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## PBDTTTZ: A Broad Band Gap Conjugated Polymer with High Photovoltaic Performance in Polymer Solar Cells

Lijun Huo,<sup>†</sup> Xia Guo,<sup>‡</sup> Shaoqing Zhang,<sup>†</sup> Yongfang Li,<sup>\*,‡</sup> and Jianhui Hou<sup>\*,†</sup><sup>†</sup>State Key Laboratory of Polymer Physics and Chemistry, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China<sup>‡</sup>CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

## Supporting Information

In recent years, great success has been made in the field of polymer solar cells (PSCs). Great effort has been employed to improve the power conversion efficiency (PCE) of PSCs, and over 7% PCE values have been reported by several research groups.<sup>1–5</sup> The design of new active layer materials with appropriate properties is one of the main approaches toward high performance PSCs. Optical band gap is one of the key parameters of active layer material for PSCs. In order to harvest more sunlight, the mismatch between absorption spectrum of the active materials and solar spectrum should be minimized, and therefore, many small band gap ( $1.5 \text{ eV} < E_g < 1.8 \text{ eV}$ ) conjugated polymers were designed and used in PSCs.<sup>6–14</sup> Besides of the band gap, electronic energy level is another key parameter for photovoltaic (PV) polymer materials. It has been clearly proved that open circuit voltage ( $V_{oc}$ ) of the PSCs with bulk heterojunction structure is directly proportional to the offset between the HOMO level of the electron donor material and the LUMO level of the electron acceptor material.<sup>15</sup> For example,  $V_{oc}$  of the PSCs based on PBDTTTz can be tuned gradually by lowering the HOMO level of the polymer donor.<sup>1,27</sup>

Although small band gap materials attract much attention due to their great success in PSCs, less effort was employed for exploring high efficient broad band gap conjugated polymers for the PSCs. Actually, this part of work is also of great importance; for example, in PSCs with tandem structure, which is equivalent to two cells in series, one cell is made by broad band gap materials and another one is made by small band gap materials.<sup>16</sup> The  $V_{oc}$  of tandem cells is equal to the sum of the two cells, but the current is limited by the lower one, and also the overlap between the absorption spectra of the two cells is still a big obstacle to realizing higher PCE of tandem cells. Since great success has been made for small band gap polymer PV materials, in order to achieve higher PCE for tandem cells, there will be a great need for high efficient broad band gap polymer materials in the near future. Moreover, semitransparent PSCs, which are attractive for the application as solar cell windows, need high PV performance broad band gap polymers. Furthermore, the broad band gap polymers have better durability/stability than small band gap polymers.

In this work, we designed and synthesized a new broad band gap conjugated polymer PBDTTTZ (see Scheme 1) with  $E_g$  of 2.0 eV. PBDTTTZ is a D–A copolymer containing 2-alkylthiophene-substituted benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) donor unit and a thiazolo[5,4-*d*]thiazole (TTZ) acceptor unit.

As reported, the TTz-based conjugated polymers exhibited excellent hole mobility in field effect transistors (FETs) with excellent stability.<sup>18–20</sup> Recently, the TTZ-based copolymers were also been applied in PSCs.<sup>21–23</sup> In the other hand, a D–A copolymer containing the planner 2-alkylthiophene-substituted BDT unit showed high photovoltaic performance,<sup>24</sup> which could be benefitted from the two-dimensional conjugated structure of the polymer.<sup>25</sup>

PBDTTTZ was synthesized by copolymerization of the 2-alkylthiophene-substituted BDT and 2,5-bis(thiophen-2-yl)thiazolo[5,4-*d*]thiazole, as shown in Scheme 1. The alkylthiophene-substituted BDT monomer can be easily synthesized through the reported method.<sup>25</sup> A typical Stille coupling reaction was employed to synthesize the polymer. Although a branched alkyl chain, 2-hexyldecyl, was used to improve solubility, only a small part of polymer can be dissolved into chloroform or dichlorobenzene. The soluble part from Soxhlet extraction was collected for PSC device application, and the molecular weight of this part polymer is only 9K ( $M_n$ ); this part of polymer exhibits good thermal stability below 300 °C in the ambient atmosphere.

The absorption spectra of PBDTTTZ in solution and solid film are shown in Figure 1. In solid state, the polymer exhibits an absorption peak at  $\sim 538 \text{ nm}$  with a shoulder at  $\sim 582 \text{ nm}$ , the absorption at long wavelength direction drops sharply, and the absorption edge is at  $\sim 620 \text{ nm}$ , corresponding to a band gap ( $E_g$ ) of 2.0 eV. Electrochemical cyclic voltammetry (CV) was used to determine the HOMO and the LUMO energy levels of the polymer. The HOMO and LUMO levels of PBDTTTZ are calculated to be  $-5.3$  and  $-3.2 \text{ eV}$ , respectively. On the basis of its HOMO level value, it can be predicted that  $V_{oc}$  of PBDTTTZ-based PSC device should be around 0.7–0.9 V.<sup>15,17</sup>

The hole mobility of the blend was measured by the space-charge-limited current (SCLC) method with a device structure of ITO/PEDOT:PSS/polymer:PC<sub>70</sub>BM/Au. A hole mobility of  $\text{ca. } 1.67 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was obtained for the blend of the polymer and PCBM. The PSC devices with a structure of ITO/PEDOT:PSS/PBDTTTZ:PC<sub>70</sub>BM/Ca/Al were fabricated to investigate PV properties of this material. Two organic solvents, chlorobenzene and dichlorobenzene, were used to make the solution of active layer for spin-coating, and dichlorobenzene

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Scheme 1. Synthesis and Molecular Structure of PBDTTTZ

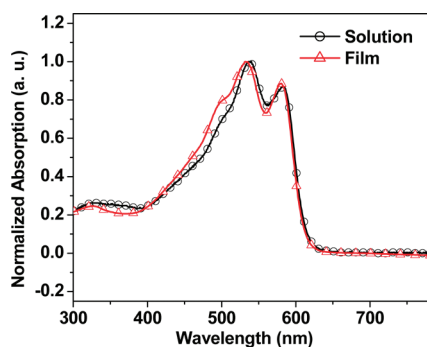
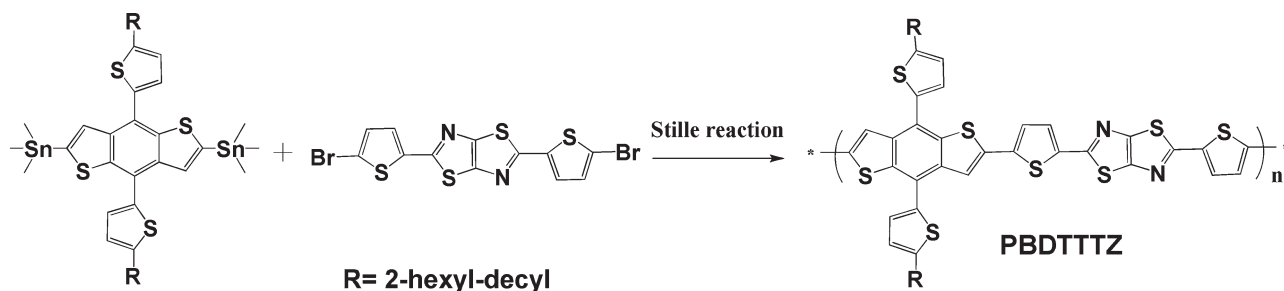


Figure 1. Absorption spectra of PBDTTTZ in chloroform solution and in solid film on quartz.

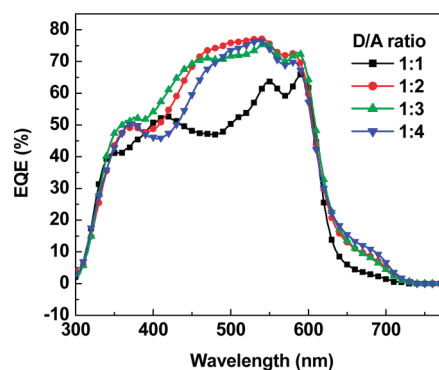
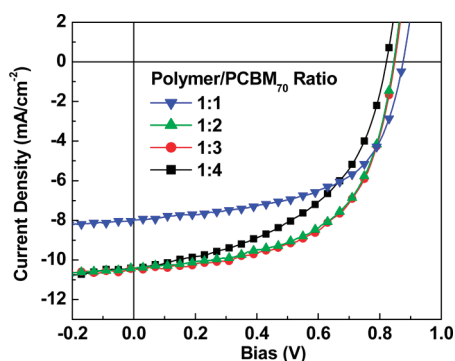


Figure 3. External quantum efficiency (EQE) curves of PBDTTTZ-based PSCs with different D/A ratios.

Figure 2.  $J$ - $V$  curves of the PSCs based on PBDTTTZ/PC<sub>70</sub>BM with different donor/acceptor ratios (1:1, 1:2, 1:3, and 1:4) under illumination of AM1.5G, 100 mW/cm<sup>2</sup>.Table 1. Photovoltaic Results of the PSCs Based on PBDTTTZ/PC<sub>70</sub>BM under the Illumination of AM1.5G 100 mW/cm<sup>2</sup>

D/A ratio	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	PCE (%)
1:1	0.88	8.1	0.51	3.64
1:2	0.85	10.3	0.59	5.17
1:3	0.85	10.4	0.59	5.22
1:4	0.82	10.3	0.51	4.31

gives better PV results. In order to further optimize PV performance, 3% (v/v) 1,8-diiodooctane (DIO) was used as additive<sup>26</sup> in the solution of active layer materials. The PCEs of the devices fabricated from the solution without DIO are slightly lower than

the device with DIO. The AFM images of the active layers spin-coated from the solutions with or without DIO are provided in the Supporting Information. It can be seen that when DIO was used as additive, smoother film with less phase separation can be obtained. Different donor/acceptor (D/A) ratios, 1:1, 1:2, 1:3, and 1:4, were also investigated to find the optimization process of device fabrication. The  $J$ - $V$  curves of the PBDTTTZ-based PSC devices with different D/A ratios under illumination of AM1.5G (100 mW/cm<sup>2</sup>) are shown in Figure 2. As listed in Table 1, the  $V_{oc}$  of PBDTTTZ/PC<sub>70</sub>BM based devices is between 0.82 and 0.88 V, and higher PC<sub>70</sub>BM content reduces the  $V_{oc}$  slightly. Interestingly, ~5.2% PCEs were recorded from the devices with D/A ratio of 1:2 and 1:3, and the  $V_{oc}$  of these devices is 0.85 V. For the champion devices, the short-circuit current density ( $J_{sc}$ ) values are around ~10.3 mA/cm<sup>2</sup> and the fill factors (FF) are ~0.59. In comparison with other BDT- and TTZ-containing polymers, the PV performance of this PBDTTTZ-based device is much better,<sup>21,22</sup> which indicates that the introduction of the thiophene conjugated side-chain on BDT unit in PBDTTTZ is much helpful for improving the photovoltaic performance of the polymers.

The external quantum efficiency (EQE) curves of the device with different D/A ratios were measured and are shown in Figure 3. The PSC devices exhibited excellent response in their absorption range. The highest EQE value of the devices reached ~80% at ca. 550 nm. As known, more than 15% sunlight can be wasted due to the reflection (5%) and absorption (>10%) of glass/ITO substrate and also the absorbance by the PEDOT:PSS layer. It means that 80% EQE has already closed to the upper limit value of a PSC device. The internal quantum efficiency (IQE) was also calculated, and we found the IQE of the champion cell reached ~100% at the range from 500 to

600 nm. Additionally, we found that  $J_{sc}$  of the devices can be improved by increasing thickness of the active layer and a  $J_{sc}$  of 11.7 mA/cm<sup>2</sup> was recorded, but the PCE of such a device dropped to <5% due to the decreasing of FF. On the basis of the standard spectrum of the solar irradiation (AM 1.5G), it can be calculated that the theoretical maximum value of the current density of the PSC device with a response range from 300 to 620 nm should be ~14.6 mA/cm<sup>2</sup>. Considering the absorbance and the reflection of the glass/ITO substrate and the absorbance by the PEDOT:PSS layer as mentioned above, the  $J_{sc}$  value of 11.7 mA/cm<sup>2</sup> is a remarkable result for such a broad band gap material as PBDTTTZ. At present, although the  $J_{sc}$  already reached 14–17 mA/cm<sup>2</sup> for the PSC devices based on small band gap polymers ( $E_g < 1.8$  eV),<sup>1,5,8</sup> it is still hard to get a  $J_{sc}$  over 10 mA/cm<sup>2</sup> from broad band gap materials ( $E_g > 2$  eV). As known, the peak value of solar photon flux (AM 1.5G) is at ~680–700 nm, and hence, high EQE is necessary to get high output current density for the PSCs based on broad band gap materials. Since only a very few small band gap polymers can provide >70% EQE, the PBDTTTZ-based PSC device demonstrates a good example for polymer PV materials with high EQE.

In conclusion, the new polymer with  $E_g = 2.0$  eV, PBDTTTZ, was designed and synthesized for the application in PSCs. The fabrication process of the PBDTTTZ-based PSC devices was optimized. The best performance was obtained when dichlorobenzene was used as solvent for active layer solution with 3% DIO as additive. Although the response range of the PBDTTTZ-based PSCs is narrower than that of small band gap polymers, a PCE of ~5.2% was recorded due to the high EQE of the devices. In comparison with the classic photovoltaic material, poly(3-hexylthiophene) (P3HT), PBDTTTZ has broader band gap and deeper HOMO level. The PBDTTTZ-based solar cell exhibited higher  $V_{oc}$  and similar  $J_{sc}$  compared to the reported results of P3HT-based devices.<sup>28</sup> Since the absorption of the PSC devices is mainly at the range from 350 to 620 nm, which is ~20 nm narrower than that of P3HT-based solar cells, PBDTTTZ is not only a good polymer donor material for semitransparent single cells but also a promising material as broad band gap polymer/blue absorber in PSCs with tandem structure.

## ■ ASSOCIATED CONTENT

**Supporting Information.** Synthesis procedure, thermogravimetry analysis (TGA) and electrochemical cyclic voltammetry (CV), atomic force microscope (AFM) of the polymer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [hjhzl@iccas.ac.cn](mailto:hjhzl@iccas.ac.cn) (J.H.), [liyf@iccas.ac.cn](mailto:liyf@iccas.ac.cn) (Y.L.).

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