

KAUNAS UNIVERSITY OF TECHNOLOGY

DAIVA TAVGENIENĖ

**LOW-MOLECULAR-WEIGHT TRIPHENYLAMINO AND
CARBAZOLYL GROUP-CONTAINING DERIVATIVES FOR
ORGANIC LIGHT-EMITTING DIODES**

Summary of Doctoral Dissertation
Technological Sciences, Materials Engineering (08T)

2017, Kaunas

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Scientific Supervisor:

Prof. Dr. Saulius GRIGALEVIČIUS (Kaunas University of Technology, Technological Sciences, Materials Engineering – 08T).

Editors:

Dovilė Dumbrasuskaitė (Publishing house “Technologija”)

Inga Nanartonytė (Publishing house “Technologija”)

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Dr. Viktoras GRIGALIŪNAS (Kaunas University of Technology, Technological Sciences, Materials Engineering, 08T) – **chairman**;

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Dr. Jūratė SIMOKAITIENĖ (Kaunas University of Technology, Physical Sciences, Chemistry, 03P);

Dr. Aivars VEMBRIS (University of Latvia, Technological Sciences, Materials Engineering, 08T).

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Address: K. Donelaičio str. 73, 44029, Kaunas, Lithuania.

Tel. no. (+370) 37 300042; fax: +370 37 324144; e-mail doktorantura@ktu.lt

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KAUNO TECHNOLOGIJOS UNIVERSITETAS

DAIVA TAVGENIENĖ

**MAŽAMOLEKULIAI TRIFENILAMINO IR
KARBAZOLILGRUPES TURINTYS DARINIAI ORGANINIAMS
ŠVIESOS DIODAMS**

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Mokslinis vadovas:

Prof. dr. Saulius Grigalevičius (Kauno technologijos universitetas, technologijos mokslai, medžiagų inžinerija, 08T).

Anglų kalbos redaktorė:

Dovilė Dumbraskaitė (leidykla „Technologija“)

Lietuvių kalbos redaktorė:

Inga Nanaronytė (leidykla „Technologija“)

Medžiagų inžinerijos mokslo krypties disertacijos gynimo taryba:

Dr. Viktoras GRIGALIŪNAS (Kauno technologijos universitetas, technologijos mokslai, medžiagų inžinerija, 08T) – **pirmininkas**;

Doc. dr. Mindaugas ANDRULIČIUS (Kauno technologijos universitetas, technologijos mokslai, medžiagų inžinerija, 08T);

Prof. habil. dr. Albertas MALINAUSKAS (Fizinių ir technologijos mokslų centras, fiziniai mokslai, chemija, 03P);

Dr. Jūratė SIMOKAITIENĖ (Kauno technologijos universitetas, fiziniai mokslai, chemija, 03P);

Dr. Aivars VEMBRIS (Latvijos universitetas, technologijos mokslai, medžiagų inžinerija, 08T).

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Adresas: K. Donelaičio g. 73-403, 44249 Kaunas, Lietuva.

Tel. + 370 37 300 042; faks. + 370 37 324 144; el. paštas doktorantura@ktu.lt.

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1. INTRODUCTION

Organic electroluminescent (EL) materials have many advantages when compared with their inorganic counterparts and, therefore, they have a wide range of potential applications in communications, information display, illumination, and so on. Phosphorescent organic light-emitting diodes (PHOLEDs) that contain late transition-metal complexes as emitters are particularly attractive due to their ability to harvest singlet and triplet excitons, which makes it possible to achieve an internal quantum efficiency of 100%. To suppress concentration quenching, a phosphorescent emitter is usually dispersed in a suitable host to obtain a high photoluminescent (PL) quantum yield. Developing a host with a suitable triplet energy level (E_T), charge-transporting ability, and thermal and film stability is thus the key to improving the performance of PHOLEDs.

A good host used in PHOLEDs should have the following characteristics:

- an E_T value higher than that of the phosphorescent guest, which facilitates efficient energy transfer from the host to the guest and prevents reverse energy transfer from the guest back to the host; different phosphorescent emitters require the hosts with their corresponding E_T values;
- appropriate values of highest occupied molecular orbital (HOMO) energy and lowest unoccupied molecular orbital (LUMO) energy to facilitate charge injection from the adjacent hole-transporting and electron-transporting layer (HTL and ETL), which is also the key to balance the transporting of holes and electrons;
- high glass-transition temperatures (T_g) and thermal-decomposition temperatures (T_d) confer better device endurance;
- appropriate film-forming and morphological stability.

In this regard, there is a contradictory issue as to how to simultaneously optimize the photophysical and electric performance of PHOLEDs. Generally, a highly crystalline film is helpful to transport carriers, but it may also lead to PL quenching. To meet these requirements and optimize the parameters which determine the device performance, intramolecular charge-transfer, charge mobility, and energy level must all be fully considered when new hosts are synthesized.

In this field, one representative example is the well-known poly(*N*-vinylcarbazole) (PVK) ($E_g = 3.5$ eV) for which the polymer bandgap is similar to that of the carbazole moiety. Carbazole is among the most stable wide bandgap molecules which has been extensively studied for the design of low molecular weight or oligomeric hosts, fully justifying the development of polymeric host with this molecule. The appealing features of PVK include a high glass transition

temperature ($T_g = 200^\circ\text{C}$), a high triplet energy level ($E_T = 2.5 \text{ eV}$), good solubility in common organic solvents and excellent film-forming properties, rendering this polymer of great interest for PHOLEDs. However, PVK is characterized by a hole-dominated transportation, limiting its scope of usability. Another drawback is that PVK is also prone to exciplex formation, lowering device performances.

Chromophores containing carbazolyl moieties were synthesized using rigid and flat structures of aromatic linkage for connecting the rings of carbazole in low-molecular-weight hosts. Compounds are prepared by changing the connection positions of substitution and are widely used as effective hosts for phosphorescent organic light emitting diodes. A shortage of such hosts is a big tendency to crystallize, thus the devices can not be formed by spin coating. Due to a high demand and necessary complex characteristics, host materials of a new structure which could be formed from solutions are intensively synthesized and applied for phosphorescent devices.

The aim of this work is the synthesis and characterization of new low-molecular-weight compounds which have electronically isolated chromophores as well as bipolar derivatives as potential host materials, and the application of these derivatives in multilayer light-emitting diodes.

The tasks proposed to achieve the aim:

1. To synthesize carbazole derivatives which have carbazolyl, phenylindolyl, indan-1,3-dione moieties.
2. To synthesize carbazole and triphenylamine compounds containing 1-phenylphenanthro[9,10-d]imidazolyl moieties.
3. To investigate the thermal and optoelectronic characteristics of the synthesized compounds.
4. To apply the obtained compounds in organic light-emitting diodes and describe their characteristics of the obtained devices.

The main statements of the doctoral thesis:

1. Branched derivatives containing electrically isolated carbazole fragments are hole-transporting hosts, which are suitable for emitting layers of phosphorescent organic light-emitting diodes.
2. Carbazole and triphenylamine-based compounds containing 1-phenylphenanthro[9,10-d]imidazole fragments demonstrate good charge transporting properties and are suitable host materials for red phosphorescent light-emitting diodes.
3. Carbazole-based compounds containing phenylvinyl, phenylindolyl or indan-1,3-dione moieties demonstrate good thermal and morphological

stability, suitable charge transporting properties and could be used as electroactive layers in various organic light-emitting diodes.

The scientific novelty of the work:

1. New carbazole-based derivatives containing different electronically isolated fragments in their structures were synthesized and characterized. These compounds were effective host materials for organic light-emitting diodes. This was confirmed by the use of these compounds in effective green and blue phosphorescent light-emitting diodes.
2. Carbazole and triphenylamine compounds containing 1-phenylphenanthro[9,10-d]imidazole fragments were synthesized and characterized. It was confirmed that these compounds are effective hosts for red electrophosphorescent organic light-emitting diodes.

Validity of the research results. The research results were presented in five scientific publications which correspond to the list of Clarivate Analytics Web of Science. The results of this research were presented in nine international and one national conference.

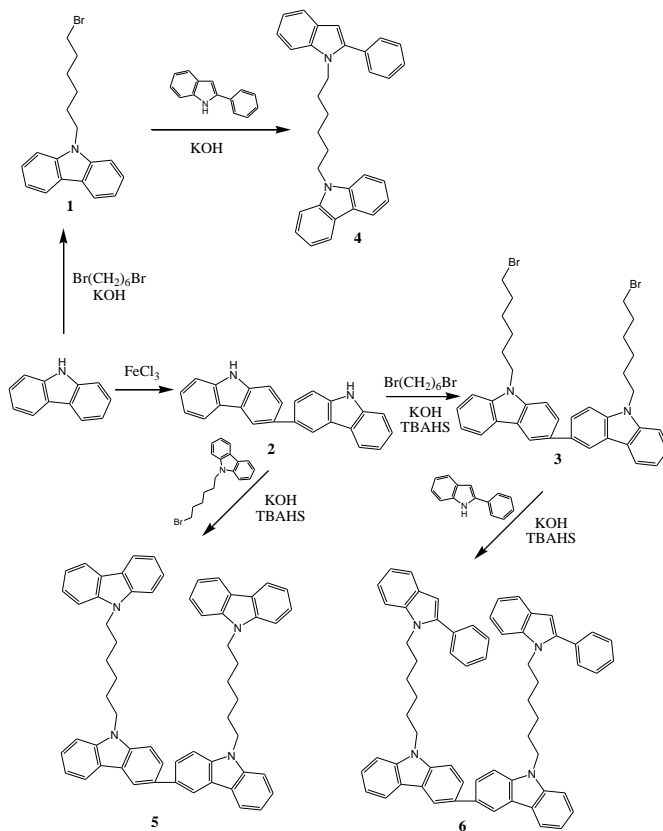
Structure of the doctoral dissertation. The doctoral dissertation consists of an introduction, three chapters, conclusions, a list of references (172 entries) and a list of scientific publications. The data of the doctoral dissertation is presented in 100 pages, including 28 figures, 5 schemes, 97 structures of compounds and seven tables.

Personal input of the author. The author has designed, synthesized, purified and characterized the compounds described in Chapter 3. The author also performed the melting point and infrared spectroscopy measurements and analysed the obtained results. The structures of the obtained compounds, their thermal properties, photophysical properties and ionization potential measurements were analysed in collaboration with the colleagues from the Department of Polymer Chemistry and Technology, Kaunas University of Technology; the obtained results were analysed by the author. OLEDs were fabricated and characterised in the group of Prof. J.H. Jou from National Tsing Hua University (Taiwan), in the group of Prof. C.H. Chang from Yuan-Ze University (Taiwan) and in the group of Prof. B. Zhang from Changchun Institute of Applied Chemistry, Chinese Academy of Science (China). The results of the OLEDs were analysed by the author.

2. THE MAIN RESULTS

2.1. Synthesis and characterization of carbazole- and phenylindole-based derivatives

The synthesis of the carbazole- and phenylindole-based derivatives was carried out by the synthetic route shown in Scheme 1.



Scheme 1

9-(6-Bromohexyl)carbazole (**1**) was prepared by reacting 9H-carbazole with an excess of 1,6-dibromohexane under basic conditions as described previously [1]. A part of compound **1** was reacted with 2-phenylindole to yield a low-molecular-weight host material **4**.

9H,9'H-[3,3']Bicarbazole (**2**) was obtained by the chemical oxidation of 9H-carbazole in the presence of FeCl_3 [2]. Derivative **2** was reacted with an

excess of 1,6-dibromohexane to yield 9,9'-bis(6-bromohexyl)[3,3']bicarbazole (**3**), which was then used to prepare the branched host material **6**. 9H,9'H-[3,3']bicarbazole (**2**) was also reacted with an excess of 9-(6-bromohexyl)carbazole (**1**) to afford the carbazole-based host material **5**.

The behavior of materials **4–6** under heating was studied using differential scanning calorimetry (DSC). All the derivatives were obtained as crystalline material by re-crystallising the solutions; however, they readily formed glasses when their melt samples were cooled on a stand in air or with liquid nitrogen. The DSC thermograms of compound **5** are shown in Figure 1 as examples. When the crystalline sample was heated, the endothermic peak caused by melting was observed at 178°C (T_m). When the melt sample was cooled down and reheated, the glass-transition phenomenon was observed at 71°C and no peaks due to crystallisation and melting appeared with further heating.

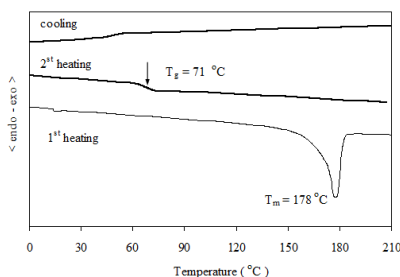


Fig. 1. DSC curves of material **5**. Heating rate: 10°C/min.

The sample of compound **4** melted at 114°C in the first heating scan and glass transition occurred at 31°C in the second heating scan. The crystalline sample of branched derivative **6** demonstrated similar behavior. During the first heating it melted at 152°C and formed glass ($T_g = 64^\circ\text{C}$) upon cooling.

Ionization potentials (I_p) of thin amorphous layers of the derivatives were determined from electron photoemission spectra of the layers. The layer of material **4** demonstrated the highest I_p of 5.95 eV. The I_p values of the layers of materials **5** and **6** were close to 5.75 eV. As it could be expected, the I_p value for the film of material **4** was similar to that of other derivatives containing unsubstituted carbazole or indole rings ($I_p > 5.9\text{ eV}$) [3, 4]. The experimentally determined E_T were 2.61 eV, 2.81 eV and 2.60 eV for materials **4**, **5** and **6**, respectively. The E_T values were calculated from the emission peak maximums of low temperature (77 K) phosphorescence spectra, which were at 474 nm, 440 nm and 476 nm for the materials **4**, **5** and **6**, respectively.

To evaluate the performance of the new host materials, phosphorescent green and blue OLEDs were fabricated by using green triplet emitter tris(2-

phenylpyridine)iridium ($\text{Ir}(\text{ppy})_3$) and blue triplet emitter iridium(III)[bis(4,6-difluorophenyl)-pyridinato-*N,C*]²picolate (Flrpic), correspondingly, as the guests. The structure of the multilayer devices was indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS)/ **4**, **5** or **6** host doped with a corresponding guest/ 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBi)/ lithium fluoride (LiF)/ aluminium (Al).

The low molecular-weight host **4** was firstly used in concentration-dependent OLED experiments with the amount of the green guest $\text{Ir}(\text{ppy})_3$ ranging from 1 to 10 wt%. Figure 2 shows the characteristics of the devices. The OLEDs exhibited turn-on voltages of 5–6 V, current efficiencies of 8.5–23 cd/A and maximal brightness of 2,670–13,660 cd/m². The green device containing 3 wt% of $\text{Ir}(\text{ppy})_3$ exhibited the best performance among all the devices with the current efficiency of 20.9 cd/A and power efficiency of 6.8 lm/W at 100 cd/m². At higher brightness, such as 1,000 cd/m², which is used for illumination applications, this OLED also showed the greatest current efficiency of 21.9 cd/A (5.6 lm/W).

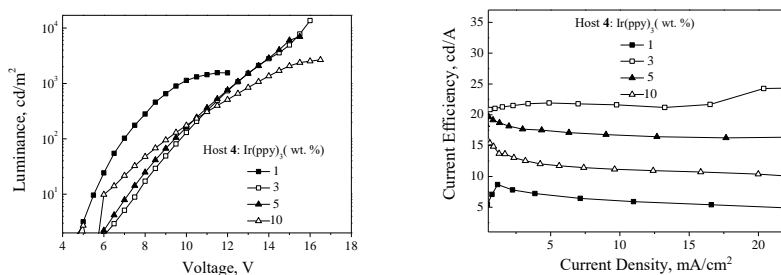


Fig. 2. OLED characteristics of compound **4**-based green host devices with $\text{Ir}(\text{ppy})_3$ guest

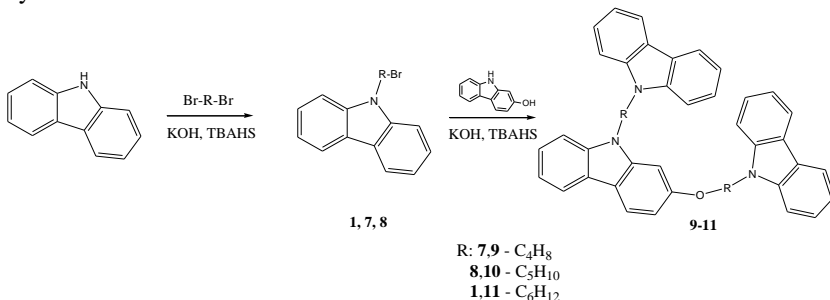
To evaluate the performance of derivative **4** as host of blue devices, phosphorescent OLEDs were fabricated by using blue emitter Flrpic as the guest. Host **4** was used in concentration-dependent experiments with the doping amount ranging from 5 to 20 wt%. The OLEDs exhibited turn-on voltages of 4.9–5.5 V, maximum current efficiencies of 6–14.2 cd/A and maximum brightness of 720–1400 cd/m². The device exhibited the best overall performance when using 15 wt% of Flrpic as the guest, including a turn-on voltage of ca. 5 V, a maximum current efficiency of 14.2 cd/A and maximum brightness of 1,160 cd/m². Efficiency roll-off at higher currents, which is typical in phosphorescent OLEDs, was also observed here; yet at brightness of 100 cd/m², an efficiency of about 9.4 cd/A (4 lm/W) could still be obtained.

Host materials **5** and **6** were also tested as components of green phosphorescent OLEDs in concentration-dependent experiments with the amount of $\text{Ir}(\text{ppy})_3$ guest ranging from 1 to 10 wt%. The devices containing compound **5**

as a host demonstrated reasonably superior performance relative to that of OLEDs containing compound **6** as a host. The OLEDs with host **5** exhibited rather low turn-on voltages of 3.1–3.2 V, power efficiencies of 5.2–16.4 lm/W and current efficiencies of 7.3–19.8 cd/A at 100 cd/m². The device containing 5 wt% of Ir(ppy)₃ exhibited the best overall performance with the current efficiency of 8.2 cd/A and power efficiency of 4.2 lm/W at higher brightness, such as 1,000 cd/m², used for illumination applications. The maximum luminance of the device exceeded 2,500 cd/m². The triplet energies of phenylindole- containing materials **4** and **6** were lower. Reverse energy transfer from the guest back to the host could be possible in this case. It appears that carbazolyl-based host **5** demonstrated better performance in the similar PHOLED devices due to this reason.

2.2. The synthesis and characterization of branched derivatives containing electrically isolated carbazole fragments

Carbazole-type host materials, 2-[4-(carbazol-9-yl)butyloxy]-9-[4-(carbazol-9-yl)butyl]carbazole (**9**), 2-[5-(carbazol-9-yl)pentyloxy]-9-[5-(carbazol-9-yl)pentyl]carbazole (**10**) and 2-[6-(carbazol-9-yl)hexyloxy]-9-[6-(carbazol-9-yl)hexyl]carbazole (**11**), were synthesized using rather simple alkylation methods as shown in Scheme 2.



Scheme 2

The key starting materials, 9-(bromoalkyl)carbazoles (**1**, **7**, **8**) were prepared from the commercially available 9H-carbazole and an excess of corresponding dibromoalkane under basic conditions using tetra-*n*-butyl ammonium hydrogen sulfate (TBAHS) as the phase transfer catalyst. Compounds **1**, **7**, **8** were reacted with 2-hydroxycarbazole under basic conditions to afford the carbazolyl containing derivatives **9–11** as host materials. The newly synthesized derivatives were confirmed by ¹H NMR, ¹³C NMR, IR spectroscopy and mass spectrometry.

When measured using DSC, host material **9** showed a glass transition temperature of 64°C, while 58°C were noticed for material **10** and 20°C for material **11** (Table 1).

Table 1. Photophysical, electrochemical and thermal characteristics of carbazole-based host materials **9–11**.

Compound	λ_{abs}^a , (nm)	λ_{em}^b , (nm)	λ_{phos}^c , (eV)	E_T^d , (eV)	HOMO ^e , (eV)	LUMO ^f , (eV)	T _g ^g , (°C)	T _m ^g , (°C)	T _d ^h , (°C)
9	345	356, 368	420	2.95	5.48	1.95	64	198	361
10	345	368	420	2.95	5.48	1.95	58	124	345
11	345	369	420	2.96	5.47	1.96	20	-	338

^a absorption maxima in tetrahydrofuran (THF) ($c = 10^{-5}$ mol/l). ^b emission maxima of fluorescence in THF ($c = 10^{-5}$ mol/l). ^c emission maxima of phosphorescence in THF ($c = 10^{-5}$ mol/l) at 77 K. ^d Estimated from the peak of phosphorescence spectrum at 77 K. ^e HOMO values are measured by the cyclic voltammetry (CV) method. ^f The energy of LUMO could be obtained by subtracting the optical bandgap (E_g) from the HOMO energy level. ^g Determined by DSC (scan rate 10°C/min, N₂ atmosphere). ^h Analysed using thermogravimetric analysis (TGA) (5% weight loss, scan rate 20°C/min, N₂ atmosphere).

The slightly higher T_g of host **9** indicated a strong intermolecular interaction of carbazole units owing to the short-chain alkyl ether and alkyl junctions. When investigated using TGA, host **9** exhibited a thermal decomposition temperature of 361°C, corresponding to a 5% weight loss, while compounds **10** and **11** decomposed at 345°C and 338°C, respectively. The higher T_g and T_d characteristic of host **9** facilitates a relatively better film integrity during the entire fabrication process, especially during solvent removal [5, 6].

The data of ultraviolet-visible (UV-vis) and PL spectra of materials **9–11** are shown in Table 1. The experimentally determined triplet-energies were 2.95 eV, 2.95 eV, and 2.96 eV for materials **9**, **10** and **11**, respectively, which were calculated from the first phosphorescent emission peak of low temperature (77 K) PL spectra at 420 nm, 420 nm and 419 nm, as shown in Figure 3.

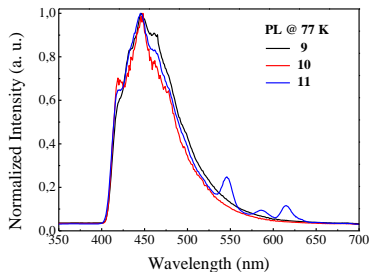


Fig. 3. PL spectra of the newly synthesized hosts **9**, **10**, and **11** measured in THF at 77 K

Most importantly, the triplet-energies of these three host materials are extensively higher than those of the green emitter, Ir(ppy)₃, which exhibited a triplet-energy value of 2.57 eV [7, 8]. These host materials should enable the occurrence of effective energy transfer from host to guest and exciton confinement on guest, resulting in good device efficiency [9, 10, 11, 12]. Both photophysical and electrochemical properties of all three compounds remained almost unchanged by increasing the length of alkyl and alkyl ether linkages.

The electrochemical properties of the carbazole-type host molecules **9–11** were measured by using cyclic voltammetry. The HOMO energy levels were estimated to be 5.48 eV, 5.48 eV, and 5.47 eV for **9**, **10**, and **11**, respectively, using the oxidation potential. The LUMO energy levels of the emitters were calculated to be 1.94 eV, 1.94 eV, and 1.95 eV for **9**, **10**, and **11**, respectively (Table 1).

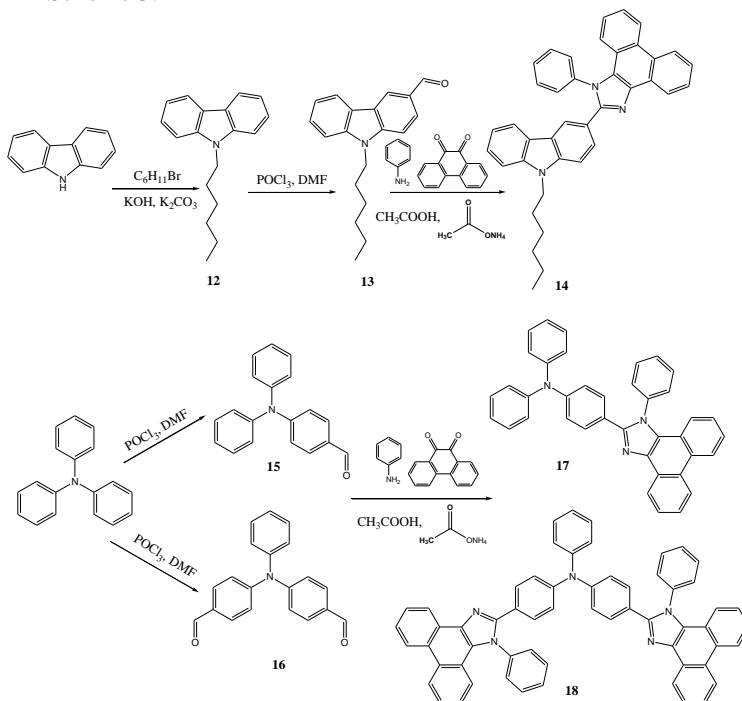
Derivatives **9**, **10** and **11** were applied in OLEDs as host materials for green phosphorescent Ir(ppy)₃ emitter. The devices were composed of a 125 nm ITO anode layer, a 35 nm PEDOT:PSS hole injection layer, a 20 nm emissive layer with the Ir(ppy)₃ emitter doped in a corresponding host, a 32 nm TPBi ETL, a 1 nm LiF layer, and a 100 nm Al cathode layer. The efficiency of the device was extensively dependent on doping concentration of the green emitter. Taking the device based on host **9** as an example, the power efficiency at 1,000 cdm⁻² increases from 14.1 to 30.3 lmW⁻¹ as the doping concentration increases from 5 to 25 wt %. The resulting device shows the highest efficiency among all studied concentrations, as 25 wt% guest was doped into host **9**. However, as the concentration is increased to 30 wt%, the power efficiency begins to decrease. This may be attributed to the concentration-quenching efficiency roll-off, resulting from the self-segregation of the emitter at high concentrations.

When material **11** was employed as the host, the resultant device exhibited the power efficiency of 15.9 lmW⁻¹ (23.1 cdA⁻¹), at 1,000 cdm⁻², with a 5 wt% doping concentration of Ir(ppy)₃ guest. The efficiency increases as the dopant

concentration increases from 5 to 20 wt%. At 20 wt%, the power efficiency was 23.3 lmW^{-1} (35.9 cdA^{-1}). As dopant concentration further increased to 35 wt%, the efficacy dropped to 18.7 lmW^{-1} (31.1 cdA^{-1}). The device which contained host **10** showed the best efficacy of 29.1 lmW^{-1} (35.9 cdA^{-1}) with a 30 wt% doping concentration of $\text{Ir}(\text{ppy})_3$. Compared to that of compound **11**, the higher efficiency exhibited by the device which contained host **10** may result mainly from the fact that material **11** showed poor film integrity owing to relatively much lower T_g (20°C).

2.3. Synthesis and characterization of carbazole and triphenylamine compounds containing 1-phenylphenanthro[9,10-d]imidazolyl fragments

The synthesis of 1-phenylphenanthro[9,10-d]imidazole-based host materials (**14**, **17**, **18**) was carried out following a multi-step synthetic route as shown in Scheme 3.



Scheme 3

9-Hexylcarbazole (**12**) was firstly synthesized by reacting 9H-carbazole with an excess of 1-bromohexane under basic conditions in acetone. 3-Formyl-9-hexylcarbazole (**13**) was then prepared from compound **12** by employing the

Vilsmeier-Haack formylation procedure [13]. 4-(Diphenylamino)benzaldehyde (**15**) and 4,4'-diformyltriphenylamine (**16**) were obtained from triphenylamine by using the Vilsmeier-Haack formylation procedure [13] in chloroform or dichloromethane, respectively. The objective materials, i.e. 2-(9-hexylcarbazolyl-3-yl)-1-phenylphenanthro[9,10-d]imidazole (**14**), 2-[4-(N,N-diphenylamino)phenyl]-1-phenylphenanthro[9,10-d]imidazole (**17**) and bis[4-(1-phenylphenanthro[9,10-d]imidazol-2-yl)phenyl]-N-phenylamine (**18**) were prepared by the reactions of aldehydes **13**, **15** or **16** with an excess of 9,10-phenanthrenequinone, aniline and ammonium acetate in acetic acid. The synthesized derivatives were identified by mass spectrometry, ^1H NMR, ^{13}C NMR and IR spectroscopy.

The behaviour of the objective materials **14**, **17**, **18** under heating was studied by using DSC and TGA under a nitrogen atmosphere. The data are summarized in Table 2 and presented in Figure 4. It was established that all the analysed compounds demonstrated high thermal stability. The onsets of mass loss were at 386°C for compound **14**, at 414°C for compound **17** and at 448°C for compound **18**, as confirmed by TGA with a heating rate of 10°C/min. the research revealed that triphenylamine-based derivatives (**17** and **18**) demonstrated slightly higher thermal stability than that of 9-alkylcarbazole containing material **14**.

Compounds **14**, **17**, **18** were obtained as crystalline materials after synthesis as confirmed by DSC; however, some of them could be converted to amorphous materials by cooling the melted samples. Derivative **17** demonstrated a very strong tendency to crystallize. DSC thermo-grams of the compound are shown in Figure 4(a). When the crystalline sample was heated during the experiment, an endothermic peak caused by melting was observed at 285°C. When the melt sample was cooled down, its crystallization (T_{cr}) was observed at 223°C to form the same crystals which were obtained by crystallization from the solution.

Compounds **14** and **18** demonstrated different behaviour during the DSC experiments. The thermo-grams of compound **18** are shown in Figure 4(b) as an example. When its crystalline sample was heated, melting was observed at 318°C followed by fast crystallization at 321°C to form a new crystalline modification, which melted at 361°C. When the melt sample was cooled down, it formed an amorphous material with high T_g of 184°C. Compound **14** demonstrated analogous behaviour during the DSC test. When its crystalline sample was heated during the experiment, melting was observed at 152°C followed by recrystallization at 166°C. The new crystalline modification then melted at 204°C. When the melt sample was cooled down, it formed an amorphous material with glass transition temperature of 52°C.

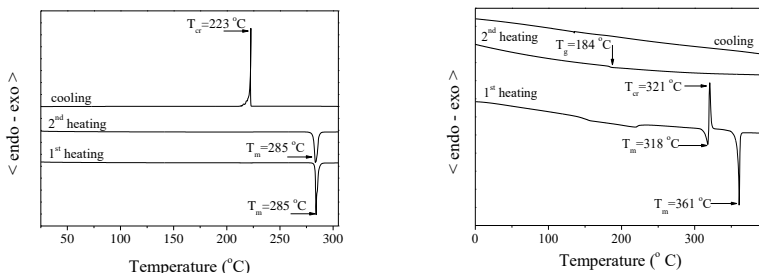


Fig. 4. DSC curves of compounds **17** (a) and **18** (b). Heating rate: 10 °C/min.

I_p's of thin amorphous layers of the derivatives were determined from electron photoemission spectra of the layers. The layer of material **14** demonstrated the highest I_p of 5.35 eV. The I_p value of the layer of compound **18** was close to 5.3 eV. The layer of material **17** demonstrated the lowest I_p of 5.1 eV (Fig. 5(a)).

Figure 5(b) shows the UV-vis absorption spectra and the PL spectra of the materials dissolved in dichloromethane recorded at 300 K and 77 K. The PL spectra measured at 77 K aimed to characterize the triplet energy of the compounds.

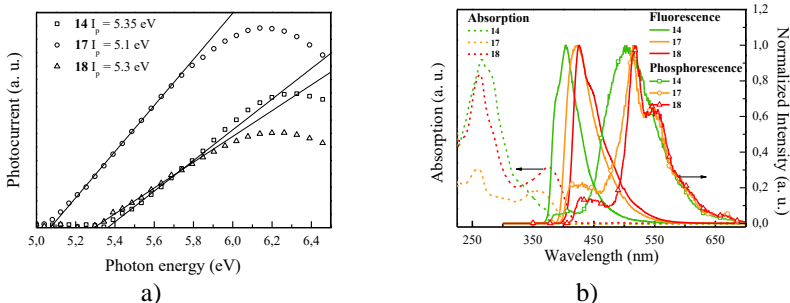


Fig. 5 (a). Electron photoemission spectra of thin layers of materials **14**, **17** and **18**; (b) absorption spectra, fluorescence spectra and phosphorescence spectra (at 77 K) of the compounds in dichloromethane ($c = 10^{-5}$ mol/l)

In the UV-vis absorption spectra, each material exhibited a peak at around 260 nm, which is related to the absorption bands of the imidazole moiety in the three compounds [14]. Notably, absorption peaks appeared at around 360 nm in compounds **17** and **18**, whereas no peak appeared for compound **14**, indicating that the absorption bands could originate from the triphenylamine moiety [15]. On the other hand, compound **14** exhibited the highest-energy fluorescence and

phosphorescence peaks at around 404 nm and 504 nm. Comparing the molecular structure of material **14**, an extension of conjugation length design was introduced in the molecules of **17** and **18**. The fluorescence (and phosphorescence) peaks of compounds **17** and **18** were respectively red-shifted to 423 nm (514 nm) and 426 nm (517 nm). Furthermore, both compounds **17** and **18** had similar spectral profiles demonstrating that the additional imidazole moiety in compound **18** did not significantly affect its photophysical properties. The triplet energy gap of each material was higher than those found in orange or red phosphors, thus enabling their use as host materials for red PHOLEDs applications. The corresponding photophysical and thermal properties are summarized in Table 2.

Table 2. Photophysical and thermal properties of compounds **14**, **17** and **18**

	λ_{abs}^a , (nm)	λ_{fluo}^b , (nm)	λ_{phos}^c , (nm)	E_T^d , (eV)	I_p^e , (eV)	T_m^f , (°C)	T_g^f , (°C)	T_{cr}^f , (°C)	T_d^g , (°C)
14	265, 279, 332, 367	404	504	2.46	5.35	152, 204 ^h	52	166	386
17	258, 359	423	514	2.41	5.1	285	-	223	414
18	263, 283, 376	426	517	2.40	5.3	318, 361 ^h	184	321	448

^a absorption maxima in dichlormethane ($c = 10^{-5}$ mol/l). ^b emission maxima of fluorescence in dichlormethane ($c = 10^{-5}$ mol/l). ^c emission maxima of phosphorescence in dichlormethane ($c = 10^{-5}$ mol/l) at 77 K. ^d Estimated from the peak of phosphorescence spectrum at 77 K. ^e Estimated from the electron photoemission spectra. ^f Determined by DSC (scan rate 10°C/min, N₂ atmosphere). ^g Analysed using TGA (5% weight loss, scan rate 20°C/min, N₂ atmosphere). ^h The materials have two different crystalline modifications.

Considering the triplet energy gaps of compounds **14**, **17** and **18** (i.e. 2.46 eV, 2.41 eV and 2.40 eV), we fabricated red phosphorescent OLEDs with a simplified tri-layer architecture and investigated their EL characteristics. Generally speaking, a host material should possess a triplet energy gap higher than that of the guest to ensure sufficient energy transfer as well as exciton confinement [16]. Furthermore, the emission of the host material and the absorption spectrum of the guest should have an adequate spectral overlap for iso-energetic transitions. In this study, a highly efficient red phosphor, bis(2-methylidibenzo[f,h]quinoxaline) (acetylacetonate) iridium (III), [Ir(MDQ)₂acac], was chosen as the emitter because of its high quantum yield and adequate energy bandgap [17]. On the other hand, to evaluate the performance of the fabricated materials, three commercially available host materials suitable for red-emitting guests were used for comparison, including 2,6-dicarbazolo-1,5-pyridine (PYD-2Cz), 4,4',4''-tris(carbazol-9-yl)triphenylamine (TCTA), and 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) [18, 19, 20].

Furthermore, di-[4-(N,N-ditolyl-amino)-phenyl] cyclohexane (TAPC) and 1,3-bis[3,5-di(pyridin-3-yl)phenyl]benzene (BmPyPhB) were respectively selected as the HTL and ETL due to their excellent carrier-transport capabilities and adequate energy gaps [21, 22]. The tested device with a tri-layer architecture was configured as ITO/TAPC (40 nm)/ host doped with 2 wt.% of Ir(MDQ)₂acac (30 nm)/ BmPyPhB (40 nm)/ LiF (0.8 nm)/ Al (150 nm), where the LiF and Al were used as the electron injection layer and the cathode, respectively. The host materials for devices A–E were as follows: PYD-2Cz, TCTA, CBP, **14**, **17**, and **18**.

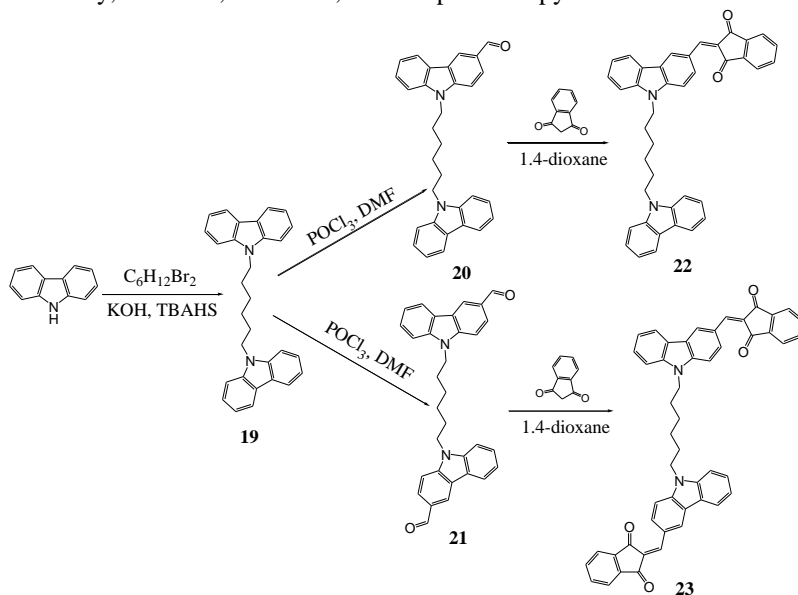
All devices showed pure Ir(MDQ)₂acac phosphorescence, except for device A, which showed an additional TCTA residual emission, indicating a lack of doping concentration of the emitter in the TCTA host. Overall, the emission peaks could be divided into two types. The emission peaks for devices with TCTA, PYD-2Cz, and CBP hosts were located at around 600 nm, while devices with the synthesized host materials exhibited red-shifted peaks (~611 nm) as well as wider spectral profiles. Considering the doping concentration of Ir(MDQ)₂acac, molecule stacking could be excluded as the cause of the red-shifted spectra. Instead, the saturated red emissions in devices D–F resulted from the environmental polarity of solid films, making these fabricated compounds more appropriate for use as hosts in red-PhOLEDs with a saturated red emission, thus reducing the difficulty of developing materials for use as red emitters. The CIE coordinates of both devices E and F were recorded at (0.62, 0.38).

Conditionally low efficiency (5.5%, 8.5 cd/A and 6.5 lm/W) of device D was attributed to the poor carrier-transport ability of compound **14**. A similar efficiency was obtained in device B with the TCTA host, but for the opposite reason. Higher hole mobility of the TCTA host resulted in the accumulation of redundant holes in the emitting layer, leading to carrier imbalance. On the other hand, the performance of devices E (**17**) and F (**18**) responded very favourably. Devices E and F exhibited the peak of EL efficiencies of up to 15.9% (21.5 cd/A and 29.9 lm/W) and 12.4% (18.3 cd/A and 23.9 lm/W), respectively. These results indicate that the gradually improved carrier-transport capabilities for compounds **17** and **18** could result in devices easily achieving the carrier balance in a simplified tri-layer architecture. In addition, although the spectral overlap between Ir(MDQ)₂acac and compound **17** (or **18**) is rather low as compared to that of the other hosts, there was no need to raise the doping concentration to achieve an effective exothermic energy transfer. In contrast, device C with the commonly used bipolar CBP host only produced a peak external quantum efficiency (EQE) of 10.4%, which is much lower than that of devices E (**17**) and F (**18**). Furthermore, the respective EQEs of devices E and F recorded at 100 (and 1000) cd/m² remained as high as 14.8% (12.7%) and 12.4% (12.1%).

2.4. Synthesis and characterization of carbazole-indan-1,3-dione-based derivatives

The synthesis of indan-1,3-dione-carbazole-based host materials (**22–23**) was carried out by a multi-step synthetic route as shown in Scheme 4.

1,6-Di-(9-carbazolyl)hexane (**19**) as the key starting material was synthesized by reacting 9H-carbazole with 1,6-dibromohexane under basic conditions in acetone. 3-Formyl-9-[(9-carbazolyl)hexyl]carbazole (**20**) and 1,6-di-(3-formylcarbazol-9-yl)hexane (**21**) were prepared from the twin compound **20** by using the Vilsmeier-Haack procedure [13]. 3-(1,3-Dioxoindan-2-ylmethylene)-9-[(carbazol-9-yl)hexyl]carbazole (**22**) and 1,6-di{[3-(dioxoindan-2-ylmethylene)carbazol-9-yl]hexane (**23**) were prepared by reacting compounds **20** or **21** with an excess of indan-1,3-dione in 1,4-dioxane or ethanol, respectively. The newly synthesized derivatives were confirmed by mass spectrometry, ¹H NMR, ¹³C NMR, and IR spectroscopy.



Scheme 4

The behaviour of the synthesized materials **22** and **23** under heating was studied by DSC and TGA under a nitrogen atmosphere. TGA analysis showed that the studied materials have very high thermal stability, and their T_d are in the range of 398–402°C. The thermal resistance of these derivatives depend on their chemical substitution to a very slight extent. For example, compound **23** containing two 1,3-dioxoindan-2-ylmethylene groups has the highest T_d (402°C),

however the value is rather close with that of the mono-substituted derivative **22** ($T_d = 398^\circ\text{C}$).

DSC experiment confirmed that both derivatives were obtained as crystalline materials by re-crystallisation from solutions; however, they readily formed glasses with high glass transition temperatures when their melt samples were cooled on a stand in air or with liquid nitrogen. The DSC thermograms of compound **22** are shown in Figure 6 as an example.

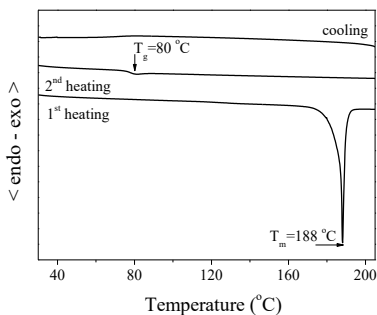


Fig. 6. DSC curves of material **22**. Heating rate: $10^\circ\text{C}/\text{min}$.

When the crystalline sample was heated, the endothermic peak due to melting was observed at 188°C . When the melt sample was cooled down and reheated, the glass-transition phenomenon was observed at 80°C and no peaks due to crystallisation and melting appeared with further heating. The crystalline sample of twin derivative **23** demonstrated the analogous behaviour. During the first heating, it melted at 275°C and formed amorphous material with T_g of 114°C upon cooling. The results demonstrate that new host materials could form thin amorphous films suitable for OLED devices. DSC analysis also revealed that the thermal transitions of the derivatives depended on their chemical structures. For example, the T_g value of di-substituted compound **23** was found to be considerably higher than that of derivative **22** having only one 1,3-dioxindan-2-ylmethylene group in its structure.

The I_p of thin amorphous layer of derivative **23** was determined from electron photoemission spectra of the layer. The layer of material **23** had I_p of 5.7 eV. The I_p value of the layer of derivative **22** could not be observed by spectroscopy. The experimentally determined triplet energies were 2.57 eV and 2.44 eV for materials **22** and **23**, respectively. The values were calculated from the first emission peaks (482 nm and 508 nm) of low temperature (77 K) phosphorescent spectra.

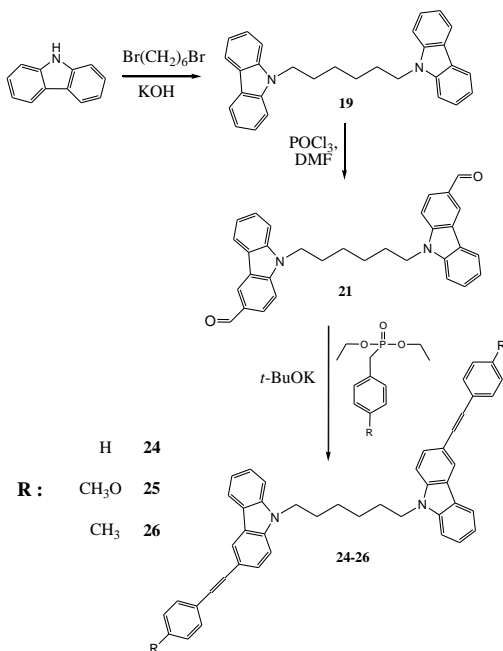
To evaluate the performance of the new host materials **22** and **23**, blue phosphorescent OLEDs were fabricated using blue emitter FIrpic as the guest.

The structure of the multilayer devices was: ITO/ PEDOT:PSS/ host **22** or **23** doped with FIrpic/ TPBi/ LiF/ Al. In all the formed devices containing hosts **22** or **23**, the electro-phosphorescence was found to originate only from the guest at different bias voltages. No host and doped transport molecular emission was visible from the OLED devices, indicating an efficient energy transfer or charge transfer from the hosts to the guest as well as the sufficient injection of both holes and electrons into the emitting layer.

The OLED prepared using the di-substituted twin derivative **23** exhibited a turn-on voltage of 5.2 V, maximum brightness of 115 cd/m² and photometric efficiency of 2.17 cd/A. The device prepared using the mono-substituted derivative **22** as the host exhibited better overall performance with low turn-on voltage of 5.0 V, maximum brightness of about 220 cd/m² and maximal photometric efficiency of about 2.7 cd/A. For the technically important brightness of 100 cd/m², the efficiency of the device containing host **22** was above 2.5 cd/A. It should be pointed out that these characteristics were obtained in non-optimized test devices under ordinary laboratory conditions. The device performance may be further improved by an optimization of the layer thickness and processing conditions.

2.5. Synthesis and characterization of twin compounds containing phenylvinyl-substituted carbazoles

The synthesis of twin derivatives (**24–26**) containing 2-phenylvinyl-substituted carbazole rings was carried out by a multi-step synthetic route shown in Scheme 5.



Scheme 5

9H-carbazole was firstly used to prepare 1,6-di(9-carbazolyl)hexane (**19**) using the procedure described in chapter 2.4. The key material, i.e. 1,6-di-(3-formylcarbazol-9-yl)hexane (**21**) was then synthesized from the twin carbazole-based derivative **19** with the Vilsmeier-Haack reaction [13]. The twin derivatives **24–26** were prepared by reacting the formylcarbazol-9-yl-containing dimer **21** with an excess of diethyl benzylphosphonate, diethyl 4-methoxybenzylphosphonate or diethyl 4-methylbenzylphosphonate, correspondingly. The synthesized compounds were identified by mass spectrometry, ¹H NMR, ¹³C NMR and IR spectroscopy. The data were found to be in good agreement with the proposed structures. Derivative **24** was obtained as a mixture of *cis*- and *trans*-isomers. Derivatives **25** and **26** were obtained as *trans*-isomers.

The behavior of the synthesized materials **24–26** under heating was studied by DSC and TGA under a nitrogen atmosphere. The results are presented in Table 3.

Table 3. Thermal characteristics of the analysed materials **24–26**

Material	T _m ^a , (°C)	T _g ^a , (°C)	T _{cr} ^a , (°C)	T _d ^b , (°C)
24	202	74	137	411
25	-	109	-	412
26	176	119	-	419

^a Determined by DSC (scan rate 10°C/min, N₂ atmosphere). ^b Analysed using TGA (5% weight loss, scan rate 20°C/min, N₂ atmosphere).

TGA analysis have showed that the analysed materials have a very high thermal stability, and their T_d values are in the range of 411–419°C. The thermal resistance of these derivatives barely depend on their chemical composition. For example, material **26** containing methylphenyl groups has the highest T_d (419°C); however, the value is rather close with those of derivatives **24** (T_d = 411°C) or **25** (T_d = 412°C).

The thermal transitions of derivatives **24–26** under heating was studied by DSC. The values of T_m, T_g and T_{cr} of the compounds are presented in Table 3. Derivative **25** containing methoxyphenyl groups was obtained after synthesis as amorphous material with a rather high T_g of 109°C. Compounds **24** and **26** were obtained as crystalline materials after synthesis; however, they could also form amorphous materials upon cooling of the melt. When the crystalline sample of material **26** was heated during the DSC test, the endothermic peak due to melting was observed at 176°C. When the melt sample was cooled down and reheated, the glass-transition was observed at 119°C and no peaks caused by crystallization and melting appeared with further heating.

The crystalline sample of compound **24** demonstrated different behaviour. The DSC thermograms of material **24** are shown in Figure 7. The crystalline sample melted at 202°C during the first heating and formed glass upon cooling. When the amorphous sample was reheated, the glass-transition was observed at 74°C, and an exothermic peak due to crystallisation was observed to produce crystals at 137°C with further heating, which melted at 202°C. It could be observed that compound **24** formed similar crystalline modifications by crystallization from the solution and from the melt.

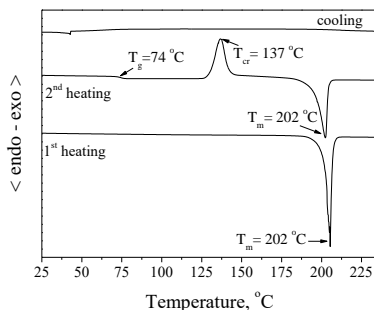


Fig. 7. DSC curves of material **24**. Heating rate: 10°C/min.

DSC analysis has shown that the thermal transitions of derivatives **24–26** depend strongly on their chemical structure. For example, the T_g value of material **24** is considerably lower than those of derivatives **25** and **26**. The crystalline derivatives **24** and **26** demonstrate very different behaviour during their heating and cooling cycles and show rather different values of T_m .

I_p 's of layers of the materials synthesized were measured by using the electron photoemission method. The photoemission spectra of thin amorphous layers of compounds **24–26** as well as the values of I_p for the layers are presented in Figure 8.

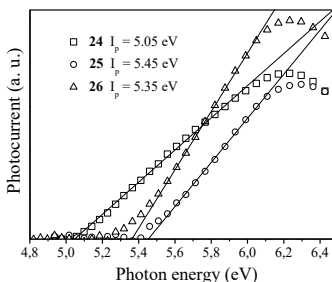


Fig. 8. Electron photoemission spectra of the layers prepared using materials **24–26** and I_p

It could be seen that values of I_p of the newly synthesized compounds depend on the nature of substituents attached to the carbazole core. Phenyl-substituted derivative **24** demonstrated the lowest I_p of 5.05 eV. The layers of materials **25** and **26** showed higher I_p values, which are in the range 5.35–5.45 eV. The I_p of all the synthesized materials are notably lower than those of derivatives having unsubstituted carbazole rings ($I_p \sim 5.9$ eV) [23]. These results demonstrate that electroactive layers of materials **24–26** should demonstrate

better hole injecting and transporting properties in optoelectronic devices than that of materials with electronically isolated carbazole rings.

To investigate the hole-transporting properties of layers of derivatives **24–26**, EL OLED devices were fabricated with a configuration of ITO/ HTL/ tris-(8-hydroxyquinoline)aluminum (Alq₃)/ LiF/ Al. In the OLED devices **24–26** were used as HTL materials, Alq₃ was used both as a light emitting and electron transporting material, ITO and LiF/Al were used as an anode and cathode, respectively. A reference device of the structure ITO/ PEDOT:PSS/ Alq₃/ LiF/ Al was also fabricated for comparison. Here the commercially available PEDOT:PSS was used as HTL material.

All the formed devices emitted bright green luminescence ($\lambda_{\text{max}} = 512\text{--}520$ nm) in agreement with the PL spectrum of Alq₃. As an example, the EL spectrum of the device containing HTL of material **24** is shown in Figure 9. The results clearly show that charge recombination occurs in the Alq₃ layer in all devices. Emission from the exciplex species at the longer wavelength formed at the interface of HTL or ETL was not seen from the OLED devices, which generally occurs in EL OLEDs containing planar molecules as the HTL derivatives.

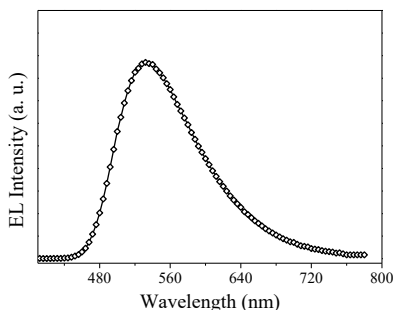


Fig. 9. EL spectrum of the OLED device: ITO/**24**/ Alq₃/LiF/Al

Figure 10 shows current density – voltage and luminance – voltage characteristics as well as the luminous efficiencies for the OLED devices containing HTL materials **24–26**. It was observed that the HTL of these derivatives demonstrate slightly different hole transporting properties in the devices due to their different hole injection properties. OLED devices in general exhibit rather low turn-on voltages of 2.6–3.8 V, a photometric efficiency of 2.0–2.34 cd/A, and a maximum brightness of about 5950–7380 cd/m² at 9–11 V. The characteristics observed for all devices are notably superior to those of reference device containing widely used PEDOT:PSS as HTL material.

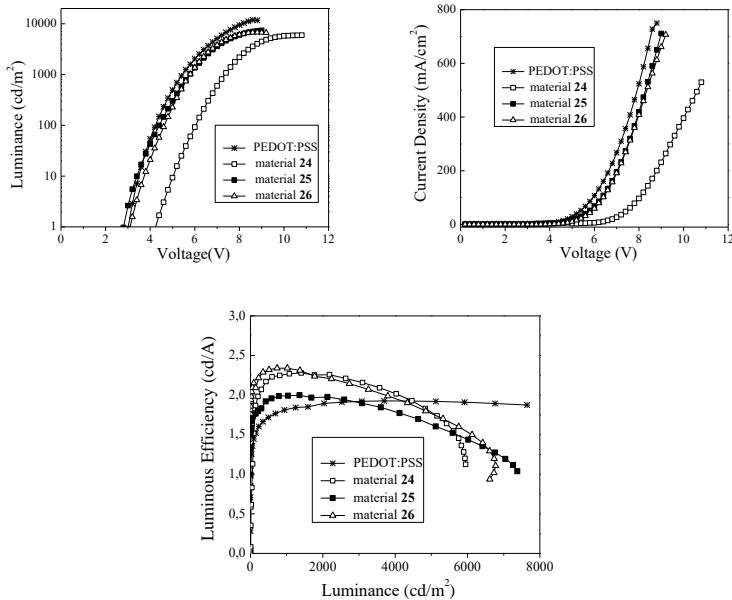


Fig. 10. OLED characteristics of the devices with the configuration: ITO/ **24**, **25**, **26** or PEDOT:PSS/ Alq₃/ LiF/ Al

Among the formed OLEDs, the device containing hole-transporting material **26** exhibited the best overall performance, i.e. maximum brightness of 7380 cd/m² and maximal photometric efficiency exceeding 2.3 cd/A. Taking the device at 1,000 cd/m², for example, the photometric efficiency was increased from 1.8 to 2.34 cd/A, an increment of 23%, as compared with that of PEDOT:PSS-based device. It should be pointed out that these characteristics were obtained in test devices under ordinary laboratory conditions. The device performance may be further improved by an optimization of the layer thickness and processing conditions [24].

3. CONCLUSIONS

1. Carbazole- and phenylindole-based compounds were synthesized, their structures were verified by ^1H NMR spectroscopy and mass spectrometry. It was established that these compounds are capable of glass formation; glass transition temperatures range from 31°C to 71°C . The ionization potentials of these materials are in the range of 5.75–5.95 eV. These materials have been confirmed as suitable hosts for green and blue phosphorescent organic light emitting diodes. The green device exhibited the best performance with the current efficiency of 20.9 cd/A and the power efficiency of 6.8 lm/W at 100 cd/m 2 .
2. Branched compounds containing three electrically isolated carbazole fragments were synthesized and characterized. Their thermal, optical, photophysical and photoelectrical properties were investigated. The synthesized compounds are capable of glass formation ($T_g = 20\text{--}64^\circ\text{C}$). Their thermal decomposition temperatures range from 338 to 361°C . These materials are suitable as hosts for effective green phosphorescent organic light emitting diodes. The most efficient device showed a power efficiency of 51 lm/W and a current efficiency of 52 cd/A at 100 cd/m 2 or 30 lm/W and 40.7 cd/A at 1,000 cd/m 2 .
3. 1-Phenylphenanthro[9,10-d]imidazole-based derivatives having carbazole or triphenylamine fragments were synthesized and characterized. These compounds demonstrate high thermal stability and glass-forming ability. Glass transition temperatures of the synthesized molecular glasses range from 52 to 184°C , and their thermal decomposition temperatures with 5% weight loss range from 386 to 448°C . Electron photoemission spectra of thin layers of the materials showed ionization potentials in the range of 5.1–5.35 eV. It was confirmed that these materials are suitable as hosts for effective red phosphorescent organic light emitting diodes. The most efficient device showed a power efficiency of 29.9 lm/W and a current efficiency of 21.5 cd/A. Efficiencies of the device were about 35–67% higher than those of devices containing commercial host materials.
4. New carbazole-indan-1,3-dione-based compounds were synthesized and characterized. These materials form glasses with the glass transition temperatures ranging from 80 to 114°C . Their thermal degradation temperatures range from 398 to 402°C . Thus these materials can be host materials for blue phosphorescent organic light emitting diodes. One of the blue OLED devices demonstrated a rather low turn-on voltage of 5.0 V, maximum brightness of about 220 cd/m 2 and a maximum luminance efficiency of 2.7 cd/A.
5. Twin compounds containing two phenylvinyl-substituted carbazole rings were synthesized and characterized. The glass transition temperatures of

the amorphous materials were in the range of 74–119°C and the thermal degradation temperatures of these materials were in the range of 411–419°C. Layers of these compounds demonstrated low I_p values, which are in the range of 5.35–5.45 eV, and the materials were suitable as hole transporting layers for organic light emitting diodes. A device containing Alq₃ emitter and hole transporting layer of 1,6-di{3-[2-(4-methylphenyl)vinyl]carbazol-9-yl}hexane exhibited the best overall performance, low turn-on voltage of 2.6 V, the maximum brightness of 7380 cd/m² and maximal photometric efficiency exceeding 2.3 cd/A. The efficiency was higher by 23% as compared with that of hole transporting layer of commercial poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) containing device.

LIST OF PUBLICATIONS ON THE TOPIC OF DISSERTATION

Publications referred in journals in the main list of Clarivate Analytics Web of Science

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2. Tavgenienė, Daiva; Kručaitė, Gintarė; Pečiulytė, Laura; Buika, Gintaras; Zaleckas, Ernestas; Dumurc, Frederic; Grigalevičius, Saulius. New carbazole-indan-1,3-dione- based host materials for phosphorescent organic light emitting diodes // *Molecular crystals and liquid crystals*. Oxon: Taylor & Francis. ISSN 1542-1406. 2016, vol. 640, iss. 1, p. 145-151. [ISI Web of Science].
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3. Tavgenienė, Daiva; Liu, Lin; Kručaitė, Gintarė; Volyniuk, Dmytro; Gražulevičius, Juozas Vidas; Xie, Zhi-Yuan; Zhang, Baohua; Grigalevičius, Saulius. Phenylvinyl - substituted carbazole twin compounds as hole transporting materials for organic light emitting diodes // Chemistry and chemical technology : international conference of Lithuanian Society of Chemistry : Lithuanian Academy of Science, Vilnius, Lithuania, April 28-29, 2016 : book of abstracts / Fizinių ir technologijos mokslų centras, Vilniaus universitetas, Lietuvos mokslų akademija, Kauno technologijos universitetas. [S.l.: s.n., 2016], ISBN 9786099551135. p. 159.
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INFORMATION ABOUT THE AUTHOR OF THE DISSERTATION

Name, Surname: Daiva Tavgenienė
Birth date and place: 11 September 1988, Marijampolė, Lithuania.
For contacts: daiva.tavgen@gmail.com

Education:

1995–2007	Sūduva Secondary School in Marijampolė
2007–2011	Bachelor's studies of Applied Chemistry, Faculty of Chemical Technologies, Kaunas University of Technology.
2011–2013	Master's studies of Applied Chemistry, Faculty of Chemical Technologies, Kaunas University of Technology.
2013–2017	Doctoral studies of Materials Engineering, Faculty of Chemical Technologies, Kaunas University of Technology.

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REZIUMÉ

Organinės šviesos diodų emiterių medžiagos turi daugybę pranašumų prieš neorganinius analogus, todėl jos gali būti plačiai naudojamos komunikacijos prietaisuose, informaciniuose ekranuose, apšvietimo prietaisuose ir kt. Fosforescuojantys organiniai šviesos diodai, turintys pereinamųjų metalų kompleksų emiterius, yra patrauklūs dėl gebėjimo šviesos emisijai panaudoti ir singletinius, ir tripletinius eksitonus, kurie suteikia galimybę pasiekti 100 % vidinį kvantinį efektyvumą. Norint gauti didelę prietaisų kvantinę išėigą, fosforescuojantys emiteriai paprastai yra disperguojami atitinkamoje matricoje tam, kad būtų nuslopintas fotoluminescencijos (FL) gesinimas. Norint pagerinti fosforescuojančių organinių šviesos diodų veiksmingumą, reikia susintetinti matricas, kurios turėtų reikiamų savybių kompleksą: turėtų tinkamas tripletinės

būsenos energijos (E_T) vertes, pasižymėtų gera krūvio pernaša ir terminiu bei morfologiniu plėvelių stabilumu.

Matricos, naudojamose fosforescuojančiuose organiniuose šviesos dioduose, įprastai turi pasižymėti šiomis charakteristikomis:

- matricos E_T turi būti didesnė už fosforescuojančio emiterio. Tai užtikrina efektyvų energijos perdavimą iš matricos į emiterį ir užkerta kelią atvirkštiniam energijos perdavimui iš emiterio atgal į matricą. Skirtingiems fosforescuojantiems emiteriams reikia skirtingų matricų su atitinkamomis E_T vertėmis;
- tinkamos aukščiausios užimtos molekulinės orbitalės (HOMO) energijos lygmenų ir žemiausios neužimtos molekulinės orbitalės (LUMO) energijos lygmenų vertės, kurios palengvina krūvininkų injekciją iš gretimų skylių pernašos ir elektronų pernašos sluoksnių (HTL ir ETL); tai yra būdas subalansuoti skylių ir elektronų pernašą;
- aukšta stiklėjimo temperatūra (T_s) ir terminės destruktijos pradžios temperatūra (T_d) lemia ilgesnį prietaiso naudojimo laiką;
- geros plėvedaros savybės ir morfologinis sluoksnių stabilumas.

Šiuo atžvilgiu kyla prieštaringi klausimai, kaip optimizuoti fotofizikines ir elektrines fosforescuojančių organinių šviesos diodų charakteristikas. Paprastai kristalinė plėvelė pasižymi gera krūvininkų pernaša, bet ji skatina FL gesinimą. Norint optimizuoti prietaisų parametrus, turi būti atsižvelgta į prieš tai paminėtus reikalavimus, keliamus sintetinant naujas matricas, kurios nulemia prietaiso ilgaamžiškumą, tarpmolekulinę krūvio pernašą, krūvininkų dreifinį judrį ir E_T lygį.

Šioje srityje gerai žinoma polimerinė matrica – poli(*N*-vinilkarbazolas) (PVK), kurios optinis draustinių energijų tarpas ($E_g = 3,5$ eV) yra panašus į nepakeisto karbazolo. Paminėtina, kad karbazolas yra vienas iš stabiliausių junginių, turintis platų draustinės juostos tarpą, todėl yra intensyviai tyrinėjamas sintetinant ir mažos molekulinės masės, ir polimerines matricas. PVK matrica pasižymi aukšta stiklėjimo temperatūra ($T_s = 200$ °C), didele tripletinės būsenos energijos verte ($E_T = 2,5$ eV), geru tirpumu įprastuose organiniuose tirpikliuose ir geromis plėvelių formavimo savybėmis, todėl plačiai naudojama fosforescuojančiuose organiniuose šviesos dioduose. Tačiau PVK yra apibūdinama kaip skyles pernešanti medžiaga, tai apriboja jos taikymo galimybes. Kitas šio polimero trūkumas yra tai, kad jis linkęs formuoti eksipleksus, kurie taip pat sumažina prietaisų efektyvumą.

Mažos molekulinės masės matricose naudojamų karbazolilfragmentus buvo susintetinta daug chromoforų, kuriuose panaudotos standžios ir plokščios struktūros aromatinės jungtys karbazolo fragmentams sujungti. Keičiant jungties pakaitų pozicijas, buvo gaunami junginiai, kurie plačiai naudojami kaip efektyvios matricos fosforescuojantiems organiniams šviesos diodams. Dažnas tokių matricų trūkumas yra didelis polinkis kristalizuotis, todėl prietaisų

negalima suformuoti liejimo iš tirpalų būdu. Dėl didelio tokių matricų poreikio ir kompleksinių charakteristikų trūkumo naujos struktūros matricų medžiagų, kurių sluoksnius galima suformuoti liejant tirpalus, sintezei ir panaudojimui šiuo metu mokslininkai skiria daug dėmesio.

Darbo tikslas – susintetinti naujos struktūros mažamolekulius junginius – potencialias matricas, turinčias elektroniškai izoliuotus chromoforus arba bipolinę sandarą, ištirti šių junginių savybes ir juos panaudoti daugiasluoksniuose organiniuose šviesos dioduose.

Tiksliui pasiekti išsikelti šie **darbo uždaviniai**:

1. Susintetinti karbazolil-, fenilindolil-, fenilvinil- ir indan-1,3-diono fragmentus turinčius karbazolo darinius.
2. Susintetinti 1-fenilfenantro[9,10-d]imidazolilfragmentus turinčius karbazolo ir trifenilamino junginius.
3. Ištirti gautų junginių termines ir optoelektronines savybes.
4. Susintetintus junginius panaudoti organiniams šviesos diodams formuoti ir charakterizuoti gautus prietaisus.

Pagrindiniai ginamieji disertacijos teiginiai

1. Šakoti dariniai, turintys elektroniškai izoliuotus karbazolilfragmentus, yra skyles pernešančios matricos, tinkamos efektyviems fosforescuojančių organinių šviesos diodų emisiniams sluoksniams formuoti.
2. 1-Fenilfenantro[9,10-d]imidazolilfragmentus turintys karbazolo ir trifenilamino junginiai pasižymi teigiamųjų krūvininkų pernašos savybėmis ir yra tinkami kaip matricų medžiagos raudona šviesa elektrofosforescuojantiems organiniams šviesos diodams formuoti.
3. Fenilvinil-, fenilindolil- arba indan-1,3-diono fragmentus turintys karbazolo junginiai pasižymi geru terminiu bei morfologiniu stabilumu ir tinkamomis skylių pernašos savybėmis, todėl gali būti naudojami kaip elektroaktyvūs sluoksniai įvairiuose organiniuose šviesos dioduose.

Mokslinio darbo naujumas

1. Susintetinti ir ištirti nauji karbazolo junginiai, turintys įvairius elektroniškai izoliuotus fragmentus. Šie junginiai yra efektyvios matricos organiniams šviesos diodams. Tai leidžia patvirtinti jų panaudojimas efektyviuose fosforescuojančiuose žalios ir mėlynos šviesos prietaisuose.
2. Susintetinti ir ištirti nauji 1-fenilfenantro[9,10-d]imidazolilfragmentus turintys karbazolo ir trifenilamino junginiai. Šie junginiai yra

efektyvios elektrofosforescuojančių šviesos diodų emisinių sluoksnių matricos. Jie buvo panaudoti raudonai šviečiančiuose prietaisuose.

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Išleido Kauno technologijos universitetas, K. Donelaičio g. 73, 44249 Kaunas
Spausdino leidyklos „Technologija“ spaustuvė, Studentų g. 54, 51424 Kaunas