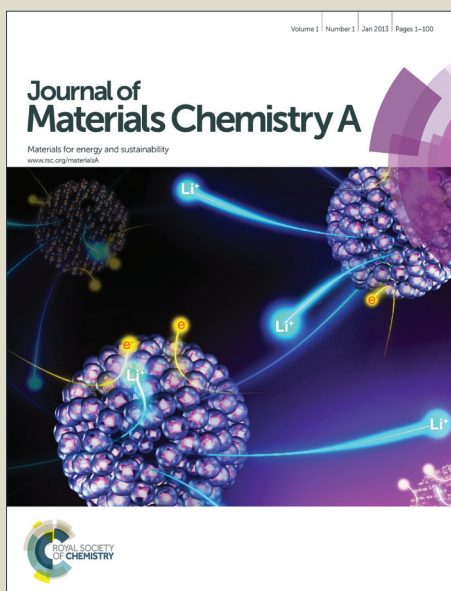


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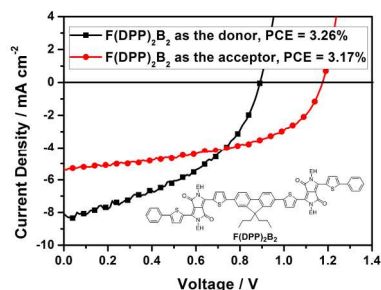
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The graphical and textual abstract for the Table of contents entry:

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

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COMMUNICATION

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*

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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 organic 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.¹ 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.² For example, with a perylene dimide 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%.^{2c} 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%.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.⁴ Thereby, this type of DPP-based material is suitable to be applied as the charge-transporting material in the field-effect transistors (FETs)⁵ and the donor in OSCs,⁶ but not for the acceptor since good molecular coplanarity will lead to large aggregates, 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, ϕ_1 and ϕ_2 , 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.

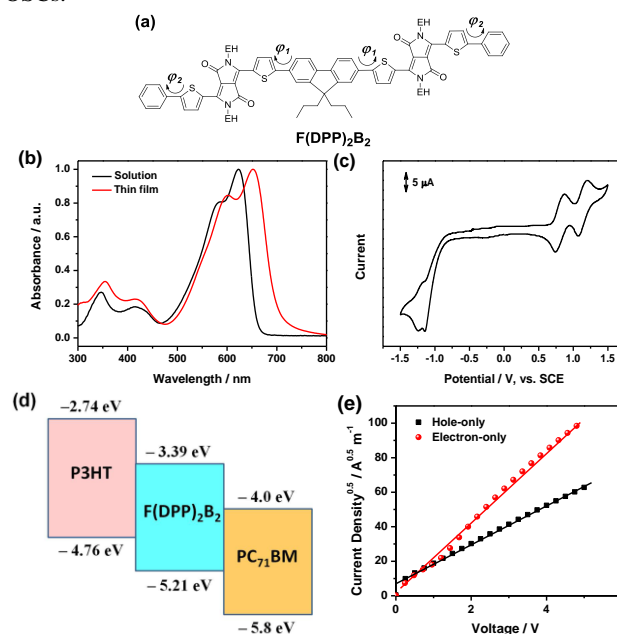


Fig. 1 (a) The molecular structure of F(DPP)₂B₂, EH stands for 2-ethylhexyl; (b) UV-vis absorption spectra of F(DPP)₂B₂ in CHCl₃ solution and thin film; (c) cyclic voltammogram of F(DPP)₂B₂ in CH₂Cl₂ solution; (d) energy level alignment of P3HT, F(DPP)₂B₂, and PC₇₁BM; (e) $J^{0.5}$ -V curves of the hole-only 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)₂B₂ is synthesized through traditional palladium-catalyzed Suzuki coupling reactions of DPP units with fluorene 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)₂B₂ in CHCl₃ solution and thin film. As expected, F(DPP)₂B₂ 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)₂B₂ 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)₂B₂. 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)₂B₂ are obtained as -5.21 and -3.39 eV, respectively. Thereby, both HOMO and LUMO energy levels of F(DPP)₂B₂ are lower than those of P3HT (-4.76 and -2.74 eV), but higher than those of PC₇₁BM (-5.8 and -4.0 eV),⁷ 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)₂B₂ and the HOMO of P3HT, as well as that between the LUMO of PC₇₁BM and the HOMO of F(DPP)₂B₂, are both very large, which can provide high V_{OC} of the OSCs. We also employ space charge limited current (SCLC) method to determine the charge-transporting property of F(DPP)₂B₂. Fig. 1e shows the J^{0.5}-V characteristics of the hole-only and electron-only devices with the as-cast F(DPP)₂B₂ film as the charge-transporting layer. From Fig. 1e, the electron and hole mobilities of F(DPP)₂B₂ are calculated as 2.8 × 10⁻⁴ and 4.3 × 10⁻⁵ cm²V⁻¹s⁻¹, respectively. The above findings demonstrate that F(DPP)₂B₂ possesses appropriate energy levels and charge-transporting characteristics for either electron donor or acceptor in the OSCs.

To evaluate potential applications of F(DPP)₂B₂ as both electron donor and acceptor in the OSCs, two types of organic photovoltaic devices are fabricated. For the first one, F(DPP)₂B₂ is used as electron donor and PC₇₁BM as electron acceptor with a device structure of ITO/PEDOT:PSS/F(DPP)₂B₂:PC₇₁BM/PFN/Al. For the second one, F(DPP)₂B₂ is functioned as electron acceptor and P3HT as electron donor with a device structure of ITO/PEDOT:PSS/P3HT:F(DPP)₂B₂/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 3.26% with a short-circuit current density (J_{SC}) of 8.08 mA cm⁻², a V_{OC} of 0.89 V, and a fill factor (FF) of 0.453 when the blend weight ratio of donor (F(DPP)₂B₂) and acceptor (PC₇₁BM) is 1:3. For the second kind of OSC, it is found that thermal annealing can improve significantly the device's photovoltaic performance. With a 1:1 blend ratio of donor (P3HT) and acceptor (F(DPP)₂B₂), the device exhibits the highest PCE of 3.17% with a J_{SC} of 5.35 mA cm⁻², an extremely big V_{OC} of 1.18 V, and a FF of 0.502 after annealing at 120 °C for 10 min. To our knowledge, this efficiency is one of the highest values ever reported for P3HT and non-

fullerene acceptor based OSCs.^{2e,8} Shown in Fig. 2c and 2d are external quantum efficiency (EQE) curves of the two kinds of OSCs. 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.

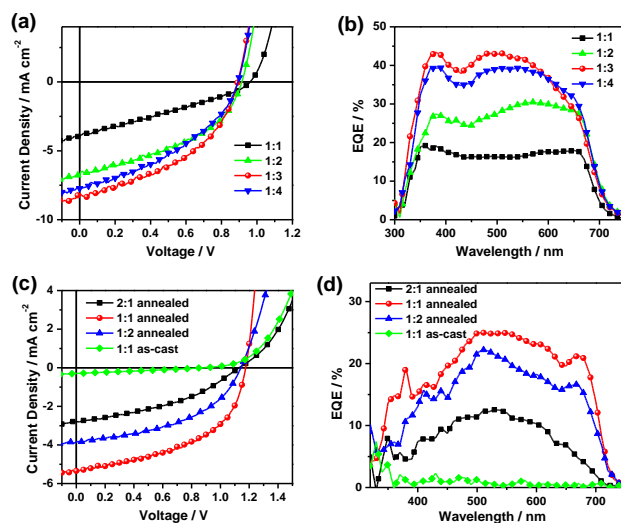


Fig. 2 J-V characteristics (a, c) and EQE spectra (b, d) of F(DPP)₂B₂:PC₇₁BM (a, b) and P3HT:F(DPP)₂B₂ (c, d) based OSCs.

Table 1. Photovoltaic performances of the two kinds of OSCs based on F(DPP)₂B₂

Active layer	Blend ratio	V _{OC} /V	J _{SC} /mA cm ⁻²	FF	PCE/%
F(DPP) ₂ B ₂ :PC ₇₁ BM ^a	1:1	0.96	3.92	0.298	1.12
F(DPP) ₂ B ₂ :PC ₇₁ BM ^a	1:2	0.91	6.75	0.426	2.62
F(DPP) ₂ B ₂ :PC ₇₁ BM ^a	1:3	0.89	8.08	0.453	3.26
F(DPP) ₂ B ₂ :PC ₇₁ BM ^a	1:4	0.89	7.73	0.400	2.75
P3HT:F(DPP) ₂ B ₂ ^b	2:1	1.13	2.79	0.395	1.25
P3HT:F(DPP) ₂ B ₂ ^b	1:1	1.18	5.35	0.502	3.17
P3HT:F(DPP) ₂ B ₂ ^b	1:2	1.15	3.83	0.467	2.05
P3HT:F(DPP) ₂ B ₂ ^a	1:1	0.89	0.30	0.267	0.07

^a As-cast; ^b annealed at 120 °C for 10 min.

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)₂B₂: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)₂B₂ film, P3HT is completely compatible with F(DPP)₂B₂, 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)₂B₂ to orderly crystalline structure (ESI†, Fig. S4), the RMS roughness of the 1:1 P3HT:F(DPP)₂B₂ 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)₂B₂ in red-light region (ESI†, Fig. S6). Therefore, thermal annealing elevates tremendously the photovoltaic performances of the P3HT:F(DPP)₂B₂ based OSCs.

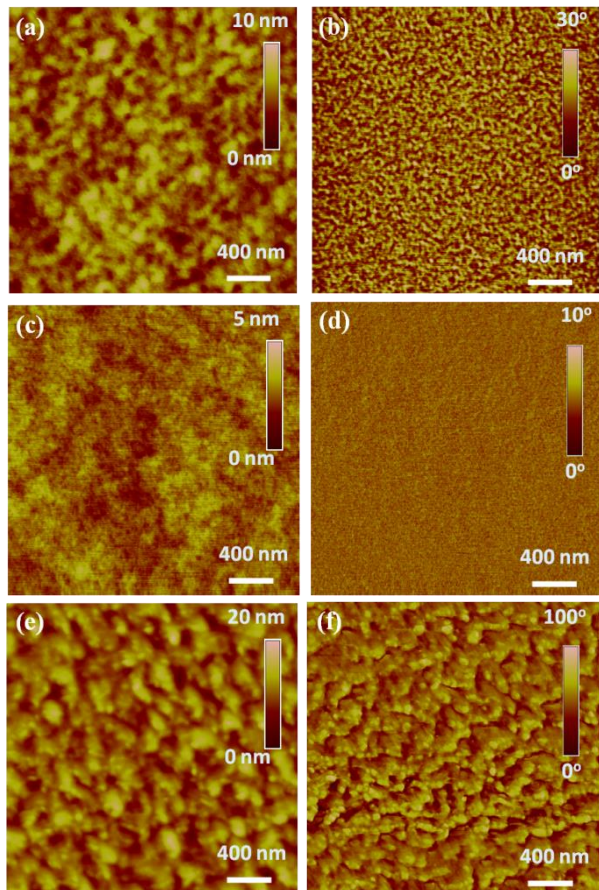


Fig. 3 AFM height images (a, c, e) and phase images (b, d, f) of the as-cast 1:3 F(DPP)₂B₂:PC₇₁BM (a, b), as-cast 1:1 P3HT:F(DPP)₂B₂ (c, d), and annealed 1:1 P3HT:F(DPP)₂B₂ (e, f) films.

In conclusion, a new DPP molecule F(DPP)₂B₂ is designed and synthesized by linking two DPP units with fluorene and benzene rings. Because of the twisted molecular conformation, F(DPP)₂B₂ exhibits suitable HOMO and LUMO energy levels matching perfectly those of PC₇₁BM and P3HT, and provides fine phase separation domains in the blended films favourable for exciton dissociation. Thus, the resulting OSCs both give the PCEs of more than 3% while F(DPP)₂B₂ 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.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis and characterization of F(DPP)₂B₂, 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/

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