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Novel Red Electroluminescent Polymers Derived from Carbazole and 4,7-Bis(2-thienyl)-2,1,3-benzothiadiazole

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Experimental Part

Materials

Carbazole, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 2,1,3-benzothiadiazole, and 2-ethylhexyl bromide were obtained from Aldrich Co. and used without further purification. Thiophene, tributylchlorostannane, and $PdCl_2(PPh_3)_2$ were purchased from Acros Co. Tetrakis(triphenylphosphane)palladium(0) obtained from TCI Co. was stored in a dry box under inert conditions to prevent oxidation of palladium(0). THF was dried over sodium and benzophenone. Compounds **1**-**4** were synthesized according to published procedures.

Syntheses

4,7-(Dithien-2-yl)-2,1,3-benzothiadiazole (**6**)

To a solution of **4** (2 g, 6.8 mmol) and tributyl(2-thienyl)stannane (6.1 g, 16.4 mmol) in THF (50 ml), $PdCl_2(PPh_3)_2$ (97 mg, 2 mol-%) was added. The mixture was refluxed under a nitrogen atmosphere for 3 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, CH_2Cl_2/hexane 1:1). Recrystallization from ethanol gave **6** (1.8 g, 88%) as red needles; m.p. 124-125 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (dd, 2 H), 7.87 (s, 2 H), 7.46 (dd, 2 H), 7.21 (dd, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.2, 126.4, 127.2, 127.9, 128.4, 139.8, 153.0.

4,7-Bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (**7**)

To a mixture of chloroform (52 ml) and acetic acid (52 ml), **6** (2 g, 6.67 mmol) was added under nitrogen. After complete dissolution of the solid, *N*-bromosuccinimide (2.5 g, 14.01 mmol) was added as one portion. The reaction mixture was stirred at room temperature overnight and the resulting dark red precipitate was removed by filtration and recrystallized from *N*,*N*-dimethylformamide to give **7** (1 g, 33%) as shiny red crystals; m.p. 251-252 ºC.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81 (dd, 2 H), 7.78 (s, 2 H), 7.15 (dd, 2 H).

Copolymers PCzDBT

Three copolymers with different compositions were synthesized from various [HCz]/[DBT] starting molar ratios: 99:1 (PCzDBT1), 95:5 (PCzDBT5), 80:20 (PCzDBT20). A mixture of **3**, **7**, **2** and $Pd(PPh_3)_4$ (1.0 mol-%) was added to a mixture of toluene and a 2 M aqueous solution of sodium carbonate. The mixture was stirred at 85-90 ºC for 72 h under argon. After the mixture had cooled to room temperature, it was poured into stirred methanol. The resulting solid was collected by filtration, and washed with methanol, water and methanol. The polymer was further purified by stirring in acetone for 24 h to remove oligomers and catalyst residues. The resulting product was dried under reduced pressure at room temperature. Red copolymers were obtained in 35-70% yield.

PCzDBT5: Found N 4.58, S 0.90.

PCzDBT20: Found N 4.68, S 5.63.

PCzDBT20: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.32-8.54, 7.88, 7.74, 7.44-7.12, 4.09, 2.17, 1.25-1.67, 0.88.

Copolymer compositions were calculated by means of elemental analysis (nitrogen and sulfur). The results are summarized in Table 1.

Table 1. Compositions of PCzDBT copolymers, as calculated from elemental analysis.

Copolymers	HCz/DBT in feed composition	HCz/DBT in the material
PCzDBT5	95:5	97:3
PCzDBT20	80:20	79:21

The number-average molecular weights of PCzDBT copolymers are listed in Table 2.

Table 2. Molecular weights of PCzDBT copolymers.

Copolymer	$M_n \times 10^{-3}$ g/mol	$M_w \times 10^{-3}$ g/mol	M_w/M_n
PCz	3.8	5.8	1.52
PCzDBT1	3.6	4.9	1.36
PCzDBT5	5.6	7.6	1.36
PCzDBT20	4.3	5.4	1.26

Measurements

^{1}H and ^{13}C NMR spectra were recorded on Varian Inova 500 and Bruker DRX 400 spectrometers in deuterated chloroform at 298 K. Number-average (M_n) and weight-average (M_w) molecular weights were determined with a Waters GPC 2410 in THF using polystyrene

standards for calibration. Elemental analysis was performed on a Vario EL elemental analyzer (Elementar Co.). UV-vis absorption spectra of spin coated films on quartz plates were recorded on a HP8453 (Agilent). Cyclic voltammetry was measured on a CHI660A electrochemical workstation with platinum electrodes at a scan rate of 50 mV/s against a calomel reference electrode in an 0.1 M anhydrous nitrogen-saturated solution of tetrabutylammonium hexafluorophosphate/propylene carbonate. PL and EL spectra were recorded with a CCD spectrograph (Intraspec IV, Oriel Co.). PL efficiencies of the copolymers in solid thin films on quartz substrates were measured with an integrating sphere (IS80, LabSphere), together with a digital photometer (S370, UDT), according to the method described by Greenham et al.[a] Excitation of the 325 nm line of a HeCd laser (OmniChrome Co.) was used for measuring both PL spectra and PL efficiency.

Device Fabrication

LEDs were fabricated on pre-patterned indium tin oxide (ITO) with sheet resistance of 20 Ω/□. The substrate was cleaned subsequently with acetone, detergent, deionized water and isopropyl alcohol using ultrasonication. Oxygen plasma treatment was applied for 10 min as the final step to improve the contact angle just before film forming. A layer of poly(ethylene dioxythiophene) doped with poly(styrene sulfonate) (PEDOT/PSS) 50 nm thick was spin coated onto the ITO glass from aqueous solution (Baytron P 4083, Bayer Co.), aiming to improve hole injection and avoid leaking. Solutions of the PCzDBT copolymers in toluene were prepared in a dry box under nitrogen and spin coated on top of the ITO/PEDOT/PSS surface. Solution blending was

[a]See: N.C. Greenham, I.D.W. Samuel, G.R. Hayes, R.T. Phillips, Y.A.R.R. Kessener, S.C. Moratti, A.B. Holmes, R.H. Friend, *Chem. Phys. Lett.* **1995**, *241*, 89.

performed by mixing and stirring calculated volumes of solutions of host and guest polymers in toluene. Typical thickness of the emitting layer was 70-80 nm. A thin layer of barium as an electron injection cathode and, subsequently, 200 nm of aluminium protection layers were thermally deposited by vapor deposition through a mask at a base pressure below 2×10^{-4} Pa. The EL layer spin coating process and device performance tests were taken within a glove box (VAC Co.) with nitrogen circulation. *I-U* and luminance characteristics were tested with a calibrated Si photodiode driven by a Keithley236 source-measure meter and voltammeter. External quantum efficiencies were verified by measurements in the integrating sphere (removed from the glove box after encapsulation with epoxy and cover glass).