# New electroactive polymers with electronically isolated 3,6,9-triarylcarbazole units as efficient hole transporting materials for organic light emitting diodes

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## ARTICLE INFO

## ABSTRACT

Polyethers containing electronically isolated 3,6,9-triarylcarbazole moieties have been synthesized by the multi-step synthetic procedures. A polymer containing unsubstituted carbazole rings was also prepared for comparison of properties. Full characterization of the materials is presented. The new polymers represent materials of high thermal stability with initial thermal degradation temperatures exceeding 367 °C. The high glass transition temperatures of the amorphous materials were in the rage of 133–146 °C. The electron photoemission spectra of thin layers of the polymers showed ionization potentials in the range of 5.52–5.6 eV. Hole-transporting properties of the electroactive materials were tested in the structures of organic light emitting diodes (OLEDs) with tris(quinolin-8-olato)aluminium as the green emitter and electron transporting material. The OLED devices in general exhibited rather low turn-on voltages of 3.2–4.2 V, high maximum brightness of 4910–7500 cd/m$^2$ and luminous efficiency of 1.7–3.1 cd/A. It was confirmed that the devices containing the polymers with 3,6,9-triarylcarbazole moieties demonstrate considerably better OLED performance than that of device with polymer containing unsubstituted carbazole rings due to its higher ionization potential and accordingly worse hole injecting properties. The device containing hole-transporting layer of polymer with 3,6-di(1-naphthyl)-9-phenylcarbazole units exhibited the best overall performance with rather low turn on voltage of 4.4 V, maximum photometric efficiency exceeding 3.1 cd/A and maximum brightness of about 7500 cd/m$^2$.

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## 1. Introduction

Organic light-emitting diodes (OLEDs) based on organic electroactive derivatives have attracted much attention because of their potential use in lighting as well as in flat panel displays [1–5], however efficient devices can be obtained only by building bilayer or multilayer structures [6–9]. One approach that is widely used to improve efficiency of the OLED devices is the appliance of effective hole transporting layers in the structures of the devices. The electroactive layers can be fabricated by vapor deposition or by spin coating from solution. The latter rout has some advantages, e. g. the

production costs are reduced due to preparation of the layers using cheap casting or spin-coating technologies, large areas can be coated and the molar mass of the materials is not limited.

Carbazole-based solution processed derivatives are among the most studied materials for electronic applications due to good chemical and environmental stability, and high hole mobility in their layers [10–14]. In addition, derivatives containing electronically isolated carbazole rings have high triplet energies and are widely used as host materials for electro-phosphorescent OLEDs [15, 1]. It should be also mentioned that derivatives containing carbazolyl fragments could be used for the photovoltaic devices [16]. We have reported earlier that low-molar-mass derivatives of 3,6-diaryl substituted carbazoles demonstrate suitable ionization potentials and hole transporting properties for application in OLEDs, however the materials have low glass transition

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temperatures and demonstrated tendency for crystallization due to their low molecular weight [17]. Here, we report on polymeric hole transporting materials containing electronically isolated 3,6,9-triaryl substituted carbazole rings as electro-active moieties. The materials were fully amorphous with high glass transition temperatures and demonstrated also high thermal stability. Hole transporting layers of the polymers were tested in OLEDs with Alq$_3$ emitter and were shown to be suitable components for preparation of efficient devices by spin-coating.

## 2. Experimental

### 2.1. Instrumentation

$^1$H NMR spectra were recorded using a Varian Unity Inova (300 MHz) apparatus. Mass spectra of low-molar-mass derivatives were obtained on a Waters ZQ 2000 spectrometer.

The molecular weights of polymers were determined by a gel permeation chromatography (GPC) system including GMH$_{HR}$-M columns and Bischoff LAMBDA 1000 detector. Polystyrene standards were used for calibration of the columns and THF was chosen as an eluent.

Differential scanning calorimetry (DSC) measurements were carried performed on a Bruker Reflex II thermosystem. Thermogravimetric analysis (TGA) was performed on carried out using a TGAQ50 apparatus. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10° C/min.

The electron photoemission method for measurement of ionization potentials (I$_p$) of the solid state layers of the studied polymers was exploited in air [18,19]. The spin-coated layers of the materials onto commercial indium tin oxide (ITO) coated glass substrates were utilized as the samples for the electron photoemission measurements. The deep-UV deuterium light source ASBN-D130-CM, CM110 1/8 m monochromator and 6517B Keithley electrometer were used in the experimental setup, which was similar as previously described [20].

The electroluminescent devices (OLEDs) were fabricated on glass substrates containing a bottom indium tin oxide (ITO) anode. Before use for the device fabrication, the ITO-coated substrates were carefully cleaned with acetone and treated with UV/ozone right before deposition of the polymeric layers. The hole-transporting layers (HTL) of 40 nm thickness were prepared by spin-coating from chloroform solutions (3 mg/ml) of the synthesized polymers **10**–**12**. HTL of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (**PEDOT-PSS**) containing device was also prepared and used for comparison of properties of the OLED devices. The **PEDOT-PSS** was also deposited by spin-coating and then the layers heated at 120 °C for 30 min. Tris(quinolin-8-olato) aluminium (Alq$_3$) was used as green light emitter as well as electron transporting material. Evaporation of Alq$_3$ (80 nm) and of LiF (1 nm)/Al (100 nm) cathode was done at a pressure of $3 \times 10^{-4}$ Pa in vacuum evaporation equipment. The final structure of the devices was ITO/HTL/Alq$_3$/LiF/Al.

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*H*-Carbazole (**1**), 4-fluorobenzaldehyde, 3-bromomethyl-3-methyloxetane, phenyl boronic acid, 1-naphtyl boronic acid, boron trifluoride diethyl ether [BF$_3$·O(C$_2$H$_5$)$_2$], tetra-*n*-butylammonium hydrogen sulphate (TBAHS), tetra-*n*-butyl ammonium

bromide (TBAB), NaBH$_4$, Na$_2$SO$_4$ and KOH were purchased from Aldrich and used as received.

4-(9-Carbazolyl)benzaldehyde (**2**) and 9-(4-hydroxymethylphenyl)carbazole (**4**) were synthesized according to the procedure described in literature [21,22].

4-(3,6-Diiodocarbazol-9-yl)benzaldehyde (**3**) was prepared using Tucker iodination reaction according to the procedure described in literature [23].

9-(4-Hydroxymethylphenyl)-3,6-diiodocarbazole (**5**). 4-(3,6-Diiodocarbazol-9-yl)benzaldehyde (**3**) (5.0 g, 10 mmol) was dissolved in mixture of methanol (150 ml) and tetrahydrofuran (50 ml) and NaBH$_4$ (0.4 g, 11 mmol) was added by small portions. The resulting mixture was stirred at reflux for 24 h. After thin layer chromatography (TLC) control the reaction mixture was cooled down to the room temperature and poured into ice water. The solution was extracted by chloroform. The organic fraction was dried by Na$_2$SO$_4$ and the solvent was removed by evaporation. The product was purified by column chromatography with silica gel using ethyl acetate/hexane (vol. ratio 1:3) as an eluent. White amorphous material, 89% (4.5 g). IR data (KBr): 3290 (O–H); 3058, 3033 (C–H, Ar); 2927, 2860 (C–H); 1609, 1588 (C=C, Ar); 1517, 1466, 1429 (C=C, Ar ir C–H); 1362, 1280, 1231 (C–N, Ar); 1041, 1016 (C–O); 868, 811, 799, 789 (C–H, Ar) cm$^{-1}$. NMR $\delta_H$ (CDCl$_3$, 400 MHz): 8.39 (d, 2H, J = 1.6 Hz); 7.66 (dd, 2H, J$_1$ = 1.6 Hz, J$_2$ = 6.6 Hz); 7.62 (d, 2H, J = 8.4 Hz); 7.48 (d, 2H, J = 8.4 Hz); 7.14 (d, 2H, J = 7.6 Hz); 4.85 (s, 2H, CH$_2$); 1.50 (s, 1H, OH). Elemental analysis for C$_{19}$H$_{13}$I$_2$NO % Calc.: C 43.46, H 2.50, N 2.27; % Found: C 43.41, H 2.54, N 2.24.

9-[4-(3-Methyloxetan-3-ylmethoxymethyl)phenyl]carbazole (**6**). 9-(4-Hydroxymethyl-phenyl)carbazole (**4**) (2.0 g, 7.3 mmol) was dissolved in acetone (10 ml) and bromomethyl-3-methyloxetane (2.4 g, 7.3 mmol) was added. KOH (1.24 g, 22 mmol), K$_2$CO$_3$ (0.96 g, 7.3 mmol) and catalytic amount of TBAHS were then added into the mixture and it was stirred at 60 °C for 2 h. After TLC control the reaction mixture was cooled down and filtered. The solvent was removed by evaporation. The product was purified by column chromatography with silica gel using ethyl acetate/hexane (vol. ratio 1:4) as an eluent. White crystals, 65% (1.7 g), mp 95 °C. IR data (KBr): 3048 (C–H, Ar); 2951, 2925, 2865 (C–H); 1624, 1594, 1573 (C=C, Ar); 1516, 1478, 1452 (C=C, Ar ir C–H); 1334, 1315, 1234 (C–N, Ar); 1106 (C–O–C, in oxetane); 1094, 980, 972 (C–O–C); 836, 824, 748, 724 (C–H, Ar) cm$^{-1}$. NMR $\delta_H$ (CDCl$_3$, 400 MHz): 8.14 (d, 2H, J = 7.6 Hz, Ar); 7.56 (d, 4H, J = 7.8 Hz, Ar); 7.42–7.40 (m, 4H, Ar); 7.31–7.27 (m, 2H, Ar); 4.69 (s, 2H, PhCH$_2$); 4.59 (d, 2H, J = 5.6 Hz, CH$_2$ of oxetane ring); 4.43 (d, 2H, J = 6.2 Hz, CH$_2$ of oxetane ring); 3,64 (s, 2H, OCH$_2$); 1,40 (s, 3H, CH$_3$). Elemental analysis for C$_{24}$H$_{23}$NO$_2$% Calc.: C 80.64, H 6.49, N 3.92; % Found: C 80.61, H 6.51, N 3.89.

9-[4-(3-Methyloxetan-3-ylmethoxymethyl)phenyl]-3,6-diiodocarbazole (**7**). 9-(4-Hydroxy-methylphenyl)-3,6-diiodocarbazole (**5**) (4.5 g, 8.6 mmol) was dissolved in acetone (10 ml) and bromomethyl-3-methyloxetane (2.9 g, 18 mmol) was added. KOH (1.6 g, 29 mmol), K$_2$CO$_3$ (1.25 g, 10 mmol) and catalytic amount of TBAHS were then added into the mixture and it was stirred at 60 °C for 4 h. After TLC control the reaction mixture was cooled down and filtered. The solvent was removed by evaporation. The product was purified by column chromatography with silica gel using ethyl acetate/hexane (vol. ratio 1:3) as an eluent. White amorphous material, 68% (3.5 g). IR data (KBr): 3053 (C–H, Ar); 2957, 2926, 2863 (C–H); 1608, 1539 (C=C, Ar); 1516, 1466, 1428 (C=C, Ar ir C–H); 1354, 1281, 1234 (C–N, Ar); 1111 (C–O–C of oxetane ring); 1095, 971 (C–O–C); 871, 847, 810 (C–H, Ar); 567 (C–I) cm$^{-1}$. NMR $\delta_H$ (CDCl$_3$, 400 MHz): 8.38 (d, 2H, J = 1.6 Hz, Ar); 7.65 (dd, 2H, J$_1$ = 1.8 Hz, J$_2$ = 8.6 Hz, Ar); 7.,57 (d, 2H, J = 8.4 Hz, Ar'); 7.48 (d, 2H, J = 8.4 Hz, Ar); 7.14 (d, 2H, J = 8.8 Hz, Ar); 4.69 (s, 2H, PhCH$_2$); 4.59