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Polyfluorenes containing pyrazine units: Synthesis, photophysics and electroluminescence

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A series of conjugated copolymers of 9,9-dioctylfluorene and symmetrical pyrazine unit (BY) were synthesized by Suzuki copolymerization and were used as novel light-emitting materials in PLEDs. Efficient energy transfer was observed in both thin film and solution. Compared with the lowest occupied molecular orbital (LUMO) energy level of the polyfluorenes homopolymer (PFO), the lower LUMO energy levels of copolymers indicated that the introduction of the BY unit would be benefit to electron injection. The turn-on voltages of their single-layer electroluminescent (EL) devices (ITO/PEDOT/polymer/LiF/Al) were at 6.1–4.0 V, which were much lower than that of PFO (7.0 V). The maximum brightness, current efficiency, and external quantum efficiency of all PFBY copolymers were higher than those of the PFO homopolymer. The single-layer device of PFBY5 was the best one in the copolymers, with a maximum brightness of 485 cd/m^2, a current efficiency of 0.29 cd/A, and an external quantum efficiency of 0.10%. The introduction of PVK and TPBI for the multilayer device of PFBY5 increased the device efficiencies, which showed a maximum brightness of 3012 cd/m^2, a maximum current efficiency of 1.81 cd/A, and an external quantum efficiency of 0.66%.

pyrazine, polyfluorenes, energy transfer, PLED

1 Introduction

Polymer light-emitting diodes (PLEDs) based on conjugated polymers have attracted a great interests of researchers due to their potential application in large-area full-color flat panel displays [1–3]. Polyfluorene and its derivatives have been widely explored as the emissive materials for PLEDs because of their high photoluminescence (PL) quantum efficiency, solution processibility, and good hole-transporting properties [4–6]. However, electron injection and transport are poor in polyfluorene homopolymers [7], which limits their PLED efficiency greatly.

The introduction of n-type molecule in copolymers is an effective method to improve electron injection properties of PLEDs, because of their lower LUMO energy levels. Polyfluorenes containing n-type units, such as benzothiadiazole, naphthoselenadiazole, oxadiazole, quinoxaline [8–11], have been reported. For example, Cao's group has synthesized a series of fluorene-*co*-dibenzothiophene-*S*,*S*-dioxide (FSO) copolymers and investigated their electrochemistry and electroluminescent performance. The n-type FSO unit lowers the LUMO energy level, balances the injection and transportation both electron and hole in the polymers, and therefore improves the EL device efficiencies. The maximum brightness (1292–6631 cd/m^2) and luminous efficiency (1.03–4.63 cd/A) of all the copolymers surpassed the PFO homopolymer [12].

In previous work, our group has synthesized a series of n-type molecules based on unsymmetrical pyrazine units (BYs) [13]. The LUMO energy levels decrease from −3.24 to −3.78 eV with an increasing number of pyrazine rings

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*Corresponding author (email: lixiang@ciac.jl.cn) and the conjugation length of the molecules. By introducing a pyrazine acceptor to the backbone of polyfluorenes, we have synthesized a series of p-n diblock conjugated copolymers. The results also demonstrated that the acceptor containing the pyrazine unit was a promising n-type building block for organic semiconductors [11].

In this work, we synthesized a series of new polyfluorenes containing the symmetrical BY unit (Chart 1) by Suzuki polymerization and studied the photophysics, electrochemical and electroluminescence properties of copolymers. A series of polyfluorene copolymers containing 1, 2, 5, and 10 mol% BY unit, denoted as PFBY1, PFBY2, PFBY5, and PFBY10. The BY unit has been proved was a strong electron acceptor in previous paper and it's LUMO energy level was −3.27 eV [13]. Thus, the introduction of BY unit will improve the electron injection property and EL performance of polymers.

2 Experimental

2.1 Materials

Pyrene-4,5,9,10-tetraones (**1**) [14], 9,9-dioctylfluorene-2-boronic acid ester (**5**) [15], 9,9-dioctylfluorene-2,7-diboronic acid ester (**6**), 9,9-dioctyl-2,7-dibromofluorene (**7**) [16] and compound **3** [13, 17] were synthesized according to the reported methods.

2.2 General experimental

Instruments

^{1}H NMR spectra data were recorded on a Bruker Avance 300-MHz NMR spectrometer in $CDCl_3$ with TMS standard. Molecular mass spectra of intermediates were measured by means of LDI-1700 MALDI-TOF mass spectroscopy. Elemental analysis was performed by Bio-Rad elemental analysis system. IR spectra were obtained on FT-IR Bruker Vertex 70 spectrometer at a nominal resolution of 2 cm^{-1}. Polymer samples were prepared to be thin films on KBr. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) on a Waters 410 instrument with polystyrene as standards and THF as eluent. Thermogravimetric analysis (TGA) measurements were performed on a Perkin-Elmer series 7 analysis systems under N_2 at a heating rate 10 °C/min. UV-vis absorption (UV) spectra were recorded with a PerkinElmer Lambda35 UV-vis Spectrometer. Photoluminescence (PL) spectra were obtained on a PerkinElmer LS50B Luminescence spectrometer. The electroluminescence (EL) spectra, Commission Internationale de L'Eclairage (CIE) coordinates, Current-Voltage and Brighness-Voltage characteristics of devices were measured with a Spectrascan PR650 spectrophotometer at the forward direction and a computer-controlled Keithley 2400 under ambient condition.

Cyclic voltammetry (CV) was performed on a Chi660b electrochemical analyzer with a three-electrode cell in 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) in dry dichloromethane solution under an argon atmosphere at a scan rate of 100 mV/s and using ferrocene as standards. A glass carbon disk (2-mm diameter) was used as working electrode with a Pt wire as the counter electrode and an Ag/AgCl electrode as the reference electrode.

EL device fabrication

The ITO glass plates were degreased in an ultrasonic solvent bath and then dried in a heating chamber at a temperature of 120 °C. The polymer light-emitting diodes with the configuration of the organic light-emitting diodes (OLED) were fabricated with the PFO and copolymers as the emissive material. The PSS-doped PEDOT was spin-coated onto the treated ITO at 3000 r/min for 1 min and heated for 1 h at 120 °C to obtain an approximate thickness of 40 nm. PVK was spin-coated from its 5 mg/mL solution in toluene to

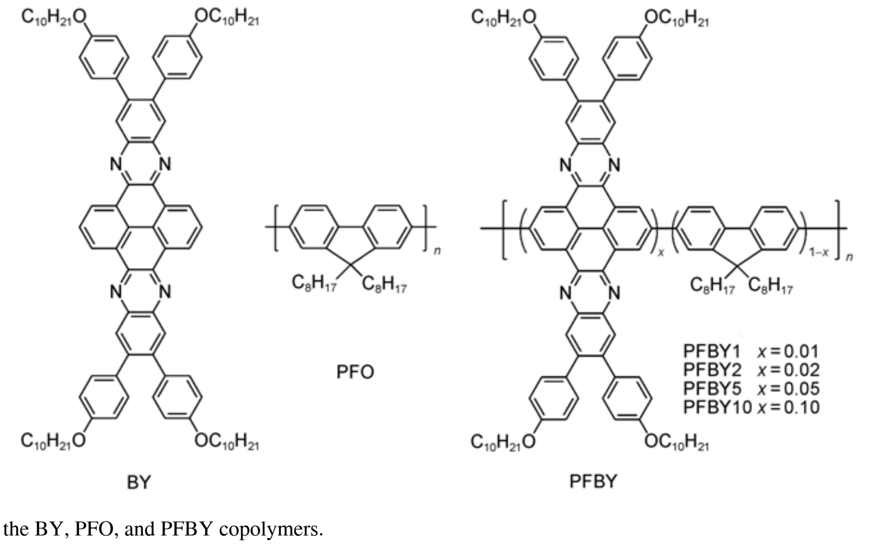


Chart 1 The structures of the BY, PFO, and PFBY copolymers.

give a 20 nm thick film on PEDOT. This film was dried in a vacuum at 80 °C for 1 h. The copolymer layer (about 70 nm) was then spin-coated onto the PVK/PEDOT/ITO-coated glass substrate in fresh toluene solution (10 mg/mL). Because of the partial solubility of PVK in toluene, the interface between PVK and the copolymers was not flat; the total thickness of the PVK/copolymer bilayers was measured instead to get the copolymer layer thickness. 20 nm thick films of TPBI were obtained by evaporation from resistively heated in a vacuum evaporator. Finally, a thin layer of LiF (1 nm) followed by a layer of aluminum (100 nm) was deposited in a vacuum thermal evaporator through a shadow mask at a pressure of $3\times10^{-4}-4\times10^{-4}$ Pa. All the devices fabrication and characterization were carried out at ambient conditions. The EL spectra, CIE coordinates, Current-Voltage and Brightness-Voltage characteristics of the devices were measured with a Spectrascan PR650 spectrophotometer at the forward direction and a computer-controlled Keithley 2400 instrument.

2.3 Monomer synthesis

*Synthesis of 2,7-dibromo-pyrene-4,5,9,10-tetraones (**2**)*

A solution of pyrene-4,5,9,10-tetraones (**3**) (0.26 g, 1 mmol) in 85% H_2SO_4 (11 mL). The solution was added *n*-bromosuccinimide (NBS) (0.54 g, 3 mmol) after 10 min and was stirred 3 h at room temperature. The mixture was poured into 200 mL water and stirred 20 min. The precipitated was filtered and dried under vacuum to afford compound **2** as a yellow solid (0.36 g, 85 %). ^{1}H NMR (300 MHz, DMSO-d_6) δ(ppm): 8.37 (s, 0.14H), 8.33 (s, 4H).

*Synthesis of compound **4***

A solution of compound **3** (1.2 g, 2.1 mmol) and **2** (0.36 g, 0.85 mmol) in 30 mL m-cresol was degassed. The reaction mixture was heated at 90 °C under nitrogen atmosphere for 20 h. The mixture was cooled to room temperature and poured into 300 mL ethanol. The precipitate was filtered and dried under vacuum. The crude product was purified by column chromatography on silica gel with chloroform: petroleum ether (1:1) as the eluent to afford the compound **4** as a yellow solid (0.6 g, 55 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 8.97 (s, 4H), 8.01 (s, 4H), 7.11 (d, $J=3.0$ Hz, 8H), 6.79 (d, $J=3.0$ Hz, 8H), 3.96 (t, $J=4.8$ Hz, 8H), 1.83 (m, 8H), 1.57–1.30 (m, 56H), 0.92 (t, $J=5.1$ Hz, 12H). Elemental Anal. calcd (%) for $C_{92}H_{108}Br_2N_4O_4$: C 74.29, H 7.08, N 3.52; found: C 73.89, H 7.29, N 3.75. [MALDI- TOF]: 1495 $[M+H]^+$.

Synthesis of model compound B2F

To a flask containing a degassed solution of **4** (0.30 g, 0.2 mmol) and 9,9-dioctylfluorene-2-boronic acid ester (0.21 g, 0.44 mmol) acid ester in 20 mL toluene added 10 mL of an aqueous 2 M K_2CO_3 solution. The $Pd(PPh_3)_4$ (5 mg, 0.004 mmol) in 10 mL toluene was added into the mixture. The mixture was stirred 2 d at 90 °C and cooled to the room temperature. The aqueous phase was extracted with CH_2Cl_2. The CH_2Cl_2 extracts were combined with the organic phase and washed with H_2O. The solution was dried with anhydrous Na_2SO_4. The crude product was dried under vacuum and purified by column chromatography on silica gel with CH_2Cl_2 as the eluent to afford the product as a yellow solid (0.38 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) 9.75 (s, 4H), 8.31 (s, 4H), 8.11 (s, 2H), 8.02 (d, $J=8.0$ Hz, 2H), 7.81 (d, $J=8.0$ Hz, 2H), 7.76 (d, $J=7.2$ Hz, 2H), 7.43 (m, 6H), 7.17 (d, $J=8.4$ Hz, 8H), 6.81 (d, $J=8.4$ Hz, 8H), 3.97 (t, $J=6.4$ Hz, 8H), 2.24–2.04 (m, 8H), 1.83 (m, 8H), 1.62–0.65 (m, 128H). Elemental analysis calcd (%) for $C_{150}H_{190}N_4O_4$: C 85.26, H 9.06, N 3.03; found: C 85.49, H 8.89, N 2.78. [MALDI-TOF]: 2113 $[M+H]^+$.

2.4 Polymerization

The polymers were synthesized by Suzuki coupling reaction in an argon atmosphere. For example the synthesis of PFBY10, to a stirred solution of 9,9-dioctylfluorene-2,7-diboronic acid ester (0.2792 g, 0.5 mmol), 9,9-dioctyl-2,7-dibromofluorene (0.2194 g, 0.4 mmol) and compound **4** (0.1495 g, 0.1 mmol) in 10 mL toluene and 5 mL 2 M K_2CO_3 solution in water were added the catalysts $Pd(PPh_3)_4$ (5.8 mg, 5 mol‰) in 5 mL toluene and Aliquat 336 (0.1 g, 0.25 mmol). The mixture was stirred for 2 d at 90 °C and be cooled to the room temperature. The solution was poured into methanol. The precipitate was collected by filtration and then dissolved in chloroform. The solution was washed with water and dried with anhydrous Na_2SO_4 for 30 min. After most of the solvent was removed, the residue was poured into stirred methanol to obtain polymer fiber. The reprecipitation procedure in chloroform/methanol was then repeated three times. This polymer fiber was extracted with acetone for 24 h. The final product was dried in vacuum. Yield: 80%–88%. Random copolymers (PFBY) and the corresponding poly(9,9-dioctylfluorene) (PFO) were synthesized by Suzuki coupling polymerization.

PFO

Yield: 82%, ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.85 (br, 2H), 7.68 (br, 4H), 2.15 (br, 4H), 1.15 (br, 20H), 0.81 (br, 10H). Calcd: C 89.63; H 10.37. Found: C 89.85; H 10.14.

PFBY10

Yield: 80%, ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.58 (m, 4H), 8.23 (m, 4H), 7.84–7.68 (m, 54H), 6.87 (m, 8H), 4.00 (s, 8H), 2.13–1.15 (m, 316H), 0.91–0.60 (m, 66H). Calcd: C 87.79; H 9.70; N 1.16. Found: C 88.65; H 9.95; N 0.89.

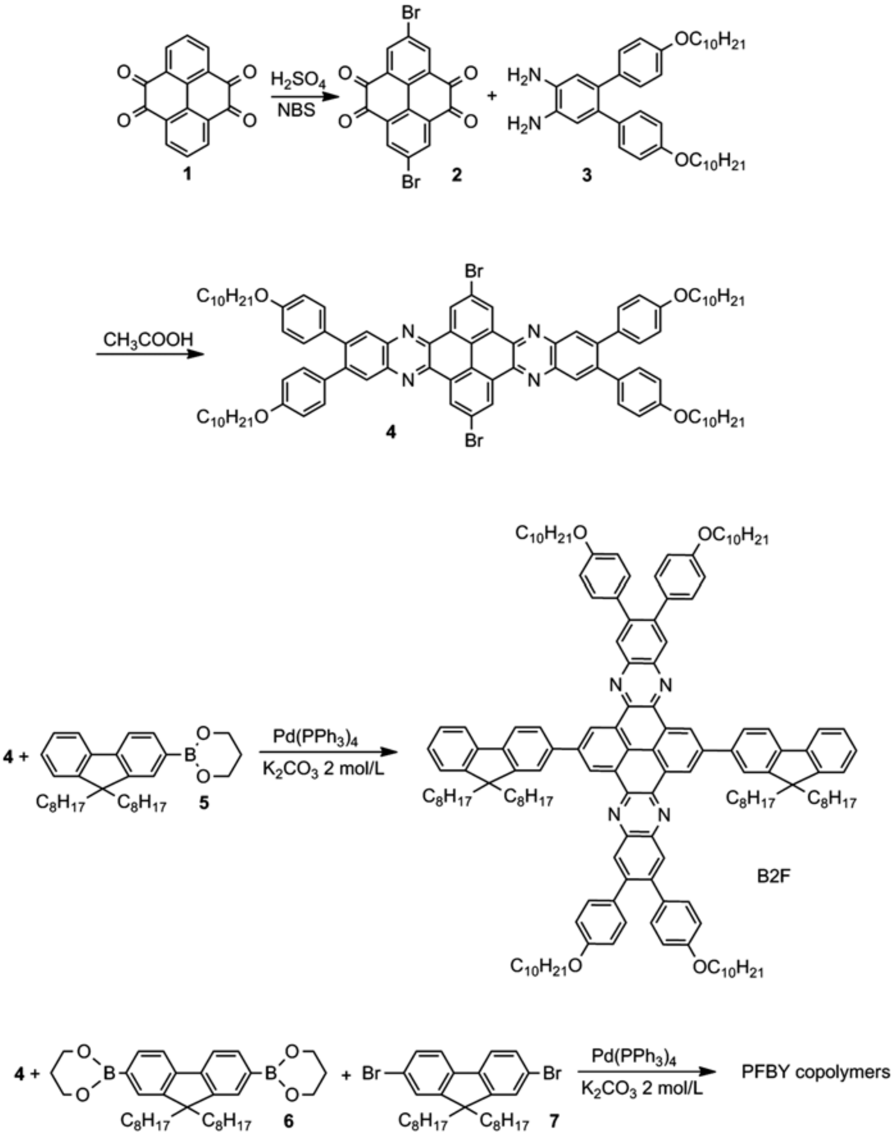
Other copolymers showed NMR and FT-IR spectra similar to PFBY10 copolymer.

3 Results and discussion

3.1 Synthesis and structure

The synthetic procedures are outlined in Scheme 1. We first reported the synthesis of 2,7-dibromo-pyrene-4,5,9,10-tetraones in 85% H_2SO_4 and NBS system. The method was simple, convenient and high yield. However, the poor solubility of crude product **2** leads to difficulty in purification. Through the reaction of compound **2** and **3**, we obtained the key monomer **4** with good solubility, which can be purified by column chromatography on silica gel easily. Then, the model compound B2F and copolymers were synthesized by the Suzuki coupling reactions. The molar ratio of BY in the copolymers was controlled by adjusting the molar ratio of **4**, **6**, and **7**. All polymers have good solubility and can be dissolved in common organic solvents, such as chloroform, toluene, dichloromethane and tetrahydrofuran (THF).

The chemical structures of the polymers were verified by ^{1}H NMR and FT-IR spectra. Representative ^{1}H NMR spectra of copolymer PFBY10, PFO, and compound **4** were shown in Figure 1. The small peaks at 8.58, 8.23, and 6.87 ppm, which belong to the aromatic ring protons in the compound **4**, and the peak at 4.0 ppm, which was assigned to the aliphatic protons (–O–CH_2–). The peaks in the range of 7.68–7.84 ppm correspond to the aromatic ring protons in fluorene units. The FT-IR spectra of PFO and PFBY10 also confirmed their molecular structures. The FT-IR spectra of PFO and PFBY10 were shown in Figure 2. The new vibrational bands at 1608 cm^{-1} and 1514 cm^{-1} were assigned to stretching vibrations of C=N group in the pyrazine ring. The number-average molecular weights (M_n) of these polymers were determined by gel permeation chromatography (GPC)



Scheme 1 Synthetic routes of model compound **B2F** and the resulting polymers.

using polystyrene as the standard in THF. The molecular weights of all polymers were 4.5 × 10^4–9.0 × 10^4 with a polydispersity index of 2.2–3.4 (Table 1). The thermal properties of the polymers were evaluated by thermogravimetric analysis (TGA) and the results were summarized in Table 1. The onset decomposition temperatures of the PFBY copolymers and PFO homopolymer were in range of 394–438 °C, which indicated their good thermal stability (Figure 3).

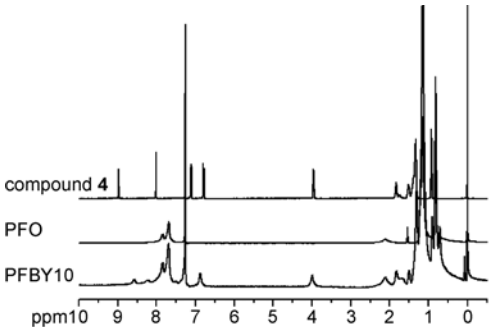


Figure 1 The ^{1}H NMR spectra of compound **4**, PFO, and PFBY10.

Table 1 The molecular weight and thermal properties of the resulting polymers

Polymer	M_n^{a}	M_w/M_n $^{a)}$	T_d (°C) $^{b)}$
PFO	8.9×10^4	2.5	438
PFBY1	9.0×10^4	2.7	412
PFBY2	7.4×10^4	3.4	404
PFBY5	7.4×10^4	2.7	397
PFBY10	4.5×10^4	2.2	394

a) Molecular weights were determined by GPC using polystyrene as a standard in THF. b) Onset decomposition temperature measured by TGA under nitrogen.

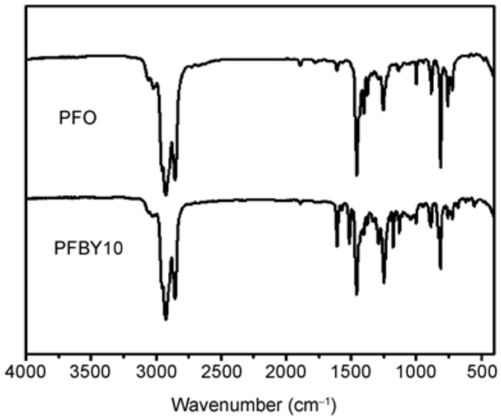


Figure 2 The FT-IR spectra of PFO and PFBY10.

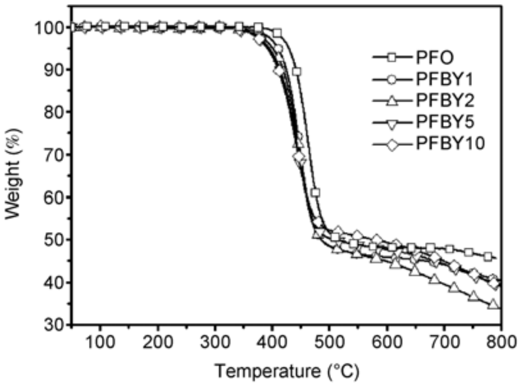


Figure 3 The thermogravimetric analysis (TGA) of the PFBY copolymers and PFO homopolymer under nitrogen at a heating rate 10 °C/min.

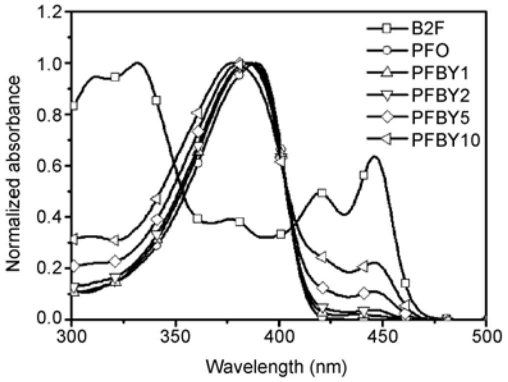


Figure 4 Normalized optical absorption spectra of 10^{-5} M toluene solutions of model compound B2F, PFO and PFBY copolymers.

3.2 Photophysical

Figure 4 showed the normalized absorption spectra of B2F, PFO and four PFBY copolymers in toluene solutions (10^{-5} M). PFO has an absorption maximum at 389 nm corresponding to the π-π* transition of poly-fluorene backbone. The main absorption band progressively blue-shifts from 386 nm in PFBY1 to 378 nm in PFBY10, suggesting the decrease of the effective conjugation length [18]. A new absorption band at 446 nm was observed for all copolymers and increased with increasing BY amount. The same absorption band also was found for the model compound B2F in toluene solution. Thus, it can be assigned to the B2F unit in copolymers.

Figure 5(a) showed the normalized emission spectra of PFO and copolymers in toluene solutions (10^{-5} M). The PL spectra of PFO showed two blue emission peaks (417 nm and 439 nm). For all the copolymers, the blue emission steadily decreased and a new emission peak at 470–490 nm increased with increasing BY content in the copolymers. The similar emission peak can be observed from the PL spectra of model compound B2F, suggesting the new emission peak could also be attributed to B2F moieties in copolymers. Considering the absorption band of B2F (446 nm) have good overlap with the blue emission of PFO (417 and 439 nm), energy transfer from the conjugated main chain to

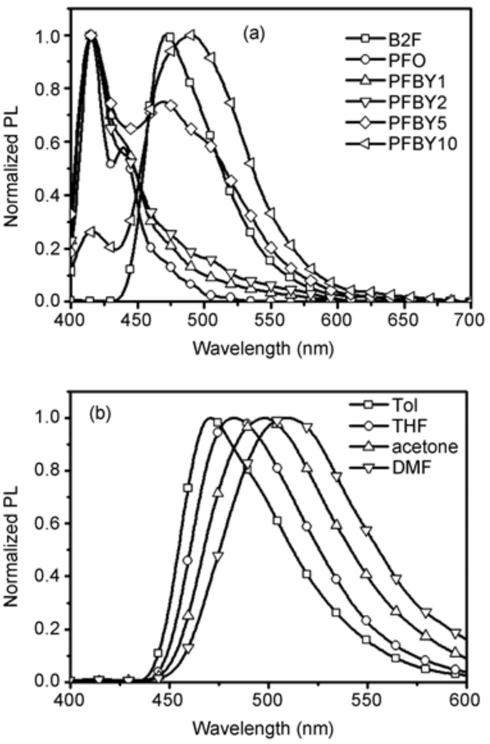


Figure 5 (a) Normalized PL emission spectra of 10^{-5} M solutions of B2F, PFO and PFBY copolymers in toluene and (b) normalized PL emission spectra of 10^{-5} M solutions of B2F in toluene, THF, acetone and DMF.

the B2F moieties would happen. Moreover, energy transfer was more and more complete as the BY content increased. The PL quantum yields of copolymers and PFO in toluene solution were 62%, 49%, 30%, 19% and 90% for PFBY1, PFBY2, PFBY5, PFBY10 and PFO, respectively. The emission characteristics of B2F in dilute solution were investigated in different solutions (Figure 5(b)). As the solvent polarity increased, the emission maximum peak was red-shifted from 471 to 509 nm indicating an intramolecular charge transfer (ICT) excited state with a large dipole moment [19]. The geometry of model compound B2F was optimized by density functional theory calculations at the B3LYP/6-31G* level [20]. Figure 6 indicated that its LUMO orbital was localized on the BY unit and the HOMO energy level was on polymer main chain, which also suggested the existence of charge transfer in B2F.

Figure 7(a) showed the normalized absorption spectra of PFO and copolymers in thin films. As increasing BY content, the change trend of the spectral shapes and peak positions are similar to those of the absorption spectra in dilute solution. The main absorption band was also blue-shifted from 385 nm in PFO homopolymer to 377 nm in PFBY10. The intensity of the new peak at 446 nm was also increased with increasing BY content. The absorption onsets (471 nm) of the four copolymers were red-shifted compared to that of PFO (414 nm). The optical band gaps of all copolymers were 2.63 eV, which were calculated from the absorption edge of the thin film spectra. The PL emission spectra of the copolymers and PFO in thin films were shown in Figure 7(b). The PL spectra of copolymers in thin film were different from those in solutions. Besides the PFBY1, the blue emission peak of all copolymers was disappeared in thin film and only the green emission around 511 nm was found, suggesting much more efficient energy transfer for copolymers in thin film than in solutions. At the same time, the PL spectra were steadily red-shifted with increasing BY content, possibly due to the larger ICT effect of the excited state in the copolymers [7]. The PL quantum yields of copolymers and PFO in film were 23.1%, 18.3%, 11.5%, 11.4% and 49% for PFBY1, PFBY2, PFBY5, PFBY10 and PFO respectively. The PL quantum yields of copolymers in film progressively reduced from 23.1% in PFBY1 to 11.4% in PFBY10, indicating the existence of aggregation.

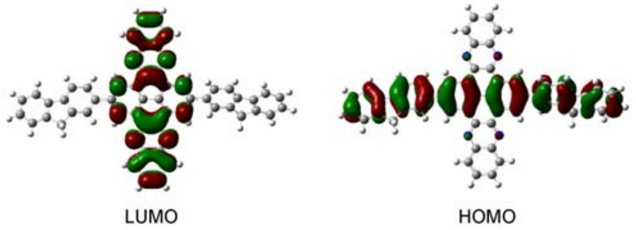


Figure 6 HOMO and LUMO molecular orbitals of B2F.

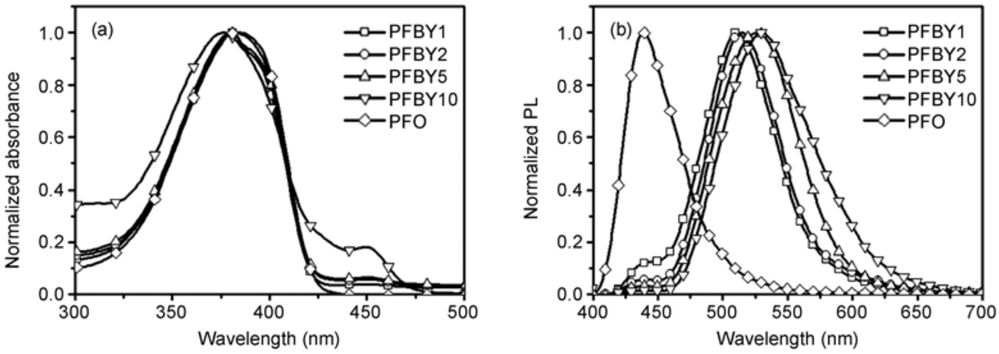


Figure 7 (a) Normalized optical absorption and (b) normalized PL emission spectra of thin films of PFO and PFBY copolymers.

3.3 Electrochemical

The electrochemical properties of copolymers and B2F were studied by a three-electrode electrochemical cell with Bu_4NClO_4 (0.1 M) as electrolyte and Ag/AgCl as reference electrode. The HOMO and LUMO energy level were calculated according to the formula $E_{HOMO} = -[4.8 - E_{FOC} + E^{ox}_{onset}]$ and $E_{LUMO} = -[4.8 - E_{FOC} + E^{red}_{onset}]$ eV [21]. The onset oxidation potential (E_{FOC}) of ferrocene (the standard) was measured to be 0.45 eV. The cyclic voltammetry of B2F exhibited two reversible reduction processes, however only irreversible oxidation process was observed. The onset reduction and oxidation potentials were −1.18 and 1.57 eV for B2F. Thus, the LUMO and HOMO energy levels of B2F were −3.17 and −5.92 eV, respectively. The HOMO level of PFBY10 was −5.77 eV by calculation from the onset oxidation potential. However no reduction process of PFBY copolymers was found, perhaps because of the low content of BY units [22]. Thus, their LUMO energy levels (around −3.14 eV) were calculated from the corresponding HOMO energy level and the band gap. The LUMO energy levels of PFBY copolymers were much lower than PFO (−2.17 eV) [11], confirmed that the importing of the BY units was benefit to improve the electron injection. The energy levels of PFO and PFBY copolymers were shown in Figure 8. However, the barrier of electron injection is still higher than that of the hole injection, suggesting the introduction of an electron transport layer will much improve the performance of devices in multilayer devices.

3.4 Electroluminescent

The single-layer PLEDs devices with the structure of ITO/ PEDOT:PSS (40 nm)/polymer (70 nm)/LiF (1 nm)/Al (100 nm) (type I) were fabricated to investigate the EL properties of the polymers [19]. The much more stable LiF/Al cathode was chosen to replace very active Ca/Al cathode due to the better electron injection properties of these copolymers. Their EL spectra under different voltages were shown in Figure 9. The EL emission maxima of all the copolymers were from 488 to 500 nm. The EL spectral shapes of the devices of these polymers kept almost unchanged at different voltages [23]. Table 2 summarizes the EL properties of the single-layer PLEDs.

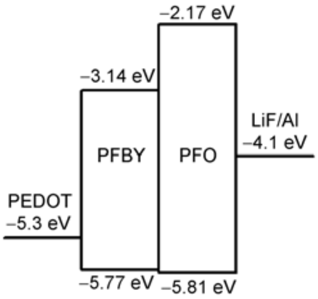


Figure 8 Energy levels of PFO and PFBY copolymers.

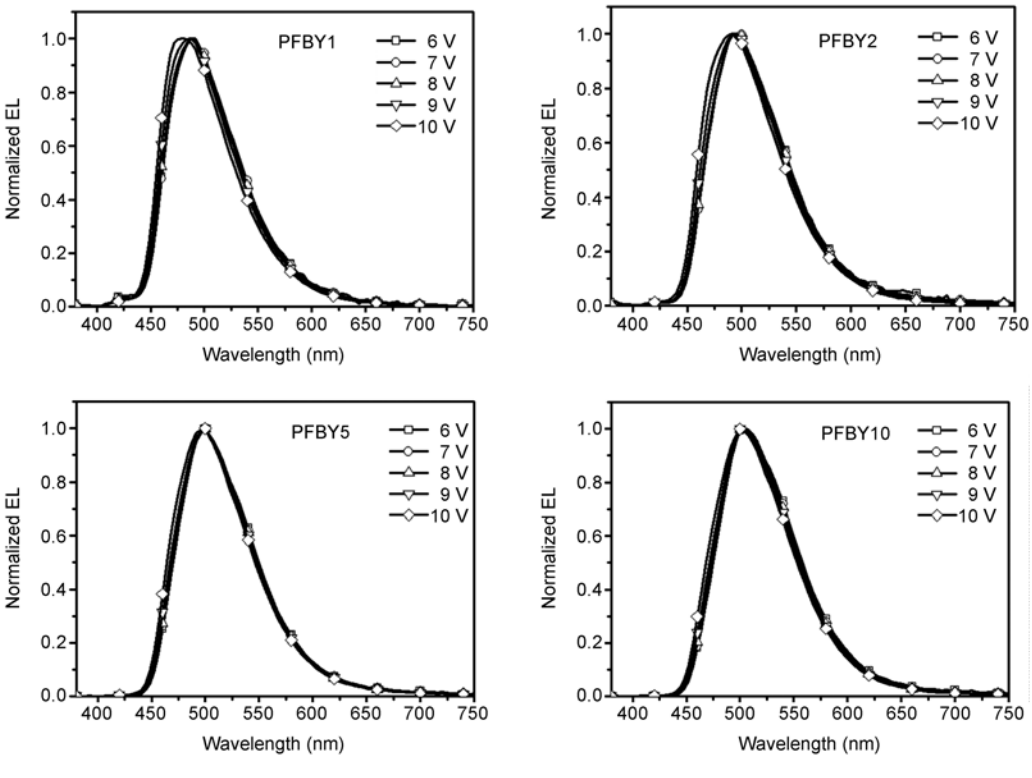


Figure 9 The EL spectra of type I diodes (ITO/PEDOT/polymer/LiF/Al) based on PFBY copolymers under 6, 7, 8, 9 and 10 V.

Figure 10 showed the current density-voltage-brightness and current efficiency-current density characteristics of single-layer devices. As shown in Figure 10(a), the turn-on voltages were at 4.0–6.1 V for all devices of copolymers, which were lower than that of PFO (7.0 V). The turn-on voltages decreased with the increasing BY content, suggesting better electron injection of copolymers. At the same voltage, the current density of the copolymer devices were higher than the PFO homopolymer diode, suggesting a better charge recombination efficiency in the copolymers due to the presence of the BY units. The PFO homopolymer diode had a maximum brightness of 74.5 cd/m^2, a maximum current efficiency of 0.06 cd/A and an external quantum efficiency (EQE) of 0.041%. The brightness and current efficiency of four copolymers diodes were higher than PFO devices. The device of PFBY5 was the best one among the copolymers, with a maximum brightness of 485 cd/m^2, a maximum current efficiency of 0.29 cd/A and an external quantum efficiency (EQE) of 0.10%. These results clearly demonstrated that the introduction of BY unit can stabilize the EL spectra and improve luminance and current efficiency.

To improve the device performance, PVK (20 nm) hole-transport layer and TPBI (20 nm) electron-transport layer were used to construct multilayer diodes of PFBY5:type II (ITO/PEDOT/PVK/PFBY5/LiF/Al), type III (ITO/PEDOT/PFBY5/TPBI/LiF/Al) and type IV (ITO/PEDOT/PVK/PFBY5/TPBI/LiF/Al). Table 3 summarizes the relevant EL properties of multilayer devices. Figure 11 showed the EL spectra of multilayer diodes. The EL spectra were stable when the voltage increases and the turn-on voltages were at 4.5–5.0 V. The current density-voltage-brightness and current efficiency-current density characteristics of multilayer diodes were displayed in Figure 12. When the PVK was

Table 2 EL performance data of the single-layer devices

Polymer	λ_{max} (nm)	V_{on} $^{a)}$ (V)	Maximum brightness (cd/m^2)	Current efficiency (cd/A)	CIE coordinate $^{b)}$	EQE (%)
PFO	424	7	74.5	0.06	(0.17，0.11)	0.04
PFBY1	488	6.1	238	0.12	(0.19，0.40)	0.05
PFBY2	492	5.8	365	0.17	(0.21，0.45)	0.07
PFBY5	500	4.6	485	0.29	(0.21，0.48)	0.10
PFBY10	500	4	112	0.15	(0.23，0.50)	0.05

a) Turn-on voltage. b) Measured at the voltage of 8 V.

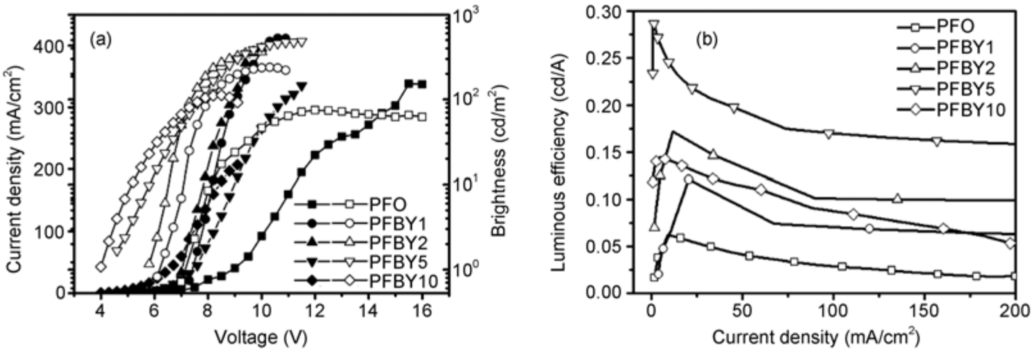


Figure 10 Current density-voltage-brightness (a) and current efficiency-current density (b) for the PFO and PFBY copolymers. In Figure 10(a), current density-voltage curves (solid symbol) and brightness-voltage curves (open symbol).

Table 3 EL performance data of the devices with different configuration based on PFBY5.

Device configuration	λ_{max} (nm)	$V_{on}$$^{a)}$ (V)	Maximum brightness (cd/m^2)	Current efficiency (cd/A)	CIE coordinates$^{b)}$	EQE (%)
Type I	500	4.5	485	0.29	(0.21，0.48)	0.10
Type II	500	4.5	628	0.30	(0.21，0.47)	0.11
Type III	500	4.5	2980	1.61	(0.20，0.47)	0.58
Type IV	500	5.0	3012	1.81	(0.20，0.47)	0.66

a) Turn-on voltage. b) Measured at the voltage of 8 V.

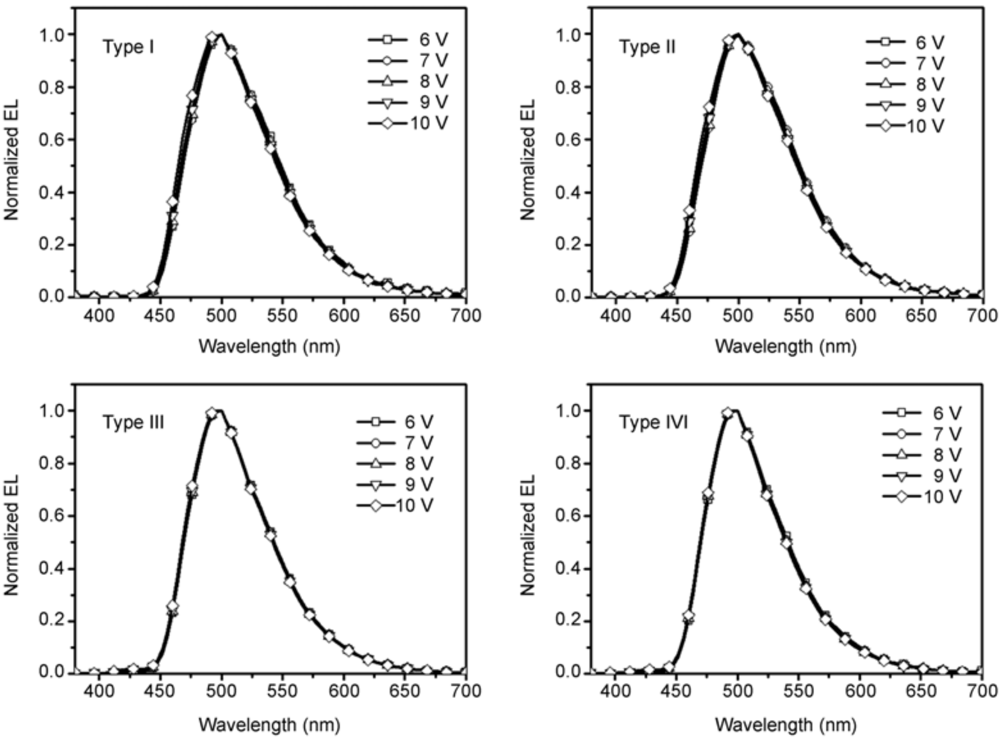


Figure 11 The EL spectra of different device structures for PFBY copolymers under 6, 7, 8, 9 and 10 V.

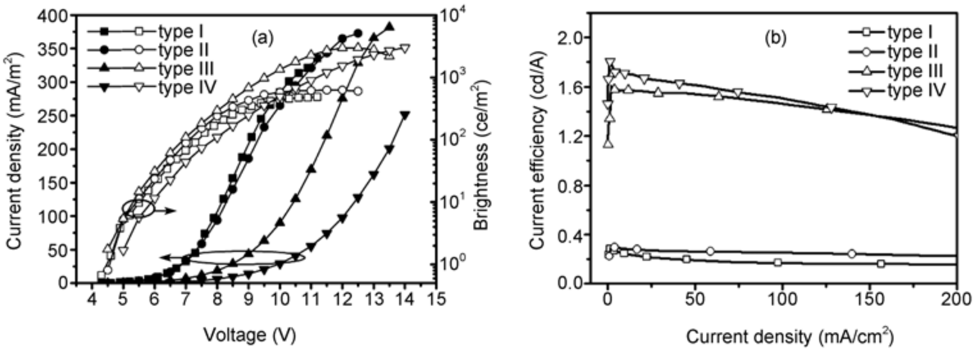


Figure 12 EL performance data of the devices with different configuration based on PFBY5.

introduced in the device (type II), there was only a little change for current efficiency (0.30 cd/A), the brightness (628 cd/m^2) and the external quantum efficiencies (0.11%). However, the introduction of TPBI significantly improved the performance. The maximum current efficiency, the maximum brightness, and the external quantum efficiencies of type III were 1.61 cd/A, 2980 cd/m^2 and 0.58%. The multilayer devices containing PVK and TPBI further improved the EL performance. The maximum current efficiency, the maximum brightness, and the external quantum efficiencies reached 1.81 cd/A, 3012 cd/m^2 and 0.66%. Overall, the EL performances of multilayer devices were significantly improved compared to the corresponding single-layer device.

4 Conclusions

We synthesized a series of polyfluorenes containing BY units by Suzuki polymerization. Energy transfer from the polymer main chain to the B2F moieties was more efficient in thin film than that in solution. For the copolymers, the blue emission of PFO steadily decreased and a new green emission increased in intensity with increasing the BY content in solution. Complete energy transfer was achieved in film besides PFBY1 copolymer. LUMO energy levels of these copolymers and PFO were −3.14 and −2.17 eV, suggesting that the introduction of BY unit would facilitate electron injection in PLED. Based on the single-layer EL device (ITO/PEDOT/polymer/LiF/Al), we found that the

EL performance of PFBY copolymers surpassed PFO due to the presence of the electron acceptor BY unit. The best efficiency among the copolymers was given by PFBY5, with a maximum brightness of 485 cd/m^2, a maximum current efficiency of 0.29 cd/A, and an external quantum efficiencies of 0.10 %. In multilayer devices of PFBY5, the introduction of PVK (20 nm) and TPBI (20 nm) further greatly improved EL performance. The type IV diodes gave the best performance, with an onset voltage of 5.0 V, a current efficiency of 1.81 cd/A, a maximum brightness of 3012 cd/m^2, and an external quantum efficiencies of 0.66% with the CIE coordinates of (0.20, 0.47). All these results clearly demonstrated that the introduction of the BY unit in the polyfluorene can reduce barrier of electron injection and effectively improve their EL performance.

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1 Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, Burns PL, Holmes AB. Light-emitting-diodes based on conjugated polymers. *Nature*, 1990, 347: 539–541

2 Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, Bradley DDC, Dos Santos DA, Bredas JL, Logdlund M, Salaneck WR. Electroluminescence in conjugated polymers. *Nature*, 1999, 397: 121–128

3 Jin Y, Song S, Park SH, Park JA, Kim J, Woo HY, Lee K, Suh H. Synthesis and properties of various PPV derivatives with phenyl substituents. *Polymer*, 2008, 49: 4559–4568

4 Chen Q, Liu N, Ying L, Yang W, Wu H, Xu W, Cao Y. Novel white-light-emitting polyfluorenes with benzothiadiazole and Ir complex on the backbone. *Polymer*, 2009, 50: 1430–1437

5 Yu W L, Pei J, Huang W, Heeger AJ. Spiro-functionalized polyfluorene derivatives as blue light-emitting materials. *Adv Mater*, 2000, 12: 828–831

6 Park JW, Park SJ, Kim YH, Shin DC, You H, Kwon SK. Pure color and stable blue-light emission-alternating copolymer based on fluorene and dialkoxynaphthalene. *Polymer*, 2009, 50: 102–106

7 Zhu Y, Gibbons KM, Kulkarni AP, Jenekhe SA. Polyfluorenes containing dibenzo[a,c]phenazine segments: Synthesis and efficient blue electroluminescence from intramolecular charge transfer states. *Macromolecules*, 2007, 40: 804–813

8 Herguch P, Jiang XZ, Liu MS, Jen AKY. Highly efficient fluorene- and benzothiadiazole-based conjugated copolymers for polymer light-emitting diodes. *Macromolecules*, 2002, 35: 6094–6100

9 Qiao Z, Peng JB, Jin Y, Liu QL, Weng JEN, He ZC, Han SH, Cao DR. Synthesis and electroluminescence properties of fluorene-*co*-diketopyrrolopyrrole-*co*-phenothiazine polymers. *Polymer*, 2000, 51: 1016–1023

10 Yang J, Jiang CY, Zhang Y, Yang RQ, Yang W, Hou Q, Cao Y. High-efficiency saturated red emitting polymers derived from fluorene and naphthoselenadiazole. *Macromolecules*, 2004, 37: 1211–1218

11 Wang M, Tong H, Cheng YX, Xie ZY, Wang LX, Jing XB, Wang FS. Synthesis and characterization of polyfluorenes containing bisphenazine units. *J Polym Sci Polym Chem*, 2010, 48: 1990–1999

12 Li YY, Wu HB, Zou JH, Ying L, Yang W, Cao Y. Enhancement of spectral stability and efficiency on blue light-emitters via introducing dibenzothiophene-*S*,*S*-dioxide isomers into polyfluorene backbone. *Org Electron*, 2009, 10: 901–909

13 Gao BX, Wang M, Cheng YX, Wang LX, Jing XB, Wang FS. Pyrazine-containing acene-type molecular ribbons with up to 16 rectilinearly arranged fused aromatic rings. *J Am Chem Soc*, 2008, 130: 8297–8306

14 Hu J, Zhang D, Harris FW. Ruthenium(III) chloride catalyzed oxidation of pyrene and 2,7-disubstitued pyrenes: An efficient, one-step synthesis of pyrene-4,5-diones and pyrene-4,5,9,10-tetraones. *J Org Chem*, 2005, 70: 707–708

15 Li SB, Zhao P, Huang YQ, Li TC, Tang C, Zhu R, Zhao L, Fan QL, Huang SQ, Xu ZS, Huang W. Poly-(*p*-phenylene vinylenes) with pendent 2,4-difluorophenyl and fluorenyl moieties: Synthesis, characterization, and device performance. *J Polym Sci Polym Chem*, 2009, 47: 2500–2508

16 Xin Y, Wen GA, Zeng WJ, Zhao L, Zhu XR, Fan QL, Feng JC, Wang LH, Wei W, Peng B, Cao Y Huang, W. Hyperbranched oxadiazole-containing polyfluorenes: Toward stable blue light PLEDs. *Macromolecules*, 2005, 38: 6755–6758

17 Lee DC, Jang K, McGrath KK, Uy R, Robins KA, Hatchett DW. Self-assembling asymmetric bisphenazines with tunable electronic properties. *Chem Mater*, 2008, 20: 3688–3695

18 Jin Y, Kim Y, Kim SH, Song S, Woo HY, Lee K, Suh H. Novel green-light-emitting polymers based on cyclopenta[def]phenanthrene. *Macromolecules*, 2008, 41: 5548–5554

19 Smith AA, Kannan K, Manavalan R, Rajendiran N. Spectral characteristics of bicalutamide drug in different solvents and beta-cyclodextrin. *J Inclusion Phenom Macrocyclic Chem*, 2007, 58: 161–167

20 Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR. *Gaussian 03 R C*. Wallingford: Gaussian Inc, 2004

21 Jiang ZQ, Zhang WJ, Yao HQ, Yang CL, Cao Y, Qin JG, Yu G, Liu YQ. Copolyfluorenes containing bridged triphenylamine or triphenylamine: Synthesis, characterization, and optoelectronic properties. *J Polym Sci Polym Chem*, 2009, 47: 3651–3661

22 Wang P, Jin H, Yang Q, Liu WL, Shen ZH, Chen XF, Fan XH, Zou DC, Zhou QF. Synthesis, characterization, and electroluminescence of novel copolyfluorenes and their applications in white light emission. *J Polym Sci Polym Chem*, 2009, 47: 4555–4565

23 Liu J, Chen L, Shao SY, Xie ZY, Cheng YX, Geng YH, Wang LX, Jing XB, Wang FS. Three-color white electroluminescence from a single polymer system with blue, green and red dopant units as individual emissive species and polyfluorene as individual polymer host. *Adv Mater*. 2007, 19: 4224–4228