



Polyether containing N-[6-(N-carbazolyl)hexyl]carbazol-3-yl side chains and its model compound as components of organic light emitting diodes

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ABSTRACT

Polyether containing electronically isolated carbazolyl fragments and its model compound were synthesized and characterized. Weight-average molecular weight of the polymer was 31,500 with polydispersity index of 2.4. Both the compounds represent amorphous materials of high thermal stability with glass transition temperatures of 137 °C for polymer and of 41 °C for model compound. The derivatives were tested as host materials in green as well as blue phosphorescent OLEDs. The green device with polymeric host exhibited turn-on voltage of 3.3 V, a maximal current efficiency of 11.5 cd/A and maximum brightness of 1312 cd/m². An efficient blue OLED using the model compound as host demonstrated a turn-on voltage of ca. 4.3 V, a maximum brightness of 6225 cd/m², and maximum current efficiency of 23.3 cd/A at 100 cd/m².

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1. Introduction

The efficiencies of organic light-emitting devices (OLEDs) have advanced rapidly in recent years because of the development of efficient phosphorescent triplet guests. In phosphor-doped OLEDs, to reduce quenching associated with relatively long excited-state lifetimes of triplet emitters and triplet-triplet annihilation etc., the triplet emitters of heavy-metal complexes are normally used as emitting guests in a host material, and thus suitable host materials are of equal importance for the phosphorescent devices [1–3]. For electro-phosphorescence from triplet guests, it is essential that the triplet level of the host be larger than that of the triplet emitter to prevent reverse energy transfer from the guest back to the host and to effectively confine triplet excitons on guest molecules [4–6]. It was reported earlier that carbazole-, indole- and arylsilane-based derivatives demonstrate rather large triplet energies and are potential host materials for solution processed blue electro-phosphorescent devices [7–11]. For example, a blue OLED with an external quantum efficiency of ~10% at 100 cd/m² has been fabricated via solution processes by So's group using a well balanced carrier injection [9].

A green device with an external quantum efficiency of ~27% at 100 cd/m² has been fabricated by Kido's group [8]. Here, we report new host materials containing electronically isolated carbazolyl fragments.

2. Experimental

2.1. Instrumentation

¹H 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 molecular weight of polymer was determined by a gel permeation chromatography (GPC) system including GMH_{HR}-M columns and Bischoff LAMBDA 1000 detector. Polystyrene standards were used for the calibration of the columns and tetrahydrofuran (THF) was chosen as an eluent.

The devices were fabricated on glass substrates and consisted of multiple organic layers sandwiched between the bottom indium tin oxide (ITO) anode and the top metal cathode (Al). The device structure used was ITO/PEDOT:PSS (ca. 300 Å)/our host doped with a triplet guest (250 Å)/LiF (5 Å)/Al (1500 Å),

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where the conducting polymer poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) was used as the hole-injection layer [12], synthesized hosts **2** or **6** doped with the green phosphorescent tris(2-phenylpyridine)iridium(III) (**Ir(ppy)₃**) or blue phosphorescent iridium(III)[bis(4,6-difluorophenyl)-pyridinato-N,C2']picolinate (**Flrpic**) were used as the emitting layers and LiF was used as the electron-injection layer [13]. All the emitting layers were prepared by spin coating from solutions. Thickness of the layers was controlled by changing speed of the substrate (rpm).

The luminance and CIE chromatic coordinates of the resulting OLEDs were measured as described earlier [14]. A Keithley 2400 electrometer was used to measure the current–voltage (*I*–*V*) characteristics. All the devices were characterized without encapsulation and all the measurements were carried out under ambient condition. The emission area of all the devices was 25 mm² and only the luminance in the forward direction was measured.

2.2. Materials

9H-Carbazole (**1**), boron trifluoride diethyl etherate [BF₃·O(C₂H₅)₂], NaBH₄, 1,6-dibromohexane, 3-bromomethyl-3-methyloxetane, tetra-*n*-butylammonium hydrogen sulfate (TBAHS), tetra-*n*-butylammonium bromide and KOH were purchased from Aldrich and used as received.

Hexane-1,6-diyl bis(9-carbazole) (**2**) was prepared by procedure described in the literature [15].

9-[6-(9H-carbazol-9-yl)hexyl]-9H-carbazole-3-carbaldehyde (**3**) was prepared by the reaction of compound **2** with POCl₃ in dimethylformamide (DMF) by Vilsmeier procedure [16]. POCl₃ (29.5 g, 192 mmol) was added drop-wise to 80 ml of dry DMF at 0 °C under nitrogen atmosphere. Compound **2** (8 g, 19.21 mmol) was added to the mixture. The resulting mixture was stirred at 80 °C for 72 h, until the starting compound **2** reacted completely. Then the mixture was cooled down to the room temperature, poured into ice water and neutralized with sodium acetate till pH 6–8. The resulting mixture was extracted by chloroform. Organic fraction was dried by MgSO₄ and the solvent was removed by evaporation. The product was purified by column chromatography with silica gel using hexane/ethyl acetate (vol. ratio 3:1) as an eluent. Yield of the product **3** was 3.4 g (40%).

MS (APCI⁺, 20 V): 445.5 ([M+1], 100%). ¹H NMR spectrum (CDCl₃, δ, ppm): 10.08 (s, 1H, ArCHO), 8.59 (s, 1H, Ar), 8.16–7.94 (m, 4H, Ar), 7.52–7.19 (m, 10H, Ar), 4.26 (t, 4H, NCH₂, *J* = 6.9 Hz), 1.88–1.79 (m, 4H, NCH₂CH₂), 1.41–1.33 (m, 4H, NCH₂CH₂CH₂). Elemental analysis for C₃₁H₂₈N₂O % Calc.: C 83.75, H 6.35, N 6.30, O 3.60; % Found: C 83.77, H 6.36, N 6.32.

{9-[6-(9H-carbazol-9-yl)hexyl]-9H-carbazol-3-yl}methanol (**4**). Formyl compound **3** (2.4 g, 5.4 mmol) was dissolved in the mixture of methanol (40 ml) and THF (30 ml). NaBH₄ (0.4 g, 10.6 mmol) was added to the solution by small portions. The resulting mixture was refluxed for 0.5 h. When the reaction was finished, the reaction mixture was poured into ice water. The product was extracted by ethyl acetate. The organic fraction was dried by MgSO₄ and the solvent was removed by evaporation. The product was purified by column chromatography with silica gel using hexane/ethyl acetate (vol. ratio 1:1) as an eluent. Yield of the product **4** was 1.9 g (83%).

MS (APCI⁺, 20 V): 429.5 ([M–OH], 100%). ¹H NMR spectrum (CDCl₃, δ, ppm): 8.59 (s, 1H, Ar), 8.16–7.94 (m, 4H, Ar), 7.52–7.19 (m, 10H, Ar), 4.53 (s, 2H, Ar–CH₂–O–), 4.26 (t, 4H, NCH₂, *J* = 6.9 Hz), 1.88–1.79 (m, 4H, NCH₂CH₂), 1.56 (s, 1H, –OH), 1.41–1.33 (m, 4H, NCH₂CH₂CH₂). Elemental analysis for C₃₁H₃₀N₂O % Calc.: C 83.37, H 6.77, N 6.27, O 3.58; % Found: C 83.38, H 6.76, N 6.29.

9-[6-(9H-carbazol-9-yl)hexyl]-3-[(3-methyloxetan-3-yl)methoxy]methyl-9H-carbazole (**5**). Compound **4** (1.5 g, 3.4 mmol) was dissolved in toluene (7 ml). 1.1 g (6.7 mmol) of

3-(bromomethyl)-3-methyloxetane and tetra-*n*-butylammonium bromide (0.11 g, 0.34 mmol) were added into the solution. After the mixture was heated to reflux, 3 ml of 50% NaOH solution was added. The resulting mixture was stirred at 60 °C for 24 h. Then new portions of the materials: 3-(bromomethyl)-3-methyloxetane (1.1 g, 6.7 mmol), NaOH solution (3 ml), and tetra-*n*-butylammonium bromide (0.11 g, 0.34 mmol) were added into the mixture and it was stirred again at 60 °C for 24 h. When the reaction was finished, the reaction mixture was poured into ice water. The product was extracted by chloroform. The organic fraction was dried by MgSO₄ and the solvent was removed by evaporation. The product was purified by column chromatography with silica gel using hexane/ethyl acetate (vol. ratio 5:1) as an eluent. Yield of the monomer **5** was 0.9 g (48%).

MS (APCI⁺, 20 V): 531.7 ([M+1], 100%). ¹H NMR spectrum (CDCl₃, δ, ppm): 8.12–8.01 (m, 3H, Ar), 7.48–7.14 (m, 12H, Ar), 4.73 (s, 2H, ArCH₂O), 4.52 (d, 2H, CH₂ of oxetanyl fragment, *J* = 5.7 Hz), 4.35 (d, 2H, CH₂ of oxetanyl fragment, *J* = 5.7 Hz), 4.26–4.19 (m, 4H, 2 × NCH₂), 3.54 (s, 2H, CCH₂O), 1.88–1.81 (m, 4H, 2 × NCH₂CH₂), 1.53 (s, 3H, CH₃), 1.41–1.33 (m, 4H, 2 × NCH₂CH₂CH₂). Elemental analysis for C₃₆H₃₈N₂O₂ % Calc.: C 81.48, H 7.22, N 5.28, O 6.03; % Found: C 81.49, H 7.24, N 5.29.

Poly{3-(3-methyloxetan-3-ylmethoxymethyl)-9-[6-(9-carbazolyl)hexyl]carbazole} (**6**). Monomer **5** (0.88 g, 1.17 mmol) was polymerized in 3.2 ml of 1,2-dichloroethane by using 1 mg (0.12 mmol) of BF₃·O(C₂H₅)₂ as an initiator. Polymerization mixture was stirred at 60 °C under nitrogen for 24 h. After precipitation into methanol, the low molecular weight fractions of the polymer were removed by Soxhlet extraction of the raw material with methanol. Yield: 0.36 g (41%) of white amorphous powder. GPC: *M_w* = 31,500, *M_n* = 13,100.

¹H NMR spectrum (CDCl₃, δ, ppm): 8.12–8.01 (m, 3H, Ar), 7.48–7.14 (m, 12H, Ar), 4.58–4.47 (m, 2H, ArCH₂O), 4.26–4.19 (m, 4H, 2 × NCH₂), 3.19–2.96 (m, 6H, 3 × CCH₂O), 1.88–1.81 (m, 4H, 2 × NCH₂CH₂), 1.59–1.33 (m, 7H, 2 × NCH₂CH₂CH₂ and CH₃). Elemental analysis for (C₃₆H₃₈N₂O₂)_{*n*} % Calc.: C 81.48, H 7.22, N 5.28, O 6.03; % Found: C 81.52, H 7.23, N 5.26.

3. Results and discussion

The synthesis of derivatives containing N-[6-(*N*-carbazolyl)hexyl]carbazol-3-yl fragments was carried out by the synthetic route shown in Scheme 1. 1,6-Di(9-carbazolyl)hexane (**2**) – a model compound for the polymer was prepared by reaction of 1,6-dibromocarbazole with an excess of 9H-carbazole as described earlier [15]. The derivative **2** was converted to aldehyde **3** using Vilsmeier procedure [16]. Hydroxymethyl-substituted N-[6-(*N*-carbazolyl)hexyl]carbazole (**4**) was obtained by reduction of the aldehyde **3** with sodium borohydride in methanol. The hydroxy compound **4** was later converted into oxetane monomer **5** by its reaction with an excess of 3-(bromomethyl)-3-methyloxetane under basic conditions. Polymer **6** was obtained by cationic polymerization of the monomer **5** in 1,2-dichloroethane solutions using BF₃·O(C₂H₅)₂ as an initiator. Low-molar-mass fractions were removed from the polymer by Soxhlet extraction of the raw polymerization material with methanol.

The newly synthesized derivatives were identified by elemental analyses, mass spectrometry and ¹H NMR spectroscopy. The data were found to be in good agreement with the proposed structures. The derivatives were soluble in common organic solvents at room temperature. Transparent thin films of these materials could be prepared by spin coating from solutions.

The number-average (*M_n*) and weight-average (*M_w*) molecular weights of the polymer **6** were determined by GPC using polystyrene standards. The GPC results indicated that the cationic

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