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Supporting information

for

Small Molecules Incorporating Regioregular Oligothiophenes and Fluorinated Benzothiadiazole Groups for Solution-Processed Organic Solar Cells

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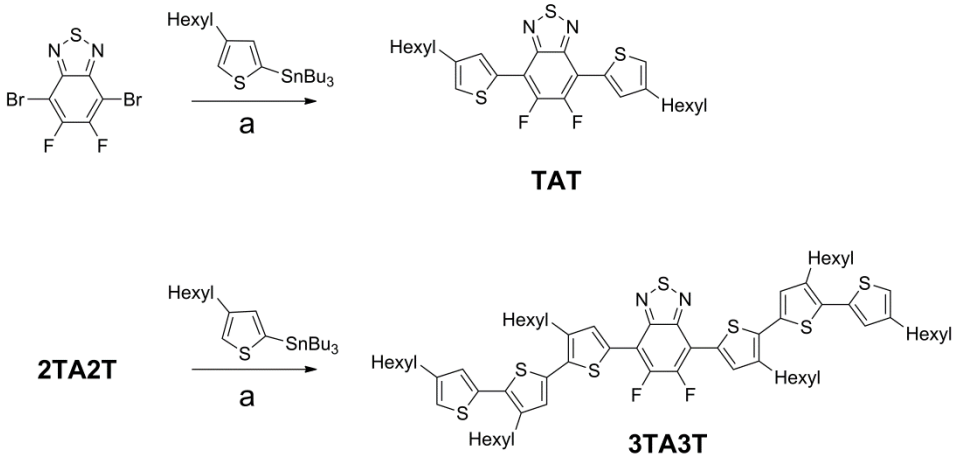

Scheme S1 Synthesis route of TAT and 3TA3T. Condition (a) $Pd(PPh_3)_4$, toluene, Ar, 115 °C, 48 h.

TAT Compound 5,6-difluoro-2,1,3-benzothiadiazole (3.3 g, 10 mmol), tributyl- (4-hexyl-thiophen-2-yl)-stannane (13.7 g, 30 mmol), and toluene (60 ml) were added into a 100ml three-neck round-bottom flask., followed by the addition of Pd $(PPh_3)_4$ (115 mg, 0.1 mmol). The reaction flask was degassed three times and purged with argon for 5 minutes, then it was refluxed for 48 hours at 110 ^oC. The reaction mixture was cooled down to room temperature, and solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography on silica gel using a mixture of dichloromethane and petroleum ether (1:10) as

eluent. TAT was collected as an orange solid (3.17 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.07 (s, 2H), 7.16 (s, 2H), 2.63 (d, 4H,), 1.65 (m, 2H), 1.22-1.45 (m, 16H), 0.80-0.95 (m, 12H). ^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ -128.16. ^{13}C(101 MHz, $CDCl_3$, ppm) δ 151.14, 150.93, 148.94, 148.90, 148.85, 148.56, 148.35, 143.67, 132.26, 132.22, 132.18, 131.20, 123.94, 123.92, 123.89, 111.73, 111.69, 111.64, 111.59, 31.71, 30.51, 30.48, 29.04, 22.65, 14.11. MS (MALDI): calculated: 504.15, found: 504.1 (M^+). Elemental Anal. Calcd. for ($C_{26}H_{30}F_2N_2S_3$): C, 61.87; H, 5.99; N, 5.55. Found: C, 61.85; H, 6.04; N, 5.61.

3TA3T 3TA3T was synthesized using the same procedure of TAT by reacting 2Br-2TA2T with tributyl-(4-hexyl-thiophen-2-yl)-stannane. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.12 (s, 2H), 7.11 (s, 2H), 7.00 (s, 2H), 6.92 (s, 2H), 2.95-2.83 (m, 4H), 2.83-2.71 (m, 4H), 2.70-2.56 (m, 4H), 1.74 (d, 4H), 1.70 (d, 8H), 1.33 (d, 36H), 0.91 (m, 18H). ^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ -128.12. ^{13}C(101 MHz, $CDCl_3$, ppm) δ 151.16, 148.79, 148.57, 148.37, 143.71, 139.74, 139.65, 135.46, 134.73, 134.10, 133.20, 131.72, 129.16, 128.97, 127.24, 120.13, 111.07, 31.71, 30.59, 30.52, 30.42, 29.54, 29.35, 29.32, 29.30, 29.04, 22.69, 22.67, 22.64, 14.13, 14.11. MS (MALDI): calculated: 1168.48, found: 1168.4 (M^+). Elemental Anal. Calcd. for ($C_{66}H_{86}F_2N_2S_7$): C, 67.76; H, 7.41; N, 2.39. Found: C, 67.63; H, 7.54; N, 2.44.

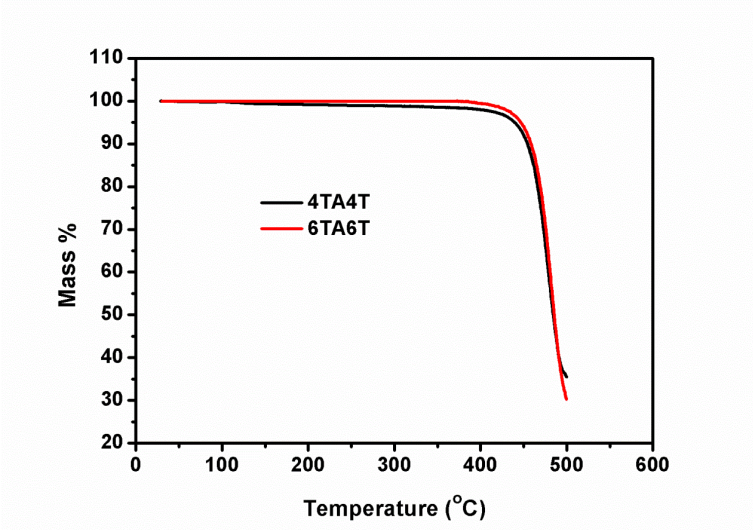

Fig. S1 TGA plot of 4TA4T and 6TA6T under nitrogen atmosphere with a heating rate of 10 °C min^{-1}.

Table S1 Photovoltaic performances of 6TA6T: $PC_{71}BM$ BHJ solar cells under AM 1.5 G-simulated solar illumination with different processing solvents.

Solvent		D/A Ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE
CB	1:0	1:1	0.73	5.81	0.50	2.15%
CB/CF	4:1	1:1	0.76	6.90	0.56	2.96%
CB/CF	3:2	1:1	0.74	7.92	0.55	3.21%
CB/CF	1:1	1:1	0.75	7.31	0.57	3.15%
CB/CF	1:4	1:1	0.74	5.85	0.60	2.61%
CF	0:1	1:1	0.78	5.85	0.43	1.97%

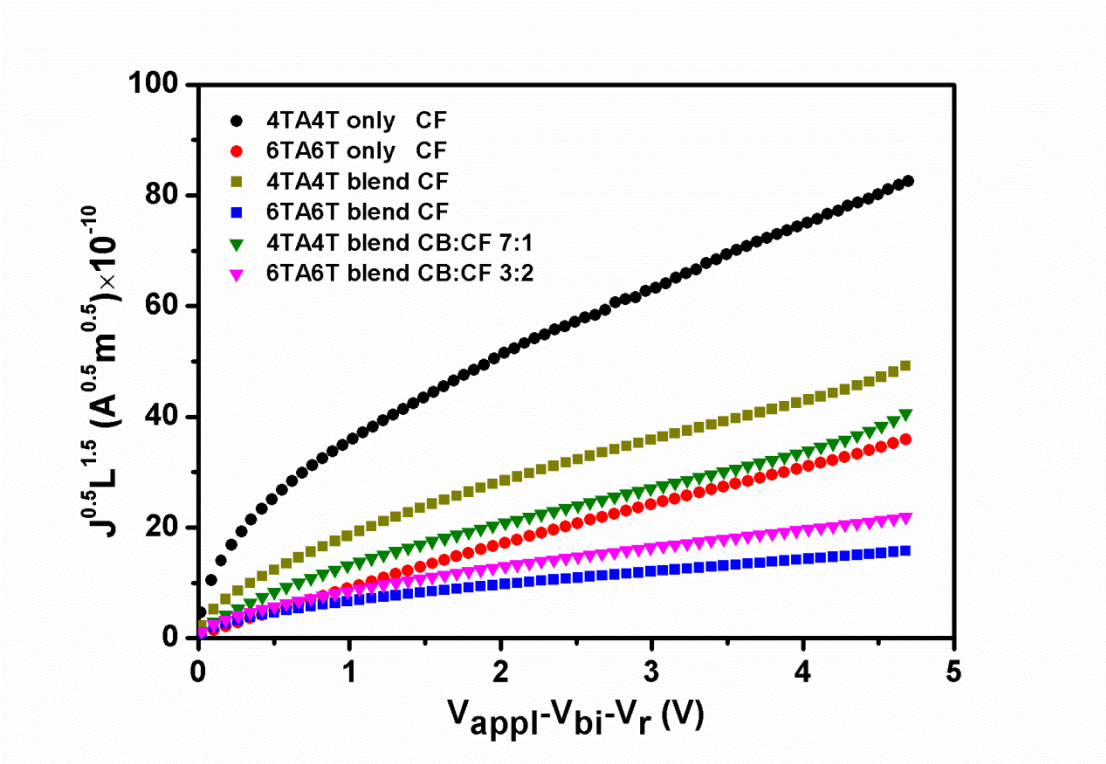

Fig. S2 SCLC model hole mobility measurement for 4TA4T and 6TA6T pristine films and their blended films with $PC_{71}BM$ casted from CF or mixed solvents.

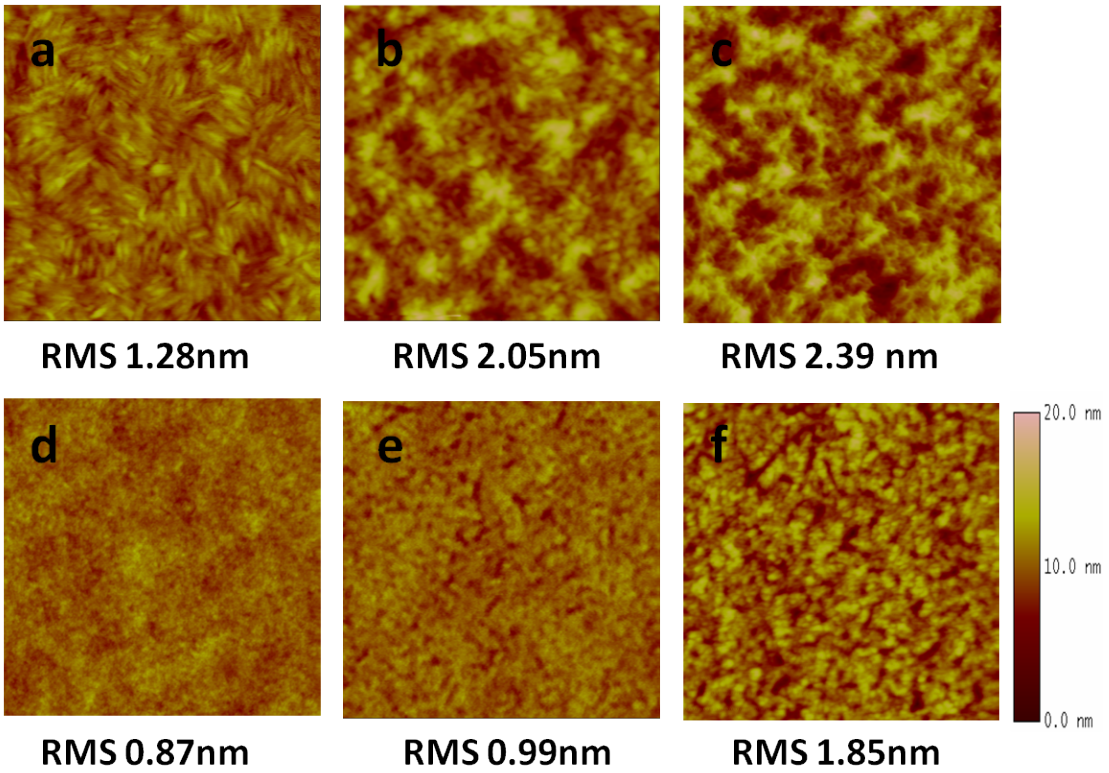

Fig. S3 AFM height images of solar cell active layers of 4TA4T processed with (a) CF, (b) CB, (c) CB/CF 7:1 and 6TA6T processed with (d) CF, (e) CB, (f) CB/CF 3:2. All the image scales are 2 μm × 2 μm with RMS roughness below.

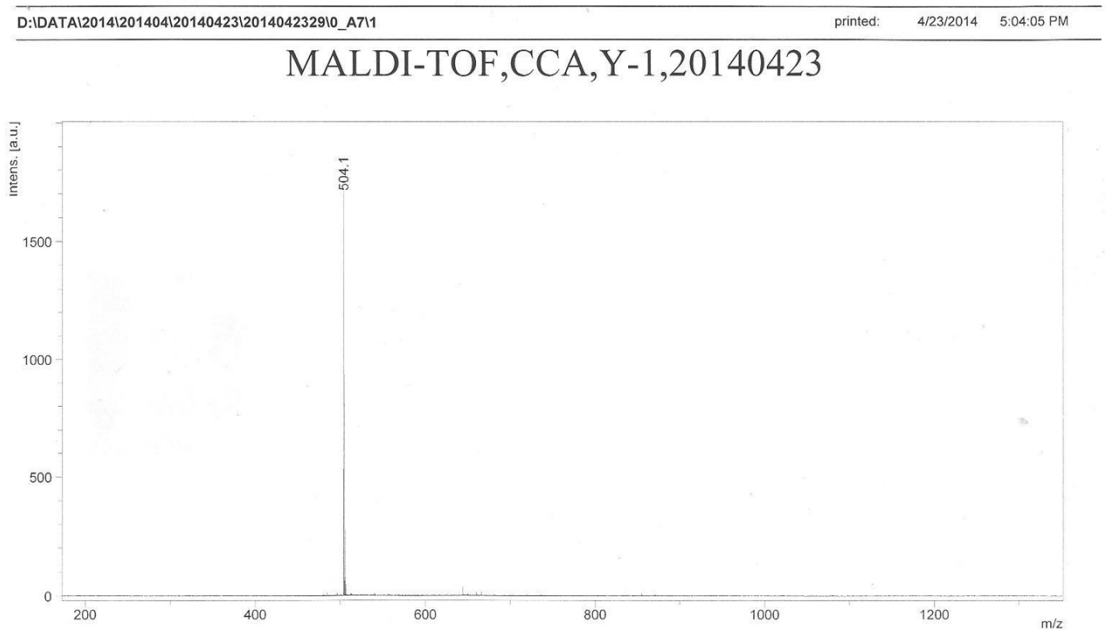

Fig. S4. MALDI-TOF spectrum of TAT

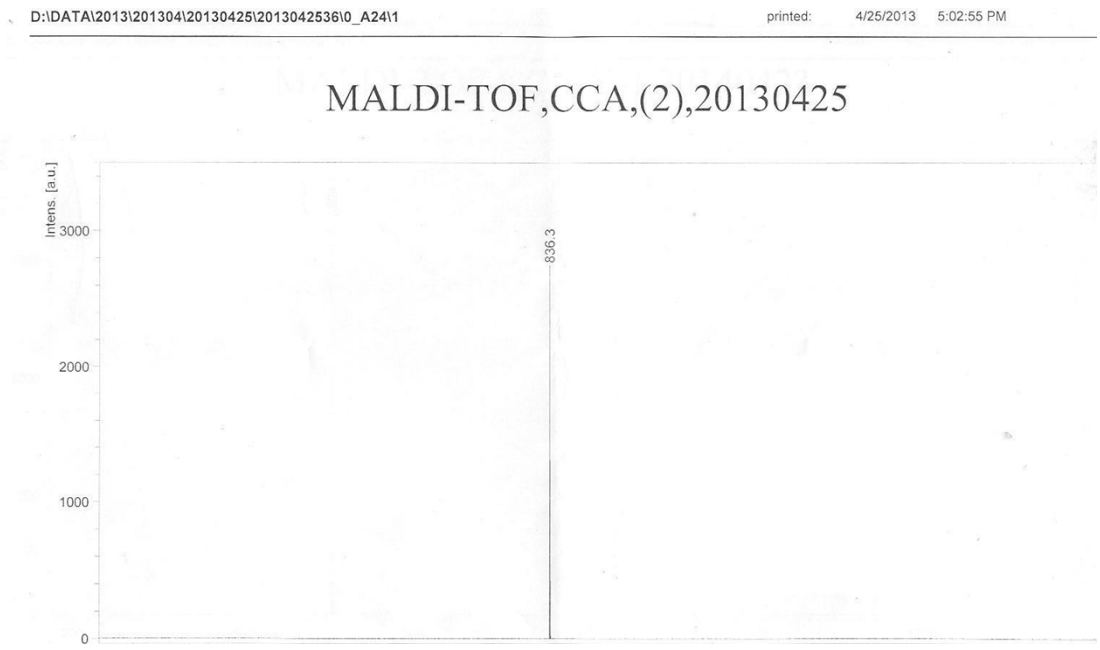

Fig. S5. MALDI-TOF spectrum of 2TA2T

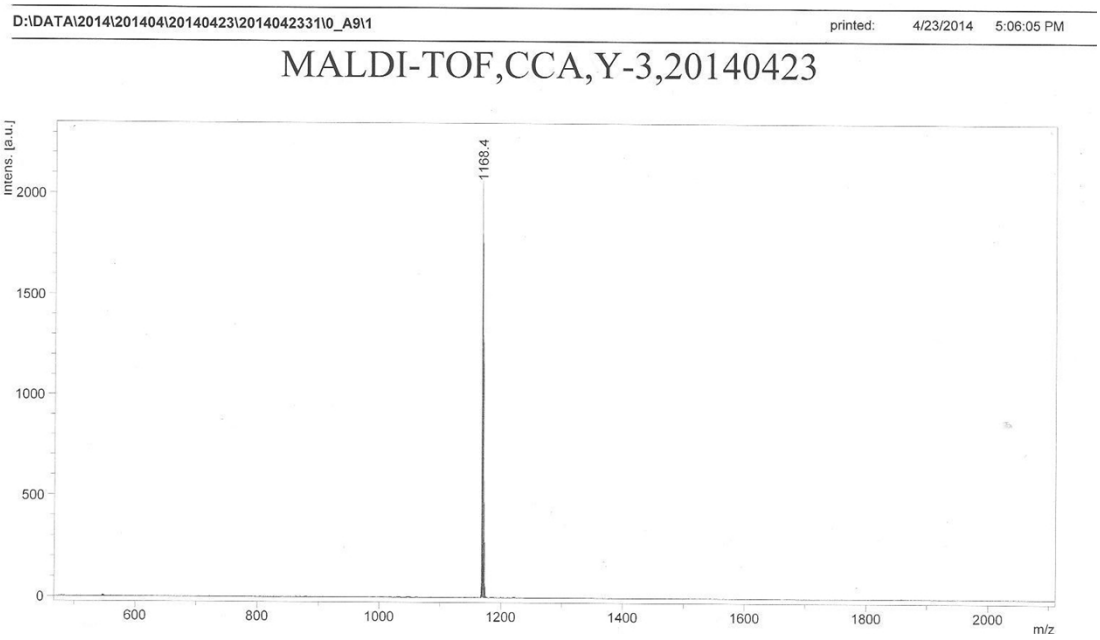

Fig. S6. MALDI-TOF spectrum of 3TA3T

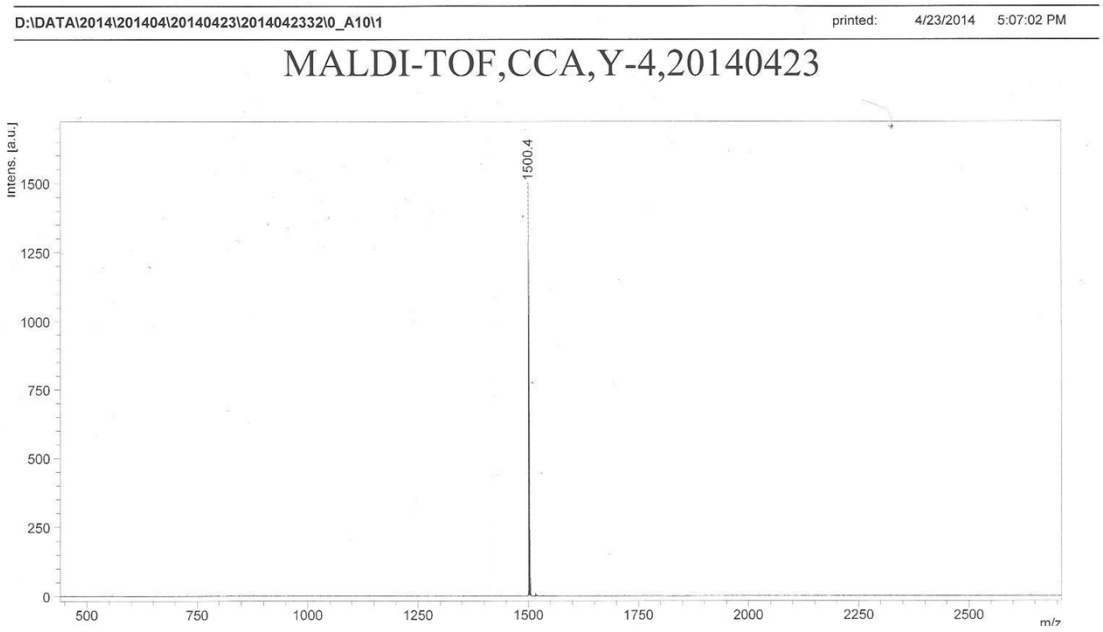

Fig. S6. MALDI-TOF spectrum of 4TA4T

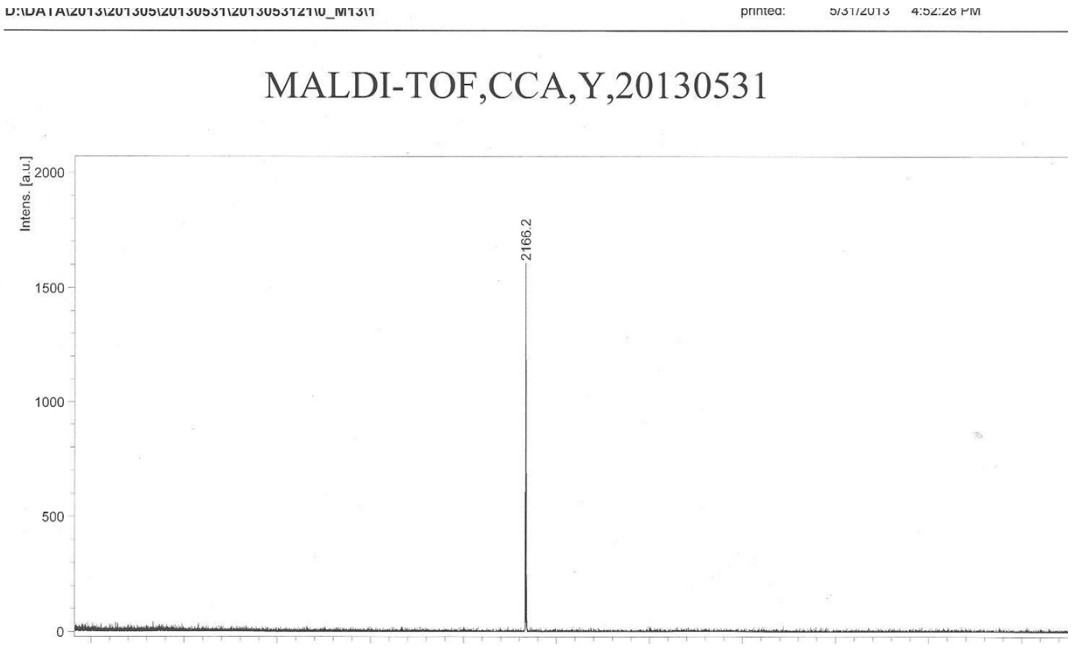

Fig. S6. MALDI-TOF spectrum of 6TA6T