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Synthesis, Characterization, and Electroluminescence of New Conjugated Polyfluorene Derivatives Containing Various Dyes as Comonomers

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ABSTRACT: Four new fluorene-based alternating polymers (PFR1-S, PFR2-S, PFR3-S, and PFR4-S) containing different comonomers (R1, R2, R3, and R4) have been designed, synthesized, and characterized. These polymers were found to be thermally stable and readily soluble in common organic solvents. Single layer LED devices fabricated from these polymers emitted bluish green to pure red light. Our results show that the color of the light emitted by the homopolymer, poly(9,9-dioctylfluorene-2,7-diyl) (PDOF), can be tuned by incorporating R1, R2, R3, and R4 comonomers, which have narrower band gaps. The absorption and emission maxima of the copolymers varied according to the position of the cyano group in the vinylene unit (α- or β-position) and the type of incorporated aromatic group (thiophene or phenylene). Notably, PFR4-S showed pure red emission (CIE coordinate values $x = 0.66$, $y = 0.33$) that is almost identical to the standard red (0.66, 0.34) demanded by the National Television System Committee. PFR3-S also exhibited pure red emission (chromaticity values $x = 0.63$, $y = 0.38$), and its maximum luminance and maximum external quantum efficiency were approximately 3100 cd/m^2 at 6 V and 0.46% at 4 V, respectively.

Introduction

Since the initial report of the fabrication of polymer light-emitting diodes (PLEDs) based on poly(*p*-phenylenevinylene) (PPV) by the Cambridge group,[1] luminescent conjugated polymers have been found to be of considerable importance as active materials in emerging new technologies, because their luminescence properties can be adjusted by manipulation of their chemical structures and because their physical properties make them suitable for use in the spin coating and printing processes required to create large-area flat-panel displays.[2−5] Although PLEDs have been developed that produce each of the three primary colors (red, green, and blue), at present only green and orange PLEDs meet the requirements of commercial use.

A number of polyfluorene (PF) polymers and their derivatives have been studied since poly(9,9-di-*n*-hexylfluorene) (PDHF) was first reported to be a blue-light-emitting polymer.[6] The interest in these polymers arose because they exhibit high photoluminescence quantum yields and excellent chemical and thermal stability as well as photostability, good solubility and film-forming properties, and can readily be prepared via high-yielding synthetic routes that produce well-defined high molar mass polymers.[7−13] However, the usefulness of PFs is compromised by their tendency to exhibit excimer and/or aggregate formation upon thermal annealing or the passage of current. Recently, keto formation of the C-9 position in fluorene has been less attractive, because some experimental results show that unwanted emission bands are caused by the keto group.[14] Therefore, the efficiency of PF-based devices is insufficient for commercial applications. The study of PFs is ongoing, and numerous attempts have been made to improve their performance.[15−17]

Although some attempts have been made to tune the color of blue-emitting PFs, appropriate red- and green-emitting materials that meet the requirements for display applications have yet to be obtained, and further improvements are necessary.[18−21] If two chromophores with different energy band gaps are mixed together, then energy transfer occurs from the chromophore with the larger band gap to that with the smaller band gap, and emission from the latter dominates.[22−24] One method for color tuning that exploits this effect is the blending of a dye chromophore into the polymer matrix. However, although blending has the advantage that diverse dyes are readily available, blends of polymers and dyes tend to phase-separate during device operation.[25] An alternative approach is to covalently attach the dye to the polymer. This approach has two significant advantages over blending: (1) aggregation is prevented and (2) efficient energy transfer from the polymer chromophores to the dye chromophores easily confines the singlet excitons.[19] Inbasekaran et al. have reported the synthesis of several fluorene-based copolymers through alternating copolymerization of 5,5′-dibromo-2,2′-bithiophene and 4,7-dibromo-2,1,3-benzothiadiazole, which exhibit yellow and green emissions, respectively.[26] Lee et al. have reported the synthesis of fluorene-based copolymers through random copolymerization of 3,9(10)-dibromoperylene, 4,4′-dibromo-α-cyanostilbene, and 1,4-bis(2-(4′-bromophenyl)-1-cyanovinyl)-2-(2′-ethylhexyl)-5-methoxybenzene.[27] Thus the introduction into PF of comonomers with band gaps narrower than that of the fluorene monomer can be used for color tuning.

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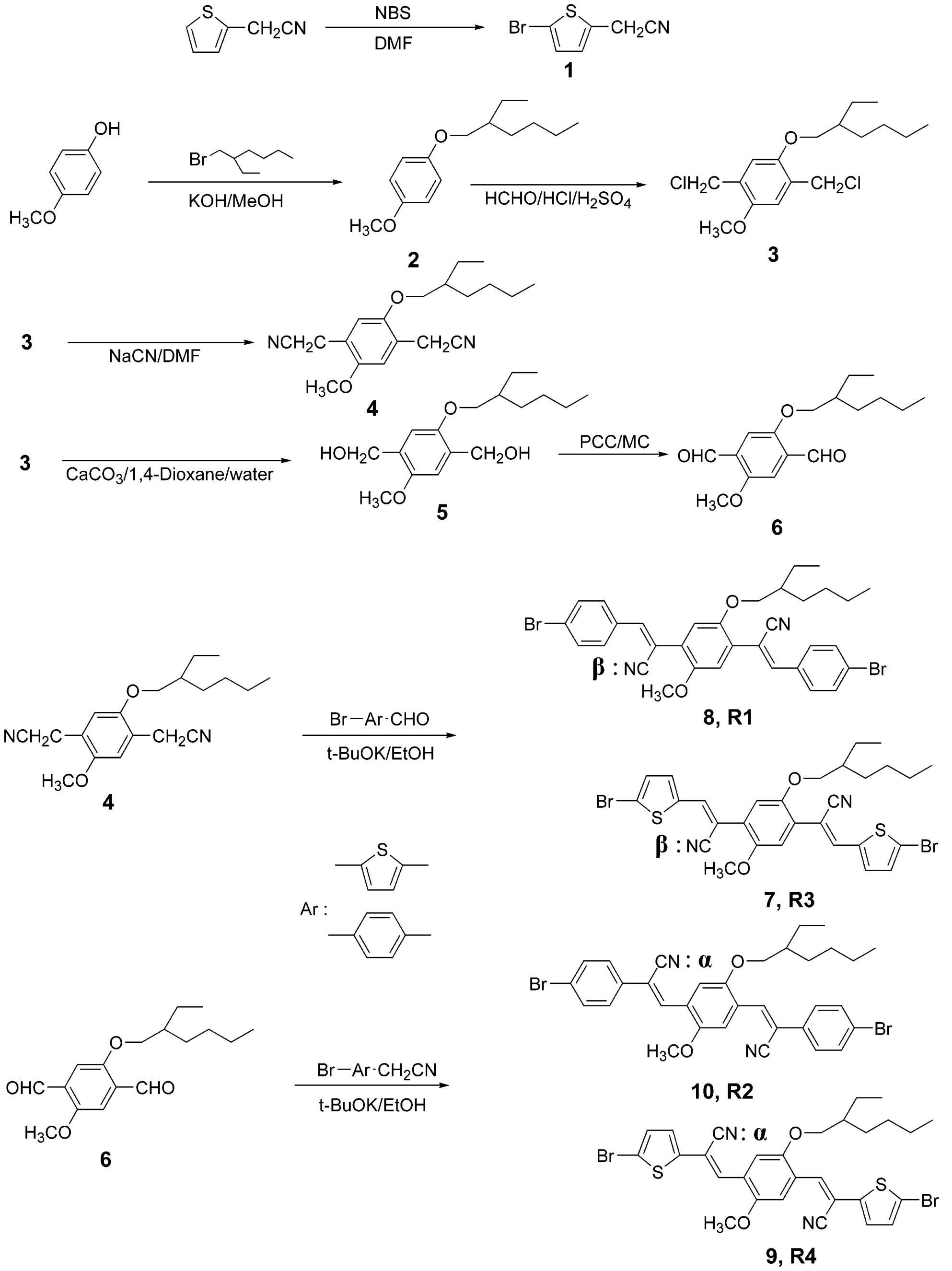
Scheme 1. Synthetic Scheme of Monomers R1, R2, R3, and R4

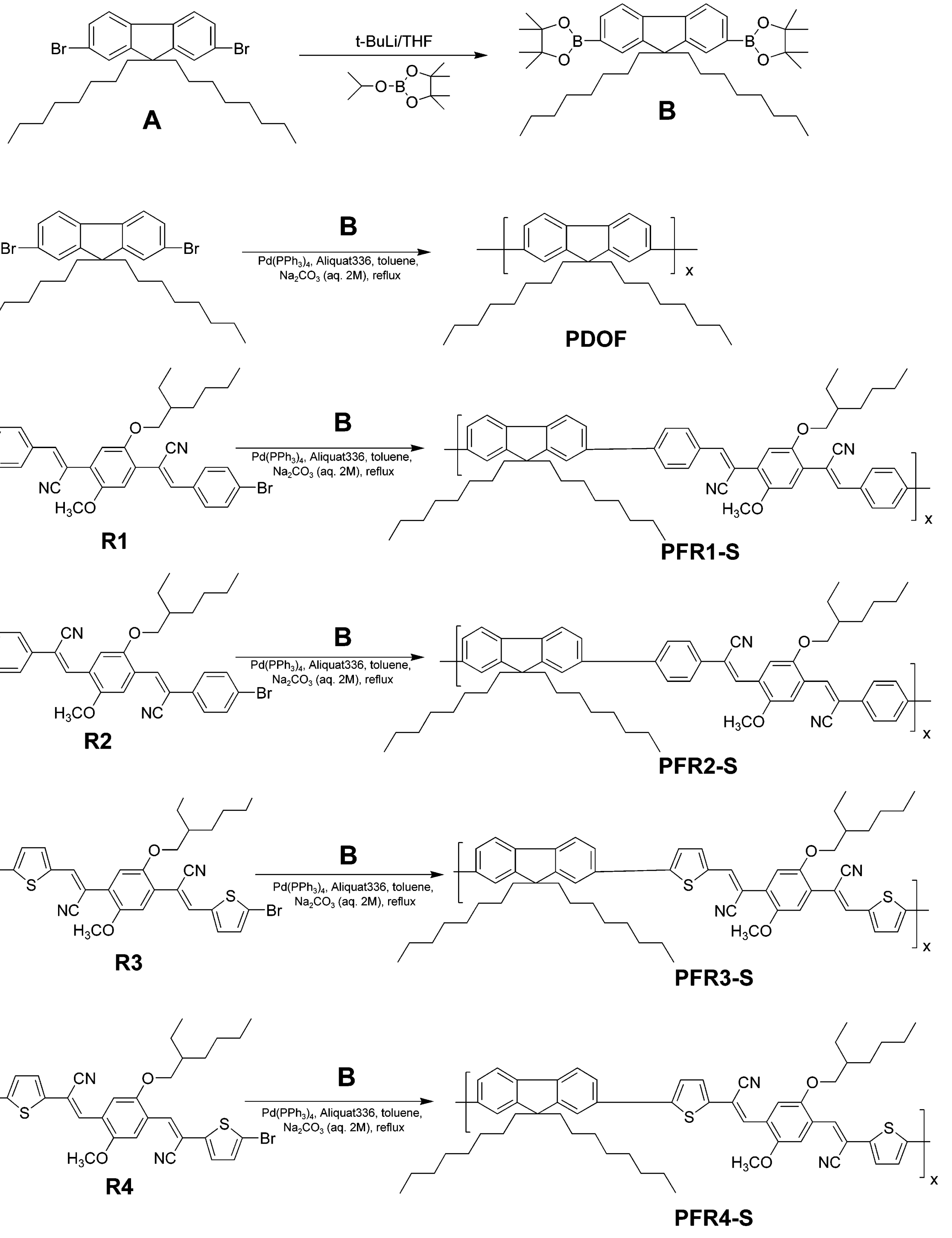


In contrast to the large body of work on blue-emitting copolymers, only a few studies have investigated red emission from copolymers based on PFs. To address this shortfall, we have systematically introduced simple narrow band gap monomers into PFs in the search for a copolymer with pure red emission. These experiments have led to the discovery of the following polymers that exhibit pure red emission: poly{9,9-dioctylfluorene-2,7-diyl-*alt*-2,5-bis(2-thienyl-2-cyanovinyl)-1-(2′-ethylhexyloxy)-4-methoxybenzene-5″,5″-diyl} (PFR4-S) and poly{9,9-dioctylfluorene-2,7-diyl-*alt*-2,5-bis(2-thienyl-1-cyanovinyl)-1-(2′-ethylhexyloxy)-4-methoxybenzene-5″,5″-diyl} (PFR3-S). Interestingly, the CIE coordinates for the EL spectra of PFR4-S and PFR3-S are (0.66, 0.33) at approximately 5 V and (0.63, 0.38) at approximately 3 V, respectively, which are very close to those of standard red (0.66, 0.34) demanded by the National Television System Committee (NTSC). We systematically prepared various copolymers in the present study by changing the position of the functional group and introducing different moieties, and then we determined the relationships between the structures of these copolymers and color tuning. The synthetic routes and the structures of the various monomers and copolymers are shown in Schemes 1 and 2.

Experimental Section

Measurements. NMR spectra were recorded using a Bruker AM 300 MHz spectrometer with tetramethylsilane as an internal reference. Elemental analysis was performed using an EA 1110 Fisons analyzer. FT-IR spectra were recorded using an EQUINOX 55 spectrometer. UV−vis and PL spectra were recorded using Jasco V-530 and Spex Fluorolog-3 spectrofluorometers. Thermogravimetric analysis (TGA) was carried out using a DuPont 9900 analyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. The number- and weight-average molecular weights of polymers were determined by gel permeation chromatography (GPC) on a Waters GPC-150C instrument, using tetrahydrofuran (THF) as eluent

Scheme 2. Synthetic Scheme of Polymers PFR1-S, PFR2-S, PFR3-S, and PFR4-S



and polystyrene as standard. Single-layer LED devices were fabricated on glass substrates coated with indium−tin oxide (ITO). The device configuration was ITO/poly(3,4-ethylenedioxythiophene)/polymer/Ca/Al. Poly(3,4-ethylenedioxythiophene) (PEDOT) was used as the hole-injection layer. The LED structure used in this study consisted of a calcium contact on the copolymer surface that is spin-cast onto a PEDOT-coated ITO glass substrate from a solution of polymers in chlorobenzene. The spin-casting yielded uniform films with thicknesses of approximately 100 nm. Aluminum was deposited onto the polymer films using the vacuum evaporation method at a pressure of 10^{-6} Torr. EL spectra of the devices were obtained using a Minolta CS-1000. Current−voltage−luminance ($I-V-L$) characteristics were recorded simultaneously with the measurement of the EL intensity by attaching the photospectrometer to a Keithley 238 and a Minolta LS-100 as the luminance detector. All measurements were carried out at room temperature under ambient atmosphere.

Materials. 4-Methoxyphenol, 2-ethylhexyl bromide, 1,5-cyclooctadiene, 2,7-dibromofluorene, 2,2′-dipyridyl, 2-thiopheneacetonitrile, *N*-bromosuccinimide, 4-bromobenzaldehyde, 4-bromophenylacetonitrile, toluene (99.8%, anhydrous), *N*,*N*-dimethylformamide (99.8%, anhydrous), tetrakis(triphenylphosphine)palladium, Aliquat 336, and 5-bromo-2-thiophenecarboxaldehyde were purchased from Aldrich. All chemicals were used without further purification. 2-(2′-Ethylhexyloxy)-5-methoxybenzene (**2**), 1,4-bis(chloromethyl)-2-(2′-ethylhexyloxy)-5-methoxybenzene (**3**), [2-(2′-ethylhexyloxy)-4-(hydroxymethyl)-5-methoxyphenyl]methan-1-ol (**5**),[22] 2,5-bis-{2-(4′-bromothienyl)-1-cyanovinyl}-2-(2′-ethylhexyloxy)-5-methoxybenzene (R3) (7),[24] and 2,7-dibromo-9,9-dioctylfluorene (**11**) were synthesized according to procedures outlined in the literature.[28]

Synthesis of 5-Bromo-2-thiopheneacetonitrile (1). *N*-Bromosuccinimide (7.58 g, 40.2 mmol) was added to a solution of 2-thiopheneacetonitrile (5 g, 40.0 mmol) in *N*,*N*-dimethylformamide (30 mL). The reaction mixture was then stirred for 5 h at room temperature. The resulting mixture was extracted with methylene chloride and brine and then dried with $MgSO_4$. After filtering, the solvent was evaporated and the pure liquid product was obtained by column chromatography. The product yield was 72% (5.81 g): ^1H NMR ($CDCl_3$, ppm) δ 6.90 (d, 1H), 6.78 (d, 1H), 3.80 (s, 2H). ^{13}C NMR ($CDCl_3$, ppm) δ 132.23, 129.92, 127.53, 116.19, 112.15, 18.62.

Synthesis of 1,4-Bis(cyanomethyl)-2-(2′-ethylhexyloxy)-5-methoxybenzene (4). A mixture of 20.0 g (60 mmol) of compound **3** and 8.8 g (180 mmol) of sodium cyanate in *N*,*N*-dimethylformamide was stirred at 45 °C for 72 h. The resulting mixture was extracted with methylene chloride and brine and then dried with $MgSO_4$. The extract was filtered and evaporated in vacuo. The resulting liquid was poured into water, yielding a pale yellow precipitate that was separated by filtering. The precipitate was recrystallized in methylene chloride and hexane two times. The product yield was 79% (15 g): ^1H NMR ($CDCl_3$, ppm) δ 6.90 (d, 2H), 3.85 (d, 2H), 3.83 (s, 3H), 3.68 (s, 4H), 1.72 (m, 1H), 1.55−1.29 (m, 8H), 0.91 (q, 6H); ^{13}C NMR ($CDCl_3$, ppm) δ 150.43, 150.30, 119.10, 119.00, 117.73, 112.48, 111.82, 71.13, 56.12, 39.48, 30.59, 29.07, 23.98, 22.99, 18.63, 18.58, 14.03, 11.16. Anal. Calcd for $C_{19}H_{26}N_2O_2$; C, 72.58; H, 8.33; N, 8.91. Found: C, 72.52; H, 8.11; N, 8.67.

Synthesis of 5-(2′-Ethylhexyloxy)-2-methoxybenzene-1,4-dicarbaldehyde (6). A solution of 4.0 g (14 mmol) of the dialcohol compound **4** in 80 mL of methylene chloride was stirred and cooled with an ice bath while pyridium chlorochromate (9.06 g, 42 mmol) was added in a portionwise manner over a period of 20 min. The mixture was then stirred for 8 h at room temperature until the oxidation was complete (as monitored by TLC). After a dark brown suspension had formed, the solution was diluted with 200 mL of diethyl ether and stirred for a further 30 min. The mixture was then filtered through silica gel to remove inorganic and insoluble particles. The solution was washed with 100 mL of 1 N HCl and then with brine, after which it was dried over $MgSO_4$. The ether solution was filtered and concentrated, and the remaining greenish-yellow solid was purified by column chromatography (eluent: hexane/ethyl acetate = 10/1). The pure greenish-yellow solid was obtained with a yield of 78% (3.2 g): ^1H NMR ($CDCl_3$, ppm) δ 10.51 (s, 1H), 10.48 (s, 1H), 7.43 (s, 2H), 3.8 (d, 2H), 3.7 (s, 3H), 1.6−1.3 (m, 9H), 0.9 (m, 6H); ^{13}C NMR ($CDCl_3$, ppm) δ 189.30, 155.60, 129.26, 111.76, 110.65, 71.57, 56.20, 39.40, 30.57, 29.04, 23.97, 22.98, 14.03, 11.13. Anal. Calcd for $C_{29}H_{28}Br_2N_2O_2S_2$: C, 52.74; H, 4.27; N, 4.24; S, 9.71. Found: C, 52.01; H, 4.41; N, 4.25; S, 12.24.

Synthesis of 2,5-Bis{2-(4′-bromophenyl)-1-cyanovinyl}-2-(2′-ethylhexyloxy)-5-methoxybenzene (R1) (8). The synthesis is analogous to that of **7**, with 62% yield: ^1H NMR ($CDCl_3$, ppm) δ 7.95 (s, 1H), 7.79 (s, 1H), 7.31 (d, 1H), 7.28 (d, 1H), 7.10−7.06 (m, 4H) 3.82 (d, 2H), 3.76 (s, 3H), 3.68 (s, 4H), 1.72 (m, 1H), 1.55−1.29 (m, 8H), 0.91 (q, 6H); ^{13}C NMR ($CDCl_3$, ppm) δ 150.94, 239.64, 138.20, 133.22, 132.84, 130.55, 123.84, 118.55, 118.21, 113.85, 113.32, 104.84, 71.79, 56.51, 39.66, 30.81, 29.16, 24.14, 23.01, 14.03, 11.24. Anal.Calcd for $C_{29}H_{28}Br_2N_2O_2S_2$: C, 52.74; H, 4.27; N, 4.84; S, 9.71. Found: C, 52.72; H, 4.10; N, 4.53; S, 9.84.

Synthesis of 2,5-Bis{2-(4′-bromophenyl)-2-cyanovinyl}-2-(2′-ethylhexyloxy)-5-methoxybenzene (R2) (10). The synthesis is analogous to that of **7**, with 72% yield: ^1H NMR ($CDCl_3$, ppm) δ 8.02 (s, 1H), 7.96 (s, 1H), 7.89 (s, 1H), 7.85 (s, 1H), 7.59−7.51 (m, 8H), 4.01 (d, 2H), 3.94 (s, 3H), 1.80 (m, 1H), 1.53−1.29 (m, 8H), 0.96−0.84 (m, 6H); ^{13}C NMR ($CDCl_3$, ppm) δ 151.89, 136.00, 133.50, 132.23, 127.50, 123.50, 117.95, 111.44, 110.61, 71.90, 56.31, 39.40, 30.85, 29.09, 24.15, 23.02, 14.02, 11.23. Anal. Calcd for $C_{33}H_{32}Br_2N_2O_2$: C, 61.32; H, 4.97; N, 4.32. Found: C, 60.28; H, 5.07; N, 4.34.

Synthesis of 2,5-Bis{2-(4′-bromothienyl)-1-cyanovinyl}-2-(2′-ethylhexyloxy)-5-methoxybenzene (R3) (7). This compound was synthesized by the literature procedure.[24] All physical and spectral properties were in accord with previously published values.

Synthesis of 2,5-Bis{2-(4′-bromothienyl)-2-cyanovinyl}-2-(2′-ethylhexyloxy)-5-methoxybenzene (R4) (9). The synthesis is analogous to that of **7**, with 67% yield: ^1H NMR ($CDCl_3$, ppm) δ 7.82 (s, 1H), 7.78 (s, 1H), 7.73 (s, 1H), 7.66 (s, 1H), 7.12 (m, 2H), 7.03 (m, 2H), 3.98 (d, 2H), 3.92 (s, 3H), 1.80 (m, 1H), 1.55−1.32 (m, 8H), 0.95−0.87 (m, 6H); ^{13}C NMR ($CDCl_3$, ppm) δ 151.90, 141.07, 133.20, 131.08, 127.42, 125.32, 116.58, 113.83, 111.09, 109.54, 105.39, 71.89, 56.33, 39.54, 30.95, 29.20, 24.21, 23.08, 14.07, 11.29. Anal. Calcd for $C_{29}H_{28}Br_2N_2O_2S_2$: C, 52.74; H, 4.27; N, 4.24; S, 9.71. Found: C, 52.01; H, 4.41; N, 4.25; S, 12.24.

Synthesis of 2,7-Bis(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-dioctylfluorene (B).[29] To a solution of 2,7-dibromo-9,9′-dioctylfluorene (7.0 g, 12.8 mmol) in THF (120 mL) at −78 °C was added, by syringe, 33.79 mL (57.42 mmol) of *tert*-butyllithium (1.7 M in hexane). The mixture was stirred at −78 °C for 2 h. 2-Isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane (7.97 mL, 38.4 mmol) was added to the solution, and the resulting mixture was stirred at −78 °C for 1 h, warmed to room temperature, and stirred for 40 h. The mixture was poured into water, extracted with dichloromethane, and dried over $MgSO_4$. The solvent was removed by solvent evaporation, and the residue was purified by several reprecipitations in hexane to provide 4.82 g (59%) of the product as a white solid: ^1H NMR ($CDCl_3$, ppm) δ 7.78 (d, 2H), 7.72 (s, 2H), 7.70 (d, 2H), 1.97 (m, 4H), 1.37 (s, 24H), 1.18−0.99 (m, 20H), 0.79 (t, 6H), 0.53 (m, 4H); ^{13}C NMR ($CDCl_3$, ppm) δ 150.45, 143.89, 133.62, 128.89, 119.35, 83.69, 55.16, 40.07, 31.76, 29.91, 29.18, 29.13, 24.92, 23.57, 22.57, 14.05. Anal. Calcd for $C_{41}H_{64}B_2O_4$: C, 76.64; H, 10.04. Found: C, 77.00; H, 10.17.

General Polymerization Procedure.[30] Into a 100 mL two-neck flask were added 2.33 mmol of comonomers—R1 (1.51 g), R2 (1.51 g), R3 (1.54 g), and R4 (1.54 g)—and 2.28 mmol (1.5 g) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxabororan-2-yl)-9′,9′-dioctylfluorene in 25 mL of anhydrous toluene. Into the mixture was transferred in a drybox 0.026 g of the water-soluble Pd(0) complex tetrakis(triphenylphosphine)palladium (1 mol %). Subsequently, 2 M aqueous sodium carbonate (5.4 mL, 10.7 mmol) deaerated for 30 min and the phase transfer catalyst Aliquat 336 (0.092 g, 0.23 mmol) in toluene purged under nitrogen for 1 h were transferred via cannula. The reaction mixture was stirred at 100 °C for 3 days, and then the excess amount of bromobenzene (0.036 g, 0.23 mmol), the end-capper, dissolved in 1 mL of anhydrous toluene was added and stirring continued for 12 h. The reaction mixture is cooled to about 50 °C and added slowly to a vigorously stirred mixture of 200 mL of methanol and 13 mL of 1 N aqueous HCl. The polymer fibers are collected by filtration and reprecipitation from methanol and acetone. The polymers are purified further by washing for 2 days in a Soxhlet apparatus, with acetone to remove oligomers and catalyst residues, and column chromatographed with a chloroform solution of the polymer. The reprecipitation procedure in chloroform/methanol is then repeated several times. The final polymers were obtained after drying in vacuo at 40 °C, yielding 67% (PFR1-S), 72% (PFR2-S), 78% (PFR3-S), and 71% (PFR4-S). PFR1-S: ^1H NMR ($CDCl_3$, ppm) δ aromatic and vinylene; 8.00−7.62 (18H), aliphatic; 4.06−3.97 (5H), 2.02−0.76 (~45H). Anal. Calcd for $(C_{62}H_{72}N_2O_2)_n$: C, 84.89; H, 8.27; N, 3.19. Found: C, 79.65; H, 8.30; N, 3.92. PFR2-S: ^1H NMR ($CDCl_3$, ppm) δ aromatic and vinylene; 8.14−7.55 (18H), aliphatic; 4.06−3.95 (5H), 2.05−0.77 (~45H). Anal. Calcd for $(C_{62}H_{72}N_2O_2)_n$: C, 84.89; H, 8.27; N, 3.19. Found: C, 81.51; H, 8.19; N, 3.59. PFR3-S: ^1H NMR ($CDCl_3$, ppm) δ aromatic and vinylene; 8.14−7.55 (14H), aliphatic; 4.06−3.95 (5H), 2.05−0.77 (~45H). Anal. Calcd for $(C_{62}H_{72}N_2O_2)_n$: C, 78.33; H, 7.71; N, 3.15; S, 7.21. Found: C, 76.77; H, 7.78; N, 3.55; S, 8.12. PFR4-S: ^1H NMR ($CDCl_3$, ppm) δ aromatic and vinylene; 7.94−7.24 (14H), aliphatic; 4.05−3.95 (5H), 2.03−0.76 (~45H). Anal. Calcd for $(C_{62}H_{72}N_2O_2)_n$: C, 78.33; H, 7.71; N, 3.15; S, 7.21. Found: C, 73.31; H, 7.50; N, 3.63; S, 8.34.

Table 1. Physical Properties of the Polymers

polymer	PDOF	PFR1-S	PFR2-S	PFR3-S	PFR4-S
M_w	82 000	28 000	32 000	45 000	26 000
M_n	40 000	11 000	18 000	21 000	14 000
PDI (M_w/M_n)	2.0	2.5	1.8	2.1	1.9
polymer yield (%)	69	67	72	78	71
$T_{d5}{}^a$ (°C)	426	370	391	400	407
T_g (°C)	78	106	112	113	118

[a] Temperature resulting in 5% weight loss based on initial weight.

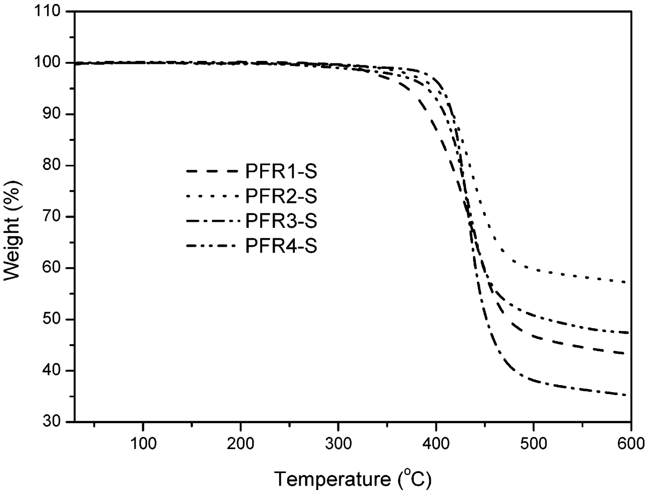


Figure 1. TGA traces of PFR1-S, PFR2-S, PFR3-S, and PFR4-S.

Poly(9,9′-dioctylfluorene) (PDOF). PDOF was synthesized using the same method as used for PFRs-S, with 0.88 g of monomer **A** (1.61 mmol) and 1.06 g of monomer **B** (1.65 mmol). The final product, a light-green polymer, was obtained after drying in vacuo, with a yield of 0.70 g (66.7%): ^{1}H NMR (CDCl$_3$, ppm) δ (ppm) aromatic; 7.80−7.75 (d, 2H), 7.60 (br, 4H), aliphatic; 2.04 (br, 4H), 1.08 (br, 20H), 0.77 (m, 10H).

Results and Discussion

Synthesis and Characterization of Polymers. All the copolymers were found to be soluble in common organic solvents. The copolymers were spin-coated onto an ITO substrate and found to produce transparent and homogeneous thin films. The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the copolymers, as determined by gel permeation chromatography using polystyrene standard, ranged from 11 000 to 21 000 (M_n) and from 26 000 to 45 000 (M_w), respectively, with polydispersity indices ranging from 1.9 to 3.1. The yields of the copolymers were from 67% to 78%. All the copolymers and the homopolymer, poly(9,9-dioctylfluorene) (PDOF), were end-capped with bromobenzene using Suzuki copolymerization. The polymerization results for the synthesized copolymers are summarized in Table 1. The thermal properties of the polymers were determined by thermal gravimetric analysis (TGA) and differencial scanning calorimetry (DSC). All the polymers were found to exhibit very good thermal stability, losing less than 5% of their weight on heating to approximately 400 °C in TGA runs under a nitrogen atmosphere, and their the glass transition temperatures (T_g) were 106−118 °C, as shown in Figure 1.

Optical and Photoluminescence Properties. Representative FT-IR spectra of the polymers are shown in Figure 2. The cyano group produces a medium-intensity, sharp band in the triple-bond region of the spectrum (2270−2210 cm^{-1}), and conjugation with double bonds or aromatic rings moves this absorption to a lower frequency. As a result, the stretch absorption band due to cyano groups in the polymers appears typically at 2210 cm^{-1}. In addition, the phenyl alkyl ether groups in polymers result in two strong bands at 1215 and 1040 cm^{-1}. Figures 3 and 4 show the UV−vis absorption and PL spectra of dilute solutions of the four comonomers (R1, R2, R3, and R4) in chloroform; the key spectral data are summarized in Table 2. The absorptions and emissions of the comonomers containing the thiophene unit are red-shifted to a greater extent than those of the corresponding comonomers containing a phenylene unit. In addition, the position of the cyano group in the vinylene linkage is an important determinant of the optical properties. In particular, the absorption maximum of R4, which appears at 465 nm, is red-shifted to a greater extent than that of R2, because the thiophene unit of R4 has a narrower energy band gap than the phenylene unit of R2. Additionally, the emission maximum of R4 (530 nm) is red-shifted to a greater extent than that of R3, because its aromatic subunits exhibit weaker torsion with the cyano group in the α-position than those of R3, which has its cyano group in the β-position. As a result, the emission maximum

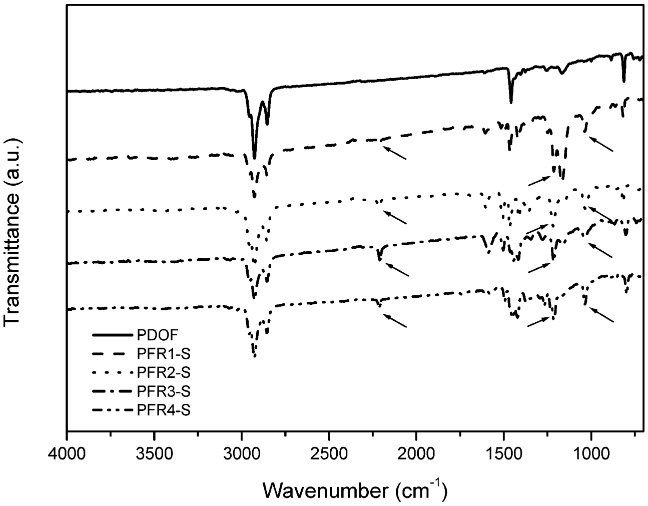


Figure 2. Infrared spectra of PDOF, PFR1-S, PFR2-S, PFR3-S, and PFR4-S coated onto NaCl plates.

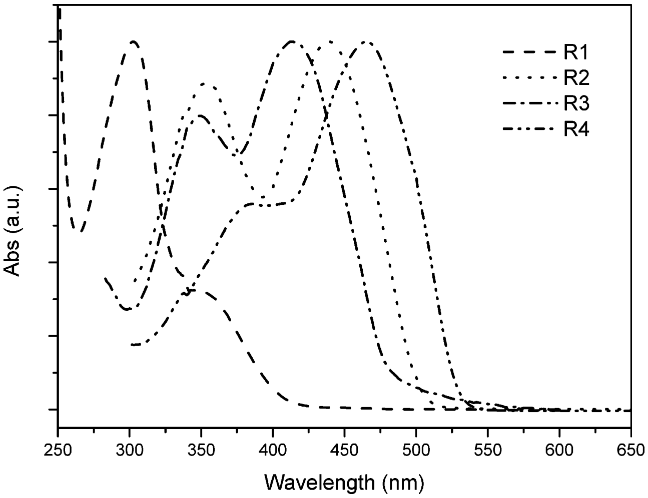


Figure 3. UV−vis absorption spectra of the monomers-R1, R2, R3, and R4 in the chloroform solutions.

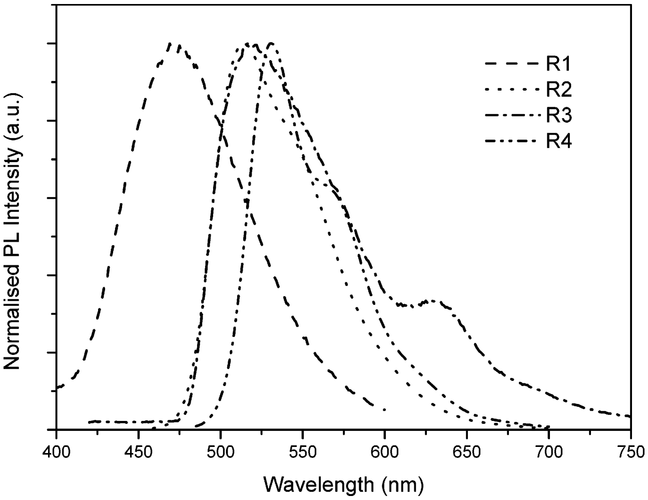


Figure 4. Photoluminescence spectra of the monomers-R1, R2, R3, and R4 in the chloroform solutions.

Table 2. Spectral Data and Energy Levels of the Polymers

	monomer, $\lambda_{\max}$ (nm)[a]		polymer, $\lambda_{\max}$ (nm)[b]			
polymer	abs	PL emission	abs	PL emission	$E_{\text{onset,ox}}$ (vs SCE, V)	HOMO[c]/ LUMO[d] (E_g[e]) (eV)
PDOF			380	420	1.41	−5.80/−2.87 (2.93)
PFR1-S	302	468	372	525	1.43	−5.82/−3.08 (2.74)
PFR2-S	439	513	468	555	1.48	−5.87/−3.59 (2.28)
PFR3-S	414	516	460	602	1.26	−5.65/−3.44 (2.21)
PFR4-S	465	530	537	674	1.20	−5.59/−3.64 (1.95)

[a] Measured in chloroform solution. [b] Measured in the thin film onto fused quartz plates. [c] Calculated from the empirical equation: $I_p(\text{HOMO}) = -(E_{\text{onset,ox}} + 4.39)$ (eV). [d] Calculated from the HOMO level and optical band gap. [e] The optical band gap, E_g, taken as the absorption onset (value in parentheses) of UV−vis spectrum of the polymer film.

of R4 is the most red-shifted of those of the four comonomers.

The UV−vis absorption spectra of the copolymers are shown in Figure 5, and the results are summarized in Table 2. The absorption spectra of the copolymers PFR1-S, PFR2-S, PFR3-S, and PFR4-S were founded to exhibit absorption maxima at 372, 468, 460, and 537 nm, respectively. The absorption maxima were founded to be shifted to longer wavelengths if a thiophene unit was present or if the cyano group was located in the α-position, as discussed above.

The film of the PDOF homopolymer exhibits PL emission maxima at 420 and 440 nm. These two strong and sharp PL peaks are markedly smaller in the PL spectra of the copolymers, as shown in Figure 6. In contrast, the emission peaks due to the comonomers dominate the copolymer PL spectra. These large shifts in PL maxima are probably due to the changing of their HOMO and LUMO energy levels, resulting in a red-shift of the PL emission maxima of the copolymers compared to that of PDOF. The largest red-shift of the PL emission maximum of the copolymer with respect to that of the homopolymer is obtained on introduction of a comonomer containing the cyano group at the α-position in the vinylene linkage and a thiophene aromatic unit. Introduction of comonomers with cyano substituents at the α-position (i.e., R2 and R4) gives rise to a red-shift in the copolymer emission compared to that of the corresponding copolymers containing comonomers with cyano substituents at the β-position (i.e., R1 and R3).[31] This effect can be explained by noting that moving the cyano groups in the vinylene linkage from the α- to the β-position causes a strong steric interaction with the alkoxy chains of the inner phenylene ring, which shortens the conjugation length of the molecules, resulting in a blue-shift in the emission.[32−34] Further, as reported by Karasz et al., the alkoxy substituent on the phenylene ring of R2 and R4 is located at the ortho position relative to the vinyl bond, which permits the resonance between the alkoxy and cyano groups to reduce the energy band gap.[35] Last, thiophene has a narrower band gap energy than phenylene, and hence the emission from copolymers containing thiophene is red-shifted still further with respect to that of the homopolymer.[36] As a result of the effects of the different substituents outlined above, the PL emission maxima of the PF-based copolymers are at 525, 555, 602, and 674 nm for PFR1-S, PFR2-S, PFR3-S, and PFR4-S, respectively. Of particular note are the PL emission

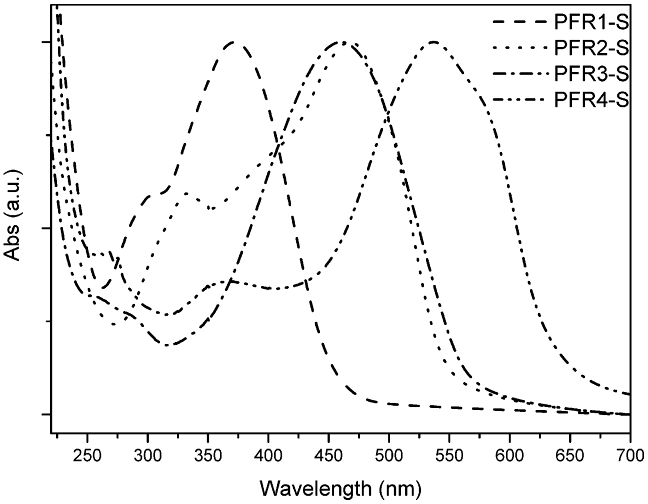


Figure 5. UV−vis absorption spectra of the thin films of PFR1-S, PFR2-S, PFR3-S, and PFR4-S coated onto fused quartz plates.

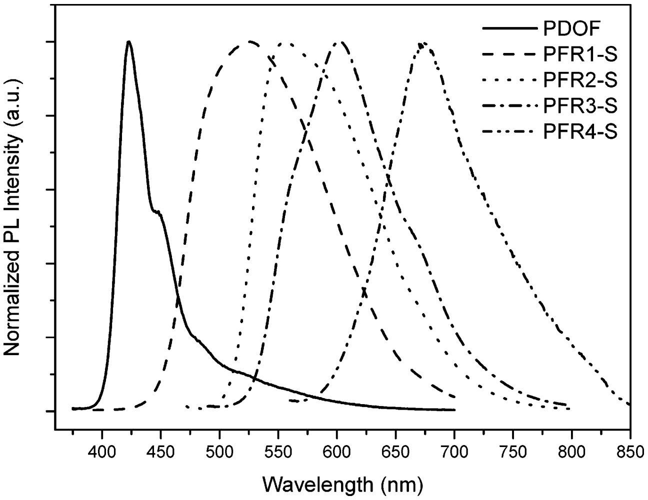


Figure 6. Photoluminescence spectra of the thin films of PDOF, PFR1-S, PFR2-S, PFR3-S, and PFR4-S coated onto fused quartz plates.

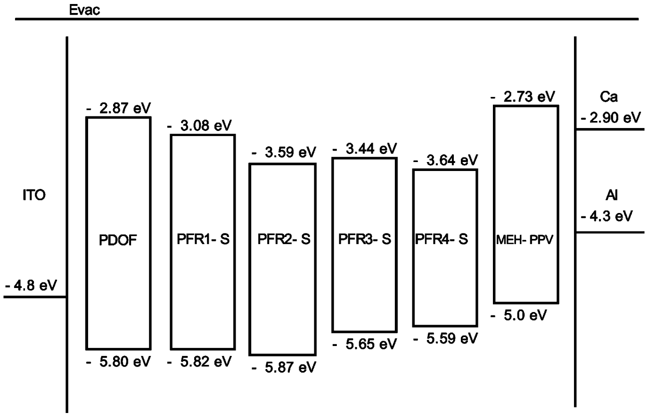


Figure 7. Energy band diagram of PFR1-S, PFR2-S, PFR3-S, PFR4-S, and MEH-PPV.

maxima of PFR4-S at 674 nm and PFR3-S at 602 nm, which suggest the strong possibility of pure red EL emission.

Electrochemical Properties of the Polymers. Cyclic voltametry (CV) was employed to investigate the redox behavior of the polymers and to estimate their HOMO and LUMO energy levels. The electrochemical processes probed by cyclic voltammetry are similar to those involved in charge injection and transport processes in LED devices.[37,38] The polymer films were coated onto Pt electrodes and scanned positively and negatively at a scan rate 50 mV/s in a 0.1 M solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in anhydrous acetonitrile. In the anodic scan, the onsets of oxidation of PFR1-S, PFR2-S, PFR3-S, and PFR4-S were found to occur at 1.43, 1.48, 1.26, and 1.20V (vs SCE), respectively, which correspond to the ionization potentials (I_p) −5.82, −5.87, −5.65, and −5.59 eV, respectively, according to the empirical relationships proposed by Leeuw et al.: ($I_p(\mathrm{HOMO}) = -(E_{\mathrm{onset,ox}} + 4.39)$ (eV), $E_a(\mathrm{LUMO}) = -(E_{\mathrm{onset,red}} + 4.39)$ (eV), where $E_{\mathrm{onset,ox}}$ and $E_{\mathrm{onset,red}}$ are the onset potentials of oxidation and reduction, repectively.[39,40] The energies of the HOMO levels of PFR1-S, PFR2-S, PFR3-S, and PFR4-S, listed in Table 2, indicate that the HOMO energy is slightly lower in copolymers in which the comonomer contains the cyano group at the α-position in the vinylene linkage and a thiophene aromatic unit. However, we were unable to record the cathodic scans for these polymers, despite many attempts. The LUMO energies of these copolymers were estimated from the optical band gaps (taken as the absorption onsets of the UV−vis spectra of the polymer films) and the HOMO energies. Using this approach, we estimate the energy band gaps of PFR1-S, PFR2-S, PFR3-S, and PFR4-S to be 2.75, 2.28, 2.21, and 1.95 eV, respectively, as shown in Figure 7. The energy band gaps of PFR3-S and PFR4-S are 2.21 and 1.95 eV, respectively, and these are narrower than the energy band gap of MEH-PPV (2.27 eV), which suggests the possibility of pure red emission. Overall, the incorporation of the electron-rich thiophene and cyano moieties leads to higher HOMO and lower LUMO levels in all of the copolymers than are found for the PDOF homopolymer.[41] All of the data, including the electrochemical band gaps, are listed in Table 2.

Electroluminescence Properties and Voltage−Luminance (*V*−*L*) Characteristics. The EL spectra of the various copolymers are similar to their PL spectra, as shown in Figure 8. The EL emission maximum is red-shifted to the greatest extent for PFR4-S, which was synthesized from the monomer containing cyano groups at the α-position and a thiophene unit. Moreover, as shown in Figure 9, PFR3-S and PFR4-S exhibit pure red emission; their chromaticity values are ($x = 0.63$, $y = 0.38$) and ($x = 0.66$, $y = 0.33$), which are almost identical to the standard red (0.66, 0.34) demanded by the NTSC.[42] Further, these systems also have low turn-on voltages, 2.5 and 4.4 V, respectively.

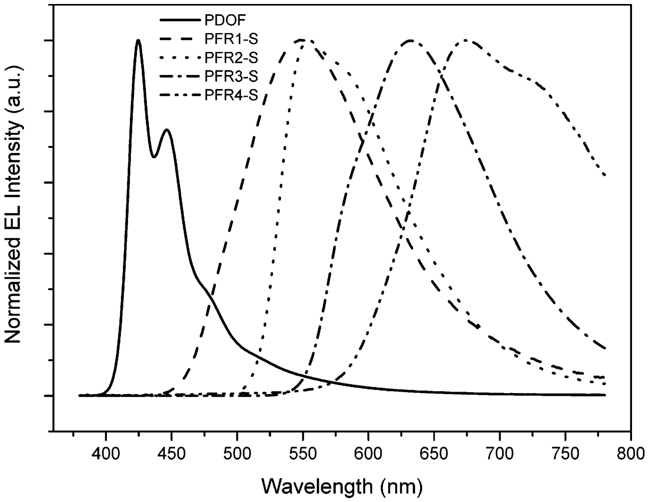


Figure 8. Electroluminescence spectra of PDOF, PFR1-S, PFR2-S, PFR3-S, and PFR4-S, which have ITO/PEDOT/polymer/Ca/Al configuration, respectively.

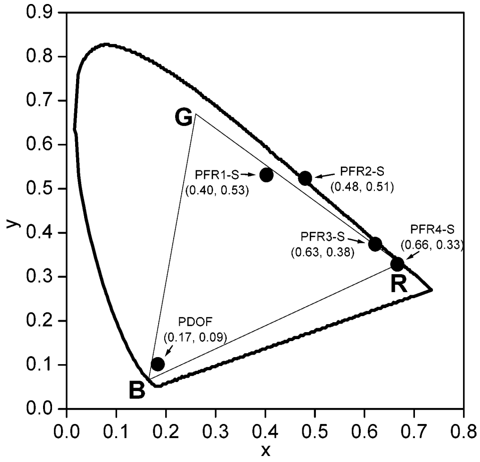


Figure 9. CIE coordinates (*x*, *y*) of PFR1-S, PFR2-S, PFR3-S, and PFR4-S (NTSC-solid line).

Figure 10 shows the voltage−luminance plots for the devices fabricated with the polymers in the configuration ITO/PEDOT/polymer/Ca/Al. The turn-on voltages of the devices ranged from about 2.5 to 6 V, and the maximum brightness of all the devices was in the range 100−3100 cd/m^2. The PFR3-S device had the highest performance, with a maximum brightness of 3100 cd/m^2 at 6 V. The external quantum efficiencies (%) (photons emitted/charges injected) of the polymers are exhibited in Figure 11. The maximum external quantum efficiency of the PFR3-S device was 0.46% at 4 V, with a brightness of 652 cd/m^2. We conclude that PFR3-S is a good candidate for use as the red-emitting layer in polymer LED devices. At present, there is no clear explanation for the different properties of the copolymers considered here; however, the present results suggest that the PFR3-S structure favors balanced electron and hole injection. We believe that further

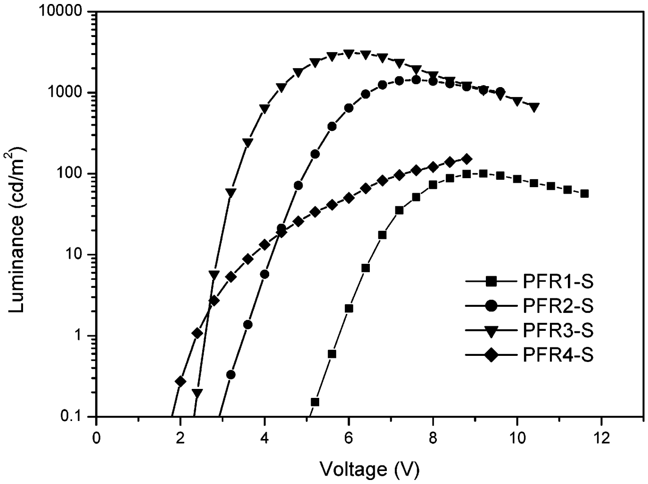


Figure 10. Voltage−luminance characteristics of PFR1-S, PFR2-S, PFR3-S, and PFR4-S, which have ITO/PEDOT/polymer/Ca/Al configuration, respectively.

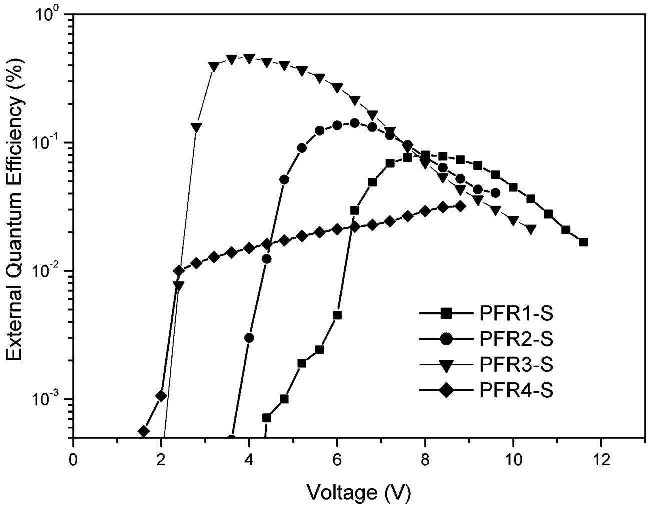


Figure 11. Voltage−external quantum efficiency characteristics of the devices.

Table 3. Performance of the Devices with the Polymers

polymer	EL emission λ_{max} (nm)	CIE coordinate (*x*, *y*)	turn-on voltage[a] (V)	max. efficiency (cd/A, %)	max. brightness (cd/m^2)
PFR1-S	547	(0.40, 0.53)	5.7	(0.20, 0.08)	100
PFR2-S	554	(0.48, 0.51)	3.5	(0.36, 0.14)	1440
PFR3-S	604	(0.63, 0.38)	2.6	(0.73, 0.46)	3100
PFR4-S	674	(0.66, 0.33)	2.4	(0.004, 0.032)	150

[a] Voltage needed for brightness of 1 cd/m^2.

improvements could be achieved in its electroluminescence characteristics by incorporating a third monomer into the polymer backbone or introducing a PVK layer into devices in order to enhance and balance the electron and hole transport of the polymer.[43] These optical properties are summarized in Table 3. A detailed study aimed at improving the efficiency of these devices and further research into the new applications in organic solar cells[44] of these narrow energy band gap polymers are currently underway.

Summary

We have systematically prepared various fluorene-based copolymers (PFR1-S, PFR2-S, PFR3-S, and PFR4-S) with the aim of achieving pure red-light emission. The UV−vis absorption maxima of these copolymers are in the range from 372 to 537 nm. Their PL and EL spectra were found to be similar to their UV−vis absorption spectra. The PL and EL maxima of the copolymers were red-shifted with respect to those of the homopolymer, poly(9,9-dioctylfluorene-2,7-diyl) (PDOF) on introduction of cyano groups located at the α-position and on changing the aromatic groups from phenylene to thiophene. The PFR3-S device exhibited a maximum brightness of about 3100 cd/m^2 and a maximum external quantum efficiency of 0.46% at 4 V, with a brightness of 652 cd/m^2. Significantly, both the PFR3-S and PFR4-S devices exhibit pure red emission, in that their chromaticity values are (x = 0.63, y = 0.38) and (x = 0.66, y = 0.33), which are almost identical to those of standard red (0.66, 0.34) demanded by the NTSC, and they also exhibit a low turn-on voltage.

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