SPECIAL ISSUE: Flexible and Stretchable Energy

A twisted monomeric perylenediimide electron acceptor for efficient organic solar cells

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ABSTRACT Perylenediimide (PDI)-based materials exhibit great potential as non-fullerene acceptors in bulk-heterojunction (BHJ) organic solar cells (OSCs). Recent investigations have revealed that PDI molecules with a twisted structure could disrupt aggregation of perylene unit. Here, we present a PDI monomer via bay-substitutions with four fused naphthalene units by three-step reactions, named TN-PDI. The introduction of four fused naphthalene rings into the bay positions of PDI unit leads to a strong steric hindrance with a twist angle of 33° between the two PDI subplanes. Blended with a wide-band gap polymer donor (PDBT-T1), the TN-PDI based non-fullerene solar cells show power conversion efficiency (PCE) of 3.0%. Our results indicate that the bay-substitutions with fused aromatic substitutions could be an efficient approach to develop monomeric PDI acceptors.

Keywords: organic solar cells, non-fullerene electron acceptors, perylene diimide, monomer

INTRODUCTION

Solution-processed bulk-heterojunction (BHJ) organic solar cells (OSCs) have emerged as one of the next-generation energy resources to meet the worldwide urgent energy demand in virtue of their merits in light weight, low fabrication cost and the capability to build on the plastics and printing manufactures [1–7]. Among various materials used for acceptors, fullerene derivatives act as the protagonists of electron acceptors, which lead the power conversion efficiencies (PCEs) to 11% for single junction OSCs [8–12]. Despite the achievements of fullerene derivatives in laboratory scale devices, the high-cost production, inflexibility in chemical modification, and weak light absorption in the visible region of fullerenes hamper their practical applications [13–16]. To this end, design and synthesis of or-

ganic fused acceptors have being considered as vital alternatives to the fullerene counterparts in terms of their tunable energy level, broad absorption, and chemical robustness [17–19]. Recently, several excellent polymer/non-fullerene systems have led to the high PCEs up to 9%, which indicates that non-fullerene OSCs have enormous potential to approach performance similar to that of fullerene-based solar cells [20–23].

Perylene diimide (PDI) derivatives are widely used as the electron acceptor in OSCs due to their excellent thermal and chemical stabilities, strong electron-accepting abilities, and high electron mobilities [24,25]. However, in the initial stage, PDI derivatives suffer from over-strong propensity of aggregation, leading to the formation of large crystalline domains [26–29]. Moreover, some PDI derivatives intend to form excimers that perform as traps for excitation energy which severely hinder the efficiency of exciton splitting and the further performance of the OSCs [30–33]. Considerable effort has been dedicated to design and synthesize PDI-based acceptors with twisted structures in order to weaken aggregation and restrict crystalline of molecules [34–39]. PDI monomers are alternative non-fullerene acceptors. Functionalized monomeric PDI derivatives were generally synthesized with alkyl-chain on the imide position or aliphatic or aromatic substituent on the bay-position [40–45]. The modification on the bay region can be of tremendous assistance to make the perylene core twisted, impede intermolecular interactions, and adjust the energy levels of the materials potentially [46–48]. Recently, we have reported a PDI monomer (TP-PDI), in which four phenyl groups are appended to the bay positions of PDI unit. OSCs based on TP-PDI acceptor showed a record

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PCE of 4.1% for monomeric PDI based polymer solar cells [45]. The high performance of TP-PDI inspired us subsequently to develop its analogue to study the relationship between photovoltaic properties and twisted molecular structures for PDI acceptors.

Herein, we reported a non-fullerene acceptor 1,6,7,12-tetra-naphthalenyl-perylenediimide (TN-PDI), in which four fused naphthalene units are inserted to the bay positions of PDI core. The incorporation of naphthalene units could afford a twisted configuration and provide a solution for inhibiting aggregation tendency and tuning the phase separation in as-casted film. Moreover, this PDI monomer could be simply synthesized in three steps and purified on a large scale [49]. TN-PDI possesses high lowest unoccupied molecular orbital (LUMO) level which leads to an impressive open-circuit voltage (V_{oc}), broad absorption in visible spectrum and complements well with the donor material. By incorporating a wide band gap polymer PDBT-T1 [50] with the monomer, an initial PCE of 3.0% was achieved with a V_{oc} of 0.95 V, short-circuit current density (J_{sc}) of 7.70 mA cm^{-2} , fill factor (FF) of 0.41.

EXPERIMENTAL SECTION

Materials

3,4,9,10-Perylenetetracarboxylic dianhydride, 2-ethylhexylamine, 1-naphthaleneboronic acid, tetrakis(triphenylphosphine)palladium, cesium fluoride, and silver(I) oxide were purchased from Acros. The wide-bandgap polymer PDBT-T1 is previously reported by our group [50]. Regular chemical reagents and solvents were obtained from Beijing Chemical Plant. Solvents for reactions and photo-physical measurements, such as N,N' -dimethylformamide (DMF), tetrahydrofuran (THF), and dichloromethane (CH_2Cl_2), were all distilled after dehydration according to conventional methods.

General

Mass spectra were recorded on an AEI-MA50-MS spectrometer for EI-MS. MALDI-TOF spectra were recorded on a Bruker BIFLEX III instrument. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer using CDCl_3 as the solvent. Thermogravimetric analyses (TGA) were performed on a NETZSCH STA 409 under N_2 flow at a heating rate of $20^\circ\text{C min}^{-1}$. UV-vis absorption spectra were obtained with SHIMADZU UV-2600. Theoretical calculations using density functional theory (DFT) were performed using the Gaussian03 package at the B3LYP level of theory with a basis

set of 6-31G(d). Atomic force microscopy (AFM) images were obtained using a NanoMan VS microscope in the tapping mode. Cyclic voltammetric (CV) measurements were performed in a conventional three-electrode cell using a Pt button as working electrode of 2 mm in diameter, a Pt wire as counter electrode, and a Ag/Ag^+ electrode as reference electrode on a computer-controlled CHI-660E electrochemical workstation at room temperature. The compound tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 mol L^{-1}) is used as a supporting electrolyte. The energy levels were calculated using the ferrocene (E_{FOC}) value of 4.8 eV as the standard: $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.80)$ (eV) (highest occupied molecular orbital (HOMO)), $E_{\text{LUMO}} = -(E_{\text{red}} + 4.80)$ (eV).

Synthesis

Compound **1** (1,6,7,12-tetrabromoperylene-3,4,9,10-tetracarboxylic acid bisanhydride) and compound **2** (N,N' -Di(2-ethylhexyl)-1,6,7,12-tetra-bromoperylene-3,4,9,10-tetra-carboxylic acid bisimide) were synthesized as reported in our previous work [49].

Compound TN-PDI (N,N' -di(2-ethylhexyl)-1,6,7,12-tetranaphthaleneperylene-3,4,9,10-tetracarboxylic acid bisimide): compound **2** (626 mg, 0.72 mmol), 1-naphthaleneboronic (528 mg, 4.32 mmol), cesium fluoride (880 mg, 5.76 mmol) and silver(I) oxide (736 mg, 3.2 mmol) were added to a three-neck flask. After the flask was degassed with nitrogen, tetrakis(triphenylphosphine)palladium (83 mg, 0.072 mmol) was added with a gentle flow of nitrogen. 15 mL THF was added. Then, the flask was cooled to -78°C and further evacuated and backfilled with nitrogen three times. The reaction mixture was stirred at 80°C for 24 h with vigorous stirring. After cooled to room temperature, the crude product was purified by flash column chromatography (SiO_2 , toluene) to give 1,6,7,12-tetraphenylperyene bisimide as a dark purple solid. Yield: 29%. ^1H NMR (400 MHz, CDCl_3 , ppm, 25°C): δ = 8.43–8.46 (4H, m, perylene-H), 7.73–7.75 (4H, m, naph-H), 7.43–7.45 (8H, br, naph-H), 7.09 (4H, s, br, naph-H), 6.82 (4H, s, br, naph-H), 6.66 (8H, m, naph-H), 4.16–4.18 (4H, d, N-CH-), 2.00 (2H, m, -CH-), 1.33–1.44 (18H, m, -CH₂-), 0.85–1.05 (12H, m, -CH₂-). ^{13}C NMR (CDCl_3 , 25°C): δ = 164.39 (C=O), 142.58, 137.94, 134.78, 134.37, 132.25, 131.98, 129.95, 128.24, 127.78, 127.16, 126.67, 126.27, 122.65, 44.44, 38.30, 32.06, 31.12, 30.91, 29.83, 29.22, 28.74, 24.49, 24.26, 23.25, 22.82, 14.30, 11.01, 10.66. MALDI-TOF-MS: calcd. for $\text{C}_{80}\text{H}_{66}\text{N}_2\text{O}_4$ 1119.39; found: 1119.5. Elemental analysis calcd. (%) for ($\text{C}_{80}\text{H}_{66}\text{N}_2\text{O}_4$): C, 85.84; H, 5.94; N, 2.50; found: C, 85.51;

H, 5.91; N, 2.52.

Device fabrication and characterization

BHJ OSCs were fabricated on indium tin oxides (ITO)-coated glass substrates, which were first cleaned in an ultrasonic bath, sequentially in detergent, water, acetone, and isopropyl alcohol. After pretreated with UV-ozone for 20 mins, ZnO precursor solution was spin-cast onto the ITO substrate and baked at 230°C for 20 min. Active layer solution containing a mixture of PDBT-T1:TN-PDI (with or without 0.25% DIO, 50:50 *w/w*) in dichlorobenzene at a total solids concentration of 20 mg mL⁻¹ was spin casted at 1300 rpm for 90s. Before transferred into a thermal evaporator, the samples were annealed at 90°C for 5 mins to achieve an optimized film. Then, MoO_x (≈ 6 nm) and Al (≈ 100 nm) layers at the vacuum condition of 8 × 10⁻⁵ Pa were deposited in the evaporator. The active area of the devices was 4.50 mm². Current density-voltage (*J*-*V*) characteristics were measured by using a Keithley 2400 Source Measure Unit. Solar cell performance was characterized by an Air Mass 1.5 Global (AM 1.5 G) solar simulator (Class AAA solar simulator, Model 94063A, Oriel) with an irradiation intensity of 100 mW cm⁻², which was measured by a calibrated silicon solar cell and a readout meter (Model 91150V, Newport). Incident photon-to-current conversion efficiency (IPCE) spectra were measured by a QEX10 Solar Cell IPCE measurement system (PV measurements, Inc.).

RESULTS AND DISCUSSION

Synthesis

As shown in Scheme 1, TN-PDI was synthesized in three

steps: first, compound **1** was synthesized by treatment of perylene bisanhydride with Br₂ in the mixture of sulfuric acid and fuming sulfuric acid with crude yield is as good as 96%. Then, compound **2** was functionalized by 2-ethylhexylamine at *N*-position in propionic acid. Finally, the four bromines in the bay position of compound **2** were successfully substituted by naphthaleneboronic to construct TN-PDI through fluoride ion-mediated and Ag₂O-promoted Suzuki coupling reaction [44]. The compound exhibits good solubility in common organic solvents such as CH₂Cl₂, THF, and toluene at room temperature, which provides convenience for purification and full characterizations. Such solubility is mainly due to both the branched alkyl side chains and the twisted molecular skeleton. For the large molecular weight of TN-PDI, a MALDI-TOF-MS measurement (*M*_w.1119.5 as found) is employed to characterize the structure and molecular weight directly. Thermogravimetric analysis (TGA) was utilized to evaluate the thermal property under a nitrogen atmosphere at a heating rate of 20°C min⁻¹. TN-PDI shows great thermal stability with 5% weight loss temperature at 446°C (see Fig. S1).

Theoretical simulation of TN-PDI

To gain a deeper insight into the electronic distribution and geometrical configuration of TN-PDI, we performed DFT calculations at B3LYP/6-31G(d) level. The corresponding electron distributions of HOMO and LUMO of the ground state optimized structures are shown in Fig. 1a. For the HOMO level of TN-PDI, more electrons are distributed around the PDI unit, with only a slight influence from the

Scheme 1 Synthetic route of TN-PDI and the chemical structure of PDBT-T1.

Figure 1 Optimized geometries of TN-PDI by DFT at the B3LYP/6-31G(d) level: (a) frontier molecular orbitals, (b) side view and top view of the molecular model.

naphthalene unit. On transition to the LUMO level, the molecular orbital of the PDI unit is dominant. Fig. 1b shows the side view and top view of the geometrical configuration of TN-PDI. The pristine PDI unit is completely planar without any substituent at the bay positions. For TN-PDI, PDI was functionalized via bay-substitution with fused naphthalene, and the determined twisted angle between the two subplanes of PDI is about 33° (Fig. S2), due to strong steric repulsion of the naphthalene units at the bay positions. And, the dihedral angle between the plane of the naphthalene unit and the PDI is about 42° (Fig. S2). Therefore, the twisted structure will reduce the tendency of aggregation of PDI unit in the solid state, which leads to a better performance of optoelectronic devices.

Optical properties

The UV-vis absorption spectra of TN-PDI were measured in solution and thin film as presented in Fig. 2a. It can be seen that TN-PDI (in chloroform, 10^{-6} mol L $^{-1}$) exhibits a broad absorption spectrum with two peaks at 528

and 613 nm. Compared with the absorption spectrum in solution, the spectrum in thin film of TN-PDI shows a similar profile with only a relatively small shift of 5 nm, indicating weak molecular aggregation and intermolecular interaction in the solid state [51]. The optical feature could be assigned to the twisted structure of the perylene unit supported by the theoretical calculations. For the BHJ OSCs constructed with TN-PDI as acceptor, we chose a wide band-gap polymer PDBT-T1 (shown in scheme 1) as the electron donor. As illustrated in Fig. 2b, the main absorption of PDBT-T1 is in the range of 550–700 nm, which complements the weak absorption of TN-PDI in this region, and should be beneficial for charge generation inside the devices. Finally, a broad absorption covering the visible range of 400–700 nm was observed for PDBT-T1: TN-PDI blend film (1:1, w/w), which may suggest a better J_{sc} for the OSCs.

Electrochemical properties

The electrochemical property of TN-PDI was investigated by CV, as shown in Fig. 3a. When potential cycling was applied, TN-PDI exhibits electrochemically stable. The CV curve was recorded vs. the potential of Ag/Ag $^+$ reference electrode. In the cathodic scan region, TN-PDI rises to one reversible reduction waves, which reflects electron reductive process of the perylene cores. In the anodic scan region, the irreversible oxidation peak was observed at ca. 1.35 V, which is attributed to the oxidation of naphthalene moieties. The onset oxidation and reduction potentials are 0.80/−0.80 V vs. Ag/Ag $^+$ electrode, so the HOMO and LUMO energies of TN-PDI are to be at −5.60 and −4.00 eV, respectively. The energy level of PDBT-T1 is also displayed in Fig. 3b. The energy offset between the HOMO of PDBT-T1 (−5.36 eV) and the LUMO of TN-PDI (−4.00 eV) is 1.36 eV. As a consequence, a high V_{oc} is expected. The LUMO gap between the PDBT-T1 and TN-PDI is 0.57

Figure 2 (a) Normalized UV-vis absorption spectra of neat TN-PDI in solution and thin film, (b) normalized thin-film absorption spectra of neat TN-PDI, PDBT-T1 and their composite (1:1 w/w, PDBT-T1 concentration is 10 mg mL $^{-1}$).

Figure 3 (a) CV plot of TN-PDI in thin film, (b) energy levels of all materials used in the solar cell device.

eV, expected to be sufficient for efficient exciton dissociation.

Photovoltaic properties

To demonstrate the potential application of TN-PDI in OSCs, an inverted structure of ITO/ZnO/PBDT-T1:TN-PDI/MoO_x/Al was used in this work, sol-gel-derived ZnO is the electron transport layer [52], and MoO_x is functioned as the hole transport layer. As known, weight ratios of donor and acceptor in active layers play important roles on the performance of OSCs. Thus, three different weight ratios at 1.5:1, 1.1 and 1:1.5 (*w/w*) were performed for the PBDT-T1:TN-PDI blend films. The corresponding photovoltaic parameters were summarized in Table 1. With weight ratios decreasing, there are almost no change for

V_{oc} , which are all above 0.9 V. But, in terms of J_{sc} and FF parameters, the devices show big difference with different weight ratios. Thus, the optimal ratio of the donor and acceptor is found to be 1:1. It is known that photovoltaic properties are greatly affected by the morphology of the active layers. 1,8-diiodooctane (DIO) was used to modify the morphology so as to further improve the cell performance (as shown in Table 2). The current density-voltage (J - V) curves of the devices fabricated with optimal conditions under simulated AM 1.5 G irradiation with intensity of 100 mW cm⁻² are shown in Fig. 4a. When 0.25% DIO was added, J_{sc} increased from 6.94 mA cm⁻² to 7.70 mA cm⁻², FF increased to 0.41, and an improved PCE of 3.0% was achieved. Compared with the reported PCEs of PDI monomer-based solar cells, this initial PCE is much higher

Figure 4 (a) J - V curves of OSCs with an inverted structure based on PBDT-T1:TN-PDI solar cells with/without DIO under simulated AM 1.5G irradiation (100 mW cm⁻²), and (b) the corresponding IPCE spectra.

Table 1 Photovoltaic performance of solar cells based on different weight ratios of PBDT-T1:TN-PDI in an inverted structure under the illumination of AM1.5G, 100 mW cm⁻²

Weight ratios (<i>w/w</i>)	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE ^a [%]	PCE _{max} [%]
1.5:1.0	0.930±0.004	6.51±0.09	0.35±0.02	2.12±0.16	2.28
1:1	0.947±0.003	7.52±0.18	0.40±0.01	2.85±0.15	3.00
1.0:1.5	0.930±0.002	6.60±0.13	0.36±0.03	2.20±0.25	2.45

a) The average PCE value was calculated from five devices for each condition.

Table 2 Photovoltaic performance of solar cells based on PBDT-T1:TN-PDI (1:1, w/w) with different DIO additive contents in an inverted structure under the illumination of AM1.5G, 100 mW cm⁻²

DIO [v/v %]	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF [%]	PCE ^a [%]	PCE _{max} [%]
0	0.950±0.001	6.87±0.07	0.35±0.01	2.28±0.11	2.38
0.25	0.947±0.003	7.52±0.18	0.40±0.01	2.85±0.15	3.00
0.50	0.937±0.007	6.97±0.10	0.41±0.01	2.68±0.12	2.80

a) The average PCE value was calculated from five devices for each condition.

than that value reported from the two bay-positions substituted PDI monomer-based solar cells [40–43], and is close to the top values of the PDI monomer-based non-fullerene cells [44,45].

Fig. 4b shows the corresponding IPCE spectra of solar cells with or without DIO additive. The addition of DIO increases the IPCE obviously in 300–400 nm. The maximum IPCE reached 46% at 630 nm for the champion cell. To make sure the accuracy of the J_{sc} values measured from J-V curves, the photocurrent values from IPCE spectra was calculated. The calculated J_{sc} was 7.40 mA cm⁻², entailing 5% mismatch with the value from J-V measurement.

The bulk charge-transport properties of PBDT-T1:TN-PDI blend films were investigated by the space-charge-limited current (SCLC) method. The device structures for electron-only measurements were ITO/Al/PBDT-T1:TN-PDI/Al for optimized device. The electron mobility of the optimized device is 1.6 × 10⁻³ cm² V⁻¹ s⁻¹ (Fig. S4) and the electron mobility of neat TN-PDI film is 9.8 × 10⁻⁴ cm² V⁻¹ s⁻¹ (Fig. S5).

Film morphology

Influence of the solvent additive DIO on the morphology of PBDT-T1:TN-PDI blended films was investigated by AFM in the tapping mode (Fig. 5). The surface of the PBDT-T1:TN-PDI film without DIO shows relatively homogeneous and smooth surface morphology with a root mean square (RMS) roughness of 5.68 nm. After the treatment of DIO additive, the film displays smaller crystalline grains and better mixed BHJ morphology with a RMS of 4.70 nm. The more smooth and uniform morphology with the introduction of DIO implies better compatibility with the donor for TN-PDI, and leads to enhanced J_{sc} and FF. The above discussions imply well that the molecule TN-PDI is an excellent acceptor candidate for efficient OSCs. Further work on optimized device is still under investigation.

CONCLUSIONS

In summary, a novel bay-substituted fused naphthalene functionalized PDI monomer (TN-PDI) was synthesized and successfully applied in BHJ OSCs. TN-PDI displayed

Figure 5 AFM topography image and phase image of PBDT-T1:TN-PDI blend films (a and c) without DIO additive, (b and d) with 0.25% DIO additive.

relatively strong absorption in the visible region, good miscibility with polymer donors. DFT calculations illuminate that the four bay-position substitutions introduce a twisting of the perylene skeleton, leading weak aggregation in the solid state. The solar cells with an inverted architecture show a PCE of 3.0%. The results demonstrate that the bay-substitutions with fused aromatic substitutions could be an effective approach to develop monomeric PDI acceptors.

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Author contributions Cai Y performed the experiments for organic solar cells and wrote the draft. Guo X synthesized the organic compounds. Sun X conceived the experiments, analyzed the results and wrote the paper. Wei D and Yu M provided theoretical simulation. Huo L analyzed the results. All authors contributed to the general discussion and revised manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supplementary data: the TGA thermogram, the calculation for the Dihedral angles of the optimized geometry of TN-PDI, the absorption features of donor-acceptor blends, the SCLC measurement for the electron mobility of TN-PDI and the mobility of optimized device are available in the online version of this paper.

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构筑扭曲花酰亚胺单分子型电荷受体材料用于高性能有机太阳能电池

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摘要 近年来, 本体异质结型有机太阳能电池领域中, 花酰亚胺类衍生物作为富勒烯类电荷受体材料的最佳替代材料而得到广泛关注. 很多研究表明扭曲构型的分子结构设计可以明显地抑制花酰亚胺的聚集行为. 本研究在花酰亚胺的四个湾位同时共轭引入氨基官能团, 从而合成一种简单结构的花酰亚胺单分子型电荷受体材料TN-PDI. 四个共轭氨基的引入使花酰亚胺平面骨架扭曲至33°. 分别以TN-PDI和一种宽带隙聚合物PDBT-T1为电荷受体材料和给体材料构筑本体异质结型有机太阳能电池, 其光电转换效率可达3.0%. 研究表明, 四个湾位同时共轭取代花酰亚胺是一种制备简单高效花酰亚胺单分子型电荷受体材料的有效方法.