

KAUNAS UNIVERSITY OF TECHNOLOGY

GINTARĖ KRUČAITĖ

**ELECTROACTIVE SUBSTITUTED CARBAZOLYL AND  
FLUORENYL GROUPS CONTAINING DERIVATIVES FOR  
ORGANIC LIGHT EMITTING DIODES**

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

2017, Kaunas

This doctoral dissertation was prepared at Kaunas University of Technology, Faculty of Chemical Technologies, Department of Polymer Chemistry and Technology during the period of 2013–2017. The studies were supported by Lithuanian Council of Science

### **Scientific Supervisor:**

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

**Editor:** Gavin Stewart (Publishing Office “Technologija”)

### **Dissertation Defence Board of Materials Engineering Science Field:**

Dr. Šarūnas MEŠKINIS (Kaunas University of Technology, Technological Sciences, Materials Engineering – 08T) – **chairman.**

Assoc. Prof. dr. Mindaugas ANDRULEVIČIUS (Kaunas University of Technology, Technological Sciences, Materials Engineering – 08T);

Prof. Dr. Saulutė BUDRIENĖ (Vilnius University, Physical science, Chemistry– 03P );

Dr. Dalius GUDEIKA (Kaunas University of Technology, Technological Sciences, Materials Engineering – 08T);

Prof. Dr. Ewa SCHAB-BALCERZAK (Katowice Silesia University, Physical science, Chemistry– 03P).

### **Official Opponents:**

The official defence of the dissertation will be held at 14 a.m. on 10<sup>th</sup> of October, 2017 at the public meeting of Dissertation defence Board of materials engineering science field in Dissertation Defence Hall at Kaunas University of Technology.

Adress: K. Donelaičio str. 73-403, 44029, Kaunas, Lithuania.

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

The Summary of the Dissertation was sent on the 8 september, 2017.

The doctoral dissertation is available on the internet (<http://ktu.edu>) and at the library of Kaunas University of Technology (K. Donelaičio str. 20, 44239 Kaunas, Lithuania).

KAUNO TECHNOLOGIJOS UNIVERSITETAS

GINTARĖ KRUČAITĖ

**ELEKTROAKTYVŪS SUBSTITUOTAS KARBAZOLIL- IR  
FLUORENILGRUPES TURINTYS DARINIAI ORGANINIAMS  
ŠVIESTUKAMS**

Daktaro disertacijos santrauka  
Technologijos mokslai, Medžiagų inžinerija (08T)

2017, Kaunas

Disertacija rengta 2013 – 2017 metais Kauno technologijos universiteto, Cheminės technologijos fakultete, Polimerų chemijos ir technologijos katedroje. Mokslinius tyrimus rėmė Lietuvos mokslo taryba.

**Mokslinis vadovas:**

Prof. dr. (HP) Saulius Grigalevičius (Kauno technologijos universitetas, Technologijos mokslai, Medžiagų inžinerija 08T).

**Redagavo:** Gavin Stewart (Leidykla “Technologija”)

**(Mokslo krypties pavadinimas) mokslo krypties disertacijos gynimo taryba:**

Dr. Šarūnas MEŠKINIS (Kauno technologijos universitetas, Technologijos mokslai, Medžiagų inžinerija – 08T) – **pirmininkas**.

Doc. dr. Mindaugas ANDRULEVIČIUS (Kauno technologijos universitetas, Technologijos mokslai, Medžiagų inžinerija – 08T);

Prof. dr. Saulutė BUDRIENĖ (Vilniaus universitetas, Fiziniai mokslai, Chemija–03P);

Dr. Dalius GUDEIKA (Kauno technologijos universitetas, Technologijos mokslai, Medžiagų inžinerija – 08T);

Prof. dr. Ewa SCHAB-BALCERZAK (Katowice Silesia universitetas, Fiziniai mokslai, Chemija–03P).

Disertacija bus ginama viešame medžiagų inžinerijos mokslo krypties disertacijos gynimo tarybos posėdyje 2017 m. spalio 10 d. 14 val. Kauno technologijos universiteto disertacijų gynimo salėje.

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

Tel. (370) 37 300 042; faks. (370) 37 324 144; el. paštas [doktorantura@ktu.lt](mailto:doktorantura@ktu.lt).

Disertacijos santrauka išsiųsta 2017 m. rugsėjo 8 d. Su disertacija galima susipažinti internetinėje svetainėje <http://ktu.edu> ir Kauno technologijos universiteto bibliotekoje (K. Donelaičio g. 20, 44239 Kaunas

## 1. INTRODUCTION

Polymers and low-molar-mass derivatives containing electroactive fragments and capable of thin amorphous film formation on the substrate, are used to fabricate functional layers for organic light emitting diodes (OLED), photovoltaic cells, field effect transistors and photorefractive materials. Amorphous layers of polymers are fabricated by spin-coating processes. In this case, devices can be formed more cheaply and over large areas/sizes. Layers of low-molar-mass derivatives usually are formed by thermal evaporation. This method is more expensive, but obtained devices have higher efficiency and longer lifetime.

Carbazolyl groups containing polymers and low-molar-mass compounds are among the most widely studied materials which are adaptable in optoelectronic and electronic. These compounds have good film forming properties, high hole mobility in their layers and photoconductive properties. Some carbazole-based materials have been commercialized in a number of devices. Fluorene moiety is also interesting for the design and synthesis of organic semiconductors. It is a fully aromatic unit providing a high thermal, morphological, chemical and environmental stability of the electroactive layers. A wide variety of aromatic and functional groups can be attached to its 2, 7 and 9 positions, and obtained compounds have different optoelectronic properties.

Electroactive charge-transporting materials can be hole transporting, electron transporting or bipolar (capable of transporting both holes and electrons). The hole transporting layer in multilayer OLED devices plays the role of facilitating hole injection from anode into the organic layer, and transporting the injected holes to the emitting layer. The hole transporting layer can also block electrons to escape from the emitting layer to the anode. They could influence the luminance and efficiency of the devices. The ideal hole transporting material should display good solubility, high thermal stability, good film forming ability and high hole mobility in its layer. In addition, hole transporting materials with high triplet energies are also used as host materials in phosphorescent OLED devices (PhOLEDs). To improve properties of the mentioned devices, it is highly desirable to design and synthesise new multifunctional materials.

**The aim of this work** was synthesis, characterization and application of new substituted carbazolyl and fluorenyl groups containing low-molecular-weight electroactive materials and polymers, which would be suitable for the formation of layers of organic light-emitting devices.

**The tasks set for the achievement of the aim** are as follows:

1. Synthesis of low-molar-mass 3,6-diaryl-9-alkylcarbazoles, 2-aryl-9-alkylcarbazoles and twin derivatives containing various substituents, investigation

of their thermal and optoelectronic properties as well as application of the materials for organic light emitting diodes.

2. Synthesis of monomers and polymers containing electronically isolated 3,6-diarylcarbazolyl, 3-arylcarbazolyl, 2-arylfluorenyl or 2,7-diarylfluorenyl fragments. Investigation of their thermal and optoelectronic properties as well as application of the obtained polymers in organic light emitting diodes.

**The main statements** of the doctoral dissertation:

1. Low-molar-mass 3,6-diaryl-9-alkylcarbazole and 2-aryl-9-alkylcarbazole based derivatives have good thermal and optoelectronic properties and are suitable materials for hole transporting layers of OLED devices.

2. Aryl substituted carbazole or fluorene fragments containing polymers, which were obtained by cationic or radical polymerization, have good thermal and optoelectronic properties and are suitable materials for hole transporting layers of OLED devices.

3. Twin compounds containing carbazole heterocyclics with electron donor or electron acceptor fragments are suitable materials for hole transporting layers or for emissive layers of organic light emitting diodes.

**Novelty of this work:**

1. New low molecular weight (di)arylcarbazoles and twin compounds with aryl substituted carbazole fragments were synthesized and explored. Some of these compounds are effective hole transporting materials suitable for the formation of organic light emitting devices. Twin compounds containing carbazole heterocyclics with electron accepting fragments are suitable host materials for emitting layers of phosphorescent OLED devices.

2. (Di)aryl substituted carbazole or fluorene fragments containing monomers and their polymers were synthesized and explored. Some of these polymers are effective hole transporting materials for the formation of electroluminescent organic light emitting diodes.

**Approval of the research results.** The research results were presented in 10 scientific publications, which correspond to the list of Clarivate Analytics Web of Science. One patent is registered in United States Patent and Trademark Office. The results of the research were also presented in 8 international conferences.

**Structure of the doctoral dissertation.** The doctoral dissertation consists of an introduction, 3 chapters, conclusions, a list of references (142 entries) and a list of scientific publications. The material of the doctoral dissertation is presents in 123 pages, including 55 figures, 9 schemes and 14 tables.

**Personal input of the author.** The author has synthesized, purified and characterized all the new derivatives. Thermal and electrochemical measurements

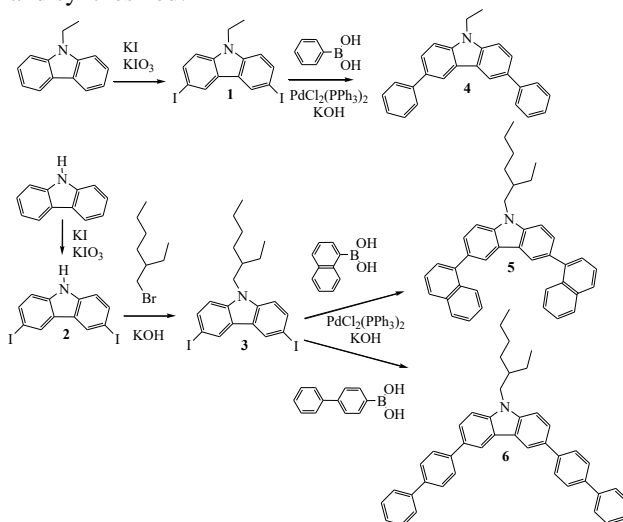
of the obtained materials were done with corresponding technicians. Habil. dr. V. Gaidelis and dr. D. Volniukas helped by measurements of ionization potentials of the synthesized materials. Dr. V. Jankauskas and dr. D. Volyniukas helped by measurements of the charge drift mobility in layers of the synthesized materials. Scientific groups of prof. Z. Xie and prof. J. H. Jou applied the newly synthesized compounds in OLEDs and measured characteristics of the devices. The author has analyzed and described all data of the investigations.

## 2. THE MAIN RESULTS

### 2.1. Synthesis and characterization of 3,6-diaryl-9-alkylcarbazoles

#### 2.1.1. Synthesis and characterization of 3,6-diphenyl, 3,6-di(1-naphthyl) or 3,6-di(4-biphenyl) substituted 9-alkylcarbazoles

Carbazole compounds, containing 9-alkylcarbazol-3-yl moieties which combined with different aromatic rings, were synthesized and described previously<sup>1</sup>. These compounds had good thermal, optoelectronic and charge transporting properties. Electroluminescent double layer hole transporting OLED devices with these compounds have reached 3470-6000 cd/m<sup>2</sup> maximum brightness, and 2.3-2.88 cd/A current efficiency. In order to obtain electronically active materials, which were expected to show enhanced hole injection and transport properties and could be suitable as hole transporting materials for multilayer OLEDs, phenyl, naphthyl or biphenyl di-substituted 9-alkylcarbazoles were designed and synthesized.



**1 Scheme.** Synthesis of 3,6-diaryl-9-alkylcarbazoles

The synthesis of aryl-disubstituted 9-alkylcarbazoles (**4-6**) was carried out by a multi-step synthetic route as shown in Scheme 1. 3,6-Diiodo-9-ethylcarbazole (**1**) as a key material was synthesized from 9-ethylcarbazole by Tucker iodination reaction<sup>2</sup>. 3,6-Diiodo-9-(2-ethylhexyl)carbazole (**3**) was prepared by two step procedure involving Tucker iodination of 9H-carbazole and alkylation of the obtained 3,6-diiodo-9H-carbazole (**2**) by using 2-ethylhexylbromide. 3,6-Diphenyl-9-ethylcarbazole (**4**) was prepared by Suzuki reaction of the diiodo-

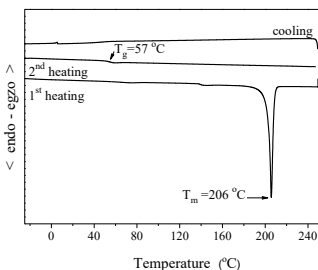


derivative **1** with an excess of phenyl boronic acid. Naphthyl- and 4-biphenyl-substituted derivatives **5** and **6** were obtained by the Suzuki reaction<sup>3</sup> of the 3,6-diiodo-9-(2-ethylhexyl)carbazole (**3**) with an excess of 1-naphthalene boronic acid or 4-biphenyl boronic acid, correspondingly.

The synthesized derivatives were all identified by mass spectrometry and <sup>1</sup>H NMR spectroscopy. The materials are soluble in common organic solvents. Transparent thin films of these materials could be prepared by spin coating from solutions or by vacuum evaporation.

The behaviour under the heating of the materials **4-6** was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under a nitrogen atmosphere. The compounds demonstrated high thermal stability. The onsets of mass loss ( $T_d$ ) were at 372 °C for **4**, at 355 °C for **5** and at 404 °C for **6**, as confirmed by TGA with a heating rate of 10 °C/min.

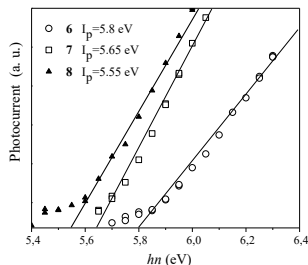
All the compounds **4-6** were obtained as crystalline materials as confirmed by DSC. The thermograms of material **5** are shown in Figure 1. When the crystalline sample was heated during the DSC test, an endothermic peak due to melting was observed at 206 °C. When the melted sample was cooled down and heated again, the glass-transition temperature ( $T_g$ ) was observed at 57 °C, and on further heating, no peaks due to crystallization and melting appeared.



**Fig 1.** DSC curves of compound **5**, heating rate 10 °C/min

Materials **4** and **6** demonstrated slightly different behaviour in the DSC measurements. The crystalline sample of **6** melted at 165 °C on first heating and formed glass upon cooling. When the amorphous sample was heated again, the glass-transition was observed at 62 °C, and on further heating an exothermic peak due to crystallisation was observed at 131 °C to give the same crystals, which were obtained from solution and melted at 165 °C. The crystalline sample of compound **4** demonstrated similar behaviour as material **6**. It melted on first heating at 187 °C, demonstrated glass transition upon second heating at 50 °C and then crystallized at 98 °C.

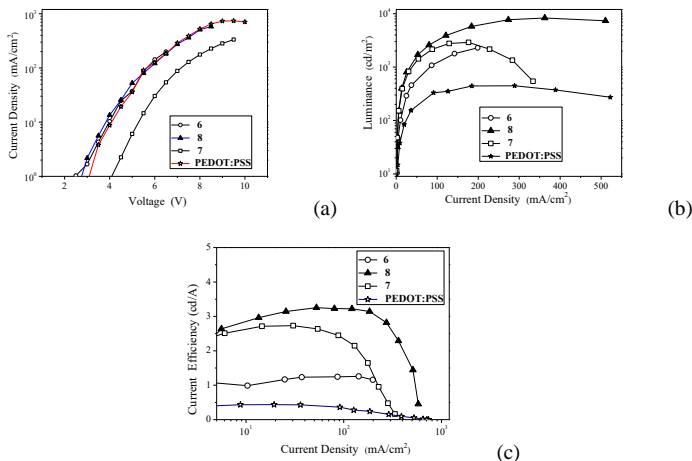
The ionization potentials ( $I_p$ ) of layers of the synthesized materials were measured by the electron photoemission method. The photoemission spectra of thin amorphous films of compounds **4-6** are presented in Figure 2.



**Fig 2.** The photoemission spectra and  $I_p$  values of thin amorphous layers of compounds **4-6**

It could be observed that values of  $I_p$  of the newly synthesized compounds depend on aromatic substituents attached to carbazole core. Biphenyl substituted derivative **4** demonstrated the lowest  $I_p$  of 5.55 eV. The layers of phenyl substituted derivative **4** showed the highest  $I_p$  of 5.8 eV. It is evident that the  $I_p$  values of the new compounds **4-6** are slightly lower than that of derivatives having electronically isolated carbazole rings ( $I_p > 5.9$  eV)<sup>4, 5</sup>. The investigations demonstrate that thin layers of **4-6** could be suitable for application in optoelectronic devices as hole transporting materials.

The compounds **4-6** were all tested in electroluminescent OLEDs as hole transporting (HT) materials. HT layer of PEDOT: PSS (poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)) containing device was also prepared for comparison. Figure 3 shows current density-voltage (a), luminance-current density (b) and current efficiency-current density (c) characteristics of the OLEDs containing the HT layers of **4-6** or PEDOT: PSS.



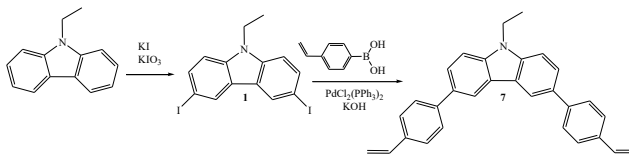
**Fig 3.** OLED: ITO/4,5,6 or PEDOT:PSS/Alq<sub>3</sub>/LiF/Al characteristics

It is seen that the current density of the devices with layers of **4-6** is higher than that of the device with PEDOT: PSS. This means that layers of **4-6** have better charge-transporting properties. The OLEDs in general exhibit turn-on voltages of 2.5-3.0 V and maximum brightness of 1270 – 8300 cd/m<sup>2</sup>. Maximal current efficiency of 3.25 cd/A was obtained in device containing HT layer of biphenyl-substituted carbazole (**6**). It is evident that the incorporation of HT layers of compounds **4-6** to the devices leads to better performance in current efficiency at the same current density in comparison with that of PEDOT: PSS-based device. The layers of the compound **6** containing the lowest  $I_p$  (5.55 eV) are better suited for hole injection from ITO (indium tin oxide) anode into Alq<sub>3</sub> (tris(quinolin-8-olato)aluminium) layer than those of materials **4** and **5** containing slightly higher  $I_p$  values. It should be pointed out that these characteristics were obtained in non-optimized test devices.

### 2.1.2. Synthesis and characterization of cross-linkable 3,6-bis(4-vinylphenyl)-9-ethylcarbazole

Efficiency of phosphorescent OLED is increasing when additional HT layers and electron transporting layers (ETL) are used in structures of the devices. If multilayer devices are fabricated by spin-coating processes, the lower HT layer should be insoluble, therefore cross-linkable materials, which after the layer formation are converted into polymeric network, are needed. The employed HT materials should possess the lowest unoccupied molecular orbital (LUMO) higher than that of the host material, so that the electrons entering in emissive layer (EML) can be effectively confined therein to lead to a higher device efficiency.

When phosphorescent blue or green light-emitting devices are formed a high triplet energy of HT material is also necessary due to prevent the out-diffusion of the triplet excitons from the emitting layer. Synthesized 3,6-bis(4-vinylphenyl)-9-ethylcarbazole (**7** in Scheme 2) conformed to the described requirements. The carbazolyl moiety in the compound structure serves to provide a high triplet energy, while the vinylphenyl fragments are useful to provide cross-linking function.

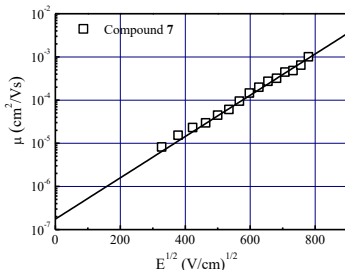


**Scheme 2.** Synthesis of 3,6-bis(4-vinylphenyl)-9-ethylcarbazole

The cross-linkable derivative (**7**) was prepared as shown in Scheme 2. 3,6-diiodo-9-ethylcarbazole (**1**) as a key material was synthesized firstly from commercially available 9-ethylcarbazole by Tucker iodination with KI/KIO<sub>3</sub> in acetic acid<sup>2</sup>. 3,6-Bis(4-vinylphenyl)-9-ethylcarbazole (**7**) was prepared by Suzuki reaction of the di-iodo-derivative **1** with an excess of 4-vinylphenyl boronic acid. The synthesized derivatives were identified by mass spectrometry, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

As determined using TGA and DSC, compound **7** showed a 5% weight loss decomposition temperature of 350 °C. The material **7** exhibited T<sub>g</sub> of 109 °C and cross-linking temperature of about 240 °C. The exothermic peak of **7** was observed only in the first heating curve of DSC and corresponded to thermal polymerization, while no peak was resulted in the second heating scan. The stable second heating thermogram was resulted because of cross-linking of compound **7** during the thermal polymerization, which is extremely consistent with the previously reported cross-linkable hole transporting materials<sup>6, 7, 8, 9, 10</sup>.

The hole drift mobility in layer of the compound **7** was characterized by the time of flight (TOF) technique. The hole drift mobility of  $1.0 \times 10^{-4}$  cm<sup>2</sup>/(V·s) at an electric field of  $3.3 \times 10^5$  V/cm was observed in the thin film (Figure 4).



**Fig 4.** The hole mobility of compound **7**

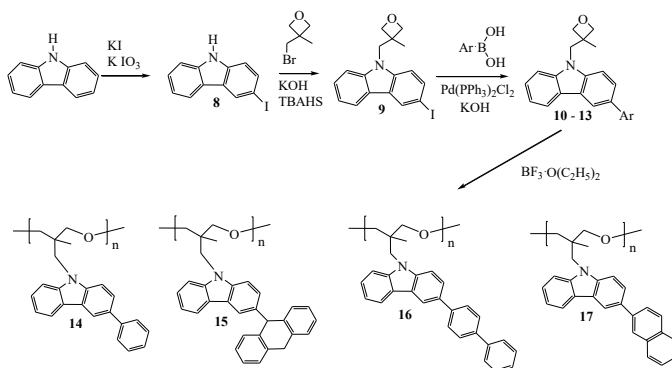
The oxidation potential of compound **7** was measured by cyclic voltammetry (CV). The highest occupied molecular orbital (HOMO) energy level was then estimated according the oxidation potential of the compound. Its LUMO energy level was calculated from the resulting HOMO energy level and the energy bandgap. The resulted HOMO value was -5.3 eV, LUMO -2.0 eV, and energy bandgap 3.3 eV. The results confirmed that compound **7** has suitable HOMO/LUMO values as for HT layer material.

The cross-linked compound **7** was used as HT polymeric network in phosphorescent OLED devices. The HT layer not only worked for devices containing low band-gap red or green emitters, but also for the counterpart with high band-gap blue emitters. With the electron confining hole transporting polymeric network, the power efficiency of a studied red device, at 1,000 cd/m<sup>2</sup> for example, was increased from 8.5 to 13.5 lm/W, an increment of 59%, and the maximum luminance was enhanced from 13000 to 19000 cd m<sup>-2</sup>, an increment of 46%, as compared with device having not the HT layer. For a high triplet energy blue emitter containing device, the power efficiency was increased from 6.9 to 8.9 lm W<sup>-1</sup>, an increment of 29%, and the maximum luminance enhanced from 9000 to 11000 cd/m<sup>2</sup>, an increment of 22%.

## **2.2. Synthesis and characterization of monomers and polymers containing oxetanyl groups**

### **2.2.1. Synthesis and characterization of 3-aryl-9-(3-methyl-oxetan-3-yl)methylcarbazole based monomers and polymers**

3-Aryl-9-alkylcarbazoles and twin derivatives with 3-arylcarbazole chromophores were describe in literature and tested as HT layers in green multilayer devices<sup>11, 12</sup>. A device containing hole-transporting layers of 3-(1-naphthyl)-9-ethylcarbazole exhibited the best overall performance with a maximum current efficiency of 5 cd/A and maximum brightness of about 9524 cd/m<sup>2</sup>. Polymeric electronically active materials generally have better film-forming properties and layers of the materials could be formed from solutions by cheap spin-coating process. Due to such advantages in this work 3-aryl-9-(3-methyloxetan-3-yl)methylcarbazole based monomers and polymers were synthesized and investigated.



**3 Scheme.** Synthetic scheme of 3-aryl-9-(3-methyloxetan-3-yl)methylcarbazole based monomers and polymers

The synthetic route demonstrating the preparation of polyethers (**14-17**) containing electroactive 3-arylcarbazolyl chromophores is shown in Scheme 3. 3-Iodo-9H-carbazole (**8**) was firstly synthesized from commercially available 9H-carbazole by Tucker iodination procedure<sup>2</sup>. The iodo-derivative **8** was then converted to oxetanyl-functionalized key derivative **9** by reaction with large excess of 3-bromomethyl-3-methyloxetane under basic conditions in the presence of phase transfer catalyst<sup>13</sup>. The monomers **10-13** were obtained from the 3-iodo-9-(3-methyloxetan-3-ylmethyl)carbazole by its Suzuki<sup>3</sup> reactions with boronic acids i.e. phenylboronic acid, 9-anthracene boronic acid, 4-biphenylboronic acid or 1-naphthalene boronic acid. Polymers **14-17** were prepared by cationic polymerization of the corresponding monomers **10-13** in dichloroethane solutions using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as an initiator. Low-molecular-weight fractions were removed from the products of polymerizations by Soxhlet extraction of the raw polymers with methanol.

The synthesized derivatives were identified by mass and  $^1\text{H}$  NMR spectroscopy. The data were found to be in good agreement with the proposed structures. Polymers **14-17** were soluble in common organic solvents at room temperature. Amorphous thin films of these materials could be prepared by spin coating from solutions.

Molecular weights and polydispersity indexes (*d*) of the synthesized polymeric materials were estimated by gel permeation chromatography (GPC). The number-average molecular weights ( $M_n$ ), weight-average molecular weights ( $M_w$ ) and values of *d* of these polymers are presented in the Table 1.

**Table 1.** Molecular weights and *d* of polymers **14-17**

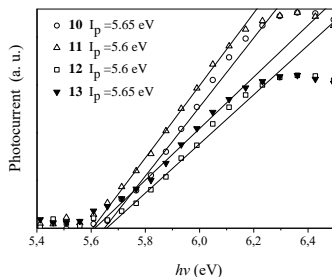
Polymer	$M_n$	$M_w$	<i>d</i>
<b>14</b>	4200	16500	3.9
<b>15</b>	1000	2400	2.4
<b>16</b>	2000	6500	3.3
<b>17</b>	1800	7100	3.9

It was observed that low-molecular-weight polymers (oligomers) were obtained after the cationic polymerization. The molecular weights of the oligomers slightly depend on the nature of chromophores attached to the polymerizable oxetane ring. The monomer containing 3-phenylcarbazolyl groups yielded the polymer with the highest molecular weight. The lowest molecular weight of oligomer **15** could probably be explained by low solubility of the formed polymeric material in dichloroethane, which was used as a solvent of the polymerization.

The behaviour under the heating of the polymeric materials **14-17** was studied by DSC and TGA under a nitrogen atmosphere. It was observed during the analyses that some of the synthesized materials demonstrate very high thermal stability. The initial thermal decomposition occurred at the temperature of 356 °C for **14**, at 378 °C for **15**, at 411 °C for **16** and at 412 °C for **17**. It was observed that the values of  $T_d$  depended on chemical structure of the polymers. For example,  $T_d$  of material **14** was notably lower than those of polymers **16** and **17**.

DSC measurements confirmed that the polymers **14-17** were amorphous materials with very high  $T_g$ 's, which are desirable for application in OLED devices. The glass-transitions were observed at 148 °C for **14**, at 175 °C for **15**, at 161 °C for **16** and at 163 °C for **17**, and no peaks due to crystallisation and melting appeared during all of the experiments. It could be observed that  $T_g$ 's of the synthesized polymers slightly depended on chemical structure of the derivatives. For example, polymer **14** containing 3-phenylcarbazolyl groups demonstrated the lowest value of  $T_g$  (148 °C), while polymer **15** with the rigid 3-(9-anthracenyl)carbazolyl moieties had the highest  $T_g$  of 175 °C.

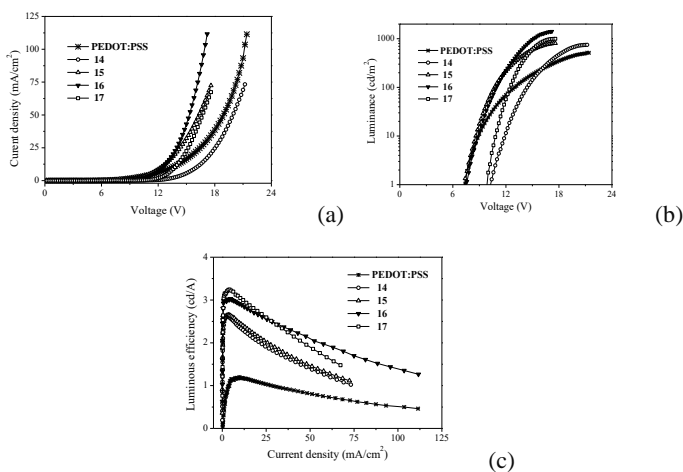
Monomers **10-13** were used for determination of  $I_p$  of the derivatives having various 3-arylcarbazolyl chromophores, since only these materials formed suitable layers for the measurements.  $I_p$  of thin amorphous films of the monomers were determined from electron photoemission spectra of the layers. The spectra as well as the values of  $I_p$  are presented in Figure 5.



**Fig 5.** The photoemission spectra and  $I_p$  values of thin amorphous layers of monomers **10-13**

It was established that  $I_p$  of the materials only slightly depended on chemical structure of the chromophores. The layers of 9-anthracenyl and 4-biphenyl substituted derivatives **10** and **11** had the lowest  $I_p$  of 5.6 eV, probably due to the longer conjugated system in the aromatic fragments.  $I_p$  of the layers of **4** and **13** reached 5.65 eV. It is evident that the values of  $I_p$  of the newly synthesized derivatives were found to be much lower than those of materials having unsubstituted carbazole rings.

Hole transporting properties of the synthesized polyethers **14-17** were tested in electroluminescent OLED devices. Hole transporting layer of PEDOT: PSS containing device was also prepared for the comparison. Figure 10 shows current density-voltage, luminance – voltage and luminous efficiency – current density characteristics for the OLEDs containing the HT layers of **14 -17** or PEDOT: PSS.



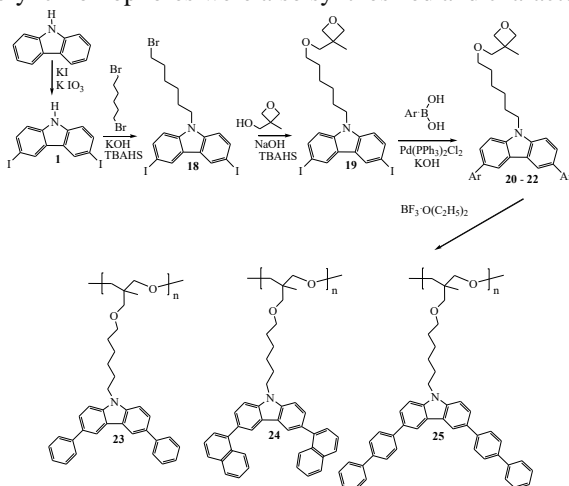
**Fig 10.** OLED: ITO/**14,15,16,17** or PEDOT:PSS/Alq<sub>3</sub>/LiF/Al characteristics



The OLEDs in general exhibited turn-on voltages of 6.8-9.0 V, a maximum brightness of 750 – 1400 cd/m<sup>2</sup> and luminous efficiency of 2.6-3.3 cd/A. It was evident that incorporation of hole transporting layers of polymers **14-17** to the devices lead to the better performance in luminous efficiency at the same current density in comparison with that of PEDOT: PSS based device. The highest efficiency of 3.3 cd/A was obtained in the device containing charge-transporting layer of polymer **17** with electro-active 3-naphthylcarbazole units. It should be pointed out that these characteristics were observed for the non-optimized test devices.

### 3.2.1. Synthesis and characterization of 3,6-diaryl-9-[6-(3-methyloxetan-3-yl)hexyl]carbazole based monomers and polymers

Low molecular weight derivatives of 3,6-diaryl-9-alkylcarbazole were described in chapter 2.1.1. Electroluminescent OLED devices using these compounds as HT materials reached maximum brightness of 1270-8300 cd/m<sup>2</sup> and current efficiency of 3.25-22.5 cd/A<sup>14</sup>. So, it has been demonstrated that aryl substituents at carbazole core improved charge transporting and injection properties of the materials. Due to that reason, monomers and polymers having 3,6-diarylcarbazolyl chromophores were also synthesized and characterized.



**4 Scheme.** Synthetic scheme of 3,6-diaryl-9-[6-(3-methyloxetan-3-yl)hexyl]carbazole monomers and polymers

The synthetic route towards the polyethers containing electroactive 3,6-diarylcarbazolyl groups (**23-25**) is shown in Scheme 4. 3,6-Diiodo-9H-carbazole (**1**) as key compound was synthesized from commercially available 9H-carbazole by Tucker iodination procedure<sup>2</sup>. The diiodo-derivative **1** was then alkylated with 1,6-dibromohexane under basic conditions to give 3,6-diiodo-9-(6-

bromohexyl)carbazole (**18**)<sup>15</sup>. Compound **18** was then treated with 3-hydroxymethyl-3-methyloxetane in two-phase system of aqueous 50 % NaOH and toluene using tetra-*N*-butylammonium hydrogen sulphate (TBAHS) as a catalyst. The oxetanyl functionalized diiodo-derivative **19** was converted to monomers (**20-22**) via the Suzuki coupling<sup>3</sup> reaction by using an excess of phenyl boronic acid, 1-naphtalene boronic acid, 4-biphenylboronic acid, respectively. Polymers **23-25** were obtained by cationic polymerization of the corresponding monomers (**20-22**) in 1,2-dichloroethane solutions using BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> as an initiator. Low-molecular-weight fractions of the products of polymerizations were removed by Soxhlet extraction of the raw polymers with methanol.

The synthesized derivatives were identified by mass spectrometry, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The data were found to be in good agreement with the proposed structures. Polymers **23-25** were soluble in common organic solvents. Transparent thin films of these materials could be prepared by spin coating from solutions.

Molecular weights and *d* of the synthesized polymeric materials were estimated by GPC. The values of M<sub>n</sub>, M<sub>w</sub> and *d* of these polymers are presented in the Table 2.

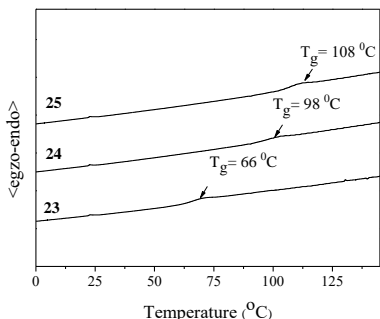
**Table 2.** Molecular weights and *d* of polymers **23-25**.

Polymer	M <sub>n</sub>	M <sub>w</sub>	<i>d</i>
<b>23</b>	1840	3860	2.1
<b>24</b>	1530	3520	2.3
<b>25</b>	1000	2520	2.5

It was observed that low-molecular-weight polymers (oligomers) were obtained after the cationic polymerization. The molecular weights of the oligomers only slightly depend on the nature of electroactive moieties attached to the polymerizable oxetane ring. The monomer containing 3,6-diphenylcarbazolyl units yielded oligomers with the highest molecular weight. The lowest molecular weight of oligomer **25** could probably be explained by low solubility of the formed polymeric material in dichloroethane.

The behaviour under the heating of the polymeric materials **23-25** was studied by DSC and TGA under a nitrogen atmosphere. It was observed by TGA that the synthesized polymers demonstrate very high thermal stability. The mass loss occurred at the temperatures of 419 °C, 426 °C and 431 °C for **23**, **24** and **25**, respectively, and little depended on molecular weight or chemical structure of the polymers.

DSC measurements confirmed that polymers **23-25** are amorphous materials with rather high glass-transition temperatures, which are sufficient for application in OLEDs. The curves of the second heating scans of the polymeric samples recorded during DSC are presented in Figure 7.

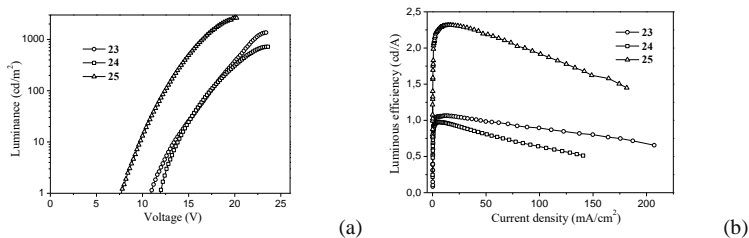


**Fig 7.** DSC curves of 2<sup>nd</sup> heating of polymers **23-25**, heating rate 10  $^{\circ}\text{C}/\text{min}$

The glass-transitions were observed at 66  $^{\circ}\text{C}$  for **23**, at 98  $^{\circ}\text{C}$  for **24** and at 108  $^{\circ}\text{C}$  for **25**, and no peaks due to crystallisation and melting appeared on further cooling and heating cycles between -10  $^{\circ}\text{C}$  and 200  $^{\circ}\text{C}$ . It is evident that  $T_g$ s of the synthesized derivatives depend on chemical structure of the polymeric materials. Polymer **23** containing 3,6-diphenylcarbazol-9-yl units demonstrated the lowest  $T_g$ , while polymer **25** with rigid 3,6-di(4-biphenyl)carbazolyl fragments has the highest  $T_g$  of 108  $^{\circ}\text{C}$ .

$I_p$  of thin amorphous films of polymers **23-25** were determined from electron photoemission spectra of the layers. It was observed that layers of polymers **23** and **25** had the lowest  $I_p$  of about 5.5 eV probably due to longer conjugated system in the aromatic fragment of 3,6-diarycarbazolyl.  $I_p$  of the layer of polymer **24** reached 5.69 eV apparently due to less effective conjugation in the 3,6-dinaphtylcarbazol-9-yl unit. The investigations demonstrated that the layers of polymers **23-25** are suitable as hole injection or transport layers for organic optoelectronic devices.

Hole transporting properties of the synthesized polymers were tested in electroluminescent devices. The two layer OLEDs containing the layers of polymers **23**, **24** or **25**, respectively, as HT layer and  $\text{Alq}_3$  as an electroluminescent/electron transporting layer were prepared. Figure 8 shows luminance-voltage (a) and photometric efficiency-current density (b) characteristics for the OLEDs containing the HT layers of **23 - 25**.



**Fig 8.** OLED characteristics of the devices with the configuration: ITO/**23, 24** or **25**/Alq<sub>3</sub>/LiF/Al

These OLEDs in general exhibited turn-on voltages of 7 – 11.5 V, a photometric efficiency of 1.0 – 2.3 cd/A, and a maximum brightness of 720 – 26300 cd/m<sup>2</sup> (at 20 - 24 V). Among these devices, the OLED using polymer **25** as the hole transporting material exhibits the best overall performance, i.e. a turn-on voltage of about 7 V and maximal photometric efficiency of 2.3 cd/A. The efficiency of this device showed only a moderate drop in the observed current density window up to 180 mA/cm<sup>2</sup>, i.e. for the technically important brightness of 100 cd/m<sup>2</sup> an efficiency above 2 cd/A was detected.

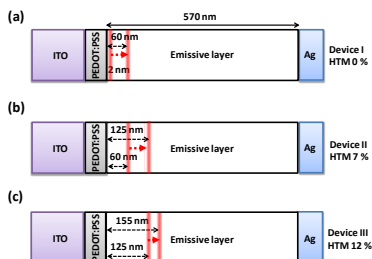
### 2.2.3. Utilization of poly{3,6-diphenyl-9-[6-(3-methyloxetan-3-ylmethoxy)hexyl]carbazole} in solid-state light-emitting electrochemical cells

Solid-state light-emitting electrochemical cells (LECs) have recently attracted intense attention since they possess several advantages as compared to OLEDs. In the active layer of LECs, electrochemically p- and n-doped layers induced by spatially separated mobile ions under an applied bias form ohmic contacts with electrodes, leading to balanced carrier injection, low operating voltages and consequently high power efficiencies<sup>16, 17</sup>. Therefore, LECs are generally composed of only a single emissive layer, which can be easily processed from solutions. If the emissive layer of the cell is composed of an ionic transition metal complex (iTMC), an imbalanced number of electrons and holes result in an off-centred recombination zone and exciton quenching deteriorates device efficiency. To improve device efficiency of iTMC-based LECs, several techniques to improve carrier balance, i.e., to achieve a centred recombination zone, have been reported. These techniques include doping a carrier trapper, adjusting carrier injection, incorporating salt additives, adjusting the thickness of the emissive layer and confinement of the recombination zone. In this work, we demonstrated the incorporation of HT material into the emissive layer of iTMC-based LECs to improve device performance.

The host complex used in the emissive layer of the LECs was Ru(dtb-bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (where dtb-bpy is 4,4'-ditertbutyl-2,2'-bipyridine). The HT material doped in LECs based on the complex was poly{3,6-diphenyl-9-[6-(3-

methyloxetan-3-ylmethoxy)hexyl]carbazole} (**23**). The chemical structure of polymer **23** was promising for HTL material of LEC. Carbazolyl moieties facilitated hole transport and alkoxy groups improved phase compatibility with ionic complex.

Three LECs were made and the concentration of polymer **23** was 0 % (I device), 7 % (II device) or 12 % (III device). Structures of the cells are shown in Figure 9. Device I with only Ru(dtb-bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> emission layer was used for characteristics comparison.



**Fig 9.** Structures of LEC (a) **I**, (b) **II** and (c) **III**

Devices were fabricated on the ITO coated glass substrate. A thin PEDOT:PSS layer (30 nm) was spin-coated onto the ITO substrate. This layer improves charge injection and contact between the anode and emission layer. The emissive layers (thicknesses 570 nm) were spin-coated from the acetonitrile/chloroform mixed solution of Ru(dtb-bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> and polymer **23** HT layer. Then Ag top contact (100 nm) was formed by thermal evaporation. The electrical and emission characteristics of LEC devices were measured using a source-measurement unit and a calibrated Si photodiode. All device measurements were performed under a constant bias voltage (2.5 V) in a nitrogen glove box and are presented in the table 3.

**Table 3.** LEC characteristics.

Device (HTM w.%)	$t_{\text{maks}}$ (min) <sup>a</sup>	$J_{\text{maks}}$ (mA/cm <sup>2</sup> ) <sup>b</sup>	$L_{\text{maks}}$ (μW/cm <sup>2</sup> ) <sup>c</sup>	$\eta_{\text{I}}^{\text{maks}}$ (%) <sup>d</sup>	$\eta_{30}$ (%) <sup>e</sup>	$\eta_{540}$ (%) <sup>f</sup>
I (0 %)	180	0,21	3,44	1,86	1,37	0,74
II (7 %)	156	0,20	5,20	2,78	2,29	1,16
III (12 %)	290	0,22	6,47	2,79	2,48	1,57

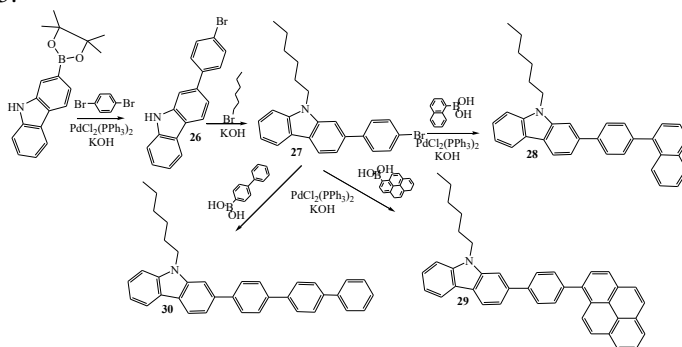
Where: <sup>a</sup>Time required to reach the maximal light output. <sup>b</sup>Maximal current density. <sup>c</sup>Maximal light output. <sup>d</sup>Maximal external quantum efficiency. <sup>e</sup>External quantum efficiency at 30 min. <sup>f</sup>External quantum efficiency at 540 min.

Although all LECs exhibited a similar trend in the temporal evolution of the recombination zone, i.e., moving from anode toward the centre of the emissive layer, the recombination zone position was dependent on the doping concentration of HT material (Figure 9). The initial recombination zone in device I was very

close to the anode (60 nm). When 7% HT material was doped in the emissive layer (device II), the initial recombination zone moved toward the centre of the emissive layer (125 nm) and the EQE at 30 min increased from 1.37 to 2.29% (Table 3). Moving the recombination zone resulted from the addition of HT material, which facilitated hole transport. The more centred recombination zone offered sufficient distance between the doped layers and recombination zone, resulting in reduced exciton quenching and improved device efficiency. Increasing the doping concentration of HT material to 12% (device III) further moved the initial recombination zone toward the centre of the emissive layer (155 nm), rendering an even higher EQE (2.48%) at 30 min. At 30 min, the EQE of LECs based on complex was enhanced by 80% upon doping with 12% polymer **23**. When the doped layers were well established, e.g., at 540 min, the intrinsic layer between the doped layers shrank significantly and exciton quenching in the off-centred recombination zone was extremely severe. These results revealed that incorporating an HT material into the emissive layer of LECs can move the recombination zone away from anode, rendering mitigated exciton quenching and thus higher light output and device efficiency.

### 2.3 Synthesis and characterization of 2-(4-arylphenyl)-9-hexylcarbazoles

A previous study found that introduction hexyl moiety in the ninth position of carbazole could increase the spatial hindrance of the carbazole moiety and the derivatives could be used for the preparation of thin amorphous layers with adequate morphology on substrates<sup>18</sup>. The synthesis of aryl-substituted 9-hexylcarbazoles (**28-30**) was carried out by a multi-step synthetic route as shown in Scheme 5.



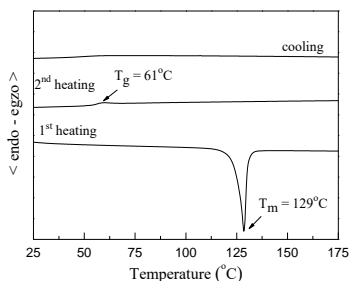
**5 Scheme.** Synthesis of 2-(4-arylphenyl)-9-hexylcarbazoles

2-(4-Bromophenyl)-9H-carbazole (**26**) as a key material was synthesized from commercially available 9H-carbazole-2-boronic acid pinacol ester by its Suzuki reaction with 1,4-dibromobenzene<sup>2</sup>. The bromo-derivative **26** was then alkylated under basic conditions using an excess of 1-bromohexane to produce 2-

(4-bromophenyl)-9-hexylcarbazole (**27**)<sup>19</sup>. Naphthyl, pyrenyl or biphenyl substituted objective derivatives **28**, **29** and **30** were finally obtained by Suzuki reaction of the 2-(4-bromophenyl)-9-hexylcarbazole (**27**) with an excesses of 1-naphthalene boronic acid, pyrene-1-boronic acid or 4-biphenyl boronic acid. The synthesized derivatives were identified by mass spectrometry and <sup>1</sup>H NMR spectroscopy. The data were found to be in good agreement with the proposed structures. The materials were soluble in common organic solvents. Transparent thin films of these materials could be prepared by spin coating from their solutions or by vacuum evaporation technique.

The behaviour under heating of the compounds **28-30** was studied by DSC and TGA under a nitrogen atmosphere. It was observed by TGA that the synthesized electroactive materials demonstrate high thermal stability. The thermal destruction occurred at 344 °C for compound **28**, at 341°C for compound **28** and 334 °C for compound **30**. It was observed that the values of  $T_d$  did not significantly depend on chemical structure of the materials.

The derivatives **28**, **29** and **30** were obtained after synthesis as crystalline material as demonstrated during the DSC measurements. DSC thermograms of the material **29** are presented in Figure 10 as an example.



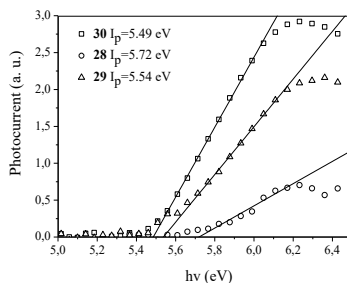
**Fig 10.** DSC curves of compound **29**, heating rate 10 °C/min

The crystalline sample of **29** melted at 129 °C on first heating and formed glass upon cooling. When the amorphous sample was heated again, only the glass-transition was observed at 61°C and, on further heating, no peaks appeared due to crystallization and melting.

A crystalline sample of derivative **28** demonstrated analogous behaviour during the DSC experiment. The material **28** melted at 121 °C on first heating and formed glass upon cooling. When the amorphous sample was heated again, only the glass-transition was observed at 58 °C and, on further heating, no peaks appeared due to crystallization and melting. The material **30** melted at 225 °C on first heating and formed glass upon cooling. When the amorphous sample was heated, the glass-transition was observed at 136 °C, however the liquid sample

crystallized at 198 °C to form the same crystals which were obtained after syntheses ( $T_m = 225$  °C).

The  $I_p$  of thin amorphous films of the compounds **28**, **29** and **30** were determined from electron photoemission spectra of the layers. The spectra as well as the values of  $I_p$  are presented in Fig. 11.



**Fig 11.** Photoemission spectra and  $I_p$  values of thin amorphous layers of compounds **28-30**

The  $I_p$  of the materials was found to depend on their chemical structure. The layers of the derivative **28** demonstrated a higher  $I_p$  value of 5.72 eV probably due to the smaller conjugated system of naphthyl fragment. The layers of the derivative **30** demonstrated a lowest  $I_p$  value of 5.49 eV. The  $I_p$  of the layers of compound **29** having pyrenyl fragments was also rather low, i.e. 5.54 eV.

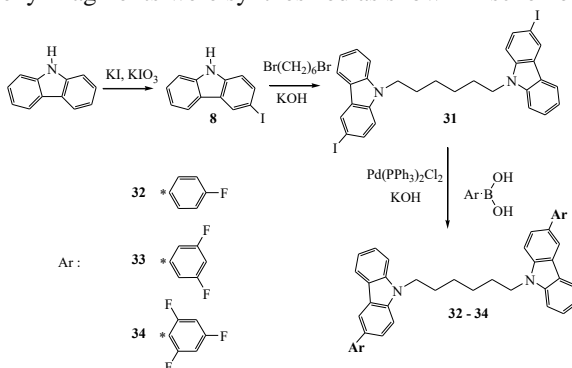
Compounds **28** and **29** were selected for use as HT layers in red phosphorescent OLEDs using a highly efficient emitter bis(2-methyl-dibenzo[f,h]quinoxaline)(acetylacetonate)iridium(III) ( $\text{Ir}(\text{MDQ})_2\text{acac}$ ). 4,4-bis(N-carbazolyl)-1,1'-biphenyl (CBP) was chosen as host for the triplet emitter. 3,5,3',5'-tetra(m-pyrid-3-yl)-phenyl[1,1']biphenyl (BP4mPy) was used as electron transport material for the devices. Furthermore, a reference device was fabricated with N,N'-bis(1-naphthalen)-N,N'-bis(phenyl) benzidine (NPB) due to its common application as HT layer in red-emitting phosphorescent OLEDs. The electroluminescent characteristics of the tested devices indicated that devices with compounds **28** and **29** exhibited a performance comparable to that of NPB-based devices. By introducing the hole transporting layers, the peak efficiencies of red phosphorescent OLEDs with compounds **28** and **29** were respectively recorded at 15.4 % (26.0 cd/A and 24.2 lm/W) and at 17.3 % (26.1 cd/A and 19.1 lm/W). The positive results of these devices with 9-hexylcarbazole compounds indicated a new path of molecular designs for HT materials.



## 2.4. Synthesis and characterization of twin carbazole-based compounds

### 2.4.1. Synthesis and characterization of twin compounds containing fluorophenyl, difluorophenyl or trifluorophenylsubstituted carbazole rings

Earlier described twin carbazole-based compounds containing phenyl, naphthyl and biphenyl substituents demonstrated good film-forming and charge transporting properties<sup>20</sup>. For example, OLED device with 1,6-di(3-(1-naphthyl)-9-carbazolyl)hexane HT layer and Alq<sub>3</sub> emitter reached 3.4 cd/A maximum current efficiency and 7940 cd/m<sup>2</sup> maximum brightness. In this work, 1,6-di(9-carbazolyl)hexane derivatives containing 4-fluorophenyl, 3,5-difluorophenyl or 2,4,6-trifluorophenyl fragments were synthesized as shown in scheme 6.



**6 Scheme.** Synthetic scheme of 1,6-di(3-aryl-9-carbazolyl)hexanes

The starting key material, i.e. 3-iodo-9H-carbazole (**8**) was synthesized from commercially available 9H-carbazole by Tucker iodination reaction by described in literature procedure<sup>2</sup>. Twin derivative **31** containing two 3-iodocarbazol-9-yl fragments was prepared by the reaction of 1,6-dibromohexane with an excess of the 3-iododerivative **8** under basic conditions as we described earlier<sup>21</sup>. The objective electro-active derivatives **32-34** were prepared by Suzuki reaction<sup>3</sup> of the 1,6-bis(3-iodocarbazol-9-yl)hexane (**31**) with an excess of 4-fluorophenyl boronic acid, 3,5-difluorophenyl boronic acid or 2,4,6-trifluorophenyl boronic acid, correspondingly. The synthesized compounds were identified by mass spectrometry and <sup>1</sup>H NMR spectroscopy. The data were found to be in good agreement with the proposed structures. The materials are soluble in common organic solvents, i.e. THF, chloroform, ethyl acetate, chlorobenzene. Transparent thin films of compounds **32-34** can be prepared from their solutions by spin coating method.

The behaviour under the heating of the synthesized materials **32-34** was studied by DSC and TGA under a nitrogen atmosphere. The results are presented in Table 4. It was observed during the TGA analysis that thermal resistance of

these derivatives depended strongly on their chemical composition. For example, material **32** containing the lowest amount of fluorine had the highest temperature of thermal destruction. Its value of  $T_d$  (395 °C) was visibly higher than that of derivative **34** ( $T_d = 278$  °C) containing the biggest amount of fluorine in its structure.

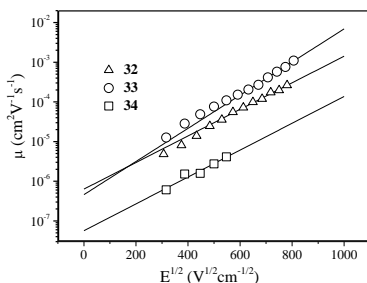
**Table 4.** Thermal characteristics and  $I_p$  values of the materials **32-34**.

Material	$T_m$ (°C)	$T_g$ (°C)	$T_d$ (°C)	$I_p$
<b>32</b>	152	54	395	5.70
<b>33</b>	86	48	346	5.75
<b>34</b>	178	51	278	5.92

The thermal transitions under heating of the derivatives **32-34** was studied by DSC. Melting temperatures ( $T_m$ ) and  $T_g$  of the compounds are presented in Table 4. It was observed that all the objective derivatives were obtained as crystalline materials after synthesis; however they could form also stable amorphous materials upon cooling of their melts. When crystalline sample **34** was heated during the DSC test, an endothermic peak due to melting was observed at 178 °C. When the melt sample was cooled down and heated again, the glass-transition was observed at 51 °C, and on further heating no peaks due to crystallization and melting appeared. The crystalline samples of compounds **32** and **33** demonstrated similar behaviour as material **34**. They melted on first heating at 152 °C (**32**) and at 86 °C (**33**), respectively, and formed amorphous state during cooling. The amorphous samples demonstrated only glass transitions upon second heating at 54 °C (**32**) and at 48 (**33**) °C, respectively. It can be observed that values of  $T_g$  of the materials did not depend considerably on the chemical composition of the derivatives and are in the narrow range from 48 °C to 54 °C.

The  $I_p$  of layers of the materials synthesized were measured by the electron photoemission method. The photoemission spectra of thin amorphous layers of the compounds **32-34** as well as values of  $I_p$  for the layers are presented in Table 4. It could be seen that  $I_p$  of the newly synthesized compounds depend on the nature of substituents attached to carbazole core, i.e number of fluorine atoms at phenyl ring. 4-Fluorophenyl substituted derivative **32** demonstrated the lowest  $I_p$  of 5.7 eV. The layers of 2,4,6-trifluorophenyl substituted derivative **34** showed the highest  $I_p$  of 5.92 eV. These results demonstrate that hole transporting properties of thin layers of **32-34** should also depend on the chemical composition of the materials.

The TOF method was used to characterize the magnitude of charge drift mobility in thin layers of the synthesized materials **32-34**. It was observed from the measurements that positive charges (holes) are transported in the thin films. Electric field dependencies of the  $\mu_h$  for the layers are shown in Figure 12.



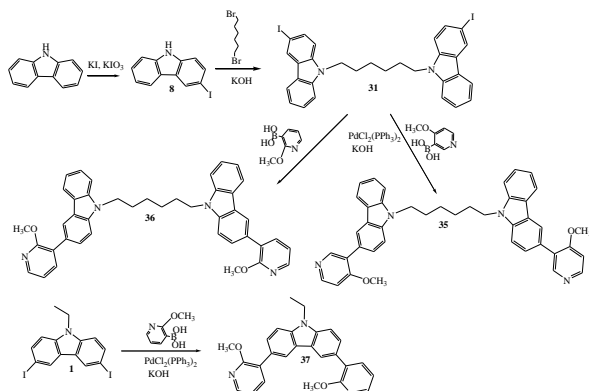
**Fig 12.** Electric field dependencies of  $\mu_h$  in charge transport layers of the materials **32–34**

The  $\mu_h$  of the materials **32–34** range from  $4 \times 10^{-6} \times 10^{-3}$  to  $1.1 \times 10^{-3}$   $\text{cm}^2/(\text{V}\cdot\text{s})$  at high electric field at 25 °C. It is obvious that charge transporting properties depend on chemical structures of the electroactive materials. The highest  $\mu_h$ , exceeding  $10^{-3}$   $\text{cm}^2/(\text{V}\cdot\text{s})$  at high electric field, was observed for the layers of the derivative **33** containing 3-(3,5-difluorophenyl)carbazolyl fragment. Charge mobility observed for the layers of material **34** containing 3-(2,4,6-trifluorophenyl)carbazolyl fragments was the lowest and reached  $4 \times 10^{-6}$   $\text{cm}^2/\text{Vs}$  at high electric field. It is evident that these results correlate with ionization potentials of the materials as well as with characteristics of OLED devices using these materials.

The compounds were tested as hole-transporting materials in organic light emitting diodes using  $\text{Alq}_3$  as a green emitter and electron transporting layer. The structure of the devices was ITO/**32**, **33** or **34**/ $\text{Alq}_3$ /LiF/Al. An OLED based on a twin derivative containing 3-(3,5-difluorophenyl)carbazolyl moieties exhibited the best overall performance with a maximal current efficiency of 2.1 cd/A and maximum brightness of about 560  $\text{cd}/\text{m}^2$ . The analogous slightly optimized device containing an additional PEDOT: PSS hole injecting layer demonstrated turn on voltage of 6.0 V, maximum brightness of about 6200  $\text{cd}/\text{m}^2$  and maximal current efficiency of 3.4 cd/A.

#### 2.4.2. Synthesis and characterization of twin carbazole based compounds containing methoxypyridinyl fragments

The twin compounds, which were described in chapter 2.4.1, demonstrated good thermal and optoelectronic properties. Therefore, the strategy of the structure was also used for synthesis of bipolar compounds, which can be used as host materials for PhOLED. Twin compounds containing methoxypyridinyl fragments were synthesized and characterized in the next step were. 3,6-Di(2-methoxy-3-pyridinyl)-9-ethylcarbazole was synthesized for comparison of characteristics.



**7 Scheme.** Synthetic scheme of 1,6-di(3-aryl-9-carbazolyl)hexanes and 3,6-di(2-methoxy-3-pyridinyl)-9-ethylcarbazole

As shown in scheme 7, the synthesis of the methoxypyridinyl substituted carbazole based materials **35-37** was carried out by Suzuki coupling reaction<sup>3</sup>. The key materials **8** and **31** were firstly synthesized as described in chapter 4.2.1. Materials **35** and **36** were prepared by coupling reaction of 1,6-bis(3-iodocarbazol-9-yl)hexane (**31**) with an excess of 6-methoxy-3-pyridinylboronic acid or 2-methoxy-3-pyridinylboronic acid, respectively. Moreover, material **37** was synthesized by a coupling reaction of 3,6-diiodo-9-ethylcarbazole with an excess amount of 2-methoxy-3-pyridinylboronic acid. The resultant compounds **35-37** were characterized by using <sup>1</sup>H NMR and <sup>13</sup>CNMR spectroscopies as well as mass spectrometry. The data were found to be good agreement with the proposed structures.

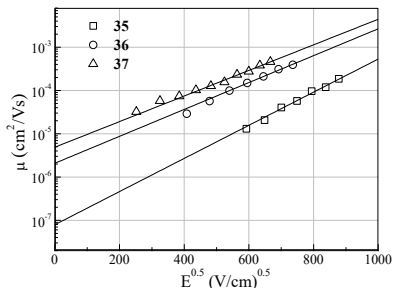
The behaviour under the heating of the synthesized materials **35-37** was studied by DSC and TGA under a nitrogen atmosphere. The results are presented in Table 5.

**Table 5.** Thermal characteristics and of the materials **35-37**.

Junginys	T <sub>m</sub> (°C)	T <sub>g</sub> (°C)	T <sub>d</sub> (°C)
<b>35</b>	167	51	409
<b>36</b>	-	54	402
<b>37</b>	137	57	353

The reason why compounds **35** and **36** showed higher thermal stability than that of compound **37** was because of their higher molecular weight, which was due to the twin molecular structures. Derivatives **35** and **37** were obtained as crystalline materials with T<sub>m</sub> of 167 °C and of 137 °C, correspondingly, however they could form also amorphous layers. T<sub>g</sub> of the materials **35-37** ranged from 51 °C to 57 °C. The reason why a single carbazole unit based compound **37** shows a slightly higher T<sub>g</sub> (57 °C) than that of twin carbazole based counterparts is because of their mono methoxypyridinyl substituted chromophore.

The charge drift mobility in layers of the materials **35-37** was characterized by TOF technique. It was established that positive charges could be transported in the thin films. The  $\mu_h$  determined for compounds **35-37** is shown as a function of the square root of electric field (Figure 13).



**Fig 13.** Electric field dependencies of  $\mu_h$  in charge transport layers of the materials **35-37**

The compounds **35**, **36**, and **37** showed hole mobility in the order **35** ( $2 \times 10^{-4}$  cm<sup>2</sup>/(V·s)) < **36** ( $4 \times 10^{-4}$  cm<sup>2</sup>/(V·s)) < **37** ( $5 \times 10^{-4}$  cm<sup>2</sup>/(V·s)). It seems that compounds **36** and **37** showed slightly higher hole mobility than that of compound **35** due to different position of methoxy group on the pyridine unit.

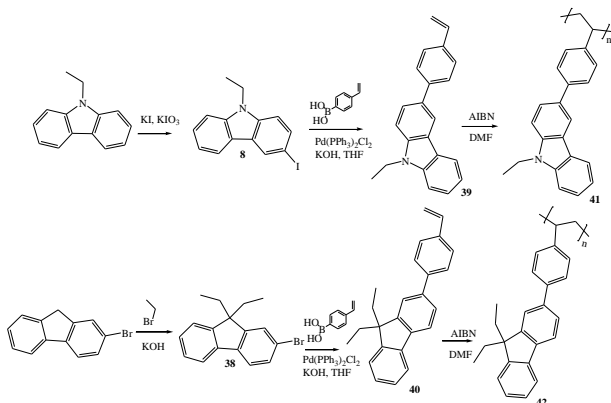
The prepared derivatives were used as host materials for green PHOLED: ITO/PEDOT: PSS/**35**, **36** or **37** with Ir(ppy)<sub>3</sub>/TPBi/LiF/ with both wet-and dry-fabrication. It was established that derivative **36** was the most effective host material. By employing this host, green PHOLED devices showed, at 100 cd/m<sup>2</sup> for example, a power efficiency of 16.1 lm/W (27 cd/A) by using spin-coating, while 52.7 lm W<sup>-1</sup> (59.4 cd/A) by using vapour-deposition. The high efficiency may be attributed to feasibility of effective exciton generation on both host and guest, high triplet energy, and effective host-to-guest energy transfer. The device efficiency can be further enhanced to 62.8 lm/W (61 cd/A) by incorporating an additional hole transporting layer of 1-bis[4-[N,N-di(4-tolyl)amine]phenyl]cyclohexane (TAPC). The results confirmed that this carbazole derivative may serve as one ideal host for fabricating energy-efficient devices for solid state lighting and flat panel display applications via either wet- or dry-processing.

## 2.5. Synthesis and characterization of monomers and polymers containing vinylphenyl fragments

### 2.5.1. Synthesis and characterization of electroactive polymers containing 3-phenylcarbazol-6-yl or 2-phenylfluoren-4-yl fragments

Polymers of 3-aryl-9-(3-methyloxetan-3-yl)methylcarbazoles, which are described in section 2.2.1, had good thermal, also charge transporting properties

and electroluminescent OLED devices with Alq<sub>3</sub> emitter reached current efficiency of 2.6-3.3 cd/A. In this section, monomers and corresponding polymers containing 3-phenylcarbazol-6-yl or 2-phenylfluoren-7-yl moiety are described. Synthetic scheme of the derivatives is shown in Scheme 8.



**8 Scheme.** Synthetic scheme of poly{3-(4-vinylphenyl)-9-ethylcarbazole} and poly{3-(4-vinylphenyl)-9,9-diethylfluorene}

The key starting compounds, 3-iodo-9-ethylcarbazole (**8**) and 2-bromo-9,9-diethylfluorene (**38**), were prepared from 9-ethylcarbazole or 2-bromofluorene, correspondingly, using the described procedures<sup>22, 23</sup>. Monomers **39** and **40** containing vinyl groups were prepared by palladium catalyzed Suzuki coupling reactions of the corresponding halogen derivatives **8** or **38** with an excess of 4-vinylphenylboronic acid<sup>3</sup>. Vinyl polymers **41** and **42** were obtained by radical polymerization of the monomers in *N,N'*-dimethylformamide (DMF) solutions under inert atmosphere using 2,2'-azoisobutyronitrile as an initiator. Low-molar-mass fractions of the products of polymerizations were removed by Soxhlet extraction of the raw polymers with methanol.

The newly synthesized derivatives were identified by mass spectrometry (low molar mass derivatives) and <sup>1</sup>H NMR spectroscopy. The synthesized polymers were soluble in common organic solvents, such as chloroform and THF at room temperature. Transparent thin films of the polymeric materials could be prepared by spin coating from solutions.

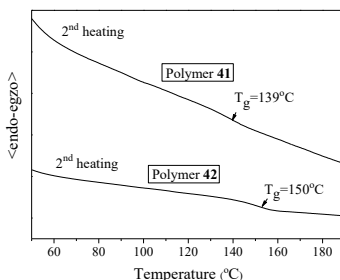
$M_n$  and  $M_w$  of the synthesized polymers were estimated by GPC. The values of  $M_n$  and  $M_w$  as well as  $d$  are summarized in Table 6.

**Table 6.** Molecular weights and values of d of polymers **41-42**.

Polymer	M <sub>n</sub>	M <sub>w</sub>	d
<b>41</b>	2100	1100	1.9
<b>42</b>	3700	1500	2.5

It was observed that the molecular weights of the polymers depend on the nature of chromophores attached to vinyl groups of the corresponding monomers. The monomer **42** containing 2-phenylfluoren-7-yl fragment yielded polymer with higher molecular weight than that of carbazole-based monomer **41**, which yielded mostly oligomers.

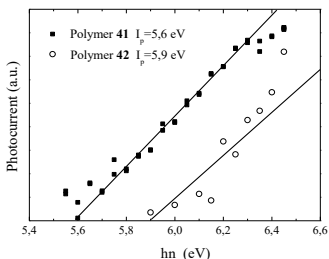
The behaviour under the heating of polymeric materials **41** and **42** were estimated by DSC and TGA. Both these materials demonstrated rather high thermal stability. The temperatures at which 5 % loss of mass was observed were found to be 361 °C for **41** and 354 °C for **42**.



**Fig 14.** DSC curves of 2<sup>nd</sup> heating of polymers **41** and **42**, heating rate 10 °C/min

DSC thermograms of the polymeric samples are shown in Figure 14. The measurements confirmed that the polymers are amorphous materials with high T<sub>g</sub>. When the samples were used for DSC heating scans the glass-transitions were observed at 139 °C for **41** and at 150 °C for **42**, and no peaks due to crystallisation and melting appeared on further cooling and heating cycles between -30 °C and 250 °C.

The I<sub>p</sub> of thin amorphous films of the polymeric materials were determined from the electron photoemission spectra of the layers. The spectra, as well as the values of I<sub>p</sub>, are presented in Figure 15.



**Fig 15.** The photoemission spectra and  $I_p$  values of thin amorphous layers of compounds **41-42**

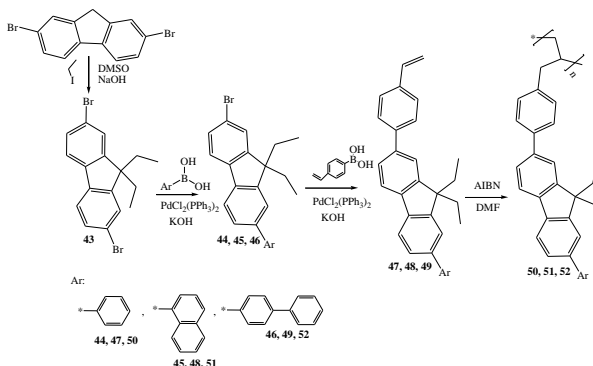
It was established that the layers of polymer **41** have lower  $I_p$  than that of fluorene-based polymer as well as other derivatives containing un-substituted carbazolyl fragments<sup>24</sup>.

The films of the polymers were tested as hole-transporting layers in bilayer OLEDs with Alq<sub>3</sub> as the emitter. A device with poly(9-vinylcarbazole) (**PVC**) as hole transporting material was also investigated for comparison of properties. Structure of the OLED was ITO/**41**, **42** or **PVK**/ Alq<sub>3</sub>/LiF/Al. The device with the polymer **42** exhibited the best overall performance (turn-on voltage: 6.8 V; maximum photometric efficiency: 1.9 cd/A; maximum brightness: about 2150 cd/m<sup>2</sup>). These OLED properties were rather promising in comparison with the **PVK**-based Alq<sub>3</sub> devices.

### 2.5.2. Synthesis and characterization of 2-aryl-7-(4-vinylphenyl)-9,9-diethylfluorene based monomers and polymers

Poly{2-(4-vinylphenyl)-9,9-diethylfluorene} was describe in chapter 2.5.1. It was used as HT layer in OLED device, which reached higher efficiency than that with HT polymer containing 3-phenylcarbazol-6-yl fragments and about 40% higher efficiency than that with PVK HT layer. Therefore, new monomers and polymers containing 2,7-diarylfuorene fragments were synthesized and characterized.





**9 Scheme.** Synthetic scheme of monomers and polymers containing 2,7-diarylf luorene fragments

The synthesis of the electroactive polymers (**50-52**) was carried out according to synthetic route shown in Scheme 9. The starting material 2,7-dibromo-9,9-diethylfluorene (**43**) was prepared from 2,7-dibromofluorene by its alkylation with iodoethane under basic conditions<sup>25</sup>. Compounds **44-45** containing phenyl, 1-naphtyl or 4-biphenyl groups were prepared by palladium catalysed Suzuki coupling reaction of the 2,7-dibromo-9,9-diethylfluorene (**43**) with an equal amounts of phenylboronic acid, 1-naphtylboronic acid or 4-biphenylboronic acid, correspondingly<sup>3</sup>. Monomers **47-49** containing vinyl groups were then prepared by palladium catalysed Suzuki coupling reaction of a corresponding halogen derivatives **44-46** with an excess of 4-vinylphenylboronic acid. The vinyl polymers **50-52** were obtained by radical polymerization of the monomers **47-49** in DMF solutions using 2,2'-azoisobutyronitrile as an initiator. Low-molar-mass fractions of the products of polymerizations were removed by Soxhlet extraction of the raw polymers with methanol.

The newly synthesized derivatives were identified by mass spectrometry and <sup>1</sup>H NMR spectroscopy. The synthesized polymers were soluble in common organic solvents, such as chloroform and THF at room temperature.  $M_n$  and  $M_w$  of the synthesized derivatives **50-52** were estimated by GPC. The values of  $M_n$  and  $M_w$  as well as  $d$  are summarized in Table 7.

**Table 7.** Molecular weights and values of  $d$  of polymers **50-52**.

Polymer	$M_n$	$M_w$	$d$
<b>50</b>	15800	3330	4.7
<b>51</b>	5090	2760	1.8
<b>52</b>	4990	2970	1.7

It was observed that low molecular weight products, i.e. oligomers were obtained after the polymerizations. The molecular weights of the oligomers

slightly depend on the nature of chromophores attached to the vinyl groups of the corresponding monomers. The monomer **47** containing 2,7-diphenylfluoren-7-yl fragment yielded oligomer with little higher molecular weight than those of monomers **48** and **49** containing, correspondingly, naphthyl or biphenyl fragments in their structures.

The behaviour under heating of synthesized monomers **47-49** and polymers **50-52** was studied by DSC and TGA under a nitrogen atmosphere. The results are presented in Table 8. It was evident that these derivatives demonstrated rather high thermal stability having onsets of  $T_d$  in the range from 275 °C to 400 °C. It should be mentioned that monomers **47-49** undergo thermal polymerization during the TGA test and established values of  $T_g$  depend to polymerized materials.

**Table 8.** Thermal characteristics and of the monomers **47-49** and polymers **50-52**

Monomer	$T_m$ , °C	$T_g$ , °C	$T_{pol}$ , °C	$T_d$ , °C
<b>47</b>	125	95	178	275
<b>48</b>	157	92	190	290
<b>49</b>	173	110	200	350
Polymer	$T_g$ , °C	$T_d$ , °C		
<b>50</b>	185	400		
<b>51</b>	151	390		
<b>52</b>	159	400		

The DSC measurements confirmed that all the monomers **47-49** were obtained as crystalline materials with high  $T_m$ . When the samples were heated, the melting was observed at 125 °C for **47**, at 157 °C for **48** and at 173 °C for **49**. During the DSC analyses, the functional derivatives **47-49** were also thermally polymerized. The polymerization of the monomers **47-49** was observed at 178 °C, 190 °C and 200 °C, respectively. The second DSC heating scan demonstrated  $T_g$  of products of the thermal polymerization and the values ranged from 92 °C to 110 °C.

Solution synthesized polymers **50-52** were obtained as fully amorphous materials with rather high glass transition temperatures ranging from 151 °C to 185 °C. It was observed that polymer **50** has a higher value of  $T_g$  than those of materials **51** and **52** due to its higher molecular weight. It is also seen that these polymers demonstrated very high thermal stability having onsets of  $T_d$  in the range from 390 °C to 400 °C.

Polymeric materials **51-52** were tested as hole transporting layers in bilayer electroluminescent organic light emitting diodes with Alq<sub>3</sub> as the emitter and electron transporting layer. The OLED structure was ITO/**50**, **51** or **52**/Alq<sub>3</sub>/LiF/Al. The device with polymer **52** containing electro-active 2-(4-biphenyl)-7-(4-vinylphenyl)-9,9-diethylfluorene units exhibited the best overall performance with maximum brightness of about 5300 cd/m<sup>2</sup> and current efficiency

of 3.1 cd. These OLED properties are rather promising among Alq<sub>3</sub>-based two-layer devices.

### 3. THE MAIN RESULTS AND CONCLUSIONS

1. Phenyl, naphthyl, biphenyl or 4-vinylphenyl fragments containing 3,6-diaryl-9-alkylcarbazoles were prepared by Suzuki coupling reactions. Structures of compounds were confirmed by spectroscopic methods. Thermal, optoelectronic and charge transporting properties of the materials were investigated and it was established that:

1.1 The yield of the low molecular weight compounds depends on boric acid which is used in the reaction. 4-Vinylphenyl boronic acid and synthesized bifunctional vinyl monomer can polymerized during the Suzuki reaction, therefore yield of 3,6-bis(4-vinylphenyl)-9-ethylcarbazole is just 10%.

1.2 The synthesized compounds exhibit considerably high thermal degradation temperatures, which are in the range of 350 °C - 404 °C. The materials form amorphous films, which glass transition temperatures are in the range of 50 °C - 62 °C. 3,6-Bis(4-vinylphenyl)-9-ethylcarbazole can form cross-linked polymer during thermal polymerization.

1.3 Ionization potentials of amorphous layers of the materials depend on their chemical structure and range from 5.5 to 5.8 eV. Holes drift mobility in layer of the bis(4-vinylphenyl)-9-ethylcarbazole reached  $1.0 \times 10^{-4} \text{ cm}^2/(\text{V} \cdot \text{s})$  at  $3.3 \times 10^5 \text{ V/cm}$  electric field.

1.4 Compound containing two 4-vinylphenyl substituents is suitable for formation of insoluble electroactive polymeric network by thermal polymerisation. The films were used as hole transporting/electron blocking layers to prepare phosphorescent organic light-emitting diodes of all the major colours. Efficiencies of the devices were considerably increased as compared with those of devices without the hole transporting/electron blocking layer.

2. Two groups of carbazole based oxetanes and their polymers containing different aryl fragments at carbazole heterocycle were synthesized and characterized. Charge transporting properties of the polymers were investigated in organic light emitting diodes with green Alq<sub>3</sub> emitters, while poly{3,6-diphenyl-9-[6-(3-methyloxetan-3-ylmethoxy)hexyl]carbazole} was also used in solid-state light-emitting electrochemical cells. It was established that:

2.1 Low molecular weight polymers (oligomers) were obtained after the cationic polymerization. Yields of the polymers reached 70%.

2.2 The synthesized polymers exhibit high thermal stability and high glass transition temperatures. The temperatures of thermal destruction of these materials range from 356 °C to 431 °C, while the glass transition temperatures range from 120 °C to 144 °C. Values of the temperatures depend on molecular weights and chemical compositions of the polymers.

2.3 The values of ionization potentials confirmed that layers of the polymers are suitable for hole injection and transport in organic light-emitting diodes. Devices with hole transporting layer of polymer containing 3,6-di(4-phenyl)carbazolyl

fragments reached maximum brightness of 2630 cd/m<sup>2</sup> and maximum current efficiency of 2.3 cd/A.

3. Naphthyl, biphenyl or pyrenyl fragments containing 2-(4-arylphenyl)-9-hexylcarbazoles were synthesized and characterized. It was established that:

3.1 Glass transition temperatures of these compounds range from 58 °C to 136 °C and temperatures of thermal destruction exceed 340 °C.

3.2 Ionization potentials of the amorphous layers of the materials range from 5.49 eV to 5.79 eV.

3.3 2-(4-(1-Naphthyl)phenyl)-9-hexylcarbazole and 2-(4-(pyren-1-yl)phenyl)-9-hexylcarbazole were tested as hole transporting layer materials in red phosphorescent OLED devices. Device with hole transporting layer of 2-(4-(pyrene-1-yl)phenyl)-9-hexylcarbazole reached 26,1 cd/A maximum current efficiency and 19,1 lm/W maximum power efficiency.

4. Twin carbazole based compounds containing fluorophenyl, difluorophenyl, trifluorophenyl or methoxypyridinyl fragments were obtained by a multistep synthetic rout. Thermal and optoelectronic properties of compounds were investigated and they were used in the formation of organic light emitting devices. It was established that:

4.1 The compounds exhibit high thermal stability and form amorphous films with glass transition temperatures exceeding 50 °C.

4.2 Layers of the compounds containing fluorophenyl or difluorophenyl substituents are characterized by better hole injection and transport properties than the layer of compound containing trifluorophenyl substituents. Hole drift mobility in layers of the compounds range from  $4 \times 10^{-6} \times 10^{-3}$  to  $1,1 \times 10^{-3}$  cm<sup>2</sup>/(V·s) at high electric fields and at 25 °C temperature.

4.3 1,6-Bis[3-(2-methoxy-3-pirydinyl)-9-carbazolyl]hexane is a very effective host material for green triplet emitter when phosphorescent OLED devices are formed. The device reached 62,8 lm/W power efficiency, 61 cd/A current efficiency and maximum luminance of 47800 cd/m<sup>2</sup>.

5. Vinyl groups containing monomers and their polymers were synthesized and characterized. Thermal and optoelectronic properties of the materials were investigated and the hole transporting polymers were used in organic light-emitting diode with green Alq<sub>3</sub> emitters. It was established that:

5.1 Low molecular-weight polymers (oligomers) were obtained after radical polymerization. Yields of the obtained polymers were lower than those of polymers received by cationic polymerisation.

5.2 The polymers exhibit high thermal stability and form homogeneous amorphous layers, which are characterized with high glass transition temperatures ranging from 139 °C to 185 °C.

5.3 Ionization potentials of amorphous layers of the polymers containing carbazolyl fragments (5.6 eV) are lower than that of polymers containing fluorenyl fragments (5.8 eV).

5.4 Alq<sub>3</sub> emitters with organic light-emitting diodes with hole transporting layer of poly{2-(4-biphenyl)-7-(4-vinylphenyl)-9,9-diethylfluorene} demonstrated the best characteristics with low turn on voltage of 3.6 V, maximum photometric efficiency of 3.1 cd/A and maximum brightness of 5300 cd/m<sup>2</sup>.

## LIST OF PUBLICATIONS ON THE THEME OF DISSERTATION

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

1. Chang, Chih-Hao; Kručaitė, Gintarė; Lo, Dain; Chen, Yun-Lan; Su, Chu-Chun; Lin, Tzu-Chun; Gražulevičius, Juozas Vidas; Pečiulytė, Laura; Grigalevičius, Saulius. Naphthyl or pyrenyl substituted 2-phenylcarbazoles as hole transporting materials for organic light-emitting diodes // Dyes and pigments. ISSN 0143-7208. 2017, vol. 136, p. 302-311.
2. Kručaitė, Gintarė; Tavgenienė, Daiva; Stulpinaitė, Beatričė; Sipavičiūtė, Diana; Buika, Gintaras; Zaleckas, Ernestas. Fluorenes substituted with fluorophenyl, difluorophenyl or trifluorophenyl fragments as materials for organic light emitting diodes // Molecular crystals and liquid crystals. ISSN 1542-1406. 2016, vol. 640, iss. 1, p. 173-179.
3. Kručaitė, Gintarė; Liu, L.; Tavgenienė, Daiva; Pečiulytė, Laura; Gražulevičius, Juozas Vidas; Xie, Zhi-Yuan; Zhang, Baohua; Grigalevičius, Saulius. Electroactive polymers containing 3-arylcarbazolyl units as hole transporting materials for OLEDs // Optical materials. ISSN 0925-3467. 2015, vol. 42, p. 94-98.
4. Jou, Jwo-Huei; Li, Tsung-Han; Kumar, Sudhir; An, Chih-Chia; Agrawal, Abhishek; Chen, Sun-Zen; Fang, Po-Hsun; Kručaitė, Gintarė; Grigalevičius, Saulius; Gražulevičius, Juozas Vidas; Sung, Chao-Feng. Enabling high-efficiency organic light-emitting diodes with a cross-linkable electron confining hole transporting material // Organic electronics. ISSN 1566-1199. 2015, vol. 24, p. 254-262.
5. Kručaitė, Gintarė; Tavgenienė, Daiva; Volyniuk, Dmytro; Gražulevičius, Juozas Vidas; Liu, L.; Xie, Zhi-Yuan; Zhang, B.; Grigalevičius, Saulius. Twin derivatives of fluorophenyl, difluorophenyl or trifluorophenyl substituted carbazoles as electroactive amorphous materials // Synthetic metals. ISSN 0379-6779. 2015, vol. 203, p. 122-126.
6. Kručaitė, Gintarė; Liu, L.; Volyniuk, Dmytro; Buika, Gintaras; Lygaitis, Ramūnas; Gražulevičius, Juozas Vidas; Xie, Zhi-Yuan; Zhang, B.; Grigalevičius, Saulius. Polyethers containing 3,6-diarylcarbazolyl groups as polymeric materials for hole transporting layers of OLEDs // Designed monomers and polymers. ISSN 1385-772X. 2015, vol. 18, iss. 6, p. 592-598.
7. Huang, Po-Chin; Kručaitė, Gintarė; Su, Hai-Ching; Grigalevičius, Saulius. Incorporating a hole-transport material into the emissive layer of solid-state light-emitting electrochemical cells to improve device performance // Physical chemistry chemical physics. ISSN 1463-9076. 2015, vol. 17, iss. 26, p. 17253-17259.
8. Jou, Jwo-Huei; Sahoo, Snehasis; Kumar, Sudhir; Yu, Hui-Huan; Fang, Po-Hsun; Singh, Meenu; Kručaitė, Gintarė; Volyniuk, Dmytro; Gražulevičius, Juozas

Vidas; Grigalevičius, Saulius. A wet- and dry-process feasible carbazole type host for highly efficient phosphorescent OLEDs // Journal of materials chemistry C. ISSN 2050-7526. 2015, vol. 3, iss. 47, p. 12297-12307.

9. Kručaitė, Gintarė; Tavgenienė, Daiva; Sipavičiūtė, Diana; Buika, Gintaras; Gražulevičius, Juozas Vidas; Liu, L.; Zhang, Baohua; Xie, Zhi-Yuan; Grigalevičius, Saulius. Electro-active oligomers containing pendent 3-phenylcarbazol-6-yl or 2-phenylfluoren-7-yl fragments as materials for OLEDs // Optical materials. ISSN 0925-3467. 2014, vol. 37, p. 788-792.

10. Kručaitė, Gintarė; Tavgenienė, Daiva; Gražulevičius, Juozas Vidas; Wang, Y. C.; Hsieh, C. Y.; Jou, Jwo-Huei; Garšva, Gintautas; Grigalevičius, Saulius. 3,6-Diaryl substituted 9-alkylcarbazoles as hole transporting materials for various organic light emitting devices // Dyes and pigments. ISSN 0143-7208. 2014, Vol. 106, p. 1-6.

### **Publications in International and Lithuanian conference proceedings**

1. Chang, C.H.; Kručaitė, Gintarė; Lo, D.; Chen, Y.L.; Su, C.C.; Lin, T.C.; Pečiulytė, Laura; Volyniuk, Dmytro; Grigalevičius, Saulius. Naphtyl or pyrenyl substituted 2-phenylcarbazoles as hole transporting materials for organic light-emitting diodes // Baltic polymer symposium 2016 : Klaipeda, September 21-24, 2016 : programme and abstracts / Kaunas University of Technology, Vilnius University, Klaipeda University. Kaunas: Kaunas University of Technology, 2016, ISBN 9786090212356. p. 51.

2. Kručaitė, Gintarė; Pečiulytė, Laura; Volyniuk, Dmytro; Grigalevičius, Saulius; Liu, L.; Xie, Zhi-Yuan; Zhang, B. 2,7-Diarylfluorene-based derivatives as hole transporting materials for OLEDs // Molecular crystals and liquid crystals : the jubilee 10th international conference on electronic processes in organic and inorganic materials, ICEPOM-10, May 23- 27, 2016, Ternopol, Ukraine. Oxon: Taylor & Francis. ISSN 1542-1406. 2016, p. 106.

3. Jou, Jwo-Huei; Sahoo, Snehasis; Kumar, Sudhir; Yu, Hui-Huan; Fang, Po-Hsun; Singh, Meenu; Kručaitė, Gintarė; Volyniuk, Dmytro; Gražulevičius, Juozas Vidas; Grigalevičius, Saulius. Wet- and dry-process feasible carbazole type hosts for highly efficient phosphorescent OLEDs // 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. 158.

4. Kručaitė, Gintarė; Liu, L.; Tavgenienė, Daiva; Pečiulytė, Laura; Gražulevičius, Juozas Vidas; Xie, Zhi-Yuan; Zhang, Baohua; Grigalevičius, Saulius. New electroactive polymers containing pendent aryl substituted carbazole unites as hole transporting materials for OLEDs // European polymer congress : June 21-26, 2015, Dresden, Germany : book of



abstracts. Dresden: Leibniz-Institut für Polymerforschung Dresden, 2015, ISBN 9783936028898. p. 316.

5. Kručaitė, Gintarė; Liu, L.; Tavgenienė, Daiva; Pečiulytė, Laura; Gražulevičius, Juozas Vidas; Xie, Zhi-Yuan; Zhang, Baohua; Grigalevičius, Saulius. New electroactive polymers containing pendent aryl substituted carbazole unites as hole transporting materials for organic light-emitting diodes // Advanced materials and technologies : book of abstracts of the 17-th international conference-school, 27-31 August 2015, Palanga, Lithuania. Kaunas: Kauno technologijos universitetas. ISSN 1822-7759. 2015, p. 106.

6. Kručaitė, Gintarė; Liu, L.; Volyniuk, Dmytro; Buika, Gintaras; Lygaitis, Ramūnas; Gražulevičius, Juozas Vidas; Xie, Zhi-Yuan; Zhang, B.; Grigalevičius, Saulius. Polyethers containing 3,6-diarylcabazolyl groups as polymeric materials for hole transporting layers of OLEDs // Baltic polymer symposium 2015 : Sigulda, Latvia, September 16-18 : programe and proceedings / Riga Technical University Institute of Polymer Materials. Riga: Riga Technical University Institute of Polymer Materials, ISBN 9789934542121. p. 93.

7. Kručaitė, Gintarė; Tavgenienė, Daiva; Buika, Gintaras; Pečiulytė, Laura; Stulpinaitė, Beatričė; Grigalevičius, Saulius; Suna, Edgars. Hole transporting polymers containing pendant 3-arylcabazolyl or 2-arylfluorenyl groups // Baltic polymer symposium 2014 : Laulasmaa, Estonia, September 24-26, 2014 : program and abstracts / Tallinn University of Technology. Tallinn: Tallinn University of Technology, 2014. p. 85.

8. Kručaitė, Gintarė; Tavgenienė, Daiva; Buika, Gintaras; Pečiulytė, Laura; Stulpinaitė, Beatričė; Grigalevičius, Saulius. Hole transporting polymers containing pendant 3-arylcabazolyl or 2-arylfluorenyl groups as materials for OLEDs // 8th International conference on advanced optical materials and devices, 25-27 August, 2014, Riga, Latvia : book of abstracts. Riga: Institute of Atomic Physics and Spectroscopy, 2014, ISBN 9789934517587. p. 45.

### **Patent registered in International Patent Office**

1. Jou, Jwo-Huei; Li, Tsung-Han; Grigalevičius, Saulius; Kručaitė, Gintarė. US 9266833 B2. Carrier transport material / Inventors: Jwo-Huei Jou, Tsung-Han Li, Saulius Grigalevičius, Gintarė Kručaitė ; Applicant: National Tsing-Hua University, Hsinchu (TW). 2016-02-23. 22 p. [USPTO Patent Full-text and Image Database].

## INFORMATION ABOUT THE AUTHOR OF THE DISSERTATION

Name, Surname: Gintarė Kručaitė  
Birth date and place: 17<sup>th</sup> May 1988, Kupiškis, Lithuania.  
For contacts: [gkgintare5@gmail.com](mailto:gkgintare5@gmail.com)

### *Education:*

1995 – 2007 Kupiškio Lauryno Stuokos-Gucevičiaus gymnasium.  
2007 – 2011 Bachelor degree studies of Applied Chemistry, Faculty of Chemical Technologies, Kaunas University of Technology.  
2011 – 2013 Master degree 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.

## ACKNOWLEDGEMENTS

Prof. Habil. Dr. Juozas Vidas Gražulevičius is greatly acknowledged for the opportunity to carry out the work at the Department of Polymer Chemistry and Technology, Kaunas University of Technology.

Prof. Habil. Dr. Saulius Grigalevičius is greatly acknowledged for the supervision of my Doctoral research and helpful advices.

M. Krenevičienė (Department of Organic Chemistry, Vilnius University), Dr. G. Ragaitė and A. Bieliauskas (Department of Organic Chemistry, Kaunas University of Technology), dr. G. Buika, dr. L. Pečiulytė, de. R. Lygaitis, A. Bučinskas (Department of Polymer Chemistry and Technology, Kaunas University of Technology) are thanked for measurements of  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, gel permeation chromatography, mass spectrometry, UV, FL, DSC ant TGA measurements.

Habil. dr. V. Gaidelis, V. Jankauskas (Department of the Solid State Electronic, Vilnius University) and dr. D. Volyniuk (Department of Polymer Chemistry and Technology, Kaunas University of Technology) are thanked for the measurements of charge carrier mobilities and ionization potentials in the layers of synthesized compounds.

The group of prof. Z. Xie (Changchun Institute of Applied Chemistry, Chinese Academy of Science, China) and prof. J.H. Jou (Department of Materials Science and Engineering, National Tsing Hua University, Taiwan) are thanked for characterization of the materials in OLEDs.

All my colleagues in the Department of Polymer Chemistry and Technology are kindly thanked for sharing their particular knowledge and experience.

## REZIUMĖ

Polimerai ir mažamolekuliniai junginiai, turintys elektroaktyvius fragmentus ir galintys suformuoti plonas amorfinės plėvelės ant pagrindo, yra pritaikomi gaminant funkcinis sluoksnius organiniams šviesos diodams (OLED), fotovoltiniams elementams, lauko tranzistoriams arba jutikliams. Amorfiniai polimerų sluoksniai formuojami liejimo iš tirpalų būdu. Šiuo atveju galima suformuoti pigius ir didelio ploto prietaisus. Sluoksniai iš mažamolekulinių medžiagų dažniausiai formuojami terminio garinimo būdu. Šis metodas yra gerokai brangesnis, tačiau gaunami efektyvesni ir ilgesniau tarnaujantys prietaisai.

Karbazolilgrupės turintys polimerai ir mažamolekuliniai junginiai yra vienos iš dažniausiai tyrinėjamų medžiagų, kurios pritaikomos optoelektronikoje ir elektronikoje. Šie junginiai pasižymi geromis plėvėdaros savybėmis, dideliu skylių judrių sluoksniuose ir geromis fotolaidumo savybėmis. Kai kurios karbazolo fragmentus turinčios medžiagos jau yra panaudotos komercializuotuose prietaisuose. Fluorenas taip pat plačiai naudojamas junginys iš kurio projektuojami ir sintetinami organiniai puslaidininkai. Jis yra aromatinis ir

elektroaktyviam sluoksniui gali suteikti aukštą terminį, morfologinį ir cheminį stabilumą. Be to, prie fluoreno 2,7 ir 9 padėčių galima prijungti įvairias aromatinės ar funkcines grupes ir pagaminti junginius, kurie pasižymėtų skirtingomis optoelektroninėmis savybėmis.

Elektroaktyvios krūvininkus pernešančios medžiagos yra skirstomos į skyles pernešančias, elektronus pernešančias ir bipolines (pernešančias ir skyles, ir elektronus). Skyles pernešantis sluoksnis OLED prietaisuose palengvina skylių injekciją iš anodo į organinį sluoksnį, taip pat perneša injektuotas skyles į emiterio sluoksnį. Skyles pernešantis sluoksnis taip pat blokuoja elektronus, kad jie iš emiterio sluoksnio nepatektų prie anodo. Tinkamas elektronų kiekis emiteryje gali turėti įtakos eksitonų formavimuisi, prietaiso skaisčiui ir efektyvumui. Ideali skyles pernešanti medžiaga turi pasižymėti puikiu tirpumu, aukštu terminiu stabilumu, geromis plėvėdaros savybėmis ir efektyvia skylių pernaša jos sluoksnyje. Be to, didelę tripletinės būsenos energiją turinčios ir skyles transportuojančios medžiagos taip pat naudojamos matricomis fosforescuojančiuose organiniuose šviestukuose (PhOLED). Norint pagerinti OLED prietaisų savybes, reikia projektuoti, sintetinti ir išbandyti prietaisuose naujas elektroaktyvias medžiagas, kurios turėtų visą kompleksą reikalingų savybių.

Šio **darbo tikslas** yra naujų, substituuotus karbazolil- arba fluorenilgrupės turinčių, mažos molekulinės masės elektroaktyvių medžiagų ir polimerų, kurie tiktų organinių, šviesą skleidžiančių prietaisų sluoksniams sintezė, charakterizavimas ir panaudojimas prietaisuose.

Siekiant įgyvendinti darbo tikslą buvo iškelti tokie **uždaviniai**:

1. Mažamolekulinių 3,6-diaril-9-alkilkarbazolo, 2-aril-9-alkilkarbazolo ir įvairius pakaitus turinčių dvynųjų karbazolo darinių sintezė, jų terminių ir optoelektroninių savybių nustatymas bei panaudojimas formuojant organinius šviesos diodus;
2. Monomerų ir jų polimerų, turinčių elektroniškai izoliuotus 3,6-diarilkarbazolil-, 3-arilkarbazolil-, 2-arilfluorenil- arba 2,7-diarilfluorenilfragmentus sintezė, jų terminių ir optoelektroninių savybių nustatymas bei panaudojimas formuojant organinius šviesos diodus.

Disertacijos pagrindiniai **ginamieji teiginiai**:

1. Mažamolekuliniai 3,6-diaril-9-alkilkarbazolo ir 2-aril-9-alkilkarbazolo dariniai pasižymi geromis terminėmis ir optoelektroninėmis savybėmis ir yra tinkamos medžiagos organinių šviestukų skyles pernešantiems sluoksniams formuoti.
2. Katijoninės arba radikalinės polimerizacijos būdu gauti polimerai, turintys arilsubstituotus karbazolo arba fluoreno fragmentus, pasižymi geromis terminėmis

ir optoelektroninėmis savybėmis ir yra tinkamos medžiagos organinių šviestukų skyles pernešantiems sluoksniams formuoti.

3. Dvynieji junginiai, kurių sandaroje yra elektrononoriniais arba elektronakceptoriniais fragmentais substitutuoti karbazolo heterociklai, yra tinkamos medžiagos organinių šviestukų skyles pernešantiems sluoksniams arba emiterio sluoksniams formuoti.

#### **Mokslinio darbo naujumas:**

1. Susintetinti ir ištirti nauji mažamolekuliniai (di)arilkarbazolo ir dvynieji arilsubstituoto karbazolo dariniai. Keletas šių junginių yra efektyvios, skyles pernešančios medžiagos, tinkamos organinių šviestukų formavimui. Dvynieji junginiai, kurių sandaroje yra elektronakceptoriniais fragmentais substitutuoti karbazolo heterociklai, yra tinkamos matricos emiterio sluoksniams formuoti.

2. Susintetinti ir ištirti nauji (di)arilsubstituotus karbazolo ir fluoreno fragmentus turintys monomerai ir jų polimerai. Keletas šių polimerų yra efektyvios, skyles transportuojančios medžiagos, tinkamos elektroluinescuojančių organinių šviestukų formavimui.

#### **Disertacijos aprobavimas**

Pagrindiniai darbo rezultatai yra paskelbti 10 mokslinių straipsnių leidiniuose įtrauktuose į *Clarivate Analytics Web of Science* duomenų bazės sąrašą. Rezultatai taip pat buvo pristatyti 8 tarptautinėse konferencijose. Tarptautinėje patentų tarnyboje įregistruotas JAV patentas.

#### **Disertacijos apimtis ir struktūra**

Bendra darbo apimtis – 123 psl. Darbą sudaro įvadas, literatūros apžvalga, metodikos ir tyrimo rezultatų skyriai, išvados, literatūros ir publikacijų darbo tema sąrašai. Darbe yra pateiktos 9 schemas, 56 paveikslai, 14 lentelių ir 149 šaltinių literatūros sąrašas.

#### **Autoriaus indėlis:**

Autorė susintetino, išgrynino ir apibūdino visus aprašomus junginius. Kartu su tos srities specialistais atliko gautų medžiagų, aprašytų 4 skyriuje terminius ir elektrocheminius tyrimus. Habil. dr. V. Gaidelis ir dr. D. Volyniukas išmatavo medžiagų jonizacijos potencialus. Dr. V. Jankauskas ir dr. D. Volyniukas atliko medžiagų krūvininkų pernašos matavimus. Prof. Z. Xie bei prof. J. H. Jou vadovaujamos mokslininkų grupės panaudojo naujai susintetintus junginius organiniuose šviestukuose ir išmatavo jų charakteristikas. Autorė išanalizavo ir aprašė visų šių tyrimų duomenis.

## LITERATŪRA

1. KRUCAITE, G., et al. Twin derivatives containing two 9-alkylcarbazol-3-yl fragments as new electro-active materials for organic light-emitting diodes. *Optical Materials*. 2014, 36, 444–448. ISSN 0925-3467.
2. TUCKER, S. H. Iodination in the Carbazole Series. *Journal of Chemical Society*, 1926, 1, 546-553.
3. SUZUKI, A. *Recent Advances in the Cross-Coupling Reactions of Organoboron Derivatives with Organic Electrophiles*, 1995-1998. *Journal of Organometallic Chemistry*. 1999, 576, 147-168. ISSN 0022-328X.
4. Grigalevicius, S., et al. Synthesis and properties of poly(3,9-carbazole) and low-molar-mass glass-forming carbazoles cpmoids. *Polymer*. 2002, 43, 2063-2608. ISSN 0032-3861.
5. STROHRIEGL, P., et al. Carbazole-containing polymers: synthesis, properties and applications. *Progress in Polymer Science*. 2003, 28, 1297-1353. ISSN 0079-6700.
6. CHENG, Y. J., et al. Thermally cross-linkable hole-transporting materials on conducting polymer: synthesis, characterization, and applications for polymer light-emitting devices. *Chemistry of Materials*. 2008, 20, 413-422. ISSN 0897-4756.
7. LIN, C. Y., et al. Hole mobilities of thermally polymerized triaryldiamine derivatives and their application as hole-transport materials in organic light-emitting diodes (OLEDs). *Organic Electronics*. 2009, 10, 181-188. ISSN 1566-1199.
8. AIZAWA, N., et al. Thermally cross-linkable host materials for enabling solution-processed multilayer stacks in organic light-emitting devices. *Organic Electronics*. 2013, 14, 1614-1620. ISSN 1566-1199.
9. JIANG, W., et al. A high triplet energy small molecule based thermally cross-linkable hole-transporting material for solution-processed multilayer blue electrophosphorescent devices. *Journal of Materials Chemistry C*. 2015, 3, 243-246. ISSN 2050-7534.
10. TSAI, C. E., et al. Triarylamine-based crosslinked hole-transporting material with an ionic dopant for high-performance PEDOT:PSS-free polymer solar cells. *Journal of Materials Chemistry C*. 2015, 3, 6158-6165.
11. KRUCAITE, G., et al. 3-Aryl substituted 9-alkylcarbazoles as tailored building blocks for hole transporting materials of OLEDs. *Synthetic Metals*. 2012, 162, 1079-10863. ISSN 0379-6779.
12. GRINIENE, R., et al. Twin derivatives of 3-arylcarbazoles as efficient hole transporting amorphous materials. *Optical Materials*. 2013, 35, 553-557. ISSN 0925-3467.
13. LENGVINAITĖ, S., et al. Functional derivatives of (bi)phenyl-substituted carbazoles as building blocks for electro-active polymers. *Reactive & Functional Polymers*. 2010, 70, 477-481. ISSN 1381-5148.
14. KRUCAITE, G., et al. 3,6-Diaryl substituted 9-alkylcarbazoles as hole transporting materials for various organic light emitting devices. *Dye and Pigments*. 2014, 106, 1-6. ISSN 0143-7208.

15. RODRIGUEZ-PARADA, J. M., & PERSEC K. Interchain Electron Donor-Acceptor Complexes: a Model to Study Polymer-Polymer Miscibility. *Macromolecules*. 1986, 19, 55–64. ISSN 0024-9297.
16. PEI, Q., et al. Polymer light-emitting electrochemical cells. *Science*, 1995, 269, 1086-1088. ISSN 1095-9203.
17. PEI, Q., et al. Polymer Light-Emitting Electrochemical Cells: In Situ Formation of a Light-Emitting p–n Junction. *Journal of American Chemical Society*. 1996, 118, 3922-3929. ISSN 0002-7863.
18. CHANG, C. H., et al. Efficient red phosphorescent OLEDs employing carbazole-based materials as the emitting host. *Dyes and Pigments*. 2015, 122, 257-263. ISSN 0143-7208.
19. HELLER, J., LYMAN, J. D. & W. A. HEWETT. The synthesis and polymerization studies of some higher homologues of 9-vinylcarbazole. *Macromolecular Chemistry and Physics*. 1964, 73, 48-59. ISSN 1521-3935.
20. GRINIENE, R., et al. Twin derivatives of 3-arylcarbazoles as efficient hole transporting amorphous materials. *Optical Materials*. 2013, 35, 553-557. ISSN 0925-3467.
21. GRIGALEVICIUS, S., et al. New Carbazole-Based Copolymers as Amorphous Hole-Transporting Materials for Multilayer Light-Emitting Diodes. *Macromolecular Chemistry and Physics*. 2007, 208, 349-355. ISSN 1521-3935.
22. JOU, J. H., et al. High-efficiency wet- and dry-processed green organic light emitting diodes with a novel iridium complex-based emitter. *Advanced Optical Materials*. 2013, 1, 657-667. ISSN 2195-1071.
23. ZHUANG, S., et al. Efficient nondoped blue organic light-emitting diodes based on phenanthroimidazole-substituted anthracene derivatives. *Organic Electronics*. 2012, 13, 3050–3059. ISSN 1566-1199.
24. ZHANG, Y. D., et al. Synthesis and characterization of polymers containing in the chain backbone carbazoles substituted with two acceptor groups as nonlinear optical chromophores. *Macromolecules*. 1966, 14, 1569-1573. ISSN 0024-9297.
25. GRIGALEVICIUS, S., et al. *Synthesis and characterization of new carbazole/fluorene-based derivatives for blue-light-emitting devices*. *Journal of Polymer Science, Part A: Polymer Chemistry*. 2006, 44, 5987-5994. ISSN 1099-0518.

UDK 547.759.057 + 547.678.3.057 + 624.315.592](043.3)

SL344. 2017-08-24, 3 leidyb. apsk. I. Tiražas 50 egz.

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