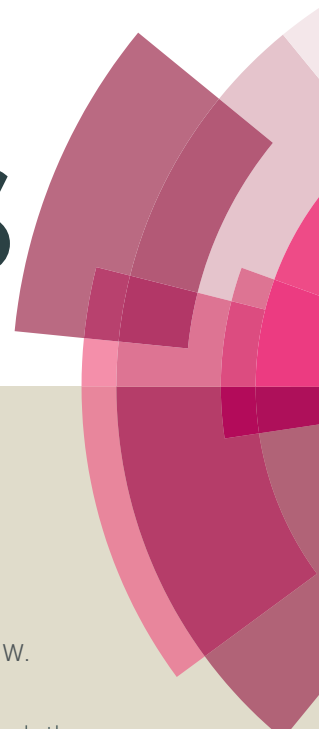


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## ARTICLE

# Triple Bond Side-Chained 2D-Conjugated Benzodithiophene based Photovoltaic Polymer

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A series of triple bond side-chained benzodithiophene copolymers, derived from 4,8-bis(1-ethynyl-3,5-bis(octyloxy)phenyl)-benzo[1,2-b:4,5-b']dithiophene, were synthesized by Still coupling reactions. Several electron acceptors are introduced into the polymer backbone to tune the photo-electronic properties of the copolymers. The obtained copolymers are readily soluble in common organic solvents, such as toluene, THF and chloroform. The number average molecular weights of these polymers were determined by GPC using a polystyrene standard, ranging from 15,400 to 28,300 which are decent results for polymers with rigid triple band side chain. These polymers show high decomposition temperature (403–419 °C), narrow band gap (1.27–1.89 eV), and low-lying HOMO energy level (–5.4 to –5.6 eV). The best polymer solar cells (PSCs) device based on the copolymer PBDTPA-TPD and PC<sub>61</sub>BM showed a power conversion efficiency (PCE) of 0.93% with a  $V_{oc}$  = 0.96 V,  $J_{sc}$  = 1.9 mA cm<sup>–2</sup>, and FF = 51%, which is one of the highest  $V_{oc}$  value achieved by benzodithiophene polymer.

## 1. Introduction

Polymer solar cells (PSCs) have attracted increasing interest due to light-weight, large-area, and flexible through solution processing.<sup>1,2,3,4</sup> PSCs usually adopt a bulk-heterojunction (BHJ) structure, and the photoactive layer consists of an interpenetrating network of  $\pi$ -conjugated polymer donors and soluble fullerene acceptors.<sup>5,6,7</sup> Among different polymer donor units, benzodithiophene (BDT) unit shows good planarity due to symmetrical molecular structure, meanwhile BDT polymer also exhibits high carrier mobility due to strong intermolecular  $\pi$ - $\pi$  stacking interaction.<sup>8,9,10</sup> 4,8-Dialkoxy substituted BDT based donor-acceptor (D-A) type conjugated polymer, have shown excellent maximum power conversion efficiency (PCE) of 9.35%<sup>11</sup> which is the highest PCE for PSCs. However, modification and optimization of BDT based polymer is still hot topic for more efficiency PSCs. For example, by replacing strong electron-donating alkoxy chains with weak electron donor, the HOMO energy level of polymer is reduced, which can increase the open circuit voltage ( $V_{oc}$ ) of PSCs devices.<sup>12</sup> By the concept of two dimensional (2D) conjugated BDT, dialkyl-thiophene substituted BDT is synthesized, which to some extents reduces the HOMO energy level and extends absorption spectrum of polymer, comparing to dialkoxy substituted BDT.<sup>13–17</sup> Besides thiophene side chain of BDT, other conjugated side chain, such as thiophene[3,2-b]thiophene, benzene etc,<sup>18</sup> have also been tried to build more efficiency BDT photovoltaic polymer.

According to the *sp* hybrid in the hybrid orbital theory, the triple bond in the alkynyl group is a weak electron withdrawing group, meanwhile performs high rigidity which is good for intermolecular stacking.<sup>19</sup> By introducing alkynyl group into BDT side chain, the HOMO energy level of polymer materials can be lowered, due to enhanced  $\pi$ - $\pi$  stacking. PCE of (tri-isopropyl-silyl) acetylene based BDT polymer have reached 5.76%,<sup>20</sup> but strong rigidity of triple bond leads to poor solubility of the polymer, which make it

inconvenient for PSCs devices processing.

In this paper, to make more soluble alkynyl substituted BDT donor materials, we have designed and synthesized two-dimension conjugated unit of dialkoxy-phenylacetylene substituted BDT, 4,8-bis(1-ethynyl-3,5-bis(octyloxy)phenyl)-benzo[1,2-b:4,5-b']dithiophene. (Scheme 1) Copolymerized with the acceptor TPD, DPP and TT (Scheme 2), three BDT based copolymers are obtained, and their optical properties, electrical properties and photovoltaic properties are studied.

## 2. Experimental section

### 2.1. Materials

Unless otherwise stated, all reagents and starting materials were used as commercially purchased without further purification. The TPD, DPP and TT comonomers were purchased from Derthon Optoelectronic Materials Science Technology Co Ltd. Tetrahydrofuran (THF) and toluene were distilled from sodium with benzophenone as indicator and N,N-dimethylformamide (DMF) was distilled from CaH<sub>2</sub> under argon atmosphere before use. All air and water sensitive reactions were performed under argon or nitrogen atmosphere.

### 2.2. Materials characterization

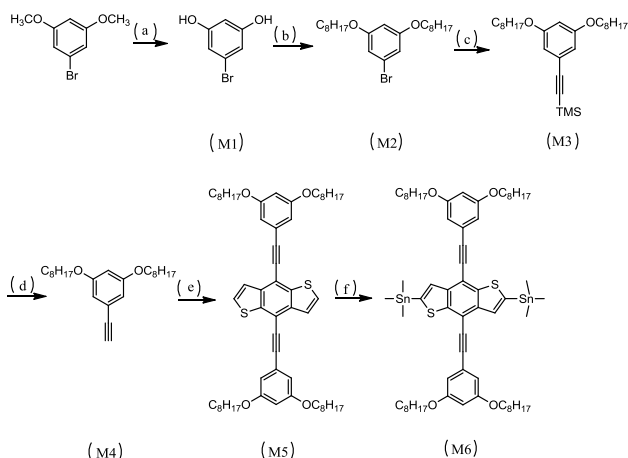
The nuclear magnetic resonance (NMR) spectra were recorded on a BrukerAvanceIII 600 (600 MHz) using CDCl<sub>3</sub> as the solvent. UV-vis absorption spectra were measured with a Hitachi U-4100 spectrophotometer. The molecular weight and polydispersity were determined by gel permeation chromatography (GPC) analysis using an ELEOS System with polystyrenes as the reference standard and THF as an eluent. Thermogravimetric analysis (TGA) was

performed on a TA-Q600 analyzer with a heating rate of 20 °C min<sup>-1</sup> under nitrogen. Electrochemical cyclic voltammetry (CV) measurements were conducted on an electrochemistry workstation (CHI660D) with a glassy carbon as working electrode, a platinum wire as counter electrode and an Ag/AgCl as reference electrode under nitrogen in a solution of Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M).

### 2.3. Device fabrication

Photovoltaic devices were fabricated on pre-patterned indium tin oxide (ITO) coated glass substrates with a layered structure of ITO/PEDOT:PSS/donor:PC<sub>61</sub>BM/Ca(10 nm)/Al(100 nm). The ITO coated glass substrates were cleaned in ultrasonic bath in acetone, toluene, methanol and isopropyl alcohol sequentially. After a twenty-minute oxygen plasma treatment, a thin layer of PEDOT:PSS (30 nm) was spin-coated onto the ITO anode and then dried at 120 °C for 20 min. The photosensitive layer was prepared by spin-coating a blend solution of the polymers and PC<sub>61</sub>BM with a weight ratio of 1:1.5 in deoxygenated anhydrous *o*-dichlorobenzene on the ITO/PEDOT:PSS substrate and then annealed at 150 °C for 10 min in a glove box. 4% of DIO was added as processing additive to the blend solutions. The active layer thickness was around 90 nm. Finally, Ca (10 nm) and aluminum (100 nm) were thermally evaporated at a vacuum of ~2×10<sup>-4</sup> Pa on top of active layer. The photovoltaic performance was measured under illumination at 100 mWcm<sup>-2</sup> AM 1.5 G irradiation using a Xe arc lamp in an argon atmosphere (<0.1 ppm H<sub>2</sub>O and O<sub>2</sub>), and the current density-voltage (*J*-*V*) curves was obtained by Keithley 2400. The external quantum efficiency (EQE) was obtained by a source meter, silicon photodiode and a computer-controlled light source-monochromator-lock-in system.

### 2.4. Synthesis



Reaction conditions: (a) BBr<sub>3</sub>, methylene chloride, 0 °C; (b) Bromooctane, K<sub>2</sub>CO<sub>3</sub>, DMF, 60 °C; (c) Ethynyl-trimethyl silicon, CuI, trans-dichlorobis(triphenyl-phosphine) Palladium(II), triethylamine, 80 °C; (d) KOH, methylene chloride; (e) *n*-BuLi, THF, 0 °C, SnCl<sub>2</sub>, reflux; (f) *n*-BuLi, Me<sub>3</sub>SnCl, THF, 0 °C.

**Scheme 1** Synthetic routes of monomers

#### 1-Bromo-3,5-di-hydroxyphenyl (M1)

3,5-Dimethoxybromobenzene (10.0 g, 46.2 mmol) was dissolved in 100 ml dry CH<sub>2</sub>Cl<sub>2</sub>. The solution of 3, 5-dimethoxybromobenzene

was cooled to -78 °C, and 1 M CH<sub>2</sub>Cl<sub>2</sub> solution of BBr<sub>3</sub> (100 ml, 100.0 mmol) was added slowly. Then, the solution was allowed to warm to ambient temperature for overnight. The stirred solution was cooled to 0 °C, and then quenched with H<sub>2</sub>O. The aqueous phase was extracted with Et<sub>2</sub>O. The combined organic layers were washed with H<sub>2</sub>O, dried over MgSO<sub>4</sub>. Solvent was removed, and the resulting white solids were used for the next step reaction without further purification.

#### 1-Bromo-3, 5-bis(octyloxy)phenyl (M2)

1-Bromo-3, 5-di-hydroxyphenyl (3 g, 15.9 mmol) and anhydrous K<sub>2</sub>CO<sub>3</sub> (16.21 g) was diluted with 90 mL of *N,N*-dimethylformamide, the mixture was stirred at ambient temperature for 30 min. After the addition of bromooctane (12.4 g, 64.4 mmol), solution was heated at 60 °C overnight. The cooled reaction mixture was filtered through Celite, and concentrated to yield the crude product which was purified by column chromatography (hexane eluent) to obtain 1-bromo-3,5-bis(octyloxy)phenyl 4.4 g (10.5 mmol, 66.8%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600MHz), δ (ppm): 6.63 (d, 2H), 6.36 (t, 1H), 3.89(t, 4H), 1.75 (m, 4H), 1.42 (m, 4H), 1.29 (m, 16H), 0.89 (t, 6H) (Figure S1)

#### 1-(Trimethylsilyl)ethynyl-3,5-bis(octyloxy)phenyl (M3)

1-Bromo-3, 5-bis(octyloxy)benzene (4.3 g, 10.5 mmol), copper iodide (27.3 mg) and bis(triphenylphosphine)dichloridepalladium (336 mg) was dissolved in 42 ml of dry triethylamine under nitrogen. After the mixture was heated to 50 °C, trimethylsilylacetylene (1.1 g, 11.4 mmol) was added. The solution was heated at 80 °C for 24 h. The cooled reaction mixture was quenched with 2 M HCl solution, washed with H<sub>2</sub>O, dried over MgSO<sub>4</sub>, and concentrated to yield crude product, which was purified by column chromatography (hexane eluent) to obtain 3.2 g of light yellow powder (7.3 mmol, 70%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600MHz), δ (ppm): 6.62 (d, 2H), 6.46 (t, 1H), 3.94 (t, 4H), 1.78 (m, 4H), 1.46 (m, 4H), 1.33 (m, 16H), 0.92 (t, 6H), 0.27 (s, 9H). (Figure S2)

#### 1-Ethynyl-3,5-bis(octyloxy)phenyl (M4)

1-(Trimethylsilyl)ethynyl-3,5-bis(octyloxy)benzene (3.2 g, 7.3 mmol) was dissolved in 35 ml of dichloromethane, and 2.3 g of potassium hydroxide was dissolved in 35 ml of methanol. These two solutions were mixed and stirred at ambient temperature for 3 h. The reactant was poured into water and extracted by dichloromethane. The organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing solvent, the crude product was purified by column chromatography (hexane eluent) to obtain 2.4 g of light yellow powder (7.68 mmol, 99%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz), δ (ppm): 6.65 (d, 2H), 6.49 (t, 1H), 3.94 (t, 4H), 3.04 (s, 1H), 1.78 (m, 4H), 1.46(m, 4H), 1.33 (m, 16H), 0.92 (t, 6H). (Figure S3)

#### 4,8-Bis(1-ethynyl-3,5-bis(octyloxy)phenyl)-benzo[1,2-b:4,5-b']dithiophene (M5)

1-Ethynyl-3, 5-bis(octyloxy)benzene (2 g, 6.4 mmol) was dissolved in 70 ml of dry THF under nitrogen. Solution was cooled to 0 °C, and then 4 ml of *n*-BuLi (6.5 mmol, 1.6 M) was added dropwise. The mixture was stirred at 0 °C for 30 min, then benzo[1,2-b:4,5-b']dithiophene-4,8-dione (0.67 g, 3.1 mmol) was added. The stirred mixture was heated at reflux for 1 h, then cooled to 0 °C again. 3.3 g of tin chloride dihydrate dissolved in 50 mL 20% HCl solution was added, and the reaction was heated at reflux for 2 h. The cooled reaction mixture was extracted with ether. The organic layer was

washed with H<sub>2</sub>O several times, dried over MgSO<sub>4</sub>, and concentrated to yield crude product, which was purified by column chromatography (hexane: dichloromethane (8:1, v/v) eluent) to obtain 1.3 g of light yellow powder (1.47 mmol, 45%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz), δ (ppm): 7.74 (d, 2H), 7.62 (d, 2H), 6.84 (d, 4H), 6.55 (t, 2H), 4.02 (t, 8H), 1.84 (m, 8H), 1.51 (m, 8H), 1.36 (m, 32H), 0.93 (t, 12H). (**Figure S4**)

### 2,6-Bis(trimethyltin)-4,8-bis(1-ethynyl-3,5-bis(octyloxy)phenyl)-benzo[1,2-b:4,5-b']dithiophene (M6)

4,8-Bis(1-ethynyl-3,5-bis(octyloxy)phenyl)-benzo[1,2-b:4,5-b']bithiophene (BDTPA) (0.6 g, 0.68 mmol), N, N, N, N-tetramethylethylenediamine (0.28 ml, 1.8 mmol) was dissolved in 30 ml of dry THF under nitrogen. The mixture was cooled to 0 °C, and 1.2 ml of n-BuLi (1.8 mmol, 1.6 M) was added dropwise. After being stirred at 0 °C for 4 h, 2.2 ml of 1 M trimethyltin chloride was added slowly. The stirred solution was warm up to ambient temperature for overnight. After the reaction, the solution was poured into water and extracted by ether. The organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing solvent under vacuum, the residue was recrystallized from isopropanol to obtain 0.67 g of product (0.544 mmol, 80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz), δ (ppm): 7.76 (t, 2H), 6.86 (d, 4H), 6.55 (t, 2H), 4.03 (t, 8H), 1.84 (m, 8H), 1.51 (m, 8H), 1.36 (m, 32H), 0.93 (t, 12H), 0.52 (t, 18H). (**Figure S5**) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz), δ (ppm): 160.1, 144.7, 143.6, 139.1, 130.9, 124.2, 110.2, 110.0, 102.9, 98.7, 85.6, 68.3, 31.8, 29.4, 29.2, 26.0, 22.7, 14.1, -8.2. (**Figure S6**) Anal. Calcd. for C<sub>64</sub>H<sub>94</sub>O<sub>4</sub>S<sub>2</sub>Sn<sub>2</sub>: C, 62.55; H, 7.71; S, 5.22. Found: C, 62.73; H, 7.62; S, 5.15. HRMS (APCI) *m/z*: calcd. 1229.4632 [M+I]<sup>+</sup>, found: 1229.4740.

### PBDTPA-TPD

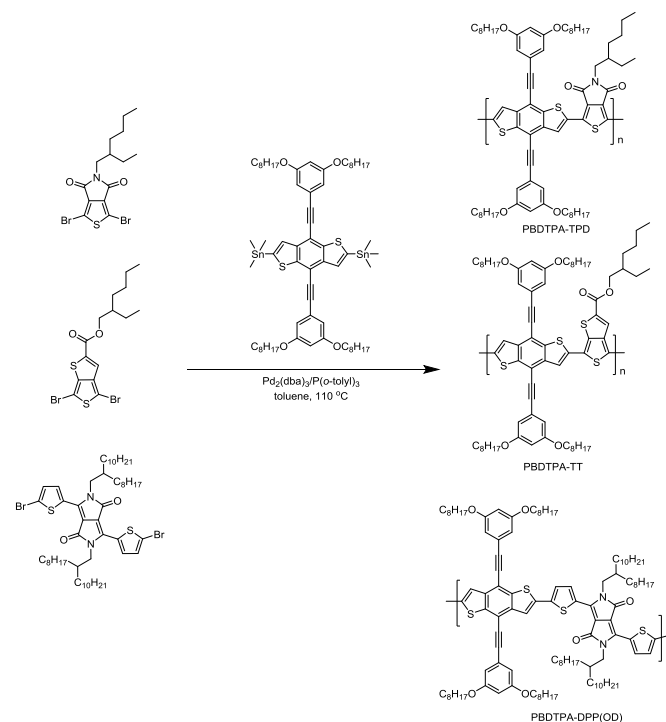
2,6-Bis(trimethyltin)-4,8-bis(1-ethynyl-3,5-bis(octyloxy)phenyl)-benzo[1,2-b:4,5-b']dithiophene (184.4 mg, 0.15 mmol), 1,3-dibromo-5-(2-ethylhexyl)-thieno[3,4-c]pyrrole-4,6-dione (TPD) (63.5 mg, 0.15 mmol), (o-tolyl)phosphine (7.3 mg, 16%) and tris(dibenzylideneacetone)dipalladium (2.8 mg, 2%) was dissolved in 5 ml dry toluene under nitrogen. The mixture was heated to 70 °C for 4 h. Then, the stirred solution was heated to 110 °C for 48 h. After the reaction, the cooled mixture was dropped into methanol. The precipitate was collected and Soxhlet-extracted in sequence with methanol, hexane and chloroform. The product was dried under vacuum for 1 day to obtain the target polymer PBDTPA-TPD as a dark red solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz), δ (ppm): 9.5-7.5 (m), 7.2-5.5 (m), 4.5-3.3 (m), 2.3-0.3 (m). (**Figure S7**) GPC (THF, polystyrene standard): *M*<sub>n</sub> = 23.9 kDa, *M*<sub>w</sub> = 57.7 kDa, PDI = 2.41.

### PBDTPA-TT

2,6-Bis(trimethyltin)-4,8-bis(1-ethynyl-3,5-bis(octyloxy)phenyl)-benzo[1,2-b:4,5-b']dithiophene (122.9 mg, 0.1 mmol), 2-ethylhexyl-4,6-dibromo-thieno[3,4-b] thiophene-2-carboxylate (TT) (48.6 mg, 0.1 mmol), tris(o-tolyl)phosphine (4.9 mg, 16%) and tris(dibenzylideneacetone)dipalladium (1.8 mg, 2%) was dissolved in 5 ml of dry toluene under nitrogen. The other procedures are just as PBDTPA-TPD polymer. Finally, the target polymer PBDTPA-TT is obtained as a dark solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz), δ (ppm): 8.5-7.5 (m), 7.2-6 (m), 4.5-3.2 (m), 2.2-0.3 (m). (**Figure S8**) GPC (THF, polystyrene standard): *M*<sub>n</sub> = 15.4 kDa, *M*<sub>w</sub> = 81.2 kDa, PDI = 5.25.

### PBDTPA-DPP (OD)

2,6-Bis(trimethyltin)-4,8-bis(1-ethynyl-3,5-bis(octyloxy)phenyl)-benzo[1,2-b:4,5-b']dithiophene (61.4 mg, 0.05 mmol), 3,6-bis(5-bromo-thiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4-(2H, 5H)-dione (DPP(OH)) (50.9 mg, 0.05 mmol), tris(o-tolyl)phosphine (2.4 mg, 16%) and tris(dibenzylideneacetone)dipalladium (0.9 mg, 2%) was dissolved in 5 ml dry toluene under nitrogen. The other procedures are just as PBDTPA-TPD polymer. Finally, the target polymer PBDTPA-DPP(OD) is obtained as a dark green solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz), δ (ppm): 9.0-8.5 (m), 7.1-6.2 (m), 4.0 (s), 2.1-1.2 (m). (**Figure S9**) GPC (THF, polystyrene standard): *M*<sub>n</sub> = 28.3 kDa, *M*<sub>w</sub> = 275.6 kDa, PDI = 9.72.

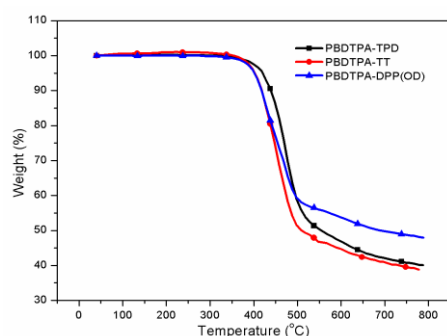


Scheme 2 Synthetic routes of polymers

## 3. Results and discussion

### 3.1. Synthesis and Characterization

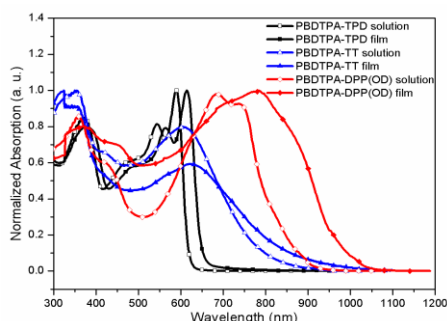
The general synthetic routes toward the monomer and copolymers are outlined in **Scheme 1** and **Scheme 2** respectively. All the compounds are characterized by <sup>1</sup>H NMR spectra. They are in accordance with the literature<sup>21</sup> for the precursors and show correctly the designed structure for polymers (see supporting information **Figure S7** to **Figure S9**). The obtained copolymers are readily soluble in common organic solvents, such as toluene, THF, and chloroform. The number-average molecular weights of these polymers were determined by GPC using a polystyrene standard, ranging from 15,400 to 28,300 with a polydispersity index (*M*<sub>w</sub>/*M*<sub>n</sub>) between 2.41 and 9.72. The molecular weights data is summarized in **Table 1**.



**Figure. 1** TGA plots of the polymers with a heating rate of 20 °C min<sup>-1</sup> under an inert atmosphere.

The thermal properties of the polymer were measured with a heating rate of 20 °C min<sup>-1</sup> under inert atmosphere. As shown in Figure 1, the decomposition temperature ( $T_d$ ) at 5% weight loss of PBDTPA-TPD, PBDTPA-TT and PBDTPA-DPP(OD) was 419.7 °C, 403.7 °C and 401.7 °C respectively. The high decomposition temperature decreases the possibility of the deformation of the polymer film morphology and the degradation of the polymer active layer under applied electric fields in solar cell devices.

### 3.2. Optical properties



**Figure. 2** Normalized absorption spectra of the polymers in chloroform solution and in thin film

The absorption spectra of the polymers were measured both in chloroform solution and in thin films (Figure 2, Table 1). Since the different electron acceptors of copolymers lead to various absorption spectral features, PBDTPA-TPD, PBDTPA-TT and PBDTPA-DPP(OD) exhibit absorption peaks at ~587, 603 and 683 nm respectively. Compared to the absorption in solution, the thin films show red-shifted UV-vis absorption spectrum, with absorption peaks at ~ 613, 624 and 784 nm, respectively. Especially for PBDTPA-DPP(OD), the absorption spectrum becomes broader and shows a 101 nm red-shifted in thin film, which can be attributed to the planar polymer chain structure and effective inter-chain  $\pi$ - $\pi$  stacking in the solid state. The introduction of alkynyl group enhances intermolecular interactions by extending the 2D conjugation of polymers. The absorption coefficients were tested in thin film and middle value ( $< 5 \times 10^4$  cm<sup>-1</sup>) were obtained for all three polymers, which may cause limited photocurrent in solar cells<sup>22</sup>.

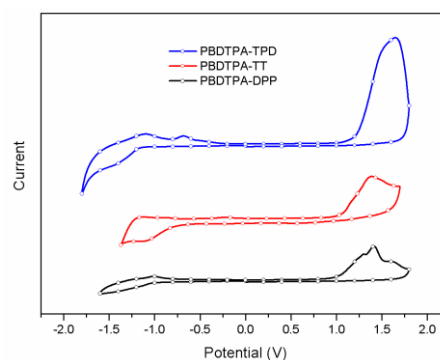
**Table 1** Molecule weight and optical properties of the polymers

polymer	$M_n$ (k)	$M_w$ (k)	PDI	$\lambda_{\max}^{\text{S}}$ (nm)	$\lambda_{\max}^{\text{F}}$ (nm)	$\epsilon$ (cm <sup>-1</sup> ) thin film	$E_g^{\text{opt}}$ (eV)
PBDTPA-TPD	23.9	57.7	2.41	587	613	$4.1 \times 10^4$	1.89
PBDTPA-TT	15.4	81.2	5.25	603	624	$2.4 \times 10^4$	1.37
PBDTPA-DPP(OD)	28.3	275.6	9.72	683	784	$4.7 \times 10^4$	1.27

$\lambda_{\max}^{\text{S}}$ : Absorption peak in solution;  $\lambda_{\max}^{\text{F}}$ : Absorption peak in film;

$E_g^{\text{opt}}$ : Optical band gap is calculated from  $1240/\lambda_{\text{onset}}$ .

### 3.3. Electrochemical characterization



**Figure. 3** Cyclic voltammogram of the polymers

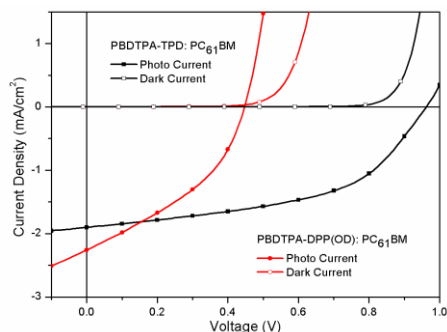
Cyclic voltammogram (CV) (Figure 3) was performed to evaluate the HOMO and LUMO energy levels of all the polymers. HOMO and  $E_{\text{LUMO}}$  were estimated from the onset oxidation potential and reduction potential of the polymer film.<sup>23</sup> The HOMO and LUMO levels are calculated according to the empirical formula  $E_{\text{HOMO}} = -e(E_{\text{ox onset}} + 4.4)$  eV and  $E_{\text{LUMO}} = -e(E_{\text{red onset}} + 4.4)$  eV. The data are listed in Table 2. The polymers show deep HOMO level around -5.6 and -5.4 eV, which may result in high open circuit voltage ( $V_{\text{oc}}$ ) in OSC device. Meanwhile, the LUMO levels were calculated from optical band gap. The materials of PBDTPA-TT and PBDTPA-DPP(OD) exhibit low  $\text{LUMO}^{\text{opt}}$  value of below -4.0 eV, which may lead to insufficient exciton dissociation at donor/acceptor interfaces<sup>24</sup>.

**Table 2** Electrochemical properties of the polymers

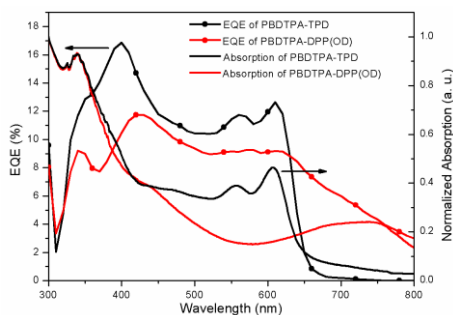
polymer	$E_{\text{ox}}$ (V)	$E_{\text{red}}$ (V)	HOMO (eV)	LUMO (eV)	$\text{LUMO}^{\text{opt}}$ <sup>a</sup> (eV)	$E_g^{\text{cv}}$ <sup>b</sup> (eV)
PBDTPA-TPD	1.24	-1.17	-5.65	-3.24	-3.76	2.41
PBDTPA-TT	1.05	-0.85	-5.44	-3.57	-4.07	1.87
PBDTPA-DPP(OD)	1.01	-1.02	-5.42	-3.39	-4.15	2.03

<sup>a</sup>  $\text{LUMO}^{\text{opt}} = \text{HOMO} - E_g^{\text{opt}}$ ; <sup>b</sup>  $E_g^{\text{cv}} = \text{LUMO} - \text{HOMO}$ .

## 3.4. Photovoltaic performance



**Figure 4** J-V curves of the PSCs based on the blend of PBDTPA-TPD or PBDTPA-DPP(OD)/PC<sub>61</sub>BM under the illumination of AM 1.5, 100 mWcm<sup>-2</sup>



**Figure 5** EQE curves of the PSCs based on the blend of PBDTPA-TPD or PBDTPA-DPP(OD)/PC<sub>61</sub>BM and optical absorptions for the corresponding polymer/PC<sub>61</sub>BM blend film.

Polymer solar cells (PSCs) devices were fabricated with the resultant polymer as the donor and PC<sub>61</sub>BM as the acceptor to investigate the photovoltaic properties of the polymer. The device structure is ITO/PEDOT:PSS/polymer:PC<sub>61</sub>BM/Ca/Al. To improve the photovoltaic performance of the device, 1, 8-diiodooctane (DIO) was used as the additive and the optimized D/A ratio of polymer:PC<sub>61</sub>BM was 1:1.5 (Figure S10). Figure 4 shows the current density-voltage curves (J-V) of the devices under the illumination of AM 1.5G (100 mW cm<sup>-2</sup>). The PBDTPA-TPD/PC<sub>61</sub>BM device exhibited the best PCE of 0.93%, V<sub>oc</sub> of 0.96 V. Due to the low-lying HOMO energy level of PBDTPA-TPD (-5.4 eV), the PSCs based on PBDTPA-TPD show nearly 1 V (0.96 V) V<sub>oc</sub> which is one of the highest V<sub>oc</sub> value achieved by benzodithiophene polymer. For PBDTPA-DPP(OD)/PC<sub>61</sub>BM based PSCs devices, the best result was obtained with a PCE = 0.39% and a V<sub>oc</sub> of 0.45 V. PBDTPA-TT based device performances wasn't listed in Table 3, because it does not show photovoltaic response in the ITO/PEDOT:PSS/polymer:PC<sub>61</sub>BM/Ca/Al device structure. For polymers PBDTPA-DPP(OD) and PBDTPA-TT, the deep LUMO level (< -4.0 eV) may be a detrimental factor for the low PCE value, because the LUMO-LUMO offset with PC<sub>61</sub>BM acceptor is less than 0.3 eV and exciton dissociation could not be sufficiently efficient. Furthermore, low value of absorption coefficient would also reduce the PCE of OSC (Table 1). The dark J-V curves were tested for polymers of PBDTPA-TPD and PBDTPA-DPP(OD) (Figure 4). It shows good diode character.

The external quantum efficiency (EQE) spectra of the devices are shown in Figure 5. EQE value of < 20% were obtained for polymers PBDTPA-TPD and PBDTPA-DPP(OD). The EQE spectrum of PBDTPA-DPP(OD) shows relatively low value beyond 500 nm, while its maximum absorption in film is at about 784 nm. This mismatch reflect insignificant contribution from the major absorption of PBDTPA-DPP(OD) to the photocurrent of solar cell<sup>25</sup>. That is to say, the conversion of the low-energy excitons (from the polymer's absorption) to harvestable free charges is not efficient. This is most probably due to the poor dissociation efficiency of the low-energy excitons as the polymer-PC<sub>61</sub>BM LUMO energy difference is too small (<0.3 eV)<sup>26</sup>. This induces less-effective utilization of the absorption and low J<sub>sc</sub> is obtained as a result.

**Table 3** Solar cells devices performance of PBDTPA-TPD and PBDTPA-DPP(OD)

Active layer	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
PBDTPA-TPD/PC <sub>61</sub> BM	0.96	1.90	51	0.93
PBDTPA-DPP(OD)/PC <sub>61</sub> BM	0.45	2.26	39	0.39

## 4. Conclusions

In summary, a series of triple bond side-chained benzodithiophene copolymer, derived from 4,8-bis(1-ethynyl-3,5-bis(octyloxy)phenyl)-benzo[1,2-b:4,5-b']dithiophene, were synthesized. By introducing soluble bis(octyloxy)phenyl substituted triple band as side chain of DBT polymer, decent molecule weight (15.4 k to 28.3 k) is achieved for polymers with rigid triple band side chain. These polymers show high decomposition temperature and low-lying HOMO energy level. The best PSCs device based on the copolymer PBDTPA-TPD and PC<sub>61</sub>BM showed a nearly 1V (0.96 V) V<sub>oc</sub>. Further work to make more efficiency triple bond side-chained benzodithiophene polymer is underway.

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## Notes

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