

Novel Oxadiazole-Containing Polyfluorene with Efficient Blue Electroluminescence

Fang-Iy Wu, D. Sahadeva Reddy, and Ching-Fong Shu*

Department of Applied Chemistry, National Chiao Tung University,
Hsin-Chu, Taiwan, 30035, Republic of China

Michelle S. Liu and Alex K.-Y. Jen*

Department of Materials Science and Engineering, Box 352120, University of Washington,
Seattle, Washington 98195-2120

Received June 21, 2002. Revised Manuscript Received October 14, 2002

A novel oxadiazole-containing polyfluorene copolymer (PF–OXD) was synthesized by attaching two electron-deficient, 4-*tert*-butylphenyl-1,3,4-oxadiazole groups onto the C-9 position of the alternating fluorene unit to form a 3-D cardo-structure. This polymer possesses a very high glass transition temperature (T_g : 213 °C) and very good thermal stability due to its rigid cardo-linkage. The results from the photoluminescence measurements of the isothermally heated PF–OXD thin film (150 °C for 20 h) show that the commonly observed aggregate/excimer formation in polyfluorenes is very effectively suppressed in this polymer due to its 3-D structure and high T_g . A double-layer LED device using this polymer as the emitting layer shows a bright blue emission with a low turn-on voltage at 5.3 V and a high brightness of 2770 cd/m² at a drive voltage of 10.8 V. The maximum external quantum efficiency is 0.52% at 537 cd/m² with a bias of 7.4 V. The improved device performance over that of poly(9,9-dioctylfluorene) (POF) may be due to better electron injection and transport in PF–OXD and the efficient energy transfer from the OXD side chain to the polyfluorene main chains.

Introduction

Since the discovery of polymer-based light-emitting diodes¹ (PLEDs) in 1990, considerable progress has been made in the development of new conjugated polymers and exploration of their applications in displays.² Organic light-emitting polymers are attractive because of the flexibility of fine-tuning their luminescent properties through the manipulation of chemical structures, and the feasibility of combining spin-coating and printing processes for large-area flat panel displays. In full-color display applications, a polymer with a large energy band gap that can efficiently emit blue light and can also serve as the energy-transfer donor in the presence of lower energy fluorophores is highly desirable.³ Poly-

fluorenes (PF), with their high photoluminescence (PL) and electroluminescence (EL) efficiencies, are among the most promising candidates as blue-emitting polymers.⁴ The facile functionalization at the C-9 position of the fluorene unit provides the opportunity to improve both the solubility and processability of the resulting polymers, while offering the ability to reduce interchain interactions⁵ and cross-linking side reactions.⁶ It also offers a good mechanism to improve the charge-injecting or -transporting properties of the polymers if either an electron- or a hole-transporter can be directly attached onto this position. Herein, we report the synthesis and characterization of a fluorene-based alternating copolymer containing oxadiazole moieties with their phenyl end group directly attached to the C-9 carbon in every alternating fluorene unit. Our motivation for the synthesis of this novel copolymer is 3-fold and can be explained as follows. First, because PF has been proven to be a better hole-transporting polymer, the incorporation of an electron-deficient oxadiazole group will result

* Authors to whom correspondence should be addressed. C.-F. Shu: Phone: 886-3-5712121, ext. 56544. E-mail: shu@cc.nctu.edu.tw. A. K.-Y. Jen: phone, 206-543-2626; fax, 206-543-3100; e-mail, ajen@u.washington.edu.

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(2) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402. (b) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121. (c) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv. Mater.* **2000**, *12*, 1737. (d) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471.

(3) Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. *Appl. Phys. Lett.* **1994**, *64*, 815. (b) Kido, J.; Shionoya, H.; Nagai, K. *Appl. Phys. Lett.* **1995**, *67*, 2281. (c) McGehee, M. D.; Bergstedt, T.; Zhang, C.; Saab, A. P.; O'Regan, M. B.; Bazan, G. C.; Srdanov, V. I.; Heeger, A. J. *Adv. Mater.* **1999**, *11*, 1349. (d) Chen, F.-C.; Yang, Y.; Thompson, M. E.; Kido, J. *Appl. Phys. Lett.* **2002**, *80*, 2308.

(4) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416. (b) Leclerc, M. J. *Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2867. (c) Neher, D. *Macromol. Rapid Commun.* **2001**, *22*, 1365. (d) Becker, S.; Ego, C.; Grimsdale, A. C.; List, E. J. W.; Marsitzky, D.; Pogantsch, A.; Setayesh, S.; Leising, G.; Müllen, K. *Synth. Met.* **2002**, *125*, 73.

(5) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946. (b) Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 6965.

(6) Klärner, G.; Lee, J.-I.; Lee, V. Y.; Chan, E.; Chen, J.-P.; Nelson, A.; Markiewicz, D.; Siemens, R.; Scott, J. C.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1800.

in increased electron affinity and transporting properties of the polymer, leading to a more balanced charge recombination in the polymer emissive layer.⁷ Second, the 3-D shaped oxadiazole structures linked on the C-9 position may help prevent π -stacking between polymer chains and suppress the formation of excimers in the solid state. Furthermore, the rigidity of the main chain will be preserved, yielding a polymer with a much higher glass transition temperature (T_g) and better thermal stability. Third, the sp^3 carbon (C-9) serves as a spacer to effectively block the conjugation between the oxadiazole side chains and the polymer backbone.⁸ Thus, the conjugation and the integrity of the emission spectrum of the PF main chain will remain unperturbed.

Experimental Section

Materials. Monomer **3**, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene, was synthesized according to literature procedures.⁹ All the reactions were performed under a nitrogen atmosphere.

9,9-Bis(4-cyanophenyl)fluorene. A mixture of fluorene (10.0 g, 60.2 mmol), 4-fluorobenzonitrile (16.3 g, 134 mmol), 18-crown ether-6 (8.2 g, 31 mmol), K_2CO_3 (19.8 g, 144 mmol), DMF (50 mL), and benzene (15 mL) was heated at 160 °C for 4 h. Water that was formed during the reaction was removed by azeotropic distillation and collected in a Dean–Stark trap. After this period, the remaining benzene was removed by distillation. The reaction mixture was then cooled to room temperature, and 200 mL of water was added. The precipitated solid was collected by filtration, washed with water, and dried. The product was purified by recrystallization from toluene/THF (2:1) to give colorless crystals (14.1 g, 63.9%). ¹H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, 4H, $J = 8.7$ Hz), 7.31–7.35 (m, 4H), 7.41–7.48 (m, 2H), 7.55 (d, 4H, $J = 8.7$ Hz), 7.83 (d, 2H, $J = 7.8$ Hz). ¹³C NMR (75 MHz, $CDCl_3$) δ 65.4, 111.0, 118.4, 120.7, 125.7, 128.3, 128.5, 128.6, 132.3, 140.1, 148.6, 150.2. HRMS [$M^+ + H$]: calcd. for $C_{27}H_{17}N_2$ 369.1392, found 369.1393.

9,9-Bis(4-tetraazolyphenyl)fluorene. A mixture of 9,9-bis(4-cyanophenyl)fluorene (1.5 g, 4.1 mmol), sodium azide (0.80 g, 12.3 mmol), and ammonium chloride (0.70 g, 13.0 mmol) in DMF (5.0 mL) was heated at 150 °C for 4 h. After cooling, the resulting mixture was poured into water (200 mL) and acidified with 1 N HCl to pH \sim 2. The precipitated solid was collected by filtration, washed with water, and dried to give a white solid (1.67 g, 90.6%). ¹H NMR (300 MHz, $DMSO-d_6$) δ 7.32–7.38 (m, 2H), 7.36 (d, 4H, $J = 8.4$ Hz), 7.46 (dd, 2H, $J = 7.5, 7.5$ Hz), 7.55 (d, 2H, $J = 7.5$ Hz), 7.95 (d, 4H, $J = 8.4$ Hz), 7.99 (d, 2H, $J = 7.8$ Hz). ¹³C NMR (75 MHz, $DMSO-d_6$) δ 65.5, 121.4, 123.4, 126.6, 127.8, 128.8, 129.2, 140.2, 148.9, 149.9. HRMS [$M^+ + H$]: calcd. for $C_{27}H_{19}N_8$ 455.1733, found 455.1732.

9,9-Bis(4-(5-(4-*tert*-butylphenyl)-2-oxadiazolyl)phenyl)fluorene (1). To a solution of 9,9-bis(4-tetraazolyphenyl)fluorene (1.5 g, 3.3 mmol) in pyridine (8.0 mL) at 25 °C was added 4-*tert*-butyl benzoyl chloride (1.9 mL, 9.9 mmol) dropwise. The reaction mixture was heated at 125 °C for 3 h. After cooling, the resulting solution was poured into a mixture of water and MeOH (150 mL, 1:3). The resulting precipitate was collected by filtration, washed with water, and dried. The

product was purified by column chromatography over silica gel ($CHCl_3$) followed by recrystallization from toluene/ $CHCl_3$ (5:1) to give **1** (2.12 g, 89.3 %). ¹H NMR (300 MHz, $CDCl_3$) δ 1.34 (s, 18H), 7.27–7.35 (m, 2H), 7.37 (d, 4H, $J = 8.4$ Hz), 7.37–7.45 (m, 4H), 7.52 (d, 4H, $J = 8.4$ Hz), 7.81 (d, 2H, $J = 7.4$ Hz), 8.01 (d, 4H, $J = 8.4$ Hz), 8.02 (d, 4H, $J = 8.4$ Hz). ¹³C NMR (75 MHz, $CDCl_3$) δ 31.0, 35.0, 65.5, 120.5, 121.0, 122.7, 125.9, 126.0, 126.7, 127.0, 128.1, 128.2, 128.7, 140.2, 149.2, 149.7, 155.3, 164.0, 164.6. HRMS [$M^+ + H$]: calcd. for $C_{49}H_{43}N_4O_2$ 719.3386, found 719.3392.

Synthesis of Monomer 2. To a solution of **1** (500 mg, 0.70 mmol) in $CHCl_3$ (25 mL) at 25 °C, phenyliodine bis(trifluoroacetate) (600 mg, 1.40 mmol), and bromine (220 mg, 1.40 mmol) were added. The reaction mixture was stirred at 25 °C for 24 h, then poured into water (80 mL) and washed with aqueous sodium thiosulfate solution until the red color of bromine disappeared. The organic layer was dried over Na_2SO_4 , and the solvent was removed in vacuo. The residue was purified by column chromatography, eluting with CH_2Cl_2 and CH_2Cl_2 /ethyl acetate (20:1) to give monomer **2** (0.38 g, 61.0%). ¹H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 18H), 7.32 (d, 4H, $J = 8.6$ Hz), 7.50 (d, 2H, $J = 1.5$ Hz), 7.53 (d, 4H, $J = 8.6$ Hz), 7.55 (dd, 2H, $J = 1.5, 8.1$ Hz), 7.65 (d, 2H, $J = 8.1$ Hz), 8.02 (4H, d, $J = 8.6$ Hz), 8.05 (4H, d, $J = 8.6$ Hz). ¹³C NMR (75 MHz, $CDCl_3$) δ 31.2, 35.2, 65.6, 121.1, 122.1, 122.3, 123.4, 126.2, 126.9, 127.5, 128.7, 129.3, 131.8, 138.2, 147.7, 151.6, 155.5, 163.9, 164.8. HRMS [M^+]: calcd. for $C_{49}H_{40}N_4O_2^{79}Br^{81}Br$ 874.1518, found 874.1535; calcd. for $C_{49}H_{40}N_4O_2^{81}Br^{81}Br$ 876.1498, found 876.1434; calcd. for $C_{49}H_{40}N_4O_2^{81}Br^{81}Br$ 878.1478, found 878.1414.

Preparation of PF–OXD. A mixture of **2** (512 mg, 0.58 mmol), **3** (376 mg, 0.58 mmol), Aliquat 336 (71 mg), 2 M $K_2CO_3(aq)$ (5.0 mL), and toluene (8.0 mL) was degassed and tetrakis(triphenylphosphine)palladium (8 mg, 1.33 mol %) was added in one portion under nitrogen atmosphere. The reaction mixture was then heated at 110 °C for 60 h. At the end of the polymerization, the terminal groups were capped by refluxing 24 h with phenylboronic acid (148 mg, 1.22 mmol) and 12 h with bromobenzene (191 mg, 1.22 mmol). The resulting polymer solution was precipitated repeatedly into methanol–water and methanol several times, followed by Soxhlet extraction with acetone, and dried over vacuum to give PF–OXD (536 mg, 83.6%). ¹H NMR (300 MHz, $CDCl_3$) δ 0.67–0.78 (m, 10H), 1.04 (br, 20H), 1.33 (s, 18H), 2.01 (br, 4H), 7.48–7.57 (m, 12 H), 7.69–7.77 (m, 6H), 7.94 (d, 2H, $J = 7.9$ Hz), 8.01 (d, 4H, $J = 8.3$ Hz), 8.09 (d, 4H, $J = 8.1$ Hz). ¹³C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.6, 23.9, 29.2, 30.0, 31.2, 31.7, 35.2, 40.3, 55.4, 65.9, 120.2, 121.0, 121.1, 121.4, 123.0, 124.6, 126.1, 126.3, 126.8, 127.4, 127.7, 129.0, 139.1, 139.8, 140.3, 141.9, 149.3, 150.9, 151.9, 155.5, 164.1, 164.8.

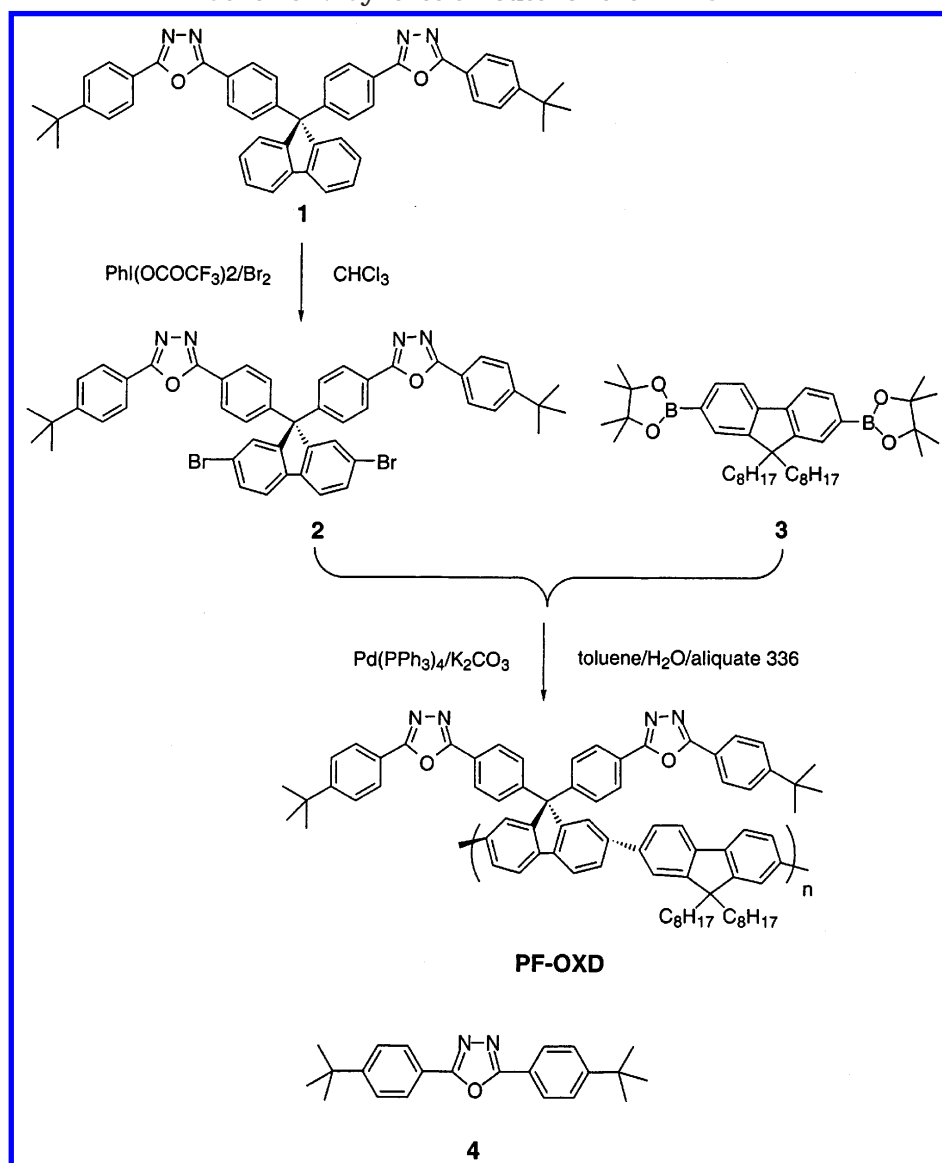
General Information. ¹H and ¹³C NMR spectra were recorded on a Varian Unity 300 MHz or a Bruker-DRX 300 MHz spectrometer. Mass spectra were obtained on a JEOL JMS-SX/SX 102A mass spectrometer. Size exclusion chromatography (SEC) was carried out on a Waters chromatography unit interfaced to a Waters 410 differential refractometer. Three 5- μ m Waters styragel columns (300 \times 7.8 mm) connected in series in decreasing order of pore size (10^4 , 10^3 , and 10^2 Å) were used with THF as eluent, and standard polystyrene samples were used for calibration. Differential scanning calorimetry (DSC) was performed on a SEIKO EXSTAR 6000 DSC unit using a heating rate of 10 °C min^{-1} and a cooling rate of 30 °C min^{-1} . Samples were scanned from 30 to 350 °C and then cooled to 30 °C and scanned for a second time from 30 to 350 °C. Glass transition temperatures (T_g) were determined from the second heating scan. Thermogravimetric analysis (TGA) was made on a Du Pont TGA2950 instrument. The thermal stability of the samples was determined in nitrogen by measuring weight loss while heating at a rate of 10 °C min^{-1} . UV–visible spectra were measured with a HP 8453 diode array spectrophotometer. Photoluminescence spectra were obtained on a Hitachi F-4500 luminescence spectrometer. The PL quantum yields (Φ_{FL}) in toluene solutions were measured by excitation of the respective polymer solutions at 375 nm and compared with the solution emission of

(7) (a) Huang, W.; Meng, H.; Yu, W.-L.; Gao, J.; Heeger, A. J. *Adv. Mater.* **1998**, *10*, 593. (b) Yu, W.-L.; Meng, H.; Pei, J.; Huang, W.; Li, Y.; Heeger, A. J. *Macromolecules* **1998**, *31*, 4838. (c) Peng, Z.; Bao, Z.; Galvin, M. E. *Chem. Mater.* **1998**, *10*, 2086. (d) Huang, W.; Meng, H.; Yu, W.-L.; Pei, J.; Chen, Z.-K.; Lai, Y.-H. *Macromolecules* **1999**, *32*, 118. (e) Peng, Z.; Zhang, J. *Chem. Mater.* **1999**, *11*, 1138. (f) Lee, Y.-Z.; Chen, X.; Chen, S.-A.; Wei, P.-K.; Fann, W.-S. *J. Am. Chem. Soc.* **2001**, *123*, 2296. (g) Zheng, M.; Ding, L.; Gürel, E. E.; Lahti, P. M.; Karasz, F. *Macromolecules* **2001**, *34*, 4124. (h) Zhan, X.; Liu, Y.; Wu, X.; Wang, S.; Zhu, D. *Macromolecules* **2002**, *35*, 2529.

(8) Chiang, C.-L.; Shu, C.-F. *Chem. Mater.* **2002**, *14*, 682.

(9) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686.

Scheme 1. Synthetic Route for the PF-OXD



the 9,10-diphenylanthracene (ca. 5×10^{-6} M solution, $\Phi_{\text{FL}} = 1.0$). Cyclic voltammetry measurements of the polymer films were performed on a BAS 100 B/W electrochemical analyzer in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at a scan rate of 50 mV/s. The potentials were measured against an Ag/AgCl reference electrode with 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.

Device Fabrication and Testing. The devices were fabricated on ITO substrates that had been ultrasonicated sequentially in detergent, deionized water, 2-propanol, and acetone, and had been treated with O₂ plasma for 10 min before use. All the evaporation of the metal electrodes was carried out in a vacuum evaporator inside an argon atmosphere drybox. A hole-injecting layer, polyethylene dioxethiophene:polystyrene sulfonate (PEDOT, Bayer Corp) was spin-coated at a spin rate of 4000 rpm from its water solution (1.3 wt %) onto the ITO substrates and cured at 160 °C for 10 min under nitrogen. Then a layer of copolymer was spin-coated from its dichloroethane solution (1 wt %) at 2000 rpm. The thickness of the films was measured on a Sloan Dektak 3030 surface profilometer. The thickness of PEDOT was about 35 nm, and the thickness of the polymer layer was around 55 nm. A layer of 30-nm-thick calcium (Ca) cathode was then vacuum deposited at below 1×10^{-6} Torr through a mask, and then a

layer of 120-nm-thick silver (Ag) was vacuum deposited on top of Ca as the protecting layer. The device testing was carried out in air at room temperature. Current-voltage characteristics were measured on a Hewlett-Packard 4155B semiconductor parameter analyzer. The power of EL emission was measured using a Newport 2835-C multi-function optical meter. Photometric units (cd/m²) were calculated using the forward output power and the EL spectra of the devices, assuming Lambertian distribution of the EL emission.¹⁰

Results and Discussion

Synthesis of Monomers and Polymer. Scheme 1 illustrates the synthetic route for the preparation of the oxadiazole-containing polyfluorene (PF-OXD). The relatively high yields and simple workup procedures render the tetrazole synthetic route to be attractive for the preparation of pure oxadiazole derivatives.¹¹ By starting from the 9,9-bis(4-cyanophenyl)fluorene, compound 1 was prepared via the tetrazole route.¹² The bromination

(10) Greenhan, N. C.; Friend, R. H.; Bradley, D. D. C. *Adv. Mater.* **1994**, *6*, 491.

(11) Greczmiel, M.; Strohriegel, P.; Meier, M.; Brütting, W. *Macromolecules* **1997**, *30*, 6042.

(12) (a) Bettenhausen, J.; Strohriegel, P. *Adv. Mater.* **1996**, *8*, 507. (b) Detert, H.; Schollmeier, D. *Synthesis* **1999**, 999.

of **1** with Br₂/phenyliodine bis(trifluoroacetate)¹³ furnished the desired dibromo monomer **2**, which was then copolymerized with the diboronate **3** using the Suzuki coupling reaction. Pd(PPh₃)₄ was used as the catalyst in a mixture of toluene and aqueous potassium carbonate (2 M) with aliquate 336 as the phase-transfer reagent, to give an alternating copolymer PF-OXD.¹⁴ The structures of the dibromo monomer **2** and PF-OXD were characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis. PF-OXD is readily soluble in common organic solvents, such as THF, chloroform, chlorobenzene, and xylene, and is only soluble in toluene upon heating. Gel permeation chromatography (GPC) analysis, which was performed at 30 °C using polystyrene as the standard and THF as the eluent, indicated that PF-OXD has a number-average molecular weight (*M_n*) of approximately 1.3 × 10⁴ g/mol, with a polydispersity index of 2.1.

Thermal Properties. The thermal properties of PF-OXD were investigated by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC was performed at a temperature range between 30 and 350 °C. A distinct *T_g* was observed at 213 °C, and no melting transition was found upon heating beyond *T_g*. The *T_g* of PF-OXD is much higher than that of poly(9,9-dioctyl-fluorene) (POF) (*T_g* ~ 51 °C),¹⁵ in which each repeating fluorene unit contains two flexible *n*-octyl chains at C-9. It is evident that the introduction of two rigid oxadiazole moieties onto the C-9 position of every alternating fluorene unit in the polymer backbone increases the chain rigidity and leads to a much higher *T_g*. This is very important for polymers that function as the emissive materials in LEDs.¹⁶ In addition, as revealed by TGA, the polymer also possesses excellent thermal stability (5% weight loss was observed at 403 °C) due to the presence of the oxadiazole units.

Optical Properties. The absorption and PL spectra of PF-OXD in diluted solution and in solid state are shown in Figures 1 and 2. PF-OXD in THF solution exhibits an absorption with a λ_{max} at 390 nm, due to a $\pi-\pi^*$ transition contributed from the conjugated polyfluorene backbone. There is an additional absorption at 297 nm contributed from the oxadiazole side chains because the model compound, 2,5-di-(4-*tert*-butylphenyl)-1,3,4-oxadiazole **4**, in THF, also has an absorption with the λ_{max} at 298 nm. Upon excitation of the polyfluorene main chain at 390 nm, the emission spectrum displays a vibronic fine-structure with two sharp bands at 419 and 444 nm, and a shoulder at 469 nm. The PL spectrum is almost identical to that obtained from POF in THF (not shown in Figure 1), with only a slightly 1-nm red-shift. This observation suggests that the introduction of oxadiazole groups onto fluorene units via the C-9 carbon does not cause perturbation of the main chain conjugation. The fluorescence yield (Φ_f) of PF-OXD in toluene solution excited at 375 nm was measured to be 1.24, using 9,10-diphenylanthracene ($\Phi_f = 1.0$) as a standard. In comparison to dilute solution, the absorption spectrum of the PF-OXD thin

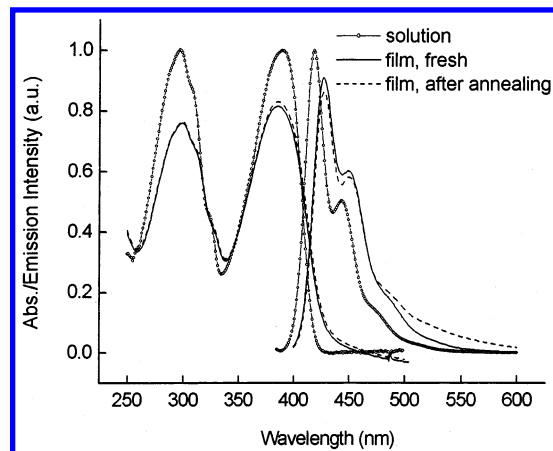


Figure 1. UV-Vis absorption and PL (excited at 390 nm) spectra of PF-OXD in THF solution and in solid state; also included is a PL spectrum of the PF-OXD film after annealing at 150 °C for 20 h under nitrogen atmosphere. The emission intensity is relative to that of a fresh film.

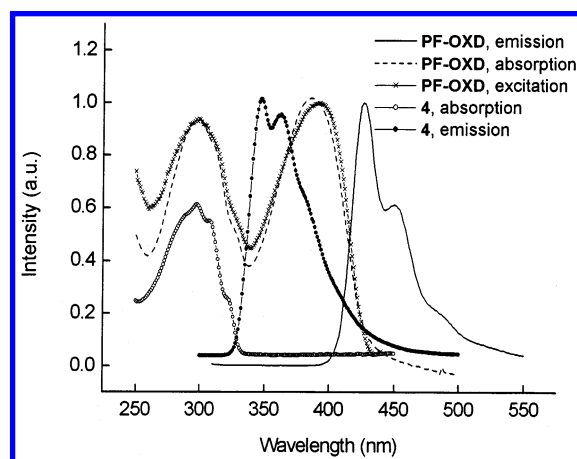


Figure 2. UV-Vis absorption, PL (excited at 300 nm), and excitation (monitored emission at 450 nm) spectra of PF-OXD film; also included are UV-vis absorption and PL (excited at 300 nm) spectra of the model compound **4** in THF solution.

film, prepared by spin-coating from its toluene solution onto a quartz plate, is slightly broadened but without spectral shift, whereas the emission spectrum shows a red-shift of 8 nm. The small red-shift of the emission observed in solid state is probably due to the different dielectric constant of the environment.¹⁷ The PL quantum yield of the PF-OXD film was estimated to be 0.43 by comparing the fluorescence intensity of the POF polymer thin film sample that was excited at 384 nm ($\Phi_f = 0.55$).¹⁸

Although bright blue LEDs based on polyfluorenes have been fabricated, a major problem with polyfluorenes exists due to their tendency to form long wavelength aggregates/excimers in the solid state upon heating.¹⁹ To examine the thermal stability of PF-OXD, the polymer thin film sample was heated on a hot plate at 150 °C under nitrogen atmosphere for 20 h. The PL

(13) Gallos, J.; Varvoglis, A. *J. Chem. Res. Miniprint* **1982**, 1649.

(14) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(15) Ding, J.; Day, M.; Robertson, G.; Roovers, J. *Macromolecules* **2002**, *35*, 3474.

(16) Tokito, S.; Tanaka, H.; Noda, K.; Okada, A.; Taga, Y. *Appl. Phys. Lett.* **1997**, *70*, 1929.

(17) Wu, F.-I.; Dodda, R.; Reddy, D. S.; Shu, C.-F. *J. Mater. Chem.* **2002**, *12*, 2893.

(18) Grice, A. W.; Bradley, D. C. D.; Bernius, M. T.; Inbasekaran, M.; Wu, W. W.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 629.

(19) Lee, J. I.; Klaerner, G.; Miller, R. D. *Synth. Mater.* **1999**, *101*, 126. (b) Teetsov, J.; Fox, M. A. *J. Mater. Chem.* **1999**, *9*, 2117. (c) Weinfurter, K. -H.; Fujikawa, H.; Tokito, S.; Taga, Y. *Appl. Phys. Lett.* **2000**, *76*, 2502.

spectra of the PF-OXD film remains almost intact without the appearance of a long wavelength tail after thermal treatment (Figure 1). For comparison, the same experiments were conducted for the POF film. The annealing of the POF film not only results in a bathochromical spectral shift in PL with a significantly reduced emission intensity, but also generates the appearance of an additional emission band between 500 and 600 nm. Thus, it is apparent that the thermal stability of PF-OXD is improved over that of POF due to the incorporation of oxadiazole moieties onto the C-9 position of the fluorene units. The 3-D shape rigid oxadiazole structure may also prevent π -stacking between polymer chains and suppress the formation of aggregates/excimers in the solid state. The higher T_g of the PF-OXD also accounts for the greater spectroscopic stability of the polymer film.

Figure 2 shows the PL spectrum of the model compound **4** in THF solution. There is some spectral overlap between the emission spectrum of **4** and the absorption spectrum of the main chain conjugated PF-OXD, indicating that there is a possibility of getting energy transfer from the excited OXD side chains to the polyfluorene backbone. Upon excitation of the OXD groups at 300 nm, the PF-OXD film emits a blue fluorescence around 440 nm which originates from the emission of conjugated backbone, whereas no luminescence was detected from the OXD side chains at 347 nm. This PL spectrum is almost identical to that of the PF-OXD excited at 390 nm (Figure 1), with a slightly higher intensity. Furthermore, the excitation spectrum of PF-OXD, monitored at 450 nm, is a perfectly superimposed image of the absorption spectrum. These results reveal that the energy transfer from excited OXD side chains to the polyfluorene backbone is quite efficient and its contribution to the emission intensity from the main chain may be significant.

Redox Properties. The electrochemical behavior of PF-OXD was investigated by using cyclic voltammetry. On the basis of the onset potentials of the oxidation and reduction, the HOMO and LUMO energy levels of PF-OXD were estimated to be -5.76 and -2.47 eV, respectively, with regard to the energy level of the ferrocene reference (4.8 eV below the vacuum level).²⁰ The HOMO energy level of the polymer is similar to that reported for POF (-5.8 eV).²¹ It is also consistent with the previous observation that the electronic structure of the conjugated polyfluorene backbone remains undisturbed after the attachment of oxadiazole moieties as side chains onto PF-OXD. The low-lying LUMO level of PF-OXD may originate from the electron-deficient nature of the oxadiazole moiety, as revealed from the comparison between the LUMO level of 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, which was estimated to be -2.4 eV.²² This result indicates that the introduction of an electron-deficient oxadiazole group leads to the increase in electron affinity and improvements in electron-injecting of the polymer.

Electroluminescent Properties. The EL properties of the polymer were examined using a double-layer LED

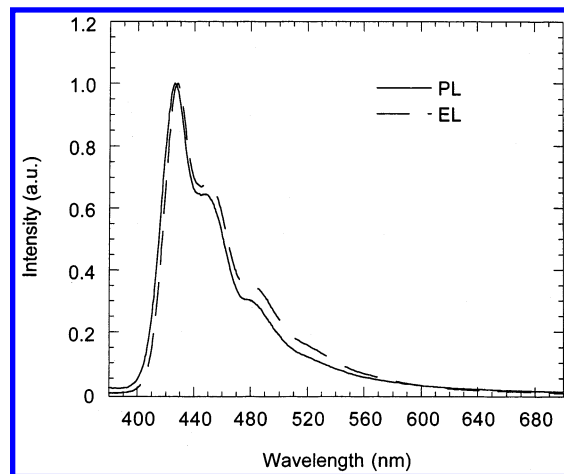


Figure 3. PL spectrum of PF-OXD superimposed with the EL spectrum of the ITO/PEDOT/PF-OXD/Ca/Ag device.

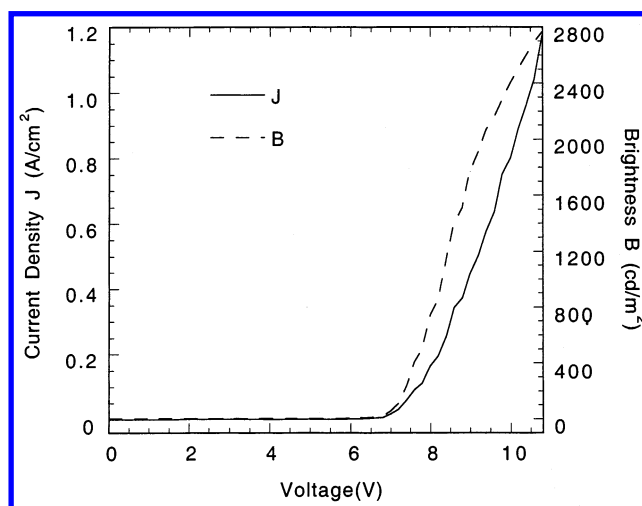


Figure 4. Current density-voltage-brightness (J - V - B) characteristics of ITO/PEDOT/PF-OXD/Ca/Ag device.

device configuration (ITO/PEDOT/PF-OXD/Ca/Ag), where a conducting polymer, poly(3,4-ethylene dioxythiophene) (PEDOT) was used as the hole-injecting layer. The typical EL spectrum from this device is shown in Figure 3 along with its PL spectrum. The EL peaks at 428 nm which is identical to its PL spectrum. No undesirable excimer/aggregate emission was observed at a long wavelength like that of POF reported in the literature. The device shows a strong blue emission with a quite low turn-on voltage (voltage needed for brightness of 1 cd/m^2) at 5.3 V. The luminance reaches 2770 cd/m^2 at a drive voltage of 10.8 V and a current density 1.12 A/cm^2 , corresponding to an efficiency of 0.25 cd/A and a luminosity of 0.08 lm/W (Figure 4). The maximum external quantum efficiency is 0.52% at 537 cd/m^2 with a bias of 7.4 V. The device based on the PF-OXD demonstrates a much higher brightness and efficiency than the device made with the unmodified POF, which had a maximum brightness around 600 cd/m^2 and an external quantum efficiency of 0.2% .¹⁸ The improved device performance is due to better electron injection and transport from PF-OXD and the efficient energy transfer from OXD side chain to polyfluorene main chains.

(20) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bässler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551.

(21) Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453.

(22) Janietz, S.; Wedel, A. *Adv. Mater.* **1997**, *9*, 403.

Conclusion

We have developed a novel polyfluorene copolymer with two electron-deficient, 4-*tert*-butylphenyl-1,3,4-oxadiazole groups functionalized on the C-9 position of the alternating fluorene unit to form a 3-D structure. This polymer possesses a very high T_g (213 °C) and very good thermal stability (5% weight loss observed at 403 °C). The results from the PL measurements of the isothermally heated PF-OXD thin film (150 °C for 20 h) show that the commonly observed aggregate/excimer formation is very effectively suppressed in this polymer due to its 3-D structure and high T_g . A double-layer LED device using this polymer as the emitting layer shows a bright blue emission with a low turn-on voltage at 5.3 V and a high brightness of 2770 cd/m² at a drive voltage of 10.8 V. The maximum external quantum efficiency

is 0.52% at 537 cd/m² with a bias of 7.4 V. The improved device performance over that of POF is due to better electron injection and transport in PF-OXD and the efficient energy transfer from OXD side chain to the polyfluorene main chains.

Acknowledgment. We thank the National Science Council of the Republic of China and the Air Force Office of Scientific Research (AFOSR) for financial support. A. J. thanks the Boeing-Johnson Foundation for financial support. M. L. is thankful for support from the Joint Institute for Nanoscience funded by the Pacific Northwest National Laboratory (operated by Battelle for the U.S. Department of Energy) and the University of Washington.

CM020688+