Tuning Wavelength: Synthesis and Characterization of Spiro-DPVF-Containing Polyfluorenes and Applications in Organic Light-Emitting Diodes

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ABSTRACT: We have synthesized polyfluorene copolymers containing bis(2,2-diphenylvinyl)fluorene pendent groups attached orthogonally to the C-9 positions of fluorene units. These polymers possess high glass transition temperatures and good thermal stability. The results from PL studies indicate that most excitons formed in the polyfluorene backbone by direct photoexcitation are likely to migrate to lower-energy pendent groups, from which emission occurs. An organic light-emitting device using the copolymer PF4-DPVF as the emitting layer exhibits a voltage-independent and stable blue emission with color coordinates (0.15, 0.17) at 11 V, with a maximum brightness of 3137 cd/m^2 at 9 V (262 mA/cm^2) and a maximum external quantum efficiency of 1.06%. In addition, we blended PF4-DPVF as the host material with 0.5 wt % of MEH-PPV to realize a white electroluminescence having CIE coordinates of (0.29,0.34) and a maximum brightness of 3258 cd/m^2 (119 mA/cm^2). We demonstrate that both Förster energy transfer and direct charge trapping/recombination on the MEH-PPV guest are responsible for the observed EL.

Introduction

Since the discovery of poly(phenylenevinylene)-based LEDs in 1990,[1] considerable efforts have been made toward the development of new conjugated polymers and in the performance of their related LEDs.[2] Organic luminescent polymers are attractive because of the flexibility available for fine-tuning their luminescence properties through the manipulation of their chemical structures and because of the feasibility of combining spin-coating and printing processes for preparing large-area flat-panel displays. Blue-emitting polymers are of special interest because they can be used either as a blue light source in full-color displays or as the host material for generating other colors through energy transfer to lower-energy fluorophores.[3] Polyfluorenes (PFs) are among the most promising candidates for blue-emitting polymers because of their high photoluminescence and electroluminescence efficiencies.[4] In addition, the facile process of functionalizing the C-9 position of the fluorene unit provides the opportunity to improve both the solubility and processability of the resulting polymers, while also offering the ability to tune the optoelectronic properties of the PFs through macromolecular engineering.[5−8]

The application of polyfluorenes in PLEDs has been hampered, however, because the formation of an undesired long-wavelength emission band occurs during device operation and results in both color instability and reduced efficiency.[9,10] Moreover, the emissions of typical dialkylpolyfluorenes are located in the deep-blue region (λ_{max} = ca. 420 nm) where the human eye is not very sensitive.[11] In this paper, we report the synthesis and characterization of fluorene-based copolymers containing bis(2,2-diphenylvinyl)fluorene (DPVF) pendent groups attached orthogonally to the C-9 positions of fluorene units. This polymer design has the advantage of permitting the incorporation of a high concentration of DPV dye without affecting the electronic properties of the polyfluorene backbone.[12] We chose DPVF dye to be the side chain because its distyrylarylene analogue, 4,4′-

bis(2,2-diphenylvinyl)-1,1′-biphenyl (DPVBi), exhibits intense fluorescence in the blue region (λ_{max} = ca. 460 nm) and been utilized as an emitting material to achieve efficient organic blue- and white-light-emitting diodes.[13,14] By attaching DPVF to the polyfluorene chain, energy transfer from the higher-energy polyfluorene backbone to the lower-energy DPVF pendant groups may occur, leading to emission solely or predominantly from the latter. As a result, the photoluminescence (PL) of the copolymer is fine-tuned to a blue region, which is closer to the maximum of a relative photopic luminous efficiency function.[15] Another special feature of DPVBi is its nonplanar molecular structure; i.e., the phenyl rings at both ends of the molecule are forced to twist as a result of steric hindrance.[16] The presence of the rigid spiro-DPVF side chain may also reduce interchain interactions and suppress the formation of long-wavelength aggregates/excimers,[9] resulting in a stable and efficient blue electroluminescence.

Experimental Section

Materials. 2,7-Dibromo-9,9′-spirobifluorene (**1**), 2,7-dibromo-9,9-dioctylfluorene (**5**), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctylfluorene (**6**), poly(2-ethylhexloxy-5-methoxy-1,4-phenylenevinylene) (MEH-PPV), and the electron-transport material 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)-benzene (TPBI) were prepared according to reported procedures.[17−20] The solvents were dried using standard procedures. All other reagents were used as received from commercial sources, unless otherwise stated.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Unity Yinova 500 MHz or a Bruker DRX 300 MHz spectrometer. Mass spectra were obtained on a JEOL JMS-SX/SX 110 mass spectrometer. Size exclusion chromatography (SEC) was carried out on a Waters chromatography unit interfaced to a Waters 410 differential refractometer. Three 5 μm Waters styragel columns (300 × 7.8 mm) connected in series in decreasing order of pore size (10^4, 10^3, and 10^2 Å) were used in conjunction with THF as the eluent. Standard polystyrene samples were used for calibration. Differential scanning calorimetry (DSC) was performed on a SEIKO EXSTAR 6000DSC unit at a heating rate of 20 °C min^{-1} and

a cooling rate of 40 °C min^{-1}. Samples were scanned from 30 to 300 °C, cooled to 0 °C, and then scanned again from 30 to 300 °C. The glass transition temperatures (T_g) were determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken on a DuPont TGA 2950 instrument. The thermal stability of each sample under a nitrogen atmosphere was determined by measuring its weight loss while heating at a rate of 20 °C min^{-1}. UV−vis spectra were measured using an HP 8453 diode-array spectrophotometer. Photoluminescence (PL) spectra were obtained on a Hitachi F-4500 luminescence spectrometer. Cyclic voltammetry (CV) measurements were performed using a BAS 100 B/W electrochemical analyzer in anhydrous acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte at a scan rate of 50 mV s^{-1}. The potentials were measured against an Ag/Ag$^+$ (0.01 M AgNO$_3$) reference electrode using ferrocene as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram.

2,7-Dibromo-2′,7′-bis(bromomethyl)-9,9′-spirobifluorene (2). 2,7-Dibromo-9,9′-spirobifluorene (378 mg, 800 µmol) was added to a stirred solution of paraformaldehyde (216 mg, 7.06 mmol) in 30 wt % HBr/AcOH (8 mL) in a medium-pressure flask at 0 °C. The flask was sealed, and the reaction mixture was heated at 120 °C for 24 h before being cooled and added dropwise to water (100 mL). The precipitate was washed with water and purified by column chromatography (hexane/CH$_2$Cl$_2$, 5:1) to afford **2** (210 mg, 41%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.35 (s, 4 H), 6.68 (s, 2 H), 6.81 (d, J = 1.6 Hz, 2 H), 7.45 (dd, J = 7.9, 1.5 Hz, 2 H), 7.51 (dd, J = 8.1, 1.8 Hz, 2 H), 7.67 (d, J = 8.1 Hz, 2 H), 7.79 (d, J = 7.9 Hz, 2 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 33.4, 65.3, 120.8, 121.5, 122.1, 124.5, 127.3, 129.7, 131.5, 138.0, 139.6, 141.2, 147.9, 149.6. HRMS [M$^+$ + H] calcd for C$_{27}$H$_{17}$^{79}Br$_4$, 656.8064; found 656.8062. Anal. Calcd for C$_{27}$H$_{16}$Br$_4$: C, 49.13; H, 2.44. Found: C, 49.22; H, 2.66.

2,7-Dibromo-2′,7′-bis(diethoxyphosphorylmethyl)-9,9′-spirobifluorene (3). A mixture of **2** (310 mg, 470 µmol) and triethyl phosphite (0.18 mL, 1.03 mmol) was heated at 150 °C for 15 h. Excess triethyl phosphite was evaporated under vacuum, and the residue was added to hexane. The precipitate was washed with hexane to yield a white solid (352 mg, 97%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.04 (t, J = 7.0 Hz, 12 H), 3.00 (d, $J_{H,P}$ = 21.6 Hz, 4 H), 3.74−3.89 (m, 8 H), 6.57 (s, 2 H), 6.77 (d, J = 1.6 Hz, 2 H), 7.34 (d, J = 7.7 Hz, 2 H), 7.46 (dd, J = 8.1, 1.7 Hz, 2 H), 7.65 (d, J = 8.1 Hz, 2 H), 7.75 (d, J = 7.8 Hz, 2 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 16.2 (d, $J_{C,P}$ = 6.0 Hz), 33.8 (d, $J_{C,P}$ = 137.1 Hz), 62.2 (d, $J_{C,P}$ = 6.8 Hz), 65.2, 120.4 (d, $J_{C,P}$ = 2.6 Hz), 121.5, 121.8, 125.2 (d, $J_{C,P}$ = 6.4 Hz), 127.1, 130.1 (d, $J_{C,P}$ = 6.3 Hz), 131.2, 131.6 (d, $J_{C,P}$ = 9.3 Hz), 139.6, 140.1 (d, $J_{C,P}$ = 1.9 Hz), 147.2 (d, $J_{C,P}$ = 2.8 Hz), 150.2. HRMS [M$^+$] calcd for C$_{35}$H$_{36}$^{79}Br$_2$P$_2$O$_6$, 772.0353; found 772.0352. Anal. Calcd for C$_{35}$H$_{36}$Br$_2$P$_2$O$_6$: C, 54.40; H, 4.70. Found: C, 54.25; H, 4.87.

2,7-Dibromo-2′,7′-bis(2,2-diphenylvinyl)-9,9′-spirobifluorene (4). Potassium *tert*-butoxide (343 mg, 2.71 mmol) was added to a solution of **3** (700 mg, 900 µmol) and benzophenone (494 mg, 2.71 mmol) in anhydrous THF (7 mL) under nitrogen. The mixture was heated under reflux for 9 h, cooled, and then added to water (100 mL). The precipitate was washed with hexane and purified by column chromatography (hexane/EtOAc, 5:1) to give **4** (459 mg, 61%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 5.98 (s, 2 H), 6.62 (d, J = 1.5 Hz, 2 H), 6.82 (s, 2 H), 6.90−6.93 (m, 4 H), 6.97−7.02 (m, 6 H), 7.14 (dd, J = 8.0, 1.4 Hz, 2 H), 7.21−7.24 (m, 10 H), 7.42 (dd, J = 8.0, 2.0 Hz, 2 H), 7.47 (d, J = 8.0 Hz, 2 H), 7.56 (d, J = 8.0 Hz, 2 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 64.9, 119.7, 121.0, 121.7, 124.8, 127.1, 127.3, 127.4, 127.7, 128.11, 128.14, 129.8, 130.2, 130.7, 137.4, 139.2, 139.7, 139.8, 142.9, 146.8, 149.8. HRMS [M$^+$ + H] calcd for C$_{53}$H$_{35}$^{79}Br$_2$, 829.1106; found 829.1104. Anal. Calcd for C$_{53}$H$_{34}$Br$_2$: C, 76.64; H, 4.13. Found: C, 76.75; H, 4.47.

Preparation of PF2−DPVF. Aqueous potassium carbonate (2.0 M, 2.4 mL) and Aliquat 336 (ca. 34 mg) were added to a mixture of monomers **4** (230 mg, 277 µmol) and **6** (178 mg,

277 µmol) in distilled toluene (3.5 mL). The mixture was degassed, and tetrakis(triphenylphosphine)palladium (8 mg, 2.5 mol %) was added in one portion under N$_2$. The solution was then heated at 110 °C for 14 h. The end groups were then capped by heating under reflux for 12 h with benzeneboronic acid (70.9 mg, 582 µmol) and then for 12 h with bromobenzene (91 mg, 582 µmol). The reaction mixture was then cooled to room temperature and precipitated into a mixture of MeOH and H$_2$O (1:1 v/v, 100 mL). The crude polymer was collected and washed with excess MeOH. The resulting polymer was dissolved in chloroform and reprecipitated into MeOH. The polymer was then washed with acetone for 24 h using a Soxhlet apparatus and dried under vacuum to give PF2-DPVF (279 mg, 95%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.69−0.77 (m, 10 H), 0.98−1.08 (m, 20 H), 2.02 (br, 4 H), 6.23 (s, 2 H), 6.83 (d, J = 7.5 Hz, 4 H), 6.85−6.94 (m, 10 H), 7.11 (d, J = 7.7 Hz, 2 H), 7.17−7.20 (m, 10 H), 7.41−7.43 (m, 2 H), 7.50−7.53 (m, 2 H), 7.57−7.66 (m, 6 H), 7.77 (d, J = 7.7 Hz, 2 H). Anal. Calcd for (C$_{82}$H$_{74}$)$_n$: C, 92.96; H, 7.04. Found: C, 92.34; H, 7.61.

Preparation of PF4-DPVF. Following the procedure described for **PF2-DPVF**, the copolymerization of monomers **4** (150 mg, 181 µmol), **5** (99.0 mg, 181 µmol), and **6** (231 mg, 362 µmol) gave PF4-DPVF (259 mg, 78%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.70−0.79 (m, 30 H), 1.05−1.11 (m, 60 H), 2.06 (br, 12 H), 6.24 (s, 2 H), 6.84−6.94 (m, 14 H), 7.14−7.18 (m, 12 H), 7.45−7.81 (m, 24 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 14.1, 22.52, 22.56, 22.59, 23.9, 29.2, 30.0, 31.6, 31.7, 31.8, 40.4, 55.3, 65.6, 119.5, 120.0, 121.1, 121.5, 122.2, 125.2, 126.1, 126.7, 127.2, 127.4, 128.0, 128.2, 128.8, 129.8, 137.2, 139.7, 140.0, 140.3, 140.5, 140.9, 142.6, 143.1, 148.7, 149.2, 151.7, 151.8. Anal. Calcd for (C$_{140}$H$_{154}$)$_n$: C, 91.55; H, 8.45. Found: C, 91.08; H, 8.38.

Farbricating Light-Emitting Devices. Polymer LED devices were fabricated having the configuration ITO/poly-(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT) (35 nm)/light-emitting layer (50−70 nm)/TPBI (30 nm)/Mg:Ag (100 nm)/Ag (100 nm). To improve hole injection and substrate smoothness, the PEDOT was spin-coated directly onto the ITO glass and dried at 80 °C for 12 h under vacuum. The light-emitting layer was spin-coated on top of the PEDOT layer using toluene as the solvent and then dried for 3 h at 60 °C under vacuum. Prior to film casting, the polymer solution was filtered through a Teflon filter (0.45 µm). The TPBI layer, which was grown by thermal sublimation in a vacuum of 3 × 10^{-6} Torr, was to be used as the electron-transport layer that would block holes and confine excitons.[21] The cathode Mg:Ag (10:1, 100 nm) alloy was deposited onto the TPBI layer by coevaporation of the two metals, followed by an additional layer of Ag (100 nm) deposited onto the alloy as a protection layer. The current−voltage−luminance was measured under ambient conditions using a Keithley 2400 source meter and a Newport 1835C optical meter equipped with an 818ST silicon photodiode.

Results and Discussion

Synthesis of the Monomer and the Polymers. Scheme 1 illustrates the synthetic route we followed to prepare a spirobifluorene monomer containing bis(2,2-diphenylvinyl) moieties. Bromomethylation of **1**[17] with paraformaldehyde in HBr/AcOH afforded compound **2**, which was then reacted with triethyl phosphite to yield the phosphonate ester **3**. The Horner−Emmons condensation of **3** and benzophenone furnished the target monomer, 2,7-dibromo-2′,7′-bis(2,2-diphenylvinyl)-9,9′-spirobifluorene (**4**). The structure of monomer **4** was characterized by ^{1}H and ^{13}C NMR spectroscopy. The vinylic protons give rise to a singlet at δ 6.82, while the signal for a quarternary carbon atom at δ 64.9 (C-9) indicates the presence of the spiro skeleton. We synthesized two random-fluorene copolymers, PF2-DPVF and PF4-DPVF, which incorporate 50 and 25 mol % of bis(2,2-diphenylvinyl) units, respectively, by the Suzuki

Scheme 1. Synthetic Route for DPVF-Containing Monomer
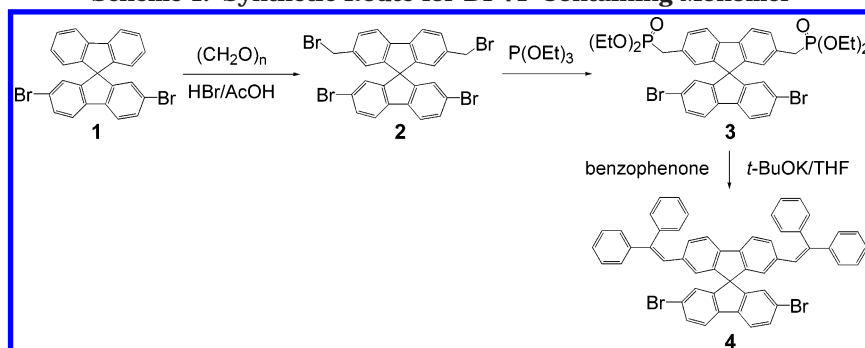
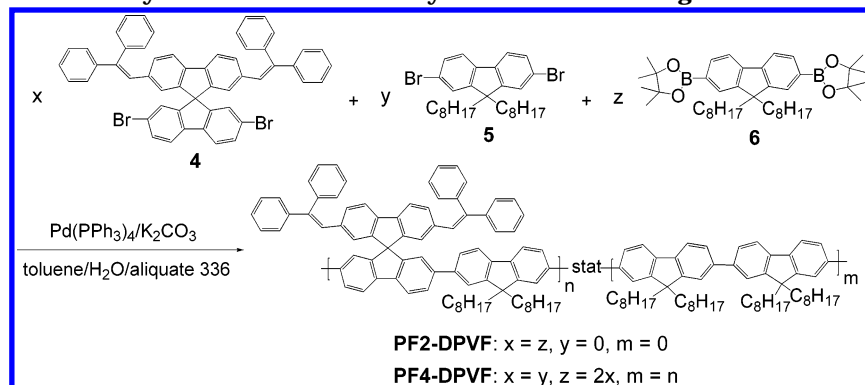**Scheme 2. Synthetic Scheme for Polyfluorenes Containing DPVF Pendants**

PF2-DPVF: x = z, y = 0, m = 0
PF4-DPVF: x = y, z = 2x, m = n

Table 1. Molecular Weights and Thermal Properties of PF2-DPVF and PF4-DPVF

polymer	$M_n{}^a \times 10^4$	$M_w{}^a \times 10^4$	DSC (°C) $T_g{}^b$	TGA^c (°C) 5%
PF2-DPVF	0.86	2.5	n.o.^{d}	410
PF4-DPVF	1.5	3.6	107	423

^{a} Molecular weights were determined by GPC, eluting with THF, by comparison with polystyrene standards. ^{b} The value of T_g was determined by DSC at a heating rate 20 °C min^{-1} under a nitrogen atmosphere. ^{c} Temperature at which a 5% weight loss occurred was determined at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere. ^{d} No noticeable phase transition was observed in the temperature range 30−300 °C.

coupling reaction between dibromides **4** and **5** and the diboronate **6** (Scheme 2).[22] We estimated the compositions of these copolymers by integrating the areas of the peaks in the ^{1}H NMR spectra. We attribute the resonance at ca. 2.04 ppm to the aliphatic protons (4 H) adjacent to the quarternary carbon atom (C-9) of the fluorene unit, whereas the peak at 6.23 ppm represents the protons (2 H) located in the spirobifluorene unit. The ratios between the integrals of the former and the latter are 1.9:1.0 and 5.8:1.0 for PF2-DPVF and PF4-DPVF, respectively, which reveals that the incorporation ratios of bis(2,2-diphenylvinyl) units are in good agreement with the monomer feed ratios.

PF4-DPVF is readily soluble in common organic solvents, such as toluene, chloroform, and THF, but PF2-DPVF is only slightly soluble in chloroform and exhibits poor solubility in other organic solvents as a result of its higher content of the rigid spiro-DPVF (50 mol %). We determined the molecular weights of these polymers by size exclusion chromatography (SEC) using THF as the eluent and calibrating against polystyrene standards; Table 1 lists the results. For PF2-DPVF, the molecular weights are probably higher than the values listed because it is only partially soluble in THF; the

insoluble portion may correspond to higher-molecular-weight material.

We investigated the thermal properties of these spiro-DPVF-containing copolymers by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC); the results are also tabulated in Table 1. Both polymers are thermally stable and have 5% weight loss temperatures in nitrogen >410 °C. We did not detect any possible phase transition signals during repeated heating/cooling DSC cycles for PF2-DPVF. This observation probably results from the stiffness of this polymer's chains, which again is due to its higher content of the rigid spiro-DPVF. In the case of PF4-DPVF, we observed a distinct glass transition temperature at 107 °C, which is higher than that of poly(9,9-dioctylfluorene) (POF; T_g = ca. 75 °C).[23] The increased value of T_g can be attributed to the presence of the rigid diphenylvinyl-9,9′-spirobifluorene unit, which enhances the molecular rigidity of the polymer and restricts its segmental mobility. It is important that PLEDs be constructed from materials having a relatively high value of T_g to avoid the problems associated with the formation of aggregates and excimers upon exposure to heat.[24]

Photophysical Properties. Because PF2-DPVF exhibits poor solubility in organic solvents, which limits this material's use in PLED applications, in this study we investigated the optical properties of PF4-DPVF only. Figure 1 presents the absorption and PL spectra of this fluorene copolymer as dilute solutions; the spectral data are summarized in Table 2. The absorption and PL spectra of compound **4**, which serves as a model compound in studying the optical properties of the bis-(2,2-diphenylvinyl)fluorene (DPVF) pendants, are also presented in Figure 1. In chloroform solution, PF4-DPVF exhibits an absorption having its λ_{max} at 387 nm, which we ascribe to the combined $\pi-\pi^*$ transitions originating from the polyfluorene backbone and pendent groups because POF and compound **4**, in chloroform,
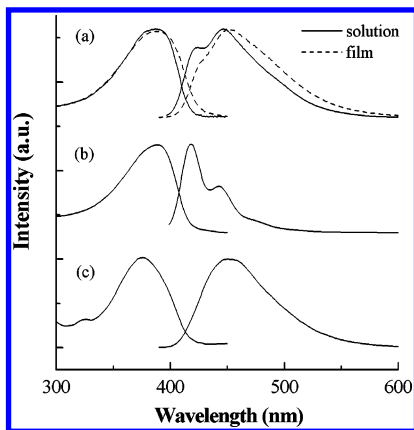
Figure 1. (a) UV−vis absorption and PL spectra of PF4-DPVF in chloroform solution and in the solid state. UV−vis absorption and PL spectra of (b) POF and (c) **4** in chloroform solutions.

Table 2. Optical Properties and Quantum Yields of PF4-DPVF, 4, and POF

	solution[a]			film[b]		
	abs (nm)	PL (nm)[c]	Φ_f[d]	abs (nm)	PL (nm)[c]	Φ_f
PF4-DPVF	387	(424) 447	0.75	388	(426) 450	0.59[e]
4	374	451				
POF	389	418 (442)	0.85	387	424 (448)	0.55

[a] Evaluated in chloroform. [b] Prepared by spin-coating from a toluene solution. [c] Excited at 380 nm. [d] Determined in toluene relative to 9,10-diphenylanthracene in cyclohexane ($\Phi_f = 0.9$) with excitation at 365 nm. [e] Relative to the thin-film quantum efficiency of POF ($\Phi_f = 0.55$) with excitation at 380 nm. [f] Peaks that appear as shoulders or weak bands are indicated in parentheses.

exhibit absorptions having λ_{max} at 389 and 374 nm, respectively. Upon excitation at 380 nm, we observed a broad PL spectrum that has a main peak at 447 nm, which is contributed from the emission of the DPVF pendants, together with a minor contribution from the PF main chain (a shoulder at 424 nm). This result reveals that an efficient intramolecular energy transfer occurs from the excited PF backbone to the DPVF side chain, even though the spectral overlap between the emission spectrum of the former and the absorption spectrum of the latter is moderate (Figure 1b,c). PF4-DPVF exhibits a high quantum efficiency in solution; we measured its fluorescence yield (Φ_f) when excited at 365 nm in toluene, using 9,10-diphenylanthrancene ($\Phi_f = 0.9$) as a standard,[25] to be 0.75, which is close to the fluorescence yield measured for POF ($\Phi_f = 0.85$).

In comparison to the dilute solution, the absorption spectrum of a PF4-DPVF thin film appears slightly broadened, probably because of aggregate formation, but without a spectral shift, while the emission spectrum shows a red shift of 3 nm. It is noteworthy that the emission from the polyfluorene is almost completely suppressed in this PF4-DPVF film; instead, the PL spectrum exhibits emission arising predominantly from the DPVF pendants. The lack of polyfluorene emission in the film indicates that an efficient Förster energy transfer is facilitated by both intra- and interchain interactions that result from the shorter polymer chain distances in the solid state. We estimated the PL quantum yield of the PF4-DPVF film to be 0.59 by comparing its fluorescence intensity to that of a thin-film sample of POF polymer that was excited at 380 nm ($\Phi_f = 0.55$).[26]
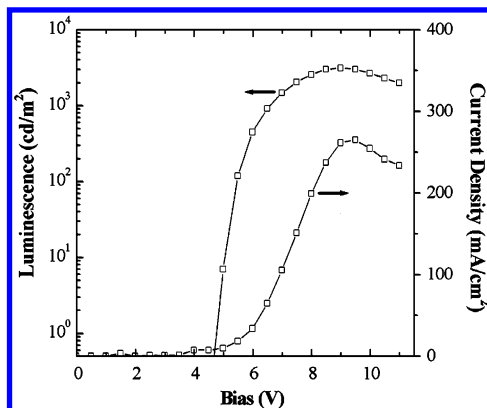

Figure 2. Current density−voltage−luminance characteristics of ITO/PEDOT/PF4-DPVF/TPBI/Mg:Ag.
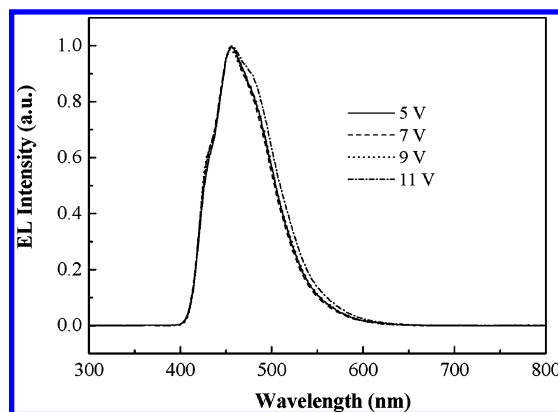

Figure 3. EL spectra of the device ITO/PEDOT/PF4-DPVF/TPBI/Mg:Ag at different voltages.

Redox Properties. Cyclic voltammetry (CV) measurements of PF4-DPVF film coated on a glassy carbon electrode were performed in an electrolyte of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in acetonitrile using ferrocene as the internal standard. On the basis of the onset potentials of the oxidation and reduction, which were 0.91 and −2.61 V, we estimated the HOMO and LUMO energy levels of PF4-DPVF to be 5.71 and 2.18 eV, respectively, with regard to the energy level of ferrocene (4.8 eV below vacuum).[27] These results are very close to the data reported for POF (I_p = 5.8 eV, E_a = 2.12 eV).[28] Because the energy level of ferrocene is determined by photoelectron spectroscopy in the solid state, this method can be considered to provide merely a rough approximation.

Electroluminescence Properties of LED Devices. To evaluate the potential of PF4-DPVF as a blue emissive material in polymer LED applications, we fabricated a triple-layered diode with a TPBI electron injection/transport layer (ETL), introduced between the light-emitting layer and the Mg:Ag cathode, for hole blocking and exciton confinement.[21] As indicated in Figure 2, the device reaches a maximum brightness of 3137 cd/m² at a bias of 9 V (261.5 mA/cm²); the maximum external quantum efficiency of 1.06% occurs at 6.5 V (64.7 mA/cm²). The EL spectra presented in Figure 3 having their peak wavelengths at ca. 455 nm are quite similar to the PL emission spectrum of PF4-DPVF (Figure 1), which indicates that both the PL and EL originate from the same radiative decay process of the singlet exciton. Moreover, Figure 3 also demonstrates that the PF4-DPVF-based device exhibits voltage-independent and stable EL spectra with Commis-
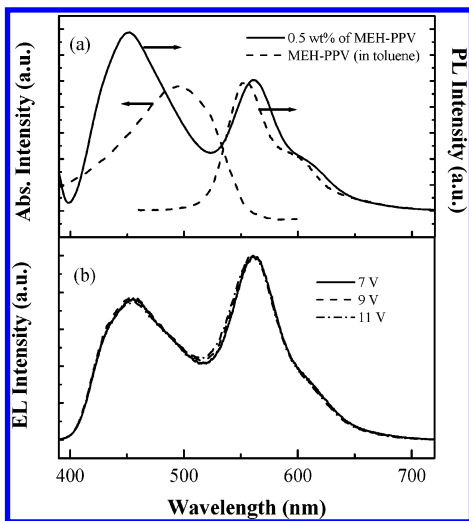
Figure 4. (a) Absorption and emission spectra of MEH-PPV in toluene and the solid-state PL spectrum of the binary blend. (b) EL spectra of the device ITO/PEDOT/MEH-PPV:PF4-DPVF/TPBI/Mg:Ag at different voltages.

Figure 5. Current density–voltage–luminance characteristics of ITO/PEDOT/MEH-PPV:PF4-DPVF/TPBI/Mg:Ag.

sion Internationale de L'Eclairage (CIE) color coordinates of (0.15, 0.15) at 7 V and (0.15, 0.17) at 11 V, which fall in the region of pure blue on a CIE chromaticity diagram.

White Electroluminescence from a Binary Blend. It has been demonstrated that white polymer LEDs can be achieved by emission from a binary blend composed of a blue host polymer and a red-orange polymer used as the guest material.[29] In this study, we used PF4-DPVF as the host material and blended it with 0.5 wt % of MEH-PPV to realize white electroluminescence. The PL spectrum of PF4-DPVF and the absorption spectrum of MEH-PPV (Figure 4a) overlap to a reasonable extent in the region 400–550 nm, which meets the requirement for efficient energy transfer. The excitons formed in the host, PF4-DPVF, by direct photoexcitation are likely to migrate to the lower-energy dopant, MEH-PPV. As a result, the PL profile of the blend contains two peaks: one centered at 450 nm that originates from the emission of the PF4-DPVF host, while another at ca. 560 nm corresponds to the emission of MEH-PPV. The emission peak of MEH-PPV from the blend is blue-shifted by 30 nm relative to that of neat MEH-PPV and is similar to that of the dilute solution of MEH-PPV in toluene (Figure 4a). This observation indicates that the interchain interactions between MEH-PPV chains are reduced in the blend as a result of the dilution effect induced by the host polymer. At a low dopant concentration of 0.5 wt %, the PL spectrum is dominated by the emission of the host because of incomplete energy transfer. In contrast, the MEH-PPV emission contrib-
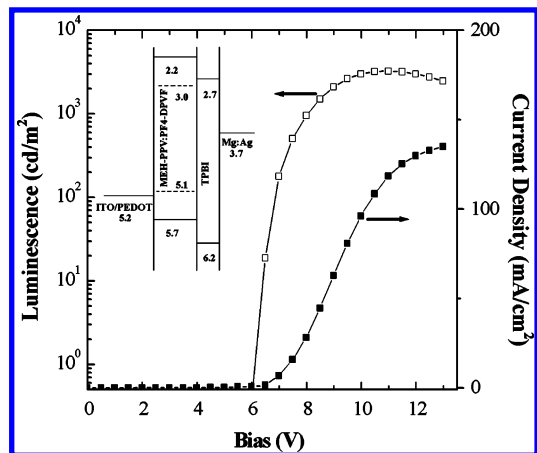
utes predominately to the corresponding EL spectrum (Figure 4b), which results in the white electroluminescence having CIE coordinates of (0.29, 0.34) at 7 V. The contribution from the MEH-PPV emission is obviously more significant in the EL process than it is in the PL process, which reveals that both Förster energy transfer and direct charge trapping/recombination on the MEH-PPV guest are responsible for the observed EL.[30] The inset of Figure 5 depicts the energy level diagram. The highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbit (LUMO) levels of PF4-DPVF are 5.7 and 2.2 eV, respectively, while the ionization potential and LUMO of MEH–PPV are 5.1 and 3.0 eV,[31] respectively. These values imply that holes or electrons can be potentially trapped by MEH-PPV with a depth of 0.6–0.8 eV and recombined with opposite charges in the blend device. Table 3 summarizes the performances of the device based on the blend. The maximum external quantum efficiency is 1.31% (3.40 cd/A) at a bias of 8 V (28.2 mA/cm^2) with a brightness of 957 cd/m^2; the maximum brightness (Figure 5) is 3258 cd/m^2 at 11 V (118.5 mA/cm^2), and the corresponding EL spectrum is almost identical to that recorded at 7 V. Furthermore, the turn-on voltage for the binary blend device is 6.1 V, while that for the host-only device is decreased to 4.6 V. This observation also supports the charge trapping mechanism previously proposed.[30a]

In summary, we have developed DPVF-containing polyfluorenes having DPVF moieties as pendent groups attached orthogonally to the 9-positions of some of the fluorene units. Our PL studies indicate that color tuning can be achieved through Förster energy transfer from the higher-energy polyfluorene backbone to the lower-energy DPVF pendants, from which the emission occurs. This moderate red shift (ca. 25 nm) leads to a higher

Table 3. Performances of Devices Having Structures ITO/PEDOT/EML/TPBI/Mg:Ag

device	PF4-DPVF	MEH-PPV (0.5 wt %): PF4-DPVF
turn-on voltage (V)^a	4.6	6.1
voltage (V)^b	6.9	10.2
brightness (cd/m^2)^b	1404	3078
luminance efficiency (cd/A)^b	1.41	3.08
external quantum efficiency (%)^b	1.05	1.19
max brightness (cd/m^2)	3137 (at 9 V)	3258 (at 11 V)
max luminance efficiency (cd/A)	1.42	3.40
max external quantum efficiency (%)	1.06	1.31
EL max (nm)^c	455	561
CIE coordinates, x and y^c	0.15, 0.15	0.29, 0.34

^{a} At 1 cd/m^2. ^{b} At 100 mA/cm^2. ^{c} At 7 V.

luminance efficiency. An EL device based on PF4-DPVF exhibits a voltage-independent and stable blue emission having color coordinates of (0.15,0.17) at 11 V, a low turn-on voltage at 4.6 V, and a maximum brightness of 3137 cd/m^2 at 9 V. Moreover, we realized a white electroluminescent device having CIE coordinates of (0.29, 0.34) and a maximum brightness of 3258 cd/m^2 using a blend of PF4-DPVF with 0.5 wt % of MEH-PPV as the emitting material.

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