Electronic Supplementary Information for:

A star-shaped oligothiophene end-capped with alkyl cyanoacetate group for solution-processed organic solar cells

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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 was synthesized according to the literature procedures.[1] 5''-Bromo-2,2':5',2''-terthiophene-5-carboxaldehyde and 2-ethylhexyl cyanoacetate were purchased from TCI.

Synthesis of S(TPA-3T-CHO):

To a three-necked round bottom flask were added tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine (93 mg, 0.15 mmol), 5''-bromo-2,2':5',2''-terthiophene-5-carboxaldehyde (160 mg, 0.45 mmol), toluene (10 mL), and potassium carbonate aqueous solution (2 M, 5 mL). The mixture was deoxygenated with nitrogen for 30 min. $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) was added under nitrogen. The mixture was refluxed for 16 h and then cooled down to room temperature. Water (50 mL) was added and the mixture was extracted with dichloromethane (2 × 200 mL). The organic phase was dried over anhydrous $MgSO_4$ and filtered. After removing the solvent from filtrate, the residue was washed by ethyl acetate and filtered. The crude product (140 mg, 87%) was obtained as an orange solid and was used directly for next step reaction without further purification due to poor solubility of this compound in common solvents. MS (MALDI): *m/z* 1067.2 (M^+).

Synthesis of S(TPA-3T-CA):

To a three-necked round bottom flask were added S(TPA-3T-CHO) (135 mg, 0.13 mmol) and dichloromethane (60 mL). The orange suspension was deoxygenated with nitrogen for 30 min. Then triethylamine (2 mL) and 2-ethylhexyl cyanoacetate (1 mL, 4.8 mmol) were added under nitrogen.

The mixture was stirred at room temperature for 3 d. After removing the solvent from mixture, the residue was purified by column chromatography on silica gel using dichloromethane as eluent yielding a black solid (80 mg, 40%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.24 (s, 3H), 7.67 (d, J = 4.0 Hz, 3H), 7.53 (d, J = 8.8 Hz, 6H), 7.34 (d, J = 4.0 Hz, 3H), 7.27 (d, J = 4.0 Hz, 3H), 7.23 (s, 6H), 7.17 (d, J = 4.0 Hz, 3H), 7.14 (d, J = 8.4 Hz, 6H), 4.19 (dd, J = 6.0 Hz, J = 2.0 Hz, 6H), 1.69 (m, 3H), 1.33 (m, 24H), 0.94 (m, 18H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.93, 146.83, 146.46, 145.63, 143.81, 139.51, 139.44, 135.07, 134.27, 134.05, 128.67, 127.38, 126.54, 125.67, 124.54, 124.43, 124.23, 123.50, 116.03, 97.73, 68.77, 38.88, 30.37, 28.99, 23.82, 23.06, 13.92, 10.87. MS (MALDI): *m/z* 1605.8 (M^+). Anal. Calcd for $C_{90}H_{84}N_4O_6S_9$: C, 67.30; H, 5.27; N, 3.49. Found: C, 67.02; H, 5.16; N, 3.43%.

Measurements. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AVANCE 400 MHz spectrometer. 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. The bright-field transmission electron microscopy (TEM) characterization was carried out on a Tecnai G2 F20 U-TWIN. The samples for the TEM measurements were prepared as follows: The active-layer films were spin-casted on ITO/PEDOT:PSS substrates, and the ITO glass with the active layers were submerged in deionized water (10 min) to make the active layers float onto the air–water interface. Then the floated films were picked up on unsupported 200 mesh copper grids for the TEM measurement.

Fabrication and characterization of photovoltaic cells. Photovoltaic cells were fabricated with a structure of ITO/PEDOT:PSS/S(TPA-3T-CA):PC$_{71}$BM/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 chloroform solution of blend of S(TPA-3T-CA):PC$_{71}$BM was subsequently spin-coated on PEDOT:PSS layer to form a photosensitive layer (*ca.* 80 nm). The thickness of the photosensitive layer was measured by Ambios Technology XP-2 profilometer. Calcium (*ca.* 25 nm) and aluminium (*ca.* 60 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.

Hole mobility measurements. Hole-only diodes were fabricated using the architectures: ITO/PEDOT:PSS/S(TPA-3T-CA)/Au. Mobilities were extracted by fitting the current density–voltage curves using the Mott–Gurney relationship (space charge limited current).[2]

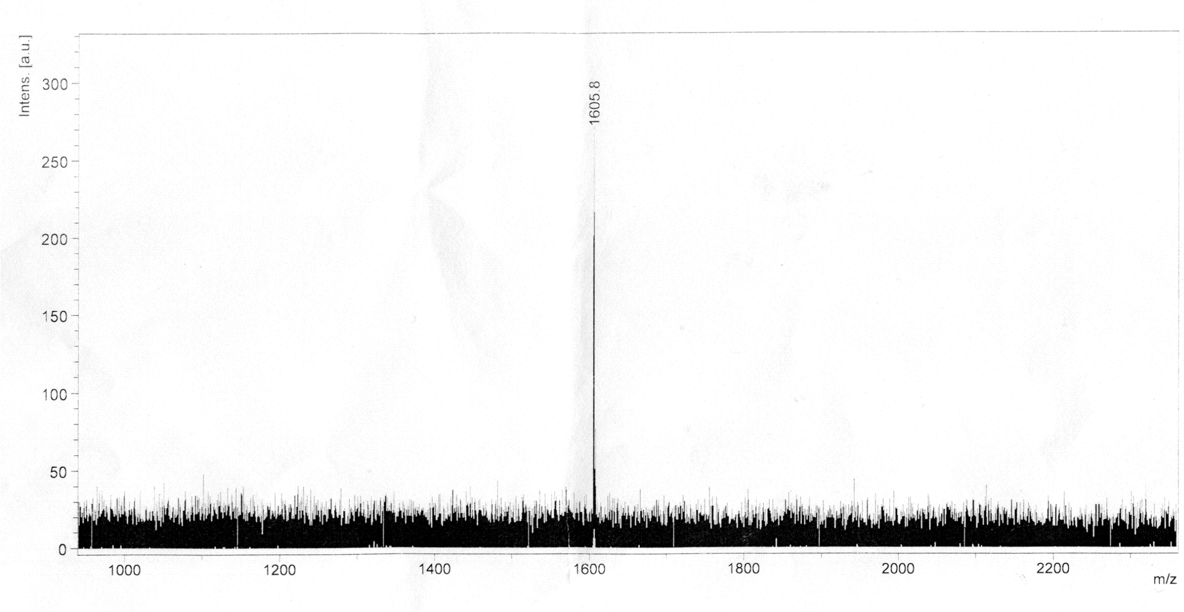

Fig. S1 MS (MALDI-TOF) spectrum of S(TPA-3T-CA).

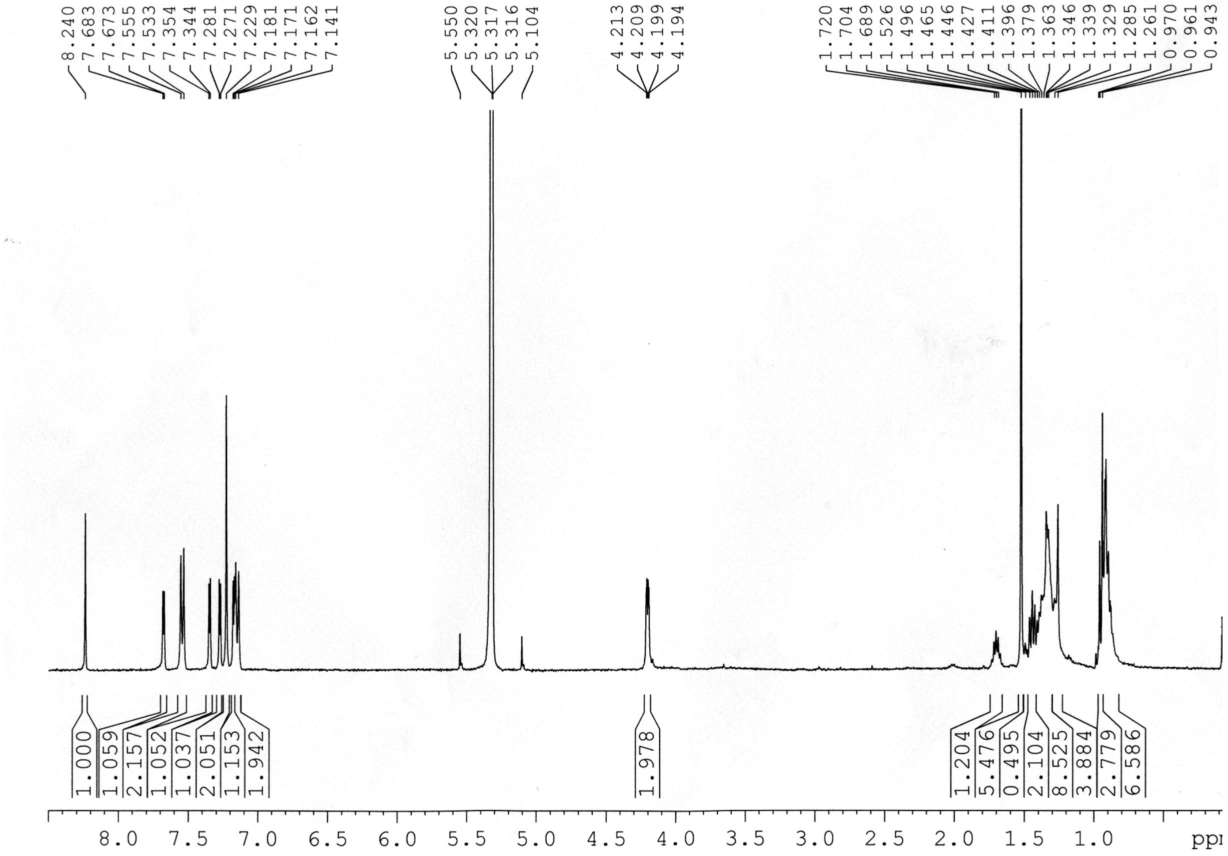

Fig. S2 ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of S(TPA-3T-CA).

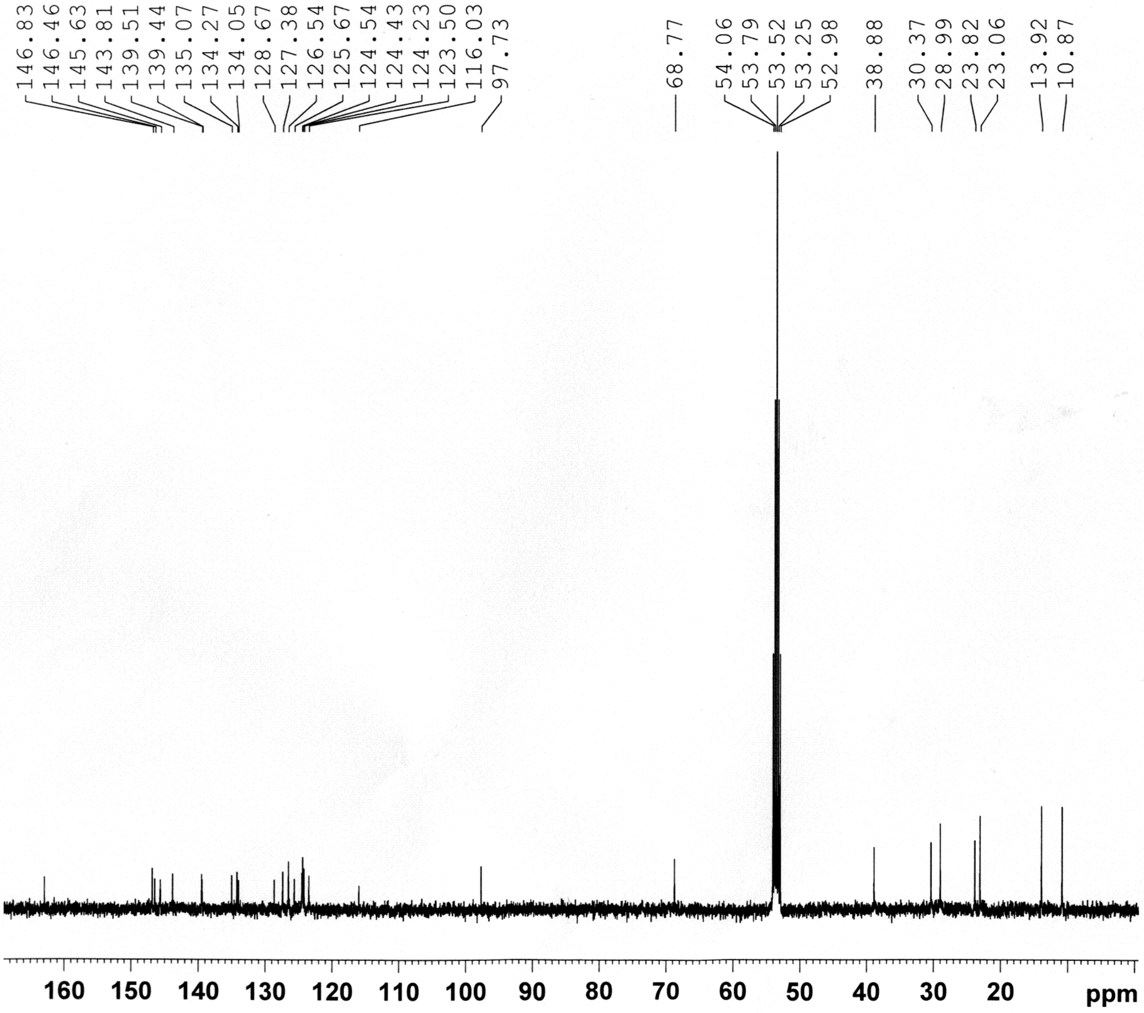

Fig. S3 ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of S(TPA-3T-CA).

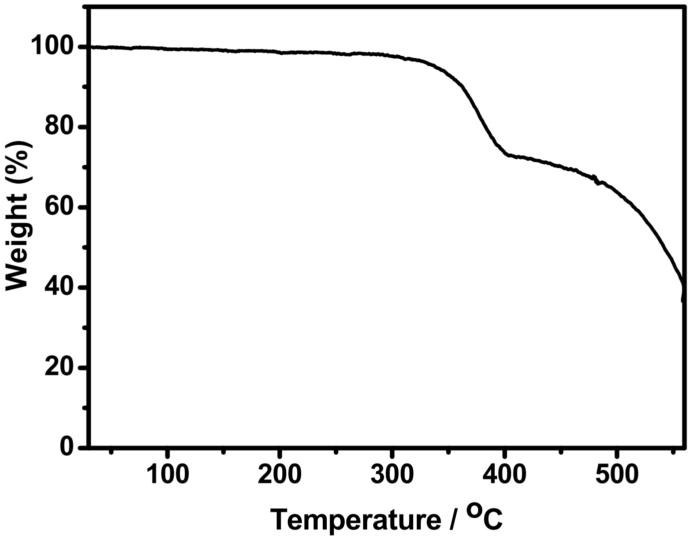

Fig. S4 TGA curve of S(TPA-3T-CA).

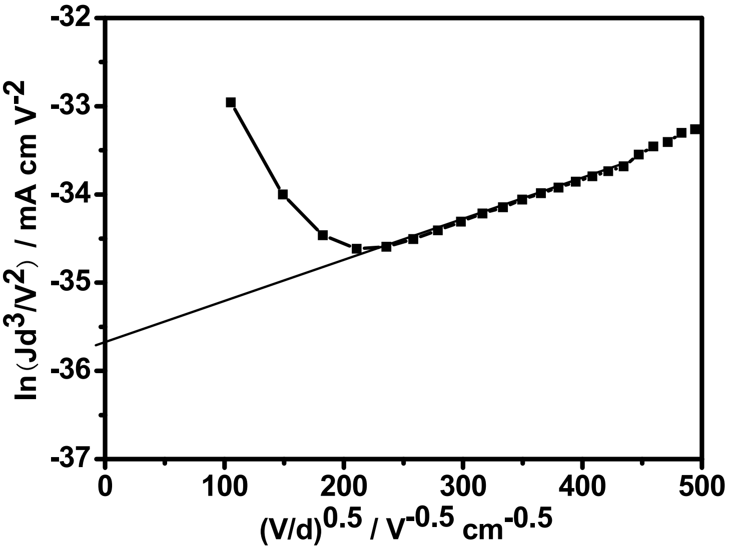

Fig. S5 Field dependence of the current for hole-only device.

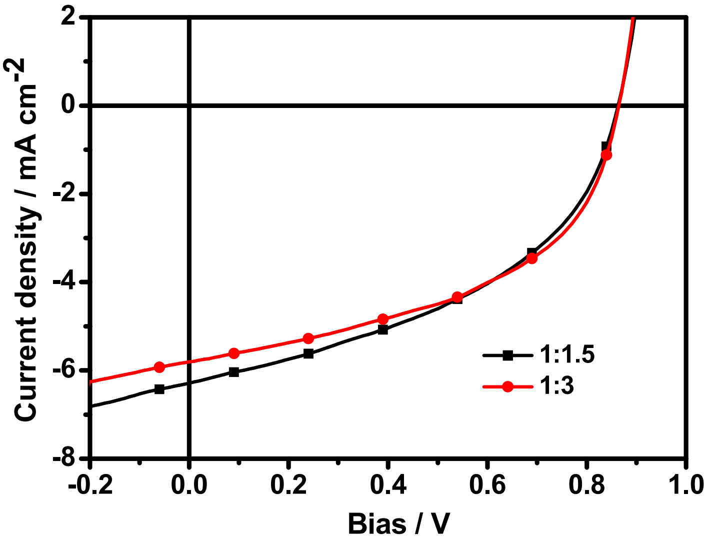

Fig. S6 *J*-*V* curves of device with the structure ITO/PEDOT:PSS/S(TPA-3T-CA):PC$_{71}$BM (1:1.5 or 1:3, w/w)/Ca/Al.

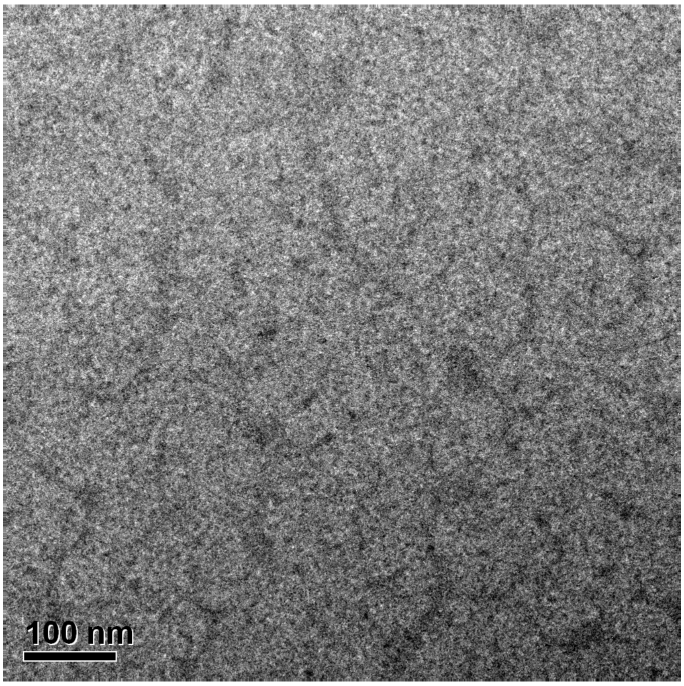

Fig. S7 TEM image of S(TPA-3T-CA):$PC_{71}BM$ blend film (1 : 2, w/w).

References

1. J. Cremer and P. Bauerle, *J. Mater. Chem.*, 2006, **16**, 874-884.
2. G. G. Malliaras, J. R. Salem, P. J. Brock and C. Scott, *Phys. Rev. B*, 1998, **58**, R13411-R13414.