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Synthesis and Characterization of 3,4-Diphenylmaleimide Copolymers That Exhibit Orange to Red Photoluminescence and Electroluminescence

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ABSTRACT: A series of newly designed 3,4-diphenylmaleimide-based π-conjugated copolymers that exhibit red fluorescence in both solution and solid state were synthesized and characterized. Bright and efficient red fluorescence in the solid state was achieved by varying the structural combination of thiophene and/or fluorene with 3,4-diphenylmaleimide fluorophore. The range of thiophene- and fluorene-derived 3,4-diphenylmaleimide model compounds revealed that thiophene moieties were effective in extending the emission wavelength to the red region, and fluorene moieties significantly enhanced fluorescence intensity. Polymer light-emitting diodes (PLEDs) fabricated from 3,4-diphenylmaleimide−terthiophene copolymer (PTTML) exhibited saturated red electroluminescence (EL) with emission $\lambda_{\max}^{\mathrm{EL}}$ of 676 nm, although the diode was inefficient and dim. TPBI (2,2′,2″-(1,3,5-phenylene)-tris(1-phenyl-1*H*-benzimidazole)) as the electron-transporting layer in PLEDs was found to improve the performance of 3,4-diphenylmaleimide−bithiophene copolymer (PBTML). PBTML PLED yielded reddish EL (emission $\lambda_{\max}^{\mathrm{EL}}$ of 620 nm) with peak efficiencies of 0.61% (0.89 cd/A) and a maximum electroluminance of 1290 cd/m^2. A rare fluorene copolymer of a 3,4-diphenylmaleimide−thiophene−fluorene triad (PFTML) emitted orange-red photoluminescence (PL) at a $\lambda_{\max}^{\mathrm{fl}}$ of 598 nm in solution and $\lambda_{\max}^{\mathrm{fl}}$ of 601 nm in a solid thin film, with relatively high fluorescence quantum yields of 37 and 22%, respectively. Its PLEDs yielded bright orange-red EL (emission $\lambda_{\max}^{\mathrm{EL}}$ of 614 nm) with a high intensity of over 2000 cd/m^2 and an enhanced peak luminous efficiency of 1.25 cd/A or an external quantum efficiency of 0.74%.

Introduction

Polyfluorene (PF) has been extensively studied owing to its distinct blue electroluminescence (EL) and relatively high carrier mobility.[1] Over the past decade, a variety of copolymers derived from 2,7-fluorenes and other comonomers that contain delocalized π-electrons have been actively investigated. The development of such copolymers has led to the preparation of an entire series of fluorene-containing copolymers, which can be used in polymeric light-emitting diodes (PLEDs) whose colors span the entire visible range.[2] Nevertheless, only a limited number of fluorene-based copolymers are known for red EL. Most of the red copolymers were developed using similar approaches, such as so-called low-band-gap conjugated fluorene copolymers, to emit the long wavelengths from orange to red or even in the near-infrared region. 2,1,3-Benzoselenadiazole,[3a] 2,1,3-naphthoselenadiazole,[3b] 4,7-dithiophen-2′-yl-2,1,3-benzothiazole,[3c] 4,7-diselenophen-2′-yl-2,1,3-benzothiazole,[3d] 4,7-diselenophen-2′-yl-2,1,3-benzoselenazole,[3d] 3,4′-dihexyl-2,2′;5′,2″-terthiophene,[3e] 3″,4″-dihexyl-2,2′:5′,2′:5″,2‴:5‴,2‴-quinquethiophene 1″,1″-dioxide,[3e] bis(2-thiophen-2′-yl-1-cyanovinyl)-2-(2′-ethylhexyloxy)-5-methoxybenzene,[3f] and 2,6-bis[2-(2-hexyloxylphenyl)vinyl]pyran-4-ylidene-malononitrile[3g] all exhibit low-band-gap π-conjugation. The maximum electroluminance of these red PLEDs has rarely exceeded 1000 cd/m^2; efficiencies seldom exceed more than 1% (external quantum efficiency), or luminous efficiencies are around 1 cd/A.[3] The development of efficient and bright fluorene-based copolymers with long-wavelength emission for PLED applications remains a challenging task.

Maleimide is an electron-deficient heterocyclic ring and similar to the larger members of phthalimide, naphthalimide, and peryleneimide, which are known to be n-type organic semiconducting materials for organic transistors.[4] We expect that *N*-alkyl-3,4-diphenylmaleimide (ML) resembles such electron-deficient heterocyclic arenas such as benzoselenadiazole, naphthoselenadiazole, and thiophene dioxide and can be involved in low-band-gap π-conjugation in the formation of long-wavelength emissive fluorene copolymers. Furthermore, *N*-alkyl derivative of 3,4-bis(4-bromophenyl)maleimide, BrML (Scheme 1), is an ideal monomer that can form polyarylenes with high molecular weights through various types of polycondensation. Several studies have utilized various different *N*-alkyl derivatives of BrML in the preparation of 3,4-diphenylmaleimide-based polyaryl macromolecules.[5] Although the authors recently developed efficient and bright small molecules of arylamine-substituted 3,4-diphenylmaleimide for use in red organic light-emitting diode (OLED),[6,7] only yellow to orange-yellow fluorescent polymers have so far been derived from maleimides.[4] This work reports the photoluminescence (PL) characteristics of a series of thiophene- and/or fluorene-based copolymers that contain 3,4-diphenylmaleimide which are fluorescent in the orange to red region. In particular, the fluorescence intensity of the solid film, which is critical to PLED applications, is investigated. The role of either thiophene or fluorene moiety in determining the PL color and the intensity of maleimide-based copolymers is elucidated. Results of this study provide further insight into the development of red light-emitting polymers based on maleimide fluorophores. PLEDs were fabricated from

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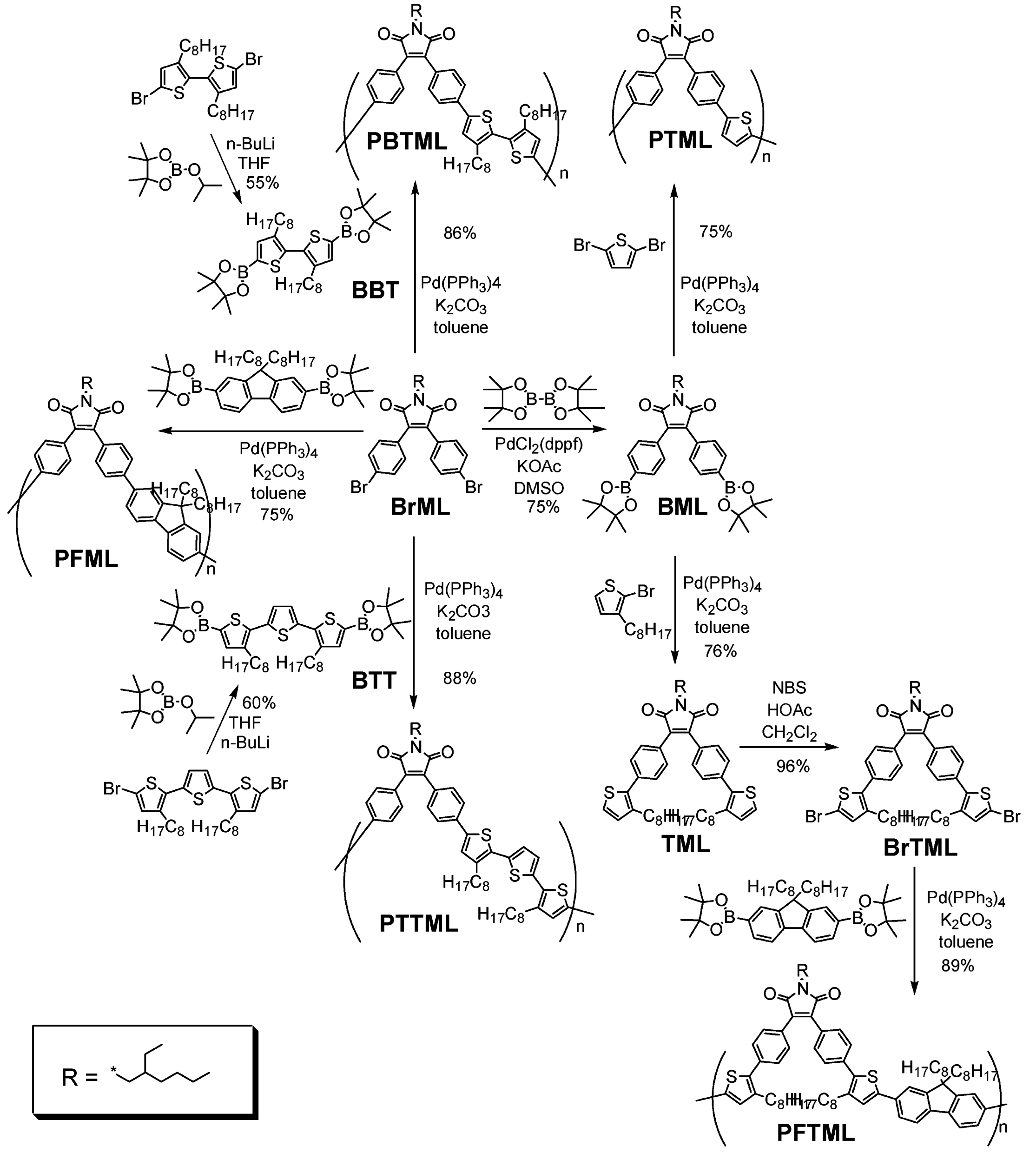
Scheme 1



these maleimide copolymers, and their EL properties were examined for practical applications.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 MHz or AMX-400 MHz Fourier transform spectrometer at room temperature. The number- and weight-average molecular weight of polymers were determined by gel permeation chromatography (GPC) on a Waters GPC-1515 with a 2414 refractive index detector, using THF as the eluent and polystyrene as the standard. Fluorescence spectra were recorded by a fluorescence spectrophotometer (Hitachi F-450). Glass transition temperatures (T_gs) and thermal decomposition temperatures (T_ds) of the copolymers were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) using Perkin-Elmer DSC-6 and TGA-7 analyzer systems, respectively. Both thermal analyses were performed with a scanning (both heating and cooling) rate of 10 deg/min in an atmosphere of nitrogen. The temperatures at the intercept of the curves on the thermogram (endothermic, exothermic, or weight loss) and the leading baseline were taken as the estimates for the onset T_g and T_d. Both solution and solid-state fluorescence quantum yields of the model compounds and the maleimide-based copolymer were determined using the integrating sphere method described by de Mello et al.[8] The thin films were spin-casted from toluene solution on the glass substrate and subjected for vacuumed drying at room temperature for at least 16 h before the experimental measurement.

Materials. All chemicals were purchased from Aldrich and Acros Chemical Co. and were used without any further purification. All the solvents such as toluene, DMSO, and THF were distilled after drying with appropriate drying agents. The dried solvents were stored over 4 Å molecular sieves before usage. Compounds 3,3′-dioctyl-2,2′-bithiophene,[9] 3,3″-dioctyl-[2,2′;5′,2″]terthiophene,[10] 2,7-dibromofluorene,[11] 2,7-dibromo-9,9-dioctylfluorene,[12] 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene,[13] 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene,[3c] and *N*-(2-ethylhexyl)-3,4-bis(4-bromophenyl)-maleimide, BrML,[7a] were synthesized according to methods in the literature. Pertinent synthesis procedures for preparing *n*-hexyl derivatives were adopted to synthesize 5-bromo-3,3′-dioctyl-[2,2′]-bithiophene,[14a,b] and 5-bromo-3,3′-dioctyl-[2,2′;5′,2″]terthiophene.[14c] Copolymer PFML[5f] has been known before and synthesized in our lab by Suzuki cross-coupling of *N*-(2-ethylhexyl)-3,4-bis(4-bromophenyl)maleimide and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene with a good yield of 75% (Scheme 1).

***N*-(2-Ethylhexyl)-3,4-diphenylmaleimide, ML.** This compound was obtained as a greenish-yellow solid according to the procedure in the literature,[7] but 2-ethylhexyl bromide was used as the alkylating reagent. ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.47 (dd, 4H, $J = 7.7$ Hz, $J = 1.5$ Hz), 7.45 (dd, 4H, $J = 7.7$ Hz, $J = 1.5$ Hz), 7.38−7.30 (m, 6H), 3.53 (d, 2H, $J = 7.1$ Hz), 1.82−1.77 (m, 1H), 1.43−1.15 (m, 8H), 0.93−0.81 (m, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz, δ/ppm): 171.1, 136.0, 129.9, 128.7, 128.5, 42.2, 38.4, 30.6, 28.6, 23.9, 23.0, 14.1, 10.4. Anal. Calcd for $C_{24}H_{27}NO_2$: C, 79.74; H, 7.53; N, 3.87. Found: C, 79.38; H, 7.87; N, 3.30.

5,5′-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,3′-dioctyl-[2,2′]bithiophenyl, BBT. *n*-Butylithium (6.4 mL of a 1.6 M solution in hexane, 10.2 mmol) was added dropwisely to a solution of 5,5′-dibromo-3,3′-dioctyl-[2,2′]bithiophenyl (2.75 g, 5 mmol) in tetrahydrofuran (50 mL) at −78 °C for 2 h, and then 2-isopropoxy-4,4,5,5-tetramethyl-13,2-dioxaborolane (10 mL, 49 mmol) was promptly injected into the flask. After stirring for 10 min at −78 °C, the reaction mixture was allowed to stand overnight at room temperature. The mixture was poured into ice−water and extracted with dichloromethane. After drying over magnesium sulfate, the extract was concentrated. The solution mixture was purified by flash silica gel column (EtOAc/hexanes, 5:95) and gave a colorless viscous oil (1.78 g, 55%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.48 (s, 2H), 2.47 (t, 4H, $J = 7.7$ Hz), 1.52−1.49 (m, 4H), 1.38 (s, 24H), 1.26−1.18 (m, 20H), 0.86−0.82 (m, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz, δ/ppm): 143.6, 138.8, 136.3, 84.1, 31.9, 30.6, 29.4, 29.3, 29.2, 28.8, 24.8, 22.6, 14.1. Anal. Calcd for $C_{36}H_{60}B_2O_4S_2$: C, 67.29; H, 9.41. Found: C, 67.16; H, 9.37.

***N*-(2-Ethylhexyl)-bis[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]maleimide, BML.** A flask charged with BrML (1.038 g, 2 mmol), bis(pinacolato)diboron (1.32 g, 5.2 mmol), PdCl$_2$(dppf) (90 mg, 3 mol %), and KOAc (1.18 g, 12 mmol) in 12 mL of DMSO was stirred at 80 °C for 4 h under a nitrogen atmosphere. After cooling, the mixture was diluted with 30 mL of benzene and then washed with H_2O (3 × 20 mL). After drying over magnesium sulfate, the solution mixture was subjected for purification by column chromatograph with silica gel (EtOAc/hexanes, 5:95) to afford a green viscous oil (0.96 g, 78%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.73 (d, 4H, $J = 7.9$ Hz), 7.42 (d, 4H, $J = 7.9$ Hz), 3.51 (d, 2H, $J = 7.0$ Hz), 1.80−1.77 (m, 1H), 1.32−1.23 (m, 8H), 0.92−0.87 (m, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz, δ/ppm): 170.8, 136.4, 134.7, 131.2, 129.0, 127.0, 84.0, 83.9, 42.2, 38.4, 30.5, 28.5, 24.8, 23.9, 23.0, 14.0, 10.4. Anal. Calcd for $C_{36}H_{49}B_2NO_6$: C, 70.49; H, 8.05; N, 2.28. Found: C, 70.16; H, 8.37; N, 2.23.

5,5″-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,3″-dioctyl-[2,2′;5′,2″]terthiophenyl, BTT. BTT was synthesized from 5,5″-dibromo-3,3″-dioctyl-[2,2′;5′,2″]terthiophenyl (0.77 g, 1.2 mmol) by using a similar method for BBT. The desired product was obtained by silica gel flash column chromatography (EtOAC/hexanes, 5:95) as a colorless viscous oil (0.54 g, 60%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.45 (s, 2H), 7.10 (s, 2H), 2.77 (t, 4H, $J = 7.8$ Hz), 1.69−1.61 (m, 4H), 1.37−1.25 (m, 44H), 0.88−0.84 (m, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz, δ/ppm): 140.8, 140.2, 137.5, 136.4, 126.3, 84.1, 31.9, 30.6, 29.6, 29.4, 29.3, 29.2, 24.7, 22.6, 14.1. Anal. Calcd for $C_{40}H_{62}B_2O_4S_3$: C, 66.29; H, 8.62. Found: C, 66.11; H, 8.73.

***N*-(2-Ethylhexyl)-3,4-bis{4-[(3-octylthien-2-yl)phenyl]}-maleimide, TML.** To a mixture of BML (1.3 g, 2.1 mmol), 2-bromo-3-octylthiophene (2.32 g, 8.4 mmol), and Pd(PPh$_3$)$_4$ (146 mg, 6 mol %) was added in a mixture solution of toluene (10.5 mL) and aqueous potassium carbonate (2 M, 10.5 mL). The reaction mixture was vigorously stirred at 85−90 °C for 8 h under a nitrogen atmosphere. After cooling, the reaction solution was extracted with dichloromethane and water. The organic layer was collected and dried over magnesium sulfate. Further purification was performed using silica gel flash column chromatography (EtOAc/hexanes, 1:9) to generate a yellow viscous oil (2.32 g, 76%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.59 (d, 4H, $J = 8.3$ Hz), 7.43 (d, 4H, $J = 8.3$ Hz), 7.23 (d, 2H, $J = 5.2$ Hz), 6.97 (d, 2H, $J = 5.5$ Hz), 3.55 (d, 2H, $J = 7.0$ Hz), 2.66 (t, 4H, $J = 7.8$ Hz), 1.83−1.80 (m, 1H), 1.63−1.56 (m, 4H), 1.40−1.22 (m, 28H), 0.95−0.82 (m, 12H). ^{13}C NMR (CDCl$_3$, 100 MHz, δ/ppm): 171.1, 139.5, 136.8, 136.5, 135.1, 130.1, 129.9, 129.2, 127.4, 124.3, 42.2, 38.4, 31.8, 31.0, 30.5, 29.7, 29.5, 29.4, 29.2, 28.8, 28.6, 23.9, 23.0, 22.6, 14.1, 10.4. Anal. Calcd for $C_{48}H_{63}NO_2S_2$: C, 76.85; H, 8.47; N, 1.87. Found: C, 76.57; H, 8.45; N, 1.72.

***N*-(2-Ethylhexyl)-3,4-bis{4-[(3,3′-dioctyl-[2,2′]bithiophen-5-yl)phenyl]}maleimide, BTML.** BTML was obtained as an orange viscous oil with isolated yields of 46% from the reaction of BML (368 mg, 0.6 mmol) and 5-bromo-3,3′-dioctyl-[2,2′]bithiophene (610 mg, 1.3 mmol) according to the procedure described for the synthesis of TML. ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.57 (d, 4H, $J = 6.8$ Hz), 7.54 (d, 4H, $J = 6.8$ Hz), 7.28 (d, 2H, $J = 4.2$ Hz), 7.22 (s, 2H), 6.95 (d, 2H, $J = 4.2$ Hz), 3.55 (d, 2H, $J = 5.7$ Hz), 2.52 (t, 4H, $J = 6.2$ Hz), 2.48 (t, 4H, $J = 6.2$ Hz), 1.81−1.79 (m, 1H), 1.55−1.52 (m, 8H), 1.38−1.21 (m, 48H), 0.94−0.80 (m, 18H). ^{13}C NMR (CDCl$_3$, 100 MHz, δ/ppm): 171.1, 143.7, 142.5, 142.4, 135.6, 134.8, 130.5, 129.5, 128.7, 128.3, 127.7, 125.5, 125.4, 125.3, 38.4, 31.9, 30.7, 30.6, 30.5, 29.7, 29.4, 29.2, 29.0, 28.8, 28.6, 23.9, 23.0, 22.6, 14.1, 10.4. Anal. Calcd for $C_{72}H_{99}NO_2S_4$: C, 75.94; H, 8.76; N, 1.23. Found: C, 75.49; H, 8.59; N, 1.32.

***N*-(2-Ethylhexyl)-3,4-bis{4-[(3,3″-dioctyl-[2,2′;5′,2″]terthiophen-5-yl)phenyl]}maleimide, TTML.** TTML was obtained as a deep red viscous oil with isolated yields of 40% from the reaction of BML (740 mg, 1.2 mmol) and 5-bromo-3,3′-dioctyl-[2,2′;5′,2″]-terthiophene (1.72 g, 3.1 mmol) following the procedure described for the synthesis of TML. ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.58−7.54 (m, 8H), 7.21 (s, 2H), 7.16 (d, 2H, $J = 5.2$ Hz), 7.09 (d, 2H, $J = 3.6$ Hz) 7.05 (d, 2H, $J = 3.6$ Hz) 6.92 (d, 2H, $J = 5.2$ Hz) 3.54 (d, 2H, $J = 6.8$ Hz) 2.79−2.75 (m, 8H), 1.82−1.752 (m, 1H), 1.67−1.62 (m, 8H), 1.39−1.25 (m, 48H), 0.94−0.83 (m, 18H). ^{13}C NMR (CDCl$_3$, 100 MHz, δ/ppm): 171.0, 140.7, 140.6, 139.8, 136.3, 135.7, 135.4, 134.8, 131.2, 130.5, 130.3, 130.1, 127.8, 127.1, 126.1, 126.0, 125.4, 123.8, 42.3, 38.4, 31.9, 30.7, 30.6, 29.6, 29.4, 29.3 (×2), 29.2, 28.6, 23.9, 23.0, 22.7, 14.1, 10.4. Anal. Calcd for $C_{80}H_{103}NO_2S_6$: C, 73.74; H, 7.97; N, 1.07. Found: C, 73.35; H, 7.88; N, 1.23.

***N*-(2-Ethylhexyl)-3,4-bis{4-[(5-bromo-3-octylthien-2-yl)phenyl]}-maleimide, BrTML.** *N*-Bromosuccinimide (NBS) (0.57 g, 3.2 mmol) was added portionwise to a solution of TML (1.2 g, 1.6 mmol) in a mixture of chloroform (16 mL) and acetic acid (16 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred overnight and then washed with water. The aqueous layer was further extracted with chloroform. The organic layers were combined and washed with saturated aqueous sodium bicarbonate, brine, and water. After drying over magnesium sulfate, the solvent was evaporated. The solid residue was purified by silica gel flash column chromatography (EtOAc/hexanes, 5:95) and gave a yellow viscous oil (1.28 g, 88%). ^{1}H NMR (CDCl$_3$, 400 MHz, δ/ppm): 7.57 (dd, 4H, $J = 8.5$ Hz, $J = 1.9$ Hz), 7.36 (dd, 4H, $J = 8.5$ Hz, $J = 1.9$ Hz), 6.92 (s, 2H), 3.55 (d, 2H, $J = 7.1$ Hz), 2.58 (t, 4H, $J = 7.7$ Hz), 1.82−1.79 (m, 1H), 1.59−1.53 (m, 4H), 1.39−1.22 (m, 28H), 0.94−0.82 (m, 12H). ^{13}C NMR (CDCl$_3$, 100 MHz, δ/ppm): 170.9, 140.1, 138.3, 135.4, 135.1, 132.5, 130.2, 129.1, 127.9, 111.2, 42.3, 38.4, 31.8, 30.8, 30.6, 29.4 (×2), 29.3, 29.2, 28.7, 28.6, 23.9, 23.0, 22.6, 14.1, 10.4. Anal. Calcd for $C_{48}H_{61}Br_2NO_2S_2$: C, 63.50; H, 6.77; N, 1.54. Found: C, 63.22; H, 6.65; N, 1.57.

***N*-(2-Ethylhexyl)-3,4-bis{4-[(5−9,9-dioctylfluoren-2-yl)phenyl]}-maleimide, FTML.** FTML was obtained as an orange-red viscous oil with isolated yields of 78% from the reaction of BrTML (908 mg, 1.0 mmol) and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (1.55 g, 3.0 mmol) according to the procedure described for the synthesis of TML. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, δ/ppm): 7.67 (d, 4H, $J = 7.2$ Hz), 7.60−7.56 (m, 8H), 7.50 (d, 4H, $J = 7.2$ Hz), 7.33−7.23 (m, 8H), 3.52 (dd, 2H, $J = 6.8$, $J = 4.2$ Hz), 2.70 (t, 4H, $J = 7.2$ Hz), 2.02 (t, 8H, $J = 7.3$ Hz), 1.82−1.79 (m, 1H), 1.78−1.67 (m, 4H), 1.32−0.73 (m, 92H), 0.70−0.57 (m, 8H). ^{13}C NMR (CDCl$_3$, 100 MHz, δ/ppm): 171.6, 152.4, 144.0, 141.5, 140.9, 136.9, 136.7, 135.8, 133.7, 130.8, 129.4, 128.4, 126.6, 125.1, 120.7, 120.3, 56.0, 42.8, 40.9, 39.1, 32.5, 32.4, 31.5, 31.2, 30.5, 30.3, 30.1, 30.0, 29.8 (×2), 29.7 (×2), 29.2, 24.5, 24.4, 23.6, 23.3, 23.2, 14.5, 14.4, 10.9. Anal. Calcd for $C_{106}H_{143}NO_2S_2$: C, 83.35; H, 9.44; N, 0.92. Found: C, 83.12; H, 9.25; N, 0.86.

Copolymer PBTML. $Pd(PPh_3)_4$ (12 mg, 1.0 mol %) and several drops of Aliquate 336 in a mixture of toluene (5 mL) and aqueous potassium carbonate (2 M, 5 mL) were added to a mixture of BrML (519.3 mg, 1.0 mmol) and BBT (642.6 mg, 1.0 mmol). The mixture was vigorously stirred at 85−90 °C for at least 48 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into a solution (400 mL) of methanol and deionized water (10:1). Fibrous precipitates were obtained by filtration. The precipitate was then dissolved in dichloromethane and reprecipitated first from water and then from methanol. The resulting polymer PBTML was obtained as a red solid with isolated yields of 86% after drying in a vacuum. ^1H NMR (CD_2Cl_2, 400 MHz, δ/ppm): 7.57 (d, 4H, $J = 8.0$ Hz), 7.51 (d, 4H, $J = 8.0$ Hz), 7.26 (s, 2H), 3.50 (d, 2H, $J = 7.0$ Hz), 2.53 (t, 4H, $J = 7.7$ Hz), 1.78−1.72 (m, 1H), 1.57−1.51 (m, 4H), 1.47−1.21 (m, 28H), 0.92−0.85 (m, 6H), 0.82−0.75 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 171.1, 143.9, 142.8, 135.6, 134.9, 130.6, 129.2, 127.9, 125.7, 125.5, 42.3, 38.5, 31.9, 30.7, 30.6, 29.4 (×2), 29.2 (×2), 29.1, 28.6, 24.0, 23.0, 22.7, 14.1, 10.5. Anal. Calcd for $C_{48}H_{61}NO_2S_2$: C, 77.06; H, 8.22; N, 1.87. Found: C, 76.37; H, 8.08; N, 1.89.

Copolymer PTML. PTML was obtained as a red solid with a yield of 75% from the reaction of BML (613.4 mg, 1.0 mmol) and 2,5-dibromothiophene (241.9 mg, 1.0 mmol) according to the procedure described for the synthesis of PBTML. ^1H NMR (CD_2Cl_2, 400 MHz, δ/ppm): 7.62−7.47 (m, 8H), 7.37−7.35 (m, 2H), 3.49 (br, 2H), 1.76 (br, 1H), 1.39−1.16 (m, 8H), 0.89−0.82 (m, 6H), 0.82−0.75 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 171.4, 144.1, 135.8, 135.6, 131.9, 129.1, 128.9, 126.0, 125.8, 42.8, 39.1, 31.2, 29.2, 24.5, 23.6, 14.4, 10.8. Anal. Calcd for $C_{28}H_{27}NO_2S$: C, 76.16; H, 6.16; N, 3.17. Found: C, 74.16; H, 6.11; N, 2.87.

Copolymer PTTML. PTTML was obtained as a deep red solid with isolated yields of 88% from the reaction of BrML (519.3 mg, 1.0 mmol) and BTT (724.7 mg, 1.0 mmol) according to the procedure described for the synthesis of PBTML. ^1H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.56 (m, 8H), 7.21 (s, 2H), 7.09 (s, 2H), 3.52 (br, 2H), 2.77 (br, 4H), 1.80−1.74 (m, 1H), 1.67−1.62 (m, 4H), 1.37−1.23 (m, 28H), 0.94−0.82 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 171.0, 140.9, 136.0, 135.3, 134.7, 131.4, 131.2, 130.5, 127.8, 127.1, 126.1, 125.4, 42.3, 38.4, 31.9, 30.6, 30.1, 29.7, 29.6 (×2), 29.4, 29.3, 28.6, 23.9, 23.0, 22.7, 14.1, 10.4. Anal. Calcd for $C_{52}H_{63}NO_2S_3$: C, 75.22; H, 7.65; N, 1.69. Found: C, 74.62; H, 7.49; N, 1.71.

Copolymer PFTML. PFTML was obtained as a deep orange solid with isolated yields of 89% from the reaction of BrTML (907.9 mg, 1.0 mmol) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (642.6 mg, 1.0 mmol) according to the procedure described for the synthesis of PBTML. ^1H NMR (CD_2Cl_2, 400 MHz, δ/ppm): 7.66 (d, 2H, $J = 7.9$ Hz), 7.61−7.56 (m, 8H), 7.50 (d, 4H, $J = 8.4$ Hz), 7.28 (s, 2H), 3.53 (d, 2H, $J = 5.3$ Hz), 2.70 (t, 4H, $J = 7.4$ Hz), 2.02 (br, 4H), 1.80−1.78 (m, 1H), 1.68−1.63 (m, 4H), 1.31−1.22 (m, 28H), 1.13−1.02 (m, 20H), 0.94−0.89 (m, 6H), 0.83−0.79 (m, 6H), 0.74−0.71 (m, 6H), 0.64 (br, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 171.6, 152.4, 144.0, 141.5, 140.9, 136.9, 136.7, 135.8, 133.7, 130.8, 129.4, 128.4, 126.6, 125.1, 120.7, 120.3, 56.0, 42.8, 40.9, 39.1, 32.5, 32.4, 31.5, 31.2, 30.5, 30.3, 30.1, 30.0, 29.8 (×2), 29.7 (×2), 29.2, 24.5, 24.4, 23.6, 23.3, 23.2, 14.5, 14.4, 10.9. Anal. Calcd for $C_{65}H_{83}NO_2S$: C, 82.84; H, 8.88; N, 1.49. Found: C, 81.94; H, 8.81; N, 1.73.

Fabrication and Characterization of PLED. A ∼90 nm thick layer of poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was initially spin-casted on precleaned ITO-coated glass substrate. After it had been bake-dried at about 140 °C, ITO/PEDOT:PSS glass substrate was spin-casted with a filtered toluene solution that contained maleimide copolymer to form a thin film with a thickness about 60 nm. TPBI (2,2′,2″-(1,3,5-phenylene)-tris(1-phenyl-1*H*-benzimidazole) was initially deposited, by vacuum thermal deposition, on a ITO/PEDOT:PSS/maleimide−copolymer glass substrate as an electron-transporting layer,[15] or LiF (0.5 nm)/Al (150 nm) was directly vacuum-deposited thereon as the cathodic top electrode. The EL characteristics, including current density (*I*, mA/cm^2), driving voltage (V), electroluminance (*L*, cd/m^2), external quantum efficiency (%), and luminious efficiency (cd/A), of complete PLEDs were examined for under ambient conditions, according to a routine procedure described elsewhere.[6]

Table 1. Characterization of Copolymers PFML, PTML, PBTML, PTTML and PFTML

	M_w[a]	M_n[a]	PDI[a]	T_g (°C)	T_d (°C)	λ_{max}^{fl}, ϕ_f, fwhm[b] (nm, %, nm)[c]	λ_{max}^{fl}, ϕ_f, fwhm[b] (nm, %, nm)[d]
PFML	12 619	6 874	1.84	75	401	549, 65, 70	580, 20, 92
PTML	16 532	10 463	1.58	105	427	582, 49, 95	610, 5, 93
PBTML	24 199	14 938	1.62	52	398	609, 36, 103	621, 13, 99
PTTML	43 135	17 185	2.51	70	395	634, 15, 100	*e*, <1, *e*
PFTML	34 060	19 135	1.78	75	405	598, 37, 92	601, 22, 91

[a] Analytical GPC was obtained in tetrahydofuran (THF) using polystyrene standard. [b] Fwhm is the full width at half-maximum of emission bands. [c] In toluene. [d] As solid film spin-casted from toluene solution. [e] Fluorescence too weak to be determined.

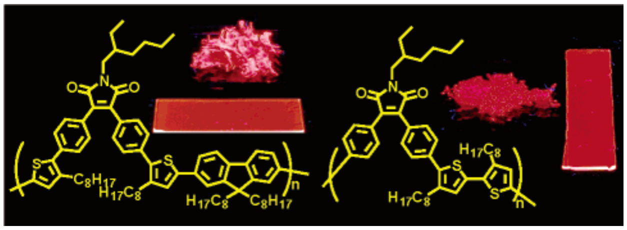


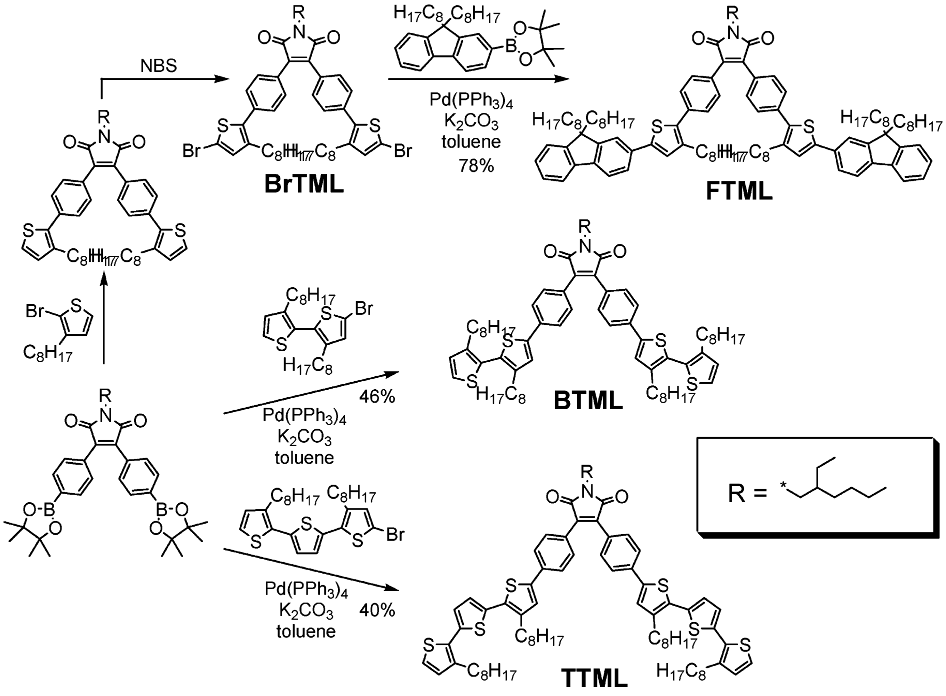
Figure 1. Fluorescence images of PBTML and PFTML in form of bulk solid and thin film on glass substrate.

Results and Discussion

Synthesis and Characterization. Thiophene−maleimide copolymers, PTML, PBTML, and PTTML, were readily prepared by facile Suzuki cross-coupling in two ways. Whereas PTML was prepared from 2,5-dibromothiophene and bis(boron ester)-substituted maleimide BML, previously known BrML was adopted in the synthesis of PBTML and PTTML with 5,5′-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,3′-dioctyl-[2,2′]-bithiophenyl (BBT) and 5,5″-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,3″-dioctyl-[2,2′;5′,2″]terthiophenyl (BTT), respectively (Scheme 1). Both bis(boronic ester)s of BBT and BTT were synthesized in two steps from known 3,3′-dioctyl-2,2′-bithiophene and 3,3″-dioctyl-[2,2′;5′,2″]terthiophene, respectively. Synthesis of the novel triad copolymer PFTML is less straightforward because it involves the heretofore unknown bromothiophene-substituted 3,4-diphenylmaleimide, *N*-(2-ethylhexyl)-3,4-bis{4-[(5-bromo-3-octylthien-2-yl)phenyl]}-maleimide (BrTML), in addition to the well-known 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene as two monomers. BrTML was obtained in high yields by the NBS (*N*-bromosuccinimide) bromination of *N*-(2-ethylhexyl)-3,4-bis{4-[(3-octylthien-2-yl)phenyl]}maleimide (TML**)**, which in turn was easily prepared by Suzuki cross-coupling between BML and 2-bromo-3-octylthiophene. Bis-(boron ester)-substituted maleimide, BML**,** served as the starting material, which was easily derived from BrML by reacting it with bis(pinacolato)diboron catalyzed by homemade $PdCl_2(dppf)$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene).

These copolymers have weight-average molecular weights (M_w) of 12 600−43 100 with polydispersity indices (M_w/M_n) of 1.62−2.51. The thermal properties of the polymers were determined by TGA and DSC measurements. All of these polymers exhibit good thermal stability with T_ds of near or above

Scheme 2



400 °C (Table 1) in an atmosphere of nitrogen. Although such copolymers have extended π-conjugation along their rigid polymer backbones, many aliphatic long alkyl substituents (2-ethylhexyl and *n*-octyl) render maleimide copolymers highly soluble in most common organic solvents, such as toluene, dichloromethane, and THF. This solubility is an advantage in the fabrication of homogeneously thin films from these copolymers by the spin-coating method. (See PBTML and PFTML in Figure 1 as examples.) However, this solubility also reduces the rigidity of these maleimide copolymers, resulting in a relatively low T_gs of 52−105 °C. Appropriately shortening the alkyl substituent of these maleimide copolymers can effectively enhance the T_gs.

In addition to TML, a series of model compounds, BTML, TTML, and FTML, were also synthesized to study the photoluminescence properties and the color tuning of the parent compound *N*-(2-ethylhexyl)-3,4-diphenylmaleimide, ML, the fundamental building block of the 3,4-diphenylmaleimide copolymers studied herein. Conventional Suzuki cross-coupling was used to prepare both BTML and TTML in reasonable yields from BML with 5-bromo-3,3′-dioctyl-[2,2′]bithiophene and 5-bromo-3,3′-dioctyl-[2,2′;5′,2″]terthiophene, respectively (Scheme 2). On the other hand, an FTML model compound was prepared from BrTML with 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene again via efficient Suzuki cross-coupling (Scheme 2). All copolymers and their synthetic precursors were characterized with elemental analysis and ^{1}H/^{13}C NMR.

Photoluminescent Characterization. Previously, we have shown that the fluorescence color of 3,4-diphenylmaleimide is quite sensitive to the substituent on the phenyl rings.[7b] A series of maleimide model compounds (Scheme 2) were prepared to examine the variation in the color of fluorescence: the parent maleimide ML has a short emission wavelength $\lambda_{\max}^{\mathrm{fl}}$ of 500 nm and so exhibits green fluorescence, and TML has an emission wavelength $\lambda_{\max}^{\mathrm{fl}}$ of 568 nm (Figure 2). As the number of the electron-rich thiophene rings attached to ML increases, the emission wavelength $\lambda_{\max}^{\mathrm{fl}}$ of TML approaches 568 nm (yellow) and that of BTML approaches 609 nm (orange-red). In fact, terthiophene-substituted ML, TTML (Figure 2), exhibited the longest emission $\lambda_{\max}^{\mathrm{fl}}$ of 626 nm, the color of which fluorescence in solution is reddish.

Comparing the fluorescence spectra shown in Figure 2 reveals that the fluorescence wavelengths of the copolymers are more or less bathochromically shifted from those of corresponding model compounds, such as $\lambda_{\max}^{\mathrm{fl}}$ of 590 nm for FTML and $\lambda_{\max}^{\mathrm{fl}}$ of 598 nm for PFTML. This finding implies the π-conjugation nature of the copolymers. This red shift in the PL makes the fluorescence of PTTML practically red ($\lambda_{\max}^{\mathrm{fl}} = 634$ nm). However, like most known red light-emitting polymers, PBTML or PTTML suffered from a serious problem of fluorescence quenching in the solid state. PBTML showed considerable fluorescence quenching with a solid-state fluorescence quantum yields (ϕ_f) of 13%, which is more than 60% lower than that in solution (Table 1). The situation for PTTML was even worse. In the solid state, the red fluorescence was almost invisible, meaning that the solid state ϕ_f of PTTML is virtually zero (Table 1).

The ϕ_f values of three copolymers reveal more thiophene rings in the copolymer structure which correspond to lower fluorescence quantum yields in the solid state (Table 1). Although thiophene potently red-shifts the fluorescence of maleimide copolymer, it is also a determining structural factor in weakening the fluorescent intensity in both solution and the solid state. This result is consistent with the fact that oligo- and polythiophene are generally not suitable as emissive materials because they form aggregates that quench fluorescence in the solid state.[16] PTML, PBTML, and PTTML have decreasing fluorescence quantum yields in solution, which are 40, 36, and 15%, respectively (Table 1). The structure of the copolymer was redesigned with a fluorene moiety to replace the thiophene rings as in PFTML to solve the problem. This structural change was motivated by the previously known fluorene−maleimide copolymer PFML, which has a relatively high ϕ_f in both toluene solution ($\phi_f = 65\%$) and the solid state ($\phi_f = 20\%$), although its fluorescence is an undesired yellow color ($\lambda_{\max}^{\mathrm{fl}}$ of 549 nm). Therefore, the new copolymer PFTML, with a maleimide−

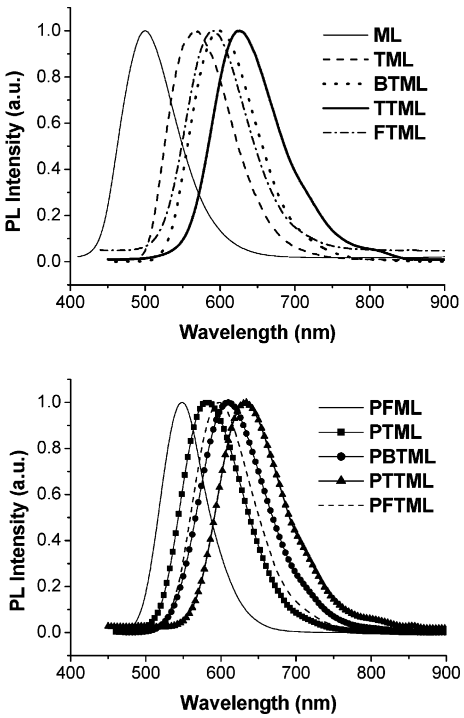


Figure 2. Solution fluorescence spectra of ML, TML, BTML TTML, and FTML (top) and of PFML, PTML, PBTML, PTTML, and PFTML (bottom).

thiophene–fluorene triad, is anticipated to have strong fluorescence in the solid state and yet possess sufficiently long wavelengths. In terms of fluorescence intensity, PFTML is quite a successful orange-red light-emitting material. PFTML has a solution emission wavelength of around 598 nm with one of the highest ϕ_f (37%) of any of the maleimide copolymers reported here. In the solid state, the fluorescent wavelength is only slightly red-shifted to $\lambda_{\max}^{\mathrm{fl}} \sim 601$ nm, and the fluorescent intensity remains high ($\phi_f \sim 22\%$), unlike from most orange-red or red light-emitting polymers. The highly efficient orange-red light-emitting polymer MEH–PPV (2-methoxy-5-(2-ethylhexyl)-polyphenylenevinylene), a bench mark of long wavelength emissive polymer for PLED, has a ϕ_f of 10–20% in the solid state.[8,17]

A structure that combines thiophene and fluorene is ideal for maleimide-based copolymers. The red shift in the fluorescence color is attributable mainly to the thiophene ring, since the emission $\lambda_{\max}^{\mathrm{fl}}$ values of PTML, PBTML, and PTTML are 33, 60, and 85 nm longer than that of PFML, respectively (Figure 2, Table 1). However, the 9,9-dioctylfluorene moiety is responsible for most of the fluorescent intensity of the copolymers, as evidenced by the high ϕ_f of PFTML (22%) in the solid state, which is almost double that of PBTML (13%). Moreover, the PBTML fluorescence in the toluene solution is significantly bathochromic-shifted (12 nm) to that in the solid film; PFTML exhibits only a 3 nm difference in emission $\lambda_{\max}^{\mathrm{fl}}$ (Table 1). This can be attributed to the rigid fluorene moiety that effectively reduces the interaction between π-conjugated polymer chains in the solid state, helping to prevent the copolymer from fluorescence quenching.

Table 2. EL Characteristics of PFML, PFTML, and PBTML Devices

	$\lambda_{\max}^{\mathrm{EL}}$, fwhm (nm, nm)	CIE[a] 1931 (x, y)	peak L (cd/m^2)	L and V[b] (cd/m^2, V)	peak efficiency (%, cd/A)
PFML	566, 102	0.45, 0.52	365	65, 11	0.13, 0.35
PFTML	620, 96	0.61, 0.39	2020	215, 7.8	0.74, 1.25
PFTML[c]	614, 86	0.60, 0.39	1901	184, 7.5	0.57, 0.95
PBTML	624, 96	0.61, 0.38	207	11, 6.5	0.05, 0.07
PBTML[c]	620, 94	0.60, 0.37	1290	200, 7.4	0.61, 0.89
PTTML	676, 104	0.65, 0.33	14	7, 12	0.16, 0.46

[a] Commission Internationale de L'Eclairage chromaticity coordinates. [b] At 20 mA/cm^2. [c] PLED devices containing TPBI as electron-transporting layer.

Electroluminescent Characterization. Four PLED devices were fabricated from toluene solutions by the spin-coating method with PFML, PBTML, PFTML, and PTTML as the light-emitting materials. PLED devices with the similar ITO/PEDOT:PSS/maleimide copolymer/LiF/Al configurations were fabricated. PFTML and PBTML devices also incorporated the electron-deficient TPBI as the electron-transporting layer to form ITO/PEDOT:PSS(90 nm)/PFTML or PBTML/TPBI/LiF/Al to balance the electron charge carriers and the hole charge carriers to elevate the EL efficiency of the devices. Without TPBI, the device, particularly the PBTML device, is expected to be inefficient because it contains an excess of hole charge carriers, which is in turn due to the electron-rich bithiophene unit of the copolymer. The yellow EL of similar maleimide–fluorene copolymers of PFML has been reported before.[4f] A PLED of PFML was also fabricated and characterized herein for comparison purposes.

Peng et al. reported that PLED of ITO/PEDOT:PSS/PFML (a *N*-octyl derivative)/Alq$_3$/Mg:Ag exhibited EL with a peak intensity of 363 cd/m^2 (18 V) and a $\lambda_{\max}^{\mathrm{EL}}$ of 559 nm,[5f] which values are very similar to those 365 cd/m^2 (15 V) and $\lambda_{\max}^{\mathrm{EL}}$ of 566 nm of the PFML device herein (Table 1). Whereas the PFML PLED herein showed a relatively low EL efficiency of 0.13% or 0.35 cd/A, the corresponding EL efficiency data are not available in Peng et al.'s previous report. Although only slight or no red-shifting of the $\lambda_{\max}^{\mathrm{EL}}$ of PFTML or PBTML was observed, PFML exhibited a blue-shifting of 14 nm (from 580 to 566 nm) from the thin film PL to device EL (Table 2). Peng et al. reported similar blue-shifting for PFML.[5f] The small or little emission red-shifting of PFTML or PBTML is quite inspiring for the implication of eximer formation of these two copolymer. The similarity between the $\lambda_{\max}^{\mathrm{EL}}$ and fwhm values (91 and 99 nm for PL vs 96 nm for EL) indicates that either the excimers are not emissive or only a little excimer formation occurs in PFTML or PBTML.

The PFTML device shows discernible orange-red EL at a low voltage of 5 V with an emission $\lambda_{\max}^{\mathrm{EL}}$ of 620 nm, corresponding to a CIE$_{x,y}$ of (0.61, 0.39). Its brightness increases with the voltage (or current density) and peaks at 2020 cd/m^2 (Figure 4). This is a relatively high peak electroluminance compared with other known orange to red PLEDs[4] and can be attributed to the relatively high fluorescence quantum yields of the copolymer in the solid state. External quantum efficiencies were nearly 1%, or luminous efficiencies exceeded 1 cd/A of (Table 2, Figure 4) at an electroluminance of 1 cd/m^2 and a driving voltage of 5 V. The efficiency performance of the PLED is reasonably good on the basis of EL characterization of the simple and unprotected (from water and oxygen) device structure. This finding is qualitatively attributed to the relatively high fluorescence quantum yields of PFTML.

PBTML exhibited slightly redder EL with an emission $\lambda_{\max}^{\mathrm{EL}}$ of 624 nm, corresponding to a CIE$_{x,y}$ of (0.61, 0.38), although its performance of electroluminance and efficiency are very poor (Table 2, Figure 4). Adding the electron-transporting TPBI into the device drastically improved the performance of PLED. The PBTML device that contained TPBI had an electroluminance of 1290 cd/m^2 and an EL efficiency of as high as 0.61% or 0.89 cd/A (Figure 4), which values are comparable with those

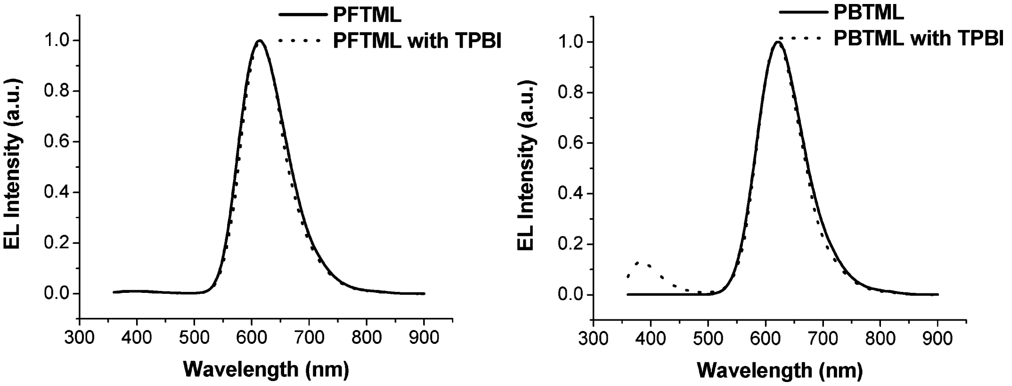


Figure 3. EL spectra of PFTML (left) and PBTML (right) devices.

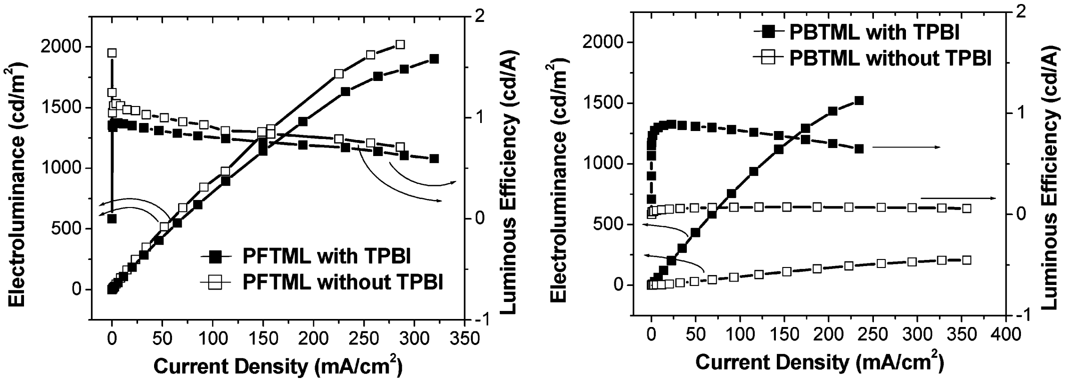


Figure 4. $L-I-$luminous efficiency characteristics of PFTML (left) and PBTML (right) devices.

of the PFTML device. Unfortunately, adding TPBI did not similarly improve the PFTML device (Table 2, Figure 4), probably because that PFTML does not have as many thiophene units as PBTML.

Finally, PLED with PTTML which emits light with a long wavelength was fabricated to test the saturated red EL of the maleimide copolymers, even though PTTML is nearly nonemissive in the solid state. As anticipated, the PTTML device showed an EL $\lambda_{\max}^{\mathrm{EL}}$ of 676 nm, corresponding to a CIE$_{x,y}$ of (0.65, 0.33), which is comparable to that of (0.64, 0.33) of the standard red color as specified by the National Television System Committee (NTSC). However, the saturated red PLED was neither bright (peak EL intensity of only 14 cd/m^2) nor efficient (peak efficiency of 0.16% or 0.46 cd/A), mainly because the ϕ_f was virtually zero in the solid state. However, the possibility of the eximer emission of PTTML in the solid state cannot currently be ruled out. PTTML has the largest redshifting of 42 nm from PL in toluene solution to device EL. This value is relatively large when compared with only 26 nm for PFTML and 11 nm for PBTML (Tables 1 and 2).

Conclusion

In summary, a series of new maleimide-based copolymers were designed and successfully synthesized. The designs support either orange or red long-wavelength fluorescence. More importantly, attention has been paid to achieve high fluorescence intensity in solid state. The model compounds and copolymers showed that the thiophene ring effectively red-shifts the fluorescence wavelength of 3,4-diphenylmaleimide, and 9,9-dioctylfluorene effectively increases fluorescent intensity, particularly in the solid state. For the first time, the PL or EL of maleimide copolymers was extended to long wavelengths from orange to the saturated red region. The PLED of PFTML and PBTML exhibited satisfactory brightness and efficiency. PFTML, a novel maleimide−thiophene−fluorene triad copolymer, exhibited the most satisfactory results. Maleimide copolymers were shown to be potential candidates for orange to red PL and EL PLEDs.

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