Articles

Synthesis and Characterization of New Red-Emitting Polyfluorene Derivatives Containing Electron-Deficient 2-Pyran-4-ylidene−Malononitrile Moieties

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ABSTRACT: A novel series of red-light-emitting copolymers derived from fluorene and 2-pyran-4-ylidene−malononitrile (PM) have been synthesized through a palladium-catalyzed Suzuki coupling reaction. The polymers were characterized by FT-IR, NMR, and elemental analysis. All these polymers are completely soluble in common organic solvents, such as THF, CH_2Cl_2, $CHCl_3$, and toluene, and they have good thermal stability with onset decomposition temperature (T_d) of 406−407 °C and glass-transition temperature (T_g) of 73−186 °C. Cyclic voltanmetry studies reveal that these copolymers have low-lying LUMO energy levels ranging from −3.53 to −3.57 eV and HOMO energy levels ranging from −5.77 to −5.79 eV, which indicated that they may be promising candidates for electron-transporting or hole-blocking materials in light-emitting diodes. These polymers in thin films can emit strong red photoluminescence (PL) around 641−662 nm with the corresponding additional peaks in the range 704−712 nm upon photoexcitation. Double-layer LEDs fabricated with the configuration of ITO/PEDOT/polymer/Ba/Al can emit red light with external quantum efficiencies of 0.21−0.38%. Preliminary electroluminescent (EL) results show that these polymers are novel promising candidates for red emissive materials in polymer light-emitting diodes.

Introduction

Since the initial report of polymer light-emitting diodes (PLEDs) based on poly(*p*-phenylenevinylene) (PPV) by the Cambridge group, conjugated polymers have received considerable attention due to their potential application in patterned light sources and flat panel displays.[1−5] In the past decade, many conjugated polymers, such as poly(*p*-phenylene)s, poly(phenylenevinylene)s, poly(oxadiazole)s, poly[2,7-(9,9-dialkylfluorene)]s, poly(3,6-carbazole)s, and poly(2,7-carbazole)s, have been synthesized in order to obtain three primary (RGB) colors.[6−16] Among these polymers, polyfluorene 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 processabililty of polymers without significantly increasing the steric interactions in the polymer backbone.[17] As a result, polyfluorene and its derivatives have emerged as the most promising light-emitting materials due to their emission at wavelength spanning the entire visible spectrum, high fluorescence efficiency, and good thermal stability.[18−29] Indeed, many blue- and green-light-emitting polyfluorene derivatives have been reported, and recently, red-light-emitting diodes, presumably made from random copolymers based on fluorene and 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole, have been briefly described.[30,31] Other red-emitting materials have also been reported from energy transfer between emissive polymers and several dyes, such as tetraphenylporphyrin or europium complexes.[28,32−34] However, most of these red-emitting polymers synthesized to date have low electron affinity. It is established that high quantum efficiency PLEDs can be obtained by achieving both efficient charge injection and balanced mobility of both charge carriers inside the emissive materials. In general, many light-emitting polymers inject and transport holes more efficiently than electrons due to their inherent richness of π-electrons. So it is a very challenging task to develop new red-light-emitting polymers with high electron affinitiy, especially for polyfluorene derivatives.

Eastman Kodak's dyes (DCM class) are well-known as low molecular weight red-emitting materials, which can be synthesized by a relatively simple procedure.[35−38] All the DCM class red dyes contain 2-pyran-4-ylidene−malononitrile (PM) derivatives as electron acceptor. In most of the studies, these dyes were usually doped in a layer of Alq_3, which was used as the electron-transporting layer (ETL) as well as the host. But the Alq_3-doped

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devices are either low in efficiency (at high dopant concentrations) or poor in color purity (at low dopant concentrations). The low efficiency at high dopant concentrations is due to the effect of aggregation and concentration quenching, which suppress, broaden, and red shift the EL spectra. However, at low dopant concentrations, the energy transfer from Alq_3 to dopant is not complete, and the red emission from dopant is usually mixed with the green emission from Alq_3 leading to an orange emission.

In this contribution, we designed and synthesized a novel series of fluorene-based red-light-emitting polymers containing a 2-pyran-4-ylidene−malononitrile (PM) unit in the main chain. These polymers possess high molecular weight, good solubility, excellent thermal stability, low-lying lowest unoccupied molecular orbital (LUMO) energy level, and good red-emitting property with improved electron affinity. The chemical doping method by introducing a PM moiety into polyfluorene main chain might enable these polymer materials to be used as red-emitting materials with improved device performance for full color (RGB) displays.

Experimental Section

Instrumentation. ^{1}H NMR and ^{13}C NMR spectra were performed on a Varian Unity INOVA-400. FT-IR spectra were recorded on a Perkin-Elmer 2000 spectrometer with KBr pellets. Elemental analysis studies were carried out with a Carlo Erba 116 elemental analyzer. UV−vis spectra in solutions and thin films were taken on a Shimadzu UV2100 UV−vis recording spectrophotometer. Photoluminescence (PL) spectra of the polymers in solutions and thin films were measured on a Hitachi 850 fluorescence spectrophotometer. The PL quantum yields in neat films were measured in an integrating sphere at room temperature. Thermal gravimetric analysis (TGA) measurements were performed on Perkin-Elmer series 7 thermal analysis system under N_2 at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were performed on Perkin-Elmer DSC 7 under N_2 at a heating rate of 10 °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 25 °C, using THF as the eluent and standard polystyrene as the reference. The cyclic voltammograms were recorded on a computer-controlled EG&G potential/galvanostat model 283. The thickness of films was measured by a Dektak surface profilometer.

Materials. All the chemicals were purchased from Aldrich and Acros Chemical Co. and were used without any further purification. All the solvents such as toluene, piperidine, and THF were dried with appropriate drying agents, then distilled under reduced pressure, and stored over 4 Å molecular sieve. The catalyst was tetrakis(triphenylphosphine)palladium Pd-$(PPh_3)_4$,[39] (2,6-dimethyl-4*H*-pyran-4-ylidine)propanedinitrile was synthesized from 2,6-dimethyl-4-pyrone as a starting material by the method of Woods,[40] and 9,9-dihexylfluorene-2,7-bis(trimethylene boronates) (**4**)[23] were synthesized using 2,7-dibromofluorene according to the previous literature.

2-{2,6-Bis[2-(4-bromophenyl)vinyl]pyran-4-ylidene}−Malononitrile (1). A mixture of 4-bromobenzaldehyde (1.85 g, 10.0 mmol), 2-(2,6-dimethylpyran-4-ylidene)−malononitrile (0.861 g, 5.00 mmol), piperidine (10 drops), and freshly distilled acetonitrile (10 mL) were refluxed under argon for 24 h. The reaction mixture was cooled to room temperature. The yellow precipitate was filtered and washed with 50 mL of acetonitrile. The crude product was purified by recrystallization from methanol to afford compound **1** as a yellow solid with a yield of 75%; mp: 290−291 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.60−7.58 (d, 4H), 7.47−7.43 (m, 6H), 6.79−6.73 (t, 4H). Anal. Calcd for $C_{24}H_{14}Br_2N_2O$: C, 56.95; H, 2.79; N, 5.53. Found: C, 56.91; H, 2.77; N, 5.54.

2-Hexyloxyl-5-bromobenzaldehyde (2a). A mixture of 2-hydroxyl-5-bromobenzaldehyde (7.9 g, 0.0393 mol), 1-bromohexane (6.5 g, 0.0393 mol), K_2CO_3 (16.4 g, 119 mol), and DMF (35 mL) was heated at 100 °C overnight under argon. The mixture was filtered, and DMF was removed under a reduced pressure. The crude product was purified by a silica gel column chromatography. Compound **2a** was obtained as light yellow oil with a yield of 90%. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 10.41 (s, 1H), 7.92 (d, 1H), 7.62−7.59 (m, 1H), 6.95−6.87 (d, 1H), 4.08−4.04 (t, 2H), 1.88−0.89 (m, 11H). Anal. Calcd for $C_{13}H_{17}O_2Br$: C, 54.75; H, 6.01. Found: C, 54.71; H, 6.03.

2-Dodecyloxyl-5-bromobenzaldehyde (2b). Compound **2b** was obtained as a white solid with a yield of 92% from the reaction of 2-hydroxyl-5-bromobenzaldehyde with 1-bromododecane according to the procedure described for **2a**; mp: 39.5−40.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 10.42 (s, 1H), 7.92 (d, 1H), 7.62−7.59 (m, 1H), 6.89−6.87 (d, 1H), 4.07−4.04 (t, 2H), 1.88−0.87 (m, 23H). Anal. Calcd for $C_{19}H_{29}O_2Br$: C, 61.79; H, 7.91. Found: C, 61.72; H, 7.93.

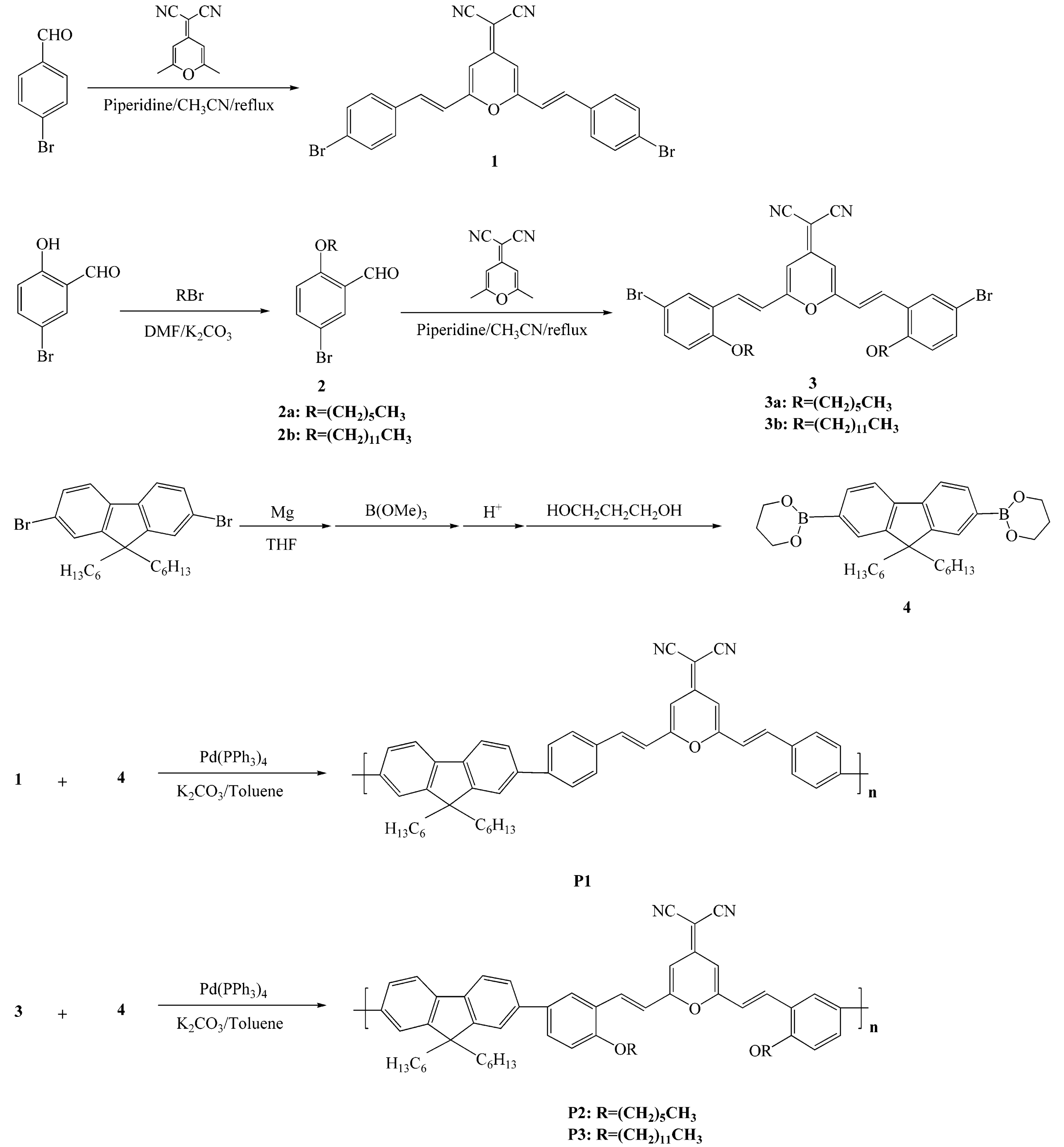
2-{2,6-Bis[2-(2-hexyloxyl-5-bromophenyl)vinyl]pyran-4-ylidene}−Malononitrile (3a). Compound **3a** was obtained as a yellow solid with a yield of 70% from reaction of **2a** with 2-(2,6-dimethylpyran-4-ylidene)−malononitrile according to the procedure described for **1**; mp: 166−167 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.75−7.62 (m, 4H), 7.46−7.43 (m, 2H), 6.98−6.68 (m, 6H), 4.09−4.06 (t, 4H), 1.91−0.81 (m, 22H). Anal. Calcd for $C_{36}H_{38}Br_2N_2O_3$: C, 61.20; H, 5.42; N, 3.96. Found: C, 61.15; H, 5.40; N, 3.98.

2-{2,6-Bis[2-(2-dodecyloxyl-5-bromophenyl)vinyl]pyran-4-ylidene}−Malononitrile (3b). Compound **3b** was obtained as a yellow solid with a yield of 65% from reaction of **2b** with 2-(2,6-dimethylpyran-4-ylidene)−malononitrile according to the procedure described for **1**; mp 112−113 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.74−7.60 (m, 4H), 7.44−7.41 (m, 2H), 6.95−6.65 (m, 6H), 4.07−4.03 (t, 4H), 1.88−0.85 (m, 46H). Anal. Calcd for $C_{48}H_{62}Br_2N_2O_3$: C, 65.90; H, 7.14; N, 3.20. Found: C, 65.86; H, 7.12; N, 3.23.

Poly{(9,9-dihexyl-9*H*-fluorene-2,7-ylene)-*alt*-(2-{2,6-bis[2-(4-phenylene)vinyl]pyran-4-ylidene}−malononitrile)} (P1). To a mixture of **4** (502.3 mg, 1.0 mmol), **1** (506.2 mg, 1.0 mmol), and $Pd(PPh_3)_4$ (12 mg, 1.0 mol %) was added a mixture of toluene (5 mL) and aqueous 2 M potassium carbonate (5 mL). The mixture was vigorously stirred at 85−90 °C for 48 h. After the mixture was cooled to room temperature, it was poured into 200 mL of methanol and deionized water (10:1). A fibrous solid was obtained by filtration; the solid was washed with methanol, water, and then methanol. After washing for 24 h in a Soxhlet apparatus with acetone, the resulting polymer P1 was obtained as a red solid with a yield of 80% after drying under vacuum. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.85−7.47 (m, 14H), 7.38−7.36 (m, 2H), 6.89−6.77 (m, 4H), 2.07 (br, 4H), 1.26−0.75 (m, 22H). ^{13}C NMR ($CDCl_3$, 400 MHz, δ/ppm): 157.01, 150.73, 148.67, 148.41, 148.13, 141.82, 139.35, 137.85, 136.09, 134.57, 134.31, 134.03, 132.53, 130.66, 127.49, 127.31, 126.31, 125.79, 124.95, 122.48, 122.24, 121.95, 120.01, 119.20, 117.29, 113.92, 105.86, 54.19, 38.93, 30.00, 28.23, 22.56, 21.10, 12.54. FTIR (KBr pellet, cm^{-1}): 3057, 3027, 2926, 2853, 2209, 1643, 1605, 1548, 1500, 1465, 1416, 1330, 1260, 1203, 1160, 1179, 1097, 1019, 943, 809, 756, 698, 536. Anal. Calcd for $(C_{49}H_{46}N_2O)_n$: C, 86.69; H, 6.83; N, 4.13. Found: C, 85.94; H, 6.95; N, 4.19.

Poly{(9,9-dihelxyl-9*H*-fluorene-2,7-ylene)-*alt*-(2-{2,6-bis[2-(2-hexyloxyl-5-phenylene)vinyl]pyran-4-ylidene}−Malononitrile)} (P2). Polymer P2 was obtained as a red solid with a yield of 84% from the reaction of **3a** with **4** according to the procedure described for the synthesis of polymer P1. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.01−7.46 (m, 12H), 7.38−7.34 (m, 2H), 7.11−6.71 (m, 4H), 4.14−4.10 (m, 4H), 2.05 (br, 4H), 1.90−0.67 (m, 44H). ^{13}C NMR ($CDCl_3$, 400 MHz, δ/ppm): 158.90, 157.33, 156.07, 151.80, 151.56, 139.90, 138.96, 134.51, 132.04, 131.95, 130.28, 128.76, 128.66, 128.54, 127.41, 127.15, 125.68, 124.14, 121.02, 120.11, 119.64, 115.37, 112.70, 106.99, 68.96, 55.38, 40.41, 31.46, 31.43, 29.63, 29.17, 29.08, 28.93, 25.89, 23.81, 22.81, 13.98, 13.92. FTIR (KBr pellet, cm^{-1}): 3507, 3028, 2925, 2853, 2209, 1640, 1609, 1544, 1506, 1463,

Scheme 1. Synthetic Route to the Monomers and Polymers



1417, 1321, 1247, 1175, 1147, 1120, 1018, 967, 944, 861, 809, 696, 536. Anal. Calcd for $(C_{61}H_{70}N_2O_3)_n$: C, 83.33; H, 8.03; N, 3.19. Found: C, 82.57; H, 8.11; N, 3.23.

Poly{(9,9-dihexyl-9*H*-fluorene-2,7-ylene)-*alt*-(2-{2,6-bis[2-(2-dodecyloxyl-5-phenylene)vinyl]pyran-4-ylidene}−Malononitrile)} (P3). Polymer P3 was obtained as a red solid with a yield of 85% from the reaction of **3b** with **4** according to the procedure described for the synthesis of polymer P1. ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 8.02−7.46 (m, 12H), 7.38−7.36 (m, 2H), 7.12−6.71 (m, 4H), 4.14−4.10 (m, 4H), 2.04 (br, 4H), 1.89−0.67 (m, 68H). ^{13}C NMR (CDCl$_3$, 400 MHz, δ/ppm): 158.86, 158.36, 157.29, 156.09, 151.85, 151.75, 151.52, 141.59, 140.06, 139.87, 138.90, 134.42, 134.13, 132.93, 132.09, 132.02, 131.51, 130.25, 128.75, 128.69, 128.54, 127.13, 126.04, 125.65, 124.05, 121.51, 120.93, 120.07, 119.59, 115.41, 112.62, 107.03, 68.90, 59.21, 55.35, 55.28, 40.41, 31.90, 31.43, 29.63, 29.60, 29.56, 29.33, 29.17, 29.05, 28.95, 26.21, 26.10, 23.79, 22.66, 22.52, 14.10, 14.00. FTIR (KBr pellet, cm^{-1}): 3059, 3029, 2925, 2852, 2209, 1640, 1611, 1545, 1505, 1462, 1418, 1249, 1179, 1120, 1017, 968, 943, 861, 811, 752, 699, 536. Anal. Calcd for $(C_{73}H_{94}N_2O_3)_n$: C, 83.70; H, 9.04; N, 2.67. Found: C, 82.94; H, 9.13; N, 2.72.

EL Device Fabrications. For the fabrication of the devices, glass substrates coated with indium−tin oxide (ITO) with a sheet resistance of 100 Ω/□ (CSG Co. Ltd.) were cleaned subsequently in ultrasonic baths of ionic detergent water, acetone, and anhydrous molecules. A thin film layer of PEDOT (Batron-P 4083) (90 nm) [(PEDOT is poly(ethylenedioxythiophene) doped with poly(styrenesulfonic acid)] and the polymers (80 nm) (from a 10 mg mL^{-1} of the polymers in toluene solution) were spin-coated on ITO at 1500 rpm for 30 s in turn; after that a thin layer of Ba (4 nm)/Al (170 mn) was deposited on the polymer film by thermal evaporation under a vacuum of 10^{-6} Torr. The active area of the device was about 0.15 cm^2. The applied dc bias voltages for EL devices were in a forward direction (ITO, positive; Ba/Al, negative). The

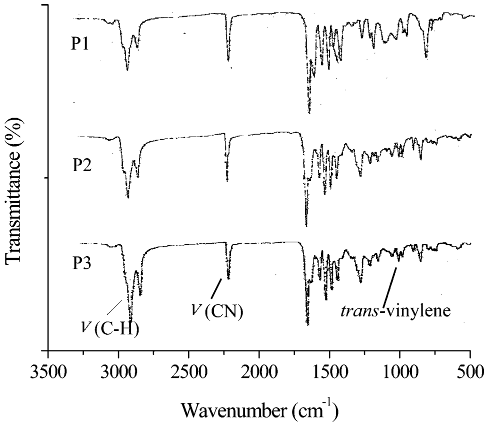


Figure 1. FT-IR spectra of the polymers.

Table 1. Molecular Weights and Thermal Properties of the Polymers

polymers	yield (%)	M_w[a]	M_w/M_n[a]	T_d[b] (°C)	T_g[c] (°C)
P1	80	35 700	1.52	407	186
P2	84	38 200	1.58	406	119
P3	85	33 400	1.61	406	73

[a] Molecular weights and polydispersity indices determined by GPC in THF using polystyrene as the standard. [b] Onset decomposition temperature measured by TGA under N_2. [c] Glass transition temperature measured by DSC under N_2.

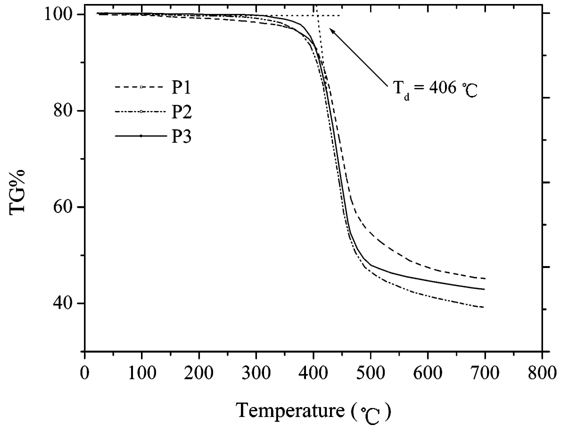


Figure 2. Thermal gravimetric analysis (TGA) curves of the polymers (under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}). The representative T_d of P3 is given in the figure to be 406 °C.

Table 2. Absorption and Emission Data for the Polymers

polymer	absorption (film) λ_{max} (nm)	band gap (eV)	PL (film) λ_{max} (nm)	fwhm[a] (nm)	η_{PL} (%)
P1	352, 457	2.22	662, 712	139	7
P2	345, 435	2.32	641, 704	148	5
P3	347, 438	2.30	641, 705	150	4

[a] Full width at half-maximum of the film PL spectra.

current−voltage characteristic was measured on a voltmeter and an amperometer. The EL efficiency and brightness measurements were carried out with a calibrated silicon photodiode. All the measurements of the EL devices were carried out in air at room temperature.

Results and Discussion

Synthesis and Characterization. The method for preparing the monomers and the polymers is outlined in Scheme 1. The monomers **1** and **3** were prepared through Knoevenagel condensation between 2-(2,6-dimethypyran-4-ylidene)−malomonitrile and the corresponding bromoarylaldehyde in a yield of over 65%. The monomer **4**, 9,9-dihexylfluorene-2,7-bis(trimethylene boronate), was prepared using 2,7-dibromofluorene following a literature procedure.[23] The polymerization reaction conducted by the well-known palladium-catalyzed Suzuki coupling reaction between compounds **1** (or **3**) and **4** in toluene yielded a dark red solid of above polymers in a yield of over 80%. The chemical structures of the polymers were confirmed by NMR, FTIR, and elemental analysis. All these polymers readily dissolve in solvents, such as THF, CH_2Cl_2, $CHCl_3$, and toluene. Uniform and transparent films on substrates can be obtained by spin-casting the solutions in toluene (1%) at a spin rate of 1500 rpm. The good solubility of these polymers may result from the hexyl side chain attached to the fluorene moiety and *n*-alkyl side chain linked to the PM unit. Figure 1 shows the FT-IR spectra. The absorption peak at about 2925 cm^{-1} corresponds to C−H stretching vibration of saturated hydrocarbon, the absorption peak at about 2209 cm^{-1} corresponds to −CN stretching vibration, and the weak absorption peaks at about 3028 cm^{-1} and relatively strong absorption at around 967 cm^{-1} correspond to C−H stretching and out-of-plane bending motions of *trans*-vinylene, respectively.[41,42] Their molecular weights were determined by gel permeation chromatography (GPC) using polystyrene as the standard. The results are listed in Table 1. These copolymers have weight-average molecular weights (M_w) of 33 400−38 200 with polydispersity indices (M_w/M_n) of 1.52−1.61. The thermal properties of the polymers were determined by TGA (heating at 10 °C min^{-1} in nitrogen) and DSC measurements. Figure 2 gives the thermogravimetric curves of the polymers. All these polymers show good thermal stability with the onset decomposition temperature (T_d) of 406−407 °C (shown in Figure 2) under nitrogen, and no weight loss was observed at lower temperatures. After the temperature increasing above 400 °C, the curves fall rapidly, indicating the decomposition of the polymer backbones. Above 600 °C, there are only 33−40 wt % residues, which are produced by charring during heating. The glass-transition temperatures (T_g) of the polymers range from 73 to 186 °C. Compared with P1 and P2, polymer P3 has a lower T_g (°C) because of two long length dodecyoxyl linked to PM units. However, their T_g values are higher than those of poly(9,9-dihexylfluorene) (PHF) (~55 °C)[43] and poly(9,9-dioctylfluorene) (POF) (~51 °C),[44] in which each repeating fluorene unit contained two flexible *n*-hexyl or *n*-octyl chains at C-9. It is obvious that the incorporation of a PM unit into the main chain can increase T_g of polyfluorenes. This is very important for such types of polymers used as emissive materials in PLEDs.[45]

Photophysical Properties. The photophysical characteristics of the polymers were investigated in the solid films. The absorption and emission spectral data for the polymers in the films casting from solution in toluene are summarized in Table 2. As shown in Figure 3, the absorption spectra of the polymers obtained from the thin films, P2 and P3, possess very similar absorption spectra maximum peaks at 345 and 347 nm with the corresponding additional absorption peaks at 435 and 438 nm, attributed to $\pi-\pi^*$ transitions of the polymers. However, P1 shows the different absorption spectrum maximum peak at 457 nm with an additional peak at 352 nm. Compared with the spectra of P2 and P3, the difference shape and red-shifted maximum peak may

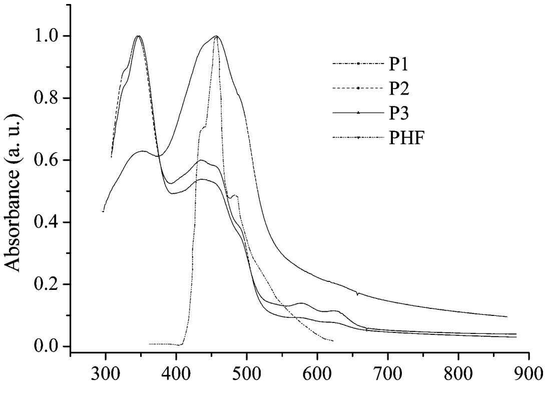


Figure 3. UV−vis absorption spectra of the polymer thin films and PL spectrum of poly(9,9-dihexylfluorene) (PHF).

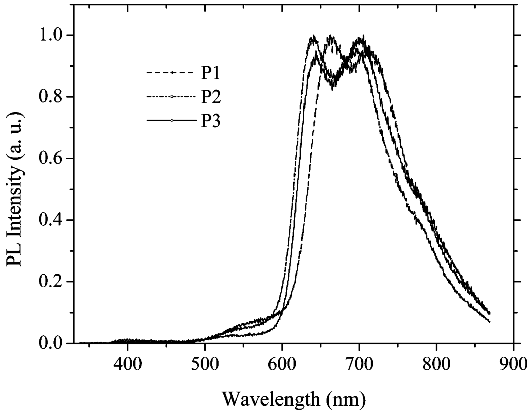


Figure 4. Photoluminescence (PL) spectra of the polymer thin films.

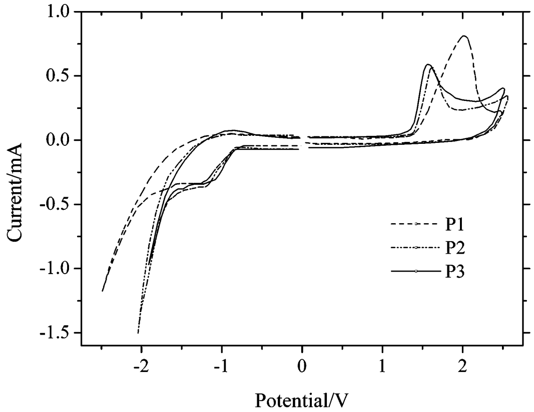


Figure 5. Cyclic voltammograms of the polymers recorded from thin films coated onto platinum plate electrodes in an electrolyte solution of Bu_4NClO_4 (0.10 M) in acetonitrile with a reference electrode of $Ag/AgNO_3$ (0.10 M) at room temperature. Scan rate = 50 mV s^{-1}.

Table 3. Electrochemical Potentials and Energy Levels of the Polymers

polymer	$[E^a_{\text{onset}}]^{\text{red}}$ (V)	$[E^b_{\text{onset}}]^{\text{ox}}$ (V)	LUMO[c] (eV)	HOMO[d] (eV)	E_g[e] (eV)
P1	−0.83	1.38	−3.57	−5.78	2.21
P2	−0.86	1.39	−3.54	−5.79	2.25
P3	−0.87	1.37	−3.53	−5.77	2.24

[a] Onset reduction potentials measured by cyclic voltammetry. [b] Onset oxidation potential measured by cyclic voltammetry. [c] Calculated from the reduction potentials. [d] Calculated from the oxidation potentials. [e] Calculated from the LUMO and HOMO energy levels.

be caused by the different structure with extended length of π-conjugation. The absorption onset wavelengths of the polymers were 534−558 nm, which correspond to band gaps of 2.22−2.32 eV.

The PL spectra of these polymers in thin films are shown in Figure 4. The polymer films with the broad band red PL emission exhibit similar vibronic features with maximum emission peaks around 641−662 and 704−712 nm. No typical emission from fluorene (at about 450 nm) was observed, which implied that the emission of fluorene was quenched in these polymers. As shown in Figure 3, there is a entire or almost entire overlap between the emission spectrum of poly(9,9-dihexylfluorene) (PHF) and the absorption spectra of these polymers. So the results indicate that there is a possibility of either the charge transfer between a fluorene segment and electron-deficient PM segment of the polymers or the efficient Föster energy transfer between different polymer chains. Compared with P2 and P3, P1 also exhibits the red-shifted PL spectrum due to the longer length of π-conjugation. The absolute PL quantum yields of the neat polymer films were measured to be about 4−7% in an integrating sphere at room temperature in air using a HeCd laser line of 325 nm as the excitation source according to the procedure described by Greenham et al.[46]

Electrochemical Properties. Cyclic voltammetry (CV) was employed to investigate the electrochemical behavior of the polymers as well as estimate the HOMO and LUMO energy levels of the materials. The polymer films deposited on a platinum plate electrode were scanned both positively and negatively separately in 0.10 M tetrabutylammonium perchlorate (Bu_4NClO_4) in anhydrous acetonitrile by using platinum wire as a counter electrode and $Ag/AgNO_3$ (0.10 M) as reference electrode. As shown in Figure 5, the onset potentials for oxidation were observed to be 1.38, 1.39, and 1.37 V for P1, P2, and P3, respectively. On the other hand, the onset potentials for reduction were −0.83, −0.86, and −0.87 V, respectively. From the onset potentials of the oxidation and reduction processes, the band gaps of the polymers were estimated to be 2.21, 2.25, and 2.24 eV for polymer P1, P2, and P3. The values are quite close to those obtained by the optical method. According to the equations[47,48] $IP = -([E_{\text{onset}}]^{\text{ox}} + 4.4)$ eV and $EA = -([E_{\text{onset}}]^{\text{red}} + 4.4)$ eV, where $[E_{\text{onset}}]^{\text{ox}}$ and $[E_{\text{onset}}]^{\text{red}}$ are the onset potentials for oxidation and reduction of the polymer vs the reference electrode, the LUMO and HOMO of the polymers were estimated to be −3.57, −3.54, and −3.53 eV and −5.78, −5.79, and −5.77 eV for P1, P2, and P3, respectively. The electrochemical data of the polymers are summarized in Table 3. From Table 3, we find that the HOMO and LUMO energy levels of these polymers are quite similar, and all the polymers show much high electron affinity due to the incorporation of the electron-deficient PM moiety.

Electroluminescence Properties of LED Devices. Double-layer LED devices based on the three polymers with the configuration of ITO/PEDOT/polymer/Ba/Al were fabricated. Poly(3,4-ethylenedionythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) (Batron-P 4083) with a thickness of 90 nm was used as the hole injection/transporting layer. A thin layer of Ba (4 nm) was employed as the cathode because it normally results in devices with longer lifetime due to its larger atomic size and mass as compared with Ca or Mg.[49] The Ba layer was coated with a 170 nm layer of Al. The

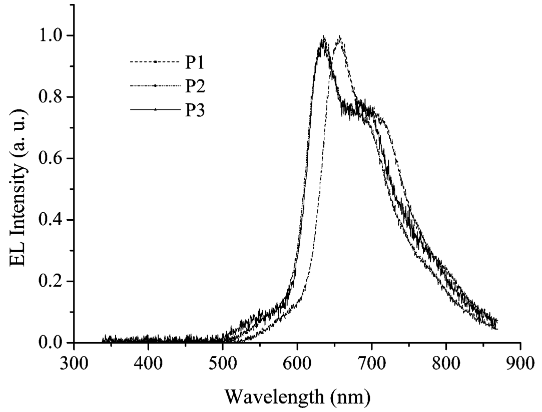


Figure 6. EL spectra of the devices with the configuration of ITO/PEDOT/polymer/Ba/Al.

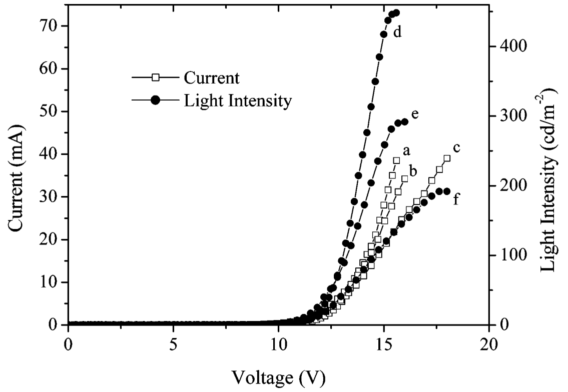


Figure 7. Current−voltage ($I-V$) and luminance−voltage ($L-V$) curves of an ITO/PEDOT/polymer/Ba/Al. The curves of a and d were recorded from the device based on P1, b and e were from the device based on P2, and c and f were from the device based on P3.

thickness of the emissive layer is around 80 nm. The electroluminescence spectra are displayed in Figure 6, in which P1, P2, and P3 follow the traces of their PL spectra, with peaks at 657, 636, and 638 nm with shoulders at 702, 694, and 696 nm, respectively. The similarity of the PL and EL spectra indicates that same excitations are involved in both cases. Figure 7 compares the $I-V-L$ curves of the double-layer devices. The devices show a good diode behavior: under the forward bias (a positive voltage applied to the ITO electrode), the current increases exponentially, with an increase in the applied voltage after exceeding the turn-on voltage. In contrast, under reverse bias, no obvious increase in the current density is observed when the applied voltage is increased. As shown in Figure 7, the red emission (from the ITO/PEDOT/P1/Ba/Al device) starts at about 10.4 V and reaches a brightness of 449 cd m^{-2} at a bias of 15.6 V. The EL external quantum efficiency of 0.27% can be obtained at a bias voltage of 13.8 V and a current density of 84 mA cm^{-2}. The devices based on polymers P2 and P3 can also emit red light, which start at about 11.7, 11.5 V and reach the brightness of 292, 192 cd m^{-2} at the bias of 16, 18 V, respectively. The EL external quantum efficiencies of ITO/PEDOT/P2/Ba/Al and ITO/PEDOT/P3/Ba/Al were measured to be about 0.38% (at 13.8 V with a current density of 78 mA cm^{-2}) and 0.21% (at 14 V with a current density of 77 mA cm^{-2}). The preliminary electrolunimescent results show these polymers are novel candidates for red emissive materials in polymer light-emitting diodes. So further improvements could be expected after optimization.

Conclusion

A novel class of conjugated fluorene-based polymers containing a 2-pyran-4-ylidene−malononitrile (PM) moiety in the main chain were designed and synthesized through the palladium-catalyzed Suzuki coupling reaction. The resulting polymers show excellent thermal stability and good red emission properties. The introduction of a PM moiety into the polyfluorene main chain can improve the electron affinity of this type of polymer. Double-layer LEDs were fabricated using these polymers as emitting layers. These devices show red emission with maximum external quantum efficiencies of 0.21−0.38%. The preliminary EL results show that these polymers are novel candidates for red emissive materials in polymer LEDS. Intensive studies on the electroluminescent and electron-transporting/hole-blocking properties of these polymers in LED devices are in progress.

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