Dyes and Pigments 85 (2010) 183–188

Contents lists available at ScienceDirect

Dyes and Pigments

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

Indolo[3,2-*b*]carbazole-based functional derivatives as materials for light emitting diodes

S. Lengvinaite [a], J.V. Grazulevicius [a], S. Grigalevicius [a,*], R. Gu [b], W. Dehaen [b], V. Jankauskas [c], B. Zhang [d], Z. Xie [d]

[a] *Department of Organic Technology, Kaunas University of Technology, Radvilenu plentas 19, LT50254 Kaunas, Lithuania*
[b] *Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium*
[c] *Department of Solid State Electronics, Vilnius University, Sauletekio aleja 9, LT10222 Vilnius, Lithuania*
[d] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China*

ARTICLE INFO

Article history:
Received 3 July 2009
Received in revised form
22 October 2009
Accepted 23 October 2009
Available online 11 November 2009

Keywords:
Indolo[3,2-*b*]carbazole
Cross-linked layer
Ionisation potential
Charge transporting properties
Light emitting diodes

ABSTRACT

Derivatives of indolo[3,2-*b*]carbazole containing reactive oxetanyl groups were characterized using ^{1}H NMR, IR spectroscopy and mass spectrometry. The synthesized materials were examined using various techniques including differential scanning calorimetry, thermogravimetry, electron photoemission spectrometry and xerographic time of flight technique. The electron photoemission spectra of layers of the derivatives showed ionisation potentials of 5.2–5.45 eV; hole drift mobilities in layers of the derivatives dispersed in the polymeric host Bisphenol Z polycarbonate (50%) ranged from 6.2×10^{-6} to 6.9×10^{-4} cm^2 V^{-1} s^{-1} at high electric fields at room temperature. The compounds were tested as hole transporting materials in bilayer OLED's using Alq$_3$ as emitter; devices comprising phenyl substituted indolo[3,2-*b*]carbazole exhibited best overall performance with a turn-on voltage of ~5 V, maximum luminance efficiency of 3.64 cd A^{-1} and maximum brightness of ~5700 cd m^{-2}. The compounds were also used for the preparation of cross-linked hole transporting layers by photoinduced polymerization, the ensuing layers being employed in light emitting diodes.

1. Introduction

Organic light emitting diodes (OLED's) based on organic small molecules and polymers have attracted much attention owing to their potential use in flat panel displays and lighting [1]. Efficient organic LEDs can be obtained only by building multilayer structures [2]. The main difficulty in the preparation of such devices by spin-coating is the solubility of the material which forms the bottom layer onto which the top layer has to be cast, because most organic semiconductors are soluble in the same solvents. One approach that has been employed to circumvent this problem is the appliance of bi-functional electroactive derivatives, which could be converted into insoluble networks by cross-linking reactions. Several series of photo-cross-linkable polymers and monomers for the fabrication of OLEDs have been reported [3–7]. Cross-linked, solvent resistant charge-transporting layers are also useful in electrophotographic photoreceptors [8]. Among the cross-linkable monomers reported earlier, derivatives having a triphenyldiamine (TPD) core prevail [4,6]. With the purpose of developing organic hole transporting layers, carbazole- and triarylamine-based derivatives were also studied [9–12]. Here we describe syntheses and properties of substituted derivatives of indolo[3,2-*b*]carbazole having reactive oxetanyl groups. It was reviewed recently that indolo[3,2-*b*]carbazole-based compounds are very promising electroactive materials [13].

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. FTIR spectra were recorded using a Perkin Elmer FT-IR System. UV spectra were measured with a Spectronic Genesys^{TM} 8 spectrometer. Fluorescence (FL) spectra were recorded with a MPF-4 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.

---

* Corresponding author.
E-mail address: saulius.grigalevicius@ktu.lt (S. Grigalevicius).

0143-7208/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2009.10.022

The ionisation potentials of the layers of the compounds synthesized were measured by the electron photoemission method in air, which was described earlier [14]. The measurement method was, in principle, similar to that described by Miyamoto et al. [15].

Hole drift mobility was measured by the xerographic time of flight technique [16,17]. The samples for the charge carrier mobility measurements were prepared by the procedure we have described earlier [18].

Organic light emitting diodes were fabricated on glass substrates and had the 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 before deposition of the organic layers. The hole transporting layers were made by spin-coating a 60 nm layer of the corresponding material (**3**–**5**) onto the substrates from chloroform solution. Evaporation of the electroluminescent tris(quinolin-8-olato)aluminium (Alq_3) layer (60 nm) and a LiF/Al electrode (1/150 nm) was done at a pressure of 3×10^{-6} mbar in vacuum evaporation equipment.

The cross-linked hole transporting layers were made by spin-coating a 25–30 nm layer of the derivatives **3**–**5** containing initiator onto the substrates and by following cross-linking as we described earlier [10,19]. 90–100 nm layer of green light emitting polymer (GEP)- poly(9,9-dioctylfluorene-2,7-diyl-co-2,5-di(phenyl-4-yl)-2,1,3-benzothiadiazole) [10] was spin-coated from toluene solution onto the cross-linked network. The current-voltage and luminance-voltage characteristics of the devices were recorded as we described earlier [20].

2.2. Materials

10H-Phenothiazine, diphenylamine, phenylboronic acid 1,3-propanediol ester, tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$] (caution: air sensitive; moisture sensitive; incompatible withmoist air or water, strong oxidizing agents), tri(*tert*-butyl)phosphine (t-Bu_3P) (caution: powder or liquid is pyrophoric; avoid ignition sources, dust generation, exposure to air, strong oxidants), bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$) (caution: avoid dust generation, moisture, excess heat; incompatible with strong oxidizing agents), sodium *tert*-butoxide (*t*-BuONa), potassium carbonate, tetrabutylammonium hydrogen sulphate (TBAHS), Alq_3 and potassium hydroxide were purchased from Aldrich and used as received. 3-Bromomethyl-3-methyloxetane was received from Chemada Fine Chemicals and used without further purification.

2,8-Dibromo-6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**1**) was prepared by the earlier reported procedure [21].

2,8-Dibromo-5,11-di(3-methyl-3-oxetanylmethyl)-6-pentylindolo[3,2-*b*]carbazole (**2**) was prepared by the reaction of 2,8-dibromo-6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**1**) with an excess of 3-bromomethyl-3-methyl oxetane under basic conditions in the presence of a phase transfer catalyst-TBAHS. Compound **1** (1.5g, 3 mmol), 3-(bromomethyl)-3-methyl oxetane (1.79 g, 10.5 mmol), powdered potassium carbonate (2.48g, 18 mmol), potassium hydroxide (1g, 18 mmol) and TBAHS (0.2 g, 0.6 mmol) were stirred at 50 °C for 18 hours. After TLC control, the mixture was quenched with water. The product was extracted by ethyl acetate and purified by silica gel column chromatography using ethyl acetate/hexane (vol. ratio 1:3) as an eluent. Yield: 1.6g (79%) of yellow crystals. M.p.: 220 °C (DSC).

^1H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 8.33–8.31 (m, 2H, Ar), 7.87 (s, 1H, Ar), 7.62–7.57 (m, 2H, Ar), 7.34–7.17 (m, 2H, Ar), 4.84 (d, 2H, CH_2 of oxetane ring, $J = 6$ Hz), 4.74 (d, 2H, CH_2 of oxetane ring, $J = 6$ Hz), 4.55(s, 4H, $2 \times CH_2N$), 4.43 (d, 2H, CH_2 of oxetane ring, $J = 6$ Hz), 4.26 (d, 2H, CH_2 of oxetane ring, $J = 6$ Hz), 1.67–1.19 (m, 14H, $2 \times CH_3$ of oxetane and $4 \times CH_2$ of alkyl chain), 1.05 (t, 3H, CH_3, $J = 3$ Hz).

MS(APCI$^+$, 20 V), m/z (%): 653 ($[M + H]^+$, 90), 582 ($[M\text{-}C_5H_{11}]^+$, 100).

IR (KBr, ν, cm^{-1}): 3070(C–H, in Ar), 2959, 2854(C–H), 1460 (C–N, in Ar), 978(C–O–C), 731 (Ar).

2,8-Di(10-phenothiazinyl)-5,11-di(3-methyl-3-oxetanylmethyl)-6-pentylindolo[3,2-*b*]carbazole (**3**). $Pd_2(dba)_3$ (5.5mg, 0.006mmol), t-Bu_3P (2.4 mg, 0.012 mmol) and toluene (8 ml) of were charged under nitrogen into a two neck flask. The mixture was stirred at room temperature for 10 min. Then 2,8-dibromo-5,11-di(3-methyl-3-oxetanylmethyl)-6-pentylindolo[3,2-*b*]carbazole (0.4 g, 0.6 mmol), 10H-phenothiazine (0.36 g, 1.8 mmol) and *t*-BuONa (0.34 g, 3.6 mmol) were added, and the mixture was stirred at 80 °C for 8 h. The reaction mixture was cooled down and quenched by the addition of ice water. The product was extracted into ethyl acetate. The extract was dried over anhydrous $MgSO_4$, and the solvent was removed by evaporation. The product was purified by silica gel column chromatography using ethyl acetate/hexane (vol. ratio 1:2) as an eluent. Yield: 0.33g (61%) of yellow crystals. M.p.: 191 °C (DSC).

^1H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 8.27–7.93 (m, 3H, Ar), 7.69–6.8 (m, 20H, Ar), 4.90–4.79 (m, 4H, $2 \times CH_2$ of oxetane ring), 4.51(s, 4H, $2 \times CH_2N$), 4.42 (d, 2H, CH_2 of oxetane ring, $J = 6$ Hz), 4.28 (d, 2H, CH_2 of oxetane ring, $J = 6$ Hz), 1.67- 1.19 (m, 14H, $2 \times CH_3$ of oxetane and $4 \times CH_2$ of alkyl chain), 0.76 (t, 3H, CH_3 of alkyl chain, $J = 7$ Hz).

MS(APCI+, 20 V), m/z (%):890.4 ($[M + H]^+$, 73), 889.4 (M^+, 100).

IR (KBr, ν, cm^{-1}): 3056(C–H, in Ar), 2955, 2870(C–H), 1492 (C–N, in Ar), 973(C–O–C), 747(Ar).

2,8-Di(diphenylamino)-5,11-di(3-methyl-3-oxetanylmethyl)-6-pentylindolo[3,2-*b*]carbazole (**4**). $Pd_2(dba)_3$ (6.9 mg, 0.0076 mmol), t-Bu_3P (3 mg, 0.015 mmol) and toluene (10 ml) were charged under nitrogen into a two neck flask. The resulting mixture was stirred at room temperature for 10 min and 2,8-dibromo-5,11-di(3-methyl-3-oxetanylmethyl)-6-pentylindolo[3,2-*b*]carbazole (0.5 g, 0.76 mmol), diphenylamine (0.64 g, 3.8 mmol) and *t*-BuONa (0.44 g, 4.56 mmol) were added, and the mixture was stirred at 80 °C for 12 h. Then the reaction mixture was cooled down and quenched by the addition of ice water. The product was extracted into ethyl acetate. The extract was dried over anhydrous $MgSO_4$, and the solvent was removed by evaporation. The product was purified by silica gel column chromatography using ethyl acetate/hexane (vol. ratio 1:2) as an eluent. Yield: 0.25g (40%) of yellow crystals. M.p.: 163 °C (DSC).

^1H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 8.08–7.76 (m, 4H, Ar), 7.39–6.97 (m, 23H, Ar), 4.88–4.79 (m, 4H, $2 \times CH_2$ of oxetane ring), 4.5 (s, 4H, $2 \times CH_2N$), 4.38 (d, 2H, CH_2 of oxetane ring, $J = 6$ Hz), 4.25 (d, 2H, CH_2 of oxetane ring, $J = 6$ Hz), 1.68–1.13(m, 14H, $2 \times CH_3$ of oxetane and $4 \times CH_2$ of alkyl chain), 0.85 (t, 3H, CH_3 of alkyl chain, $J = 3$ Hz).

MS(APCI+, 20 V), m/z (%):830.5 ($[M + H]^+$,65), 829.5 (M^+, 100).

IR (KBr, ν, cm^{-1}): 3058(C–H, in Ar), 2954, 2869(C–H), 1459 (C–N, in Ar), 979(C–O–C), 745(Ar).

2,8-Diphenyl-5,11-di(3-methyl-3-oxetanylmethyl)-6-pentylindolo[3,2-*b*]carbazole (**5**). 2,8-Dibromo-5,11-di(3-methyl-3-oxetanylmethyl)-6-pentylindolo[3,2-*b*]carbazole (0.4 g, 0.6 mmol), phenylboronic acid 1,3-propanediol ester (0.2 ml, 1.8 mmol), potassium hydroxide (0.23 g, 6 mmol) and $Pd(PPh_3)_2Cl_2$ (0.03 g, 0.04 mmol) were charged into two neck flask. The reaction vessel was evacuated and filed with argon. Degassed THF (6 ml) and degassed distilled water (0.2 ml) were added, and the reaction mixture was stirred at 80 °C for 20 h. After TLC control, the reaction mixture was cooled down and quenched by the addition of ice water. The crude product was extracted into ethyl acetate. The organic solution was dried over anhydrous $MgSO_4$, and the solvent was removed by evaporation. The product was purified by silica gel column chromatography using ethyl acetate/hexane (vol. ratio 1:2) as an eluent. Yield: 0.22g (56%) of yellow crystals. M.p.: 275 °C (DSC).

^{1}H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 8.52–8.26 (m, 2H, Ar), 8.06–7.32 (m, 15H, Ar), 4.96–4.83 (m, 4H, 2 × CH_2 of oxetane ring), 4.78–4.26 (m, 6H, 2 × CH_2N and CH_2 of oxetane ring), 4.31 (d, 2H, CH_2 of oxetane ring, $J = 6$ Hz), 1.72 (s, 3H, CH_3 of oxetane), 1.67 (s, 3H, CH_3 of oxetane), 1.66–1.27(m, 8H, 4 × CH_2 of alkyl chain), 1.03 (t, 3H, CH_3 of alkyl chain, $J = 7$ Hz).

$\mathrm{MS(APCI+, 20\,V), m/z(\%) : 647.4([M+H]^+, 50)}$.

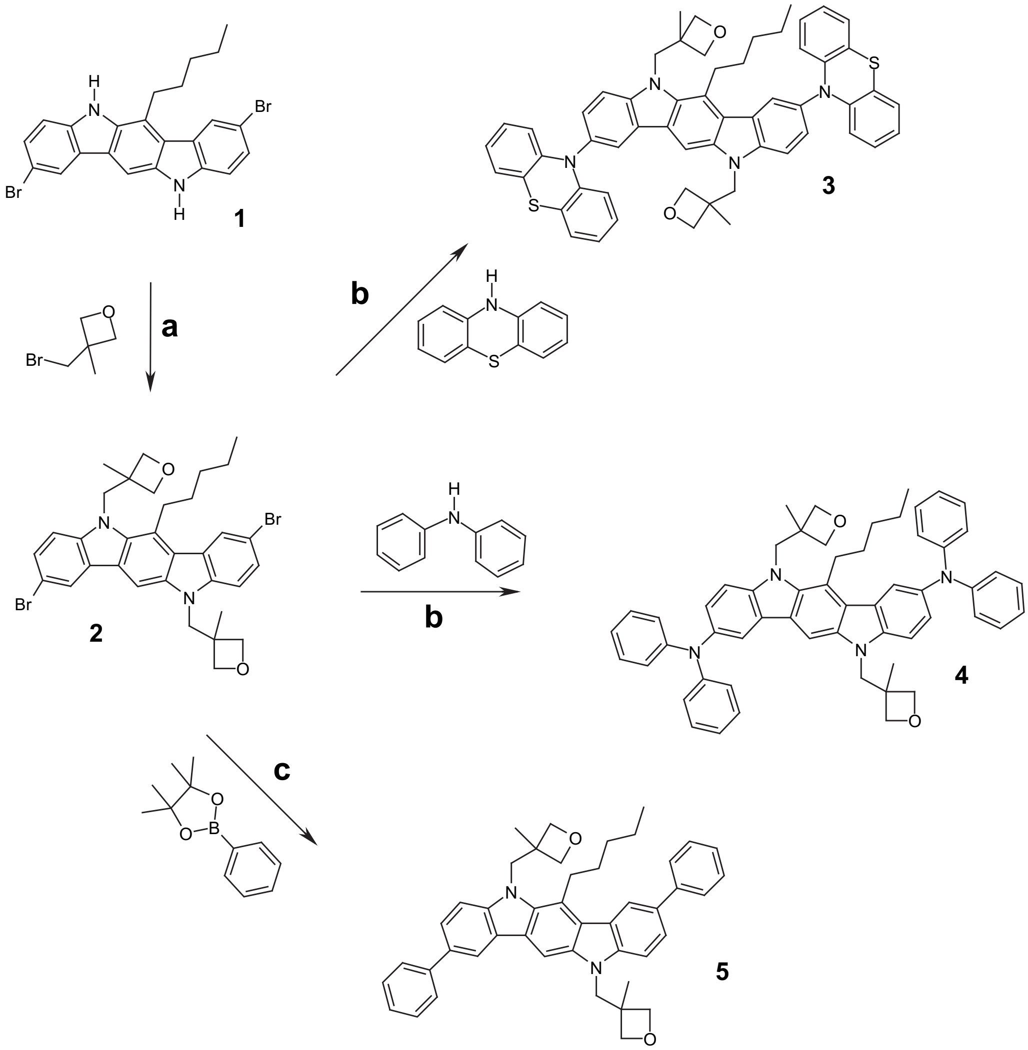
IR (KBr, ν, cm^{-1}): 3058(C–H, in Ar), 2954, 2866(C–H), 1470, 1455 (C–N, in Ar), 979(C–O–C), 753, 762(Ar).

3. Results and discussion

The synthesis of indolo[3,2-*b*]carbazole-based derivatives with reactive oxetanyl groups (**3**–**5**) was carried out by a multi-step synthetic route as shown in Scheme 1. 2,8-Dibromo-6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**1**) as a key compound was obtained by one-pot synthesis starting from 5-bromoindole with *n*-hexanal catalysed by hydroiodic acid as described earlier [17]. Compound **1** containing two secondary amine moieties was then treated with an excess of 3-bromomethyl-3-methyloxetane under basic conditions in the presence of a phase transfer catalyst TBAHS to obtain 2,8-dibromo-5,11-di(3-methyl-3-oxetanylmethyl)-6-pentylindolo[3,2-*b*] carbazole (**2**). Compound **2** was treated by Buchwald-Hartwig [22,23] procedure with 10H-phenothiazine or diphenylamine to yield phenothiazinyl- or diphenylamino-substituted derivatives **3** and **4** respectively. 2,8-Diphenyl-5,11-di(3-methyl-3-oxetanylmethyl)-6-pentylindolo[3,2-*b*]carbazole (**5**) was obtained by Suzuki- Miyaura [24,25] coupling of compound **2** with an excess of phenylboronic acid 1,3-propanediol ester.

All the newly synthesized compounds were identified by mass spectrometry, IR-, and ^{1}H NMR spectroscopy. The data were found to be in good agreement with the proposed structures. The materials (**3**–**5**) were soluble in common organic solvents, such as chloroform and THF at room temperature. Transparent thin films of these materials could be prepared by spin-coating from solutions.

The behaviour on heating of compounds **3**–**5** was studied by DSC and TGA under a nitrogen atmosphere. The values of glass transition temperatures (T_g), melting points (T_m) and the temperatures at which 5% loss of mass was observed (T_{ID}) are summarized in Table 1. Compounds **3**–**5** demonstrate high thermal stability. The mass loss occurs at a temperature ranging from 382 °C to 400 °C as confirmed by TGA with a heating rate of 10o C/min. It is evident that the phenothiazinyl-substituted derivative **3** exhibits slightly lower



Scheme 1. a) KOH, K_2CO_3, b) $Pd_2(dba)_3$, *t*-Bu_3P, *t*-BuONa, c) $Pd(PPh_3)_2Cl_2$, KOH.

Table 1
Thermal characteristic of compound **3**–**5**.

Compound	T_g (°C)	T_m (°C)	T_{ID} (°C)
3	155	191	382
4	123	163	398
5	172	275	400

thermal stability than diphenylamino- or phenyl-substituted compounds **4** and **5**.

Compounds **3**–**5** all were obtained as crystalline materials. When the crystalline samples were heated, endothermic peaks due to melting were observed in the region from 163 °C to 275 °C by DSC (Table 1). However, the melt samples readily formed glasses when they were cooled on standing in air or with liquid nitrogen. When the amorphous samples were heated again, glass-transitions were observed at 155°C, 123°C and 172°C, respectively, for compounds **3**–**5**, and on further heating no peaks due to crystallization and melting appeared.

UV absorption and FL spectra of dilute solutions of the compounds synthesized are shown in Fig. 1. For comparison, the corresponding spectra of 5,11-di(2,3-epoxypropyl)-6-pentyl[3,2-*b*] carbazole (**DInCz**) [26] are given in the Figure. All the compounds (**3**–**5**) exhibit a broad absorption with λ_{max} in the range of 265–360 nm and demonstrate a red shift of the UV absorption edge with respect of that of **DInCz**. The strongest red shift of the absorption band is observed for compound **4**. These red shifts show that the molecules synthesized have an interaction between the chromophores and that π electrons are de-localized over these molecules.

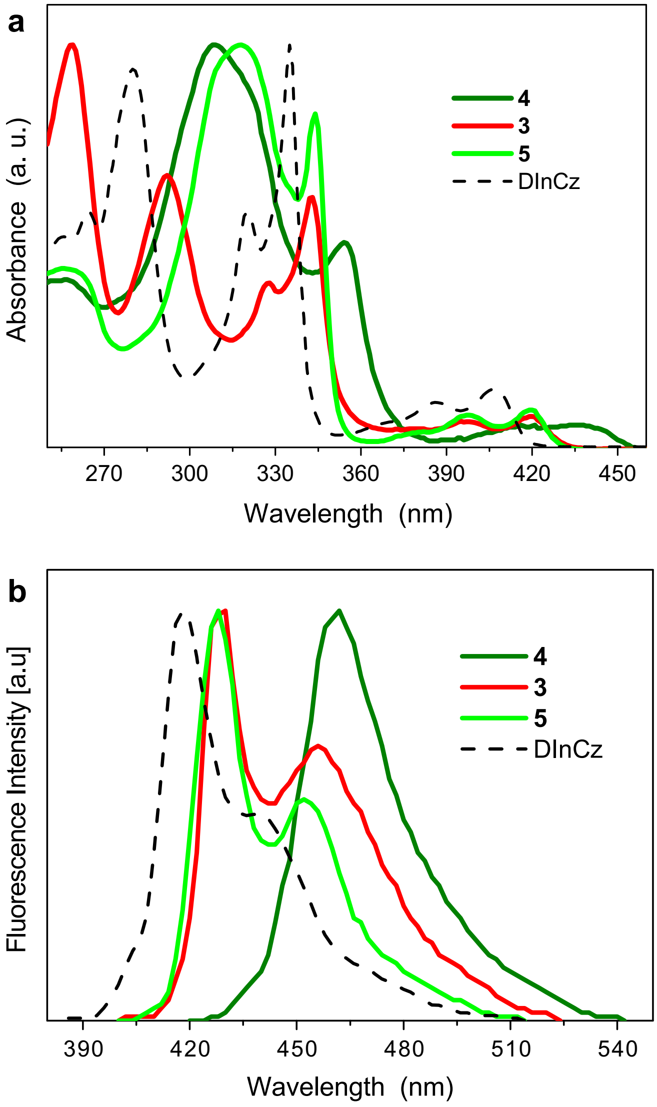


Fig. 1. UV absorption (a) and FL emission (b) spectra of dilute THF solutions of **3**–**5** and **DInCz**.

The FL emission spectra of the synthesized derivatives also show a red shift with respect of the **DInCz** spectrum (Fig. 2b). The fluorescence spectra of **3** and **5** have similar shape compared to that of **DInCz**, however they are red shifted by ca 10 nm. The spectrum of diphenylamino-substituted derivative **4** shows a considerable bathochromic shift with the emission maximum at 462 nm. The highest Stokes shift of **4** can apparently be explained by the highest relaxation energy in the excited state, which is determined by the possibility of an independent rotation of the two phenyl groups at the nitrogen atom.

Electron photoemission spectra of the amorphous layers of compounds **3**–**5** as well as the values of their I_p are presented in Fig. 2. The I_p values of amorphous layers of the materials synthesized range from 5.2 to 5.45 eV. The layers of **4** show the lowest I_p probably due to the most extended conjugation of π electrons, which was confirmed by comparison of UV absorption and FL spectra of the materials.

The I_p values of these materials demonstrate that their layers or cross-linked systems would be suitable for application in optoelectronic devices. Positive charges could be easily injected into the layers of **3**–**5** from compounds widely used in electrophotography as pigments, such as titanyl phthalocyanines, perylene derivatives, and bisazo pigments, which have I_p in the range of 5.1–5.6 eV [27]. The I_p values of compounds **3**–**5** are also close to that of indium-tin oxide which is widely used as an anode in electroluminescent devices [28]. Compounds **3**–**5** or their cross-linked networks can be suitable as hole transporting layers in multilayer devices.

Xerographic time of flight measurements were used to characterize the magnitudes of hole drift mobility (μ_h) for compounds **3**–**5** molecularly dispersed in polymer host bisphenol Z polycarbonate (PC-Z). For the molecular dispersions of compounds **3**–**5** in PC-Z (50%) the room temperature μ_h shows the linear dependencies on the square root of the electric field (Fig. 3). This characteristic dependence is observed for the majority of amorphous

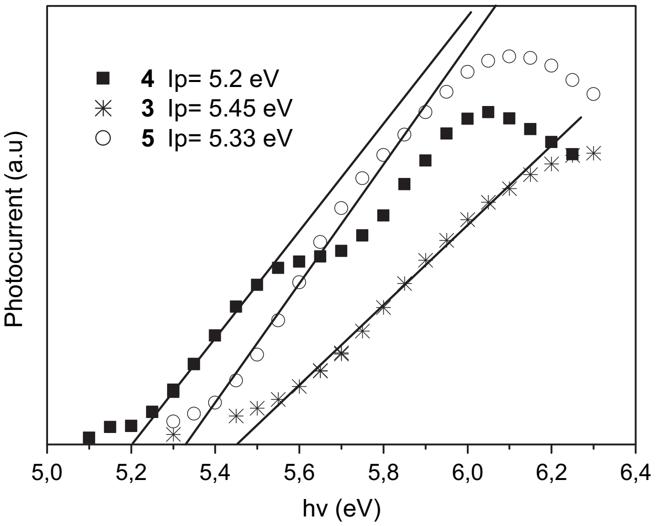


Fig. 2. Electron photoemission spectra of the layers of **3**–**5**.

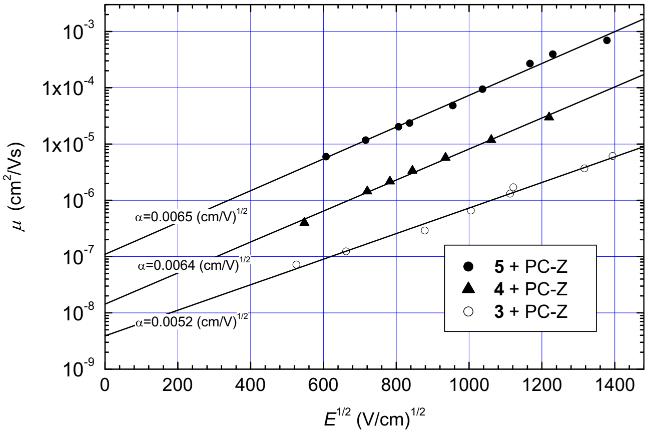


Fig. 3. Electric field dependencies of hole drift mobility in charge transport layers of compounds **3**–**5** molecularly doped in PC-Z.

organic systems and can be attributed to the effects of disorder on charge transport [29].

A μ_h value of 6.2×10^{-6} cm^2 V^{-1} s^{-1} was observed for the amorphous layer of compound **3** dispersed in PC-Z at an electric field of 1.93×10^6 Vcm^{-1} at 25 °C. A layer containing a molecular dispersion of compound **4** showed a μ_h well exceeding 10^{-5} cm^2 V^{-1} s^{-1} at high electric fields at 25 °C. The highest μ_h was observed in the layers of phenyl-disubstituted derivative **5**. The charge mobility reached almost 10^{-3} cm^2 V^{-1} s^{-1} at high electric field. It should be mentioned that these charge mobilities were estimated in layers having only 50 wt.% of the electroactive materials **3**–**5**. Charge mobilities higher by at least one order of magnitude can be predicted for amorphous films of the pure compounds. The different charge transporting properties of the synthesized compounds **3**–**5** are predetermined probably by different chemical structures of the materials as well as by different positional and energetic disorder in their layers.

The compounds 3–5 were also tested in OLEDs as hole transporting (HT) materials. The two layer OLED devices were prepared using these compounds for the HT layers and Alq_3 for the electroluminescent/electron transporting layers. The cathode used was aluminium with a thin LiF electron injection layer. When a positive voltage was applied the bright green electroluminescence of Alq_3 was observed with an emission maximum at around 520 nm [30,31]. This implies that the hole mobility in the HT layers of 3–5 is fully sufficient for an effective charge carrier recombination occurring within the Alq_3 layer. No exciplex formation at the interface between HT and Alq_3 layer was observed.

Fig. 4 shows luminance – voltage (a) and efficiency – current density (b) characteristics for the OLEDs containing the HT layers of **3**–**5**. These devices in general exhibit turn-on voltages of 5–8 V (defined as the voltage where electroluminescence becomes detectable) and a maximum brightness of 1090–5670 cd/m^2 (at 13–17 V). Current efficiency of the OLEDs range from 2.21 to 3.64 cd/A. Among these devices, the OLED using derivative **5** as the HT material exhibits the best overall performance, i.e. a turn-on voltage of ~5 V and maximal photometric efficiency of 3.64 cd/A. The efficiency shows an only a moderate drop in the observed current density window up to 120 mA/cm^2, for the technically important brightness of 100 cd/m^2, an efficiency above 3.4 cd/A is detected. These findings are rather promising also in comparison to similar Alq_3-based bilayer devices [1,32].

Cross-linked layers of the material **3**–**5** were also tested as hole transporting networks in two-layer OLEDs of the configuration ITO/PEDOT/cross-linked material/GEP emitter/(Ca/Al). The hole transporting layers were made by spin-coating from solution a layer of the derivatives **3**–**5** containing initiator onto PEDOT and by following cross-linking as we described earlier [10,19].

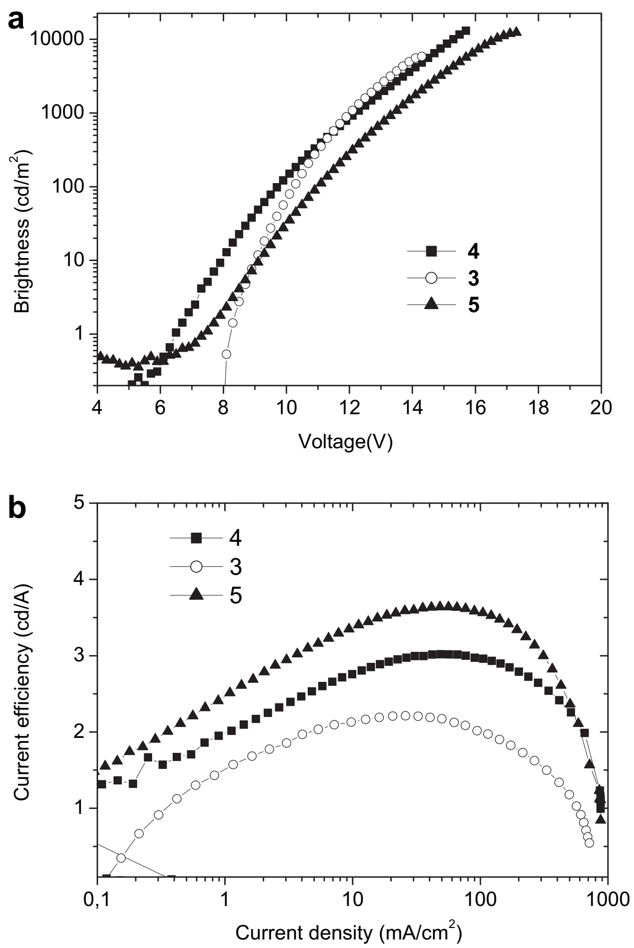


Fig. 4. OLED characteristics of the devices with the configuration: ITO/**3**, **4** or **5**/Alq_3/LiF/Al.

When a positive voltage was applied to the devices bright green electroluminescence of GEP emitter was observed with an emission maximum at around 528 nm. This implies that the hole mobility in the hole transporting networks is sufficient for an effective charge carrier recombination occurring within the GEP layer. No exciplex formation at the interface between hole transporting and emitting layer was observed.

Turn–on voltages of the devices were 2.5–3 V and maximum brightness was 3500–7790 cd/m^2. The best performance was achieved from the device having cross-linked HT layer of derivative 5 (Fig. 5), which demonstrated the highest charge drift mobility. EL efficiency of the device reached 2.8 cd/A and the maximum brightness exceeded 7700 cd/m^2. It should be pointed out that these characteristics were obtained in a non-optimized test device under ordinary laboratory conditions. The device performance may be further improved by an optimization of the layer thicknesses and processing conditions [33].

In conclusion, cross-linkable materials with 2,8-disubstituted indolo[3,2-*b*]carbazole core as hole transport agent, and oxetanyl groups as reactive moieties have been synthesized and characterized. The materials show high thermal stability and form glasses with glass transition temperatures in the range of 123–155 °C. The ionization potential values (5.2–5.45 eV) of amorphous layers of the derivatives and the hole drift mobility studies show that these compounds are potential materials for the preparation of hole

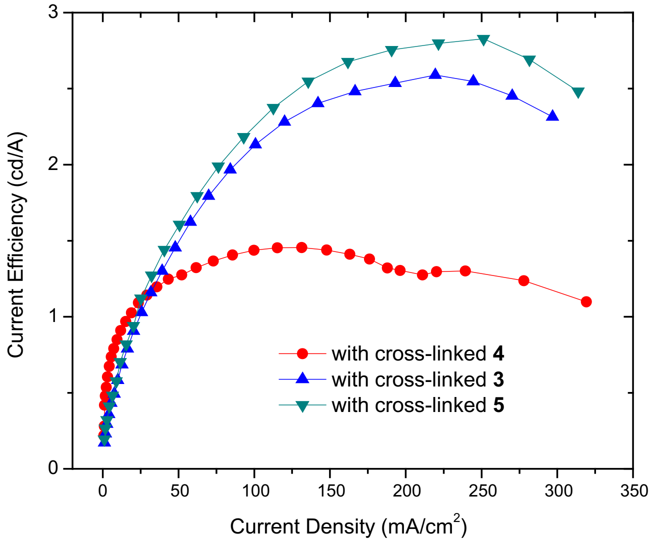


Fig. 5. Current efficiency of the devices ITO/cross-linked HT layer/GEP/(Ca/Al).

transporting layers for multilayer optoelectronic devices. These derivatives have been studied as hole transporting materials in bilayer OLEDs with Alq_3 as an emitter. The devices with phenyl substituted indolo[3,2-*b*]carbazole exhibited the best overall performance (turn-on voltage: ~5 V; maximum luminance efficiency: 3.64 cd/A; maximum brightness: approx. 5700 cd/m^2). Cross-linked networks of these derivatives have also been tested as hole transporting structures in multilayer OLEDs with green light emitting polymer. The device containing cross-linked layer of phenyl substituted indolo[3,2-*b*]carbazole demonstrated maximum photometric efficiency of 2.8 cd/A and maximum brightness of 7790 cd/m^2.

Acknowledgements

Financial support of this research by the Lithuanian Science and Studies Foundation and by the Alexander von Humboldt Foundation (Germany) is gratefully acknowledged. Habil. dr. V. Gaidelis is thanked for the help in ionisation potential measurements.

References

[1] Mullen K, Scherf U, editors. Organic light emitting devices – synthesis, properties and applications. Weinheim: Wiley-VCH; 2005.
[2] Mitschke U, Bauerle P. J Mater Chem 2000;10:913.
[3] Muller CD, Falcou A, Reckefuss N, Rojahn M, Wiederhirn V, Rudati P, et al. Nature 2003;421:829.
[4] Nuyken O, Jungermann S, Wiederhirn V, Bacher E, Meerholz K. Monatsh Chem 2006;137:811.
[5] Huang F, Cheng Y-J, Zhang Y, Liu MS, Jen AK-Y. J Mater Chem 2008;18:4495.
[6] Wen G-A, Zhu X-R, Wang L-H, Feng J-C, Zhu R, Wei W, et al. J Polym Sci Part A: Polym Chem 2007;45:388.
[7] Meerholz K, Muller CD, Nuyken O. In: Mullen K, Scherf U, editors. Organic light emitting devices – synthesis, properties and applications. Weinheim: Wiley-VCH; 2005.
[8] Daskeviciene M, Getautis V, Grazulevicius JV, Stanisauskaite A, Antulis J, Gaidelis V, et al. J Imag Sci Technol 2002;46:467.
[9] Lengvinaite S, Grazulevicius JV, Grigalevicius S. Synth Met 2009;159:91.
[10] Lengvinaite S, Grazulevicius JV, Grigalevicius S, Zhang B, Yang J, Xie Z, et al. Synth Met 2008;158:213.
[11] Du P, Zhu W-H, Xie Y-Q, Zhao F, Ku C-F, Cao Y, et al. Macromolecules 2004;37:4387.
[12] Ning Z, Tian H. Chem Commun 2009:5483.
[13] Wakim S, Aich B-R, Tao Y, Leclerc M. Polym Rev 2008;48:432.
[14] Kirkus M, Lygaitis R, Tsai M-H, Grazulevicius JV, Wu C-C. Synth Met 2008;158:226.
[15] Miyamoto E, Yamaguchi Y, Yokoyama M. Electrophotography 1989;28:364.
[16] Montrimas E, Gaidelis V, Pazera A. Lith J Phys 1966;6:569.
[17] Vaezi-Nejad SM. Int J Electron 1987;62:361.
[18] (a) Balionyte A, Grigalevicius S, Grazulevicius JV, Garsva G, Jankauskas V. J Photochem Photobiol A: Chem 2004;162:249;
(b) Grigalevicius S, Lideikis E, Grazulevicius JV, Gaidelis V, Antulis J, Jankauskas V, et al. Polymer 2002;43:5693.
[19] Lengvinaite S, Grazulevicius JV, Grigalevicius S, Zhang B, Xie Z. Mol Cryst Liq Cryst 2008;497:496.
[20] Grigalevicius S, Ma L, Qian G, Xie Z, Forster M, Scherf U. Macromol Chem Phys 2007;208:349.
[21] Gu R, Hameurlaine A, Dehaen W. J Org Chem 2007;72:7207.
[22] Louie J, Hartwig JF. Tetrahedron Lett 1995;36:3609.
[23] Wolfe JP, Buchwald SL. Org Synth 2004;10:423.
[24] Miyaura N, Suzuki A. Chem Rev 1995;95:2457.
[25] Suzuki AJ. Organomet Chem 1999;576:147.
[26] Kirkus M, Grazulevicius JV, Grigalevicius S, Gu R, Dehaen W, Jankauskas V. Eur Polym J 2009;45:410.
[27] Blazys G, Grigalevicius S, Grazulevicius JV, Gaidelis V, Jankauskas V, Kampars V. J Photochem Photobiol A: Chem 2005;174:1.
[28] Tao XT, Zhang YD, Wada T, Sasabe H, Suzuki H, Watanabe T, et al. Adv Mater 1998;10:226.
[29] Borsenberger M, Weiss DS. Photoreceptors for imaging systems. New York: Marcel Dekker; 1993.
[30] Hosokawa C, Higashi H, Kusumoto T. Appl Phys Lett 1992;60:1220.
[31] Kepler RG, Beeson PM, Jacobs SJ, Anderson RA, Sinclair MB, Valencia VS, et al. Appl Phys Lett 1995;66:36118.
[32] Li W, Jones RA, Allen SC, Heikenfeld JC, Steckl AJ. J Disp Technol 2006;2:143.
[33] Jou JH, Hsu MF, Wang WB, Liu CP, Wong ZC, Shyue JJ, et al. Org Electron 2008;9:291.