

NOVEL RED LIGHT-EMITTING POLYMERS BASED ON 2,7-CARBAZOLE AND THIOPHENE DERIVATIVES*

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Abstract A series of conjugated copolymers derived from 9-ethylhexyl-2,7-carbazole (Cz) and 4,7-di(4-hexylthien-2-yl)-2,1,3-benzothiadiazole (DHTBT) was synthesized by Suzuki polycondensation. The photo- and electro-luminescent properties of these polymers were investigated. Efficient energy transfer from the Cz segment to the DHTBT unit occurs even if the DHTBT content as low as 1 mol%. PL emission was red-shifted significantly from 645 nm to 700 nm with the increase in DHTBT content by 1–50 mol%. PL efficiencies decreased with the increase in DHTBT content in the polymers from 55% for PCzDHTBT1 gradually down to 7% for PCzDHTBT50. EL emission of these polymers red-shifted from 640 nm to 690 nm when the DHTBT content increased from 1 mol% to 50 mol%. The highest external quantum efficiency was 1.67% for PCzDHTBT25 with the maximum luminescence of 870 cd/m² in the device configuration of ITO/PEDOT:PSS/polymer/PFN/Ba/Al. The enhancement of device performances could be due to the improved electron injection by inserting the amino-containing polyfluorene (PFN) layer. These polymers are promising candidates as a red emitter in the full-color polymer light emitting diodes (PLEDs).

Keywords: 2,7-Carbazole; Thiophene derivatives; Red light-emitting polymer.

INTRODUCTION

Conjugated polymers are extensively investigated by both academic and industrial laboratories^[1] because of their great potential for optoelectronic applications as light-emitting diodes^[2], chemo- and biosensors^[3], solar cells^[4], etc. Depending on the target applications, different conjugated building blocks, such as thiophene^[5], *p*-phenylene-vinylene^[6] and fluorene moieties^[7], have been utilized. As far as the research of active materials in light-emitting diodes is concerned, polymers derived from fluorene have been one of the most extensively studied materials because of their excellent solubility, good film-forming property, high luminescence quantum yield and color tunability^[8]. As a close analog of polyfluorene, carbazole-based polymers were widely used as hole transport materials and active materials in light-emitting diodes^[9]. Of the great number of papers related to polycarbazole^[10], only a few papers reported the syntheses and properties of 2,7-carbazole-based polymers^[11]. Nevertheless, this type of materials could be very interesting to electroactive and photoactive devices, for the carbazole units linked at the 2,7-positions should lead to a longer conjugation length than any other known carbazole derivative^[12, 13].

Morin *et al.* reported the first synthesis of homopolymers and copolymers derived from *N*-alkyl-2,7-

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carbazoles^[14]. Light-emitting devices fabricated from poly(*N*-alkyl-2,7-carbazole) derivatives^[15] in the configuration: ITO/LiF/PEHC+TPD/ Bu-PBD/LiF/Al/Ag emit blue light peaked at 432–452 nm with a maximum luminance of 372 cd/m². 2,7-Carbazole-based alternating copolymers, poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-2,3-diheptyl-5,8-quinoxaline) and poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-2,2'-diiodo-3,3',4'',3'''-tetramethyl-3'',4''-dihexyl-2,2':5',2'':5'',2''':5''',2'''-quinoxathiophene-1'',1''-dioxide) giving off green and red light emission were also synthesized. The PL spectra of the copolymers show peak emission of 502 nm and 671 nm in solid films, and the fluorescence quantum yield are respectively 83% and 25% in solution^[14]. Lately, the synthesis of highly conjugated 2,7-carbazole-based polymers has been developed and an extensive characterization of their electrochemical properties was reported^[16–19]. However, the EL properties of this type of polymers was not fully investigated^[9].

Recently, a series of copolymers based on fluorene and 4,7-di(4-hexylthien-2-yl)-2,1,3-benzothiadiazole (DHTBT) was synthesized and characterized^[20]. All the copolymers emit saturated red light. The alkyl side chain in the 4-position of both thiophene rings gives the material a good solubility. More important, the PL efficiencies of such copolymers are significantly enhanced in the solid state in comparison with its unsubstituted analogue, PFO-DBT^[21]. For the synthesis of red light emitters, DHTBT is a good candidate as a narrow band gap comonomer. Unfortunately, the copolymers derived from 2,7-carbazole and DHTBT have not been reported so far.

In this paper, a series of red light-emitting polymer derived from Cz and DHTBT was synthesized by Suzuki polycondensation. We expect that the incorporation of Cz and DHTBT sites can improve the EL efficiency of the polymers due to the good hole transportability of Cz segment. Devices based on these copolymers were fabricated and optimized. A layer of PFN was used in the diodes to improve the electron injection.

EXPERIMENTAL

Materials and Measurement

All reagents, unless otherwise specified, were purchased from Aldrich, TCI, and Acros and were used as they were received. All solvents were carefully dried and purified in a nitrogen flow. All manipulations involving air-sensitive reagents were performed in a dry argon atmosphere. ¹H- and ¹³C-NMR spectra were recorded on Bruker DRX 300 in deuterated chloroform solution. Number-average (*M_n*) and weight-average (*M_w*) molecular weights were determined by a Waters GPC 2410 in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. The elemental analysis was performed on Vario EL elemental analysis instrument (ELEMENTAR Co.). UV-Vis absorption spectra were recorded on a HP 8453 spectrophotometer. Cyclic voltammetry was measured on a Potentiostat/Galvanostat model 283 electrochemical workstation (Princeton Applied Research) at a scan rate of 50 mV/s with a nitrogen-saturated solution of 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile (CH₃CN), respectively with platinum and saturated calomel electrodes (SCE) as the working and reference electrodes. The deposition of polymers on the electrode was done by the evaporation of a dilute chloroform solution. The PL quantum yields were determined in integrating sphere IS080 (Labsphere) with 405 nm excitation of UV diode laser (CL-2000, crystal laser). PL spectra were determined by Instaspec 4 CCD spectrophotometer (Oriel) of 325 nm line of the HeCd laser.

Monomers Synthesis

4,7-Bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (6) was prepared following the published procedures^[20]. ¹H-NMR (300 MHz, CDCl₃, δ): 7.75 (s, 2H), 7.69 (s, 2H), 2.63 (m, 4H), 1.67 (m, 4H), 1.33–1.40 (m, 12H), 0.90 (t, 6H). ¹³C-NMR (100 MHz, CDCl₃, δ): 126.15, 126.38, 127.21, 127.90, 128.42, 139.75, 153.02. Element Anal. Calcd for C₂₆H₃₀N₂S₃Br₂: C, 49.84%; H, 4.79%; N, 4.47%; S, 15.34%; Br, 25.26%. Found: C, 50.61%; H, 5.26%; N, 4.37%; S, 14.86%; Br, 24.9%.

4,4'-Dibromo-2,2'-dinitrobiphenyl (1)^[22]

In a 500 mL three-necked flask, a mixture of 2,5-dibromonitrobenzene (50 g, 179 mmol) and activated copper

powder (27.8 g, 434 mmol) were added to 180 mL of DMF and stirred for 3 h at 120°C in N₂. After cooling to the room temperature, 240 mL of toluene was added. The mixture was stirred for a few minutes before the brown residue was filtered off. The organic layer was washed with water and brine, the solution dried with MgSO₄, and the solvent evaporated at a reduced pressure. Recrystallization from ethanol yielded 28.8 g (80 %) of **1** as a light brown solid. ¹H-NMR (300 MHz, CDCl₃, δ): 7.15 (d, *J* = 8.22 Hz, 2H), 7.82 (dd, *J*₁ = 8.20 Hz, *J*₂ = 2.00 Hz, 2H), 8.38 (d, *J* = 2.00 Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃, δ): 147.40, 136.63, 132.04, 131.97, 128.09, 122.93 MS: *m/z* ([M+]) 402.

4,4'-Dibromo-2,2'-diaminobiphenyl (**2**)^[22]

A mixture of **1** (12.0 g, 29.9 mmol), 60 mL of concentrated HCl and 100 mL of ethanol were stirred, SnCl₂ (48 g, 355.5 mmol) were added. The reaction mixture was heated to reflux for 12 h. The mixture was poured into 300 mL of cold water, and 2 mol/L NaOH solution was added until pH 8 was reached. The solution was extracted several times with diethyl ether. The organic layer was washed with water and dried with MgSO₄ and the solvent was evaporated. Recrystallization from ethanol yielded **2** 8.67 g (85%) of light yellow solid. ¹H-NMR (300 MHz, CDCl₃, δ): 3.78 (brs, 4H), 6.92 (s, 6H); ¹³C-NMR (100 MHz, CDCl₃, δ) : 145.41, 132.27, 122.74, 122.08, 121.71, 118.17. MS: *m/z* ([M+]) 342.

2,7-Dibromocarbazole (**3**)^[22]

A mixture of **2** (6 g, 17.5 mmol) and 60 mL of concentrated H₃PO₄ were refluxed at 190°C for 24 h in N₂. After cooling to the room temperature, the crude product was filtered off and thoroughly washed with water. The residue was dissolved into toluene and filtered over silica gel. After the solvent was evaporated, the product was recrystallized from toluene/hexane (10:1). Yield: 3.5 g (61%) of a white solid. ¹H-NMR (300 MHz, CDCl₃, δ): 7.36 (dd, *J*₁ = 1.67 Hz, *J*₂ = 1.67 Hz, 2H), 7.58 (d, *J* = 1.63 Hz, 2H), 7.88 (d, *J* = 8.32 Hz, 2H), 8.09 (brs, N—H, 1H). ¹³C-NMR (100 MHz, CDCl₃, δ): 140.27, 123.30, 121.77, 121.46, 119.74, 113.82 MS: *m/z* ([M+]) 325.

2,7-Dibromo-9-ethylhexylcarbazole (**4**)^[23]

In a 150 mL three-necked flask, 60 mL of THF(dry) and 2.4 g of NaH (60% in mineral oil) were purged by continuous nitrogen flow, then 13 g of 2,7-dibromocarbazole was slowly added, and then the mixture was stirred. 1 h later, 9.26 g of 1-bromo-2-ethylhexane was added dropwise. The mixture was refluxed for 12 h. After cooling to the room temperature, 60 mL of water was added slowly, and then the solution was extracted with methylene chloride. The extracted solution was washed with brine and water, and dried with anhydrous MgSO₄. After the solvent was evaporated, the residue was purified by column chromatography on silica gel using ethyl acetate-hexane (1:10) as the eluent to yield 15.2 g white crystals in 87% yield. ¹H-NMR (300 MHz, CDCl₃, δ): 8.33 (d, *J* = 8.28 Hz, 2H), 7.96 (d, *J* = 1.53 Hz, 2H), 7.78 (dd, *J*₁ = 8.28 Hz, *J*₂ = 1.59 Hz, 2H), 4.49 (dd, *J*₁ = 3.48 Hz, *J*₂ = 3.03 Hz, 2H), 2.44 (t, 1H), 1.80 (m, 8H), 1.73 (m, 6H). ¹³C-NMR (100 MHz, CDCl₃, δ): 141.83, 122.51, 121.42, 119.65, 112.29, 112.29, 47.66, 39.13, 30.77, 28.55, 24.32, 23.04, 14.04, 10.90 MS: *m/z* ([M+]) 437.

9-Ethylhexyl-2,7-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)carbazole (**5**)^[23]

6 g (13.7 mmol) of 2,7-dibromo-9-ethylhexylcarbazole was dissolved in absolute THF in argon. The solution was cooled to −78°C before 20.8 mL of *n*-BuLi (1.6 mol/L solution in hexane) was added dropwise. The reaction mixture was stirred for 2 h before 12.5 mL (61.7 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added. The reaction mixture was allowed to be warmed to the room temperature and stirred for 24 h before it was poured into ice-water. The solution was extracted with diethyl ether and the organic layer was washed with brine and dried with MgSO₄ before the solvent was evaporated. The residue was purified by column chromatography with hexane/ethyl acetate (10:1) as eluent yielded 4.58 g (63%) of white crystals. ¹H-NMR (300 MHz, CDCl₃, δ): 8.14 (d, *J* = 7.77 Hz, 2H), 7.91(s, 2H), 7.69 (d, *J* = 7.80 Hz, 2H), 4.26 (t, 2H), 1.37 (m, 33H), 0.91(m, 6H). ¹³C-NMR (100 MHz, CDCl₃, δ): 140.91, 125.00, 124.72, 119.96, 115.64, 83.77, 47.14, 39.20, 30.62, 28.48, 24.97, 24.93, 24.29, 23.07, 14.18, 11.01 MS: *m/z* ([M+]) 531.

Synthesis of Polymer

The synthesis of the copolymers was carried out using palladium-catalyzed Suzuki polycondensation. Purified 2,7-dibromo-9-ethylhexylcarbazole (4), 9-ethylhexyl-2,7-(4,4,5,5-tetramethyl[1,3,2] dioxaborolan-2-yl)-carbazole (5), 4,7-bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (6) and $(\text{PPh}_3)_4\text{Pd}$ (0) (0.5–1.5 mol%) and several of drops of Aliquat 336 were dissolved in a mixture of toluene and aqueous solution of 2 mol/L Na_2CO_3 . The mixture was first put in the nitrogen atmosphere and was refluxed with vigorous stirring for two days. Then 9-ethylhexyl-2,7-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)carbazole and 2-dibromo-9-ethylhexylcarbazole were added to end-cap the polymer chain. The whole mixture was poured into methanol. The resulting solid was filtered and washed with acetone to remove oligomers and catalyst residues. The resulting polymers were soluble in THF, CHCl_3 and toluene. Yield: 55%–70%.

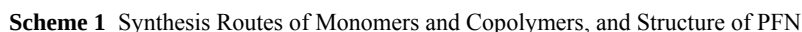
NMR results: for PCzDHTBT1 ^1H -NMR (300 MHz, CDCl_3 , δ): 8.26–8.16, 8.00–7.97, 7.77–7.57, 7.46–7.36, 4.30, 2.26–2.16, 1.58–1.40, 1.33–1.28, 1.03–0.88. For PCzDHTBT5 ^1H -NMR (300 MHz, CDCl_3 , δ): 8.25–8.16, 8.0–7.96, 7.76–7.53, 7.46–7.36, 4.29, 2.90, 1.88–1.79, 1.58–1.44, 1.33–1.28, 1.01–0.89. For PCzDHTBT10 ^1H -NMR (300 MHz, CDCl_3 , δ): 8.25–8.14, 8.0–7.93, 7.77–7.48, 7.46–7.36, 4.29, 2.90, 1.81–1.70, 1.58–1.28, 1.01–0.91. For PCzDHTBT15 ^1H -NMR (300 MHz, CDCl_3 , δ): 8.24–8.15, 8.00–7.93, 7.77–7.64, 7.59–7.28, 4.30, 2.90, 2.38–2.19, 1.87–1.81, 1.58–1.28, 1.02–0.90. For PCzDHTBT25 ^1H -NMR (300 MHz, CDCl_3 , δ): 8.24–8.14, 7.77–7.58, 7.48–7.28, 4.27, 2.90, 2.38–2.19, 1.81, 1.58–1.28, 1.04–0.91. For PCzDHTBT50: ^1H -NMR (300 MHz, CDCl_3 , δ): 8.35 (m, 4H), 7.90 (m, 3H), 7.56 (m, 2H), 7.28 (s, 1H), 4.23 (m, 2H), 2.88 (s, 4H), 2.16 (m, 1H), 1.79 (m, 4H), 1.35–1.43 (m, 24H), 0.90–0.98 (m, 8H). ^{13}C -NMR (100 MHz, CDCl_3 , δ): 152.71, 141.55, 139.77, 137.35, 131.75, 125.68, 122.57, 120.79, 109.65, 47.67, 39.49, 31.79, 31.02, 29.73, 24.56, 22.73, 14.14, 11.07.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymers

The synthetic routes of the monomers and polymers are shown in Scheme 1. Syntheses of 4-(hexyl-2-thienyl)stannane, 4,7-di(4-hexyl-2-thienyl)-2,1,3-benzothiadiazole, and 4,7-bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole have been reported in the literature^[20]. For compounds, 4,4'-dibromo-2,2'-dinitrobiphenyl, 4,4'-dibromo-2,2'-diaminobiphenyl, 2,7-dibromo-carbazole, 2,7-dibromo-9-ethylhexylcarbazole and 9-ethylhexyl-2,7-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)carbazole, slightly different synthetic procedures were utilized to improve the yield^[22, 23]. In the synthesis of 4,4'-dibromo-2,2'-diaminobiphenyl, we used SnCl_2 as a reductant instead of Sn and HCl, and the yield was improved to 85%.

Copolymers were prepared from 9-ethylhexyl-2,7-(4,4,5,5-tetramethyl[1,3,2] dioxaborolan-2-yl)carbazole (Cz) and narrow-band-gap comonomer 4,7-bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (DHTBT) by Suzuki polycondensation (Scheme 1). The comonomer feed molar ratios of Cz to DHTBT are 99:1, 95:5, 90:10, 85:15, 75:25 and 50:50, and the corresponding copolymers were named PCzDHTBT1, PCzDHTBT5, PCzDHTBT10, PCzDHTBT15, PCzDHTBT25 and PCzDHTBT50, respectively. At the end of polymerization, 9-ethylhexyl-2,7-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)carbazole was added to remove the bromine end groups, and 2-bromo-9-ethylhexylcarbazole was added as a monofunctional end capping reagent to remove end groups of boronic isopropyl ester because boron and bromine units could quench emission and contribute to red shift of EL emission in PLEDs^[24, 25]. The monomer molar ratios have been adjusted in order to investigate the effect of copolymer composition on the physical and optical properties. The actual molar ratio of Cz/DHTBT in the copolymer calculated from elemental analysis is close to the feed ratio, as listed in Table 1. The number-average molecule weights (M_n) of the synthesized copolymers, PCzDHTBT1 to PCzDHTBT50, were determined by gel permeation chromatography (GPC) using a polystyrene standard (Table 1). As shown in Scheme 1, the advantage of Suzuki polycondensation is that each individual narrow-band-gap unit is separated from both sides by the wide-band-gap segments for copolymers with under or equal to 50 mol% in the copolymer. In this case, the narrow-band-gap unit as an exciton trap allows most efficient intramolecular energy transfer from carbazole segment to DHTBT unit, as shown in other random copolymers synthesized via Suzuki polycondensation^[21, 26].



Polymers	M_n	M_w/M_n	Cz/DHTBT ratio	
			In feed composition	In polymers
PCz	4510	1.46	—	—
PCzDHTBT1	3560	1.25	99:1	—
PCzDHTBT5	5066	1.39	95:5	94.2:5.8
PCzDHTBT10	10509	1.20	90:10	88.6:11.4
PCzDHTBT15	7319	1.66	85:15	84.3:15.7
PCzDHTBT25	9797	1.77	75:25	72.7:27.3
PCzDHTBT50	7118	1.50	50:50	49.4:50.6

The UV-Vis absorption spectra of copolymers are shown in Fig. 1. The absorption spectra of the copolymers consist of two absorption peaks both in the solution and in solid states. The absorption peak appeared at *ca.* 370 nm in the solid films is from the Cz segment^[18]. This peak can be attributed to the π - π^* transition of carbazole segment in the copolymer. We notice that the onset of these absorption peaks in the film red-shifted 10–20 nm further than that in THF solution. This may be due to the aggregation of the Cz segment in the neighboring backbone. The intensity of absorption peaked at about 530 nm increases with increasing DHTBT content, which can be attributed to the DHTBT unit incorporated into the poly(2,7-carbazole) main chain.

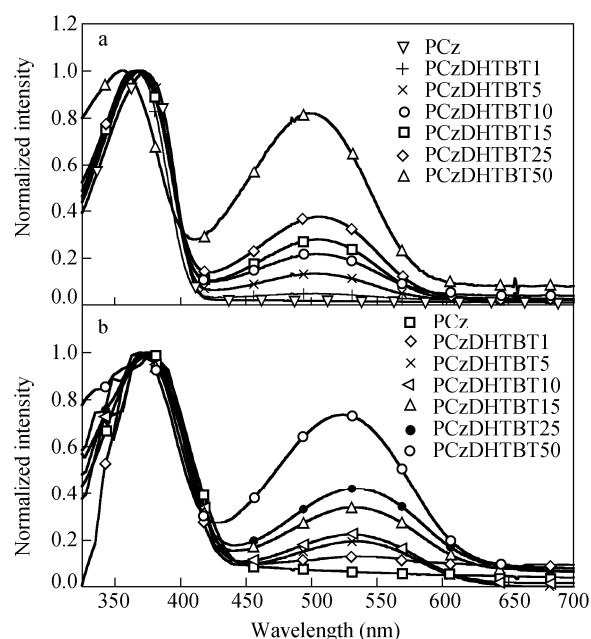


Fig. 1 UV-Vis absorption spectra for polymers in THF solution (a) and in thin film (b)

The redox behavior of the copolymers was investigated by cyclic voltammetry (CV). For copolymers, the p-doping waves were between 1.04 V to 1.19 V. Since the oxidation potential of poly(2,7-carbazole) homopolymer and DHTBT was observed typically at 0.85 V^[9], and 1.28 V^[20]. The oxidation wave observed at 1.04–1.19 V in the copolymers must be attributed to the mixture of the two oxidation processes for the carbazole and DHTBT unit. HOMO (highest occupied molecular orbital) level is calculated according to the empirical formula $(E_{\text{HOMO}}) = -(E_{\text{ox}} + 4.4) \text{ eV}^{[27]}$. LUMO level is estimated from the difference between the HOMO levels and the optical band gap. All the electrochemical data as well as calculated HOMO and LUMO levels are listed in Table 2, HOMO levels of the copolymers lying between -5.44 eV and -5.59 eV . Since the copolymer based on 2,7-carbazole has higher HOMO level than that of the PFO-DHTBT, better hole injection ability for the copolymer can be expected.

Table 2. Optical and electrochemical properties of polymers

Polymers	$\lambda_{\text{abs,max}}$ (nm)	$\lambda_{\text{PL,max}}$ (nm)	Q_{PL} (%)	E_{g}^{a} (eV)		E_{ox} (V)	HOMO (eV)	LUMO ^b (eV)
				Cz	DHTBT			
PCz	370	440	5	2.82	—	0.85	-5.25	-2.43
PCzDHTBT1	370, —	645	55	2.82	—	1.08	-5.48	-2.66
PCzDHTBT5	370, 538	668	17	2.82	1.93	1.04	-5.44	-3.51
PCzDHTBT10	377, 530	690	15	2.82	1.93	1.10	-5.50	-3.57
PCzDHTBT15	370, 530	690	17	2.85	1.91	1.14	-5.54	-3.63
PCzDHTBT25	370, 530	693	16	2.88	1.89	1.19	-5.59	-3.70
PCzDHTBT50	377, 525	700	7	2.95	1.88	1.14	-5.54	-3.66

^a Estimated from the onset wavelength of optical absorption in solid film;

^b Calculated from the onset of optical absorption of DHTBT unit

Photoluminescent Properties

Figure 2(a) shows PL spectra of PCzDHTBT copolymers in film. Emission of the Cz segment was completely quenched for copolymers with a DHTBT unit concentration as low as 1 mol%. The dominance of the emissions due to the DHTBT unit indicates that the energy transfer from Cz segment to the DHTBT unit is efficient. We note that PL peaks were red-shifted 55 nm from PCzDHTBT1 to PCzDHTBT50 with increasing DHTBT content in the polymer, as seen in other thiophene narrow band gap units, and that the red-shift is due to

molecular polarization effects between DHTBT units^[28]. This is consistent with the fact that, in Table 2, the PL efficiencies decrease with increasing the DHTBT content from 55% for PCzDHTBT50 gradually down to 7% for PCzDHTBT50. Contrast to PFODHTBT, the analog with same narrow band gap unit, PL peaks of PCzDHTBT were red-shifted 15–30 nm for the copolymer with same DHTBT content^[20].

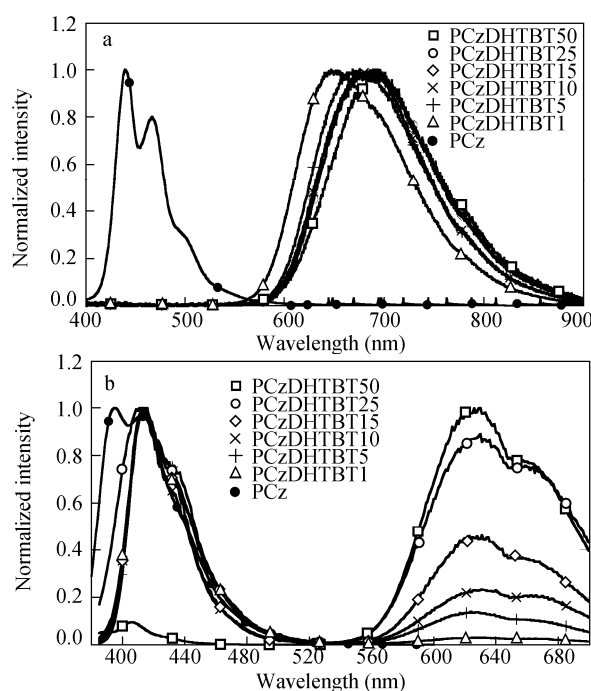


Fig. 2 PL spectra of polymers in thin films (a) and in THF solution (1×10^{-5} mol/L) (b)

Since no great red shift was observed for absorption spectra of the corresponding copolymers (Fig. 1), the great red shift in PL emission indicates that the Stokes shift increases with the increase in DHTBT content of the copolymers. The reason for the increase of Stokes shift due to increasing DHTBT units in the copolymers is probably attributed to the higher polarizability of DHTBT heterocycles, allowing greater adjustment in the excited state^[29]. Similar phenomena were observed for PFO-DHTBT copolymers^[20]. The fact that the emission of the carbazole segment completely disappeared at very low loading of narrow band gap comonomers indicates that an efficient energy transfer occurs from the carbazole segment to the DHTBT unit, which serves as a powerful trap in the copolymer chain. Excitons are confined and recombined on narrow band gap units isolated from both sides by carbazole segment and emit red light corresponding to DHTBT unit emission. Energy transfer from carbazole segments to the DHTBT unit may occur *via* the intra- or intermolecular mechanism. To elucidate the relative role of intra- and interchain energy transfer, the concentration dependence of PL spectra of the copolymers was investigated in THF solution. The Comparison in the PL spectra of the copolymers with different DHTBT contents is shown in Fig. 2(b) at a concentration of 10^{-5} mol/L (a sufficiently dilute solution to avoid strong intermolecular interaction between polymer chains). At this relatively dilute concentration PCzDHTBT50 copolymer exhibits a dominated DHTBT emission with a very small shoulder peak of carbazole segment emission. This seems to indicate that the transfer of the exciton energy from carbazole segment to the narrow-band-gap site (DHTBT) occurs mainly along the polymer chain. In other words, the efficient energy transfer from carbazole segment to DHTBT unit occurs when an intramolecular energy transfer takes place^[30, 31]. However, when the DHTBT content was less than 25 mol%, the main emission peak is in the blue region, and a shoulder peak in the red region due to DHTBT segment emission can be observed in the PL spectra, and its intensity increases with increasing DHTBT content (Fig. 2b). Compared with the PL spectra in thin films

(Fig. 2a), carbazole emission completely disappears for 1 mol% DHTBT content, which indicates that the energy transfer in such a concentration is incomplete for copolymers with low DHTBT content in the solution. The interchain energy transfer must take place in the solid-state film in order to completely quench the PL emission from carbazole segment.

Electroluminescent Properties

The EL performances of the copolymers were examined in the device configuration of ITO/PEDOT:PSS/polymer/Ba/Al and ITO/PEDOT:PSS/polymer/PFN/Ba/Al. For the same polymer, the EL emission did not vary over the different device configuration. The typical EL spectra from such devices are shown in Fig. 3. We note that, due to the introduction of a small amount of DHTBT into polycarbazole chain, EL emission of Cz segment at around 420 nm is completely quenched (Fig. 3). For devices fabricated from PCzDHTBT copolymers, starting from DHTBT content as low as 1 mol%, only a saturated red emission responsible for DHTBT unit has been observed. There are two mechanisms to explain the EL and PL emission, charge trapping and energy transfer, and both of them are very important^[32]. In PL spectra, the dominance of the emissions due to the DHTBT unit indicates that the energy transfer from Cz segment to the DHTBT unit is efficient. From Fig. 2(a) and Fig. 3, it's clearly seen that the PL spectra are similar with the EL spectra. So we guess the energy transfer plays a more important role in the EL emission. EL emissions are generally blue-shifted for 10–20 nm (Figs. 2 and 3) in comparison with the PL emission of corresponding copolymers. The same phenomenon was observed for fluorene-*co*-DHTBT polymers^[20]. The EL emission also red-shifted with increasing the DHTBT content in copolymers as the PL emission (from 640 nm for PCzDHTBT1 to 695 nm for PCzDHTBT50, Figs. 2 and 3). The red shift in EL emission with the increase in DHTBT content indicates an aggregation between DHTBT units of neighboring polymer backbone. Similar behavior was reported for the fluorine-*co*-DHTBT and 3,6-carbazole-*co*-benzothiadiazole copolymers^[20, 22].

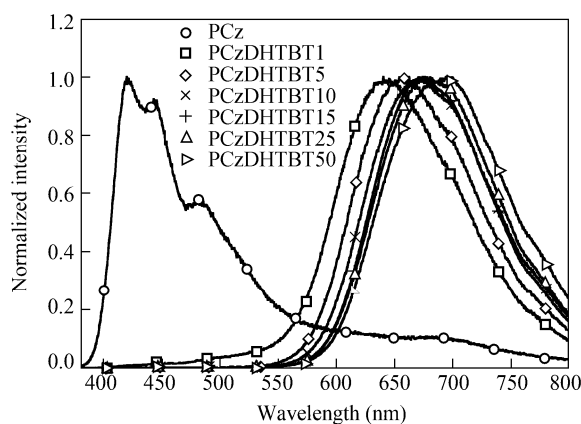


Fig. 3 EL Spectra of polymers

The device performances in configuration of ITO/PEDOT:PSS/polymer/Ba/Al are presented in Table 3. The external quantum efficiencies increase initially with the DHTBT content, up to the maximum for copolymer with 25 mol% DHTBT content. The highest external EL quantum efficiency in such a device configuration was 0.72% with a luminance of 215 cd/m² for PCzDHTBT25.

Since the carbazole based conjugated copolymer is the p-type polymer, the electron injection and transport in EL devices based on these types of conjugated polymers are usually limited by the low electron affinity and low mobility of electrons^[33]. In order to improve electron injection and transport, amino-containing polyfluorene (PFN, a new type of electron injection material in PLEDs first used by our group^[34], shown in Scheme 1) was coated on the top of EL polymer prior to Ba cathode deposition. Table 3 shows the device performances for PCzDHTBT copolymers with PFN interlayer. The highest EL external quantum efficiency reached 1.67% for

PCzDHTBT25 with the maximum luminescence of 870 cd/m². The device performance was significantly enhanced in contrast to the device without PFN interlayer, however, the turn-on voltage of these devices increased slightly. As shown in Fig. 4, the current density (J) applied field (F) curves of devices provide further insight into the roles of functional material PFN playing in the device. The increase of current density versus the applied field indicates clearly the electron-injecting character of PFN layer. Similar J - F characteristics can be observed for the devices from other copolymers (not shown here). These results suggest that the insertion of PFN between emitting layer and cathode Ba/Al effectively reduces barrier height for electron injection and enhances the electron injection, thereby leading to more balanced electron-hole current. The similar phenomenon was also reported for MEH-PPV, P-PPV, and PFO^[34–36]. The device stability is very important, especially for commercial applications. As far as the PLEDs are concerned, the thermal stability and efficiency stability with increasing voltage and current are the most important two parameters. The efforts are in progress and will be reported in a forthcoming paper.

Table 3. Device performance of polymers

Polymers	$B_{\max}$ (cd/m ²)	$V_{\text{turn on}}$ (V)	QE _{ext} (%)	LE (cd/A)
PCzDHTBT1 ^a	28	5.0	0.05	0.01
PCzDHTBT5	12	4.0	0.01	0.002
PCzDHTBT10	55	5.2	0.19	0.03
PCzDHTBT15	350	3.6	0.54	0.08
PCzDHTBT25	503	3.0	0.72	0.10
PCzDHTBT50	220	4.0	0.26	0.04
PCzDHTBT1 ^b	30	5.5	0.35	0.15
PCzDHTBT5	29	6.0	0.33	0.08
PCzDHTBT10	130	6.0	0.99	0.14
PCzDHTBT15	605	3.8	1.08	0.19
PCzDHTBT25	870	4.0	1.67	0.24
PCzDHTBT50	442	5.2	0.80	0.14

^a Device configuration: ITO/PEDOT:PSS/polymer/Ba/Al;

^b Device configuration: ITO/PEDOT:PSS/polymer/PFN/Ba/Al

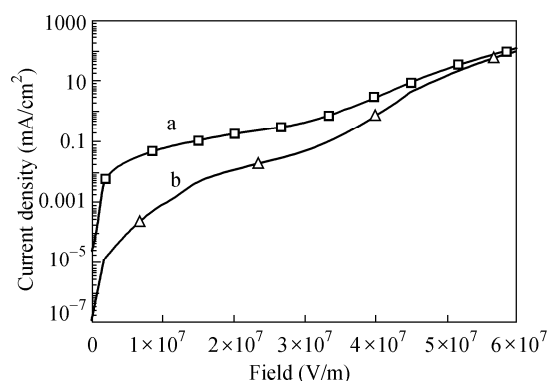


Fig. 4 J - F curves of device based on PCzDHTBT25 with PFN (a) and without PFN (b)

CONCLUSIONS

In summary, a series of red-light-emitting copolymers derived from 9-ethylhexyl-2,7-carbazole and DHTBT was synthesized by Suzuki polycondensation. Efficient energy transfer from the Cz segment to the DHTBT sites occurred even if the DHTBT concentration was as low as 1 mol%. PL emission was red-shifted significantly with increasing DHTBT content in the polymers. PL efficiencies decreased with the increase in DHTBT content in the polymers from 55% for PCzDHTBT1 gradually down to 7% for PCzDHTBT50. Double- and triple-layer

devices with these polymers showed a saturated red emission. EL emission was red-shifted from 640 nm to 690 nm with the increasing of DHTBT content in the copolymers. The highest EL external quantum efficiency reached 1.67% from PCzDHTBT25 with the maximum luminescence of 870 cd/m² in device configuration of ITO/PEDOT:PSS/polymer/PFN/Ba/Al.

REFERENCES

- Burroughes, J.H., Bradley, D.D.C., Brown, A.R., Marks, R.N., Mackay, K., Friend, R.H., Burns, P.L. and Homes, A.B., *Nature (London)*, 1990, 347: 539
- Gaylord, B.S., Heeger, A.J. and Bazan, G.C., *J. Am. Chem. Soc.*, 2003, 125: 896
- Huang, F., Hou, L.T., Wu, H.B., Wang, X.H., Shen, H.L., Cao, W., Yang, W. and Cao, Y., *J. Am. Chem. Soc.*, 2004, 126: 9845
- Sariciftci, N.S., Braun, D., Zhang, C., Srdanov, V.I., Heeger, A.J., Stucky, G. and Wudl, F., *Appl. Phys. Lett.*, 1993, 62: 585
- Pei, J., Yu, W.L., Ni, J., Lai, Y.H., Huang, W. and Heeger, A., *J. Macromolecules*, 2001, 34: 7241
- Gustasson, G., Cao, Y., Treacy, G.M., Klavetter, F., Colaneri, N. and Heeger, A.J., *Nature (London)*, 1992, 357: 477
- Fukuda, M., Sawada, K. and Yoshino, K., *J. Polym. Sci. Part A: Polym. Chem.*, 1993, 31: 2465
- Bernius, M.T., Inbasekaran, M., O'Brien, J. and Wu, W., *Adv. Mater.*, 2000, 12: 1737
- Morin, J.F., Leclerc, M., Ades, D. and Siove, A., *Macromol. Rapid. Commun.*, 2005, 26: 761
- Belletête, M., Bédard, M., Bouchard, J., Leclerc, M. and Durocher, M., *Can. J. Chem.*, 2004, 82: 1280
- Brière, J.F. and Côté, M., *J. Phys. Chem. B*, 2004, 108: 3123
- Morin, J.F. and Leclerc, M., *Macromolecules*, 2001, 34: 4680
- Morin, J.F. and Leclerc, M., *Macromolecules*, 2002, 35: 8413
- Zotti, G., Schiavon, G., Zecchin, S., Morin, J.F. and Leclerc, M., *Macromolecules*, 2002, 35: 2122
- Morin, J.F., Beaupré, S., and Leclerc, M., *Appl. Phys. Lett.*, 2002, 80: 341
- Morin, J.F., Drolet, N., Tao, Y. and Leclerc, M., *Chem. Mater.*, 2004, 16: 4619
- Morin, J.F., Boudreault, P.L. and Leclerc, M., *Macromol. Rapid. Commun.*, 2002, 23: 1032
- Yang, L., Feng, J.K., Ren, A.M. and Sun, J.Z., *Polymer*, 2006, 47: 1397
- Belletête, M., Bouchard, J., Leclerc, M. and Durocher, G., *Macromolecules*, 2005, 38: 880
- Hou, Q., Zhou, Q.M., Zhang, Y., Yang, W., Yang, R.Q. and Cao, Y., *Macromolecules*, 2004, 37: 6299
- Hou, Q., Xu, Y.S., Yang, W., Yuan, M., Peng, J.B. and Cao, Y., *J. Mater. Chem.*, 2002, 12: 2887
- Sonntag, M. and Stroehriegel, P., *Chem. Mater.*, 2004, 16: 4736
- Huang, J., Niu, Y.H., Yang, W., Mo, Y.Q., Yuan, M. and Cao, Y., *Macromolecules*, 2002, 35: 6080
- Yang, X.H., Yang, W., Yuan, M., Hou, Q., Huang, J., Zeng, X.R. and Cao, Y., *Synth. Met.*, 2003, 135-136: 189
- Yang, J., Jiang, C.Y., Zhang, Y., Yang, R.Q., Yang, W., Hou, Q. and Cao, Y., *Macromolecules*, 2004, 37: 1211
- Huang, J., Xu, Y.S., Hou, Q., Yang, W., Yuan, M. and Cao, Y., *Macromol. Rapid. Commun.*, 2002, 23: 709
- Leeuw, D.M., Simenon, M.M.J., Brown, A.R. and Einerhand, R.E.F., *Synth. Met.*, 1997, 87: 53
- Bulovic, V., Shoustikov, A., Baldo, M.A., Bose, E., Kozlov, V.G., Thompson, M.E. and Forrest, S.R., *Chemical Physics Letters*, 1998, 287: 455
- Yang, R.Q., Tian, R.Y., Hou, Q., Yang, W. and Cao, Y., *Macromolecules*, 2003, 36: 7453
- Gong, X., Moses, D., Heeger, A.J. and Xiao, S., *Synth. Met.*, 2004, 141: 17
- Gong, X., Moses, D., Heeger, A.J. and Xiao, S., *J. Phys. Chem. B*, 2004, 108: 8601
- Zhen, H.Y., Xu, W., Yang, W., Chen, Q.L., Xu, Y.H., Jiang, J.X., Peng, J.B. and Cao, Y., *Macromol. Rapid Commun.*, 2006, 27: 2095
- Wu, H.B., Huang, F., Mo, Y.Q., Yang, W., Wang, D.L., Peng, J.B. and Cao, Y., *Adv. Mater.*, 2004, 16: 1826
- Huang, F., Wu, H.B., Wang, D.L., Yang, W. and Cao, Y., *Chem. Mater.*, 2004, 16: 708
- Wu, H.B., Huang, F., Peng, J.B. and Cao, Y., *Organic Electronics*, 2005, 6: 118
- Wang, L., Liang, B., Huang, F., Peng, J.B. and Cao, Y., *Appl. Phys. Lett.*, 2006, 89: 151115