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A new series of random conjugated copolymers containing 3,4-diphenylmaleimide and thiophene units for organic photovoltaic cell applications

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ABSTRACT

A series of random conjugated copolymers (labeled PMLTQT, PMLT2T, and PMLT3T) consisting of 3,4diphenyl-maleimide and various thiophene derivatives has been designed and synthesized via Stille cross-coupling for application in polymer solar cells. These copolymers were readily soluble in common organic solvents, thermally stable from 405 to 437 °C upon heating, and exhibited good absorption in the UV and visible regions from 300 to 650 nm. The intensities of the PL emission spectra of these copolymers in a solid film were dramatically quenched by the addition of 50 wt% [6,6]-phenyl C₆₁ butyric acid methyl ester (PC₆₁BM). Their electrochemical properties indicated that the highest occupied molecular orbital levels of these copolymers were in the range of -5.63-5.73 eV, characteristic of better air stability and a high open-circuit voltage (V_{oc}) suitable for application to photovoltaic cells. Bulk heterojunction photovoltaic devices composed of an active layer of electron-donor copolymers blended with the electron acceptor PC₆₁BM or [6,6]-phenyl C₇₁ butyric acid methyl ester (PC₇₁BM) at a weight ratio of 1:3 were investigated. The photovoltaic device containing PMLT3T and PC₇₁BM (1:3, w/w) as the active layer afforded the best performance among these copolymers, with a V_{oc} of 0.74 V, J_{sc} of 7.4 mA cm⁻² and a PCE of 1.20% under AM 1.5 G simulated solar light.

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1. Introduction

During the past decade, polymer solar cells (PSCs) have been attracting extensive attention because they are flexible, lightweight, and potentially low-cost materials suitable for large-area manufacturing, and they present a renewable energy alternative to fossil energy [1–6]. In the past two years, significant progress has been achieved on polymer/fullerene hybrid systems based on the concept of bulk heterojunction (BHJ) [7-9]. For most BHJ cells, the photoactive layer of a PSC is based on a blend of an electron-donating polymer and an electron-accepting fullerene derivative [6,6],-phenyl C₆₁ butyric acid methyl ester (PC₆₁BM) or [6,6]-phenyl C₇₁ butyric acid methyl ester (PC₇₁BM). Regioregular poly(3-hexylthiophene) (rr-P3HT) is one such electron-donating polymer that is most widely investigated in PSC applications [10,11]. A high power conversion efficiency (PCE) of around 4% has been achieved with a BHJ-structure PSC based on rr-P3HT and PC₆₁BM [11]. Although the rr-P3HT: PC₆₁BM blend system represents encouraging progress in PSCs

[12–14], the mismatch or narrow absorption of polythiophenes (PTs) with the solar spectra might hinder further enhancement of the PCE.

To further improve the absorption properties of polymers, the intramolecular charge transfer interactions between electrondonor and electron acceptor moieties have been extensively applied to the development of low bandgap π -conjugated polymers with better PSC performance. Among several π -conjugated D-A polymer systems, aromatic heterocycles such as benzothiadiazole-[15–19], diketopyrrolopyrrole- [20,21], guinoxaline- [22–24], and thienopyrazine-based [25-27] derivatives have been widely used as electron-accepting moieties in absorbing light of longer wavelengths. Maleimide is an electron-deficient heterocyclic ring and similar to the larger members of phthalimide, naphthalimide, and peryleneimide, which are known as *n*-type organic semiconducting materials for organic transistors [28-31]. Furthermore, N-alkyl derivatives of 3,4-bis(4-bromophenyl)maleimide BrML (Scheme 1) are ideal monomers that can form polyarylenes with high molecular weights through various types of polycondensation reactions. In several studies, various N-alkyl derivatives of BrML have been utilized in the preparation of 3,4-diphenyl-maleimide-based polyaryl macromolecules [32-36]. Recently, we have developed efficient and highly fluorescent small molecules of arylamine-



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Scheme 1. Synthetic routes for monomers as well as copolymers PMLTQT, PMLT2T, and PMLT3T.

substituted 3,4-diphenyl-maleimide for use in red organic lightemitting diodes (OLEDs) [37–40], in addition to orange-yellow to red fluorescent polymers derived from maleimides [41–43]. We demonstrated that *N*-alkyl-3,4-diphenyl-maleimide (ML) resembles such electron-deficient heterocyclic arenes as benzoselenadiazole, naphthoselenadiazole, and thiophene dioxide, and can be involved in low bandgap π -conjugation in the formation of longwavelength-emissive fluorene copolymers. More recently, we have developed randomly configured PT derivatives that show promising results for application in PSCs [44,45].

Based on the above discussion, a series of random copolymers containing 3,4-diphenyl-maleimide and different thiophene derivatives has been designed and synthesized via Stille coupling with random configurations for application in PSCs. To generate copolymers for use in PSCs, we first utilized a 3,4-diphenyl-maleimide derivative copolymerizing with quaterthiophene. The 3,4-diphenylmaleimide derivative was designed as an electron-accepting unit, whereas an electron-sufficient thiophene was the electron-donating unit. A donor-acceptor (D-A) copolymer could be readily synthesized. In order to enhance the ability to harvest the light of the solar spectrum, a thiophene unit was further converted into a 3,4-diphenylmaleimide unit. The 3,4-diphenyl-maleimide-thiophene derivative was then copolymerized with different fused thiophene derivatives to improve the coplanarity and conjugation lengths. Several groups have reported that introduction of fused thiophene derivatives into the polymer backbone can reduce steric hindrance, extend conjugation, enhance absorption, and improve charge transport properties [46–51]. Hence, the resulting random copolymers exhibit electron D-A architectures, which promise the merits of low bandgaps and broad absorption bands. In this work, the influence of coplanarity and number of thiophenes for these copolymers on their photophysical and electrochemical properties were investigated in detail. Moreover, the morphological and photovoltaic (PV) characteristics of the copolymer/fullerene derivative-blend films were also discussed.

2. Experimental details

2.1. Chemical materials

The starting materials 2,5-bis(trimethyl-stannyl)thiophene and bis(pinacolato)diboron, reagents, and chemicals were purchased from Aldrich, Alfa, and TCI Chemical Co. They were used as received without any further purification. All solvents, including diethyl ether, dichloromethane (DCM), tetrahydrofuran (THF) or dimethylformamide (DMF), and toluene were freshly distilled over appropriate drying agents prior to use and purged with nitrogen. 2-bromo-3octylthiophene [52], 5,5-dibromo-2,2'-bithiophene [53,54], 3,3'dioctyl-2,2'-bithiophene [55], thieno[3,2-b]thiophene [46,56], and dithieno[3,2-b:2',3'-d]thiophene [57,58] were synthesized according to methods in the literature. N-(2-Ethylhexyl)-3,4-bis(4-bromoph enyl)maleimide (BrML), N-(2-ethylhexyl)-bis[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]maleimide (BML), N-(2-ethylhexyl)-3,4-bis{4-[(5-bromo-3-octylthien-2-yl)phenyl]}maleimide (BrTML), and N-(2-ethylhexyl)-3,4-bis{4-[(3-octylthien-2-yl)phenyl]}maleim ide (TML) have been known before and synthesized in our lab [38,41-43].

2.1.1. 1,1'-(3,3'-Dioctyl[2,2'-bithiophene]-5,5'-diyl)bis[1,1,1trimethylstannane] (BTT)

n-Butyllithium (2.5 mL of a 2.5 M solution in hexane, 6.25 mmol) was added dropwise to a solution of 5,5'-dibromo-3,3'-dioctyl-2,2'bithiophene (1.62 g, 2.95 mmol) in THF (15 mL) at -78 °C for 2 h, after which trimethyltin chloride (1.76 g, 8.80 mmol) was added 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 iced water and extracted with DCM. After drying over magnesium sulfate, the extract was concentrated. The solution mixture was purified by flash silica gel column (hexanes/triethylamine, 10:1) to yield a yellow viscous oil (1.81 g, 86%). ¹H NMR (CDCl₃, 300 MHz, δ /ppm): 7.02 (s, 2H), 2.52 (t, 4H, *J* = 7.8 Hz), 1.59–1.51 (m, 4H), 1.29–1.24 (m, 20H), 0.89–0.85 (m, 6H), 0.37 (s, 18H). ¹³C NMR (CDCl₃, 75 MHz, δ /ppm): 142.97, 137.43, 136.96, 135.34, 32.05, 31.08, 30.89, 29.72, 29.54, 29.39, 28.90, 22.83, 14.27. HRMS calculated for C₃₀H₅₄S₂Sn₂: 718.1711, found 718.1696.

2.1.2. 2,5-Dibromothieno[3,2-b]thiophene (2T)

To an ice-cooled solution of thieno[3,2-b]thiophene (0.70 g, 5.0 mmol) in DMF (20 mL), NBS (1.95 g, 11.0 mmol) was added portionwise, and the mixture was stirred for 3 h. The resulting mixture was extracted with CH₂Cl₂. The organic layer was washed with water, dried over MgSO₄, and evaporated. The residue was recrystallized in mixed solvent (ethanol:water = 5:1, v/v) to yield a colorless crystal (0.96 g, 65%). ¹H NMR (CDCl₃, 300 MHz, δ /ppm): 7.17 (s, 2H). ¹³C NMR (CDCl₃, 75 MHz, δ /ppm): 113.60, 121.79, 138.24. HRMS calculated for C₆H₂Br₂S₂: 295.7965, found 295.7972.

2.1.3. 2,6-Dibromo-dithieno[3,2-b; 2',3'-d]thiophene (3T)

Dithieno[3,2-b; 2',3'-d]thiophene was prepared according to a literature preparation [59]. To a solution of dithieno[3,2-b; 2',3'-d] thiophene (0.98 g, 5.0 mmol) in DMF (20 mL), NBS (1.95 g, 11.0 mmol) was added portionwise and then the mixture was stirred at room temperature overnight. The light yellow suspension was treated with water and filtered off. Subsequently, silica column chromatography with hexane yielded a light yellow solid (1.50 g, 85%). ¹H NMR (300 MHz, CDCl₃): 7.27 (s, 2H). ¹³C NMR (CDCl₃, 75 MHz, δ /ppm): 112.32, 123.19, 130.79, 139.02. HRMS calculated for C₈H₂Br₂S₃: 351.7685, found 351.7671.

2.1.4. PMLTQT

PMLTQT was synthesized via a Stille coupling route, as shown in Scheme 1. BrML (0.39 g, 0.75 mmol), 5,5-dibromo-2,2'-bithiophene (0.24 g, 0.75 mmol), and BTT (1.07 g, 1.50 mmol) were dissolved in 15 mL of dry toluene under a nitrogen atmosphere. Then, $Pd(PPh_3)_4$ (53 mg, 3.0 mol% with respect to ditin monomer) was added to the reaction mixture and the reactions were continued at 85-90 °C for at least 48 h. After the mixture was cooled to room temperature, it 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 DCM, and reprecipitated first from water and then from methanol. Further purification was performed by Soxhlet extractions with methanol and hexane. The resulting polymer PMLTQT was obtained as a red solid with isolated yields of 68% after drying under vacuum. Gel permeation chromatography (GPC) (THF): $M_w = 10.4$ kg/mol and PDI = 1.5. ¹H NMR (CDCl₃, 300 MHz, δ/ppm): 7.61–7.56(br, 8H), 7.09–7.04 (m, 8H), 3.57–3.53 (br, 2H), 2.59-2.52 (m, 8H), 1.85-1.75 (br, 1H), 1.70-1.53 (m, 8H), 1.43–1.20 (m, 40H), 0.98–0.85 (m, 18H). ¹³C NMR (CDCl₃, 75 MHz, δ/ ppm): 171.07, 143.93, 143.56, 142.80, 137.02, 136.72, 136.23, 135.92, 135.55, 134.86, 131.96, 131.46, 130.57, 129.16, 129.00, 128.69, 127.86, 127.68, 127.53, 125.70, 125.47, 125.34, 124.28, 42.31, 38.46, 31.92, 30.67, 29.43, 29.27, 29.08, 28.61, 23.94, 23.04, 22.71, 14.15, 10.48. Anal. Calcd. for $[(C_{48}H_{61}NO_2S_2)_{0.48} + (C_{32}H_{40}S_4)_{0.52}]$: C, 73.63; H, 7.74; N, 1.04; S, 15.06. Found: C, 72.02; H, 7.79; N, 0.86; S, 16.16.

2.1.5. PMLT2T

PMLT2T was obtained as a red solid with a yield of 78% from the reaction of BrTML (0.62 g, 0.68 mmol), 2,5-bis(trimethyl-stannyl) thiophene (0.56 g, 1.36 mmol), 2T (0.20 g, 0.68 mmol), and Pd(PPh_3)₄ (47 mg, 3.0 mol% with respect to ditin monomer) according to the procedure described for the synthesis of PMLTQT. GPC (THF):

$$\begin{split} M_{\rm W} &= 47.0 \ \text{kg/mol} \ \text{and} \ \text{PDI} = 4.3. \ ^1\text{H} \ \text{NMR} \ (\text{CDCl}_3, 300 \ \text{MHz}, \ \delta/\text{ppm}); \\ 7.70-7.58 (br, 8H), \ 7.35-7.50 \ (br, 6H), \ 7.09-6.90 \ (br, 2H), \ 3.57-3.53 \\ (br, 2H), \ 2.70-2.52 \ (br, 4H), \ 1.85-1.82 \ (br, 1H), \ 1.70-1.53 \ (br, 4H), \\ 1.43-1.10 \ (m, 28H), \ 0.95-0.70 \ (m, 12H). \ ^{13}\text{C} \ \text{NMR} \ (\text{CDCl}_3, 75 \ \text{MHz}, \ \delta/\text{ppm}); \\ 171.09, \ 140.55, \ 139.50, \ 135.99, \ 135.03, \ 130.21, \ 128.95, \ 127.66, \\ 126.53, \ 124.30, \ 123.62, \ 109.98, \ 42.29, \ 38.44, \ 31.85, \ 30.85, \ 30.59, \ 29.54, \\ 29.39, \ 29.24, \ 29.06, \ 28.62, \ 27.21, \ 23.94, \ 23.00, \ 22.67, \ 14.12, \ 10.47, \ \text{Anal.} \\ \text{Calcd. for} \ [(\text{C}_{52}\text{H}_{63}\text{NO}_2\text{S}_3)_{0.53} + (\text{C}_{10}\text{H}_4\text{S}_3)_{0.47}]; \ \text{C}, \ 71.21; \ \text{H}, \ 6.48; \ \text{N}, \\ 1.36; \ \text{S}, \ 17.65, \ \text{Found}: \ \text{C}, \ 69.67; \ \text{H}, \ 6.27; \ \text{N}, \ 1.30; \ \text{S}, \ 16.30. \end{split}$$

2.1.6. PMLT3T

PMLT3T was obtained as a deep red solid with isolated yields of 72% from the reaction of BrTML (0.63 g, 0.69 mmol) 2,5bis(trimethyl-stannyl)thiophene (0.57 g, 1.38 mmol), 3T (0.24 g, 0.69 mmol), and Pd(PPh₃)₄ (48 mg, 3.0 mol% with respect to ditin monomer) according to the procedure described for the synthesis of PMLTQT. GPC (THF): $M_w = 15.0$ kg/mol and PDI = 1.9. ¹H NMR (CDCl₃, 300 MHz, δ/ppm): 7.71–7.61 (m, 8H), 7.51–7.40 (br, 6H), 7.06–6.90 (br, 2H), 3.65-3.45 (br, 2H), 2.73-2.57 (br, 4H), 1.87-1.74 (br, 1H), 1.70–1.55 (br, 4H), 1.54–1.26 (m, 28H), 0.99–0.78 (m, 12H). ¹³C NMR (CDCl₃, 75 MHz, δ/ppm): 171.07, 143.87, 143.51, 142.80, 141.79, 140.55, 136.70, 136.21, 135.99, 135.79, 135.55, 135.01, 131.96, 131.44, 130.55, 130.22, 129.47, 128.93, 127.85, 127.65, 126.52, 125.69, 125.46, 125.34, 124.27, 116.75, 109.98, 42.30, 38.45, 31.89, 30.86, 30.65, 29.56, 29.42, 29.25, 29.08, 28.63, 27.22, 23.94, 23.02, 22.69, 14.13, 10.48. Anal. Calcd. for $[(C_{52}H_{63}NO_2S_3)_{0.56}+(C_{12}H_4S_4)_{0.44}]$: C, 70.37; H, 6.31; N, 1.33; S, 18.76. Found: C, 69.94; H, 6.21; N, 1.33; S, 17.60.

2.2. Characterization of copolymers

General. ¹H and ¹³C NMR spectra were recorded on a Varian Unity Inova 300WB NMR spectrometer at room temperature. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer. The number- and weight-average molecular weights of polymers were determined by GPC on a Waters GPC-1515 with refractive index detector 2414, using THF as the eluent and polystyrene as the standard. The glass transition temperatures (T_{α}) and thermal decomposition temperatures (T_d) of the copolymers were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) with 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. UV-visible absorption and fluorescence spectra were recorded by Hewlett-Packard 8453 and Hitachi F-450 spectrophotometers, respectively. The thin films were spin-cast from toluene solution on the glass substrate and subjected to vacuumed drying at room temperature for at least 16 h before experimental measurements. The redox potentials of the polymers were determined by cyclic voltammetry (CV) with an electrochemical analyzer CHI 612D (scanning rate: 50 mV s^{-1}), equipped with platinum (Pt) electrodes and an Ag/Ag⁺ (0.10 M AgNO₃ in MeCN) reference electrode in an anhydrous N₂-saturated solution of 0.1 M Bu₄NClO₄ in MeCN. Bu₄NClO₄ (98%, TCl) was recrystallized three times from mixed solvent methanol/water (1:1) and then dried at 100 °C under reduced pressure. A Pt plate coated with a thin polymer film was used as the working electrode, and a Pt wire and an Ag/Ag⁺ electrode were used as the counter and reference electrodes, respectively. The electrochemical potential was calibrated against Ferrecene/Ferrocene⁺. The morphologies of the polymer solid films were studied with an atomic force microscope (AFM, Seiko SII SPA400) operated in the tapping mode.

2.3. Fabrication and characterization of PSCs

All PSCs were prepared by using the following device fabrication procedure. Glass substrates [Sanyo, Japan (8Ω /sq.)] coated with

indium tin oxide (ITO) were sequentially patterned lithographically, cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, dried on a hot plate at 120 °C for 5 min, and treated with oxygen plasma for 5 min. The hole-transporting material poly(3,4ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS, Clevios P-VP AI4083) was passed through a 0.45-µm filter prior to being deposited on the ITO-coated glass by the spin-coating method (5000 rpm). The sample was then dried on a hot plate at 150 °C for 30 min. A mixture solution of fullerene derivatives (both PC61BM and PC₇₁BM were used) and the copolymer with various weight ratios (w/w) [36 mg/mL in o-dichlorobenzene (o-DCB)] was stirred overnight and then filtered through a 0.2-µm poly(tetrafluoroethylene) (PTFE) filter. The composite film-based photoactive layer of the copolymer/fullerene derivative was formed above the PEDOT: PSS layer by spin-coating (600 rpm, 60 s) of the mixture solution. By using AFM, film thickness of the photoactive layer in PSCs was found in the range of 65-82 nm. The Ca-based (30 nm)/Al (100 nm) cathode was thermally deposited onto the photoactive thin film in a high-vacuum chamber. The active area of the PSC was 4 mm². After Al electrode deposition, the PSCs were examined under ambient conditions. Current density-voltage (I-V) curves of the PSCs were measured on a programmable electrometer with current and voltage sources (Keithley 2400) under the illumination of 100 mW cm⁻² solar light from an AM 1.5G solar simulator (Oriel solar simulator). The illumination intensity was calibrated by using a standard Si photodiode detector equipped with a KG-5 filter. The output photocurrent was adjusted to match the photocurrent of the Si reference cell to obtain a power density of 100 mW cm⁻².

3. Results and discussion

3.1. Characterization of copolymers

The synthetic routes towards the monomers and copolymers are outlined in Scheme 1. BrML was synthesized according to the literature. Another monomer, BML, was easily derived from BrML by reacting it with bis(pinacolato)diboron catalyzed by PdCl₂(dppf) (dppf = 1,1'-bis(diphenylphosphino)ferrocene). BrTML was obtained in high yield by NBS (N-bromosuccinimide) bromination of TML, which in turn was easily prepared by Suzuki cross-coupling between BML and 2-bromo3-octylthiophene. PMLTQT was synthesized by Stille coupling of BrML, BTT, and 5,5-dibromo-2,2'bithiophene. PMLT2T and PMLT3T were synthesized with the same method by coupling BrTML, 2,5-bis(trimethyl-stannyl)thiophene, and 2T or 3T, respectively. The chemical structures of these conjugated polymers were characterized by ¹H NMR spectra, as shown in Fig. 1. In the ¹H NMR spectrum of PMLTQT, there was a peak at 7.60 ppm (peak *a*), which is attributed to the hydrogens on the phenyl group of BrML. Moreover, there were peaks from 7.04 to 7.09 ppm (peak b, c), which were assigned to the hydrogens of the thiophenes. Thus, the repeat unit ratio (m/n) of PMLTQT calculated from the integral areas was about 1.09:1. By the same concept, the peaks at 7.60 and 7.06 ppm (peak a, b) for PMLT2T were attributed to the phenyl and alkyl thiophene moieties of BrTML. The peak at 7.45 ppm (peak c) is assigned to the hydrogens of 2T and unsubstituted thiophenes. Therefore, the repeat unit ratio (m/n) calculated from the integral areas of the above-mentioned peaks for PMLT2T was about 1.14:1. Calculating the integral areas from the hydrogens assigned to BrTML as well as 3T and unsubstituted thiophenes in the ¹H NMR spectrum of PMLT3T with the same method (peak a, b and peak c), the repeat unit ratio (m/n) was about 1.27:1.

The molecular weights and polydispersity indices (PDIs, M_w/M_n) were characterized by GPC with THF as the eluent and polystyrenes as the internal standards. The results summarized in Table 1. These



Fig. 1. ¹H NMR spectra of (a) PMLTQT, (b) PMLT2T, and (c) PMLT3T.

copolymers were readily soluble in common organic solvents such as chloroform, THF, and toluene. The number-average molecular weights (M_n) of PMLTQT, PMLT2T, and PMLT3T were found to be 6.9, 11.0, and 8.0 kg mol⁻¹ respectively, with corresponding polydispersity indices of 1.50, 4.27, and 1.87.

The operational stability of an optoelectronic device is directly related to the thermal stability of the conjugated polymers. Thus, a high T_g and high T_d are desirable for the application of a conjugated polymer to PSCs. As shown in Table 1, the values of T_d (at which a 5% weight loss occurred) of PMLTQT, PMLT2T, and PMLT3T were in the range of 405–431 °C under an atmosphere of nitrogen. It was apparent that these copolymers exhibited good thermal stability, which was adequate for their application to PSCs. Regarding the DSC experiments, PMLTQT exhibited a glass transition centered at 45 °C, whereas PMLT2T and PMLT3T showed thermal transitions temperatures at 85 and 90 °C, respectively. The rigidity of PMLT2T and PMLT3T results in their values of T_g becoming higher than PMLTQT. This suggests that appropriately

Table 1			
Molecular weights and	l thermal	properties of	f conolymer

Ì	Copolymers	$M_n^{\rm a}$ (kg/mol)	M _w ^a (kg/mol)	PDI (M_w/M_n)	$T_g(^{\circ}C)$	$T_d{}^{\mathbf{b}}({}^{\circ}\mathbf{C})$
	PMLTQT	6900	10,400	1.50	45	431
	PMLT2T	11,000	47,000	4.30	90	405
	PMLT3T	8000	15,000	1.87	85	417

^a M_n , M_w and PDI of the polymers were determined by GPC using polystyrene standards in THF.

^b Temperature of 5% weight loss.

Table 1

shortening the alkyl substituent of these copolymers can effectively enhance the values of T_{g} .

3.2. Optical properties of the conjugated copolymers

Fig. 2 shows the normalized absorption spectra of copolymers and blended copolymer/PC₆₁BM in both toluene solution and thin films. The photophysical properties of these copolymers are summarized in Table 2. In solution, absorption peaks were observed at 435, 428, and 457 nm for PMLTQT, PMLT2T, and PMLT3T, respectively. These copolymers displayed a broad absorption, which originated from the π - π^* transition of its conjugated main chain and intramolecular charge transfer (ICT) interactions between the donors (thiophene derivatives units) and acceptors (maleimide units) along the main chain [60,61]. Compared to PMLT2T, PMLTQT shows a slight red-shift in the absorption peak—an effect attributed to the longer effective conjugated length in the main chain. However, it was noted that PMLT2T has a broader absorption range than PMLTQT. This implies the presence of a copolanar moiety in the main chain that increases the conjugation length as well as the ICT interactions [62]. As a result, the fact that PMLT3T exhibited the absorption peak with the longest wavelength could be attributed to the coplanarity of 3T monomer. If correct, this suggests that the incorporation of a coplanar moiety into the polymer main chain would lead to the capture of sunlight at longer wavelengths and contribute to the performance of the resultant PSC devices. In general, conjugated polymers with relatively broad absorption were favorable for the harvesting of solar light. This broad absorption characteristic was expected to improve the absorption efficiency of the photoactive layer and, thus, induce a larger photocurrent in PSCs.

The same trend was observed in thin films of these copolymers, also as shown in Fig. 2. The maximal absorption wavelengths of PMLTQT, PMLT2T, and PMLT3T were observed at around 454, 446, and 472 nm, respectively. A red-shift and an enhancement of the full-width at half-maximum of the absorption bands were observed for these copolymers, as compared to those in solution. These results were attributed to the interaction of and π - π stacking between the polymer chains. In particular, highly coplanar fused thiophene rings introduced to the main chain resulted in a broader

absorption range in the UV–vis region. The normalized UV–Vis absorption spectra of PMLTQT/PC₆₁BM-, PMLT2T/PC₆₁BM-, and PMLT3T/PC₆₁BM-blend films in various weight ratios are also shown in Fig. 2. The absorption band of the conjugated polymer ranged from 350 to 600 nm, whereas the absorption band of PC₆₁BM ranged from 300 to 375 nm. Moreover, the absorption intensity of the conjugated polymer decreased as the PC₆₁BM content increased for the conjugated polymer/PC₆₁BM-based blend films. From a photon-absorption viewpoint, employing less PCBM in the photoactive layer was preferred. However, the typical stoichiometry of a polymer/PCBM blend is 1:4 by weight, which has



Fig. 2. UV-vis absorption spectra of copolymers and copolymer/PC₆₁BM (w/w, 1:1 and 1:3) in solution (a-c) and thin films (d-f).

Table 2	
Optical and electrochemical properties of copolymers.	

Copolymer	rs In solu	tion ^a (nm)	nm) In film ^b (nm)		HOMO/LUMO ^c (eV)	$E_g^{ecd}(V)$
	λ_{\max}^{abs}	λ_{\max}^{em}	λ_{\max}^{abs}	λ_{\max}^{em}		
PMLTQT	435	619	454	631	-5.63/-3.55	2.08
PMLT2T	428	620	446	634	-5.67/-3.58	2.09
PMLT3T	457	622	472	643	-5.73/-3.65	2.08

^a Measured in toluene solution.

^b Casted from o-DCB solution.

^c The energy levels were calculated according to: HOMO = $-e(E_{on}^{ox} - E_{on}^{ferrocene} + 4.8)$ (eV), LUMO = $-e(E_{on}^{red} - E_{on}^{ferrocene} + 4.8)$ (eV).

^d Estimated using empirical equations: $E_g^{ec} = E_{HOMO} - E_{LUMO}$.

been found to be optimal for devices in several PSC systems [63]. A high proportion of PCBM limits optical absorption in the composite layer because PCBM absorption is quite inefficient in the visible region [64]. In addition, the maximal absorption wavelengths of the conjugated polymer/PC₆₁BM-blend films varied with PC₆₁BM content. Noticeably, the maximal absorption wavelength showed a blue shift as the blending content of PC₆₁BM was further enhanced. A blue shift of the maximal absorption wavelength was observed for the polymer/PC₆₁BM-blend (w/w = 1:1) film as compared to the polymer film. This was attributed to the excellent compatibility between the polymer and PC₆₁BM. The intercalating of PC₆₁BM into the polymer chains led to perturbing the aggregation between copolymer chains. Hence, the maximal absorption wavelength of the polymer/PC₆₁BM-blend (w/w = 1:1) film.

The photoluminescence (PL) spectra of the copolymers PMLTQT, PMLT2T, and PMLT3T in toluene solution and in the copolymer/ PC61BM-based blend films spin-coated from o-dichlorobenzene with various weight ratios are shown in Fig. 3. The PL emission maxima of PMLTOT, PMLT2T, and PMLT3T in solution were observed at 619, 620, and 622 nm, respectively. The three copolymers exhibited almost the same PL emission maxima. This is because the fused thiophene rings were introduced into the PMLT2T and PMLT3T polymer backbone, which can enhance the coplanarity and ICT interactions along the main chains. Hence, the emission peaks of PMLT2T and PMLT3T are slightly red-shifted in comparison with that of PMLTQT. A similar trend was found in solid films, which showed maximum emission at wavelengths of 631, 634, and 643 nm for PMLTQT, PMLT2T, and PMLT3T, respectively (Table 2). The PL emissions were almost completely quenched upon the addition of $PC_{61}BM(w/w = 1:1)$ for the copolymers, as shown in Fig. 3. The same quenched PL emissions were observed for the polymer-blend film with higher $PC_{61}BM$ content (w/w = 1:3). The highly efficient PL quenching phenomena suggest that the excitons generated by the absorbed photons completely dissociate to free charge carriers (electrons and holes). Moreover, this achieves effective charge transfer from the copolymer to PC₆₁BM—a basic requirement for preparing a PSC with excellent PV performance [65].

3.3. Electrochemical properties of conjugated copolymers

Cyclic voltammetry (CV) was employed to investigate electrochemical behavior and to estimate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the conjugated polymers. The oxidation and reduction behaviors in the CV curves of the copolymers are shown in Fig. 4. The oxidation potentials of PMLTQT, PMLT2T, and PMLT3T were 1.31, 1.35, and 1.38 V, respectively. From these values, the HOMO levels of the copolymers were calculated according to the follow equation:

HOMO =
$$-e\left(E_{on}^{ox} - E_{on}^{ferrocene} + 4.8\right)(eV)$$



Wavelength (nm)

Fig. 3. PL spectra of copolymers (a) PMLTQT, (b) PMLT2T, and (c) PMLT3T in solution and copolymer/ $PC_{61}BM$ (w/w, 1:1 and 1:3) in thin films.

where 4.80 eV is the energy level of ferrocene below the vacuum level Hence, the corresponding HOMO levels were -5.63, -5.67, and -5.73 eV for PMLTQT, PMLT2T, and PMLT3T, respectively. In the same way, the reduction potentials of PMLTQT, PMLT2T, and



Fig. 4. Cyclic voltammograms of copolymer films on platinum plates in acetonitrile solution of 0.1 mol L^{-1} Bu₄NClO₄.

PMLT3T were found to be -1.01, -0.98, and -0.91 V, respectively. The corresponding LUMO levels were estimated with the equation:

$$LUMO = -e\left(E_{on}^{red} - E_{on}^{ferrocene} + 4.8\right)(eV)$$

As a result, the LUMO levels were -3.55, -3.58, and -3.65 eV for PMLTQT, PMLT2T, and PMLT3T, respectively. The electrochemical bandgaps (E_{σ}^{ec}) calculated from the differences between the oxidation and reduction potentials were found to be around 2.08 eV for these polymers. Although the electrochemical bandgaps were almost identical for these polymers, the HOMO levels were lowered by incorporation of the fused thiophene moiety into the polymer backbone. Delocalization of electrons from the fused thiophene unit into the backbone is less favorable than that from a single thiophene ring, because the resonance stabilization energy of the fused ring is larger than that of the single thiophene ring. This reduced delocalization along the backbone results in a lowering of the polymer HOMO level [66]. In BHJ solar cells, the $V_{\rm oc}$ value is directly proportional to the difference between the HOMO level of the polymer and the LUMO level of the PCBM derivatives [67]. Superior efficiencies were obtained with PSC devices fabricated from PMLT2T and PMLT3T with low HOMO levels. Given that the reduction potential of the D-A structure copolymer is mainly determined by the electron-accepting moiety, all copolymers that possess the same maleimide moiety with electron-accepting ability showed similar reduction potentials. The electrochemical properties of the copolymers are summarized in Table 2. All the copolymers showed good air stability with a HOMO energy level below the air oxidation threshold (ca. -5.2 eV), and the relatively low HOMO level of the copolymers can allow a high open-circuit voltage (V_{oc}) for the PV cell [68,69] Meanwhile, the difference in the LUMO energy levels between the donor and acceptor (e.g., PCBM) is more than 0.3 eV, which implies a sufficient driving force for exciton dissociation [70,71].

To provide further insight into the fundamentals of molecular architecture, the geometries and electron-state density distributions of three copolymers were performed by using Q-Chem employing the B3LYP functional with 6-31G* basic set. Note that the calculations were performed on model systems of copolymers where all alkyl chain substituents were replaced with ethyl groups to avoid excessive computation demand, since this has only minimal effect on the electronic properties. Fig. 5 shows the geometries and the HOMO and LUMO surface plots for these copolymers. For each copolymer, the HOMO state density is distributed entirely over the thiophene units, while the electron density of LUMO is mainly localized on the maleimide units. These results indicated that the HOMO-LUMO transition for the three copolymers is mainly accompanied by charge transfer from the electro-rich segments to maleimide units due to electron deficiency of maleimide units. The insertion of fused thiophene rings can provide improved planarity and greater conjugation length as demonstrated by the optimized geometry of PMLT2T and PMLT3T in Fig. 5. The calculated HOMO levels were -4.97 eV for all copolymers, while the LUMO levels were -2.62, -2.67, -2.68 eV for PMLTQT, PMLT2T, and PMLT3T, respectively. Although discrepancies exist between the calculation and experimental results, the trend of variation in the LUMO energies are similar.

3.4. Atomic force microscope investigation

The film morphology of the active layer has been found to be the one of the key elements in determining the PCE of PSCs [11,72,73]. Therefore, the compatibility and morphology of the conjugated copolymer/PCBM composite films were investigated using AFM microscopy. The topography (a–c) and phase (d–f) nanoscale images of the PMLTQT/PC₆₁BM, PMLT2T/PC₆₁BM, and PMLT3T/PC₆₁BM-blend films are shown in Fig. 6. As shown in Fig. 6, the copolymer/PC₆₁BM (w/w = 1:3) films displayed low levels of rootmean-square (RMS) (0.39, 0.36, and 0.27 nm for PMLTQT, PMLT2T and PMLT3T, respectively), which implies that all blend films exhibited satisfactory miscibility. PMLTQT/PC₆₁BM showed the highest surface roughness among the blend films; this suggests that the introduction of fused thiophene rings into the polymer main chain enhanced the compatibility by providing sufficient room for PC₆₁BM intercalation. However, the PMLT2T/PC₆₁BM



Fig. 5. Calculated HOMO and LUMO levels and surface plots for PMLTQT, PMLT2T, and PMLT3T at B3LYP/6-31G* level.







Fig. 6. Topographic (a-c) and phase (d-f) images of PMLTQT/PC₆₁BM (w/w = 1:3) (a, d), PMLT2T/PC₆₁BM (w/w = 1:3) (b, e), and PMLT3T/PC₆₁BM (w/w = 1:3) (c, f) in the tapping mode. The area was 300 nm \times 300 nm.



Fig. 7. Topographic (a-c) and phase (d-f) images of PMLTQT/PC₇₁BM (w/w = 1:3) (a, d), PMLT2T/PC₇₁BM (w/w = 1:3) (b, e), and PMLT3T/PC₇₁BM (w/w = 1:3) (c, f) in the tapping mode. The area was 300 nm \times 300 nm.

blend film showed clearer grain aggregation and homogeneous dispersion of PC₆₁BM than the other blend films, which resulted in large-scale phase separation between the copolymer and $PC_{61}BM$, and hence decreased the J_{sc} of the PMLT2T/PC₆₁BM-based device. This may explain why the performance of PMLTQT and PMLT3T were superior to that of PMLT2T. Fig. 7 shows the topography (a-c)and phase (d-f) nanoscale images of the PMLTOT/PC₇₁BM. PMLT2T/ PC71BM, and PMLT3T/PC71BM blend films. As shown in Fig. 7. $PMLTQT/PC_{71}BM$ (w/w = 1:3) films displayed relatively high levels of RMS compared to the other films (0.89, 0.48, and 0.39 nm for PMLTQT, PMLT2T, and PMLT3T, respectively). A large degree of phase segregation appeared again in the PMLTQT/PC71BM blend film; however, a clear nanoscale-segregated phase was observed in both PMLT2T/PC71BM and PMLT3T/PC71BM blend films. The purported ideal morphology is comprised of a nanoscale interpenetrating network between donor and acceptor, which enables a large interface area for exciton dissociation and continuous percolating paths for hole and electron transport to the corresponding electrodes [74]. It is important to note that the PMLT2T/ PC71BM and PMLT3T/PC71BM blend films showed a relatively smooth morphology in the AFM height image; therefore, the PMLT2T- and PMLT3T-based solar cells gave a higher J_{sc}, suggesting the appropriate coarse phase separation between the copolymers and PC₇₁BM in these cells. Clearly, the suitable morphology of the blend films is consistent with the higher PV performance of the PSCs. This result indicates that the introduction of fused thiophene rings into the polymer main chain enhanced the percolation of PC₇₁BM and thus enabled a smooth phase to be obtained.

3.5. PV properties of PSCs

The PSCs were fabricated from copolymer/PC₆₁BM- and copolymer/PC₇₁BM-blend films at the weight ratio of 1:3 via the spincoating method, where the blending ratio of copolymers with the acceptor PC₆₁BM or PC₇₁BM were optimized. The PCE performance of the PSCs was observed when the photoactive layer was spincoated (600 rpm) from the *o*-DCB solution. The photocurrent density–voltage (*I*–*V*) characteristics of the PSCs prepared from copolymer/PC₆₁BM and copolymer/PC₇₁BM, measured under the illumination of simulated AM 1.5 G conditions (100 mW/cm²), are shown in Fig. 8. The PV properties of these PSCs, including the V_{oc},



Fig. 8. Current density-potential characteristics of illuminated (AM 1.5 G, 100 mW/ $\rm cm^2)$ bulk heterojunction solar cells.

Table 3

Photovoltaic performances of the bulk heterojunction solar cells.

Active laver(w/w ratio)	$V_{\rm ex}(V)$	$I_{\rm ex}$ (mA/cm ²)	FF	n(%)
netive layer(w/w ratio)	• 86 (•)	Jsc (mayerin)		1(,0)
PMLTQT:PC ₆₁ BM (1:3)	0.76	4.7	0.16	0.57
PMLT2T:PC61BM (1:3)	0.78	2.7	0.18	0.38
PMLT3T:PC61BM (1:3)	0.80	4.9	0.21	0.82
PMLTQT:PC71BM (1:3)	0.70	6.2 (6.28) ^a	0.19	0.85
PMLT2T:PC71BM (1:3)	0.70	7.9 (7.98) ^a	0.20	1.08
PMLT3T:PC71BM (1:3)	0.74	7.4 (7.38) ^a	0.22	1.20

^a Calculated from the EQE spectrum.

short-circuit current density (I_{sc}) , fill factor (FF), and PCE are summarized in Table 3. As shown in Fig. 8, all devices exhibited a high $V_{\rm oc}$ in the range of 0.76–0.80 V, having benefited from the deep HOMO energy levels of the copolymers, which correlated with their HOMO levels. In organic solar cells, the Voc is generally governed by the energy difference between the HOMO of the donor and the LUMO of the acceptor [67]. As expected, the $V_{\rm oc}$ of the PMLT3T/PC₆₁BM-based (w/w = 1:3) PSC was higher than that of the $PMLTQT/PC_{61}BM$ -based (w/w = 1:3) PSC owing to the deeper HOMO level of PMLT3T. Compared to the absorption spectra of the blend films (see Fig. 2), they are almost identical. Therefore, the PCE difference of these devices is ascribed to the morphology of the blend films, which lead to different J_{sc} values for the corresponding devices. The larger Voc and higher Jsc values led to a superior PCE value; thus, the PMLT3T/PC₆₁BM-based (w/w = 1:3) PSC exhibited the highest PCE among all PSCs. The relatively low J_{sc} for the PMLT2T-based device could be explained by the large number of carrier recombinations due to the clear grain aggregation in the blend film. Solar cell efficiency was further optimized by using the 1:3 blending ratio of copolymers with the acceptor $PC_{71}BM$. Higher current is usually obtained by replacing $PC_{61}BM$ with $PC_{71}BM$ as an acceptor in the active layer, as the latter has higher absorption in the visible region [6]. When $PC_{71}BM$ was used instead of $PC_{61}BM$ as the electron acceptor in the devices, significant improvements in J_{sc} were recorded. However, slightly lower V_{oc} values were observed in the copolymer/PC₇₁BM based devices. A similar drop in the V_{oc} could be explained by the formation of a charge transfer complex (CTC) in a polymer/PCBM film, which reduces the effective LUMO level of PCBM [75]. An optimized PCE of 1.20% could be achieved by using PMLT3T with PC71BM (1:3 blend ratio). Although PMLT3T/



Fig. 9. EQE curves of the photovoltaic cells with (copolymer: $\mbox{PC}_{71}\mbox{BM}=1:3)$ as the active layer.

 $PC_{71}BM$ -based (w/w = 1:3) PSC exhibited the highest PCE among all PSCs, the deficits of the PCE values in our PSCs were mainly caused by low FFs which indicated lacks of ordered continuity in the copolymer/PC₆₁BM or PC₇₁BM blend films [76]. The preliminary experimental results could offer some clues for the design of maleimide-based copolymers for PSCs, such as broadening of the absorption band to long wavelengths by the introduction of an electron-donating low bandgap as well as high coplanarity comonomer to the polymer main chain.

Fig. 9 depicts the external quantum efficiency (EQE) curves of the PSCs based on copolymers: $PC_{71}BM$ (w/w = 1:3). It is apparent that all PSCs exhibited a broad response range, coving from 350 to 700 nm, which indicated that the copolymer and PC71BM all contributed to the photo-electronic conversion. Obviously, the PMLT2T/PC₇₁BM-based PSC shows the higher EQE value of 60% at ca. 460 nm. The higher EQE of the device based on PMLT2T than that on PMLTQT or PMLT3T is consistent with the higher J_{sc} value obtained from the *I*–*V* measurements. To evaluate the accuracy of the photovoltaic results, the Jsc values were calculated by integrating the EQE data with the AM 1.5G reference spectra. The Jsc values obtained using integration and I-V measurements are similar. For example, the calculated Jsc value of the device based on PMLT3T was 7.38 mA cm⁻², while the value obtained from the *I*–*V* measurement was 7.4 mA cm⁻² (Table 3). The EQE results indicate that the photovoltaic results are reliable.

4. Conclusion

In summary, we synthesized three new random D-A conjugated copolymers (PMLTQT, PMLT2T, and PMLT3T) containing a maleimide derivative as an acceptor unit and a donor unit of BTT, 2T, or 3T, by Stille cross-coupling polymerization reactions. The synthesized copolymers exhibited good solubility and good absorption in the visible region. By incorporating fused thiophene rings into the polymer backbone, the coplanarity and effective conjugated length can be enhanced. The electrochemical data indicated the fused thiophene rings incorporated into the polymer backbone would reduce the delocalization along the backbone and thus resulted in a lowering of the polymer HOMO level. The relatively low HOMO energy levels promised good air stability and high V_{oc} for photovoltaic cells application. Moreover, the coplanarity provides sufficient space for PC₆₁BM or PC₇₁BM percolation, which leads to a smooth morphology as demonstrated by the AFM measurements. Improved compatibility was observed for both PMLT2T/PC₆₁BM (or PC71BM) and PMLT3T/PC61BM (or PC71BM) blend films as compared to the PMLTQT/PC₆₁BM (or PC₇₁BM) blend film. PV devices based on copolymer/PC₆₁BM (or PC₇₁BM) blend films spin-coated from odichlorobenzene solution were investigated. Preliminary studies revealed that PV cells with blends of PMLT3T and PC71BM (1:3, w/ w) as the active layer afforded the best performance among these copolymers, which implies that better compatibility would lead to better film morphology thus enhance the PSC efficiency. The PV results clearly demonstrated that BrML derivative is promising electron-accepting unit for constructing D-A copolymers. A higher PCE can be achieved through the careful engineering of devices by varying factors such as layer thickness, additives, and postproduction treatment conditions.

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