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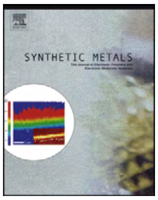

Polyethers containing 2-phenylindol-1-yl moieties as host materials for light emitting diodes

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ABSTRACT

Oxetane monomers and polyethers containing electroactive 2-phenylindol-1-yl or 3-(2-phenylindol-1-yl)carbazol-9-yl fragments were synthesized and characterized by NMR spectroscopy and elemental analysis. The polymers represent amorphous materials of high thermal stability with glass transition temperatures of 94–179 °C and thermal decomposition starting at temperatures above 400 °C. The electron photoemission spectra of layers of the synthesized polymers showed ionization potentials of 5.7–5.8 eV. The polymers were tested as host materials in phosphorescent OLEDs with iridium(III)[bis(4,6-difluorophenyl)-pyridinato-*N*,*C*2′]picolinate as the guest. The device based on polymer containing 2-phenylindol-1-yl fragments exhibited the best overall performance with a driving voltage of 5.9 V, maximum power efficiency of 8.46 lm/W and maximum brightness of 718 cd/m^2.

1. Introduction

Improvements in organic light emitting diodes (OLEDs) performance over the past decade have resulted in commercially available products. Organometallic small molecule phosphor-doped devices have demonstrated by far the highest efficiency [1–3]. In phosphorescent devices, to reduce quenching associated with relatively long excited-state lifetimes of triplet emitters, triplet–triplet annihilation etc., 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 blue phosphorescent OLEDs. For electrophosphorescence 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- and indole-based derivatives demonstrate rather large triplet energies and are potential host materials for blue electro-phosphorescent devices [7–10]. Here, we report the electroactive polymers containing pendent 2-phenylindol-1-yl or 3-(2-phenylindol-1-yl)carbazol-9-yl fragments. The polymeric hosts can be suitable for preparation of large area devices.

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

The molecular weights of polymers were determined by a gel permeation chromatography (GPC) system including GMH$_{\text{HR}}$-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 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 (I_{p}) of the materials were measured by the electron photoemission in air method, similar to the method described in [11]. The samples for the ionization potential measurement were prepared by the earlier reported procedure [12]. The materials were dissolved in THF and were 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 elim-

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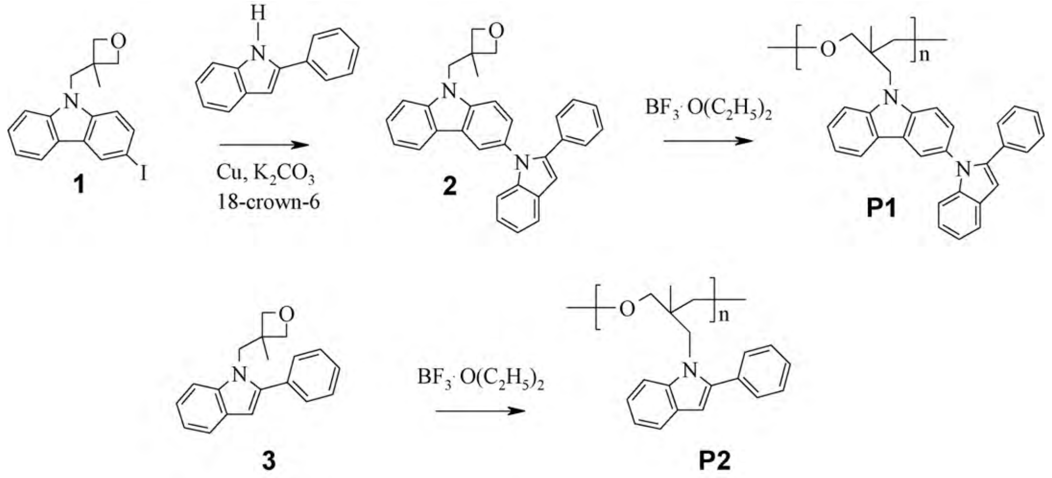

Scheme 1.

inate 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 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)/**P1** or **P2** doped with 10–22 wt% of **Firpic** (250 Å)/TPBi (500 Å)/LiF (5 Å)/Al (1500 Å), where the conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was used as the hole-injection layer [13], **P1** or **P2** doped with the blue phosphorescent iridium(III)[bis(4,6-difluorophenyl)-pyridinato-*N*,*C*2′]picolinate (**FIrpic**) was used as the emitting layer [7,8,14], 1,3,5-Tris(2-*N*-phenylbenzimidazolyl)benzene (TPBi) was used as the electron-transport layer and LiF was used as the electron-injection layer [15].

The luminance and CIE chromatic coordinates of the resulting OLEDs were measured using a Minolta CS-100 luminance meter. 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 mm^2 and only the luminance in the forward direction was measured.

2.2. Materials

2-Phenyl-1H-indole, copper powder, 18-crown-6, $BF_3 \cdot O(C_2H_5)_2$, potassium carbonate 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.

3-Iodo-9-(3-methyloxetan-3-ylmethyl)carbazole (**1**) was prepared by the reaction of 3-iodo-9H-carbazole with large excess of 3-bromomethyl-3-methyloxetane under basic conditions in the presence of a phase transfer catalyst. The synthesis was described earlier [16].

3-(2-Phenylindol-1-yl)-9-(3-methyloxetan-3-ylmethyl)carbazole (**2**): 1.2 g (3.1 mmol) of 3-iodo-9-(3-methyloxetan-3-ylmethyl)carbazole (**1**), 1.84 g (9.4 mmol) of 2-phenylindoline, 3.05 g (22.12 mmol) of powdered potassium carbonate, 0.79 g (12.64 mmol) of copper powder and 0.16 g (0.63 mmol) of 18-crown-6 were stirred in 7 ml of *o*-dichlorobenzene at 170 °C under nitrogen for 18 h. After TLC control the copper and inorganic salts were filtered off and the solvent was removed by distillation. After precipitation into hexane the crude product was purified by silica gel column chromatography using mixture of ethyl acetate and hexane (vol. ratio 1:3) as an eluent. Yield: 0.6 g (42.5%) of white crystals. M.p.: 152–154 °C. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 8.07–7.98 (m, 2H, Ar), 7.72–7.13 (m, 15H, Ar), 4.74 (d, 2H, CH_2 of oxetane ring, *J* = 6 Hz), 4.42 (s, 2H, CH_2N), 4.35 (d, 2H, CH_2 of oxetane ring, *J* = 6 Hz), 1.46 (s, 3H, CH_3). IR (KBr, ν, cm^{-1}): 3054 (aromatic C–H), 2929; 2853 (aliphatic C–H), 1490; 1456 (C–N), 977 (C–O–C in oxetane ring), 746, 697 (CH=CH of monosubstituted benzene). Elemental analysis for $C_{31}H_{28}N_2O$ % Calc.: C 83.75, H 6.35, N 6.30, O 3.60; % Found: C 83.71, H 6.43, N 6.36.

1-(3-Methyloxetan-3-ylmethyl)-2-phenylindole (**3**) was prepared by the reaction of 2-phenyl-1H-indole with large excess of 3-bromomethyl-3-methyloxetane by the published procedure [17].

Poly{oxy[2-methyl-2-(3-[2-phenylindol-1-yl]carbazol-9-yl) methylpropylene]} (**P1**) of 3-(2-Phenylindol-1-yl)-9-(3-methyl-3-oxetanylmethyl)carbazole (**2**) (0.44 g, 0.98 mmol) was polymerized in 2 ml of 1,2-dichlorethane using $BF_3 \cdot O(C_2H_5)_2$ (0.004 g, 0.032 mmol) as initiator. The 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: 0.25 g (56%) of white amorphous powder. $M_w = 18{,}940$, $M_n = 5080$. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 8.36–6.88 (m, 17H, Ar), 4.55–3.08 (m, 6H, 2× CH_2 and CH_2N), 1.3–0.97 (m, 3H, CH_3). IR (KBr, ν, cm^{-1}): 3051 (aromatic C–H), 2870 (aliphatic C–H), 1491; 1465 (C–N), 1230, 1096 (C–O), 760, 746 (CH=CH). Elemental analysis for $(C_{31}H_{28}N_2O)_n$ % Calc.: C 84.13, H 5.92, N 6.33, O 3.62; % Found: C 84.11, H 6.03, N 6.26.

Poly{oxy[2-methyl-2-(2-phenylindol-1-yl)methylpropylene]} (**P2**) was prepared by cationic polymerization of 1-(3-methyloxetan-3-ylmethyl)-2-phenylindole (**3**) using $BF_3 \cdot O(C_2H_5)_2$ as an initiator by the same procedures as described for polymer **P1**. $M_w = 1440$, $M_n = 880$. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm): 8.09–7.05 (m, 8H, Ar), 6.75 (s, 2H, Ar), 4.42–4.16 (m, 2H, N–CH_2–), 3.51–3.23 (m, 4H, O–CH_2–C), 1.13–0.85 (m, 3H, CH_3). IR (KBr, ν, cm^{-1}): 3424 (OH, br); 3049 (aromatic C–H); 2964, 2932, 2875 (aliphatic C–H); 1598 (N–C=C); 1483, 1453 (N–C); 1099 (C–O); 833, 749, 723 (CH=CH). Elemental analysis for $(C_{20}H_{23}NO)_n$ % Calc.: C 81.87, H 7.90, N 4.77, O 5.45; % Found: C 81.91, H 8.02, N 4.65.