



# A non-fullerene electron acceptor with a spirobifluorene core and four diketopyrrolopyrrole arms end capped by 4-fluorobenzene



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## ABSTRACT

In this paper, a non-fullerene electron acceptor, SF(DPPFB)<sub>4</sub>, which owns a spirobifluorene core and four diketopyrrolopyrrole (DPP) arms end capped by 4-fluorobenzene, is designed and synthesized for solution-processable organic solar cells (OSCs). SF(DPPFB)<sub>4</sub> shows similar absorption bands as those of its non-fluorinated parent compound, SF(DPPB)<sub>4</sub>. However, the terminal fluorine atoms reduce the energy levels of SF(DPPFB)<sub>4</sub>, especially, its lowest unoccupied molecular orbital level decreases by 0.04 eV than that of SF(DPPB)<sub>4</sub>, which enlarges the energy offset between the electron donor and acceptor, favorable for the dissociation of excitons in OSCs. Moreover, the fluorination improves the electron mobility of SF(DPPFB)<sub>4</sub>. Thus, the OSCs with poly(3-hexylthiophene) as the electron donor and SF(DPPFB)<sub>4</sub> as the electron acceptor can provide a maximum power conversion efficiency of 4.42%, with a lifted short-circuit current ( $J_{sc}$ ) of 8.48 mA cm<sup>-2</sup>.

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## 1. Introduction

In the past few years, non-fullerene electron acceptors have emerged as a research hotspot in the field of organic solar cells (OSCs) because they own some advantages beyond their fullerene-based counterparts, such as strong light absorption, easily tunable energy levels, and improved morphological stability, etc [1–8]. Recently, through elaborate design of non-fullerene acceptors and the matched donors, fullerene-free OSCs have made huge strides with the maximum power conversion efficiency (PCE) over 12%, which is comparable to or even better than those of fullerene-based OSCs [9–13]. Nevertheless, most of the above researches use the newly-developed medium or narrow band-gap conjugated polymers, not poly(3-hexylthiophene) (P3HT), as the donors of OSCs. It is worth noting that P3HT-based OSCs are particularly attractive because this simple and easy-synthesis polymer, as one of the most profoundly studied donor materials, has been demonstrated to show the excellent compatibility with roll-to-roll process [14], i.e.

the most promising industrial technique for the fabricating of OSCs. Unfortunately, few literatures report OSCs based on P3HT and non-fullerene acceptors with PCEs over 3% until now [15–20].

In the previous work [16], we designed and synthesized a non-fullerene acceptor, SF(DPPB)<sub>4</sub>, through installing four benzene (B) end capped diketopyrrolopyrrole (DPP) arms onto a spirobifluorene (SF) core. Due to the cross-shaped molecular configuration, SF(DPPB)<sub>4</sub> can prevent from forming large aggregates when blended with P3HT to fabricate OSCs. And SF(DPPB)<sub>4</sub> possesses the absorption bands and energy levels well matching with those of P3HT. Thus, the P3HT:SF(DPPB)<sub>4</sub> OSCs exhibit a best PCE of 5.16%, which is one of the highest values reported to date for P3HT-based fullerene-free OSCs, with an extremely high open-circuit voltage ( $V_{oc}$ ) of 1.14 V. However, the short-circuit current density ( $J_{sc}$ ) of these devices is not high enough (8.29 mA cm<sup>-2</sup>) while the broad absorption range from 300 to 700 nm is considered. Since the fine phase separation domains of 20–30 nm are observed for P3HT:SF(DPPB)<sub>4</sub> blended films, which is in favor of the dissociation of excitons in OSCs, we guess that the relatively low electron mobility of SF(DPPB)<sub>4</sub> and small driving force for the splitting of excitons into free charges, i.e. the energy difference between the lowest unoccupied molecular orbitals (LUMOs) of P3HT and SF(DPPB)<sub>4</sub>, may be responsible for the inadequate utilization of absorbed solar photons into current in the P3HT:SF(DPPB)<sub>4</sub> OSCs.

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Taking the above considerations into account, we develop herein a new non-fullerene electron acceptor, SF(DPPFB)<sub>4</sub>, through the chemical modification of SF(DPPB)<sub>4</sub> by the introduction of fluorine atoms at 4-positions of benzene end-groups. The main reasons for such modification are: 1. the fluorine atom, due to its strong electron-withdrawing ability, can decrease effectively the LUMO level of organic semiconductors [21,22], thereby, enlarge the energy offset between the donor (P3HT) and acceptor (SF(DPPFB)<sub>4</sub>), promoting the dissociation of excitons in the resulting OSCs; 2. Fluorination can induce stronger intermolecular interactions, and enhance  $\pi$ - $\pi$  stacking [21,23], thus, a higher electron mobility of SF(DPPFB)<sub>4</sub> is expected. Then, the absorption, energy levels, and photovoltaic property of SF(DPPFB)<sub>4</sub> are investigated, to prove the feasibility of the above molecular design.

## 2. Experimental

### 2.1. Instrument

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker Advance III 400 (400 MHz) nuclear magnetic resonance (NMR) spectroscope. Matrix-assisted laser desorption/ionization time of flight mass spectra (MALDI-TOF MS) were performed on a Walters Maldi Q-TOF Premier mass spectrometry. Thermogravimetric analyses (TGA) were carried out on a WCT-2 thermal balance under protection of nitrogen at a heating rate of 10 °C min<sup>-1</sup>. Differential scanning calorimetry (DSC) curve was recorded on a Pekin-Elmer Pyris 1 differential scanning calorimeter. UV-vis spectra were taken on a Shimadzu UV-2450 spectrophotometer. Cyclic voltammetry (CV) was done on a CHI600A electrochemical workstation with Pt disk, Pt plate, and standard calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol L<sup>-1</sup> tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) CH<sub>2</sub>Cl<sub>2</sub> solution. The CV curves were recorded *versus* the potential of SCE, which was calibrated by the ferrocene-ferrocenium (Fc/Fc<sup>+</sup>) redox couple (4.8 eV below the vacuum level). Topographic images of the films were obtained on a Veeco MultiMode atomic force microscopy (AFM) in the tapping mode using an etched silicon cantilever at a nominal load of ~2 nN, and the scanning rate for a 10  $\mu$ m  $\times$  10  $\mu$ m image size was 1.5 Hz.

### 2.2. Materials

All reagents and solvents, unless otherwise specified, were purchased from Aladdin, Aldrich, and J&K Scientific Co., and were used without further purification. P3HT (96% H-T regioregularity,  $M_n = 26$  kg/mol, polydispersity = 2.0) was purchased from Merck Co. 2,2',7,7'-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-spirobifluorene (**1**) [24] and 2,5-bis(2-ethylhexyl)-3-(5-(4-fluorophenyl)thiophen-2-yl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo [3,4-c]pyrrole-1,4-dione (**2**) [25] were synthesized according to the reported procedures, respectively.

### 2.3. Synthesis of SF(DPPFB)<sub>4</sub>

The general synthetic route toward SF(DPPFB)<sub>4</sub> is outlined in Fig. 1a. The detailed synthetic process is as follows.

6,6',6'',6'''-(9,9'-spirobifluorene-2,2',7,7'-tetrayltetrakis-(thiophene-5,2-diyl))tetrakis (2,5-bis(2-ethylhexyl)-3-(5-(4-fluorophenyl)thiophen-2-yl)-2,5-dihydropyrrolo [3,4-c]pyrrole-1,4-dione) (SF(DPPFB)<sub>4</sub>)

Compound **1** (110 mg, 0.138 mmol), compound **2** (580 mg, 0.831 mmol), K<sub>2</sub>CO<sub>3</sub> (1.56 g, 11.3 mmol), toluene (50 mL), ethanol (3 mL), and H<sub>2</sub>O (8 mL) were added into a two-necked round bottom flask. The mixture was first frozen by liquid nitrogen, followed

by three times of successive vacuum and nitrogen fill cycles. Pd(PPh<sub>3</sub>)<sub>4</sub> (36 mg, 0.0311 mmol) was added in nitrogen atmosphere, and another three times of successive vacuum and nitrogen filling cycles was made. Then, the mixture was refluxed at 80 °C for 72 h. After removing the solvent, the product was purified using column chromatography (silica gel) with hexane/dichloromethane (1:4) as the first eluent and dichloromethane/ethyl acetate (50:1) as the second eluent, yielding a dark purple solid (270 mg, 70.3%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.89 (b, 4H), 8.80 (b, 4H), 7.98 (d,  $J = 8.4$  Hz, 4H), 7.81 (d,  $J = 8.0$  Hz, 4H), 7.62 (m, 8H), 7.37 (d,  $J = 4.0$  Hz, 4H), 7.34 (d,  $J = 4.4$  Hz, 4H), 7.04–7.16 (m, 12H), 3.90–4.10 (m, 16H), 1.75–1.92 (m, 8H), 1.15–1.40 (m, 64H), 0.76–0.91 (m, 48H).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  164.27, 161.78, 161.67, 161.59, 149.31, 149.15, 148.40, 141.63, 139.73, 139.54, 136.72, 136.52, 133.58, 129.50, 129.47, 128.97, 128.82, 127.93, 127.85, 126.80, 124.83, 124.42, 121.45, 121.32, 116.35, 116.14, 108.27, 108.23, 65.95, 45.92, 45.90, 45.87, 39.20, 39.18, 30.30, 28.51, 28.38, 23.72, 23.66, 23.09, 23.03, 14.06, 10.62, 10.59.

MALDI-TOF MS ( $m/z$ ): [M]<sup>+</sup> calcd for C<sub>169</sub>H<sub>180</sub>F<sub>4</sub>N<sub>8</sub>O<sub>8</sub>S<sub>8</sub>, 2783.82; Found, 2783.84.

### 2.4. DFT calculation

Geometry optimizations were carried out by the density functional theory (DFT) method at the B3LYP/6-31G level. All the calculations were performed using Gaussian 03 program. All *N*-ethylhexyl substituents were replaced with methyl groups in calculations to save computational time due to the fact that the geometries and energies negligibly depended on the pendant alkyl groups.

### 2.5. Device fabrication and characterization

OSC devices were fabricated on glass substrates commercially pre-coated with a layer of ITO. Prior to fabrication, the substrates were cleaned using detergent, de-ionized water, acetone, and isopropanol consecutively for every 15 min, and then treated in an ultraviolet ozone generator for 15 min before being spin-coated at 3000 rpm with a layer of 30 nm thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). After baking the PEDOT:PSS layer in air at 150 °C for 15 min, the substrates were transferred into a glovebox. The active layer was spin-cast at 3000 rpm from a solution of P3HT and SF(DPPFB)<sub>4</sub> in chloroform with different blend weight ratios at a total solid concentration of 15 mg mL<sup>-1</sup>. The samples might be annealed at 120 °C for 10 min. Then a 5 nm thick poly [(9,9'-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9'-dioctylfluorene)] (PFN) film was deposited as the cathode buffer layer by the spin-coating of a solution of 0.4 mg mL<sup>-1</sup> PFN in methanol because PFN could reduce greatly the work function of the cathode, in favor of electron collection in the OSCs. Subsequently, the samples were loaded into a vacuum deposition chamber (background pressure  $\approx 5 \times 10^{-4}$  Pa) to deposit 100 nm thick aluminum cathode with a shadow mask (the device area was 5.2 mm<sup>2</sup>).

The current density-voltage ( $J$ - $V$ ) curves were measured with a Keithley 2400 measurement source units at room temperature in air. The photocurrent was measured under a calibrated solar simulator (Abet 300W) at 100 mW cm<sup>-2</sup> and the light intensity was calibrated with a standard photovoltaic (PV) reference cell. External quantum efficiency (EQE) spectra were measured with a Stanford lock-in amplifier 8300 unit.

The charge carrier mobilities of the P3HT:SF(DPPFB)<sub>4</sub> films were measured using the space-charge-limited current (SCLC) method. Hole-only devices were fabricated in a structure of ITO/PEDOT:PSS/

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