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Fullerene-free small molecule organic solar cells with high open circuit voltage of 1.15V

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A new small molecule named DTBTF with thiobarbituric acid as terminal group were designed and synthesized as acceptor for organic photovolataic application.. DTBTF exhibits strong absorption in the visible region, and relatively high lying LUMO energy level (-3.62 eV). All-small-molecule organic solar cells based on DR3TSBDT:DTBTF blend films show a considerable PCE of 3.84% with a high $V_{\rm oc}$ of 1.15 V.

Organic photovoltaics (OPVs) are considered as promising candidates for the production of renewable energy with advantages such as solution processability, low cost, light weight and flexibility. Power conversion efficiencies (PCEs) over 10% have been achieved for single junction organic solar cells with bulk heterojunction (BHJ) architecture with fullerene derivatives as acceptors.² The rapid progress is mainly ascribed to the development of new electron-donor materials including polymers and small molecules.3 With the advantages of high electron mobility and high electron affinity, fullerene derivatives are the most commonly used electron acceptors in organic solar cells.4 However, these fullerene derivatives also have some disadvantages such as weak absorption in the visible region, difficulty in tuning energy levels and high cost in synthesis. Therefore, recently more and more attention has been given to design and synthesis of non-fullerene electron acceptor materials including polymers and small molecules.5 PCEs over 6% have been achieved for the devices based on polymer donor materials and non-fullerene electron acceptor materials.⁶ It is worth to note that nearly all the fullerene-free

based devices employed polymers as donor materials.^{5a, 7} Incomparison with polymer materials, small molecules control, several advantages such as well-defined structure and therefore less batch-to-batch variation, easier energy local control, etc.^{3b, 8} Even with those advantages of small molecule based devices, it is interesting to note that fullerene-free all small-molecule organic solar cells were relatively rare. studied and PCEs over 3% have been achieved ⁹.

It is most accepted that open-circuit voltage (V_{oc}) depends on the difference between the highest occupied molecular orbital (HOMO) energy level of the donor material and the low lying lowest unoccupied molecular orbital (LUMO) level of the acceptor material, 10 and an off-set energy of 0.3 eV between the LUMO level of donor and acceptor materials could provide efficient exciton dissociation. In order to maximize the V_{oc} , it is satisfying that the LUMO energy level of the electron acceptor is as high as possible while still guaranteeing for efficient electron transfer from the donor to the acceptor material. For many reported efficient small molecule done materials such as $p\text{-DTS}(\text{FBTTh}_2)_2$ and DR3TSBDT, ¹² the LUMO energy levels are around -3.3 eV, indicating a relatively big offset energy of ~0.6 eV between the LUMO levels of these small molecule donors and PC71BM (~ -3.90 eV for LUMO4). This there is enough space for up-shift of the LUMO energy level to achieve higher V_{oc} , thus further improving the PCE of sm(1 molecule organic solar cells. In addition, the energy loss (E_{los} , which is the loss in energy of the V_{oc} relative to the optic... band gap (E_g) , defined as $E_{loss} = E_g - qV_{oc}$, is an importar parameter to evaluate the $V_{\rm oc}$ of BHJ organic solar cells .¹³ Th minimum E_{loss} is suggested to be 0.6 eV, and the corresponding $V_{\rm oc}$ is often considered as the maximum achievable $V_{\rm oc.}$ 11

As one type of donor-acceptor (D-A) type small molecules. A-D-A small molecules have been demonstrated to be efficier, photovoltaic materials in the past years. ¹⁴ In our pervious works, we have demonstrated that choosing terminal acceptor units with suitable electron withdrawing ability could obtain desirable LUMO energy levels. Herein, we designed an 'synthesized an A-D-A small molecule electron acceptor

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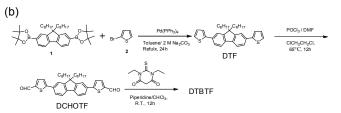


Fig. 1 a) Chemical structures of DTBTF and DR3TSBDT, b) synthetic route of DTBTF.

material named DTBTF (Fig. 1a) with weak electron- donating unit fluorene as central building block and strong electron withdrawing unit thiobarbituric acid as the terminal. The new small molecule exhibited strong absorption in the visible region, a deep HOMO (-5.68 eV) and relatively ideal LUMO energy level (-3.62 eV). All-small-molecule organic solar cells based on our reported small molecule donor DR3TSBDT (Fig. 1a) and the new electron acceptor DTBTF exhibited a PCE of 3.84% and an impressively high $V_{\rm oc}$ of 1.15 V which is among the highest V_{oc} values reported for single junction organic solar cells. The devices based on DTBTF as acceptor showed a low energy loss of only 0.59 eV, indicating that nearly maximum achievable $V_{\rm oc}$ for DR3TSBDT based BHJ organic solar cells was realized. The results demonstrate that DTBTF is a promising acceptor material for achieving high-performance fullerenefree organic solar cells.

The synthetic route of DTBTF is shown in **Fig. 1b**. DTF was synthesized using Suzuki coupling between 1 and 2. The intermediates of dialdehyde DCHOTF was obtained by Vilsmeier-Haack reaction. The target molecule DTBTF were then prepared by Knoevenagel condensation of DCHOTF with thiobarbituric acid. The details are shown in Supporting Information. The new molecule exhibits good solubility in common organic solvents, such as dichloromethane, chloroform, tetrahydrofuran, etc. Thermogravimetric analysis (TGA) indicates that DTBTF exhibits excellent thermal stability up to 350 °C under N_2 atmosphere (**Fig. S1**).The UV-Vis absorption spectra of DTBTF in chloroform and in thin film are shown in **Fig. 2a**. DTBTF in chloroform (10^{-6} M) shows an absorption peak at 540 nm with a maximum absorption

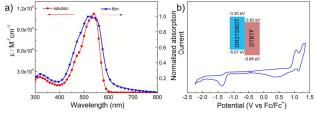


Fig.2 a) Absorption spectra of DTBTF in chloroform solution and as-cast film, b) Cyclic voltammogram of DTBTF in a dichloromethane solution of 0.1 mol L^{-1} Bu₄NPF₆ with a scan rate of 100 mV s⁻¹.

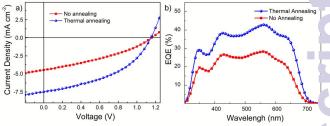


Fig. 3 a) Characteristic current density versus voltage (*J*-') curves of DR3TSBDT:DTBTF based devices without and with thermal annealing; b) The external quantum efficiency (EQ_, curves of the DR3TSBDT:DTBTF based devices without and with thermal annealing.

coefficient of 1.12×10⁵ M⁻¹ cm⁻¹. The DTBTF film casted from chloroform shows a blue-shifted maximum absorption peak c 520 nm, and a broad absorption band from 300 to 620 nm. The optical band gap of DTBTF is 2.03 eV estimated from the or of the film absorption spectrum.

The electrochemical properties of **DTBTF** investigated by cyclic voltammetry with ferrocene/ ferrocenium of the (Fc/Fc+) redox couple (4.8 eV below vacuum level) as the internal calibration. As shown in Fig. 2. the HOMO and LUMO energy levels of DTBTF, which are -5.6° and -3.62 eV, respectively, are estimated based on the onse oxidation potential and the onset reduction potential of redox curves. Both the HOMO offset and LUMO offset between DR3TSBDT and DTBTF were large enough for photoinduced hole and electron transfer, respectively. 11 Due to the higher LUMO energy level compared to PC71BM, and improved V_{oc} could be expected by using DTBTF as the electron acceptor material.

BHJ organic solar cells were fabricated using DR3TSBDT as the electron donor material and DTBTF as the electron acceptor material with structure glass/ITO/PEDOT:PSS/DR3TSBDT:DTBTF/PDIN/AI, using conventional solution spin-coating process. PDIN is a perylendiimide derivative, developed as cathode interlayer by Li et al,15 and its structure is shown in Fig. S2. The optimized devices parameters of V_{oc} , J_{sc} , FF and PCE are summarized Table 1, and more performance data under various conditions are shown in Table S1 and S2. The optimized D/A weight ratio of DR3TSBDT:DTBTF is 1:0.5. The current density-voltage (J-) curves of the devices (with D/A weight ratio of 1:0.5) with different treatments measured under 100 mW cm⁻² simulate... sunlight illumination are shown in Fig. 3a. The device without

Table 1 Device performance parameters of the BHJ solar cells based on DR3TSBDT: DTBTF (1:0.5, w/w) blend films.

Post treatment	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF	PCE [%] ^{a,b}
No annealing	1.15	4.51	0.34	1.65±0.11 (1.76)
Thermal annealing	1.15	7.42	0.45	3.64±0.20 (3.84)

a) Average values from 30 devices, b) The best PCEs are provided in parentheses.

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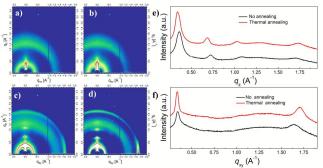


Fig. 4 GIWAXS images of (a, b) DTBTF pure films and (c, d) DR3TSBDT:DTBTF blend films. (a, c) The films without post-treatment. (b, d) The films with thermal annealing. (e) Out-of-plane line-cuts of GIWAXS patterns for the DR3TSBDT:DTBTF blend films. (f) In-plane line-cuts of GIWAXS patterns for the DR3TSBDT:DTBTF blend films.

post-treatment showed a PCE of 1.76%, with a $V_{\rm oc}$ of 1.15V, a J_{sc} of 4.51 mA cm⁻² and a FF of 0.34. After thermal annealing at 100 °C for 10 min, the performance was significantly improved to a PCE of 3.84%, with a $V_{\rm oc}$ of 1.15 V, a $J_{\rm sc}$ of 7.42 and a FF of 0.45. The devices with DTBTF as electron acceptor exhibited much higher $V_{\rm oc}$ (1.15 V) than the devices with PC₇₁BM as electron acceptor (with $V_{\rm oc}$ of 0.96 V). The higher $V_{\rm oc}$ could be attributed to the high-lying LUMO energy level of DTBTF. Furthermore, the E_{loss} is 0.59 eV, calculated from the difference between the optical band gap of DR3TSBDT and the qV_{oc} . Since the minimum E_{loss} is suggested to be 0.6 eV and the corresponding V_{oc} is also often considered as the maximum achievable $V_{\rm oc}$ in the BHJ organic solar cells, replacing PC71BM with non-fullerene acceptor DTBTF in OPV devices could almost realized the maximized $V_{\rm oc}$ for DR3TSBDT based BHJ organic solar cells. External quantum efficiency (EQE) spectra of the OPV devices are shown in Fig. 3b. The DR3TSBDT:DTBTF blend film with thermal annealing showed broad photo-tocurrent response from 300 to 700 nm with the maximum value of 41% at 560 nm. The calculated J_{sc} obtained by integration of the EQE curves were 4.41 and 7.06 mA cm⁻², respectively, for the devices without and with thermal annealing, respectively, which showed a $2^{\sim}5\%$ mismatch compared with the J_{sc} values obtained from the J-V curves.

The hole and electron mobilities of the BHJ blend films were measured using the space-charge limited current (SCLC) method with device structures ITO/PEDOT:PSS/DR3TSBDT:DTBTF/Au and AI/DR3TSBDT: DTBTF/AI, respectively (Fig. S3). For the devices without annealing, the hole and electron mobilities were 6.70×10⁻⁵ $cm^2V^{-1}S^{-1}$ and 1.91 ×10⁻⁵ $cm^2V^{-1}S^{-1}$, respectively. After thermal annealing, the hole and electron mobilities increased to 1.14×10^{-4} and 4.13×10^{-5} cm² V ⁻¹ S⁻¹, respectively. The microstructural features of the pure DTBTF films and DR3TSBDT:DTBTF blend films with different treatments were investigated by two dimensional (2D) grazing-incidence wideangle X-ray scattering (GIWAXS) (Fig. 4). The pure DTBTF films showed weak (100) diffraction peak at 0.39 Å⁻¹, corresponding to interchain distance of 16.1 Å, indicating poor molecular packing in the solid state. For the blend film without annealing,

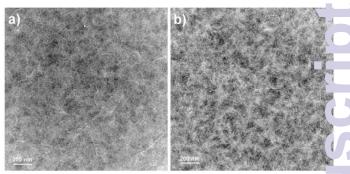


Fig. 5 TEM images of DR3TSBDT:DTBTF blend films (a) without annealing and (b) with thermal annealing.

both (h00) and (010) reflections of DR3TSBDT were observed. After thermal annealing, the reflection intensity of both (h0), and (010) was strengthened, which indicats that a more ordered structure was formed after thermal annealing treatment. In addition, from photoluminescence (PL) spectrate of the pure and blend films (Fig. S5), Compared with an DR3TSBDT:DTBTF blend film without annealing, the DR3TSBDT:DTBTF blend film with thermal annealing exhibited a decreased PL emission, indicating the enhancement of intermolecular interaction between the donor and acceptor. The enhanced intermolecular interaction and more ordered packing in the blend film with thermal annealing could promote charge separation and transport, thus higher J_{sc} .

The morphologies of the blend films were investigated by atomic force microscopy (AFM) and transmission electron microscopy (TEM). From AFM imges (Fig. S4), the blend filn s without and with thermal annealing are smooth and uniform with low root-mean-square (RMS) roughness of 0.78 and 1.(5 nm, respectively. The TEM images clearly showed the differences between the morphologies of the blend films win different treatments. As shown in Fig. 5, the blend film without post-treatment showed poor interpenetrating networks of the donor and acceptor phases. After thermal annealing, the ble... film exhibited clear phase separation, and obvious fiber like crystalline structures. The better morphology could increase charge transport efficiency, thus resulting in higher J. However, the large domains with size of ~120 nm in the bler 1 film which is much larger than the ideal exciton diffusion length (10~20 nm), 16 would lead to serious charge recombination, thus inferior FF and relatively low EC response. It is believed that higher PCEs could be expected through further efforts focused on device optimization t improve the J_{sc} and FF in the future.

In conclusion, a new A-D-A small molecule electron acceptor DTBTF containing a central fluorene unit as the central block unit and and thiobarbituric acid as the enucapping groups was designed and synthesized. The introduction of electron withdrawing group thiobarbituric acid could finely tune the LUMO energy level of the acceptomolecule. The new molecule DTBTF exhibited strong absorption in the visible region and a high LUMO energy level compared to PCBM. The devices based on the DR3TSBDT:DTBTF blend film exhibited a PCE of 3.84% and a Vas high as 1.15 V with a low energy loss of only 0.59 eV. The

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results indicate that the OPV performance of fullerene-free all-small-molecule organic solar cells could have great improvement room if desirable $J_{\rm sc}$ and FF could be obtained simultaneously. We demonstrate that the A-D-A molecules could serve as not only good donors but also good acceptors. Through careful molecule design and device optimization, fullerene-free all-small- molecule organic solar cells would achieve better performance in the near future.

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