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Synthesis and Characterization of Blue-Light-Emitting Poly(aryl ether)s Containing Oligofluorenes in the Main Chain

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ABSTRACT: A series of blue light-emitting poly(aryl ether)s (PAEs) containing ter- or pentafluorenes in the main chain have been synthesized via nucleophilic substitution polycondensation reaction. The energy levels of the polymers were tuned by introducing hole-transporting triaryamine groups in the side chains and/or incorporating electron-transporting oxadiazole segments in the main chain. The optical properties of the polymers are dominantly determined by the well-defined oligofluorene segments, and therefore all polymers show high photoluminescence quantum yield. Differential scanning calorimeter (DSC) characterizations indicate that they are vitrified polymers with high glass transition temperature (up to 156 °C). The polymers comprising pentafluorenes exhibit electroluminescent properties equal to or better than fully conjugated fluorene homopolymers. With the device structure of ITO/PEDOT:PSS/polymer/Ca/Al, an external quantum efficiency of 1.4% along with Commission Internationale de L'Eclairage (CIE) coordinates of (0.17, 0.09) has been realized.

Introduction

Organic light-emitting diodes offer an attractive opportunity for the material science society due to their significant advantages over liquid crystal displays, including broader viewing angle, shorter response time, and lower power consumption. Among the different classes of light-emitting materials, light-emitting polymers (LEPs) are always dramatically pursued because of their cost-effectiveness to produce large area flat-panel displays by simple solution processes.[1] Promising LEPs to date are generally fully conjugated polymers, such as poly(phenylenevinylene)s, polythiophenes, and polyfluorenes (PFs). PFs are of particular interest due to their high thermal and chemical stability, high photoluminescence (PL) quantum yield, and ease of color modulation. However, PFs exhibit complicated morphologies such as the ease of β phase and liquid crystalline mesophase formation, which can cause problems in the applications, e.g., unstable spectra or emission color upon device operation.[2] How to remove the catalyst residues from PFs is another puzzle even today.[3] In the past several years, tremendous effort has been made to solve the above two problems by tailoring monomer structures and improving posttreatment process.[3,4] Meanwhile, many light-emitting nonconjugated polymers have been prepared by incorporating optoelectronically active species in the side chain or main chain.[5] However, although this approach can eliminate the influence of catalyst residues or chain defects on light-emitting properties of the materials, which are often problematic in fully conjugated polymers, unfortunately, the relatively poor device performance renders most of them less attractive compared to fully conjugated polymers. Their inferior performance should be able to be ascribed to poorer charge-carrier injection and transportation capability caused by the interruption of conjugated chain[6] or relative small portions of electrically and optically active components.[7] In some cases, the polymers also exhibit low PL quantum yield.[5e]

Conjugated oligomers have been known as a class of promising materials due to their excellent chemical purity and well-defined structure and properties. Especially, oligofluorenes have been intensively studied as model compounds for establishment of structure−property relationship as well as blue light-emitting materials.[8] Incorporating them into a polymer side chain or main chain by radical or condensation polymerization of macromonomers is a desirable approach to obtain blue-light-emitting polymers.[5,9] In this approach, the content of optoelectronically inactive components must be very low and, therefore, have negligible effect on the optoelectronic properties of the polymers. In fact, we have recently reported a series of poly(aryl ether)s (PAEs) with oligofluorenes in the side chains, in which the poly(aryl ether) main chain mainly serves as a skeleton to control the condensed state of the polymers, and the optoelctronic properties of the polymers are determined by oligofluorene pendants.[9] By tailoring the structures of oligofluorene pendants, high-performance light-emitting materials with a capability of vitrification have been demonstrated. Herein, we further present the design, synthesis, and characterizations of light-emitting PAEs with oligofluorenes in the main chain.

Experimental Section

Materials. Dimethylacetamide (DMAc) and dichloromethane (DCM) were distilled from calcium hydride. Tetrahydrofuran (THF) and toluene were distilled over sodium/benzophenone. The compounds 4-methoxyphenylboronic acid and 4-fluorophenyl sulfone were purchased from Acros, and the latter one was recrystallized with ethanol before use. The compound 2,5-bis(4-fluorophenyl)-[1,3,4]oxadiazole was synthesized according to the reported methods.[5e] All other chemicals, reagents, and solvents were used as received from commercial sources without further purification.

7-(4-Methoxyphenyl)-9,9-di-*n*-octylfluorenyl-2-boronic Acid (3). A mixture of compound **1** (4.50 g, 30.0 mmol), 2,7-dibromo-9,9-di-*n*-octylfluorene (27.0 g, 48.0 mmol), Pd(PPh$_3$)$_4$ (400 mg, 0.400 mmol), K$_2$CO$_3$ (2.0 M aqueous solution, 60 mL, 120 mmol), and toluene (100 mL) was stirred at 80 °C for 1 day. After the mixture was cooled to room temperature, a large amount of DCM was added. The organic portion was separated and washed with

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brine before drying over anhydrous Na_2SO_4. The solvent was evaporated off, and the solid residues were purified by column chromatography on silica gel with petroleum ether (PE)/DCM (12:1) to afford 2-bromo-7-(4-methoxyphenyl)-9,9-di-*n*-octylfluorene (**2**) as a white solid (8.80 g, 51.0%). Then, to a solution of **2** (8.80 g, 15.3 mmol) in anhydrous THF (150 mL) was slowly added *n*-BuLi (1.6 M in hexane, 11.0 mL, 17.6 mmol) at −78 °C. The reaction mixture was stirred for 1 h before adding trimethyl borate (2.50 mL, 23.2 mmol). It was then warmed to room temperature and stirred overnight followed by quenching with 50 mL of HCl (2.0 M). After extraction with diethyl ether three times, the ethereal extracts were washed with brine before drying over anhydrous Na_2SO_4. Solid residues collected by evaporating off the solvent were purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1:10 and then 1:2) to afford **3** as a white solid (7.00 g, 85.0%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, 1H, J = 7.7 Hz), 8.23 (s, 1H), 7.90 (d, 1H, J = 7.5 Hz), 7.85 (d, 1H, J = 7.7 Hz), 7.68 (d, 2H, J = 8.7 Hz), 7.59 (d, 1H, J = 7.5 Hz), 7.03 (d, 2H, J = 8.7 Hz), 3.87 (s, 3H), 2.15−2.12 (m, 4H), 1.09−0.74 (m, 30H).

7-(4-Methoxyphenyl)-9,9,9′,9′-tetra-*n*-octyl-2,2′-bifluorenyl-7′-boronic Acid (5). The procedure for **2** was followed to prepare 7-bromo-7′-(4-methoxyphenyl)-9,9,9′,9′-tetra-*n*-octyl-2,2′-bifluorenyl (**4**) from **3** (5.00 g, 9.30 mmol) to yield a white solid (5.20 g, 5.40 mmol). Then, compound **5** was prepared as a white solid (4.00 g, 79.6%) by the same procedure for **3** from **4** (5.20 g, 5.40 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (d, 1H, J = 7.6 Hz), 8.28 (s, 1H), 7.96−7.93 (m, 2H), 7.86−7.55 (m, 10H), 7.03 (d, 2H, J = 8.6 Hz), 3.73 (s, 3H), 2.18−2.07 (m, 8H), 1.26−0.76 (m, 60H).

9,9-Bis(4-*p*-tolylphenylaminophenyl)-2,7-dibromofluorene (6). 2,7-Dibromofluorenone (2.00 g, 5.90 mmol), diphenyl-*p*-tolylamine (15.50 g, 60.0 mmol), and methanesulfonic acid (0.60 g, 6.20 mmol) were added to a two-necked round-bottom flask. The reaction mixture was stirred thoroughly at 140 °C for 6 h. The cooled mixture was extracted with DCM and washed with water before drying over anhydrous Na_2SO_4. Then the solid residues collected by evaporating off the solvent were purified by column chromatography on silica gel with ethyl acetate/ methanesulfonic acid (1:10) to afford **6** as a white solid (3.40 g, 67.0%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, 2H, J = 8.1 Hz), 7.54 (d, 2H, J = 1.4 Hz), 7.50 (dd, 2H, J = 8.1 Hz, 1.4 Hz), 7.29−7.22 (m, 6H), 7.11−6.90 (m, 20H), 2.28 (s, 6H).

General Procedure for the Preparation of 7 and 9 via Suzuki Coupling Reaction. Toluene or THF (for **6**) and a 2.0 M aqueous solution of K_2CO_3 (8 equiv, toluene/water at a 3:2 volume ratio) were added to a two-necked round-bottom flask containing **6** or 2,7-dibromo-9,9-di-*n*-octylfluorene (1 equiv), **3** or **5** (2.2 equiv), and $Pd(PPh_3)_4$ (1 mol %). The reaction mixture was stirred thoroughly at 80 °C for 2 days followed by extraction and dried over anhydrous Na_2SO_4. After the solvent had been removed, the residue was purified by column chromatography on silica gel to afford the target compounds **7** and **9** with a yield of 70−80%.

2,7″-Bis(7-(4-methoxyphenyl)-9,9,9′,9′,9″,9″-hexa-*n*-octyl-7,2′;7′,2″-terfluorene (7a). Yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88−7.80 (m, 6H), 7.72−7.56 (m, 16H), 7.03 (d, 4H, J = 8.6 Hz), 3.89 (s, 6H), 2.15−2.08 (m, 12H), 1.24−0.81 (m, 90H).

2,7⁗-Bis(7-(4-methoxyphenyl)-9,9,9′,9′,9″,9″,9‴,9‴,9⁗,9⁗-deca-*n*-octyl-7,2′;7′,2″; 7″,2‴;7‴,2⁗-pentafluorene (7b). Yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88−7.80 (m, 12H), 7.75−7.58 (m, 22H), 7.06 (d, 4H, J = 8.7 Hz), 3.92 (s, 6H), 2.16−2.09 (m, 20H), 1.17−0.82 (m, 150H).

2,7″-Bis(7-(4-methoxyphenyl)-9,9,9″,9″-tetra-*n*-octyl-9′,9′-di-(4-p-tolyl-phenyl-aminophenyl)-7,2′;7′,2″-terfluorene (9a). Yield: 75%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, 2H, J = 7.8 Hz), 7.76−7.52 (m, 20H), 7.21−7.16 (m, 8H), 7.06−6.92 (m, 22H), 3.88 (s, 6H), 2.28 (s, 6H), 2.15−2.07 (m, 8H), 1.17−0.75 (m, 60H).

2,7⁗-Bis(7-(4-methoxyphenyl)-9,9,9′,9′,9‴,9‴,9⁗,9⁗-octa-*n*-octyl-9″,9″-di(4-*p*-tolylphenylaminophenyl)-7,2′;7′,2″; 7″,2‴;7‴,2⁗-pentafluorene (9b). Yield: 75%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, 2H, J = 7.8 Hz), 7.82−7.54 (m, 32H), 7.23−7.17 (m, 8H), 7.08−6.94 (m, 22H), 3.88 (s, 6H), 2.29 (s, 6H), 2.15−2.07 (m, 16H), 1.10−0.76 (m, 120H).

General Procedure for Preparation of Monomers 8 and 10. To a solution of **7** or **9** (1 equiv) in anhydrous DCM (0.1 M) was slowly added BBr_3 (1.0 M in DCM, 3 equiv) at 0 °C. After 5 h, it was poured into a large amount of water and extracted with DCM three times. The combined organic portions were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The solid residues were purified by column chromatography on silica gel with PE/DCM (1:3) to afford the monomers **8** and **10**.

2,7″-Bis(7-(4-hydroxyphenyl)-9,9,9′,9′,9″,9″-hexa-*n*-oc-tyl-7,2′;7′,2″-terfluorene (8a). Yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87−7.79 (m, 6H), 7.72−7.68 (m, 8H), 7.63−7.56 (m, 8H), 7.00 (d, 4H, J = 8.6 Hz), 4.80 (−OH, 2H), 2.16−2.08 (m, 12H), 1.24−0.81 (m, 90H). MS (Maldi-TOF): *m*/*z*: 1352.5 [M$^+$].

2,7⁗-Bis(7-(4-hydroxyphenyl)-9,9,9′,9′,9″,9″,9‴,9‴,9⁗,9⁗-deca-*n*-octyl-7,2′;7′,2″; 7″,2‴;7‴,2⁗-pentafluorene (8b). Yield: 98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88−7.80 (m, 12H), 7.74−7.68 (m, 14H), 7.63−7.57 (m, 8H), 6.98 (d, 4H, J = 8.6 Hz), 4.80 (−OH, 2H), 2.16−2.09 (m, 20H), 1.17−0.82 (m, 150H). MS (Maldi-TOF): *m*/*z*: 2128.9 [M$^+$].

2,7″-Bis(7-(4-hydroxyphenyl)-9,9,9″,9″-tetra-*n*-octyl-9′,9′-di-(4-*p*-tolyl-phenyl-aminophenyl)-7,2′;7′,2″-terfluorene (10a). Yield: 94%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, 2H, J = 8.1 Hz), 7.76−7.68 (m, 8H), 7.59−7.52 (m, 12H), 7.21−7.17 (m, 8H), 7.07−6.94 (m, 22H), 4.75 (−OH, 2H), 2.29 (s, 6H), 2.16−2.07 (m, 8H), 1.12−0.76 (m, 60H). MS (Maldi-TOF): *m*/*z*: 1640.0 [M$^+$].

2,7⁗-Bis(7-(4-hydroxyphenyl)-9,9,9′,9′,9‴,9‴,9⁗,9⁗-octa-*n*-octyl-9″,9″-di(4-*p*-tolyl-phenyl-aminophenyl)-7,2′;7′,2″; 7″,2‴; 7‴,2⁗-pentafluorene (10b). Yield: 92%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, 2H, J = 7.8 Hz), 7.81−7.53 (m, 32H), 7.22−7.17 (m, 8H), 7.07−6.93 (m, 22H), 4.72 (−OH, 2H), 2.35 (s, 6H), 2.15−2.07 (m, 16H), 1.10−0.76 (m, 120H). MS (Maldi-TOF): *m*/*z*: 2416.5 [M$^+$].

General Polymerization Procedure.[10] A mixture of 4-fluorophenyl sulfone or 2,5-bis(4-fluorophenyl)-[1,3,4]oxadiazole (0.306−0.309 mmol), bisphenol monomers **8** or **10** (0.300 mmol), toluene (5.0 mL), DMAc (5.0 mL), and K_2CO_3 (0.166 g, 1.200 mmol) in a two-necked 20 mL glass reactor equipped with a Dean−Stark trap was heated to 140 °C for 2.0 h until the toluene was all condensed in the Dean−Stark trap. The reaction temperature was then enhanced to 170 °C for an extra 3−4 h. Then the mixture was cooled to room temperature and diluted with 200 mL of DCM. The organic portion was washed with water, dried with anhydrous Na_2SO_4, and concentrated to a viscous solution. The polymers were precipitated with methanol and further purified by means of Soxhlet extraction with acetone and again by precipitation into methanol twice to afford the polymer as a white fiber in a yield of 70−85%.

P3FSF. Yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, 4H, J = 8.7 Hz), 7.86−7.84 (m, 4H), 7.76−7.61 (m, 16H), 7.19 (d, 4H, J = 8.4 Hz), 7.14 (d, 4H, J = 8.7 Hz), 2.16−2.08 (m, 12H), 1.24−0.81 (m, 90H). Anal. Calcd for $C_{111}H_{136}O_4S$ (%): C, 85.12; H, 8.75. Found: C, 85.19; H, 8.68.

P2A3FSF. Yield: 71%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, 4H, J = 8.7 Hz), 7.91 (d, 2H, J = 8.1 Hz) 7.83−7.73 (m, 8H), 7.62−7.59 (m, 12H), 7.25−6.96 (m, 34H), 2.32 (s, 6H), 2.19−2.07 (m, 8H), 1.17−0.80 (m, 60H). Anal. Calcd for $C_{133}H_{134}N_2O_4S$ (%): C, 86.04; H, 7.27; N, 1.51. Found: C, 85.40, H, 6.49 N, 1.63.

P3FOXD. Yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, 4H, J = 8.7 Hz), 7.88−7.84 (m, 4H), 7.78−7.63 (m, 16H), 7.26−7.22 (m, 8H), 2.16−2.08 (m, 12H), 1.24−0.81 (m, 90H). Anal. Calcd for $C_{113}H_{136}N_2O_3$ (%): C, 86.43; H, 8.73; N, 1.78. Found: C, 86.70; H, 8.66; N, 1.69.

P2A3FOXD. Yield: 81%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, 4H, J = 8.7 Hz), 7.91 (d, 2H, J = 8.1 Hz), 7.84−7.74 (m, 8H), 7.64−7.61 (m, 12H), 7.24−7.20 (m, 12H), 7.01−6.96 (m, 22H), 2.32 (s, 6H), 2.19−2.07 (m, 8H), 1.17−0.80 (m, 60H). Anal. Calcd for $C_{135}H_{134}N_4O_3$ (%): C, 87.15; H, 7.26; N, 3.01. Found: C, 86.75, H, 6.89, N, 3.15.

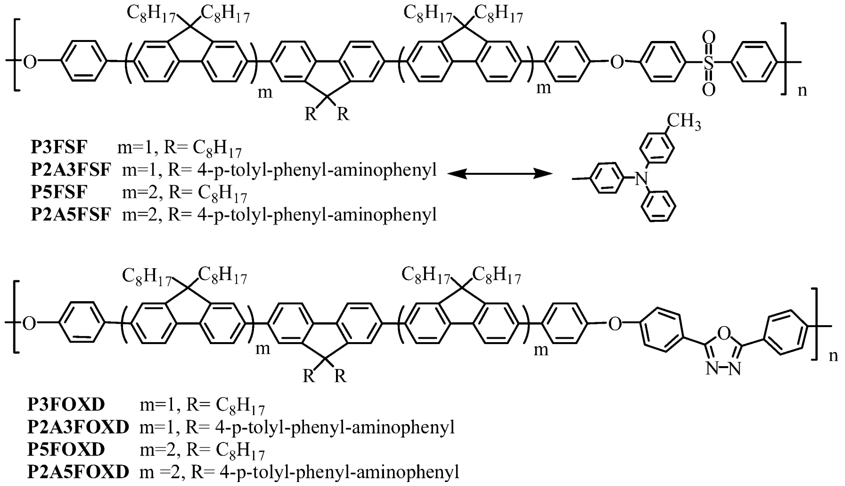


Chart 1. Structures of the PAEs Containing Ter- and Pentafluorene Segments in the Main Chain

P3FSF m=1, R= C_8H_{17}
P2A3FSF m=1, R= 4-p-tolyl-phenyl-aminophenyl
P5FSF m=2, R= C_8H_{17}
P2A5FSF m=2, R= 4-p-tolyl-phenyl-aminophenyl

P3FOXD m=1, R= C_8H_{17}
P2A3FOXD m=1, R= 4-p-tolyl-phenyl-aminophenyl
P5FOXD m=2, R= C_8H_{17}
P2A5FOXD m =2, R= 4-p-tolyl-phenyl-aminophenyl

P5FSF. Yield: 85%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, 4H, $J = 8.7$ Hz), 7.88−7.84 (m, 4H), 7.74−7.61 (m, 24H), 7.20 (d, 4H, $J = 8.4$ Hz), 7.15 (d, 4H, $J = 8.7$ Hz), 2.16−2.09 (m, 20H), 1.17−0.82 (m, 150H). Anal. Calcd for $C_{169}H_{216}O_4S$ (%): C, 86.61; H, 9.29. Found: C, 86.49; H, 9.22.

P2A5FSF. Yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, 4H, $J = 8.7$ Hz), 7.91 (d, 2H, $J = 7.8$ Hz), 7.85−7.61 (m, 32H), 7.25−6.97 (m, 34H), 2.32 (s, 6H), 2.15−2.07 (m, 16 H), 1.10−0.76 (m, 120H). Anal. Calcd for $C_{191}H_{214}N_2O_4S$ (%): C, 87.10; H, 8.19; N, 1.06. Found: C, 86.97, H, 7.96, N, 1.19.

P5FOXD. Yield: 75%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, 4H, $J = 8.7$ Hz), 7.88−7.84 (m, 8H), 7.78−7.63 (m, 24H), 7.26−7.22 (m, 8H), 2.16−2.09 (m, 20H), 1.17−0.82 (m, 150H). Anal. Calcd for $C_{171}H_{216}N_2O_3$ (%):C, 87.49; H, 9.27; N, 1.19. Found: C, 87.52; H, 9.12; N, 1.20.

P2A5FOXD. Yield: 73%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, 4H, $J = 8.7$ Hz), 7.91 (d, 2H, $J = 7.8$ Hz), 7.85−7.62 (m, 32H), 7.25−7.20 (m, 12H), 7.10−6.96 (m, 22H), 2.32 (s, 6H), 2.15−2.07 (m, 16 H), 1.10−0.76 (m, 120H). Anal. Calcd for $C_{193}H_{214}N_4O_3$ (%): C, 87.88; H, 8.18; N, 2.12. Found: C, 87.57 H, 7.71, N, 2.24.

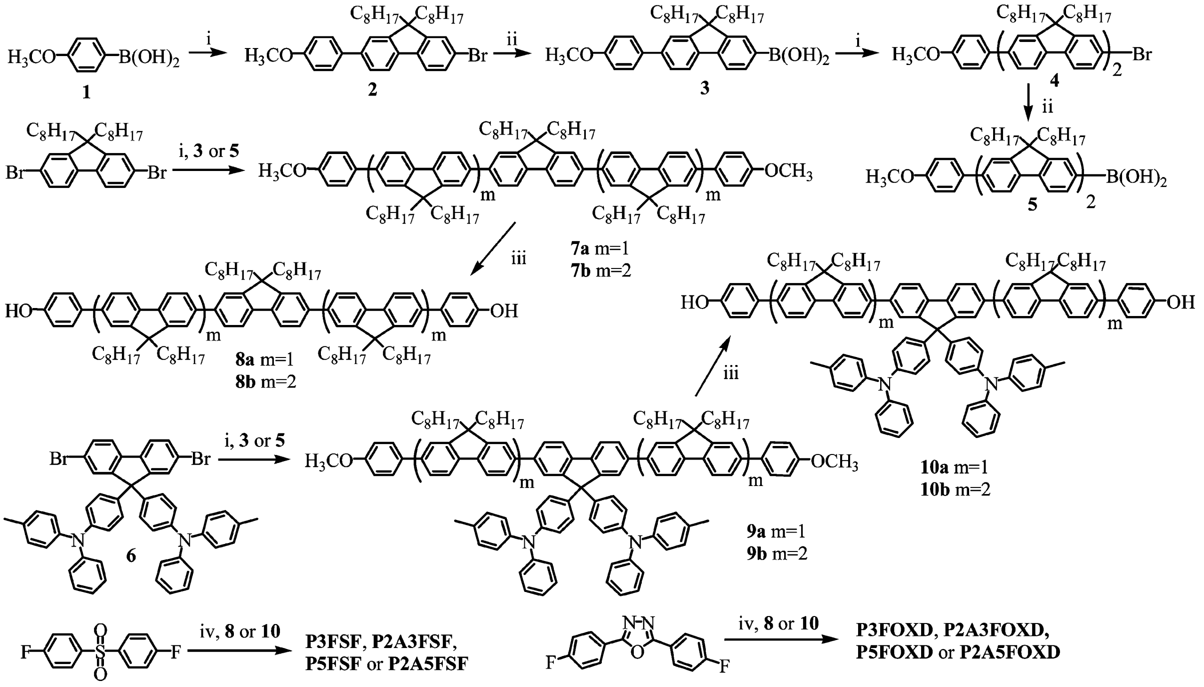
Instrumentation. ^{1}H NMR spectra were recorded on a Bruker 300 MHz or a 600 MHz FT-NMR spectrometer. Molecular mass of all synthesized monomers used for polymerization was measured by a LDI-1700 matrix-assisted laser desorption/ionization time-of-flight (MALDI TOF) mass spectrometer (American Linear Scientific Inc.). The elemental analysis was performed using a Bio-Rad elemental analysis system. The UV−vis absorption and PL spectra were recorded on a Perkin-Elmer Lambda 35 UV/vis spectrometer and a Perkin-Elmer LS50B luminescence spectrometer, respectively. The cyclic voltammetry was measured on an EG&G model 283 potentiostat/galvanostat system at room temperature using a Ag/AgCl electrode as the reference electrode, a platinum wire as the auxiliary electrode, and a platinum plate as the working electrode in acetonitrile solution of $(n\text{-Bu})_4NClO_4$ (0.1 M) with the scan rate of 100 mV/s. Thermal properties of the polymers were measured using Perkin-Elmer DSC7 and TGA7 equipment at a heating/cooling rate of 10 °C/min under a nitrogen atmosphere. Device fabrication and characterizations are identical to previous publication.[9]

Results and Discussion

Synthesis and Characterization of Polymers. The structures of the polymers are depicted in Chart 1. In polymers **P3FSF**, **P2A3FSF**, **P3FOXD**, and **P2A3FOXD**, there are three fluorene units in each oligofluorene segment, while in other polymers, oligofluorenes with five fluorene units were used. Oxadiazole derivatives and triaryamine compounds are believed to be promising electron- and hole-transporting materials, respectively.[11,12] Therefore, 2,5-diphenyl-[1,3,4]oxadiazole and *N*,*N*-diphenyl-*p*-tolylamine were introduced into the main chain and side chain, respectively, to tune the electrochemical properties of the polymers. The synthetic route of the monomers and polymers is outlined in Scheme 1. The oligofluorenes **7** and **9** were synthesized by means of Suzuki coupling reaction in a yield of 70−80%. The macromonomers **8** and **10** were prepared by treatment of **7** and **9** with BBr_3 in high yield. All polymers were synthesized via the nucleophilic displacement reaction often adopted in the synthesis of traditional PAEs. To reduce the possibility of phenol terminals in the polymers, the feed ratio of fluoro-monomers to phenol-monomers is controlled at the level of 1.02−1.03. Compared with the Suzuki or Yamamoto coupling reaction, this polymerization method can easily afford high molecular weight polymers within 6 h. Furthermore, purification process is extremely simple, and there is no need to use chromatography or other techniques to remove metal catalyst residues. In fact, the pure polymers as white fibers can be obtained by one-step precipitation. In our previous report,[9] we only obtained PAEs with molecular weight in the range of 12 000−34 600 g/mol. The relative low molecular weight was owing to the low solubility of the polymers in the polymerization solvent dimethyl sulfoxide (DMSO); hence, the polymers precipitated during the polymerization. In the current work, DMAc instead was used as the solvent to improve the solubility of the polymers, and the molecular weight of the polymers was dramatically enhanced. As shown in Table 1, the weight-average molecular weight (M_w), determined by gel permeation chromatography (GPC) using polystyrene as the standard, is up to 562 000 g/mol with the number of repeat units up to 91. Meanwhile, the polydispersity index is in the range 1.71−2.63, identical to PFs synthesized by the Suzuki coupling reaction. The structures of the polymers were verified by ^{1}H NMR spectra and elemental analysis (EA). All polymers are soluble in common organic solvents such as DCM, chloroform, toluene, and THF.

Thermal Properties. Thermal properties of the polymers were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) with a scan rate of 10 °C/min under a nitrogen atmosphere, and the results are tabulated in Table 1. All polymers exhibit decomposition temperature higher than 400 °C. DSC characterizations along with polarizing optical microscopy observations indicate that all polymers are noncrystalline from room temperature to 300 °C. Figure 1 shows the DSC heating curves of **P5FSF**, **P2A5FSF**, **P5FOXD**, and **P2A5FOXD**. It is clear that only a

Scheme 1. Synthetic Routes of Oligofluorene Monomers and Polymers[a]



[a] (i) Pd(PPh$_3$)$_4$, K$_2$CO$_3$ (2.0 M aq), toluene; (ii) *n*-BuLi, B(OCH$_3$)$_3$ and then 2.0 M HCl; (iii) CH$_2$Cl$_2$, 1.0 M BBr$_3$; (iv) K$_2$CO$_3$, toluene, DMAc, 140 °C and then 170 °C.

Table 1. Weight-Average Molecular Weight (M_w), Polydispersity Index (PDI), Degree of Polymerization (DP), Glass Transition Temperature (T_g), Decomposition Temperature (T_d), PL Quantum Yield (Φ_{PL}), and Absorption and Photoluminescence Maxima ($\lambda_{abs,max}$ and $\lambda_{PL,max}$) of the Polymers

polymer	M_w ($\times 10^4$)[a]	PDI[a]	DP[b]	T_g (°C)	T_d (°C)[c]	Φ_{FL}[d] (%)	$\lambda_{abs,max}$ (nm)[e] solution	$\lambda_{abs,max}$ (nm)[e] film	$\lambda_{PL,max}$ (nm)[f] solution	$\lambda_{PL,max}$ (nm)[f] film
P3FSF	14.0	1.94	46	101	417	97	361	361	406, 429	416, 435
P3FOXD	4.2	1.83	15	99	423	95	317, 361	316, 361	406, 429	416, 435
P2A3FSF	6.8	1.72	21	152	409	93	312, 362	311, 363	408, 431	419, 437
P2A3FOXD	11.9	1.70	37	156	404	91	310, 362	310, 363	408, 431	419, 437
P5FSF	56.2	2.63	91	97	404	100	372	372	413, 436	422, 442
P5FOXD	12.5	2.06	26	92	413	97	317, 372	316, 372	413, 436	422, 442
P2A5FSF	13.5	1.71	30	128	406	98	312, 374	312, 374	414, 438	424, 445
P2A5FOXD	22.4	1.77	48	130	410	88	314, 374	314, 374	414, 438	424, 445

[a] M_w and PDI values of the polymers were determined with GPC in THF using polystyrene as the standard. [b] Degree of polymerization was calculated with number-average molecular weight measured by GPC. [c] Onset decomposition temperature measured by TGA under nitrogen. [d] Fluorescence quantum yield was measured in toluene with a chromophore concentration of 10^{-7} M and 9,10-diphenylanthracene ($\Phi = 0.9$) as the standard. [e] Solution spectra were measured in toluene with a concentration of 10^{-6} M (terfluorene or pentafluorene units). The films were spin-cast from CH$_3$Cl solution with the concentration of 8 mg/mL. The excitation wavelength for PL measurements is 340 nm.

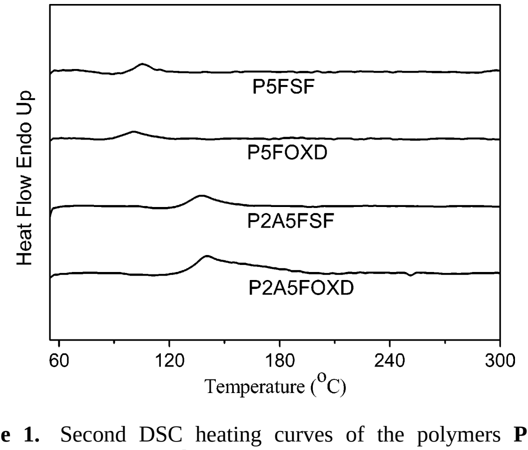


Figure 1. Second DSC heating curves of the polymers **P5FSF**, **P5FOXD**, **P2A5FSF**, and **P2A5FOXD**.

second-order transition is observed, which corresponds to glass transition temperature (T_g). The polymers exhibit T_g from 92 to 156 °C, depending on the length of oligofluorenes and structure of the central fluorene unit. Nevertheless, all these T_g values are much higher than that of poly(9,9-dioctylfluorene) (PFO, $T_g = 75$ °C), a well-studied blue-light-emitting polymer.[2b] Introduction of two triarylamine groups in the central fluorene unit resulted in dramatic enhancement of the T_g. As shown in Table 1, the T_g of **P2A3FSF**, **P2A3FOXD**, **P2A5FSF**, and **P2A5FOXD** is 51, 57, 31, and 38 °C higher, respectively, than their octyl-substituted counterparts. Similar to PAEs with oligofluorene segments as pendants,[9] all polymers show much higher T_g values than the corresponding oligofluorenes.[8e] We propose that the rigid PAE chain can significantly restrict the movement of the oligofluorene segments and increase the T_g. Meanwhile, saturated oxygen and sulfur atoms in polymer main chain have significant impact on the geometry and hence thermal properties of the polymers. Figure 2 shows the geometry of the one segment of **P3FSF** or **P2A3FSF** based on full geometry optimization of oligomers (Ph−terfluorene−Ph and Ph−O−Ph−SO$_2$−Ph−O−Ph) at the HF/3-21G level with the aid of the Gaussian 98 package,[13] in which the substituents at the

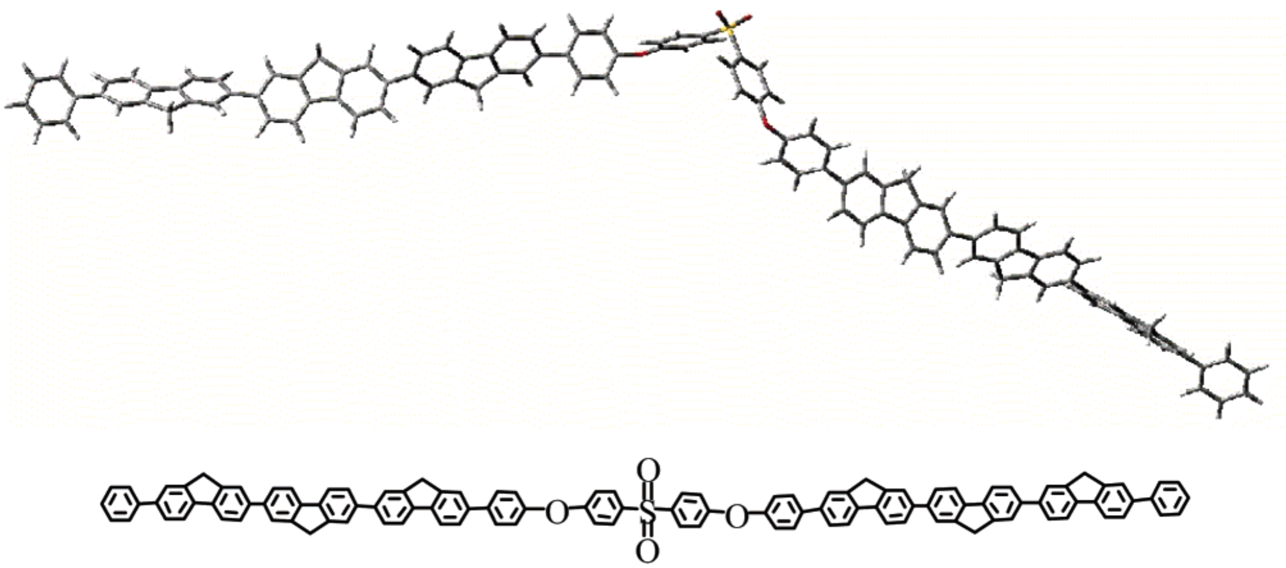


Figure 2. Simulated stereo-structure of a chain segment of **P3FSF** or **P2A3FSF** without substituents at the 9-position.

9-position of fluorene units were ignored in order to simplify the simulation. It indicates that the polymer chain is severely deviated from linear due to sp^3 hybridization of the ether oxygen and sulfur atoms. This structural feature should be able to prevent the polymers from mesophase formation and crystallization. As well-known, high T_g and glassy forming ability are imperative features of morphologically stable light-emitting polymers. Therefore, the film morphology of the herein polymers should be highly stable.

Optical Properties. The absorption and emission spectra of the polymers are shown in Figure 3, and the related data are summarized in Table 1. With 9,10-diphenylanthracene as the reference, the PL quantum yield (Φ_{PL}) of the polymers in toluene is 88−100%, maintaining the high quantum yield feature of oligofluorenes. There are two absorption bands in the absorption spectra of the polymers, which are at 310−317 and 361−374 nm and correspond to the absorption of oxadiazole/triarylamine units[5e,8f] and oligofluornene segments,[8] respectively. The film absorption spectra of the polymers are almost the same with those in solution, implying no aggregation in the solid state, which is consistent with the glassy characteristics of the polymers. The absorption of the polymers containing triarylamine at the 9-position of the central fluorene shows about a 2 nm red-shift relative to those without triarylamine groups because of the electron donation effect of these groups. This effect is much weaker compared with PAEs containing diphenylamine end-capped oligofluorenes in the side chain, as reported in our previous paper,[9] because the triarylamine groups in the current polymers are introduced to the oligofluorene segments through a saturated carbon. The PL spectra in solution and film state are also quite similar except for a several nanometers bathochromic shift in the solid state, which may be caused by the environmental or geometrical difference of the oligofluorene-emitting segments in solution and solid state. Because of self-absorption effect in film state, the intensity of the emission peak at the shorter wavelength (e.g., 422 nm for **P5FSF**) relative to that at the longer wavelength (e.g., 442 nm for **P5FSF**) is lower in comparison with the spectra in solution. This is supported by the fact that the relative intensity of the former peak decreases with increasing film thickness.

To study the spectral stability of the polymers, the films of **P5FSF** and **P2A3FOXD** were annealed at 90 °C in air and 180 °C under vacuum, and the PL spectra before and after annealing are shown in Figure 4. The PL spectra of annealed films at 90 and 180 °C are identical and almost similar to those of pristine ones. In contrast, the PL spectrum of PFO in general exhibits obvious change upon annealing.[9,14] This should be attributed to better morphological stability and higher T_g of the current polymers.

Electrochemical Properties. The electrochemical properties of the polymers were investigated by means of cyclic voltammetry (CV) with a typical three-electrode cell. Figure 5 shows the energy level diagram. From the onset potential of the oxidation and reduction, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the polymers can be estimated. The polymers **P3FSF** and **P5FSF** show the HOMO level of −5.8 to −5.9 eV and LUMO level of −2.0 to −2.1 eV, respectively, identical to those of oligofluorene.[8] This indicates that the oxidation and reduction processes must occur at oligofluorene segments as expected. For other polymers, the first oxidation and reduction should occur at the triarylamine or oxadiazole units, respectively. Indeed, the HOMO level of **P2AnFSF** and **P2AnFOXD** ($n = 3$ and 5) is −5.4 eV, and the LUMO level of **PnFOXD** and **P2AnFOXD** ($n = 3$ and 5) is −2.4 eV. These values are quite close to what has been reported for LEPs containing triarylamine and oxadiazole segments.[11a,12d] However, the emission spectra of the polymers are not affected obviously by introduction of the triarylamine or oxadiazole units since they are connected to the oligofluorene segments (which are responsible for the emission) through a nonconjugated linkage and have negligible effect on electronic structures of oligofluorene segments. That means the HOMO and LUMO levels of the polymers can be tuned independently through introducing isolated hole- and electron-injecting segments without affecting emission properties of the polymers.

Device Properties. The polymer light-emitting diodes (PLEDs) were fabricated with a configuration of ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS)/polymer (80 nm)/Ca/Al, and the device performances are summarized in Table 2. The polymers exhibit electroluminescence (EL) spectra similar to their PL counterparts (Figure 6), except that the polymers **P2A3FSF** and **P2A3FOXD** show two new emission peaks at lower energy. The polymers comprising of terfluorene units exhibited much worse EL properties than those carrying pentafluorenes, which is consistent with our

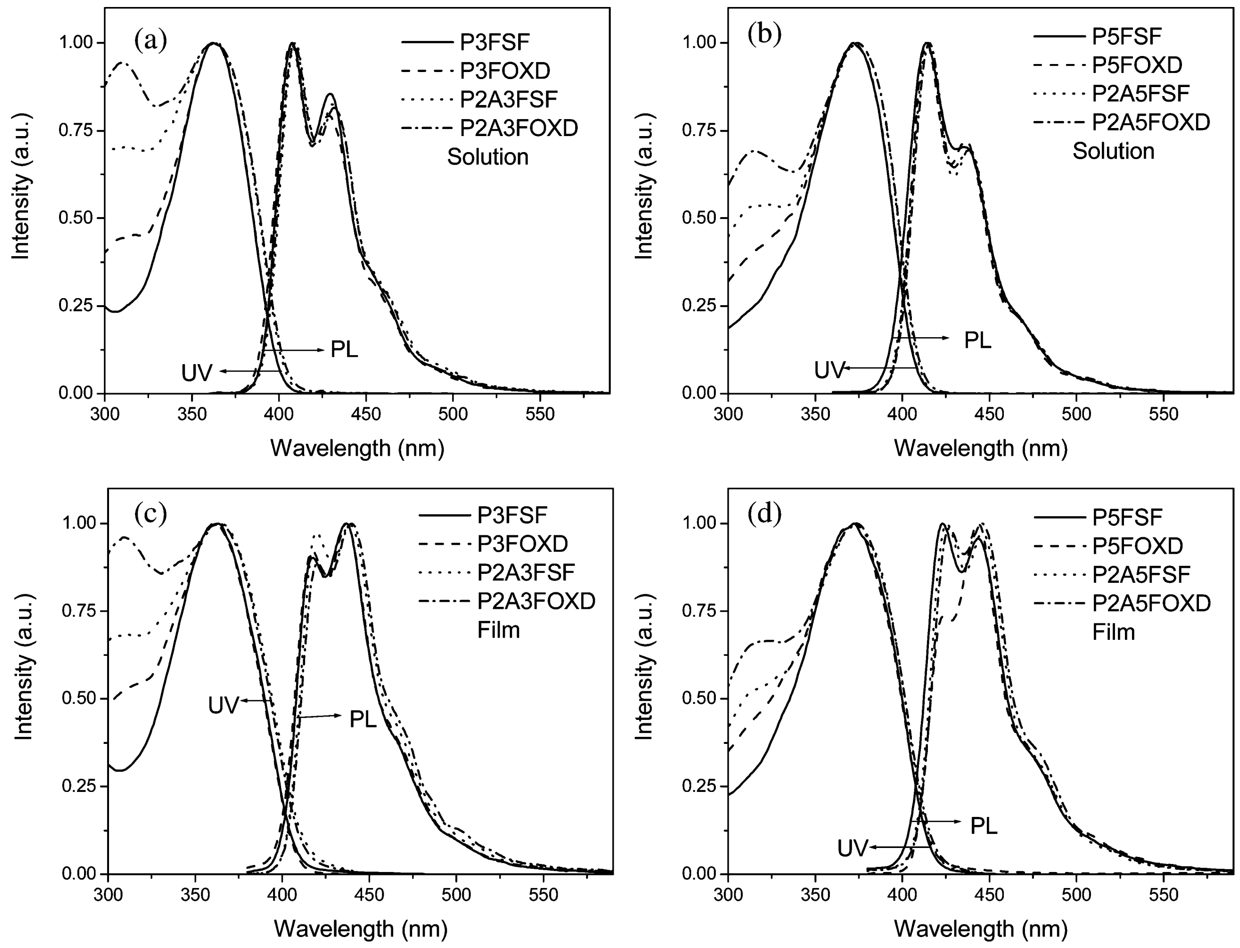


Figure 3. Absorption and PL spectra of polymers in toluene solution (a and b) with an oligofluorene segment concentration of 10^{-6} M and those in film state (c and d).

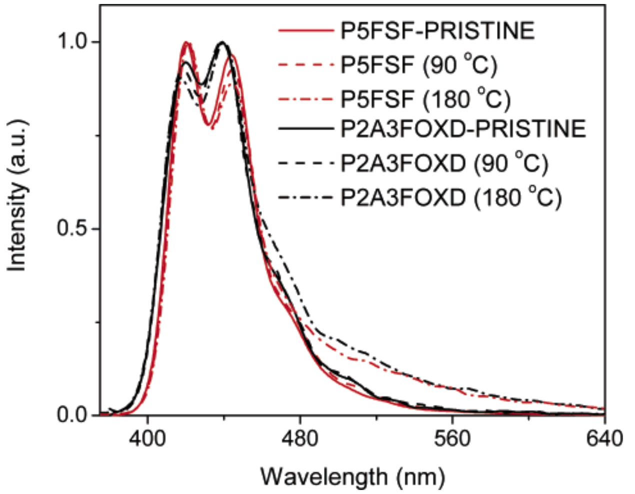


Figure 4. PL spectra of **P2A5F** and **P2A3FOXD** films before and after thermal annealing at 90 °C (36 h) in air and 180 °C (24 h) under vacuum.

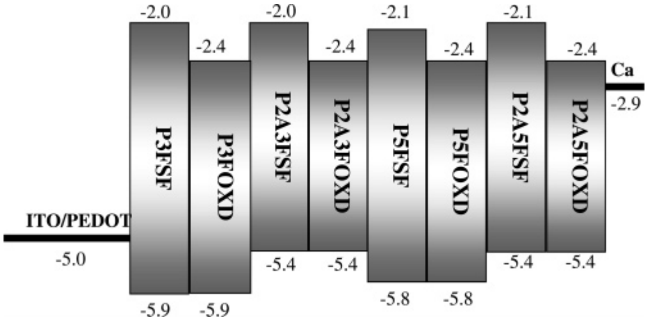


Figure 5. Energy diagram of the polymers.

previous observation[9] and others' work.[5a] Although the luminous efficiencies of **P2A3FSF** and **P2A3FOXD** are about 2 times those of **P3FSF** and **P3FOXD**, their external quantum efficiencies are almost the same because people's eyes are more sensitive to green light. Figure 7 shows the luminous efficiency–voltage relationship of the devices based on **P5FSF**, **P5FOXD**, **P2A5FSF**, and **P2A5FOXD**. With increasing number of fluorene unit from 3 to 5, the polymers show significantly improved EL performance. A luminous efficiency of 0.7 cd/A at 100 cd/m² and a maximum brightness of 2593 cd/m² were realized for **P5FSF**. These values are identical to those of the device based on PFO in the same fabrication condition and device configuration. In comparison with **P5FSF**, the polymers **P5FOXD**,

Table 2. Turn-On Voltage (V_{on}), Maximum Brightness (L_{max}), Luminous Efficiency (*LE*), External Quantum Efficiency (QE_{ext}), and *CIE* Coordinates of the Devices with the Configuration of ITO/PEDOT:PSS/Polymer/Ca/Al

polymer	V_{on}[a] (V)	L_{max} (cd/m²)	*LE*[b] (cd/A)	QE_{ext}[b] (%)	*CIE*(*x*, *y*)[b]
P3FSF	6	274	0.2	0.3	0.16, 0.07
P3FOXD	5	276	0.3	0.4	0.16, 0.08
P2A3FSF	5	629	0.6	0.4	0.21, 0.13
P2A3FOXD	5	769	0.6	0.4	0.23, 0.16
P5FSF	4	2593	0.7	0.8	0.17, 0.10
P5FOXD	4	2083	1.0	1.2	0.17, 0.11
P2A5FSF	4	2471	1.0	1.4	0.17, 0.09
P2A5FOXD	4	2244	1.2	1.4	0.18, 0.11

[a] The voltage at the brightness of 1 cd/m². [b] The values at 100 cd/m².

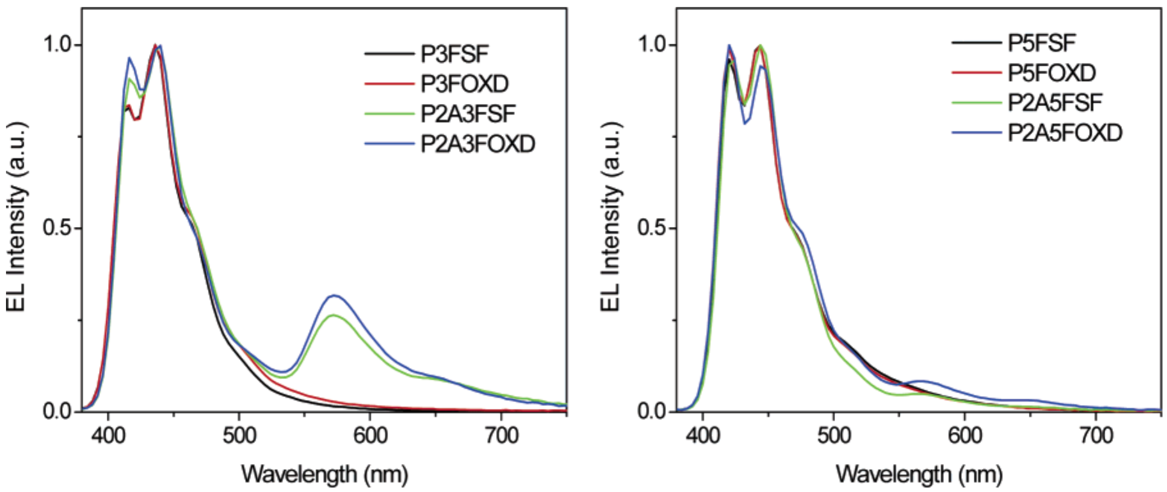


Figure 6. EL spectra of the polymers with device structure of ITO/PEDOT:PSS/polymers/Ca/Al.

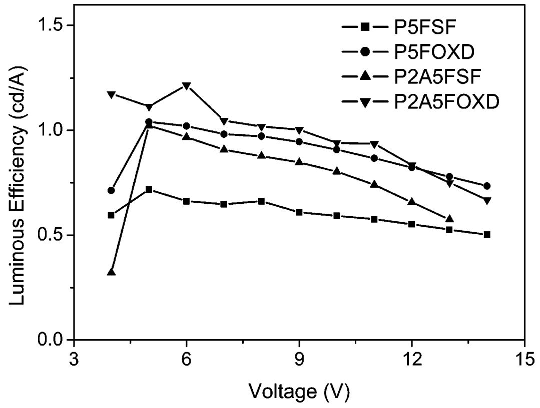


Figure 7. Luminous efficiency−voltage relationship of the devices based on the polymers **P5FSF**, **P5FOXD**, **P2A5FSF**, and **P2A5FOXD**.

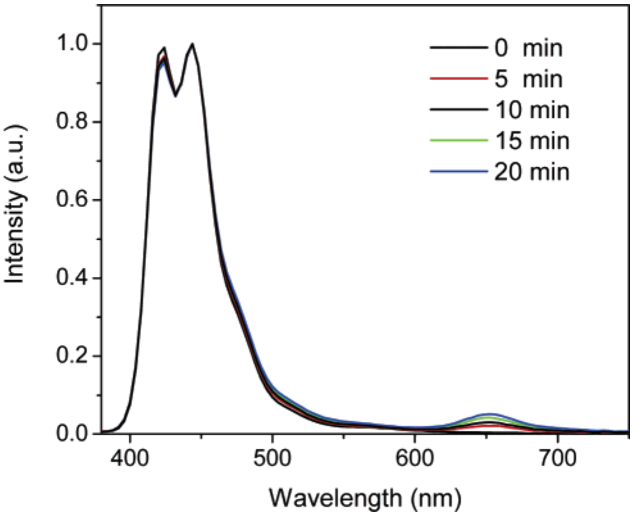


Figure 8. EL spectra of **P2A5FOXD** with operation time from 0 to 20 min.

P2A5FSF, and **P2A5FOXD** show better EL performance due to diminished injection energy barrier. A luminous efficiency of 1.0, 1.0, and 1.2 cd/A at 100 cd/m^2 along with the maximum brightness of 2083, 2471, and 2244 cd/m^2 for **P5FOXD**, **P2A5FSF**, and **P2A5FOXD**, respectively, were realized. Meanwhile, the external quantum efficiencies of the devices based on these polymers are in the range 0.8−1.4%. Especially, with the negligible emission at long wavelength for **P2A5FSF** and **P2A5FOXD**, the polymers containing pentafluorene segments show comparable Commission Internationale de L'Eclairage (CIE) coordinates of (0.17, 0.10), (0.17, 0.11), (0.17, 0.09), and (0.18, 0.11) for **P5FSF**, **P5FOXD**, **P2A5FSF**, and **P2A5FOXD**, respectively. All these CIE coordinates are close to the National Television System Committee Standard blue, viz. (0.14, 0.08). In comparison with previously reported PAEs with oligofluorene segments as pendants, current main-chain PAEs exhibit better CIE coordinates. It is worthy pointing out that the EL performance of these materials is comparable with those of the triarylamine end-capped PFs[15] and PFs with triarylamine and oxadiazole groups in the side chain.[11a,16] However, nonconjugated polymers based on phenylenevinylene building blocks exhibited much inferior device performance in comparison with fully conjugated ones.[17]

PLEDs based on PFO often emit undesired green light upon operation.[18,19] To test the color stability of the current polymers, a device of **P2A5FOXD** with the structure of ITO/PEDOT:PSS/polymer/Ca/Al was fabricated and encapsulated with an aluminum sheet. As shown in Figure 8, the EL spectra show almost no change upon operation in the period of 20 min with the initial brightness of 110 cd/m^2. This indicates that this type of polymers is relative stable in terms of emission color. The lifetime of the devices so far is still low and should be improved by optimizing the device structures and improving the encapsulation techniques.

As aforementioned, the polymers **P2A3FSF** and **P2A3FOXD** show a long wavelength EL emission peak with a maximum of ∼570 nm. The PFs containing triarylamine and oxadiazole pendants at the C-9 position of fluorene reported by Shu etc. also showed a similar phenomenon.[16] The authors tentatively ascribed it to the formation of emissive fluorenone defects as a result of the electrooxidative degradation of dioctylfluorene units. However, this long wavelength emission band is quite different from that caused by fluorenone defects and should be attributed to other reasons. The first, the undesired green emission peak due to the fluorenone defects, generally locates at the wavelength shorter than 550 nm[18,19] (but around 570 nm here), and the second, the current polymers without triarylamine groups, do not show such phenomenon. Even for the polymers with pentafluorene containing triarylamine groups, the emission band at long wavelength is very weak. Therefore, we suspect that this phenomenon is attributed to the efficient hole-transporting properties of triarylamine-containing polymers, which result in an unbalanced hole/electron injection/transportation, and consequently the holes can easily transport to the light-emitting layer−cathode interface to induce the long wavelength

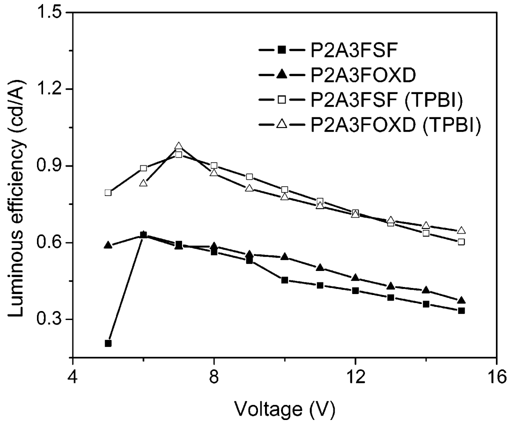


Figure 9. Luminous efficiency of the devices based on **P2A3FSF** and **P2A3FOXD** with and without TPBI hole-blocking layer.

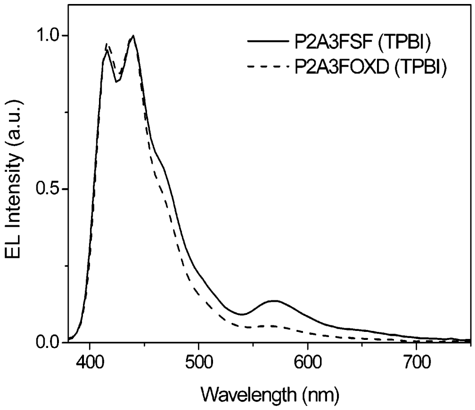


Figure 10. EL spectra of the polymers **P2A3FSF** and **P2A3FOXD** with device structure of ITO/PEDOT:PSS/polymers/TPBI/LiF/Al.

emission due to the formation of unknown emission species. For the polymers without triarylamine groups or with less triarylamine groups (i.e., polymers with pentafluorene segments), hole transportation of the polymers may be relatively less efficient; therefore, the emission region is apart from the cathode avoiding the long wavelength emission. To verify this hypothesis, we inserted a thin layer of hole blocking layer between the emission layer and the cathode and fabricated the multilayer devices with a configuration of ITO/PEDOT:PSS/**P2A3FSF** or **P2A3FOXD** (50 nm)/TPBI (30 nm)/LiF/Al (TPBI:1,3,5-tris-(2-phenylbenzimidazolyl)benzene). The device performance was improved obviously as shown in Figure 9, and the long wavelength emission can be suppressed as shown in Figure 10. On the basis of these results, we propose that the long wavelength emission probably comes from the interface between the emissive layer and the cathode layer.

Conclusions

We have designed and synthesized a series of novel high molecular weight light-emitting PAEs with oligofluorene segments in the main chain. This procedure for the preparation of light-emitting polymers is quite simple compared to metal-mediated cross-coupling reactions. Especially, the resulting polymers can be easily purified via precipitation. Owing to the rigid characteristics of PAE chain and sp^3 hybridization of ether oxygen and sulfur atoms, the polymers are amorphous with a glass transition temperature much higher than typical fluorene–homopolymer PFO. Furthermore, their optoelectronic properties can be adjusted by tuning the length of the oligofluorene segments or introducing hole- and electron-transport units into the polymers. EL devices with the structure of ITO/PEDOT:PSS/polymer/Ca/Al were fabricated. The polymers comprising of pentafluorene segments show better EL performance, and an external quantum efficiency of 1.4% along with the CIE coordinates of (0.17, 0.09) at 100 cd/m^2 was realized. These results along with our previous publication about side chain PAEs indicate that high-performance light-emitting polymers can also be prepared by means of traditional polymerization through the carefully designing light-emitting building blocks.

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