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New Series of Blue-Emitting and Electron-Transporting Copolymers Based on Fluorene

Xiaowei Zhan, Yunqi Liu,* Xia Wu, Shuai Wang, and Daoben Zhu*

Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

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ABSTRACT: A novel series of conjugated copolymers having oxadiazole, quinoline, quinoxaline, and phenylenecyanovinylene moieties in the main chain based on fluorene were synthesized in good yields by palladium-catalyzed Suzuki coupling reaction, a new approach different from the traditional polyhydrazide precursor route (oxadiazole-containing polymers), acid-catalyzed Friedländer condensation reaction (polyquinolines), and Knoevenagel condensation polymerization (poly(phenylenecyanovinylene)). The thermal, electrochemical, and optical properties of these copolymers were examined. All these polymers possess excellent thermal stability with glass transition temperatures of 114−208 °C and onset decomposition temperatures of 387−415 °C. Cyclic voltammetry studies reveal that these copolymers possess low-lying LUMO energy levels ranging from −3.01 to −3.37 eV and low-lying HOMO energy levels ranging from −6.13 to −6.38 eV and may be promising candidates for electron-transporting or hole-blocking materials in light-emitting diodes. The polymers in thin films emit strong blue luminance around 414−476 nm with narrow bandwidth upon photoexcitation. Photoluminescence spectra of the polymers in the films are only red-shifted by 7−11 nm compared to those in the solution, indicating that the aggregation and the excimer fluorescence are suppressed.

Introduction

Since the discovery of an electroluminescent (EL) polymer in 1990, EL conjugated polymers have attracted much interest in recent years because of potential application in large-area flat panel displays.[1] It is established that high quantum efficiency EL devices can be obtained by achieving both efficient charge injection and balanced mobility of both charge carriers inside the EL materials. In general, most of the EL polymers inject and transport holes more efficiently than electrons due to their inherent richness of π-electrons. Thus, synthesis of novel efficient electron transport (ET) polymers is needed to improve device performance. Polyquinolines and polyquinoxalines have recently been demonstrated as ET layers in light-emitting diodes (LEDs) due to their high thermal and oxidative stability, outstanding mechanical property, and good film-forming ability.[2,3] However, polyquinolines and polyquinoxalines possess poor solution processability.

2-(4-Biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) is one of the most widely used electron injection/transport or hole-blocking materials.[4] Its function is believed to result from the high electron affinity of the oxadiazole ring in the molecule. Several oxadiazole-containing polymers have been synthesized as electron-transporting materials;[5] oxadiazole-containing light-emitting polymers have also been prepared in recent years.[6−8] Poly(*p*-phenylenecyanovinylene) (CN-PPV) and its derivatives are well-known electron-transporting electroluminescent polymers.[9]

Fluorene derivatives show interesting and unique chemical and physical properties because they contain a rigid planar biphenyl unit, and the facile substitution at the remote C_9 position can improve the solubility and processability of polymers without significantly increasing the steric interactions in the polymer backbone.[10] As a result, homopolymers and copolymers of fluorene have emerged as the most attractive blue-emitting materials due to their high efficiency and good thermal stability.[11−13] To our knowledge, electron-transporting polymers based on fluorene are still rare.[14] No effort has been devoted to synthesis of fluorene-based conjugated electron-transporting electroluminescent polymers containing oxadiazole, quinoxaline, and phenylenecyanovinylene.

In this work, we describe the synthesis of a novel series of electron-deficient oxadiazole-, quinoline-, quinoxaline-, and phenylenecyanovinylene-containing conjugated copolymers based on fluorene in hope of combining both excellent electron-affinitive properties of the formers and blue light-emitting and high quantum efficiency of the latter into a polymer. Moreover, we introduced sterically hindered substituents into fluorene moiety to enhance processability and amorphicity of polymers. These copolymers possess good solubility, excellent thermal stability, low-lying LUMO energy levels, and blue-emitting properties.

Experimental Section

Materials. 3,3-Diaminobenzidine (Acros), phenylacetylene (Fluka), 1,4-diacetylbenzene (Acros), ethyl 4-bromobenzoate (Acros), dimethyl terephthalate (Acros), 4-bromophenylacetonitrile (Acros), and 4-bromobenzaldehyde (Acros) were used as received without further purification. 2,7-Dibromo-9,9-bis(2-ethylhexyl)fluorene,[15] 2-amino-5-bromobenzophenone,[16] tetrakis(triphenylphosphine)palladium(0),[17] and bis(triphenylphosphine)palladium dichloride[17] were synthesized by literature methods. Toluene was freshly distilled from sodium benzophenone ketyl under nitrogen prior to use. Triethylamine was dried over CaH_2 and distilled under a N_2 atmosphere prior to use. *m*-Cresol was purified by distillation under reduced pressure.

Monomer Synthesis. 9,9-Bis(2-ethylhexyl)fluorene-2,7-bis(trimethylene boronate) was synthesized according to our previous literature.[15] The synthesis of other monomers is shown in Scheme 1.

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* To whom correspondence should be addressed. E-mail: liuyq@infoc3.icas.ac.cn.

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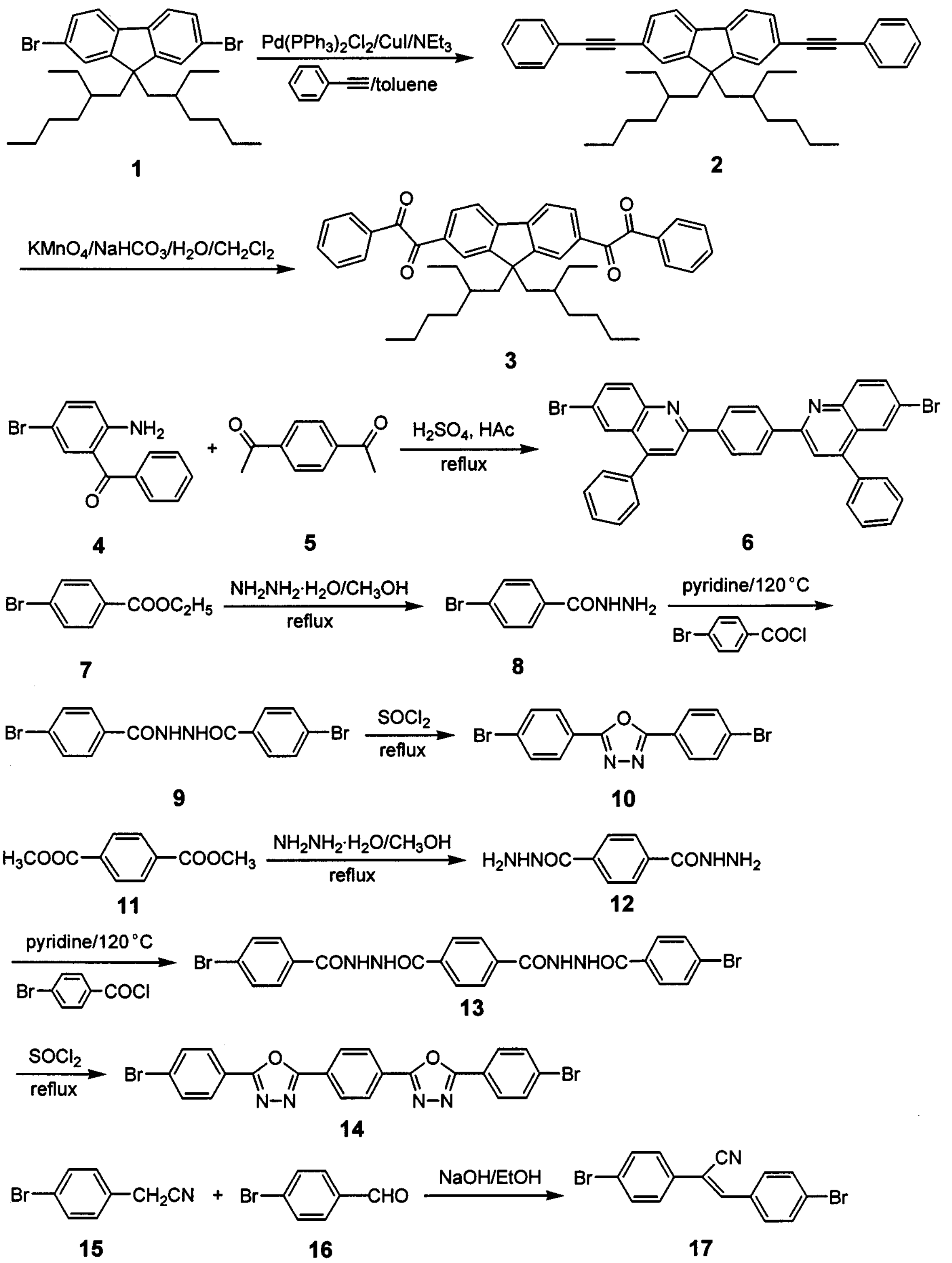
Scheme 1. Synthetic Route to the Monomers



2,7-Bis(phenylethynyl)-9,9-bis(2-ethylhexyl)fluorene (2). To a solution of 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene (**1**) (2.2 g, 4 mmol) in dry triethylamine (30 mL) was added phenylacetylene (1.1 mL, 10 mmol). After the solution was degassed with nitrogen for 30 min while stirring, $Pd(PPh_3)_2Cl_2$ (70 mg, 0.10 mmol) and CuI (38.0 mg, 0.20 mmol) were added. The reaction mixture was then refluxed under nitrogen for 24 h. After the reaction was complete, the crude mixture was filtered at room temperature to remove triethylammonium bromide precipitate. The precipitate was rinsed with diethyl ether, and the combined filtrates were evaporated to dryness. The residue was purified by flash column chromatography (silica gel, 20% ethyl acetate in petroleum ether) to give compound **2** (2.1 g, 87%) as an orange oil. Anal. Calcd for $C_{45}H_{50}$: C, 91.47; H, 8.53. Found: C, 91.05; H, 8.68%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, 2H), 7.58 (m, 8H), 7.38 (m, 2H), 7.28 (d, 2H), 7.20 (d, 2H), 2.05 (d, 4H), 1.32 (s, 2H), 0.94–0.75 (m, 22H), 0.59 (t, 6H). MS (EI) 590.89 (calcd for $C_{45}H_{50}$), 590 (found). FT-IR (Nujol mulls): ν 2958, 2926, 2857, 1597, 1493, 1462, 1378, 822, 755, 690 cm^{-1}.

2,7-Bis(phenyloxoacetyl)-9,9-bis(2-ethylhexyl)fluorene (3). To a solution of **2** (2.4 g, 4 mmol) in 20 mL of dichloromethane was added 200 mg of tetrabutylammonium bromide, 40 mL of water, 0.8 g of $NaHCO_3$, and 4.0 g of $KMnO_4$. After vigorous stirring at room temperature for 48 h, sodium bisulfite (6 g) and hydrochloric acid (3.0 mL) were slowly added to reduce excess oxidizing agents. The mixture was extracted with CH_2Cl_2 and washed with water, and the organic layer was dried over magnesium sulfate. The solvent was evaporated to afford a yellow viscous oil (2.6 g, 97%). Anal. Calcd for $C_{45}H_{50}O_4$: C, 82.53; H, 7.70. Found: C, 82.08; H, 7.68%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (m, 4H), 7.92 (m, 2H), 7.82 (m, 2H), 7.57 (m, 4H), 7.47−7.38 (m, 4H), 1.98 (d, 4H), 1.18 (s, 2H), 0.81−0.57 (m, 22H), 0.36 (t, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 194.4, 152.5, 145.7, 134.8, 133.6, 132.9, 132.2, 130.0, 129.7, 129.4, 128.9, 128.3, 125.3, 121.3, 55.6, 43.7, 34.6, 33.7, 27.9, 26.9, 22.5, 13.8, 10.1. MS (FAB) 654.89 (calcd for $C_{45}H_{50}O_4$), 654 (found). FT-IR (Nujol mulls): ν 2959, 2928, 2872, 2858, 1671, 1601, 1579, 1452, 1319, 1206, 1162, 889, 750, 715, 689, 649 cm^{-1}.

2,2′-(*p*-Phenylene)bis(6-bromo-4-phenylquinoline) (6). Under nitrogen atmosphere, 2-amino-5-bromobenzophenone (**4**) (5.52 g, 20 mmol), 1,4-diacetylbenzene (**5**) (1.62 g, 10 mmol), sulfuric acid (0.1 mL), and acetic acid (10 mL) were placed in a three-necked flask and refluxed for 18 h. After cooling, the mixture was slowly added to a stirred mixture of crushed ice (40 g) and 25% ammonia solution in water (15 mL) to give a precipitate. The obtained solid was washed with hot water, ethanol, and chloroform to afford a white solid (5.33 g, 83%); mp >300 °C. Anal. Calcd for $C_{36}H_{22}Br_2N_2$: C, 67.31; H, 3.45; N, 4.36. Found: C, 67.09; H, 3.53; N, 4.22%. ^{1}H NMR (300 MHz, CF_3COOD): δ 8.56 (s, 2H), 8.42 (d, 4H), 8.35 (m, 6H), 7.76 (m, 10H). ^{13}C NMR (50 MHz, CF_3COOD): δ 152.1, 139.8, 137.7, 135.1, 134.1, 131.9, 130.2, 129.6, 129.2, 128.1, 126.1, 122.2, 121.9. MS (FAB) 642.39 (calcd for $C_{36}H_{22}Br_2N_2$), 642 (found).

4-Bromobenzoic Hydrazide (8). To a solution of ethyl 4-bromobenzoate (**7**) (5.7 g, 25 mmol) in 25 mL of methanol was added hydrazine monohydrate (4.7 mL, 75 mmol), and then the mixture was refluxed for 16 h under a nitrogen atmosphere. After the reaction was complete, water was poured into the mixture and extracted with ethyl acetate. The solvent was evaporated to give white needlelike crystals (5.1 g, 95%); mp 166−167 °C. Anal. Calcd for $C_7H_7BrN_2O$: C, 39.10; H, 3.28; N, 13.03. Found: C, 39.23; H, 3.27; N, 13.12%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.88 (s, 1H), 7.79 (d, 2H), 7.68 (d, 2H), 4.54 (s, 2H).

Bis(4-bromophenyl)hydrazine (9). Equimolar amounts of **8** (2.15 g, 10 mmol) and 4-bromobenzoic chloride (2.19 g, 10 mmol) were dissolved in 50 mL of pyridine. The reaction mixture was refluxed for 6 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into 200 mL of ethanol and was frozen to afford white plate crystals (3.2 g, 80%); mp 319−320 °C. Anal. Calcd for $C_{14}H_{10}Br_2N_2O_2$: C, 42.24; H, 2.53; N, 7.04. Found: C, 42.01; H, 2.57; N, 7.12%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.63 (s, 2H), 7.85 (d, 4H), 7.77 (d, 4H).

2,5-Bis(4-bromophenyl)-1,3,4-oxadiazole (10). A solution of **9** (4.0 g, 10 mmol) in $SOCl_2$ (10 mL) was refluxed for 5 h under nitrogen atmosphere. Excess $SOCl_2$ was distilled off, and then the residue was slowly poured into 50 mL of water to give a precipitate. The crude produce was purified by sublimation to yield white crystals (2.7 g, 71%); mp 258 °C. Anal. Calcd for $C_{14}H_8Br_2N_2O$: C, 44.25; H, 2.12; N, 7.37. Found: C, 44.08; H, 2.17; N, 7.31%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, 4H), 7.68 (d, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.0, 132.5, 128.3, 126.6, 122.6. MS (EI) 380.04 (calcd for $C_{14}H_8Br_2N_2O$), 380 (found).

1,4-Bis[5-(4-bromophenyl)-1,3,4-oxadiazole-2-yl]benzene (14). This compound was prepared by a procedure similar to that of **10**, using dimethyl terephthalate (**11**) instead of ethyl 4-bromobenzoate (**7**), and the product was isolated as a white crystalline solid (64%); mp >300 °C. Anal. Calcd for $C_{22}H_{12}Br_2N_4O_2$: C, 50.41; H, 2.31; N, 10.69. Found: C, 50.13; H, 2.36; N, 10.77%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.04 (m, 4H), 7.85 (m, 4H), 7.75 (m, 4H). MS (EI) 524.17 (calcd for $C_{22}H_{12}Br_2N_4O_2$), 524 (found).

1,2-Bis(4-bromophenyl)-1-cyanovinylene (17). 4-Bromophenylacetonitrile (**15**) (1.96 g, 10 mmol) and 4-bromobenzaldehyde (**16**) (1.85 g, 10 mmol) were dissolved in ethanol (50 mL). To the mixture was added dropwise a solution of NaOH (50 mg) in ethanol (30 mL) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h. The product was obtained as a precipitate, was filtered, and was washed with water to give a yellow powder (3.30 g, 91%). Anal. Calcd for $C_{15}H_9Br_2N$: C, 49.63; H, 2.50; N, 3.86. Found: C, 49.64; H, 2.54; N, 3.80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, 2H), 7.62−7.52 (m, 6H), 7.45 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 140.9, 132.8, 132.2, 130.5, 127.3, 125.1, 123.6, 117.2, 111.0. MS (EI) 363.05 (calcd for $C_{15}H_9Br_2N$), 363 (found).

Polymer Synthesis. The two synthetic routes to copolymers are illustrated in Scheme 2. The quinoxaline-containing copolymer (**PFQx**) was prepared by a condensation reaction between 2,7-bis(phenyloxoacetyl)-9,9-bis(2-ethylhexyl)fluorene and 3,3-diaminobenzidine in *m*-cresol. Other polymers were synthesized through a palladium-catalyzed Suzuki coupling reaction between diboronate and dibromide in toluene.

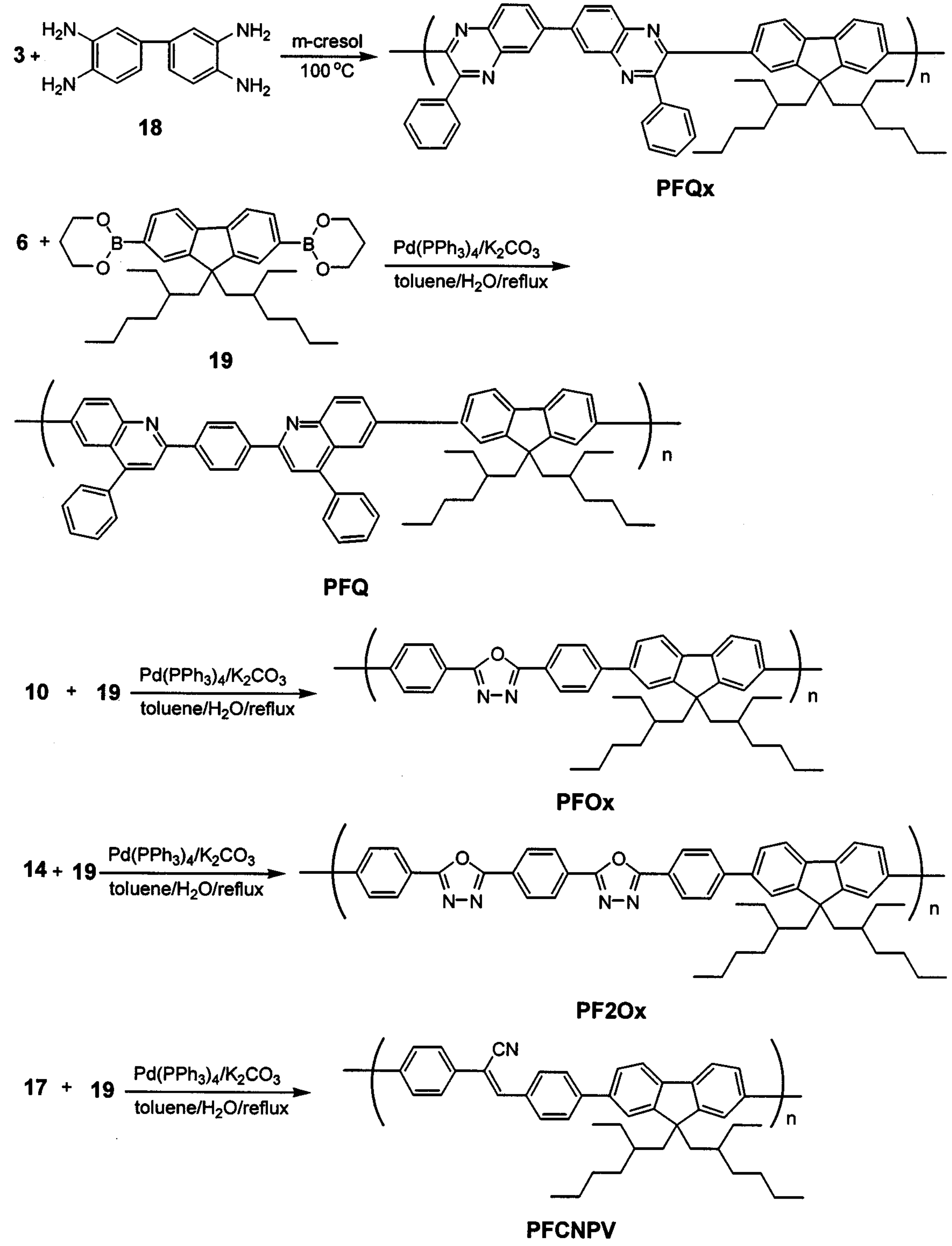
Poly{9,9-bis(2-ethylhexyl)fluorene-2,7-diyl]-*alt*-[6,6′-bis(3-phenylquinoxaline)-2,2′-diyl]} (PFQx). Equimolar amounts of monomer **3** (654 mg, 1.0 mmol) and 3,3-diaminobenzidine (**18**) (214 mg, 1.0 mmol) were dissolved in 4 mL of freshly distilled *m*-cresol in a 50 mL three-necked flask. The reaction mixture was stirred under nitrogen purge at 100 °C for 48 h during which progressive increase of the solution viscosity was observed. After cooling to room temperature, the reaction mixture was poured into 100 mL of methanol to give a precipitate. The obtained solid was redissolved in *m*-cresol and reprecipitated from methanol, followed by Soxhlet extraction with ethanol for 24 h to give a pale yellow powder (600 mg, 75%). Anal. Calcd for $(C_{57}H_{56}N_4)_n$: C, 85.89; H, 7.08. Found: C, 85.35; H, 7.18%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.72 (m, 2H), 8.41 (m, 4H), 7.87 (m, 2H), 7.64 (m, 6H), 7.41 (m, 8H), 2.00 (d, 4H), 1.26 (s, 2H), 1.02−0.62 (m, 28H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 154.2, 154.0, 153.6, 151.6, 141.6, 141.1, 140.7, 139.4, 137.8, 129.8, 129.3, 129.2, 128.9, 128.4, 127.5, 127.3, 125.7, 119.6, 55.0, 44.5, 34.9, 33.7, 28.2, 26.9, 22.9, 14.1, 10.5. FT-IR (KBr): ν 3060, 2957, 2925, 2856, 1733, 1613, 1537, 1463, 1383, 1342, 1261, 1193, 1059, 1029, 827, 805, 769, 697 cm^{-1}.

Poly{[9,9-bis(2-ethylhexyl)fluorene-2,7-diyl]-*alt*-[2,2′-(*p*-phenylene)bis(4-phenylquinoline)-6,6′-diyl]} (PFQ). Under a nitrogen atmosphere, 9,9-bis(2-ethylhexyl)fluorene-2,7-bis(trimethylene boronate) (**19**) (280 mg, 0.5 mmol), **6** (320 mg, 0.5 mmol), $Pd(PPh_3)_4$ (6.0 mg, 0.005 mmol), toluene (5 mL), and 2 M K_2CO_3 (5 mL) were placed in a three-necked flask and refluxed for 72 h. After cooling, the mixture was diluted with $CHCl_3$ (20 mL) and washed with water, and the organic layer was dried over magnesium sulfate. The solvent was evaporated to 2 mL and then poured into methanol to give a precipitate. The obtained solid was redissolved in $CHCl_3$ and reprecipitated from methanol, followed by Soxhlet extraction with the same solution for 24 h to give a pale yellow powder (426 mg, 98%). Anal. Calcd for $(C_{65}H_{62}N_2)_n$: C, 89.61; H, 7.17. Found: C, 89.29; H, 7.23%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, 4H), 8.05 (m, 4H), 7.91 (s, 2H), 7.68 (m, 2H), 7.59−7.36 (m, 16H), 2.12 (d, 4H), 1.15 (s, 2H), 0.70−0.36 (m, 28H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.7, 151.5, 140.5, 140.0, 138.9, 138.2, 130.1, 129.6, 128.8, 128.2, 126.5, 126.4, 126.2, 123.2, 120.1, 119.9, 55.2, 44.4, 34.5, 33.8, 28.0, 27.0, 22.6, 13.9, 10.3. FT-IR (KBr): 2957, 2924, 2855, 1588, 1546, 1470, 1383, 1354, 1262, 1095, 1066, 1018, 874, 818, 701 cm^{-1}.

Poly{[9,9-bis(2-ethylhexyl)fluorene-2,7-diyl]-*alt*-[2,5-bis(*p*-phenylene)-1,3,4-oxadiazole]} PFOx. This polymer was prepared by a procedure identical to **PFQ** using **10** instead of **6**; the product was isolated as an off-white powder in a yield of 75%. Anal. Calcd for $(C_{43}H_{48}N_2O)_n$: C, 84.83; H, 7.95. Found: C, 85.44; H, 8.17%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (d, 4H), 7.78 (m, 6H), 7.63 (d, 4H), 2.08 (d, 4H), 1.19 (s, 2H), 0.81−0.46 (m, 28H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.6, 151.6, 145.0, 140.9, 138.3, 127.6, 127.4, 126.8, 126.3, 122.8, 122.4, 120.4, 119.8, 55.2, 44.4, 34.8, 34.0, 28.2, 27.2, 22.7, 14.0, 10.4. FT-IR (KBr): 2961, 2926, 2872, 2857, 1613, 1500, 1465, 1408, 1378, 1262, 1098, 1018, 852, 817, 804, 752 cm^{-1}.

Poly{[9,9-bis(2-ethylhexyl)fluorene-2,7-diyl]-*alt*-{1,4-bis[5-(*p*-phenylene)-1,3,4-oxadiazole-2-yl]benzene}} PF2Ox. This polymer was prepared by a procedure identical to **PFQ**

Scheme 2. Synthetic Route to the Polymers



using **14** instead of **6**; the product was isolated as an off-white powder in a yield of 95%. Anal. Calcd for $(C_{51}H_{52}N_4O_2)_n$: C, 81.35; H, 6.96. Found: C, 81.94; H, 7.13%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (m, 8H), 7.80 (m, 4H), 7.74 (m, 6H), 2.06 (d, 4H), 1.17 (s, 2H), 0.80−0.44 (m, 28H). FT-IR (KBr): 2961, 2913, 2854, 1601, 1509, 1462, 1267, 1091, 805, 464 cm^{-1}.

Poly{[9,9-bis(2-ethylhexyl)fluorene-2,7-diyl]-*alt*-[1,2-bis(*p*-phenylene)-1-cyanovinylene]} PFCNPV. This polymer was prepared by a procedure identical to **PFQ** using **17** instead of **6**; the product was isolated as a greenish-yellow powder in a yield of 79%. Anal. Calcd for $(C_{44}H_{49}N)_n$: C, 89.29; H, 8.34. Found: C, 88.64; H, 8.29%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.96−7.51 (m, 14H), 2.07 (d, 4H), 1.26 (s, 2H), 0.88−0.58 (m, 28H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.5, 143.8, 141.2, 140.7, 138.4, 129.9, 127.6, 127.5, 127.2, 126.8, 126.4, 126.2, 122.7, 120.3, 55.3, 44.5, 34.7, 33.8, 28.1, 27.1, 22.7, 14.0, 10.4. FT-IR (KBr): 3031, 2957, 2926, 2871, 2857, 2215, 1605, 1518, 1465, 1409, 1378, 1260, 1099, 1016, 894, 847, 817, 742 cm^{-1}.

Instrumentation. FT-IR spectra were taken on a Perkin-Elmer System 2000 FT-IR spectrometer with KBr pellets or Nujol mulls. UV−vis spectra in chloroform solution and in thin films on quartz substrates were recorded on a Hitachi U-3010 UV−vis spectrophotometer. Photoluminescence (PL) spectra of the polymers in chloroform solution and in thin films on quartz substrates were measured on a Hitachi F-4500 spectrophotometer. ^{1}H NMR spectral data are expressed in ppm relative to internal standard tetramethylsilane and were obtained in $CDCl_3$ or other deuterated solvents on a Bruker dmx 300 NMR spectrometer. ^{13}C NMR spectra were observed in deuterated solvents (20% w/v) on a Varian Unity 200 MHz NMR spectrometer. Mass spectra were determined with the instruments AEI-MS50 for EI-MS and KYKY-ZH-P-5 for FAB-MS. Elemental analyses were carried out by a Carlo Erba model 1106 elemental analyzer. Thermal gravimetric analysis (TGA) measurements were performed on Perkin-Elmer series 7 thermal analysis system under N_2 at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) measurements were performed on Perkin-Elmer DSC 7 under N_2 at a heating rate of 20 °C/min. The weight-average molecular weights (M_w) and polydispersity indices (M_w/M_n) of the polymers were measured on a PL-GPC model 210 chromatograph at 35 °C, using THF as eluent and standard polystyrene as reference. For study on electrochemical behavior, a polymer thin film was prepared on a platinum wire as a working electrode, using a platinum wire as the counter electrode and Ag/Ag^+ as the reference electrode in a solution of tetrabutylammonium hexafluorophosphate (0.1 M) in acetonitrile. The reference electrode potential vs normal hydrogen electrode (NHE) is 0.2223 V.[18] The cyclic voltammogram was recorded on a computer-controlled EG&G potentiostat/galvanostat model 283. The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energy levels of the polymers were converted from the onset reduction and oxidation potentials, respectively, with the assumption that the energy level of ferrocene/ferrocenium (Fc) is 4.8 eV below vacuum.[19]

Results and Discussion

Synthesis and Characterization of Polymers. The synthesis of aromatic poly(1,3,4-oxadiazole) compounds has been reviewed recently.[20] The widespread route involves the preparation of polyhydrazide precursors followed by cyclodehydration. However, this synthetic route has some disadvantages. One is the difficult purification of the polyhydrazide precursors because of their poor solubility in common organic solvents, resulting in impurity of the final polymers. It should be emphasized that purity of the polymers is an important criterion of EL materials since the impurity of the polymers leads to the poor performance of the EL devices. Another is the incompleteness of the heterogeneous cyclodehydration reaction because of low solubility of the precursors and their corresponding final polymers in dehydrating solvents such as $POCl_3$.[7b] We used a different synthetic approach which is outlined in Schemes 1 and 2. At first we synthesized easily purified (by sublimation) 1,3,4-oxadiazole-containing monomers **10** and **14**. Finally, we prepared polymers by employing palladium-catalyzed Suzuki coupling reactions between fluorene diboronate and 1,3,4-oxadiazole dibromide in toluene. Two oxadiazole-containing polymers **PFOx** and **PF2Ox** were synthesized successfully in good yields of 75% and 95%. These polymers are off-white powders. Polymer **PFOx** has good solubility in common organic solvents such as chloroform and tetrahydrofuran (THF), while polymer **PF2Ox** has poor solubility in chloroform and THF because of higher 1,3,4-oxadiazole content in the latter.

In general, polyquinolines were synthesized by acid-catalyzed Friedländer condensation reaction between bis(*o*-aminoketone) and diacetylaryl compound in *m*-cresol.[14,21] *m*-Cresol is known to catalyze the polycondensation. However, the use of the high boiling and polar *m*-cresol has one disadvantage, that is, the poor removability of the solvent from bulk material or cast films for LED applications. Here, we employed a different synthetic route which is outlined in Schemes 1 and 2. First of all, we synthesized a new bisquinoline monomer **6** by acid-catalyzed condensation reaction between *o*-aminoketone **4** and diacetylbenzene **5**. Then we prepared the polymer **PFQ** composed of fluorene and quinoline units using palladium-catalyzed Suzuki coupling reactions between fluorene diboronate and quinoline dibromide in toluene. The polymer **PFQ** was obtained as a pale yellow powder in a high yield of 98%. In contrast to polyquinolines reported in the literature,[16] **PFQ** is completely soluble in common organic solvents, such as chloroform and tetrahydrofuran, due to the 2-ethylhexyl side chain attached to the fluorene moiety.

The copolymer constituted of fluorene and quinoxaline, **PFQx**, was synthesized according to Scheme 2. The monomer **3** was prepared according to Scheme 1. Phenylacetylene and 2,7-dibromofluorene (**1**) were cross-coupled in a palladium-catalyzed Heck reaction to compound **2**. The compound **2** could easily be oxidized to the tetraketone **3** with $KMnO_4$ in CH_2Cl_2 according to the procedure for the oxidation of 2,5-bis(phenylethynyl)thiophene described by Jenekhe.[3d] The route to the tetraketone **3** avoids the use of highly toxic selenium dioxide as the oxidizing agent.[3c] The last step is the polycondensation of the tetraketone **3** and 3,3-diaminobenzidine **18** in *m*-cresol, leading to the new substituted polyquinoxaline **PFQx**. The obtained polyquinoxaline **PFQx** is a pale yellow powder. In contrast to polyquinoxalines reported in the literature,[3d] **PFQx** is completely soluble in common organic solvents, such as chloroform, tetrahydrofuran, and *m*-cresol. This was partially due to the 2-ethylhexyl side chain attached to the fluorene moiety.

The established synthetic route to poly(*p*-phenylenecyanovinylene) (CN-PPV) involves Knoevenagel condensation polymerization of terephthalaldehyde with benzenediacetonitrile.[9a] However, the molecular weight of the CN-PPV obtained by the above method is not high; for example, the number-average molecular weight (M_n) of the CN-PPV synthesized by Greenham et al. is 4000 by gel permeation chromatography (GPC) against polystyrene standard.[9a] Here, we report a different synthetic route which is outlined in Schemes 1 and 2. We synthesized a phenylenecyanovinylene monomer **17** by base-catalyzed condensation reaction between 4-bromophenylacetonitrile (**15**) and 4-bromobenzaldehyde (**16**) in ethanol. Then we prepared the polymer **PFCNPV** consisting of fluorene and phenylenecyanovinylene units using palladium-catalyzed Suzuki coupling reactions between fluorene diboronate and phenylenecyanovinylene dibromide in toluene. The polymer **PFCNPV** was obtained as a greenish-yellow powder in a yield of 79%. The prepared **PFCNPV** is soluble in chloroform and THF. The M_n of **PFCNPV** was measured to be 13 140 by GPC on the basis of polystyrene standard, 3 times that for the reported CN-PPV.[9a]

The molecular weights of these polymers were determined by gel permeation chromatography using polystyrene as the standard and are listed in Table 1. These copolymers have weight-average molecular weights (M_w) of 20 000−81 400 with polydispersity indices (M_w/M_n) of 2.3−2.9. The thermal properties of the polymers were determined by TGA and DSC measurements. Figure 1 gives thermogravimetric curve of the polymer **PFQx**. TGA reveals good thermal stability of this polymer with the onset decomposition temperature (T_d) of 415 °C under nitrogen. As shown in Table 1, all these polymers possess excellent thermal stability with T_d ranging from

Table 1. Molecular Weights and Thermal Properties of the Polymers

polymer	yield (%)	M_w[a]	M_w/M_n[a]	T_d[b] (°C)	T_g[c] (°C)
PFOx	75	20 000	2.3	399	137
PF2Ox	95	20 100	2.2	394	194
PFQ	98	66 100	2.5	387	146
PFQx	75	81 400	2.9	415	208
PFCNPV	79	38 110	2.9	411	114

[a] Weight-average molecular weight (M_w) and polydispersity index (M_w/M_n) determined by means of GPC in THF on the basis of polystyrene calibration. [b] Onset decomposition temperature measured by TGA under N_2. [c] Glass transition temperature measured by DSC under N_2.

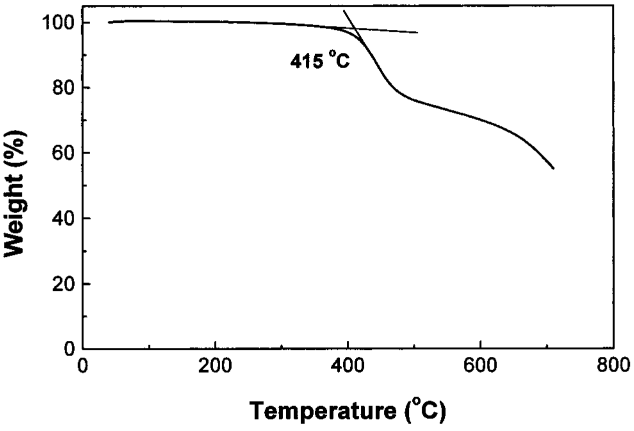


Figure 1. Representative TGA curve (**PFQx**).

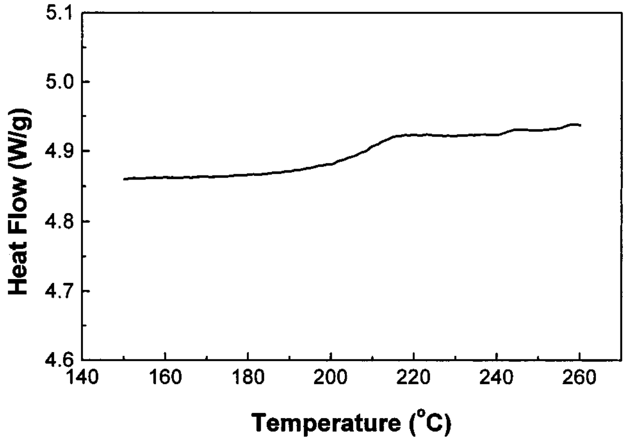


Figure 2. DSC chart of **PFQx**.

Table 2. Absorption and Emission Spectral Data of the Polymers in Chloroform and in Thin Solid Films

	absorption λ_{max}[a] (nm)		band	emission λ_{max}[c] (nm)		fwhm[d]
polymers	solution	film	gap[b] (eV)	solution	film	(nm)
PFOx	366	369	3.02	405	414	76
PF2Ox	349	352	3.09	428	422	82
PFQ	391	394	2.81	432	441	115
PFQx	404	402	2.80	448	455	80
PFCNPV	399	403	2.66	465	476	65

[a] Absorption maxima in solution (chloroform, 10^{-4} mol/L) and in films on quartz substrates. [b] Optical band gap derived from film absorption spectra. [c] Emission maxima in solution (chloroform, 10^{-4} mol/L) and in films on quartz substrates; the excitation wavelength corresponds to the absorption maximum. [d] Full width at half-maximum of the film PL spectra.

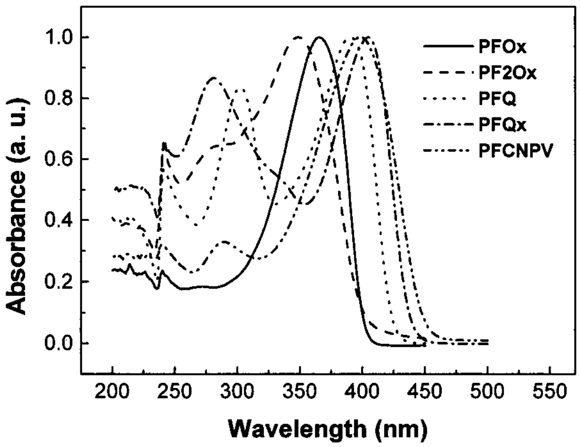


Figure 3. Absorption spectra of the polymers in chloroform solution.

387 to 415 °C. The DSC thermogram of **PFQx** (Figure 2) shows a clear glass transition at 208 °C. The glass transition temperature (T_g) of the polymers ranges from 114 to 208 °C (Table 1). These T_g values are much higher than that of typical polyfluorene (~55 °C),[22] indicating that the incorporation of oxadiazole, quinoline, and quinoxaline rings and phenylenecyanovinylene unit significantly enhances the thermal stability of the fluorene-based polymers. The T_g of the polymer containing two oxadiazole rings per repeated unit, i.e., **PF2Ox**, is 194 °C, higher than that of its cousin containing one oxadiazole ring per repeated unit, i.e., **PFOx** (137 °C). The T_g of the quinoxaline-containing polymer, i.e., **PFQx**, is 208 °C, higher than that of its cousin containing quinoline ring, i.e., **PFQ** (146 °C). Clearly, the glass transition temperature increases as the chain rigidity of the polymer increases.

Photophysical Properties. The photophysical characteristics of the polymers were investigated in solution and in the solid state. The absorption and emission spectral data for the polymers in solution and in the films casting from solution in $CHCl_3$ are summarized in Table 2. The absorption spectra of the polymers obtained for diluted $CHCl_3$ solution are illustrated in Figure 3 to reveal the effects of changing the polymer backbone structure on band gap and $\pi-\pi^*$ transition maximum (λ_{max}). All the polymers show the maximum absorptions in the range 349−404 nm, attributed to $\pi-\pi^*$ transition of the polymers. The optical band gaps (E_g) of the polymers were determined to be 2.66−3.09 eV from the film absorption spectra. Compared to the absorption spectrum of the polymer containing one oxadiazole ring per repeated unit, i.e., **PFOx**, the introduction of an additional oxadiazole ring in the polymer **PF2Ox** containing two oxadiazole rings per repeated unit brings about change to the absorption peak in the short wavelength region. Replacing the oxadiazole moiety in **PFOx** with quinoline or phenylenecyanovinylene moiety results in a bathochromic shift in λ_{max} and a reduction in E_g. Further red shift and smaller E_g are induced when the quinoline ring in **PFQ** is replaced by the quinoxaline ring. In other words, the electronic structures and properties of the fluorene-based polymers can be readily tuned by molecular engineering of a counit in the main chain. Figure 4 shows the absorption spectra of the thin solid films of the polymers, which are similar to those measured in the solution. Thus, the electronic transitions of the polymers are primarily determined by their molecular structures, which are insignificantly affected by their aggregation states.

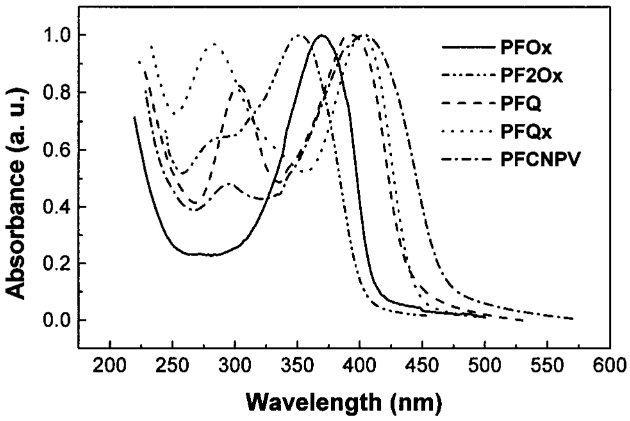


Figure 4. Absorption spectra of the polymers in thin films.

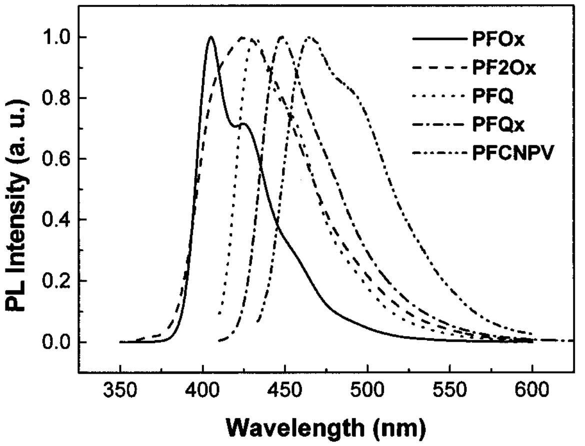


Figure 5. Fluorescence spectra of the polymers in chloroform solution.

The great similarity between PL and EL spectra of many light-emitting materials suggests that similar mechanisms are at play or that the same emitting species (a singlet exciton) is involved in each case.[23] Because of the simplicity of the PL measurements, we first checked the PL behaviors of the polymers. Figure 5 shows the PL spectra of the polymers in chloroform solution. All the polymers in chloroform solution emit strong blue fluorescence around 405−465 nm under ultraviolet irradiation. Compared to those of the oxadiazole-containing polymers (**PFOx** and **PF2Ox**), the PL spectra of the polymers containing quinoline or quinoxaline units (**PFQ** and **PFQx**) locate in the longer wavelength region. Further a red shift is observed in the PL spectrum of the polymer **PFCNPV** containing a CN-PPV unit. CN-PPV is a red-emitting material, while our copolymer **PFCNPV** consisting of CN-PPV and fluorene units is a blue-emitting material.

The PL spectra of the polymers in thin solid films are illustrated in Figure 6. All the polymers in thin films emit strong blue luminance around 414−476 nm upon photoexcitation. In comparison with its solution fluorescence, **PF2Ox** as solid films has emission blue-shifted by 6 nm. It is worth noting that the PL maxima of the polymers films except for **PF2Ox** are only red-shifted by 7−11 nm compared to those of the polymers solution. Full width at half-maximum (fwhm) of the film PL spectra is in the range of 65−82 nm except for **PFQ**. It should be emphasized that polyfluorene derivatives trend to undergo various degrees of aggregation and the excimer formation in the films, leading to concentration-dependent EL quenching, emission band broadening, and bathochromic shift.[13a] In contrast to the polyfluorene derivatives reported in the literature, our copolymers based on fluorene emit narrow-peak blue light with slight red shifts. We explain this interesting phenomenon by the assumption that sterically demanding groups such as 2-ethylhexyl prevent "disklike" molecules from stacking on top of each other, and consequently excimer fluorescence is suppressed.

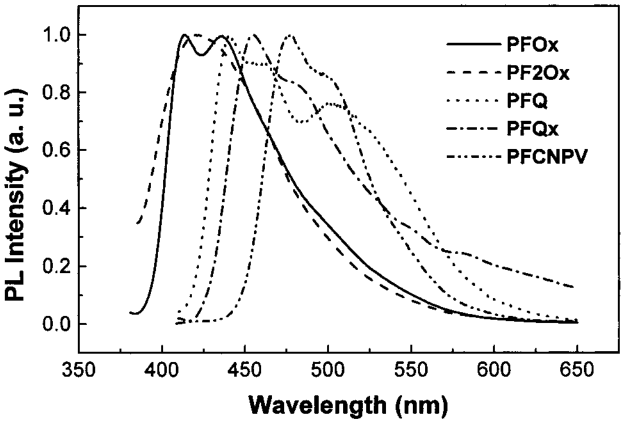


Figure 6. Photoluminescence spectra of the polymers in thin solid films.

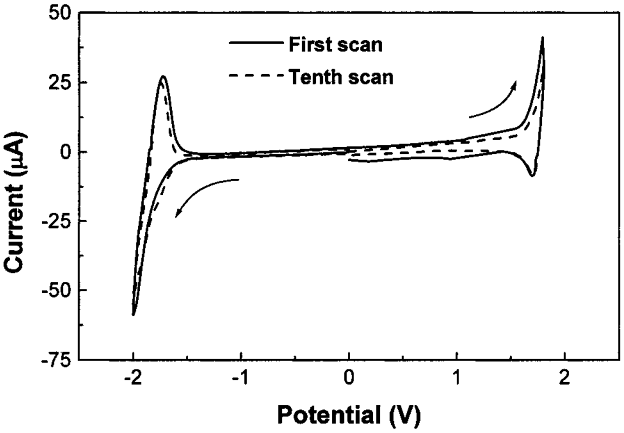


Figure 7. Cyclic voltammograms of **PFOx** recorded from a thin film deposited on a platinum wire electrode in an electrolyte solution of Bu_4NPF_6 (0.1 M) in CH_3CN at a scan rate of 50 mV/s. The potentials were measured relative to Ag/Ag^+ reference electrode.

Electrochemical Properties. Cyclic voltammetry (CV) was employed to investigate the redox behaviors of the polymers. Regarding the energy level of the ferrocene/ferrocenium (Fc) reference, one can calculate the LUMO and HOMO energies with the assumption that the energy level of Fc is 4.8 eV below vacuum.[19] Since the energy level of Fc is determined by photoelectron spectroscopy in the solid state, this method can only be considered to be a rough approximation. It is worth mentioning that obtaining absolute HOMO and LUMO levels from electrochemical data in combination with the energy gap is still in debate. An example of typical cyclic voltammograms is shown in Figure 7. Quasi-reversible oxidation and reduction waves were revealed for **PFOx** (Figure 7). On sweeping the polymer cathodically, the onset of the reduction occurs at about ca. −1.67 V vs Ag/Ag^+ above which the cathodic current quickly increases, and a cathodic peak appears at −2.00 V. A corresponding reoxidation peak appears at −1.74 V. For oxidation, the onset potential is ca. 1.56 V and an anodic peak occurs at 1.79 V with the corresponding rereduc-

Table 3. Electrochemical Potentials and Energy Levels of the Polymers

polymers	E_{red}[a] (V vs Ag/Ag$^+$)	E_{ox}[b] (V vs Ag/Ag$^+$)	LUMO[c] (eV)	HOMO[d] (eV)
PFOx	−1.67	1.56	−3.01	−6.24
PF2Ox	−1.49	1.70	−3.19	−6.38
PFQ	−1.44	1.58	−3.24	−6.26
PFQx	−1.31	1.51	−3.37	−6.19
PFCNPV	−1.60	1.45	−3.08	−6.13

[a] Reduction potentials measured by cyclic voltammetry. [b] Oxidation potentials measured by cyclic voltammetry. [c] Calculated from the reduction potentials assuming the absolute energy level of ferrocene/ferrocenium to be 4.8 eV below vacuum.[19] [d] Calculated from the oxidation potentials assuming the absolute energy level of ferrocene/ferrocenium to be 4.8 eV below vacuum.[19]

tion peak at 1.70 V. As shown in Figure 7, after 10 scans for the same polymer film, only slight changes for both the potentials and the current intensities of the redox process were observed, demonstrating that the polymer is stable to cycling through the reduction and oxidation.

The HOMO and LUMO energy levels are summarized in Table 3. Their LUMO levels range from −3.01 to −3.37 eV. These reduction potentials are lower than those of PBD (∼−2.4 eV) and other oxadiazole-containing materials[7] and comparable with that of CN−PPV (−3.10 eV), which shows good electron-transporting ability in polymeric LEDs.[9] Such energy levels may provide a closer match to the work function of Al when they are used as electron-transporting materials in polymer LEDs. The HOMO energy levels of these polymers range from −6.13 to −6.38 eV, much lower than those of most currently known EL materials. Thus, all these polymers can also be employed as hole-blocking materials in LEDs.

The LUMO level of **PFOx** is −3.01 eV, while the LUMO level of **PF2Ox** is −3.19 eV. It is clear that the higher the oxadiazole content, the lower the LUMO level of the polymer and therefore the better the electron injection properties. The LUMO level of **PFQ** is −3.24 eV, comparable to that of polyquinolines reported in the literature.[14] It is believed that the low-lying LUMO of polyquinolines originates from the electron-deficient nature of the quinoline ring. The increased electron deficiency of the quinoxaline ring due to an additional imine nitrogen, compared to the quinoline ring, brings about the lower LUMO level of **PFQx** (−3.37 eV).

Conclusions

We synthesized a novel series of conjugated copolymers having oxadiazole, quinoline, quinoxaline, and phenylenecyanovinylene moieties in the main chain based on fluorene by palladium-catalyzed Suzuki coupling reaction, a new approach different from the traditional polyhydrazide precursor route (polyoxadiazoles), acid-catalyzed Friedländer condensation reaction (polyquinolines), and Knoevenagel condensation polymerization (CN-PPV). These copolymers possess good solubility and excellent thermal stability. Cyclic voltammetry reveals that these polymers have a low-lying LUMO energy level ranging from −3.01 to −3.37 eV and a low-lying HOMO energy levels ranging from −6.13 to −6.38 eV and may be attractive candidates for electron-transporting or hole-blocking materials in LEDs. The polymers in thin films emit strong blue luminance with narrow bandwidth upon photoexcitation. PL spectra of the polymers in the films are only red-shifted by 7−11 nm compared to those in the solution, indicating that the aggregation and the excimer fluorescence are suppressed. Intensive studies on the electroluminescent and electron-transporting/hole-blocking properties of these polymers in LED devices are in progress.

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References and Notes

(1) (a) Blasse, G.; Grabmaier, B. C. *Luminescent Materials*; Springer-Verlag: Berlin, 1994. (b) *Organic Electroluminescent Materials and Devices*; Miyata, S., Nalwa, H. S., Eds.; Gordon and Breach Publishers: Amsterdam, 1997. (c) 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 (London)* **1999**, *397*, 121.

(2) (a) Jenekhe, S. A.; Zhang, X.; Chen, X. L.; Choong, V. E.; Gao, Y.; Hsieh, B. R. *Chem. Mater.* **1997**, *9*, 409. (b) Parker, I. D.; Pei, Q.; Marrocco, M. *Appl. Phys. Lett.* **1994**, *65*, 1272. (c) Chen, T. A.; Jen, A. K.-Y.; Cai, Y. M. *Chem. Mater.* **1996**, *8*, 607. (d) Jen, A. K.-Y.; Wu, X. M.; Ma, H. *Chem. Mater.* **1998**, *10*, 471.

(3) (a) Fukuda, T.; Kanbara, T.; Yamamoto, T.; Ishikawa, K.; Takezeo, H.; Fukuda, A. *Appl. Phys. Lett.* **1996**, *68*, 2346. (b) O'Brien, D.; Weaver, M. S.; Lidzey, D. G.; Bradley, D. D. C. *Appl. Phys. Lett.* **1996**, *69*, 881. (c) Jandke, M.; Strohriegl, P.; Berleb, S.; Werner, E.; Brütting, W. *Macromolecules* **1998**, *31*, 6434. (d) Cui, Y.; Zhang, X.; Jenekhe, S. A. *Macromolecules* **1999**, *32*, 3824.

(4) (a) Adachi, C.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1989**, *55*, 1489. (b) Adachi, C.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1990**, *56*, 799.

(5) Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* **1995**, *267*, 1969.

(6) (a) Pei, Q.; Yang, Y. *Chem. Mater.* **1995**, *7*, 1568. (b) Buchwald, E.; Meier, M.; Karg, S.; Pösch, P.; Schmidt, H.-W.; Strohriegel, P.; Riess, W.; Schwoerer, M. *Adv. Mater.* **1995**, *7*, 839.

(7) (a) Yu, W.-L.; Meng, H.; Pei, J.; Huang, W. *J. Am. Chem. Soc.* **1998**, *120*, 11808. (b) Huang, W.; Yu, W.-L.; Meng, H.; Pei, J.; Li, S. F. Y. *Chem. Mater.* **1998**, *10*, 3340. (c) Yu, W.-L.; Meng, H.; Pei, J.; Lai, Y.-H.; Chua, S.-J.; Huang, W. *Chem. Commun.* **1998**, 1957. (d) Yu, W.-L.; Meng, H.; Pei, J.; Huang, W.; Li, Y.; Heeger, A. J. *Macromolecules* **1998**, *31*, 4838. (e) Huang, W.; Meng, H.; Yu, W.-L.; Pei, J.; Chen, Z.-K.; Lai, Y.-H. *Macromolecules* **1999**, *32*, 118.

(8) (a) Peng, Z.; Bao, Z.; Galvin, M. E. *Chem. Mater.* **1998**, *10*, 2086. (b) Peng, Z.; Zhang, J. *Chem. Mater.* **1999**, *11*, 1138.

(9) (a) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature (London)* **1993**, *365*, 628. (b) Liu, Y.; Li, Q.; Jiang, X.; Zhu, D. *Synth. Met.* **1997**, *85*, 1279. (c) Peng, Z.; Galvin, M. E. *Chem. Mater.* **1998**, *10*, 1785.

(10) (a) Klaerner, G.; Miller, R. D. *Macromolecules* **1998**, *31*, 2007. (b) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765.

(11) (a) Yang, Y.; Pei, Q. *J. Am. Chem. Soc.* **1996**, *118*, 7416. (b) He, Y.; Gong, S.; Hattori, R.; Kanicki, J. *Appl. Phys. Lett.* **1999**, *74*, 2265. (c) Yu, W.; Cao, Y.; Pei, J.; Huang, W.; Heeger, A. J. *Appl. Phys. Lett.* **1999**, *75*, 3270. (d) Yu, W.; Pei, J.; Cao, Y.; Huang, W.; Heeger, A. J. *Chem. Commun.* **1999**, 1837. (e) Liu, B.; Yu, W.; Lai, Y.; Huang, W. *Chem. Commun.* **2000**, 551.

(12) (a) Redecker, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 1565. (b) Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453. (c) Grell, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *Adv. Mater.* **1997**, *9*, 798. (d) Grell, M.; Knoll, W.; Lupo, D.; Meisel, A.; Miteva, T.; Neher, D.; Nothofer, H.; Scherf, U.; Yasuda, A. *Adv. Mater.* **1999**, *11*, 671. (e) Virgili, T.; Lidzey, D. G.; Bradley, D. D. C. *Adv. Mater.* **2000**, *12*, 58.

(13) (a) Sainova, D.; Miteva, T.; Nothofer, H.; Scherf, U.; Glowacki, I.; Ulanski, J.; Fujikawa, H.; Neher, D. *Appl. Phys. Lett.* **2000**, *76*, 1810. (b) Weinfurtner, K.; Fujikawa, H.; Tokito, S.; Taga, Y. *Appl. Phys. Lett.* **2000**, *76*, 2502. (c) Jiang, X.; Liu, S.; Ma H.; Jen, A. K.-Y. *Appl. Phys. Lett.* **2000**, *76*, 1813.

(14) (a) Kim, J. L.; Kim, J. K.; Cho, H. N.; Kim, D. Y.; Kim, C. Y.; Hong, S. II. *Macromolecules* **2000**, *33*, 5880. (b) Kim, J. L.; Cho, H. N.; Kim, J. K.; Hong, S. II. *Macromolecules* **1999**, *32*, 2065. (c) Kim, J. L.; Kim, J. K.; Cho, H. N.; Kim, D. Y.; Hong, S. II. *Synth. Met.* **2000**, *114*, 97.

(15) Zhan, X.; Liu, Y.; Zhu, D.; Huang, W.; Gong, Q. *Chem. Mater.* **2001**, *13*, 1540.

(16) Sybert, P. D.; Beever, W. H.; Stille, J. K. *Macromolecules* **1981**, *14*, 493.

(17) (a) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121. (b) Tayim, H. A.; Bouldoukian, A.; Awad, F. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3799.

(18) Milazzo, G.; Caroli, S. *Tables of Standard Electrode Potentials*; Wiley-Interscience: New York, 1977.

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

(20) Schulz, B.; Bruma, M.; Brehmer, L. *Adv. Mater.* **1997**, *9*, 601.

(21) Liu, Y.; Ma, H.; Jen, A. K.-Y. *Chem. Mater.* **1999**, *11*, 27.

(22) Fukuda, M.; Sawada, K.; Yoshino, K. *J. Polym. Sci., Polym. Chem.* **1990**, *31*, 2465.

(23) Li, X.-C.; Moratti, S. C. In *Photonic Polymer Systsms: Fundamentals, Methods, and Applications*; Wise, D. L., Wnek, G. E., Trantolo, D. J., Cooper, T. M., Gresser, J. D., Eds.; Marcel Dekker: New York, 1998; Chapter 10, pp 335−371.

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