Copolyfluorenes Containing Pendant Bipolar Carbazole and 1,2,4-Triazole Groups: Synthesis, Characterization, and Optoelectronic Applications

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ABSTRACT: Three novel copolyfluorenes (P1-P3) containing pendant bipolar groups (2.5–7.7 mol %), directly linked holetransporting carbazole and electron-transporting aromatic 1,2,4-triazole, were synthesized by the Suzuki coupling reaction and applied to enhance emission efficiency of polymer lightemitting diodes based on conventional MEH-PPV. The bipolar groups not only suppress undesirable green emission of polyfluorene under thermal annealing, but also promote electronand hole-affinity of the resulting copolyfluorenes. Blending the bipolar copolyfluorenes with MEH-PPV results in significant enhancement of device performance [ITO/PEDOT:PSS/MEH-

INTRODUCTION Since the discovery of green-yellow electroluminescence of poly(p-phenylene vinylene) (PPV) by Holmes and coworkers in 1990,¹ polymeric light-emitting diodes (PLEDs) continue to attract intensive interests due to their potential applications in large-area display and solidstate lighting.² In general, polymeric materials possess many advantages over inorganic ones, such as facile fabrication via spin-coating, roll-to-roll processing and other printing methods,^{3,4} and susceptible to structural modification. However, for conventional electroluminescent MEH-PPV {poly[2methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene]}, holes are more readily injected and transported than electrons, leading to unbalanced carriers currents in PLEDs.⁵⁻⁹ Maintaining a balance between electron and hole currents in PLEDs is an important factor for achieving high device efficiency. Various methods have been attempted to improve the device efficiency. One is to insert an additional electron injection/ transport layer between the emitter and the cathode. $^{\rm 10-12}$ Nevertheless, fabrication of the multilayer polymer LEDs is usually a difficult task, since the emitting layer might be redissolved during subsequent spin-coating of the electron injection/transport layer. Single-layer devices are preferred from the viewpoints of process simplicity and cost effectiveness.

Another method is to fabricate single-layer LEDs which blend charge injection/transport molecules such as oxadia-

PPV+**P1**, **P2** or **P3**/Ca(50 nm)/Al(100 nm)]. The maximum luminance and luminance efficiency were enhanced from 3230 cd/m² and 0.29 cd/A of MEH-PPV-only device to 15,690 cd/m² and 0.81 cd/A (blend device with MEH-PPV/**P3** = 94/6 containing about 0.46 wt % of pendant bipolar residues), respectively. Our results demonstrate the efficacy of the bipolar copolyfluorenes in enhancing emission efficiency of MEH-PPV. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3928–3938, 2011

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zole, 1,2,4-triazole (TAZ), triphenylamine or carbazole (CAZ) derivatives. However, crystallization-induced degradation and thermal breakdown during device operation might readily happen on account of their poor thermal stability.¹³⁻¹⁵ Therefore, many research groups prepared thermally stable polymers carrying electron- and/or hole-transporting groups in an attempt to improve device performance.¹⁶⁻²² For instance, Jung et al. synthesized thermally stable fluorenebased poly(iminoarylene)s with a triarylamine unit as holeinjection layers to enhance efficiency (with max. brightness: 12,370 cd/m²).^{18(c)} Alam et al. synthesized electron-transporting conjugated poly(2,2'-(3,3'-dioctyl-2,2'-bithienylene)-6,6'-bis(4-phenylenequinoline)) (POBTPQ) as acceptor to enhance performance of devices based on poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) or poly(3-octylthiophene) (POT).^{20(f)} Similarly, Tonzola et al. improved performance of (MEH-PPV)-based device using a soluble n-type conjugated copolymers incorporated with bis(phenylquinoline) and region-regular dialkylbithiophene in the backbone.^{20(h)} Lim et al. synthesized an organosilicate polymer based on N,N'-diphenyl- N,N'-bis(4-((E)-2-(triethoxysilyl)vinyl)phenyl)biphenyl-4,4'-diamine (TEVS-TPD) and used as a hole injection/transport layer to enhance OLED device performance, as compared to the device with PEDOT:PSS.^{22(c)} To our knowledge, few researches have been focused on directly blending functional polymers containing

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bipolar groups to enhance emission efficiency of another light-emitting polymer. In addition, in our previous study, the device performances were significantly enhanced (11,090 cd/m² and 0.56 cd/A), using blends of the pendant bipolar copolyfluorenes (with triphenylamine and 1,2,4-triazole moieties) and MEH-PPV as emitting layer.^{21(d)}

In this work, we demonstrate the synthesis of a new bipolar monomer (M1) and the following preparation of three copolyfluorenes (P1-P3) containing 2.5-7.7 mol % pendant bipolar groups by the Suzuki coupling reaction. The bipolar unit consists of electron-transporting aromatic 1,2,4-triazole directly linked with hole-transporting carbazole. The copolyfluorenes not only enhance the injection of holes and electrons but also lessen excimer formation under thermal annealing due to non-planar structure of the bipolar groups. Finally, the influence of bipolar contents on device performance is investigated, using blends of the copolyfluorenes and MEH-PPV as emitting layer. Both maximum luminance and maximum luminance efficiency of the blends-based PLEDs are further enhanced to $15,690 \text{ cd/m}^2$ and 0.81 cd/A, respectively, relative to those of our previous study.^{21(d)} Consequently, the copolyfluorenes containing pendant bipolar groups are applicable to effectively enhance emission efficiency of PPV-based polymers.

EXPERIMENTAL

Measurements

Newly synthesized compounds were identified by NMR spectra, FT-IR spectra and elemental analysis (EA). ¹H NMR and ¹³C NMR spectra were obtained on a Bruker AMX-400 MHz or an AV500 MHz FT-NMR spectrometer, with the chemical shifts reported in ppm using tetramethylsilane (TMS) as an internal standard. The FT-IR spectra were measured as KBr disk on a Fourier transform infrared spectrometer, model 7850 from Jasco. Elemental analysis was carried out on a Heraus CHN-Rapid elemental analyzer. The weight-average molecular weight (M_w) and polydispersity index (PDI) of polymers were measured with a gel permeation chromatograph (GPC), using chloroform (CHCl₃) as eluent and monodisperse polystyrenes as calibration standards. Thermogravimetric analysis (TGA) of polymers was performed under nitrogen atmosphere at a heating rate of 20 °C /min using a Perkin-Elmer TGA-7 thermal analyzer. Thermal transition properties of polymers were investigated using a differential scanning calorimeter (DSC), PerkinElmer DSC 7, under nitrogen atmosphere at a heating rate of 10 °C/min. Absorption and photoluminescence (PL) spectra were measured with a Jasco V-550 spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Cyclic voltammograms were recorded with a voltammetric analyzer (model CV-50W from Bioanalytical Systems) at room temperature under nitrogen atmosphere. The measuring cell was made up of a glassy carbon as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire as the auxiliary electrode. The concentration of low MW compounds (M0, TAZ and CAZ) in the cell was 3 mg/1 mL acetonitrile, while polymers (PF, P1-P3) were directly coated on glassy



SCHEME 1 Synthesis of monomer M1 and structures of M0, TAZ, and CAZ.

carbon to form as thin films. The electrodes were immersed in acetonitrile containing 0.1 M $(n-Bu)_4NClO_4$ as electrolyte. The energy levels were calculated using ferrocene (FOC) as standard (-4.8 eV with respect to vacuum level).²³

Materials

9,9-Dihexyl-2,7-dibromofluorene (Aldrich), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (Aldrich), aliquat 336 (Alfa Aesar), tetrakis(triphenylphosphine) palladium $[Pd(PPh_3)_4]$ (Acros), methyl 2,5-dibromobenzoate (Acros), benzoyl chloride (Acros), phosphorous pentachloride (PCl₅, Riedel-Dehaen), 9-phenyl-9H-carbazole (CAZ, Aldrich) N,N-dimethylaniline (Acros), dimethyl sulfoxide (DMSO, Tedia), toluene (Tedia), chloroform (CHCl₃, Tedia) and other solvents were of commercial sources and used without further purification. 1-((2,5-Dibromophenyl)chloromethylene)-2-(chloro(phenyl)methylene) hydrazine (4) was prepared from 2,5-dibromobenzohydrazide (2) by reacting consecutively with benzoyl chloride and phosphorous pentachloride (PCl₅) (Scheme 1). 4-(9*H*-carbazol-9-yl)benzenamine (8) was synthesized via direct reduction of 9-(4-nitrophenyl)-9H-carbazole (7) by hydrazine monohydrate, in which 7 was obtained from 1-fluoro-4-nitrobenzene (5) and 9Hcarbazole (6). For a comparative study, triazole model





SCHEME 2 Synthesis of bipolar copolyfluorenes (P1-P3) and polyfluorene (PF).

3,4,5-triphenyl-4*H*-1,2,4-triazole (**TAZ**) containing electrontransporting core was also prepared from aniline and 1,2-bis(chloro(phenyl)methylene)hydrazine. The synthetic procedures of bipolar model compound **M0** were similar to those of bipolar **M1**.

Synthesis of Bipolar Monomer (M1) and Model Compound (M0) (Scheme 1)

A mixture of 1-((2,5-dibromophenyl)chloromethylene)-2-(chloro(phenyl)methylene) hydrazine (4: 0.87 g, 2 mmol) and 4-(9H-carbazol-9-yl)benzenamine (8: 0.52 g, 2 mmol) in 10 mL of N,N-dimethylaniline was stirred at 135 °C for 12 h under nitrogen atmosphere. After adding aqueous solution of HCl (30 mL, 2 N), the mixture was stirred for additional 30 minutes. The precipitated solid was collected by filtration, dried in vacuo, and recrystallized from acetone to afford 9-(4-(3-(2,5-dibromophenyl)-5-phenyl-4H-1,2,4-triazol-4-yl)phenyl)-9*H*-carbazole (**M1**) (54%); mp >250 °C. ¹H NMR (CD₂Cl₂, ppm): δ 8.15 (s, 1H, Ar-H), 8.13 (s, 1H, Ar-H), 7.68 (d, J = 2.0 Hz, 1H, Ar-H), 7.60–7.56 (m, 4H, Ar-H), 7.54–7.41 (m, 7H, Ar-H), 7.36-7.29 (m, 6H, Ar-H). FTIR (KBr pellet, cm⁻¹): v 1507 (C=N), 1262 (C-N), 1070 (C-Br). Anal. Calcd. (%) for $C_{32}H_{20}Br_2N_4$: C, 61.96; H, 3.25; N, 9.03. Found: C, 61.65; H, 3.18; N, 8.96.

9-(4-(3,5-Diphenyl-4*H*-1,2,4-triazol-4-yl)phenyl)-9*H*-carbazole (**M0**), model compound of bipolar unit, was synthesized by analogous procedures used in the preparation of monomer **M1** with a yield of 61%; mp >250 °C. ¹H NMR (CDCl₃, ppm): δ 8.18–8.15 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.67–7.65 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.57–7.55 (m, 4H, Ar-H), 7.47–7.32 (m, 14H, Ar-H). FTIR (KBr pellet, cm⁻¹): ν 1509 (C=N), 1270 (C–N). Anal. Calcd. (%) for C₃₂H₂₂N₄: C, 83.09; H, 4.79; N, 12.11. Found: C, 83.00; H, 4.81; N, 12.14.

Synthesis of Bipolar Copolyfluorenes (P1-P3) and Poly(9,9-dihexylfluorene) (PF)

Copolyfluorenes (**P1-P3**) containing pendant bipolar groups and poly(9,9-dihexylfluorene) (**PF**) were prepared by the Suzuki coupling reaction using $(PPh_3)_4Pd$ as the catalyst

(Scheme 2).²⁴ For instance, stoichiometric amounts of 9,9dihexylfluorene-2,7-bis(trimethyleneborate) (9: 0.251 g, 0.50 mmol), 9,9-dihexyl-2,7-dibromofluorene (10: 0.222 g, 0.45 mmol), 9-(4-(3-(2,5-dibromophenyl)-5-phenyl-4H-1,2,4-triazol-4-yl)phenyl)-9H-carbazole (M1: 0.031 g, 0.05 mmol), 10 mg of (PPh₃)₄Pd and several drops of Aliquat 336 were added to a mixture containing toluene (10 mL) and 2 M aqueous solution of K₂CO₃ (8 mL). The mixture was refluxed for 48 h under nitrogen atmosphere. Extra monomer 9 (16 mg, 0.03 mmol) was added to the reaction mixture and stirred for additional 12 h. Finally, mono-functional bromobenzene (10 mg, 0.07 mmol) was added and stirred for 12 h to end-cap polymer chain with phenyl group. After cooling to room temperature, the reaction mixture was precipitated from methanol and distilled water (v/v = 10/1). The precipitate was collected by filtration, dissolved in chloroform and reprecipitated from methanol twice. Then it was Soxhlet extracted with acetone for 48 h to remove trace oligomers and catalyst residues and then dried *in vacuo* to give **P2**. ¹H NMR (CDCl₃, ppm): δ 7.86–7.84 (m, 2H, Ar-H), 7.71–7.67 (m, 4H, Ar-H), 7.65 (m, 4H, Ar-H), 7.59-7.56 (m, 7H, Ar-H), 7.52-7.34 (m, 6H, Ar-H), 2.12 (s, 4H, -CH2-), 1.26-1.25 (s, 4H, --CH₂--), 1.14-1.11 (s, 12H, --CH₂--), 0.84-0.78 (s, 6H, $-CH_3$). FTIR (KBr pellet, cm⁻¹): v 2930 (Ar-H), 1509 (C=N), 1455 (C=C), 1274 (C-N). Anal. Calcd. (%) for P2: C, 89.36; H, 9.80; N, 0.84. Found: C, 87.34; H, 9.12; N, 0.53.

The synthetic procedures of PF, P1 and P3 were analogous to those used in the preparation of P2, except with varied molar feed ratios in 9, 10 and M1. PF: 9 (0.251 g, 0.50 mmol), **10** (0.246g, 0.50 mmol). ¹H NMR (CDCl₃, ppm): δ 7.85-7.83 (m, 2H, Ar-H), 7.71-7.67 (m, 4H, Ar-H), 2.12 (s, 4H, --CH₂--), 1.25 (s, 4H, --CH₂--), 1.13 (s, 12H, --CH₂--), 0.84–0.78 (m, 6H, –CH₃). FTIR (KBr pellet, cm⁻¹): v 2928 (Ar-H), 1455 (C=C). Anal. Calcd. (%) for PF: C, 90.26; H, 9.74. Found: C, 88.37; H, 9.43. P1: 9 (0.251 g, 0.50 mmol), **10** (0.231 g, 0.47 mmol) and **M1** (0.018 g, 0.03 mmol). ¹H NMR (CDCl₃, ppm): δ 7.86-7.84 (m, 2H, Ar-H), 7.71-7.67 (m, 4H, Ar-H), 7.65 (m, 4H, Ar-H), 7.59-7.56 (m, 7H, Ar-H), 7.52-7.34 (m, 6H, Ar-H), 2.12 (s, 4H, -CH₂-), 1.25-1.23 (s, 4H, --CH₂--), 1.14-1.11 (s, 12H, --CH₂--), 0.84-0.78 (s, 6H, -CH₃). FTIR (KBr pellet, cm⁻¹): v 2928 (Ar-H), 1509 (C=N), 1455 (C=C), 1274 (C-N). Anal. Calcd. (%) for P1: C, 89.54; H, 9.95; N, 0.51. Found: C, 88.27; H, 9.37; N, 0.38. P3: 9 (0.251 g, 0.50 mmol), 10 (0.197 g, 0.40 mmol) and M1 (0.062 g, 0.10 mmol). ¹H NMR (CDCl₃, ppm): δ 7.86–7.84 (m, 2H, Ar-H), 7.72-7.68 (m, 4H, Ar-H), 7.65 (m, 4H, Ar-H), 7.59-7.56 (m, 7H, Ar-H), 7.52-7.34 (m, 6H, Ar-H), 2.13 (s, 4H, -CH₂-), 1.25-1.23 (s, 4H, -CH₂-), 1.50 (s, 12H, $-CH_2$ -), 0.84–0.78 (s, 6H, $-CH_3$). FTIR (KBr pellet, cm⁻¹): v 2930 (Ar-H), 1509 (C=N), 1455 (C=C), 1274 (C-N). Anal. Calcd. (%) for P3: C, 88.91; H, 9.45; N, 1.64. Found: C, 87.66; H, 8.82; N, 1.28.

Fabrication of Polymer Light-Emitting Diodes

Double-layer polymer light-emitting diodes (ITO/PEDOT: PSS/polymer/Ca/Al) were fabricated to investigate their optoelectronic characteristics. Transparent indium tin oxide (ITO) glass was successively cleaned with neutraler

reiniger/de-ionized water (1/3 = v/v) mixture, de-ionized water, acetone and 2-propanol, and then dried *in vacuo* overnight. Aqueous dispersion of PEDOT:PSS was spin-coated on top of the cleaned ITO glass as hole-injection layer and dried at 150 °C for 15 min. Emitting layer was then deposited by spin-coating (1000 rpm) onto the PEDOT:PSS layer from a polymer solution in 1,2-dichlorobenzene (10 mg/mL). Finally, calcium and aluminum were consecutively vacuum-deposited as cathode using a vacuum coater at a pressure of 2×10^{-6} Torr. Luminance versus voltage and current density versus voltage characteristics of the devices were measured using a combination of a Keithley power source (model 2400) and an Ocean Optics usb2000 fluorescence spectrophotometer. The optoelectronic measurements were conducted in a glove-box filled with nitrogen.

RESULTS AND DISCUSSION

Characterization of Bipolar Monomer (M1) and Copolyfluorenes (P1-P3)

Scheme 1 illustrates the synthetic routes employed in the preparation of novel bipolar monomer M1. 9-(4-nitrophenyl)-9*H*-carbazole $(7)^{2^{5}(d)}$ and 4-(9*H*-carbazol-9-yl)benzenamine $(8)^{25(d)}$ were prepared according to the procedures reported previously. The copolyfluorenes (P1-P3) were synthesized by the Suzuki coupling reaction of 9,9dihexylfluorene-2,7-bis(trimethyleneborate) (9) with functionalized dibromo aromatic monomers (10 and M1) (Scheme 2), using Pd(PPh₃)₄ as the reaction catalyst and Aliquat 336 as the phase-transfer catalyst. The feed ratios of monomer M1 in the preparation of P1, P2, and P3 were 3, 5, and 10 mol %, respectively. Extra monomer 9 and monofunctional bromobenzene were added to end-cap polymer chain after the polymerization. Supporting Information (Fig. S1) shows the ¹H NMR, ¹³C NMR, DEPT135, H-H COSY, and C-H HMQC spectra of M1. Assignments of each carbon and proton were assisted by the two-dimensional NMR spectra [Supporting Information Fig. S1(d,e)], which agree well with the proposed molecular structure of M1. The existence of M1 residue in P3 is confirmed by ¹³C NMR and DEPT135 spectra of M1, PF and P3 as shown in Supporting Information Figures S1(b,c) and S2. In ¹³C NMR spectra of P3 chemical shifts of M1 residue are obviously observed at 132.2 ppm (12), 128.8 ppm (2), 128.6 ppm (4), 128.4 ppm (3), and 127.2 ppm (14). The actual molar percents of M1 residues in P1, P2 and P3 are 2.5, 3.2 and 7.7 mol %, respectively, as estimated from the elemental analysis data. This indicates that the bipolar monomer M1 is less reactive than 9,9-dihexyl-2,7-dibromofluorene (10), which is probably due to steric hindrance and electron-deficient characteristic of its bipolar moiety. The copolyfluorenes are readily soluble in common organic solvents such as toluene, chloroform, chlorobenzene and 1,2-dichlorobenzene. Their weight-average molecular weights (M_w) and polydispersity indexes (PDI) are in the range of $(1.70-4.79) \times 10^4$ and 1.95-2.33 (Table 1), respectively, as determined by gel permeation chromatography using mono-disperse polystyrenes as calibration standards.

TABLE 1 Polymerization Results and Characterization of Polymers

Polymer	Yield (%)	<i>M</i> _n (×10 ⁴) ^a	<i>M</i> _w (×10 ⁴) ^a	PDI ^a	<i>T</i> g (°C)	T _d (°C) ^b	у (%) ^с
PF	66	2.06	4.79	2.33	91	440	0
P1	64	1.61	3.40	2.11	101	469	2.5
P2	59	1.21	2.63	2.17	104	475	3.2
P3	60	0.87	1.70	1.95	120	482	7.7

 $^{\rm a}$ $M_{\rm n},$ $M_{\rm w},$ and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards.

^b The temperature at 5 wt % loss under nitrogen atmosphere.

 $^{\rm c}$ The molar fractions of M1 residues were estimated from elemental analysis.

Thermal decomposition temperatures (T_d) (at 5 wt % loss) and glass transition temperatures (T_g) of the copolyfluorenes were evaluated with thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. The residual weights of P1-P3 and PF (at 800 °C) are above 50% under nitrogen atmosphere (Supporting Information Fig. S3). As shown in Table 1, the thermal decomposition temperatures (T_d : 469–482 °C) of the copolyfluorenes (P1-P3) are higher than that of **PF** (T_d : 440 °C). Moreover, the copolyfluorenes reveal higher glass-transition temperatures (101-120 °C) than **PF** (91 °C) and the $T_{\rm g}$ increases gradually with increasing M1 residues in main chain. This is attributable to rigid and non-planar structure of M1 residues which not only raises chain rigidity but also restrict chain mobility of the copolyfluorenes.^{21(c),26} Accordingly, the copolyfluorenes exhibit better thermal stability than **PF**; i.e., their thermal decomposition (469-482 °C) and glass-transition temperatures (101-120 °C) are higher than those of **PF** (440 °C, 91 °C).

Photophysical Properties of Model Compound M0 and Bipolar Copolyfluorenes (P1-P3)

Figure 1 illustrates the absorption and photoluminescence (PL) spectra of bipolar model compound (MO), carbazole model (CAZ) and triazole model (TAZ) in CHCl₃ with the characteristic optical data summarized in Table 2. The absorption maximum and main emission peak of the bipolar model **M0** in CHCl₃ appear at about 283, 292 nm (with shoulders at 310, 323 and 337 nm) and 347 nm (with a shoulder at 359 nm), respectively. These absorption and emission bands are mainly attributed to carbazole part as judged from their spectral features (similar to those of CAZ). However, the absorption and emission of MO are slightly blue-shifted (3-5 nm) relative to those of CAZ due to the presence of electron-accepting triazole moiety. Moreover, the PL spectra of MO were almost the same whether they were excited with 261 nm (absorption maximum of TAZ) or 286 nm (absorption maximum of CAZ), suggesting efficient intramolecular energy transfer from TAZ to CAZ moiety under the photo-excitation.

Figure 2 illustrates the absorption and photoluminescence (PL) spectra of poly(9,9-dihexylfluorene) (**PF**) and bipolar copolyfluorenes (**P1-P3**) in CHCl₃ and as films spin-coated





FIGURE 1 Absorption and PL spectra of **M0**, **CAZ**, and **TAZ** in chloroform (1 × 10⁻⁵ M) (λ_{ex} = 283 nm for **M0**, 286 nm for **CAZ** and 261 nm for **TAZ**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

from CHCl₃ solutions, with the characteristic optical data summarized in Table 2. The absorption maxima of P1-P3 in $CHCl_3$ locate at 386, 385 and 380 nm with only small shorter-wavelength absorptions at about 292 nm. The major absorption of P1-P3 (380-386 nm) can be attributed to the π - π * transitions of their conjugated backbone, whereas the shorter-wavelength absorption (ca. 292 nm) is definitely originated from bipolar M1 residues. The major absorption shifts slightly from 389 nm (PF) to 380 nm (P3) because the conjugation of polyfluorene main chain is interrupted by the bipolar moieties. This can be substantiated by the existence of twist angles (ca. 90°) between heterocyclic ring and adjacent benzene rings of bipolar M1 units (Fig. 3), simulated by minimizing energy via semi-empirical MNDO calculations in the gas states.²⁷ Solid state absorption maxima of PF and P1-P3 are slightly red-shifted (5-7 nm) relative to solution state ones due to aggregate formation via intra- or inter-chain interactions. Copolyfluorenes P1-P3 exhibit PL peaks at 418-419 nm which are very close to 419 nm of PF. Moreover, the PL spectra of P1-P3 were almost the same whether they were excited with 292 nm (absorption maximum of M0) or 380 nm, confirming efficient Förster energy transfer from bipolar M1 residues to fluorene segments

TABLE 2 Optical Properties	s of Model N	10 and Polymers
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FIGURE 2 Absorption and PL spectra of **PF** and **P1-P3**: (a) in chloroform $(1 \times 10^{-5} \text{ M})$ ($\lambda_{ex} = 389 \text{ nm}$ for **PF**, 386 nm for **P1**, 385 nm for **P2** and 380 nm for **P3**), (b) in film state ($\lambda_{ex} = 391$ nm for **PF**, 391 nm for **P1**, 390 nm for **P2** and 387 nm for **P3**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

under the photo-excitation. Partial overlap between emission spectrum of **M1** residues and absorption spectrum of **PF** contributes greatly to the energy transfer.^{21(c),26,28} It is note-worthy that the emission spectrum of **PF** partially overlaps with the absorption spectrum of MEH-PPV, indicating that energy transfer from **PF** to MEH-PPV can be expected.^{21(c)} Based on this characteristic we fabricated efficient PLEDs using blends of MEH-PPV and **P1-P3** as emitting layer and will be discussed later.

Molecule/Polymer	UV-vis λ _{max} Solution (nm) ^a	UV-vis λ_{\max} Film (nm)	PL λ_{max} Solution (nm) ^b	PL λ _{max} Film (nm) ^b	$\Phi_{PL}{}^{c}$
MO	283,292,310s,323s,337s	-	347,359s	-	-
CAZ	261,286,293,327s,341s	_	352,364s	_	_
TAZ	261	_	346	_	_
PF	389	391	419,441s	425,449s	0.82
P1	292,386	293,391	419,441s	425,449s	0.79
P2	292,385	293,390	419,441s	424,449s	0.77
P3	292,380	293,387	418,441s	424,449s	0.72

 a In chloroform (1 \times 10 $^{-5}$ M).

^b s: wavelength of shoulder.

 c Φ_{PL} : Determined in CHCl₃, relative to quinine sulfate in 1N H₂SO_{4(aq)} at a concentration of 10⁻⁵ M ($\Phi_{PL}=$ 0.55).



FIGURE 3 Optimized geometry of a model bipolar compound obtained from semiempirical MNDO calculation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Relative PL quantum yields (Φ_{PL}) of **PF**, **P1**, **P2**, and **P3** in chloroform (at a concentration of 10^{-5} M) are 0.82, 0.79, 0.77, and 0.72, respectively. The $\Phi_{PL}s$ of the copolyfluorenes are slightly lower than that of PF, probably caused by torsion-induced non-radiative deactivation occurred at the nonplanar bipolar groups.²⁹ Polyfluorenes usually show undesirable green emission after thermal annealing or under device operation, which has been attributed to enhanced intermolecular interactions.³⁰ To examine stability in emission color, PF and P1-P3 films were thermally annealed at 150 °C for 24 h to observe their PL spectral variations. As shown in Figure 4, the green emission appears at about 500-600 nm in PF film after the thermal treatment; however, it is significantly suppressed in P1-P3 films. This result suggests that the non-planar bipolar M1 residues are effective in suppressing the intermolecular interactions in the copolyfluorenes.

Electrochemical Investigations

Cyclic voltammetry (CV) was employed to investigate the electrochemical properties of PF, bipolar copolyfluorenes P1-P3, bipolar model M0, triazole model TAZ and carbazole model CAZ. Their HOMO and LUMO energy levels were esti-



FIGURE 4 PL spectra of PF and P1-P3 after annealing in vacuum at 150 °C for 24 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



(a)

TAZ CAZ

100

0

-200

-300

Current (µA) -100

FIGURE 5 Cyclic voltammograms of (a) M0, TAZ, and CAZ are 3 mg/1 mL acetonitrile (b) PF and P1-P3 coated on glassy carbon working electrode (scan rate: 100 mV/s). [Color figure can be viewed in the online issue, which is available at

-2

-3

mated by the equations: E_{HOMO} (eV) = $-(E_{\text{ox,FOC}} + 4.8)$ and $E_{
m LUMO}$ (eV) = - ($E_{
m red,FOC}$ + 4.8), where $E_{
m ox,FOC}$ and $E_{
m red,FOC}$ are the onset oxidation and onset reduction potentials, respectively, relative to the ferrocene/ferrocenium couple whose energy level is already known (-4.8 eV). The cyclic voltammograms are shown in Figure 5, with the representative electrochemical data summarized in Table 3. Bipolar model M0 would emit blue-green light corresponding to its band-gap (2.80 eV), but its main emission peak (347 nm) with a shoulder at 359 nm obviously strays from blue-green emission. To elucidate above interesting phenomena, we also estimated the LUMO and HOMO energy levels of bipolar model M0, triazole model TAZ and carbazole model CAZ from their cyclic voltammograms. The LUMO levels of MO, TAZ and CAZ are -2.79, -2.71, and -2.45 eV, and the estimated HOMO levels are -5.59, -6.12, and -5.53 eV, respectively (Table 3). Obviously, the LUMO and HOMO energy levels of MO are close to LUMO level of TAZ and HOMO level of CAZ, respectively. This indicates that the LUMO and HOMO levels of MO are attributed to triazole and carbazole moieties, respectively. Accordingly, when MO is subjected to external potentials, the reduction starts from electron-deficient aromatic 1,2,4-triazole and the oxidation begins from electron-rich 9-phenyl-9H-carbazole groups, respectively.

Molecule/Polymer	$E_{\rm ox}$ vs. FOC (V) ^a	$E_{\rm red}$ vs. FOC (V) ^a	Е _{номо} (eV) ^ь	E _{LUMO} (eV) ^b	$E_{\rm g}^{\rm el}$ (eV) ^c	E_{g}^{opt} (eV) ^d
MO	0.79	-2.01	-5.59	-2.79	2.80	_
TAZ	1.32	-2.09	-6.12	-2.71	3.41	_
CAZ	0.73	-2.35	-5.53	-2.45	3.08	_
PF	0.85	-2.31	-5.65	-2.49	3.16	2.91
P1	0.84	-2.30	-5.64	-2.50	3.14	2.91
P2	0.83	-2.28	-5.63	-2.52	3.11	2.90
P3	0.81	-2.25	-5.61	-2.55	3.06	2.90

TABLE 3 Electrochemical Properties of M0, TAZ, CAZ and Polymers (PF, P1-P3)

^a E_{FOC} = 0.48 V vs. Ag/AgCl.

^b E_{HOMO} = - ($E_{ox, FOC}$ + 4.8) eV; E_{LUMO} = - ($E_{red, FOC}$ + 4.8) eV.

In this study, copolyfluorenes P1-P3 contain 2.5-7.7 mol % of bipolar M1 residues derived from electron-transporting triazole and hole-transporting carbazole. The estimated HOMO energy levels of **PF**, **P1-P3** are -5.65, -5.64, -5.63, and -5.61 eV, whereas the estimated LUMO levels are -2.49, -2.50, -2.52, and -2.55 eV, respectively. The HOMO levels of P1-P3 are raised gradually from -5.65 eV to -5.61 eV with an increase in M1 residues (2.5-7.7 mol %; Fig. 6), suggesting that their hole affinity is in the order of P3 > P2 > P1. On the contrary, the LUMO levels of P1-P3 are lowered slightly (-2.49 to -2.55 eV) with increasing M1 residues meaning that their electron injection ability is improved in the order of P3 > P2 > P1. Accordingly, both hole and electron affinity of P1-P3 is slightly enhanced with increasing M1 residues, resulting in improved carriers injection and transport. Both LUMO and HOMO levels of bipolar model MO (-2.79 and-5.59 eV) are lower than those of conventional MEH-PPV (-2.70 and -5.02 eV) because of the electron-withdrawing aromatic 1,2,4-triazole moiety.^{21(b,c),31} Therefore, blending MEH-PPV with P1-P3 containing bipolar residues would increase electron affinity; the hole affinity, however, would be reduced simultaneously. The blending might be an effective way to improve charges injection and transport balance in MEH-PPV, whose hole injection and transport are more facilitated.



FIGURE 6 Energy band diagrams of **M0**, **TAZ**, **CAZ**, **PF**, **P1-P3**, and MEH-PPV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

^c Electrochemical band gap: $E_{q}^{el} = LUMO - HOMO$.

^d Optical band gap: $E_{g}^{opt} = hc / \check{\lambda}_{onset}$.

Electroluminescent Enhancement of MEH-PPV by Bipolar Copolyfluorenes

Polymer light-emitting devices using P1-P3 as emitting layer [ITO/PEDOT:PSS/P1-P3/Ca(50 nm)/Al(100 nm)] were fabricated to study their current density and luminance (vs. bias) characteristics. The turn-on voltages of P1-P3 devices increased from 5.3 to 7.3 V with increasing M1 moieties (from 2.5 to 7.7 mol %). In addition, the maximum luminance and maximum luminance efficiency of P1-P3 devices decreased from 410 to 230 cd/m² and from 0.15 to 0.10 cd/ A, respectively, with increasing M1 moieties (2.5-7.7 mol %). Moreover, the LUMO and HOMO levels of bipolar model MO (-2.79 and -5.59 eV) are encompassed within those of PF (-2.49 and -5.65 eV) (Fig. 6). Accordingly, the performance degradation at high M1 contents is probably caused by charges trapping in the bipolar moieties that reduce charge recombination in polyfluorene segments.^{32,33} As mentioned earlier, both LUMO and HOMO levels of bipolar model MO are lower than those of MEH-PPV (Fig. 6). This suggests that the M1 residues will promote electron injection/transport and block hole transport in MEH-PPV device. To elucidate this reasoning, MEH-PPV was blended with bipolar P1-P3 and used as emitting layers to solve its common defect of unbalanced charges injection and transport. Double-laver diodes [ITO/PEDOT:PSS/(MEHpolymer light-emitting PPV+P1, P2 or P3)/Ca(50 nm)/Al (100 nm)] were fabricated to investigate their device performances. The weight ratios of MEH-PPV to the bipolar copolyfluorenes (MEH-PPV/P1, MEH-PPV/P2 and MEH-PPV/P3) were controlled at 91/9, 94/6 and 97/3, respectively, to adjust the ratios of bipolar residues to be about 0.2 wt %. Figure 7 shows the current density and luminance versus bias characteristics of the blend devices, with the representative data summarized in Table 4. The maximum luminance efficiency of the neat MEH-PPV device (0.29 cd/A) is moderate relative to those reported in literatures.^{20(a-c,h,i),22(d,e)} The discrepancy of luminance efficiency among these EL devices is probably due to their device structural difference. The blend devices exhibit slightly higher turn-on voltages (3.3-4.1 V) than MEH-PPV device (3.3 V), indicating that electron injection enhancement by the bipolar residues seems inferior to their hole-blocking effect that higher bias is needed to turn on the devices.^{21(c),34} However, the maximum luminance and

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FIGURE 7 (a) Current density versus bias and (b) luminance versus bias characteristics of PLEDs using blends of MEHPPV and P1-P3 (3–9 wt %) as emitting layer. Device configuration: ITO/PEDOT:PSS/MEH-PPV + P1, P2 or P3 (90–110 nm)/Ca(50 nm)/Al(100 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

maximum luminance efficiency of the blend devices are significantly enhanced to $8780-13,350 \text{ cd/m}^2$ and 0.56-0.79 cd/A, respectively, when compared with 3230 cd/m^2 and 0.29 cd/A of the MEH-PPV device. Apparently the bipolar **M1** residues in emitting layer effectively balance charges injection and transport under device operation. In addition, the device performance seems mainly dependent on the con-

ARTICLE

tents of fluorene segments (from copolyfluorenes). For instance, **P3**-based blend device reveals the best EL performance, due probably to the least content of fluorene segments (ca. 2.8 wt %) relative to **P1**- and **P2**-based devices (ca. 8.8 wt %) and 5.8 wt %). This means that higher percents of fluorene segments in emitting layer (as in **P1**- and **P2**-based devices) leads to inferior device performance. As shown in Figure 6, the HOMO (-5.02 eV) and LUMO energy levels (-2.70 eV) of MEH-PPV lies between those of poly(9,9-dihexylfluorene) (**PF**: -5.65 eV, -2.49 eV). Therefore, charges injection and transport ability of the blend is reduced with increasing contents of fluorene segments.

The influence of bipolar residues' contents on electroluminescent performance was also investigated using P3-based blend devices as an example. The current density and luminance versus bias characteristics are shown in Figure 8, with the corresponding performance data summarized in Table 4. The turn-on voltages increase slightly from 3.3 to 4.8 V with increasing P3 contents (3-15 wt %) because hole-blocking effect of the bipolar residue surpasses its enhancement in electron injection.^{21(c),34} To clarify the hole-blocking effect of P3 in the blends, hole-only devices [ITO/PEDOT:PSS/(MEH-PPV+ P3)/Au(20 nm)/Al (100 nm)] were fabricated to investigate their current density versus bias characteristics. As shown in Figure 9, the curve shifts horizontally to higher bias as P3's ratio is increased from 0 to 6 wt %, indicating diminished current density under the same bias. For instance, at an electric field of 9 \times 10⁵ V/cm the current density decreases from 1000 mA/cm² to about 700 mA/cm², which is obviously due to increased hole-blocking at high P3 contents (6 wt %). The maximum luminance and the maximum luminance efficiency of the device are enhanced from 3230 cd/m^2 and 0.29 cd/A to 15,690 cd/m² and 0.81 cd/A, respectively, as the weight ratio of P3 is increased from 0 to 6%. This performance is superior to that obtained for our previous copolyfluorene with 8.2 mol % pendant bipolar groups derived from triphenylamine and aromatic 1,2,4-triazole (11,090 cd/m² and 0.56 cd/A).^{21(d)} The EL performance difference is probably due to varied LUMO and HOMO energy levels, resulting from different chemical structures (carbazole vs. triphenylamine) and contents of the bipolar

TABLE 4	Optoe	lectronic	Performance	of Po	lymer Li	ght-Emitting	Diodes ^a
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Emitting–Layer Composition ^b	Turn on Voltage (V) ^c	Maximum Luminance Efficiency (cd/A)	Maximum Luminance (cd/m²)	CIE Coordinates $(x, y)^d$
MEH-PPV	3.3	0.29	3,230	(0.54, 0.46)
MEH-PPV/ P1 (91/9)	4.1	0.56	8,780	(0.49, 0.50)
MEH-PPV/ P2 (94/6)	3.5	0.67	11,950	(0.49, 0.50)
MEH-PPV/ P3 (97/3)	3.3	0.79	13,350	(0.50, 0.49)
MEH-PPV/ P3 (94/6)	3.6	0.81	15,690	(0.48, 0.51)
MEH-PPV/P3 (91/9)	3.6	0.71	11,470	(0.52, 0.48)
MEH-PPV/ P3 (88/12)	4.3	0.56	9,620	(0.48, 0.51)
MEH-PPV/P3 (85/15)	4.8	0.44	5,060	(0.53, 0.47)

^a Device structure: ITO/PEDOT:PSS/emitting layer/Ca/Al.

^b The weight ratios are given in parentheses.

 $^{\rm c}$ The voltage required for the luminance of 10 cd/m².

^d The CIE coordinates at maximum luminance.



ARTICLE



FIGURE 8 (a) Current density versus bias and (b) luminance versus bias characteristics of PLEDs using blends of MEHPPV and P3 (3–15 wt %) as emitting layer. Device structure: ITO/ PEDOT:PSS/MEH-PPV + P3 (90–110 nm)/Ca(50 nm)/Al(100 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

groups (7.7 vs. 8.2 mol %). Accordingly, the significantly enhanced device performance in P3-based device is mainly resulted from more balanced charges recombination. However, further increase in P3 contents leads to quick degrada-



FIGURE 9 Current density versus bias characteristics of the hole-only devices using blends of MEH-PPV and P3 (0–6 wt %) as emitting layer. Device structure: ITO/PEDOT:PSS/MEH-PPV + P3 (90–110 nm)/Au(20 nm)/Al(100 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tion in maximum luminance and maximum current efficiency; i.e., diminish to 5060 cd/m² and 0.44 cd/A at MEH-PPV/P3 = 85/15. The results of morphology investigation can reasonably explain this performance reversion at higher P3 contents. As shown in Figure 10, the root-mean-square surface roughness of the blend films increases from 0.97 to 1.33 nm with increasing P3 weight ratio from 6 to 15%. The increased surface roughness at high P3 weight ratio is due to its limited compatibility with MEH-PPV. Therefore, the quick performance degradation of the blend device is probably attributed to higher surface roughness formed during film preparation.

However, at low **P3** content (MEH-PPV/**P3** = 94/6) the device performance is effectively enhanced. As shown in Figure 11, the electroluminescent emission of all devices is exclusively originated from MEH-PPV, with full width at half-



FIGURE 10 AFM images of blend films (Scan size: $5 \times 5 \mu m^2$): (a) MEH-PPV/**P3** = 94/6, RMS roughness = 0.97 nm, (b) MEH-PPV/**P3** = 85/15, RMS roughness = 1.33 nm.



FIGURE 11 Emission spectra of PLEDs using blends of MEH-PPV and P1-P3 as emitting layer. Device configuration: ITO/ PEDOT:PSS/MEH-PPV + P1, P2, or P3 (90–110 nm)/Ca(50 nm)/ Al(100 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

maxima (fwhm) being about 80 nm. The 1931 CIE coordinates (*x*, *y*) of the EL emission only shift slightly from (0.54, 0.46) of MEH-PPV-based device to (0.48, 0.51) of blend devices (MEH-PPV/**P3** = 94/6, MEH-PPV/**P3** = 88/12). Furthermore, the excimer emission of MEH-PPV at about 625 nm is also diminished due probably to reduced aggregation after blending with the bipolar copolyfluorenes. Consequently, slight amount of copolyfluorenes **P1-P3** containing pendant bipolar groups (**M1** residues) is effective in enhancing device performance of the conventional MEH-PPV.

CONCLUSIONS

We have successfully synthesized three copolyfluorenes (P1-P3) containing pendant bipolar groups (M1 residues: 2.5, 3.2, and 7.7 mol %). The copolyfluorenes were soluble in common organic solvents and thermally stable (T_d at 5 wt % loss: 469-482 °C and T_g : 101-120 °C). The PL spectra of bipolar model ${\bf M0}$ were almost the same whether they were excited with absorption maximum of TAZ or CAZ, suggesting efficient intra-molecular energy transfer. Moreover, the PL spectra of P1-P3 were identical to that of poly(9,9-dihexylfluorene) (PF), due to efficient Förster energy transfer. Estimated LUMO and HOMO levels of model M0 were -5.59 eV and -2.79 eV, which are mainly attributed to LUMO levels of TAZ and HOMO levels of CAZ, respectively. The HOMO levels of PF and P1-P3 were raised gradually from -5.65 eV to -5.61 eV with increasing bipolar residues (from 0 to 7.7 mol %), while their LUMO levels lowered slightly from -2.49 to -2.55 eV. The device performance of EL device based on MEH-PPV was significantly enhanced by blending with the bipolar copolyfluorenes, due to more balanced charges recombination in the blends. P3-based blend device (MEH-PPV/P3 = 94/6) showed the best performance with maximum luminance of 15,690 cd/m² and maximum luminance efficiency of 0.81 cd/A. Current results indicate that the copolyfluorenes containing bipolar moieties are promising additives in effectively improving device performance of MEH-PPV and other conjugated polymers.

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