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Short Communication

5H-dithieno[3,2-b:2′,3′-d]pyran-5-one unit yields efficient wide-bandgap polymer donors

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Recently, great progress has been made in organic solar cells due to the emergence of high-performance nonfullerene acceptors [1–6]. Over 16% and 17% power conversion efficiencies (PCEs) were achieved for nonfullerene-acceptor-based single-junction and tandem cells, respectively [7,8]. Owing to complementary light absorption, wide-bandgap donor-acceptor (D-A) copolymers are ideal electron-donating partners for nonfullerene acceptors. However, efficient D-A copolymer donors are still limited. The reported donors include: copolymers based on carboxylic ester-functionalized thiophene [9], copolymers based on benzo[1,2-c:4,5-c′]dithiophene-4,8-dione [10], copolymers based on benzo[d][1,2,3]triazole [11] and copolymers based on polycyclic aromatic lactam units [12,13]. Novel and high-performance D-A copolymer donors are desired. In this context, we propose using fused-ring aromatic lactone (FRAL) as a building block to develop D-A copolymer donors. The strong electron-withdrawing capability of FRAL unit could lower the highest occupied molecular orbital (HOMO) levels, thus enhancing open-circuit voltage (V_{oc}) for solar cells. The extended and rigid molecular plane of FRAL could favour π-π stacking, thus improving the hole mobility of the copolymers and enhancing short-circuit current density (J_{sc}) and fill factor (FF). FRAL-based D-A copolymer donors have not been reported yet. In this communication, we report two D-A copolymers, L1 and L2, based on 5H-dithieno[3,2-b:2′,3′-d]pyran-5-one unit (Fig. 1a). L1 and L2 present wide bandgaps and deep HOMO levels. Inverted solar cells with them as the donor and Y6 [14] as the acceptor gave decent PCEs up to 14.36%.

The copolymers L1 and L2 were synthesized via Stille copolymerization of the lactone monomer M1 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) and (4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b′,]dithiophene-2,6-diyl)bis(trimethylstannane) (FBDT-Sn), respectively (Scheme S1 online). The synthesis details are given in the Supplementary materials. L1 and L2 show good solubility in common solvents such as chloroform and chlorobenzene. The number-average molecular weights (M_n) for L1 and L2 are 49.4 and 27.9 kDa, respectively, and the polydispersity indexes (PDI) are 1.73 and 1.88, respectively.

The absorption spectra for L1 and L2 in chloroform and as films are shown in Fig. S9 (online) and Fig. 1b, respectively. In solution, L1 and L2 show similar spectra with a low-energy peak at 590 and 592 nm, respectively, and a high-energy peak at 551 and 549 nm, respectively. For films, the high-energy peak intensifies and no peak shifts. The absorption onsets for L1 and L2 films are ~634 nm, corresponding to a large optical bandgap (E_g^{opt}) of 1.96 eV. The above results indicate that fluorine substitution has insignificant influence to the optical property of the copolymers. Y6 film shows strong absorption at 570–920 nm, which is complementary with that of L1 and L2. The HOMO and the lowest unoccupied molecular orbital (LUMO) levels for L1 and L2 were estimated by cyclic voltammetry (CV) (Fig. S10 online). The HOMO levels for L1 and L2 are −5.45 and −5.52 eV, respectively, and the LUMO levels are −2.79 and −2.91 eV, respectively (Fig. 1c). The fluorine atoms push down HOMO and LUMO levels for L2. The deep HOMO levels of L1 and L2 favor to produce high V_{oc} in solar cells. The acceptor Y6 has a HOMO of −5.65 eV and a LUMO of −4.10 eV [14].

Inverted solar cells with a structure of ITO/ZnO/active layer/MoO_3/Ag were made to evaluate the performance of L1 and L2. *J-V* curves and external quantum efficiency (EQE) spectra are

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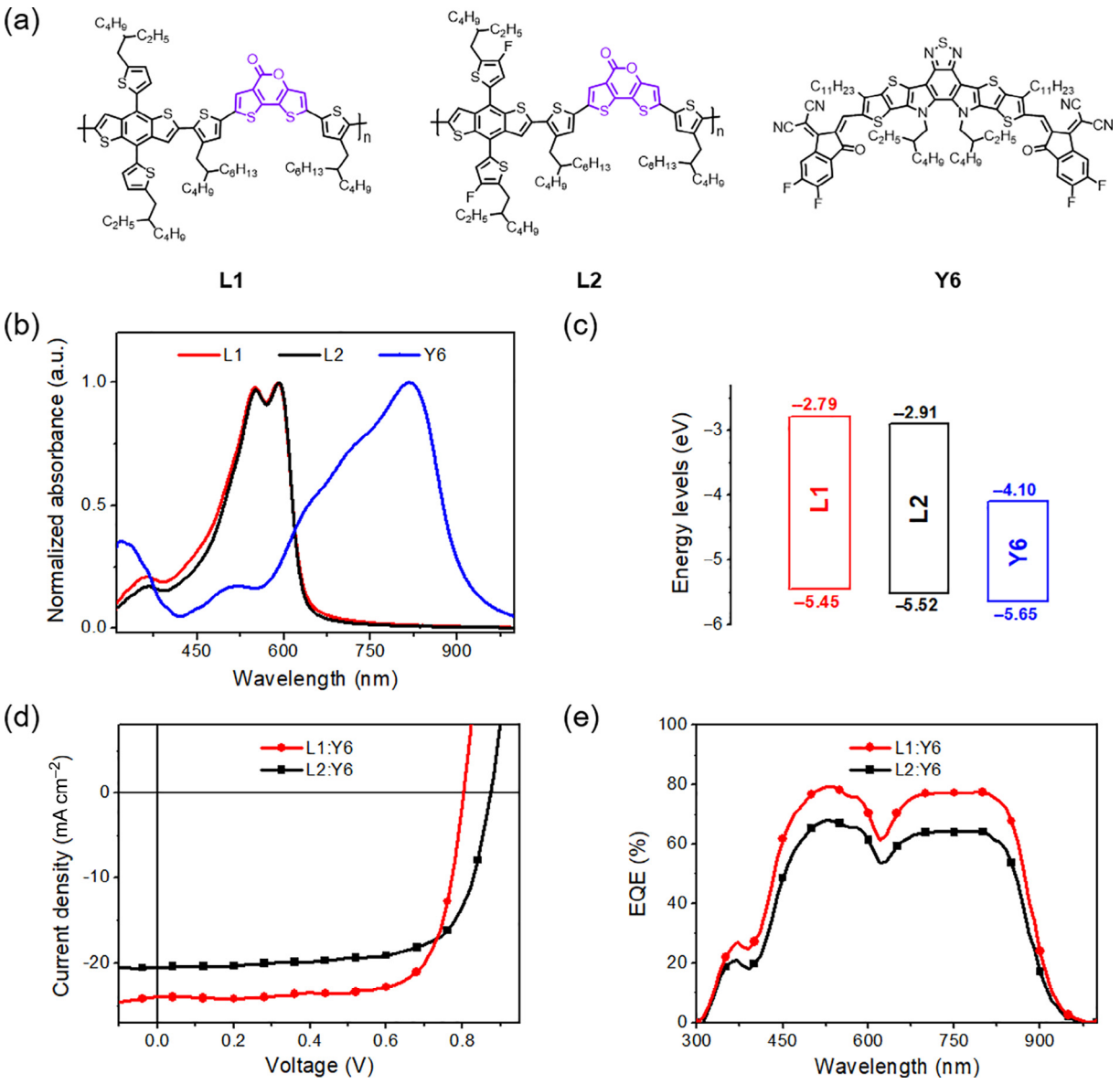

Fig. 1. Efficient D-A copolymer donors based on a fused-ring aromatic lactone unit. (a) The structures for L1, L2 and Y6; (b) absorption spectra for L1, L2 and Y6 films; (c) energy level diagram; (d) *J-V* curves for the solar cells; (e) EQE spectra for the solar cells.

shown in Fig. 1d and e, respectively. The best L1:Y6 solar cells gave a PCE of 14.36%, with a V_{oc} of 0.80 V, a J_{sc} of 23.93 mA cm^{-2} and a FF of 74.7%. These cells have a D/A ratio of 1:1 (w/w), an active layer thickness of 103 nm and no additive (Tables S1–S3 online). The best L2:Y6 solar cells gave a PCE of 12.57%, with a V_{oc} of 0.87 V, a J_{sc} of 20.52 mA cm^{-2} and a FF of 70.2%. These cells have a D/A ratio of 1:1 (w/w), an active layer thickness of 102 nm and no additive (Tables S4–S6 online). The V_{oc} for L1 cells is 0.07 V smaller than that of L2 cells because of the higher HOMO level of L1. J_{sc} and FF for L1 cells are much higher than that of L2 cells. L1 cells gave higher EQE than L2 cells in 340–950 nm region. The maximum EQE for L1 and L2 cells are 79% and 68%, respectively. The integrated current densities from EQE spectra are 23.05 and 19.10 mA cm^{-2}, respectively, which are consistent with the J_{sc} from *J-V* measurements. Exciton dissociation probabilities (P_{diss}) were evaluated (Fig. S11 online). P_{diss} for L1 and L2 cells are 96.7% and 94.7%, respectively. The higher P_{diss} for L1 cells suggests more efficient charge generation, thus benefiting J_{sc}. Hole and electron mobilities (μ_h and μ_e) were measured by using space charge limited current (SCLC) method (Figs. S12, S13 and Table S7 online). Compared with L2:Y6 blend film, L1:Y6 blend film shows higher μ_h (5.62×10^{-4} cm^2 V^{-1} s^{-1}) and μ_e (4.77×10^{-4} cm^2 V^{-1} s^{-1}), and more balanced charge carrier transport (μ_h/μ_e closer to 1). We investigated bimolecular recombination by plotting J_{sc} against light intensity (P_{light}) (Fig. S14 online). The data were fitted to a power law: $J_{sc} \propto P_{light}^{\alpha}$. The α values for L1 and L2 cells are 0.971 and 0.951, respectively, suggesting less charge recombination in the former. Faster and more balanced charge transport as well as suppressed charge recombination account for the higher J_{sc} and FF for L1 solar cells. The morphology of the active layers was studied by using atomic force microscope (AFM) (Fig. S15 online). L1:Y6 and L2:Y6 blend films present typical nanofiber structures, which favor exciton dissociation and charge transport.

In summary, FRAL unit was first used to develop efficient polymer donors. The strong electron-withdrawing capability and the extended and rigid molecular plane of FRAL building block gift

the materials high V_{oc} and decent PCEs in nonfullerene solar cells. Continuous work in developing high-performance FRAL-based polymer donors is ongoing.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Jinfeng Liu and Ling Liu performed the experiments. Chuantian Zuo, Zuo Xiao, Yingping Zou and Zhiwen Jin 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.2019.09.001.

References

[1] Yan C, Barlow S, Wang Z, et al. Non-fullerene acceptors for organic solar cells. Nat Rev Mater 2018;3:18003.
[2] Xiao Z, Yang S, Yang Z, et al. Carbon-oxygen-bridged ladder-type building blocks for highly efficient nonfullerene acceptors. Adv Mater 2019. https://doi.org/10.1002/adma.201804790.
[3] Xiao Z, Liu F, Geng X, et al. A carbon-oxygen-bridged ladder-type building block for efficient donor and acceptor materials used in organic solar cells. Sci Bull 2017;62:1331–6.
[4] Xiao Z, Jia X, Li D, et al. 26 mA cm^{-2} J_{sc} from organic solar cells with a low-bandgap nonfullerene acceptor. Sci Bull 2017;62:1494–6.
[5] Xiao Z, Jia X, Ding L. Ternary organic solar cells offer 14% power conversion efficiency. Sci Bull 2017;62:1562–4.
[6] Liu L, Liu Q, Xiao Z, et al. Induced *J*-aggregation in acceptor alloy enhances photocurrent. Sci Bull 2019;64:1083–6.
[7] An Q, Ma X, Gao J, et al. Solvent additive-free ternary polymer solar cells with 16.27% efficiency. Sci Bull 2019;64:504–6.
[8] Meng L, Zhang Y, Wan X, et al. Organic and solution-processed tandem solar cells with 17.3% efficiency. Science 2018;361:1094–8.
[9] Li S, Ye L, Zhao W, et al. A wide band gap polymer with a deep highest occupied molecular orbital level enables 14.2% efficiency in polymer solar cells. J Am Chem Soc 2018;140:7159–67.
[10] Zhao W, Qian D, Zhang S, et al. Fullerene-free polymer solar cells with over 11% efficiency and excellent thermal stability. Adv Mater 2016;28:4734–9.
[11] Lin Y, Zhao F, Prasad S, et al. Balanced partnership between donor and acceptor components in nonfullerene organic solar cells with > 12% efficiency. Adv Mater 2018;30:1706363.
[12] An M, Xie F, Geng X, et al. A high-performance D-A copolymer based on dithieno[3,2-b:2′,3′-d]pyridin-5(4H)-one unit compatible with fullerene and nonfullerene acceptors in solar cells. Adv Energy Mater 2017;7:1602509.
[13] Gao Y, Li D, Xiao Z, et al. High-performance wide-bandgap copolymers with dithieno[3,2-b:2′,3′-d]pyridin-5(4H)-one units. Mater Chem Front 2019;3:399–402.
[14] Yuan J, Zhang Y, Zhou L, et al. Single-junction organic solar cell with over 15% efficiency using fused-ring acceptor with electron-deficient core. Joule 2019;3:1140–51.

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