17 (1.002)
3	339/492	338/471	347/478	2/29	1.10/2.44 (1.015)	0.89/4.18 (1.032)
4	347/532	350/458	360/486	1/18	0.66/2.34 (1.013)	1.083/9.055 (1.008)

λ_{abs} : wavelength of LEB for THF, TOL solutions and neat film; λ_{em} : wavelength of emission peak for THF, TOL solutions and neat films; η_{PL} : PLQY for THF solutions and neat films; τ_1/τ_2 : PL lifetimes.

To examine AIEE properties, compounds were dispersed in THF/water mixtures with *water fractions* (F_w) ranging from 0% to 95%. The PL spectra of the dispersions along with the plot of PL intensity versus the water fraction are shown in **Fig. 34**. As the studied compounds are not soluble in water, they tend to form aggregates with the increase of the water fraction in aqueous mixtures, thus causing **Mie scattering**, which is evident spectroscopically [113].

The redshift of the LEB of absorption spectra and the appearance of a spectral tail at long wavelengths in the water/THF mixtures (the Mie effect) manifest the formation of aggregates. Due to the ICT character of emission of the compounds, the redshifts of their emission wavelengths were caused by the increasing polarity of the THF/water mixtures when the water fraction was being increased. When the water fraction in the dispersions reached ca. 60% for compound **3** and 90% for the other compounds, significant enhancements of the emission intensities occurred due to the formation of aggregates, and thus, the restriction of intramolecular rotations was compelled. Due to this, a hypsochromic shift of the spectra occurred for compounds **3** and **4**. The redshift remains consistent for compounds **1** and **2** corresponding to the bathochromically shifted PL spectra of neat films compared to both respective non-polar TOL and polar THF solutions caused by the effects of stacking. For compounds **1** and **4**, PL intensities increase slightly with an increase of the water fraction from 0% to 60%. Meanwhile, compounds **2** and **3** experience a monotonous decrease of the PL intensity with the increase of the water fraction from 0% to 80% and 60%, respectively. Due to the ICT nature of the emission of the studied compounds, their PL spectra should be sensitive to the polarity of the solvent in which the compounds are dissolved. Thus, the red shift of the PL spectra and a decrease of PL intensity are expected with the increasing percentages of water fractions, which results in the increase of the polarity of water/THF mixtures. Apparently, the balance of the quenching effect of the polar water/THF mixtures and the AIEE effect was different for the studied compounds, which resulted in their different PL intensity dependencies.

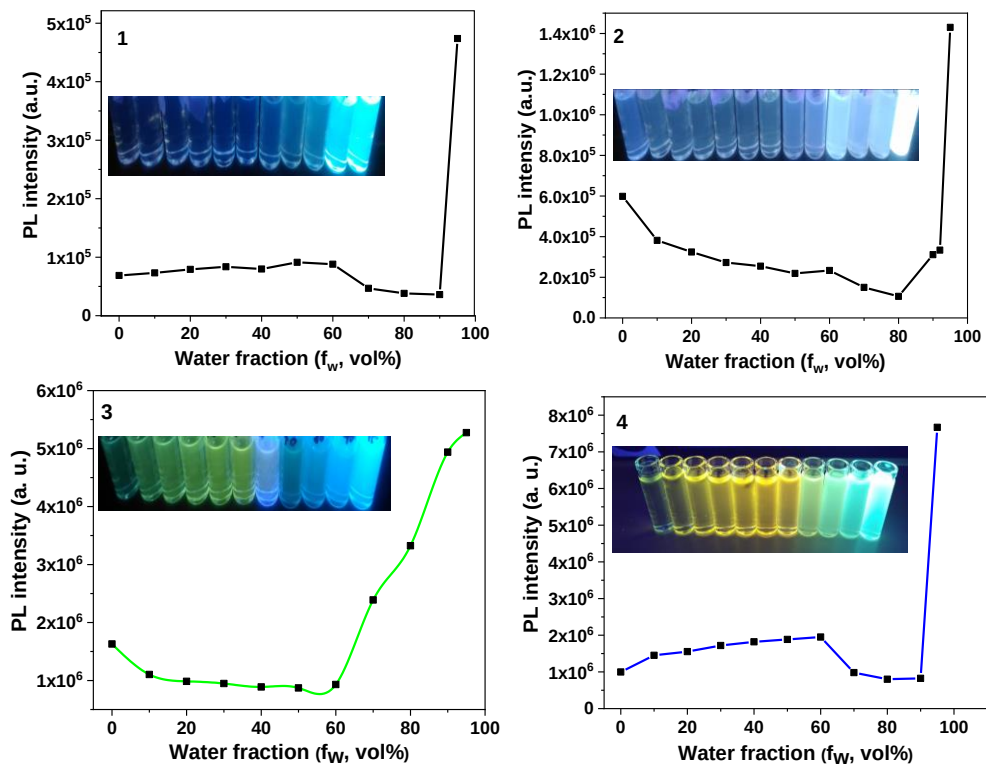


Fig. 34. Plots of PL intensities vs. water fractions of compounds 1–4.

The ToF measurements of vacuum-deposited layers of compounds 1–4 were performed to estimate their charge transporting properties. The experiment indicated bipolar dispersive charge transport in all the samples. Balanced electron and hole transport was observed for all compounds, except for compound 4, which was characterized with a considerably higher electron mobility relative to the hole mobility. The highest hole and electron drift mobilities reaching $3.07 \times 10^{-3} \text{ cm}^2 / \text{Vs}$ and $4.2 \times 10^{-3} \text{ cm}^2 / \text{Vs}$, respectively, were observed at an electric field of $3.67 \times 10^5 \text{ V / cm}$ for compound 1.

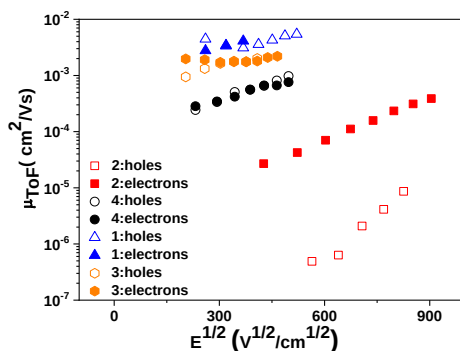
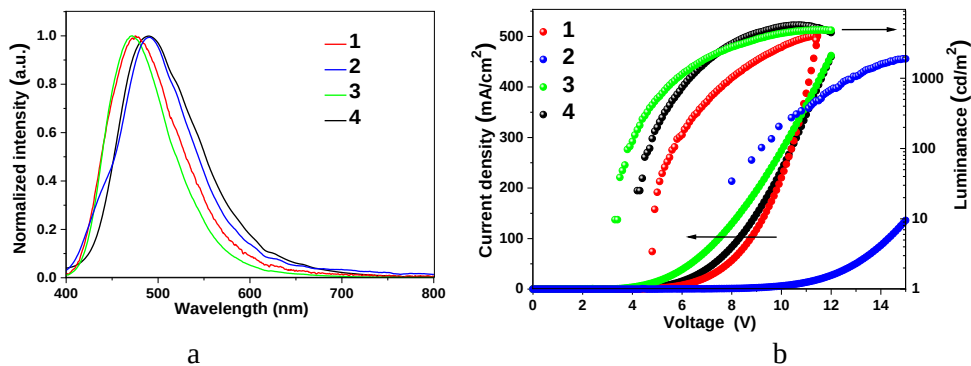


Fig. 35. Electric field dependencies of hole and electron mobilities of compounds **1–4**.

OLEDs with the neat layers of compounds **1–4** were fabricated. The EL properties are summarized in **Table 4**. The EL spectra shown in **Fig. 36** revealed that the peaks were structureless across the entire range of applied electric power, thus disclosing the absence of exciplex/electroplex formations. The EL spectra of OLEDs correspond to the PL spectra of materials with sky-blue emission peaks (**Table 4**). The low driving voltage indicates efficient injection and transport of holes and electrons to the recombination state. However, there is an increase in the driving voltage due to the blocking layers of *1,3-bis (N-carbazolyl) benzene* (mCP) and *diphenyl [4- (triphenylsilyl) phenyl] phosphine oxide* (TSPO1). Acridan-based compounds **3** and **4** displayed better device properties due to a high PLQY along with 2% EQE (**Table 4**).



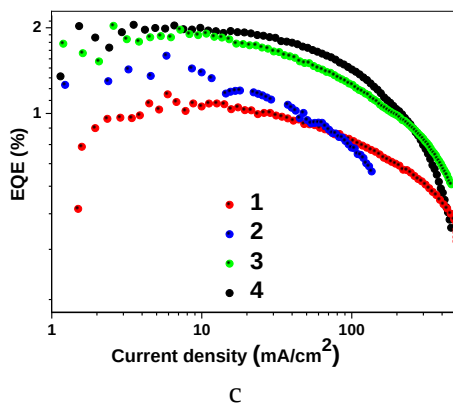


Fig. 36. OLEDs: (a) Normalized electroluminescence spectra; (b) Luminance-current density characteristics; (c) EQE-current density characteristics.

Table 4. Characteristics of nondoped OLEDs

Emitt er	Drivi ng volta ge, (V) ^A	λ_{EL} max, (nm)	Brightne ss $\times 10^3$, (cd/m ²) ^B	EQ E, (%) _B	Power efficien cy, (lm/W) _B	EQE, PE, CE at 100 (cd/m ²) ^C	CIE ^D
ITO / MoO ₃ (1 nm) / NPB (50 nm) / TCTA (10 nm) / non-doped layer of emitter (25 nm) / TPBi (45 nm) / LiF (0.5 nm) / Al (>200 nm)							
1	5.7	475	4.1	1.2	1.2	1.1%, 1.2 lm/W, 2.1 cd/A	0.17, 0.25
3	3.8	472	4.9	2	3.1	2%, 3 lm/W, 3.3 cd/A	0.16, 0.21
4	4.7	489	5.7	2	3.2	1.7%, 2.8 lm/W, 4.6 cd/A	0.20, 0.35
ITO / HAT-CN (1 nm) / TCTA (55 nm) / mCP (7.5 nm) / non-doped layer of emitter (30 nm) / TSPO1 (5 nm) / TPBi (55 nm) / LiF (0.5 nm) / Al (>200 nm)							
2	9.2	490	1.9	1.6	1.1	1.4%, 1.1 lm/W, 3.2 cd/A	0.19, 0.32
Electroluminescence parameters of OLEDs; A: Voltage at 100 cd/m ² brightness; B: Maximum values; C: Values of EQE, power and current efficiency at 100 cd/m ² ; D: (x, y) CIE 1931 UCS coordinates estimated from EL spectra [114]							

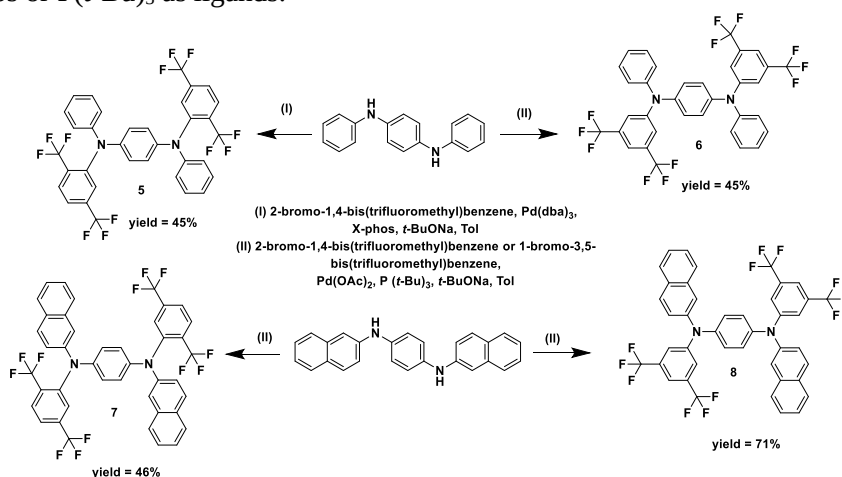
All devices displayed a moderate roll-off of the current and power efficiencies, and compound **2** displayed the lowest driving voltage. Relatively high EQE, power efficiency of 3.2 lm/W and luminance up to 5700 cd/m² for OLED based on compound **4**, can also be explained by almost ideally bipolar charge transport in its layer and the efficient radiative relaxation of the excited states.

3.2. Bis(trifluoromethyl)phenyl disubstituted aromatic diamines

This chapter is based on the work published by Ronit Sebastine Bernard, Viktorija Andrulevičienė, Oleksandr Bezikonnyi, Dmytro Volyniuk, Juratė Simokaitienė, Rimantas Henrikas Kublickas, Juozas Vidas Grazulevicius. *Impact of the substitution pattern of the acceptor on the properties of the bis(trifluoromethyl)phenyl disubstituted aromatic diamines* // Journal of Photochemistry & Photobiology, A: Chemistry 430 (2022) 113969. JIF:4.29. DOI: 10.1016/j.jphotochem.2022.113969

Triphenylamine (TPA) and *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenylbenzidine (TPD) displayed strong electron donating and hole transporting capabilities [115,116]. This led to a great interest toward TPA-based OLEDs, perovskite solar cells and organic transistors [117,118,119,120,121,122]. To improve the performance of organic electronic devices, CF₃ groups were added. It is well established that fluorene (F) atoms reduce the undesired steric hindrance, which leads to the improved planarization of the conjugated polymer backbone, thus, the charge mobility is enhanced, and the ionization potentials are reduced in polymers due to the contribution of F atoms [123,124]. Due to the electron negativity, F atoms demonstrate the 'Inductive effect'. However, F atoms can also be used as electron substituents through the 'mesomeric effect', in which the F atom enters conjugation with π -electrons of the molecular backbone [125,126].

Aromatic diamines **5–8** with CF₃ groups at different positions were synthesized and investigated. The π -conjugated heteroaromatic backbone of TPD acted as the donor, and the CF₃ groups acted as the acceptor moieties. In this work, we shall discuss the steric hindrance properties and effects of the donor and acceptor moieties. The synthetic routes of compounds **5–8** are given in **Scheme 2**. Buchwald–Hartwig amination was used to achieve the target materials. The synthesis of compounds **5–8** was implemented by using Pd(OAc)₂ or Pd₂(dba)₃ as catalysts and X-Phos or P(*t*-Bu)₃ as ligands.



Scheme 2. Synthetic routes of compounds **5–8**

Thermal measurements revealed that the 5% weight loss temperatures were observed in the range of 258–294 °C. The melting points were recorded for compounds **5** and **6**, while their counterparts **7** and **8** were amorphous. Thus, no signals of melting of compounds **7** and **8** were observed in the DSC thermograms. Glass transition signals were observed for all four compounds. All the data was compiled in **Table 5**.

Due to the presence of naphthalene moieties, compounds **7** and **8** displayed higher weight loss temperatures compared to compounds **5** and **6**. The naphthalene moieties in compounds **7** and **8** increased the number of conformers and changed the packing mode of the molecules. The higher molecular weight of naphthalene-based compounds **7** and **8** resulted in higher glass transition temperatures than those of compounds **5** and **6**. Additionally, it was observed that compounds **5** and **7**, containing CF₃ groups in the *ortho* position, demonstrated slightly higher 5% weight loss, glass transition, melting, and crystallization temperatures than analogous compounds **6** and **8** having CF₃ groups in the *meta* position, see **Table 5**.

Table 5. Thermal properties of compounds **5–8**

Compound	T _d , °C	T _g , °C	T _m , °C	T _c , °C
5	267	28	180	115
6	258	26	170	95
7	294	74	-	-
8	285	54	-	-
T _d – 5% weight loss temperature; T _g – glass transition temperature; T _m – melting point; T _c – crystallization temperature				

The crystal structures of compounds **5** and **6** obtained by XRD are presented in **Fig. 37**. XRD indicated that the single crystal of compound **5** contains two types of conformers and a variety of packing of molecules colored in blue and red in **Fig. 37 A**. The analysis of the interatomic contacts in the conformers revealed different types of interactions between the central phenyl ring and the side fragments. The C–H... π interactions of 2.830 and 2.817 Å were observed in the conformer having a dihedral angle between the phenyl unit and the C–N–C bond of 33°, while the fluorine atom was established to interact with the hydrogen atom of the neighboring molecule CH...F with a bond distance of 2.545 (**Fig. 37 A, C**). The other conformer, adopted by compound **5** molecule in the crystal structure, demonstrated interactions between the π system of the central phenyl ring system and the fluorine atom (F... π) of 3.157 and 2.928 Å (**Fig. 37 A, C**). In the case of compound **6**, only one type of conformer was found (**Fig. 37 B**), with inter- and intramolecular C–H... π interactions of 2.883, 2.886 Å and 2.851 Å (**Fig. 37 D**).

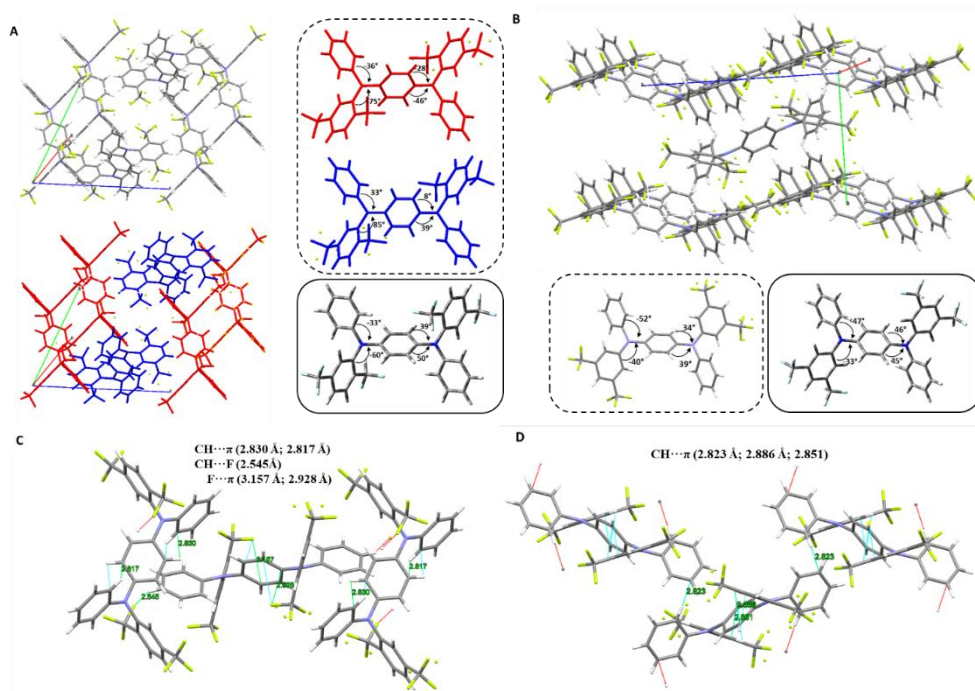


Fig. 37. Packing patterns, experimental (the dash line) and theoretically calculated at DFT-B3LYP/6-311G(d,p) level (the solid line) molecular structures of compounds **5** (**A**) and **6** (**B**) and interactions between the atoms of **5** (**C**) and **6** (**D**) in single crystal structures.

The frontier molecular orbitals demonstrate that the HOMO of the four synthesized compounds is distributed over the length of the conjugated molecular backbone. The electron density of HOMO in compounds **5** and **7** was observed on the fluorine atoms located close to the central phenyl ring. The LUMO of compounds **6** and **8** is extended across the entire molecules. In the case of compounds **5** and **7**, the CF₃ group at the *ortho* position of the phenyl ring predetermines the distribution of LUMO mainly on the electron-accepting fragments containing CF₃. The data of the theoretical calculations are shown in **Table 6**.

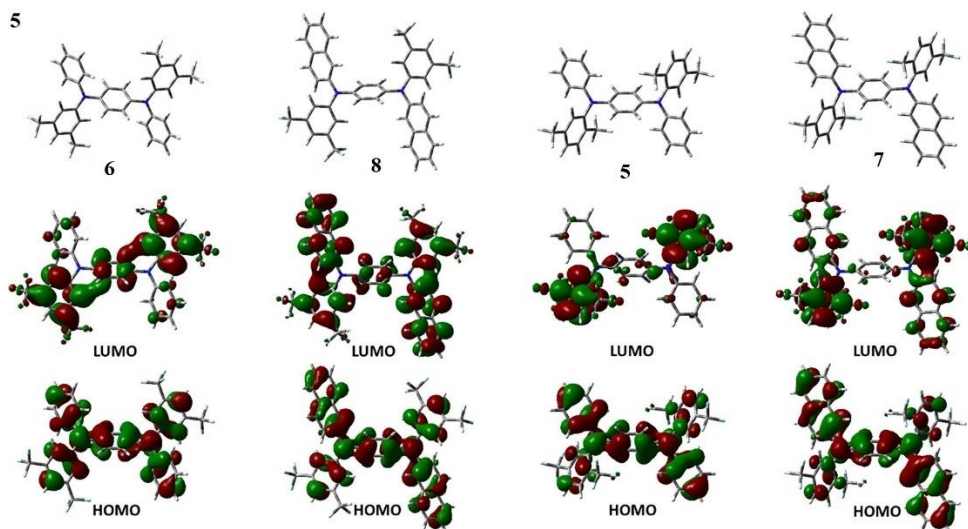


Fig. 38. Geometries and frontier molecular orbitals of compounds calculated at the DFT-B3LYP/6-31G(d,p) level.

CV and PE spectrometry measurements were performed to determine the $IP_{(PE, CV)}$ of the synthesized compounds, see **Table 6**. All the compounds exhibited irreversible reduction and reversible oxidation waves over the measured potential range. The onset potentials of the first reduction ($E_{redonset}$) and oxidation ($E_{oxonset}$) waves of dilute solutions in THF of the compounds with respect to ferrocene were used to determine the EA_{CV} and IP_{CV} values. The estimated EA_{CV} values of the compounds were in the range from 2.10 to 2.41 eV, while the IP_{CV} values ranged from 5.19 to 5.28 eV. The IP_{CV} values of the compounds decreased in the same order as the absolute values of the compounds of HOMO energies **6** > **8** > **5** > **7** (**Table 6**). The IP_{PE} of the layers of the compounds measured by PE spectrometry ranged from 5.75 eV to 6.17 eV. They were higher than the IP_{CV} values due to the different measurement conditions. The trend of IP_{PE} is not consistent with the trend of IP_{CV} (**Table 6**). This observation can be explained by the possible formation of different types of conformers in the solid layers of the compounds, resulting in the change of dihedral angles and conjugation lengths in the molecules. However, in all cases, IP_{CV} , IP_{PE} , as well as the absolute values of the HOMO energies of compounds **5** and **7** were lower than those of compounds **6** and **8**. This observation can be attributed to the combination of two effects caused by CF_3 attached at the *ortho* position of the phenyl unit. Firstly, the lone pair of electrons of fluorine atoms interacts with the π -electrons of the central phenyl ring via the mesomeric effect. This assumption is supported by the $F \cdots \pi$ interaction detected in the single crystal of compound **5**. Second, the CF_3 group attached at the *ortho* position causes steric hindrance between the acceptor unit and the C-N-C bond, thus reducing the extension of HOMO into the acceptor part and of LUMO into the donor moiety.

Table 6. Theoretical, electrochemical and photophysical characteristics of compounds **5–8**

Compound	LUMO, eV	HOMO, eV	H-L, eV	EA ^{CV a} , eV	IP ^{CV b} , eV	E _g ^{CV c} , eV	IP ^{PE} , eV
5	-1.46	-5.15	3.69	2.40	5.20	2.80	5.84
6	-1.36	-5.31	3.95	2.14	5.28	3.14	5.95
7	-1.54	-5.14	3.60	2.41	5.19	2.78	5.75
8	-1.49	-5.25	3.76	2.10	5.26	3.16	6.17

^a Electron affinity, ^b ionization potential and ^c band gap values were calculated according to equations $EA^{CV} = 4.8 - (E_{ox}^{Fe^{onset}} - E_{red}^{onset})$, $IP^{CV} = 4.8 + (E_{ox}^{onset} - E_{ox}^{Fe^{onset}})$ and $E_g^{CV} = IP^{CV} - EA^{CV}$, respectively. The determined onset potential of ferrocene was $E_{ox}^{Fe^{onset}} = 0.2$ V, Theoretical bandgap (H-L) = HOMO-LUMO.

ToF measurements were carried out to estimate the charge transporting properties of the films of compounds **5**, **7** and **8**. Unfortunately, the film of compound **6** was not appropriate for measuring the charge mobilities because of the low glass transition temperature ($T_g = 26$ °C). Even though the synthesized compounds have CF₃ acceptor moieties, only hole transport was detected in the films of the compounds. The room-temperature electric field dependencies of the hole drift mobilities of the films of compounds **5**, **7** and **8** are presented in **Fig. 39 b**. The best charge transporting properties were observed for the films of compounds having a CF₃ group at the *ortho* position. Compounds **5** and **7** showed hole drift mobility of 2.2×10^{-3} cm²/Vs and 3.0×10^{-4} cm²/Vs, respectively, at an electric field of 4.1×10^5 V/cm. Meanwhile, compound **8** with CF₃ groups at the *meta* positions demonstrated roughly one order of magnitude lower hole mobility relative to that of compounds **5** and **7**. It is assumed that the difference in charge transporting properties appeared because of the different molecular packing in the films of fluorinated compounds [127,128]. The larger number of inter and intramolecular interactions found in the single crystal of compound **5** as compared to that of compound **6**, **Fig. 37 C, D** may indicate the closer packing of the molecules with *ortho*-substituted phenyl groups. Furthermore, interactions between the π system of the central phenyl ring and the fluorine atom in compounds **5** and **7** can lead to a decrease of the number of geometrical conformers. These interactions may result in a decrease in the energetic disorder parameter and in the enhancement of hole mobilities in the amorphous films of the compounds [129].

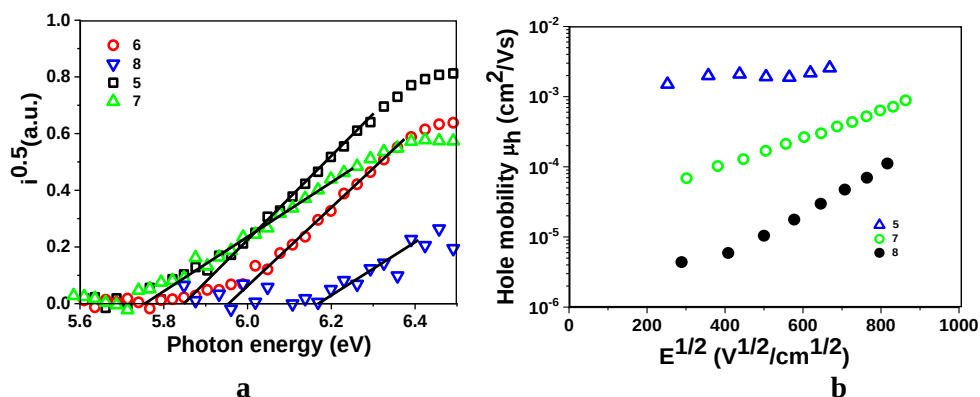


Fig. 39. (a) Photoelectron emission spectra of the films of the compounds and (b) electric field dependencies of hole drift mobilities in the films of the compounds.

The absorption and PL spectra of the dilute TOL, THF solutions, and films of the compounds are presented in **Fig. 40**. The results of theoretical calculations indicated that the experimental spectra of the compounds exhibit an absorption band in the region of 350–400 nm stemming from $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$. The transitions $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ of all the compounds can be attributed to the transitions $\text{HOMO} \rightarrow \text{LUMO}$ and $\text{HOMO} \rightarrow \text{LUMO}+1$, respectively, which are dominated by CT between the conjugated backbone and the CF_3 disubstituted phenyl units. Usually, the steric hindrance between donor and acceptor moieties leads to the spatial separation of the frontier orbitals in the molecules resulting in small oscillator strength [130]. However, the oscillator strengths at S_1 of compounds **5** and **7** are larger than those of compounds **6** and **8** (**Table 7**). It can be assumed that the mesomeric effect increases the overlap between HOMO and LUMO in compounds **5** and **7**. Additionally, the mesomeric effect leads to a much stronger destabilization of HOMO with respect to the LUMO narrowing of the HOMO-LUMO gap [131]. Thus, the theoretical HOMO-LUMO gaps, as well as the *band gaps* (E_g^{CV}) of compounds **5** and **7** are smaller compared to those of compounds **6** and **8**, see **Table 6**. The experimental absorption band of the solutions and solid films of compounds **5** and **6**, peaked at ca. 305 nm, and those of compounds **7** and **8** exhibited maxima at ca. 320 nm. Additionally, the absorption spectra of compounds **5** and **7** exhibited an absorption band at ca. 350 nm. The theoretical results indicate that these bands for all the studied compounds can be attributed to the local excitation transitions with the contribution from CT. The redshift of the absorption bands of compounds **5** and **6** relative to those of compounds **7** and **8** is due to an extension of the π conjugation caused by the presence of the naphthalene unit. The CT state and the length of π conjugation determine the position of the PL peaks of the compounds in the sequential order $7 > 5 > 6 > 8$ (**Table 7**). The bathochromic shift of the PL peaks of the solutions caused by changing non-polar TOL with polar THF is the evidence of a stronger solvatochromic effect characteristic of compounds **6** and **8** (42 nm and 40 nm) compared to compounds **5** and **7** (32 nm and 27 nm). This observation indicates

a greater degree of emission from the CT state in the PL spectra of the compounds having CF₃ groups in the *meta* positions. The PL bands of the films were found to be hypsochromically shifted up to 27 nm with respect to the PL bands of TOL solutions due to the lower values of the dipole moment (μ) of the films relative to that of TOL ($\mu = 0.31$ D). This was confirmed by theoretical calculations which revealed the values of μ of 0 D for compounds **5–8**. The PL decay curves of neat films showed short lifetimes of up to 12.7 ns which were derived from the multi-exponential fitting of the curves highlighting the prompt emission of the local excited states and CT interactions between the moieties of the compounds.

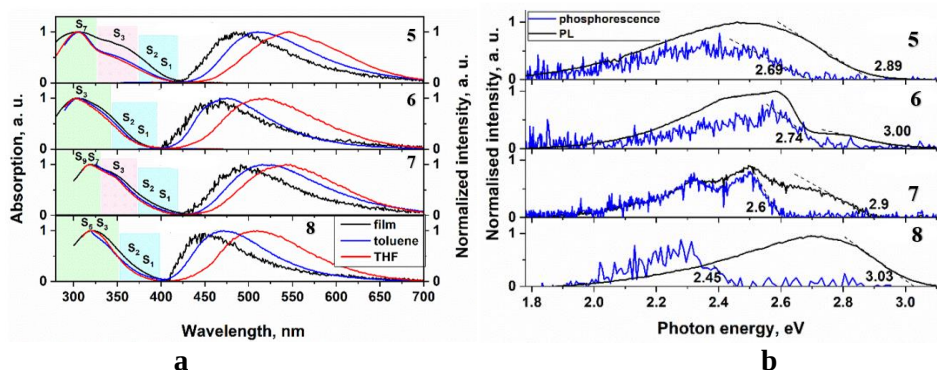


Fig. 40. (a) Absorption spectra with corresponding theoretical transitions and PL spectra of TOL, THF solutions and neat films of the compounds; (b) phosphorescence and PL spectra of THF solutions recorded at 77K.

The experimental energy values for E_{S1} and E_{T1} excited states were taken from the onsets of the phosphorescence and fluorescence spectra, respectively, of the compounds' dilute THF solutions recorded at 77 K, see **Table 7**. The fluorescence bands were almost not affected by the low temperature following the spectral character of the PL spectra of THF solutions recorded at room temperature. Compounds **7** and **8**, containing naphthalene units, displayed a lower E_{T1} than compounds **5** and **6**. Also, the steric hindrance between the donor and acceptor parts caused by CF₃ at the *ortho* position lowers the ΔE_{ST} of compounds **5** and **7** compared to that of compounds **6** and **8**.

Table 7. Photophysical characteristics of the compounds **5–8**

Compound	f^a	λ_{PL} film/TOL/THF, nm	E _{S1} ^b , eV	E _{T1} ^b , eV	ΔE_{ST} , eV
5	0.131	485/512/544	2.89	2.69	0.20
6	0.016	460/473/515	3.00	2.74	0.26
7	1.133	492/519/546	2.90	2.60	0.30
8	0.060	450/470/510	3.03	2.45	0.58

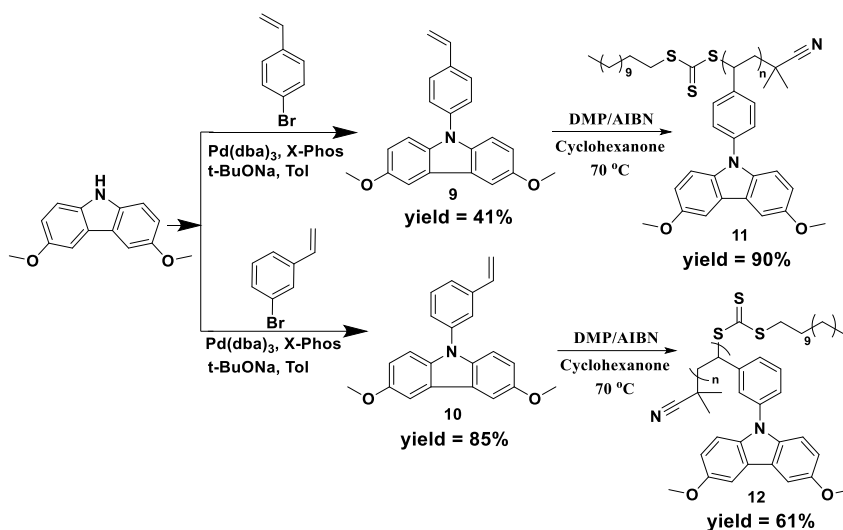
^a oscillator strength of the S₀→S₁ transition, ^b excited states measured from the onsets of photoluminescence PL and phosphorescence bands of dilute solutions in THF at 77 K

3.3. Methoxy-substituted carbazole-based polymers for solution-processable organic light emitting diodes

This chapter is based on the published work by Ronit Sebastine Bernard, Viktorija Andrulevičienė, George K. Belousov, Aliaksei A. Vaitusionak, Uliana Tsiko, Dmytro Volyniuk, Sergei V. Kostjuk, Rimantas Henrikas Kublickas, Juozas Vidas Gražulevičius. *Methoxy-substituted carbazole-based polymers obtained by RAFT polymerization for solution-processable organic light-emitting devices* // European Polymer Journal 174 (2022) 111323. JIF: 4.59. DOI: 10.1016/j.eurpolymj.2022.111323

Carbazole-based organic semiconductors are denoted by great potential in optoelectronic applications due to their remarkable *charge transporting* (CT) properties, a high luminescence efficiency, etc. [132]. Numerous carbazole-based compounds have been reported as hosts, emitters, or CT materials [133,134,135]. The fabrication of optoelectronic devices is often based on the expensive vacuum deposition technique. However, solution-process techniques enable simple and cost-effective fabrication of OLEDs [136,137,138]. In comparison to low-molar-mass compounds, polymers are more appropriate for large-scale solution processing because of the ability to form amorphous, morphologically stable, and flexible films [139]. *Poly(N-vinylcarbazole)* (PVK) is the most widely used as a host for emitters in *phosphorescent OLEDs* (PhOLEDs). However, the high ionization potential (5.9 eV) and the high resistivity of PVK can lead to a high operating voltage [140]. The introduction of methoxy groups is an effective approach to reduce the ionization potential due to the strong π donor effect and to improve the charge mobility due to the additional hydrogen bonds [141]. In the synthesis of functional polymers for optoelectronic application, *2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid* (DDMAT) was reported to be advantageous as a *reversible addition–fragmentation chain transfer* (RAFT) agent which allows to obtain low-dispersity polymers with a well-defined structure and composition [142].

Monomers **9** and **10** were synthesized by using Buchwald–Hartwig amination. The radical polymerization of these monomers was performed by using DDMAT as RAFT and AIBN as the initiator agent yielding polymers **11** and **12**, see Scheme 3.



Scheme 3. Synthesis of compounds **9–12**

The thermal characteristics of monomers **9** and **10** and polymers **11** and **12** are summarized in **Table 8**. Monomers **9** and **10** showed endothermic melting signals in the first heating scan at 76 °C and 62 °C, respectively. During the second heating scan, the thermal self-polymerization of compounds **9** and **10** was detected [143]. The glass transition temperatures of polymers **11** and **12** were found to be higher than those of the corresponding monomers. The polymers were obtained as amorphous materials, and no peaks due to crystallization and melting were observed in their DSC curves. The glass transition temperature of polymer **12** was lower than that of polymer **11** because of the higher mobility of the polymer chains in polymer **12**. The larger free volume in polymer **12** structure is caused by the less dense packing of the polymer. Polymers **11** and **12** demonstrated high thermal stability, and their weight loss temperatures were found to be 414 °C and 406 °C, respectively. It was impossible to estimate the thermal stability of monomers **9** and **10** due to their polymerization at a high temperature.

Table 8. Thermal characteristics of monomers **9**, **10** and polymers **11**, **12**

Compound	M_n (g mol ⁻¹)	T_m^a (°C)	T_g^b (°C)	T_{ID}^c (°C)
9	329/3450 ^d	76	151	404 ^e
11	7900	—	191	414
10	329/1680 ^d	62	138	430 ^e
12	7200	—	161	406

^aDSC: T_m = melting point; ^bDSC T_g = glass transitions. ^c T_{ID} = 5% weight. ^d M_n values of polymers obtained during thermal self-polymerization. ^e 5% weight loss of polymer formed during measurement

Theoretical calculations revealed that the position of the vinyl group does not have a noticeable effect on the shape and energy of the frontier orbitals of monomers **9** and **10**, as shown in **Fig. 41**. In both cases, HOMO is distributed across the entire molecular backbone, while LUMO is essentially localized on the vinyl phenyl moiety. The addition of methoxy groups at **C-3** and **C-6** positions of the carbazole moiety led to an increase of the HOMO energies. The orbitals of the oxygen atoms contribute to the π -conjugation system of the molecules. The estimated HOMO (-4.80 eV) and LUMO (-1.07 eV and -1.09 eV) energies of the monomers were almost identical because of the similar electronic cloud distribution of the frontier orbitals in the molecules. CV measurements revealed the experimental IP^{CV} values which are related to the HOMO energies. The theoretical results correlate with the IP^{CV} values of the monomers. The measured IP^{CV} values of 5.35 eV and 5.34 eV were estimated for monomers **9** and **10**, respectively.

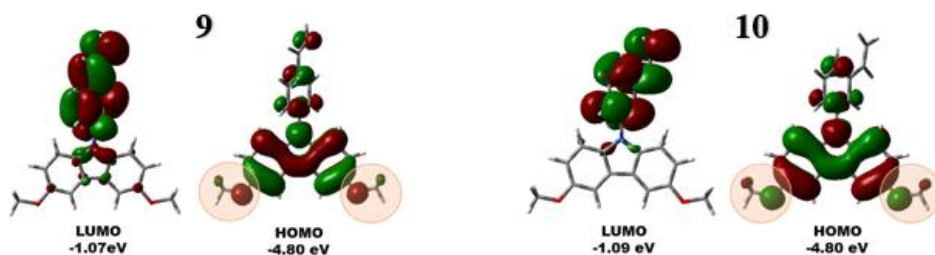


Fig. 41. Frontier orbitals of monomers **9** and **10** obtained by using B3LYP/6-31G(d,p) level at gas phase.

The absorption spectra of the dilute THF solutions of compounds **9–12** unambiguously demonstrated the same character of the absorbance of the carbazole moiety shown in **Fig. 42**. However, a redshift of 30 nm was observed due to the extension of the π -conjugation onto the phenylene group and/or methoxy substituents at positions **C-3** and **C-6**. The characteristics of emission spectra of the solutions and thin films of compounds **9–12** are presented in **Table 9**. According to the results, both the absorption and the PL spectra of the solutions of compounds **9–12** are mostly characterized by the lowest $\pi\pi^*$ transition on the carbazole core [144].

In contrast to the PL spectra of the solutions, the thin films of the compounds showed complicated PL spectra because of aggregation and molecular packing. The additional intensive emission peaks were observed at 510 nm for the film of polymer **12** and up to 447 nm for the film of polymer **11**. These emission bands suppressed carbazole-related peaks. As the compounds do not have intramolecular CT clear donor-acceptor structures, the additional peak can be assigned to the excimer emission [145] at the blue-green region and can be attributed to the intermolecular or through-space CT.

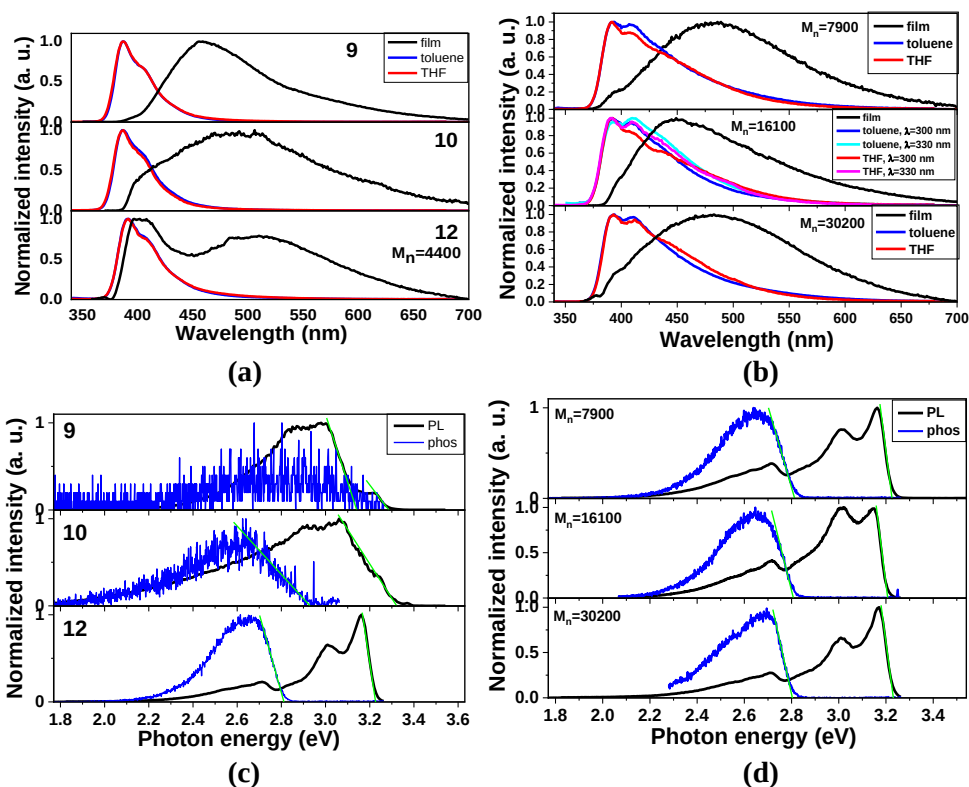


Fig. 42. PL spectra of the films and dilute TOL and THF solutions of **9**, **10** and **12** (a) and **11** (b) recorded at room temperature. PL and phosphorescence spectra of THF solutions of **9**, **10** and **12** (c) and **11** (d) recorded at 77 K.

Table 9. Photophysical characteristics of the monomers and polymers

Compound	M_n (g mol ⁻¹)	$\lambda_{PL}^a/b/c$ (nm)	$^1\pi\pi^*$ (eV)	^3CT (eV)	PLQY ^d / _e (%)
9	329	387 /387 /458	3.29	-	40 /24
11_8K	7900	391 /391 /483	3.23	2.81	19 /6
11_16K	16100	391 /391 /447	3.23	2.81	19 /2
11_30K	30200	392 /392 /483	3.23	2.81	21 /3
10	329	386 /386 /490	3.32	2.93	9 /1
12	4400	391 /391 /402,510	3.23	2.81	8 /≈0

Wavelength of photoluminescence PL maximum of ^aTHF solutions, ^b TOL solutions and ^csolid samples. Photoluminescence quantum yield PLQY of ^d TOL solution and ^e film; 8K, 16K, 30K – different temperatures in the presence of liquid nitrogen (K-Kelvin)

The PL decay curves of the solutions of compounds **9–12** in TOL showed single exponential decay curves with the lifetime of emission of nearly 5 ns for monomers and 7 ns for polymers (**Table 10**). However, the emission lifetime of 27.45 ns was detected for the TOL solution of polymer **11** when the PL decay curve was recorded at 472 nm, attributing to a probable CT, although the amplitude of this component of intensity is only 0.77% (**Table 10**). The PL curve of the film of monomer **9** was adequately represented by the triple exponential function at the peak wavelength of 458 nm with fluorescence lifetimes of 11.56 ns. The PL decay curve of the thin film of monomer **10** shows a lifetime of 480.85 ns at 490 nm, thus demonstrating signs of excimer formation.

Table 10. Characteristics of PL decay dynamics

Compound	Sample	λ , nm	τ_1 , ns	A_1 , %	τ_2 , ns	A_2 , %	τ_3 , ns	A_3 , %	χ^2
9	TOL	387	4.92	100	-	-	-	-	1.041
		405	4.82	100	-	-	-	-	1.016
	film	458	1.54	24.43	4.17	44.99	11.56	30.58	1.116
10	TOL	410	5.08	100	-	-	-	-	1.012
	film	490	13.44	56.41	44.51	38.76	480.85	4.83	1.121
11_8K	TOL	392	2.34	35.84	7.26	64.16	-	-	1.196
	TOL	412	2.77	43.76	7.25	56.24	-	-	1.164
11_16K	TOL	409	2.75	39.28	7.10	60.72	-	-	1.090
	TOL	472	4.21	64.75	8.22	34.48	27.45	0.77	1.199
11_30K	TOL	394	2.33	33.90	6.91	66.10	-	-	1.219
	TOL	413	2.92	40.49	7.12	59.51	-	-	1.271
11_8K	film	483	4.01	50.99	12.83	41.48	72.86	7.53	1.282
11_16K	film	490	82.57	37.27	2465.33	62.73	-	-	1.200
11_30K	film	483	9.34	52.19	42.59	36.87	339.42	10.95	1.014
12	TOL	392	1.76	46.65	6.00	53.35	-	-	1.172
		410	1.76	46.42	5.99	53.58	-	-	1.223
	film	398	6.47	100	-	-	-	-	1.085
		510	19.73	53.95	129.20	11.87	2612.58	34.18	1.273

λ – wavelength of analysis; τ_1 , τ_2 , τ_3 – lifetimes of the components of a PL decay curve; A_1 , A_2 , A_3 – amplitudes of intensity of the components of a PL decay curve; χ^2 – weighted sum of squares of deviations of calculated fit points of a PL decay curve; 8K, 16K, 30K – different temperatures in the presence of liquid nitrogen (K – Kelvin)

The films of polymers **11** and **12** exhibited multi-exponential PL decay curves with the lifetimes up to 2.5 μ s at 490 nm and 2.6 μ s at 510 nm, respectively. The delayed components of excimer emission of polymers **11** and **12** were relatively high, i.e., of 63 and 34% in comparison to prompt excimer emission (**Table 10**). In

contrast, the lifetime of the emission of the film of polymer **12** recorded at 398 nm was of 6 ns. This observation of the excimer CT emission can be described similarly to the through-space TADF emitters [146].

The PL spectra of the THF solutions of compounds **9** and **10**, and **12** recorded at the temperature of liquid nitrogen were redshifted in relation to the PL spectrum of carbazole [147] recorded at room temperature. The $^1\pi\pi^*$ energy levels were estimated from the onsets of the fluorescence bands to be of ca. 3.23 eV for polymers **11** and **12** and of 3.29 and 3.32 eV for monomers **9** and **10**, respectively. For the solutions of polymers **11** and **12** in polar THF, ^3CT energies were estimated to be of ca. 2.81 eV. The energy levels of ^3CT of the polymers were lower compared to the corresponding monomers.

The PLQY values were measured to be 40 and 9% for the solutions of monomers **9** and **10** in TOL, respectively. The PLQY of the solutions of polymers **11** and **12** were recorded to be 19–21 and 8%. The estimated PLQY values were dramatically suppressed for the films of monomers **9** and **10** in comparison to those of TOL solutions and were found to be 24 and 1%, respectively. The decrease of PLQY in the solid films appeared because of the formation of CT leading to delayed fluorescence. These results correlate with the results obtained by PL decay dynamics. The PLQYs of the films of polymers **11** and **12** were also lower than those of the solutions. The PLQYs of the solutions and films of compounds **9–12** are presented in **Table 10**. It was found that the molecular weight of polymer **11** affects more significantly the efficiency of the solid-state emission than that of the solution. The PLQY values estimated for the samples with the M_n values of 7900 to 16100 to 30200 g mol⁻¹ were found to be of 6, 2 and 3%, respectively. The dependence of the extent of PL quenching on the length of the polymeric chain agrees with the above formulated presumption related to the formation of excimers and/or through-space CT.

Two series of solution processed OLEDs were fabricated to examine the EL properties of the investigated polymers. For this purpose, polymers **11** and **12** and poly(9,9-dioctylfluorene-alt-*N*-(4-sec-butylphenyl)-diphenylamine) TFB were utilized as HTL, and a non-doped TADF emitter 4,6-di(9*H*-carbazol-9-yl)pyrimidine-5-carbonitrile (CzPCN) [148] was employed for EML. PhOLEDs **D–J** were fabricated to test the polymers as hosts for red phosphors. PhOLEDs **D–J** were fabricated by using solution processed EML based on well-known red phosphor bis(1-phenylisoquinoline)(acetylacetonate)iridium(III) (Ir(piq)₂(acac)) as a dopant, whereas polymers **11** and **12** and TFB served as host materials. TFB was used as a reference. The fabrication of emitting layers by spin-coating is attractive due to the possibility to thoroughly control the concentration of a dopant. The EL characteristics of the OLEDs are listed in **Table 11** and **Fig. 43**.

OLEDs **A** and **B** were found to exhibit lower turn-on voltages compared to OLED **C** fabricated by using TFB, which proved that polymers **11** and **12** can provide charge carrier balance in EMF. The undoped TADF devices had an EQE of 0.8%.

Table 11. Characteristics of OLEDs

Device	EML	Turn-on voltage (V)	Current efficiency (cd/A)	Power efficiency (lm/W)	EQE (%)
A	11 / CzPCN	4.9	2.2	1.1	0.8
B	12 / CzPCN	5.6	1.8	1	0.6
C	TFB / CzPCN	7.1	2.1	0.7	0.8
D	TFB / Ir(piq) ₂ (acac): 11 , 1 wt%	6.8	11.3	5.2	10.6
E	TFB / Ir(piq) ₂ (acac): 11 , 4 wt%	10.6	4.2	1.2	3.9
F	TFB / Ir(piq) ₂ (acac): 11 , 9 wt%	8.6	3	0.7	3.1
G	TFB / Ir(piq) ₂ (acac): 12 , 1 wt%	5.9	6.1	3	5.8
H	TFB / Ir(piq) ₂ (acac): 12 , 4 wt%	6.6	1.1	0.3	1
I	TFB / Ir(piq) ₂ (acac):TFB, 4 wt%	8.6	7.2	2.4	6.8
J	TFB / Ir(piq) ₂ (acac):TFB, 9 wt%	7.5	3.5	0.8	3.7

PhOLED **D** with EML of 1 wt% of Ir(piq)₂(acac) doped in polymer **11** exhibited the highest EQE in the series of devices **D–J**, **Table 11**. The maximum EQE of nearly 11% is comparable with the state-of-the-art efficiency values of the solution-processed Ir(piq)₂(acac)-based PhOLEDs. Nevertheless, the obtained EQE is still lower in comparison to the state-of-the-art efficiency values due to the incomplete electronic excitation energy transfer from the host to the guest manifested by the EL contribution of TFB [149] in the UV region of the spectra, see **Fig. 43**. The emission of HTL observed for the PhOLEDs is due to aggregation-caused quenching, high charge mobilities of polymers **11** and **12**, and a possible partial diffusion of the layers made by spin-coating despite the preventive thermal annealing.

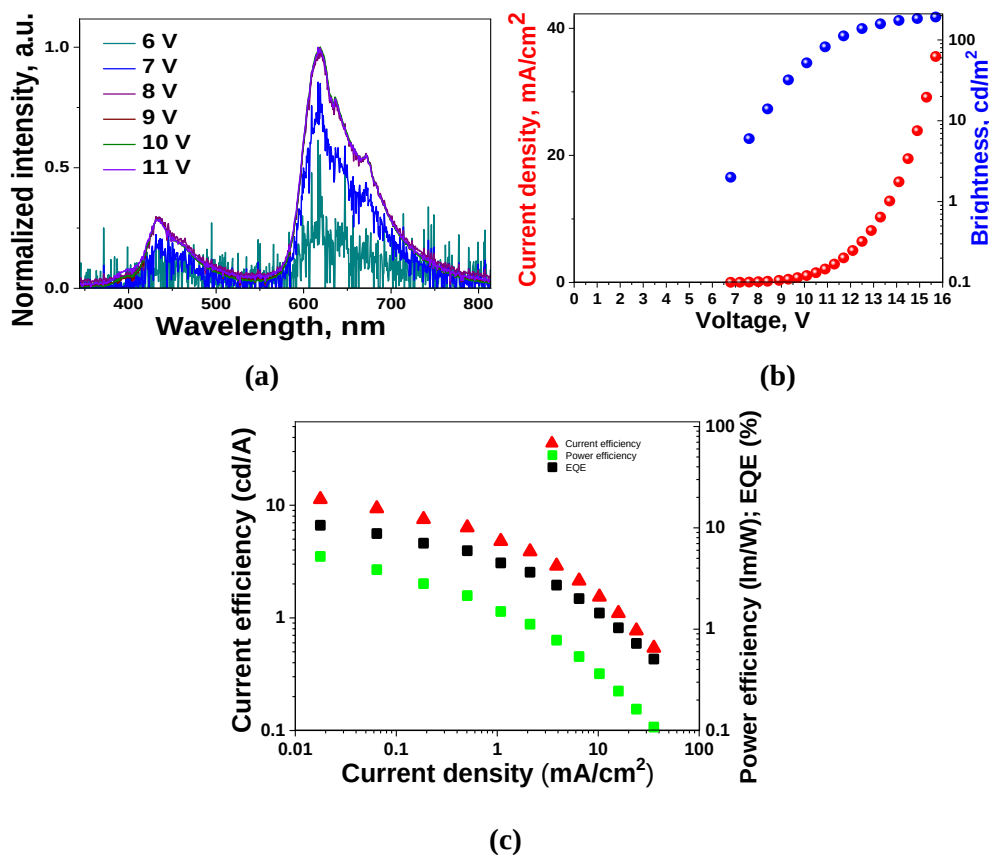


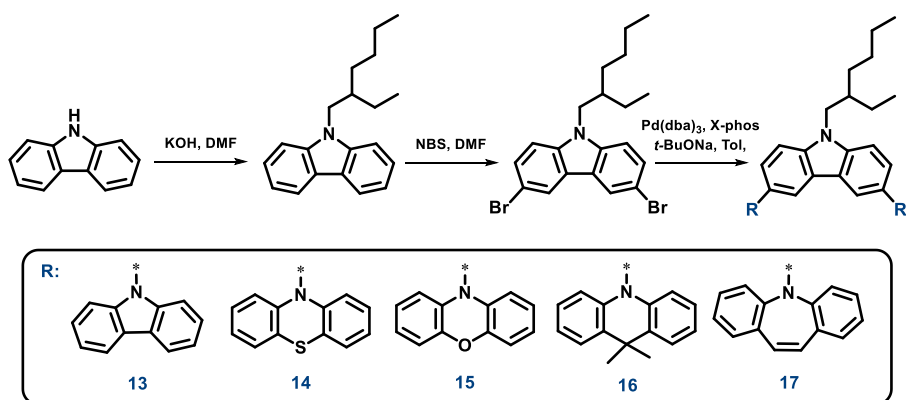
Fig. 43. PhOLED D: (a) EL spectra; (b) current density-, brightness-voltage curves; current efficiency-, power efficiency-, (c) EQE- current density curves.

The relatively high turn-on voltage and low brightness of PhOLEDs **D–J** was apparently caused by the big overall thickness of the layers suppressing the formation of excitons and charge balance. The charge distribution in the layers may be a/the cause of the inferior performance of PhOLEDs with 9 wt% dopant concentration for polymer **12**, whereas 1 wt% for TFB can be explained by the inefficient energy transfer from the host to the emitter stimulating TFB-facilitated radiative recombination of excitons. The highest EQE achieved for polymer **12** based devices was that of 5.8%. Similarly to the observation done for OLEDs **A–C**, polymer **11** showed better performance in PhOLEDs than polymer **12**. PhOLED **D** based on host **11** produced an EQE of 10.6%, while the best TFB-based device exhibited an EQE of only 6.8%. The obtained EL data shows that the synthesized polymers are promising for the utilization as hosts for red PhOLEDs, see **Fig. 43**.

3.4. Derivatives containing three donor fragments for organic light emitting diodes

Among the wide-band gap materials, carbazole derivatives are among the most studied due to their good hole transporting properties, high triplet energy and the rigid molecular framework [150]. The carbazole ring can be easily modified by attaching various electron accepting units [151]. Derivatives of carbazole with benzimidazole [152], or phenanthro[9,10-d] imidazole [153] substituents demonstrate suitable triplet energies, efficient bipolar charge transport, and a relatively high PLQY. The donor-acceptor derivatives of carbazole containing aromatic moieties with cyano, fluoro, sulfoxide and keto groups exhibit the TADF behavior [154]. Consequently, these compounds can be exploited for practical electroluminescent applications including OLEDs. Recently, there has been a great deal of interest in the use of TADF compounds as emitters in systems utilizing delayed fluorescence. Such an approach results in the harvesting of triplet excitons via RISC into singlet excitons that can emit light [155].

V-shaped compounds **13–17** having three donor moieties were synthesized, and their TADF properties were investigated. Donor fragments, such as carbazole, phenothiazine, phenoxazine, acridine, and dibenzazepine, were chosen. These moieties were attached to 3,6-dibromocarbazole by using the Buchwald–Hartwig reaction, yielding five compounds **13–17**.



Scheme 4. Synthesis of derivatives **13–17**

Thermal measurements revealed that 5% weight loss temperatures of compounds **13–17** were found to be in the range from 365 to 391 °C, see **Fig. 45**. Compounds **13–16** were obtained as crystalline materials. During the first DSC heating scan, endothermic melting signals were observed at 169, 173, 237 and 289 °C, respectively. Compound **17** was obtained as an amorphous material with the glass transition temperature of 88 °C. In terms of compounds **13–15** and **17**, the cooling and second heating scans did not show any crystallization or melting

signals, as only glass transition was observed. The DSC thermogram of compound **14** is presented in **Fig. 44**. Exceptionally, compound **16** demonstrated crystallization at 208 °C in the course of cooling and melting during the second heating at 285 °C.

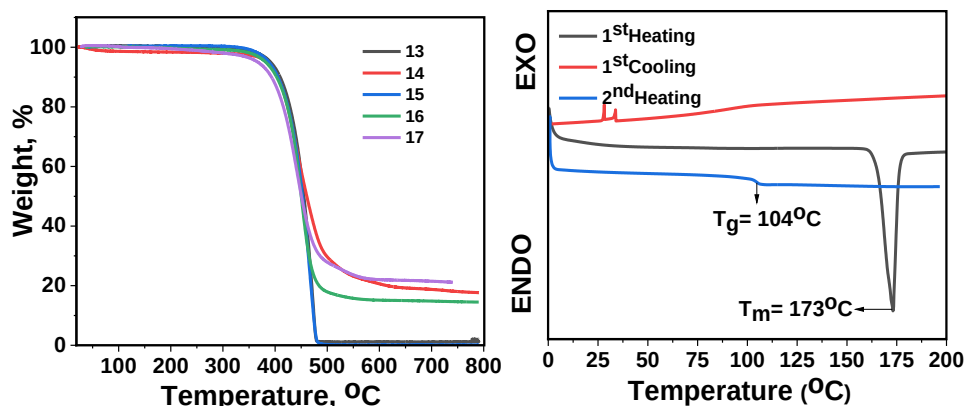


Fig. 44. TGA curves of compounds **13–17** (left) and DSC thermograms of compound **14** (right).

The PL and phosphorescence spectra of compounds **13–17** are presented in **Fig. 46**. The maximum of the PL spectra of dilute solutions of compound **13** in TOL and THF can be attributed to the relaxation of the locally excited states. There are well observed differences between the PL spectra of the solutions of compound **13** and the corresponding spectra of the other compounds **14–17**, **Fig. 45**, **Table 12**. The structureless PL spectra of these compounds are of the CT nature. The maxima of the PL spectra of compound **14** in TOL and THF solutions are peaked at 453 and 475 nm, respectively. In the case of compounds **15** and **16**, the maximum of the PL spectrum in the THF solution is red shifted with respect to that in TOL by 32 and 10 nm, respectively. Compounds **14–16** exhibited positive solvatochromism manifested in CT from the phenothiazine/phenoxazine/acridane donating units to the core carbazole acting as an acceptor. A different shape of the PL spectrum was detected for compound **17**. The two PL bands of LE and CT were recorded in the spectra of the solutions of compound **17** in the TOL and THF solutions. The PLQY in TOL reached 22% for compound **13** and 10% for compound **16**, see **Table 12**. Significantly lower PLQY values were recorded for other compounds **14**, **15**, and **17** ranging from 1 to 3%.

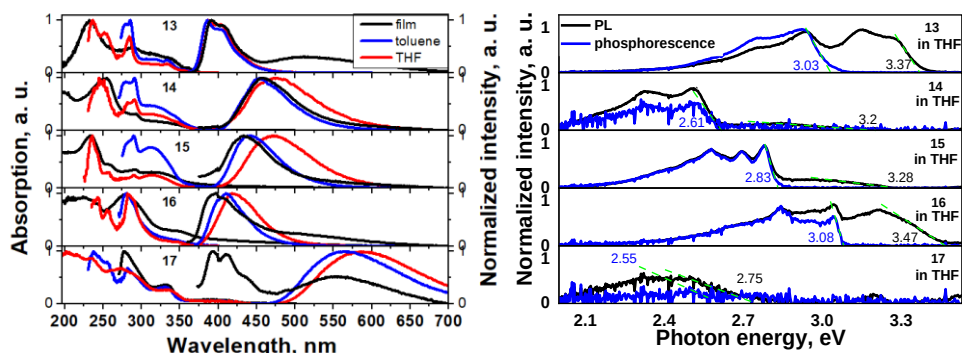


Fig. 45. Absorption and PL spectra (a) of either film, toluene or THF solutions, PL, and phosphorescence spectra (b) of THF solutions recorded at 77 K.

The PL and phosphorescence spectra of THF solutions of compounds **13–17** were recorded at 77K temperature to calculate the energy levels of S_1 and T_1 from the onset of the corresponding spectral bands (**Table 12**), **Fig. 45**. Since compound **13** has only carbazole donating units, its phosphorescence is totally characterized by the phosphorescence of carbazole. It is shown that the energy splitting for the energy levels vary from 0.20 to 0.59 eV, see **Table 12**. The largest ΔE_{ST} value of 0.59 eV and the lowest value of 0.20 eV were determined for compounds **14** and **17**, respectively.

Table 12. Photophysical properties of compounds **13–17**

Compound	13	14	15	16	17
$\lambda_{em}^{tol/THF}$, nm	386/386	453/475	441/473	411/421	408, 563/408, 587
PLQY _{deox. tol} ^a , %	22	1	3	10	1
E_{S1}^b , eV	3.37	3.20	3.28	3.47	2.75
E_{T1}^b , eV	3.03	2.61	2.83	3.08	2.55
ΔE_{ST} , eV	0.34	0.59	0.45	0.39	0.20
a – estimated from measurement of deoxygenated TOL solution; b – estimated from measurement of THF solution					

The PL spectra of the neat films of compounds **13–17** were similar to the spectra of their TOL solutions, see **Fig. 46**. However, a low energy band and/or a low energy tail can be recognized at least for the PL spectra of the films of compounds **13**, **16** and **17**. Those peaks/shoulders can be attributed to the aggregation effects. To mitigate the aggregation effects, the solid-state mixtures of compounds **13–17** (1 wt%) and Zeonex were tested, see **Fig. 46**. The high energy bands remain the same for all the compounds except for compound **17** which demonstrated only the low-energy band. The low energy shoulder was still left for the solid-state mixtures of compounds **13** and **16**, **Fig. 46**. In contradistinction to

compounds **14**, **16** and **17**, the solid-state mixture of compounds **13** and **15** doped in Zeonex exhibited an increase of the UV peak under vacuum conditions. Consequently, the radiative path of the deactivation of excitons is enhanced at the energy levels of the UV peak excited states for **13** and **15** after suppressing the collisional interactions of the molecules of the compound and oxygen [156]. Nevertheless, the short lifetime of 6 ns estimated for the PL decay curve of the solid-state mixture of compound **13** recorded at 400 nm showed that the emission of the band takes place due to the radiative recombination of singlet excitons, see **Fig. 46**. The solid-state mixture of compound **14** and Zeonex revealed room temperature phosphorescence. The low-energy bands of compounds **16** and **17** are apparently originated in ICT allowing TADF. The obtained values of long lifetimes of the emission at the selected wavelengths in the green spectral range are in agreement with this assumption, see **Fig. 46**.

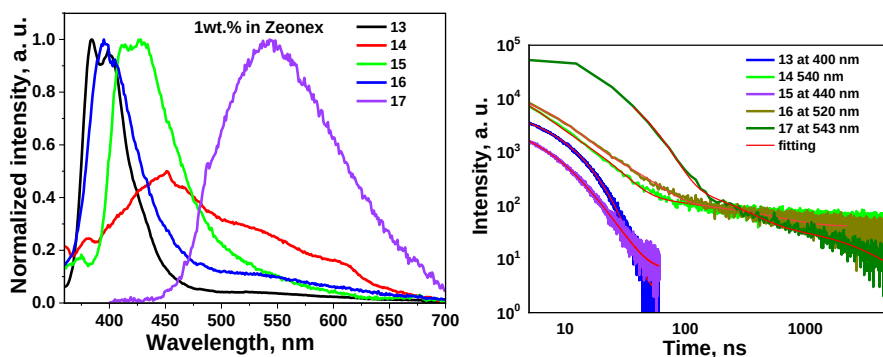


Fig. 46. PL spectra (left) and PL decay curves (right) of the solid-state mixtures of compounds **13**–**17** and Zeonex.

To provide additional evidence of TADF for compounds **16** and **17**, the PL spectra and PL decays at different temperatures of solid-state mixtures of compounds **16** and **17** (20 wt%) and bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) were investigated, see **Fig. 47**. DPEPO as the high polar host was selected due to the aim to decrease the ΔE_{ST} of compounds **16** and **17**. The lower values (0.3 and 0.16 eV) of ΔE_{ST} were recorded for the solid state mixtures of compounds **16** and **17** (20 wt%) in DPEPO in comparison to those values (0.61 and 0.2 eV) of solutions of compounds **16** and **17** in THF, respectively, see **Fig. 45**, **46**. The long-lived emission was detected for the solid-state mixture of compound **17** and DPEPO, see **Fig. 46**. The lifetime of 159 μ s of the delayed emission of compound **17** doped in DPEPO was obtained. The shape of the PL spectra of compound **17** at different temperatures is practically the same, thus additionally proving the similarity of the fluorescence and phosphorescence spectra, the small ΔE_{ST} . In the case of the solid-state mixture of compound **16** and DPEPO, the PL spectra were characterized by the high-energy band at 410 nm and the low-energy shoulder at ca. 500 nm. Their PL decay curves recorded at different temperatures display that the band at 410 nm is

attributable to the prompt fluorescence, whereas the shoulder at 500 nm is characterized by a very weak TADF.

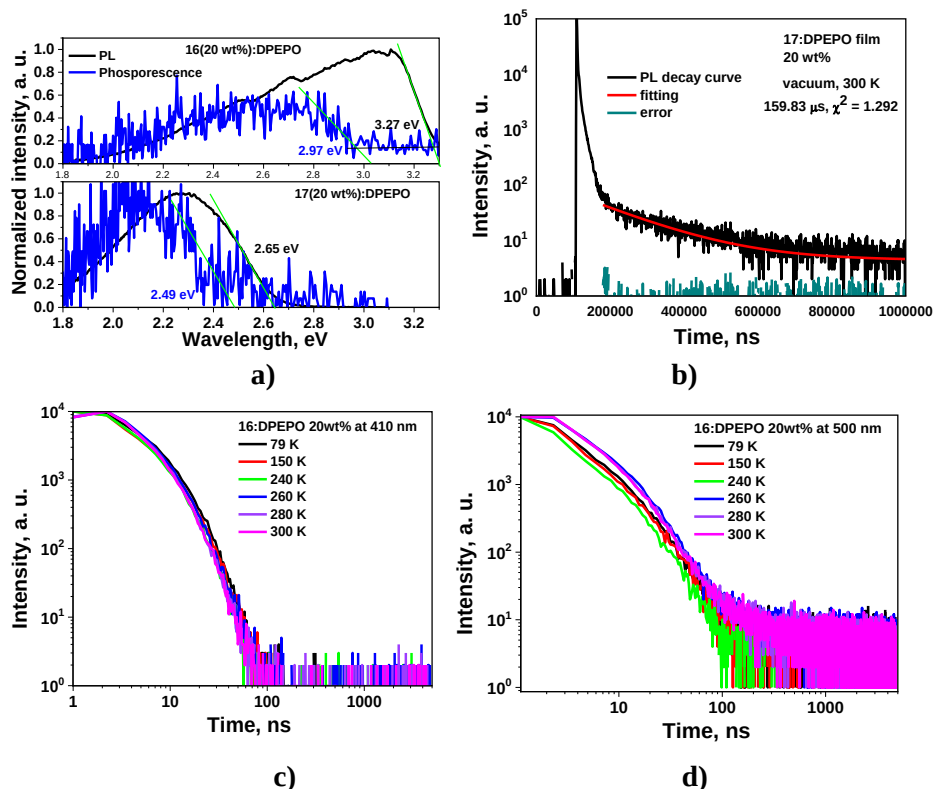


Fig. 47. PL and phosphorescence spectra (a) of the solid-state mixtures of compounds **16** and **17** (20 wt%) doped in DPEPO. PL decay curve (b) recorded at room temperature of **17**: DPEPO. PL decay curves (c, d) recorded at deoxygenated atmosphere at various temperatures of **16**: DPEPO.

The synthesized compounds **13**–**17** were used as hosts for red emitter bis(1-phenylisoquinoline) (acetylacetonate)iridium(III) ($\text{Ir}(\text{piq})_2\text{acac}$). The IP^{EP} values of these compounds were obtained in the range from 5.1 to 5.58 eV, see **Fig. 48**. Except for compound **17**, the remaining compounds **13**–**16** should provide good injection of holes to the HOMO level of $\text{Ir}(\text{piq})_2\text{acac}$ because their IP^{EP} values are slightly above the corresponding level of $\text{Ir}(\text{piq})_2\text{acac}$ which is 5.3 eV. The charge transporting properties of vacuum-deposited layers were studied by considering ToF, see **Fig. 48**. Compound **16** showed the highest hole and electron mobility values of $1.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $9.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, at an electric field of $1.6 \times 10^5 \text{ V/cm}$. Compound **13** also showed ambipolar charge-transporting properties, while compounds **14**, **15**, and **17** were HTMs.

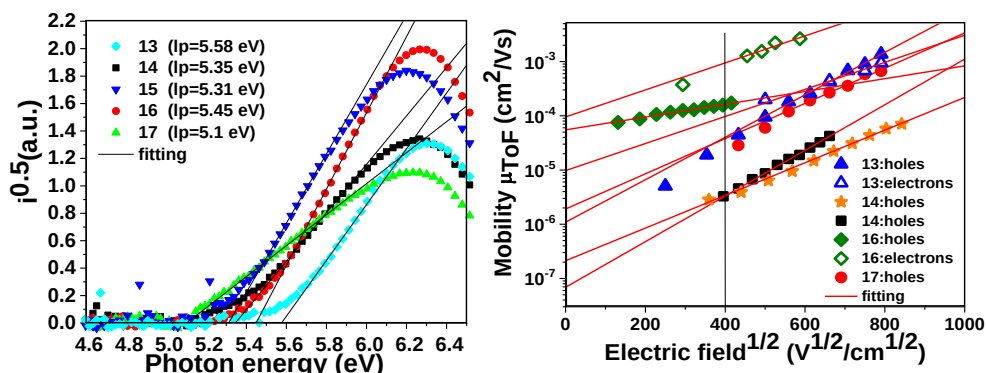


Fig. 48. Photoelectron emission spectra (left) and electric field dependencies of hole/electron drift mobilities (right) of vacuum-deposited films of compounds **13**–**17**.

PhOLEDs R1–R5 with a structure of indium tin oxide (ITO)/ 1,1-bis[(di-4-tolylamino)phenyl] cyclohexane TAPC (50 nm)/ N, N-dicarbazolyl-3,5-benzene *m*CP (10 nm)/ emitting layer (EML) (30 nm)/ 4,7-diphenyl-1,10-phenanthroline Bphen (50 nm)/ LiF (0.8 nm)/ Al (100 nm) have been fabricated. The key characteristics of the devices R1–R5 are summarized in **Table 13**.

Table 13. EL performance for devices R1–R5

Device	Voltage ^a , V	Luminance ^b , cd/m ²	CE ^b , cd/A	PE ^b , lm/W	EQE ^b , %	λ _{EL} , nm
R1 (host 14)	5.61	9650	15.92	15.92	11.65	618
R2 (host 15)	4.87	11070	13.47	13.47	8.92	617
R3 (host 16)	6.71	6193	14.27	14.27	12.61	622
R4 (host 17)	4.13	5812	5.05	5.05	4.67	620
R5 (host 13)	5.98	4999	9.75	9.75	9.29	622

^a at J=10 mA/cm²; ^b at maximum; ^c at 4 V

Compounds **13**–**17** were employed as hosts for the EML in devices R1–R5, respectively. Red emitter Ir(piq)₂acac, was doped into the hosts with a volume concentration of 7%. The hosts exhibited a high triplet energy (approximately 2.61–3.03 eV) to guarantee an effective energy transfer from the host to the dopant. The structures of PhOLEDs R1–R5 are presented in **Fig. 49**, and their EL characteristics are shown in **Fig. 50**.

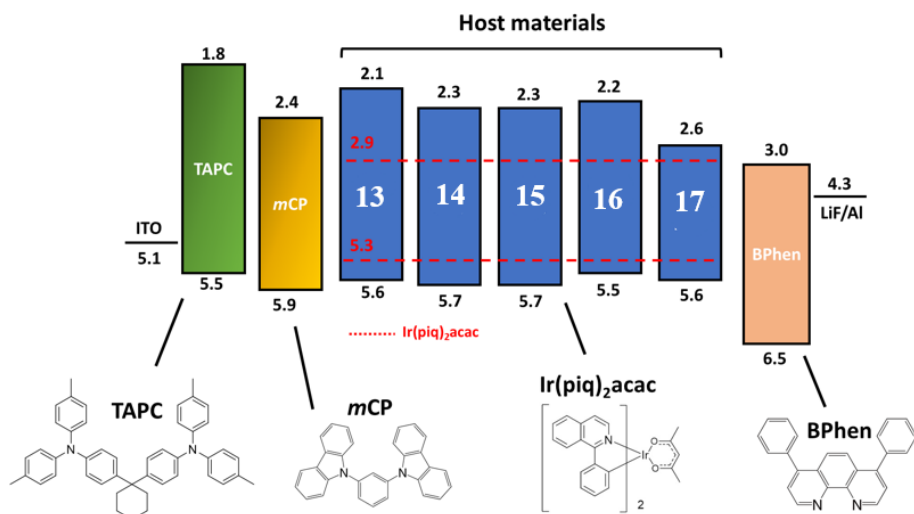


Fig. 49. Energy band diagram and chemical structure of compounds for red PhOLEDs.

As shown in **Fig. 49**, and **Table 13**, among the five red PhOLEDs, device R3 with compound **16** as the host achieved the best performance with the maximum current efficiency (CE), power efficiency (PE) and EQE of 41.98 cd/A, 37.66 lm/W and 12.61%, respectively. It was estimated that all devices R1–R5 show pure emission from Ir(piq)₂acac without any other impure emissions from the hosts, HTLs, or ETLs. This observation means that the exciton energy completely transfers from the host to the guest, and that no exciton leakage occurs during the energy transfer procedure. The driving voltage (at 10 mA/cm²) of these devices is ranged from 4.13–6.71 V, and their maximum luminance values are as high as 4999–11070 cd/m², see **Fig. 50 c**.

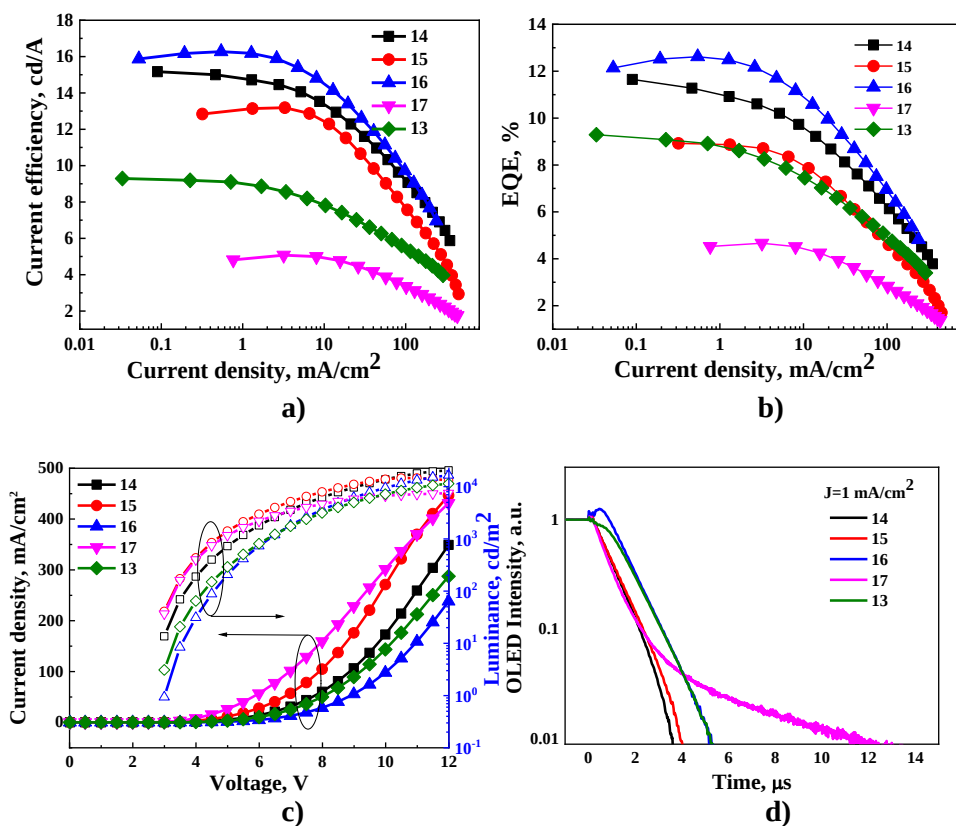


Fig. 50. (a) CE as a function of current density; (b) EQE as a function of current density; (c) J–V–L characteristics; (d) TREL signals of devices R1–R5.

To understand the emission mechanism, *transient electroluminescence* (TREL) was employed, see **Fig. 50 d**. Except for device R5, devices R1–R4 showed an EL decay which lasted several microseconds (4~5 μs), which indicates a typical decay behavior of Ir(piq)₂acac. However, device R5 showed a significantly longer EL decay (~12 μs) than the others, which is probably due to the inefficient energy transfer from the host to the dopant. Thus, the observation is deduced as the most possible reason of the low efficiency of PhOLED R5.

4. CONCLUSIONS

1. Four new triphenylethene-based derivatives containing 3,6-di-tertbutylcarbazole or 9,9-dimethyl-9,10-dihydroacridine as donor moieties and phenylene or tetrafluorophenylene linking bridges have been synthesized. It has been determined that:
 - a. Compounds exhibited aggregation induced emission enhancement, and their neat films demonstrated photoluminescence quantum yields of 16–29%.
 - b. The solid films of the obtained compounds emitted blue light with the emission maxima in the range of 478–487 nm.
 - c. The solid-state ionization potential and the electron affinity values of the compounds were in the range of 5.88–6.37 eV and 2.30–2.89 eV, respectively.
 - d. The highest hole and electron drift mobilities reaching $3.07 \times 10^{-3} \text{ cm}^2/\text{V}$ and $4.2 \times 10^{-3} \text{ cm}^2/\text{V}$, respectively, were observed in an electric field of $3.67 \times 10^5 \text{ V/cm}$ for the compound having 3,6-di-tert-butylcarbazole donor moiety and a phenylene linking bridge.
 - e. All the compounds were used as fluorescent emitters in OLEDs. The highest external quantum efficiency of 2% was observed for devices based on emitters containing 9,9-dimethyl-9,10-dihydroacridine moieties.
2. Four new aromatic diamines have been synthesized, and the impact of the linking topology of the CF_3 group has been investigated. It has been determined that:
 - a. Compounds containing 2,5-bis(trifluoromethyl)benzene moieties exhibited interactions between the π system of the central phenyl ring and the fluorine atom.
 - b. The detected intermolecular interactions in 2,5-bis(trifluoromethyl)benzene substituted compounds led to a closer packing of molecules.
 - c. Higher thermal temperatures, a lower ionization potential, and enhanced hole mobilities were detected for compounds containing 2,5-bis(trifluoromethyl)benzene moieties as compared to their counterparts containing 3,5-bis(trifluoromethyl)benzene moieties.
3. 3,6-Dimethoxy-9-(4-vinylphenyl)-9H-carbazole and 3,6-dimethoxy-9-(3-vinylphenyl)-9H-carbazole monomers and their polymers have been synthesized. It has been determined that:

- a. The RAFT polymerization of monomers with 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid as a chain-transfer agent proceeded in a living fashion affording polymers with a controlled molecular weight up to $M_n = 20,000$ and relatively low polydispersity ($\text{Đ} < 1.5$).
 - b. The polymerization rate of the monomer containing 3-vinylbenzene moiety was by more than one order of magnitude lower than that of the monomer featuring a 4-vinylbenzene fragment.
 - c. Thermal measurements revealed that the obtained polymers formed glasses with glass transition temperatures exceeding 160 °C. The PL of the films of the monomers and polymers revealed through-space thermally activated delay fluorescence or/and excimer emission.
 - e. The synthesized polymers were tested as hole transporting materials and hosts in solution-processed OLEDs. The best phosphorescent device exhibited an external quantum efficiency of 10.6%.
4. Five 9-(2-ethylhexyl)carbazole derivatives containing carbazole, phenothiazine, phenoxazine, acridane or dibenzazepine donor fragments have been synthesized. It has been determined that:
 - a. The photoluminescence bands of compounds exhibited charge transfer and/or local excited character in the different media.
 - b. The origin of the low-energy bands of photoluminescence of solid mixtures of compounds and zeonex, having acridane or azepine moieties, was attributed to the thermally activated fluorescence.
 - c. The ionization potential values of the vacuum-deposited films of compounds were in the range from 5.10 to 5.58 eV.
 - d. The compounds demonstrated good charge transporting abilities with the hole mobility exceeding $10^{-4} \text{ cm}^2/\text{Vs}$ at high electric fields. The derivatives, having carbazole and acridane moieties attached to 9-(2-ethylhexyl)carbazole, revealed ambipolar charge transporting properties.
 - e. The synthesized compounds were investigated as hosts in red phosphorescent OLEDs; they demonstrated the maximum quantum efficiency of 12.61%.

5. SANTRAUKA

5.1. ĮVADAS

Civilizacija siekia gerinti gyvenimo kokybę. Technologinė pažanga padeda žmonėms pasiekti šį tikslą [1]. Viena iš tokių pažangių technologijų – veiksminga ir patikima apšvietimo technologija. Tai paskatino sukurti ir atrasti tokius šviesos šaltinius, kaip ugnies fakelas senovės civilizacijoje, o šiuolaikinėje eroje – *šviesos diodas* (LED) [2]. Dėl šių šviesą skleidžiančių prietaisų tyrimų buvo sukurti pagrindiniai komerciniai produktai, pavyzdžiui, televizorių, monitorių ar mobiliųjų įrenginių ekranai. Siekdami išsaugoti planetą ir komercializuoti aplinkai saugesnes technologijas, mokslininkai pradėjo tirti organinės elektronikos sritį. Ši sritis susijusi su tokiomis technologijomis, kaip organiniai plonasluoksniai tranzistoriai, organiniai saulės elementai, *organiniai šviesos diodai* (OLED) ir kt. Įdomu tai, kad OLED yra palyginti nauja sąvoka, kuri mokslininkų dėmesio sulaukė per pastaruosius du dešimtmečius. Toks prietaisų konstrukcijos projektavimo metodas turėjo didelę įtaką gamybos sąnaudoms, o tai savo ruožtu sumažino išmetamo anglies dioksido kiekį ekranų gamybos technologijoje [3-5].

Pirmą kartą organinius junginius OLED gamyboje 1987 m. panaudojo Tang ir jo kolegos. Dėl mažos molekulinės masės, lankstumo ir perdirbimo sąnaudų, taip pat dėl unikalių elektrinių ir fotofizikinių savybių didžiulio dėmesio sulaukė organinės elektroaktyviosios medžiagos [6,7]. Organiniai elektroaktyvūs junginiai buvo laikomi tinkamais kandidatais optoelektroniniams prietaisams [3-5]. Organinių molekulių universalumas suteikia galimybę kurti π konjuguotus mažos molekulinės masės ir polimerinius puslaidininkius [8,9]. Organiniai spinduoliai laikomi pagrindine OLED sudedamąja dalimi ir yra lemiamas OLED efektyvumo veiksnys. Pagrindinės medžiagos, turinčios atitinkamą energijos lygį ir tripletų energiją, subalansuotą krūvininkų pernašą, taip pat didelį jų sluoksnių terminį stabilumą ir morfologinį stabilumą, gali leisti pasiekti puikų *fosforescencinių OLED* (PHOLED) veikimą [10].

Pagrindinę OLED konstrukciją sudaro organinis sluoksnis, esantis tarp neigiamai įkrauto anodo ir teigiamai jonizuoto katodo. Organinis sluoksnis sukurtas iš π konjuguotų junginių, pasižyminčių elektroliuminescencinėmis savybėmis, kad būtų pasiekta subalansuota ir (arba) efektyvi skylių ir elektronų rekombinacija. Be to, pagrindiniai reikalavimai, keliami organinėms elektroaktyviosioms medžiagoms, yra optinės ir fotofizikinės, terminės ir morfologinės savybės bei tinkami energetiniai lygmenys [11-13]. Elektronus atiduodančių (D) ir elektronus prisijungiančių (A) grupių ir jungiamųjų fragmentų (L) derinys organinių puslaidininkių konstrukcijoje naudojamas įvairioms naudingoms savybėms pasiekti [14].

Nors organinės elektronikos pažanga pagerėjo, dar liko keletas spęstinių problemų. Svarbiausios spęstinos problemos yra, pavyzdžiui, didelės OLED gamybos sąnaudos, trumpas tarnavimo laikas ir nepakankamas efektyvumas [15]. Medžiagos, turinčios tam tikrą savybių derinį, gali padėti įveikti šiuos trūkumus ir pagerinti norimas prietaiso savybes. Tai gali būti sudėtingas uždavinys, todėl labai svarbu

gerai suprasti elektroaktyviųjų junginių struktūros poveikį jų savybėms. Efektyvios medžiagos, pasižyminčios dideliu fotoluminescencijos kvantiniu našumu, reikiamais energetiniais lygmenimis, didele skylių ir elektronų pernašos geba, gali būti susintetintos tinkamai parinkus donorinius ir (arba) akceptorinius ir jungiamuosius fragmentus. Didelį susidomėjimą kelia paprastos organinės fluorescencinės arba fosforescencinės medžiagos. Daugiafunkciai paprasti organiniai junginiai yra palankūs konkurentai siekiant pagerinti organinių elektroluminescencinių OLED veikimą.

Šio darbo tikslas: naujų organinių elektroaktyvių trifeniletano, karbazolo ir trifenilamino darinių modeliavimas, sintezė, tyrimas ir potencialus pritaikymas OLED.

Disertacijos tikslui pasiekti buvo suformuluoti šie uždaviniai:

- Naujų trifeniletano darinių, bis(trifluormetil)fenilpakeistų aromatinių diaminių, metoksipakeistų karbazolo polimerų ir V formos karbazolo darinių su įvairiais donoriniais fragmentais sintezė.
- Susintetintų medžiagų savybių tyrimas ir analizė.
- Junginių, kaip skylių pernešančiųjų medžiagų, spinduolių arba matricų tyrimas fluorescenciniuose ir fosforescenciniuose OLED.

Disertacijos ginamieji teiginiai:

- Trifeniletano darinių sintezė yra efektyvi strategija gauti emisinius junginius, pasižyminčius agregacijos sukelta emisija.
- F atomai elektroaktyviuose junginiuose sudaro tarpmolekulinės ir intramolekulinės sąveikas, dėl kurių sumažėja jonizacijos potencialo vertės bei pagerėja krūvininkų judrio savybės.
- Polimerai yra tinkami formuoti OLED tirpalų liejimo metodu, nes sudaro amorfinius, morfologiškai stabilius ir lanksčius sluoksnius.
- Aromatinių fragmentų suvaržymas mažamolekuliniuose junginiuose įgalina termiškai aktyvintos uždelstosios fluorescencijos vyksmą.

Darbo naujumas:

- Pirmą kartą buvo pastebėtas agregacijos sukeltas padidintas trifeniletano darinių, kurių donorų fragmentai yra 2,6-di-tret-butylkarbazolas arba 9,9-dimetil-9,10-dihidroakridinas, emisija ir jų panaudojimas OLED spinduliuotėse. buvo įrodyta.
- Susintetinti nauji aromatiniai diaminais su bis(trifluormetil)fenilo pakaitais ir nustatytas mezomerinis efektas junginiams su 2,5-bis(trifluormetil)benzeno dalimis.

- Nauji 3,6-dimetoksi-karbazolo polimerai, gauti RAFT polimerizacijos būdu, buvo išbandyti kaip skyles pernešančiosios medžiagos ir matricos OLED, suformuotuose tirpalų liejimo metodu. Geriausio fosforescencinio prietaiso išorinis kvantinis efektyvumas buvo 10,6 %.
- Susintetinti keturi nauji karbazolo dariniai su donoriniais 9,9-dimetil-9,10-dihidroakridino, 10*H*-fenotiazino, 10*H*-fenoksazino ir 5*H*-dibenzo[*b,f*]azepino fragmentais ir pademonstruotas jų pritaikymas fosforescenciniuose OLED. Nustatytas didžiausias prietaiso su 10,10'-(9-(2-etilheksil)-9*H*-karbazol-3,6-diyl)bis(9,9-dimetil-9,10-dihidroakridinu), pasižyminčiu termiškai aktyvuota uždelsta fluorescencija, išorinis kvantinis efektyvumas, siekiantis 12,6%.

Asmeninis autorius indėlis

Skyriai 3.1–3.4. Disertacijos autorius (Kauno technologijos universiteto Polimerų chemijos ir technologijos katedra) modeliavo, susintetino ir išgrynino naujus organinius elektroaktyvius junginius. Autorius atliko ir išanalizavo teorinių skaičiavimų, struktūros, UV-VIS absorbcijos, fotoluminescencijos, įskaitant kvantinę išeigą ir sužadintos būsenos gyvavimo trukmę, bei ciklinės voltamperometrijos matavimų rezultatus. Dr. Viktorija Andrulevičienė ir prof. Juozas Vidas Gražulevičius (Kauno technologijos universiteto Polimerų chemijos ir technologijos katedra) konsultavo molekulių modeliavimo ir sintezės klausimais, analizuojant susintetintų junginių savybes bei rengiant mokslines publikacijas. Dr. Jūratė Simokaitienė (Kauno technologijos universiteto Polimerų chemijos ir technologijos katedra) atliko terminius matavimus DSC ir TGA. Masių spektrų matavimus atliko dr. Eigirdas Skuodis (Kauno technologijos universiteto Polimerų chemijos ir technologijos katedra), rezultatus toliau analizavo autorius. Elektronų fotoemisijos matavimus, krūvininkų judrio matavimus, OLED gamybą ir charakterizavimą atliko dr. Dmytro Volyniuk ir dr. Oleksandr Bezvikonnyi (Kauno technologijos universiteto Polimerų chemijos ir technologijos katedra); rezultatus toliau analizavo autorius. Monokristalų rentgeno spindulių difrakcinės analizės matavimus atliko doc. dr. Audrius Bučinskas (Kauno technologijos universiteto Polimerų chemijos ir technologijos katedra). Dr. Galyna Sych (Kauno technologijos universiteto Polimerų chemijos ir technologijos katedra) konsultavo molekulių modeliavimo, sintezės ir struktūros analizės klausimais. Prof. dr. Azhar Ariffin (Malaizijos universiteto Gamtos mokslų fakulteto Chemijos katedra) konsultavo BMR analizės ir ciklopaladavimo reakcijos mechanizmų paaiškinimo klausimais. Dr. Sohrab Nasiri (Kauno technologijos universiteto Polimerų chemijos ir technologijos katedra) padėjo atlikti fotofizikinių savybių matavimus. Dr. Dalius Gudeika (Kauno technologijos universiteto Polimerų chemijos ir technologijos katedra) ir dr. Rimantas Henrikas Kublickas (Kauno technologijos universiteto Maisto mokslo ir technologijos katedra) padėjo redaguoti rankraštį ir atlikti reikiamus pataisymus. George Belousov, dr. Aliaksei Vaitusionak ir dr. Sergej Kostjuk (Baltarusijos valstybinio universiteto Fizikinių cheminių problemų tyrimų institutas) atliko monomerų polimerizaciją ir polimerų kinetikos eksperimentus.

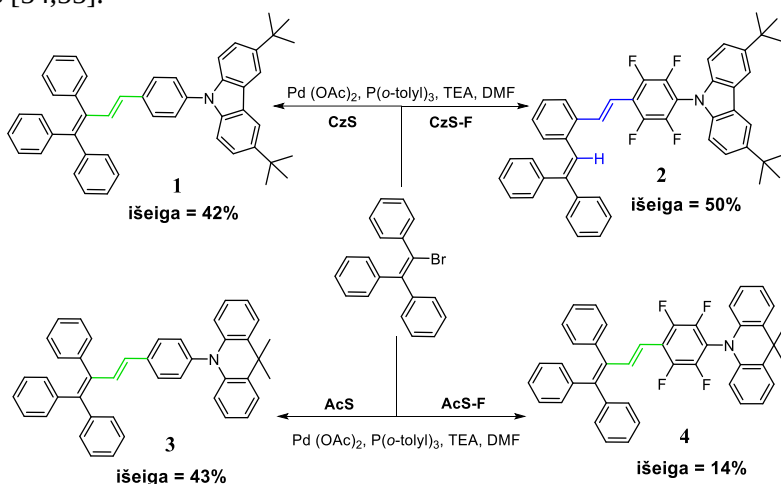
Dr. Uliana Tsiko (Kauno technologijos universiteto Polimerų chemijos ir technologijos katedra) padėjo redaguoti rankraštį bei atlikti reikiamus pataisymus. Bo-Yen Lin (Yuan Ze universiteto Elektros inžinerijos katedra), Chia-Hsun Chen (Taivano nacionalinio universiteto Fotonikos ir optoelektronikos institutas ir Elektros inžinerijos katedra), Jing-Xiang Huang (Taivano nacionalinio universiteto Fotonikos ir optoelektronikos institutas ir Elektros inžinerijos katedra) ir Chi-Feng Lin (Nacionalinio jungtinio universiteto Elektrooptinės inžinerijos katedra) pagamino ir charakterizavo fosforescencinius OLED. Tien-Lung Chiu (Yuan Ze universiteto Elektros inžinerijos katedra) ir Jiun-Haw Lee (Taivano nacionalinio universiteto Fotonikos ir optoelektronikos institutas ir Elektros inžinerijos katedra) analizavo fosforescencinių OLED elektroliuminescencines charakteristikas.

5.2. TRIFENILETENO DARINIAI, SKIRTI MĖLYNOS SPALVOS NELEGIRUOTIEMS ORGANINIAMS ŠVIESOS DIODAMS

Šis skyrius parengtas remiantis publikuotu straipsniu: Ronit Sebastine Bernard, Galyna Sych, Sohrab Nasiri, Oleksandr Bezikonnyi, Dmytro Volyniuk, Juratė Simokaitienė, Audrius Bučinskas, Dalius Gudeika, Azhar Ariffin, Juozas V. Gražulevičius. *Triphenylethene-based emitters exhibiting aggregation induced emission enhancement and balanced bipolar charge transport for blue non-doped organic light-emitting diodes* // *Synthetic Metals* 271 (2021) 116641. JIF: 3.266. DOI:10.1016/j.synthmet.2020.116641.

Pastaraisiais metais fluorescencinės medžiagos, pasižyminčios agregacijos sukelta emisija (AIE) arba agregacijos sustiprinta emisija (AIEE), sulaukė didelio tyrėjų dėmesio jas pritaikant organinėje optoelektronikoje [104]. Trifenileteno (TPE) ir tetrafenileteno (TEPE) dariniai yra plačiai tyrinėjami dėl jų unikalių AIE ir AIEE savybių [105-107]. Šios medžiagos atlieka svarbų vaidmenį sprendžiant agregacijos sukulto emisijos gesimo (ACQ) problemą emisiniame prietaiso sluoksnyje [109].

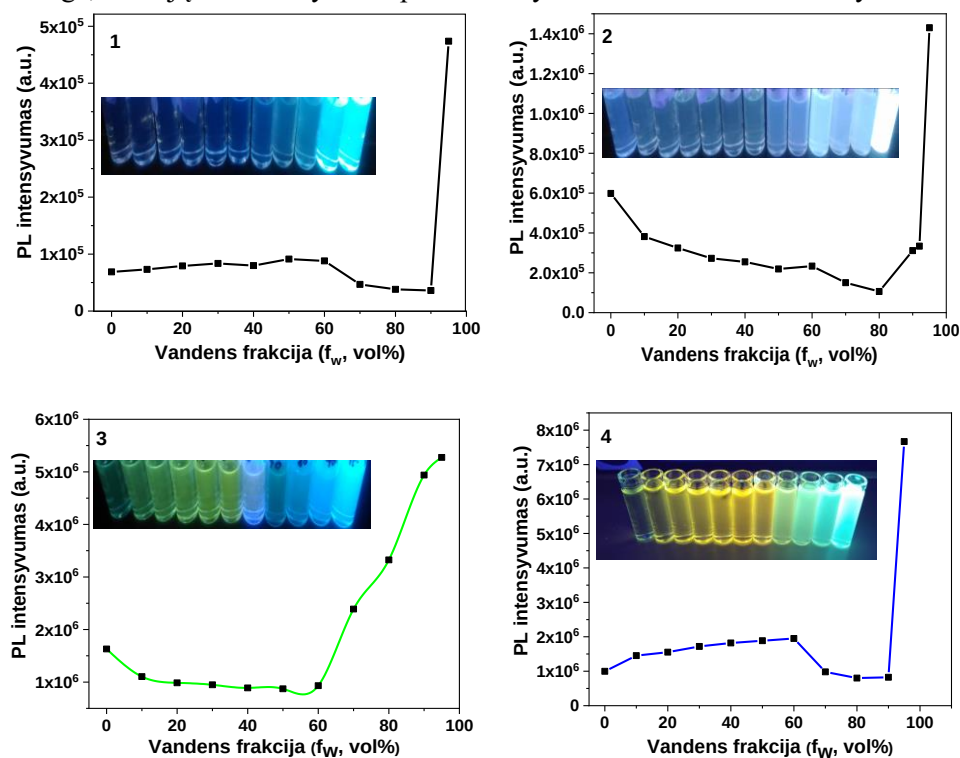
Tiksliniai junginiai **1–4**, pavaizduoti 5.2.1 **schema**je, buvo susintetinti taikant Heck reakciją. Vykdamas junginio **2** sintezę buvo užfiksuotas retas ciklopaladavimo reiškinys [54,55].



5.2.1 schema. Junginių **1–4** sintezė

Tiriant AIEE savybes, junginiai **1–4** buvo disperguoti tetrahidrofurano (THF) ir (arba) vandens (H₂O) mišiniuose, kuriuose vandens kiekis (F_w) svyruoja nuo 0 % iki 95 %. Dispersijų fotoluminescencijos (PL) spektrų maksimumų intensyvumo priklausomybė nuo vandens kiekio pateikta 5.2.1 **pav.** Tiriami junginiai yra netirpūs vandenyje, todėl, didėjant vandens kiekiui THF:H₂O mišiniuose, junginiai formuoja agregatus, kurie sukelia Mie sklaidą [113]. Agregatų formavimąsi THF:H₂O mišiniuose įrodo junginių **1–4** absorbcijos spektrų mažiausios energijos juostos batochrominis poslinkis ir mažo intensyvumo absorbcijos juostos atsiradimas ilgujų

bangų diapazone. Analizuojant junginių **1–4** PL spektrus THF:H₂O mišiniuose, pastebėtas PL maksimumo poslinkis ilgesnių bangų kryptimi didėjant vandens kiekiui. Ši tendencija gali būti aiškinama junginiuose vykstančia intramolekuline krūvio pernaša (ICT). PL intensyvumo nuo vandens kiekio diagramos (5.2.1 pav.) rodo, kad, vandens kiekiui pasiekus 60 % junginio **3** ir 90 % junginių **1, 2, 4** dispersijose, pastebimas smarkus emisijos intensyvumo padidėjimas, matomas AIEE efektas. Nustatyta, kad junginių **1** ir **4** PL maksimumo intensyvumas šiek tiek didėja didėjant vandens kiekiui nuo 0 % iki 60 %. Junginių **2** ir **3** atveju PL spektrų maksimumų intensyvumas nuosekliai mažėja didėjant vandens kiekiui, atitinkamai nuo 0 % iki 80 % ir 60 %. Junginių **1–4** PL spektrai yra jautrūs tirpiklio, kuriame yra tirpinami, poliškumui dėl ICT emisijos pobūdžio. Todėl PL spektrų maksimumų poslinkis ilgesnių bangų linkme ir PL intensyvumo mažėjimas yra tikėtini didėjant THF:H₂O mišinio poliškumui, didėjant vandens kiekiui. Akivaizdu, kad tirtų junginių **1–4** emisijos gesimo ir AIEE pusiausvyra THF:H₂O mišiniuose buvo skirtinga, todėl jų PL intensyvumo priklausomybės nuo vandens kiekio skyrėsi.



5.2.1 pav. Junginių **1–4** PL intensyvumo priklausomybės nuo vandens kiekio diagramos

Junginių **1–4** sluoksnių jonizacijos potencialai (IP_{PE}) buvo išmatuoti pasitelkiant fotoelektronų emisijos (PE) spektrometriją. Ciklinės voltamperometrijos (CV) metodu gautos junginių **1–4** tirpalų jonizacijos potencialo (IP_{CV}) ir elektroninio giminingumo (EA_{CV}) reikšmės. PE ir CV rezultatai pateikti 5.2.1

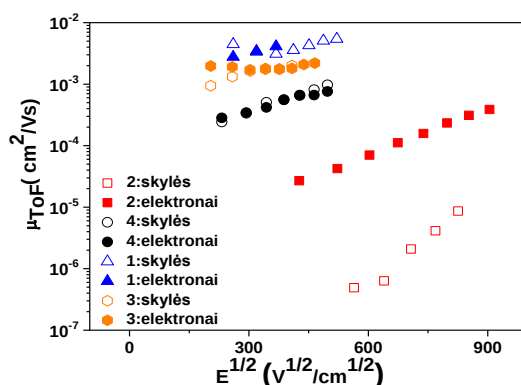
lentelėje. Nustatyta, kad IP_{PE} yra nuo 5,88 eV iki 6,37 eV. CV metodu gautos junginių **1–4** IP_{CV} reikšmės buvo 0,24–0,68 eV mažesnės nei IP_{PE} . Ši neatitikimą galima paaiškinti skirtingu molekulių agregacijos laipsniu tirpale ir kietoje būsenoje. Pastebėta, kad junginių **2** ir **4**, turinčių tetrafluorfenilo fragmentus, jonizacijos potencialų reikšmės yra didesnės nei jų fenilpakeistų analogų **1** ir **3**. Apskaičiuotos junginių **1–4** EA_{CV} išsidėsto nuo 2,54 eV iki 3,09 eV.

5.2.1 lentelė. Elektrocheminės ir fotoelektrinės medžiagų charakteristikos

Junginys	CV (CH ₂ Cl ₂)				Teorinės vertės, eV		Sluoksnių, eV		
	E_{ox}^a , V	E_{red}^a , V	IP_{cv}^b , eV	EA_{cv}^c , eV	HOMO _d	LUMO _d	IP_{PE}^e	EA^f	E_g^{opt} _g
1	0,91	-2,00	5,71	2,80	-4,95	-1,68	6,02	2,72	2,83
2	1,14	-1,71	5,94	3,09	-5,30	-1,90	6,18	2,78	2,9
3	0,82	-2,26	5,62	2,54	-4,80	-1,74	5,88	3,08	2,84
4	0,89	-1,74	5,69	3,06	-5,07	-2,01	6,37	2,63	2,81

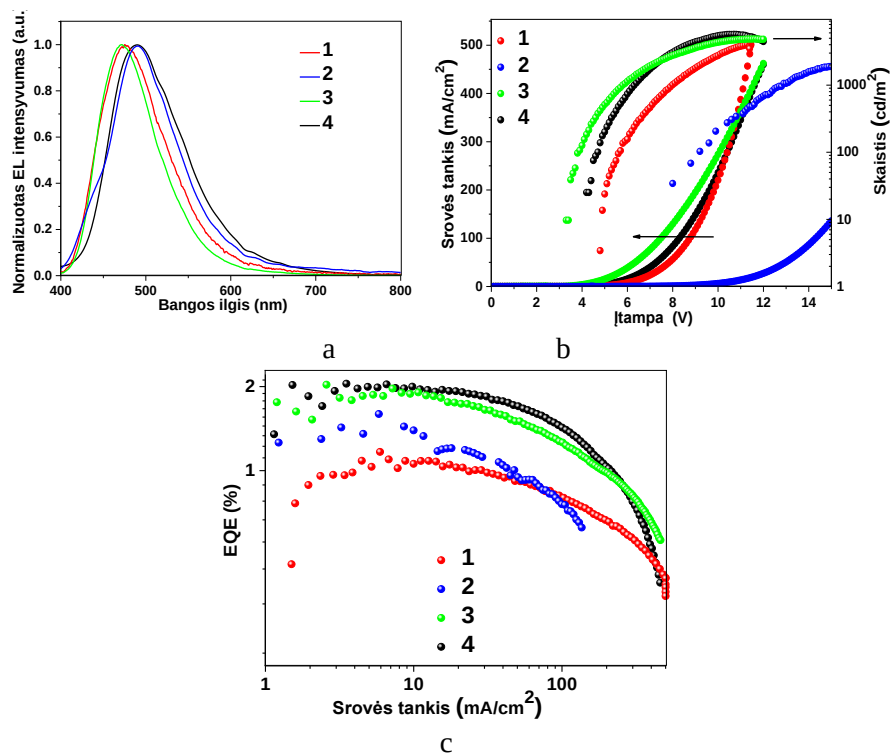
^a Oksidacijos / redukcijos bangų pradžia; ^b IP_{cv} – jonizacijos potencialas ($E_{ox} BS+4,8$); ^c EA_{cv} – giminingumas elektronui ($E_{red} +4,8$); ^d Teoriškai apskaičiuotos energijos (HOMO, LUMO); ^e Jonizacijos potencialas; ^f Giminingumas elektronui ($IP_{PE} - E_g$); ^g Optinės juostos tarpas ($1239,84/\lambda_{abs}^{film}$).

Junginių **1–4** sluoksnių krūvininkų judris buvo išmatuotas lėkio trukmės metodu. (ToF). Subalansuotas elektronų ir skylių judris buvo užfiksuotas junginių **1**, **2** ir **3** sluoksniuose. Tačiau junginys **4** pasižymėjo daug didesniu elektronų judriu, palyginti su skylių judriu. Junginio **1** buvo didžiausias skylių ir elektronų dreifinis judris, atitinkamai $3,07 \times 10^{-3} \text{ cm}^2/\text{Vs}$ ir $4,2 \times 10^{-3} \text{ cm}^2/\text{Vs}$, esant elektros lauko stipriui $3,67 \times 10^5 \text{ V/cm}$.



5.2.2 pav. Junginių **1–4** sluoksnių skylių dreifinio judrio priklausomybė nuo elektros lauko stiprio

Susintetinti junginiai **1–4** buvo išbandyti kaip spinduoliai nelegiruotų OLED struktūrose. Suformuotų prietaisų elektroluminescencijos (EL) spektrai ir EL charakteristikos pateiktos 5.2.2 **pav.** ir 5.2.2 **lentelėje**.



5.2.3 pav. OLED parametrai: a) normalizuoti EL spektrai; b) srovės tankio ir skaisčio priklausomybė nuo įtampos; c) *EQE* priklausomybė nuo srovės tankio

Prietaisų EL spektrai (5.2.3 **pav.**) atitinka junginių **1–4** PL spektrus, jų emisijos smailės yra mėlynos spalvos. Maža prietaisų darbinė įtampa nuo 3,8 V iki 5,7 V rodo veiksmingą skylių ir elektronų injekciją ir pernašą į rekombinacijos zoną. Nustatyta, kad, įterpus krūvininkus blokuojančius sluoksnius OLED, kurio emisinio sluoksnio gamybai buvo naudojamas junginys **2**, darbinė įtampa padidėjo iki 9,2 V. Junginių **3** ir **4**, turinčių akridano fragmentus, buvo geresnės OLED charakteristikos. Šių prietaisų *EQE* siekė 2 % (5.2.2 **lentelė**). Prietaiso, kuriame junginys **4** buvo naudojamas kaip spinduolis, buvo didžiausios galios efektyvumo (3,2 lm/W) ir skaisčio (5700 cd/m²) reikšmės dėl suderinto bipolinio krūvininkų judrio ir efektyvios sužadintų būsenų relaksacijos emisiniu būdu.

5.2.2 lentelė. Nelegiruotų OLED charakteristikos

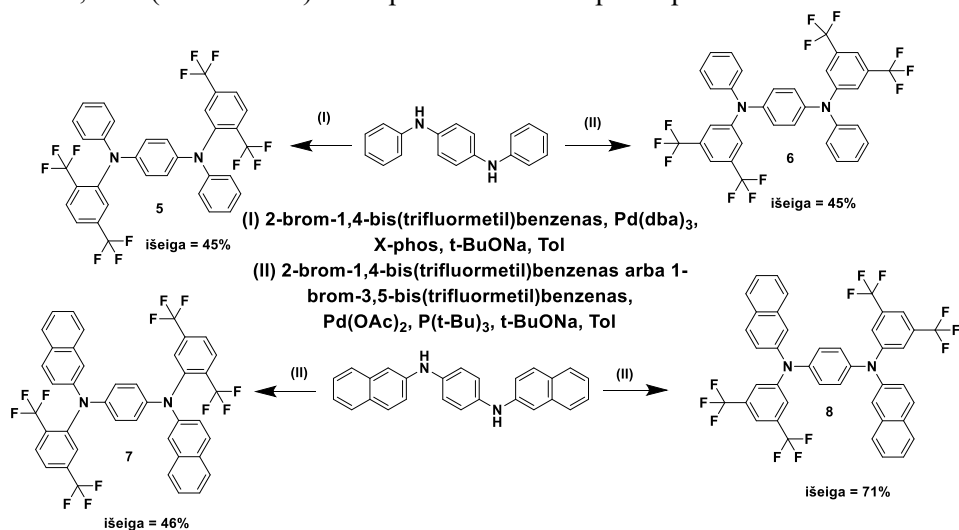
Spinduolis	Darbinė įtampa, (V) ^A	$\lambda_{EL, max}$, (nm)	Skaistis $\times 10^3$, (cd/m ²) ^B	<i>EQE</i> , (%) ^B	Galios efektyvumas, (lm/W) ^B	<i>EQE</i> , <i>PE</i> , <i>CE</i> , esant 100 (cd/m ²) _C	<i>CIE</i> ^D
ITO / MoO ₃ (1 nm) / NPB (50 nm) / TCTA (10 nm) / nelegiruotas spinduolio sluoksnis (25 nm) / TPBi (45 nm) / LiF (0,5 nm) / Al (> 200 nm)							
1	5,7	475	4,1	1,2	1,2	1,1 %, 1,2 lm/W, 2,1 cd/A	0,17, 0,25
3	3,8	472	4,9	2	3,1	2 %, 3 lm/W, 3,3 cd/A	0,16, 0,21
4	4,7	489	5,7	2	3,2	1,7 %, 2,8 lm/W, 4,6 cd/A	0,20, 0,35
ITO / HAT-CN (1 nm) / TCTA (55 nm) / mCP (7,5 nm) / nelegiruotas spinduolio sluoksnis (30 nm) / TSPO1 (5 nm) / TPBi (55 nm) / LiF (0,5 nm) / Al (> 200 nm)							
2	9,2	490	1,9	1,6	1,1	1,4 %, 1,1 lm/W, 3,2 cd/A	0,19, 0,32
OLED elektroluminescencijos parametrai; A: įtampa esant 100 cd/m ² skaisčiui; B: didžiausios vertės; C: <i>EQE</i> , galios ir srovės efektyvumo vertės esant 100 cd/m ² ; D: (x, y) <i>CIE</i> 1931 UCS koordinatės, apskaičiuotos pagal EL spektrus [114].							

5.3. BIS(TRIFLUORMETIL)FENILO DIPAKEISTI AROMATINIAI DIAMINAI

Šis skyrius parengtas remiantis publikuotu straipsniu: Ronit Sebastine Bernard, Viktorija Andrulevičienė, Oleksandr Bezikonnyi, Dmytro Volyniuk, Jūratė Simokaitienė, Rimantas Henrikas Kublickas, Juozas Vidas Gražulevičius. *Impact of the substitution pattern of the acceptor on the properties of the bis(trifluoromethyl)phenyl disubstituted aromatic diamines* // Journal of Photochemistry & Photobiology, A: Chemistry 430 (2022) 113969. JIF:4.29. DOI: 10.1016/j.jphotochem.2022.113969.

Trifenilaminas (TPA) ir *N,N'*-bis(3-metilfenil)-*N,N'*-difenilbenzidinas (TPD) turėjo stiprias elektronų donorystės ir skylių pernašos savybes, taip pat gebėjimą formuoti stabilų amorfinį sluoksnį [115,116]. Šių junginių dariniai buvo pradėti plačiai naudoti OLED, perovskitinių saulės elementų ir organinių tranzistorių gamybai [117-122]. Siekiant pagerinti organinių optoelektroninių prietaisų charakteristikas, TPA ir TPD darinių struktūros buvo modifikuotos fluora (F) turinčiomis grupėmis. Žinoma, kad F atomai junginiuose gali padidinti krūvininkų judrį ir sumažinti jonizacijos potencialą [123, 124].

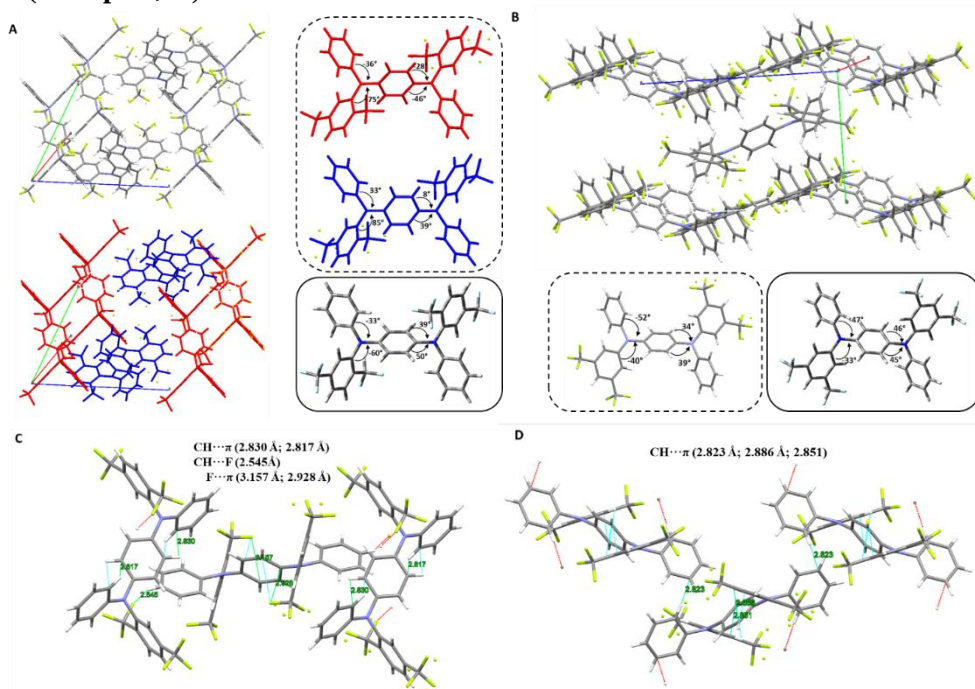
Aromatiniai diaminai **5–8** su trifluormetilo (CF₃) grupėmis skirtingose padėtyse buvo susintetinti naudojant Buchwaldo ir Hartwigo kryžminio jungimo reakciją (**5.3.1 schema**). π -Konjuguotas aromatinis diamino fragmentas veikė kaip donoras, o bis(trifluormetil)fenilo pakaitai veikė kaip akceptorius.



5.3.1 schema. Junginių **5–8** sintezė

Junginių **5** ir **6** kristalinės struktūros (**5.3.1 pav.**) buvo ištirtos atlikus *rentgeno spindulių difrakciją* (XRD). Junginio **5** monokristaluose buvo aptikti dviejų tipų konformeriai ir skirtingas molekulių išsidėstymas. **5.3.1 pav, A**, skirtingi konformeriai nuspalvinti mėlyna ir raudona spalva. Tarpatominių kontaktų konformeruose analizė atskleidė skirtingas centrinio fenilo žiedo ir šoninių

fragmentų sąveikas. Konformere, kuriame dvisienis kampas tarp fenilo žiedo ir C-N-C jungties yra 33° , C-H $\cdots\pi$ sąveikos yra 2,830 Å ir 2,817 Å, o F atomas sąveikauja su kaimyninės molekulės vandenilio atomu (C-H $\cdots$ F) atstumu 2,545 Å (5.3.1 pav., A, C). Taip pat junginio 5 konformere buvo aptiktos sąveikos tarp centrinio fenilo žiedo π sistemos ir fluoro atomo (F $\cdots\pi$) 3,157 Å ir 2,928 Å (5.3.1 pav., A, C). Junginio 6 atveju buvo nustatytas tik vieno tipo konformeras (5.3.1 pav., B), kurio tarpmolekulinės ir intramolekulinės C-H $\cdots\pi$ sąveikos yra 2,883 Å, 2,886 Å ir 2,851 Å. (5.3.1 pav., D).



5.3.1 pav. 5 (A) ir 6 (B) junginių molekulinės struktūros (eksperimentinės (brūkšninė linija) ir teoriškai apskaičiuotos DFT-B3LYP/6-311G(d, p) lygmenyje (ištiesinė linija) bei 5 (C) ir 6 (D) atomų sąveikos monokristaluose

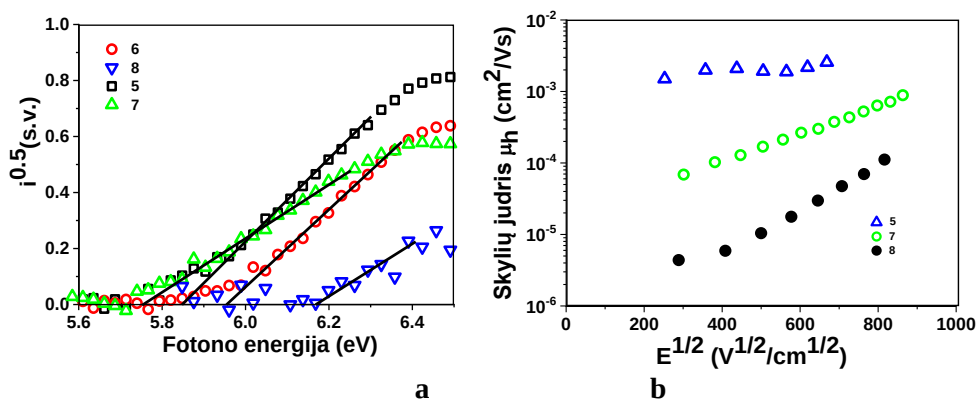
Teorinių skaičiavimų, CV ir PE duomenys yra pateikti 5.3.1 lentelėje. Molekulių orbitalių analizė parodė, kad susintetintų junginių 5–8 aukščiausia užimta molekulinė orbitalė (HOMO) yra pasiskirsčiusi per visą π -konjuguotą molekulinės ilgį. HOMO elektronų tankis junginiuose 5 ir 7 buvo matomas F atomuose, esančiuose arti centrinio fenilo žiedo. Junginiuose 6 ir 8 elektronų tankis žemiausioje neužimtoje molekulinėje orbitalėje (LUMO) yra lokalizuotas visoje molekulėje. Tačiau 5 ir 7 junginių atveju LUMO daugiausia yra ant bis(trifluormetil)fenilo pakaitų.

5.3.1 lentelė. Teorinės, elektrocheminės ir fotofizinės junginių charakteristikos

Junginys	LUMO, eV	HOMO, eV	H-L, eV	EA^{CV^a} , eV	IP^{CV^b} , eV	$E_g^{CV^c}$, eV	IP^{PE} , eV
5	-1,46	-5,15	3,69	2,40	5,20	2,80	5,84
6	-1,36	-5,31	3,95	2,14	5,28	3,14	5,95
7	-1,54	-5,14	3,60	2,41	5,19	2,78	5,75
8	-1,49	-5,25	3,76	2,10	5,26	3,16	6,17

^a Elektroninio giminingumo, ^b jonizacijos potencialo ir ^c draustinės juostos vertės, apskaičiuotos pagal lygtis $EA^{CV} = 4,8 - (E_{ox}^{Fer_{onset}} - E_{red}^{onset})$, $IP^{CV} = 4,8 + (E_{ox}^{onset} - E_{ox}^{Fer_{onset}})$ ir $E_g^{CV} = IP^{CV} - EA^{CV}$. Feroceno pradžios potencialas buvo $E_{ox}^{Fer_{onset}} = 0,2$ V.

Nustatant junginių **5–8** EA_{CV} ir IP_{CV} vertes, buvo naudojami junginių pirmosios redukcijos ir oksidacijos bangų pradžios potencialai praskiestuose tetrahidrofurano tirpaluose feroceno atžvilgiu. Apskaičiuotos junginių EA_{CV} vertės svyravo nuo 2,10 iki 2,41 eV, o IP_{CV} vertės – nuo 5,19 iki 5,28 eV (**5.3.1 lentelė**). Junginių IP_{CV} vertės mažėjo ta pačia tvarka, kaip ir junginių **6 > 8 > 5 > 7** HOMO energijų vertės. PE spektrometrijos metodu išmatuoti junginių **5–8** sluoksnių IP_{PE} vertės svyravo nuo 5,75 eV iki 6,17 eV (**5.3.1 lentelė, 5.3.2 pav., a**). Dėl skirtingų matavimo sąlygų jos buvo didesnės nei IP_{CV} vertės. IP_{PE} tendencija neatitinka IP_{CV} verčių tendencijos. Šį pastebėjimą galima paaiškinti skirtingų konformerų susidarymu kietuose junginių sluoksniuose, dėl kurių molekulėse pasikeičia dvisieniai kampai ir π -konjugacijos ilgis. Tačiau visais atvejais junginių **5** ir **7** IP_{CV} , IP_{PE} ir HOMO energijų vertės buvo mažesnės nei junginių **6** ir **8**. Šis pastebėjimas gali būti siejamas su dviejų efektų, kuriuos sukelia CF_3 grupė, prijungta prie fenilo *orto* padėtyje, deriniu. Pirma, F atomų nesuporuoti elektronai sąveikauja su centrinio fenilo žiedo π elektronais mezomeriniu efektu. Šią prielaidą patvirtina junginio **5** monokristale aptinkama $F \cdots \pi$ sąveika. Antra, *orto* padėtyje prijungta CF_3 grupė sukelia sferinį trukdį tarp akceptoriaus fragmento ir C-N-C jungties, todėl sumažinamas HOMO išplitimas į akceptoriaus dalį, o LUMO – į donorinę dalį.



5.3.2 pav. (a) Junginių 5–8 sluoksnių fotoemisijos spektrai ir **(b)** skylių dreifinio judrio priklausomybė nuo elektrinio lauko stiprio

ToF matavimai buvo atlikti junginių 5, 7 ir 8 sluoksnių krūvininkų pernašos savybėms įvertinti. Deja, junginio 6 sluoksniu nebuvo tinkamas krūvininkų judriui matuoti dėl žemos stiklėjimo temperatūros ($T_g = 26\text{ }^{\circ}\text{C}$). Nepaisant to, kad susintetinti junginiai 5, 7 ir 8 turi CF_3 akceptorinius fragmentus, junginių sluoksniuose buvo aptiktas tik skylių judris. Junginių 5, 7 ir 8 sluoksnių skylių dreifinio judrio priklausomybė nuo elektrinio lauko stiprio pateikta 53.2. pav., b. Geriausiomis krūvininkų pernašos savybėmis pasižymėjo junginiai 5 ir 7, turintys CF_3 grupę *orto*- padėtyje. Junginių 5 ir 7 sluoksnių skylių dreifinis judris siekė atitinkamai $2,2 \times 10^{-3}\text{ cm}^2/\text{Vs}$ ir $3,0 \times 10^{-4}\text{ cm}^2/\text{Vs}$, esant elektrinio lauko stipriui $4,1 \times 10^5\text{ V/cm}$. Junginys 8 su CF_3 grupėmis *meta*- padėtyse pasižymėjo maždaug viena eile mažesniu skylių judriu, palyginti su junginiais 5 ir 7. Daroma prielaida, kad krūvininkų pernašos savybių skirtumas atsirado dėl skirtingo molekulių išsidėstymo junginių sluoksniuose [127, 128]. Didesnis tarpmolekulių ir intramolekulių sąveikų skaičius junginio 5 monokristale, palyginti su junginio 7 monokristalu (5.3.1 pav., C, D), gali rodyti glaudesnę molekulių susikaupimą. Be to, sąveika tarp centrinio fenilo žiedo π sistemos ir F atomo junginiuose 5 ir 7 gali sumažinti geometrinių konformerų skaičių. Dėl šių sąveikų gali sumažėti energetinės tinklelos parametras ir padidėti skylių dreifinis judris amorfiniuose junginių sluoksniuose [129].

5.3.2 lentelė. Fotofizikinės junginių charakteristikos

Junginys	f^a	λ_{PL} film/TOL/THF, nm	E_{S1}^b , eV	E_{T1}^b , eV	ΔE_{ST} , eV
5	0,131	485/512/544	2,89	2,69	0,20
6	0,016	460/473/515	3,00	2,74	0,26
7	1,133	492/519/546	2,90	2,60	0,30
8	0,060	450/470/510	3,03	2,45	0,58
^a $S_0 \rightarrow S_1$ perėjimo osciliatoriaus stipris, ^b sužadintų būsenų energijos, išmatuotos pagal praskiestų tirpalų THF fotoluminescencijos ir fosforescencijos juostų pradžios kraštą, esant 77 K temperatūrai.					

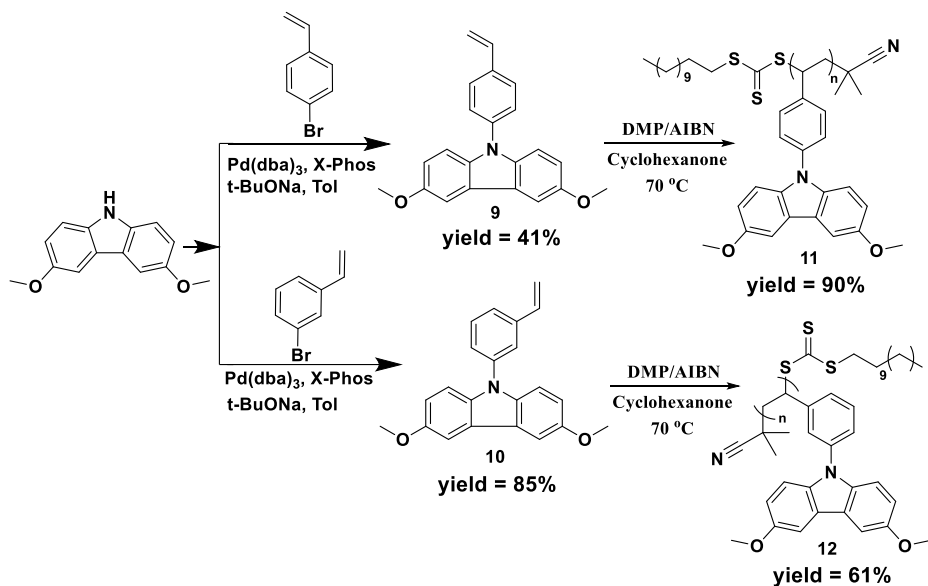
Pirmojo *singleto* (E_{S1}) ir *tripleto* (E_{T1}) sužadintos būsenos eksperimentinės energijos vertės buvo paimtos iš junginių **5–8** praskiestų THF tirpalų fluorescencijos ir fosforescencijos spektrų, užregistruotų 77 K temperatūroje (5.3.2 lentelė). Naftanepakeistų junginių **7** ir **8** buvo mažesnė E_{T1} nei jų analogų **5** ir **6**. Nustatyta, kad sferinė kliūtis tarp donoro ir akceptoriaus fragmentų, kurią sukelia CF_3 pakaitai fenilo žiedo *orto*- padėtyje, sumažina junginių **5** ir **7** ΔE_{ST} , palyginti su junginių **6** ir **8**.

5.4. METOKSIPAKEISTI KARBAZOLO POLIMERAI, SKIRTI TIRPALŲ LIEJIMO METODU GAMINAMIEMS ORGANINIAMS ŠVIESOS DIODAMS

Šis skyrius parengtas remiantis publikuotu straipsniu: Ronit Sebastine Bernard, Viktorija Andrulevičienė, George K. Belousov, Aliaksei A. Vaitusionak, Uliana Tsiko, Dmytro Volyniuk, Sergei V. Kostjuk, Rimantas Henrikas Kublickas, Juozas Vidas Gražulevičius. *Methoxy-substituted carbazole-based polymers obtained by RAFT polymerization for solution-processable organic light-emitting devices* // European Polymer Journal 174 (2022) 111323. JIF: 4.59. DOI: 10.1016/j.eurpolymj.2022.111323.

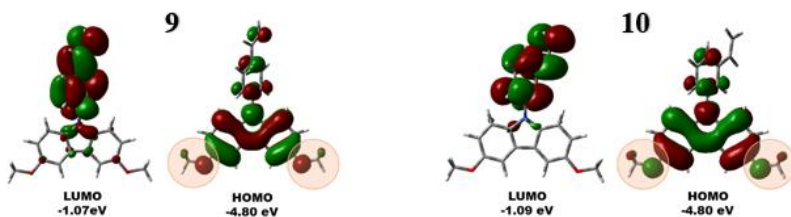
Karbazolo dariniai turi didelį potencialą optoelektronikoje dėl puikių krūvininkų pernašos savybių, didelio liuminescencijos efektyvumo ir kt. [132]. Daugelis junginių, turinčių karbazolilfragmentą, yra naudojami kaip matricos, spinduoliai arba CT medžiagos [133-135]. Optoelektroninių prietaisų gamybai yra dažnai naudojama brangi vakuuminio garinimo technika. Tirpalų liejimo metodas yra ekonomiškesnis ir paprastesnis gaminant OLED [136-138]. Palyginti su mažamolekuliniais junginiais, polimerai yra tinkamesni sluoksniams formuoti liejant jų tirpalus, nes jie geba formuoti amorfinius, morfologiškai stabilius ir lanksčius sluoksnius [139]. Poli(*N*-vinilkarbazolas) (PVK) yra plačiausiai naudojamas kaip matrica PhOLED. Tačiau didelis jonizacijos potencialas (5,9 eV) ir didelė PVK savitoji varža gali lemti aukštą PhOLED darbinę įtampą [140]. Metoksigrupių naudojimas yra efektyvus būdas junginių jonizacijos potencialui sumažinti dėl stipraus π donorinio efekto ir krūvininkų judriui pagerinti dėl formuojamų papildomų vandenilinių ryšių [141].

Monomerai **9** ir **10** buvo susintetinti naudojant Buchwaldo ir Hartwigo kryžminio jungimo reakciją. Šių monomerų RAFT polimerizacija buvo atlikta naudojant DDMAT kaip RAFT agentą ir AIBN kaip iniciatorių, gaunant polimerus **11** ir **12** (**5.4.1 schema**).



5.4.1 schema. Junginių **9**–**12** sintezė

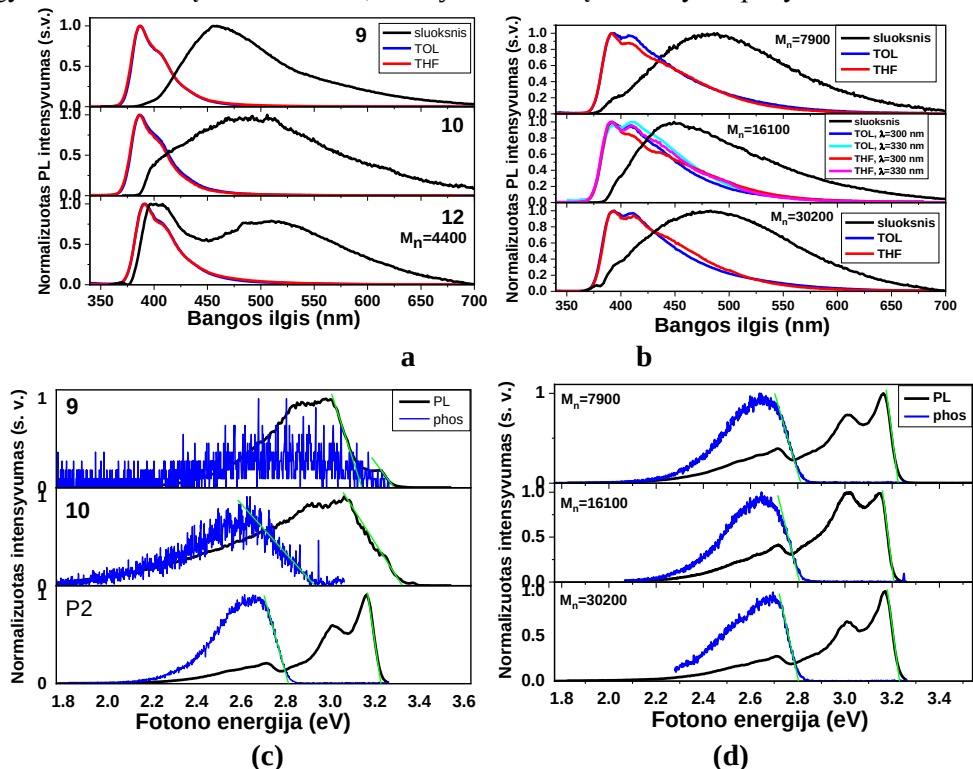
Teoriniai skaičiavimai atskleidė, kad vinilgrupės padėtis fenilo žiede neturi pastebimos įtakos monomerų **9** ir **10** HOMO ir LUMO orbitalių išsidėstymui ir jų energijai (**5.4.1 pav.**). Abiem atvejais HOMO pasiskirsto visoje molekulėje, o LUMO iš esmės yra lokalizuotas vinilfenilo fragmente. Metoksigrupių prijungimas karbazolo fragmento C-3 ir C-6 padėtyse padidina HOMO energiją, nes deguonies atomų orbitalės prisideda prie molekulių π konjuguotos sistemos. Apskaičiuotos monomerų **9** ir **10** HOMO (–4,80 eV) ir LUMO (–1,07 eV ir –1,09 eV) energijos buvo beveik identiškos dėl panašaus elektronų pasiskirstymo molekulėse. Eksperimentinės IP^{CV} vertės yra susijusios su HOMO energijomis. Monomerų **9** ir **10** IP^{CV} reikšmės, išmatuotos CV metodu, taip pat yra artimos, atitinkamai 5,35 eV ir 5,34 eV.



5.4.1 pav. Monomerų HOMO/LUMO ir jų energijos apskaičiuotos naudojant B3LYP/6-31G(d,p)

Priešingai nei tirpalų PL spektrai, junginių **9**–**12** sluoksniai parodė papildomas intensyvias PL smailes, atsiradusias dėl molekulių agregacijos (**5.4.2 pav.**). Buvo tiriama junginių **9**–**12** PL gesimo dinamika (**5.4.1 lentelė**). Monomerų **9** ir **10** praskiestuose tolueno (TOL) tirpaluose buvo fiksuojamos monoeksponentinės PL

gesimo kreivės, kurių emisijos trukmė yra beveik 5 ns. Ši vertė padidėjo iki maždaug 7 ns polimerų **11** ir **12** tirpaluose. Monomero **9** sluoksnio PL gesimo kreivė ties 458 nm atitinka triguba eksponentinę funkciją, o fluorescencijos trukmė yra 11,56 ns. Monomero **10** sluoksnio PL gesimo kreivė rodo 480,85 ns emisijos gyvavimo trukmę esant 490 nm, o tai yra eksimerų susidarymo požymiai.



5.4.2 pav. 9, 10 ir 12 (c) ir 11 (d) THF tirpalų PL ir fosforescenciniai spektrai, užregistruoti 77 K temperatūroje

Polimerų **11** ir **12** sluoksniai pasižymėjo daugiaeksponentinėmis PL gesimo kreivėmis, kurių emisijos gyvavimo trukmė siekė atitinkamai 2,5 μ s (490 nm) ir 2,6 μ s (510 nm). Polimerų **11** ir **12** uždelstosios eksimerinės emisijos komponentai buvo santykinai dideli, t. y. 63% ir 34 %. Ši eksimerinė CT emisija, užfiksuota **11** ir **12** polimerų sluoksniuose, gali būti apibūdinama kaip ir TADF spinduolių, kuriuose CT vyksta tarp molekulių [145].

Susintetinti polimerai **11** ir **12** buvo panaudoti formuojant OLED sluoksnius tirpalų liejimo metodu. Gaminant prietaisus A–C polimerai **11** ir **12** bei poli(9,9-dioktylfluoreno-alt-N-(4-sec-butylfenil)-difenilaminas) TFB buvo naudojami kaip skyles pernešančios medžiagos (HTM), o 4,6-di(9H-karbazol-9-il)pirimidin-5-karbonitrilas (CzPCN) kaip TADF spinduolis. PhOLED D–J buvo pagaminti siekiant išbandyti polimerus kaip matricas raudonam fosforescenciniam spinduoliui. PhOLED D–J buvo pagaminti liejant emisinio sluoksnio (EML) tirpalą, sudarytą iš gerai žinomo raudonojo fosforescencinio spinduolio bis(1-

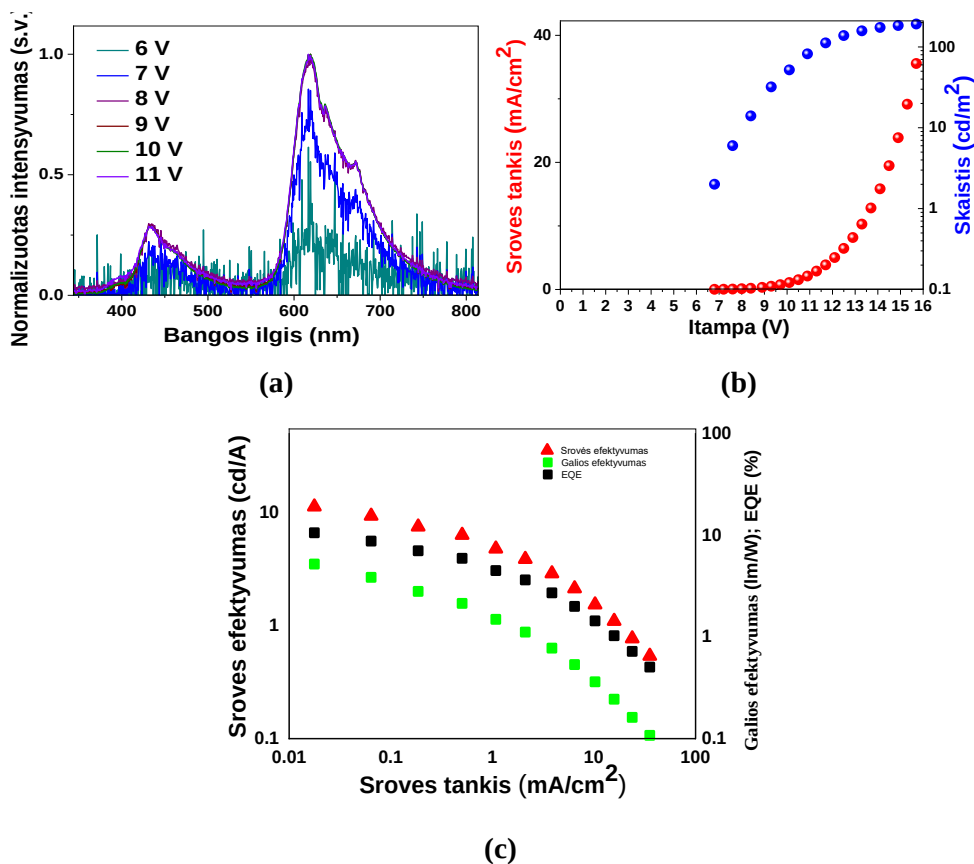
fenilizochinolino)(acetilacetono)iridžio (III) ($\text{Ir}(\text{piq})_2(\text{acac})$), ir polimerų **11** ir **12** bei TFB matricos. EML formavimas naudojant tirpalų liejimą yra patrauklus dėl galimybės kruopščiai kontroliuoti spinduolio koncentraciją. Prietaisų **A–J** EL charakteristikos pateiktos **5.4.1 lentelėje** ir **5.4.3 pav.**

Nustatyta, kad OLED **A** ir **B** pasižymėjo mažesne įjungimo įtampa, palyginti su OLED **C**, pagaminto naudojant TFB, tai įrodo, kad polimerai **11** ir **12** gali užtikrinti krūvininkų pusiausvyrą EML. Nelegiruotų TADF prietaisų *EQE* siekė 0,8 %.

5.4.1 lentelė. Prietaisų charakteristikos

Prietaisas	EML	Įjungimo įtampa (V)	Srovės efektyvumas (cd/A)	Galios efektyvumas (lm/W)	<i>EQE</i> (%)
A	11 / CzPCN	4,9	2,2	1,1	0,8
B	12 / CzPCN	5,6	1,8	1	0,6
C	TFB / CzPCN	7,1	2,1	0,7	0,8
D	TFB / $\text{Ir}(\text{piq})_2(\text{acac})$: 11 , 1 %	6,8	11,3	5,2	10,6
E	TFB / $\text{Ir}(\text{piq})_2(\text{acac})$: 11 , 4 %	10,6	4,2	1,2	3,9
F	TFB / $\text{Ir}(\text{piq})_2(\text{acac})$: 11 , 9 %	8,6	3	0,7	3,1
G	TFB / $\text{Ir}(\text{piq})_2(\text{acac})$: 12 , 1 %	5,9	6,1	3	5,8
H	TFB / $\text{Ir}(\text{piq})_2(\text{acac})$: 12 , 4 %	6,6	1,1	0,3	1
I	TFB / $\text{Ir}(\text{piq})_2(\text{acac})$:TFB, 4 %	8,6	7,2	2,4	6,8
J	TFB / $\text{Ir}(\text{piq})_2(\text{acac})$:TFB, 9 %	7,5	3,5	0,8	3,7

PhOLED **D** su EML 1 % $\text{Ir}(\text{piq})_2(\text{acac})$ polimero **11** matricoje pasižymėjo didžiausiu *EQE* iš **D–J** prietaisų serijoje (**5.4.1 lentelė**). *EQE*, siekiantis 11 %, yra panašus į naujausias tirpalų liejimo metodu pagamintų PhOLED efektyvumo vertes. Nepaisant to, gautas *EQE* vis tiek yra mažesnis, palyginti su naujausiomis efektyvumo vertėmis, dėl neviseiško energijos perdavimo iš matricos į spinduolį, kurį įrodo atsiradusi TFB EL emisija [149]. HTL emisija atsiranda dėl agregacijos sukkelto PL gesimo, aukšto polimerų **11** ir **12** krūvininkų judrio ir dėl galimo sluoksnių susimaišymo liejant tirpalus.



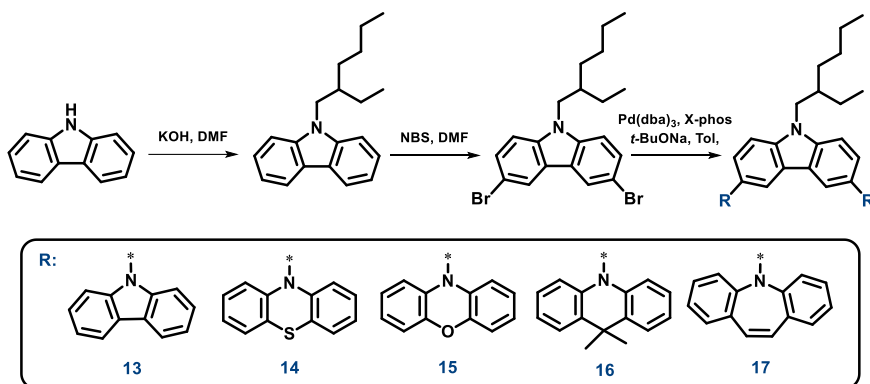
5.4.3 pav. D OLED: EL spektrai; srovės tankio, ryškumo ir įtampos kreivės; srovės efektyvumo, galios efektyvumo, *EQE* srovės tankio kreivės

Santykinai aukštą įjungimo įtampą ir mažą PhOLED **D**–**J** skaitį tikriausiai lėmė didelis bendras sluoksnių storis, slopinantis eksitonų susidarymą ir krūvininkų pusiausvyrą. Naudojant polimero **12** matricą, didžiausias *EQE* (5,8 %) buvo prietaiso **G**. PhOLED **D** su polimero **11** matrica *EQE* siekė 10,6 %, o geriausio prietaiso su TFB matrica *EQE* buvo 6,8 %. Pagamintų PhOLED EL duomenys rodo, kad susintetinti polimerai **11** ir **12** yra perspektyvūs ir gali būti naudojami kaip raudonųjų PhOLED matricos.

5.5. TRIDONORINIAI KARBAZOLO DARINIAI, SKIRTI ORGANINIAMS ŠVIESOS DIODAMS

Tarp organinių puslaidininkių karbazolo dariniai yra vieni iš labiausiai tyrinėjamų dėl gerų skylių pernašos savybių, aukštos tripletinės energijos ir standžios molekulės struktūros [150]. Karbazolo dariniai su akceptoriniais aromatiniais ciano, fluoro, sulfoksido ir keto fragmentais pasižymi TADF [154]. Šie junginiai yra potencialūs TADF spinduliai optoelektronikos prietaisams, nes rISC proceso metu tripletiniai eksitonai virsta singletiniais ir rekombinuoja emisiniu būdu [155]. Taip OLED IQE gali siekti 100%. Būtina TADF proceso sąlyga junginiuose yra silpna HOMO ir LUMO banginių funkcijų sanklota. Tokiose molekulėse vyksta ICT tarp donorinio ir akceptorinio fragmentų.

Junginių **13–17**, turinčių tris donorinius fragmentus, sintezė pavaizduota **5.5.1 scheme**. Buchwaldo ir Hartwigo metodu karbazolas, fentiazinas, fenoksazinas, akridanas ir dibenzazepinas buvo prijungti prie 3,6-dibromkarbazolo. Dėl donorinių fragmentų vandenilio atomų stūmos jėgų centrinio karbazolo atžvilgiu molekulėse galima ICT. Efektyvi ICT užtikrintų silpną sanklotą tarp HOMO ir LUMO ir galėtų inicijuoti TADF vyksmą.



5.5.1 schema. Junginių **13–17** sintezė

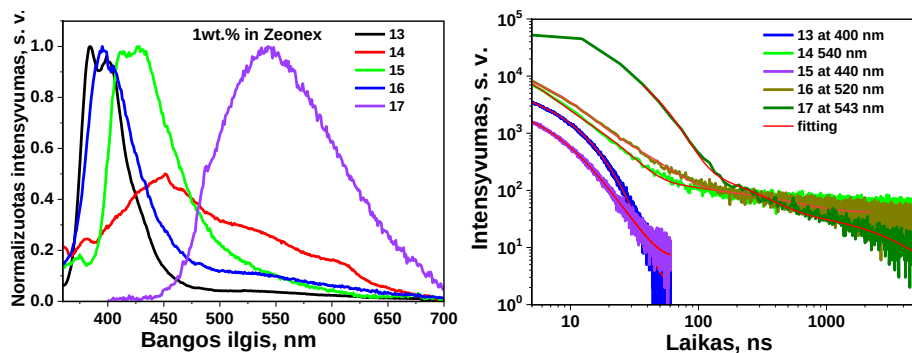
Junginių **13–17** fotoluminescencinės charakteristikos pateiktos **5.5.1 lentelėje**. Junginio **13** praskiestų tirpalų TOL ir THF PL spektrai gali būti priskirti lokaliai sužadintos (LE) būsenos relaksacijai. Pastebėti skirtumai tarp junginio **13** PL spektrų tirpaluose ir kitų junginių **14–17** atitinkamų spektrų. Šių junginių PL spektrai turi CT pobūdį. Junginio **14** PL juostų maksimumai TOL ir THF tirpaluose yra atitinkamai ties 453 ir 475 nm. Junginių **15** ir **16** atveju PL juostos maksimumas THF tirpale yra pasislinkęs į ilgesnių bangų pusę PL juostos maksimumo TOL tirpalo atžvilgiu, atitinkamai 32 ir 10 nm. Nustatyta, kad junginiams **14–16** yra būdingas solvatochromizmas, pasireiškiantis dėl ICT tarp donorinio fentiazino / fenoksazino / akridano pakaito ir centrinio karbazolo fragmento, veikiančio kaip akceptorius. Junginio **17** tirpalų TOL ir THF spektruose užfiksuotos dvi PL juostos LE ir CT. Susintetintų tridonorinių junginių **13–17** PLQY TOL tirpaluose svyruoja

nuo 1% iki 22 %. Aukščiausia *PLQY* verte pasižymėjo junginiai **13** ir **16**, atitinkamai 22 % ir 10 %. Junginių **13–17** S_1 ir T_1 energijos, nustatytos iš PL ir fosforescencijos spektrų, yra pateiktos **.5.5.1 lentelėje**. Skirtumas tarp šių energijų svyruoja nuo 0,20 iki 0,59 eV.

5.5.1 lentelė. Junginių fotoluminescencinės charakteristikos

Junginys	13	14	15	16	17
$\lambda_{em}^{tol/THF}$, nm	386/386	453/475	441/473	411/421	408, 563/408, 587
$PLQY_{deoks. tol}^a$, %	22	1	3	10	1
E_{S1}^b , eV	3.37	3.20	3.28	3.47	2.75
E_{T1}^b , eV	3.03	2.61	2.83	3.08	2.55
ΔE_{ST} , eV	0.34	0.59	0.45	0.39	0.20
a – nustatyta tiriant junginių praskiestus TOL tirpalus; b – nustatyta tiriant junginių praskiestus THF tirpalus.					

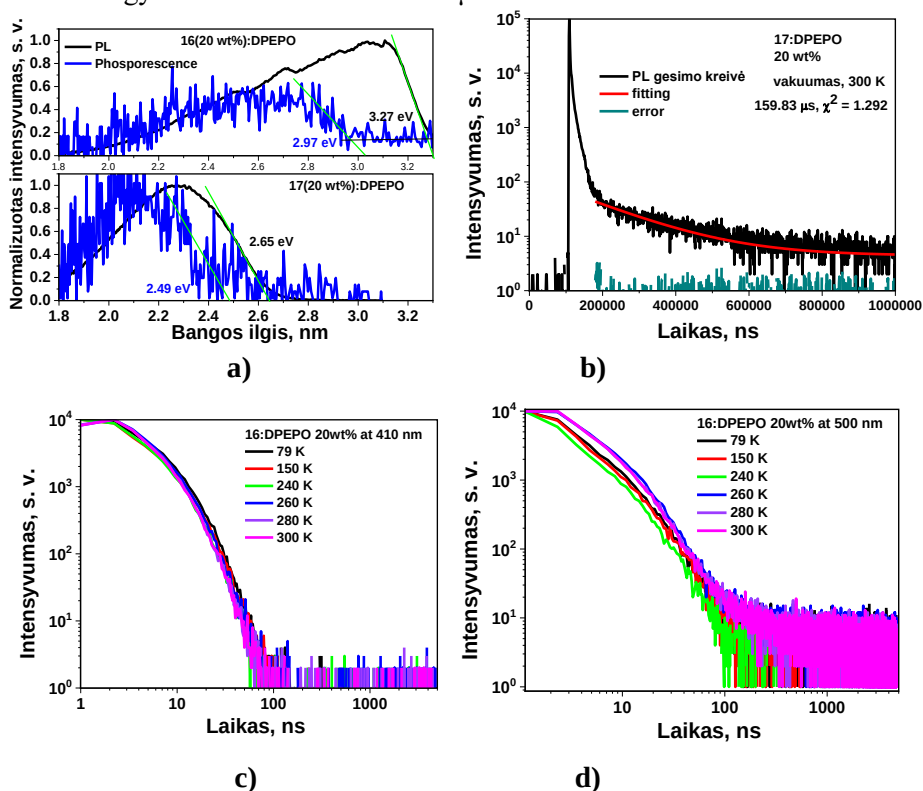
Nustatyta, kad junginių **13–16** ir Zeonex kietųjų tirpalų amorfinių sluoksnių intensyvios PL juostos fiksuojamos 400–450 nm intervale (**5.5.1 pav.**). Skirtingai junginio **17** kietojo tirpalo Zeonex sluoksnio PL juosta yra ties 550 nm. Tiriant junginių **13–16** mišinių sluoksnių PL gesimo dinamiką (**5.5.1 pav.**), nustatyta, kad trikarbazolo **13** ir junginio **15** emisijos, atitinkamai ties 400 nm ir 440 nm, gyvavimo trukmės yra trumpos, būdingos singletų rekombinacijai. Junginio **14** ir Zeonex mišinys parodė kambario temperatūros fosforescenciją. Nustatyta, kad junginių **16** ir **17** mažo intensyvumo PL juostoms, atitinkamai ties 520 nm 543 nm, yra būdingos ilgos emisijos gyvavimo trukmės (**5.5.1 pav.**). Daroma prielaida, kad šiuose tridonoriniuose junginiuose vyksta TADF.



5.5.1 pav. Junginių **13–17** ir Zeonex mišinių sluoksnių (a) PL spektrai; (b) PL gesimo kreivės

TADF vyksmas buvo įrodytas tiriant kietųjų tirpalų junginių **16** ir **17** ir bis[2-(difenilfosfino)fenil] eterio oksido (DPEPO) amorfinių sluoksnių PL

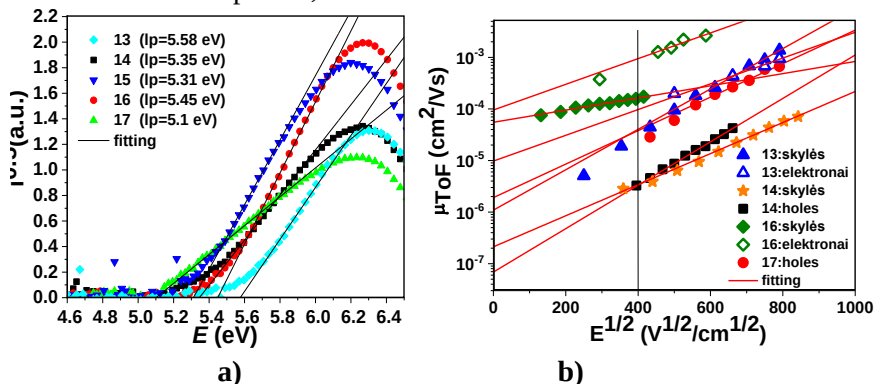
gyvavimo trukmes skirtingose temperatūrose (5.5.2 pav.). DPEPO, kaip didelio poliškumo matrica, buvo pasirinkta siekiant sumažinti junginių **16** ir **17** ΔE_{ST} . Gautas junginių **16** ir **17** bei DPEPO mišinių sluoksnių ΔE_{ST} vertės buvo žemesnės (0,3 ir 0,16 eV), palyginti su šių junginių ΔE_{ST} vertėmis THF tirpale (0,61 ir 0,2 eV). Tiriant junginio **16** ir DPEPO mišinio sluoksnį, buvo aptiktos dvi PL juostos ties 410 nm ir 500 nm. Fiksuojant abiejų PL juostų gyvavimo trukmes skirtingose temperatūrose, nustatyta, kad PL juosta ties 410 nm rodo paprastą fluorescenciją, o PL juosta ties 500 nm gali būti priskirta TADF. Junginio **17** ir DPEPO kietojo tirpalo amorfinis sluoksnis turėjo vienodą fluorescencijos ir fosforescencijos spektrų formą skirtingose temperatūrose. Maža ΔE_{ST} vertė junginyje **17** įgalino rISC ir TADF procesus. Kambario temperatūroje junginio **17** ir DPEPO mišinio amorfinio sluoksnio PL gyvavimo trukmė siekė 159 μ s.



5.5.2 pav. (a) Junginių **16** ir **17** PL ir fosforescencijos spektrai; (b) **17**: DPEPO sluoksnio PL gesimo kreivė; (c, d) **16**: DPEPO sluoksnio PL gesimo kreivės skirtingose temperatūrose

Susintetintų junginių **13–17** fotoelektronų emisijos spektrai pavaizduoti **5.5.2 pav.** Šių junginių IP_{PE} reikšmės išsidėsto nuo 5,1 iki 5,58 eV. Išskyrus junginį **17**, kiti junginiai **13–16** yra suderinami su fosforescencinio spindulio $Ir(piq)_2acac$ HOMO lygmeniu, nes jų IP_{PE} reikšmės šiek tiek viršija atitinkamą $Ir(piq)_2acac$ lygmenį, kuris yra 5,3 eV. Junginių **13–17** sluoksnių krūvininkų pernašos savybės

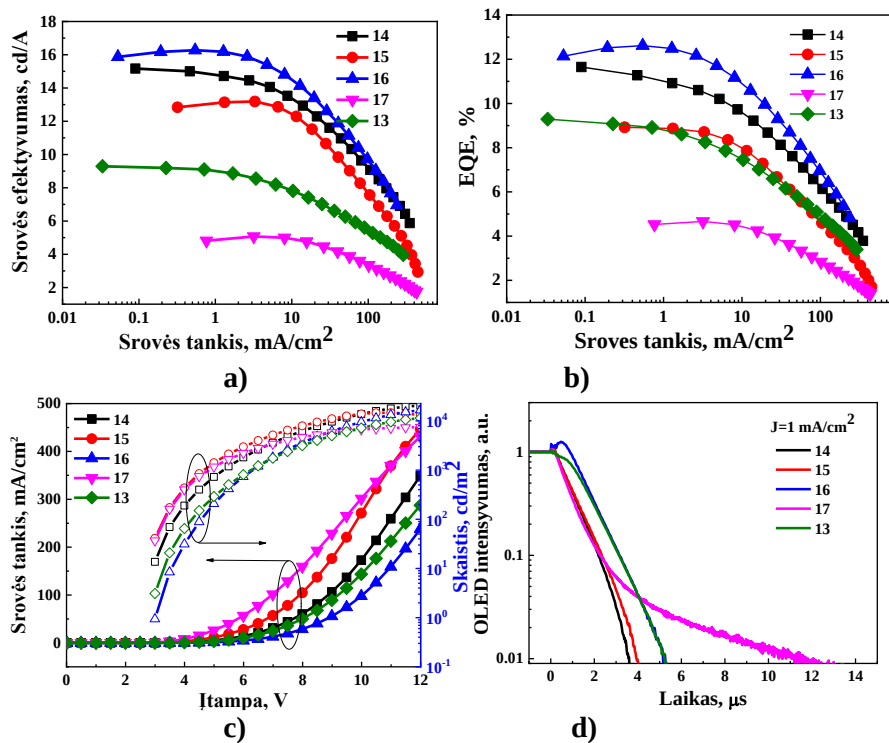
buvo ištirtos ToF metodu (5.5.3 pav.) Junginys **16** turėjo aukščiausias skylių ir elektronų judrio reikšmes, atitinkamai $1,4 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{ s}^{-1}$ ir $9,2 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{ s}^{-1}$, esant elektrinio lauko stipriui $1,6 \times 10^5 \text{ V/cm}$.



5.5.3 pav. Junginių **13–17** sluoksnių (a) fotoemisijos spektrai ir (b) krūvininkų dreifinio judrio priklausomybė nuo elektrinio lauko stiprio

Tridonoriniai junginiai **13–17** buvo naudojami kaip matricos Ir(piq)₂acac spinduoliui PhOLED R1–R5 struktūrose. Prietaisų R1–R5 charakteristikos pateiktos **5.5.4 pav.**

Prietaisų R1–R5 EL spektruose buvo fiksuojama tik Ir(piq)₂acac emisija, parodanti, kad eksitonai iš matricos yra perduodami spinduoliui. PhOLED R4 su junginio **16** matrica emisiniame sluoksnyje buvo geriausios EL charakteristikos (**5.5.4 pav.**). Prietaiso R4 išmatuotos didžiausios srovės efektyvumo, galios efektyvumo ir EQE reikšmės atitinkamai buvo 41,98 cd/A, 37,66 lm/W ir 12,61 %. Prasčiausios EL charakteristikos buvo PhOLED R4, kuriame kaip matrica buvo naudojamas junginys **17**. Šio prietaiso EQE siekė tik 4,67 %. Siekiant suprasti PhOLED R1–R5 emisijos mechanizmą, buvo išmatuota elektroluminescencijos trukmė (TREL) (**5.5.4 pav.**). Išskyrus R4, prietaisų R1–R3 ir R5 EL gesimo trukmė buvo 4–5 μs, kuri yra būdinga spinduoliui Ir(piq)₂acac. PhOLED R4 EL gesimo trukmė (~12 μs) buvo daug ilgesnė nei kitų prietaisų. Šis pastebėjimas yra įmanoma mažo PhOLED R4 efektyvumo priežastis.



5.5.4 pav. OLED R1–R5 (a) srovės efektyvumo priklausomybė nuo srovės tankio; (b) EQE priklausomybė nuo srovės tankio; (c) J–V–L charakteristikos; (d) elektroluminescencijos trukmė

5.6. IŠVADOS

1. Buvo susintetinti keturi nauji trifeniletено dariniai, kurių donorinės dalys yra 3,6-di-*tert*-butilkarbazolas arba 9,9-dimetil-9,10-dihidroakridinas, o jungiamieji fragmentai – fenilenas arba tetrafluorfenilenas. Nustatyta, kad:
 - a. junginiai pasižymi agregacijos indukuotu emisijos padidėjimu, jų sluoksnių fotoluminescencijos kvantinė išeiga buvo 16–29 %;
 - b. junginių sluoksniai skleidė mėlynąją šviesą, jų emisijos maksimumas buvo 478–487 nm intervale;
 - c. junginių jonizacijos potencialas ir elektroninis giminingumas kietoje būsenoje buvo atitinkamai 5,88–6,37 eV ir 2,30–2,89 eV;
 - d. Didžiausias skylių ir elektronų dreifo judrumas, atitinkamai siekęs $3,07 \times 10^{-3} \text{ cm}^2/\text{V}$ ir $4,2 \times 10^{-3} \text{ cm}^2/\text{V}$, buvo pastebėtas $3,67 \times 10^5 \text{ V/cm}$ elektriniame lauke junginiui, turinčiam 3,6-di-*tert*-butilkarbazolo donoro fragmentas ir fenileną jungiantis tiltelis.
 - e. visi junginiai buvo naudojami kaip fluorescenciniai OLED spinduoliai. Didžiausias išorinis kvantinis efektyvumas – 2 % – nustatytas prietaisuose, kurių spinduoliai, turi 9,9-dimetil-9,10-dihidroakridino fragmentus.
2. Buvo susintetinti keturi nauji aromatiniai diaminai ir ištirta CF₃ grupės padėties įtaka junginių savybėms. Nustatyta, kad:
 - a. junginiai, kuriuose yra 2,5-bis(trifluormetil)benzeno fragmentų, pasižymėjo sąveika tarp centrinio fenilo žiedo π sistemos ir fluoro atomo;
 - b. aptiktos tarpmolekulinės sąveikos 2,5-bis(trifluormetil)benzenų pakeistuose junginiuose lėmė glaudesnę molekulių išsidėstymą;
 - c. junginiuose, kuriuose yra 2,5-bis(trifluormetil)benzeno fragmentų, nustatytos aukštesnės terminės temperatūros, mažesnis jonizacijos potencialas ir didesnis skylių dreifinis judris, palyginti su junginiais, kuriuose yra 3,5-bis(trifluormetil)benzeno fragmentų.
3. Susintetinti 3,6-dimetoksi-9-(4-vinilfenil)-9H-karbazolo ir 3,6-dimetoksi-9-(3-vinilfenil)-9H-karbazolo monomerai ir jų polimerai. Nustatyta, kad:
 - a. monomerų RAFT polimerizacija su 2-(dodeciltiokarbonotioilto)-2-metilpropiono rūgštimi kaip grandinės pernašos agentu vyko gyvybingosios polimerizacijos principu, todėl gauti polimerai, kurių kontroliuojama molekulinė masė siekė $M_n=20\,000$ ir pasižymėjo santykinai maža polidispersija ($\text{Đ}<1,5$);
 - b. monomero, turinčio 3-vinilbenzeno fragmentą, polimerizacijos greitis buvo daugiau nei viena eile mažesnis nei monomero, turinčio 4-vinilbenzeno fragmentą;
 - c. atlikus terminius matavimus paaiškėjo, kad polimerai formavo stiklus, jų stiklėjimo temperatūra viršijo 160 °C;

- d. monomerų ir polimerų sluoksnių fotoluminescencijos spektrai atskleidė tarpmolekulinę termiškai aktyvintą uždelstąją fluorescenciją ir (arba) eksimerų emisiją;
 - e. susintetinti polimerai buvo išbandyti tirpalų liejimo būdu pagamintuose OLED kaip skylės pernešančiosios medžiagos ir matricos. Geriausio fosforescencinio prietaiso išorinis kvantinis efektyvumas buvo 10,6 %.
4. Susintetinti penki 9-(2-etilheksil)karbazolo dariniai, turintys donorinius karbazolo, fentiazino, fenoksazino, akridano ar dibenzazepino fragmentus. Nustatyta, kad:
- a. junginių fotoluminescencijos juostos skirtingose terpėse turėjo krūvio pernašos ir (arba) vietinio sužadavimo pobūdį;
 - b. kietųjų tirpalų junginių, turinčių akridano arba azepino dalis, ir Zeonex amorfinių sluoksnių fotoluminescencijos juostoms yra būdinga termiškai aktyvinta uždelstoji fluorescencija;
 - c. vakuuminio užgarinimo metodu gautų junginių sluoksnių jonizacijos potencialo vertės svyravo nuo 5,10 iki 5,58 eV;
 - d. junginiai pasižymėjo geromis krūvininkų pernašos savybėmis, skylių dreifinis judris viršijo 10^{-4} cm²/Vs, esant stipriam elektros lauko stipriui. Dariniai, turintys karbazolo ir akridano fragmentus, prijungtus prie 9-(2-etilheksil)karbazolo, pasižymėjo ambipoline krūvininkų pernaša;
 - e. susintetinti junginiai buvo tiriami kaip matricos raudonuose fosforescenciniuose OLED. Prietaiso didžiausias išorinis kvantinis efektyvumas siekė 12,61%.

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Scientific papers related to the topic of dissertation:

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