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Performance Enhancement of BODIPY-Dimer Based Small-Molecule Solar Cells by Using a Visible-Photons-Capturing Diketopyrrolopyrrole π -Bridge

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We report herein that use of a diketopyrrolopyrrole instead of a 4,8-dithienyl benzodithiophene π -bridge makes BODIPY-dimer become capable of capturing and exploiting visible solar photons by intramolecular energy transfer and affording crystalline blend film with PC₇₁BM, and consequently, a 7.3% absorption enhancement leads to a 70% increase in photocurrent and efficiency.

Since the first report by Treibs and Kreuzer,¹ 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) dyes have been extensively investigated for decades, for example, in the fields of chemical sensors and cell imaging and labelling, due to the intense absorption and emission profiles together with small Stoke's shifts.² Recent efforts on the molecular design leads to an important approach to red-shift the low-energy absorption band to capture near infrared solar photons by extending the π -system with electron-donating groups at their α - and/or β -positions.³ For instance, the α -positions thienyl-functioned BODIPY dyes show two absorption bands, one is in the near-infrared region, typically around 700 nm, the other usually appears at near-ultraviolet region, around 400 nm.⁴ Both absorption bands have a maximum absorption coefficient on the magnitude of $10^5 \text{ M}^{-1} \text{ cm}^{-1}$, while, unfortunately, leaves an absorption "gap" (480 – 650 nm) in the visible region. The onset of the film absorption extends even beyond 900 nm with a narrow bandgap of < 1.4 eV. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels are of around -3.7 and -5.0 eV, respectively. All of these excellent optoelectronic properties strongly demonstrate that BODIPY core is a good chromophoric candidate for designing narrow bandgap donor materials with excellent solar photons capturing capability.

Although the α - and β -positions π -extending BODIPY based donors have excellent light-harvesting ability, the reported molecules

often gave inferior cell performance when blended with [6,6]-phenyl-C₆₁ (or C₇₁)-butyric acid methyl ester (PC₆₁BM or PC₇₁BM), normally exhibited a power conversion efficiency (PCE), approaching or exceeding 2%.⁵ So far, there only reported two efficient derivatives. One showed a PCE of 3.2%,⁶ the other gave a PCE of 4.7%, which is the highest value reported from the BODIPY based donor materials. The low PCE is associated with its low carrier mobility, and, therefore, improvement of molecular ordering is a strategy to enhance the short-circuit current (J_{sc}), for example, the intermolecular I...F interactions and π - π stacking between the planar dyes favor short-distance organization of the molecules of the α -positions dithienyl-functioned BODIPY, which enhances the hole mobility, and, yet the J_{sc} , up to about 14 mA cm^{-2} .⁴ In contrast to this highest J_{sc} value reported to date, values from other reported BODIPY dyes were normally $\leq 7 \text{ mA cm}^{-2}$. We have recently presented a twisted BODIPY-dimer's approach to enhance the J_{sc} , which two α -positions π -extending BODIPY moieties are covalently linked via their meso positions by a central planar trithiophene π -bridge. The resulting dimer molecule possesses enhanced π - π stacking, compared to the monomeric BODIPY dye, and the twisted dimeric conformation can lead to so-called steric pairing effects,⁷ both of which improve molecular ordering in pristine and blend film, and, therefore yielding a J_{sc} of 11.28 mA cm^{-2} and a PCE of 3.1%.⁸ However, the trithiophene-mediated dimer yet unfortunately leave an absorption gap between 480 – 650 nm, as the mother BODIPY monomer does.

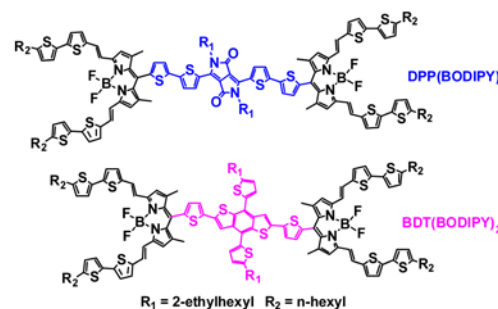


Figure 1 Chemical structures of the two dimers.

In this contribution, we present that the absorption gap of BODIPY-dimer can be filled and its crystallinity can be efficiently

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[†] Electronic Supplementary Information (ESI) available: Synthesis and general methods, device fabrication, characterizations, the relevant figures and tables. See DOI: 10.1039/x0xx00000x

controlled, both of which are achievable simply by using a diketopyrrolopyrrole (DPP), instead of a 4,8-dithienyl-benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) π -bridge (Fig. 1). As a result, a 1.07-time enhancement of the absorption can lead to a 1.7-fold increase of the J_{sc} , from 7.8 to 13.4 mA cm⁻², hence, the PCE from 2.1% to 3.6%.

The two dimers were synthesized successfully *via* Pd-catalysed Suzuki-Miyaura coupling and Stille coupling reactions, respectively. The final structures and purity of the products were convinced by NMR, MALDI-TOF-MS and elemental analysis (ESI⁺). Both dimers show highly twisted conformations with the dihedral angles between the π -bridge and the BODIPY planes are all of nearly 90°, indicating poor electronic communication between them, as simulated by Gaussian 09 at the B3LYP/6-31G level (Fig. S1, ESI⁺).

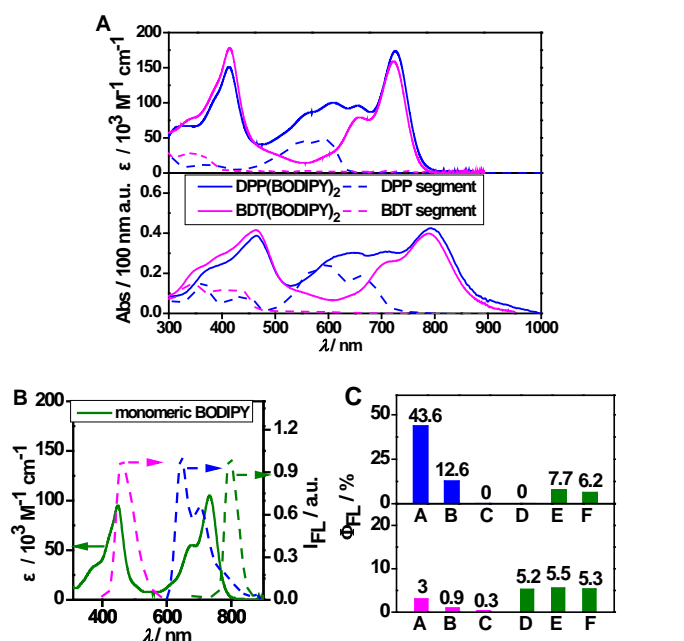


Figure 2 (A) Absorption spectra of the dimers and the central DPP and BDT segments in dilute chloroform solution (upper, 1×10^{-6} M) and in solid (lower). (B) Absorption spectrum of BODIPY segment (left, solid) and fluorescence spectra of DPP (blue), BDT (pink) and BODIPY (olive) segments (right, dash). The molecular structures of the three segments are given in Fig. S2 (ESI⁺). (C) The absolute quantum yield (Φ_{FL}) of the three segments. Upper one shows the Φ_{FL} of the DPP (A, B and C) and the BODIPY (D, E and F) part, measured from the pure DPP or BODIPY segment solution, 1:2 mixed DPP-to-BODIPY segment solution (in molar) and the DPP-mediated dimer solution, respectively. All solution samples are excited by the 580 nm light. Lower one gives the Φ_{FL} of the BDT (A, B and C) and the BODIPY (D, E and F) part, measured from the pure BDT or BODIPY segment solution, 1:2 mixed BDT-to-BODIPY segment solution (in molar) and the BDT-mediated dimer solution, respectively. All solution samples are excited by the 330 nm light.

The absorption spectra both in the dilute chloroform solution and in the pristine film (Fig. 2A) clearly confirm that the central DPP segment just complements the absorption “gap” between the two absorption bands of the BODIPY moieties, i.e. one from 350–500 nm and the other from 650–800 nm, because of the reduced π -electron conjugation between the two segments. To find how the dimer can possibly utilize the solar photons absorbed by the central DPP segment, we measured fluorescence spectra (Figs. 2B, S3 and S4)

and the absolute fluorescence quantum yields (Φ_{FL}) (Fig. 2C) of the BODIPY, DPP and BDT segments, the 1:2 DPP-to-BODIPY and BDT-to-BODIPY mixture (both in molar), and the two dimers in solution. Experimental details are given in Supporting Information (ESI⁺). Overlap between the fluorescence of DPP/BDT segment and the absorption of the BODIPY implies the possible intramolecular energy transfer, going from the DPP/BDT π -bridge to the terminal BODIPY. Under excitation at 580 nm where the BODIPY segment has a very much weaker absorption ($12 \times 10^3 M^{-1} cm^{-1}$) than the DPP ($45 \times 10^3 M^{-1} cm^{-1}$), the Φ_{FL} of DPP segment, as detected in between the wavelengths of 600 – 850 nm, dramatically decreases from 43.6% to 12.6%. Simultaneously, the Φ_{FL} of BODIPY segment increases from 0% to 7.7%, as detected in between the wavelengths of 750 – 850 nm. This clearly reveals that the fluorescence emission from DPP can be absorbed by BODIPY segment as they are both physically mixed in the dilute solution. As the two segments are covalently linked to form the DPP-mediated dimer, the fluorescence from the DPP π -bridge is fully quenched, indicating efficient Förster resonance energy transfer takes place between the DPP π -bridge and the BODIPY terminals. The slightly decrease of the Φ_{FL} detected from the BODIPY part, from 7.7% to 6.2%, can be attributed to the existing of other deactivated processes within the dimer. Similar energy transfer processes can be also observed in the case of BDT-based system. All these data strongly support that the photons absorbed by the DPP/BDT π -bridge can be efficiently exploited through the cascade energy transfer from the DPP/BDT π -bridge to the BODIPY terminal.

The HOMO/LUMO of the dimers were determined by cyclic voltammetry (Fig. S5, ESI⁺) to be $-5.01/-3.73$ and $-5.02/-3.73$ eV for the DPP- and BDT-mediated dimer, respectively.

The photovoltaic properties of the dimers were studied with the normal cell structure of ITO / PEDOT:PSS / active layer / Ca / Al with PC₇₁BM as acceptor. Detailed information of optimizations of the solar cells is available in Supporting Information (ESI⁺) and Table S3 (ESI⁺). Fig. 3A and B display the current density-voltage (J - V) and external quantum efficiency (EQE) curves of the optimal cells. The cells based on DPP(BODIPY)₂ exhibit the best PCE of 3.62% (average 3.40%) with a J_{sc} of 13.39 mA cm⁻², an open-circuit voltage (V_{oc}) of 0.73 V and a fill-factor (FF) of 0.373. While the best cell based on BDT(BODIPY)₂ only gives a moderate PCE of 2.10% (average 1.98%), with an inferior J_{sc} of 7.76 mA cm⁻², a similar V_{oc} of 0.76 V and a slightly lower FF of 0.356. The integrated current densities (J_{EQE}) from the EQE curves are of 13.13 and 7.32 mA cm⁻², respectively, each of which is in well accord with the corresponding J_{sc} value gotten from the J - V curve.

The contribution of the DPP π -bridge to the photocurrent is strongly evidenced by the comparisons of the EQE spectra of the best cells and the absorption spectra of the solar cell blend films (Fig. 3B). The blend films of the two dimers show nearly identical absorption in the wavelength range of the BODIPY segments, while the DPP-mediated one possesses stronger absorbance between 520 and 760 nm, the absorption wavelength range of the DPP segment. The total absorption, as described by the integrated area, is enhanced by 7.3%. The EQE curve from the DPP(BODIPY)₂ based cell is higher over the spectral wavelength range than that from BDT(BODIPY)₂ based cell. As Fig. S6 (ESI⁺) displays, the EQE of the BDT(BODIPY)₂ based cell multiplied by 1.26 is very close to

that of the **DPP(BODIPY)₂** based cell in the absorption wavelength range of the BODIPY segments. This allows us to possibly estimate the contribution of the central DPP π -bridge to the photocurrent, which is about 3.9 mA cm^{-2} , as calculated according to the equation $J_{\text{EQE}}^{\text{DPP(BODIPY)}_2} = 1.26 \times J_{\text{EQE}}^{\text{BDT(BODIPY)}_2}$. This value suggests that the 7.3% enhancement of the absorption from the DPP π -bridge can contribute to about 42.3% increase of the photocurrent, as calculated by $3.9/(1.26 \times 7.32)$, strongly suggesting that the DPP π -bridge contributes to the J_{sc} enhancement not only by the absorption improvement, but also greatly by other morphological factors. This is further supported by the 1.26-fold higher EQE in the absorption wavelength range of the BODIPY segments.

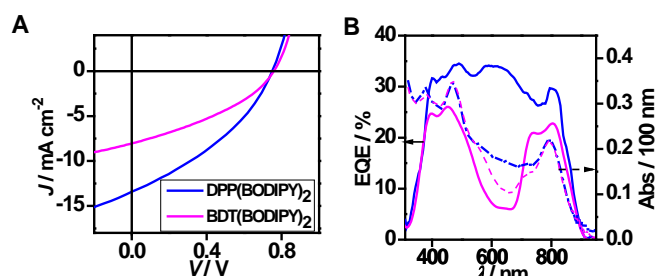


Figure 3 (A) The J - V and (B) the EQE curves (left, solid lines) of the best cells based on **DPP(BODIPY)₂** or **BDT(BODIPY)₂**:PC₇₁BM blends, respectively. In (B) the absorption spectra of the blend films are shown for comparisons (right, dashed lines).

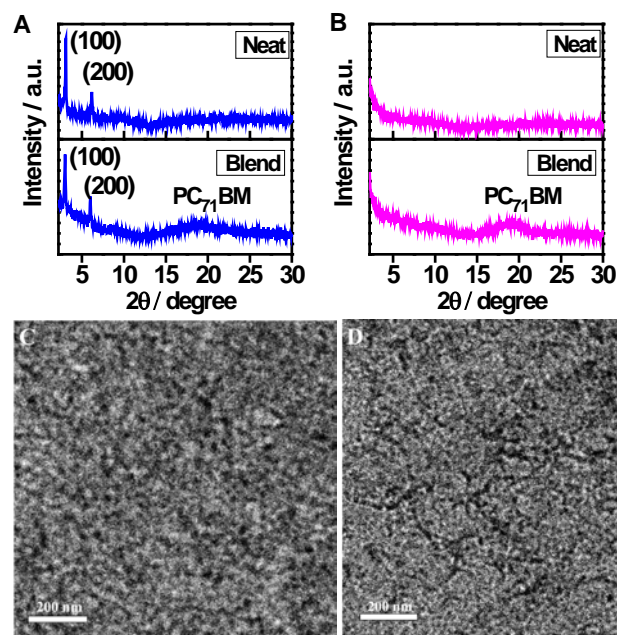


Figure 4 XRD data (A and B) and TEM images (C and D) of **DPP(BODIPY)₂** (A, C) and **BDT(BODIPY)₂** (B, D) solar cell blend films, respectively. Scale bar: 200 nm.

Both hole and electron (μ_{h} and μ_{e}) mobilities of the solar cell blends were estimated with space-charge-limited current method. The values of $\mu_{\text{h}}/\mu_{\text{e}}$ are of $2.10/3.48 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $2.58/7.02 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **DPP(BODIPY)₂**:PC₇₁BM and **BDT(BODIPY)₂**:PC₇₁BM blended films, respectively (Fig. S7, ESI[†]). With respect to the **BDT(BODIPY)₂** based blend, the **DPP(BODIPY)₂** based blend shown an about 10-fold increase in both the μ_{h} and μ_{e} values, which is consistent well with the larger J_{sc}

value ($13.39 \text{ vs. } 7.76 \text{ mA cm}^{-2}$) from the DPP-mediated molecule. X-Ray diffraction (XRD) data of the solar cell blend films (Fig. 4A and B) indicates the DPP-mediated dimer is highly crystalline, as judged from the intense and sharp (100) and (200) diffractions, while the BDT-mediated one is amorphous, in both the pristine and the blend films, however. Transmission electron microscope (TEM) images (Fig. 4C and D) demonstrate that the phase size of **DPP(BODIPY)₂** based blend (30-40 nm) is slightly larger than that of **BDT(BODIPY)₂** based one (15-25 nm), both of which are in the scope of exciton diffusion length. Moreover, atomic force microscopy (AFM) (Fig. S8, ESI[†]) was used to investigate the surface morphologies of the blends, bicontinuous interpenetrating network with the phase sizes of 20-40 and 10-25 nm can be seen from the AFM phase images of **DPP(BODIPY)₂** and **BDT(BODIPY)₂** based blend (Fig. S8A and C, ESI[†]), and the root-mean-square (RMS) roughness deduced from the height images (Fig. S8B and D, ESI[†]) is 0.323 nm for **DPP(BODIPY)₂** based blend, slightly larger than that of **BDT(BODIPY)₂** based blend (0.261 nm).

In summary, we have clearly shown that utilization of the DPP π -bridge instead of the 4,8-dithienyl BDT one, can not only afford enhanced absorption for capturing more visible solar photons but also can greatly improve the crystallinity of the BODIPY dimer in both the neat and blend films, leading to a significant increase in the photocurrent by 1.7 times, and, hence in the PCE value from 2.1% to 3.6%, which is the second best PCE achievable from the BODIPY based organic solar cells so far. However, the low FF of **DPP(BODIPY)₂** is still far from satisfactory. In fact, the low FF can always be seen in BODIPY based cells, largely due to the small parallel resistance (R_{shunt}) and the large series resistance (R_{s}). To further improve the FF and the PCE of BODIPY based solar cells, continuous efforts should be made to rationally tailor the molecular structure, optimize the processing procedures and the structure of the devices.

Acknowledgements

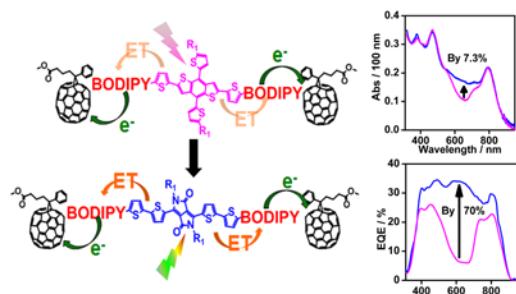
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TOC



Utilization of the visible-photons-capturing DPP instead of BDT π -bridge leads to a 70% increase of the photocurrent.