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Development of a new benzo(1,2-*b*:4,5-*b'*)dithiophene-based copolymer with conjugated dithienylbenzothiadiazole–vinylene side chains for efficient solar cells†Zhaojie Gu,^a Ping Shen,^{*a} Sai-Wing Tsang,^b Ye Tao,^b Bin Zhao,^a Peng Tang,^a Yujuan Nie,^a Yan Fang^a and Songting Tan^{*a}

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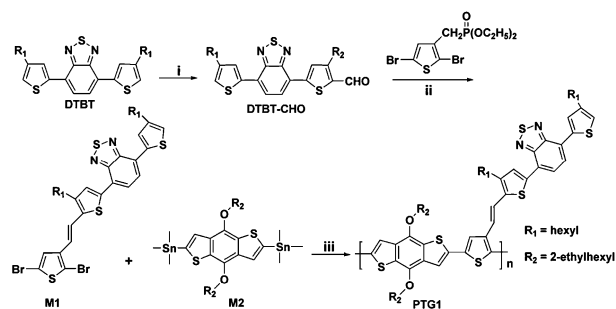
A new benzodithiophene-based copolymer PTG1 with dithienylbenzothiadiazole–vinylene side chains exhibits excellent film-forming ability, a deep HOMO energy level, and a good miscibility with PC₇₁BM. Bulk heterojunction polymer solar cells fabricated from PTG1 and PC₇₁BM showed a promising power conversion efficiency over 4.0%.

Polymer solar cells (PSCs) based on the bulk heterojunction (BHJ) structure that consists of a polymeric donor and a fullerene-based acceptor have attracted considerable attention because of their fascinating potential for low-cost, large-area production through solution processing.¹ In recent years, extensive research efforts have focused on improving the polymeric electron donor component of the BHJ while retaining fullerene derivatives as the electron acceptor. Key developments have involved narrowing the polymer bandgap, in order to better match the optical absorption with the solar spectrum, and optimizing the energy level offsets with fullerene to achieve maximum open-circuit voltage (V_{oc}).² Very recently, many of the low band gap polymers with deep highest occupied molecular orbital (HOMO) energy levels were developed for achieving high V_{oc} in PSCs. For example, a polymer containing benzo(1,2-*b*:4,5-*b'*)dithiophene (BDT) unit with a deep HOMO level (−5.31 eV) exhibited a high V_{oc} of 0.92 V and a power conversion efficiency (PCE) of 5.66% using [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as the electron acceptor.^{2c} At the same time, it has become increasingly apparent that a balance among the competing effects of solution processability, miscibility with the fullerene component, and solid-state packing needs to be established.³

One of the most efficient methods to lower the bandgap of polymers is to develop alternating donor–acceptor copolymers

by combining electron-rich (donor) and electron-deficient (acceptor) units in their repeating units to form internal donor–acceptor (D–A) structures. Among these main chain D–A copolymers, it has been demonstrated that 4,7-dithien-5-yl-2,1,3-benzodithiazole (DTBT) and benzo(1,2-*b*:4,5-*b'*)dithiophene (BDT) are the most effective electron-deficient and electron-rich units, respectively.⁴ Many of the main chain D–A copolymers have shown great success for achieving high performance PSCs. However, some polymers based on BDT and DTBT exhibit only moderate efficiency (<2%)^{4b,d} because of their relatively narrow absorption spectra, low hole mobility, and inappropriate frontier molecular orbital energy levels.

A new family of polymers with conjugated side chains has been developed by several research groups, including ours.⁵ This type of polymers features high hole mobility benefiting from the overlapping of the conjugated side chains and their interactions with the conjugated backbones, and broad absorptions deriving from both the main chains and the conjugated side chains, thus demonstrated prominent device performances in PSCs.^{5c–e} Here, we are trying to introduce DTBT as the conjugated side chains to design a novel copolymer **PTG1** (as shown Scheme 1) based on BDT and thiophene. Different from well-developed main chain D–A low band gap copolymers, this new copolymer possesses two distinctive characteristics on molecular design: (1) 4,7-dithien-5-yl-2,1,3-benzodithiazole (DTBT) moiety as an electron-deficient unit is for the first time to be introduced as side chains instead of a main chain to construct a polymer; (2) attaching the



Scheme 1 Synthesis of **PTG1**. Reagents and conditions: (i) POCl₃/DMF, CH₂ClCH₂Cl, reflux, 12 h; (ii) *t*-BuOK, THF, ambient temp., 12 h; (iii) Pd(PPh₃)₄, toluene, reflux, 48 h.

^a College of Chemistry and Key Laboratory of Advanced Functional Polymeric Materials, College of Hunan Province, Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, Xiangtan University, Xiangtan 411105, P. R. China. E-mail: shenping802002@163.com, tanst2008@163.com; Fax: +86(0)731 58292251; Tel: +86(0)731 58292207

^b Institute for Microstructural Sciences, National Research Council of Canada, 1200 Montreal Road, Ottawa, Ontario, Canada K1A 0R6

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DTBT moiety to the main chain of the polymer *via* vinylene groups is another strategy to effectively tune the electronic and optical properties. The vinylene linkage serves to enhance the co-planarity of the polymer backbone and extend the π -conjugation by further eliminating torsional strains between the main chain and the electron-deficient side chain, leading to a lower optical band gap and tunable frontier molecular orbital energy levels. Our first results demonstrate that the introduction of DTBT as conjugated side chains could become an alternative and effective strategy to tune the photoelectronic properties of a polymer and achieve efficient solar cells.

The synthesis of the DTBT moiety containing monomer **M1** and the polymer is shown in Scheme 1 and the procedure is described in detail in the ESI.† **DTBT-CHO** was synthesized by formylation of the DTBT with Vilsmeier reaction, then it reacted with 2,5-dibromo-3-bromomethylthiophene to form the monomer **M1**. The polymer **PTG1** was obtained by Stille coupling reaction of **M1** with the bis(trimethylstannane) derivative of BDT (**M2**)^{4c} using Pd(PPh₃)₄ as the catalyst. **PTG1** has excellent film-forming property and solubility in common organic solvents such as chloroform, chlorobenzene and tetrahydrofuran, providing convenience for characterization and device processing. Gel permeation chromatography (GPC) shows a weight-averaged molecular weight (M_w) of 51.8 kg mol⁻¹ and a polydispersity index (PDI) of 2.56. The polymer is thermally stable up to ~360 °C (Fig. S4, ESI†) and shows a glass transition at ~155 °C (Fig. S5, ESI†).

The UV-vis absorption spectra of the copolymer in chloroform solution and the solid film are shown in Fig. 1. In solution, the polymer shows two obvious absorption peaks, where the first absorption peak at ~340 nm corresponds to the π - π^* transition of the polymer backbone and the peak at the longer wavelength (~454 nm) is attributed to the weak intramolecular charge transfer (ICT) interaction between the main chain and the conjugated DTBT side chain. The absorption spectrum of the polymer film is slightly red-shifted as compared with the corresponding spectrum in dilute solution, indicating the presence of intermolecular interactions in the solid state. This slight red-shift indicates that the interaction is not as strong as those of linear D-A type polymers, probably due to the bulky side chains that retard the efficient packing of the polymer

chains in the solid state. The optical band gap (E_g^{opt}) of **PTG1** calculated from the onset of the film absorption is 2.03 eV.

Cyclic voltammetry (CV) of the polymer thin film coated on a platinum electrode indicates that the onset oxidation and reduction potentials (vs. SCE) are about 1.16 and -0.77 V, respectively (Fig. S6, ESI†). The corresponding HOMO and LUMO energy levels of **PTG1** are calculated to be -5.56 and -3.63 eV, respectively.⁶ It should be noted that the HOMO energy level is not only lower than that of its analogue (-5.05 eV for **H6**^{4b}) of BDT-thiophene without the conjugated DTBT side chain but also lower than that of the main chain D-A copolymer (-4.80 eV for **Z3**^{4e}) based on BDT and DTBT. The relatively low HOMO energy level of the polymers will lead to a good air stability and a high V_{oc} for the photovoltaic cells,^{4c,d} indicating that **PTG1** should achieve higher V_{oc} value than those of **H6** and **Z3**. Moreover, field effect transistor (FET) mobility measurement on the pristine polymer confirms a relatively high hole mobility of $2.2 (\pm 0.2) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Fig. S7, ESI†).

The photovoltaic properties of **PTG1** were studied in PSCs using PC₇₁BM as the acceptor in a conventional device configuration of ITO/PEDOT-PSS/**PTG1**:PC₇₁BM (1/1, w/w)/BCP/LiF/Al. PC₇₁BM was chosen as the acceptor because it has electronic properties similar to those of PC₆₁BM but a much stronger absorption in the visible region with a broad peak from 440 to 530 nm.⁷ Other details concerning device fabrication and characterization are provided in the ESI.† The polymer has excellent solubility in chlorobenzene (CB) and it forms very nice network with PC₇₁BM in thin film. Therefore the active layers were spin-cast from CB to allow for extensive characterization.

The current density-voltage (J - V) curves of the solar cells (Fig. 2) were recorded under air mass 1.5 global (AM 1.5 G) irradiation of 100 mW cm⁻², and PCEs were calculated for different preparation conditions. The solar cell parameters of four devices A-D are shown in Table S1 (ESI†). Fig. 2 presents the clear impact of the active layer thickness and additive 1,8-diiodooctane (DIO) on the performance of devices. In optimized devices, the PCEs increase from 3.00% (device A) and 3.45% (device C) with an active layer thickness of 90 nm to 3.07% (device B) and 4.32% (device D) with an active layer thickness of 80 nm, respectively. On the other

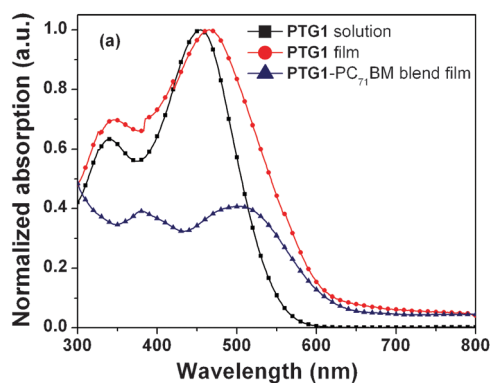


Fig. 1 UV-vis absorption spectra of **PTG1** in dilute chloroform solution and a film of a pure polymer or polymer/PC₇₁BM (1/1, w/w, 120 nm) blend on a glass substrate.

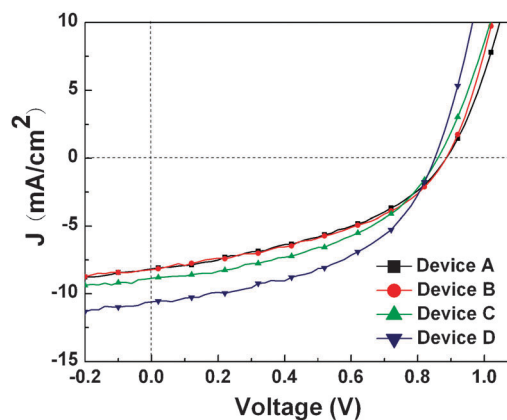


Fig. 2 J - V curves for **PTG1**-based four solar cell devices A-D under an illumination of AM 1.5 G, 100 mW cm⁻².

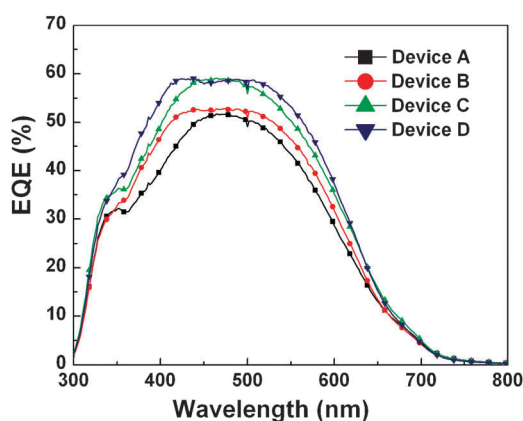


Fig. 3 EQE of the PTG1-based four solar cell devices A–D.

hand, device C (or D) with 3.0% DIO as an additive exhibits a relatively better PCE as compared with device B (or A) without an additive. Obviously, the enhanced PCEs benefit from a small amount of the high boiling-point DIO as an additive in devices C and D which has been proved to promote the packing of the polymer by avoiding excessive crystallization of the fullerene,⁸ and thus improved J_{sc} of the devices. However, there is no dramatic difference in device performance with and without the DIO additive like other reports,^{4d,9} which indicates that DIO only has a little influence on the morphology of the blend films. From atomic force microscopy (AFM) images (Fig. S8, ESI†) of the blend films of devices B and D, we can see that the morphology of both the blend films is moderately homogeneous and there is no large phase separation, which indicates good miscibility between PTG1 and PC₇₁BM, and the polymer itself with PC₇₁BM can form a reasonably good bulk heterojunction without using DIO as an additive. Therefore, the additional DIO additive does not give a significant improvement in the overall device performance. We obtained a maximum PCE value of 4.32% in our best device D with a V_{oc} of 0.84 V, a short-circuit current density (J_{sc}) of 10.59 mA cm⁻², and a fill factor (FF) of 0.49. The average V_{oc} (~0.86) of these devices (A–D) is higher than those of previously reported polymers H6 (0.75 V)^{4b} and Z3 (0.84 V)^{4c} attributed to the much lower HOMO energy level. Total absorption (1-reflectance) spectra and the external quantum efficiency (EQE) curves of the four devices are shown in Fig. S9 (ESI†) and Fig. 3, respectively. As shown in Fig. 3, those devices exhibit broad response covering 300–700 nm, and the EQE exceed 40% in the spectral region from 400 to 600 nm. The J_{sc} values calculated by integrating the EQE curves with the AM 1.5 G spectrum are lower than those obtained from the J - V curves, due to the spectral mismatch of the solar simulator. Therefore, the EQE-calibrated short-circuit current density (J_{EQE}) and power conversion efficiency (PCE_{EQE}) values are also reported in Table S1 (ESI†).

In conclusion, a novel BDT–thiophene copolymer PTG1 with conjugated DTBT side chains has been designed and synthesized for photovoltaic application. The polymer features excellent film-forming property, a relatively deep HOMO energy level, and a good miscibility with PC₇₁BM. Preliminary tests on PTG1/PC₇₁BM photovoltaic devices demonstrate the best PCE over 4.0%. Our results show that using DTBT as conjugated side chains instead of a main chain could become

an alternative and effective strategy to tune the optoelectronic properties of conjugated polymers and achieve high performance solar cells. Further structural functionalization and device optimization based on PTG1 to improve the photovoltaic performance are just ongoing.

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