



Isomeric small molecule acceptors based on perylene diimide and spirobifluorene for non-fullerene organic solar cells



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ABSTRACT

Two isomeric small molecules based on perylene diimide with 4,4'-/2,4'-substituted spirobifluorene as the core were designed and synthesized as acceptor materials for organic solar cells. According to density functional theory calculations, the different sites of the substitution, either the 4-position or the 2-position of the spirobifluorene led to significant distinction in both molecular structure and electronic distribution. The dihedral angles between the two perylene diimide units were calculated as well, indicating the 2-position linkage molecule had a more isotropic spatial arrangement. X-ray diffraction results showed the more ordered molecular packing of the 2-position linked molecule. In consequence, when blended with a donor, these two acceptors exhibited different device performance, especially the short circuit currents. The solar cell based on the 2-position linkage molecule achieved the best power conversion efficiency of 4.56% with 2% 1-chloronaphthalene as an additive. The hole and electron mobilities were also improved greatly after adding 2% 1-chloronaphthalene, which benefited the short circuit currents.

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1. Introduction

With the energy shortage and environmental deterioration issues, more and more studies are focused on organic solar cells (OSCs) for the advantages such as light weight, low cost, ready flexibility and simple processing [1–4]. Fullerene derivatives are widely used as electronic acceptors in bulk-heterojunction (BHJ) OSCs and the power conversion efficiencies (PCEs) have surpassed 10% [5–8]. Nevertheless, narrow absorption, small molar extinction coefficient, high cost, poor solubility, difficulty in functionalization and limited bandgap variability impede further promotion in fullerene-based device performance [9–11]. To overcome these

shortcomings, several other kinds of materials collectively known as non-fullerene acceptors such as rylene dimides [12,13] and subphthalocyanine [14–16], have been developed in the last decade [17–24]. Generally, the molecular structures of these materials are based on various electron deficient groups, including fluoranthene-fused imide [25], perylene diimide (PDI) [20,22,24,26,27], naphthalimide [28], benzothiadiazole [29,30], diketopyrrolopyrrole [21,23,31,32] and 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile (INCN) [33–35]. Among these, PDI is becoming the most widely used moiety because of the excellent absorption, chemical and thermal stabilities, strong electron-withdrawing ability and high electron mobility [4]. Since PDI monomer is particularly easy to aggregate owing to its large planar structure, which may lead to excessive phase separation [36], PDI based non-fullerene acceptors are preferably designed as 3D spatial configurations. Additionally, such designs can even simulate the isotropy of fullerene derivatives, which is well known as one of the reasons for their outstanding performance in OSCs [17,36–41].

There are diverse methods to construct a 3D structure a PDI component. One method is to introduce functional groups into the

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nitrogen atom of the imide group while the more general approach is connecting several PDI units with a core containing multidirectional reaction sites, such as triphenylamine [17,22,42], tetraphenylmethane [26], tetraphenylsilane [40] and spirobifluorene (SPF) [41,43,44]. Among these, SPF is widely utilized because of the intramolecular orthorhombic structure in which the two fluorene planes are connected through an sp^3 carbon as a bridging atom. Up to now, the overwhelming majority of investigations related to PDI and SPF are connecting PDI with the 2-position of SPF, while no investigation has anything to do with the 4-position of SPF in OSCs. In our previous work, we have reported the SPF derivatives constructed by partially or fully ortho-linking (referred to the 4-position linkage) and their application in organic light-emitting diodes (OLEDs) [45,46]. This kind of linkage brings about considerably twisted structures, which is also desirable for PDI-based acceptor materials. Consequently, here we report two novel 3D-configuration small molecule acceptors: SPFPDI44 and SPFPDI24 (Fig. 1a), where two PDIs are connected with SPF through the 4,4'-position and 2,4'-position, respectively. Their photovoltaic properties have been investigated by blending with a narrow-band gap polymer donor poly[[4,8-bis[5-(2-ethylhexyl)thiophene-2-yl]benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-*b*]thiophenediyl]] (PTB7-Th) (Fig. 1b). The different torsional angles between PDI and fluorene lead to different conditions of π - π stacking in blended films, which significantly affects the PCEs.

2. Synthesis

2.1. Synthesis of SPFPDI44

4,5'-di(2,2,3,3-tetramethyl-2,3-butanedionato)boron-9,9'-spirobifluorene (284 mg, 0.5 mmol) was mixed with 1-bromoperylene diimide (1.55 g, 2 mmol), KOH (448 mg, 8 mmol), Pd(PPh₃)₄ (70 mg, 0.06 mmol), toluene (12 mL), EtOH (6 mL) and water (3 mL), and the mixture was refluxed at 110 °C for 48 h under Ar. After cooling to room temperature, the mixture was adjusted to neutral by dilute hydrochloric acid and then extracted with chloroform three times. The organic layer was washed with aqueous NaCl solution three times and dried over anhydrous Na₂SO₄ for 30 min. The crude product was purified by silica gel chromatography using an eluent of petroleum ether: ethyl acetate = 10: 1 (v/v) and recrystallized from chloroform/hexane, to give a red solid (345 mg, yield: 40%). ¹H NMR (CDCl₃, 400 MHz): δ [ppm]: 8.85–8.72 (m, 10H), 8.30–8.06 (m, 4H), 7.50–7.35 (m, 5H), 7.12–7.02 (m, 3H), 6.91–6.82 (m, 6H), 5.18 (d, *J* = 5.20 Hz, 4H), 2.29–2.20 (m, 8H), 1.90–1.79 (m, 12H),

1.31–1.22 (br, 44H), 0.87–0.79 (br, 24H); ¹³C NMR (CDCl₃, 100 MHz): δ [ppm]: 164.80, 164.44, 163.76, 163.46, 151.37, 151.25, 150.74, 148.92, 148.20, 140.86, 140.51, 139.56, 138.29, 137.40, 137.27, 136.39, 135.85, 135.22, 135.01, 134.32, 133.24, 131.83, 131.63, 131.09, 130.11, 129.95, 129.27, 129.18, 128.67, 128.43, 127.95, 127.44, 124.74, 124.35, 124.22, 123.94, 123.84, 123.34, 123.01, 122.66, 122.03, 121.87, 65.74, 54.93, 54.62, 32.24, 31.81, 26.56, 22.62, 13.90. FTIR (KBr pellet): ν (cm⁻¹) 2954, 2926, 2856, 1698, 1658, 1591, 1406, 1331, 1251, 1132, 1076, 813, 750. Mp: 215 °C. MS (MALDI-TOF): calcd for C₁₁₇H₁₂₀N₄O₈, 1710.3; found, 1710.2. Elem. Anal. calcd for C₁₁₇H₁₂₀N₄O₈: C, 82.17; H, 7.07; N, 3.28. Found: C, 82.16; H, 7.06; N, 3.30.

2.2. Synthesis of SPFPDI24

The synthesis of SPFPDI24 was similar to the SPFPDI44. 2,5'-di(2,2,3,3-tetramethyl-2,3-butanedionato)boron-9,9'-spirobifluorene (284 mg, 0.5 mmol) was mixed with 1-bromoperylene bisimide (1.55 g, 2 mmol), KOH (448 mg, 8 mmol), Pd(PPh₃)₄ (70 mg, 0.06 mmol), toluene (12 mL), EtOH (6 mL) and water (3 mL), and the mixture was refluxed at 110 °C for 48 h under Ar, to get a dark red solid (405 mg, yield: 47%). ¹H NMR (CDCl₃, 400 MHz): δ [ppm]: 8.74–8.55 (m, 10H), 8.19–8.00 (m, 5H), 7.88–7.70 (m, 2H), 7.54–7.30 (m, 3H), 7.19–6.89 (m, 4H), 6.76–6.60 (m, 4H), 5.14 (s, 4H), 2.30–2.08 (m, 8H), 1.90–1.60 (m, 12H), 1.23 (br, 44H), 0.80–0.50 (br, 24H); ¹³C NMR (CDCl₃, 100 MHz): δ [ppm]: 171.23, 164.83, 164.45, 163.70, 150.58, 150.09, 149.00, 148.16, 142.64, 142.33, 141.56, 140.45, 136.96, 134.21, 130.92, 130.65, 129.72, 129.26, 129.09, 128.83, 128.58, 128.35, 127.97, 127.51, 127.32, 124.61, 124.26, 123.80, 123.40, 122.87, 122.66, 121.74, 120.83, 65.83, 60.45, 54.76, 54.42, 32.32, 31.73, 26.59, 22.60, 21.11, 14.07. FTIR (KBr pellet): ν (cm⁻¹) 2954, 2925, 2857, 1697, 1656, 1591, 1404, 1331, 1251, 1195, 1132, 1105, 812, 751. Mp: 218 °C. MS (MALDI-TOF): calcd for C₁₁₇H₁₂₀N₄O₈, 1710.3; found, 1710.2. Elem. Anal. calcd for C₁₁₇H₁₂₀N₄O₈: C, 82.17; H, 7.07; N, 3.28. Found: C, 82.15; H, 7.07; N, 3.30.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes to the isomeric molecules is shown in Scheme 1. The target products were synthesized through Suzuki coupling reaction between the SPF-core and 1-bromoperylene diimide. The two compounds were fully characterized by ¹H and ¹³C nuclear magnetic resonance (NMR, Fig. S1-S4), infrared

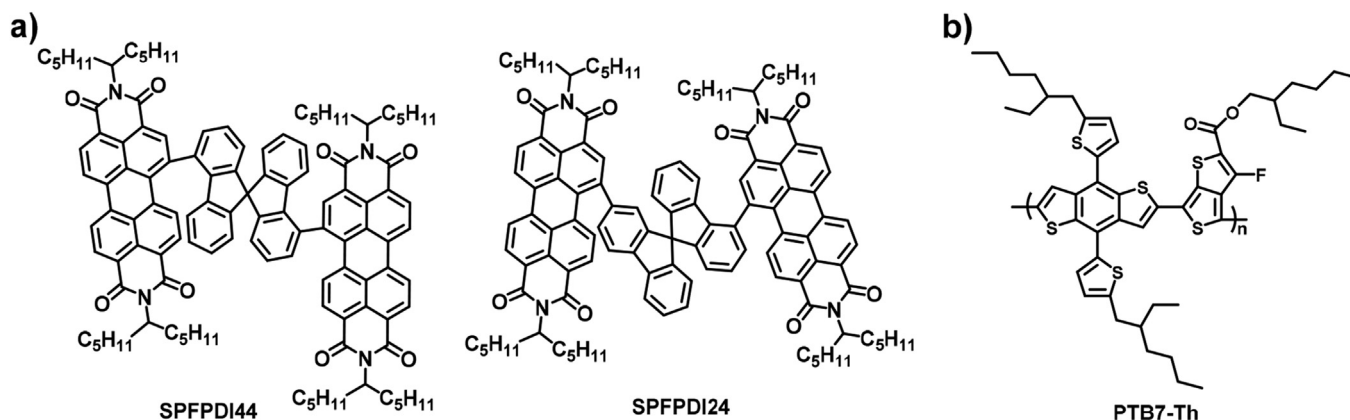


Fig. 1. a) Molecular structures of SPFPDI44 and SPFPDI24 acceptors. b) Chemical structure of the donor PTB7-Th.

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