

# The effect of intramolecular donor–acceptor moieties with donor– $\pi$ -bridge–acceptor structure on the solar photovoltaic performance

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**Abstract.** A series of intramolecular donor–acceptor polymers containing different contents of (*E*)-1-(2-ethylhexyl)-6,9-dioctyl-2-(2-(thiophen-3-yl)vinyl)-1*H*-phenanthro[9,10-*d*]imidazole (thiophene-DOPI) moiety and 4,4-diethylhexyl-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) unit was synthesized via Grignard metathesis (GRIM) polymerization. The synthesized random copolymers and homopolymer of thiophene-DOPI contain the donor– $\pi$ -bridge–acceptor conjugated structure to tune the absorption spectra and energy levels of the resultant polymers. UV-vis spectra of the three polymer films exhibit panchromatic absorptions ranging from 300 to 1100 nm and low band gaps from 1.38 to 1.51 eV. It is found that more thiophene-DOPI moieties result in the decrease of band gap and lower the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) values of polymers. Photovoltaic performance results indicate that if the content of the intramolecular donor–acceptor moiety is high enough, the copolymer structure may be better than homopolymer due to more light-harvesting afforded by both monomer units.

**Keywords:** polymer synthesis, intramolecular donor–acceptor, Grignard metathesis polymerization, polymer solar cells

## 1. Introduction

In order to harvest the sunlight over the range of maximum photon flux (500–800 nm) to achieve the high performance of polymer solar cells (PSCs), the most promising approach is to lower the band gaps of conjugated polymer donor materials. One of the effective ways to lower the band gap of conjugated polymers is to make  $-(A)_m-(B)_n-$  random type copolymers by adjusting the ratio of the two monomer unit [1–3]. On the other hand, it is found that the introduction of electron-acceptor units onto the side chain of conjugated polymers could extend the absorption breadth of sunlight and lower the energy gap to some extent [4, 5]. In other words, conjugated polymers that con-

tain side-chain-tethered acceptor moieties can not only exhibit multiple absorptions but also enhance charge transfer ability. This type of conjugated polymers falls into the intramolecular donor–acceptor systems. This system typically consists of conjugated polymers as electron donating groups, another conjugated groups or long alkyl chains as the bridges, and electron acceptors which can increase the interior charge transfer rate of molecules and broaden the absorption spectrum [5, 6]. For this type of conjugated polymers, the electron donating groups are present in the main chain, while the electron accepting units are pendent as side chains. After photoexcitation, the generated excitons are stabilized and fur-

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ther separated because of the extended conjugation length, and the electrons are subsequently transferred from the donors to the acceptors very rapidly [6, 7]. Furthermore, the charge separation and transfer process within the planar intramolecular donor-acceptor structure is more effective than the one in the twisted intramolecular donor-acceptor structure, therefore, the charge transfer rate will be higher if the acceptor units are tethered on the polymeric main chains in a coplanar manner [5, 6, 8].

Recently, a series of intramolecular donor-acceptor conjugated copolymers of  $-(A)_m-(B)_n-$  random type have been synthesized by Wei's group and used as the donor materials in the active layers of PSCs [4, 5, 9]. For this kind of conjugated polymers, thiophene derivatives were used as the electron donating groups and presented in the main chain, and phenanthrenyl-imidazole (PI) moieties with the characteristic of coplanar were employed as the side-chain-tethered electron accepting units. More recently, a new imidazole unit as the acceptor moiety has been synthesized by Neophytou *et al.* [10] and this kind of copolymer exhibits fast exciton dissociation at the polymer-fullerene heterointerfaces. Lee *et al.* [11] also reported a kind of intramolecular donor-acceptor copolymer with electron-rich carbazole presenting in the backbone as the donor unit and electron-deficient 14H-benzo[4,5]isoquino[2,1-a]perimidin-14-one moiety as pendant side chains. In a recent report, we have presented a new kind of intramolecular donor-acceptor copolymers containing side-chain-tethered perylenebis(dicarboximide) (PDI) moieties [12]. For the above-mentioned intramolecular donor-acceptor polymers, by the attachment of electron accepting moieties as side chains, the electrons can be transferred sequentially from the donor main chains to the pendant side chains, and then to n-type PCBM after photoexcitation, hence the charge separation and transfer process occurs more efficiently.

For choosing suitable monomer units to achieve the high performance of PSCs, it has been stated that using the fused thiophene family as the donor resulting in a low band gap accompanied by good electrochemical stability [13–16]. Molecules containing fused-ring systems can make the polymer backbone more rigid and coplanar, therefore enhancing effective  $\pi$ -conjugation, lowering band gap and extending absorption. The carbon-bridged 4,4-diethylhexyl-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) has attracted considerable research interests due to

the forced coplanarity of the two thienyl subunits resulting in the low energy gaps of the D-A copolymers based on this donor unit [17–23]. Recently, poly[2,6-(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) comprising of CPDT and benzothiadiazole (BT) unit was demonstrated to be one of the most promising low band gap polymers for the use in PSCs [21]. Even if the PCPDTBT is promising for PSCs, the highest power conversion efficiency (PCE) in this family of polymers has been presented very recently by Yau *et al.* [24]. By using the CPDT as the donor unit, an extremely low band gap ( $E_g = 1.20$  eV) donor-acceptor copolymer with a panchromatic absorption ranging from 280 to 1285 nm was synthesized by our group [22].

Furthermore, to optimize the material properties, conjugated polymers with an electron-rich main chain and a donor- $\pi$ -bridge-acceptor (D- $\pi$ -A) conjugated side chain has been proposed [25]. The designed polymers take advantage of the well-established knowledge of nonlinear optical chromophores to optimize the absorption spectra and energy levels of the resultant polymers [26, 27]. Based on this design concept, the PSC devices using these donor materials exhibited a high  $V_{oc}$  (0.99 V) and their absorption spectra can be easily tuned by controlling the acceptor strength of their side chains or by using a more efficient  $\pi$ -bridge.

As stated above, to build a low band gap and wide optical absorption conjugated polymer to raise the PCE of the devices, the intramolecular donor-acceptor structure with side-chain-tethered acceptor moieties might be an efficient approach. In addition, insertion of a  $\pi$ -bridge between the donor main chain and pendant side chains to tune the molecular energy levels and absorption spectra of the resultant polymers might also be a promising way. Consequently, we synthesized a series of intramolecular donor-acceptor polymers consisting of different molar ratios of 4,4-diethylhexyl-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) unit and (*E*)-1-(2-ethylhexyl)-6,9-dioctyl-2-(2-(thiophen-3-yl)vinyl)-1*H*-phenanthro[9,10-*d'*]imidazole (thiophene-DOPI) moiety. In the thiophene-DOPI unit (DOPI tethered to thiophene unit), an ethylenic double bond as the  $\pi$ -bridge was inserted into the side-chain-tethered phenanthrenyl-imidazole (PI) moiety and thiophene backbone, where the thiophene,  $\pi$ -bridge and PI moiety formed the intramolecular charge transfer system. The effect

of molar ratio of thiophene-DOPI unit on the optoelectronic properties and the photovoltaic performance of the fabricated PSCs were investigated.

## 2. Experimental

### 2.1. Materials

Palladium acetate (Sigma-Aldrich, USA), 1,4-benzoquinone (Sigma-Aldrich, USA), acrolein (Sigma-Aldrich, USA), acetonitrile (J. T. Baker, USA), neocuproine (Sigma-Aldrich, USA), 3-thienylboronic acid (Alfa Aesar, USA), diethyl ether (Echo Chemical, Taiwan), 9,10-phenanthraquinone (Acros, Belgium), bromine (Sigma-Aldrich, USA), nitrobenzene (Acros, Belgium), dibenzoyl peroxide (Sigma-Aldrich, USA), acetic acid (Acros, Belgium), ammonium acetate (Showa Chemical Co., Japan), 2-ethyl-1-hexylamine (Alfa Aesar, USA), ammonium hydroxide (Acros, Belgium), 2-ethylhexyl magnesium bromide (1.0 M in diethyl ether, Acros, Belgium), [1,3-bis(diphenylphosphino)propane] nickel (II) chloride (Acros, Belgium), *n*-bromosuccinimide (Acros, Belgium), ethyl acetate (Echo Chemical, Taiwan), sodium bicarbonate (Showa Chemical Co., Japan), magnesium sulfate anhydrous (Showa Chemical Co., Japan), *o*-dichlorobenzene (DCB, Echo Chemical, Taiwan), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Sigma-Aldrich, USA) and [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM, FEM Tech., Germany) were used as received. All other reagents were used as received.

### 2.2. Monomer synthesis

The monomer M1, 4,4-diethylhexyl-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT), was prepared according to a reported literature method [19]. The monomer M2, (*E*)-2-(2-(2,5-dibromothiophen-3-yl)vinyl)-1-(2-ethylhexyl)-6,9-dioctyl-1*H*-phenanthro[9,10-*d*]imidazole, was synthesized according to the following steps and the synthetic route is shown in Figure 1. For convenience, the monomer M2 is also designated as thiophene-DOPI.

#### 2.2.1. Synthesis of

##### (*E*)-3-(thiophen-3-yl)acrylaldehyde (**1**)

A glass reactor charged with a mixture of acrolein (0.144 g, 2.57 mmol), 1,4-benzoquinone (0.275 g, 2.52 mmol) and 3-thienylboronic acid (0.660 g, 5.06 mmol) in 10 mL of acetonitrile was purged with argon bubbling for 10 min. To prepare the solution of

catalyst, neocuproine (0.015 g, 0.07 mmol) and palladium acetate (0.013 g, 0.06 mmol) were dissolved in 5 mL of acetonitrile with stirring and argon bubbling for 30 min. To the above reactor was then added the catalyst solution. The reaction mixture was stirred at room temperature for 24 h. The solution was evaporated to dryness by rotary evaporation. The residue was chromatographically purified on silica gel eluting with *n*-pentane/diethyl ether (2:1, v:v) to afford **1** as a brown oil. Yield: 0.549 g, 65%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 6.75 (t, 1H), 6.88 (t, 1H), 7.08 (d, 1H), 7.22 (d, 1H), 7.32 (s, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 126.1, 126.7, 128.3, 130.2, 134.9, 152.6, 193.5. Anal. Calcd for C<sub>7</sub>H<sub>6</sub>OS: C, 60.84; H, 4.38. Found: C, 60.81; H, 4.42.

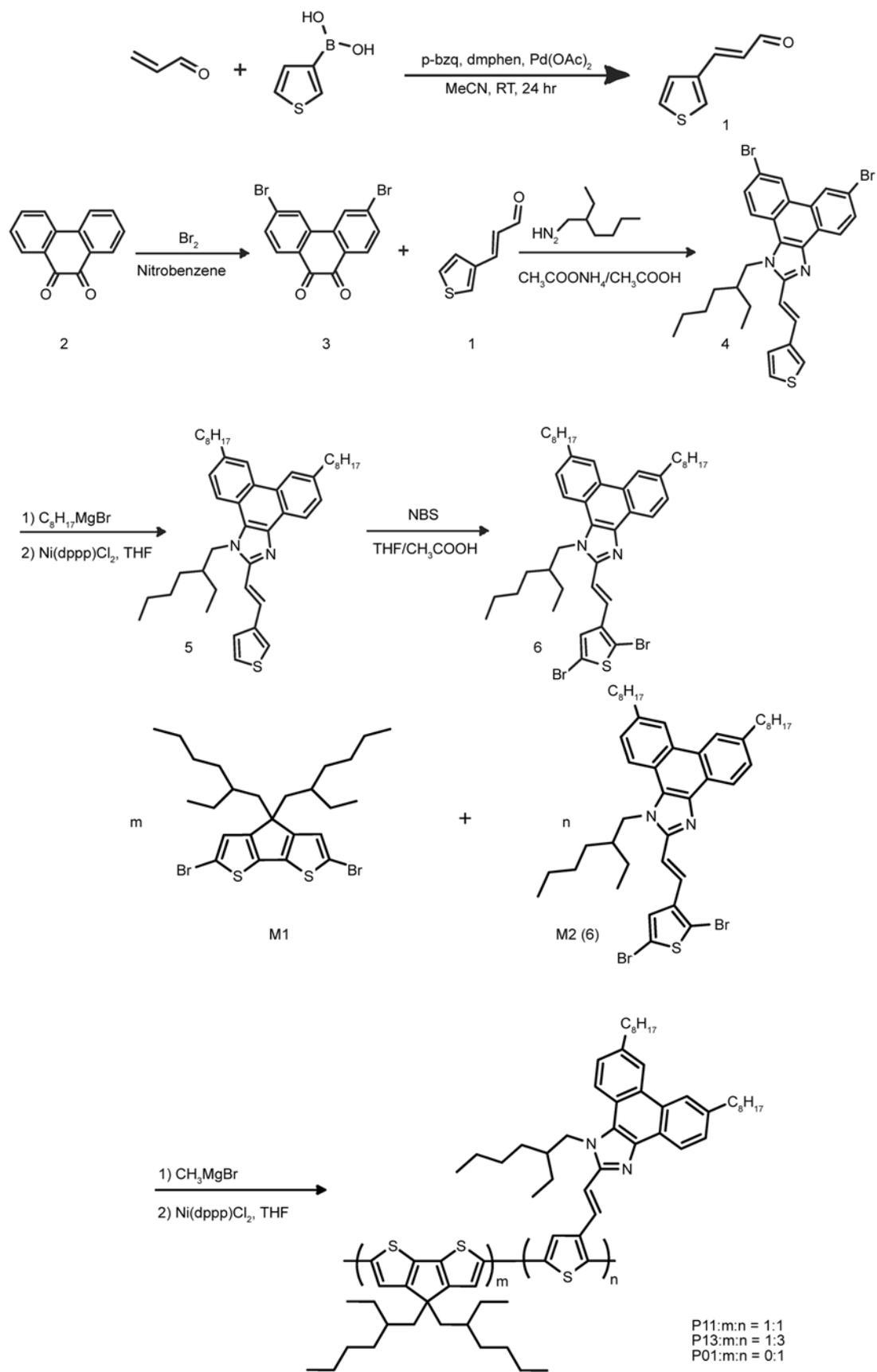
#### 2.2.2. Synthesis of

##### 3,6-dibromophenanthrene-9,10-dione (**3**)

9,10-Phenanthrenequinone (7.03 g, 33.4 mmol) (compound **2**) was dissolved in 50 mL of nitrobenzene with stirring and argon bubbling for 10 min and then 0.35 g of benzoyl peroxide was added. The solution was heated by a tungsten lamp with stirring and argon bubbling for 30 min. Liquid bromine (5 mL, 97.6 mmol) was added dropwise into the reactor through a dropping funnel under the illumination of a tungsten lamp with stirring for 8 h. After turning off the tungsten lamp, the reaction had been continuously run for 18 h at room temperature. The reaction mixture was then poured into 50 mL of diethyl ether. The precipitate was then triturated in diethyl ether for 30 min followed by filtration. The residue was washed twice with diethyl ether and then dried in a vacuum to afford **3** as a golden yellow solid. Yield: 6.41 g, 52%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.0 (s, 1H), 7.74 (d, 2H), 7.51 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 180.2, 136.3, 134.0, 132.5, 131.5, 130.2, 129.4. Anal. Calcd for C<sub>14</sub>H<sub>6</sub>Br<sub>2</sub>O<sub>2</sub>: C, 45.94; H, 1.65. Found: C, 45.98; H, 1.62.

#### 2.2.3. Synthesis of (*E*)-6,9-dibromo-1-(2-ethylhexyl)-2-(2-(thiophen-3-yl)vinyl)-1*H*-phenanthro[9,10-*d*]imidazole (**4**)

In a 100 ml glass reactor was suspended compound **3** (0.549 g, 1.50 mmol) with stirring in acetic acid (30 mL) and ammonium acetate (0.238 g, 3.00 mmol) for 10 min then 2-ethyl-1-hexylamine (0.528 g, 4.00 mmol) was added dropwise over a period of 20 min. Compound **1** (0.207 g, 1.50 mmol) was dis-



**Figure 1.** Synthetic route for the preparation of P11, P13 and P01 conjugated polymers

solved in 10 mL of acetic acid and then added dropwise into the reaction. The stirring mixture was heated at reflux for 3 h. After cooling down to room temperature, the reaction mixture was filtered and the solid was washed with an aqueous solution of acetic acid (1:1, v:v) until the washings were almost colorless. The washings were discarded and the solid was further washed with distilled water (~200 mL) until the washings were colorless. The residue was recrystallized from isopropyl alcohol. The product was dried under vacuum giving **4** as a red solid. Yield: 0.501 g, 56%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.80 (s, 1H), 8.01 (d, 1H), 7.35 (s, 2H), 7.55 (d, 2H), 8.65 (d, 2H), 4.65 (d, 2H), 2.01 (t, 1H), 0.9–1.5 (m, 15H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 11.6, 14.1, 23.0, 26.0, 29.3, 32.0, 37.2, 52.0, 118.7, 120.9, 125.7, 126.1, 126.5, 126.6, 126.7, 128.3, 130.2, 130.5, 133.4, 133.6, 141.5. Anal. Calcd for C<sub>29</sub>H<sub>28</sub>Br<sub>2</sub>N<sub>2</sub>S: C, 58.40; H, 4.73; N, 26.79. Found: C, 58.32; H, 4.85; N, 26.73.

#### 2.2.4. Synthesis of (E)-1-(2-ethylhexyl)-6,9-dioctyl-2-(2-(thiophen-3-yl)vinyl)-1H-phenanthro[9,10-d]imidazole (**5**)

In a glass reactor, (E)-6,9-dibromo-1-(2-ethylhexyl)-2-(2-(thiophen-3-yl)vinyl)-1H-phenanthro[9,10-d]imidazole (0.700 g, 1.18 mmol) was dissolved in 10 mL dry THF with stirring and argon bubbling for 10 min. (2-Ethylhexyl)magnesium bromide (2.37 mL, 2.37 mmol) was then added dropwise into the reactor in an ice bath under argon atmosphere. After returning to room temperature, this mixture was heated at 60°C for 2 h and then Ni(dppp)Cl<sub>2</sub> (0.005 g, 0.010 mmol) was added. The stirring mixture was continuously heated for 24 h. After cooling down to room temperature, the reaction mixture was filtered and the solid was washed with distilled water (~200 mL) until the washings were colorless. The product was dried under vacuum to give **5** as a dark red solid. Yield: 0.492 g, 63%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.35 (s, 1H), 7.90 (d, 1H), 7.75 (d, 1H), 9.20 (s, 2H), 7.95 (d, 2H), 8.55 (d, 2H), 3.81 (m, 6H), 0.9–3.5 (m, 45H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 11.6, 14.1, 22.7, 23.0, 26.0, 28.9, 29.3, 31.2, 31.8, 32.0, 36.0, 37.2, 52.0, 118.7, 120.5, 124.7, 126.1, 126.3, 126.6, 126.7, 128.1, 128.3, 130.2, 131.2, 133.4, 137.2, 141.5. Anal. Calcd for C<sub>37</sub>H<sub>45</sub>N<sub>2</sub>S: C, 80.82; H, 8.25; N, 5.10. Found: C, 80.36; H, 8.14; N, 5.21.

#### 2.2.5. Synthesis of (E)-2-(2-(2,5-dibromothiophen-3-yl)vinyl)-1-(2-ethylhexyl)-6,9-dioctyl-1H-phenanthro[9,10-d]imidazole (**6**)

*N*-bromosuccinimide (NBS) (0.284 g, 1.60 mmol) was added into a solution of (E)-1-(2-ethylhexyl)-6,9-dioctyl-2-(2-(thiophen-3-yl)vinyl)-1H-phenanthro[9,10-d]imidazole (0.530 g, 0.800 mmol) in 20 mL of THF and 20 mL of acetic acid. The mixture was stirred at room temperature under an argon atmosphere for 1 h. Water (50 mL) was added to the mixture and it was extracted with ethyl acetate three times. Organic fractions were combined and washed with 5% (w/w) NaHCO<sub>3</sub> and then distilled water three times. After drying over anhydrous MgSO<sub>4</sub>, the organic phase was purified by column chromatography on silica gel with chloroform to afford a dark brown solid. Yield: 0.288 g, 44%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 9.25 (s, 2H), 8.5 (d, 2H), 7.80 (d, 2H), 7.65 (s, 1H), 3.81 (m, 6H), 0.9–3.8 (m, 45H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 11.6, 14.1, 22.7, 23.0, 26.0, 29.2, 29.3, 29.6, 31.2, 31.8, 32.0, 36.0, 37.2, 52.0, 110.5, 115.0, 118.7, 120.5, 124.7, 126.3, 126.6, 128.1, 131.2, 133.4, 137.2, 140.0, 141.5. Anal. Calcd for C<sub>37</sub>H<sub>45</sub>Br<sub>2</sub>N<sub>2</sub>S: C, 62.62; H, 6.39; N, 3.95. Found: C, 63.15; H, 6.18; N, 3.72.

#### 2.2.6. Synthesis of the copolymers (P11 and P13) and homopolymer (P01)

All polymers were synthesized through Grignard metathesis (GRIM) polymerizations in THF except the molar ratio of M1 to M2 was different. The copolymer P11 was synthesized using a 1:1 molar ratio of M1 to M2, while the molar ratio of M1:M2 for the copolymer P13 and homopolymer P01 was 1:3 and 0:1, respectively. The detail synthetic procedures for the copolymer P11 are described below. In a three-necked 100 mL round-bottom flask, (E)-2-(2-(2,5-dibromothiophen-3-yl)vinyl)-1-(2-ethylhexyl)-6,9-dioctyl-1H-phenanthro[9,10-d]imidazole (1.20 g, 1.49 mmol) and 2,6-dibromo-4,4-di-(2-ethylhexyl)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (0.834 g, 1.49 mmol) were dissolved in 40 mL of freshly distilled THF and then flushed by argon for 10 min and CH<sub>3</sub>MgBr (0.672 mL, 2.98 mmol) was added dropwise to the solution. After reflux for 1 h, Ni(dppp)Cl<sub>2</sub> (0.016 g, 0.03 mmol) was added, and the solution was purged by argon for another 20 min.

Another portion of Ni(dppp)Cl<sub>2</sub> (0.016 g, 0.03 mmol) was added after refluxed for 45 min. The reaction mixture was then refluxed for 48 h under the protection of argon. The solution was cooled and poured into 200 mL of methanol, where the crude polymer was precipitated and collected as a dark brown solid, which was then subjected to Soxhlet extraction with methanol, hexane, and THF. The polymer was recovered from the THF fraction by rotary evaporation to afford a brownish-yellow solid. The synthetic route is shown in Figure 1. Yield: 0.672 g, 28%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.7 (d, 2H), 7.5 (s, 2H), 7.2 (d, 2H), 5.02 (d, 2H), 3.81 (m, 6H), 2.50 (d, 4H), 0.9~0 (m, 90H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 11.6, 11.9, 14.1, 15.1, 15.5, 22.7, 23.0, 26.0, 26.5, 29.2, 29.3, 29.6, 31.2, 31.8, 32.0, 33.5, 33.6, 36.0, 37.2, 49.0, 50.5, 52.0, 118.7, 120.5, 121.9, 124.7, 126.3, 126.6, 128.1, 128.2, 131.2, 133.4, 133.9, 134.4, 135.2, 135.9, 136.1, 137.1, 137.2, 138.0, 139.1, 141.5. Anal. Calcd for (C<sub>62</sub>H<sub>81</sub>N<sub>2</sub>S<sub>3</sub>)<sub>n</sub>: C, 78.34; H, 8.59; N, 2.95. Found: C, 77.86; H, 8.83; N, 3.14.

### 2.3. Device fabrication

The device structure of PSCs for current density-voltage (*J-V*) measurements is ITO/PEDOT:PSS/Polymer:PC<sub>71</sub>BM/Al. P11, P13, and P01 were used as the p-type donor polymers and PC<sub>71</sub>BM acted as the n-type acceptor in the active layer. Before device fabrication, the ITO-coated glass substrates were first cleaned by ultrasonic treatment in acetone, detergent, de-ionized water, methanol and isopropyl alcohol sequentially. The ITO surface was spin-coated with ca. 80 nm layer of poly(3,4-ethylene dioxythiophene): poly(styrene) (PEDOT:PSS) in the nitrogen-filled glove-box. The substrate was dried for 10 min at 150°C and then continued to spin coat the active layer. The polymer:PC<sub>71</sub>BM blend solutions were prepared with a weight ratio of 1:1 in 1,2-dichlorobenzene (DCB) as the active layer. The solution blends were spin-cast onto the PEDOT:PSS layer at 800 rpm for 30 s. The obtained thicknesses for the blend films were ca. 110 nm. The devices were completed by evaporation of metal electrodes Al with area of 6 mm<sup>2</sup> defined by masks.

### 2.4. Instrumentation

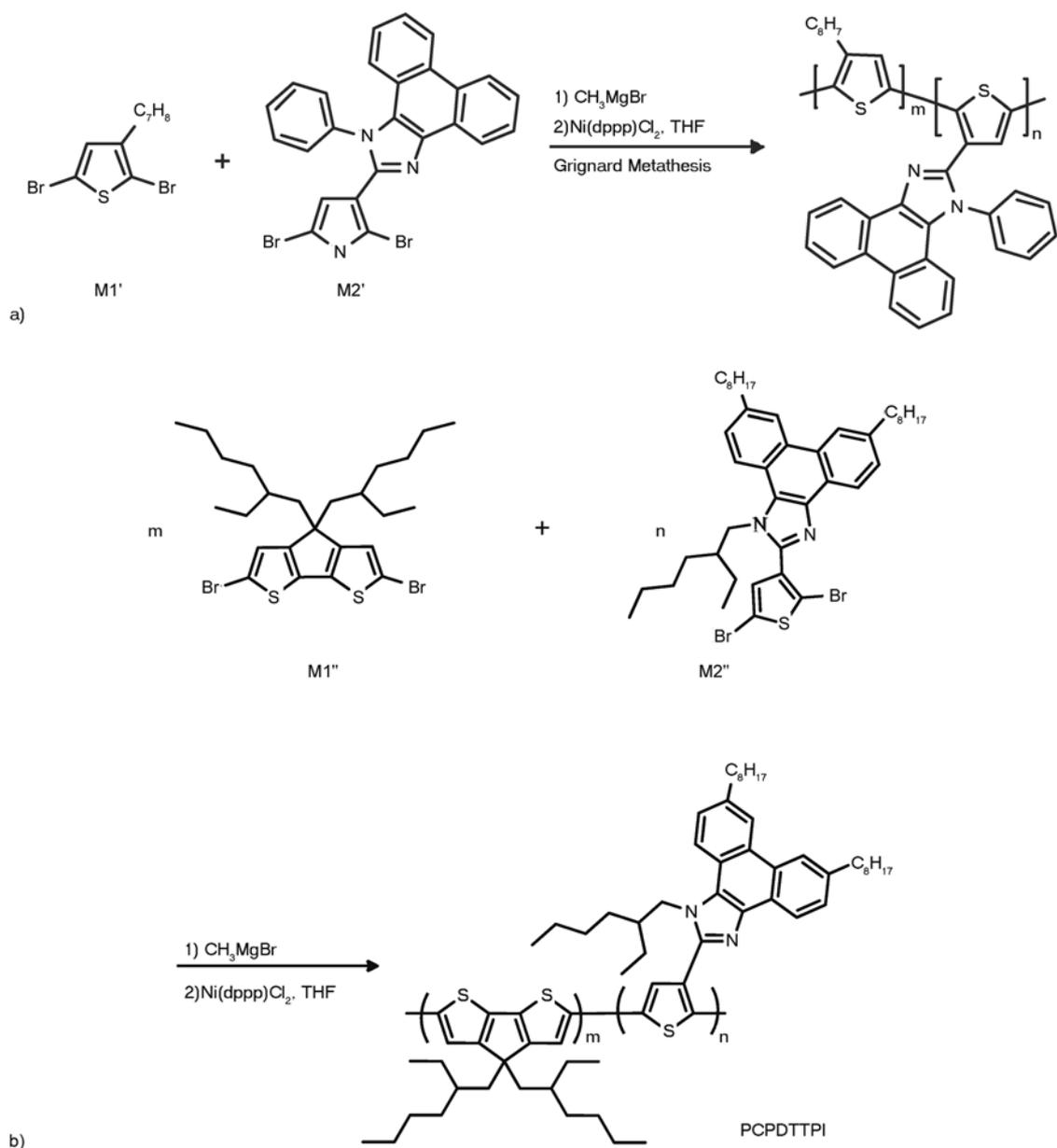
Thermogravimetric analyses (TGA) were performed using a TA Instruments SDT-2960 analyzer operated at a heating rate of 10°C/min in the air. Dif-

ferential scanning calorimetry (DSC) thermograms were obtained with a TA Instruments modulated DSC 2920 analyzer operated at a heating rate of 10°C/min under a dry nitrogen purge. Ultraviolet-visible (UV-vis) spectroscopic analysis was conducted on a Perkin-Elmer Lambda 35 UV-vis spectrophotometer. Photoluminescence (PL) spectrum was recorded on a Hitachi F-7000 fluorescence spectrophotometer. The *J-V* curves were measured under illumination from a solar simulator, using a Keithley 2400 source meter. The intensity of solar simulator was set with a primary reference cell and a spectral correction factor to give the performance under the AM 1.5 (100 mW/cm<sup>2</sup>) global reference spectrum (IEC 60904-9). EQE was detected with a QE-3000 (Titan Electro-Optics Co., Ltd.) lock-in amplifier under monochromatic illumination. Calibration of the incident light was performed with a monocrystalline silicon diode. Molecular weights of the copolymers were determined by gel permeation chromatography (GPC) using Young Lin Acme 9000 liquid chromatograph equipped with a 410 RI detector and a μ-Styragel columns with THF as the carrier solvent. Cyclic voltammetric (CV) measurements were performed in 0.1 M tetrabutylammonium perchlorate solution using a PGSTAT30 electrochemical analyzer (AUTOLAB Electrochemical Instrument, The Netherlands).

## 3. Results and discussion

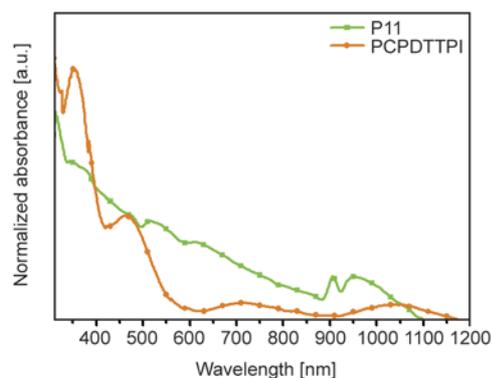
### 3.1. Material design and structural characterization

Since the charge separation and transfer process within a planar intramolecular donor-acceptor structure is more effective than that of a twisted intramolecular donor-acceptor structure, therefore, the charge transfer rate will be higher if the acceptor units are tethered on the polymeric main chains in a coplanar manner. As reported by Wei's group, the electron transfer probability of the polymer with the planar intramolecular donor-acceptor structure is at least twice higher than the pure poly(3-hexylthiophene) when blended with PC<sub>61</sub>BM [5, 9]. This type of random copolymer synthesized by Wei's group contains a thiophene monomer and a side-chain-tethered phenanthrenyl-imidazole moiety as the other monomer unit, as shown in Figure 2a. Although the intramolecular donor-acceptor conjugated copolymers reported by Wei and coworkers exhibit lower band gaps (1.77–1.89 eV) than regioregular poly(3-



**Figure 2.** (a) The synthesized copolymers reported by Chang *et al.* [4] (b) Synthetic route of PCPDTTPI copolymers

hexylthiophene) (rr-P3HT), the optical band gaps are still considered too large and ranges of light-harvesting are not broad enough [4, 5, 9]. To compare with the results of Wei's group, in an unpublished report, we designed and synthesized an intramolecular donor–acceptor type of conjugated copolymer with an ethylhexyl and two octyl chains attached to the PI moiety. The molecular structure is shown in Figure 2b and the copolymer is designated as PCPDTTPI. For the copolymer PCPDTTPI synthesized from 1:1 molar ratio of M1'' to M2'', although the UV-vis spectrum of the polymer film exhibited a panchromatic absorption ranging from 280 to 1170 nm and a low band gap of 1.42 eV as seen in Figure 3, the



**Figure 3.** Normalized UV-vis absorption spectra of P11 and PCPDTTPI

weak absorption in the range between 600 to 1170 nm resulted in a low PCE of 0.52%.

Therefore, further improvement based on this structure was carried out to obtain a copolymer with an enhanced absorption of UV-vis spectrum in the long wavelength region to afford a higher PCE. In the present study, we designed a new random copolymer containing the donor- $\pi$ -bridge-acceptor moiety as a monomer unit (M2 in Figure 1). As compared to the molecular structure reported by Wei's group (Figure 2a) [4], because the structure of PI moiety was too rigid to be soluble in common organic solvents, we attached an ethylhexyl and two octyl chains to the PI moiety. In addition, to reduce the steric hindrance of the copolymer for increasing the effective packing and to tune the molecular energy levels and absorption spectra of the resultant polymers for charge transfer and light-harvesting, an ethylenic double bond as the  $\pi$ -bridge was inserted into the PI moiety and thiophene backbone. For the other monomer unit, CPDT was chosen due to the forced coplanarity of the two thienyl subunits resulting in the more extended conjugation and stronger intermolecular interaction. In this regard, we synthesized a series of intramolecular donor-acceptor polymers containing the conjugated thiophene-DOPI moieties and CPDT units via GRIM polymerization (Figure 1). Employing the GRIM method can shorten polymerization times and lower reaction temperatures, facilitating the preparation of aryl and heteroaryl conjugating polymers. Using this approach also paves the way toward the production of block or random copolymers. Because our synthesized copolymers are also the intramolecular donor-acceptor type, which is similar to the copolymers synthesized by Wei's group (Figure 2a), we adopt the same synthetic approach and the same Grignard reagent like them. Their synthetic approach is referred to McCullough's publication [28], so we also used  $\text{CH}_3\text{MgBr}$  as the Grignard reagent in our synthesis. However, it was found that yields of this series

of copolymer were relatively low. Hence, it is suggested that for the synthesis of this series of copolymers, other Grignard reagents such as isopropylmagnesium chloride (*i*-PrMgCl) or isopropylmagnesium bromide (*i*-PrMgBr) together with lithium chloride (LiCl) may be used to afford the copolymers in good yields [29, 30].

Since the copolymer synthesized by Wei's group comprising of equal molar ratio of M1' and M2' (Figure 2a) exhibited an optical bandgap of 1.82 eV and a HOMO value of  $-5.21$  eV [4], the copolymer consisting of equal molar ratio of CPDT unit and thiophene-DOPI unit was synthesized for comparison and designated as P11. As shown in Table 1 (the data will be discussed in the following section), it can be seen that the incorporation of CPDT unit and insertion of an ethylenic double bond could significantly reduce the band gap (1.40 eV) and lower the energy level of HOMO ( $-5.27$  eV) of the conjugated polymer. On the other hand, compared to the UV-vis spectrum of the copolymer PCPDTTPI synthesized from equal molar ratio of M1'' and M2'' (Figure 2b), the copolymer P11 exhibited much enhanced absorption in the region between 550 to 1050 nm. From the TGA thermogram of P11, the onset decomposition temperature of this copolymer is around  $275^\circ\text{C}$  in the air. The thermal stability of this kind of copolymer is adequate for its application in PSCs and other optoelectronic devices. In addition, due to the insertion of an ethylenic double bond into the PI moiety and thiophene backbone, the copolymer P11 is more flexible, exhibiting a lower  $T_g$  of  $53.5^\circ\text{C}$  compared with the similar type of copolymer synthesized by Chang *et al.* [5]. These findings encouraged us to vary the content of thiophene-DOPI moiety to proceed further study. Therefore, we further synthesized a copolymer with a mole ratio of 1:3 for CPDT to thiophene-DOPI. The copolymer was designated as P13. Besides, the homopolymer of thiophene-DOPI, P01, was also prepared for comparison. The data of synthesized polymers are summarized in Table 1. In

**Table 1.** Molecular weights and optoelectronic properties of the synthesized polymers

Polymer	$M_n$ [ $\text{kg}\cdot\text{mol}^{-1}$ ]	$M_w$ [ $\text{kg}\cdot\text{mol}^{-1}$ ]	PDI	$E_g^a$ [eV]	HOMO <sup>b</sup> [eV]	LUMO <sup>c</sup> [eV]
P11	11.8	16.0	1.36	1.40	$-5.27$	$-3.87$
P13	10.5	13.4	1.28	1.38	$-5.39$	$-4.01$
P01	12.3	16.9	1.37	1.51	$-5.42$	$-3.91$
P3HT (commercial)	13.2	17.0	1.29	1.90	$-5.20$	$-3.30$

<sup>a</sup>Obtained by Tauc relation.

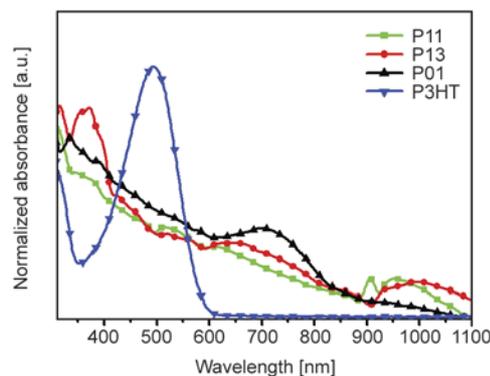
<sup>b</sup>Obtained by cyclic voltammetry.

<sup>c</sup>Obtained from  $\text{LUMO} = \text{HOMO} + E_g$ .

particular, for this kind of intramolecular donor-acceptor polymer, the electron donating groups (CPDT and thiophene units) are present in the main chain as the polymer backbone, while the electron accepting units (DOPI moieties) are pendent as side chains. By the attachment of a coplanar type of DOPI moieties as side chains, the electrons can be transferred sequentially from the donor main chains to the acceptor side chains, and then to n-type PCBM after photoexcitation, hence the charge separation and transfer process are more readily and enhanced in this intramolecular donor-acceptor system. Therefore, it was expected that a low band gap polymer with wide sunlight absorption band and high power conversion efficiency could be achieved for this type of copolymer using the thiophene-DOPI moieties as the intramolecular donor-acceptor units.

### 3.2. Optical properties and band gaps

The normalized UV-vis absorption spectra for the films of the three synthesized polymers and P3HT are presented in Figure 4. As seen from Figure 4, the UV-vis absorption spectrum of the P11 film exhibits a wide absorption band ranging from 300 to 1100 nm with four absorption peaks positioned at about 312, 516, 906 and 952 nm. The strong absorption at 312 nm is attributed to  $\pi$ - $\pi^*$  transition within the polymer backbone, whereas the other weak absorption peaks are ascribed to the intramolecular charge transfer (ICT) between CPDT and thiophene units in the polymer backbone and thiophene donor and DOPI acceptor units of the thiophene-DOPI moieties. In other words, the weak and broadened absorption bands may imply that an effective and enhanced ICT between thiophene backbone and DOPI moieties has occurred. Consequently, with the incorporation of DOPI moieties as acceptor side chains and thiophene unit as the donor backbone, the synthesized copolymer exhibits the enhanced characteristic of intramolecular donor-acceptor polymers. Moreover, since the UV-vis absorption regions of the copolymers stated in Wei's report only extend to ca. 700 nm, the incorporation of CPDT unit and insertion of an ethylenic double bond as the  $\pi$ -bridge between thiophene and PI moiety may extend the absorption breadth of sunlight and lower the energy gap. In addition, as compared to the spectrum of PCPDTTPI and evident from Figure 3, the intensified absorption for P11 in the region from 550 to 1050 nm may indicate that an enhanced ICT has occurred. This tes-

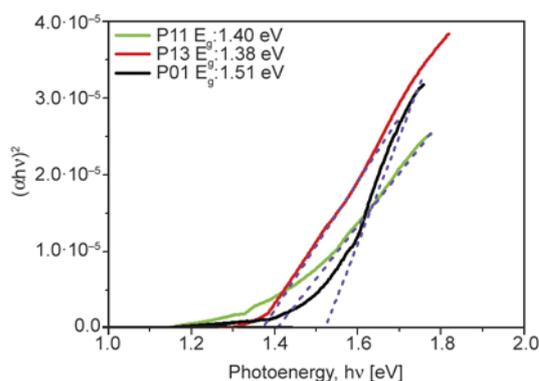


**Figure 4.** Normalized UV-vis absorption spectra of P11, P13, and P01

tifies to the fact that the insertion of a  $\pi$ -bridge between the donor and acceptor unit may optimize the absorption spectrum and harvest more light.

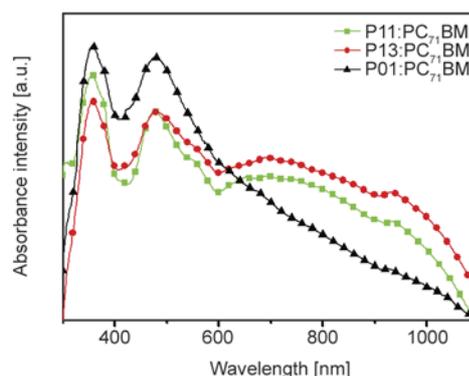
In a similar manner, the spectrum of P13 film also exhibits a panchromatic absorption ranging from 300 to 1100 nm with two strong  $\pi$ - $\pi^*$  transitions (centered at 314 and 373 nm) arising from both CPDT and thiophene units of the polymer backbone. As compared to the spectrum of P11 film, it is noticeable that the absorption bands in the region of 600–900 and 900–1100 nm are significantly enhanced. It may be ascribed to the increased mole ratio of thiophene-DOPI unit raising the ICT between the thiophene donor and DOPI acceptor. For the homopolymer of thiophene-DOPI, the absorption peak at 334 nm is assigned to the  $\pi$ - $\pi^*$  transition of thiophene backbone, while the broad absorption band ranging from 600 to 850 nm and centered at 700 nm is attributed to the ICT between thiophene and DOPI. It is worth noting that the absorption band in the region of 600–850 nm is stronger as compared to that of P11 and P13 film, indicating that the thiophene-DOPI structure has a remarkable effect of ICT between thiophene backbone and DOPI side chains. On the other hand, for the copolymer P11 and P13, the broad absorption around 900 to 1100 nm may arise from the ICT of the polymer backbone between CPDT and thiophene-DOPI units since no obvious absorption for P01 was observed in this region.

The optical band gaps obtained from the Tauc relation [31]  $ah\nu = B(h\nu - E_{opt})^n$  for P11, P13 and P01 are 1.40, 1.38, and 1.51 eV (Figure 5), respectively, and are shown in Table 1. The HOMO and LUMO energy levels of the three polymers can be determined from the oxidation potentials of cyclic voltammetry (CV) measurements and the curve-fitting opti-



**Figure 5.** Plot of  $(ah\nu)^2$  vs.  $h\nu$  via Tauc relation for P11, P13, and P01 film

cal band gaps ( $E_g^{\text{opt}}$  by Tauc relation). The related data are listed in Table 1. As compared to the data reported by Chang *et al.* [4], it is noteworthy that the incorporation of CPDT unit and insertion of an ethylenic double bond can not only lower the HOMO of the copolymer but also reduce the band gap. Both of them are important characteristics for high-performance solar cells. In addition, comparing the data of P13 with those of P11, it may suggest that more thiophene-DOPI moieties may result in the decrease of band gap and lower the HOMO and LUMO values. However, if no CPDT units present in the polymer backbone, as in the case of P01, only the HOMO value is reduced whereas the band gap is raised. Therefore, for reducing the band gap and extending the sunlight absorption of the conjugated polymer, the copolymer structure may be more favorable than that of the homopolymer structure. Since PC<sub>71</sub>BM possesses a strong absorption of UV-vis spectrum around 450–600 nm to compensate the weak absorptions of the three synthesized polymers in this region, we expected that the polymer/PC<sub>71</sub>BM blend films would be beneficial to raise the power conversion efficiency of the fabricated solar cells. Figure 6 displays the UV-vis absorption spectra of the three polymers blended with PC<sub>71</sub>BM in a weight ratio of 1:1. As evident from Figure 4 and Figure 6, the absorption range of UV-vis spectrum for the three blend films increases in the order of P01/PC<sub>71</sub>BM  $\approx$  P11/PC<sub>71</sub>BM < P13/PC<sub>71</sub>BM, resembling the absorption profiles of the three polymers. It is apparent that the ICT interaction between donor (thiophene) and acceptor (DOPI) moieties in this kind of intramolecular donor-acceptor polymers is a practical approach to lower the band gap and broaden the absorption bands of conjugated polymers. In addition, in comparison of copolymer P13 with P11, it is

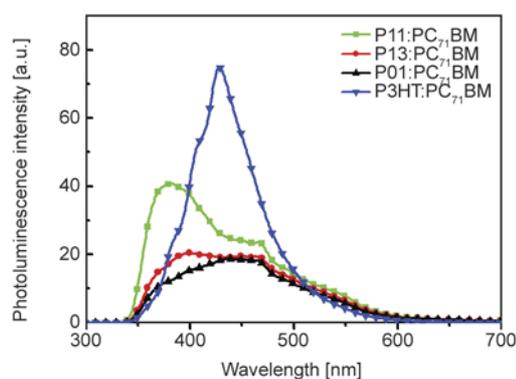


**Figure 6.** UV-vis absorption spectra of P11, P13, and P01 blended with PC<sub>71</sub>BM in a weight ratio of 1:1

obvious that the increase of molar ratio of thiophene-PDI enhances the absorption intensity in both the  $\pi$ - $\pi^*$  transition and ICT (600–1100 nm) regions, and results in the red-shifted absorption bands as well. Conversely, for the homopolymer P01, the weak absorption in the ICT region (600–1100 nm) results in the lower PCE as compared to that of P13, which we will see in the following section.

### 3.3. Photoluminescence spectra

The photoluminescence (PL) emission spectra of the three polymers in comparison with that of P3HT are shown in Figure 7. All of the spectra were obtained from the blend film of polymer/PC<sub>71</sub>BM in a weight ratio of 1:1 without annealing and any additives. The PL of the P11 blend film is dramatically quenched relative to that of P3HT blend film with two peaks centered at 379 and 468 nm. The former peak may result from the PL of CPDT units while the latter peak is associated with the PL of thiophene-DOPI moieties. Upon increasing the content of thiophene-DOPI unit in the copolymer, as in the case of P13, the degree of quenching in both regions is further

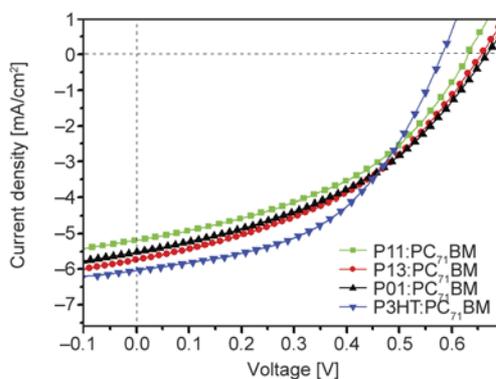


**Figure 7.** Photoluminescence emission spectra of the polymer/PC<sub>71</sub>BM blend films in a weight ratio of 1:1 with excitation at 320 nm

enhanced, especially in the region around 379 nm because of the reduction of the CPDT content, as seen in Figure 7. It is evident that an efficient intramolecular charge transfer between CPDT and thiophene unit in the polymer backbone and thiophene backbone and the electron-withdrawing DOPI side chains has occurred. For the homopolymer P01, the peak arising mainly from CPDT units is further reduced, whereas the PL around 468 nm shows not much change. Therefore, it seems that a 3:1 mole ratio of thiophene-DOPI to CPDT may be enough for the efficient intramolecular charge transfer to occur.

### 3.4. Photovoltaic properties

The photovoltaic performances of the devices for the blend films cast at room temperature (RT) with a 1:1 weight ratio of polymer:PC<sub>71</sub>BM as the active layer were measured under illumination from solar simulator at 100 mW/cm<sup>2</sup> light intensity. The current density-voltage (*J-V*) curves of the cells are shown in Figure 8. The corresponding  $V_{oc}$ , short-circuit current ( $J_{sc}$ ), fill factor (FF), and power conversion efficiency (PCE) are also listed in Table 2. As seen in Figure 8 and Table 2, comparing both copolymers (P11 and P13), the value of  $J_{sc}$  increases with the increase of the molar ratio of thiophene-DOPI moiety. In addition, it is worth noting that the  $V_{oc}$  value is also related with the content of the thiophene-DOPI unit and the more the thiophene-DOPI content, the higher the  $V_{oc}$ . Since the values of  $J_{sc}$  and  $V_{oc}$  increase with the increase of the thiophene-PDI moiety simultaneously, the PCE of the solar cell increases with the increase of thiophene-DOPI moiety in the copolymers. However, the homopolymer P01 displays a lower  $J_{sc}$  and results in a lower PCE as compared to those of P13. This



**Figure 8.** *J-V* characteristics of devices under AM 1.5 simulated solar illumination at an intensity of 100 mW/cm<sup>2</sup> for the polymer/PC<sub>71</sub>BM blend films cast at room temperature in a weight ratio of 1:1

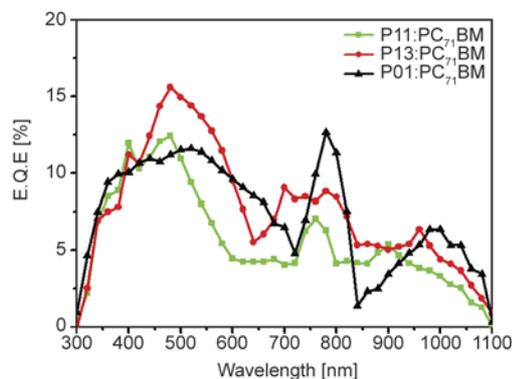
**Table 2.** Photovoltaic characteristics of the polymer solar cells

Polymer	$V_{oc}$ [V]	$J_{sc}$ [mA/cm <sup>2</sup> ]	FF [%]	PCE [%]
P11	0.63	5.18	34.5	1.13
P13	0.66	6.15	34.7	1.41
P01	0.67	5.87	34.0	1.34
P3HT (commercial)	0.58	6.25	46.4	1.68

may imply that if the content of the intramolecular donor-acceptor moiety is high enough, the copolymer structure may be a better choice than homopolymer due to more light-harvesting afforded by both monomer units (CPDT and thiophene-DOPI).

### 3.5. External quantum efficiency

External quantum efficiency (EQE) measurements with monochromatic wave from 300 to 1100 nm were also performed on the solar cell devices with a 1:1 weight ratio of polymer:PC<sub>71</sub>BM (Figure 9). As seen in the figure, both of the EQE spectra of the copolymer P11 and P13 blend films exhibit a dominant region ranging from 300–600 and 300–640 nm, respectively, along with a remarkable peak positioned at 480 nm. Both spectra also show a broad band in the region of 600–1100 and 640–1100 nm, respectively. The broad band in the red to near-infrared region fulfills the expectations for panchromatic photovoltaic applications. Comparing both spectra, it is apparent that the EQE value increases with the increase of thiophene-DOPI content and shows a red-shifted trend for the P13 blend film. The higher EQE values and enhanced  $J_{sc}$  for P13 blend film are attributed to the rapid electron transfer of the dissociated excitons in polythiophene backbone to the conjugated DOPI side chains. It may indicate that more thiophene-DOPI



**Figure 9.** External quantum efficiency curves of polymer/PC<sub>71</sub>BM blends in a weight ratio of 1:1

units may facilitate the charge separation and the intramolecular charge transfer between the thiophene backbone and DOPI moieties. As for the P01 film, the EQE spectrum displays three dominant regions ranging from 300–720, 720–840, and 840–1100 nm with three peaks positioned at 518, 780, and 990 nm, respectively. The EQE values in the first dominant region are apparently smaller than those of P11 and P13 blend films. Conversely, due to the remarkable effect of ICT between thiophene backbone and DOPI side chains in the region of 600–850 nm from the UV-vis spectrum of P01 (Figure 4) as mentioned above, the EQE values are higher in this region as compared to both copolymers. This may suggest that more thiophene-DOPI moiety may facilitate the charge separation and charge transfer process.

#### 4. Conclusions

We have designed and synthesized a series of intramolecular donor–acceptor polymers with different contents of thiophene-DOPI unit that has the D– $\pi$ –A structure. The spectra of the polymer films exhibited panchromatic absorptions and low band gaps (1.38 to 1.51 eV), which were attributed to the incorporation of thiophene-DOPI moieties. A more efficient charge transfer occurred between thiophene (donor) backbone and DOPI (acceptor) side chains, which could be ascribed to the intramolecular donor–acceptor structure. When increasing the content of the thiophene-DOPI unit, the  $V_{oc}$  could be raised and the PCEs of the photovoltaic devices showed significant improvements. In comparison with the device of P11, since the values of  $J_{sc}$  and  $V_{oc}$  increased with the increase of the thiophene-DOPI moiety in the polymers, the PCEs of the solar cells for P13 and P01 were much enhanced.

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