

Polyfluorene Presenting Dipolar Pendent Groups and Its Application to Electroluminescent Devices

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ABSTRACT: We have synthesized a blue-light-emitting polyfluorene derivative (PF-TPAOXD) that presents sterically hindered, dipolar pendent groups functionalized at the C-9 positions of alternating fluorene units. The incorporation of the dipolar side chains, each comprising an electron-rich triphenylamine group and an electron-deficient oxadiazole group connected through a π -conjugated bridge, endows the resultant polymer with higher highest occupied molecular orbital and lower lowest unoccupied molecular orbital energy levels, which, consequently, lead to an increase in both hole and electron affinities. An electroluminescent device incorporating this polymer as the emitting layer exhibited a stable blue emission with a maximum brightness of 2080 cd/m² at 12 V and a maximum external quantum efficiency of 1.4% at a brightness of 137 cd/m². Furthermore, atomic force microscopy measurements indicated that the dipolar nature of PF-TPAOXD, in contrast to the general nonpolarity of polydialkylfluorenes, provided a stabilizing environment allowing the polar organometallic triplet dopant to be dispersed homogeneously. We also fabricated an electrophosphorescent device incorporating PF-TPAOXD as the host material doped with a red-emitting osmium complex to realize red electroluminescence with Commission Internationale de l'Eclairage color coordinates of (0.66, 0.34). The resulting device exhibited a maximum external quantum efficiency of 7.3% at a brightness of 1747 cd/m² and a maximum brightness of 7244 cd/m². © 2007 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 45: 2073–2084, 2007

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INTRODUCTION

Since the first discovery of polymer light-emitting devices in 1990, electroluminescence (EL) polymers have been studied widely in an effort to realize their potential applications in flat-panel displays and in solid-state lighting.¹ Polymeric materials are attractive because of the feasibility of using solution processing techniques,^{2–5} includ-

ing spin coating and ink-jet printing, which are generally less expensive than the high-vacuum deposition approaches used commonly for depositing small molecules. For full-color-display applications, blue-, green-, and red-light-emitting materials that possess sufficient luminous efficiency and appropriate chromaticity must be developed. Polymers having such large band-gap energies that they emit blue light are of particular interest because they can be used either as blue light sources in full-color displays or as host materials for lower energy fluorescent or phosphorescent dyes to achieve green and red emis-

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Among the known light-emitting polymers, polyfluorenes (PFs) are regarded as the most promising candidates for blue-light-emitting materials because of their high luminescence and thermal stability^{17–23} and the ability to readily tune their colors through grafting with low-band-gap fluorophores or phosphors.^{24–40} Nevertheless, there are several drawbacks that may hinder their potential development, especially the phenomenon of an undesired green emission that appears upon thermal annealing or device operation.⁴¹ This long-wavelength emission is believed to occur as a result of the formation of interchain excimers or aggregates^{42–44} or from the presence of keto defects arising from oxidation at the C-9 positions of the fluorene units.^{45–52} Another problem encountered when PFs are used in polymeric light-emitting diode applications is the high ionization potential (usually 5.8 eV),⁵³ that is, a high energy barrier exists for holes to travel into PFs from the indium tin oxide (ITO)/poly(3,4-ethylene dioxythiophene) (PEDOT) layer (5.2 eV),⁵⁴ and this results in higher driving voltages.

The ability to readily functionalize the C-9 position of fluorene units provides the opportunity to improve both the solubility and processability of the resulting polymers, while offering the possibility of tuning the optoelectronic properties of PFs through macromolecular engineering.^{13,55–63} In this study, we report the synthesis and characterization of the fluorene-based alternating copolymer PF-TPAOXD, which contains a sterically hindered, dipolar pendent group attached directly to the C-9 carbon atom of every alternating fluorene unit to form a 3D cardo structure. PFs, which are π -excessive in nature, are typical *p*-dope-type polymers that are hole-transport-dominated materials.^{64,65} We incorporated a dipolar side chain, consisting of an electron-rich triphenylamine group and an electron-deficient oxadiazole group connected through a π -conjugated bridge, with the aim of improving the charge-injection/transport characteristics of PFs.^{66,67} In addition, we hoped that the introduction of the sterically demanding pendent group would help to prevent π stacking between the polymer chains and suppress the formation of excimers in the solid state, which, in turn, would enhance the thermal stability of the resultant copolymer. Moreover, we anticipated that the dipolar characteristic of PF-TPAOXD, in contrast to the generally nonpolar nature of polydialkylfluorenes, would provide a compatible environment in which polar organometallic triplet dopants could

be dispersed homogeneously.^{68,69} When using PF-TPAOXD as the emitting layer in a device setting, we achieved an efficient and stable deep blue EL with a maximum external quantum efficiency of 1.43% and color coordinates of (0.15, 0.07). We also prepared a high-performance red-electrophosphorescent device, using PF-TPAOXD as the polymeric host doped with a red-emitting osmium complex.⁷⁰

EXPERIMENTAL

General Directions

2,7-Dibromo-9-phenyl-9*H*-fluorene-9-ol (**2**),⁷¹ 2,7-dibromo-9-(4-tolyl)-9-phenyl-9*H*-fluorene (**3**),⁷¹ *N*-[4-(1*H*-tetrazol-5-yl)phenyl]-*N*-phenylbenzenamine (**5**),⁶⁷ and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**7**)⁷² were synthesized according to reported procedures. The solvents were dried with standard procedures. All other reagents were used as received from commercial sources, unless otherwise stated. ¹H and ¹³C NMR spectra were recorded on a Varian Unity Inova 500-MHz spectrometer, a Varian Unity 300-MHz spectrometer, and a Bruker-DRX 300-MHz spectrometer. Mass spectra were obtained with a JEOL JMS-HX 110 mass spectrometer. Size exclusion chromatography was performed on a Waters chromatography unit interfaced with a Waters 410 differential refractometer. Three 5- μ m Waters Styragel columns (300 \times 7.8 mm) were connected in series in order of decreasing pore size (10⁴, 10³, and 10² Å), THF was the eluent, and standard polystyrene samples were used for calibration. Differential scanning calorimetry (DSC) was performed with a Seiko Exstar 6000DSC unit at a heating rate of 20 °C/min and at a cooling rate of 50 °C/min. Samples were scanned from 30 to 350 °C, cooled to 0 °C, and then scanned again from 30 to 350 °C; the glass transition temperatures (T_g 's) were determined from the second heating scan. Thermogravimetric analysis (TGA) was performed with a PerkinElmer TGA Pyris 1 instrument. The thermal stabilities of the samples were determined under a nitrogen atmosphere by the measurement of their weight losses during heating at a rate of 10 °C/min. UV-vis spectra were measured with an HP 8453 diode-array spectrophotometer. Photoluminescence (PL) spectra were obtained with a Hitachi F-4500 luminescence spectrometer. Cyclic voltammetry (CV) measurements were performed with a BAS 100 B/W electrochemical analyzer operated at a

scanning rate of 50 mV/s; the solvent was anhydrous acetonitrile, and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) was the supporting electrolyte. The potentials were measured against a Ag/Ag⁺ (0.01 M AgNO₃) reference electrode; ferrocene was the internal standard. Atomic force microscopy (AFM) measurements were performed in the tapping mode with a Digital Nanoscope IIIa under ambient conditions.

Light-Emitting Devices

The devices were fabricated in the ITO/PEDOT (35 nm)/polymer (50–70 nm)/TPBI (1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene) (30 nm)/Mg:Ag (100 nm)/Ag (100 nm) configuration. The ITO substrates were precleaned sequentially in detergent, deionized water, acetone, and ethanol. To improve the hole-injection performance and the substrate smoothness, PEDOT was spin-coated onto the ITO substrates and dried at 80 °C for 12 h *in vacuo*. A solution of the polymer in chlorobenzene was then spin-coated on top of the PEDOT layer and dried for 3 h at 60 °C *in vacuo*. Before film casting, the polymer solution was filtered through a Teflon filter (0.45 μm). The TPBI layer, which was grown through thermal sublimation in a vacuum of 3×10^{-6} Torr, was used as an electron-transport layer that would block holes and confine excitons. The cathode Mg:Ag (10:1, 100 nm) alloy was deposited onto the TPBI layer through coevaporation of the two metals; an additional layer of Ag (100 nm) was deposited onto the alloy as a protection layer. The current–voltage–luminance characteristics were measured under ambient conditions with a Keithley 2400 source meter and a Newport 1835C optical meter equipped with an 818ST silicon photodiode.

4-(2,7-Dibromo-9-phenyl-9*H*-fluoren-9-yl)benzoic Acid (4)

KMnO₄ (12.9 g, 81.6 mmol) was added in four portions over a period of 8 h to a solution of **3** (4.0 g, 8.2 mmol), pyridine (48 mL), and water (24 mL) under refluxing. The mixture was heated under refluxing for 24 h more, and then it was filtered to remove MnO₂. The filtrate was acidified with 2 N HCl; the product precipitated as a white solid and was collected after filtration (3.70 g, 87.3%).

¹H NMR (500 MHz, DMSO-*d*₆): δ 7.12 (d, *J* = 7 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.28–7.32 (m, 3H), 7.61–7.65 (m, 4H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 8 Hz, 2H). ¹³C NMR (125 MHz,

DMSO-*d*₆): δ 65.2, 121.4, 123.1, 127.4, 127.6, 127.8, 128.7, 128.8, 129.7, 129.8, 131.3, 137.8, 143.7, 149.1, 152.0, 166.9. HRMS [M⁺ + H] calcd for C₂₆H₁₇⁷⁹Br₂O₂: 518.9595. Found: 518.9592. ELEM. ANAL. calcd for C₂₆H₁₆Br₂O₂: C, 60.24%; H, 3.11%. Found: C, 60.33%; H, 3.68%.

Monomer 6

A mixture of **4** (1.0 g, 1.9 mmol) and thionyl chloride (10 mL) was heated under refluxing in a nitrogen atmosphere for 4 h. Excess thionyl chloride was evaporated under reduced pressure, and the residue was reacted with **5** (595 mg, 1.90 mmol) in anhydrous pyridine (6 mL) under refluxing for 4 h. The reaction mixture was cooled, poured into water (20 mL), and extracted with CH₂Cl₂. The combined extracts were dried (MgSO₄), and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (CH₂Cl₂) to afford **6** (900 mg, 65.2%).

¹H NMR (500 MHz, CDCl₃): δ 7.09–7.17 (m, 10H), 7.29–7.34 (m, 9H), 7.51–7.53 (m, 4H), 7.62 (d, *J* = 8 Hz, 2H), 7.90 (d, *J* = 8.5 Hz, 2H), 8.00 (d, *J* = 8.5 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 66.3, 116.6, 121.8, 122.5, 122.7, 123.8, 125.1, 126.4, 127.8, 128.2, 128.6, 128.7, 129.3, 129.5, 130.0, 130.3, 132.0, 138.8, 144.4, 147.3, 149.0, 151.7, 152.9, 164.3, 165.3. HRMS [M⁺] calcd for C₄₅H₂₉⁷⁹Br⁸¹BrN₃O: 787.0658. Found: 787.0654. ELEM. ANAL. calcd for C₄₅H₂₉Br₂N₃O: C, 68.78%; H, 3.75%; N, 5.35%. Found: C, 68.37%; H, 3.77%; N, 5.34%.

Model Compound F-TPAOXD

A solution of 4-(9-phenyl-9*H*-fluoren-9-yl)benzoic acid (1.01 g, 2.80 mmol) and thionyl chloride (10 mL) was heated under refluxing in a nitrogen atmosphere for 4 h. Excess thionyl chloride was evaporated under reduced pressure, and the residue was reacted with **5** (865 mg, 2.80 mmol) in anhydrous pyridine (6 mL) under refluxing for 4 h. The reaction mixture was cooled, poured into water (20 mL), and extracted with CH₂Cl₂. The combined extracts were dried (MgSO₄), and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (CH₂Cl₂) to afford F-TPAOXD (1.24 g, 71.1%).

¹H NMR (300 MHz, CDCl₃): δ 7.09 (d, *J* = 8.8 Hz, 2H), 7.12–7.17 (m, 5H), 7.22–7.24 (m, 4H), 7.29–7.37 (m, 10H), 7.39–7.43 (m, 4H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 65.5, 116.0, 120.3, 121.1, 122.4, 124.4, 125.6, 126.1, 126.7, 126.9, 127.8, 127.9, 128.0, 128.4, 128.8,

129.6, 140.2, 145.1, 146.6, 149.9, 150.4, 150.9, 163.8, 164.4. HRMS [M^+] calcd for $C_{45}H_{31}N_3O$: 629.2467. Found: 629.2488. ELEM. ANAL. calcd for $C_{45}H_{31}N_3O$: C, 85.83%; H, 4.96%; N, 6.67%. Found: C, 85.58%; H, 5.21%; N, 6.43%.

PF-TPAOXD

Aqueous potassium carbonate (2.0 M, 0.72 mL) and Aliquat 336 (ca. 20 mg) were added to a mixture of monomers **6** (300 mg, 380 μ mol) and **7** (245 mg, 380 μ mol) in distilled toluene (1.45 mL). The mixture was degassed, and $Pd(PPh_3)_4$ (12 mg, 5.5 mol %) was added in one portion under nitrogen; the solution was then heated at 110 °C for 48 h. The end groups were capped through the heating of the resulting mixture under refluxing for 12 h with benzene boronic acid (163 mg, 760 μ mol) and then for 12 h with bromobenzene (126 mg, 760 μ mol). The reaction mixture was cooled to room temperature, and the product was precipitated into a mixture of MeOH and H_2O (7:3 v/v, 50 mL). The crude polymer was collected and washed with excess MeOH. The resulting material was dissolved in THF and reprecipitated into MeOH. The polymer was then washed with acetone for 48

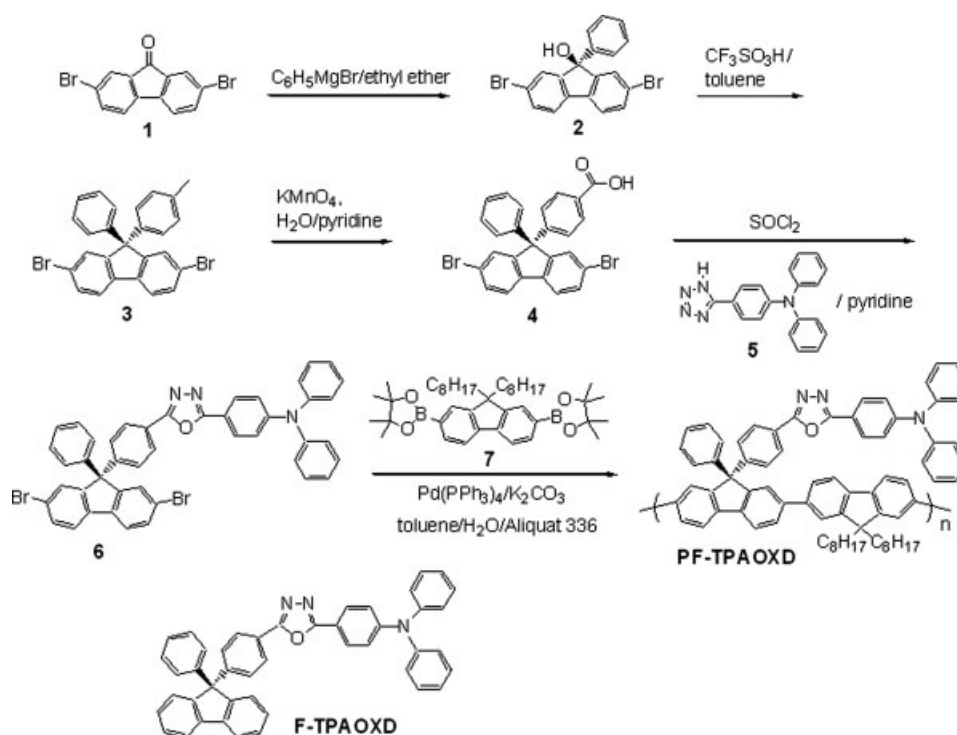
h with a Soxhlet apparatus and dried *in vacuo* to give PF-TPAOXD (209 mg, 74.8%).

1H NMR (500 MHz, $CDCl_3$): δ 0.74–0.81 (m, 10H), 1.07–1.14 (m, 20H), 2.02 (br, 4H), 7.08–7.16 (m, 8H), 7.29–7.33 (m, 7H), 7.38 (d, $J = 7$ Hz, 2H), 7.53–7.54 (m, 6H), 7.71–7.74 (m, 6H), 7.90–7.93 (m, 4H), 8.05 (d, $J = 8$ Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.4, 22.8, 24.2, 29.5, 30.3, 32.0, 40.6, 55.6, 66.1, 116.3, 120.4, 121.0, 121.4, 121.7, 123.0, 124.7, 125.0, 126.0, 126.5, 127.3, 127.5, 128.3, 128.6, 129.0, 129.3, 129.9, 139.3, 140.2, 140.4, 141.8, 145.6, 147.0, 151.3, 151.8, 152.1, 164.1, 164.9. ELEM. ANAL. calcd for $C_{74}H_{71}N_3O$: C, 87.27%; H, 7.03%; N, 4.13%. Found: C, 87.63%; H, 7.18%; N, 3.65%.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

Scheme 1 illustrates the synthetic route followed for the preparation of PF-TPAOXD. The Grignard reaction of 2,7-dibromofluorenone (**1**) with phenyl magnesium bromide gave the corresponding alcohol (**2**), which after an acid (CF_3SO_3H)-mediated Friedel–Crafts-type substitution reaction with toluene yielded **3**.⁷¹ The methyl group of com-



Scheme 1

pound **3** was then oxidized with KMnO_4 in H_2O /pyridine to provide the carboxylic acid (**4**). The treatment of **4** with thionyl chloride and subsequent coupling with the triphenylamine tetrazole derivative (**5**) in pyridine furnished the desired dibromo monomer (**6**), which contained a triphenylamino phenyloxadiazole (TPOXD) moiety substituted at the C-9 position of 2,7-dibromo-9-phenylfluorene. Finally, the PF copolymer PF-TPOXD, presenting TPOXD pendent groups on alternating fluorene units, was synthesized through the Suzuki polymerization of equimolar amounts of dibromide **6** and diborolane **7** in toluene in the presence of aqueous K_2CO_3 (2 M) and Aliquat 336 (as phase-transfer catalyst) under a nitrogen atmosphere. After the addition of $\text{Pd}(\text{PPh}_3)_4$ as a catalyst and the heating of the reaction mixture under refluxing for 48 h, the polymerization was terminated by the end capping of the polymer chains through the sequential treatment of the reaction mixture with phenyl boronic acid and bromobenzene, each for a period of 12 h under refluxing. The structure of PF-TPOXD was characterized with ^1H and ^{13}C NMR spectroscopy and elemental analysis. In the ^{13}C NMR spectrum, two signals that were almost superimposed with the signals of the C-9 carbon atoms of monomers **6** and **7** appeared at δ values of 66.1 and 55.6; we ascribe these signals to the C-9 carbon atoms of the two different fluorene units in the copolymer. Gel permeation chromatography analysis, which we performed using polystyrene as the standard and THF as the eluent, indicated that PF-TPOXD had a number-average molecular weight of about 4.2×10^4 g/mol, with a polydispersity index of 1.7. PF-TPOXD is readily soluble in common polar organic solvents, such as THF, chloroform, and chlorobenzene, but it is soluble in toluene only upon heating.

We used TGA and DSC to investigate the thermal properties of PF-TPOXD. As indicated in Figure 1, PF-TPOXD exhibits good thermal stability: its 5% weight loss occurred at 450 °C. In the DSC measurements, we observed a distinct glass transition at 186 °C, but we detected no peaks for crystallization or melting at temperatures up to 300 °C (see the inset of Fig. 1). We believe that the incorporation of the rigid, nonplanar triphenylamino oxadiazole moiety at the C-9 position of alternating fluorene units in the polymer backbone enhanced the chain rigidity and restricted its segmental mobility, resulting in a significant increase in the value of T_g . In comparison, poly(9,9-dioctylfluorene) (POF), which con-

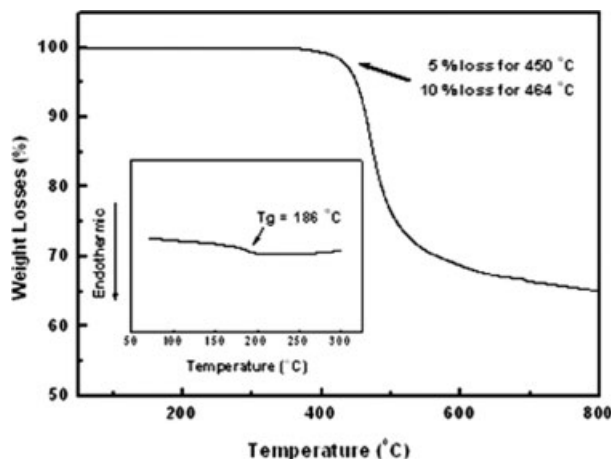


Figure 1. TGA trace of PF-TPOXD recorded at a heating rate of 10 °C/min. The inset shows DSC measurements recorded at a heating rate of 20 °C/min.

tains two flexible *n*-octyl chains at the C-9 positions of each repeating fluorene unit, exhibits, in succession, a T_g at 67 °C, an exothermic crystallization peak at 94 °C, and a melting peak at 152 °C.⁷³ The relatively high value of T_g of PF-TPOXD implies that it would not be susceptible to morphological changes upon exposure to heat; that is, it would suppress the formation of aggregates and excimers at elevated temperatures, which is a desirable property for polymers to be used as emissive materials for light-emitting applications. The thermal properties of the model compound F-TPOXD were also studied with DSC. F-TPOXD melted at 238 °C on the first heating only, and then it changed into a glassy state upon cooling from the melt. When an amorphous glassy sample was heated again, a glass transition occurred at 126 °C, and no exothermic peak due to crystallization was observed up to 350 °C.

Photophysical Properties

Figure 2 displays the UV-vis absorption and PL spectra of PF-TPOXD in a dilute solution; Table 1 summarizes the spectral data. For comparison, Figure 2 also presents the absorption and PL spectra of POF and F-TPOXD, the latter serving as a model compound for studying the optical properties of the pendent groups. In a THF solution, PF-TPOXD exhibited its main absorption peak at 378 nm, with an absorption shoulder appearing at 287 nm. From a comparison with the absorption spectra of POF and the model compound F-TPOXD, we ascribe the band at 378 nm

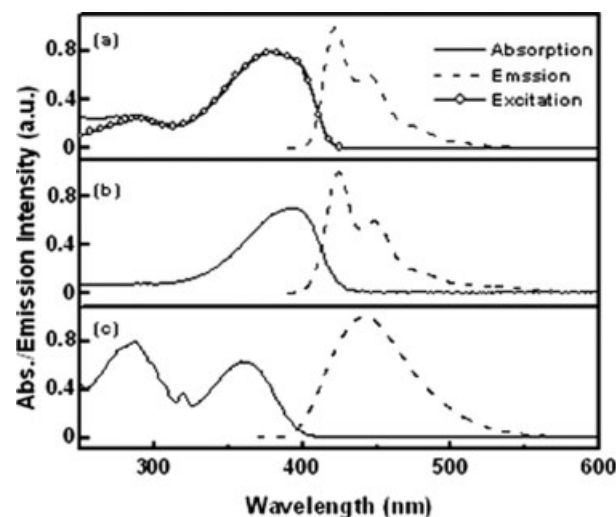


Figure 2. UV-vis absorption and PL spectra recorded from THF solutions of (a) PF-TPAOXD (excited at 390 nm), (b) POF (excited at 390 nm), and (c) F-TPAOXD (excited at 370 nm). The excitation spectrum of PF-TPAOXD (the emission is monitored at 450 nm) is also included in part a.

to a composite absorption originating from the conjugated PF backbone and the pendent TPAOXD groups; the shorter wavelength shoulder appears to result from a transition that occurs predominantly from the dipolar pendent unit. Because the pendent group is connected to the PF main chain through an sp^3 -hybridized C-9 atom, the electronic characteristics (i.e., the absorption) of each individual unit are preserved in the resultant copolymer.^{56,57} Upon the excitation of the polymer backbone at 390 nm, the PL spectrum displays a vibronic fine structure with two sharp emission bands appearing at 419 and 443 nm; these features are nearly identical to those of PF. This finding reconfirms the fact that linking TPAOXD groups to fluorene units through their

C-9 carbon atoms does not perturb the main chain's conjugation. In addition, upon irradiation at 290 nm—a wavelength at which the absorption of the pendent units contributes significantly—instead of detecting a broad emission band derived from the side chains at about 442 nm, we still observed a structured emission that was identical to that obtained after excitation of the PF backbone at 390 nm. Moreover, the excitation spectrum of PF-TPAOXD, monitored at 450 nm, is a perfectly superimposed image of the absorption spectrum. These results reveal that efficient intramolecular energy transfer takes place from the excited pendent groups to the PF backbone—from which the emission occurs—even though the spectral overlap between the emission spectrum of the former and the absorption spectrum of the latter is moderate. The PL quantum yield in toluene excited at 365 nm was 0.95, as measured with respect to 9,10-diphenylanthracene (quantum yield = 0.9) as a standard.⁷⁴

In comparison with the results obtained with dilute solutions, the absorption spectrum of the PF-TPAOXD film is slightly broadened, whereas the emission spectrum displays a redshift of 9 nm (Fig. 3). The PL quantum yield of the film was estimated to be 0.42 by the comparison of its fluorescence intensity with that of the POF polymer thin-film sample excited at 380 nm (quantum yield = 0.55).⁷⁵ A key issue for the applicability of blue-emitting PFs is their spectral stability. To examine the effect that incorporating bulky and rigid TPAOXD pendent groups has on the thermal stability of PF-TPAOXD, we heated the polymer film for 20 h on a hot plate at 150 °C under a nitrogen atmosphere. As indicated in Figure 3, the absorption and PL spectra remained virtually unchanged after such thermal treatment. In contrast, the PL spectrum of an annealed POF film

Table 1. Photophysical Properties of PF-TPAOXD and F-TPAOXD

	Solution ^a			Film ^b		
	Absorption (nm)	PL (nm)	Φ_f^c	Absorption (nm)	PL (nm)	Φ_f^d
PF-TPAOXD	287, 378	419, 443	0.95	289, 380	428, 452	0.42
F-TPAOXD	287, 361	442	0.53			

^a Evaluated in THF.

^b Evaluated in the solid state and prepared from a toluene solution.

^c Quantum yield determined in toluene with respect to that of 9,10-diphenylanthracene in cyclohexane (0.9) upon excitation at 365 nm.

^d Quantum yield determined with respect to that of POF (0.55), as measured in an integrating sphere (ref. 75).

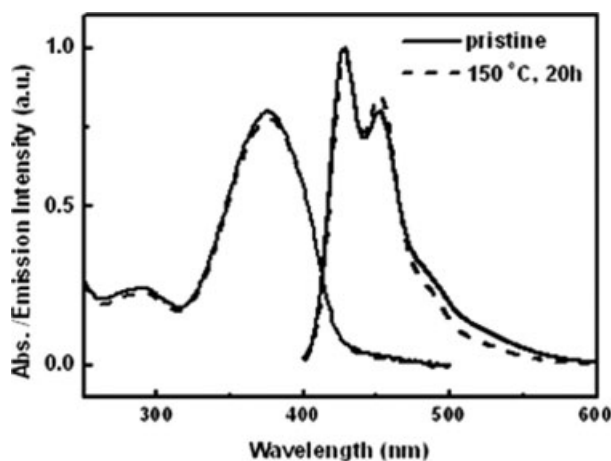


Figure 3. UV-vis absorption and PL spectra of PF-TPAOXD films recorded before and after annealing at 150 °C for 20 h under a nitrogen atmosphere.

displays a moderate redshift with respect to the pristine film, together with the appearance of a long-wavelength emission band at 500–600 nm.⁷⁶ The cause of the undesirable emissive color instability of the POF film has been accredited to either the formation of aggregates and interchain excimers or to the presence of keto defects.^{42–52} We attribute the enhanced spectral stability of PF-TPAOXD to the presence of the rigid, nonplanar TPAOXD pendent groups, the steric demand of which restricts close packing of the polymer chains and reduces the probability of interchain interactions; consequently, the presence of the pendent groups suppresses the tendency of the PF backbones to form aggregates and excimers in the polymer film upon thermal treatment. The higher value of T_g of PF-TPAOXD also accounts for the enhanced thermal stability of the polymer film.

Electrochemical Studies

We employed CV to investigate the redox behavior of PF-TPAOXD and to estimate the energy levels of its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The electrochemical processes of this polymer film coated on a glassy carbon electrode were monitored in a standard three-electrode electrochemical cell, with ferrocene as the internal standard in an electrolyte of 0.1 M in acetonitrile. On the basis of the onset potentials of the oxidation and reduction, which were +0.66 and –2.25 V, respectively, we estimated the HOMO and LUMO energy levels of PF-TPAOXD to be –5.46 and –2.55 eV, respectively, with respect to

the energy level of the ferrocene reference (4.8 eV below the vacuum level).⁷⁷ We also performed CV measurements of the model compound F-TPAOXD, which exhibited the onset potentials of the oxidation and reduction at +0.64 and –2.28 V, respectively. The HOMO and LUMO energy levels of F-TPAOXD, estimated from the onset potential, are –5.44 and –2.52 eV, respectively; these values are very close to the HOMO and LUMO energy levels of PF-TPAOXD. In comparison with the HOMO and LUMO energy levels of POF (–5.8 and –2.1 eV, respectively),⁵³ the higher HOMO energy level of PF-TPAOXD, originating from the electron-donating triphenylamine moiety, is better matched to the work function of the ITO/PEDOT electrode (5.2 eV),⁵⁴ and so it may facilitate hole injection into the polymer layer from the anode. In addition, the lower LUMO energy level of PF-TPAOXD, which derives from the electron-accepting oxadiazole moiety, suggests that there may be an increase in the electron affinity and an improvement in the electron injection of the polymer.

EL Properties

To evaluate the use of PF-TPAOXD as a blue-light-emitting material for polymeric light-emitting diode applications, we fabricated EL devices having the configuration ITO/PEDOT (35 nm)/polymer (50–70 nm)/TPBI (30 nm)/Mg:Ag (100 nm)/Ag (100 nm). As depicted in the inset of Figure 4, the EL spectrum displayed a deep-blue emission at 429 nm and a shoulder at 451 nm [corresponding to Commission Internationale de l'Eclairage (CIE)

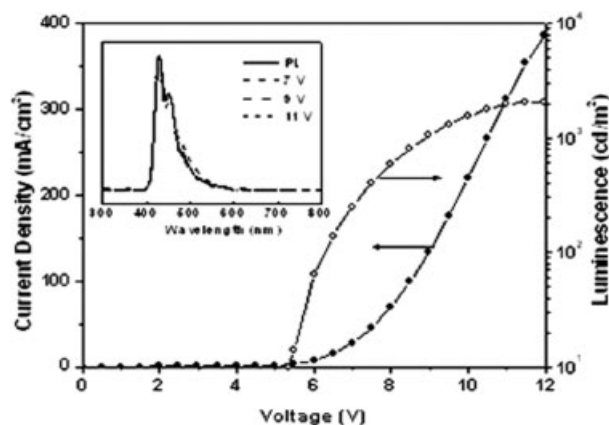


Figure 4. Current density/voltage/luminance characteristics of ITO/PEDOT/PF-TPAOXD/TPBI/Mg:Ag. The inset shows the PL spectrum and corresponding EL spectra recorded at different applied voltages.

Table 2. Performances of Devices with an ITO/PEDOT/Polymer/TPBI/Mg:Ag Structure

	1.5 mol % Os(fppz)-Doped		
	PF-TPAOXD	PF-TPAOXD	POF
Turn-on voltage (V)	5.0	9.0	9.0
Voltage (V) ^a	6.7 (8.5)	12.5 (15.5)	13.8 (17.9)
Brightness (cd/m ²) ^a	183 (813)	1830 (7235)	522 (769)
Luminance efficiency (cd/A) ^a	0.92 (0.81)	9.2 (7.2)	2.6 (0.78)
External quantum efficiency (%) ^a	1.4 (1.3)	7.3 (5.8)	2.1 (0.63)
Maximum brightness (cd/m ²)	2080 (at 12 V)	7244 (at 16 V)	843 (at 16.5 V)
Maximum luminance efficiency (cd/A)	0.92	9.2	2.9
Maximum external quantum efficiency (%)	1.4%	7.3%	2.4%
EL maximum (nm)	430, 454 ^b	624 ^c	626 ^c
CIE coordinates	(0.15, 0.07) ^b	(0.66, 0.34) ^c	(0.66, 0.33) ^c

^a Recorded at 20 mA/cm². The data in parentheses were recorded at 100 mA/cm².

^b Recorded at 9 V.

^c Recorded at 11 V.

coordinates of (0.15, 0.07)] at 9 V. The EL spectrum is almost identical to the PL spectrum, and this indicates that both the PL and EL originate from the same radiative decay process of the singlet exciton. It is noteworthy that the PF-TPAOXD-based device exhibits a voltage-independent, stable EL spectrum. Upon increasing the operating voltage from 7 to 11 V (i.e., close to the voltage required to achieve maximum brightness), we observed no significant change in the appearance of the low-energy emission band (between 500 and 600 nm, a blue-green color) in the EL spectrum. In contrast, devices using POF as the active layer displayed undesirable long-wavelength emissions resulting from the formation of keto defects and/or excimers and aggregates.^{42–52} Table 2 summarizes the performance of the PF-TPAOXD-based device. The rather low turn-on voltage of 5.0 V (corresponding to 1 cd/m²) suggests that the dipolar TPAOXD pendent group may facilitate charge injection. The maximum external quantum efficiency of the device was 1.4% at a brightness of 137 cd/m²; the maximum brightness was 2080 cd/m² at a bias of 12 V and a current density of 387 mA/cm². In addition, we fabricated a reference device using POF as the light-emitting material. In comparison to the PF-TPAOXD-based device, the POF-based device exhibited inferior performance, with a maximum

external quantum efficiency of 0.78% and a brightness of 703 cd/m² at a bias of 12 V.

Red Electrophosphorescence

Because EL devices based on phosphorescent dyes can harvest both singlet and triplet excitons, they often exhibit higher quantum efficiencies than those based on fluorescent dyes. The preparation of electrophosphorescent light-emitting diodes using polymers as host materials for the emitting layer is attractive because of the potential for their application in large-area devices prepared through simple solution processing. In this study, we used PF-TPAOXD, which possesses a blue-emitting PF backbone and dipolar TPAOXD side chains, as the polymeric host and doped it with 1.5 mol % (corresponding to 2.63 wt %) of the red-emitting phosphorescent dye Os(fppz)⁷⁰ to realize efficient EL in conjunction with a high current and luminance. For comparison, we also prepared a controlled-reference device based on POF doped with 1.5 mol % (3.45 wt %) Os(fppz). The osmium complex, which contains both 3-trifluoromethyl-5-(2-pyridyl) pyrazolate and phosphine ligands (for the chemical structure, see the inset in Fig. 5), was selected for this study because of its highly efficient saturated-red emission. In addition, its shorter triplet lifetime

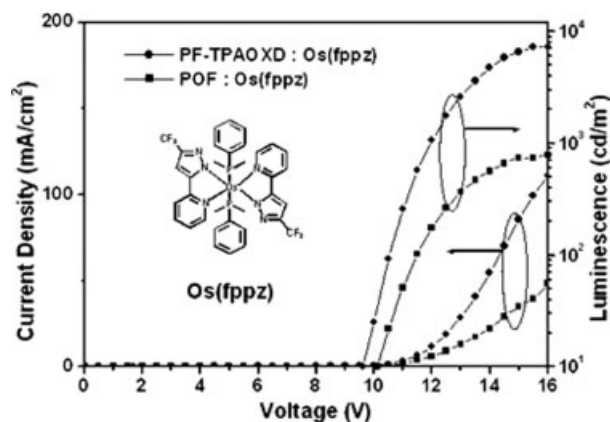


Figure 5. Current density/voltage/luminance characteristics of 1.5 mol % Os(fppz)-doped devices and chemical structure of Os(fppz).

(0.7 μ s) can help to minimize the degree of exciton quenching through triplet–triplet annihilation at a high current density.^{78,79}

From previous investigations,^{13,14} we have found that the absorption spectra of Os(fppz) and the emission spectra of PF overlap to a moderate extent to meet the requirements for energy transfer. Figure 6 displays the PL spectra of Os(fppz)-doped polymer films. Upon photoexcitation of the backbone of the host materials, the PL profiles of both blends feature two emission bands: one at about 424 nm, which originates from the residual emission of the host, and the other at about 620 nm, which corresponds to radiative decay from

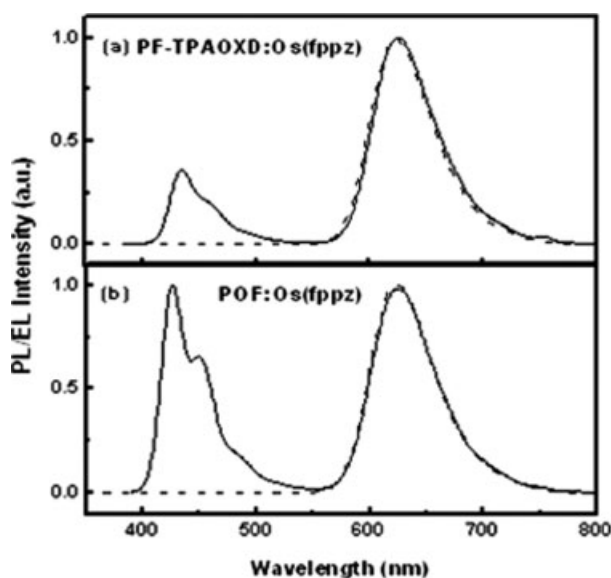


Figure 6. (—) PL spectra (excited at 390 nm) and (---) EL spectra (at 11 V) of (a) PF-TPAOXD and (b) POF doped with 1.5 mol % Os(fppz).

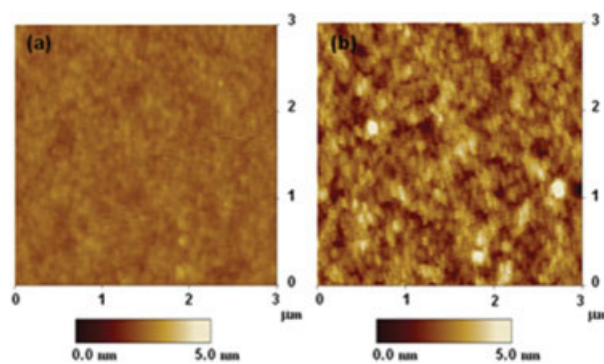


Figure 7. AFM images (tapping mode) of (a) PF-TPAOXD and (b) POF doped with 1.5 mol % Os(fppz). The films were spin-coated onto silicon wafers from 1.2 wt % solutions in chlorobenzene.

the triplet state of Os(fppz) to the ground state. We note that the energy transfer in the POF:Os(fppz) film is relatively inefficient compared with that of the PF-TPAOXD:Os(fppz) film. The efficiency of Förster energy transfer is proportional to the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor. Because the two fluorene-based polymer hosts exhibited similar emission spectra, it appears that there might be other factors required for achieving efficient energy transfer. One possibility results from the different chemical compatibilities of Os(fppz) within the two polymer hosts. For an Ir(ppy)₃ [tris(2-phenylpyridine) irridium(III)]-doped PF derivative, it was reported that the formation of aggregates prevents the dopant molecules from coming into close proximity with the host molecules, thereby inhibiting the energy-transfer processes.⁶⁹ Thus, we used AFM to investigate the phase morphologies in both blending systems; Figure 7 displays the surface topographies of the films. The POF:Os(fppz) film clearly displays an aggregated domain with a root-mean-square (RMS) surface roughness of 0.531 nm, and this suggests the formation of aggregates. In contrast, the PF-TPAOXD:Os(fppz) film is smooth and featureless, with an RMS surface roughness of 0.187 nm; this indicates that the film is homogeneous with no phase separation or aggregation. We infer that the Os complexes were dispersed well in PF-TPAOXD, probably because the polar pendent groups in PF-TPAOXD provide a stabilizing environment for the osmium dopant.

Figure 6(a) also depicts the corresponding EL spectrum of the PF-TPAOXD:Os(fppz) film recorded at 11 V. In contrast to the PL spectrum, the

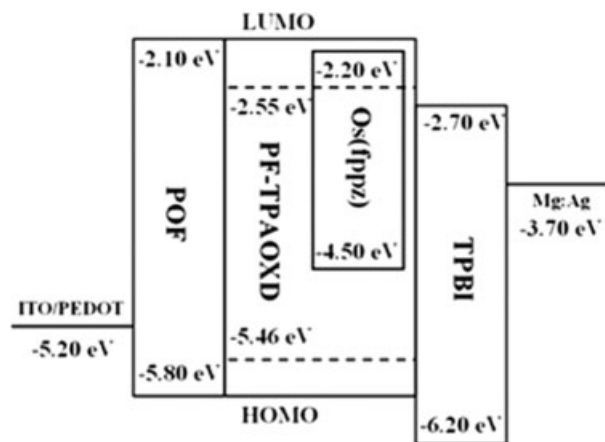


Figure 8. Energy diagram for materials involved in EL devices having an ITO/PEDOT/polymer/TPBI/Mg:Ag configuration.

host emission was quenched completely when it was stimulated by an electric field; this process resulted in a dominating red triplet emission from the Os complex that had CIE color coordinates of (0.66, 0.34), which are very close to those [(0.67, 0.33)] for standard red as demanded by the NTSC (National Television System Committee). This result implies that both energy transfer and direct charge trapping/recombination on the Os(fppz) guest are responsible for the observed EL.^{8,80} According to the energy level diagram constructed in Figure 8, the HOMO and LUMO levels of Os(fppz) are -4.5 and -2.2 eV, respectively;¹⁴ these values indicate that a hole potentially can be trapped at the HOMO of Os(fppz) by a barrier depth of 1.0 eV after injection from the ITO/PEDOT electrode and can then wait for recombination with an opposite charge (electron) to form excitons. This charge-trapping mechanism is also consistent with the EL spectrum of POF:Os(fppz) [Fig. 6(b)], in which the dopant emission dominates completely to result in a red emission having CIE color coordinates of (0.66, 0.33). Figure 5 displays the current density/voltage/luminance characteristics of the saturated-red-light-emitting device based on PF-TPAOXD:Os(fppz), together with those of a reference device based on POF:Os(fppz); Table 2 summarizes their performances. The doped PF-TPAOXD device produced a bright red emission having a maximum external quantum efficiency of 7.3% (corresponding to a luminance efficiency of 9.2 cd/A) at a current density of 19 mA/cm², together with a brightness of 1747 cd/m². Even at a higher current density of 100 mA/cm², about 80% of the peak efficiency was sustained from the red-

emitting devices, with bright phosphorescence (7235 cd/m²). Furthermore, the turn-on voltage for the host-only device was 5.0 V, whereas that for the doped device increased to 9.0 V. This observation also supports our proposed charge-trapping mechanism; that is, holes are trapped at the Os(fppz) sites to construct a positive space-charge field that impedes further injection of holes, in turn leading to a higher onset voltage.^{8,80} On the other hand, the doped POF reference device performed poorly with a maximum external quantum efficiency of 2.6% at 6 mA/cm², which decreased rapidly to 0.78% at 100 mA/cm². We attribute the higher performance of the PF-TPAOXD-based device to the improved charge injection and transport supported by the dipolar TPAOXD pendent groups. Moreover, the presence of polar moieties provides a compatible environment for the osmium dopant to prevent the formation of aggregates; this feature could also account for the superior performance of the PF-TPAOXD-based device and particularly its much lower efficiency roll-off at high current densities.

CONCLUSIONS

We have synthesized a thermally stable blue-light-emitting polymer, PF-TPAOXD, containing sterically demanding dipolar pendent groups on alternating fluorene units. The presence of these dipolar groups, which combine electron-rich triphenylamine and electron-deficient oxadiazole groups, improves the charge-injection/transport characteristics of the resultant copolymer. A blue-light-emitting device using PF-TPAOXD as the emitting layer exhibited a low turn-on voltage at 5.0 V, a maximum external quantum efficiency of 1.4%, and a maximum brightness of 2080 cd/m². Moreover, the dipolar characteristics of PF-TPAOXD provided a stabilizing environment in which the polar organometallic triplet dopants were dispersed homogeneously. Consequently, using PF-TPAOXD as the host material doped with 1.5 mol % Os(fppz) allowed us to realize a saturated-red electrophosphorescent device having CIE coordinates of (0.66, 0.34). The device exhibited a maximum external quantum efficiency of 7.3% at a brightness of 1747 cd/m², together with a maximum brightness of 7244 cd/m².

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