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A simple small molecule as the acceptor for fullerene-free organic solar cells

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A simple small molecule named DICTiF was designed, synthesized and used as the acceptor for solution processed bulk-heterojunction solar cells with polymer PBDB-T as the donor. A power conversion efficiency of 7.11% was obtained.

non-fullerene acceptor, A-D-A type, small acceptor molecule, fullerene-free, alkyl chain changing

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1 Introduction

Solution-processed organic photovoltaics (OPVs) have attracted great attention for their potential to be flexible, lightweight and effective device for power generation [1–3]. Over the past decade, due to the development of electron-donor materials, power conversion efficiencies (PCEs) of over 10% have been achieved for organic photovoltaics with bulk heterojunction (BHJ) architectures [4–13]. However, the progress for electron-acceptor materials is relatively lagging behind. To date, most commonly employed electron-acceptor materials are fullerene derivatives, such as $PC_{61}BM$ and $PC_{71}BM$. Even though fullerene based acceptor materials have advantages including deep-lying lowest unoccupied molecular orbital (LUMO, –3.8– –4.2 eV), ultra-fast three-dimensional charge transfer and high electron mobility, these acceptor materials suffer from some disadvantages including less tunable energy level, weak absorption in the visible region and high cost of production [14,15]. Therefore, it is highly desirable to develop non-fullerene acceptor materials. Indeed, recently, much attention has been focused on non-fullerene acceptor materials and exciting breakthroughs with PCEs over 10% have been achieved [16,17]. Generally, several important parameters should be considered to obtain high-efficiency non-fullerene acceptor materials [18–25], such as suitable energy level, good electron transport property, strong absorption ability in the visible and near infrared (NIR) regions, easy accessibility and purification of production [26–30].

In last few years, our group [31–33] have designed and reported series of A-D-A type small donor molecules materials and PCEs over 10% have been obtained with fullerene derivatives as the acceptors. We have found that the LUMO of those A-D-A type small molecules are mainly determined by the terminal electron withdrawing groups. Thus, those A-D-A type small molecules could be used as acceptor materials if proper end groups were selected and the molecules backbones were modified to be compatible with donor materials

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for good morphology. Just recently, we have reported a rather simple small molecule acceptor, named DICTF, with fluorene as the central block and 2-(2,3-dihydro-3-oxo-1*H*-inden-1-ylidene) propanedinitrile as the end-capping groups. The molecule was synthesized from widely available and cheap commercial materials with only three steps and a high overall yield of ~60%. Initial studies show that the fullerene-free organic solar cells with DICTF as the acceptor material and polymer PTB7-Th as the donor material gave a high PCE of 7.93%. Continuing the studies of this series for new and better acceptor materials, herein, we report a new small molecule named DICTiF through modifying the molecules DICTF by changing the alkyl chain on the fluorine from normal octyl to 2-ethylhexyl for both solubility and morphology control/optimization. Organic solar cells based on PBDB-T (Figure 1(a)) as the donor material and DICTiF as the acceptor material exhibited a PCE of 5.02% without any further treatment. After optimization, a high PCE of 7.11% was achieved, which is comparable with that of PBDB-T:$PC_{71}BM$ based OPV devices (7.51%) [34] and even higher than that of PBDB-T:$PC_{61}BM$ based devices (6.67%) [35]. The high photovoltaic performance demonstrates that DICTiF is a promising acceptor material for fullerene-free organic solar cells.

2 Experimental

The molecule DICTiF was synthesized with the similar procedure to DICTF and the detailed synthesis methods were given in the Supporting Information online. Theoretical calculations were performed by using the density functional theory (DFT) to determine the geometric structure of DICTiF. As shown in Figure 1(c), the geometry optimizations yielded a twisted structure for DICTiF. The dihedral angle between the plane of fluorene group and the thiophene ring is about 23°, which is expected to prevent the large aggregation of DICTiF when blends with donor material in order to form effective phase separation.

The UV-Vis absorption spectra of DICTiF in diluted $CHCl_3$ solution and in solid film are shown in Figure 1(b). The absorption of DICTiF in diluted $CHCl_3$ shows a peak at 589 nm. The absorption spectra of DICTiF film was broadened and showed two absorption peaks at 576 and 603 nm, which indicates effective π-π stacking between molecule backbones. The optical band gap of DICTiF estimated from the onset of the film absorption is 1.75 eV. The electrochemical cyclic voltammetry with ferrocene/ferrocenium of the (Fc/Fc^+) redox couple (4.8 eV under the vacuum level) as the internal calibration was used to investigate the energy levels. The highest occupied molecular orbital (HOMO) energy level calculated from the onset oxidation potential is –5.55 eV. The LUMO energy level calculated from the onset reduction potential is –3.62 eV. The electrochemical band gap of DICTiF is estimated to be 1.93 eV. Both the HOMO and the LUMO energy level of DICTiF are much lower than those of most donor materials, which indicates that OPV devices using DICTiF as their electron acceptor material will exhibit

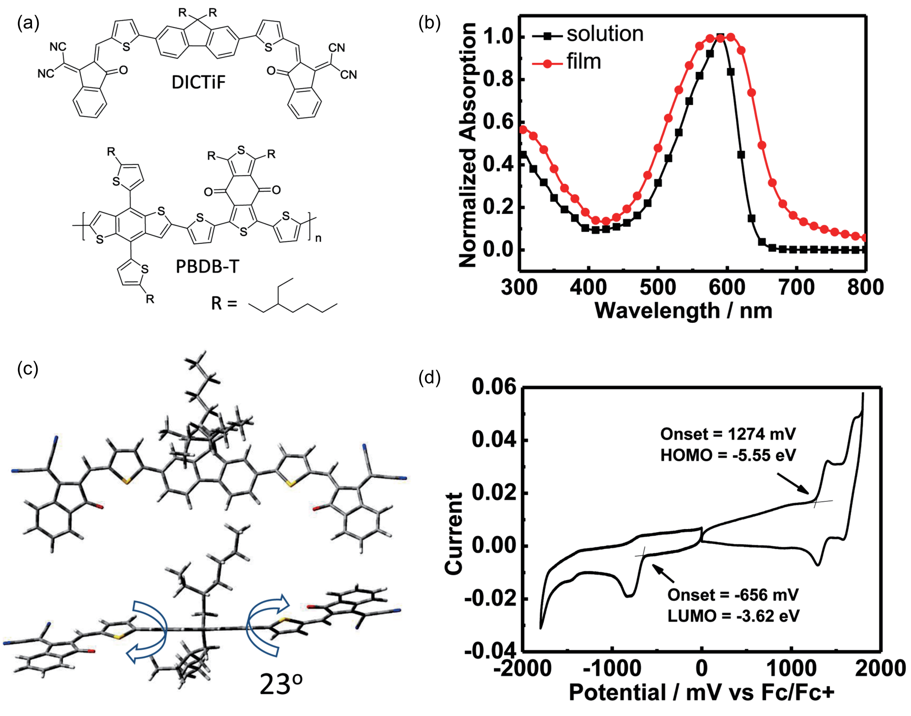

Figure 1 (a) Chemical structures of DICTiF and PBDB-T; (b) UV-Vis absorption spectra of DICTiF in solution and solid film; (c) optimized molecular geometries (side view and top view) of DICTiF using DFT; (d) the electrochemical cyclic voltammetry curveof DICTiF (color online).

effective charge separation properties. In addition, the relatively higher HOMO energy level of DICTiF than that of fullerene derivatives (–3.8––4.2 eV) indicate that using DICTiF as electron acceptor material in OPV devices will lead to an increased open voltage (V_{oc}).

3 Results and discussion

Solution-processed BHJ organic solar cells were fabricated using PBDB-T as the electron donor material and DICTiF as the electron acceptor material with a conventional device structure of ITO/PEDOT:PSS/PBDB-T:DICTiF/PDIN/Al. The *J-V* curves of the devices before and after optimization were presented in Figure 2(a), and the corresponding photovoltaic parameters are summarized in Table 1. The optimized donor/acceptor weight ratio was 1:1.4, and other optimization process of the device performance are shown in the Supporting Information. The device without any treatment shows a PCE of 5.02%, an V_{oc} of 0.97 V, a short-circuit (J_{sc}) of 10.12 mA cm^{-2}, and a fill factor (*FF*) of 51%. After optimization (using di-phenyl ether (DPE) as an additive and thermal annealing at 80 °C for 10 min) the PCE increased to 7.11%, with a V_{oc} of 0.98 V, a J_{sc} of 11.20 mA cm^{-2}, and a *FF* of 65%. The PCE (Table 1) is comparable to that of PBDB-T:PC$_{71}$BM based devices (7.51% [34]), and even higher than that of PBDB-T:PC$_{61}$BM based devices (6.67% [35]). Note, the device based on PBDB-T:DICTiF exhibits higher V_{oc} than that of devices based on both PBDB-T:PC$_{71}$BM (0.87 V) and PBDB-T:PC$_{61}$BM (0.86 V), and this should result from the high lying LUMO energy level of DICTiF. External quantum efficiency (EQE) spectrum of OPV devices based on PBDB-T:DICTiF is shown in Figure 2(b). The optimized device showed photo-to-current response from 300 to 700 nm with a maximum of 64.5% and over 57% across the range of 420 to 625 nm, indicating effective photoelectron conversion. The J_{sc} calculated from EQE spectrum of optimized devices was 10.66 mA cm^{-2}, in agreement with the J_{sc} value obtained from *J-V* curves (11.20 mA cm^{-2}) with a 4.8% mismatch. Additionally, it is worth to note that the devices based on PTB7-Th:DICTiF also achieved a high PCE of 7.03% (see Table S1 and Figure S6 in the Supporting Information online), which indicates that DICTiF possesses the potential to be applied generally with other high performance donor materials.

The mobilities of the blend films were measured by the space charge limited current (SCLC) method (Figure S5). The hole and electron mobilities were measured with the device structures of ITO/PEDOT:PSS/PBDB-T:DICTiF/Au and Al/PBDB-T:DICTiF/Al, respectively. The devices before optimization showed hole mobility and electron mobility of 3.60×10^{-5} and 2.63×10^{-5} cm^2 V^{-1} s^{-1}, respectively, with μ_h (hole mobility)/μ_e (electron mobility) of 1.37. After optimization, the device exhibits a higher and much more balanced hole and electron mobility of 8.45×10^{-5} and 7.46×10^{-5} cm^2 V^{-1} s^{-1}, respectively, with μ_h/μ_e of 1.13, which is favorable for a higher FF.

The morphology of the active layer was investigated by atomic force microscopy (AFM) and transmission electron microscopy (TEM). As shown in AFM images (Figure 3(a, b)), the root-mean-square (RMS) roughness is 0.963 nm for as-cast film. After optimization, the RMS roughness increases slightly to 1.48 nm. Figure 3(c, d) shows the TEM images of the blend films. Compared with the as-cast film, better interpenetrating networks of donor and acceptor phases could be observed after optimization, which is favorable for exciton dissociation and charge transport. Therefore, impro-

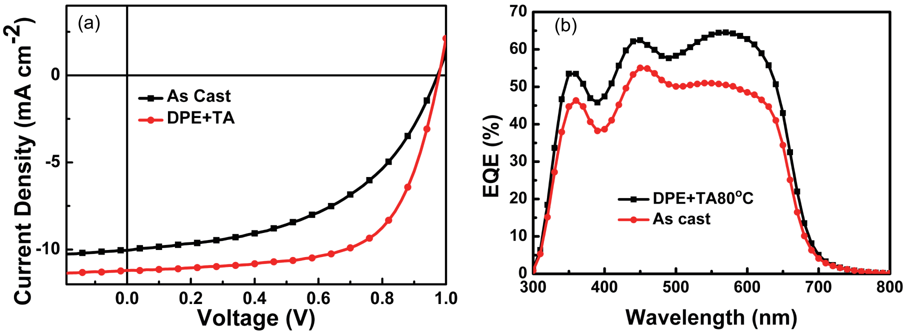

Figure 2 (a) *J-V* curves of devices based on PBDB-T:DICTiF; (b) EQE curves of optimal devices based on PBDB-T:DICTiF (color online).

Table 1 Device performance for BHJ solar cells based on PBDB-T:DICTiF

Treatment	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%) a) b)	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h/μ_e
as-cast	0.98	10.12	0.51	4.81±0.21 (5.02)	3.60×10^{-5}	2.63×10^{-5}	1.37
DPE+TA c)	0.98	11.20	0.65	6.97±0.14 (7.11)	8.45×10^{-5}	7.46×10^{-5}	1.13

a) The average PCE is obtained from 30 devices; b) the best PCEs are provided in parentheses; c) with thermal annealing at 80 °C for 10 min and using 0.5% DPE as additive.

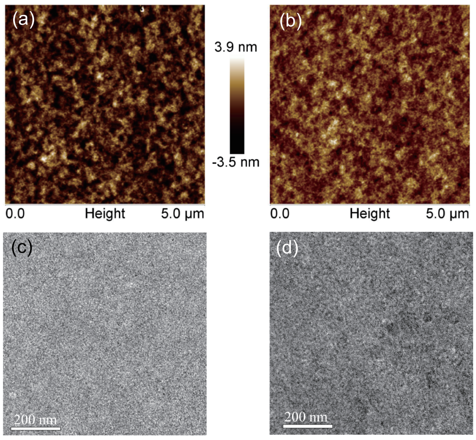

Figure 3 (a, b) AFM images and (c, d) TEM images of PBDB-T:DICTiF blend films. (a, c) as-cast; (b, d) after optimization (color online).

ved J_{sc} and FF were achieved after optimization.

4 Conclusions

In summary, a rather simple small molecular named DICTiF as the acceptor material in organic solar cells was designed and synthesized. The OPV devices using this material as the electron acceptor exhibits a high PCE of 7.11%, with a high V_{oc} of 0.98 V, a J_{sc} of 11.20 mA cm^{-2}, and a FF of 65%. It is important to note that this simple and easily accessible material gives comparable or even better performance than the corresponding conventional PCBM devices. This indicates that not only this simple acceptor material DICTiF but also other new acceptor materials might have great potential to bring the entire OPV studies to a new stage.

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Conflict of interest The authors declare that they have no conflict of interest.

Supporting information The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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