This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
The graphical and textual abstract for the Table of contents entry:

**A solution-processable bipolar diketopyrrolopyrrole molecule used as both electron donor and acceptor for efficient organic solar cells†**

Hangqi Shi, Weifei Fu, Minmin Shi,* Jun Ling and Hongzheng Chen*

A DPP molecule owns appropriate energy levels and bipolar charge-transporting property for both donor and acceptor in OSCs.
A solution-processable bipolar diketopyrrolopyrrole molecule used as both electron donor and acceptor for efficient organic solar cells†

Hangqi Shi, Weifei Fu, Minmin Shi,* Jun Ling and Hongzheng Chen*

Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX

A new diketopyrrolopyrrole derivative with appropriate energy levels and bipolar charge-transporting property is designed and synthesized. When this molecule is used as either electron donor or acceptor, the resulting solar cells both give the power conversion efficiencies over 3%. Until now, fullerene and its derivatives (e.g. [6,6]-phenyl-C71-butyric acid methyl ester, abbreviated as PC71BM) are still the predominant electron acceptors for organic solar cells (OSCs). When PC71BM is blended with some high-performance polymer or small molecule electron donors to fabricate bulk-heterojunction (BHJ) OSCs, the power conversion efficiencies (PCEs) as high as ca. 10% can be achieved. However, fullerene derivatives have some obvious drawbacks, such as poor light-harvesting ability and high-cost purification process. These limitations will inevitably hinder the future commercialization of OSCs. Therefore, the exploration of new organic electron acceptors for OSCs attracts more and more interests, and has made impressive progresses in the recent years. For example, with a perylene diimide derivative as the acceptor and a low band gap polymer as the donor, respectively, the resulting BHJ OSC shows a PCE up to about 6%. Nevertheless, if the most frequently used polymer donor, poly(3-hexylthiophene) (P3HT), is applied in the non-fullerene acceptors-based OSCs, the PCEs are normally below 3%. Diketopyrrolopyrrole (DPP) is an excellent building block to construct high-performance small molecules and polymers for electronic and opto-electronic applications due to the advantages of good photochemical stability, strong light absorption, and well-conjugated structure. When DPP is copolymerized or linked with an aromatic five-membered ring (e.g. thiophene), the resulting molecules adopt easily a quinoid state to delocalize π-electrons along the chemical bonds, in favour of molecular coplanarity, the narrowing of the band gap, and intermolecular π-π stacking. Thereby, this type of DPP-based material is suitable to be applied as the charge-transporting material in the field-effect transistors (FETs) and the donor in OSCs, but not for the acceptor since good molecular coplanarity will lead to large aggregations, which can disrupt efficient exciton dissociation in the active layer of OSCs. Taking these considerations into account, in this communication, we design and synthesize a new DPP derivative, F(DPP)2B2, in which a fluorene ring is functioned as the core, two DPP units as the arms, and two benzene rings as the end-groups (Fig. 1a). Here we select two kinds of aromatic six-membered rings (fluorene and benzene) to connect two DPP moieties because there exist moderate dihedral angles between DPP and aromatic six-membered rings (Through theoretical simulations, two dihedral angles, φ1 and φ2, are calculated as 22.2° and 24.4°, respectively. Fig. 1a). Thus, the obtained DPP molecule would show the narrowed band gap as well as the lower-lying highest occupied molecular orbital (HOMO) energy level, i.e. the appropriate energy levels for the use as the acceptor. More importantly, due to the bad molecular coplanarity of F(DPP)2B2, the active layer is expected to exhibit fine phase separation domains when F(DPP)2B2 is blended with P3HT, assuring high exciton dissociation efficiency of the non-fullerene OSCs.

Fig. 1 (a) The molecular structure of F(DPP)2B2. EH stands for 2-ethylhexyl; (b) UV-vis absorption spectra of F(DPP)2B2 in CHCl3 solution and thin film; (c) cyclic voltammogram of F(DPP)2B2 in CH2Cl2 solution; (d) energy level alignment of P3HT, F(DPP)2B2, and PC71BM; (e) J−V curves of the hole-only device with a structure of ITO/PEDOT:PSS/F(DPP)2B2/MoO3/Al and the electron-only device with a structure of ITO/PFN/F(DPP)2B2/PFN/Al, the symbols represent experimental data and the solid lines are fitted according to the Mott–Gurney law.
F(DPP)B2 is synthesized through traditional palladium-catalyzed Suzuki coupling reactions of DPP units with fluoren- and benzene rings, and its chemical structure is fully characterized by 1H NMR, 13C NMR, and MALDI-TOF MS (ESI†, Figs. S1-S3). Fig. 1b depicts the UV-visible absorption spectra of F(DPP)B2 in CHCl3 solution and thin film. As expected, F(DPP)B2 film shows intense absorptions in the range of 550-700 nm, which are red-shifted relatively to those of DPP unit (300-500 nm), and complement well those of P3HT (400-600 nm), suggesting excellent light-harvesting capability of the OSCs if F(DPP)B2 is used as the electron acceptor and P3HT as the electron donor. The cyclic voltammetry (CV) measurements are done to characterize the energy level structure of F(DPP)B2. From the onset oxidation potential (0.81 V versus SCE) and the onset reduction potential (-1.01 V versus SCE) presented in Fig. 1c, the HOMO and the lowest unoccupied molecular orbital (LUMO) energy levels of F(DPP)B2 are obtained as -5.21 and -3.39 eV, respectively. Thereby, both HOMO and LUMO energy levels of F(DPP)B2 are lower than those of P3HT (-4.76 and -2.74 eV), but higher than those of PC71BM (-5.8 and -4.0 eV)11, as illustrated in Fig. 1d. We observe that, the differences between their LUMOs are big enough to dissociate exciton, in the mean time, the offset between the LUMO of F(DPP)B2 and the HOMO of P3HT, as well as that between the LUMO of PC71BM and the HOMO of F(DPP)B2, are both very large, which can provide high Voc of the OSCs. We also employ space charge limited current (SCLC) method to determine the charge-transporting property of F(DPP)B2. Fig. 1e shows the 2D-V characteristics of the hole-only and electron-only devices with the as-cast F(DPP)B2 film as the charge-transporting layer. From Fig. 1e, the electron and hole mobilities of F(DPP)B2 are calculated as 2.8 x 10⁻⁶ and 4.3 x 10⁻⁵ cm²/Vs, respectively. The above findings demonstrate that F(DPP)B2 possesses appropriate energy levels and charge-transporting characteristics for either electron donor or acceptor in the OSCs.

To evaluate potential applications of F(DPP)B2 as both electron donor and acceptor in the OSCs, two types of organic photovoltaic devices are fabricated. For the first one, F(DPP)B2 is used as electron donor and PC71BM as electron acceptor with a device structure of ITO/PEDOT:PSS/F(DPP)B2:PC71BM:PFN/Al. For the second one, F(DPP)B2 is functionalized as electron acceptor and P3HT as electron donor with a device structure of ITO/PEDOT:PSS/P3HT:F(DPP)B2:PFN/Al. Fig. 2a and 2b present the current density-voltage (J-V) characteristics of the two kinds of OSCs under AM 1.5G illumination at an intensity of 100 mW cm⁻², and all photovoltaic data are summarized in Table 1. We can observe that, the first kind of OSC give a maximum PCE of 5.35%, with a short-circuit current density (JSC) of 8.08 mA cm⁻², a Voc of 0.89 V, and a fill factor (FF) of 0.453. From the EQE spectra (Fig. 2c), it is apparent that the shapes of the EQE spectra resemble those of the combination absorptions of donor and acceptor, suggesting that each component in the active layers contributes to the photovoltaic responses of the two types of OSCs.

We investigate the morphologies of the active layers in the two kinds of OSCs with atomic force microscopy (AFM) (Fig. 3). It can be seen from Fig. 3a that the as-cast 1:3 F(DPP)B2:PC71BM film is very smooth with a root-mean-square (RMS) roughness of 0.87 nm, leading to perfectly fine phase separation domains in a scale of 20-30 nm, as shown in Fig. 3b. For the as-cast 1:1 P3HT:F(DPP)B2 film, P3HT is completely compatible with F(DPP)B2, and the RMS roughness of the blended film is only 0.40 nm, so that no obvious donor-acceptor phase separation can be observed (Fig. 3c and 3d). After thermal annealing, due to the self-organization of P3HT and F(DPP)B2 to orderly crystalline structure (ESI†, Fig. S4), the RMS roughness of the 1:1 P3HT:F(DPP)B2 film increases to 2.14 nm, and the donor-acceptor phase separation domains at the size of 40-60 nm are formed and well interconnected, giving the percolated network for charge transportation (Fig. 3e and 3f), which can be proved by the improvement of electron and hole mobilities (ESI†, Fig. S5).

The above changes in the morphology are beneficial to efficient exciton dissociation and charge collection in the OSCs. In
addition, we observe that thermal annealing also induces stronger absorptions of P3HT and F(DPP)\(_2\)_B\(_2\) in red-light region (ESI†, Fig. S6). Therefore, thermal annealing elevates tremendously the photovoltaic performances of the P3HT:F(DPP)\(_2\)_B\(_2\) based OSCs.

In conclusion, a new DPP molecule F(DPP)\(_2\)_B\(_2\) is designed and synthesized by linking two DPP units with fluorene and benzene rings. Because of the twisted molecular conformation, F(DPP)\(_2\)_B\(_2\) exhibits suitable HOMO and LUMO energy levels matching perfectly those of PC\(_2\)_BM and P3HT, and provides fine phase separation domains in the blended films favorable for exciton dissociation. Thus, the resulting OSCs both give the PCEs of more than 3% while F(DPP)\(_2\)_B\(_2\) is used as either electron donor or acceptor. The above results also demonstrate that the accurate tuning of the molecular conformation is one feasible route to obtain high-performance organic photovoltaic materials, especially non-fullerene acceptors.

The authors would like to gratefully acknowledge the financial support from the National Natural Science Foundation of China (Nos. 21474088, 51261130582, 91233114) and Zhejiang Province Natural Science Foundation (No. LR13E030001). The work was also partly supported by 863 program (No. 2011AA050520) and 973 program (No. 2014CB643503).

Notes and references

30 MOE Key Laboratory of Macromolecular Synthesis and Functionalization, State Key Laboratory of Silicon Materials, & Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China. Fax: +86 571 87957332; Tel: +86 571 8795257; E-mail: minminshi@zju.edu.cn; hzchen@zju.edu.cn

† Electronic Supplementary Information (ESI) available: Synthesis and characterization of F(DPP)\(_2\)_B\(_2\) procedures for device fabrication, and photovoltaic and mobility characterization, XRD patterns and UV-Vis absorption spectra of the blended films. See DOI: 10.1039/b000000x/


