Electronic Supplementary Information for:

A triphenylamine-based four-armed molecule for solution-processed organic solar cells with high photo-voltage

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Materials and measurement

All reagents, unless otherwise specified, were purchased from Alfa Aesar and were used as they were received. All solvents were carefully dried and purified under a nitrogen flow. ^{1}H and ^{13}C NMR spectra were recorded on Varian Inova 400 (Varian in American) in deuterated chloroform solution at 298 K. Elemental analysis was performed on FlashEA1112 Elemental Analysis Instrument (Elementar Co.). UV-visible absorption spectra were recorded on a UV-2550 spectrophotometer (shimadzu Co. in Japan). Cyclic voltammetry were done by using a CHI610A electrochemical workstation (shanghai in China) with glass-carbon electrodes at a scan rate of 50mV/s against a calomel reference electrode with an anhydrous and nitrogen-saturated solution of 0.1 mol L^{-1} Tetrabutyl-ammonium Perchlorate (TBAP)–acetonitrile (CH_3CN). The deposition of small molecule on the electrode was done by the evaporation of a dilute chloroform solution. The TG curve was recorded on a Netzschsta409P (NETZSCH-Gerätebau GmbH in German) with a heating rate of 10 ℃ min^{-1} at N_2 atmosphere. PL and EL spectra were obtained with an Andor spectrometer (Shamrock sr-303i-B, coupled to a Newton EMCCD detector) and both pure Th_4(DTPAB) and blend based devices connected to an external current/voltage source for the measurements of EL. A green CW He-Ne 532 nm laser with an intensity of 2 mW cm^{-2} was used as pumping light source for the absolute PL measurements. AFM was performed directly on these films, with a Dimension 3100 system (Digital Instruments/Veeco) by using Antimony (n) doped Silicon cantilevers (SCM-PIT, Veeco) in tapping mode.

N,N-diphenyl-4-phenylamine stannane[1], 4-(hexyl-2-thienyl)stannane[2] were prepared following the already published procedures.

4,7-bis(4-(diphenylamino)phenyl)-2,1,3-benzothiadiazole

In a three-necked flask, 15 mg $Pd(PPh_3)_2Cl_2$ was added to a solution of N,N-diphenyl-4-phenylamine stannane (2.24 g, 4.2 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (0.588 g, 2.0 mmol) in tetrahydrofuran (THF) under an N_2 atmosphere. The mixture was refluxed for 24 h, cooled to room temperature, poured into water, and then extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, petroleum ether/$CHCl_3$ (1:1)) to produce the title product as a yellow solid (0.933 g, 75%). ESI-MS: 622. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.88-7.90 (d, 4H); 7.74 (s, 2H); 7.28-7.32 (t, 8H); 7.19-7.23 (t, 12H); 7.06-7.09 (t, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 154.14, 147.96, 147.47, 132.14, 130.99, 129.88, 129.34, 127.42, 124.87, 123.28, 122.93. Elem. Anal. for

$C_{42}H_{30}N_4S$ Calc.: C, 81.03; H, 4.82; N, 9.00; S, 5.15. Found: C, 81.15; H, 4.91; N, 9.10; S, 4.84.

4,7-bis(4-(di(4-bromophenyl)amino)phenyl)-2,1,3-benzothiadiazole

Under an N_2 atmosphere, NBS (0.712 g, 4.0 mmol) was added to the solution of 4,7-bis(4-(diphenylamino)phenyl)-2,1,3-benzothiadiazole (0.5 g, 0.8 mmol) in $CHCl_3$ (15 mL). The mixture was stirred for 5 h at room temperature under dark. Then, the reaction solution was poured into water, extracted with dichloromethane, dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, petroleum ether/$CHCl_3$ (1:1)) to produce the title product as an orange solid (0.525 g, 70%). ESI-MS: 938. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.89-7.91 (dd, 4H); 7.75 (s, 2H); 7.38-7.41 (t, 8H); 7.19-7.21(t, 4H); 7.03-7.06 (t, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 154.03, 147.03, 146.18, 132.50, 130.19, 127.58, 126.03, 123.57, 116.11. Elem. Anal. for $C_{42}H_{26}N_4SBr_4$ Calc.: C, 53.73; H, 2.77; N, 5.97; S, 3.41. Found: C, 53.88; H, 2.85; N, 5.83; S, 3.32.

Four-armed Th_4(DTPAB) molecule

Carefully purified 4,7-bis(4-(di(4-bromophenyl)amino)phenyl)-2,1,3-benzothiadiazole (**1**) (0.235 g, 0.25 mmol), 4-(hexyl-2-thienyl)stannane (0.571 g, 1.25 mmol) (**2**) and $Pd(PPh_3)_2Cl_2$ (10 mg) were dissolved in a mixture of toluene. The mixture was first put in the argon atmosphere and was refluxed with vigorous stirring for 48 h. The reaction solution was poured into water, extracted with dichloromethane, the organic layer was washed with brine, dried over anhydrous sodium sulfate. Filtered, and the solvent was removed, and the residue was purified by column chromatography (silica gel, petroleum ether/$CHCl_3$ (1:1)) to produce the title product as an orange solid (0.225 g, 70%).

ESI-MS: 1286. ^{1}H-NMR: (400MHz, $CDCl_3$, ppm): 7.91-7.93 (d, 4H); 7.76 (s, 2H); 7.50-7.52 (d,4H); 7.38-7.40 (d, 4H); 7.22-7.28 (m, 8H); 7.03-7.19 (m, 8H); 6.84 (s, 4H); 2.59-2.63 (t, 8H); 1.61-1.66 (m, 8H); 1.26-1.33 (m, 24H); 0.88-0.91 (t, 12H). ^{13}C-NMR: (100MHz, $CDCl_3$, ppm): 154.11, 147.35, 146.32, 144.30, 143.55, 132.39, 130.03, 129.79, 127.50, 126.65, 125.97, 124.78, 123.94, 123.45, 118.95, 31.69, 30.65, 30.42, 29.00, 22.62, 14.10. Elem. Anal. for $C_{82}H_{86}N_4S_5$ Calc.: C, 76.52; H, 6.69; N, 4.35; S, 12.44. Found: C, 76.68; H, 6.82; N, 4.21; S, 12.29.

Fabrication and characterization of photovoltaic cells

The OSCs were fabricated using a device structure glass/ITO/PEDOT:PSS (40 nm)/active layer/LiF (0.6 nm)/Al (100 nm). The device architecture of the OSCs is schematically illustrated in Fig. S3. The ITO covered glass substrates were cleaned by detergent and acetone prior to TL-1 (a mixture of water, ammonia (25%), and hydrogen peroxide (28%) (5:1:1 by volume)) treatment. PEDOT:PSS (40 nm) was spin-cast onto the cleaned substrate and heated for 30 minutes at 120 ℃. Then, the substrates were transferred into a glove box filled with N_2. The active layers (60 nm) were spin-coated from CF solutions on top of the PEDOT:PSS coated ITO glass substrates. The substrates were moved into a vacuum chamber where 0.6 nm LiF and 80 nm Al were thermally evaporated at a pressure less than 4×10^{-4} Pa. The active areas of all OSCs are roughly 4.5 mm^2 defined by the overlap between two electrodes, which were measured by optical microscopy. Current density–voltage ($J-V$) curves were measured by using Keithley 2400 Source Meter under illumination of AM 1.5 filtered light, with intensity of 100 mW cm^{-2} (solar simulator Model SS-50A, Photo Emission Tech., Inc.). EQE spectra were obtained using a Newport Merlin lock-in with the solar cells illuminated with chopped monochromatic light through the ITO side.

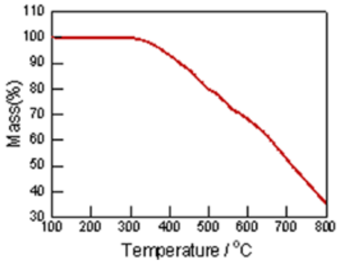

Fig. S1. TG curve of Th_4(DTPAB) at 10 ℃ min^{-1} under nitrogen

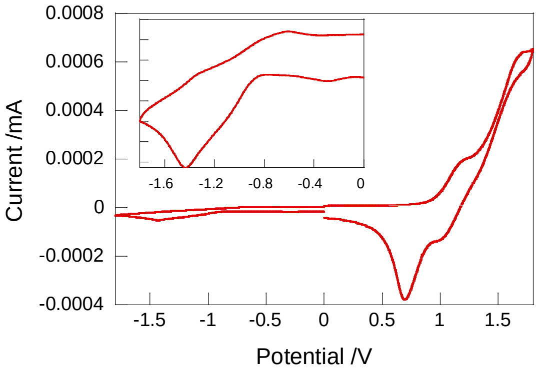

Fig. S2. Cyclic voltammograms of Th_4(DTPAB) film on glass-carbon electrode in an acetonitrile solution of 0.1 mol L^{-1} TBAP with a scan rate of 50 mV/s.

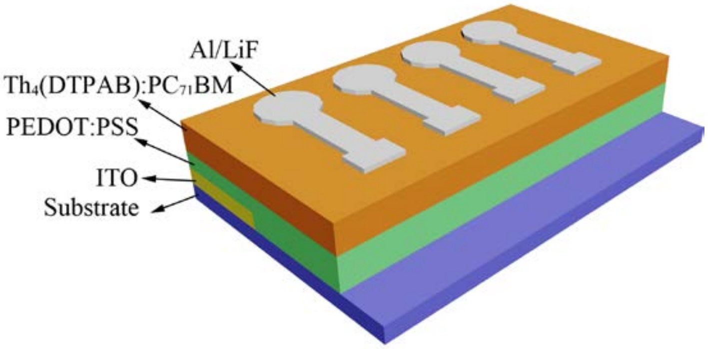

Fig. S3. Schematic device structure of the OSCs

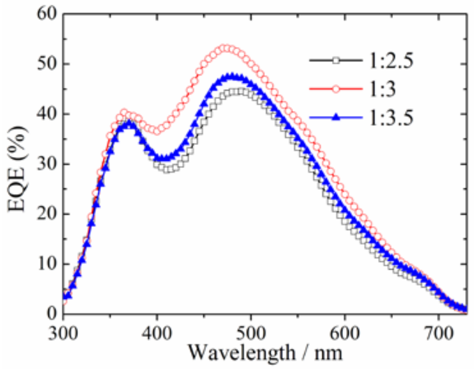

Fig. S4. EQEs of the OSCs based on Th_4(DTPAB):PC_{71}BM with different stichoimetries

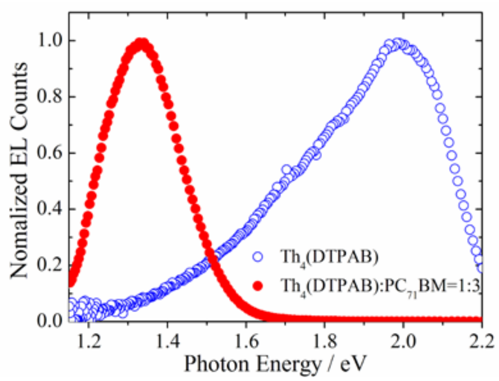

Fig. S5. EL spectra of Th_4(DTPAB) and its blend with PC_{71}BM with the ratio of 1:3

References

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2. Q. Hou, Q. Zhou, Y. Zhang, W. Yang, R. Yang and Y. Cao, Macromolecules, 2004, 37, 6299.