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Electroactive polymers containing pendant harmane, phenoxazine or carbazole rings as host materials for OLEDs

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ABSTRACT

Polystyrenes containing electronically isolated harmane, phenoxazine or carbazole rings were synthesized and characterized by NMR spectroscopy, elemental analysis and gel permeation chromatography. The new polymers represent amorphous materials of high thermal stability with glass-transition temperatures of 139–179 °C. The electron photoemission spectra of layers of the synthesized polymers showed ionization potentials of about 5.6–6.0 eV. The polymers were tested as host materials in phosphorescent green OLEDs with bis(2-phenylpyridine)(acetylacetonato)iridium(III) as the guest. The device based on polymer containing phenoxazine fragments exhibited the best overall performance with a turn-on voltage of 2.8 V, maximum photometric efficiency of about 17 cd/A and maximum brightness of 2920 cd/m^2.

1. Introduction

Improvements in the performance of organic light emitting diodes (OLEDs) over the past decade have resulted in commercially available products. The efficiencies of OLED devices have advanced rapidly in recent years because of the development of efficient emitters [1–5] as well as efficient phosphorescent guest molecules containing transition metals [6–8]. In the phosphorescent devices, to reduce quenching associated with relatively long excited-state lifetimes of triplet emitters and triplet–triplet annihilation, the emitters are normally used as emitting guests in a host material, and thus suitable host materials are of equal importance for electro-phosphorescent OLEDs. The triplet level of the hosts should be larger than that of the triplet emitter to prevent energy transfer from the guest back to the host and to confine effectively triplet excitons to the guest molecules [9–11]. It was reported earlier that carbazole- and indole-based derivatives demonstrate rather large triplet energies and are potential host materials for electro-phosphorescent devices [12–14]. Here, we report on new electroactive polymers containing electronically isolated pendant harmane, phenoxazine or carbazole rings. The fragments of aromatic heterocyclic compounds are attached to long and neural alkyl chains of the macromolecules and have not an electronic interaction. The polymers should have high triplet energy and are suitable as polymeric hosts for large area OLED devices.

2. Experimental

2.1. Instrumentation

^{1}H NMR spectra were recorded using a Varian Unity Inova (300 MHz) instrument. Mass spectra were obtained on a Waters ZQ 2000 spectrometer. UV spectra were measured with a Spectronic Genesys™ 8 spectrometer. Fluorescence (FL) spectra were recorded with a Hitachi MPF-4 spectrometer.

The molecular weights of polymers were determined by a gel permeation chromatography (GPC) system including GMH$_{HR}$-M

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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 out using a Bruker Reflex II thermosystem. Thermogravimetric analysis (TGA) was performed on a TGAQ50. 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 [15]. The samples for the ionization potential measurement were prepared as we described earlier [16].

The devices were fabricated on glass substrates and consisted of multiple layers sandwiched between the bottom indium tin oxide (ITO) anode and the top metal cathode (Al). The device structure used was ITO/PEDOT:PSS(40 nm)/host **7**, **8** or **9** doped with 10 wt% of **Ir(ppy)$_2$(acac)** (40 nm)/**SPPO13**(45 nm)/LiF (1 nm)/Al (100 nm). The PEDOT:PSS layer was deposited onto the pre-cleaned ITO substrate via spin-coating (Convac 1001 spin-coater, 2500 rpm, 30 s) and annealed at 120 °C for 45 min in air. The emissive layer was subsequently spin-coated (Convac 1001 spin-coater, 2900 rpm, 20 s) onto the PEDOT:PSS layer from chlorobenzene solution and annealed at 100 °C for 30 min in glove box. The layers of **SPPO13**, LiF and Al were deposited in a vacuum chamber at a base pressure of less than 4×10^{-4} Pa.

Luminance of the resulting OLEDs was measured using a Keithley source measurement unit (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. The EL spectra of the devices were measured using a SpectroScan PR650 spectrophotometer. All the devices were characterized without encapsulation and all the measurements were carried out under ambient condition.

2.2. Materials

1-Methyl-*9H*-pyrido[3,4-*b*]indole (harmane) (**1**), *10H*-phenoxazine (**2**), *9H*-carbazole (**3**), 4-vinylbenzyl chloride, sodium hydroxide, tetrabutylammonium hydrogen sulphate (TBAS), 2,2′-azoisobutyronitrile (AIBN) and organic solvents were purchased from Aldrich and used as received. 2,7-Bis(diphenylphosphoryl)-9,9′-spirobi[fluorene] (**SPPO13**), bis(2-phenylpyridine)(acetylacetonato)iridium(III) [**Ir(ppy)$_2$(acac)**] were purchased from Luminescence Technology Corp.

1-Methyl-9-(4-vinylbenzyl)pyrido[3,4-*b*]indole (**4**) was prepared by the reaction of 1-methyl-*9H*-pyrido[3,4-*b*]indole (harmane) (**1**) with an excess of 4-vinylbenzyl chloride under basic conditions in the presence of a phase transfer catalyst – TBAS. Harmane (**1**) (0.44 g, 2.4 mmol) and 4-vinylbenzyl chloride (0.41 g, 2.7 mmol) were stirred in acetone (20 ml) and heated to 75 °C. Then powdered sodium hydroxide (0.11 g, 2.8 mmol) and a catalytic amount of TBAS (0.02 g) were added to the mixture, and it was stirred for 4 h at 75 °C. After TLC control the mixture was filtered, the solvent was evaporated and the product was purified by column chromatography with silica gel using hexane/ethyl acetate (vol. ratio 2:1) as an eluent. Yield: 46% (0.34 g) of colourless crystals. M.p.: 177 °C (DSC).

MS (APCI$^+$, 20 V): 299.6 ([$M + 1$], 100%). ^{1}H NMR spectrum (300 MHz, CDCl$_3$, δ, m.d): 8.36 (d, 1H, $J = 6.8$ Hz, Ar); 8.17 (d, 1H, $J = 10.4$ Hz, Ar); 7.88 (d, 1H, $J = 7.2$ Hz, Ar); 7.61–7.52 (m, 1H, Ar); 7.37–7.27 (m, 4H, Ar); 6.99–6.93 (m, 2H, Ar); 6.65 (dd, 1H, $J_1 = 6.4$ Hz, $J_2 = 18.0$ Hz, $-\underline{CH}{=}CH_2$); 5.79 (s, 2H, N–CH$_2$); 5.69 (dd, 1H, $J_1 = 1.0$ Hz, $J_2 = 23.6$ Hz, $-CH{=}\underline{CH_2}$); 5.21 (dd, 1H, $J_1 = 1.0$ Hz, $J_2 = 14.4$ Hz, $-CH{=}\underline{CH_2}$); 2.89 (s, 3H, CH$_3$). Elemental analysis for $C_{21}H_{18}N_2$ % Calc.: C 84.53, H 6.08, N 9.39; % Found: C 84.59, H 6.12, N 9.41.

10-(4-Vinylbenzyl)phenoxazine (**5**) was prepared by similar procedure as described for monomer **4**. *10H*-phenoxazine (**2**) (2 g, 10.9 mmol) and 4-vinylbenzyl chloride (1.87 g, 12.3 mmol) were stirred in acetone (50 ml) and heated to 75 °C. Then powdered sodium hydroxide (0.49 g, 12.3 mmol) and a catalytic amount of TBAS (0.08 g) were added to the mixture, and it was stirred for 14 h at 75 °C. After TLC control the mixture was filtered, the solvent was evaporated and the product was purified by column chromatography with silica gel using hexane/ethyl acetate (vol. ratio 2:1) as an eluent. Yield: 62% (2.2 g) of colourless crystals. M.p.: 85 °C (DSC).

MS (APCI$^+$, 20 V): 300.5 ([$M + 1$], 100%). ^{1}H NMR spectrum (400 MHz, CDCl$_3$, δ, ppm): 7.39–7.23 (m, 4H, Ar); 6.73–6.64 (m, 7H, Ar and $-\underline{CH}{=}CH_2$); 6.32 (d, 2H, $J = 7.6$ Hz, Ar); 5.73 (d, 1H, $J = 17.6$ Hz, $-CH{=}\underline{CH_2}$); 5.22 (d, 1H, $J = 11.2$ Hz, $-CH{=}\underline{CH_2}$); 4.75 (s, 2H, N–CH$_2$). Elemental analysis for $C_{21}H_{17}NO$ % Calc.: C 84.25, H 5.72, N 4.68; % Found: C 84.19, H 5.78, N 4.61.

9-(4-Vinylbenzyl)carbazole (**6**) was prepared by similar procedure as described for monomer **4**. *9H*-carbazole (**3**) (5 g, 30 mmol) and 4-vinylbenzyl chloride (5 g, 30.4 mmol) were stirred in THF (50 ml) and heated to 75 °C. Then powdered sodium hydroxide (1.3 g, 32.5 mmol) and a catalytic amount of TBAS (0.22 g) were added to the mixture, and it was stirred for 24 h at 75 °C. After TLC control the mixture was filtered, the solvent was evaporated and the product was purified by column chromatography with silica gel using hexane/ethyl acetate (vol. ratio 5:1) as an eluent. After crystallization from the eluent yield of the product was 20% (1.7 g). M.p.: 186 °C (DSC).

MS (APCI$^+$, 20 V): 284.5 ([$M + 1$], 100%). ^{1}H NMR spectrum (300 MHz, CDCl$_3$, δ, ppm): 8.12 (d, 2H, $J = 7.8$ Hz, Ar); 7.40 (t, 2H, $J = 7.5$ Hz, Ar); 7.33 (d, 2H, $J = 8.1$ Hz, Ar); 7.29–7.05 (m, 6H, Ar); 6.62 (dd, 1H, $J_1 = 10.8$ Hz, $J_2 = 17.7$ Hz, $-\underline{CH}{=}CH_2$); 5.65 (dd, 1H, $J_1 = 0.9$ Hz, $J_2 = 17.7$ Hz, $-CH{=}\underline{CH_2}$); 5.45 (s, 2H, N–CH$_2$); 5.17 (dd, 1H, $J_1 = 0.9$ Hz, $J_2 = 10.8$ Hz, $-CH{=}\underline{CH_2}$). Elemental analysis for $C_{21}H_{17}N$ % Calc.: C 89.01, H 6.05, N 4.94; % Found: C 88.94, H 6.08, N 4.91.

Homopolymers **7**–**9** were synthesized by free radical polymerization of the vinyl monomers **4**, **5** and **6** using AIBN as an initiator. A corresponding monomer and initiator were charged in a Schlenk flask and subjected to three vacuum/nitrogen refill cycles. Anhydrous N-methyl-2-pyrrolidone (NMP) was added sequentially then the mixture was heated at 75 °C for 24 h, and poured into methanol. The crude polymer was purified by extracting with methanol for 24 h using a Soxhlet extractor. M_n, M_w and polydispersity index (PDI) of the polymers were estimated from results of gel permeation chromatography.

Poly{1-methyl-9-(4-vinylbenzyl)pyrido[3,4-*b*]indole} (**7**). 1-Methyl-9-(4-vinylbenzyl)pyrido[3,4-*b*]indole (**4**) (0.32 g, 1.1 mmol) was polymerized in NMP (0.5 ml) using AIBN (6 mol%, 10.4 mg) as initiator. After precipitation and extraction yield of the product was 63% (0.2 g). $M_w = 8370$, $M_n = 5900$. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, δ, ppm): 8.31–8.05 (m, 1H, Ar); 8.02–7.78 (m, 1H, Ar); 7.77–7.47 (m, 1H, Ar); 7.24–6.60 (m, 3H, Ar); 6.50–5.70 (m, 4H, Ar); 5.51–4.81 (m, 2H, N–CH$_2$); 2.74–2.26 (m, 3H, CH$_3$); 1.71–1.24 (m, 1H, $-\underline{CH}-CH_2-$); 1.17–0.72 (m, 2H, $-CH-\underline{CH_2}-$). Elemental analysis for $(C_{21}H_{18}N_2)_n$ % Calc.: C 84.53, H 6.08, N 9.39; % Found: C 84.49, H 6.12, N 9.32.

Poly[10-(4-vinylbenzyl)phenoxazine] (**8**). One gram of 10-(4-vinylbenzyl)phenoxazine (**5**) (3.2 mmol) was polymerized in NMP (1 ml) using AIBN (6 mol%, 31.2 mg) as initiator. After precipitation and extraction yield of the product was 30% (0.3 g). $M_w = 13{,}400$, $M_n = 6700$. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, δ, ppm): 8.30–8.05 (m, 1H, Ar); 8.02–7.78 (m, 1H, Ar); 7.77–7.47 (m, 1H, Ar); 7.24–6.60 (m, 3H, Ar); 6.50–5.70 (m, 4H, Ar); 5.51–4.81 (m, 2H, N–CH$_2$); 2.74–2.26 (m, 3H, CH$_3$); 1.70–1.24 (m, 1H, $-\underline{CH}-CH_{2}-$); 1.17–0.72 (m, 2H, $-CH-\underline{CH_2}-$). Elemental analysis for $(C_{21}H_{17}NO)_n$ % Calc.: C 84.25, H 5.72, N 4.68; % Found: C 84.17, H 5.81, N 4.62.