Electronic Supplementary Information for:

A 3D star-shaped non-fullerene acceptor for solution-processed organic solar cells with high open-circuit voltage of 1.18 V

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Materials. Unless stated otherwise, solvents and chemicals were obtained commercially and were used without further purification. Toluene was distilled from sodium-benzophenone under nitrogen prior to use. Tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine[1] and 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione[2] were synthesized according to the literature procedures.

Synthesis of S(TPA-DPP): To a three-necked round bottom flask were added tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine (63 mg, 0.1 mmol), 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (183 mg, 0.3 mmol), toluene (8 mL), and potassium carbonate aqueous solution (2 M, 4 mL). The mixture was deoxygenated with nitrogen for 30 min. $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) was added under nitrogen. The mixture was refluxed for 72 h and then cooled down to room temperature. Water (25 mL) was added and the mixture was extracted with dichloromethane (2 × 25 mL). The organic phase was dried over anhydrous $MgSO_4$ and filtered. After removing the solvent from filtrate, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (3:1) as eluent yielding a black blue solid (130 mg, 72%). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.99 (d, J = 4.1 Hz, 3H), 8.86 (d, J = 3.3 Hz, 3H), 7.68 (m, 9H), 7.49 (d, J = 4.1 Hz, 3H), 7.31 (t, J = 4.4 Hz, 3H), 7.24 (d, J = 8.6 Hz, 6H), 4.08 (m, 12H), 1.94 (m, 3H), 1.85 (m, 3H), 1.32 (m, 48H), 0.88 (m, 36H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 161.62, 161.41, 149.22, 147.17, 140.05, 139.48, 137.07, 134.93, 130.44, 130.19, 128.48, 128.29, 127.19, 124.70, 123.89, 108.18, 107.92, 45.78, 39.40, 39.25, 30.39, 30.29, 28.63, 28.48, 23.72, 23.60, 23.18, 13.97, 13.92, 10.43, 10.35. MS (MALDI): *m/z* 1812 (M^+). Anal. Calcd for $C_{108}H_{129}N_7O_6S_6$: C, 71.52; H, 7.17; N, 5.41. Found: C, 71.46; H, 7.16; N, 5.31%.

Measurements. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AVANCE 400 MHz spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard. Mass spectra were measured on a Bruker Daltonics BIFLEX III MALDI-TOF Analyzer using MALDI mode. Elemental analyses were carried out using a FLASH EA1112 elemental analyzer. Solution (dichloromethane) and thin film (on quartz substrate) UV-vis absorption spectra were recorded on a JΛSCO V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) in CH_3CN using a computer-controlled CHI660C electrochemical workstation, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag wire anodized with AgCl as a pseudo-reference electrode. Potentials were referenced to ferrocenium/ferrocene ($FeCp_2^{+/0}$) couple by using ferrocene as an internal standard. Thermogravimetric analysis (TGA) measurements were performed on Shimadzu thermogravimetric analyzer (model DTG-60) under a nitrogen flow at a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) measurements were performed using a METTLER differential scanning calorimeter (DSC822e) under nitrogen at a heating rate of 10 °C min^{-1}. The nanoscale morphology of blend film was observed by using a Veeco Nanoscopy V atomic force microscopy (AFM) in tapping mode.

Fabrication and characterization of photovoltaic cells. Photovoltaic cells were fabricated with a structure of ITO/PEDOT:PSS/P3HT:S(TPA-DPP)/Ca/Al. The patterned indium tin oxide (ITO) glass (sheet resistance = 30 Ω□ $^{-1}$) was pre-cleaned in an ultrasonic bath of acetone and isopropanol, and treated in ultraviolet-ozone chamber (Jelight Company, USA) for 30 min. A thin layer (30 nm) of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Baytron P VP AI 4083, Germany) was spin-coated onto the ITO glass and baked at 150 °C for 30 min. An o-dichlorobenzene solution of blend of P3HT:S(TPA-DPP) was subsequently spin-coated on PEDOT:PSS layer to form a photosensitive layer (*ca.* 120 nm). The thickness of the photosensitive layer was measured by Ambios Technology XP-2 profilometer. Calcium (*ca.* 15 nm) and aluminium (*ca.* 50 nm) layers were subsequently evaporated onto the surface of the photosensitive layer under vacuum (*ca.* 10^{-5} Pa) to form the negative electrode. The active area of the device was 4 mm^2. *J–V* curve was measured with a computer-controlled Keithley 236 Source Measure Unit. A xenon lamp coupled with AM1.5 solar spectrum filters was used as the light source, and the optical power at the sample was 100 mW cm^{-2}. The incident photon to converted current efficiency (IPCE) spectrum was measured by Stanford Research Systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and 500 W xenon lamp.

Mobility measurements. Hole- or electron-only diodes were fabricated using the architectures: ITO/PEDOT:PSS/P3HT:S(TPA-DPP)/Au for holes and Al/P3HT:S(TPA-DPP)/Al for electrons. Mobilities were extracted by fitting the current density–voltage curves using the Mott–Gurney relationship (space charge limited current).[3]

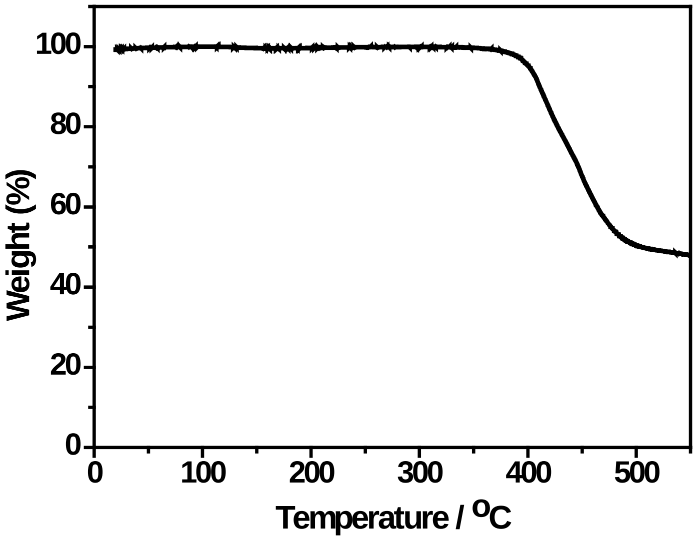

Fig. S1 TGA curve of S(TPA-DPP).

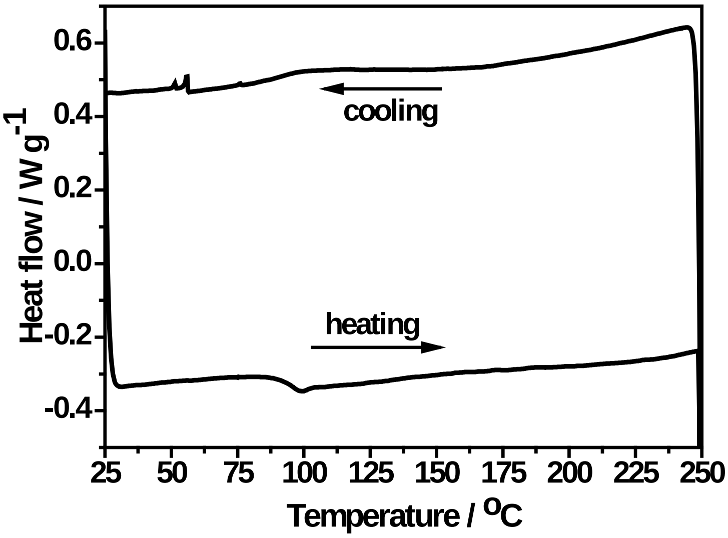

Fig. S2 DSC curves of S(TPA-DPP).

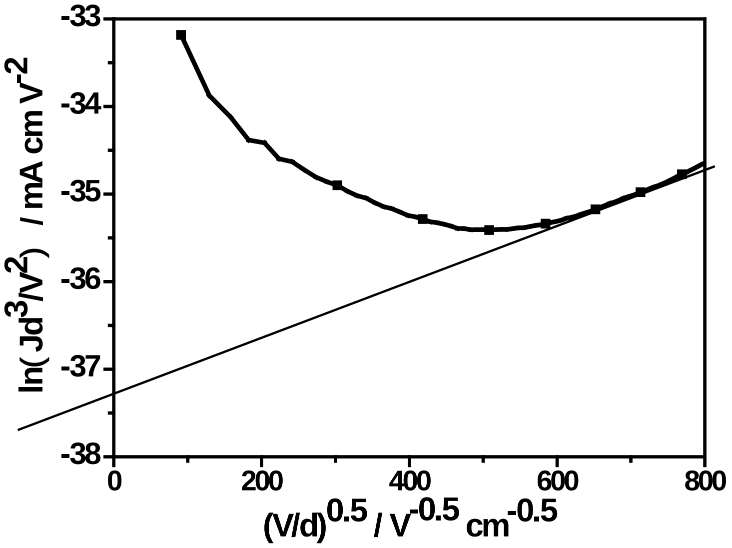

Fig. S3 Field dependence of the current for hole-only device annealed at 150 ° C for 10 min.

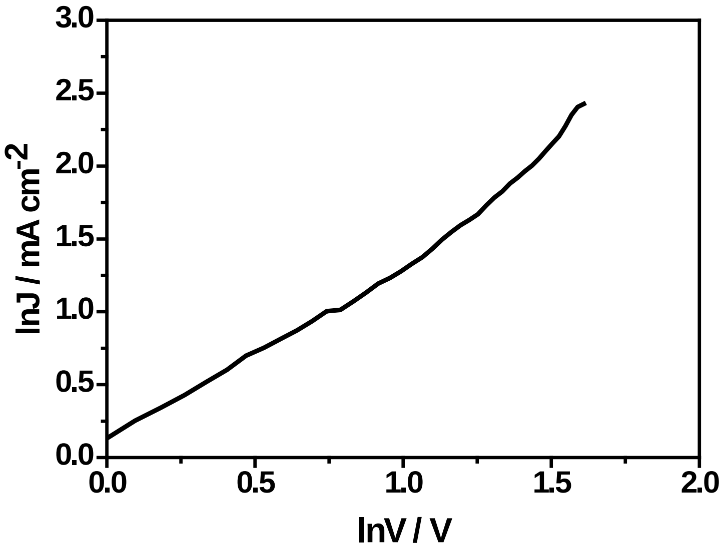

Fig. S4 Field dependence of the current for electron-only device annealed at 150 °C for 10 min.

References

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