Electronic Supplementary Information (ESI)

Simple-Structured Small Molecule Acceptors Constructed by a Weak Electron-Deficient Thiazolothiazole Core for High-Efficiency Non-fullerene Organic Solar Cells

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1. Experimental Section

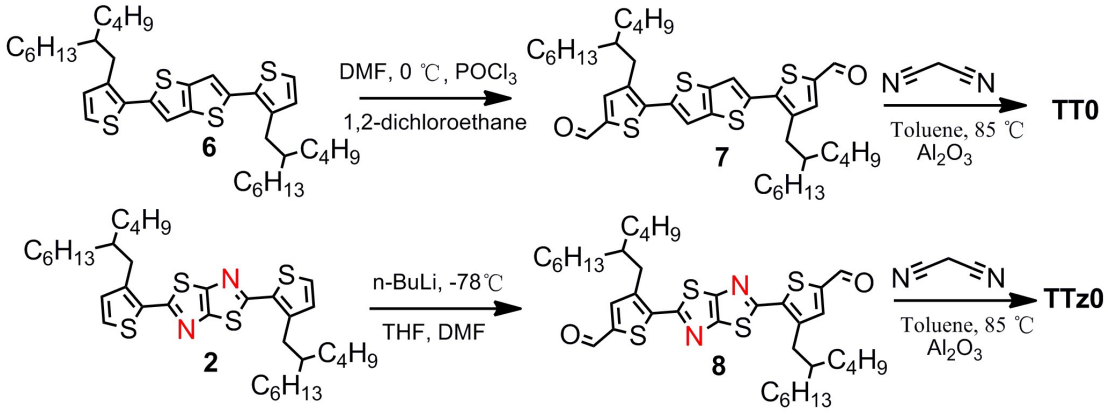
The synthetic route to **TT0 and TTz0** was displayed in Scheme S1, compound **6** and **7** were synthesized by following the literature method.[1-2] The detailed synthetic procedures as follows:

Synthesis of compound 8: To a solution of anhydrous THF (45 mL) and **2** (600 mg, 0.93 mmol), n-BuLi (2.5 M, 1.12 mL, 2.80 mmol) was added dropwise over the period of 5 min at -78 °C under nitrogen atmosphere. The mixture was stirred at -78 °C for 120 min and DMF (3 mL) was added into the flask in one portion. The reaction was then stirred for 12 h at room temperature, and then was quenched by 50 mL water and was extracted by CH_2Cl_2, the combined organic phase was dried over anhydrous $MgSO_4$. After concentration, the crude product was purified by a silica gel column (petroleum ether / CH_2Cl_2, 1: 4 v/v) to afford **8** as a yellow solid (208 mg, yield: 32%).^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.61 (s, 1H), 2.97 (d, J = 7.2 Hz, 2H), 1.84 - 1.56 (m, 1H), 1.42 - 1.13 (m, 16H), 0.90 - 0.85 (m, 6H).

Synthesis of compound TT0: A mixture of **7** (557 mg, 0.80 mmol), malononitrile (528 mg, 8.0 mmol), and alkaline aluminum oxide (400 mg) in anhydrous toluene (50 mL) was heated to 85 °C and stirred for 12 h. The reaction mixture was then cooled to room temperature, the solvent was removed by rotary evaporation, the crude product was purified by a silica gel column (petroleum ether / CH_2Cl_2, 5: 1 v/v) to give **TT0** as a red-orange sticky solid (220 mg, yield: 35%).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.60 (s, 1H), 2.95 (d, J = 7.3 Hz, 2H), 1.84 - 1.79 (m, 1H), 1.44 - 1.18 (m, 16H), 0.91 - 0.85 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.22, 151.08, 149.05, 144.54, 135.58, 130.75, 114.55, 113.30, 40.27, 33.96, 33.27, 32.96, 31.79, 29.54, 28.69, 26.46, 22.93, 22.63, 14.09.

Synthesis of compound TTz0: A mixture of **8** (180 mg, 0.26 mmol), malononitrile (170 mg, 2.60 mmol), and alkaline aluminum oxide (200 mg) in anhydrous toluene (50 mL) was heated to 85 °C and stirred for 12 h. The reaction mixture was then cooled to room temperature, the solvent was removed by rotary evaporation, the crude product was purified by a silica gel column (petroleum ether / CH_2Cl_2, 1:2 v/v).

Then, the resulting product was recrystallized from $CHCl_3$ and acetone to give **TTz0** as a red solid with metallic luster (166 mg, yield: 81%).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.60 (s, 1H), 2.95 (d, J = 7.3 Hz, 2H), 1.84 - 1.79 (m, 1H), 1.44 - 1.18 (m, 16H), 0.91 - 0.85 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.45, 152.53, 149.78, 143.63, 142.07, 141.40, 135.29, 113.70, 112.80, 79.65, 38.43, 34.80, 33.39, 33.10, 31.85, 29.67, 28.58, 26.36, 23.04, 22.67, 14.12. MS (MALDI-TOF): calcd. for $C_{44}H_{54}N_6S_4[M]^+$ 795.20; found 795.37.



Scheme S1 Synthesis routes of simplified small molecules TT0 and TTz0.

2. Supplementary Figures S1-23

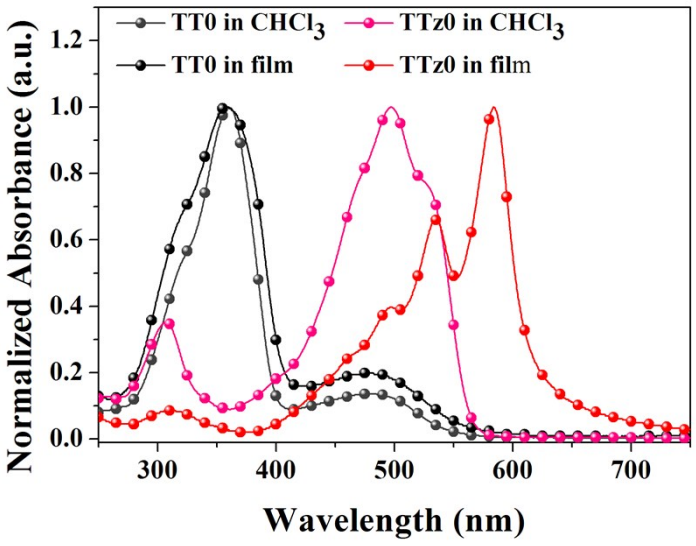


Fig. S1 Normalized UV-Vis absorption spectra of TT0 and TTz0 in $CHCl_3$ solution and film.

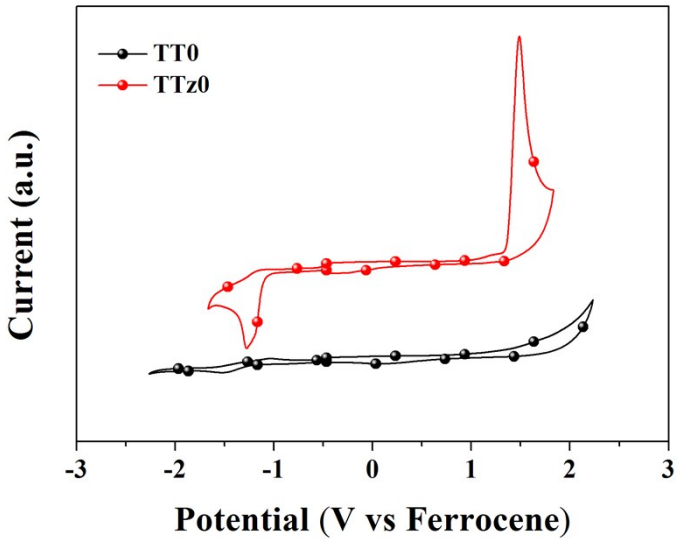


Fig. S2 Cyclic voltammogram curves of TT0 and TTz0 pristine films.

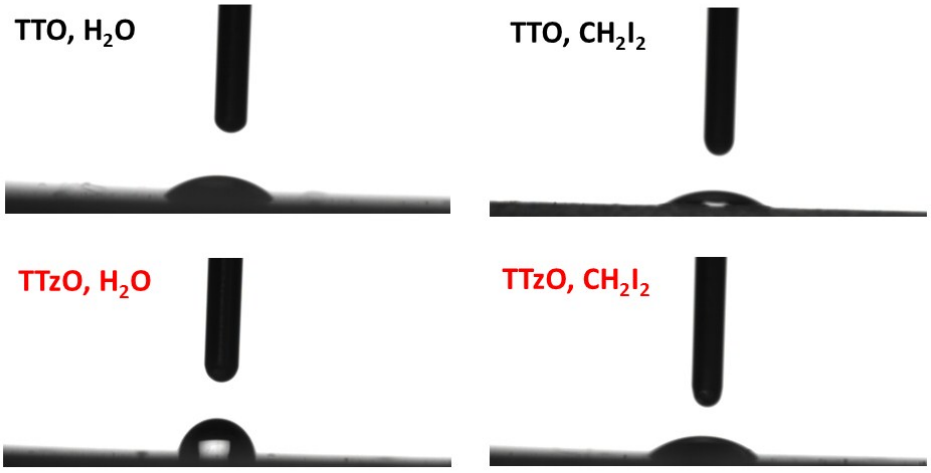


Fig. S3 Views of surface contact measurements with the corresponding films.

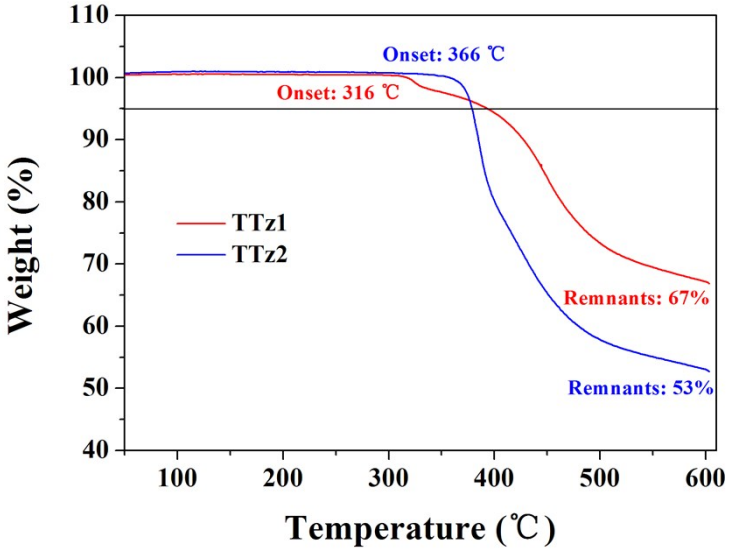


Fig. S4 TGA plots of TTz1 and TTz2.

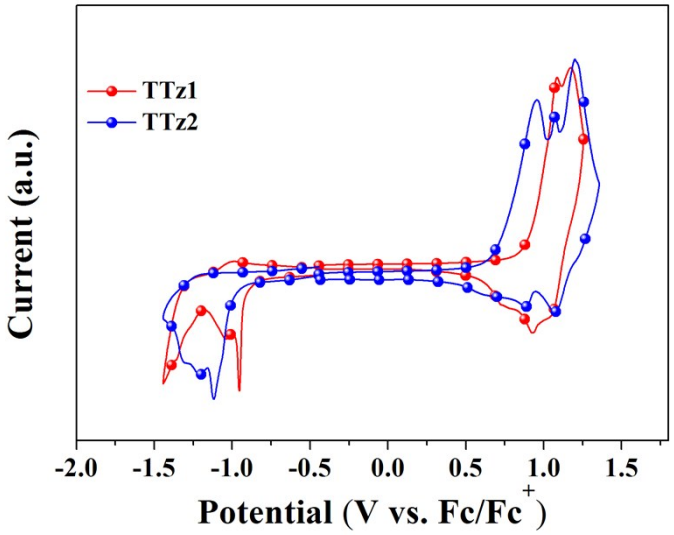


Fig. S5 Cyclic voltammogram curves of TTz1 and TTz2 pristine films.

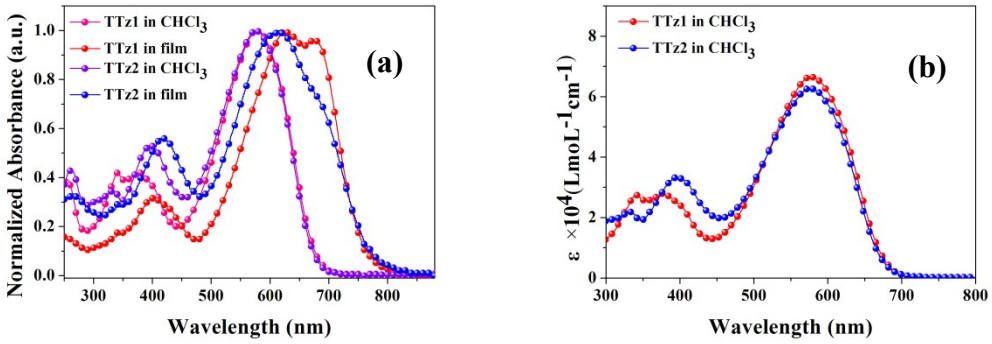


Fig. S6 (a) Normalized UV-Vis absorption spectra of TTz1and TTz2 in $CHCl_3$ solution and film; (b) the absorption coefficients of TTz1and TTz2 in $CHCl_3$ solution.

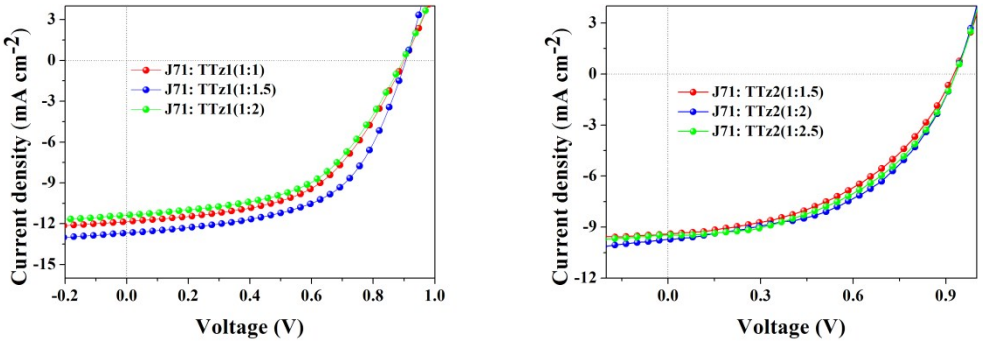


Fig. S7 The *J-V* curves of the inverted structured OSCs based on J71: TTz1/TTz2 in different ratios.

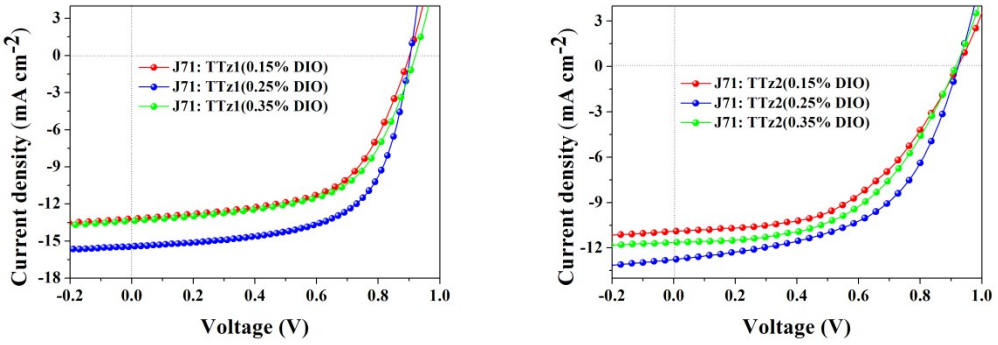


Fig. S8 The *J-V* curves of the inverted structured OSCs based on J71: TTz1/TTz2 in different additive ratios.

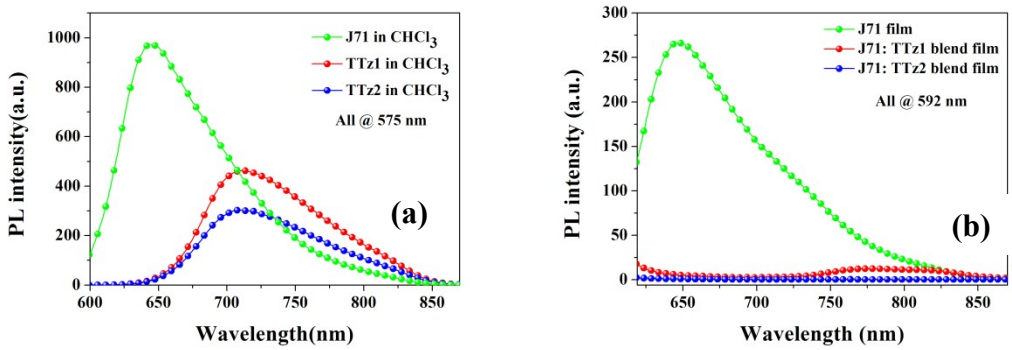


Fig. S9 (a) PL spectra of J71, TTz1and TTz2 at the same concentrations; (b) PL spectra of the thin films with J71, or the J71/TTz1 and J71/TTz2 blends (1: 2, wt/wt).

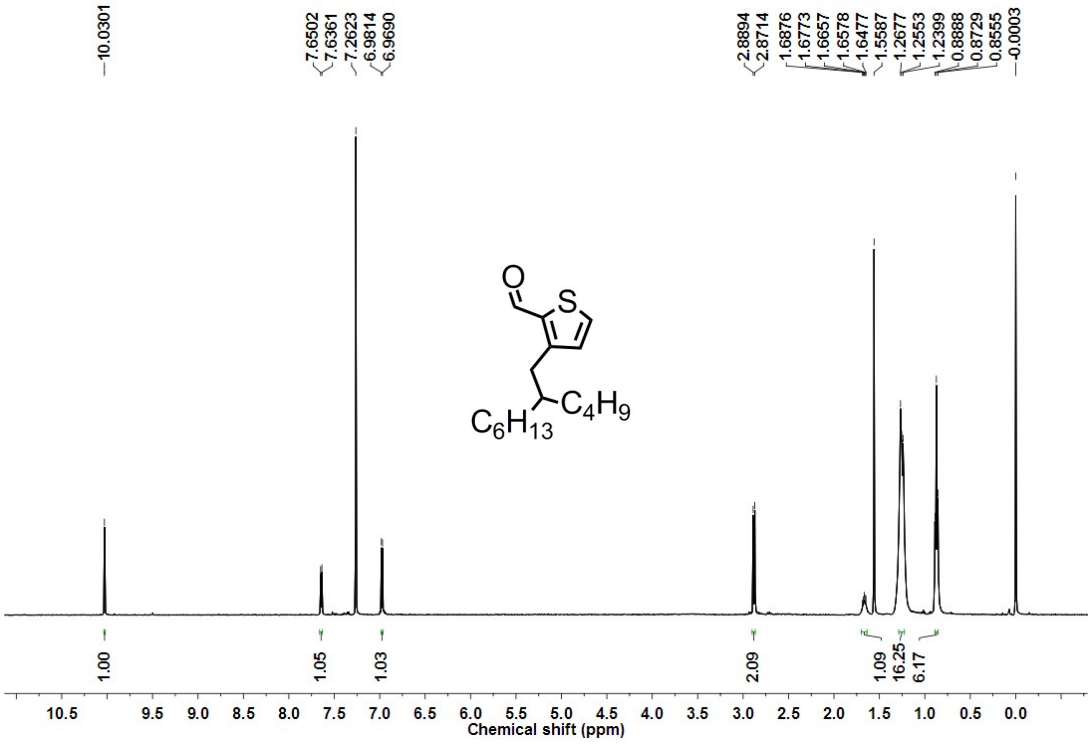


Fig. S10 ^{1}H NMR plot of compound 1.

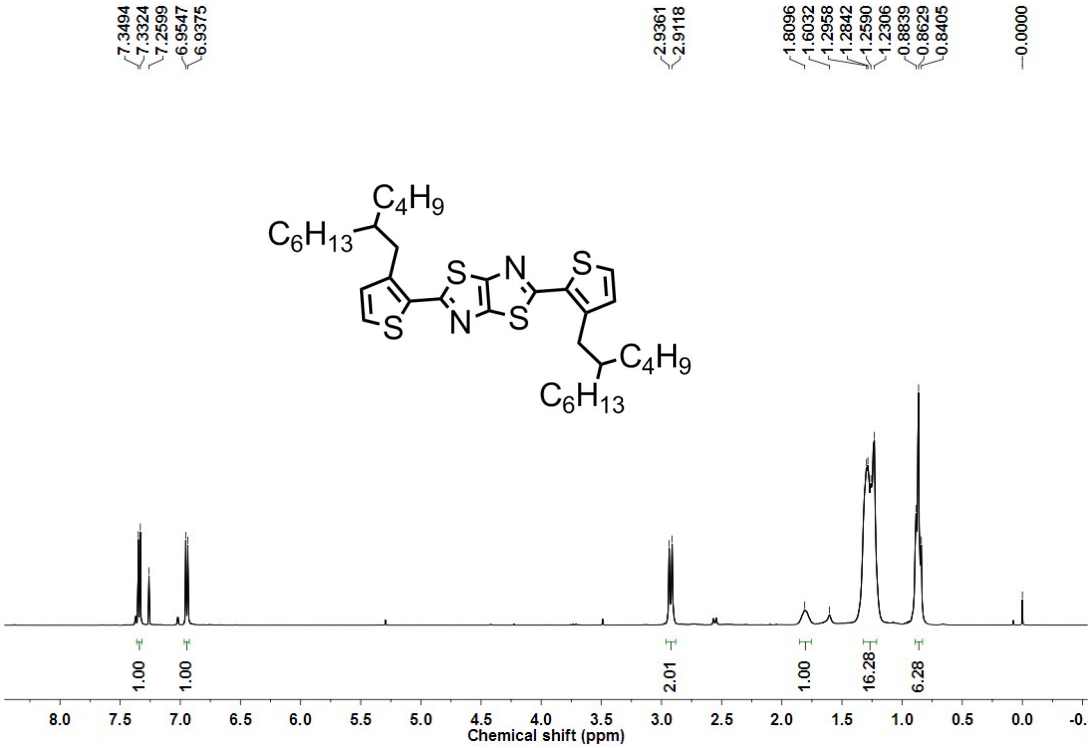


Fig. S11 [1]H NMR plot of compound 2.

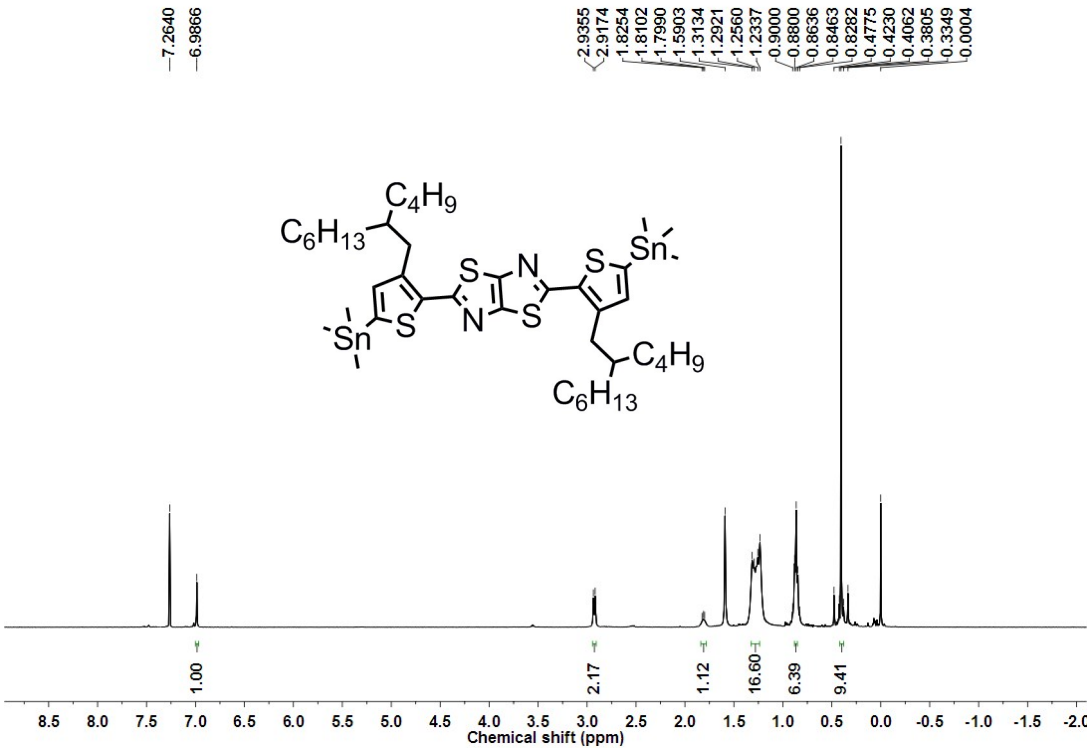


Fig. S12 [1]H NMR plot of compound 3.

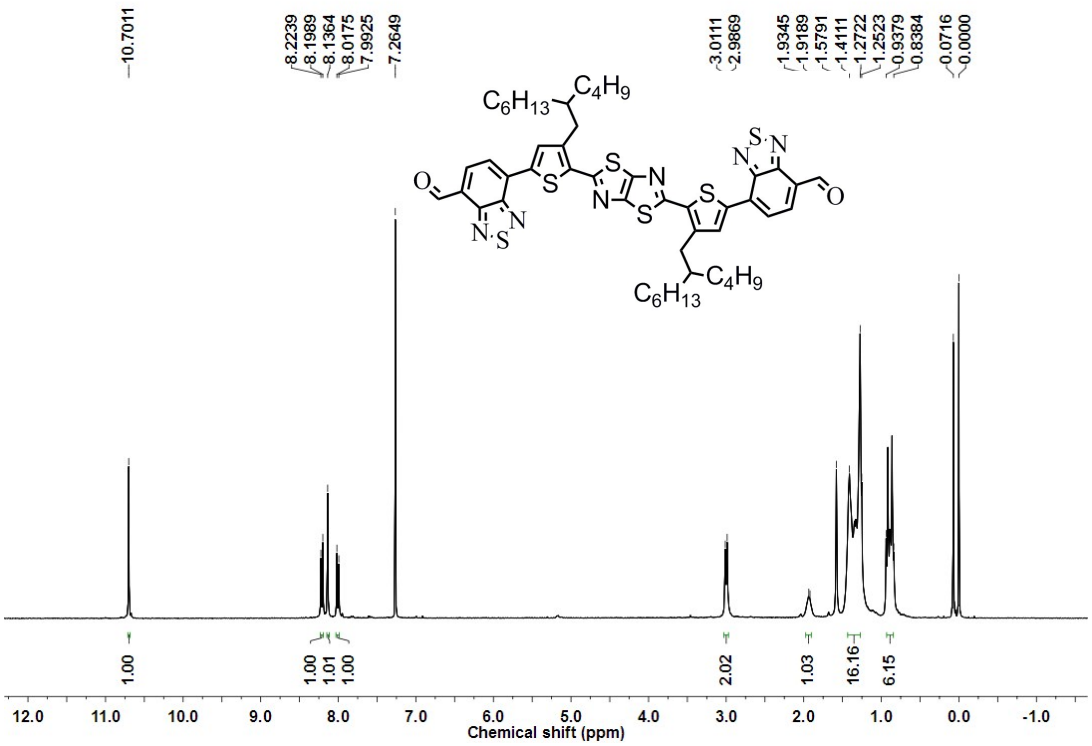


Fig. S13 [1]H NMR plot of compound 5.

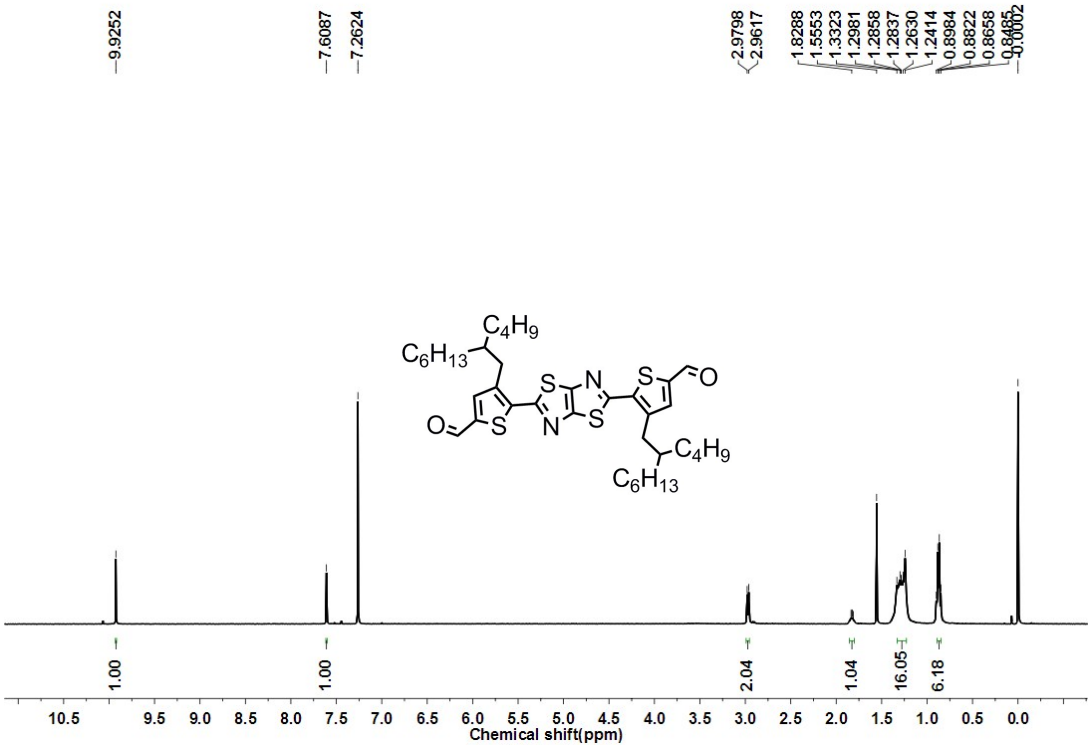


Fig. S14 [1]H NMR plot of compound 8.

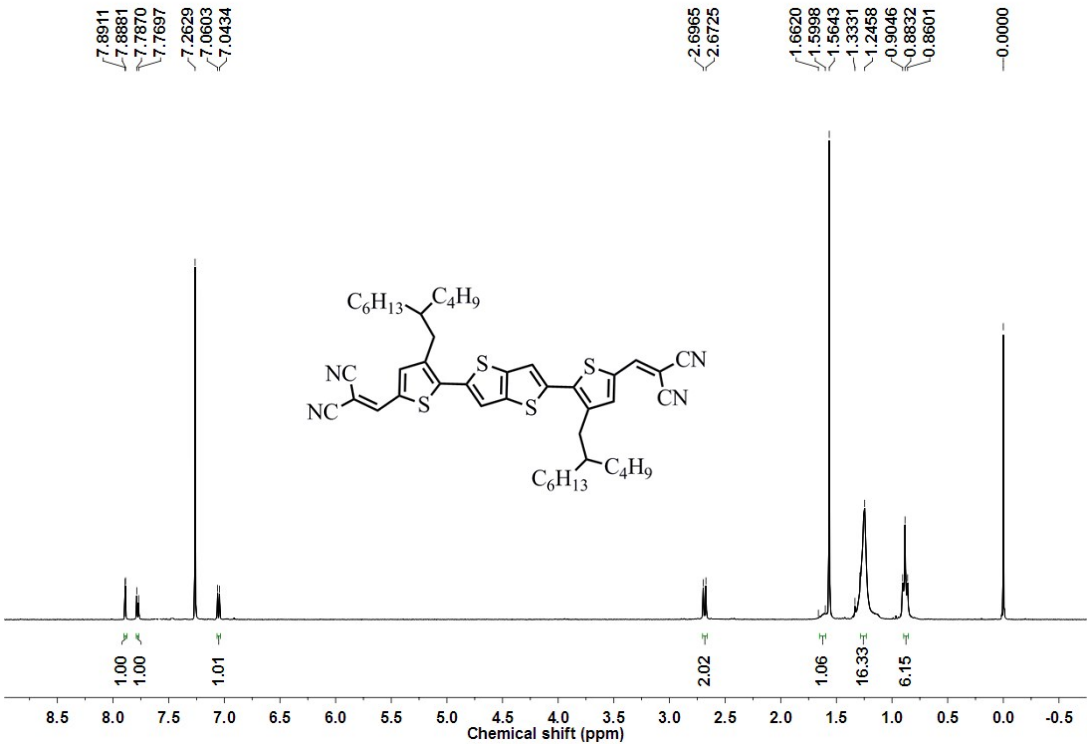


Fig. S15 ^{1}H NMR plot of TT0.

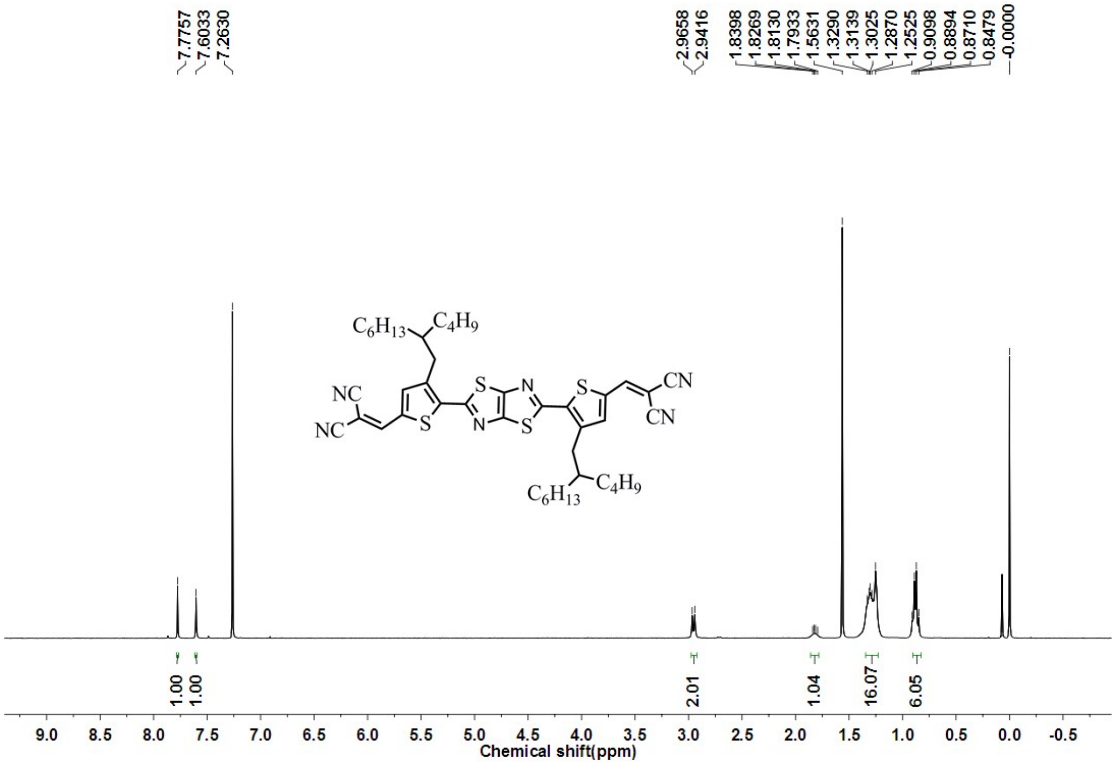


Fig. S16 ^{1}H NMR plot of TTz0.

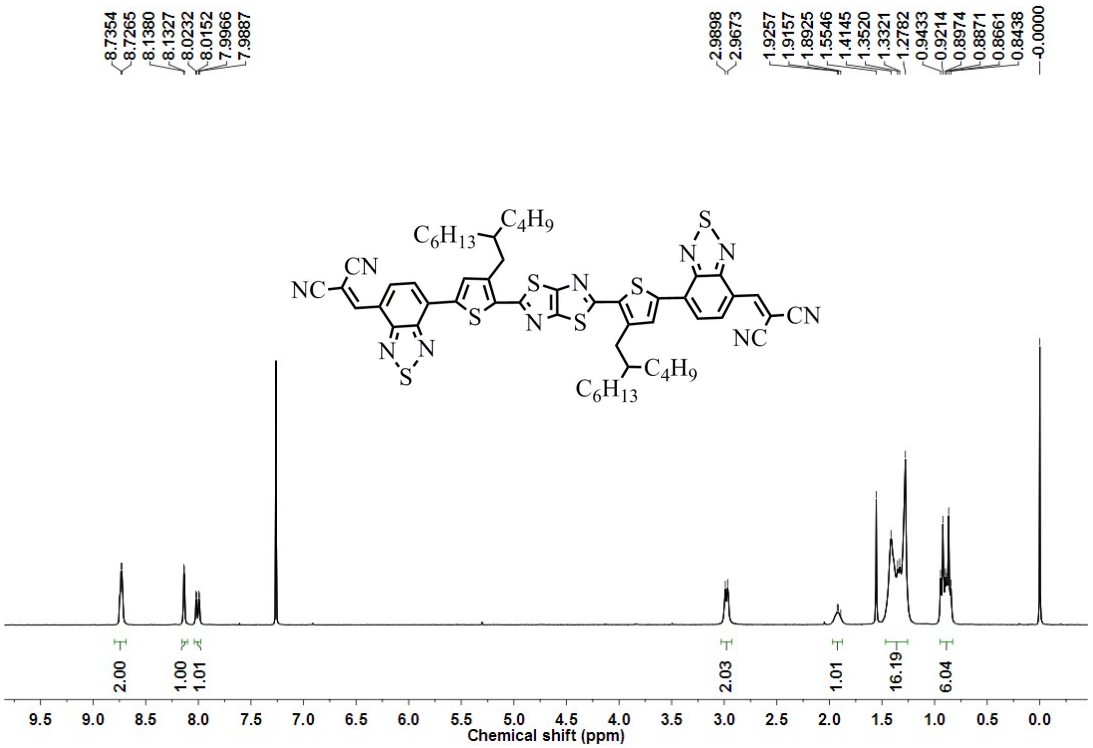


Fig. S17 ^{1}H NMR plot of TTz1.

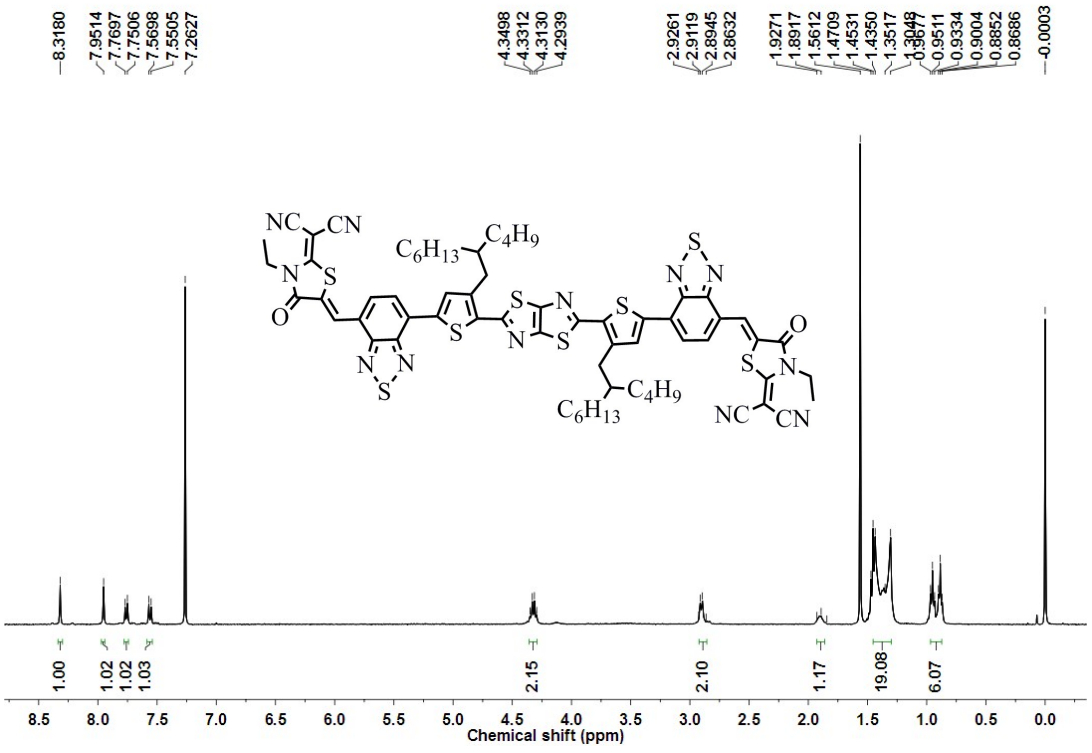


Fig. S18 ^{1}H NMR plot of TTz2.

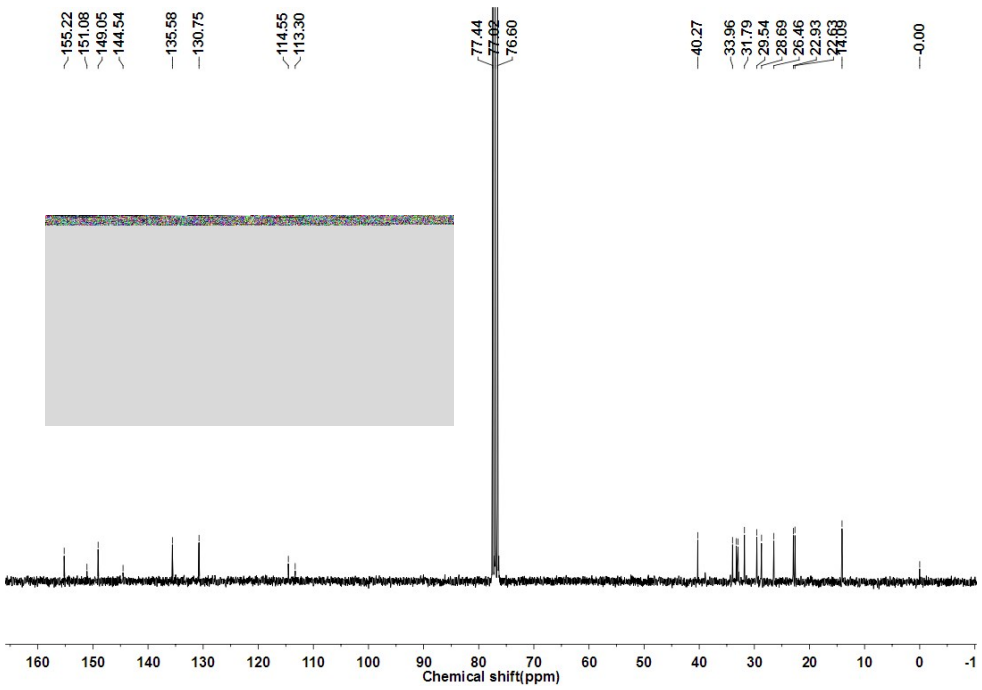


Fig. S19 ^{13}C NMR plot of TT0.

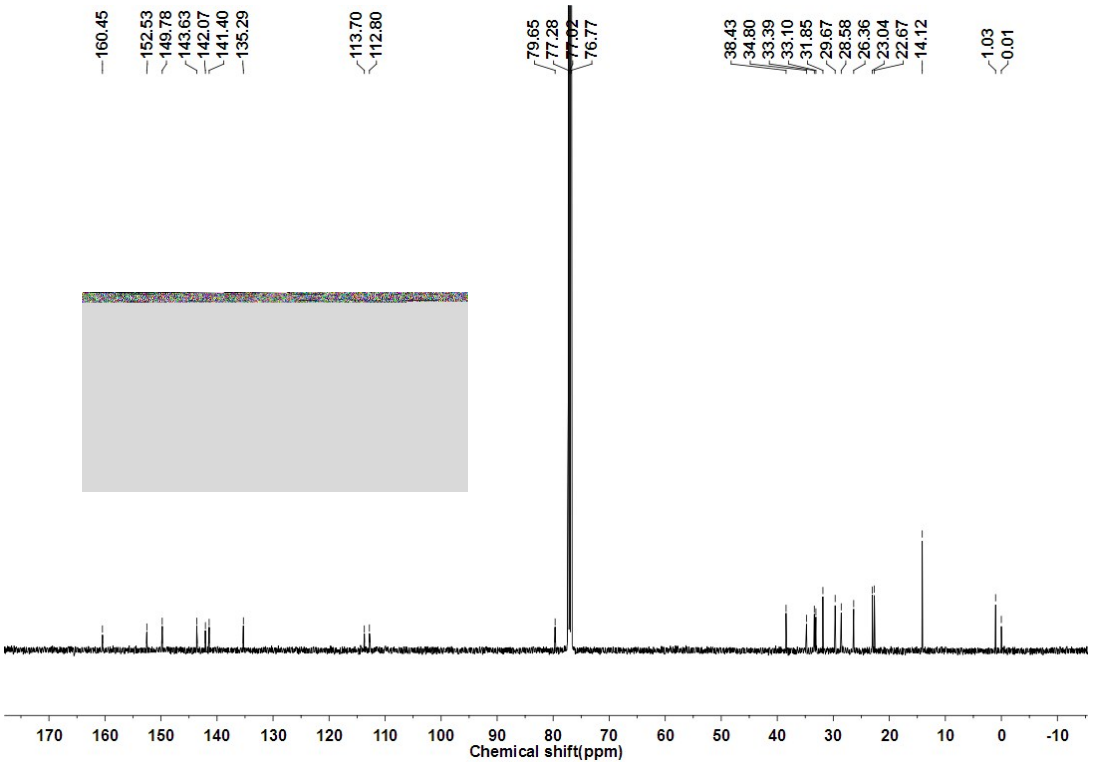


Fig. S20 ^{13}C NMR plot of TTz0.

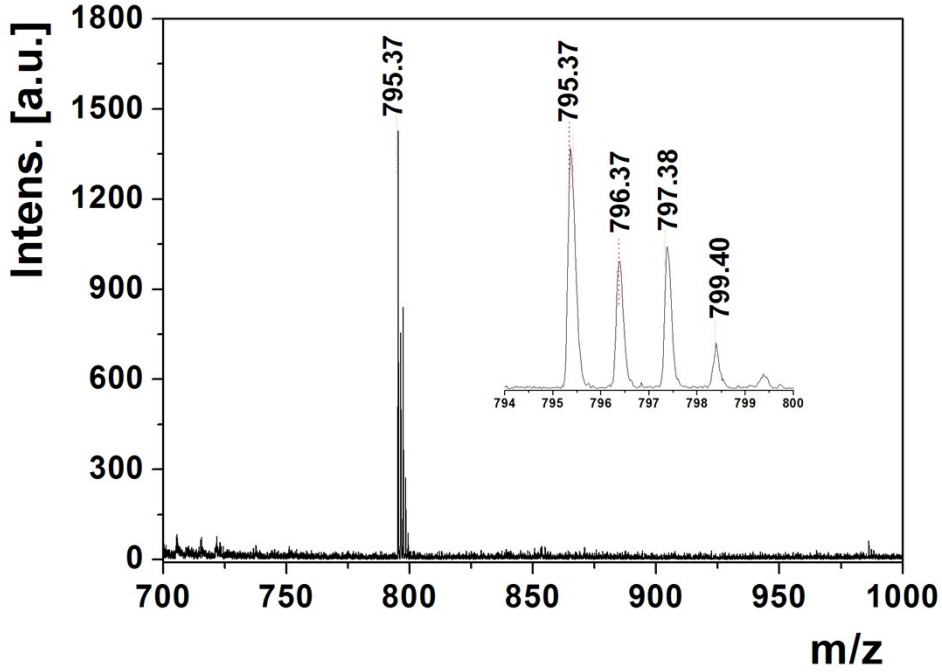


Fig. S21 MS plot of TTz0.

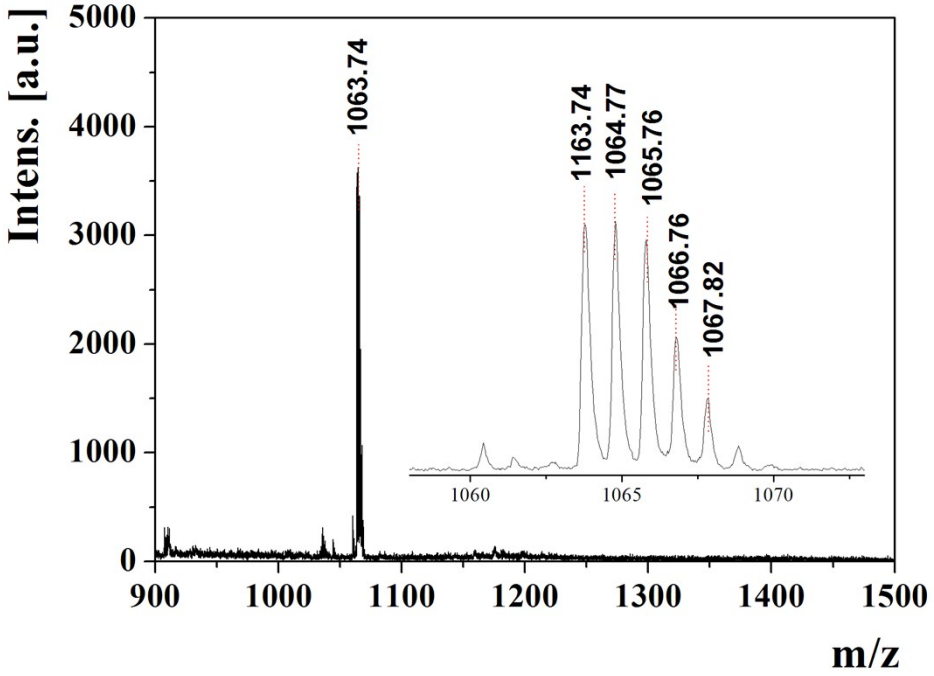


Fig. S22 MS plot of TTz1.

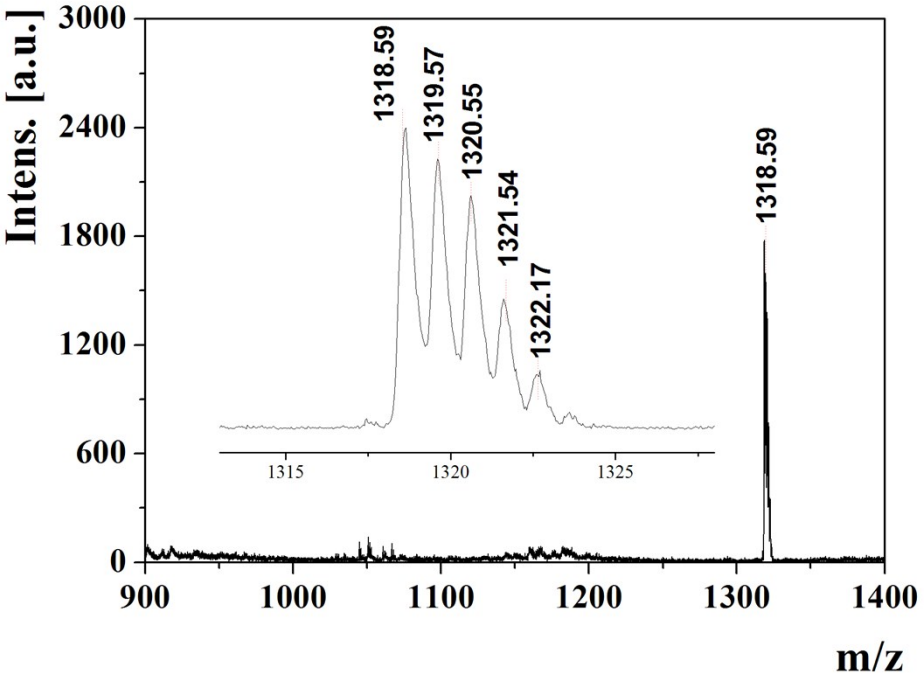


Fig. S23 MS plot of TTz2.

3. Supplementary Table S1-8

Table S1 Optical and electrochemical properties of TT0 and TTz0.

Compounds	λ_{max} (nm)		λ_{onset}	E_g^{opt}	E_{ox}/E_{red}	$E_{HOMO}/$	E_g^{ec}
	solution[a]	film[b]	(nm)[c]	(eV)[d]	(V)[e]	E_{LUMO} (eV)[f]	(eV)[h]
TT0	360, 480	362, 482	561	2.19	1.31/-1.26	-6.11/-3.54	2.57
TTz0	496, 525	535, 584	615	2.02	1.37/-1.11	-6.17/-3.69	2.48

[a]Measured in 10^{-6} M $CHCl_3$ solution. [b] Measured as the neat film cast from 3 mg/mL $CHCl_3$ solution. [c]Obtained from the onset wavelength of the film. [d]Evaluated by $E_g^{opt} = 1240/\lambda_{onset}$. [e]The onset potentials of oxidation and reduction as referenced to ferrocene. [f]$E_{HOMO} = -(E_{ox} + 4.8$ eV) and $E_{LUMO} = -(E_{red} + 4.8$ eV). The formal potential for ferrocene vs. Ag/AgCl is 0.43 V. [h] Calculated according to E_{LUMO} - E_{HOMO}.

Table S2 2θ and *d*-spacings calculated from XRD patterns.

Acceptors	$2\theta_1$(º)	*d*(001)-spcing(Å)	$2\theta_2$(º)	*d*(010)-spcing (Å)
TTz1	5.77	15.304	25.73	3.460
TTz2	5.28	16.723	25.51	3.488

Table S3 The photovoltaic properties of J71: TTz1 blend device at different D/A ratios, measured under the illumination of AM 1.5G (100 mW cm^{-2}).

J71: TTz1	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	R_s ($\Omega \cdot cm^2$)	R_{sh} ($\Omega \cdot cm^2$)
1: 1.5	0.90	11.84	53.03	5.65, (5.36) [a]	61.2	159.5
1: 2	0.90	12.67	56.91	6.49, (6.20) [a]	52.3	165.2
1: 2.5	0.89	11.36	53.11	5.37, (5.05) [a]	64.9	154.2

[a] Average of 20 devices.

Table S4 The photovoltaic properties of J71: TTz2 blend device at different D/A ratios, measured under the illumination of AM 1.5G (100 mW cm^{-2}).

J71: TTz2	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	R_s ($\Omega \cdot cm^2$)	R_{sh} ($\Omega \cdot cm^2$)
1:1.5	0.92	9.39	46.42	4.01, (3.81) [a]	70.2	145.5
1:2	0.92	9.72	49.59	4.43, (4.19) [a]	65.8	149.2
1:2.5	0.92	9.46	48.52	4.22, (4.02) [a]	67.9	146.1

[a] Average of 20 devices.

Table S5 The photovoltaic properties of J71: TTz1(1: 2)blend device in different additive ratios, measured under the illumination of AM 1.5G (100 mW cm^{-2}).

DIO	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	R_s ($\Omega \cdot cm^2$)	R_{sh} ($\Omega \cdot cm^2$)
0.15%	0.90	13.20	59.06	7.02, (6.88) [a]	40.5	235.3
0.25%	0.90	15.43	63.18	8.77, (8.46) [a]	37.6	245.1
0.35%	0.89	13.36	61.1	7.26, (7.01) [a]	39.5	237.5

[a] Average of 20 devices.

Table S6 The photovoltaic properties of J71: TTz2(1: 2)blend device in different additive ratios, measured under the illumination of AM 1.5G (100 mW cm^{-2}).

DIO	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	R_s ($\Omega \cdot cm^2$)	R_{sh} ($\Omega \cdot cm^2$)
0.15%	0.92	10.35	50.86	5.10, (4.98)[a]	62.2	158.1
0.25%	0.92	12.75	53.73	6.30, (6.05)[a]	56.3	150.6
0.35%	0.91	11.63	52.48	5.55, (5.26)[a]	58.5	155.2

[a] Average of 20 devices.

Table S7 Charge mobilities and AFM of the J71: TTz1/TTz2 blends.

Active layer	μ_h[b] ($cm^2\ V^{-1}\ s^{-1}$)	μ_e[b] ($cm^2\ V^{-1}\ s^{-1}$)	μ_h/μ_e	RMS (nm)[a]	RMS (nm)[b]
J71: TTz1	4.24×10^{-4}	1.46×10^{-4}	2.90	1.98	1.03
J71: TTz2	2.92×10^{-4}	8.74×10^{-5}	3.34	2.14	1.85

[a] without DIO ; [b] with 0.25% DIO.

Table S8 The contact angle and surface energy parameters of the corresponding films.

Surface	θ_{H_2O} (°)	$\theta_{CH_2I_2}$ (°)	γ^d (mN m^{-1})[a]	γ^p (mN m^{-1})[a]	γ(mN m^{-1})[a]
H_2O	-	-	21.80	51.00	72.80
CH_2I_2	-	-	49.50	1.30	50.80
TT0	43.5	33.5	33.77	24.95	58.72
TTz0	81.5	43.0	35.17	3.89	39.06
TTz1	91.0	33.5	42.22	0.58	42.79
TTz2	87.0	37.0	39.57	1.56	41.14
J71	98.5	55.5	30.67	0.52	31.19

[a] γ^d and γ^p represent the surface free energies generated from the dispersion forces and the polar forces, respectively.

4. References

1 M. O. Ahmed, C. M. Wang, P. Keg, W. Pisula, Y.-M. Lam, B. S. Ong, S.-C. Ng, Z.-K.Chen and S. G. Mhaisalkar, *J. Mater. Chem*., 2009, **19**, 3449-3456.

2 S. Subramaniyan, H. Xin, F. S. Kim, S. Shoaee, J. R. Durrant, S. A. Jenekhe, *Adv. Energy Mater*., 2011, **1**, 854-860.