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Two perylenediimide (PDI) derivatives (FP₄TT2T, FP₄3T) with extended conjugation have been successfully synthesized. Due to the long fused D-A (D: donor, A: acceptor) molecular structures, the PDI-based heteroacenes are rigid in backbones, and exhibit strong light absorption within 300-600 nm. Contributed by the PDI moiety with strong electron affinity, the molecules possess low energy levels of LUMOS (ca. -3.7 eV), fitting well as the acceptors for fullerene-free organic solar cells (OSCs). The OSC devices containing FP₄TT2T, FP₄3T were fabricated and fully characterized. It is found that geometric twist in the PDI-based heteroacenes as acceptors could enhance the performance of OSCs device. OSCs based on FP₄3T with more twisted geometry achieved higher power conversion efficiency of 6.05% than the FP₄TT2T counterpart.

1. Introduction

Organic solar cells (OSCs), capable of directly converting the sunlight into the electric energy in organic films, are considered as next-generation energy harvesting technology owing to numbers of potential advantages, such as low cost solution-processable, flexible, light-weighted, environmentally friendly, etc.¹⁻³ However, the power conversion efficiency (PCE) of OSCs still lags far behind that of its inorganic counterparts. To address this issue, researchers have made strenuous efforts to improve the performance of OSCs through development of novel materials and also device engineering.⁴⁻⁹ In recent years, exploiting non-fullerene acceptors for highly efficient OSCs is one of the research focus in this field.¹⁰⁻¹⁴ Compared to the fullerene acceptors with untunable energy levels, weak absorption in the visible region and poor photostability, e.g.,

[†] Electronic supplementary information (ESI) available. See 10.1039/x0xx00000x





Perylenediimide (PDI), which is composed of strong electronwithdrawing imide groups, and possesses high electron affinity, strong light absorption and high electron mobility, is appropriate for the building blocks for non-fullerene acceptors.²²⁻²⁴ However, owing to its planar molecular configuration, unmodified PDI is prone to form unfavorable aggregates in film,^{25,26} which will generally result in poor performances in bulk-heterojunction solar cells. Hence, modification of the basic structure of PDI is essential to acquire high photovoltaic performance.²⁷⁻³² To solve this problem, various strategies have been developed to suppress the large aggregation of PDI-based acceptors. The dimerization of PDI moieties with functional groups at bay position is a successful strategy for designing twisted or non-planar PDI-based acceptors.³³⁻³⁵ On the other hand, designing new PDI-based molecular structures such as PDI derivatives with threedimensional (3D) structures was considered as a more effective strategy for PDI-based acceptors.³⁶⁻³⁸ Although designing twisted or non-planar molecular structures seem to be a successful method for overcoming the strong aggregation tendency for PDIs, the detrimental effects on $\pi-\pi$ stacking of PDIs induced by steric hindrance weaken their charge transport ability in the blend film. Hence, designing three-dimensional (3D) structures with a proper degree of steric hindrance was considered as an effective way for building a balance between the optimal phase separation morphology and better $\pi-\pi$ stacking of molecules.²⁸ Recently, Peng reported two novel PDI trimers (named Ta-PDI and Ph-PDI) based on 1,3,5-triazine and benzene as the core. By eliminating the H-H steric hindrance between the benzene and PDI units, the Ta-PDI exhibited a less twisted structure that leads to higher crystallinity, better $\pi - \pi$

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stacking, and higher carrier mobility of the acceptors. With these merits, the Ta-PDI-based OSCs exhibited a higher PCE of 9.15% than that (5.57%) of the Ph-PDI devices.³⁹

Among the derivatives of PDI, PDI-based heteroacenes, normally constructed by fusing PDI fragments with other aromatic rings, can largely extend the π electron delocalization. Therefore, PDI-based heteroacenes demonstrate enhanced light absorption and higher electron mobility, and are intensively investigated in OSCs and also organic field effect transistors (OFETs).^{29, 40-45} In addition, fused ring structure also imparts the molecules with rigidity and twisted geometry between two planar π moieties. Such a configuration is closely associated with the intermolecular interaction of the molecules in solid state and their device performance.^{29,42,43}

In this work, two PDI-based derivatives composed of four PDI units fused by aromatic rings with π extension, FP₄TT2T and FP₄3T, were successfully synthesized. To form fused ring structures, thiophene or thienothiophene linkers were implanted through the Stille and Scholl coupling reactions. Both FP₄TT2T and FP₄3T have the merits of suitable energy levels, strong light absorption and rigid molecular structures, which contribute to the high photovoltaic performance in their OSCs. Moreover, geometric twist in FP₄TT2T and FP₄3T is found as an important factor impacting on the photovoltaic performance.⁴⁶⁻⁴⁸ FP₄3T with larger twist angle between PDI blocks, achieved higher efficiency than that of FP₄TT2T. This work demonstrates that tuning torsional twist between the building blocks is an effective strategy in developing high-performance PDI-based heteroacene acceptors.

2. Results and discussion

The chemical structures of FP₄TT2T and FP₄3T are shown in Figure 1a. The two compounds were synthesized through multistep Stille coupling and Scholl reactions (Scheme S1). Details of the synthetic procedures are provided in the supporting information. NMR spectroscopy and MALDI-TOF-Mass spectroscopy were used to characterize and confirm the structures of the two compounds (Figure S1-S15). Due to the thiophene rings used as the bridges in the two heteroacenes, both FP₄TT2T and FP₄3T contain isomers which can't be isolated in the synthetic processes. Nevertheless, we pay our attentions to the relationship between molecular structures and photovoltaic performances in this content. According to the thermo-gravimetric analysis (TGA), FP₄TT2T and FP₄3T exhibited favorable thermal stability with decomposition temperatures of 407 °C and 409 °C at 5% weight loss (Figure S16). The differential

scanning calorimetry measurement (DSC) did $_{V100}$ true while it melting or crystallization peaks between 30° C 40° 350° C (Figure S17), which indicated that FP₄TT2T and FP₄3T are amorphous in solid state. Owing to the solubilizing alkyl-chains introduced to the PDI units, the two compounds exhibited good solubility in most common polar solvents (e.g., chlorobenzene, chloroform, etc.).

UV-vis absorption spectra of FP4TT2T and FP43T are shown in Figure 1b and Figure S18. Due to the long conjugation skeletons, strong intramolecular charge transfer (ICT) induced by the Donor-Acceptor molecular structure, FP₄TT2T and FP₄3T showed intensive absorption from 300 nm to 600 nm, with a large molar absorption coefficient of $1.4 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at 383 nm for FP₄3T and 1.1×10^5 M⁻¹ cm⁻¹ at 404 nm for FP₄TT2T (Figure S26). The absorption spectra of FP₄TT2T in solution and film states demonstrated almost identical profiles. Whereas, the onset of the absorption spectrum from the FP43T films showed a red-shift of 11 nm compared with that from the solution (Figure S18b). The red-shift of the UV spectra is ascribed to the π - π interactions of the molecules in the solid state which was expected to achieve high charge mobilities and good performance in OSCs.^{27,38,49} The optical bandgaps of FP₄TT2T and FP₄3T are 2.11 eV and 2.01 eV estimated from the absorption onsets in films. The energy levels of the lowest unoccupied molecular orbitals (LUMOs) and the highest occupied molecular orbitals (HOMOs) FP₄TT2T and FP₄3T were calculated from the reduction onset potential (*E*^{red}_{onset}) measured by electrochemical cyclic voltammetry measurement (Figure 1c) and optical bandgaps, and the values are -3.62 eV/-5.73 eV and -3.70 eV/-5.71 eV, respectively. The optical and electrochemical data of FP₄TT2T and FP₄3T are summarized in Table 1. The energy levels of FP4TT2T and FP43T match well with most donors (like PTB7-Th) which guarantee the effective exciton separation and charge transport in bulk-heterojunction (BHJ) OSC

The BHJ-OSCs devices were fabricated with a conventional device architecture of ITO/PEDOT:PSS/PTB7-Th:FP₄TT2T or FP₄3T/PDIN/AI to characterize the photovoltaic performance of FP₄TT2T and FP₄3T. Because of the wide-bandgap properties of FP₄TT2T and FP₄3T, the narrow-bandgap p-type polymer PTB7-Th was selected as the donor for effective light harvesting. The chemical structures of PTB7-Th, PDIN and energy levels of different layers are shown in Figure 2a, b. Batches of BHJ-OSCs devices were fabricated and tested with different process conditions. The best photovoltaic performances were obtained with donor/acceptor (D/A) ratio of 1:1 without any postfabrication treatment for both FP₄TT2T and FP₄3T. The photovoltaic parameters were summarized in Table 2. The

Table 1. (Table 1. Optical and electrochemical properties of FP4TT2T and FP43T.										
-	Matarial	λ_{max} (sol)	$\lambda_{\scriptscriptstyle max}$ (film)	λ_{onset} (sol)	λ_{onset} (film)	E_{onset}^{red}	LUMO	Bandgap	НОМО		
	Material	[nm] ^{a)}	[nm]	[nm] ^{a)}	[nm]	[V] ^{b)}	[eV] ^{c)}	[eV] ^{d)}	[eV] ^{e)}	-	
•	FP₄TT2T	404	406	587	587	-0.50	-3.62	2.11	-5.73	•	
	FP₄3T	380	385	606	617	-0.42	-3.70	2.01	-5.71		

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^{a)}Obtained in CH₂Cl₂ solution; ^{b)}Measured by cyclic voltammetry; ^{c)}Calculated by using LUMO = $-[E_{onset}^{red} - E_{Fc/Fc+} + 4.8]$ eV; ^{d)}Estimated based on film absorption on set. ^{e)}Calculated by using LUMO and E_{eet}^{s} . DOI: 10.1039/DONJ01733G



Figure 1. (a) Chemical structures of FP₄TT2T and FP₄3T. (b) UV-vis absorption spectra of FP₄TT2T, FP₄3T and PTB7-Th thin films. (c) Cyclic voltammograms of FP₄TT2T and FP₄3T measured in 0.1 M solutions of tetra-*n*-butylammonium hexafluorophosphate in dry dichloromethane.

current density-voltage (J-V) curves of the optimized devices and corresponding external quantum efficiencies (EQE) spectra are shown in Figure 2c, d. The devices based on PTB7-Th:FP₄TT2T showed the highest PCE of 4.62% with an open circuit voltage (V_{oc}) of 0.92 V, a short circuit current density (J_{sc}) of 11.9 mA/cm² and fill factor (FF) of 42.1%. In comparison with PTB7-Th:FP4TT2T, PTB7-Th:FP43T based OSCs exhibited better performance with PCE of 6.05%, V_{oc} of 0.86 V, J_{sc} of 14.7 mA/cm² and FF of 48.1%. The decreased V_{oc} of FP₄3T-based OSCs corresponds to the slightly lower LUMO energy level of FP₄3T in contrast with FP₄TT2T. Owing to the complementary absorption spectra between donor and acceptors, the devices based on FP₄TT2T and FP₄3T exhibited broad spectral response in the range of 300 nm to 800 nm, as shown in Figure 2d. Both donor (PTB7-Th) and acceptors (FP₄TT2T and FP₄3T) contributed to photocurrent generation. The peak EQEs for both devices located at 570 nm are coincident with the UV absorption peaks of FP₄TT2T and FP₄3T, which also prove the contribution of the acceptors in the active layers to the photocurrent generation. The calculated J_{sc} integrated from the EQE spectra matched well with the corresponding J-V test. To characterize the bulk charge transport properties of the active layers, space-charge-limited current (SCLC) model was applied to investigate the hole and electron mobilities with the device configurations of ITO/PEDOT:PSS/PTB7-Th:Acceptors/MoO₃/Al for hole and ITO/ZnO/PTB7-Th:Acceptors/PDIN/Al for electron (Figure S21, S22). The calculated hole (μ_h) and electron (μ_e) mobilities of the PTB7-Th:FP₄TT2T based active layer are $3.45 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and 1.68×10⁻⁴ cm²V⁻¹s⁻¹ with μ_h/μ_e value of 2.05. The calculated μ_h

and μ_e of PTB7-Th:FP₄3T blend film are 6.30×10⁻⁴ cm²V⁻¹s⁻¹ and 5.27×10⁻⁴ cm²V⁻¹s⁻¹ respectively, with μ_h / μ_e value of 1.20. Compared with FP₄TT2T, FP₄3T based OSCs exhibited higher and more balanced charge mobilities which is in consistent with the higher J_{sc} and FF.

Although the chemical structures are similar between FP₄TT2T and FP₄3T, FP₄3T showed much better photovoltaic performance. Except for the lower V_{oc} caused by lower LUMO, FP₄3T-based OSCs exhibited enhanced J_{sc} and FF. To understand the reasons behind the results, density functional theory (DFT) calculations using the Gaussian package at the B3LYP/6-31G(d) level were performed to evaluate the differences in their molecular geometries and electronic properties between FP_4TT2T and FP_43T . As depicted in Figure 3, both FP_4TT2T and FP₄3T exhibit extended conjugation resulting from the ring fusion. The central two PDI units of FP₄TT2T show planar conformation because of the enough space provided by thieno[3,2-b]thiophene. Arising from the limited space of thiophene, the lateral two PDI units of FP₄TT2T present twisted conformation with dihedral angles between PDIs and thiophenes estimated to be 22.1° and 21.7°. In contrast with FP₄TT2T, FP₄3T has more condensed molecular structures with composition units of PDI-thiophene. The dihedral angles caused by the steric hindrance between PDI and thiophene were estimated to be 22.8°, 13.6° and 22.8° successively. Corresponding to the extended π -conjugation, both FP₄TT2T and FP₄3T illustrated well delocalization on the HOMO and LUMO orbitals. However, some distinctions between FP₄TT2T and FP₄3T can be observed. For FP₄TT2T, although the LUMO

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orbital distributes around the four PDI units, the whole continuity of LUMO orbital is attenuated on thieno[3,2-

b]thiophene part. The HOMO orbital of FP4TT2Twistimainly delocalized on the central two PDI units 1840 2018 2018



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Figure 2. (a) Chemical structures of PTB7-Th and PDIN. (b) Energy levels of active layers in the BHJ-OSCs. (c) *J-V* curves of the PTB7-Th:FP₄TT2T/PTB7-Th:FP₄3T based optimal solar cells devices under AM 1.5G irradiation (100 mW cm⁻²). (d) EQE spectra of the corresponding devices.

b]thiophene. In the case of FP₄3T, both LUMO and HOMO orbitals distribute continuously throughout the entire backbones. Concerning on the PDI-based non-fullerene acceptors, the structural twist is critical to the molecular interactions, the compatibility with donors and the film morphology. Combined with the UV characterization, the proper torsional twisty of FP₄3T is inferred to induce molecular interaction in film state. Besides, the fully delocalized frontier orbitals of FP₄3T can stabilize the free charges and finally improve the charge mobilities. The calculation results coincide with the optical properties and photovoltaic performance.

To observe the relationship between chemical structure and photovoltaic performance in visual, atomic force microscopy (AFM) and X-ray diffraction (XRD) were adopted to characterize the film morphology and intermolecular interaction in solid states. As illustrated in Figure 4, both PTB7-Th:FP₄TT2T and PTB7-Th:FP₄3T blend films exhibit smooth and uniform surface morphology due to the rigid and twisted molecular conformations of the new PDI-based heteroacenes.⁵⁰ The rootmean-square (RMS) roughness of the blend films were estimated to be 1.12 nm for PTB7-Th:FP4TT2T and 1.02 nm for PTB7-Th:FP₄3T, respectively, which indicates good miscibility of the donor and acceptor and could be beneficial to the enhancement of FF and J_{sc} in the devices. However, no desired distinct molecular aggregation, thus nano phase separation was observed from AFM images. As mentioned above, PTB7-Th:FP₄3T blend films also exbibit higher and more balanced charge mobilities. The higher electron mobility of FP₄3T is rationalized as the stronger intermolecular interaction of FP₄3T in solid state, which is evidenced by the XRD measurement (Figure S23) and red-shift UV absorption in film state. Hence, the optimized twisted geometry of FP₄3T which finally lead to favorable film morphology and enhanced charge mobilities are responsible for the improved J_{sc} and FF in BHJ-OSCs.

Table 2. Photovoltaic performances of PTB7-Th:FP4TT2T and PTB7-Th:FP43T solar cells, under illumination of AM 1.5G (100 mW cm ⁻²).										
	D:A ^{a)}	<i>V_{oc}</i> [V]	J _{sc} [mA cm ⁻²]	FF [%]	PCE [%] ^{b)}	μ _h [cm² V ⁻¹ s ⁻¹] ^{c)}	μ _e [cm² V ⁻¹ s ⁻¹] ^{c)}	μ_h/μ_e		
	PTB7-Th: FP₄TT2T	0.92	11.9	42.1	4.62 (4.34)	3.45 × 10 ⁻⁴	1.68 × 10 ⁻⁴	2.05		
	PTB7-Th: FP₄3T	0.86	14.7	48.1	6.05 (5.92)	6.30 × 10 ⁻⁴	5.27 × 10 ⁻⁴	1.20		

^{a)}The optimized donor:acceptor ratio was 1:1 (w/w%); ^{b)}The average data obtained from analysis of 10 devices are shown in brackets; ^{c)}Measured using space charge-limited current method.

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Figure 3. Optimized molecular geometries of (a) FP₄TT2T and (b) FP₄3T. Frontier molecular orbitals of (c) FP₄TT2T and (d) FP₄3T.

To investigate the crystallinity and molecular orientation of the films of neat FP₄3T, FP₄TT2T and their blends with PTB7-Th, grazing-incidence X-ray scattering (GIXRD) measurement was performed. The 2D-GIXRD patterns and the corresponding inplane/out-of-plane line cuts were shown in Figure S25. The neat and blend films didn't show any Bragg reflections, indicating lack of crystalline domains for the neat and blend films. The amorphous nature of the four films should be ascribed to the twisted geometry of FP₄3T and FP₄TT2T molecules. The results illustrated that incorporation of geometric twist into the fused PDI molecules is a promising approach to control the molecular aggregation in the films while keeping high charge mobility and good power conversion efficiency in OPV devices.



Figure 4. AFM height images (scale bar: 1 µm) of (a) PTB7-Th:FP4TT2T, (c) PTB7-Th:FP43T blend films and their corresponding phase images (b), (d).

3. Conclusions

Herein, two PDI-based heteroacenes were successfully synthesized and characterized. The well conjugated skeletons of FP₄TT2T and FP₄3T endow the two molecules with strong light absorption from 300 nm to 600 nm. The two PDI-based heteroacenes possess suitable LUMO energy levels as the nonfullerene acceptors in BHJ-OSCs. BHJ-OSCs based on PTB7-Th:FP₄TT2T and PTB7-Th:FP₄3T achieved PCEs up to 4.62% and 6.05%, respectively. The molecular geometries of FP₄TT2T and FP_43T , playing a critical role for their photovoltaic performance, are deeply investigated. FP₄3T with proper twisted molecular conformation induced stronger intermolecular interaction and favorable film morphology. In comparison with PTB7-Th:FP4TT2T blend film, PTB7-Th:FP43T blend film exhibit higher and more balanced charge mobilities and thus better photovoltaic performance. The results demonstrate that the geometrically twist in PDI-based heteroacenes as non-fullerene acceptors has a significantly influence on the photovoltaic performance in BHJ-OSCs.

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Conflicts of interest

There are no conflicts to declare.

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