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Crystalline conjugated polymer containing fused 2,5-di(thiophen-2-yl)thieno[2,3-b]thiophene and thieno[3,4-c]pyrrole-4,6-dione units for bulk heterojunction solar cells†

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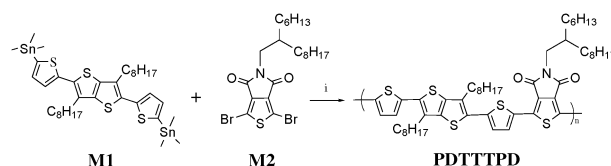
A new conjugated polymer, PDTTTPD, comprising 2,5-di-(thiophen-2-yl)thieno[3,2-b]thiophene and thieno[3,4-c]pyrrole-4,6-dione units, exhibits high crystallinity and excellent thermal stability. A device incorporating PDTTTPD and [6,6]-phenyl-C_{71}-butyric acid methyl ester (1:1, w/w) exhibited a power conversion efficiency of 5.1%.

Bulk heterojunction (BHJ) solar cells incorporating conjugated polymers possessing extended delocalized π electrons are being investigated intensively because they allow the fabrication of light-weight, large-area, flexible devices using low-cost solution processing methods.[1] In recent years, conjugated polymers containing alternating donor (D) and acceptor (A) units in their main[2] or side[3] chains have been applied widely in BHJ solar cells because of their readily tunable electronic properties (*e.g.*, band gaps, molecular energy levels). For solar cell applications, the use of D/A conjugated polymers incorporating tunable electron-donating and -withdrawing units has several advantages: a low-energy highest occupied molecular orbital (HOMO) that enhances the open-circuit voltage (V_{oc}) of BHJ devices, a low band gap, and crystalline characteristics resulting from the presence of coplanar units in the polymeric back-bone. To date, only a few synthesized D/A conjugated polymers have displayed the appropriate crystalline characteristics that are critical for not only good charge mobility but also future device durability—because crystalline polymers have higher density than amorphous polymers, they provide superior resistance toward water and oxygen permeation. It is critical to choose suitable D and A units when designing polymers expected to exhibit crystalline characteristics. The electron-rich and planar 2,5-di(thiophen-2-yl)thieno[3,2-b]thiophene (**DTT**) unit can be polymerized to produce homopolymers exhibiting the ordered packing and π–π stacking required for high charge mobility when applied in organic field effect transistors.[4] D/A conjugated polymers incorporating **DTT** moieties as the D units have also been used in BHJ solar cell applications, providing power conversion efficiencies (PCEs) of up to 2.7%.[5] For choosing an acceptor unit that would lower the HOMO level of a D/A polymer and also generate crystallinity in the polymer, one has to select strong electron-withdrawing and planar units. Thieno[3,4-c]pyrrole-4,6-dione (**TPD**) has a planar and rigid structure and is strongly electron-withdrawing; therefore, it increases the degree of intramolecular charge transfer (ICT) between the D and A units and lowers the HOMO energy levels of the polymer, resulting in enhanced values of V_{oc}, which, in turn, lead to high PCEs (up to 6%) for BHJ solar cells.[6]

In this study, we prepared a new crystalline conjugated polymer, **PDTTTPD**, featuring alternating rigid, coplanar, electron-rich **DTT** units and rigid, electron-deficient **TPD** units as D and A units, respectively. We anticipated that incorporating **DTT** and **TPD** units into the polymer backbone would provide crystalline polymer chains and relatively low-lying HOMO energy levels.

Scheme 1 displays the structures of the monomeric **DTT** and **TPD** derivatives, 2,5-bis[5-(trimethylstannyl)thiophen-2-yl]-3,6-dioctylthieno[3,2-b]thiophene (**M1**) and 1,3-dibromo-5-(2-hexyldecyl)-5H-thieno[3,4-c]pyrrole-4,6-dione (**M2**), respectively, that we used to synthesize **PDTTTPD** through Stille coupling (detailed descriptions of the syntheses of the monomers are provided in the ESI†). The number-average molecular weight (M_n) of the synthesized **PDTTTPD** was 9.2 kg mol^{-1}, with a polydispersity of 1.20, as measured using gel permeation chromatography (GPC). **PDTTTPD** featured a 5%-weight-loss temperature (T_d) of 454 °C, as determined through thermogravimetric analysis (TGA; Fig. S1, ESI†). In addition,

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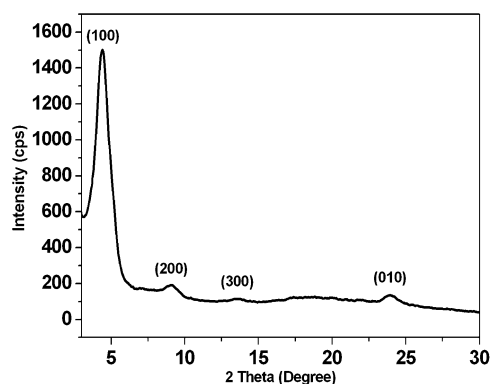

Scheme 1 Synthesis of **PDTTTPD**. Reagents and conditions: (i) Pd$_2$dba$_3$, Ph$_3$P, 135 °C, 24 h.

Fig. 1 X-ray diffraction pattern of the pristine **PDTTTPD** film.

PDTTTPD exhibited a melting point (T_m) of 351 °C and a crystallization point (T_c) of 331 °C, but no glass transition, as determined using differential scanning calorimetry (DSC; Fig. S2, ESI†). Fig. 1 reveals that a **PDTTTPD** film provided (100), (200), and (300) diffraction peaks at 4.4, 8.8, and 13.2°, respectively, indicating its highly ordered structure. More specifically, we assign the *d*-spacing of 20.1 Å at the (100) plane to the interchain spacing separated by the alkyl side chains; a broad peak at 23.9° in the (010) plane reveals a close π–π stacking distance of 3.7 Å between the **PDTTTPD** backbones. Fig. 2 displays the absorption spectra of **PDTTTPD** in dilute $CHCl_3$ solution and as a solid film. In solution, we assign the absorption maximum at 500 nm to ICT interactions between the **DTT** and **TPD** moieties; the absorption maximum of the **PDTTTPD** thin film on quartz was red-shifted by *ca.* 23 nm relative to that in solution as a result of intermolecular interactions and aggregation in the solid state. Furthermore, a vibronic shoulder appeared at 620 nm, attributable to strong π–π stacking between the polymer backbones; the presence of this peak is consistent with the X-ray diffraction peak of **PDTTTPD** at the (010) plane. The optical bandgap (E_g^{opt}) of **PDTTTPD**, calculated from the absorption edges of the UV–vis spectrum of the thin solid film, was 1.84 eV.

We used electrochemical cyclic voltammetry (CV) to determine HOMO and lowest unoccupied molecular orbital (LUMO) energy levels of **PDTTTPD** (Fig. S3, ESI†), calculated from the oxidation and reduction onsets, of −5.54 and −3.00 eV, respectively, relative to ferrocene (4.80 eV below the vacuum) as the reference. The 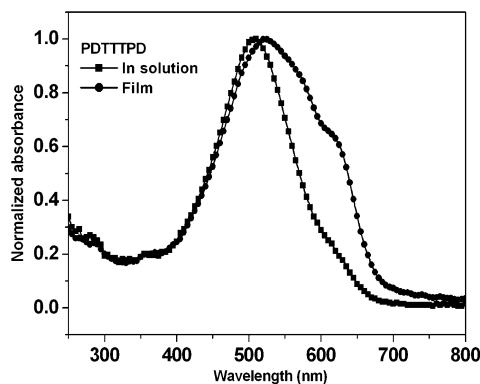low HOMO energy level of **PDTTTPD**, relative to those of other polymers containing **DTT** units,[5] was presumably caused by the presence of the strongly electron-withdrawing **TPD** moieties; in addition, its low HOMO energy level suggested that **PDTTTPD** would be stable against oxidation in air. The electrochemical bandgap, estimated from the difference between the HOMO and LUMO energy levels, was 2.54 eV—significantly larger than its optical bandgap (1.84 eV). The discrepancy might have been caused by the presence of an energy barrier at the interface between the polymer film and the electrode surface;[7] similar phenomena have been reported for other polymer systems.[8] The hole mobility, measured using the space-charge-limited current (SCLC) method (Fig. S4 and Table S1, ESI†), of the pristine **PDTTTPD** film was 2.2×10^{-4} cm^2 V^{-1} s^{-1}; those of **PDTTTPD**/PCBM blended films prepared at weight ratios of 1 : 0.8, 1 : 1, and 1 : 1.2 were 1.7×10^{-4}, 1.5×10^{-4}, and 1.3×10^{-4} cm^2 V^{-1} s^{-1}, respectively. The hole mobility decreased dramatically to 7.1×10^{-5} cm^2 V^{-1} s^{-1} upon increasing the weight ratio to 1 : 2. The hole mobility of **PDTTTPD**/ [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) at a blend ratio of 1 : 1 was 1.5×10^{-4} cm^2 V^{-1} s^{-1}.

We fabricated BHJ solar cell devices having the structure indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) : polystyrenesulfonate (PEDOT : PSS)/**PDTTTPD** : PCBM/Al to investigate the photovoltaic properties of **PDTTTPD**. Fig. 3 displays the current density–voltage curves of the BHJ solar cells fabricated with various blend weight ratios; Table 1 summarizes the corresponding data. The devices fabricated from **PDTTTPD** and PCBM blends exhibited values of V_{oc} of 0.84–0.86 V, which were related to the energy difference between the HOMO energy level of the polymer and the LUMO energy level of PCBM.[9] The optimal **PDTTTPD**/ PCBM device, prepared at a blend weight ratio of 1 : 1, exhibited a value of V_{oc} of 0.85 V, a value of J_{sc} of 7.85 mA cm^{-2}, a fill factor (FF) of 0.69, and a resulting PCE of 4.6%. Increasing the loading weight ratio of PCBM to 1 : 2, the value of J_{sc} decreased to 5.96 mA cm^{-2}, presumably because of deceased hole mobility and increased phase segregation. Fig. S5 displays height and phase images of **PDTTTPD**/ PCBM blend films probed using atomic force microscopy.† The surface of the 1 : 1 (w/w) **PDTTTPD**/PCBM blend was more homogeneous than that of the 1 : 2 (w/w) **PDTTTPD**/PCBM.

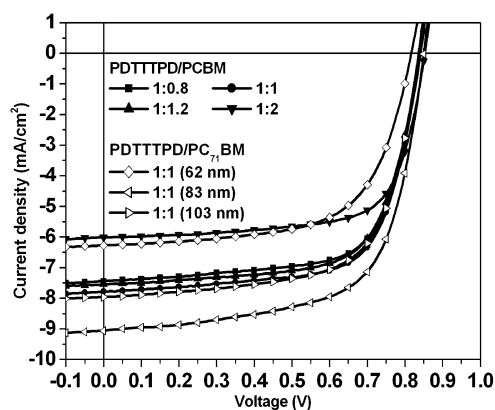**Fig. 2** UV–vis absorption spectra of **PDTTTPD** in $CHCl_3$ (1×10^{-5} M) and as a solid film.

Fig. 3 Current density–voltage (*J*–*V*) curves of polymer solar cells incorporating **PDTTTPD**/PCBM and **PDTTTPD**/PC_{71}BM blends.

Table 1 Photovoltaic Properties of BHJ Solar Cells[a]

PDTTTPD/PCBM (w/w)	Thickness (nm)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
1 : 0.8	123	0.85	7.32	0.70	4.3
1 : 1	119	0.85	7.85	0.69	4.6
1 : 1.2	116	0.84	7.58	0.69	4.4
1 : 2	102	0.86	5.96	0.71	3.6
PDTTTPD/PC$_{71}$BM (w/w)[b]	**Thickness (nm)**	**V_{oc} (V)**	**J_{sc} (mA cm^{-2})**	**FF**	**PCE (%)**
1 : 1	62	0.82	6.24	0.64	3.3
1 : 1	83	0.85	8.99	0.67	5.1
1 : 1	103	0.84	7.93	0.67	4.5

[a] Polymer solar cell device having the structure ITO/PEDOT : PSS/active layer/Al. [b] DIO (1 vol%) was added as an additive.

We also fabricated devices incorporating 1,8-diiodooctane (DIO, 1 vol%) as an additive for **PDTTTPD**/PC$_{71}$BM active layers of various thicknesses. The optimal device, based on **PDTTTPD**/PC$_{71}$BM (1 : 1, w/w) at an active layer thickness of 83 nm, exhibited a value of J_{sc} of 8.99 mA cm^{-2}, a value of V_{oc} of 0.85 V, a FF of 0.67, and a PCE of 5.1%. Fig. S6 displays external quantum efficiency (EQE) spectra of the **PDTTTPD**/PCBM and **PDTTTPD**/PC$_{71}$BM devices prepared at various blend weight ratios; all of these devices exhibited a broad response from 300 to 700 nm.† The EQE curve of the optimal device based on **PDTTTPD**/PC$_{71}$BM (1 : 1, w/w) exhibited a maximum intensity of 54% at 520 nm. The theoretical value of J_{sc} of this device, calculated through integration of its EQE spectrum, was 8.54 mA cm^{-2}, in reasonable agreement with the measured value of 8.99 mA cm^{-2}. The **PDTTTPD**/PC$_{71}$BM film incorporating DIO (1 vol%) as an additive has displayed higher light absorption than the **PDTTTPD**/PCBM film in the range from 380 to 580 nm due to the better light absorption by PC$_{71}$BM than by PCBM[1c] (see Fig. S8, ESI†), resulting in enhanced photocurrent and better device performance.

In conclusion, we have used Stille coupling to prepare a new crystalline conjugated polymer, **PDTTTPD**, featuring alternating **DTT** and **TPD** units in its backbone. This polymer possessed good thermal stability and intense crystallinity, as evidenced by strong X-ray diffraction patterns and π–π stacking between the polymer backbones. **PDTTTPD** also exhibited a low-lying HOMO energy level, due to the presence of strongly electron-withdrawing **TPD** units. A device incorporating **PDTTTPD** and PC$_{71}$BM (blend weight ratio, 1 : 1), with DIO as an additive, exhibited a high value of V_{oc} of 0.85 V and a PCE of 5.1%.

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