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Short Communication

Thiolactone copolymer donor gifts organic solar cells a 16.72% efficiency ☆

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Since 1995, bulk-heterojunction organic solar cells consisting of one or two organic donors and one or two organic acceptors have been fighting for high power conversion efficiencies (PCEs) and good stability [1]. Until recent years, this next-generation photovoltaic technology starts to offer decent PCEs, shedding the light on commercialization, and attracting great attention again [2–14]. Compared with the continuously emerging high-performance nonfullerene acceptors, high-performance donors are rare. Only a few donor-acceptor (D-A) copolymer donors like PM6 [15] and P2F-EHp [16] gave >15% PCEs. Developing more high-performance donors is a great mission for the field. Recently, our group reported new D-A copolymers based on fused-ring aromatic lactone (FRAL) building block. Owing to the strong electron-withdrawing capability and extended molecular plane of FRAL, the copolymers present deep the highest occupied molecular orbital (HOMO) levels and good hole mobility. The copolymer L1 based on a tricyclic lactone unit, 5H-dithieno[3,2-b:2′,3′-d]pyran-5-one (DTP), offered a 14.36% PCE in inverted solar cells [17]. To fully exploit the potential of FRAL copolymers, in this work, we developed a new copolymer D16 by using a thiolactone unit, 5H-dithieno[3,2-b:2′,3′-d]thiopyran-5-one (DTTP) (Fig. 1a). From L1 to D16, the simple replacement of lactone with thiolactone enhanced π-π stacking, gifting D16 higher hole mobility. Conventional solar cells with D16 as the donor and Y6 [15] as the acceptor gave high PCEs up to 16.72%.

The synthetic route for D16 is shown in Scheme S1 (online). 3-Bromothiophene coupled with 2-ethylhexyl 3-mercaptopropanoate gave 2-ethylhexyl 3-(thiophen-3-ylthio)propanoate in 82% yield. Treating 2-ethylhexyl 3-(thiophen-3-ylthio)propanoate with *N*-bromosuccinimide (NBS) afforded 2-ethylhexyl 3-((2-bromothiophen-3-yl)thio)propanoate in 87% yield. Stille coupling of 2-ethylhexyl 3-((2-bromothiophen-3-yl)thio)propanoate and ethyl 2-(tributylstannyl)thiophene-3-carboxylate gave compound **1** in 72% yield. Treating **1** with NaOEt followed by acidification afforded the thiol intermediate, ethyl 3′-mercapto-[2,2′-bithiophene]-3-carboxylate. This intermediate was not purified and was directly used in next-step intramolecular transesterification reaction, and the thiolactone DTTP was obtained in 74% yield. Treating DTTP with NBS gave DTTP-Br in 88% yield. Stille coupling of DTTP-Br and (4-(2-butyloctyl)thiophen-2-yl)trimethylstannane gave compound **2** in 91% yield. Bromination of compound **2** with NBS gave the monomer, compound **3**, in 86% yield. Finally, Stille copolymerization of compound **3** with (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl) benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT-Sn) gave D16 in 81% yield. All compounds were characterized by spectroscopic techniques, i.e., ^{1}H NMR, ^{13}C NMR and mass spectrometry. To further confirm the structure of DTTP, we prepared its derivative DTTP-2T and obtained its single crystals (Scheme S2 online). The structure of DTTP-2T from single-crystal XRD analysis

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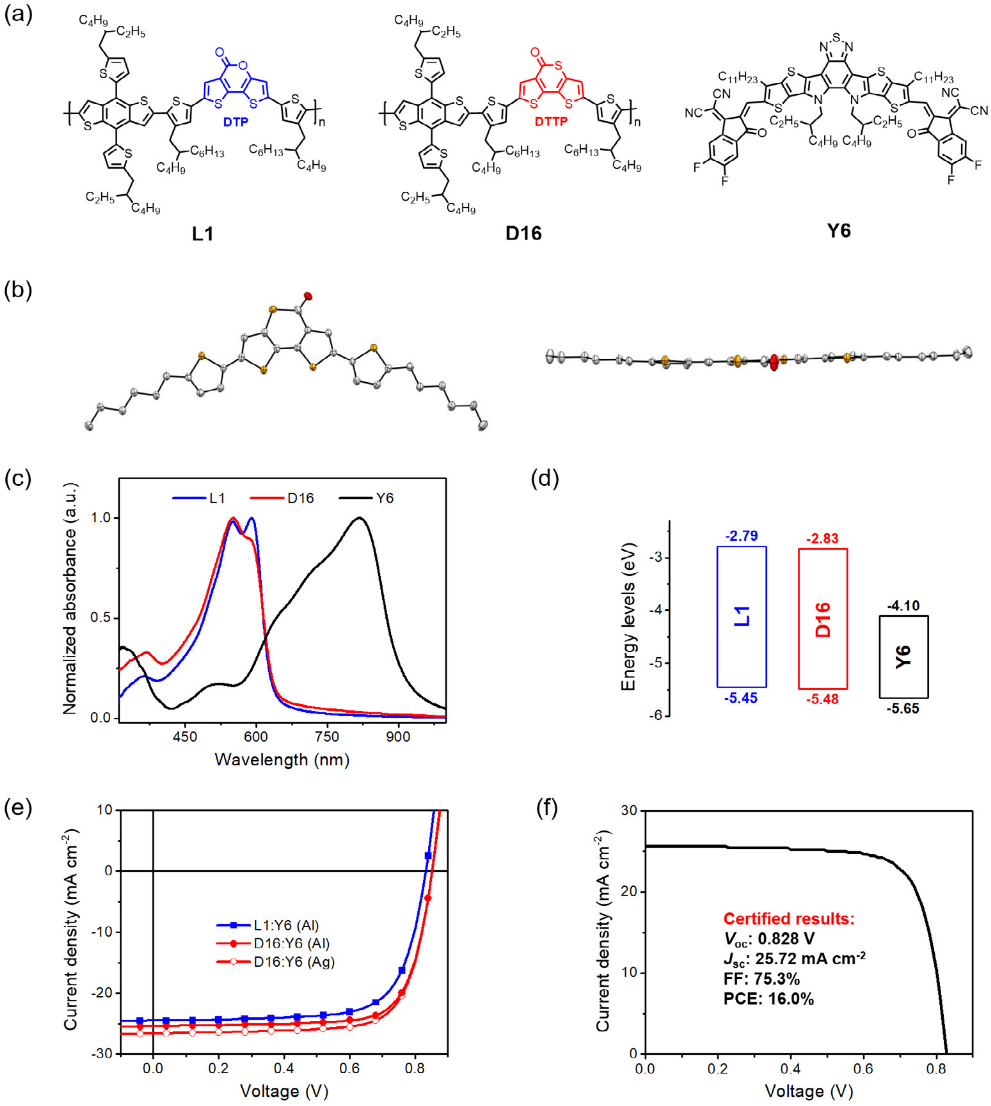

Fig. 1. A highly efficient D-A copolymer donor based on a thiolactone unit. (a) The chemical structures for L1, D16 and Y6; (b) top view (left) and side view (right) for the single crystal structure of DTTP-2T; (c) absorption spectra for L1, D16 and Y6 films; (d) energy level diagram; (e) *J-V* curves for the solar cells; (f) NIM measurement result for D16:Y6 solar cells with Ag electrode.

is presented in Fig. 1b. The top view confirmed the thiolactone structure of DTTP. The side view shows the good coplanarity of DTTP with the two adjacent thiophenes. The dihedral angle between DTTP and thiophene is less than 6°. The good coplanarity favors intermolecular π-π stacking and charge carrier transport. D16 shows good solubility in common solvents such as chloroform and chlorobenzene. The number-average molecular weights (M_n) and the polydispersity index (PDI) for D16 are 35.8 kDa and 1.86, respectively.

The absorption spectra for L1, D16 and Y6 films are shown in Fig. 1c. D16 presents a peak at 551 nm and a shoulder at 588 nm. Compared with L1, D16 shows higher absorbance at short wavelength. The optical bandgap (E_g^{opt}) of D16 estimated from the absorption onset is 1.95 eV, which is slightly smaller than that of L1 [17]. The HOMO and the lowest unoccupied molecular orbital (LUMO) levels of D16 estimated from cyclic voltammetry (CV) measurement are −5.48 and −2.83 eV, respectively (Fig. S18 online and Fig. 1d). Compared with L1, D16 has lower HOMO and LUMO levels, suggesting the stronger electron-withdrawing capability of DTTP than that of DTP. The deeper HOMO level of D16 favors to produce higher open-circuit voltage (V_{oc}) in solar cells. The X-ray diffraction (XRD) profiles for L1 and D16 films are presented in Fig. S19 (online). Compared with L1, D16 shows a stronger (0 1 0) diffraction peak ($2\theta = \sim 23.6°$), indicating its enhanced π-π stacking. The additional S atom in DTTP might strengthen the interaction between polymer backbones via S···S interaction, thus enhancing π-π stacking [18]. This benefits charge carrier mobility. The hole mobilities (μ_h) for L1 and D16 were measured by using space charge limited current (SCLC) method (Fig. S20 online). As expected, D16 film has a μ_h of 1.19×10^{-3} cm^2 V^{-1} s^{-1}, which is higher than that of L1 (7.20×10^{-4} cm^2 V^{-1} s^{-1}).

Conventional solar cells with a structure of ITO/PEDOT:PSS/active layer/PDIN/Al were made to evaluate the performance of donors L1 and D16. The D/A ratio, active layer thickness and additive content were optimized (Tables S1–S6 online). The best L1:Y6 cells gave a PCE of 14.63%, with a V_{oc} of 0.83 V, a short-circuit current density (J_{sc}) of 24.49 mA cm^{-2} and a fill factor (FF) of 71.8%, while the best D16:Y6 cells gave a PCE of 16.22%, with a V_{oc} of 0.85 V, a J_{sc} of 25.41 mA cm^{-2} and a FF of 74.9% (Fig. 1e). Compared with L1 cells, D16 cells present simultaneously enhanced V_{oc}, J_{sc} and FF. The higher V_{oc} is due to the deeper HOMO level of D16. The higher J_{sc} originates from the enhanced external quantum efficiency (EQE) of D16 cell (Fig. S23 online). D16 cells gave higher EQE than L1 cells at 300–950 nm. The maximum EQE for L1 and D16 cells are 76% and 83%, respectively. The exciton dissociation probabilities (P_{diss}) for L1 and D16 cells are 96.7% and 97.8%, respectively, suggesting more efficient charge generation in the latter (Fig. S24 online). Hole and electron mobilities (μ_h and μ_e) were measured for L1:Y6 and D16:Y6 blend films (Figs. S21, S22 and Table S8 online). Compared with L1:Y6 blend film, D16:Y6 blend film has higher μ_h (2.82×10^{-4} cm^2 V^{-1} s^{-1}) and μ_e (2.81×10^{-4} cm^2 V^{-1} s^{-1}), and more balanced charge carrier transport ($\mu_h/\mu_e = 1.01$). The study on bimolecular recombination indicated less charge recombination in D16 cells (α closer to 1) (Fig. S25 online). Faster and more balanced charge transport as well as suppressed charge recombination account for the higher J_{sc} and FF for D16 cells. The atomic force microscope (AFM) images for D16:Y6 blend film show clear nanofiber structures with a diameter around 16 nm (Fig. S26 online). Such morphology favors exciton dissociation and charge transport, thus leading to high J_{sc} and FF.

To further improve the efficiency for D16 solar cells, we made devices by using Ag electrode, considering the higher reflectance of Ag at visible and near-infrared region [19]. The D16 cells with Ag electrode show enhanced EQE and higher J_{sc} compared with cells with Al electrode. The best cells gave a PCE of 16.72%, with a V_{oc} of 0.85 V, a J_{sc} of 26.61 mA cm^{-2} and a FF of 73.8% (Fig. 1e). D16 solar cells with Ag electrode were also measured at the National Institute of Metrology, Beijing (NIM), and a certified PCE of 16.0% (V_{oc}, 0.828 V; J_{sc}, 25.72 mA cm^{-2}; FF, 75.3%; effective area, 4.911 mm^2) was recorded (Figs. 1f and S27 online). The PCE difference might result from the device decay.

In summary, a FRAL copolymer donor D16 based on a thiolactone unit DTTP was developed. Compared with the lactone analogue L1, D16 presents enhanced π-π stacking and higher hole mobility. The solar cells based on the D16:Y6 blend afforded >16% PCE. This work demonstrates the great potential of FRAL copolymer donors in organic solar cells. Further work in optimizing the chemical structure for D16 family is underway.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scib.2019.10.002.

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