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Synthesis, optical and electrochemical properties of luminescent polymers containing 1,2-diphenylmaleimide and thiophene segments

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Abstract

In an attempt to balance energy barriers of hole and electron injection we prepared and characterized homopolymer containing electron-transporting 1,2-diphenylmaleimide chromophores (**P1**) and copolymers consisting of 1,2-diphenylmaleimide and hole-transporting 2,5-thiophene moieties (**P2**, **P3**) via dehalogenation polycondensation. The copolymers are amorphous materials with decomposition temperature greater than 450 °C. Absorption and fluorescence spectra were employed to investigate their optical properties both in solution and film state. Photoluminescence maxima of **P1**, **P2** and **P3** films are 564, 559 and 558 nm, respectively. The HOMO and LUMO energy levels have been estimated from their cyclic voltammograms. The HOMO levels of **P1**, **P2**, and **P3** were readily raised with increasing thiophene content (-5.99, -5.59, and -5.43 eV, respectively), whereas their LUMO levels were very similar (-3.61 to -3.65 eV). Double-layer light-emitting diodes (Al/PEDOT:PSS/**P1**–**P3**/ITO) were fabricated to evaluate their optoelectronic characteristics. Incorporation of thiophene units successfully reduced the turn-on electric field from 11.0×10^5 to 2.9×10^5 V/cm, but it decreased the luminescent efficiency and the maximum brightness.

Keywords: Synthesis; Photoluminescence; Light-emitting diodes

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1. Introduction

Since the discovery of electroluminescence (EL) of poly(*p*-phenylenevinylene) (PPV) in 1990, EL conjugated polymers have attracted much interest in recent years [1–3].Compared with organic light-emitting diode (OLED), PLED offers various advantages, such as low cost and easy fabrication by spin-coating and ink-jetting. Many conjugated polymers, such as PPV, poly(*p*-phenylene)s (PPPs) [4,5], polyfluorenes (PFs) [6], and polythiophenes (PTs) [7,8], have been synthesized for tentative application as emissive layers in organic light-emitting diodes. However, most of these polymers synthesized to date have low electron affinity. This causes imbalance of injection rate between electrons and holes. To reduce the turn-on electric field, it is necessary to balance the injection rates of opposite charges and decrease the barriers of charge injection from the opposite contacts [9].

In order to solve this problem, one approach is to use metals with low work function (such as Ca and Mg) as cathode materials [10]. Such metals, however, are highly susceptible to atmospheric degradation and are difficult to encapsulate that the resulting devices suffer from poor stability. Therefore, many conjugated polymers containing electron-transporting chromophores have been synthesized to overcome these problems about work function and balance of injection [11–13]. Maleimide and its derivatives have been known to exhibit excellent thermal stability and electron-withdrawing properties due to the rigid imide rings in the backbone; the 1,2-substituents of the maleimide ring form a kink structure of about 80° [14–19].

In this paper, we prepared homopolymer of 1,2-diphenylmaleimide (**P1**) and random copolymers containing 1,2-diphenylmaleimide and thiophene chromophores in main chain (**P2**, **P3**) by dehalogenation polycondensation (Yamamoto reaction), and systematically investigated the influences of the thiophene content on photophysical, electrochemical and electroluminescent properties of the resulting copolymers.

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2. Experimental section

2.1. Materials and measurements

1,2-Bis(4-bromophenyl)maleimide (**2**) was synthesized by a modified procedure described in the literatures elsewhere [20,21]. Reagent chemicals were purchased from Aldrich, Lancaster, TCI, and Acros Chemical Co. All new compounds were characterized using ^{1}H NMR, FT-IR, and elemental analyzer (EA). ^{1}H NMR spectra were recorded on a Bruker 400 MHz FT-NMR and chemical shifts were reported in ppm using tetramethylsilane (TMS) as internal standard. Infrared spectra were measured as KBr pellets on a Fourier transform infrared spectrometer, model Valor III from Jasco. Elemental analyses were carried out on a Heraus CHN-Rapid elemental analyzer. The thermogravimetric analyses (TGA) of the polymers were measured under nitrogen atmosphere at a heating rate of 20 °C/min using a Perkin–Elmer TGA-7 thermal analyzer. Thermal properties of the polymers were measured using a differential scanning calorimeter (DSC), Perkin–Elmer DSC 7, under nitrogen atmosphere at a heating rate of 10 °C/min. The UV/visible spectra were measured using a Jasco V-550 spectrophotometer. The photoluminescence (PL) spectra were obtained using a Hitachi F-4500 spectrofluorometer. The cyclic voltammograms (CV) of polymer films were measured at room temperature under nitrogen atmosphere using polymer-coated ITO glass as working electrode, Ag/AgCl electrode as reference electrode, and platinum wire electrode as auxiliary electrode supporting in $(n\text{-Bu})_4\text{NClO}_4$/acetonitrile solvent, the scanning speed was 100 mV/s.

Double-layer light-emitting diodes (LED)s with a configuration of ITO/PEDOT:PSS/**P1**–**P3**/Al have been successfully fabricated. The polymer layer (**P1**–**P3**) was obtained by spin-coating (1000 rpm) polymer solutions of 7–10 mg/mL in $C_2H_2Cl_4$ on ITO glass (25 Ω/square). The pretreatment of ITO included routine sonication in a detergent solution and then distilled water and isopropyl alcohol in sequence. The thin layer aluminum was deposited as the cathode by thermal evaporation at about 10^{-5} Torr. All the fabrication and characterization of the devices were performed in ambient conditions.

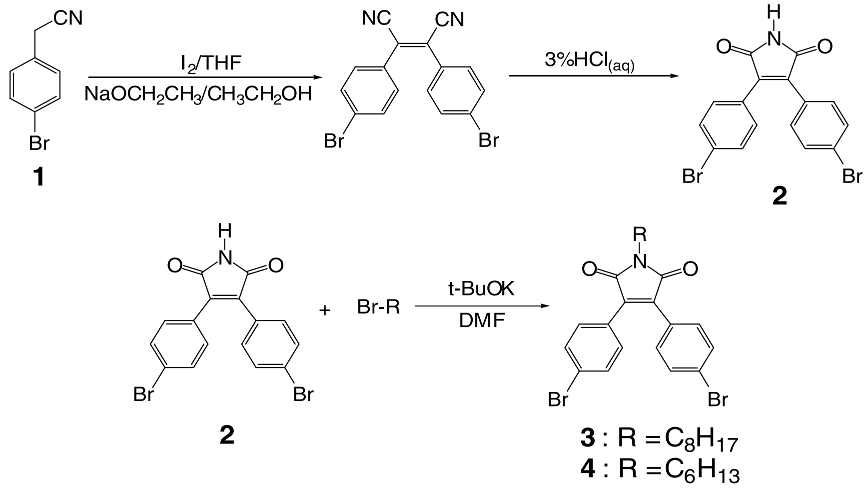
2.2. Monomer synthesis

2.2.1. 1,2-Bis(4-bromophenyl)maleimide (2) (Scheme 1)

To a two-necked 50-mL glass reactor was added with sodium ethoxide (9.777 g, 30 mmol) dissolved in ethanol (10 mL). The mixture was stirred for 30 min under ice bath in nitrogen atmosphere and then added with 10 mL tetrahydrofuran (THF) solution of 4-bromobenzylcyanide (**1**:1.968 g, 10 mmol) and one equivalent amount of iodine (2.563 g, 10 mmol). The solution was stirred for another 2 h and then the reaction was quenched with 3% hydrochloric acid (50 mL) for 14 h at 26 °C. It was poured into 300 mL water and then extracted with chloroform (300 mL × 2). The residual crude product, obtained after drying of organic phase, was then purified by column chromatography on silica gel using ethyl acetate/toluene ($v/v = 1/3$) as eluent. After drying, the solids were recrystallized from *n*-hexane/benzene to obtain yellow needle-like crystal of **2** (yield: 31.3%, mp: 217–218 °C). FT-IR (KBr pellet, cm^{-1}): ν 3212, 3065 (–NHCO–), 1768, 1717 (maleimide), 1583, 1476, 1391, 1342, 1071 (–CBr), 1007. ^{1}H NMR (acetone-d_6, ppm): δ 10.16 (s, 1H, –N*H*), 7.60 (4H, d, $J = 8.4$ Hz, Ar–*H*), 7.41 (4H, d, $J = 8.4$ Hz, Ar–*H*). Anal. Calcd for $C_{16}H_9Br_2NO_2$: C, 47.21%; H, 2.23%; N, 3.44%. Found: C, 47.20%; H, 2.23%; N, 3.44%.

2.2.2. 1,2-Bis(4-bromophenyl)-N-n-octylmaleimide (3)

1,2-Bis(4-bromophenyl)maleimide (**2**: 0.816 g, 2 mmol), *t*-BuOK (0.339 g, 3 mmol) and 4 mL DMF were stirred for 30 min under ice bath in nitrogen atmosphere. 1-Bromooctane (0.460 g, 2.4 mmol) was dissolved in 1 mL DMF and then added into the above mixture. The mixture was



Scheme 1.

allowed to react at room temperature for 18 h and then poured into water, neutralized with 6 N $HCl_{(aq)}$. It was extracted with chloroform and the extract was washed with distilled water, dried with anhydrous magnesium sulfate, and then concentrated under reduced pressure. The residual crude product was then purified by column chromatography on silica gel using ethyl acetate/*n*-hexane ($v/v=1/9$) as eluent. After drying the solids were recrystallized from methanol to obtain yellow needle-like crystal of **3** (yield: 81.2%, mp: 83–84 °C). ^1H NMR (acetone-d_6, ppm): δ 7.60 (4H, d, $J=11.2$ Hz, Ar–*H*), 7.42 (4H, d, $J=11.2$ Hz, Ar–*H*), 3.57–3.62 (2H, t, $J=9.6$ Hz, $-NCH_2-$), 1.28–1.65 (m, 12H, $-CH_2-$), 0.86 (3H, t, $J=8$ Hz, $-CH_3$). Anal. Calcd for $C_{24}H_{25}Br_2NO_2$: C, 55.51%; H, 4.85%; N, 2.70%. Found: C, 55.54%; H, 4.84%; N, 2.63%.

2.2.3. 1,2-Bis(4-bromophenyl)-N-n-hexylmaleimide (4)

The synthetic procedures of **4** were similar to those employed in the preparation of **3** except that 1-bromohexane was used instead of 1-bromooctane. Yield: 76.7%, mp: 88–89 °C. ^1H NMR (acetone-d_6, ppm): δ 7.61 (4H, d, $J=11.2$ Hz, Ar–*H*), 7.42 (4H, d, $J=11.2$ Hz, Ar–*H*), 3.60 (2H, t, $J=9.6$ Hz, $-NCH_2-$), 1.32–1.70 (m, 8H, $-CH_2-$), 0.88 (3H, t, $J=8$ Hz, $-CH_3$). Anal. Calcd for $C_{22}H_{21}Br_2NO_2$: C, 53.79%; H, 4.31%; N, 2.85%. Found: C, 53.84%; H, 4.31%; N, 2.85%.

2.3. Polymer synthesis (Scheme 2)

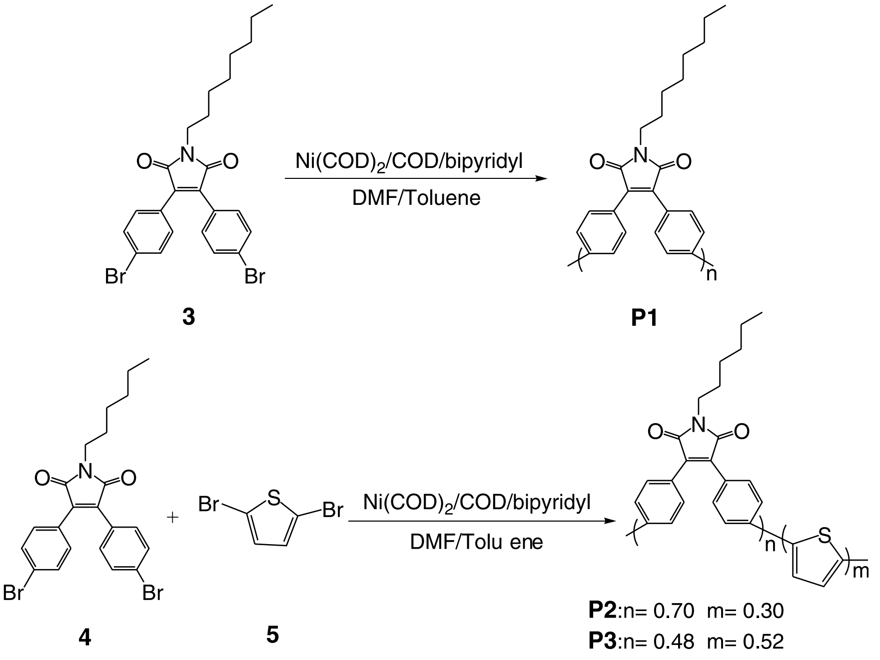
The copolymers **P1**–**P3** were synthesized from dehalogenation polycondensation (Yamamoto reaction) of 1,2-bis(4-bromophenyl)maleimide (**2**) or 1,2-bis(4-bromophenyl)-*N*-*n*-octylmaleimide (**3**) with 2,5-dibromothiophene using $Ni(COD)_2$ and 2,2′-bipyridyl as catalysts [22–24]. For instance, to a two-necked 10-mL glass reactor were added with required monomers (**3**, **4**, 2,5-dibromothiophene), 1,5-cyclooctadiene, and 2,2′-bipyridyl. The mixture was then added with $Ni(COD)_2$, toluene and *N*,*N*-dimethylformamide (DMF) in dry box. It was stirred at 80 °C for 60 h, then poured into acidic methanol (with HCl), and the appearing precipitates were collected by filtration. The precipitates were washed successively with acidic methanol, acetone, deionized water and dried under vacuum. The solid was further purified with isopropanol using a Soxhlet apparatus for 24 h to remove oligomers and catalyst residues, followed with drying under vacuum at room temperature.

P1: Monomer **3** (0.219 g, 0.42 mmol), 1,5-cyclooctadiene (0.051 g, 0.47 mmol), 2,2′-bipyridyl (0.074 g, 0.47 mmol), $Ni(COD)_2$ (0.169 g, 0.63 mmol), DMF (1.5 mL), and toluene (1.5 mL).

Yield: 72.5%, FT-IR (KBr pellet, cm^{-1}): ν 3352 (–NHCO–), 2923, 2851 ($-CH_3$, $-CH_2-$), 1770, 1705 (maleimide), 1445, 1400, 1365, 1257, 1085. ^1H NMR ($C_2D_2Cl_4$, ppm): δ 7.33–7.79 (m, 8H, Ar–*H*), 3.43–3.82 (m, 2H, $-NCH_2-$), 1.08–1.45 (m, 12H, $-CH_2-$), 0.76–0.92 (m, 3H, $-CH_3$). Anal. Calcd (%) for $C_{24}H_{25}NO_2$: C, 80.19; H, 7.01; N, 3.90. Found: C, 79.66; H, 7.00; N, 3.73.

P2: Monomer **4** (0.196 g, 0.40 mmol), 2,5-dibromothiophene (0.032 g, 0.13 mmol), 1,5-cyclooctadiene (0.067 g, 0.60 mmol), 2,2′-bipyridyl (0.094 g, 0.60 mmol), $Ni(COD)_2$ (0.222 g, 0.80 mmol), DMF (2 mL), and toluene (2 mL).

Yield: 80.4%, FT-IR (KBr pellet, cm^{-1}): ν 3345 (–NHCO–), 2921, 2853 ($-CH_3$, $-CH_2-$), 1769, 1701 (maleimide), 1446, 1403, 1366, 773 (–C–S–C–). ^1H NMR ($C_2D_2Cl_4$, ppm): δ 7.49–7.82 (m, 56H, Ar–*H*), 7.31–7.44



Scheme 2.

(m, 6H, Ar–*H*), 3.47–3.77 (m, 14H, –NCH_2–), 1.11–1.43 (m, 56H, –CH_2–), 0.84–1.06 (m, 21H, –CH_3).

Anal. Calcd (%): C, 77.72; H, 5.97; N, 3.82; S, 3.75. Found: C, 76.86; H, 6.13; N, 3.67; S, 3.52.

P3: Monomer **4** (0.196 g, 0.40 mmol), 2,5-dibromothiophene (0.097 g, 0.40 mmol), 1,5-cyclooctadiene (0.103 g, 0.90 mmol), 2,2′-bipyridyl (0.141 g, 0.90 mmol), Ni(COD)$_2$ (0.334 g, 1.20 mmol), DMF (3 mL), and toluene (3 mL).

Yield: 80.6%, FT-IR (KBr pellet, cm^{-1}): ν 3342 (–NHCO–), 2920, 2854 (–CH_3, –CH_2–), 1772, 1703 (maleimide), 1443, 1405, 1368, 770 (–C–S–C–). ^{1}H NMR ($C_2D_2Cl_4$, ppm): δ 7.51–7.80 (m, 104H, Ar–*H*), 7.30–7.46 (m, 24H, Ar-*H*), 3.45–3.79 (m, 26H, –NCH_2–), 1.19–1.41 (m, 104H, –CH_2–), 0.83–0.96 (m, 39H, –CH_3). Anal. Calcd (%): C, 75.72; H, 5.52; N, 3.33; S, 8.37. Found: C, 74.60; H, 5.51; N, 3.08; S, 8.26.

3. Results and discussions

3.1. Synthesis and characterization of **P1–P3**

We prepared homopolymer of 1,2-diphenylmaleimide (**P1**) and copolymers (**P2**, **P3**) consisting of 1,2-diphenylmaleimide and 2,5-thiophene segments by the Yamamoto reaction using Ni(COD)$_2$ and 2,2′-bipyridyl as catalysts. The ratios of 1,2-diphenylmaleimide to thiophene groups were 0.7:0.3 and 0.48:0.52 for **P2** and **P3**, respectively. The compositions of **P2** and **P3** were estimated from peak areas (in ^{1}H NMR) of protons belong to benzene rings (δ 7.55–7.62 ppm) and thiophene units (δ 7.31–7.34 ppm). The key 1,2-diphenylmaleimide monomers (**3**, **4**) exhibit good solubility in common solvents and low tendency to crystallization due to the *n*-alkyl substituents. Accordingly, **P1–P2** also show good solubility in some common solvents such as THF, chloroform, NMP, and 1,1,2,2-tetrachloroethane. But **P3** is soluble only in NMP and 1,1,2,2-tetrachloroethane among the solvents tested, which can be attributed to decreased amount of side *N*-hexyl substituents in 1,2-diphenylmaleimide units and increased backbone rigidity due to thiophene moieties. As shown in Table 1, the weight-average molecular weights (M_w) of **P1–P3**, determined by gel permeation chromatography using polystyrene as standard, are 16.4×10^3, 9.0×10^3 and 7.2×10^3, respectively, with polydispersity indexes (PDIs) of 1.6, 2.7 and 2.4. All copolymers exhibit excellent thermal stability and their weight losses are less than 5% on heating to 450 °C (Fig. 1). Moreover, the residual weights at 800 °C are still very high (**P1**: 42.2%; **P2**: 43.8%; **P3**: 48.7%), suggesting that these polymers are readily carbonized or graphitized at elevated temperature. However, no glass-transition and melting temperature was detected before 250 °C using a differential scanning calorimeter (DSC).

3.2. Optical properties

Fig. 2 illustrates the absorption spectra of **P1**, **P2**, and **P3** in chloroform and as spin-cast film, and their optical properties are summarized in Table 2. All three polymers (**P1–P3**) show very similar absorption spectra (both in solution and as films) with peaks locating at 263–272 nm, which are attributable to the π–π* electronic transitions of the 1,2-diphenylmaleimide units. The absorption bands at 411–420 nm are due to the n–π* transition of the 1,2-diphenylmaleimide units in the main chain. Therefore, incorporation of thiophene moieties renders only in broadening of the bands at 411–420 nm. From the onset wavelengths (523, 541, and 548 nm) of their film absorption spectra, the optical band gaps (E_g) of **P1**, **P2**, and **P3** are estimated to be 2.37, 2.29, and 2.26 eV, respectively. The UV absorptions of **P1–P3** films show slight red-shifts of 9, 5, and 2 nm relative to those measured in solution state (Table 2), and the red-shift decreases with increasing thiophene content. This is probably due to formation of different conformations depending on thiophene contents. The spatial models of **P1–P3** are depicted in Fig. 3, which are generated by a MM2 semi-empirical calculation in Chem3D. As shown in Fig. 3(a), **P1** demonstrates a kinked backbone structure (at 1,2-diphenylmaleimide segments) with high planarity and symmetry. However, when the thiophene units are introduced as in **P2**, the symmetric structure is disrupted and leads to main chain torsion. Moreover, when the ratio of 1,2-diphenylmaleimide to thiophene units is about 1:1, like in **P3**, the copolymer will become spiral-like structure (Fig. 3(c)). Therefore, the conformational structure of **P1** is more planar than that of **P3**, facilitating **P1** to form regular packing and hence aggregate in the film state.

Fig. 4 illustrates the PL spectra of **P1**, **P2**, and **P3** in chloroform and as spin-cast films. They show similar spectral shape with slight difference in peak wavelength. Moreover, the PL maxima in film state red-shifts slightly

Table 1
Polymerization results and characterization of **P1–P3**[a]

	Yield (%)	M_n[b] ($\times10^3$)	M_w[b] ($\times10^3$)	PDI[b]	T_d[c] (°C)
P1	72.5	10.2	16.4	1.6	476
P2	80.4	3.3	9.0	2.7	475
P3	80.6	3.0	7.2	2.4	472

[a] Reaction temperature, 80 °C; reaction time, 60 h.

[b] M_n, M_w, and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards in $CHCl_3$.

[c] Temperature at 5% weight loss.

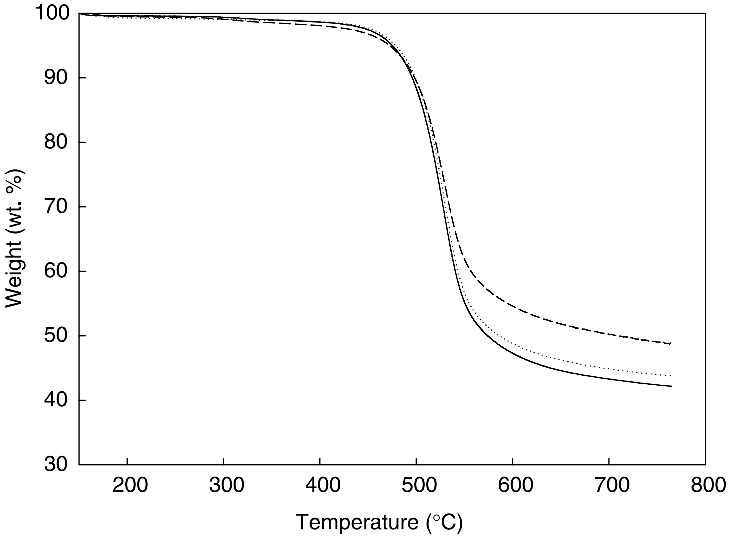


Fig. 1. Thermogravimetric curves of **P1** (—), **P2** (…) and **P3** (— —) at a heating rate of 20 °C/min in nitrogen.

relative to that in $CHCl_3$, i.e. from 546 to 564 nm for **P1**, from 549 to 559 nm for **P2**, and from 552 and 558 nm for **P3** (Table 2). The PL spectral red-shifts of **P1**–**P3** films are 18, 10, 6 nm when compared to those measured in solution, indicating that the bathochromic shifts decrease with increasing thiophene content. The Stokes shifts of **P1**–**P3** are greater than 140 nm, so the self-absorption effect would be small when fabricated as LED devices. Meanwhile, PL efficiency (Φ_{PL}) of **P1**–**P3** are 0.31, 0.24, and 0.20, respectively, which is gradually decreasing with increasing thiophene content in the copolymer. This is because thiophene group has intrinsically lower emission efficiency than 1,2-diphenylmaleimide group [25].

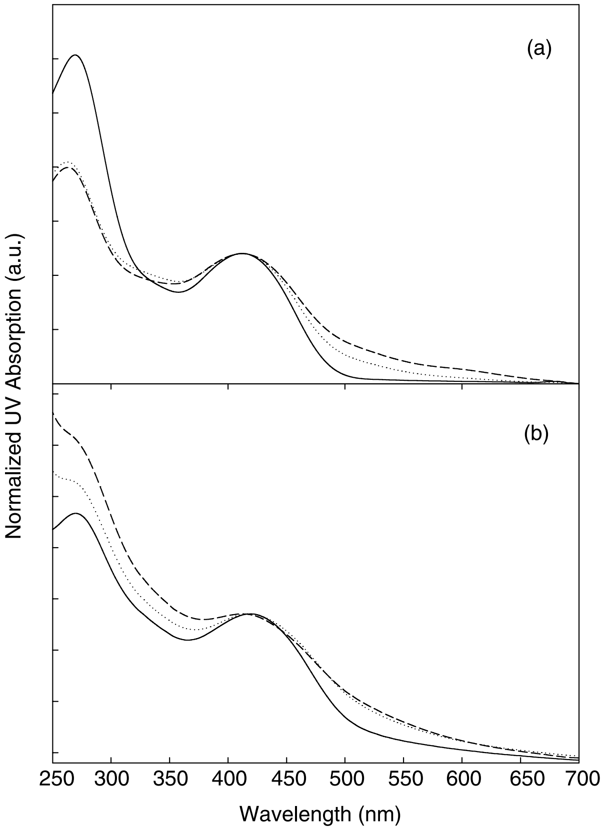


Fig. 2. Absorption spectra of **P1** (—), **P2** (…) and **P3** (— —) in chloroform (a) and as spin-cast films (b).

3.3. Electrochemical properties

The ionization potential (IP) and electron affinity (EA) are two important parameters in evaluating the redox property of electroluminescent polymers. Fig. 5 depicts the cyclic voltammograms of **P1**–**P3**, through which we investigated their redox behaviors and estimated the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) energy levels [26,27]. The electrochemical properties and band-gaps of the polymers are summarized in Table 3. The onset reduction potentials of **P1**, **P2**, and **P3** are almost the same and locate at −0.70 to −0.74 V regardless of their different thiophene contents (0, 30, and 52 mol%, respectively). Therefore, it is reasonable to propose that reduction starts at 1,2-diphenylmaleimide groups. However, the onset oxidation potentials of **P1**, **P2**, and **P3** depend heavily on thiophene content and locate at 1.64, 1.24, and 1.08 V, respectively. Therefore, it is confirmed that the onset oxidation potentials of the copolymers can be reduced by increasing the thiophene content [28]. These results directly prove that the oxidation and reduction starts at the hole-transporting thiophene and the electron-transporting 1,2-diphenylmaleimide segments, respectively.

Accordingly, the HOMO and LUMO energy level of **P1**–**P3** can be calculated from onset oxidation and reduction

Table 2
Optical properties of **P1**–**P3**

Polymer	UV–vis $\lambda_{\max}$		PL λ_{max}		Stokes shift (nm)[a]	Φ_{PL}[b] solution
	Solution (nm)	Film (nm)	Solution (nm)	Film (nm)		
P1	268, 411	272, 420	546	564	144	0.31
P2	264, 412	268, 417	549	559	142	0.24
P3	263, 412	265, 414	552	558	144	0.20

The solvent for solution preparation or spin-coating is chloroform for **P1**–**P3**.

[a] Stokes shift = PL λ_{max} (nm) − UV–vis $\lambda_{\max}$ (nm).

[b] These values were estimated by using quinine sulfate (dissolved in 1 N $H_2SO_{4(aq)}$ with a concentration of 10^{-5} M, assuming Φ_{PL} of 0.55) as a standard. The excitation wavelengths were 350 nm for **P1**–**P3** solutions (10^{-5} M repeating unit), respectively.

potentials by comparing with the ferrocence value of 4.8 eV below the vacuum level [29]. The HOMO energy level of **P1**–**P3** are −5.99, −5.59 and −5.43 eV, respectively, and the LUMO energy levels are −3.65, −3.61 and −3.61 eV. The HOMO energy levels of the copolymers are readily raised (from −5.99 to −5.43 eV) by increasing the thiophene content. In general, the raising in HOMO energy level leads to reduced hole-injection barriers (from ITO

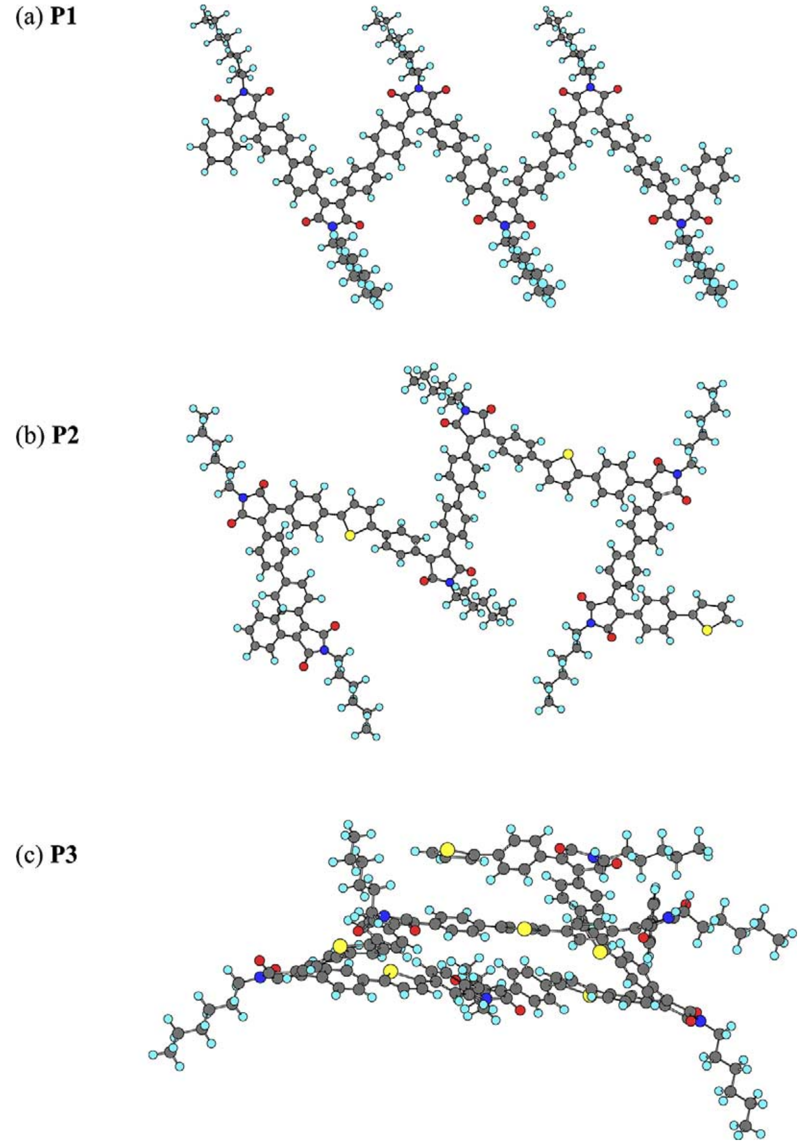


Fig. 3. Spatial models of (a) **P1**, (b) **P2**, and (c) **P3** generated by semi-empirical calculation (Chem3D).

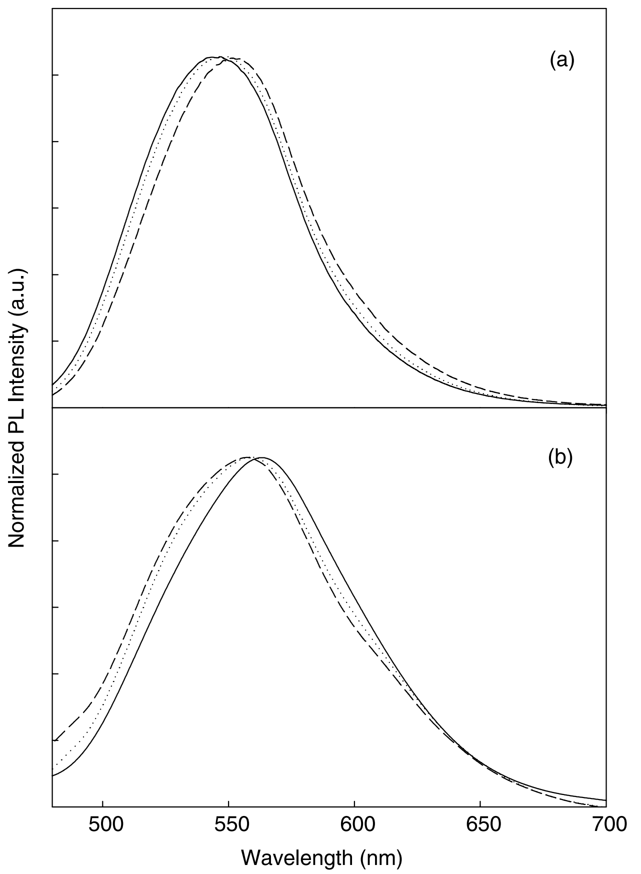


Fig. 4. Photoluminescence spectra of **P1** (—), **P2** (…) and **P3** (— —) in chloroform (a) and as spin-cast films (b).

glass) and enhanced the hole affinity. Therefore, it indicates that thiophene units play the role of enhancing hole-injection. The energy barriers relative to ITO anode (work function: −4.8 eV) are 0.79 and 0.63 eV for **P2** and **P3**, respectively, which are much lower than that for **P1** (1.19 eV). In addition, **P1**–**P3** with 1,2-diphenylmaleimide as electron-transporting segments show lower electron-injection barriers [0.65, 0.69, and 0.69 eV, respectively, relative to work function (−4.3 eV) of aluminum cathode]. Therefore, the rates of electron and hole injection in **P2** and **P3** are more balanced due to the simultaneous incorporation of 1,2-diphenylmaleimide and thiophene chromophores. The energy band diagrams of the copolymers are proposed as shown in Fig. 6.

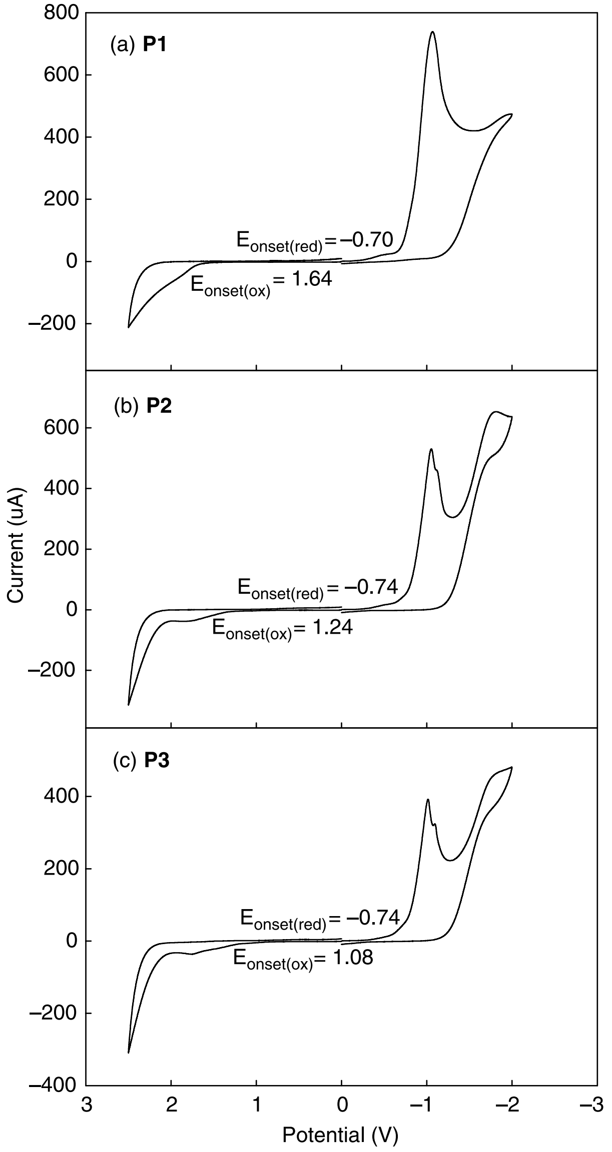


Fig. 5. Cyclic voltammograms of **P1**–**P3** films coated on ITO glass, supporting in 0.1 M acetonitrile solution of $(n\text{-Bu})_4NClO_4$, at a scanning rate of 100 mV/s.

3.4. Electroluminescence properties

In order to evaluate the optoelectronic performance of these copolymers, we fabricated three double-layer devices with a configuration of ITO/PEDOT/**P1**–**P3**/Al to study the

Table 3
Electrochemical properties and band gap of **P1**–**P3**

Polymer	$E_{onset(ox)}$ vs. Ag/Ag^+ (V)	$E_{onset(red)}$ vs. Ag/Ag^+ (V)	HOMO[a] (eV)	LUMO[a] (eV)	$E_g^{el\,b}$ (eV)
P1	1.64	−0.70	−5.99	−3.65	2.34
P2	1.24	−0.74	−5.59	−3.61	1.98
P3	1.08	−0.74	−5.43	−3.61	1.82

[a] HOMO and LUMO levels were calculated from the onset oxidation and the onset reduction potentials by comparing with the ferrocence value of 4.8 eV below the vacuum level.

[b] Electrochemically-determined band gap: $E_g^{el} = |\text{HOMO}| - |\text{LUMO}|$.

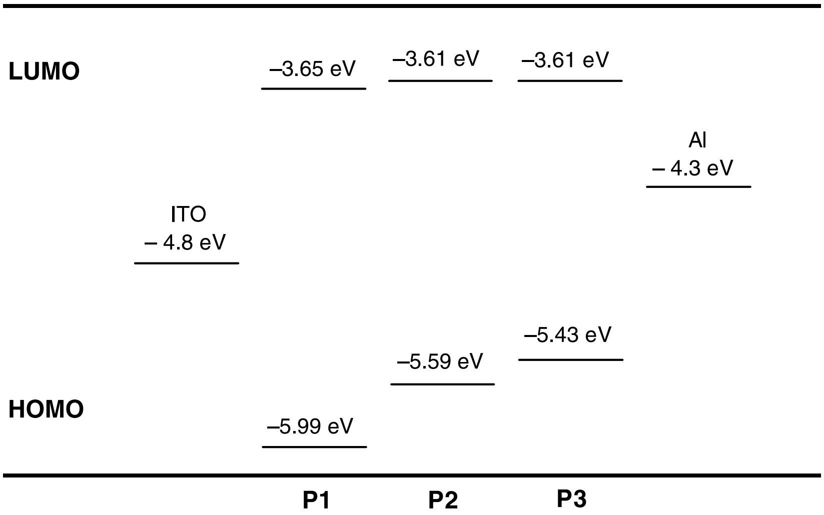


Fig. 6. The energy band diagrams of **P1**, **P2** and **P3**.

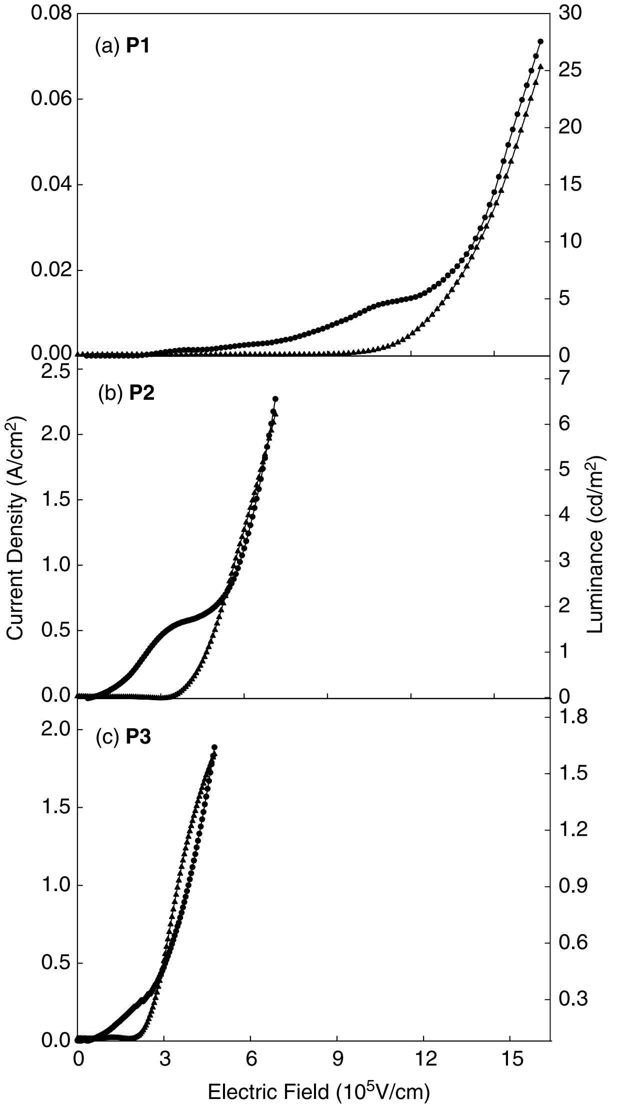


Fig. 7. Current density (●)-Electric field-Luminance (▲) characteristics of the double-layer light-emitting diodes (ITO/PEDOT:PSS/**P1**–**P3**/Al).

effect of thiophene contents. Fig. 7 shows the current density (*J*)–electric field (*F*)–luminance (*L*) diagrams of the devices, and the EL properties of the devices are summarized in Table 4. The turn on electric field were 11.0×10^5, 4.2×10^5, and 2.9×10^5 V/cm, maximum luminance were 25.3, 6.2, and 1.6 cd/m^2 and maximum current efficiency were 2.1×10^{-2}, 3.3×10^{-4}, and 1.2×10^{-4} for **P1**, **P2**, and **P3** devices, respectively. The turn on electric field decreases with increasing thiophene contents, this is because thiophene groups raise HOMO level of **P2**–**P3** and improve hole injection and/or transporting. But the maximum luminance and the current efficiency degrade significantly after incorporating thiophene chromophores. This is due to intrinsic lower emission efficiency of thiophene groups [25] and non-planar molecular structures that make recombination of electron-hole pairs difficult. From Fig. 8, EL spectral maxima of **P1**–**P3** locate at 583, 577, and 576 nm, respectively, which correspond to the orange–red region. As compared with PL emission, the EL spectral maxima red-shift slightly (18–19 nm) and the band width become broader.

4. Conclusions

We have successfully prepared one homopolymer (**P1**) from electron-transporting 1,2-bis(4-bromophenyl)-*N*-*n*-octylmaleimide (**3**) and two copolymers (**P2**, **P3**) from

Table 4
EL device characteristics and EL spectral maxima of **P1**–**P3**

Device[a]	Max. luminance (cd/m^2)	Turn-on electric field (10^5 V/cm)	Max. current efficiency (cd/A)	EL $\lambda_{\max}$ (nm)
P1	25.3	11.0	2.1×10^{-2}	583
P2	6.2	4.2	3.3×10^{-4}	577
P3	1.6	2.9	1.2×10^{-4}	576

[a] Double layer device: ITO/PEDOT:PSS/polymer/Al.

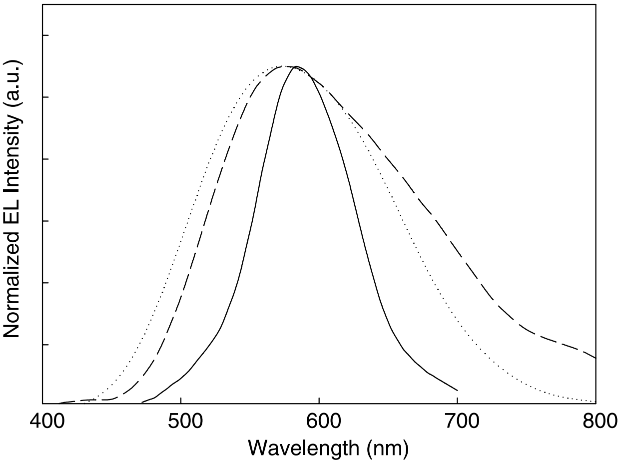


Fig. 8. Electroluminescent spectra of **P1** (—), **P2** (…) and **P3** (— —).

1,2-bis(4-bromophenyl)-*N*-*n*-hexylmaleimide (**4**) and hole-transporting 2,5-dibromothiophene through the Yamamoto reaction using Ni(COD)$_2$ and 2,2′-bipyridyl as catalysts. The polymers exhibit good thermal stability with 5% weight loss temperature above 450 °C. The absorptions of **P1–P3**, both in CHCl$_3$ and as films, are very similar and locate around 263–272 nm and 411–420 nm, whereas the emission maxima are at 546, 549, and 552 nm in CHCl$_3$. The Stokes shifts of **P1–P3** are greater than 140 nm, so the self-absorption effect would be small when fabricated as LED devices. PL efficiency (Φ_{PL}) of **P1–P3** are 0.31, 0.24, and 0.20, respectively, which decreases gradually with increasing thiophene contents due to lower emission efficiency of thiophene group. The HOMO levels of **P1–P3** have been estimated to be -5.99, -5.59, and -5.43 eV, respectively, whereas the LUMO levels are -3.65, -3.61, and -3.61 eV. The HOMO levels are readily raised by increasing thiophene contents. Double-layer light-emitting diodes (ITO/PEDOT/**P1–P3**/Al) were successfully fabricated and their turn-on electric fields were 11.0×10^5, 4.2×10^5, and 2.9×10^5 V/cm, respectively. Therefore, **P2** and **P3** with thiophene segments demonstrate higher HOMO energy level and lower turn-on electric fields than **P1**.

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