Synthesis and Characterization of Polyfluorenes Containing Bisphenazine Units

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ABSTRACT: Novel conjugated copolymers based on 9,9-dioctylfluorene and bisphenazine (BP) were synthesized by Suzuki polymerization. Energy transfer from the conjugated main chain to the BP moieties was observed. Full energy transfer was achieved when the molar content of the bisphenazine was 20% (20BPPF) in toluene solution. The similar phenomena were observed even for 1% bisphenazine content copolymer (1BPPF) in film. The lowest occupied molecular orbital (LUMO) energy levels (-3.06 eV) of the copolymers were lower than that of the polyfluorene homopolymer (PFO; -2.65 eV), indicating that the introduction of the BP unit was benefit to electron injection. Single-layer electroluminescent devices (ITO/PEDOT:PSS/polymer/LiF/AI) were fabricated to investigate their electrolumines-

INTRODUCTION Polymer light-emitting diodes (PLEDs) have received much attention of researchers in the past decades because of their potential application in the large-area, flatpanel display field.¹⁻¹⁸ Among many promising conjugated polymers, polyfluorene (PF), and its derivatives have been widely studied for PLEDs because of their processibility, high photoluminescence efficiency, and good hole-transporting properties.¹⁹⁻²⁵ On the basis of the idea of energy transfer from a host to a dopant, blue-emissive PF has also been used as a host to realize green, yellow, and even red emission when a corresponding dopant is incorporated into the main chain or side chain of PF.²⁶⁻²⁹ However, high lowest occupied molecular orbital (LUMO) energy level and poor electron-transporting properties of PFs result in a high electron injection barrier and imbalance of charge carrier transport for the PLED application,³⁰ which will greatly limit their device efficiencies.

It is well known that introduction of *n*-type units into conjugated polymers could improve their electron injection and transport properties.^{31–33} Recently, many PF derivatives containing various *n*-type building blocks were reported in the literatures,^{27,34–37} such as benzothiadiazole, pyridine, naphthoselenadiazole, quinoxaline, oxadiazole, etc. For example, Samon A. Jenekhe's group have synthesized a series of PFs

cence (EL) performances. The maximum brightness and current efficiency of all BPPF copolymers surpassed the PFO homopolymer. The best single-layer device was based on 5BPPF, with a maximum brightness of 1532 cd/m² and current efficiency of 1.09 cd/A. Much higher efficiency could be achieved for multilayer EL devices of 5BPPF (ITO/PEDOT:PSS/ PVK/polymer/TPBI/LiF/AI), which showed a maximum current efficiency of 10.01 cd/A. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1990–1999, 2010

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composed of dioctylfluorene and dibenzo[a,c]phenazine units. The dibenzo[a,c]phenazine moieties greatly improved PLED performance of the copolymers. All the copolymers achieve much more efficient blue electroluminescence compared to PF homopolymer (PFO), with the maximum brightness of 1260–4600 cd/m² and luminous efficiency of 0.47–2.69 cd/A.³⁰

Our group has reported a series of novel acene-type conjugated molecules containing *n*-type pyrazine units in a previous paper.³⁸ With the increasing the number of pyrazine rings and the conjugation length of the molecules, the LUMO energy levels significantly decrease from -3.24 to -3.78 eV, according to the electrochemical data. At the same time, their absorption and emission peaks are red shifted step by step. In dilute solution, their emission color can be easily tuned from blue to even red. Their high electron affinity, high environmental stability, and ease of structural modification make these pyrazine-containing conjugated molecules excellent candidates as a new class of *n*-type semiconductors.

In this article, we reported the synthesis and characterization of a series of new PFs containing bisphenazine (BP), a pyrazine-containing conjugated molecule, as the *n*-type unit (Chart 1). As shown in Scheme 1, the copolymers were synthesized by the Suzuki coupling reaction, containing 1, 5, 10,

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and 20 mol % bisphenazine, denoted 1BPPF, 5BPPF, 10BPPF, and 20BPPF, respectively. The BP unit was chosen because two pyrazine rings in its molecular structure could promise it to be a strong electron acceptor.³⁹ Its introduction into the main chains of BPPF copolymers may improve the electron injection properties and enhance the recombination efficiency of electrons and holes, which would ultimately obtain highly efficient electroluminescence while using a stable LiF/Al cathode instead of a very active Ca/Al cathode in PLEDs. On the other hand, BP unit can also be used as a dopant to tune the emission color of the copolymers. Photophysical properties of the copolymers were studied both in dilute solutions and in thin films. PLEDs based on these copolymers as emissive layers were fabricated and characterized.

EXPERIMENTAL

BP, PFO, BPPF copolymers.

Measurements

¹H NMR spectra data were recorded on a Bruker Avance 300-MHz NMR spectrometer in CDCl₃ with TMS standard. Elemental analysis was performed by Bio-Rad elemental analysis system. Thermogravimetric analysis (TGA) measurements were performed on a Perkin-Elmer series 7 analysis systems under N2 at a heating rate 10 °C/min. Molecular mass spectra of intermediates were measured by means of LDI-1700 MALDI-TOF mass spectroscopy. 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. UVvis 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 brightness-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 ananlyzer with a three-electrode cell in 0.1 M tetrabutylammonium perchlorate (Bu₄NClO₄) in dry dichloromethane so-

lution under an argon atmosphere at a scan rate of 100 mV/ s and using ferrocene as standards. A glass carbon disk (2mm diameter) was used as the working electrode with a Pt wire as the counter electrode and an Ag/AgCl electrode as the reference electrode.

EL Device Fabrication and Characterization

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 PLEDs with the configuration of the organic light-emitting diodes (OLED) were fabricated with the PFO and copolymers as the emissive material, poly(N-vinyl-carbazole) (PVK) as the hole-transport/electron-blocking layer and 1,3,5-tris(N-phenylbenzimidizol-2-yl)benzene (TPBI) as the electron transport/hole-blocking layer Type I ITO/ PEDOT:PSS/polymer/LiF/Al, Type II ITO/PEDOT:PSS/PVK/ polymer/LiF/Al, Type III ITO/PEDOT:PSS/polymer/TPBI/ LiF/Al and Type IV ITO/PEDOT:PSS/PVK/polymer/TPBI/ LiF/Al. The PSS-doped PEDOT was spin-coated onto the treated ITO at 3000 rpm 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 0.5 mg/mL solution in toluene to 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. Films of TPBI thickness 20 nm 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 \times 10^{-4} to 4 \times 10^{-4} Pa. All the device fabrication and characterization were carried out at ambient conditions. The active area of the devices was 12 mm². 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.



Materials

All reagents were purchased from Aldrich, Acros, or TCI companies. 2,7-di-*t*-butyl-pyrene-4,5,9,10-tetraones (**1**),⁴⁰ 3,6-dibromobenzene-1,2-diamine (**4**),⁴¹ 9,9-dioctylfluorene-2-diboronic acid ester (**6**),⁴² 9,9-dioctylfluorene-2,7-diboronic acid ester (**7**),⁴³ and compound $2^{38,44}$ were synthesized according to the reported methods.

Synthesis

Compound 3

Into a stirred solution of **1** (0.78 g, 2.1 mmol) in 100 mL acetic acid compound **2** (1.0 g, 1.7 mmol) in 30 mL acetic acid was added dropwise for 30 min at 80 °C. The mixture was stirred for 4 h, and the precipitate was filtered. This crude product was dried under vacuum and purified by column chromatography on silica gel with chloroform : petroleum ether (2:1) as the eluent to afford compound **3** as a red solid (1.14 g, 74%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) 9.69 (s, 2H), 8.64 (s, 2H), 8.40 (s, 2H), 7.28 (d, J = 6.4 Hz, 4H), 6.89 (d, J = 7.2

Hz, 4H), 4.00 (t, J = 7.2 Hz, 4H), 2.01 (t, J = 6.9 Hz, 4H), 1.85–1.70 (m, 22H), 1.48–1.30 (m, 28H), 0.90 (t, J = 6.4 Hz, 6H). Anal. Calcd. for $C_{62}H_{74}N_2O_4$: C, 81.72; H, 8.19; N, 3.07. Found: C, 81.41; H, 8.14; N, 3.09. m/z [MALDI-TOF]: 912 [M

Compound 5

 $+ H]^{+}$.

A solution of compound **3** (1.1 g, 1.2 mmol) and **4** (0.43 g, 1.6 mmol) in 140 mL acetic acid was degassed and heated at reflux for 20 h. The mixture was cooled to room temperature, and the precipitated product was filtered. The crude product was dried under vacuum and purified by column chromatography on silica gel with chloroform: petroleum ether (1:2) as the eluent to afford the key compound **5** as a yellow solid (1.2 g, 85%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) 9.73 (d, J = 5.1 Hz, 4H), 8.28 (s, 2H), 7.92 (s, 2H), 7.18 (d, J = 3.9 Hz, 4H), 6.82 (d, J = 3.9 Hz, 4H), 3.97 (t, J = 6 Hz, 4H), 1.83–1.70 (m, 22H), 1.49–1.30 (m, 28H), 0.91 (t, J = 6.4 Hz, 6H). Anal Calcd for $C_{68}H_{76}Br_2N_4O_2{:}$ C, 71.57; H, 6.71; N, 4.91. Found: C, 71.19; H, 6.51; N, 4.12. m/z [MALDI-TOF]: 1141 $[M\ +\ H]^+.$

Compound B2F

Model compound (B2F) was prepared by the Suzuki reaction. To a flask containing a degassed solution of **5** (0.23 g, 0.2 mmol), 9,9-dioctylfluorene-2-diboronic (0.21 g, 0.44 mmol) acid ester in 20 mL toluene added 10 mL of an aqueous solution of 2 M K_2CO_3 . The Pd(PPh₃)₄ (5 mg, 0.004 mmol) in 10 mL toluene was added into the mixture. The mixture was stirred 2 days at 90 °C and be cooled to the room temperature. The aqueous phase was extracted with CH₂Cl₂. The CH₂Cl₂ extracts were combined with the organic phase and washed with H₂O. The solution was dried with anhydrous Na₂SO₄. After most of the solvent was removed, the crude product was dried under vacuum and purified by column chromatography on silica gel with chloroform: petroleum ether (1:1) as the eluent to afford the product as a yellow solid (0.32 g, 92%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) 9.79 (s, 2H), 9.68 (s, 2H), 8.54 (s, 2H), 8.44 (d, J = 8.1 Hz, 2H), 8.16 (s, 2H), 8.00 (d, J = 8.1 Hz, 2H), 7.89 (d, J = 7.8 Hz, 2H), 7.76 (s, 2H), 7.49–7.27 (m, 10H), 6.87 (d, J = 8.1 Hz, 4H), 3.99 (t, J = 6.3 Hz, 4H), 2.08–0.60 (m, 124H). Anal Calcd for C₁₂₆H₁₅₈N₄O₂: C, 85.96; H, 9.05; N, 3.18. Found: C, 85.89; H, 9.08; N, 3.12. m/z [MALDI-TOF]: 1760 [M + H]⁺.

General Polymerization Procedure

The polymer was prepared from palladium-catalyzed Suzuki coupling reaction. All handling of catalysts and polymerization was done in an argon atmosphere. For example, for the synthesis of 5BPPF, to a stirred solution of 9,9-dioctylfluorene-2,7-diboronic (0.2792 g, 0.5 mmol) acid ester, 9,9-dioctyl-2,7dibromofluorene (0.2194 g, 0.4 mmol), and compound 5 (0.1141 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 days at 80 °C and be cooled to the room temperature. The mixture was poured into methanol. The precipitate was collected by filtration, dried and then dissolved in chloroform. The solution was washed with water and dried with anhydrous Na₂SO₄. After most of the solvent was removed, the residue was poured into stirred methanol to obtain polymer fiber. This polymer fiber was further purified by extracting with acetone for 24 h. The reprecipitation procedure in chloroform/methanol was then repeated three times. The final product was dried in vacuum. Random copolymers (BPPF) and the corresponding poly(9,9-dioctylfluorene) (PFO) were synthesized by Suzuki coupling polymerization. The molar ratio of BP in the copolymers was controlled by adjusting the molar ratio between 9,9-dioctylfluorene and 5. Yield: 70-83%.

PFO: Yield: 82%, ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.85 (br, 2H), 7.68 (br, 4H), 2.15 (br, 4H), 1.15 (br, 20H), 0.81 (br, 10H). Calculated: C, 89.63; H, 10.37. Found: C, 89.85; H, 10.14.

20BPPF: Yield: 70%, ¹H NMR (300 MHz, CDCl₃) δ (ppm): 9.85 (m, 1H), 8.51 (m, 0.5H), 8.22 (s, 0.5H), 7.85–7.68 (m, 6H), 7.31 (m, 1H), 6.84 (m, 1H), 4.00 (s, 1H), 2.20 (br, 3H), 1.90–0.98 (m, 37H), 0.95–0.60 (m, 11.5H). Calculated: C, 87.12; H, 9.32; N, 2.21. Found: C, 86.90; H, 9.52; N, 1.88.

The ¹H NMR spectra of other copolymers were similar to the spectra of 20BPPF copolymer, except that the relative intensities of signals are different due to the different composition of the copolymers.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Copolymers

The synthetic routes of the monomers and the corresponding copolymers were outlined in Scheme 1. The compound **3** was synthesized according to the reported methods, from 2,7-di-*t*-butyl-pyrene-4,5,9,10-tetraones (**1**) and the compound **2** in 74% yield. The key monomer **5** was obtained by the reaction of **3** and 3,6-dibromobenzene-1,2-diamine (**4**) in a high yield (85%). By the Suzuki coupling reactions of **5**, **6**, and **7** in an argon atmosphere with Pd(PPh₃)₄ as the catalysts, we obtained the model compound B2F and polymers. The molar ratio of BP in the copolymers was controlled by adjusting the molar ratio of **5**, **6**, and **7**. The molar ratio between the dibromides and the diboronic acid ester was 1:1. All the copolymers could be soluble in common organic solvents, such as toluene, chloroform, dichloromethane, and tetrahydrofuran (THF).

¹H NMR spectra of the copolymers were in good agreement with their structures. The number-average molecular weights (M_n) of these polymers were determined to be 7.3×10^4 to 12.7×10^4 with a polydispersity index of 2.5–3.3 by GPC using polystyrene as the standard in THF (Table 1). The thermal properties of the polymers were evaluated by TGA. The TGA measurement revealed that the onset decomposition temperatures of the BPPF copolymers and PFO homopolymer under nitrogen were similar at 436 °C, which indicated their good thermal stability (see in Fig. S1 in Supporting Information).

Photophysical Properties

Normalized optical absorption spectra of B2F, PFO, and four BPPF copolymers in toluene solutions (10^{-5} M) were shown in Figure 1. The main absorption band, which was associated with the π - π ^{*} transition of the conjugated backbone,⁴⁵ progressively blue-shifted from 389 nm in PFO homopolymer to 370 nm in 20BPPF, indicating the reduction of the effective conjugation length as reported in other papers.^{27,46} The full width at half-maximum (FWHM) of the absorption spectra increased with increasing BP content, suggesting greater inhomogeneous broadening due to the local disorder induced by the presence of BP units.²⁷ For all copolymers, a new absorption band at 436 nm was found, and it increased in intensity with increasing BP amount from 1 to 20%. At the same time, a similar absorption peak at 436 nm was also observed for the model compound B2F in toluene solution (10^{-5} M) . Thus, it is reasonable to assign the new absorption band at 436 nm to the B2F moieties in copolymers.

Polymer	<i>M</i> _n ^a	$M_{\rm w}/M_{\rm n}^{\rm a}$	<i>T</i> _d ^b (°C)
PFO	8.9×10^4	2.5	438
1BPPF	$7.3 imes 10^4$	2.6	434
5BPPF	8.3×10^4	2.8	436
10BPPF	8.2×10^4	3.1	437
20BPPF	12.7×10^4	3.3	436

TABLE 1 Molecular Weight and Thermal Properties of

 Polymers

^a Molecular weights were determined by GPC using polystyrene as a standard.

^b Onset decomposition temperature measured by TGA under nitrogen.

The normalized PL emission spectra of PFO and the four copolymers in 10^{-5} M toluene solutions were shown in Figure 2(a). The PL spectrum of PFO showed the blue emission with peaks at 414 nm and 438 nm. Besides the two similar blue emission peaks at 414 and 440 nm, a new green-yellow emission peak at 523 nm was observed in the PL emission spectrum of 1BPPF. As the BP content increased in the copolymers, the blue emission steadily decreased and a new green-yellow emission increased in intensity. In 20BPPF, only the green-yellow emission at 523 nm was observed. As the emission peak of B2F in toluene was at 511 nm, which was very close to the green-yellow emission of copolymers, suggesting this new green-yellow emission was resulted from the B2F moieties. Considering a large spectra overlap between the blue emission of PFO (414 and 438 nm) and the absorption band of B2F (436 nm), energy transfer from the conjugated main chain to the B2F moieties would happen. Thus, energy transfer would be more and more efficient as the BP content increased. Finally, the original blue emission disappeared for 20BPPF, indicating a complete energy transfer. The PL characteristics of B2F in dilute solution (10^{-5} M) were investigated in different solutions with increasing solvent polarity of toluene, THF, acetone, and DMF [Fig. 2(b)]. The emission peaks of these solutions were at 511, 529, 543, and 555 nm, respectively. The PL emission



FIGURE 1 Normalized optical absorption spectra of 10^{-5} M solutions of model compound (B2F), PFO and BPPF copolymers in toluene solution.

maximum peak was red-shifted with increasing the solvent polarity. Such positive solvatochromism indicates an intramolecular charge transfer (ICT) excited state with a large dipole moment.⁴⁷ To further clarify its optical properties, the geometry of B2F was optimized by density functional theory calculations at the B3LYP/6-31G* level.⁴⁸ The HOMO and LUMO molecular orbitals (see in Fig. S2 in Supporting Information) indicated that the LUMO and HOMO were localized on the BP unit and the polymer main chain, respectively, which also supported the existence of charge transfer.

The normalized optical absorption spectra of thin films of PFO and the four copolymers were shown in Figure 3(a). Their absorption spectra were similar to those in toluene solutions. The main absorption band was also progressively blue-shifted from 380 nm in PFO homopolymer to 365 nm in 20BPPF. Similarly, a new long wavelength band at 439 nm was observed for BPPF copolymers, and its intensity increased with increasing BP content. The absorption onsets (471 nm) of the four copolymers were very close, which is much red-shifted compared with that of PFO (413 nm). The



FIGURE 2 (a) Normalized PL emission (380 nm excitation) spectra of 10^{-5} M solutions of B2F, PFO, and BPPF copolymers in toluene and (b) normalized PL emission (410 nm excitation) spectra of 10^{-5} M solutions of B2F in toluene, THF, acetone, and DMF.



FIGURE 3 (a) Normalized optical absorption and (b) normalized PL emission (380 nm excitation) spectra of thin films of PFO and BPPF copolymers in toluene.

optical band gaps, calculated from these absorption onsets, were 3.00 eV for PFO and 2.63 eV for copolymers, respectively. Figure 3(b) showed the PL emission spectra of the copolymer in thin films. Again, only blue emission was observed for PFO as in its solution. However, the PL spectra of copolymers in thin films were different from those in solutions. Even for 1BPPF, no blue emission peak could be found in thin film and only a green-yellow emission around 522 nm was observed, suggesting much more efficient energy transfer for copolymers in thin film. With increasing BP content, the PL spectra were steadily red-shifted with emission maximum ranging from 522 nm (1BPPF) to 560 nm (20BPPF), possibly due to the larger ICT effect of the excited state in going from 1BPPF to 20BPPF, as other PFs containing *n*-type units.³⁰

Electrochemical Properties

The electrochemical properties of B2F and polymers in dichloromethane were studied in a three-electrode electrochemical cell with Bu₄NClO₄ (0.1 M) as electrolyte and Ag/ AgCl as reference electrode. The highest occupied molecular orbital (HOMO) and the LUMO energy level were determined according to the empirical formula $E_{\rm HOMO} = -[4.8 - E_{\rm FOC} + E_{\rm onset}^{\rm ox}]$ and $E_{\rm LUMO} = -[4.8 - E_{\rm FOC} + E_{\rm onset}^{\rm red}]$ eV.⁴⁹ The halfwave potential (E_{FOC}) of ferrocene (the standard) was 0.56 eV. B2F exhibited two reversible redox processes in the negative potential region, however only irreversible oxidation process was observed. The onset reduction and oxidation potentials were -1.10 and 1.48 eV for B2F, respectively, (see in Fig. S3 in Supporting Information). Thus, LUMO and HOMO energy levels of B2F were calculated to be -3.14 and -5.72 eV. Similarly, HOMO level of PFO (-5.65 eV) was obtained. However, no reduction process of the PFO was found, so its LUMO energy level (-2.65 eV) was calculated from the corresponding HOMO energy level and the band gap (3.00 eV). The LUMO energy level of the B2F was much low than the LUMO energy level of PFO, suggesting the introduction of BP might be benefit to the electron injection. Again, the reduction process of four copolymers were hardly observed, perhaps because of the low content of BP units.⁵⁰ Thus, their LUMO energy levels were obtained in the same

way as PFO. All the four copolymers had similar HOMO (around -5.69 eV) and LUMO (around -3.06 eV) energy levels. Their LUMO energy levels were much lower than PFO. The results confirmed that the importing of the BP units really improved the electron injection. The energy levels of PFO and BPPF copolymers in single-layer devices were shown in Figure 4. For BPPF copolymers, the energy barrier for electron injection was lower than PFO, which will facilitate the electron injection. However, the electron injection barrier is still much higher than the hole injection, suggesting the introduction of an electron transport layer is more favorable in multilayer devices than the introduction of a hole transport layer.

EL Properties

To investigate the EL properties and performances of the polymers, the EL devices were fabricated with the configuration of ITO/PEDOT:PSS (40 nm)/polymer (70 nm)/LiF (1 nm)/Al (100 nm).⁵¹ Instead of using very active Ca/Al cathode for PF-based PLEDs as reported in many literatures, much more stable LiF/Al cathode was selected here because of the better electron injection ability of these copolymers. Their EL spectra were shown in Figure 5. In comparison with the blue-emissive PFO homopolymer, the EL emission maximum of all the copolymers was about 520 to 534 nm, and the EL spectra of four copolymers exhibited very good spectral stability: the EL spectra kept unchanged when the voltage increased from 8 to 16 V.⁵² The EL spectra of the copolymers were nearly the same as the PL emission in thin film, indicating that EL and PL phenomena originated from



FIGURE 4 Energy levels of PFO and BPPF copolymers.



FIGURE 5 The EL spectra of Type I diodes (ITO/PEDOT/polymer/LiF/AI) based on BPPF copolymers under 8, 10, 12, 14, and 16V.

the same excited state.⁴⁶ As shown in Table 2, the CIE coordinates of the EL emission of the copolymers indicated the green-yellow emission of the devices.

Luminance-voltage characteristics of the Type I devices were displayed in Figure 6(a). At the same voltage, the luminances of copolymers diodes were higher than PFO devices. For all devices of copolymers, the turn-on voltages were at 6.0-5.5 V, which were lower than that of PFO (7.0 V), suggesting better electron injection and transport of copolymers. The maximum brightness of devices based on copolymers were all much larger than that of PFO (74.5 cd/m²). Current efficiency-current density characteristics of the Type I device was displayed in Figure 6(b). The same current density, the current efficiencies of the copolymers diodes were far greater than PFO devices. The PFO homopolymer diode had a maximum current efficiency of 0.06 cd/A. The best effi-

ciency among the copolymers was also given by 5BPPF, with a maximum current efficiency of 1.09 cd/A, which is 17 times higher than that of PFO devices. Overall, incorporation of BP unit in PFO main chain led to more stable EL spectra and higher current efficiency.

It is well known that introduction of buffer layers might increase the device efficiencies. According to the HOMO and LUMO energy levels of PVK and TPBI were estimated to be -5.8 /-2.3 eV and -6.2/-2.7 eV, PVK (20 nm) hole-transport layer and TPBI (20 nm) electron transport layer were used to construct multilayer diodes of 5BPPF: Type II (ITO/PEDOT/PVK/5BPPF/LiF/AI), Type III (ITO/PEDOT/PVK/5BPPF/TPBI/LiF/AI), and Type IV (ITO/PEDOT/PVK/5BPPF/TPBI/LiF/AI). All the data of the devices were summarized in Table 3. The EL spectra of these diodes were similar to the corresponding Type I and were stable when the voltage

TAB	LE 2	EL	Performance	Data of the	Devices	with the	Configuration	of ITO/PEDOT	:PSS/Polymer/LiF/Al
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Polymer	λ _{max} (nm)	V _{on} ^a (V)	Maximum Brightness (cd/m ²)	Current Efficiency (cd/A)	CIE Coordinate ^b
PFO	424	7	74.5	0.06	(0.17, 0.11)
1BPPF	520	6	620	0.44	(0.31, 0.59)
5BPPF	532	5.5	1,532	1.09	(0.35, 0.60)
10BPPF	532	5.5	778	0.36	(0.36, 0.59)
20BPPF	534	5.5	550	0.29	(0.36, 0.59)

^a Turn-on voltage.

^b Measured at the voltage of 8 V.



FIGURE 6 Luminance-voltage (a) and current efficiency-current density (b) for the PFO and BPPF copolymers.

TABLE 3 EL Performance Data of the Devices with Different Configuration Based on 5BPPF

Device Configuration	$\lambda_{\max}(nm)$	V _{on} ^a (V)	Maximum Brightness (cd/m ²)	Current Efficiency (cd/A)	CIE Coordinates ^b
Туре I	532	5.5	1,532	1.09	(0.35, 0.60)
Type II	532	5.5	1,480	1.38	(0.34, 0.59)
Type III	528	5.0	5,269	8.68	(0.33, 0.59)
Type IV	528	5.0	5,939	10.01	(0.33, 0.59)

^a Turn-on voltage.

^b Measured at the voltage of 8 V.



FIGURE 7 The EL spectra of different device structures for 5BPPF under 6, 8, 10, 12, 14, and 16V.



FIGURE 8 Luminance-voltage (a) and current efficiency-current density (b) for 5BPPF under different device structures.

increases from 6 to 16 V (Fig. 7). The EL emission maximum of Types III and IV even exactly matched its PL emission in thin film, which also proved the EL emission arose solely from the copolymer layer.

Addition of the PVK layer in Type II diode, EL performance was similar to the corresponding Type I diode with a very little change of the current efficiency change from 1.09 to 1.38 cd/A. In contrast, introduction of TPBI significantly increased the current efficiency to 8.68 cd/A in Type III devices. The maximum brightness (5269 cd/m²) was also much higher than the Types I and II diodes. Both the PVK (20 nm) and TPBI (20 nm) were added in Type IV diodes, which further improved the EL performance. The maximum current efficiency and the maximum brightness even reached 10.01 cd/A and 5939 cd/m². Overall, by constructing the multilayer devices, especially introduction of the electron-transport layer (TPBI), the EL performances were significantly improved compared to the corresponding single-layer device, as shown in Figure 8.

CONCLUSIONS

In this article, we synthesized a series of novel PFs containing BP units by Suzuki reaction. As the BP content increased in the copolymers, the original blue emission of PFO steadily decreased and a new green-yellow emission increased in intensity due to energy transfer. Complete energy transfer was achieved when the molar content of the BP reached 20% (20BPPF) in toluene solution. In film, the similar phenomena were observed even for 1% BP content copolymer (1BPPF). LUMO energy levels (-3.06 eV) of these copolymers were lower than that of PFO (-2.65 eV), which would facilitate electron injection in PLED. Single-layer EL device (ITO/ PEDOT/polymer/LiF/Al) was fabricated. The EL performance of single-layer EL devices based on all the BPPF copolymers surpassed PFO due to the presence of the electron-deficient BP moiety. The device of 5BPPF was the best one among the copolymers. The addition of PVK (20 nm) and TPBI (20 nm) further greatly improved EL performance in multilayer devices of 5BPPF, while kept their EL emission from 5BPPF layer. The Type IV diodes gave the best performance, with an onset voltage of 5.0 V, a current efficiency of 10.01 cd/A,

and maximum brightness of 5939 cd/m^2 with the CIE coordinates of (0.33, 0.59). These results clearly demonstrated that BPPF copolymers were novel efficiency green-yellow emission materials for PLEDs.

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