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

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A new small molecule named DTBTF with thiobarbituric acid as a terminal group was designed and synthesized as an acceptor for organic photovoltaic applications. DTBTF exhibits strong absorption in the visible region, and a 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_{oc} of 1.15 V.

Organic photovoltaic devices (OPVs) are considered as promising candidates for the production of renewable energy with advantages such as solution processability, low cost, lightweight and flexibility.¹ 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 the energy levels and high cost of synthesis. Therefore, recently more and more attention has been paid to the 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 noting that nearly all the fullerene-free based devices employed

polymers as donor materials.^{5a,7} In comparison with polymer materials, small molecules offer several advantages such as well-defined structure and therefore less batch-to-batch variation, and easier energy level control.^{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 rarely 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.¹¹ 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 donor materials such as *p*-DTS(FBTTh₂)₂ and DR3TSBDT,¹² the LUMO energy levels are around −3.3 eV, indicating a relatively big off-set energy of ~0.6 eV between the LUMO levels of these small molecule donors and PC₇₁BM (~−3.90 eV for LUMO⁴). Thus there is enough space for the up-shift of the LUMO energy level to achieve higher V_{oc} , thus further improving the PCE of small molecule organic solar cells. In addition, the energy loss (E_{loss}), which is the loss in energy of the V_{oc} relative to the optical band gap (E_g), defined as $E_{loss} = E_g - qV_{oc}$, is an important parameter to evaluate the V_{oc} of BHJ organic solar cells.¹³ The minimum E_{loss} is suggested to be 0.6 eV, and the corresponding V_{oc} is often considered as the maximum achievable V_{oc} .¹¹

As a class of donor–acceptor (D–A) type small molecules, A–D–A small molecules have been demonstrated to be efficient photovoltaic materials in the past years.¹⁴ In our previous studies, we have demonstrated that choosing terminal acceptor units with suitable electron withdrawing ability could obtain desirable LUMO energy levels. Herein, we designed and synthesized an A–D–A small molecule electron acceptor material named DTBTF (Fig. 1a) with a weak electron-donating unit fluorene as the central

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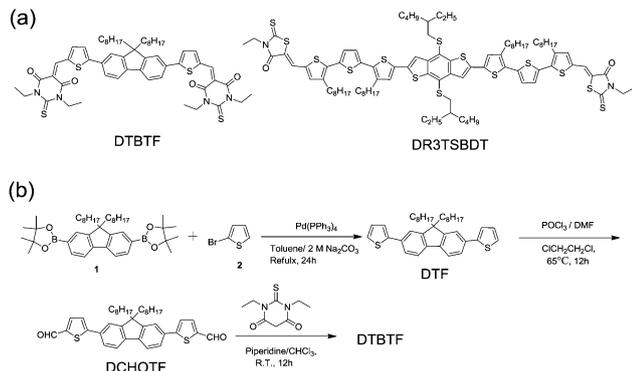


Fig. 1 (a) Chemical structures of DTBTF and DR3TSBDT, and (b) synthetic route of DTBTF.

building block and a strong electron withdrawing unit thio-barbituric 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_{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 an acceptor showed a low energy loss of only 0.59 eV, indicating that nearly maximum achievable V_{oc} for DR3TSBDT based BHJ organic solar cells was realized. The results demonstrate that DTBTF is a promising acceptor material for achieving high-performance fullerene-free 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 was then prepared by Knoevenagel condensation of DCHOTF with thiobarbituric acid. The details are shown in the ESI†. The new molecule exhibits good solubility in common organic solvents, such as dichloromethane, chloroform, and tetrahydrofuran. Thermogravimetric analysis (TGA) indicates that DTBTF exhibits excellent thermal stability up to 350 °C under a N_2 atmosphere (Fig. S1, ESI†). 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 coefficient of 1.12×10^5 $M^{-1} cm^{-1}$. The DTBTF film casted from chloroform shows a blue-shifted maximum absorption peak at 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 onset of the film absorption spectrum.

The electrochemical properties of DTBTF were investigated by cyclic voltammetry with ferrocene/ferrocenium of the (Fc/Fc⁺) redox couple (4.8 eV below the vacuum level) as the internal calibration. As shown in Fig. 2b, the HOMO and LUMO energy levels of DTBTF, which are -5.68 and -3.62 eV, respectively, are estimated based on the onset oxidation potential and the onset reduction potential of the 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

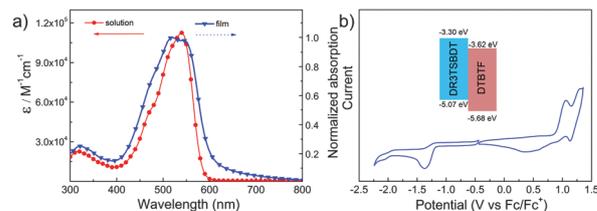


Fig. 2 (a) Absorption spectra of DTBTF in chloroform solution and as-cast film, and (b) cyclic voltammogram of DTBTF in a dichloromethane solution of 0.1 mol L⁻¹ Bu₄NPF₆ with a scan rate of 100 mV s⁻¹.

higher LUMO energy level compared to PC₇₁BM, an 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 a device structure of glass/ITO/PEDOT:PSS/DR3TSBDT:DTBTF/PDIN/Al, using the conventional solution spin-coating process. PDIN is a perylene diimide derivative, developed as a cathode interlayer by Li *et al.*,¹⁵ and its structure is shown in Fig. S2 (ESI†). The optimized device parameters of V_{oc} , J_{sc} , FF and PCE are summarized in Table 1, and more performance data under various conditions are shown in Tables S1 and S2 (ESI†). The optimized D/A weight ratio of DR3TSBDT:DTBTF is 1:0.5. The current density–voltage (J - V) curves of the devices (with the D/A weight ratio of 1:0.5) with different treatments measured under 100 mW cm⁻² simulated sunlight illumination are shown in Fig. 3a. The device without post-treatment showed a PCE of 1.76%, with a V_{oc} of 1.15 V, 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_{oc} of 1.15 V, a J_{sc} of 7.42 and a FF of 0.45. The devices with DTBTF as electron acceptors exhibited much higher V_{oc} (1.15 V) than the devices with PC₇₁BM as electron acceptors (with a V_{oc} of 0.96 V).^{12b} The higher V_{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_{oc} in the BHJ organic solar cells, replacing PC₇₁BM with non-fullerene acceptor DTBTF in OPV devices could almost realize the maximized V_{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 a broad photo-to-current response from 300 to 700 nm with the maximum value of 41% at 560 nm. The calculated J_{sc} values obtained by integration of the EQE curves were 4.41 and

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.

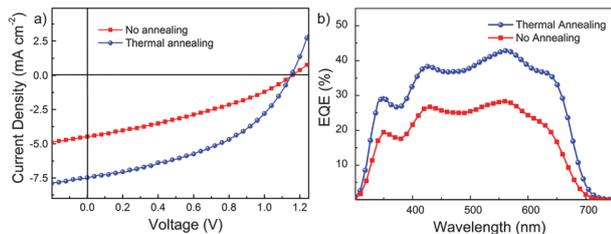


Fig. 3 (a) Characteristic current density versus voltage (J - V) curves of DR3TSBDT:DTBTF based devices without and with thermal annealing; (b) the external quantum efficiency (EQE) curves of the DR3TSBDT:DTBTF based devices without and with thermal annealing.

7.06 mA cm⁻², respectively, for the devices without and with thermal annealing, respectively, which showed a 2–5% 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 of ITO/PEDOT:PSS/DR3TSBDT:DTBTF/Au and Al/DR3TSBDT:DTBTF/Al, respectively (Fig. S3, ESI[†]). For the devices without annealing, the hole and electron mobilities were 6.70×10^{-5} cm² V⁻¹ S⁻¹ and 1.91×10^{-5} cm² V⁻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 wide-angle X-ray scattering (GIWAXS) (Fig. 4). The pure DTBTF films showed a weak (100) diffraction peak at 0.39 \AA^{-1} , corresponding to the interchain distance of 16.1 \AA , indicating poor molecular packing in the solid state. For the blend film without annealing, both ($h00$) and (010) reflections of DR3TSBDT were observed. After thermal annealing, the reflection intensity of both ($h00$) and (010) was strengthened, which indicates that a more ordered structure was formed after thermal annealing treatment. In addition, from the photoluminescence (PL) spectra of the pure and blend films (Fig. S5, ESI[†]), it can be seen that compared with the DR3TSBDT:DTBTF blend film without annealing, the DR3TSBDT:DTBTF blend film with thermal annealing exhibited decreased PL emission, indicating the enhancement of intermolecular interaction between the donor

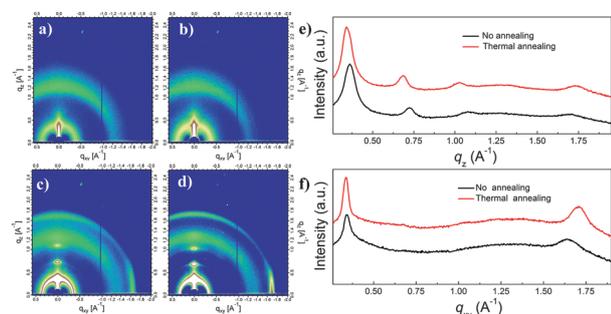


Fig. 4 GIWAXS images of (a and b) DTBTF pure films and (c and d) DR3TSBDT:DTBTF blend films. (a and c) The films without post-treatment. (b and d) The films with thermal annealing. (e) Out-of-plane line-cuts of GIWAXS patterns for the DR3TSBDT:DTBTF blend films. (f) In-plane line-cuts of GIWAXS patterns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

and the 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 images (Fig. S4, ESI[†]), the blend films without and with thermal annealing are smooth and uniform with low root-mean-square (RMS) roughness of 0.78 and 1.06 nm, respectively. The TEM images clearly showed the differences between the morphologies of the blend films with 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 blend film exhibited clear phase separation, and obvious fiber like crystalline structures. The better morphology could increase charge transport efficiency, thus resulting in higher J_{sc} . However, the large domains with a size of ~ 120 nm in the blend film, which is much larger than the ideal exciton diffusion length (10–20 nm),¹⁶ would lead to serious charge recombination, thus an inferior FF and a relatively low EQE response. It is believed that higher PCEs could be expected through further efforts focused on device optimization to 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 thiobarbituric acid as the end-capping group was designed and synthesized. The introduction of electron withdrawing group thiobarbituric acid could finely tune the LUMO energy level of the acceptor molecule. 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 V_{oc} as high as 1.15 V with a low energy loss of only 0.59 eV. The results indicate that the OPV performance of fullerene-free all-small-molecule organic solar cells could have a great room for improvement if desirable J_{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 molecular design and device optimization, fullerene-free all-small-molecule organic solar cells would achieve better performance in the near future.

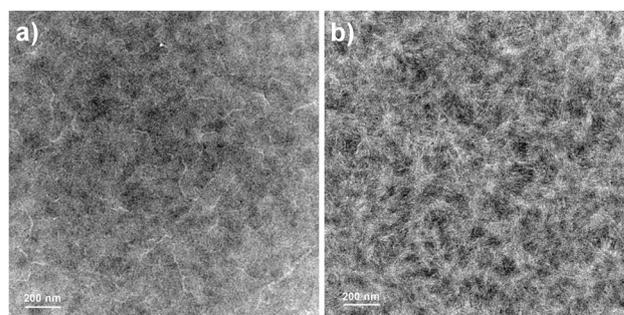


Fig. 5 TEM images of DR3TSBDT:DTBTF blend films (a) without annealing and (b) with thermal annealing.

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