Science Bulletin 64 (2019) 1083–1086

Contents lists available at ScienceDirect

Science Bulletin

journal homepage: www.elsevier.com/locate/scib

Short Communication

Induced *J*-aggregation in acceptor alloy enhances photocurrent

Ling Liu [a,b,1], Qishi Liu [a,1], Zuo Xiao [a,*], Shangfeng Yang [c,*], Yongbo Yuan [d,*], Liming Ding [a,b,*]

[a] *Center for Excellence in Nanoscience (CAS), Key Laboratory of Nanosystem and Hierarchical Fabrication (CAS), National Center for Nanoscience and Technology, Beijing 100190, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*
[c] *Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China*
[d] *School of Physics & Electronics, Central South University, Changsha 410083, China*

ARTICLE INFO

Article history:
Received 31 May 2019
Received in revised form 1 June 2019
Accepted 3 June 2019
Available online 7 June 2019

Carbon-oxygen-bridged (CO-bridged) ladder-type units already proved to be promising electron-donating building blocks for making acceptor-donor-acceptor (A-D-A) nonfullerene acceptors [1]. Compared with traditional carbon-bridged (C-bridged) units, CO-bridged units present stronger electron-donating capability due to electron-rich oxygen atoms. Their A-D-A acceptors show lower bandgaps and stronger light-harvesting capability due to enhanced intramolecular charge transfer (ICT). Ding et al. have designed pentacyclic [2], hexacyclic [3], heptacyclic [4] and octacyclic [5,6] CO-bridged units, and corresponding A-D-A acceptors. Among CO-bridged units, the octacyclic unit CO$_i$8 shows the strongest electron-donating capability and the largest molecular plane, rendering A-D-A acceptor CO$_i$8DFIC a very low bandgap of 1.26 eV and good electron mobility. CO$_i$8DFIC shows excellent near infrared (NIR) light-harvesting capability and outstanding performance in organic solar cells. Single-junction and tandem solar cells based on CO$_i$8DFIC gave record power conversion efficiencies (PCEs) of 14.62% and 17.36%, respectively [7,8]. In this work, a decacyclic CO-bridged unit CO$_i$10 and its A-D-A acceptor CO$_i$10DFIC were developed (Fig. 1a). CO$_i$10DFIC possesses a larger molecular plane and a lower bandgap than CO$_i$8DFIC. PTB7-Th:CO$_i$10DFIC solar cells afforded a PCE of 10.90%. CO$_i$10DFIC can induce remarkable *J*-aggregation of CO$_i$8DFIC. Ternary solar cells based on PTB7-Th, CO$_i$10DFIC and CO$_i$8DFIC gave high photocurrent and a decent PCE of 13.48%.

CO$_i$10DFIC was synthesized via a "demethylation-trans esterification" approach [1]. The synthetic details are given in the Supplementary data. The overall yield for CO$_i$10DFIC is 32%. CO$_i$10-DFIC was characterized by nuclear magnetic resonance (NMR) and mass spectroscopy (see the Supplementary data). Considering the relatively large molecular plane of CO$_i$10DFIC, we used (2-butyloctyl)phenyl instead of the commonly used hexylphenyl as the side chains. The bulky (2-butyloctyl)phenyl side chains can prevent over aggregation of the A-D-A acceptors with large molecular planes and ensure good solubility [9]. CO$_i$10DFIC is soluble in common solvents like chloroform, toluene and chlorobenzene. The absorption spectra for CO$_i$10DFIC, CO$_i$8DFIC and PTB7-Th films are shown in Fig. S13 (online). Compared with CO$_i$8DFIC, CO$_i$10DFIC presents a red shift in its absorption spectrum, with a peak at 887 nm and an absorption onset at 1,003 nm. The optical bandgap (E_g^{opt}) for CO$_i$10DFIC is 1.24 eV. The smaller E_g^{opt} for CO$_i$10DFIC than CO$_i$8DFIC suggests the stronger electron-donating capability of CO$_i$10 than CO$_i$8. The absorption spectrum of CO$_i$10DFIC is complementary with that of the donor PTB7-Th (absorption band at 500–800 nm). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels for CO$_i$10DFIC were evaluated by cyclic voltammetry (CV) (Fig. S14 online). The HOMO and LUMO energy levels were calculated from the onset potentials of oxidation (E_{ox}^{on}) and reduction (E_{red}^{on}), respectively, i.e., $\mathrm{HOMO} = -(E_{ox}^{on} + 4.8)$ and $\mathrm{LUMO} = -(E_{red}^{on} + 4.8)$. The energy level diagram is shown in Fig. S15 (online). Compared with CO$_i$8DFIC, CO$_i$10DFIC shows higher LUMO (−3.86 eV) and HOMO (−5.45 eV) levels. The higher LUMO for CO$_i$10DFIC can lead to a higher open-circuit voltage (V_{oc}) in solar cells. From PTB7-Th to CO$_i$10DFIC and CO$_i$8DFIC, an energy level cascade forms in either HOMO or LUMO, suggesting that they can be applied in a ternary solar cell [10].

Binary and ternary solar cells with a structure of ITO/ZnO/active layer/MoO_3/Ag were made to evaluate the performance of CO$_i$10-DFIC. *J-V* curves and external quantum efficiency (EQE) spectra are shown in Fig. 1b and c, respectively. The best PTB7-Th:CO$_i$10DFIC cells gave a PCE of 10.90%, with a V_{oc} of 0.75 V, a short-circuit current density (J_{sc}) of 21.97 mA cm^{-2} and a fill factor

---

[*] Corresponding authors.
E-mail addresses: xiaoz@nanoctr.cn (Z. Xiao), sfyang@ustc.edu.cn (S. Yang), yuanyb@csu.edu.cn (Y. Yuan), ding@nanoctr.cn (L. Ding).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.scib.2019.06.005
2095-9273/

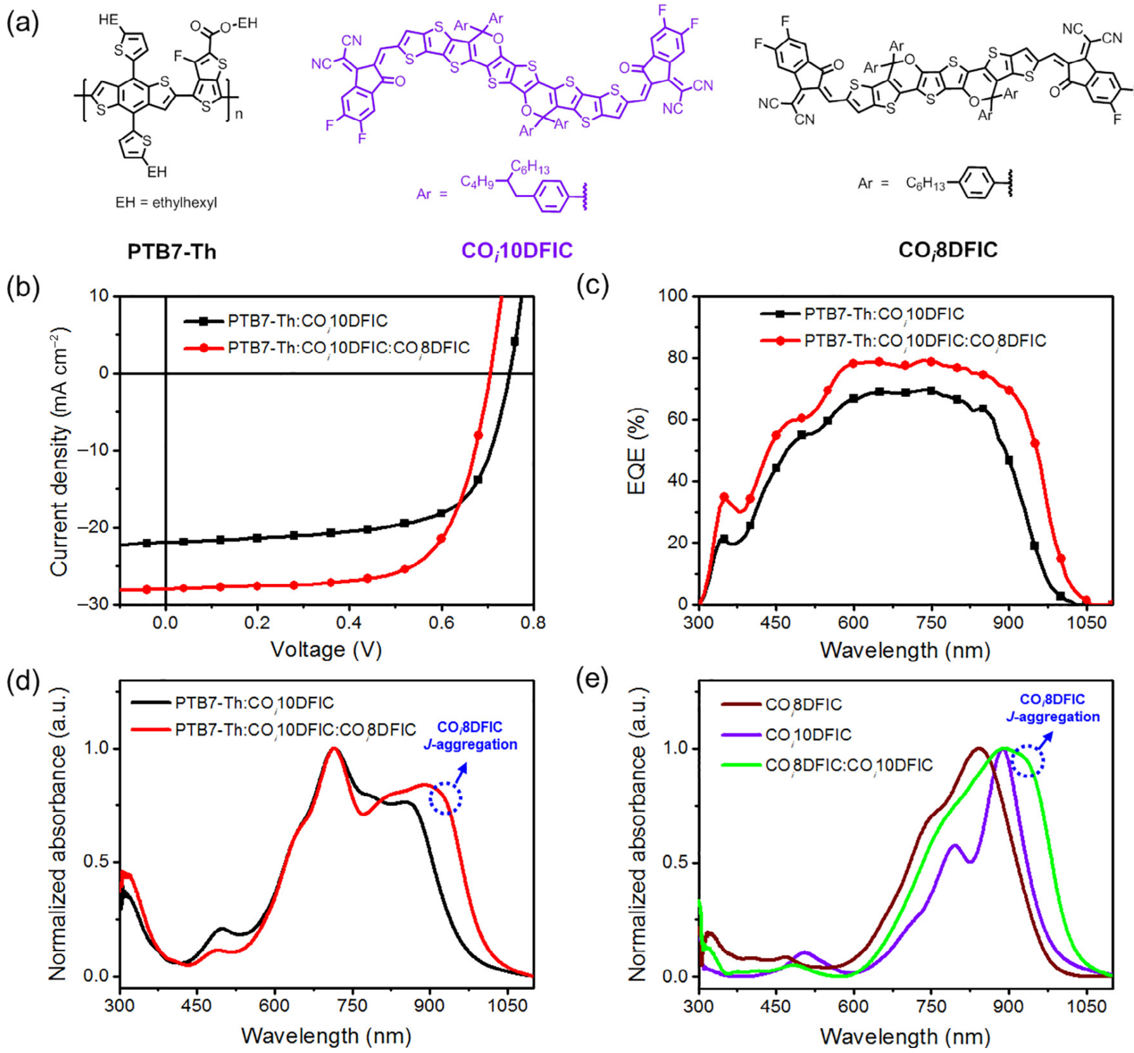

Fig. 1. Induced *J*-aggregation in acceptor alloy enhances photocurrent. (a) The structures for PTB7-Th, CO$_i$10DFIC and CO$_i$8DFIC; (b) *J-V* curves for the binary and ternary solar cells; (c) EQE spectra for the binary and ternary solar cells; (d) absorption spectra for PTB7-Th:CO$_i$10DFIC (1:1.4) and PTB7-Th:CO$_i$10DFIC:CO$_i$8DFIC (1:0.4:1) blend films; (e) absorption spectra for CO$_i$8DFIC, CO$_i$10DFIC and CO$_i$8DFIC:CO$_i$10DFIC (1:0.4) films.

(FF) of 66.4%. These cells have a D/A ratio of 1:1.4 (w/w), an active layer thickness of 98 nm and 0.2 vol.% 1-chloronaphthalene (CN) as the additive (Tables S1–S3 online). PTB7-Th:CO$_i$10DFIC cells gave higher V_{oc} than the reported PTB7-Th:CO$_i$8DFIC cells due to the higher LUMO of CO$_i$10DFIC [5]. The best PTB7-Th:CO$_i$10DFIC:CO$_i$8-DFIC (D:A$_1$:A$_2$) ternary cells gave a PCE of 13.48%, with a V_{oc} of 0.71 V, a J_{sc} of 27.97 mA cm^{-2} and a FF of 68.3%. These cells have a D/A$_1$/A$_2$ ratio of 1:0.4:1 (w/w/w), an active layer thickness of 103 nm and 1.3 vol.% 1,8-diiodooctane (DIO) as the additive (Tables S4–S6 online). Compared with the binary cells, the ternary cells afforded much higher J_{sc} due to the stronger and broader EQE response. Over 70% EQE at 550–900 nm was observed for ternary cells, while the maximum EQE for binary cells is 69% (Fig. 1c). The exciton dissociation probabilities (P_{diss}) for the binary and ternary cells are 94.1% and 98.1%, respectively, suggesting more efficient charge generation in the latter (Fig. S16 online). To understand why ternary cells gave a broader EQE spectrum, we investigated the absorption spectra for the binary and ternary blend films (Fig. 1d). Compared with PTB7-Th:CO$_i$10DFIC blend film, PTB7-Th:CO$_i$10DFIC:CO$_i$8DFIC blend film gave a broader absorption spectrum with a new NIR peak at ~910 nm. According to our previous study, this peak originates from the *J*-aggregation of CO$_i$8DFIC [11]. Fullerene or nonfullerene molecules can promote the *J*-aggregation of CO$_i$8DFIC, thus broadening the absorption and EQE spectra [6,12,13]. CO$_i$10DFIC can induce the *J*-aggregation of CO$_i$8DFIC, as the absorption spectrum for CO$_i$10DFIC:CO$_i$8DFIC blend film can confirm this (Fig. 1e). Since both HOMO and LUMO levels of CO$_i$10-DFIC are higher than that of CO$_i$8DFIC, there might be photo-induced charge transfer between CO$_i$10DFIC and CO$_i$8DFIC. To figure out this, we made three cells with CO$_i$10DFIC, CO$_i$8DFIC and CO$_i$10DFIC:CO$_i$8DFIC as the active layer, respectively (Fig. S17 and Table S7 online). The J_{sc} for CO$_i$10DFIC:CO$_i$8DFIC cell is between that for CO$_i$10DFIC cell and CO$_i$8DFIC cell, suggesting negligible photo-induced charge transfer between CO$_i$10DFIC and CO$_i$8DFIC [14].

Hole and electron mobilities (μ_h and μ_e) were measured by using space charge limited current (SCLC) method (Figs. S18, S19 and Table S8 online). From binary cells to ternary cells, μ_h increased from 1.55×10^{-4} to 4.31×10^{-4} cm^2 V^{-1} s^{-1}, μ_e from 1.95×10^{-5} to 7.03×10^{-5} cm^2 V^{-1} s^{-1}, and μ_h/μ_e decreased from 7.9 to 6.1. The charge carrier transport is more balanced in ternary cells, leading to higher J_{sc} and FF. We studied bimolecular recombination by plotting J_{sc} against light intensity (P_{light}). The data were fitted to a power law: $J_{sc} \propto P_{light}{}^{\alpha}$. The α values for binary and ternary cells are 0.988 and 0.996, respectively, suggesting less bimolecular recombination in ternary cells (Fig. S20 online). The suppressed charge recombination in ternary cells is beneficial to J_{sc} and FF.

The thermal stability for the solar cells was tested by continuously heating them at 120 °C. PTB7-Th:CO$_i$10DFIC cells show higher thermal stability than PTB7-Th:CO$_i$8DFIC cells (Fig. S21 online). After being heated for 120 h, PTB7-Th:CO$_i$10DFIC and PTB7-Th:CO$_i$8DFIC cells retained 58% and 50% of the initial PCE, respectively. The higher molecular weight of CO$_i$10DFIC might reduce the mobility of molecules and enhance the phase stability. PTB7-Th:CO$_i$10DFIC:CO$_i$8DFIC ternary cells kept 61% of the initial PCE after being heated for 120 h. In ternary cells, CO$_i$10DFIC and CO$_i$8DFIC could form an alloy, thus increasing the entropy of the blend system and improving the thermal stability [15].

In summary, a decacyclic ladder-type building block CO$_i$10 and its A-D-A acceptor CO$_i$10DFIC were developed. Compared with CO$_i$8DFIC, CO$_i$10DFIC possesses a larger molecular plane, a lower bandgap and a higher LUMO level. PTB7-Th:CO$_i$10DFIC solar cells present higher V_{oc} and better thermal stability than PTB7-Th:CO$_i$8DFIC cells. PTB7-Th:CO$_i$10DFIC:CO$_i$8DFIC ternary cells gave a decent PCE of 13.48%. CO$_i$10DFIC can be applied in organic solar cells as a NIR-absorbing electron acceptor. The *J*-aggregation inducement in the acceptor alloy can be a very useful approach for enhancing PCE for organic solar cells.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (2017YFA0206600), the National Natural Science Foundation of China (51773045, 21572041 and 21772030) and the Youth Association for Promoting Innovation (CAS).

Author contributions

Ling Liu and Qishi Liu performed the experiments. Zuo Xiao, Shangfeng Yang, and Yongbo Yuan participated in the discussion on experimental results. Liming Ding directed this project.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scib.2019.06.005.

References

[1] 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.
[2] 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.
[3] Li T, Zhang H, Xiao Z, et al. A carbon-oxygen-bridged hexacyclic ladder-type building block for low-bandgap nonfullerene acceptors. Mater Chem Front 2018;2:700–3.
[4] Jin K, Deng C, Zhang L, et al. A heptacyclic carbon-oxygen-bridged ladder-type building block for A-D-A acceptors. Mater Chem Front 2018;2:1716–9.
[5] 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.
[6] Xiao Z, Jia X, Ding L. Ternary organic solar cells offer 14% power conversion efficiency. Sci Bull 2017;62:1562–4.
[7] Li H, Xiao Z, Ding L, et al. Thermostable single-junction organic solar cells with a power conversion efficiency of 14.62%. Sci Bull 2018;63:340–2.
[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] Chang M, Wang Y, Yi Y, et al. Fine-tuning side-chains of non-fullerene small molecule acceptors to match with appropriate polymer donors. J Mater Chem A 2018;6:8586–94.
[10] Liu X, Yan Y, Yao Y, et al. Ternary blend strategy for achieving high-efficiency organic solar cells with nonfullerene acceptors involved. Adv Funct Mater 2018;28:1802004.
[11] Li W, Chen M, Cai J, et al. Molecular order control of non-fullerene acceptors for high-efficiency polymer solar cells. Joule 2019;3:819–33.
[12] Zhang M, Xiao Z, Gao W, et al. Over 13% efficiency ternary nonfullerene polymer solar cells with tilted up absorption edge by incorporating a medium bandgap acceptor. Adv Energy Mater 2018;8:1801968.
[13] Zhao Q, Xiao Z, Qu J, et al. Elevated stability and efficiency of solar cells via ordered alloy co-acceptors. ACS Energy Lett 2019;4:1106–14.
[14] An Q, Zhang F, Zhang J, et al. Enhanced performance of polymer solar cells through sensitization by a narrow band gap polymer. Sol Energy Mater Sol Cells 2013;118:30–5.
[15] de Zerio A, Müller C. Glass forming acceptor alloys for highly efficient and thermally stable ternary organic solar cells. Adv Energy Mater 2018;8:1702741.

Ling Liu got her B.S. degree from Sichuan Agricultural University in 2017. Now she is a Ph.D. student at University of Chinese Academy of Sciences under the supervision of Prof. Liming Ding. Since February 2017, she has been working in Liming Ding Group at National Center for Nanoscience and Technology. Her work focuses on organic solar cells and perovskite solar cells.

Zuo Xiao got his B.S. and Ph.D. degrees from Peking University under the supervision of Professor Liangbing Gan. He did postdoctoral research in Eiichi Nakamura Group at the University of Tokyo. In March 2011, he joined Liming Ding Group at National Center for Nanoscience and Technology as an Associate Professor. His current research focuses on organic solar cells.

Shangfeng Yang got his Ph.D. degree from Hong Kong University of Science and Technology in 2003. He then joined Leibniz Institute for Solid State and Materials Research, Dresden, Germany as an Alexander von Humboldt Fellow. In December 2007, he joined University of Science and Technology of China as a full professor. His research interests include the synthesis of fullerene-based nanocarbons toward applications in energy devices.

Yongbo Yuan got his B.S. degree in 2004 and Ph.D. degree in 2009 at Zhongshan University. Then he joined Jinsong Huang Group at University of Nebraska-Lincoln as a postdoc. In March 2016, he joined Central South University as a full professor. His research interests include perovskite/polymer solar cells, organic thin-film transistors and photodetectors.

Liming Ding got his B.S., M.S. and Ph.D. degrees from Anhui University, Changchun Institute of Applied Chemistry and University of Science and Technology of China, respectively. He started his research on OSCs and PLEDs in Olle Inganäs Lab in 1998. Later on, he worked with Frank Karasz and Tom Russell at PSE, UMASS Amherst. He joined Konarka as a Senior Scientist in 2008. In June 2010, he joined National Center for Nanoscience and Technology as a full professor. His research interests include perovskite solar cells, organic solar cells and photodetectors.