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Short Communication

A 2.16 eV bandgap polymer donor gives 16% power conversion efficiency

Tan Wang [a,b,1], Jianqiang Qin [b,c,1], Zuo Xiao [b,*], Xianyi Meng [b], Chuantian Zuo [d], Bin Yang [e], Hairen Tan [f], Junliang Yang [g], Shangfeng Yang [h], Kuan Sun [c,*], Suyuan Xie [a,*], Liming Ding [b,*]

[a] Department of Chemistry, Xiamen University, Xiamen 361005, China
[b] Center for Excellence in Nanoscience (CAS), Key Laboratory of Nanosystem and Hierarchical Fabrication (CAS), National Center for Nanoscience and Technology, Beijing 100190, China
[c] MOE Key Laboratory of Low-grade Energy Utilization Technologies and Systems, School of Energy and Power Engineering, Chongqing University, Chongqing 400044, China
[d] CSIRO Manufacturing, Bag 10, Clayton South, Victoria 3169, Australia
[e] College of Materials Science and Engineering, Hunan University, Changsha 410082, China
[f] College of Engineering and Applied Sciences, Nanjing University, Nanjing 210093, China
[g] School of Physics and Electronics, Central South University, Changsha 410083, China
[h] Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China

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Nowadays, wide-bandgap (WBG) copolymers attract great attention in the field of organic photovoltaics [1]. They are ideal electron-donating partners for low-bandgap small molecule acceptors [2–12]. With good energy levels matching, the blend of WBG copolymer donor and small molecule acceptor can harvest most of the sunlight and deliver high power conversion efficiencies (PCEs) in solar cells. >16% PCEs have been achieved [13–15]. WBG copolymers especially those with ultra-wide bandgaps (i.e., optical bandgap (E_g^{opt}) > 2.07 eV, absorption onset <600 nm) can find applications in ternary solar cells [16] and tandem solar cells [17]. Currently, ultra-WBG copolymer donors are less efficient, generally giving PCEs below 13% [18]. Designing highly efficient ultra-WBG copolymers is needed. In this work, we use fluorine- and alkoxyl-substituted benzene (FAB) as the building block to construct ultra-WBG copolymer donors. The highly aromatic benzene ring of FAB can widen the bandgap. The S···O, S···F and H···F interactions caused by fluorine and alkoxyl can lock the conformation and improve charge-transporting capability of copolymers [19]. Moreover, the fluorine atoms can lower the HOMO level and improve the open-circuit voltage (V_{oc}), and alkoxyl can improve the solubility of copolymers. Here, we report an ultra-WBG copolymer donor W1 based on 1,2-difluoro-4,5-bis(octyloxy)benzene unit (Fig. 1a). W1 has a large E_g^{opt} of 2.16 eV and a deep HOMO of −5.36 eV. W1:Y6 [13] solar cells gave a PCE of 16.16%, which is the highest efficiency for ultra-WBG donors to date.

The synthetic route for W1 is shown in Scheme S1 (online). The alkylation of 4,5-difluorobenzene-1,2-diol with 1-bromooctane afforded compound **1** in 66% yield. Treating **1** with N-bromosuccinimide (NBS) and sulfuric acid gave compound **2** in 87% yield. Stille coupling of **2** and tributyl(thiophen-2-yl) stannane gave compound **3** in 82% yield. Bromination of compound **3** with NBS gave the monomer, compound **4**, in 86% yield. Finally, Stille copolymerization of compound **4** with (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) gave W1 in 60% yield. All compounds were characterized by spectroscopic techniques, i.e. ^{1}H NMR, ^{13}C NMR and mass spectrometry. W1 shows good solubility in common solvents such as chloroform and chlorobenzene. The number-average molecular weights (M_n) and the polydispersity index (PDI) for W1 are 80.9 kDa and 1.67, respectively. The absorption spectra for W1 in chloroform and as film are shown in Fig. 1b. In solution, W1 shows an absorption band at 400–570 nm, with two peaks at 509 and 528 nm, respectively. For film, the absorption band slightly broadens, and the two peaks shift to 502 and 535 nm, respectively. The absorption onset for W1 film is 574 nm, corresponding to an E_g^{opt} of 2.16 eV. The Y6 film shows intense absorption at 600–900 nm, which is complementary with that of W1. The HOMO and LUMO levels of W1 estimated from cyclic voltammetry (CV) measurement are −5.36 and −2.81 eV, respectively (Fig. S10 online and Fig. 1c). The deep HOMO level of W1 favors to produce high V_{oc} in solar cells.

* Corresponding authors.
E-mail addresses: xiaoz@nanoctr.cn (Z. Xiao), kuan.sun@cqu.edu.cn (K. Sun), syxie@xmu.edu.cn (S. Xie), ding@nanoctr.cn (L. Ding).
[1] These authors contributed equally to this work.

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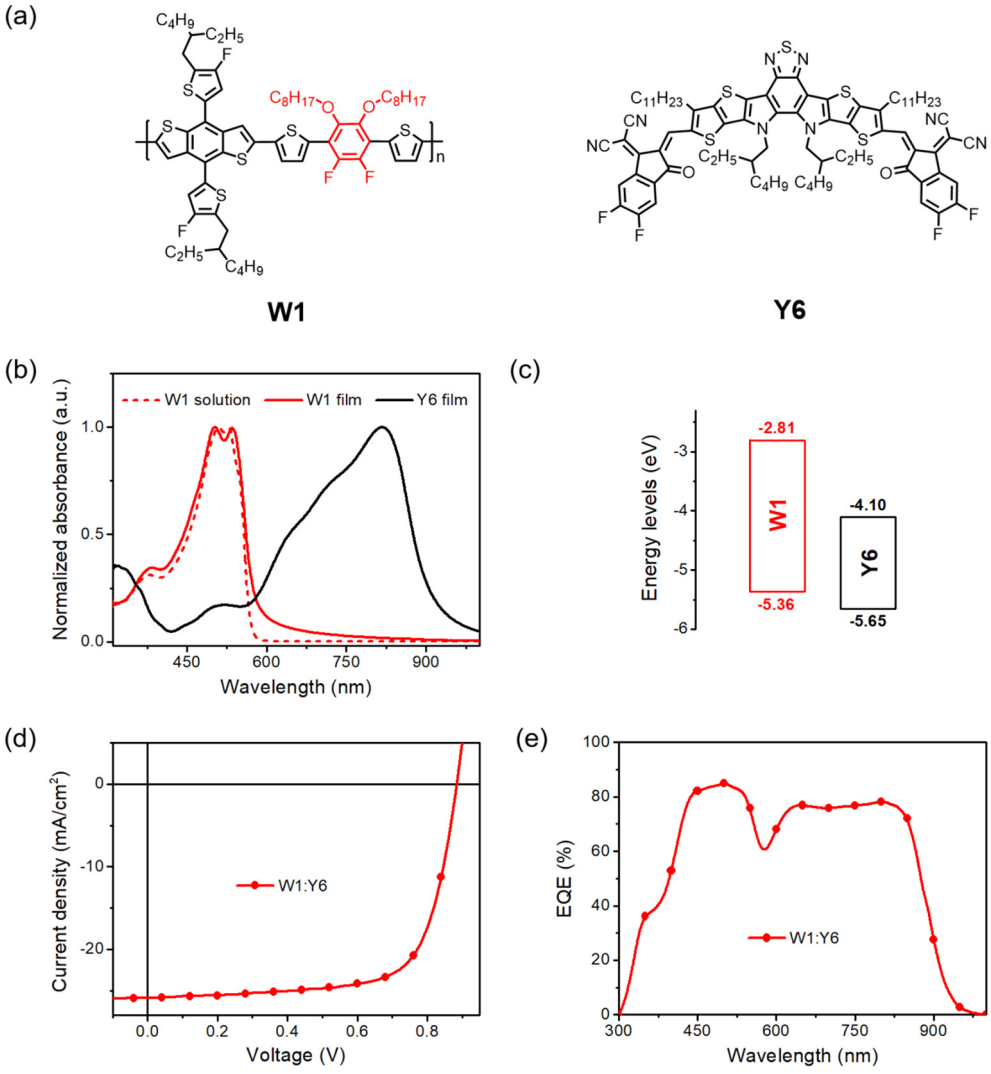

Fig. 1. An efficient ultra-WBG D-A copolymer donor based on an FAB unit. (a) The chemical structures for W1 and Y6; (b) the absorption spectra for W1 solution, W1 film and Y6 film; (c) the energy level diagram; (d) *J-V* curve for W1:Y6 solar cells; (e) EQE spectrum for W1:Y6 solar cells.

The solar cells with a structure of ITO/PEDOT:PSS/W1:Y6/PDIN/Ag were made. The *J-V* curve and external quantum efficiency (EQE) spectrum are shown in Fig. 1d and e, respectively. The best W1:Y6 solar cells gave a PCE of 16.16%, with a V_{oc} of 0.88 V, a short-circuit current density (J_{sc}) of 25.87 mA cm^{-2} and a fill factor (FF) of 70.7%. These cells have a D/A ratio of 1:1.2 (w/w), an active layer thickness of 105 nm and no additive (Tables S1–S3). To the best of our knowledge, the 16.16% PCE is the highest efficiency from ultra-WBG donor materials (E_g^{opt} > 2.07 eV) to date. As shown in Fig. 1e, W1 contributed considerable EQE response at the short wavelength region. The maximum EQE (85%) at 500 nm correlates to the maximum absorption at 502 nm for W1. The exciton dissociation probability (P_{diss}) for W1 cells is 94.6%, suggesting the charge generation is efficient (Fig. S11 online). Hole and electron mobilities (μ_h and μ_e) were measured by using space charge limited current (SCLC) method (Figs. S12, S13 and Table S4 online). The W1:Y6 blend film presents μ_h and μ_e of 3.23×10^{-4} and 1.51×10^{-4} cm^2 V^{-1} s^{-1}, respectively. We studied bimolecular recombination by plotting J_{sc} against light intensity (P_{light}) (Fig. S14 online). The data were fitted to a power law: $J_{sc} \propto P_{light}^{\alpha}$. A α of 0.959 is extracted, suggesting less recombination. The efficient charge generation and transport as well as suppressed charge recombination account for the good J_{sc} and FF for W1 cells. The morphology for W1:Y6 blend film was studied by using atomic force microscope (AFM) (Fig. S15 online). The height image indicates a smooth surface, with a root-mean-square (RMS) roughness of 0.98 nm. The phase image shows nanofiber structures with a diameter around 15 nm.

In summary, an ultra-WBG copolymer donor W1 based on a 1,2-difluoro-4,5-bis(octyloxy)benzene unit was developed. W1 has a large E_g^{opt} of 2.16 eV and intense absorption at 400–570 nm. The W1:Y6 solar cells gave a 16.16% PCE, the best efficiency offered by ultra-WBG-donor-based solar cells to date. Further application of W1 in ternary solar cells and tandem solar cells is ongoing.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

Author contributions

Tan Wang and Jianqiang Qin performed the experiments. Zuo Xiao, Xianyi Meng, Chuantian Zuo, Bin Yang, Hairen Tan, Junliang Yang, Shangfeng Yang, Kuan Sun and Suyuan Xie participated in

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the discussion on experimental results. Liming Ding directed this project.

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Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2019.11.030.

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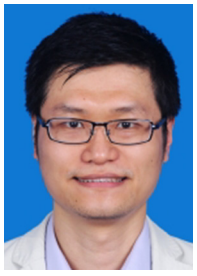
Tan Wang got his B.S. degree from Xiamen University in 2015. Now he is a Ph.D. student at Xiamen University under the supervision of Prof. Suyuan Xie. Since February 2018, he has been working in Liming Ding Group at National Center for Nanoscience and Technology as a visiting student. His work focuses on organic solar cells.

Jianqiang Qin got his M.S. degree from Henan University in 2018. Now he is a Ph.D. student at Chongqing University under the supervision of Prof. Kuan Sun. Since January 2019, he has been working in Liming Ding Group at National Center for Nanoscience and Technology as a visiting student. His current research focuses on organic solar cells.

Zuo Xiao got his B.S. and Ph.D. degrees from Peking University under the supervision of Prof. Liangbing Gan. He did postdoctoral research in Eiichi Nakamura Lab 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.



Kuan Sun is a tenured associate professor at School of Energy and Power Engineering, Chongqing University. He received B.S. and Ph.D. degrees from National University of Singapore (NUS), and did postdoctoral research at University of Melbourne and NUS. He was a visiting scholar at Karlsruhe Institute of Technology and Max-Planck Institute for Polymer Research. His current research focuses on functional materials, solar cells, and thermoelectric or photothermal energy conversions.

Suyuan Xie is a full professor at Xiamen University. He got his Ph.D. degree from Xiamen University under the supervision of Prof. Lan-Sun Zheng. He ever worked at Clemson University during 2003–2005 and Cardiff University in 2017. His research focuses on fullerenes and related carbon clusters and photovoltaics.

Liming Ding got his Ph.D. degree from University of Science and Technology of China. 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 2010, he joined National Center for Nanoscience and Technology as a Full Professor. His research includes perovskite solar cells, organic solar cells and photodetectors.