



## Short Communication

## 18% Efficiency organic solar cells

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In 1995, Yu et al. [1] first reported bulk-heterojunction (BHJ) solar cells with a conjugated polymer donor and a fullerene acceptor as the active materials. From then on, BHJ organic solar cells (OSCs) have attracted academic and industrial interests due to the advantages like lightweight, flexibility and roll-to-roll fabrication. Nowadays, 17% power conversion efficiencies (PCEs) have been achieved in the state-of-the-art OSCs [2,3]. The remarkable progress in OSCs relies on the continuously emerging new materials and device fabrication technologies, and the understanding on film morphology and device physics [4,5].

Donor and acceptor materials determine the performance of OSCs [5]. The past 25 years have witnessed an odyssey in developing high-performance donors and acceptors. Fullerenes are initially used as acceptors in BHJ solar cells. Hummelen et al. [6,7] first synthesized fullerene monoadducts PC<sub>61</sub>BM and PC<sub>71</sub>BM, which are the most widely used acceptors. To enhance the open-circuit voltage ( $V_{oc}$ ) for OSCs, He et al. [8,9] developed efficient fullerene bisadduct acceptors IC<sub>60</sub>BA and IC<sub>70</sub>BA, which gave PCEs up to 7.40%. To eliminate the energetic disorder of isomers, Xiao et al. [10] developed an isomer-free fullerene bisadduct *e*-PPMF via regioselective synthesis and pushed PCE to 8.11%, which is the highest PCE for OSCs with fullerene bisadduct acceptors to date. Despite the early success in OSCs, the intrinsic weak light-harvesting capability of fullerenes limits their further application. In this context, Lin et al. [11,12] developed nonfullerene acceptors for OSCs, the fused-ring acceptor–donor–acceptor (A–D–A) small molecules, e.g., ITIC and IDIC. These nonfullerene acceptors have strong visible–NIR light-harvesting capability and good electron

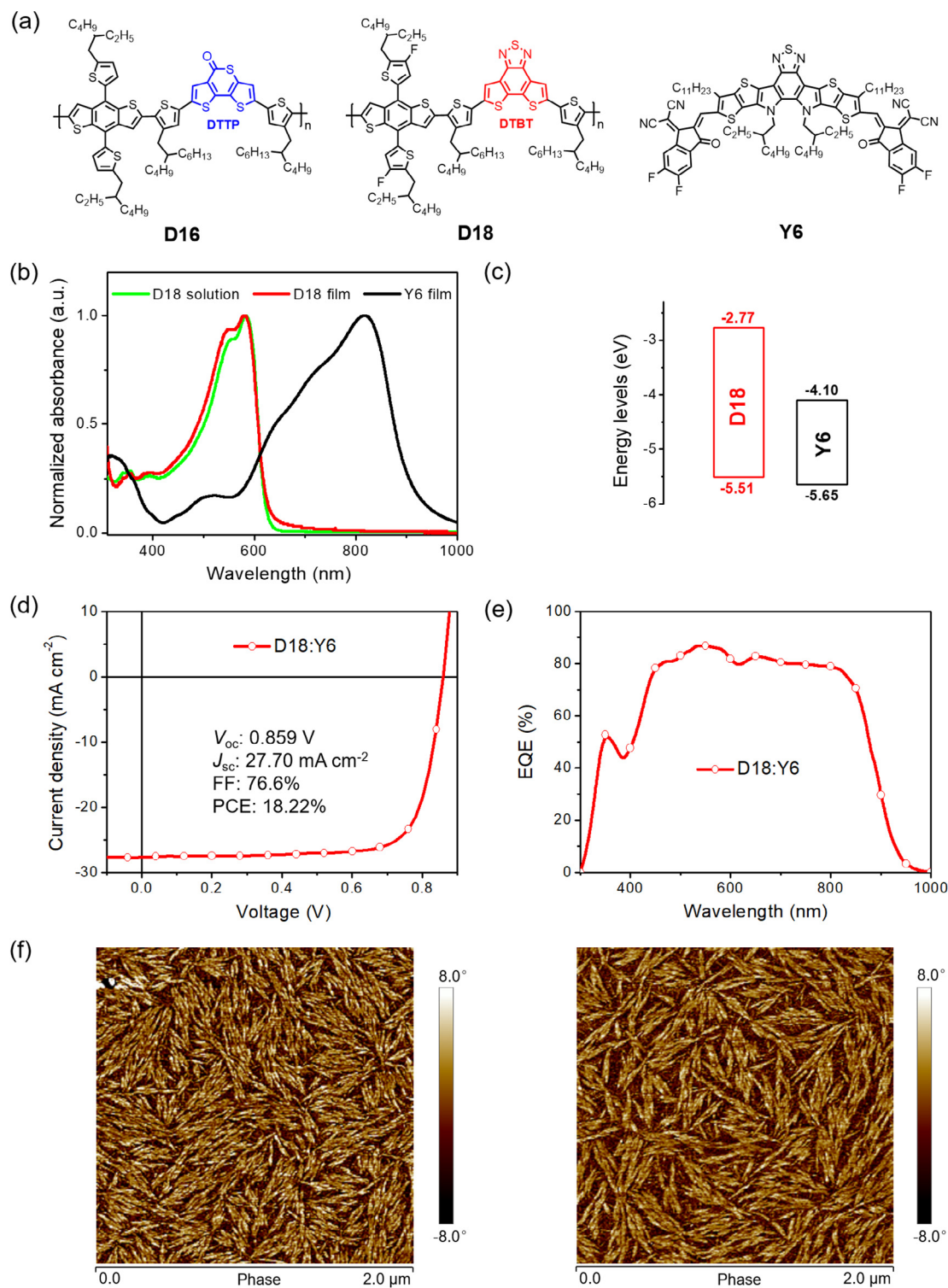
mobility, delivering higher short-circuit current density ( $J_{sc}$ ) and PCE in solar cells than fullerene acceptors. To further enhance light absorption, Xiao et al. [13–26] developed stronger light-harvesting A–D–A acceptors by using more electron-rich carbon–oxygen-bridged (CO-bridged) core units. The acceptor CO<sub>8</sub>DFIC, based on an octacyclic CO-bridged unit, CO<sub>8</sub>, presents a narrow bandgap of 1.26 eV and strong absorption at 600–1000 nm [15]. Ternary solar cells based on CO<sub>8</sub>DFIC gave an outstanding  $J_{sc}$  of 28.20 mA cm<sup>−2</sup> and a PCE of 14.08%. This is the first report demonstrating that the PCE for OSCs exceeds 14% [16]. These work indicated the great potential of low-bandgap nonfullerene acceptors. Recently, Yuan et al. [27] developed a highly efficient low-bandgap acceptor Y6 by using a fused-ring benzothiadiazole core unit. The blend of Y6 and a certain wide-bandgap donor–acceptor (D–A) copolymer donor can harvest most of the visible and NIR light and give excellent PCEs (15%–17%) [3,27–31]. On the other hand, high-performance donors matching those low-bandgap nonfullerene acceptors are still limited. Only a few D–A copolymer donors, such as PM6, PTQ10, P2F-EHp, D16 and W1 developed by Hou [32], Li [33], Huang [29] and Ding [30,31] groups, have delivered >15% PCEs. Developing more high-performance donors would keep lifting the PCE of OSCs, which is a great mission for the field!

Previously, our group reported high-performance wide-bandgap copolymers based on fused-ring acceptor units [30,34–39]. These units have strong electron-withdrawing capability and extended molecular planes, gifting copolymers deep the highest occupied molecular orbital (HOMO) levels, enhanced  $\pi$ – $\pi$  stacking and high hole mobility, thus leading to simultaneously improved  $V_{oc}$ ,  $J_{sc}$  and fill factor (FF). For example, a copolymer D16 based on a fused-ring thiolactone unit, 5H-dithieno[3,2-b:2',3'-d]thio pyran-5-one (DTTP), delivered a PCE of 16.72% when blending with Y6 (Fig. 1a) [30]. In continuing our effort, here we report a more efficient copolymer donor D18 by using a fused-ring acceptor unit,

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**Fig. 1.** An 18% efficiency polymer donor based on DTBT unit. (a) The chemical structures for D16, D18 and Y6; (b) absorption spectra for D18 solution, D18 film and Y6 film; (c) energy level diagram; (d) J-V curve for D18:Y6 solar cells; (e) EQE spectrum for D18:Y6 solar cells; (f) AFM phase images for D18:Y6 blend films without (left) and with (right) SVA.

dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]thiadiazole (DTBT) [40]. Compared with DTTP, DTBT has a larger molecular plane and gifts D18 a higher hole mobility. D18:Y6 solar cells demonstrate a PCE of 18.22% (certified 17.6%), which is the highest efficiency for organic solar cells to date.

The synthetic route for D18 is shown in Scheme S1 (online). Stille coupling of 5,8-dibromodithieno[3',2':3,4;2'',3'':5,6]benzo[1,

2-c][1,2,5]thiadiazole (DTBT-Br) and tributyl(4-(2-butyloctyl)thiophen-2-yl)stannane gave compound **1** in 93% yield. Bromination of compound **1** with NBS gave the monomer, compound **2**, in 90% yield. Stille copolymerization of compound **2** with (4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (FBTD-Sn) gave D18 in 84% yield. All compounds were characterized by spectroscopic

techniques, i.e.,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectrometry. The number-average molecular weight ( $M_n$ ) and the polydispersity index (PDI) for D18 are 72.4 kDa and 1.51, respectively. The absorption spectra for D18 in chloroform and as film are shown in Fig. 1b. In solution, D18 shows an absorption band at 410–620 nm, with a peak at 584 nm and a shoulder at 559 nm. For film, the two peaks shift to 581 and 555 nm, respectively. The absorption onset for D18 film is 625 nm, corresponding to an  $E_g^{\text{opt}}$  of 1.98 eV. The absorption of Y6 film is complementary with that of D18. The HOMO and the lowest unoccupied molecular orbital (LUMO) levels of D18 estimated from cyclic voltammetry (CV) measurement are  $-5.51$  and  $-2.77$  eV, respectively (Fig. S6 online). Y6 shows a HOMO of  $-5.65$  eV and a LUMO of  $-4.10$  eV (Fig. 1c) [27].

The solar cells with a structure of ITO/PEDOT:PSS/D18:Y6/PDIN/Ag were made to evaluate the performance of D18. The D/A ratio, active layer thickness, additive content and solvent vapor annealing (SVA) time were optimized. The best D18:Y6 cells gave a PCE of 18.22%, with a  $V_{\text{oc}}$  of 0.859 V, a  $J_{\text{sc}}$  of  $27.70 \text{ mA cm}^{-2}$  and a FF of 76.6% (Fig. 1d). These cells have a D/A ratio of 1:1.6 (w/w), an active layer thickness of 103 nm, no additive and a chloroform SVA for 5 min (Tables S1–S4 online). To the best of our knowledge, the 18.22% PCE is the highest value achieved from organic solar cells to date. The best cells were also measured at the National Institute of Metrology (NIM), Beijing, and a certified PCE of 17.6% ( $V_{\text{oc}}$ , 0.842 V;  $J_{\text{sc}}$ ,  $26.67 \text{ mA cm}^{-2}$ ; FF, 78.4%; effective area,  $2.580 \text{ mm}^2$ ) was recorded (Fig. S7 online). The 17.6% certified efficiency is the highest value for organic solar cells to date. The external quantum efficiency (EQE) spectrum for D18 cells is shown in Fig. 1e. The cells afford > 80% EQE at 460–740 nm, with a maximum of 87% at 540 nm, suggesting efficient photocurrent generation. D18 cells present a high exciton dissociation probability ( $P_{\text{diss}}$ ) of 98.6% (Fig. S8 online). Hole and electron mobilities ( $\mu_h$  and  $\mu_e$ ) were measured by using space charge limited current (SCLC) method (Figs. S9–S11 and Table S5 online). Pure D18 film shows a  $\mu_h$  of  $1.59 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . This mobility is higher than that of D16 reported previously ( $\mu_h$ ,  $1.19 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) [30], suggesting that the larger molecular plane of DTBT than DTTP might promote polymer packing and enhance  $\mu_h$ . The D18:Y6 blend film presents a  $\mu_h$  of  $1.49 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and a  $\mu_e$  of  $1.40 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The balanced charge carrier transport ( $\mu_h/\mu_e = 1.06$ ) accounts for the high FF. We investigated bimolecular recombination by plotting  $J_{\text{sc}}$  against light intensity ( $P_{\text{light}}$ ) (Fig. S12 online). The data were fitted to a power law:  $J_{\text{sc}} \propto P_{\text{light}}^\alpha$ . An  $\alpha$  of 0.980 is extracted, suggesting less recombination. The surface morphology for D18:Y6 blend films with and without SVA were studied by using atomic force microscope (AFM) (Fig. S13 online). Nanofibers with a diameter around 20 nm were observed in both films. The SVA promotes the aggregation of nanofibers to form bundle-like structures (Fig. 1f), which may favor to generate more free charge carriers, reduce charge recombination, facilitate charge transport, thus improving  $J_{\text{sc}}$  and FF.

In summary, a D-A copolymer donor D18 based on a fused-ring acceptor unit DTBT was developed. D18 has a high hole mobility of  $1.59 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The D18:Y6 solar cells gave a PCE of 18.22%, which is the highest efficiency achieved from organic solar cells to date. This work demonstrates the great potential of DTBT-based copolymer donors for organic solar cells. With a wide band-gap of 1.98 eV, D18 will find interesting application in ternary solar cells and tandem solar cells.

## Conflict of interest

The authors declare that they have no conflict of interest.

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## Author contributions

Qishi Liu, Yufan Jiang, Ke Jin, Jianqiang Qin, Jingui Xu, Wenting Li, Ji Xiong and Jinfeng Liu performed the experiments. Zuo Xiao, Kuan Sun, Shangfeng Yang and Xiaotao Zhang participated in the discussion on experimental results. Liming Ding directed this project.

## Appendix A. Supplementary materials

Supplementary materials to this article can be found online at <https://doi.org/10.1016/j.scib.2020.01.001>.

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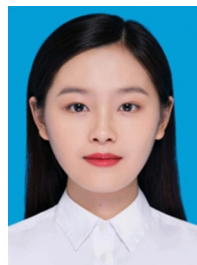
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