

Novel Efficient Light-Emitting Polyfluorene Derivatives Modified by Electron-Deficient Moieties with Nonlinear Structure

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Two novel fluorene-based copolymers (**PFSD** and **PFMD**) containing squaric acid or maleimide unit in the main chain were synthesized in good yields by Suzuki coupling reaction. The resulting polymers possess excellent thermal stability, high electron affinity and high photoluminescence (PL) quantum yields. They can fluoresce in yellow-light range due to either the charge transfer between a fluorene segment and an electron-deficient containing squaric acid/maleimide segment of the polymers or the Förster energy transfer between different polymer chains. The results from PL measurements of the isothermally heated polymer thin films show that the commonly observed aggregate excimer formation in polyfluorenes is very effectively suppressed in these two polymers due to the nonlinear structures of maleimide and squaric acid moieties. Double-layer polymer light-emitting diodes (PLED) were fabricated using the resulting polymers as the emitting layers and Ba or Mg : Ag ($V : V=10 : 1$) as cathodes. All the devices show bright yellow emission (562—579 nm) with different maximum external quantum efficiencies (0.006%—1.13%). Compared with the other devices, indium-tin oxide (ITO)/polyethylenedioxythiophene (PEDOT) : polystyrene sulfonic acid (PSS)/**PFMD**/Mg : Ag has the higher maximum external quantum efficiency of 1.13% at 564 cd/m² with a bias of 8.4 V.

Keywords Light-emitting diode, polyfluorene, electron-deficient, aggregate excimer, external quantum efficiency

Introduction

Since the first report on polymer light-emitting diodes¹ (PLED) in 1990, great progress has been made in the development of new conjugated polymers and exploration of their application in displays.² Among these polymers, polyfluorenes (PF) are regarded as the very promising candidates for PLED due to their good thermal and chemical stability, high photoluminescence (PL) quantum efficiencies, and high hole mobilities.³ However, these wide band gap materials have a relatively low electron affinity, which makes electron injection rather difficult with the use of conventional cathode materials.⁴ The electron-transporting properties of polyfluorenes (PF) can be improved by incorporating electron-deficient comonomers, such as benzothiadiazole, oxadiazole, quinoxaline and cyano-substituted olefins into the polymer main chain.⁵ These moieties can elongate conjugation length and improve charge transfer of polyfluorenes to realize their color-tunability. Another common problem of polyfluorenes is the long wave

length tail in the emission spectra, resulting from the formation of aggregates and/or the formation of inter-chain excimers.⁶ So it is a very challenging task to develop new polyfluorenes and their derivatives to resolve above problems. Herein, the synthesis and characterization of two novel fluorene-based alternating copolymer containing maleimide or squaric acid moiety in the main chain are reported. Our motivation for synthesis of the copolymers can be explained as follows. First, because PF has been proven to be a better hole-transporting polymer, the incorporation of an electron-deficient squaric acid or maleimide unit will increase electron affinity and transporting properties of these two polymers. Second, squaric acid and maleimide have nonlinear *trans*-vinyl group,⁷ so their incorporation will change the linear structure of PF to avoid the formation of excimers in solid state. Furthermore, the incorporation of squaric acid or maleimide unit will increase the glass transition temperature (T_g) and thermal stability of PF due to their rigidity of structures.

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Experimental

Materials

All the chemicals were purchased from Aldrich and Acros chemical company and used without any further purification. All the solvents such as toluene and triethylamine were dried with appropriate drying agents, then distilled under reduced pressure, and stored over 0.4 nm molecular sieve. The catalyst tetrakis(triphenylphosphine)palladium [Pd(PPh₃)₄],⁸ 3,4-bis(4-bromophenyl)-3-cyclobutene-1,2-dione (**1**),⁹ 3,4-bis(4-bromophenyl)-2,5-furandione (**2**),⁷ and 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) (**4**)¹⁰ were synthesized according to the reported methods.

1,2-Bis(4-bromophenyl)-*N-n*-octyl maleimide (**3**)

A mixture of **2** (2.04 g, 5 mmol), *n*-octylamine (0.67 g, 5.2 mmol) and triethylamine (Et₃N, catalytic amount) in toluene (40 mL) was refluxed for 24 h. Water was removed from the mixture by a Dean stark trap. Then toluene was removed under a reduced pressure. The residue was purified by a silica gel column chromatography (eluent: CH₂Cl₂). Thus, compound **3** was obtained as yellow powders with a yield of 88%, m.p. 88 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 7.49—7.53 (m, 4H), 7.33—7.37 (m, 4H), 3.63 (t, *J*=7.2 Hz, 2H), 0.86—1.68 (m, 15H). Anal. calcd for C₂₄H₂₅Br₂NO₂: C 55.51, H 4.85, N 2.70; found C 55.49, H 4.86, N 2.72.

Poly{(9,9-dehexylfluorene-2,7-diyl)-alt-[3,4-bis(*p*-phenylene)-3-cyclobutene-1,2-dione]} (PFSD)

To a mixture of **4** (502.3 mg, 1.0 mmol), **1** (392.1 mg, 1.0 mmol) and Pd(PPh₃)₄ (12 mg, 1 × 10⁻² mmol) was added a mixture of toluene (5 mL) and aqueous potassium carbonate (2 mol/L, 5 mL). The mixture was vigorously stirred at 85—90 °C for 48 h. After the mixture was cooled into room temperature, it was poured into 200 mL of methanol and deionized water (*V* : *V*=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 PFSD was obtained as light yellow powders with a yield of 75% after drying under vacuum. ¹H NMR (DMSO, 400 MHz) δ: 8.02—7.99 (m, 4H), 7.91—7.64 (m, 6H), 7.42—7.34 (m, 4H), 2.50 (br, 4H), 1.23—0.64 (m, 22H); ¹³C NMR (C₅D₅N, 400 MHz) δ: 191.81, 167.79, 152.28, 146.97, 141.58, 140.44, 139.17, 132.08, 131.60, 130.87, 130.57, 130.30, 127.75, 127.40, 126.94, 126.42, 121.96, 121.50, 120.74, 55.79, 40.27, 33.27, 31.34, 29.64, 24.10, 22.48, 13.84; FT-IR (KBr) *v*: 2928, 2854, 1692, 1649, 1601, 1511, 1465, 1402, 1316, 1248, 1211, 1170, 1088, 1018, 965, 816 cm⁻¹. Anal. calcd for (C₄₁H₄₀O₂)_{*n*}: C 87.19, H 7.08; found C 86.74, H 7.23.

Poly{(9,9-dihexylfluorene-2,7-diyl)-alt-(1,2-diphenyl-*N-n*-octyl maleimide)} (PFMD)

Polymer PFMD was obtained as light yellow powders with a yield of 87% from the reaction of **3** with **4**

according to the procedure described for the synthesis of polymer PFSD. ¹H NMR (CDCl₃, 400 MHz) δ: 7.50—7.79 (m, 14H), 3.69 (d, *J*=7.6 Hz, 2H), 2.04 (br, 4H), 0.72—1.72 (m, 37H); ¹³C NMR (CDCl₃, 400 MHz) δ: 170.95, 151.88, 142.87, 140.54, 139.15, 138.89, 135.31, 130.45, 129.91, 128.78, 128.61, 127.74, 127.21, 126.11, 121.38, 120.25, 120.11, 55.38, 40.42, 38.56, 31.80, 31.44, 29.66, 29.17, 28.68, 26.91, 23.80, 22.63, 22.53, 14.07, 13.94; FT-IR (KBr) *v*: 2954, 2926, 2854, 1766, 1703, 1604, 1464, 1402, 1370, 1079, 966, 818, 725, 469 cm⁻¹. Anal. calcd for (C₄₉H₅₇NO₂)_{*n*}: C 85.05, H 8.30, N 2.02; found C 84.48, H 8.12, N 2.07.

Measurements

¹H NMR and ¹³C NMR spectra were performed on a Varian Unity INOVA-400 photospectrometer. 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 (Φ_{FL}) in solutions (PFSD in THF solution and PFMD in CHCl₃ solution) were measured by excitation of the respective polymer solutions at 310 nm and compared with the solution emission of the Rhodamine 6G (*ca.* 2 × 10⁻⁶ mol/L in ethanol solution, Φ_{FL} =0.95), and 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 N₂ at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC 7 apparatus under N₂ 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 instrument. The thickness of films was measured by a Dektak surface profilometer.

EL device fabrications

For the fabrication of the devices, glass substrates coated with indium-tin oxide (ITO) with a sheet square resistance of 110 Ω (CSG Co. Ltd.) were cleaned subsequently in ultrasonic baths of ionic detergent water, acetone and anhydrous alcohol. A thin film layers of PEDOT (*w*=0.14% in water) : PSS (*w*=2.6% in water) (80 nm) (PEDOT : PSS is polyethylenedioxythiophene doped with polystyrene sulfonic acid) and the polymers (75 nm) (from a 10 mg/mL PFSD in THF and PFMD in toluene solution) were spin-coated on ITO at 1500 r/min for 30 s in turn, after that a thin layer of Ba (3 nm)/Al (180 nm) or Mg : Ag (*V* : *V*=10 : 1) (150 nm)

was deposited on the polymer film by thermal evaporation under a vacuum of 1.33×10^{-4} Pa. 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 or Mg : Ag, negative). The current-voltage characteristic was measured on a voltmeter and an amperometer, respectively. 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.

Result and discussion

Synthesis of monomers and polymers

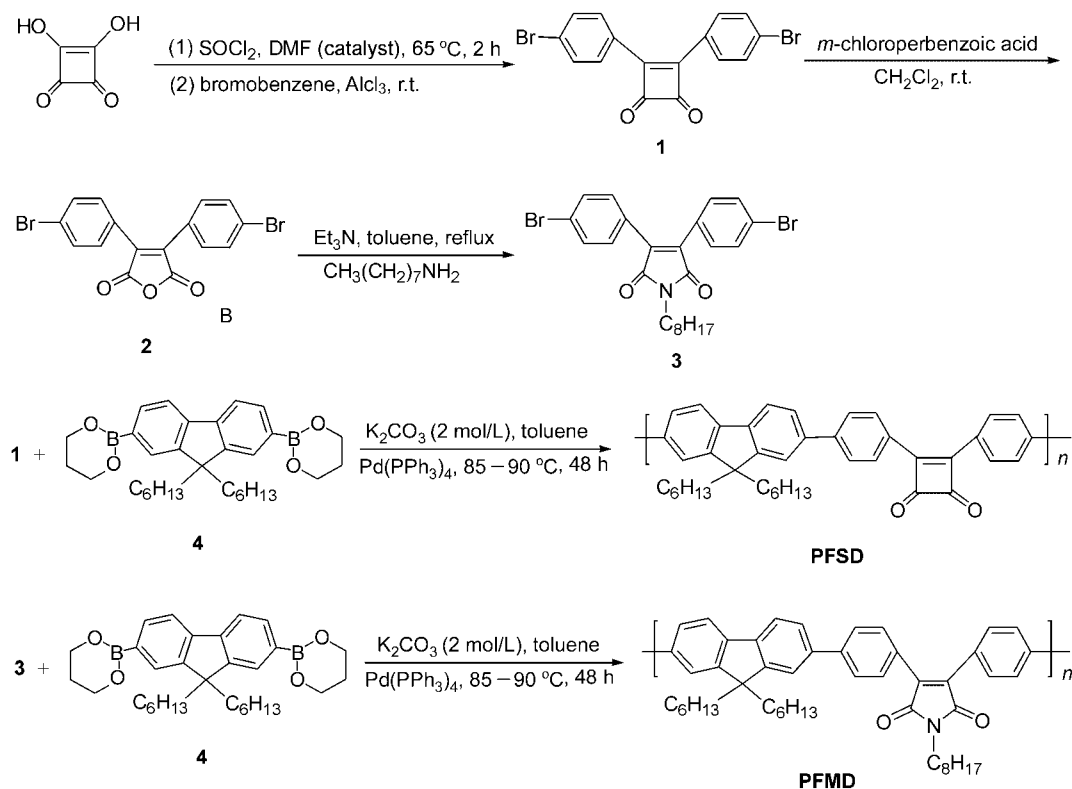
Scheme 1 shows the synthetic route for the monomers and the polymers. Compound **1** was prepared through a Friedel-Crafts reaction of bromobenzene with squaryl dichloride (treatment of squaric acid with SOCl_2 to afford squaryl dichloride).⁹ Compound **2** was prepared from **1** by a Beayer-Villiger oxidation reaction using *m*-Chloroperbenzoic acid as an oxidizing agent.⁷ By a conventional thermal imidization process, compound **2** reacted with *n*-octylamine to afford **3**.⁷ Then the dibromo monomer **1** and **3** copolymerized with the diboronate **4** using the Suzuki coupling reaction in a mixture of toluene and aqueous potassium carbonate ($2 \text{ mol} \cdot \text{L}^{-1}$) with $\text{Pd}(\text{PPh}_3)_4$ as catalyst to give **PFSD** and

PFMD. The structures of intermediate monomers were characterized by ^1H NMR spectroscopy and elemental analysis, and those of the polymers were characterized by ^1H NMR, ^{13}C NMR, FT-IR spectroscopy and elemental analysis. **PFMD** is readily soluble in common organic solvents, such as chloroform, chlorobenzene, toluene and xylene. However, **PFSD** has relative poor solubility in above solvents. But the latter polymer can easily dissolve in polar aprotic solvents, *e.g.* THF, DMF, DMAC and DMSO. Gel permeation chromatography (GPC) analysis, which was performed at $25 \text{ }^\circ\text{C}$ using polystyrene as the standard and THF as the eluent, indicated that **PFSD** has a number-averaged molecular weight (M_n) of approximately 23100 with a polydispersity index of 1.56, and **PFMD** has a M_n of about 39000 with a polydispersity index of 1.83.

Thermal properties

The thermal properties of **PFSD** and **PFMD** were investigated by using differential scanning calorimetry (DSC: heating at $10 \text{ }^\circ\text{C}/\text{min}$ in nitrogen) and thermogravimetric analysis (TGA: heating at $10 \text{ }^\circ\text{C}/\text{min}$ in nitrogen). Both of the polymers possess excellent thermal stability with onset high decomposition temperatures (T_d : $411 \text{ }^\circ\text{C}$ for **PFSD** and $427 \text{ }^\circ\text{C}$ for **PFMD**), and no weight loss was observed at lower temperatures. The glass transition temperatures (T_g) of the **PFSD** and **PFMD** were observed at $126 \text{ }^\circ\text{C}$ and $122 \text{ }^\circ\text{C}$, respec-

Scheme 1 Synthetic route of **PFSD** and **PFMD**



tively. These T_g values are much higher than those of poly(9,9-dioctyl-fluorene) (**POF**) (*ca.* 51 °C)¹¹ and poly(9,9-dihexyl-fluorene) (**PHF**) (*ca.* 55 °C),¹² in which each repeating fluorene unit contains two flexible *n*-octyl or *n*-hexyl chains at C-9. It is evident that the incorporation of squaric acid or maleimide unit in the main chain can obviously increase T_g of fluorene-based polymers. This is very important for such type of polymers used as emissive materials in PLED.¹³

Optical properties

The UV-Vis absorption and PL spectra of **PFSD** and **PFMD** in diluted solution and in thin films are shown in Figure 1. The concentration of the solution for measurements of UV-Vis and PL spectra was 2×10^{-6} mol/L (**PFSD** in THF solution and **PFMD** in CHCl_3). The thin film for UV-Vis and PL measurements was prepared by spin-coating from the solution (**PFSD** in THF solution and **PFMD** in CHCl_3 , 10 mg/mL, 1500 r/min) on a quartz plate followed by drying under vacuum for 2 h at room temperature. As shown in Figure 1, the solution (THF) and film of **PFSD** show the absorption maximum at 337 and 345 nm, due to π - π^* electronic transitions of the conjugated polymer backbones. And the solution (CHCl_3) and film of **PFMD** respectively exhibit two absorption maximum peaks at 300, 402 and 301, 403 nm. The peaks at 300 and 301 nm are due to the π - π^* electronic transitions of the conjugated polymer backbones and the peaks at 402 and 403 nm are n - π^* transitions of the maleimide units in the main chain. From the onset wavelengths (in films), the optical band gaps (E_g) of **PFSD** and **PFMD** can be estimated to be 2.65 eV ($\lambda_{\text{onset}}=468$ nm) and 2.40 eV ($\lambda_{\text{onset}}=516$ nm), respectively.

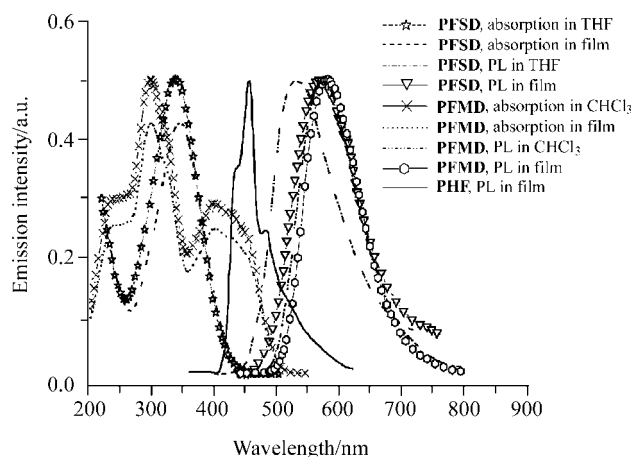


Figure 1 UV-Vis absorption and PL (excited at 310 nm) spectra of the polymers (**PFSD** and **PFMD**) in solutions and in films.

Figure 1 shows good spectral overlap of **PHF** emission with the absorption spectra of **PFSD** and **PFMD**. These two polymers can emit strong yellow fluorescence both in solution and film under UV light irradiation. The PL spectra of **PFSD** in THF solution and film peak at 538 and 567 nm, and those of **PFMD** in CHCl_3

solution and film peak at 577 and 580 nm. The results can be attributed to either the charge transfer between a fluorene segment and an electron-deficient containing squaric acid/maleimide segment of the polymers or the Förster energy transfer between different polymer chains. The fluorescence yields (Φ_{FL}) of **PFSD** in THF solution and **PFMD** in CHCl_3 solution excited at 310 nm were measured to be 1.16 and 0.32, using Rhodamine 6G (in ethanol solution, $\Phi_{\text{FL}}=0.95$) as a standard. And the PL quantum yields of **PFSD** and **PFMD** in neat films, as measured in an integrating sphere at room temperature, were found to be 0.51 and 0.08, respectively.¹⁴

Although bright PLED based on polyfluorenes have been fabricated, a common problem with polyfluorenes exists due to their tendency to form long wavelength aggregates/excimers in the solid state upon heating.⁶ To examine the thermal stability of **PFSD** and **PFMD**, polymer films were spin-cast onto quartz plates, then the film-coated plates were heated on a hot plate in nitrogen at different temperatures for 5 h. After the films were cooled to room temperature, the PL spectra were recorded. For comparison, the same experiments were carried out for the film of **PHF** (spin-cast from solution in toluene). The results are shown in Figure 2. Heating at 100 °C did not cause any spectral change in the emissions from **PFSD** and **PFMD**. When the annealing temperature was increased to 150 °C, the second emission bands appeared between 650 and 750 nm. It is evident that this formation of the additional emission peaks between 650 and 750 nm upon heating relates to the T_g of **PFSD** and **PFMD**. This may be caused by the aggregates/excimers in solid state upon heating. As shown in Figure 2, under T_g , there are no addition peaks appearing between 650–750 nm, indicating that the excimers may be efficiently avoided in these two polymers. So the thermal stability of the resulting polymers is improved over that of polyfluorenes.

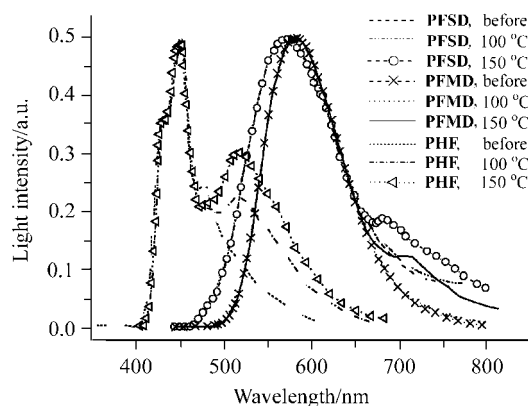


Figure 2 PL spectra of the polymers (**PFSD**, **PFMD** and **PHF**) films before and after annealing at 100 and 150 °C in air.

Electrochemical properties of the polymers

The information on the electronic structures of the

light-emitting polymers is essential in the device fabrication. Cyclic voltammetry (CV) was employed to investigate the redox behavior of the polymers and to assess the HOMO and LUMO energy levels.^{15,16} The CV was performed on a thin film of the polymer coated onto a platinum plate electrode (*ca.* 6 mm²) in a 0.1 mol/L tetrabutylammonium perchlorate (Bu₄NClO₄) solution in acetonitrile with the scan rate of 50 mV/s at room temperature. A platinum wire was used as counter electrode, and Ag/AgCl was employed as reference electrode. All measurements were calibrated against an internal standard, ferrocene (Fc), which has the IP value (−4.8 eV) of the Fc/Fc⁺ redox system.^{3d} The potential of Fc/Fc⁺ was measured as 0.1 V vs. Ag/AgCl in this work. As shown in Figure 3, **PFSD** exhibits an irreversible *n*- and *p*-doping process, but **PFMD** possesses a reversible *n*- and *p*-doping process. The reason may be that maleimide units exist in a small donor-accepter system in the molecule structure compared with square acid unit. So **PFMD** has better carrier-transporting (both electron and hole) properties than **PFSD**. On sweeping cathodically for the polymer **PFSD**, the onset of the *n*-doping process occurs at the potential of −1.54 V and gives a reduction peak at −1.93 V. In the anodic scan, the *p*-doping process onsets at 1.10 V and then gives an oxidation peak at 1.67 V. For the polymer **PFMD**, the onset of the *n*-doping process occurs at the potential of −0.95 V and gives a reduction peak at −1.56 V with the corresponding re-oxidation peak appearing at −0.94 V. In the anodic scan, the *p*-doping process onsets at 1.48 V, and then gives an oxidation peak at 1.91 V with the corresponding re-reduction peak at 1.36 V. Accordingly, the HOMO and LUMO energy levels of the polymer **PFSD** and **PFMD** can be estimated as −5.80, −6.18 eV and −3.16, −3.75 eV from the *p*-doping and *n*-doping onset potentials. The electrochemically measured band gaps of the polymers are 2.64 and 2.43 eV, which agree well with the HOMO and LUMO energy gaps as estimated from the UV-Vis absorption onsets. Compared with polyfluorene and

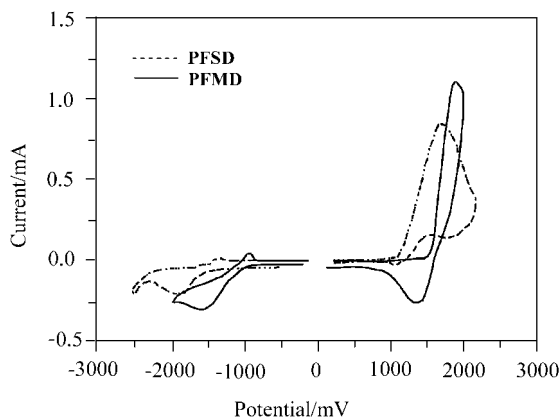


Figure 3 Cyclic voltammograms of the polymers (**PFSD** and **PFMD**) recorded from a thin film deposited on a platinum plate electrode at a scan rate of 50 mV/s. The potentials were measured relative to the Ag/AgCl.

their derivatives, these polymers have the higher electron affinity, especially the latter polymer **PFMD**, which could be attributed to the electron withdrawing property of squaric acid or maleimide unit in the polymer backbones.

Electroluminescent properties

The EL properties of the polymers were examined using double-layer PLED with configurations of **ITO/PEDOT : PSS/polymer/Ba/Al** or **ITO/PEDOT : PSS/polymer/Mg : Ag**. Here, **PEDOT : PSS** is polyethylenedioxythiophene doped with polystyrene sulfonic acid and it was used as hole-transporting layer with a thickness of 80 nm. For **PFSD**, the device using Mg : Ag as cathode turned on at about 16 V. Considering the energy barrier for electron injection at the cathode, the device of **ITO/PEDOT : PSS/PFSD/Ba/Al** was fabricated. By employing Ba as the cathode, the turn-on voltage for light output was reduced to about 6 V, and the maximum external quantum efficiency was increased from 0.006% (at 29 cd•m^{−2} with a bias of 24 V) to 0.24% (at 343 cd•m^{−2} with a bias of 10 V). The reason is that the work function of Ba cathode can match better with the LUMO energy level of **PFSD** leading to more efficient electron injection than that of Mg : Ag. The EL spectra of above devices peak at 565 and 562 nm are much similar to the PL spectrum of **PFSD** in film. For **PFMD**, **ITO/PEDOT : PSS/PFMD/Mg : Ag** was more efficient than **ITO/PEDOT : PSS/PFMD/Ba/Al**. The maximum external quantum efficiency of the former device was 1.13% (at 564 cd•m^{−2} with a bias of 8.4 V), and that of the latter was 0.2% (at 224 cd•m^{−2} with a bias of 10 V). The result can be also explained by the theory of energy level matching. The results of these PLEDs are summarized in Figures 4 and 5. The EL spectra of these two devices peak at 579 and 575 nm. Compared with the PL spectrum of **PFMD**, the EL spectra are also similar to the PL spectrum. The EL spectra of **PFSD** and **PFMD** are shown in Figure 6.

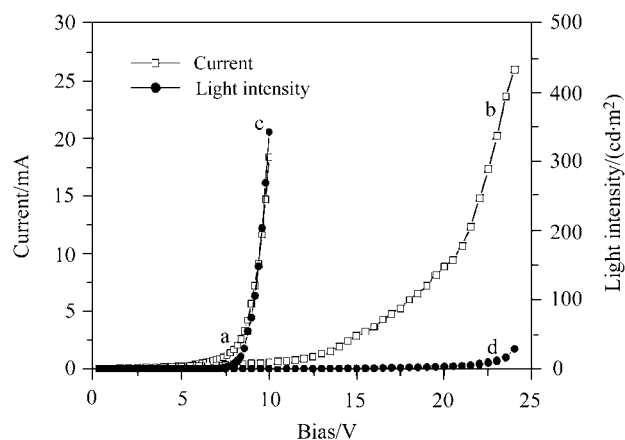


Figure 4 Current-voltage characteristics of **ITO/PEDOT : PSS/PFSD/Mg : Ag** (b), **ITO/PEDOT : PSS/PFSD/Ba/Al** (a) and brightness-voltage characteristics of **ITO/PEDOT : PSS/PFSD/Mg : Ag** (d), **ITO/PEDOT : PSS/PFSD/Ba/Al** (c).

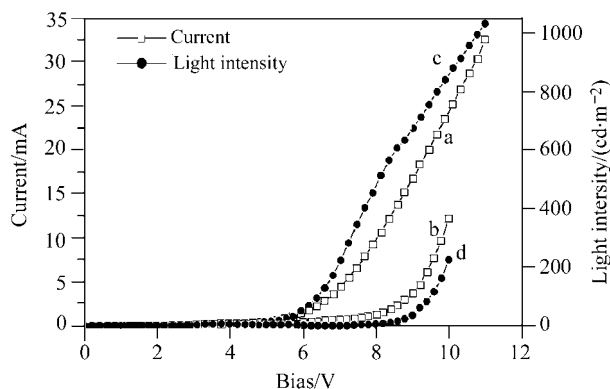


Figure 5 Current-voltage characteristics of ITO/PEDOT : PSS/PFMD/Mg : Ag (a), ITO/PEDOT : PSS/PFMD/Ba/Al (b) and brightness-voltage characteristics of ITO/PEDOT : PSS/PFMD/Mg : Ag (c), ITO/PEDOT : PSS/PFMD/Ba/Al (d).

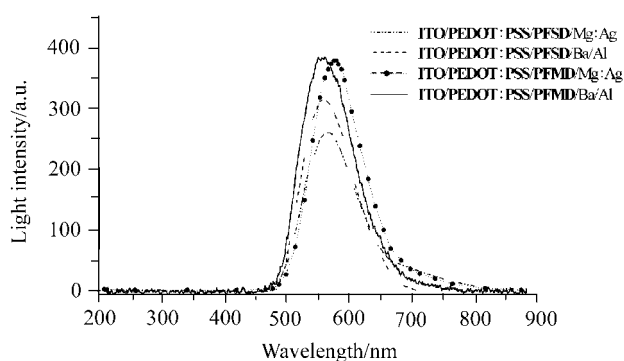


Figure 6 EL spectra of the devices in this work.

Conclusions

Two novel fluorene-based copolymers (PFSD and PFMD) containing electron-deficient squaric acid or maleimide moiety in the main chain have been developed. Both of the polymers possess high T_g and excellent thermal stability. The CV measurements indicate that PFSD and PFMD have high electron affinity. The results from PL measurements of the isothermally heated polymer thin films of PFSD and PFMD show that the commonly observed aggregate/excimer formation is very effectively suppressed in these two polymers. Four PLEDs were designed and fabricated to research the EL properties of these two polymers. All these devices show bright yellow emission (562–579 nm) with different maximum external quantum efficiency (0.006%—1.13%).

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