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Electronic Supplementary Information

Triazine Cored Star-shape Compounds as Cathode Interlayers for Efficient Inverted Polymer Solar Cells

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Materials and Characterization: Unless otherwise indicated, all the materials were obtained from commercial suppliers and used without further purification. Solvents for synthesis were purified by routine procedure and distilled under dry argon prior to use. The electron donor material PTB7 and the electron acceptor $PC_{71}BM$ were purchased from 1-material chemscitech and American Dye Source Incorporated, respectively. ^{1}H NMR and ^{13}C NMR spectra were measured on a MECUYR-VX300 spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. EI mass spectra were measured on a ZAB 3F-HF mass spectrophotometer. MALDI-TOF mass spectra were performed on Bruker BIFLEX III TOF mass spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Cyclic voltammetry (CV) was carried out at room temperature with a CHI voltammetric analyzer.n-Bu_4PF_6 (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudoreference electrode with ferrocenium-ferrocene (Fc^+/Fc) as the internal standard. Cyclic voltammograms were obtained at a scan rate of 100 mV s^{-1}. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram. The work functions of ITO were obtained by Kelvin probe (KP020, KP Technology). Ultraviolet photoelectron spectroscopy (UPS) were carried out in a Multifunctional X-ray Photoelectron Spectroscope (Kratos AXIS ULTRA DLD) using a He I (21.22 eV) discharge lamp. The thicknesses of interlayer films were calculated from combination of UV-vis absorption spectra and step profiler (Dektak150, Vecco). The tapping-mode AFM images were obtained by using a scanning probe microscope (Dimension 3100V). Contact angle measurements were performed on a video-based optical contact angle measuring instrument (OCA20, Dataphysics Corp.).

2,4,6-tris(9,9-bis(6-bromohexyl)-9H-fluoren-2-yl)-1,3,5-triazine (1)

1.14g 2-carbonitrile-9,9-bis(6-bromohexyl)-9*H*-fluorene (2 mmol) in 10mL CH_2Cl_2 was added dropwise to a solution of trifluoromethanesulfonic acid (1.5 mL) in 5mL CH_2Cl_2 over 30 min at 0 ^{o}C under Ar atmosphere. The mixture was stirred at room temperature for another 48 hours and then diluted with 50mL CH_2Cl_2, NH_4OH aqueous solution was added until the appearance of the solution is colorless. The organic layer was seperated and washed with water and then dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography using hexane/ethyl acetate (20:1, v/v) as the eluent to obtain the product as white powder (yield: 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 8.87 (d, *J*=4.1Hz, 3H), 8.75 (s, 3H), 7.97 (d, *J*=3.8Hz, 3H), 7.85-7.84 (m, 3H), 7.43-7.42 (m, 9H), 3.26 (t, *J*=6.9Hz, 12H), 2.19-2.12 (m, 12H), 1.68-1.61 (m, 12H), 1.22-1.14 (m, 24H), 0.73 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm]: 171.93, 151.61, 150.89, 145.75, 140.41, 135.44, 128.59, 128.35, 127.27, 123.22, 120.77, 120.02, 98.65, 55.28, 40.34, 34.03, 32.72, 29.19, 27.89, 23.73. MS (MALDI-TOF, m/z): $[M]^+$ Calcd for $C_{78}H_{93}Br_6N_3$: 1551.2. Found: 1552.3.

9',9'-bis(6-bromohexyl)-9,9-dihexyl-9H,9'H-[2,2'-bifluorene]-7-carbonitrile (2)

To a mixture of 7-bromo-9,9-dihexyl-9H-fluorene-2-carbonitrile (0.87 g, 2 mmol) and 2-(9,9-bis(6-bromohexyl)-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.50 g, 2.4 mmol), $Pd(PPh_3)_4$ (0.15 g, 0.2 mmol) and K_2CO_3 (1.38 g, 10 mmol) were added degassed toluene (18 mL), ethanol (6mL) and water (3 mL). The mixture was refluxed under argon for 36 hours. The resulting mixture was poured into water and extracted with chloroform. The combined organic layer was washed with water, and dried over Na_2SO_4. After removed the solvent under reduced pressure, the residue was purified with a silica gel column chromatography using hexane/ethyl acetate (12:1, v/v) as eluent to obtain the product as white powder (yield: 73%). ^{1}H NMR (300 MHz, CDCl$_3$) δ [ppm]: 7.84-7.74 (m, 4H), 7.71-7.60 (m, 6H), 7.35 (s, 3H), 3.27 (t, J = 6.6Hz, 4H), 2.07-2.05 (m, 8H), 1.68-1.61 (m, 4H), 1.26-1.08 (m, 24H), 0.80-0.75 (m, 6H), 0.69-0.67 (m, 4H). ^{13}C NMR (75 MHz, CDCl$_3$) δ [ppm]: 166.74, 152.14, 151.58, 151.15, 150.52, 145.29, 142.22, 140.74, 140.52, 139.79, 138.31, 131.26, 127.25, 126.94, 126.56, 126.37, 126.27, 122.81, 121.33, 121.19, 120.21, 120.06, 119.85, 109.72, 70.57, 55.58, 55.03, 40.02, 33.77, 32.52, 31.35, 29.47, 28.95, 27.94, 27.65, 25.36, 23.70, 23.52, 22.46, 14.00. MS (EI, m/z): [M]$^+$ Calcd for $C_{51}H_{63}Br_2N$: 849.33. Found: 848.88.

2,4,6-tris(9',9'-bis(6-bromohexyl)-9,9-dihexyl-9H,9'H-[2,2'-bifluoren]-7-yl)-1,3,5-triazine (3)

4 was prepared by using the similar procedure for preparation of 2, from 3 and trifluoromethanesulfonic acid. The crude product was purified by a silica gel column chromatography using hexane/ethyl acetate (15:1, v/v), giving 4 as light yellow powder (yield: 67%). ^{1}H NMR (300 MHz, CDCl$_3$) δ [ppm]: 8.91-8.82 (m, 6H), 8.02-7.92 (m, 6H), 7.84-7.65 (m, 18H), 7.37 (s, 9H). 3.29 (t, J = 6.9 Hz, 12H), 2.24-2.07 (m, 24H), 1.71-1.66 (m, 12H), 1.25-1.13 (m, 72H), 0.85-0.75 (m, 30H). ^{13}C NMR (75 MHz, CDCl$_3$) δ [ppm]: 172.03, 152.91, 151.53, 151.27, 150.70, 145.34, 141.55, 140.83, 140.48, 139.47, 128.62, 127.11, 126.44, 123.53, 122.96, 121.42, 121.00, 120.00, 55.55, 55.18, 40.35, 34.00, 32.72, 31.62, 29.85, 29.16, 27.85, 24.05, 23.72, 22.70, 14.19. MS (MALDI-TOF, m/z): [M]$^+$ Calcd for $C_{153}H_{189}Br_6N_3$: 2549.0. Found: 2548.6.

((1,3,5-triazine-2,4,6-triyl)tris(9H-fluorene-9,9,2-triyl))hexakis(N,N-diethylhexan-1-amine) (Tf1)

To a mixture of 2 (0.77g, 0.5mmol) in DMF (10mL) under Ar atmosphere, 3 mL of diethylamine was added in one portion. The reaction mixture was refluxed with vigorously stirring overnight. After cooling to room temperature, the mixture was poured into ice water and extracted with dichloromethane. The combined organic layer was washed with water, and dried over Na_2SO_4. After removed the solvent under reduced pressure, the residue was purified with a silica gel column chromatography using hexane/methanol/triethtyamine (100:5:1, v/v/v) to afford Tf1 as white solid (yield: 85%). ^{1}H NMR (300 MHz, CD_3OD) δ [ppm]: 8.91-8.85 (m, 6H), 8.01-7.95 (m, 6H), 7.47-7.40 (m, 9H), 2.55-2.50 (m, 36H), 2.21-2.17 (m, 12H), 1.24-1.18 (m, 36H), 1.08-1.01 (m, 48 H). ^{13}C NMR (75 MHz, CD_3OD) δ [ppm]: 178.86, 173.72, 172.01, 151.47, 150.93, 146.06, 140.10, 136.06, 135.13, 130.04, 128.32, 127.89, 126.93, 124.30, 122.45, 120.44, 119.87, 58.86, 55.83, 54.75, 40.32, 39.89, 29.33, 27.32, 25.88, 23.67, 22.96. MS (MALDI-TOF, m/z): $[M]^+$ Calcd for $C_{102}H_{153}N_9$: 1505.2. Found: 1505.3.

(1,3,5-triazine-2,4,6-triyl)tris(9',9'-dihexyl-9H,9'H-[2,2'-bifluorene]-9,9,7'-triyl))hexakis(N,N-diethylhexan-1-amine) (Tf2)

Tf2 was prepared by using the similar procedure for preparation of Tf1, from 4 and diethylamine. The crude product was purified by a silica gel column chromatography using hexane/methanol/triethtyamine (100:5:1, v/v/v/), giving Tf2 as light yellow solid (yield: 83%). ^{1}H NMR (300 MHz, CD_3OD) δ [ppm]: 8.97-8.80 (m, 6H), 8.25-7.97 (m, 6H), 7.78-7.65 (m, 18H), 7.32 (s, 9H), 2.52-2.49 (m, 36H), 2.30-2.09 (m, 24H), 1.29-1.20 (m, 84H), 1.05-1.01 (m, 48H), 0.85-0.72 (m, 18H). ^{13}C NMR (75 MHz,CD_3OD) δ [ppm]: 170.93, 152.57, 151.20, 150.40, 150.22, 146.04, 142.05, 140.66, 140.68, 139.43, 129.02, 127.11, 126.81, 123.43, 122.56, 121.62, 120.90, 119.75, 58.98, 55.85, 55.35, 54.43,40.35, 39.88,29.85, 29.34, 29.02, 26.58, 25.87, 23.49, 23.34, 22.18, 21.95, 13.06. MS (MALDI-TOF, m/z): $[M]^+$ Calcd for $C_{177}H_{249}N_9$: 2502.0. Found: 2502.1.

Device Fabrication and Measurement: ITO-coated glass substrates were cleaned by sonication in detergent, deionized water, acetone and isopropyl alcohol and dried with a nitrogen stream, followed by a UV ozone treatment. Then the cathode interlayer was deposited by spin-coating from various concentration solutions of Tf1 or Tf2 in methanol at 1000 rpm for 1min. Subsequently, a photoactive layer of PTB7/$PC_{71}BM$ (10:15, w/w) was spin-coated from chlorobenzene solution with 3% (w) 1,8-diiodooctane, which resulted in an active layer with the thickness of 90 nm ± 10 nm. Finally, a 10 nm MoO_3 layer and a 160 nm Al layer were evaporated in sequence through a shadow mask to define the active area of the devices (0.06 cm^2). The anode thickness was monitored upon deposition by using a crystal thickness monitor (Sycon). The device fabrication was carried out in a nitrogen atmosphere inside the glovebox. The *J-V* characteristics were recorded with a Keithley 236 source meter. The spectral response was measured with a commercial 40 photomodulation spectroscopy setup (Oriel). A calibrated Si photodiode was used to determine the photosensitivity. PCE was measured under an AM1.5G solar simulator. The power of the sun simulation was calibrated before the measurement using a standard silicon solar cell.

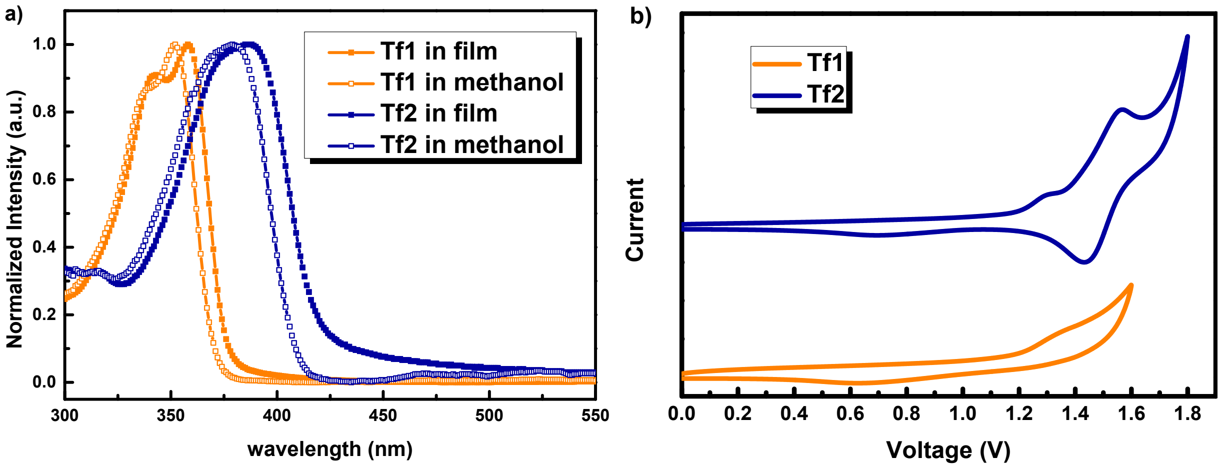

Fig. S1 a) Normalized UV-vis absorption spectra of Tf1 and Tf2 in methanol solution and in solid-state films, respectively; b) cyclic voltammograms Tf1 and Tf2 in acetonitrile for oxidation, respectively.

Table S1 The absorption peak wavelengths and HOMO/LUMO of Tf1 and Tf2, respectively.

Molecule	$\lambda_{abs}{}^{a}$ [nm]	$\lambda_{abs,\ film}$ [nm]	$E_g{}^{b}$ [eV]	$E_{ox}{}^{c}$ [V]	HOMO[d] [eV]	LUMO[e] [eV]
Tf1	352	358	3.28	1.22	-5.49	-2.21
Tf2	379	386	2.97	1.21, 1.39	-5.48	-2.51

[a] Measured in 1 x 10^{-6} M methanol solutions. [b] Calculated from the edge of low-energy absorption edge. [c] Recorded at scan rate = 100 mV s^{-1}, and $E_{1/2}$ (ferrocene) = 0.24 V versus $AgNO_3$/Ag reference electrode. [d] Determined from the onset of oxidation potentials. [e] Deduced from HOMO and E_g estimated from the edge of the long wavelength absorption in the solid-film sample.

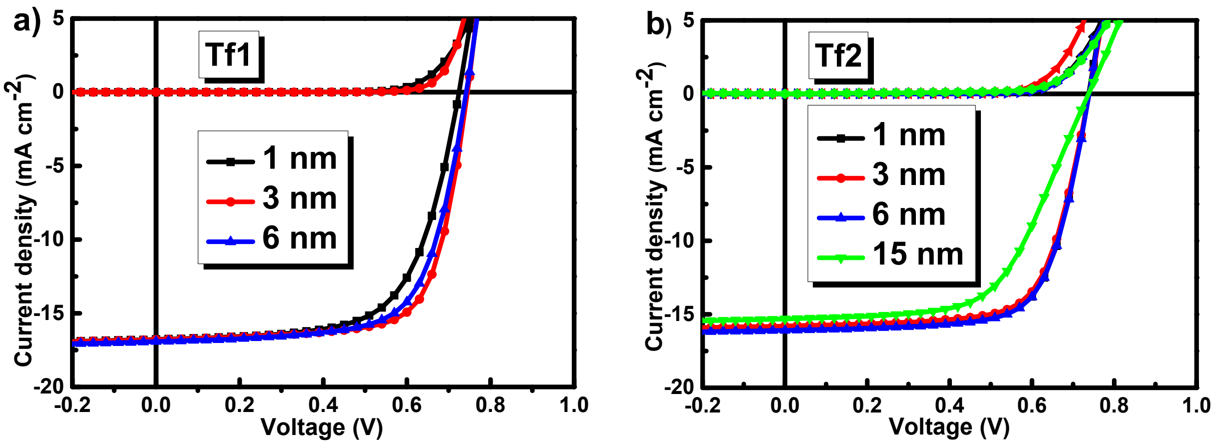

Fig. S2 *J*-*V* characteristics of the inverted PSCs with PTB7:PC$_{71}$BM as active layer, and a) Tf1, b) Tf2 as the interlayers in various thicknesses.

Table S2 Photovoltaic properties of the PSCs with various interlayers under AM 1.5G irradiation (100 mW cm^{-2})

Interlayer	Thickness (nm)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
Bare ITO	-	0.25[a](0.22)[b]	14.02 (12.97)	33.46 (30.89)	1.18 (0.92)
Tf1	1	0.72 (0.71)	16.76 (16.90)	65.09 (62.50)	7.91 (7.56)
	3	0.74 (0.74)	16.78 (16.58)	71.72 (71.67)	8.97 (8.86)
	6	0.75 (0.74)	16.44 (16.19)	67.95 (68.11)	8.38 (8.22)
Tf2	1	0.74 (0.74)	15.95 (15.82)	70.62 (69.01)	8.31 (8.07)
	3	0.74 (0.74)	15.78 (15.66)	69.84 (68.18)	8.14 (7.90)
	6	0.74 (0.74)	16.08 (15.99)	70.13 (69.62)	8.33 (8.21)
	15	0.74 (0.74)	15.93 (15.59)	55.75 (52.67)	6.56 (6.07)

a) Best device; b) Average values calculated over six devices.

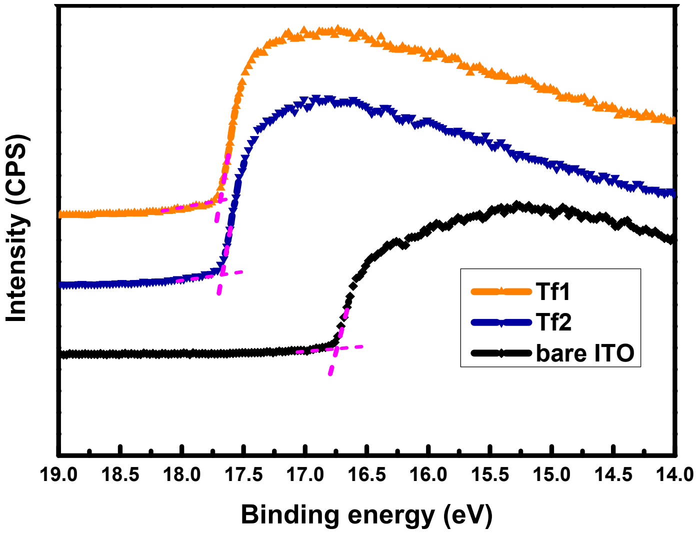

Fig. S3 UPS spectra of bare ITO, ITO/Tf1 and ITO/Tf2 thin films, respectively.

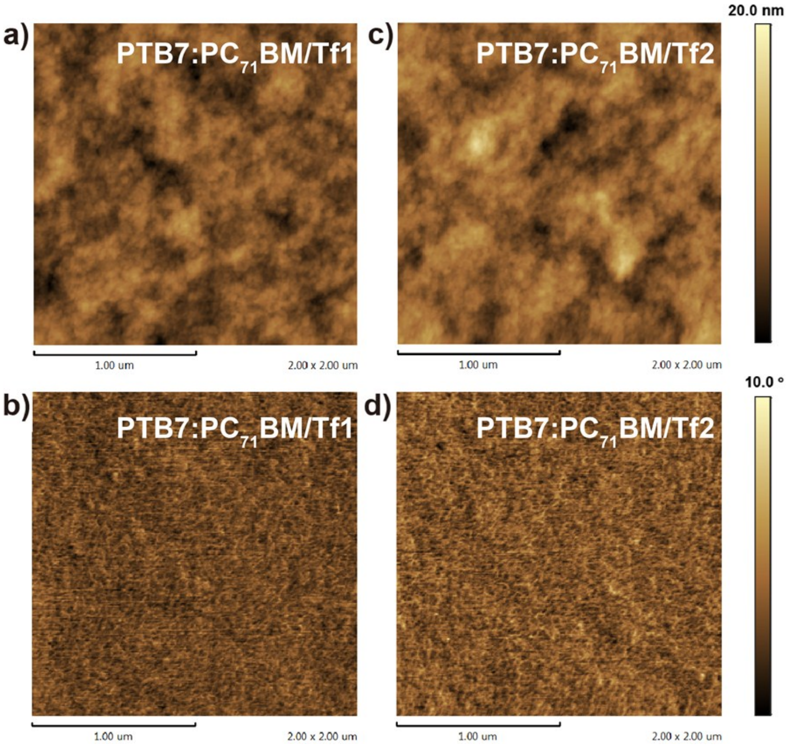

Fig. S4 Surface topographic AFM (a and c) height and (b and d) phase images of PTB7:PC$_{71}$BM atop of Tf1 or Tf2 interlayers, respectively. Scan size is 2 μm × 2 μm.

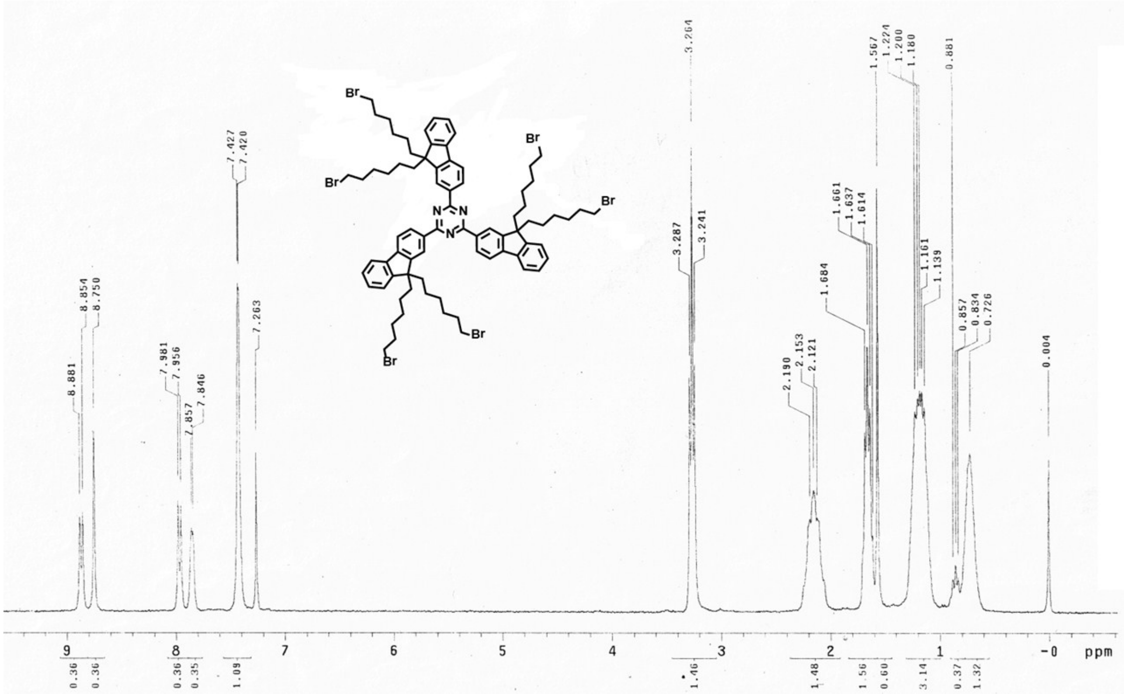

Fig. S5 ^{1}H NMR spectra of compound 1.

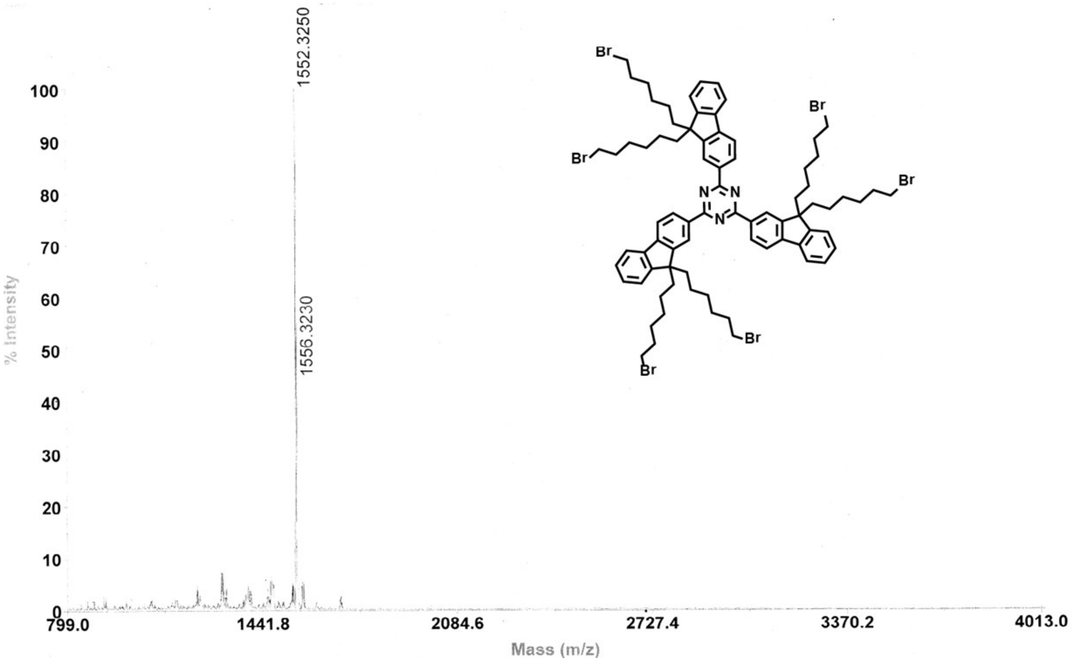

Fig. S6 MALDI-TOF mass spectra of compound 1.

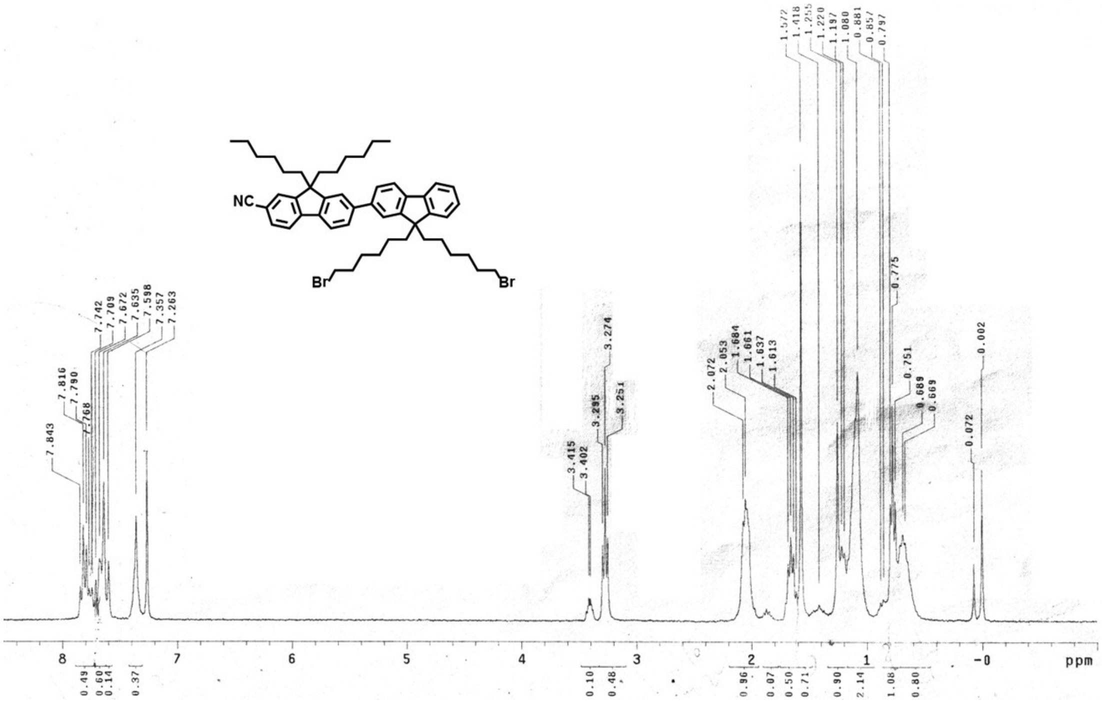

Fig. S7 ^{1}H NMR spectra of compound 2.

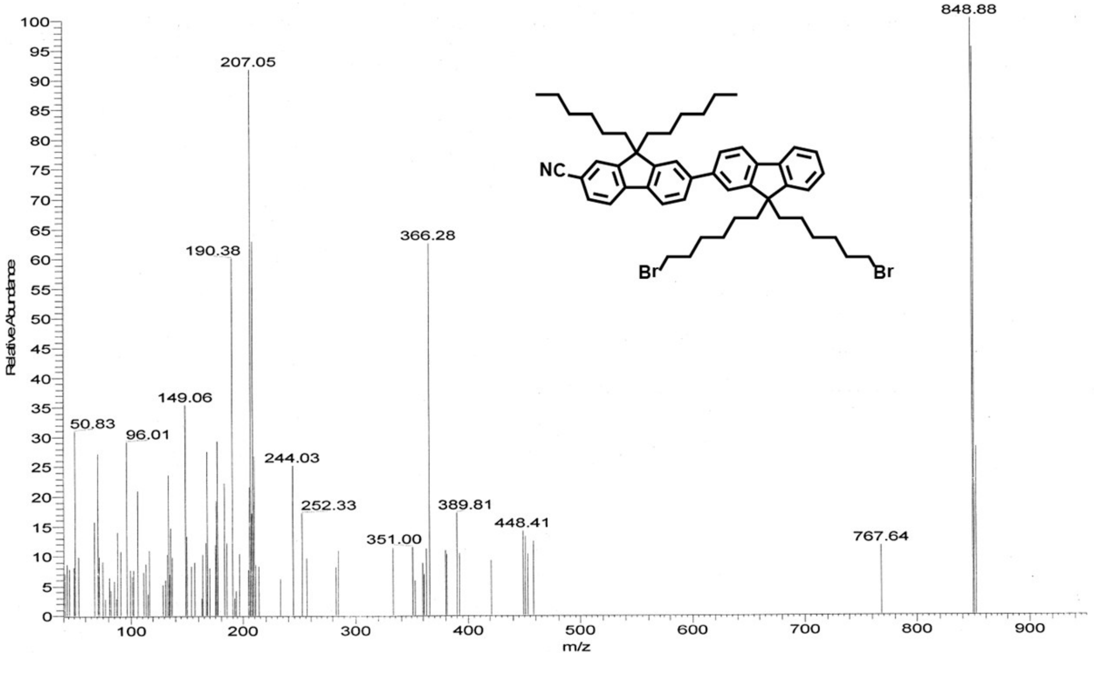

Fig. S8 Mass spectra of compound 2.

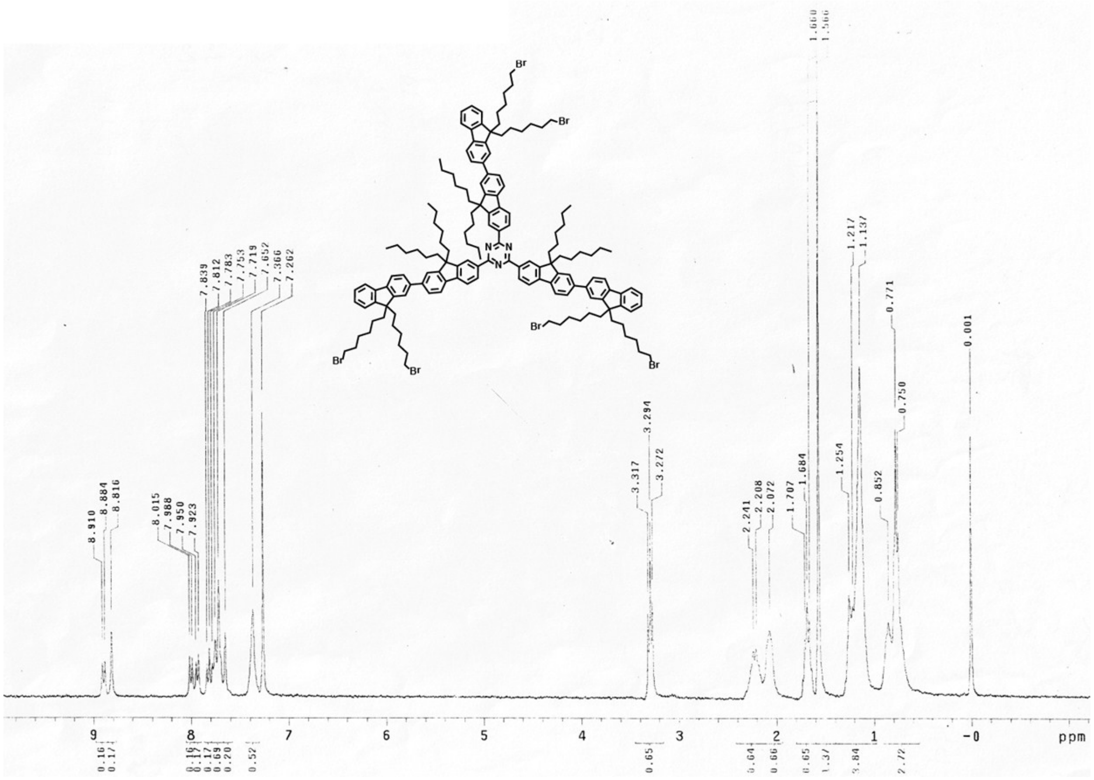

Fig. S9 ^{1}H NMR spectra of compound 3.

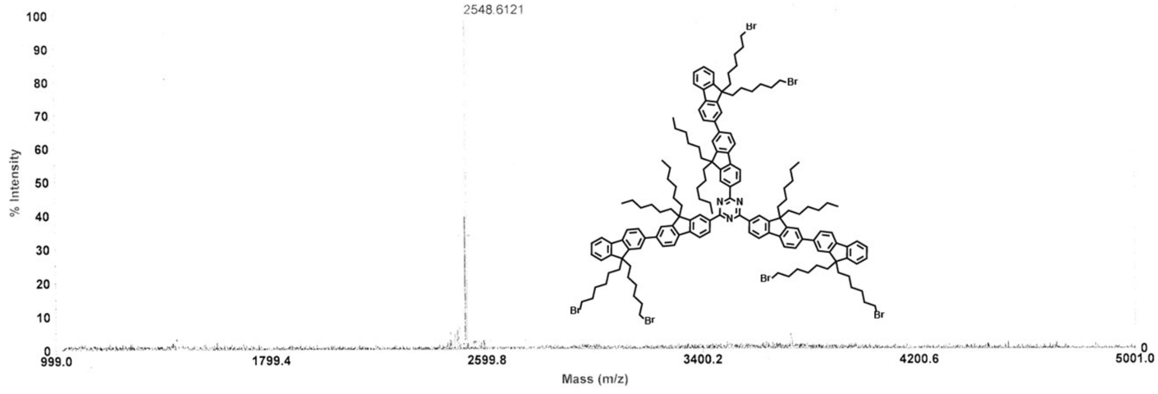

Fig. S10 MALDI-TOF mass spectra of compound 3.

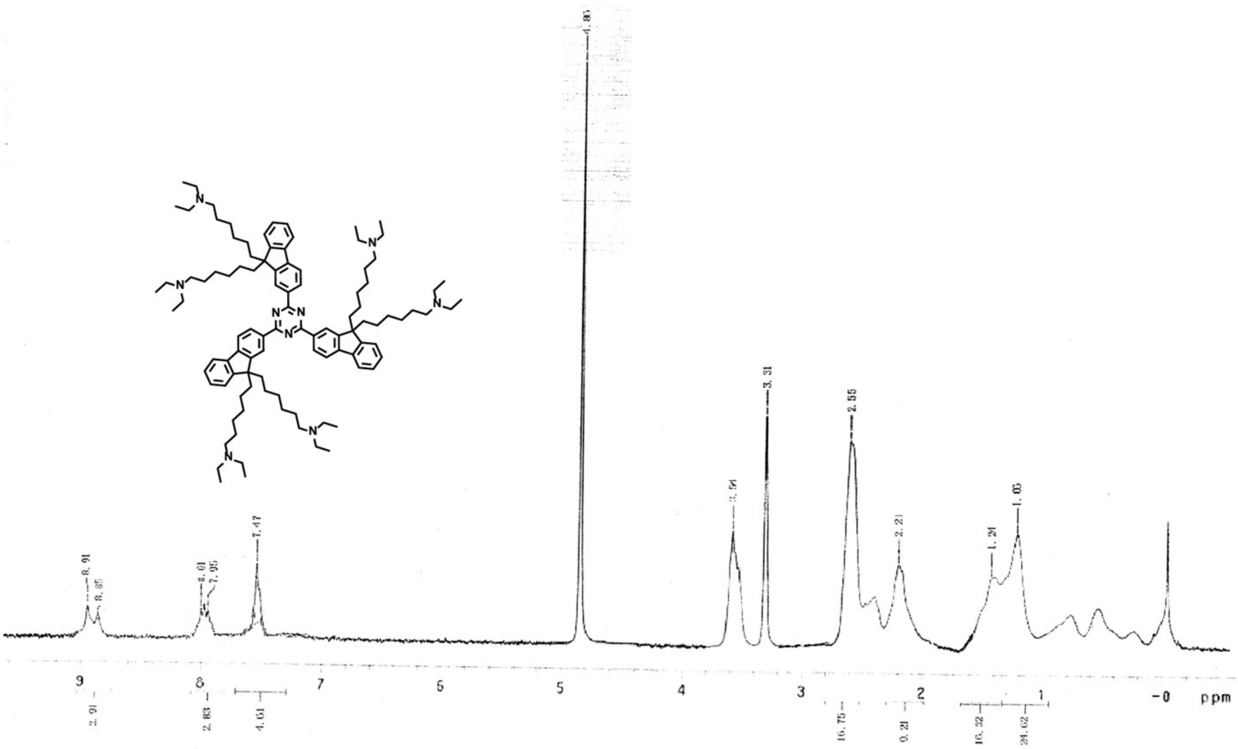

Fig. S11 ^{1}H NMR spectra of Tf1.

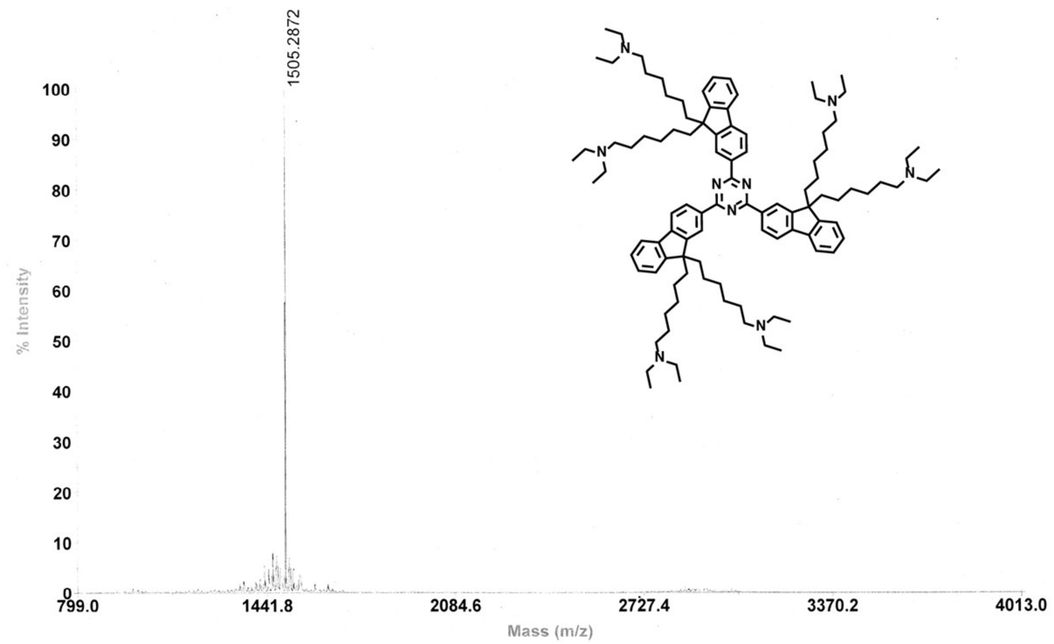

Fig. S12 MALDI-TOF mass spectra of Tf1.

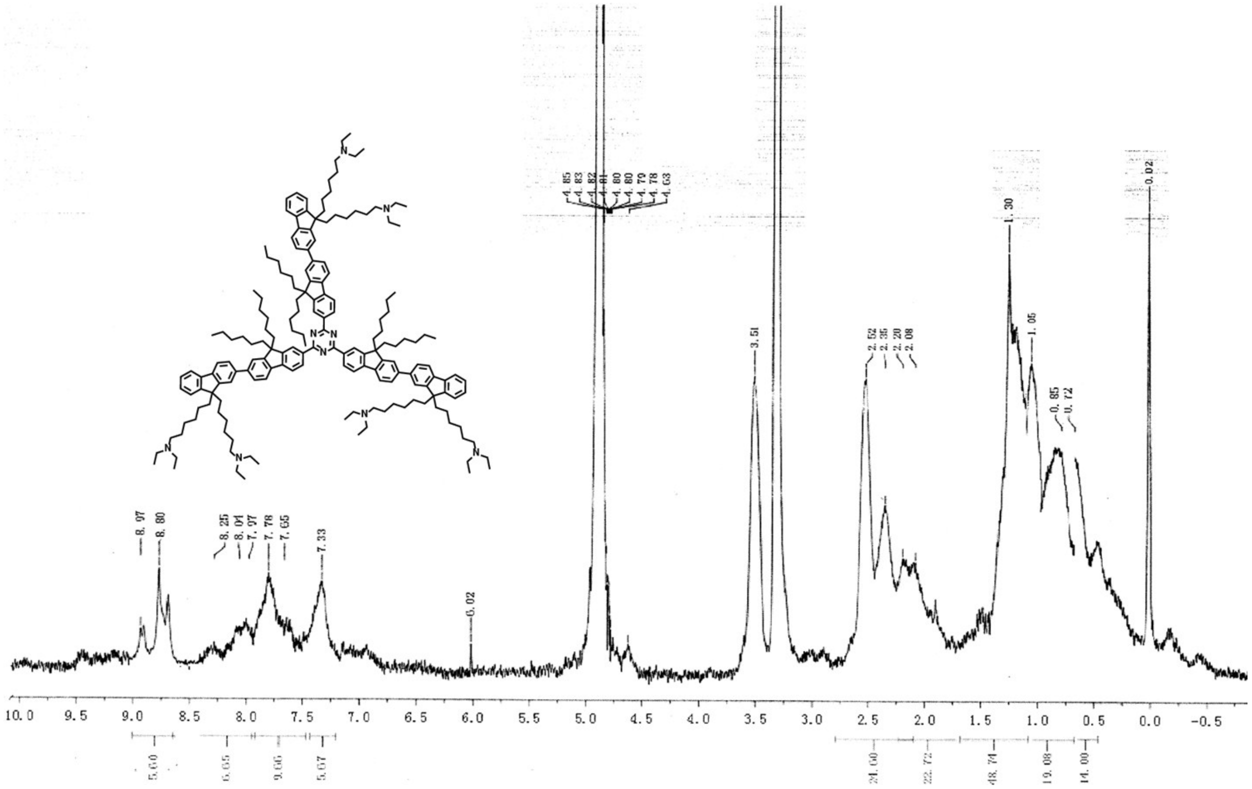

Fig. S13 ^{1}H NMR spectra of Tf2.

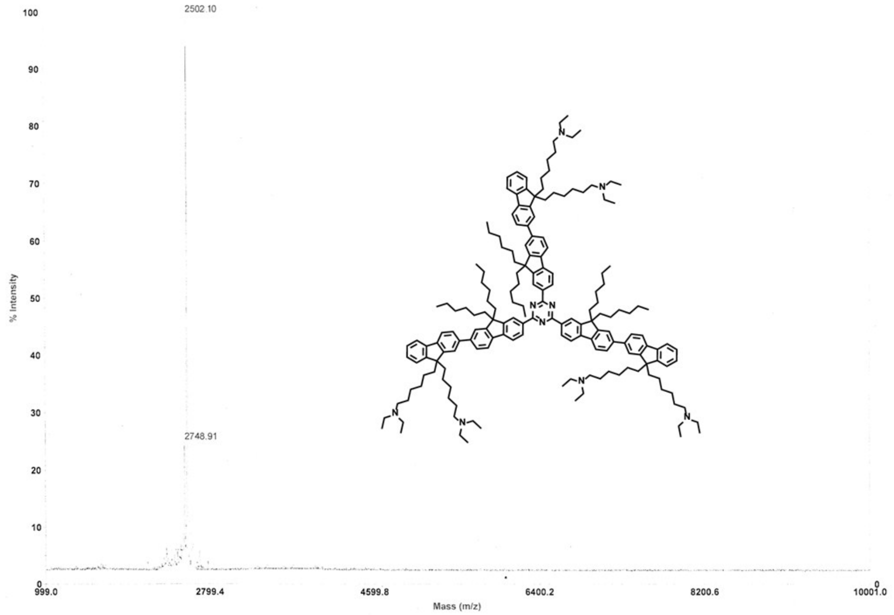

Fig. S14 MALDI-TOF mass spectra of Tf2.