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-bromo thiophen-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-bromo thiophen-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 \(\times\) 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%). \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 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\(_2\)Cl\(_2\)): \(\delta\) 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\(_7\)O\(_6\)S\(_6\): C, 71.52; H, 7.17; N, 5.41. Found: C, 71.46; H, 7.16; N, 5.31%.

2
**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 JASCO V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-$n$-butylammonium hexafluorophosphate (0.1 M) in CH$_3$CN 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$_2$/$^0$/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 $\Omega$ $\square^{-1}$) 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).\(^3\)

![TGA curve of S(TPA-DPP)](image)

**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**

