Dyes and Pigments 106 (2014) 1–6

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

3,6-Diaryl substituted 9-alkylcarbazoles as hole transporting materials for various organic light emitting devices

G. Krucaite [a], D. Tavgeniene [a], J.V. Grazulevicius [a], Y.C. Wang [b], C.Y. Hsieh [b], J.H. Jou [b,*], G. Garsva [c], S. Grigalevicius [a,*]

[a] Department of Organic Technology, Kaunas University of Technology, Radvilenu plentas 19, LT50254 Kaunas, Lithuania
[b] Department of Materials Science and Engineering, National Tsing-Hua University, No. 101, Kaungfu Rd., Hsin-Chu 30013, Taiwan, ROC
[c] Vilnius University, Kaunas Faculty, Department of Informatics, Muitines St 8, LT44280 Kaunas, Lithuania

ARTICLE INFO

Article history:
Received 7 January 2014
Received in revised form
7 February 2014
Accepted 8 February 2014
Available online 25 February 2014

Keywords:
Substituted carbazole
Electro-active material
Amorphous material
Ionization potential
Light emitting diode
Current efficiency

ABSTRACT

Phenyl, naphthyl or biphenyl disubstituted 9-alkylcarbazoles were synthesized by a multi-step synthetic rout. The materials were examined by various techniques including thermogravimetry, differential scanning calorimetry, and electron photoemission spectroscopy. These derivatives were tested as hole transporting materials in OLEDs with Alq_3 as the emitter. Some of the devices exhibited promising overall performance with a turn-on voltage of 2.5 V, a maximal current efficiency of 3.25 cd/A and maximum brightness of 8300 cd/m^2. The compounds were also applied as hole transporting layers in phosphorescent OLEDs with green phosphorescent emitter of tris(2-phenylpyridine)iridium(III) dispersed in *N,N*′-dicarbazolyl-4,4′-biphenyl host. An efficient device using 3,6-diphenyl-9-ethylcarbazole as hole transporting layer demonstrated a turn-on voltage of ca. 5 V, a maximum brightness of 9800 cd/m^2, and maximum current efficiency of 22.5 cd/A.

1. Introduction

Organic light- emitting diodes (OLEDs) based on organic derivatives have attracted much attention because of their potential use in flat panel displays and lighting [1–4], however efficient devices can be obtained only by building multilayer structures [5,6]. One approach that has been widely used to improve efficiency of the OLEDs is the appliance of effective hole transporting layers in the multilayer devices.

Carbazole-based polymers and low-molecular-weight derivatives are among the most studied materials for electronic applications due to high hole mobility in their layers and good photoconductive properties [7]. Derivatives containing electronically isolated carbazole rings also have high triplet energies and are widely used as host materials for electro-phosphorescent OLEDs [8]. We have previously synthesised a series of hole-transporting carbazole-, [3,3′]bicarbazole- and indolo[3,2-*b*]carbazole-based derivatives [9–11]. It was observed that aryl substituted derivatives demonstrate better charge transporting properties than the compounds containing unsubstituted heteroaromatic rings [12]. In this work, we have designed and synthesized phenyl, naphthyl or biphenyl di-substituted 9-alkylcarbazoles, which were expected to show enhanced hole injection and transport properties and could be suitable as hole transporting (HT) materials for multilayer OLEDs.

2. Experimental

2.1. Instrumentation

^{1}H NMR spectra were recorded using a Varian Unity Inova (300 MHz) apparatus. Mass spectra were obtained on a Waters ZQ 2000 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out using a Bruker Reflex II thermosystem. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10 °C/min.

The ionization potentials of the layers of the compounds synthesized were measured by the electron photoemission method in air, which was described earlier [13]. The measurement method was, in principle, similar to that described by Miyamoto et al. [14]. The samples for the ionization potential measurements were prepared as follows [15]. The materials were dissolved in THF and were

---

* Corresponding authors.
E-mail addresses: jjou@mx.nthu.edu.tw (J.H. Jou), saulius.grigalevicius@ktu.lt (S. Grigalevicius).

http://dx.doi.org/10.1016/j.dyepig.2014.02.008
0143-7208/© 2014 Elsevier Ltd. All rights reserved.

coated on Al plates pre-coated with ~0.5 μm thick methylmethacrylate and methacrylic acid copolymer (MKM) adhesive layer. The function of this layer is not only to improve adhesion, but also to eliminate the electron photoemission from Al layer. In addition, the MKM layer is conductive enough to avoid charge accumulation on it during the measurements. The thickness of the layers was 0.5–1 μm.

The electroluminescent devices were fabricated on glass substrates and had a typical structure with the organic layers sandwiched between a bottom ITO anode and a top metal cathode. Before use in device fabrication, the ITO-coated glass substrates were carefully cleaned and treated with UV/ozone immediately before deposition of the organic layers. The hole transporting layers were made by spin-coating ca 40 nm layer of the corresponding material onto the substrates from chloroform solutions. Evaporation of the electroluminescent tris(quinolin-8-olato)aluminium (Alq_3) layer (40 nm) and a LiF/Al electrode (1/150 nm) was performed at a pressure of 1×10^{-5} torr in vacuum evaporation equipment. The size of the emitting areas was 0.25 cm^2.

The electro-phosphorescent devices were also fabricated on glass substrates having ITO anode. The device structure used was ITO/**PEDOT**:PSS/HTM/CBP:$Ir(ppy)_3$/TPBi/LiF/Al, where the conducting polymer poly(3,4-ethylenedioxythiophene): poly(-styrenesulfonate) (**PEDOT**:PSS) was used as the hole-injection layer [16], synthesized derivatives **6** and **8** were tested as hole transporting materials (HTM) and *N*,*N*′-dicarbazolyl-4,4′-biphenyl (CBP) host doped with the green phosphorescent tris(2-phenylpyridine) iridium(III) ($Ir(ppy)_3$) was used as an emitting layer. LiF/Al was applied as the electron-injection layer and cathode, correspondingly.

The luminance of the fabricated OLEDs was measured using a Minolta CS-100 luminance-meter. A Keithley 2400 electrometer was used to measure the current–voltage characteristics of the devices. All the measurements were performed at ambient conditions in air.

2.2. Materials

9-Ethylcarbazole (1), *9H*-carbazole (3), 2-ethylhexylbromide, 1-naphthalene boronic acid, phenyl boronic acid, 4-biphenyl boronic acid, bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$), Alq_3, and potassium hydroxide were purchased from Aldrich and used as received.

3,6-Diiodo-9-ethylcarbazole (2), 3,6-diiodo-*9H*-carbazole (4) and 3,6-diiodo-9-(2-ethylhexyl)carbazole (5) were synthesized according to the procedures outlined in literature [17–19].

2.2.1. 3,6-Diphenyl-9-ethylcarbazole (6)

3,6-Diiodo-9-ethylcarbazole (2) (1.5 g, 3.4 mmol), phenyl boronic acid (1.2 g, 9.8 mmol), $PdCl_2(PPh_3)_2$ (0.09, g 0.1 mmol) and powdered potassium hydroxide (0.94 g, 16.7 mmol) were stirred in THF (15 mL) containing degassed water (1.5 mL) at 80 °C under nitrogen for 24 h. After TLC control the reaction mixture was cooled and quenched by the addition of ice water. The product was extracted by ethyl acetate. The combined extract was dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:15) as an eluent. Yield: 0.6 g of white crystals. M.p.: 124 °C (DSC). MS ($APCI^+$, 20 V): 348.5 ([M + H], 100%). ^1H NMR spectrum ($CDCl_3$, δ, ppm): 8.37 (s, 2H, Ar), 7.77–7.71 (m, 6H, Ar), 7.51–7.06 (m, 8H, Ar), 4.42 (q, 2H, NCH_2, $J = 7.5$ Hz), 1.49 (t, 3H, CH_3, $J = 7.5$ Hz).

Elemental analysis for $C_{26}H_{21}N$ % Calc.: C 89.88, H 6.09, N 4.03; % Found: C 89.85, H 6.11, N 4.06.

2.2.2. 3,6-Di(1-naphthyl)-9-(2-ethylhexyl)carbazole (7)

3,6-Diiodo-9-(2-ethylhexyl)carbazole (5) (1 g, 1.8 mmol), 1-naphthalene boronic acid (0.8 g, 4.6 mmol), $PdCl_2(PPh_3)_2$ (0.05 g, 0.07 mmol) and powdered potassium hydroxide (0.53 g, 9.4 mmol) were stirred in THF (15 mL) containing degassed water (1.5 mL) at 80 °C under nitrogen for 24 h. After TLC control the reaction mixture was cooled and quenched by the addition of ice water. The product was extracted by ethyl acetate. The combined extract was dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:5) as an eluent. Yield: 0.6 g of yellowish crystals. M.p.: 206 °C (DSC). MS ($APCI^+$, 20 V): 532.5 ([M + H], 100%). ^1H NMR spectrum ($CDCl_3$, δ, ppm): 8.22 (s, 2H, Ar), 8.01–7.84 (m, 6H, Ar), 7.67–7.34 (m, 12H, Ar), 4.31 (d, 2H, NCH_2, $J = 7.2$ Hz), 2.21–2.11 (m, 1H, $\underline{CH}(CH_2)_3$), 1.51–1.28 (m, 8H, $4 \times CH_2$), 1.04–0.88 (m, 6H, $2 \times CH_3$).

Elemental analysis for $C_{40}H_{37}N$ % Calc.: C 90.35, H 7.01, N 2.63; % Found: C 90.38, H 7.04, N 2.61.

2.2.3. 3,6-Di(4-biphenyl)-9-(2-ethylhexyl)carbazole (8)

3,6-Diiodo-9-(2-ethylhexyl)carbazole (5) (1 g, 1.8 mmol), 4-biphenyl boronic acid (0.93 g, 4.6 mmol), $PdCl_2(PPh_3)_2$ (0.05 g, 0.07 mmol) and powdered potassium hydroxide (0.53 g, 9.4 mmol) were stirred in THF (15 mL) containing degassed water (1.5 mL) at 80 °C under nitrogen for 24 h. After TLC control the reaction mixture was cooled and quenched by the addition of ice water. The product was extracted by ethyl acetate. The combined extract was dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:5) as an eluent. Yield: 0.55 g of yellowish crystals. M.p.: 165 °C (DSC). MS ($APCI^+$, 20 V): 584.5 ([M + H], 100%). ^1H NMR spectrum ($CDCl_3$, δ, ppm): 8.43 (s, 2H, Ar), 7.84–7.38 (m, 22H, Ar), 4.24 (d, 2H, NCH_2, $J = 7.2$ Hz), 2.19–2.09 (m, 1H, $\underline{CH}(CH_2)_3$), 1.51–1.24 (m, 8H, $4 \times CH_2$), 1.04–0.86 (m, 6H, $2 \times CH_3$).

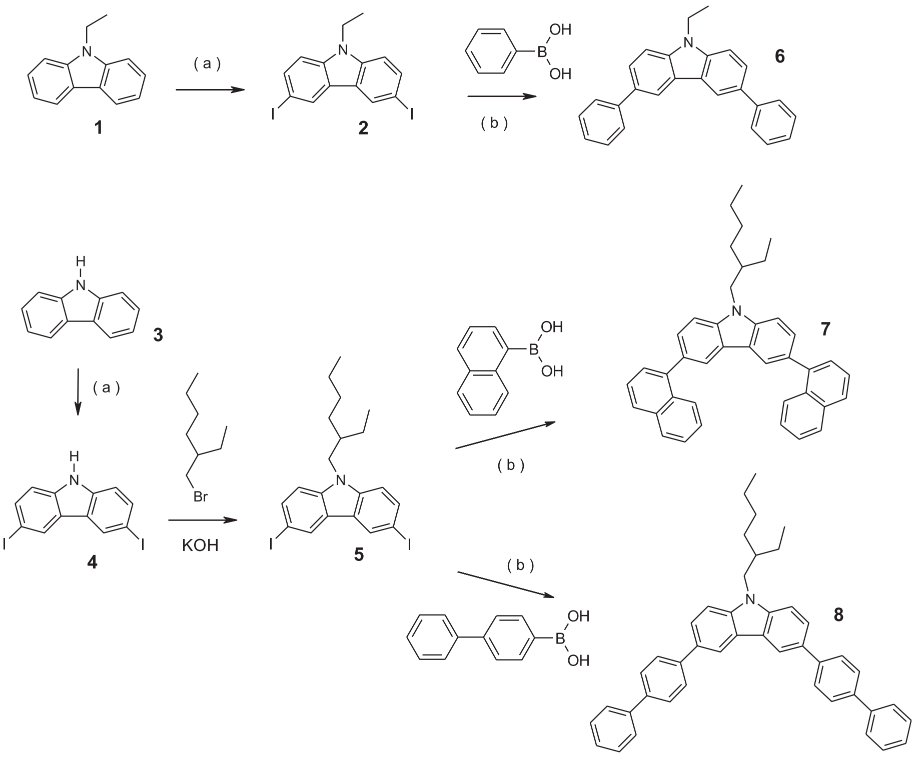
Elemental analysis for $C_{44}H_{41}N$ % Calc.: C 90.52, H 7.08, N 2.40; % Found: C 90.55, H 7.04, N 2.43.

3. Results and discussion

The synthesis of aryl-disubstituted 9-alkylcarbazoles (6–8) was carried out by a multi-step synthetic route as shown in Scheme 1. 3,6-Diiodo-9-ethylcarbazole (2) as a key material was synthesized from commercially available 9-ethylcarbazole by Tucker iodination with KI/KIO_3 in acetic acid [17]. 3,6-Diiodo-9-(2-ethylhexyl)carbazole (5) was prepared by two step procedure involving Tucker iodination of *9H*-carbazole (3) and alkylation of the obtained 3,6-diiodo-9H-carbazole (4) by using 2-ethylhexylbromide. 3,6-Diphenyl-9-ethylcarbazole (6) was prepared by Suzuki reaction [20] of diiodo-derivative 2 with an excess of phenyl boronic acid. Naphthyl- and 4-biphenyl- substituted derivatives 7 and 8 were obtained by the Suzuki reaction of the 3,6-diiodo-9-(2-ethylhexyl) carbazole (5) with an excess of 1-naphthalene boronic acid or 4-biphenyl boronic acid, correspondingly.

The synthesized derivatives were all identified by mass spectrometry, elemental analyses and ^1H NMR spectroscopy. The data were found to be in good agreement with the proposed structures. 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 heating of the materials **6**–**8** was studied by DSC and TGA under a nitrogen atmosphere. The compounds demonstrated high thermal stability. The onsets of mass loss were at 372 °C for **6**, 355 °C for **7** and at 404 °C for **8**, as confirmed by TGA with a heating rate of 10 °C/min.



Scheme 1.

All the compounds **6**–**8** were obtained as crystalline materials as confirmed by DSC. The thermograms of material **7** are shown in Fig. 1. When the crystalline sample was heated during the DSC test, the endothermic peak due to melting was observed at 206 °C. When the melt sample was cooled down and heated again, the glass-transition was observed at 57 °C and on further heating no peaks due to crystallization and melting appeared.

Materials **6** and **8** demonstrated slightly different behaviour in the DSC measurements. The DSC thermograms of material **8** are depicted in Fig. 2. The crystalline sample of **8** 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 **6** demonstrated similar behaviour as material **8**. It melted on first heating at 187 °C, demonstrated glass transition upon second heating at 50 °C and then crystallized at 98 °C. The investigations confirmed that the crystalline derivatives **6**–**8** could be converted into amorphous materials and used for preparation of thin amorphous layers on substrates. X-ray scattering analyses also confirmed that thin layers of the derivatives **6**–**8** are stable in the amorphous state.

The ionization potentials (Ip) of layers of the materials synthesized were measured by the electron photoemission method. The photoemission spectra of thin amorphous layers of compounds **6**–

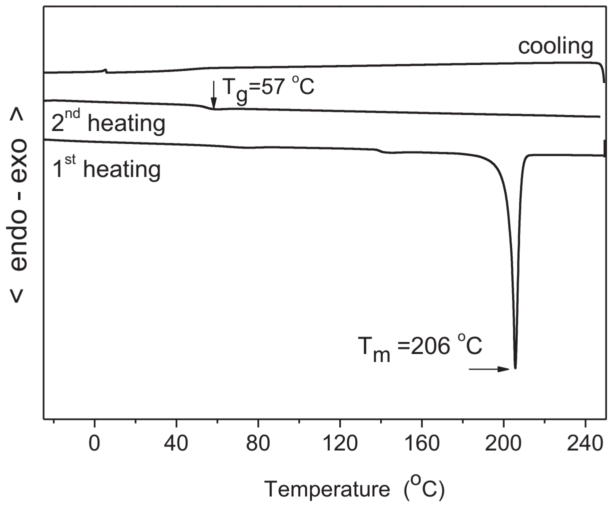


Fig. 1. DSC curves of compound **7**. Heating rate: 10 °C/min.

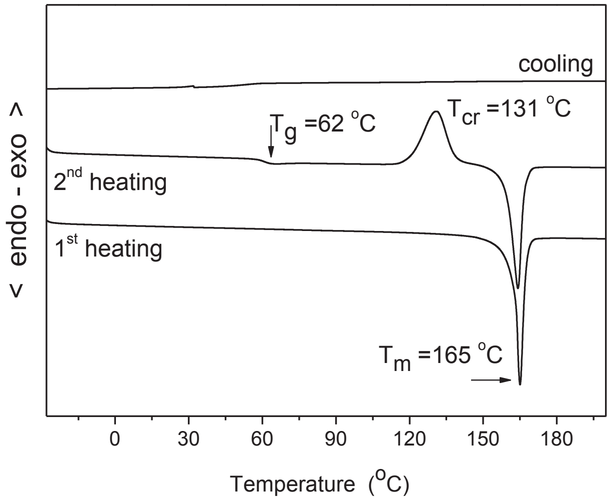


Fig. 2. DSC curves of compound **8**. Heating rate: 10 °C/min.

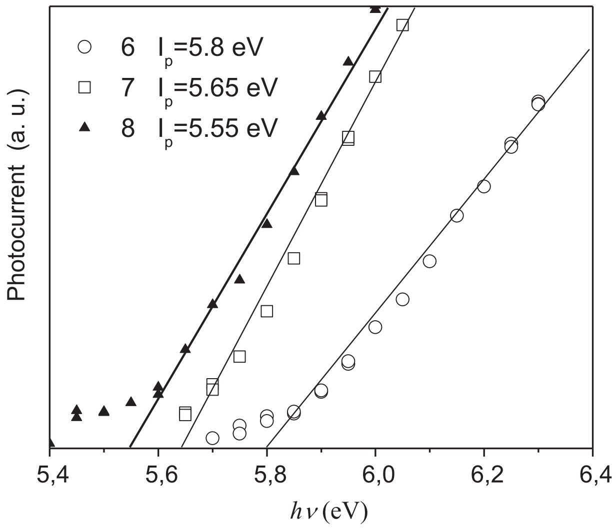


Fig. 3. Electron photoemission spectra of layers prepared using materials **6**–**8**.

8 are presented in Fig. 3. It could be observed that values of Ip of the newly synthesized compounds depend on aromatic substituents attached to carbazole core. Biphenyl substituted derivative **8** demonstrated the lowest Ip of 5.55 eV. The layers of phenyl substituted derivative **6** showed the highest Ip of 5.8 eV. It is evident that Ip's of the new compounds **6**–**8** are slightly lower than that of derivatives having electronically isolated carbazole rings (Ip > 5.9 eV) [21,22]. The investigations demonstrate that thin layers of **6**–**8** could be suitable for application in optoelectronic devices as hole transporting materials. Their layers should demonstrate better hole injecting and transporting properties in multilayer electroluminescent devices than that of widely used PVK [21].

The compounds **6**–**8** were all tested in electroluminescent OLEDs as hole transporting (HT) materials. An HT layer of **PEDOT** containing device was also prepared for comparison. The two layer OLED devices were prepared using Alq_3 for the electroluminescent(EL)/electron transporting layers. Aluminium was used as a cathode with a thin electron injection layer of LiF. When a positive voltage was applied to the device a bright green electroluminescence of Alq_3 was observed with an emission maximum at around 520 nm. This confirmed that hole injection and charge mobility in the HT layers of **6**–**8** is fully sufficient for an effective charge carrier recombination occurring within the Alq_3 layer.

Fig. 4 shows current density-voltage (a), luminance – current density (b) and current efficiency – current density (c) characteristics for the OLEDs containing the HT layers of **6**–**8** or **PEDOT**. It is seen that current density of the devices with layers of **6**–**8** is higher than that of the device with **PEDOT**. The OLEDs in general exhibit turn-on voltages of 2.5–3.0 V and a maximum brightness of 1270–8300 cd/m^2. Maximal current efficiency of 3.25 cd/A was obtained in device containing HT layer of biphenyl-substituted carbazole (**8**). It is evident that incorporation of HT layers of compounds **6**–**8** to the devices leads to better performance in current efficiency at the same current density in comparison with that of **PEDOT**-based device. It seems that layers of the compound **8** containing the lowest Ip (5.55 eV) are better suited for hole injection from ITO anode into Alq_3 layer than those of materials 6 and 7 containing slightly higher Ip's. It should be pointed out that these characteristics were obtained in a non-optimized test device. The performance may be further improved by an optimization of the layer thicknesses and processing conditions [23].

The HT materials **6** and **8**, which demonstrated suitable film forming properties by spin-coating, were also applied as HT layers in electro-phosphorescent OLEDs of the form: ITO/**PEDOT**:PSS/**6** or **8**/CBP:Ir(ppy)$_3$/TPBi/LiF/Al. Emitting layers of the devices consisted of a green phosphorescent guest of tris(2-phenylpyridine)iridium(III) (Ir(ppy)$_3$) dispersed in N,N′-dicarbazolyl-4,4′-biphenyl (CBP) host. Formation of the OLEDs is described in the Experimental Section.

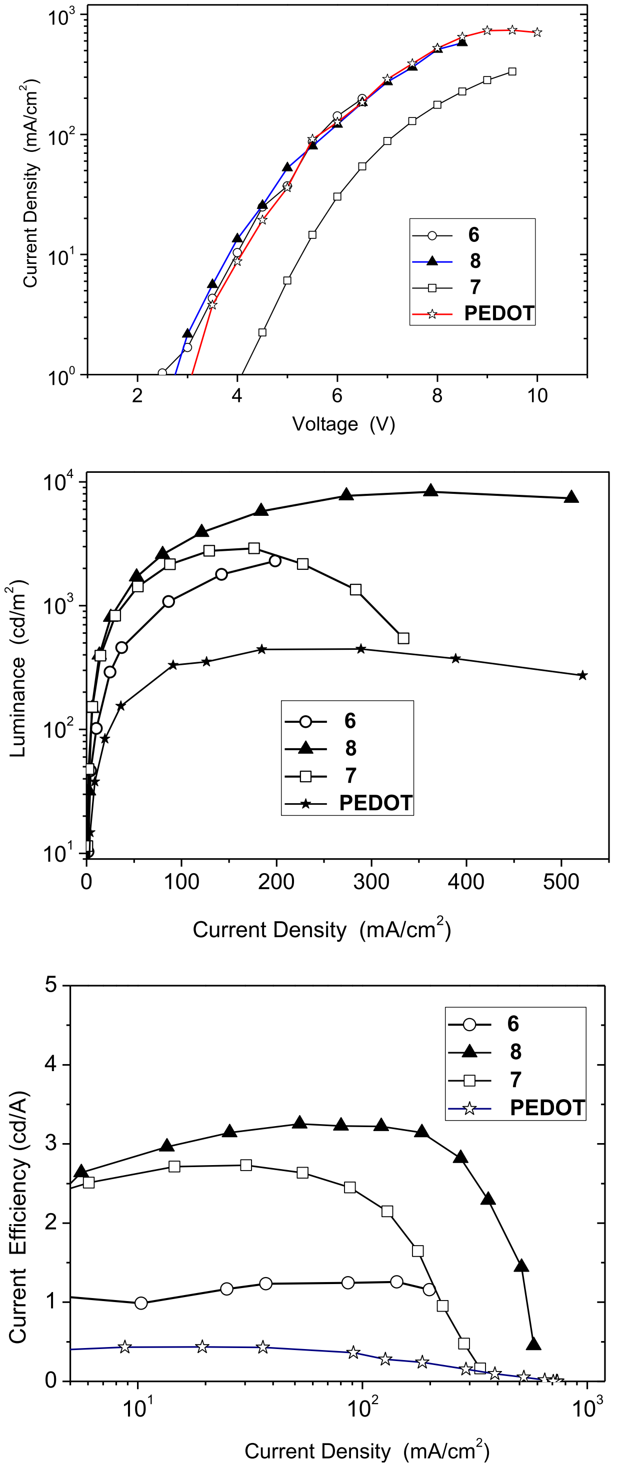


Fig. 4. OLED characteristics of the devices with the configuration: ITO/**6**, **7**, **8** or **PEDOT**/Alq_3/LiF/Al.

Current density-voltage (a), luminance – current density (b) and current efficiency – current density (c) characteristics for the OLEDs are presented in Fig. 5. It could be observed that the electrophosphorescent devices with HT layers of **6** or **8** both demonstrate rather similar characteristics. It seems that the hole injection layers of PEDOT reduce barrier for charge injection into layer of HT material 6, which has higher Ip than that of 8. The both devices exhibit turn-on voltage of ca. 5 V (defined as the voltage where electrophosphorescence becomes detectable) and a maximum brightness of 9800–11600 cd/m^2. Maximal current efficiencies of the OLEDs are about 22.5 cd/A and 20 cd/A for the materials **6**- and **8**-based devices. The efficiencies show noticeable drop in the observed current density window; however for the technically important brightness of 100 cd/m^2, an efficiency about 20 cd/A is detected. These characteristics were also obtained in non-optimized test devices and may be improved by an optimization.

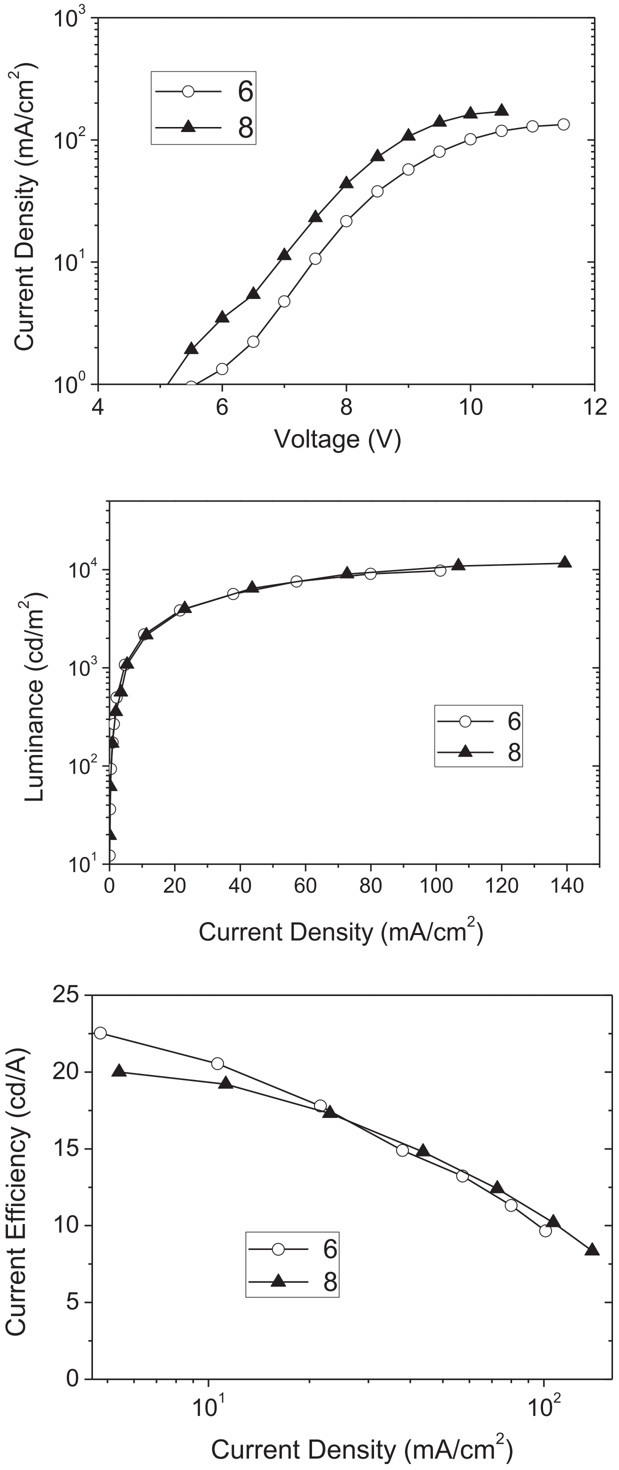


Fig. 5. OLED characteristics of the devices with the configuration: ITO/**PEDOT**/**6** or **8**/CBP:$Ir(ppy)_3$/TPBi/LiF/Al.

In conclusion, phenyl, naphthyl or biphenyl disubstituted 9-alkylcarbazoles have been synthesized and characterized as materials for hole transporting layers. The derivatives show high thermal stability and form amorphous layers with glass transition temperatures of 50–62 °C. The electron photoemission spectra of the layers showed ionisation potentials of about 5.55–5.8 eV. The materials have been tested as the hole transporting layers in OLEDs. One Alq_3-based device exhibited good overall performance (turn-on voltage: 2.5 V; maximum photometric efficiency: ~3.25 cd/A; maximum brightness: 8300 cd/m^2). These OLED properties are rather promising among Alq_3-based two-layer devices. An green electro-phosphorescent device using 3,6-diphenyl-9-ethylcarbazole as hole transporting layer demonstrated a turn-on voltage of ca. 5 V, a maximum brightness of 9800 cd/m^2, and maximum current efficiency of 22.5. For the technically important brightness of 100 cd/m^2, an efficiency exceeding 20 cd/A was detected in the OLED.

Acknowledgements

This research was funded by a grant No. MIP-024/2013 from the Research Council of Lithuania.

References

[1] Mullen K, Scherf U. Organic light emitting devices – synthesis, properties and applications. Weinheim: Wiley-VCH; 2005.
[2] AlSalhi MS, Alam J, Dass LA, Raja M. Recent advances in conjugated polymers for light emitting devices. Int J Mol Sci 2011;12:2036–54.
[3] Huang J, Xu B, Su JH, Chen CH, Tian H. Efficient blue lighting materials based on truxene-cored anthracene derivatives for electroluminescent devices. Tetrahedron 2010;66:7577–82.
[4] Zhang BH, Liu LH, Tan GP, Yao B, Ho CL, Wang SM, et al. Interfacial triplet confinement for achieving efficient solution-processed deep-blue and white electrophosphorescent devices with underestimated poly(N-vinylcarbazole) as the host. J Mater Chem 2013;1:49337–9.
[5] Huang JH, Su JH, Tian H. The development of anthracene derivatives for organic light-emitting diodes. J Mater Chem 2012;22:10977–89.
[6] Baoxiu M, Wang H, Gao ZQ, Wang XP, Chen Runfeng RF, Huang Wei W. Development of devices and materials for small molecular organic light-emitting diodes and hurdles for applications. Prog Chem 2011;23:136–52.
[7] Morin JF, Ades D, Siove A, Leclerc M. Polycarbazoles: 25 years of progress. Macromol Rapid Commun 2005;26:761–78.
[8] Tao Y, Yang C, Qin J. Organic host materials for phosphorescent organic light-emitting diodes. Chem Soc Rev 2011;40:2943–70.
[9] Grigalevicius S. 3,6(2,7),9-Substituted carbazoles as electroactive amorphous materials for optoelectronics. Synth Met 2006;156:1–12.
[10] Tomkeviciene A, Grazulevicius JV. Glass-forming organic semiconductors for optoelectronics. Mater Sci Medziagotyra 2011;17:335–42.
[11] Kirkus M, Grazulevicius JV, Grigalevicius S, Gu R, Dehaen W, Jankauskas V. Hole-transporting glass-forming indolo[3,2-b]carbazole-based diepoxy monomer and polymers. Eur Polym J 2009;45:410–7.
[12] Lengvinaite S, Grazulevicius JV, Grigalevicius S, Gu R, Dehaen W, Jankauskas V, et al. Indolo[3,2-b]carbazole-based functional derivatives as materials for light emitting diodes. Dyes Pigments 2010;845:183–8.
[13] Kirkus M, Lygaitis R, Tsai MH, Grazulevicius JV, Wu CC. Triindolylmethane-based high triplet energy glass-forming electroactive molecular materials. Synth Met 2008;158:226–32.
[14] Miyamoto E, Yamaguchi Y, Yokoyama M. Near-infrared sensitive photoreceptors incorporating a new polymorph of oxotitanium phthalocyanine. Electrophotography 1989;258:364–9.
[15] Simokaitiene J, Danilevicius A, Grigalevicius S, Grazulevicius JV, Getautis V, Jankauskas V. Phenotiazinyl-based hydrazones as new hole-transporting

materials for electrophotographic photoreceptors. Synth Met 2006;156:926–31.
[16] Elscher A, Bruder F, Heuer HW, Jonas F, Karbach A, Kirchmeyer S, et al. PEDT/PSS for efficient hole-injection in hybrid organic light-emitting diodes. Synth Met 2000;111:139–43.
[17] Tucker SH. Iodination in the carbazole series. J Chem Soc 1926;1:548–53.
[18] Rodriguez-Parada JM, Persec K. Interchain electron donor-acceptor complexes: a model to study polymer-polymer miscibility. Macromolecules 1986;19:55–64.
[19] Vaitkeviciene V, Kruzinauskiene A, Grigalevicius S, Grazulevicius JV, Rutkaite R, Jankauskas V. Well-defined [3,3′]bicarbazolyl-based electroactive compounds for optoelectronics. Synth Met 2008;158:383–90.
[20] Suzuki A. Recent advances in the cross-coupling reactions of organoboron derivatives with organic electrophiles, 1995–1998. J Organomet Chem 1999;576:147–68.
[21] Strohriegl P, Grazulevicius JV, Pielichowski J, Pielichowski K. Carbazole-containing polymers: synthesis, properties and applications. Prog Polym Sci 2003;28:1297–353.
[22] Grigalevicius S, Grazulevicius JV, Gaidelis V, Jankauskas V. Synthesis and properties of poly(3,9-carbazole) and low-molar-mass glass-forming carbazole compounds. Polymer 2002;43:2603–8.
[23] Lin WC, Lin YC, Wang WB, Yu BY, Lida S, Tozu M, et al. Effect of fabrication process on the microstructure and the efficiency of organic light-emitting diode. Org Electron 2009;10:459–64.