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# A new multi-functional conjugated polymer for use in high-performance bulk heterojunction solar cells†

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**We report a new multi-functional copolymer, PDTP-DTBDT, containing DTP and DTBDT units. Surprisingly, the introduction of novel DTP and DTBDT units brings not only superior charge transfer properties but also charge transport characteristics for efficient bulk heterojunction solar cells.**

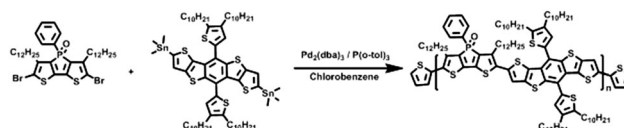
Polymer solar cells (PSCs) have attracted attention in both the academic and industrial communities because they can be fabricated to be lightweight, large-area, and flexible devices using low-cost solution processing methods.<sup>1–3</sup> In an attempt to improve the photovoltaic performance of the PSCs, tremendous efforts have been devoted to designing, synthesizing, and optimizing the photovoltaic properties of polymers by preparing suitable molecular energy levels, broadening the absorption bands, and increasing the hole mobility.<sup>4–6</sup> To date, power conversion efficiencies (PCEs) exceeding 9% in a single junction cell have been achieved.<sup>7</sup>

Several strategies for designing organic donors for use in high-performance PSCs have been established. These strategies involve (1) forming a repeating unit having the large, localized dipole moment in a polymer chain to render the excited state highly polarized and facilitate efficient electron transfer to the PCBM acceptor;<sup>8,9</sup> or (2) incorporating planar molecular structures that pack closely to form crystalline structures, thereby enhancing the charge carrier mobility and yielding a large short-circuit current ( $J_{SC}$ ).<sup>10,11</sup>

With this strategy in mind, we designed a novel multi-functional conjugated polymer, **PDTP-DTBDT**, that displayed a large internal dipole moment unit and highly ordered intermolecular stacking properties. This new polymer with multi-functional characteristics was synthesized using dithieno[3,2-*b*:2',3'-*d'*]phosphole oxide (DTP) as a highly polarized group and dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (DTBDT) as a rigid segment.

DTP provides an excellent acceptor unit with a large dipole moment for preparing highly efficient low band gap polymers. The highly polarizable properties of the phosphole oxide unit imparts superior charge carrier transport properties to the fullerene acceptor.<sup>12,13</sup> Moreover, the DTBDT unit was a linearly fused derivative of benzodithiophene, with an enlarged planar area that could enhance the structural ordering of the polymers, thereby introducing superior intermolecular charge transport properties.<sup>14,15</sup> As expected, the newly synthesized polymer was found to exhibit a sufficiently large dipole moment in the DTP unit and produced effective intermolecular charge transfer into PCBM. The **PDTP-DTBDT** polymer displayed a relatively high hole mobility due to the incorporation of the rigid DTBDT unit. Bulk heterojunction (BHJ) devices were fabricated using this multi-functional polymer as the donor and (6,6)-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) as the acceptor, and a PCE of 6.81% with a high photocurrent density of 15.1 mA cm<sup>−2</sup> was achieved in the optimized device. To the best of our knowledge, this is the first time that a multi-functional polymer composed of DTP and DTBDT units has been reported.

The chemical structure and synthetic route to prepare **PDTP-DTBDT** are depicted in Scheme 1 (full figure; Scheme S1, ESI†). The obtained polymer was purified by sequential Soxhlet



Scheme 1 Synthesis and structure of **PDTP-DTBDT**.

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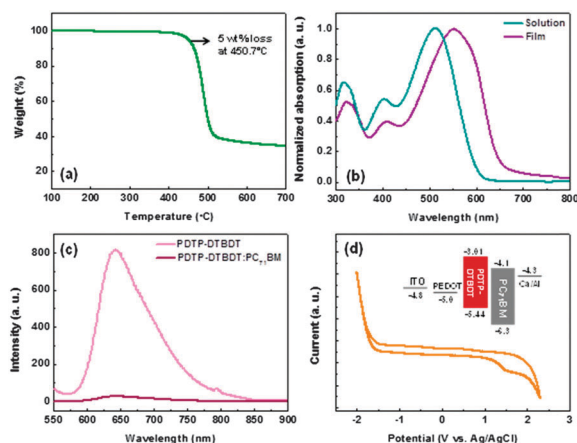


Fig. 1 (a) TGA curve. (b) Normalized UV-vis absorption spectra in solution and in the thin film. (c) PL spectra obtained from pure and blend films; (d) cyclic voltammogram (the inset: the energy level diagram of the component materials of the devices).

extraction using methanol, acetone, hexane, and toluene. The synthesized polymer displayed good solubility in common chlorinated solvents. Gel permeation chromatography (GPC) analysis revealed that the molecular weight ( $M_n$ ) of **PDTP-DTBDT** was  $46\,300\text{ g mol}^{-1}$  with a polydispersity index of 1.84. The thermal behavior of **PDTP-DTBDT** was investigated by thermogravimetric analysis (TGA) under a nitrogen atmosphere. As illustrated in the TGA plot (Fig. 1a), **PDTP-DTBDT** exhibited a decomposition temperature ( $T_d$ ) of  $450.7\text{ }^\circ\text{C}$ , indicating that the polymer displayed excellent thermal stability and was suitable for solar cell applications.<sup>16</sup>

The absorption spectra of the target polymer in dilute chloroform solution and in the thin film are shown in Fig. 1b. The absorption maxima and optical band gap are summarized in Table 1. The **PDTP-DTBDT** polymer displayed one absorption band at shorter wavelengths due to the localized  $\pi$ - $\pi^*$  transitions and one absorption band at longer wavelengths due to intramolecular charge transfer.<sup>17</sup> In solution, **PDTP-DTBDT** exhibited a maximum absorption peak ( $\lambda_{\text{max}}$ ) at 512 nm with a shoulder peak at 404 nm. The conjugated polymer in the thin film displayed a bathochromic absorption band, unlike the solution spectrum, indicating strong intermolecular stacking among the polymer molecules in the solid state.<sup>18</sup> The optical band gap deduced from the absorption edges of the thin film spectrum was estimated to be 1.85 eV. The photoluminescence (PL) spectra of the pure polymer and the corresponding polymer:PC<sub>71</sub>BM blends were recorded, and the quenching spectra are shown in Fig. 1c. The **PDTP-DTBDT**:PC<sub>71</sub>BM blend showed a much lower intensity relative to **PDTP-DTBDT** (~97% PL quenching efficiency),

Table 1 Optical and electrochemical properties of the **PDTP-DTBDT** blend films

Polymer	$\lambda_{\text{max}}$ (nm) solution	$\lambda_{\text{max}}$ (nm) film	$E_g^{\text{opt}}$ (eV)	$E_{\text{onset}}^{\text{ox}}$ (eV)	$E_{\text{onset}}^{\text{red}}$ (eV)
<b>PDTP-DTBDT</b>	512	554	1.85	1.04	-1.39

<sup>a</sup> From the edge of absorption spectra in thin film.

indicating effective charge transfer between **PDTP-DTBDT** and PC<sub>71</sub>BM.<sup>19</sup> This finding was consistent with the hypothesis outlined above, in which the DTP unit of **PDTP-DTBDT** enabled efficient photoinduced charge transfer. The PL analysis results were corroborated by calculating the dipole moment of a DTP unit (see Fig. S1, ESI<sup>†</sup>). As expected, the DTP unit displayed a large excited state dipole moment of 6.00 D with a ground state dipole moment of 3.94 D. Furthermore, the DTP-DTBDT monomer also exhibited highly large dipole moment values both at the ground state (3.78 D) and the excited state (12.51 D). Thus, the highly polarizable DTP-DTBDT unit with DTP was capable of providing excellent charge separation.

Cyclic voltammetry measurements were performed to determine the HOMO and LUMO energy levels of the copolymer (see Fig. 1d), and the electrochemical data are listed in Table 1. The equation  $E_{\text{HOMO/LUMO}} = -(E_{\text{ox/red}} - 0.40) - 4.8\text{ (eV)}$ <sup>20</sup> was used to calculate the  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  levels, which were -5.44 eV and -3.01 eV, respectively. Importantly, the **PDTP-DTBDT** polymer exhibited sufficient highest occupied molecular orbital (HOMO) energy levels to ensure a high open circuit voltage ( $V_{\text{OC}}$ ) in solar cell applications. The lowest unoccupied molecular orbital (LUMO) energies were 1.0 eV above those of the PCBM n-type acceptor (-4.1 eV), which generated a driving force for energetically favorable electron transfer (see the inset in Fig. 1d).<sup>21,22</sup> The oxidative and reductive properties of **PDTP-DTBDT** were explored by examining the geometry and electronic structure of **PDTP-DTBDT** using DFT methods (Fig. S2, ESI<sup>†</sup>). The HOMO was localized along the polymer backbone, whereas the LUMO contained DTP acceptor character. The calculated HOMO and LUMO energies of the ground state optimized geometry of **PDTP-DTBDT** were -4.82 eV and -2.31 eV, respectively.

The photovoltaic properties of **PDTP-DTBDT** were evaluated in a simple conventional device structure consisting of ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM/Ca/Al, and the device fabrication process is described in detail in the ESI<sup>†</sup>. The photovoltaic properties were optimized by preparing devices with different weight ratios of donor vs. acceptor, from different solvents, and using different active layer thicknesses (see Fig. S3-S5 and Tables S1-S3, ESI<sup>†</sup>). The optimized solar cells fabricated using a polymer-PC<sub>71</sub>BM blend in a weight ratio of 1:4, prepared in a  $40\text{ mg ml}^{-1}$  DCB solution, and with a 95 nm active layer thickness gave the best performance. A PCE of 6.05% with a  $V_{\text{OC}}$  of 0.82 V, a short circuit current ( $J_{\text{SC}}$ ) of  $13.4\text{ mA cm}^{-2}$ , and a fill factor (FF) of 55.1% was obtained under 1 sun simulated AM 1.5 G ( $100\text{ mW cm}^{-2}$ ) (Fig. 2a). The high photocurrent of  $13.4\text{ mA cm}^{-2}$  represents one of the highest  $J_{\text{SC}}$  values yet achieved in DTBDT-based polymers, such as PTBD1, PDTT, and PBT-T-DPP-C12.<sup>23-25</sup> This result indicated that the polarizable DTP unit in the polymer chain indeed contributed to the photocurrent enhancement by improving the charge separation. The addition of 1% 1-chloronaphthalene (CN) (by volume) as an additive significantly increased  $J_{\text{SC}}$  to  $15.1\text{ mA cm}^{-2}$ . Typically, the concentration of a solvent additive in a polymer solution can range between 1 and 3% v/v.<sup>26</sup> We introduced CN concentrations of 1 vol% into the blend solutions. A high  $V_{\text{OC}}$  of

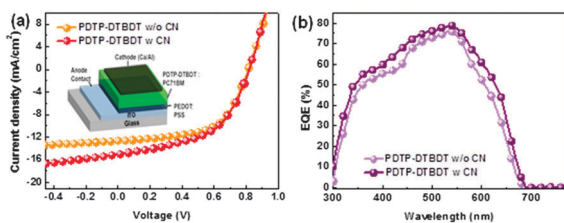


Fig. 2 (a)  $J$ - $V$  characteristics of the BHJ devices, and (b) EQE spectra of the corresponding devices.

0.83 V was obtained, and the PCE increased from 6.05% to 6.81%.  $J_{SC}$  depended strongly on the film morphology, nano-structural order, and charge carrier mobility, as discussed below. The external quantum efficiency (EQE) spectra of these devices are shown in Fig. 2b. The photovoltaic devices exhibited efficient photon conversion properties with a broad response from 300 to 700 nm. The broad coverage of the EQE obtained by the PDTP-DTBDT:PC<sub>71</sub>BM device with a 1 vol% CN significantly increased the  $J_{SC}$  values.<sup>27</sup> The PDTP-DTBDT:PC<sub>71</sub>BM blend prepared without additives exhibited a maximum EQE of 75% at 540 nm, whereas the PDTP-DTBDT:PC<sub>71</sub>BM device prepared with CN yielded a maximum EQE of 80% at 541 nm. These results indicated that the photocurrent in the device treated with the additive was 1.2 times the photocurrent measured in the as-cast PDTP-DTBDT:PC<sub>71</sub>BM device.

The morphology of the polymer:PC<sub>71</sub>BM blend film, which is closely related to the device performance of a BHJ PSC, was investigated using atomic force microscopy (AFM) and two-dimensional grazing-incidence X-ray diffraction (2D-GIXD). As shown in Fig. 3, the as-cast PDTP-DTBDT:PC<sub>71</sub>BM film (a) showed a relatively small root-mean-square (RMS) roughness of 1.24 nm and a homogeneously formless surface morphology. On the other hand, the spin-coated blend films prepared with CN (b) exhibited aggregated domains and a phase-separated surface with a large RMS roughness of 3.18 nm. The aggregated domains and large surface roughness most likely originated from the self-organized polymer structure,<sup>28</sup> which was expected to provide separate pathways for holes and electrons and to

increase  $J_{SC}$ . The 2D-GIXD results shown in Fig. 3c and d support the morphological observations. The PDTP-DTBDT:PC<sub>71</sub>BM film processed without CN displayed two broad reflections in the out-of plane direction of the 2D-GIXD pattern at  $q_z = 0.17 \text{ \AA}^{-1}$  and  $q_z = 0.54 \text{ \AA}^{-1}$ , respectively. The PDTP-DTBDT:PC<sub>71</sub>BM blend film processed with CN displayed a greater degree of self-assembly among the PDTP-DTBDT molecules, and the intensity of this reflection clearly increased. Two strong reflection peaks became apparent along the nominal direction in the CN-treated film. (The out-of-plane and the in-plane GIXD profiles extracted from the 2D profiles in Fig. S6, ESI† are provided in Fig. 3c and d.) These results suggest that the order in the crystallites of PDTP-DTBDT improved, and that the improvements in the PCE of the device processed with the CN additive could be attributed to improvements in the ordering of the donor domains.<sup>29,30</sup>

We next sought insights into the performance improvements of the PDTP-DTBDT:PC<sub>71</sub>BM device prepared with CN, compared with the performances of the devices prepared without CN, by measuring the charge carrier mobilities using the space charge limited current (SCLC) method (Fig. S7, ESI†). First, we measured the hole mobility of pure PDTP-DTBDT to examine the effects of the DTBDT unit. The hole mobility was found to be  $2.05 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . This result was supported by a synthesis strategy in which the DTBDT units incorporated into the polymer chain facilitated charge transport due to their rigid conformational properties. The blend film performance comparison revealed that the hole mobility in the PDTP-DTBDT:PC<sub>71</sub>BM blend film prepared with 1 vol% CN was  $3.73 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , more than three times the value obtained from the as-cast PDTP-DTBDT:PC<sub>71</sub>BM blend film ( $1.02 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}$ ). Significantly higher carrier mobilities were measured in the device treated with an additive, thereby increasing the  $J_{SC}$  value of the device fabricated using a PDTP-DTBDT:PC<sub>71</sub>BM blend prepared with CN.<sup>31,32</sup>

In conclusion, a novel multi-functional conjugated polymer that incorporated DTBDT as the donor unit and DTP as the acceptor unit, PDTP-DTBDT, was developed for use in PSCs. The incorporation of the DTBDT and DTP units into PDTP-DTBDT resulted in a large internal dipole moment and improved the intermolecular stacking structure in the film state. Interestingly, a PCE of 6.81%, with a  $V_{OC}$  of 0.83 V, a high  $J_{SC}$  of  $15.1 \text{ mA cm}^{-2}$ , and a FF of 54.3%, was achieved using a simple conventional device. Our results indicated that this novel multi-functional PDTP-DTBDT polymer is useful for preparing high-performance PSCs.

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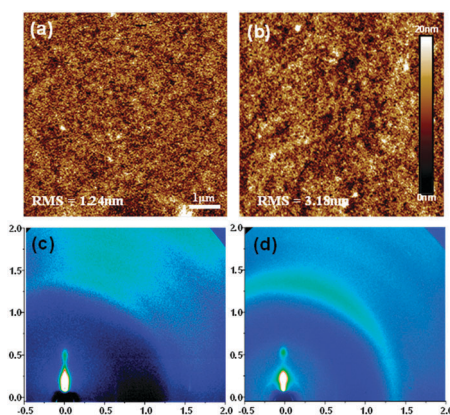


Fig. 3 AFM height images (a and b) and XRD patterns (c and d) obtained from films prepared without or with DIO.

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