

Synthesis and Application of Perylene-Embedded Benzoazoles for Small-Molecule Organic Solar Cells

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S Supporting Information

ABSTRACT: Two new building blocks of perylene-embedded benzoazoles containing both rigid 2D-conjugated aromatic rings and flexible branched alkyl chains were designed and facilely synthesized in high yields for organic solar cells (OSCs). With a typical acceptor of diketopyrrolopyrrole, small molecular OSC donors constructed in an acceptor-fused donor-acceptor motif exhibit excellent solubility, stability, and light absorption with tunable frontier orbitals, leading to a power conversion efficiency of up to 2.88% in preliminary OSCs.



C olution-processed bulk heterojunction (BHJ) organic solar Cells (OSCs) with a large interfacial area between the donor and acceptor materials have drawn tremendous attention because of their unique advantages such as light weight, high flexibility, and excellent device performance.¹ Owing to the evolution of novel donor materials, including polymers and small molecules, power conversion efficiencies (PCEs) higher than 10% have been achieved.^{2,3} An effective strategy in designing OSC donors involves employing a conjugated framework with multiple fused aromatic rings in a ladder-type building block; the fused donors with a planar molecular geometry and a delocalized π -electron cloud are beneficial to bathochromically shift photoabsorptions, restrict rotational motions, extend effective conjugation length, improve charge carrier transport and intermolecular $\pi - \pi$ stacking, as well as enhance the physical, chemical, and mechanical stabilities.⁴ Moreover, OSC donors with the acceptor-donor-acceptor (A-D-A) motif are also of particular interest due to their widely tunable energy levels, high device performance, and facile synthetic approaches.⁵ Therefore, by introducing the fused donor (FD) into the A-D-A architecture to afford A-FD-A materials has been met with great success in either polymers or small molecules for both OSC donors and acceptors.^{6,7}

Among the various polycyclic aromatic hydrocarbons (PAHs), perylene is the most studied one, due to its unique chemical and photoelectronic properties.^{8,9} Through 12 functionalizable positions (3,4,9,10: peri-positions; 1,6,7,12: bay-positions; 2,5,8,11: ortho-positions), various perylenes can be developed. Modified at the peri-positions, perylene imides

(PDIs) are one of the most important derivatives of perylene, which have shown extensive applications in organic electronics.^{10,11} By introducing heteroatoms or heterocycles into the bay-position of perylene, the S-heterocyclic annulated perylene exhibits high hole mobility due to the significant S…S interactions for enhanced solid-state packing arrangement.¹² However, these bay-position modified perylenes are difficult to introduce flexible alkyl chains on the skeletons, leading to poor solubilities.¹³ Moreover, fused aromatic perylenes often cause excessive aggregation in the solid states because of their extended π -surfaces, and the excessive aggregation is usually harmful to the construction of optimal phase-separated morphology for OSCs.^{14,15} Therefore, it is urgent to develop efficient synthetic routes to introduce flexible alkyl chains on the rigid PAH of pervlene with both high optoelectronic properties and good solubility for processing and crystalline domain control in blend films for high-performance OSCs.

Here, we present an efficient approach to prepare perylenebased OSC building blocks by covalently fusing benzoazoles with thiophene to construct an embedded 2D-conjugated pervlene core with flexible chains at the bay-positions of the synthetically formed perylenes. This approach can fuse the famous strong acceptors of 4,7-dithien-2-yl-2,1,3-benzothiadiazole $(\mathbf{DTBT})^{16}$ and 4,7-di(thiophene-2-yl)-2H-benzo[d]-[1,2,3]triazole (DTBTA)¹⁷ to afford BThP-Br and BTrP-Br through the classical Suzuki-Miyaura coupling and FeCl₃ oxidative cyclization. The rigidification and planarization of

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BThP and **BTrP** can restrict rotational motions, extend effective conjugation length, and promote intermolecular interactions, leading to broad light absorption and improved mobilities; while, two or three branched alkyl chains on the fused aromatic units could offer good solubility for material purification, device fabrication and morphology control. Considering that diketopyrrolopyrrole (**DPP**), as a widely used acceptor unit, has many advantages including good photochemical stability, strong light absorption, and highly ordered molecular packing,¹⁸ we then attempt to construct new A–FD–A-type OSC molecules using **BThP** or **BTrP** as the FD and **DPP** as the terminal acceptor unit, respectively.

Starting from the easily prepared compds **3**, **4**, and **8** (Schemes S1–S3), two building blocks of **BThP-Br** and **BTrP-Br** with simultaneously embedded perylene, benzoazoles, and alkyl chains of 2-ethylhexyl (EH) were facilely synthesized in three steps of conventional Suzuki–Miyaura coupling,¹⁹ bromination, and oxidative cyclization²⁰ in high yields of up to 85%, 95%, and 72%, respectively (Scheme 1).





Then they were coupled with **DPP** boronic ester by a Suzuki– Miyaura reaction, resulting in the corresponding target molecules of **BThP–DPP** and **BTrP–DPP** with total yields over 43%; these new compounds were fully characterized (Figures S1–S18). Owing to the presence of long and branched EH substituents, these molecules are readily soluble in common solvents, while the highly rigid perylene-embedded backbone leads to high thermal stabilities with decomposition temperatures (T_d) higher than 380 °C as revealed by the thermogravimetric analysis (TGA) (Figure S19). These perylene-benzoazoles with both good solubility and high thermal stability are applausive for solution processing of OSC devices and long-term stability upon solar luminance on operation.¹

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were investigated by both density functional theory (DFT) calculations (Figures 1 and S20) and experimental cyclic voltammetric (CV) measurements (Figure S21). In the A–FD–A molecules, the acceptor of **DPP** has deep HOMO and LUMO energy levels;¹⁸ the perylene-embedded **BThP** and **BTrP** units with fused molecular structures show slightly higher frontier orbitals than that of **DPP**, demonstrating the weak donor characteristic of **BThP** and **BTrP**. The **BTrP** unit seems to be a stronger donor than **BThP** from its high-lying HOMO level, due to the



Figure 1. DFT-calculated HOMO, LUMO, bandgap (E_g) , and frontier orbital isosurface (the isosurface value is 0.02) of **BThP**, **BThP–DPP**, **DPP**, **BTrP–DPP**, and **BTrP**.

stronger electron-donating ability of N in DTBTA. Therefore, BTrP-DPP has a higher HOMO than that of BThP-DPP, and both of them exhibit much lower bandgap (E_{σ}) than either DPP or BTrP/BThP, demonstrating a typical feature of D-A materials.^{6,7} However, owing to the much higher LUMO of BTrP, the corresponding BTrP-DPP also shows higher LUMO than BThP-DPP, which could provide higher energetic offset for the exciton dissociation into holes and electrons at the BTrP-DPP/fullerene interfaces. The A-FD-A molecular feature can be also distinguished by frontier orbital isosurfaces. The dominated LUMO wave function distribution on DPP unit suggests clearly the acceptor nature of DPP; while, the nearly equal contributions of DPP and BTrP/BThP on HOMO indicate that BTrP and BThP are indeed weak donors in these small molecular solar cell materials. It should be noted that **BTrP** and **BThP** also participate to some extent in the LUMO isosurface, possibly due to the electron-deficient nature of benzoazoles embedded in DTBT and DTBTA.^{16,17} From the onset of the oxidation waves of BThP-DPP and BTrP-DPP at -0.50 and -0.44 V vs Ag/Ag⁺ (Figure S21), their HOMO energy levels were determined to be -5.30 and -5.24 eV, respectively. Also, with the onset of reduction waves, their LUMOs were found to be at -3.37 and -3.24 eV, in good accordance with the computational results (Figure 1). The optical E_{gs} of **BThP-DPP** and **BTrP-DPP** were measured to be 1.55 and 1.60 eV from their absorption onsets at 801 and 776 nm in solid films (Table S1), which are close to that of ideal OPV donor with HOMO and E_g of -5.4 and 1.5eV based on traditional acceptor of fullerenes. These energy levels of BThP-DPP and BTrP-DPP are promising when they are used as donor materials in [6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM)-based OSCs.

High photon absorption ability in a wide range of wavelengths covering the whole sun-light spectrum is important for an efficient OSC material.²² From the absorption spectra **BThP-Br**, **BThP–DPP**, **BTrP-Br**, and **BTrP–DPP** in both diluted CH₂Cl₂ solutions and thin films (Figure 2a), red-shifted absorption bands of **BThP**-based molecules were observed in both solution and film with lower E_g than that of **BTrP-Br** and **BTrP–DPP**, which is in line with the theoretical predictions (Figure 1). The sunlight absorption range of the building block of **BThP-Br** is slightly wider than that of **BTrP-Br** in dilute CH₂Cl₂ solution with absorption peaks at 556 and 478 nm, respectively; however, **BTrP–DPP** exhibits a much higher molar extinction coefficient ($\varepsilon = 1.3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) than **BThP–DPP** ($\varepsilon = 7.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$),



Figure 2. UV-vis absorption spectra of BThP-Br, BThP-DPP, BTrP-Br, and BTrP-DPP in CH_2Cl_2 (~10⁻⁵ M) and thin film (a). DFT-simulated absorption spectra of the intermediates and target compounds (b).

probably owing to its higher oscillator strength for stronger photoabsorption (Figure 2b). Moreover, the significantly redshifted, stronger and broader absorption bands around 500– 750 nm compared to that of the building blocks demonstrate clearly the characteristic features of D–A molecules.⁵ It should be also noted that these molar extinction coefficients are among the highest values of OSC donors.¹⁸

In the solid films, very small red-shifts (<10 nm) of the absorption peaks were observed in both the building blocks and almost no shift in target donors, owing to the rigid molecular structures of these compounds. Interestingly, an additional absorption shoulder peak appears at 723 and 701 nm for BThP-DPP and BTrP-DPP, respectively, implying efficient $\pi - \pi$ stacking of these perylene-embedded A-FD-A molecules in the solid states.^{6,7} To further study the effects of bromination, rigid fusing, and D-A coupling of these A-FD-A molecules, theoretical simulations of their absorption spectra were performed. From Figure 2b, the bromination of BThP and BTrP only leads to slightly red-shifted absorption peaks, while the fusing of compounds 9 and 10 to prepare the building blocks of BThP and BTrP results in much red-shifted absorption bands (~100 nm), since the fused rigid perylene skeleton favors the delocalization of π electrons.⁴ Interestingly, BThP-DPP and BTrP-DPP show stronger absorption with 3-4-fold higher oscillator strengths at long wavelength ranges (>600 nm) compared to either the acceptor unit of DPP or fused donors of BThP and BTrP.

To evaluate the potential of these two perylene-embedded small molecules in the A-FD-A structure as donor materials of OSCs, preliminary BHJ cells were fabricated in a conventional device structure of ITO/PEDOT:PSS/BThP-DPP or BTrP-DPP:PC71BM/LiF/Al, where ITO and PEDOT:PSS are indium tin oxide and poly(3,4ethylenedioxythiophene):poly(styrenesulfonate), respectively (Figure S22).²³ Under AM 1.5 illumination, the current density-voltage (I-V) characteristics of these BHJ cells show the highest PCEs at varied additive and thermal annealing conditions (Figure 3a). For BThP-DPP/PC₇₁BM blend system, the 3 vol % diiodooctane (DIO)-processed devices give the highest PCE of 2.45% with an open-circuit voltage (V_{oc}) of 0.63 V, a short-circuit current density (J_{sc}) of 7.37 mA cm⁻², and a fill factor (FF) of 52.7%. Regarding the BTrP-DPP/PC₇₁BM blend film, the best PCE of 2.88% with



Figure 3. J-V characteristics (a) and incident photon to current efficiency (IPCE) spectra (b) of DIO-processed **BThP-DPP**/PC₇₁BM and TA-processed **BTrP-DPP**/PC₇₁BM OSCs. CV measurements (c, d) and TEM images (e, f) of **BThP-DPP**/PC₇₁BM (c, e) and **BTrP-DPP**/PC₇₁BM (d, f) films treated at different conditions. Note that the thermal treatment (TA) is at 100 °C for 10 min.

relatively larger J_{sc} of 9.44 mA cm⁻² was achieved by the thermal-annealing (TA) at 100 °C for 10 min (Table 1). The

Table 1. Photovoltaic Properties of BThP-DPP- and BTrP-DPP-Based BHJ Solar Cells

molecule	cond	$V_{\rm oc}~({\rm V})$	$J_{\rm sc} \left({\rm mA/m^2}\right)$	FF (%)	PCE (%)
BThP-DPP	w/o	0.66	2.72	55.2	0.99
	TA	0.66	2.55	50.6	0.85
	DIO	0.63	7.37	52.7	2.45
BTrP-DPP	w/o	0.72	4.45	40.7	1.30
	TA	0.69	9.44	44.3	2.88
	DIO	0.63	8.13	50.3	2.57

incident photon to current efficiency (IPCE) spectra reveal that the DIO-processed **BThP-DPP**/PC₇₁BM device has the efficiencies over 20% throughout the 350–750 nm range with a maximum of 27.6% at 670 nm, while **BTrP-DPP**/PC₇₁BM device exhibits significantly improved efficiencies throughout the whole visible region with the maximum IPCE up to 48% at 599 nm (Figure 3b). This higher IPCE in a wide range should be related to high ε for sunlight absorption, leading to better photovoltaic performance of **BTrP-DPP**/PC₇₁BM system, although **BThP-DPP** and **BTrP-DPP** have similar HOMO energy levels and molecular structures.

To understand the higher PCEs of **BTrP–DPP**-based OSCs with higher V_{oc} and larger $J_{sc'}$ cyclic voltammetry (CV) measurements were performed.²⁴ The **BThP–DPP**/PC₇₁BM and **BTrP–DPP**/PC₇₁BM blended films show varied onset potential of oxidative wave (E_{onset}^{ox}). The close E_{onset}^{ox} of **BThP–DPP**/PC₇₁BM films treated at different conditions may be responsible for their similar V_{oc} in devices (Figure 3c), while the quite different E_{onset}^{ox} of **BTrP–DPP**/PC₇₁BM films could result in different V_{oc} of their OSCs. The larger E_{onset}^{ox} of **BTrP–DPP**/PC₇₁BM should be a main reason for the higher

 V_{oc} of their devices (Figure 3d), although **BThP–DPP** has relatively lower HOMO than **BTrP–DPP**. Additionally, the transmission electron microscopy (TEM) images show high phase separation and severe aggregation in pristine **BThP– DPP**/PC₇₁BM-blended films (Figure 3e), which may be attributed to the poor miscibility of **BThP–DPP** with PC₇₁BM due to its intermolecular S…S interactions to form large aggregation domains.¹²

In summary, we succeed in developing an efficient synthetic route to prepare fused OSC building blocks of BThP-Br and BTrP-Br with a rigid perylene core for high photovoltaic property and branched alkyl chains for good solubility and morphology control; the consequently constructed two novel small molecular OSC donors of BThP-DPP and BTrP-DPP in the A-FD-A structure with the widely used acceptor of DPP show excellent solubility, high thermal stabilities, and good optical and electrochemical properties for photovoltaic applications, owing to the synergistic effects of heteroatom substitution, fused 2D-conjugation, flexible alkyl introduction, and A-FD-A architecture. Specifically, by only replacing the central S atom in the perylene-fused benzoazoles of BThP-DPP with an N atom, the band gap and HOMO/LUMO energy levels of the resulting BTrP-DPP are slightly increased owing to the electron-donating feature of N, but the lightabsorption ability is significantly enhanced and the additional branched alkyl chine on N of BTrP-DPP would be helpful for increasing its solubility and morphology/domain control of the blend films with PC71BM for OSCs. Therefore, the BTrP-DPP/PC71BM-based OSCs show higher photovoltaic performance than those of BTrP-DPP/PC71BM with PCEs up to 2.45% and 2.88%, respectively. These findings provide important clues for the design of fused 2D-conjugated molecules with simultaneously high solubility, stability, and optoelectronic properties for OSCs.

ASSOCIATED CONTENT

S Supporting Information

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Synthesis and characterization, thermal properties, electrochemical properties, DFT calculations and device fabrication, and characterization data including Schemes S1–S3, Figures S1–S18, and Table S1 (PDF)

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