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A solution-processable bipolar diketopyrrolopyrrole molecule used as both electron donor and acceptor for efficient organic solar cells

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Supporting Information

Contents

Instrument

^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker Advance DMX-300 (300 MHz) and a Bruker Advance DMX-600 (600 MHz) nuclear magnetic resonance spectroscope. UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Elemental analyses were carried out on a LECO 932 CHNS elemental analyzer. MALDI-TOF MS spectra were measured on a Waters Maldi Q-TOF Premier mass spectrometry. 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 tetrabutylammonium hexafluorophosphate (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 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 μm × 10 μm image size was 1.5 Hz.

Materials

All reagents and solvents, unless otherwise specified, were purchased from Aldrich, Acros, and J&k Scientific Ltd. and were used without further purification. 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(5-phenylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**3**) was synthesized according to the reported procedure.[1] P3HT (96% H-T regioregularity, Mn = 26 kg/mol, polydispersity = 2.0) was purchased from Merck Co. Poly [(9,9-bis(3′-(*N*,*N*-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9–dioctylfluorene)] (PFN, Mn = 20.0 kg/mol, polydispersity = 2.1) was synthesized in our lab according to the published procedure.[2]

Theoretical calculations

Geometry optimizations were carried out by the density functional theory (DFT) method at the B3LYP/6-31G(d) level. All the calculations were performed using the Gaussian 03 program. Model compound of $F(DPP)_2B_2$ was simplified by replacing pendant alkyl side chains with ethyl groups to save computational time due to the fact that the geometries and energies negligibly depended on the pendant alkyl groups.[3]

Device fabrication and characterization

Organic solar cells (OSCs) 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 with a layer of 35 nm thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P AI4083). After baking the PEDOT:PSS layer in air at 140 ^{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 F(DPP)$_2$B$_2$ and PC$_{71}$BM or P3HT and F(DPP)$_2$B$_2$ in chloroform with different blend weight ratio at a total solid concentration of 20 mg ml^{-1}. The samples might be annealed at 120 ^{o}C for 10 min. The thickness of the active layers was 90-100 nm, which was measured by a Veeco Multimode atomic force microscopy (AFM). Then a 5 nm thick 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 favour of electron collection in the OSCs.[4] 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).

The current density–voltage (*J–V*) curves of OSCs were measured with Keithley 2400 measurement source units at room temperature in air. The photocurrent was measured under a calibrated solar simulator (Abet 300 W) at 100 mW cm^{-2}, and the light intensity was calibrated with a standard silicon photovoltaic reference cell. External quantum efficiency (EQE) spectra were measured with Stanford lock-in amplifier 8300 unit.

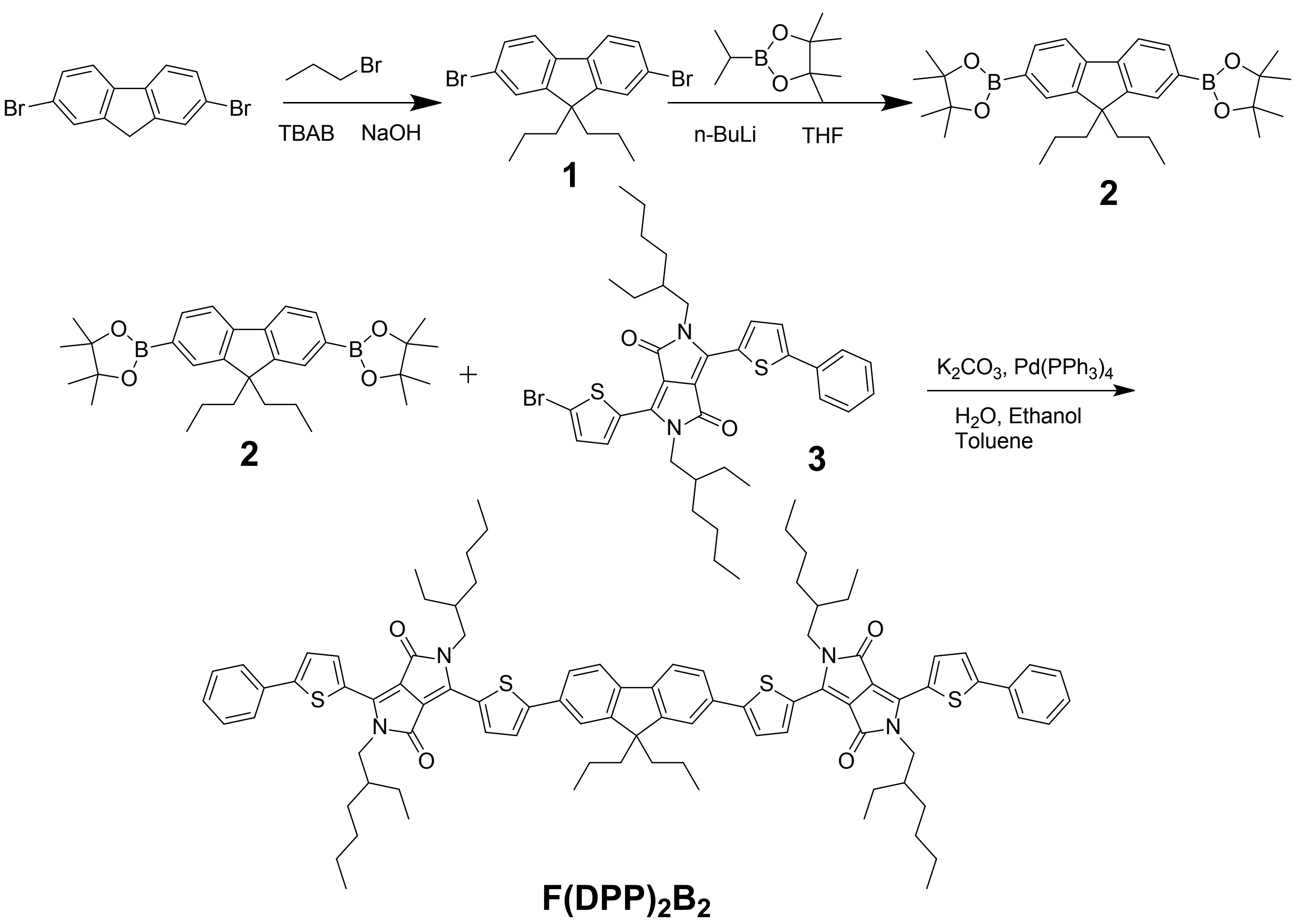
The charge carrier mobilities of the pristine F(DPP)$_2$B$_2$, F(DPP)$_2$B$_2$:PC$_{71}$BM, and P3HT:F(DPP)$_2$B$_2$ films were measured using the space-charge-limited current (SCLC) method. Hole-only devices were fabricated in a structure of ITO/PEDOT:PSS(35 nm)/the active layer/MoO$_3$(10 nm)/Al(100 nm), electron-only devices were fabricated in a structure of ITO/PFN(5 nm)/the active layer/PFN(5 nm)/Al(100 nm). The device characteristics were extracted by modelling the dark current under forward bias using the SCLC expression described by the Mott-Gurney law:

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

Here, $\varepsilon_r \approx 3$ is the average dielectric constant of the blended 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 general synthetic route towards the target compound F(DPP)$_2$B$_2$ is outlined in Scheme S1. The detailed synthetic processes are as follows.



Scheme S1 Synthetic route to F(DPP)$_2$B$_2$

*2,7-dibromo-9,9-dipropyl-9H-fluorene (**1**)*

2,7-dibromofluorene (4.95 g, 15.28 mmol), 1-bromopropane (27 ml, 30 mmol), tetrabutyl ammonium bromide (TBAB, 0.3 g), and aqueous sodium hydroxide solution (30 ml, 50 wt %) were mixed together in a 250 ml two-neck flask and stirred at 70 °C for 9 h under the protection of nitrogen. When the reaction was finished, the mixture was extracted with CH_2Cl_2, washed with brine, and dried over anhydrous $MgSO_4$. After CH_2Cl_2 was evaporated, the crude product was purified by column chromatography on silica gel (eluent: CH_2Cl_2/petroleum ether, 2:1, v/v) to provide a white crystal (3.28 g, 52.7%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.54-7.42 (m, 6H), 1.90 (t, 4H), 0.72-0.56 (m, 10H).

*2,2'-(9,9-dipropyl-9H-fluorene-2,7-diyl)-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2**)*

Compound **1** (2.04 g, 5.0 mmol) was dissolved in 20 ml dry THF in 100 ml flask and purged with nitrogen. The flask was cooled to -78 °C with a liquid nitrogen/ethanol bath and 5 ml 2.5 M *n*-BuLi solution in pentane (12.5 mmol) was added dropwise. The mixture was stirred for 2 h at -78 °C and followed by adding 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4 ml, 20.0 mol). Then the reaction was stirred overnight at room temperature and quenched by water. The resulting solution was concentrated by rotary evaporation, extracted with CH_2Cl_2, washed with brine, and dried over anhydrous $MgSO_4$. After CH_2Cl_2 was evaporated, the crude product was purified by column chromatography on silica gel (eluent: CH_2Cl_2/petroleum ether, 3:1, v/v) to provide a white crystal (0.81 g, 32.2%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.83~7.67(m, 6H), 1.98 (t, 4H), 1.39 (s, 24H), 0.67-0.55(m, 10H).

*6,6'-[5,5'-(9,9-dipropyl-9H-fluorene-2,7-diyl)-bis(thiophene-5,2-diyl)]-bis[2,5-bis(2-ethylhexyl)-3-(5-phenylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione] (**F(DPP)$_2$B$_2$**)*

Compound **2** (0.29 g, 0.57 mmol), 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl) -6-(5-phenylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**3**) (0.93 g, 1.37 mmol), 2.0 M aqueous K_2CO_3 solution (9 ml), ethanol (4 ml), and toluene (50 ml) were mixed thoroughly in 250 ml two-neck flask and purged with nitrogen for 20 min. Then, 48 mg tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] was added. The mixture was refluxed at 80 °C for 48 h. The resulting solution was concentrated by rotary evaporation, extracted with CH_2Cl_2, washed with brine, and dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography on silica gel (eluent: CH_2Cl_2/petroleum ether, 3:1, v/v) to provide a dark purple powder (0.57 g, 69.5%). ^{1}H NMR (600 MHz, $CDCl_3$) , δ (ppm): 8.99 (br, 4H), 7.77-7.63 (m, 10H), 7.55 (d, 2H), 7.48 (d, 2H), 7.46-7.42 (m, 4H), 7.40-7.35 (m, 2H), 4.18-4.05 (m, 8H), 2.21-1.82 (m, 8H), 1.44-1.26 (m, 32H), 0.97-0.86 (m, 24H), 0.83-0.69 (m, 10H). ^{13}C NMR (600 MHz, CDCl$_3$), δ (ppm): 161.83, 152.33, 141.32, 139.92, 137.11, 133.26, 132.59, 129.20, 129.01, 128.83, 126.29, 125.62, 124.53, 120.73, 120.39, 108.41, 55.82, 46.10, 42.80, 39.40, 30.61, 30.49, 28.72, 23.86, 23.28, 17.41, 14.60, 14.26, 10.76. Anal. Calcd for $C_{91}H_{106}N_4O_4S_4$: C, 75.43; H, 7.43; N, 3.71. Found: C, 75.48; H, 7.38; N, 3.87. MALDI-TOF MS:1448.44; Calcd.for $C_{91}H_{106}N_4O_4S_4$: 1448.71.

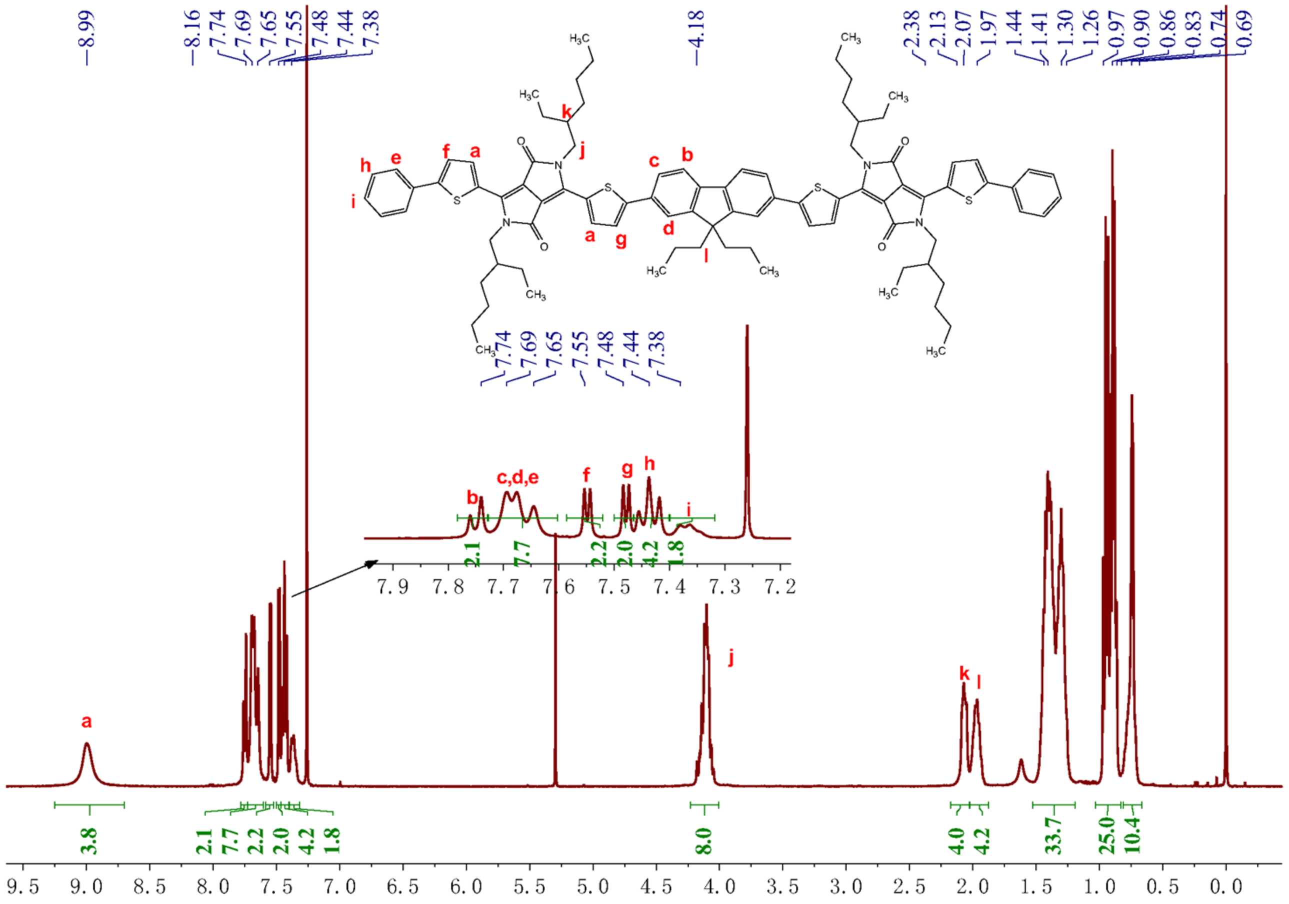


Fig. S1 ^{1}H NMR spectrum of F(DPP)$_2$B$_2$ solution in CDCl$_3$.

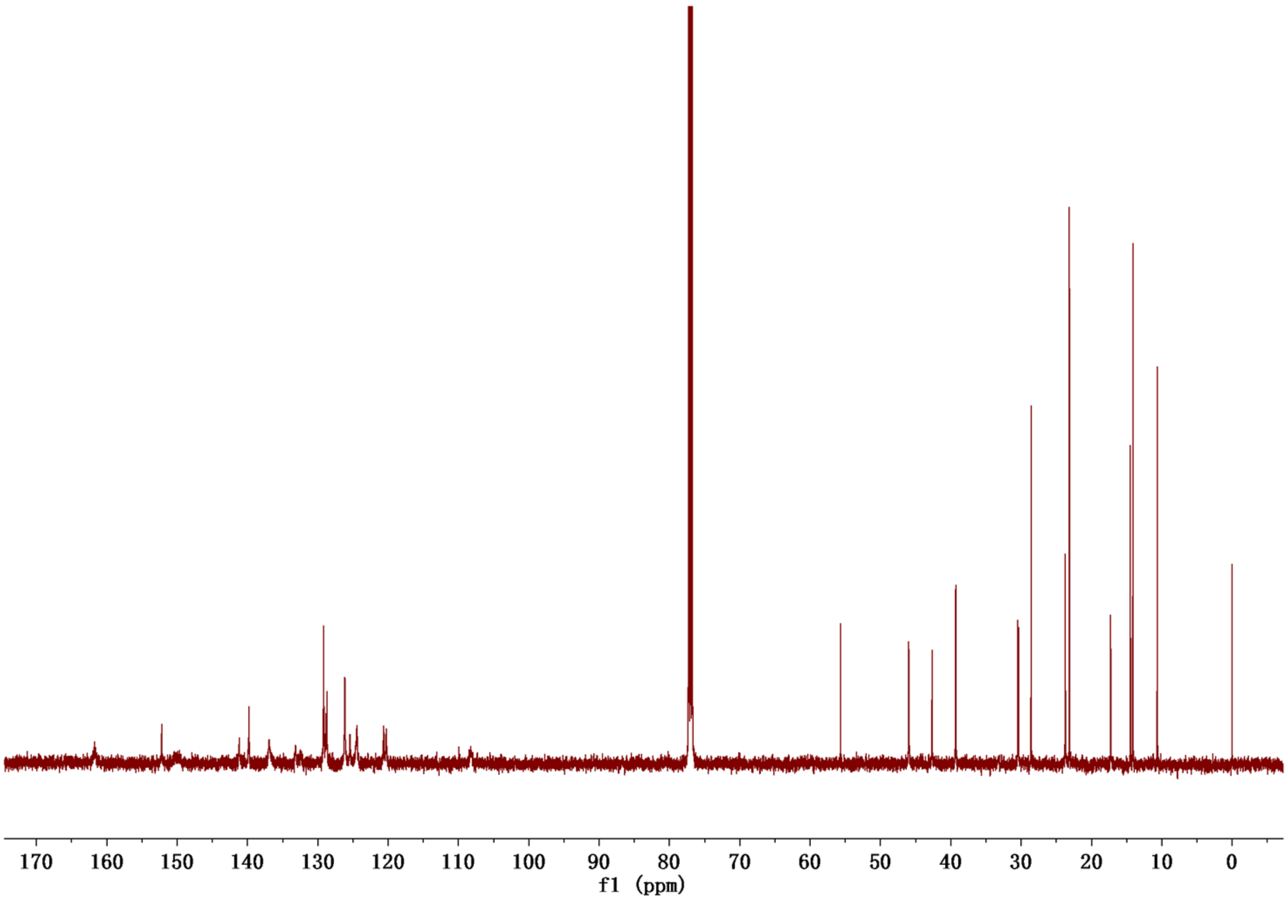


Fig. S2 ^{13}C NMR spectrum of F(DPP)$_2$B$_2$ solution in CDCl$_3$.

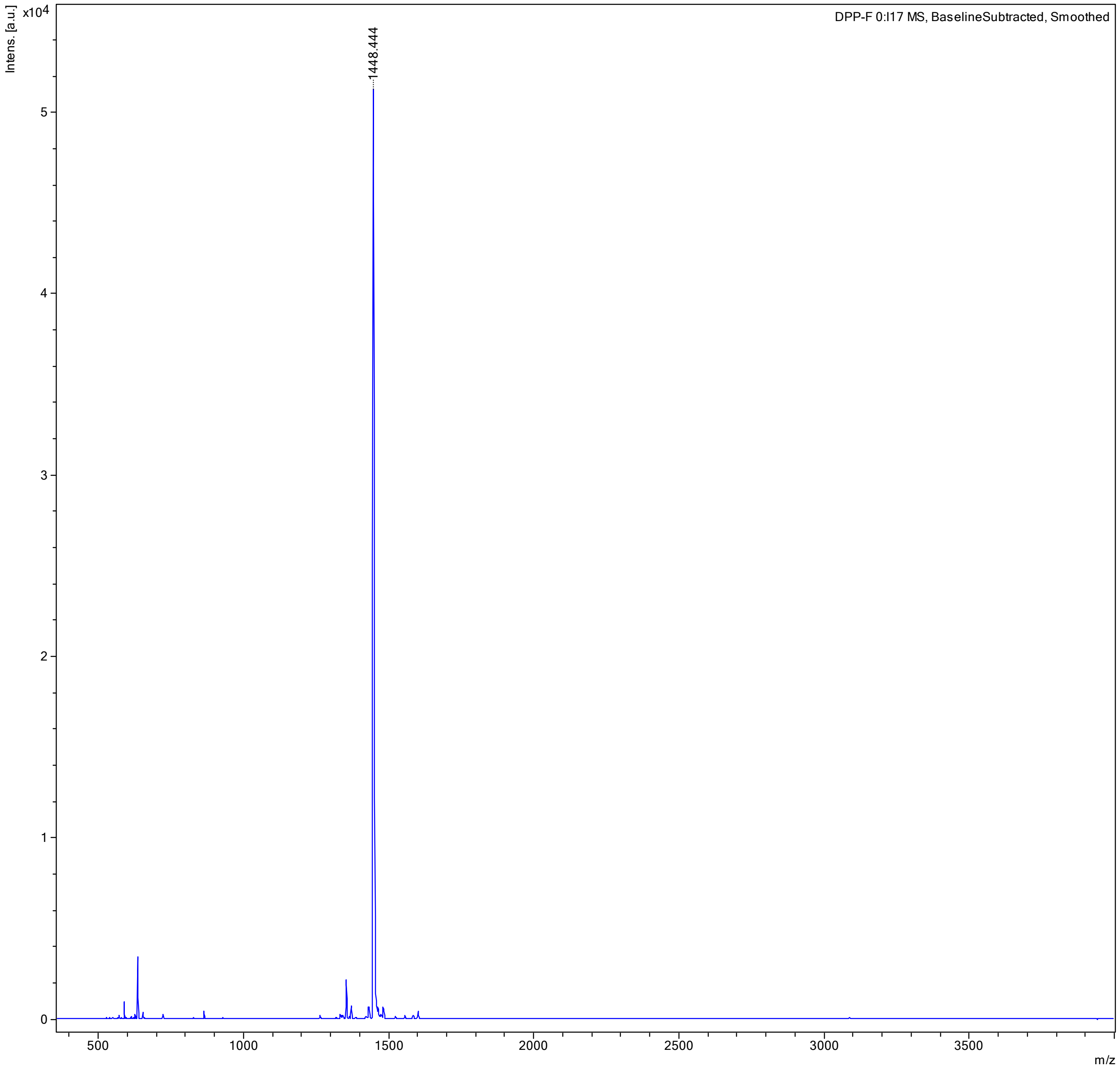


Fig. S3 MALDI-TOF MS spectrum of $F(DPP)_2B_2$.

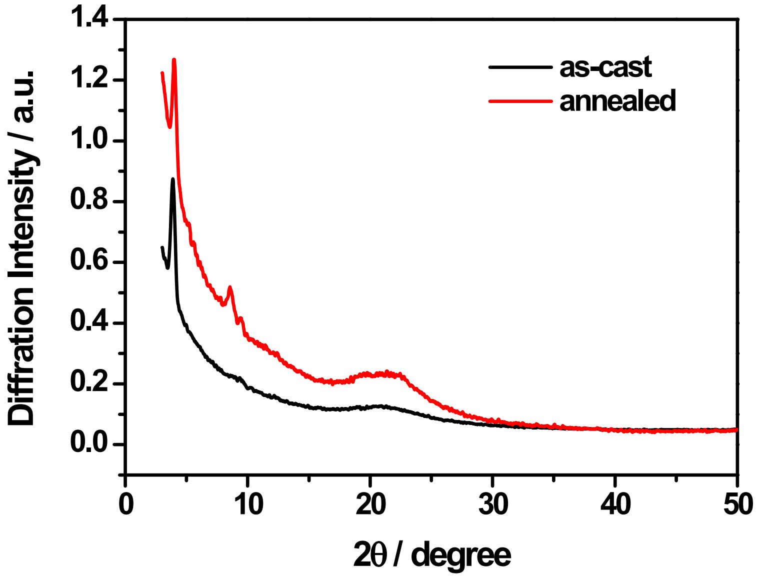


Fig. S4 X-ray diffraction (XRD) patterns of P3HT:F(DPP)$_2$B$_2$ (1:1, by wt.) films with or without the thermal annealing at 120 °C for 10 min.

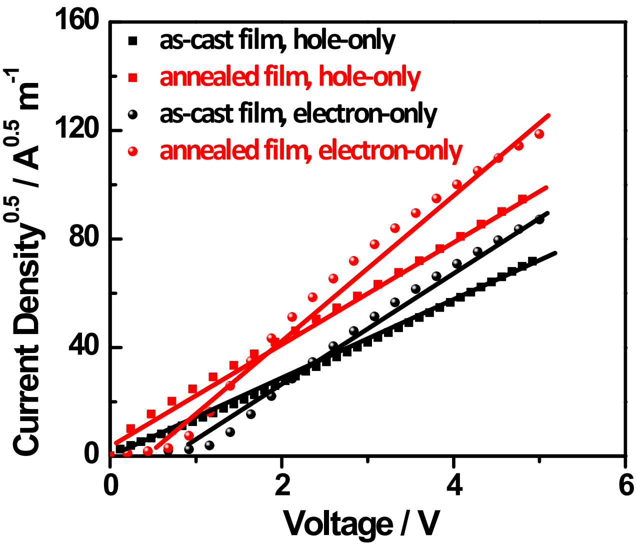


Fig. S5 $J^{0.5}$-V curves of the hole-only devices for ITO/PEDOT:PSS/P3HT:F(DPP)$_2$B$_2$(1:1, by wt.)/MoO$_3$/Al and electron-only devices for ITO/PFN/P3HT:F(DPP)$_2$B$_2$(1:1, by wt.)/PFN/Al. The symbols represent experimental data and the solid lines are fitted according to the Mott-Gurney law.

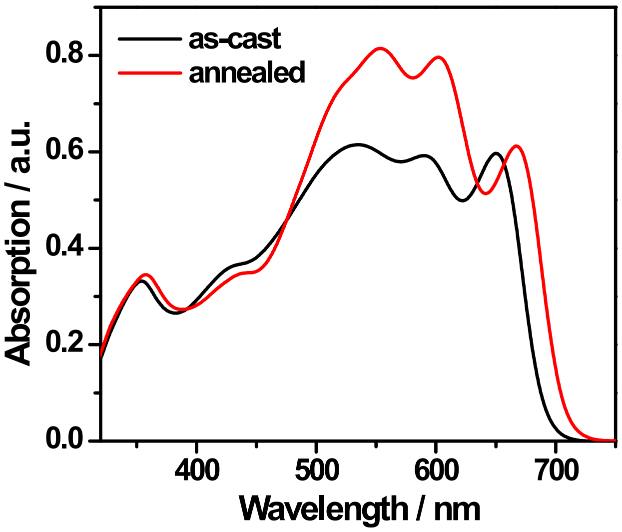


Fig. S6 UV-vis absorption spectra of P3HT:F(DPP)$_2$B$_2$ (1:1, by wt.) films with or without the thermal annealing at 120 ^{o}C for 10 min.

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