Electronic Supplementary Material (ESI) for Energy & Environmental Science.
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Electronic Supplementary Information for:

A spirobifluorene and diketopyrrolopyrrole moieties based non-fullerene acceptor for efficient and thermally stable polymer solar cells with high open-circuit voltage

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Materials and Methods

Instrument. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker Advance III 400 (400 MHz) and 500 (500 MHz) nuclear magnetic resonance (NMR) spectroscope. UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. MALDI-TOF MS spectra were measured on a Walters Maldi Q-TOF Premier mass spectrometry. Thermogravimetric analysis (TGA) was carried out on a WCT-2 thermal balance under protection of nitrogen at a heating rate of 10 ^oC/min. Differential scanning calorimetry (DSC) was recorded on a Pekin-Elmer Pyris 1 differential scanning calorimeter. 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 tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) CH_2Cl_2 solution. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium (Fc/Fc^+) redox couple (4.8 eV below the vacuum level). Topographic images of the films were obtained on a VeecoMultiMode 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 μm×10 μm image size was 1.5 Hz.

Materials. All reagents and solvents, unless otherwise specified, were purchased from Aladdin, Aldrich and J&K Scientific Ltd. 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'-spirobi[fluorene] (**1**) and 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(5-phenylthiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**2**) were synthesized according to the reported procedures.[1,2]

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.

2D-GIWAXS Measurements. The GIWAXS measurements were conducted at 23A SWAXS beamline of a superconductor wiggler at the National Synchrotron Radiation Research Center, Hsinchu, Taiwan. We probed the samples with 0.15^{o} incident angle, using a 10 keV beam of 0.15 mm in height and 0.2 mm in width and C9728DK area detector.

Device fabrication and characterization. Polymer solar cells (PSCs) were fabricated on glass substrates commercially pre-coated with a layer of indium tin oxide (ITO). Prior to fabrication, the substrates were cleaned using detergent, deionized 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, Baytron P AI4083). After baking the PEDOT:PSS layer in air at 150 ^{o}C for 15 min, the substrates were transferred to a glovebox. The Active layer was spin-cast at 3000 rpm from a solution of P3HT and SF(DPPB)$_4$ in chloroform with different blend weight ratios at a total solid concentration of 15 mg ml^{-1}. The samples might be annealed at 120 ^{o}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^{-1} PFN in methanol because PFN could reduce greatly the work function of the cathode, in favor of electron collection in the PSCs. Subsequently, the samples were loaded into a vacuum deposition chamber (background pressure $\approx 5\times10^{-4}$ Pa) to deposit 100 nm thick aluminum cathode with a shadow mask (the device area was 5.2 mm^2). PSCs based on P3HT:PC$_{61}$BM blend films were also fabricated according to the above method, just replacing SF(DPPB)$_4$ with PC$_{61}$BM, changing the spin speed to 1000 rpm for the active layer, using the D/A weight ratio of 1:0.8 and increasing the annealing temperature to 170 ^{o}C.

The current density-voltage (*J*-*V*) curves of PSCs were measured with 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^{-2} and the light intensity was calibrated with a standard photovoltaic (PV) reference cell. External quantum efficiency (EQE) spectrum was measured with a Stanford lock-in amplifier 8300 unit.

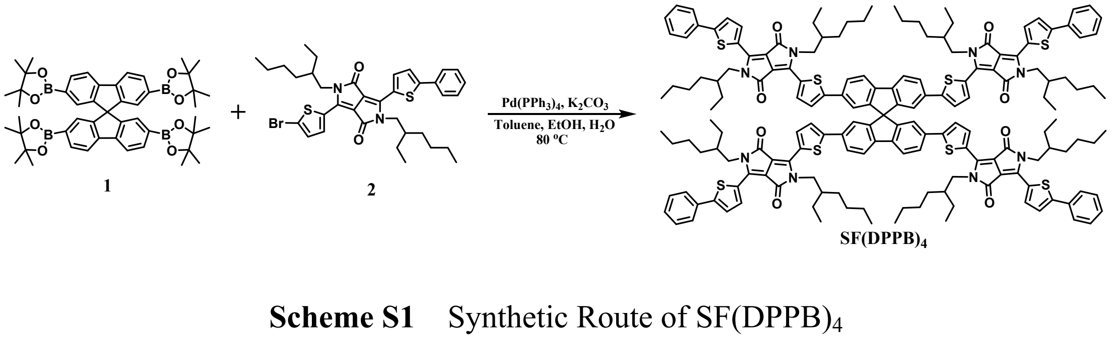
The charge carrier mobilities of the P3HT:SF(DPPB)$_4$ films were measured using the space-charge-limited current (SCLC) method. Hole-only devices were fabricated in a structure of ITO/PEDOT:PSS/P3HT:SF(DPPB)$_4$(2:1)/MoO$_3$/Al, electron-only devices were fabricated in a structure of ITO/PFN/P3HT:SF(DPPB)$_4$(2:1)/PFN/Al. The device characteristics were extracted by modeling the dark current under forward bias using the SCLC expression described by the Mott-Gurney law:

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3} \qquad (1)$$

Here, $\varepsilon_r \approx 3$ is the average dielectric constant of the blend film, ε_0 is the permittivity of the free space, μ is the carrier mobility, $L \approx 100$ nm is the thickness of the film, and V is the applied voltage.

Synthesis

The synthetic route of **SF(DPPB)$_4$** is outlined in Scheme S1:



Scheme S1 Synthetic Route of SF(DPPB)$_4$

*6,6',6'',6'''-(9,9'-spirobi[fluorene]-2,2',7,7'-tetrayltetrakis(thiophene-5,2-diyl))tetrakis(2,5-bis(2-ethylhexyl)-3-(5-phenylthiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) (**SF(DPPB)$_4$**)*

Compound **1** (0.146 g, 0.18 mmol), compound **2** (0.721 g, 1.06 mmol), K$_2$CO$_3$

(2.212 g, 16 mmol), toluene (50 mL), H_2O (8 mL), and ethanol (3 mL) were added to a two-necked round bottom flask. The mixture was frozen by liquid nitrogen, followed by three times of successive vacuum and nitrogen fill cycles. $Pd(PPh_3)_4$ (0.05 g, 0.043 mmol) was added under the protection of nitrogen, and another three times of successive vacuum and nitrogen fill cycles was made. Then, the mixture was refluxed at 80 ^{o}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 brown solid (0.39 g, 80%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (b, 4H), 8.80 (b, 4H), 7.99 (d, *J*=8.0 Hz, 4H), 7.80 (d, *J*=8.0 Hz, 4H), 7.66 (d, *J*=8.0 Hz, 8H), 7.47-7.38 (m, 12H), 7.38-7.31 (m, 8H), 7.09 (s, 4H), 4.10-3.94 (m, 16H), 1.87 (m, 8H), 1.38-1.16 (m, 64H), 0.90-0.75 (m, 48H). ^{13}C NMR (500 MHz, $CDCl_3$): δ = 161.59, 149.68, 149.64, 149.31, 149.09, 149.04, 141.59, 139.91, 139.39, 136.86, 136.47, 136.42, 133.58, 133.13, 129.12, 128.98, 128.77, 126.76, 126.08, 124.82, 124.80, 124.43, 121.42, 121.28, 108.29, 108.13, 65.95, 45.92, 45.85, 39.19, 39.16, 30.30, 29.70, 28.50, 28.38, 23.73, 23.72, 23.66, 23.08, 23.01, 14.04, 10.61, 10.57. MS (MALDI-TOF): Calcd for $C_{168}H_{184}N_8O_8S_8$ (M^+): 2711.86, Found: 2712.21.

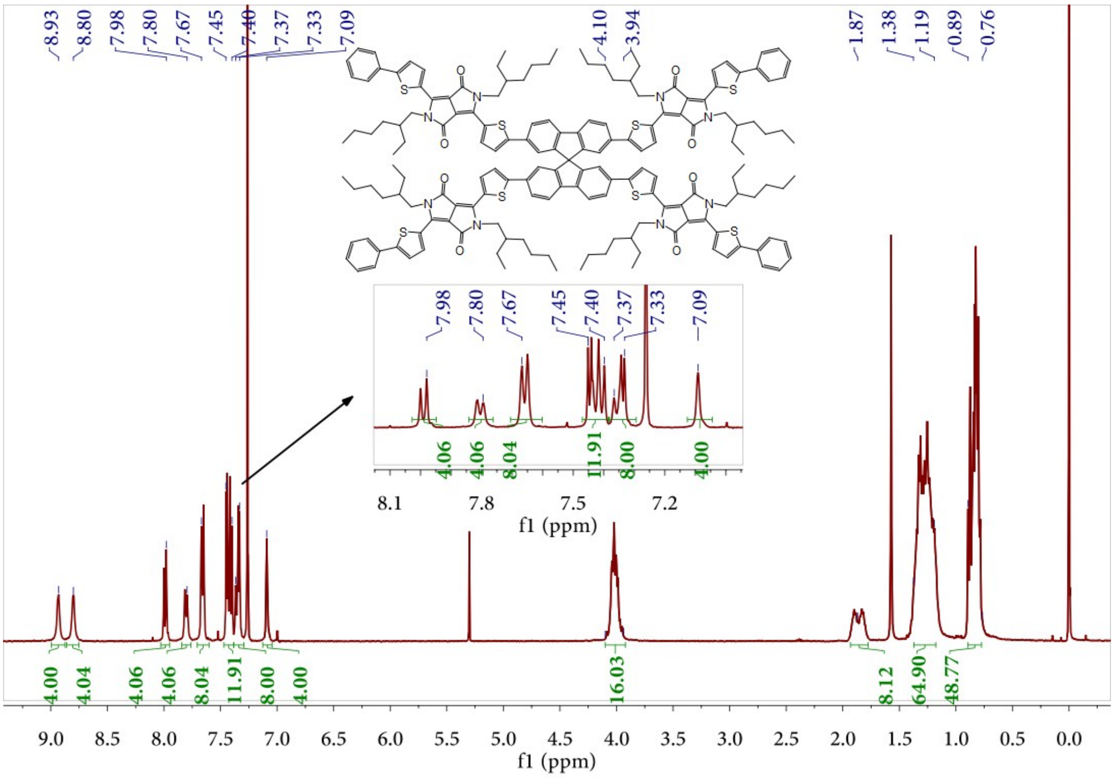


Fig. S1 ^{1}H NMR spectrum of SF(DPPB)$_4$ solution in CDCl$_3$.

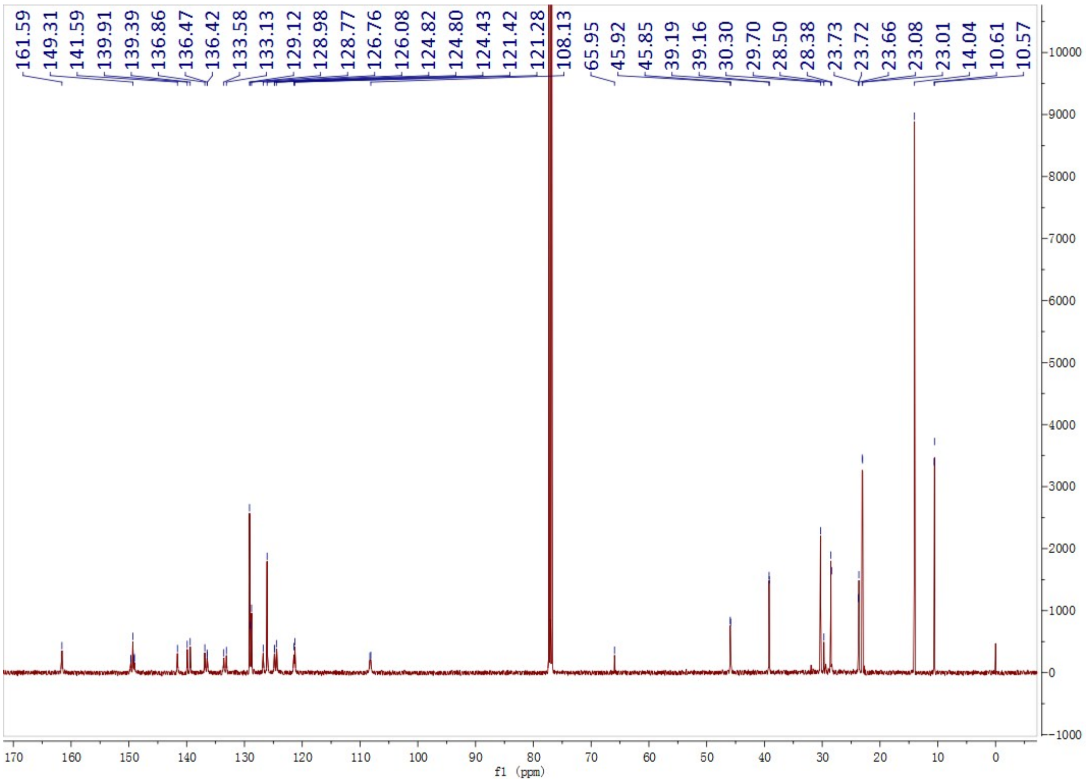


Fig. S2 ^{13}C NMR spectrum of SF(DPPB)$_4$ solution in CDCl$_3$.

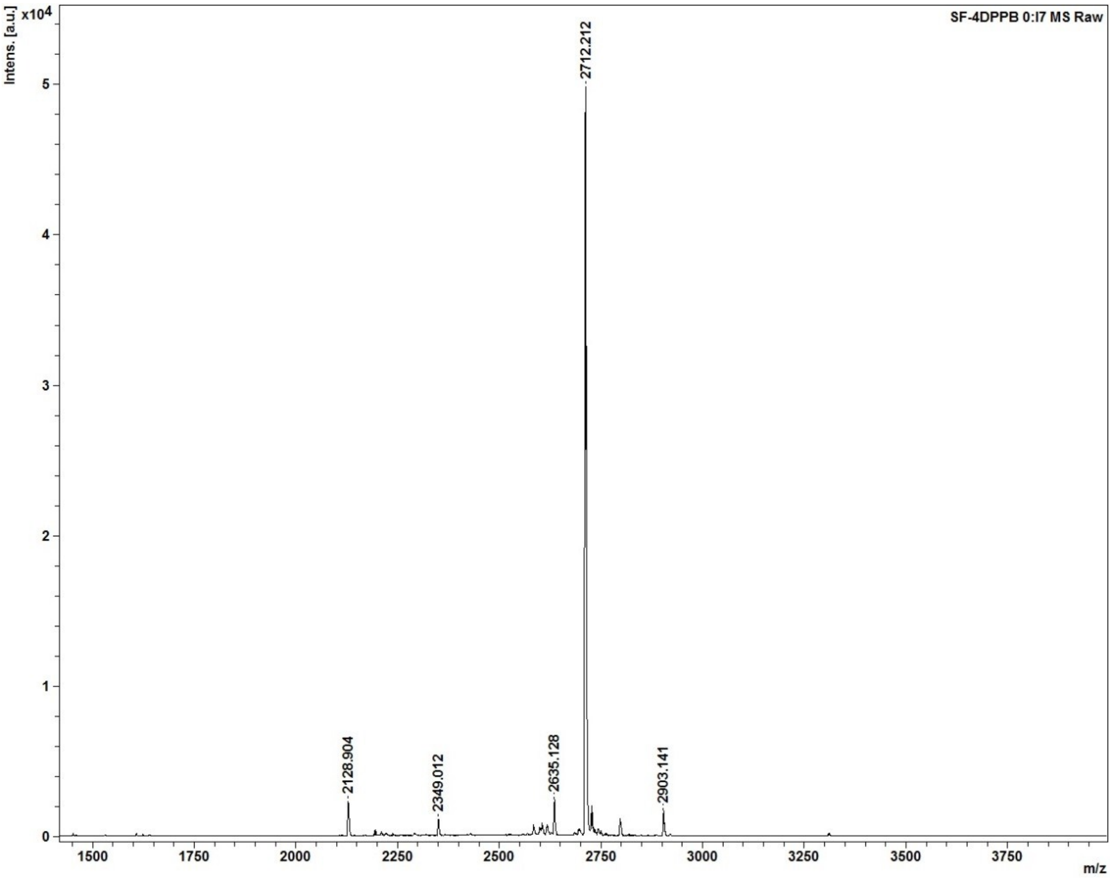


Fig. S3 Mass spectrum of SF(DPPB)$_4$.

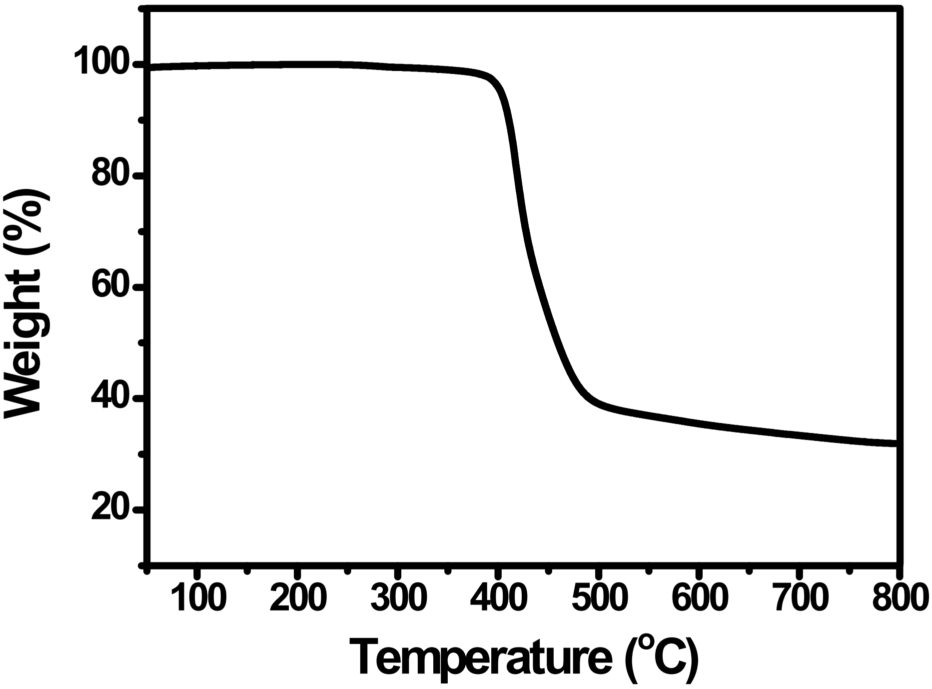


Fig. S4 TGA curve of SF(DPPB)$_4$.

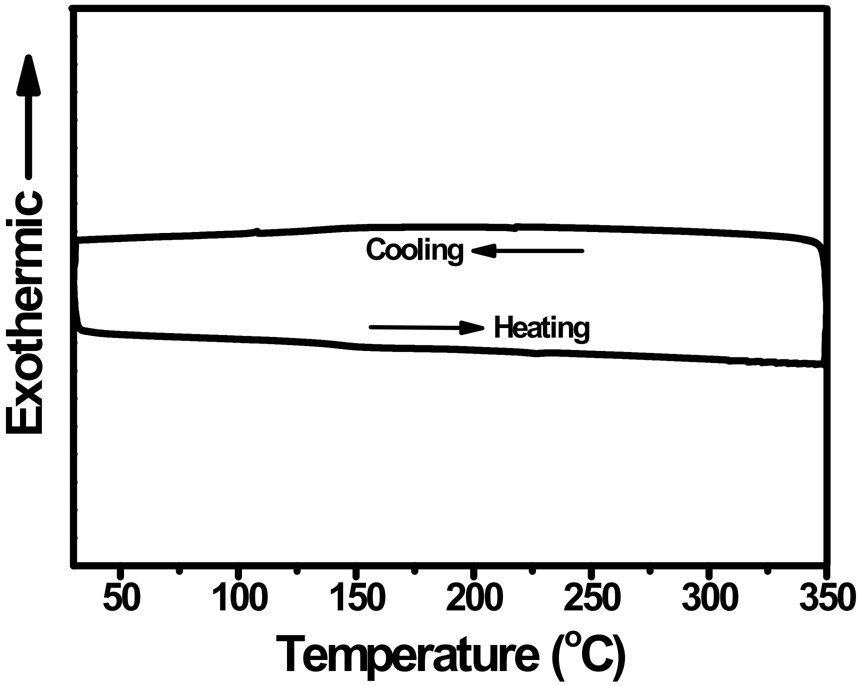


Fig. S5 DSC curve of SF(DPPB)$_4$.

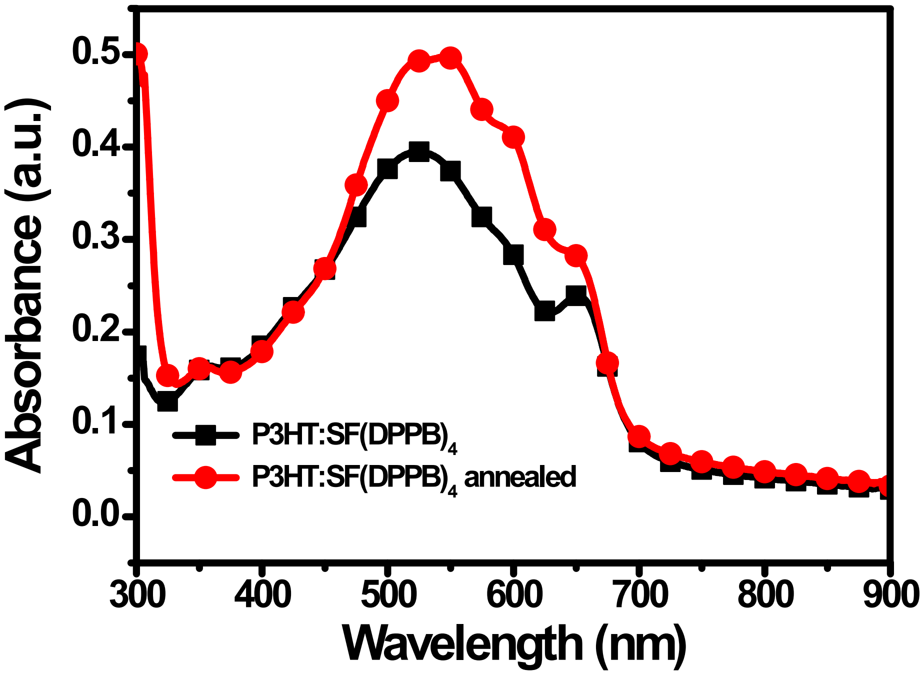


Fig. S6 UV-vis absorption spectra of P3HT:SF(DPPB)$_4$ (2:1, by wt.) films with or without the thermal annealing at 120 °C for 10 min.

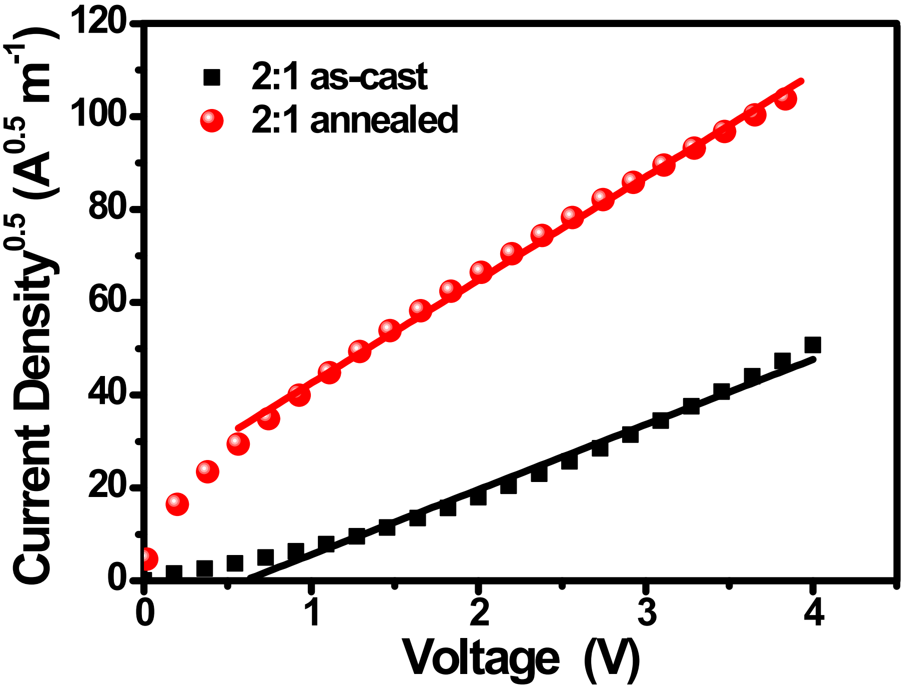


Fig. S7 $J^{0.5}$-V curves of the hole-only devices based on P3HT:SF(DPPB)$_4$ films.

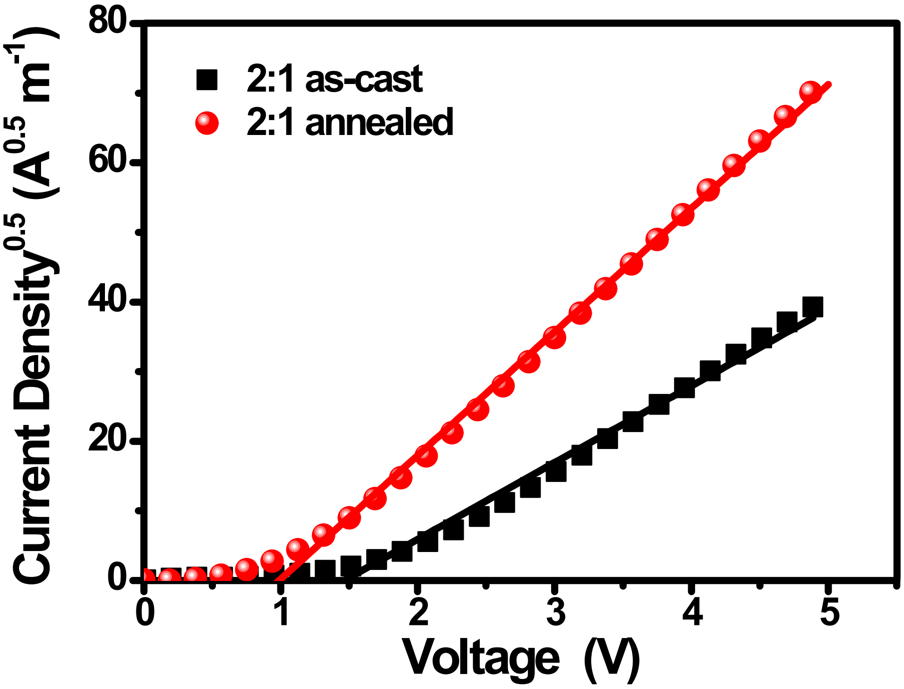


Fig. S8 $J^{0.5}$-V curves of the electron-only devices based on P3HT:SF(DPPB)$_4$ films.

References

1. S. Ma, Y. Fu, D. Ni, J. Mao, Z. Xie and G. Tu, *Chem. Commun.*, 2012, **48**, 11847-11849.
2. J. Y. Pan, L. J. Zuo, X. L. Hu, W. F. Fu, M. R. Chen, L. Fu, X. Gu, H. Q. Shi, M. M. Shi, H. Y. Li and H. Z. Chen, *ACS Appl. Mater. Interfaces*, 2013, **5**, 972-980.