

**Impact of the length of the branched alkyl side chains on the
thiazolothiazole-based small molecular acceptors in non-fullerene
polymer solar cells**

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1. Experimental section

1.1. Materials and Instruments

All solvents and chemicals used in this work were all commercially available, and used without further purification. General measurements and devices fabrication are the same as the previous work.^{1,2}

¹H NMR spectra was measured on a Bruker Dex-400 MHz NMR spectrometer using tetramethylsilane as a reference in deuteriated chloroform solution at 298 K. Mass spectra was estimated on a Bruker Autoflex III Mass Spectrometer. Fourier Transform Infrared Spectroscopy (FT-IR) spectra was performed by the NICOLET IS 10 FT-IR instrument. The sample preparation involved the use of the pelletizing method, which entailed mixing KBr (100-200 mg) with the solid sample (1-2 mg) in an agate mortar and grinding them into fine powder with a micrometer-scale consistency. Subsequently, the powders were pressed into a transparent pellet with a thickness of approximately 1 mm using a specialized pelletizing device. Finally, the pellet was analyzed and characterized against an air background. Thermogravimetric analysis (TGA) was conducted under a flow of dry nitrogen gas at a heating rate of 10 °C min⁻¹ with a NETZSCH TG 209 F1 Libra instrument. The differential scanning calorimetric (DSC) measurement was made on a TA DSCQ10 instrument at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. UV-vis absorption spectra were obtained using a Shimadzu UV-1800 PC spectrometer. The electrochemical cyclic voltammetry (CV) was measured with a CHI630E electrochemical work station dipped in an acetonitrile solution of 0.1 M tetrabutylammonium hexafluorophosphate

(Bu₄NPF₆) under nitrogen at room temperature. Powder X-ray diffraction (PXRD) was carried out to investigate the crystalline characteristics of two SMA materials by a RINT2000 vertical goniometer operated at 40 kV voltage and a 250 mA current with Cu K α radiation. AFM images were obtained by using a Bruker Inova atomic microscope in tapping mode to observe the surface morphologies of the blend films.

1.2. Synthetic details

Schemes 1 shows the synthetic routes of TTz3(C4C6) and TTz3(C2C4), and the detailed synthesis procedures are described as following.

Synthesis of 2-C2C4: Compound 1 (10.4 g, 91.09 mmol), 2-ethylhexanol (23.7 g, 182.18 mmol) and NaHSO₄ (1.09 g, 9.11 mmol) were dissolved in 50 mL toluene, then stirred for 24 h at 130 °C under nitrogen protection. The mixture was poured into water (50 mL) and then extracted with dichloromethane (DCM). The combined organic layer was washed with water and brine, dried over anhydrous MgSO₄. After removal of solvent, the residue was purified by column chromatography on silica gel using petroleum ether (PE) as eluent, yielding a golden-yellow oil (13.85 g, 71.6%). ¹H NMR (400 MHz, CDCl₃) δ 7.16 (d, J = 8.4 Hz, 1H), 6.76 (d, J = 5.2 Hz, 1H), 6.22 (d, J = 4.7 Hz, 1H), 3.83 (d, J = 6.7 Hz, 2H), 1.73 - 1.67 (m, 1H), 1.52 - 1.42 (m, 4H), 1.40 - 1.29 (m, 4H), 0.94 - 0.88 (m, 6H).

Synthesis of 2-C4C6: The synthesis procedure is the same as compound 2-C2C4, a colorless oil was obtained with a yield of 68.2%. ¹H NMR (400 MHz, CDCl₃) δ 7.16 (d, J = 8.4 Hz, 1H), 6.75 (d, J = 6.7 Hz, 1H), 6.22 (d, J = 4.6 Hz, 1H), 3.81 (d, J = 5.7 Hz, 2H), 1.76 - 1.72 (m, 1H), 1.48 - 1.24 (m, 16H), 0.91 - 0.86 (m, 6H).

Synthesis of 3-C2C4: Under N₂, 70 mL N, N-dimethylformamide (DMF) was added in a 250 mL three-necked flask, at 0 °C, phosphorus oxychloride (11.26 g, 73.46 mmol) was added into the flask dropwise. The mixture was stirred at room temperature for 1 hour. Then, a solution of compound 2-C2C4 (13.00 g, 61.22 mmol) in 5 mL dry DMF was subsequently added into the flask dropwise. After being stirred at 70 °C for 1.5 hours, the mixture was poured into ice-cold water (40 mL), and then extracted three times with dichloromethane. The combined organic layers were washed with water and brine and dried over MgSO₄. After removal of solvent, the residue was purified by column chromatography on silica gel using dichloromethane/petroleum ether (1:1, v/v) as eluent, yielding a light-yellow oil (8.86 g, 60%). ¹H NMR (300 MHz, CDCl₃) δ 10.01 (s, 1H), 7.63 (d, *J* = 5.4 Hz, 1H), 6.85 (d, *J* = 5.4 Hz, 1H), 4.05 (d, *J* = 5.7 Hz, 2H), 1.79 - 1.71 (m, 1H), 1.52 - 1.38 (m, 4H), 1.34 - 1.29 (m, 4H), 0.96 - 0.88 (m, 6H).

Synthesis of 3-C4C6: The synthesis procedure is the same as compound 3-C2C4, a light-yellow oil was obtained with a yield of 81%. ¹H NMR (300 MHz, CDCl₃) δ 10.01 (s, 1H), 7.63 (d, *J* = 6.6 Hz, 1H), 6.84 (d, *J* = 5.4 Hz, 1H), 4.03 (d, *J* = 5.6 Hz, 2H), 1.84 - 1.76 (m, 1H), 1.42 - 1.28 (m, 16H), 0.92 - 0.86 (m, 6H)

Synthesis of 4-C2C4: Under N₂ protection, compound 3-C2C4 (8.80 g, 36.60 mmol), dithiooxalamide (2.21 g, 18.30 mmol), and phenol (25 mL) were added in a 100 mL three-necked flask, and the mixture was then stirred for 8 h at 200 °C. After cooling to room temperature, the residue was purified by column chromatography on silica gel using dichloromethane/petroleum ether (1:2, v/v) as eluent, yielding a

yellow solid (2.31 g, 22%). ^1H NMR (300 MHz, CDCl_3) δ 7.33 (d, $J = 5.5$ Hz, 2H), 6.90 (d, $J = 5.6$ Hz, 2H), 4.15 (d, $J = 7.2$ Hz, 4H), 1.83 - 1.75 (m, 2H), 1.70 - 1.53 (m, 8H), 1.37 - 1.32 (m, 8H), 0.99 - 0.89 (m, 12H).

Synthesis of 4-C4C6: The synthesis procedure is the same as compound 4-C2C4, a yellow solid was obtained with a yield of 27%. ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, $J = 5.5$ Hz, 2H), 6.89 (d, $J = 5.5$ Hz, 2H), 4.14 (d, $J = 4.8$ Hz, 4H), 1.87 - 1.81 (m, 2H), 1.34 - 1.22 (m, 32H), 0.92 - 0.85 (m, 12H).

Synthesis of 5-C2C4: Compound 4-C2C4 (1.50 g, 2.67 mmol) was placed in an oven-dried 100 mL Schlenk flask and degassed by three vacuum/nitrogen cycles. Anhydrous THF (50 mL) was injected and the solution was cooled to -78 °C. *n*-butyllithium (2.5 M in hexanes, 2.66 mL, 6.66 mmol) was subsequently added into the flask dropwise, and the reaction was stirred for 2 hours. Tributyltin chloride (1.0 M in hexanes, 7.99 mL, 7.99 mmol) was then injected. After warming to room temperature, and stirred for overnight. The reaction mixture was poured into water (80 mL), and then extracted three times with dichloromethane. The combined organic layers were dried over MgSO_4 , after removal of solvent, the residue is precipitated in methanol, and a bright yellow solid 5-C2C4 (2.20 g, 94%) was obtained by suction filtration. ^1H NMR (400 MHz, CDCl_3) δ 6.93 (s, 2H), 4.17 (t, $J = 4.6$ Hz, 4H), 1.81 - 1.76 (m, 2H), 1.72 - 1.49 (m, 8H), 1.37 - 1.33 (m, 8H), 0.99 - 0.89 (m, 12H), 0.48 - 0.34 (m, 18H).

Synthesis of 5-C4C6: The synthesis procedure is the same as compound 5-C2C4, a brownish yellow solid was obtained with a yield of 73%. ^1H NMR (400 MHz,

CDCl₃) δ 6.92 (s, 2H), 4.16 (d, $J = 4.6$ Hz, 4H), 1.85 - 1.82 (m, 2H), 1.34 - 1.28 (m, 32H), 0.92 - 0.85 (m, 12H), 0.51 - 0.31 (m, 18H).

Synthesis of 7-C2C4: In a 50 mL flask, compound 5-C2C4 (2.03 g, 1.53 mmol), 7-bromobenzo [C][1,2,5] thiadiazole-4-formaldehyde (0.78 g, 3.21 mmol) were dissolved in anhydrous toluene (130 mL). Under N₂ protection, Pd(PPh₃)₄ (88.43 mg, 5%) was added and the mixture was stirred for 24 h at 110 °C. After cooling to room temperature, the reaction mixture was poured into methanol (180 mL). The precipitate was filtered, and purified by column chromatography on silica gel using chloroform as eluent, yielding a blue black solid (1.85 g, 91%). ¹H NMR (400 MHz, CDCl₃) δ 10.75 (s, 2H), 8.27 (d, $J = 7.6$ Hz, 2H), 8.23 (s, 2H), 8.06 (d, $J = 7.7$ Hz, 2H), 4.35 (d, $J = 4.2$ Hz, 4H), 1.93 - 1.87 (m, 2H), 1.78 - 1.63 (m, 8H), 1.44 - 1.38 (m, 8H), 1.05 (t, $J = 7.5$ Hz, 6H), 0.95 (t, $J = 6.8$ Hz, 6H).

Synthesis of 7-C4C6: The synthesis procedure is the same as compound 7-C2C4, a blue-black solid was obtained with a yield of 86%. ¹H NMR (400 MHz, CDCl₃) δ 10.71 (s, 2H), 8.23 (d, $J = 7.5$ Hz, 2H), 8.18 (s, 2H), 8.01 (d, $J = 7.5$ Hz, 2H), 4.33 (d, $J = 4.6$ Hz, 4H), 1.98 - 1.93 (m, 2H), 1.69 - 1.58 (m, 8H), 1.37 (m, 24H), 0.93 (dt, $J = 12.9, 6.7$ Hz, 12H).

Synthesis of TTz3(C2C4): In a 500 mL flask, compound 7-C2C4 (1.63 g, 1.84 mmol), malononitrile (1.21 g, 18.37 mmol) were dissolved in anhydrous toluene (420 mL). Under N₂ protection, alkaline alumina (1 g) was added and the mixture was stirred for 12 h at 85 °C. After cooling to room temperature, the reaction mixture was poured into methanol (200 mL). The precipitate was filtered, and the crude product

was purified by flash chromatography on silica, using chloroform as the eluent. The product TTz3(C2C4) was subsequently recrystallized from chloroform and acetone as a purplish-red solid with metallic luster (1.14 g, 63%). ¹H NMR (400 MHz, CDCl₃) δ 8.75 (d, *J* = 6.9 Hz, 4H), 8.19 (s, 2H), 8.01 (d, *J* = 7.9 Hz, 2H), 4.34 (d, *J* = 5.3 Hz, 4H), 1.93 - 1.88 (m, 2H), 1.77 - 1.61 (m, 8H), 1.45 - 1.39 (m, 8H), 1.06 (t, *J* = 7.2 Hz, 6H), 0.97 (t, *J* = 6.6 Hz, 6H). MS (MALDI-TOF): calcd. for C₄₈H₄₂N₁₀O₂S₆[M]⁺ 983.29; found 983.02.

Synthesis of TTz3(C4C6): The synthesis procedure is the same as compound TTz3(C2C4), a purplish-red solid with metallic luster was obtained with a yield of 85%. ¹H NMR (400 MHz, CDCl₃) δ 8.70 (d, *J* = 7.9 Hz, 2H), 8.68 (s, 2H), 8.14 (s, 2H), 7.95 (d, *J* = 7.9 Hz, 2H), 4.33 (d, *J* = 4.7 Hz, 4H), 1.99 - 1.94(m, 2H), 1.72 - 1.60(m, 8H), 1.44 - 1.33 (m, 24H), 1.00 - 0.89 (m, 12H). MS (MALDI-TOF): calcd. for C₅₆H₅₈N₁₀O₂S₆[M]⁺ 1095.51; found 1095.03.

2. Supplementary Figure. S1-18

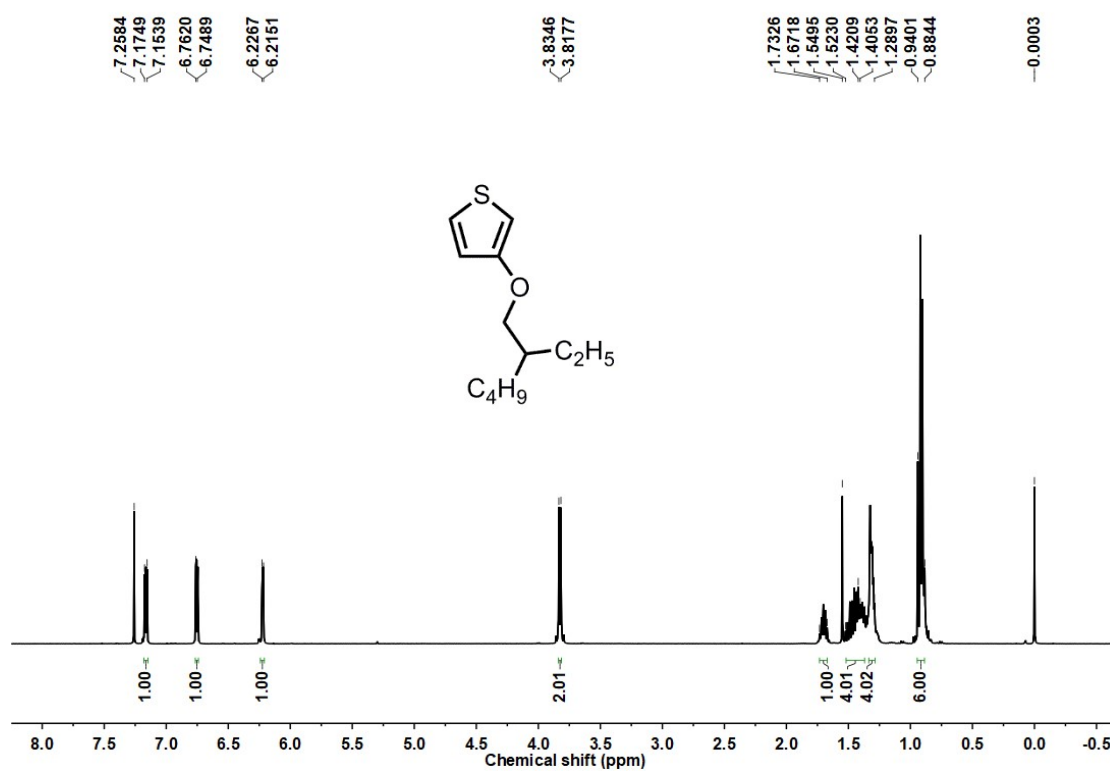


Figure S1. ¹H NMR plot of compound 2-C2C4.

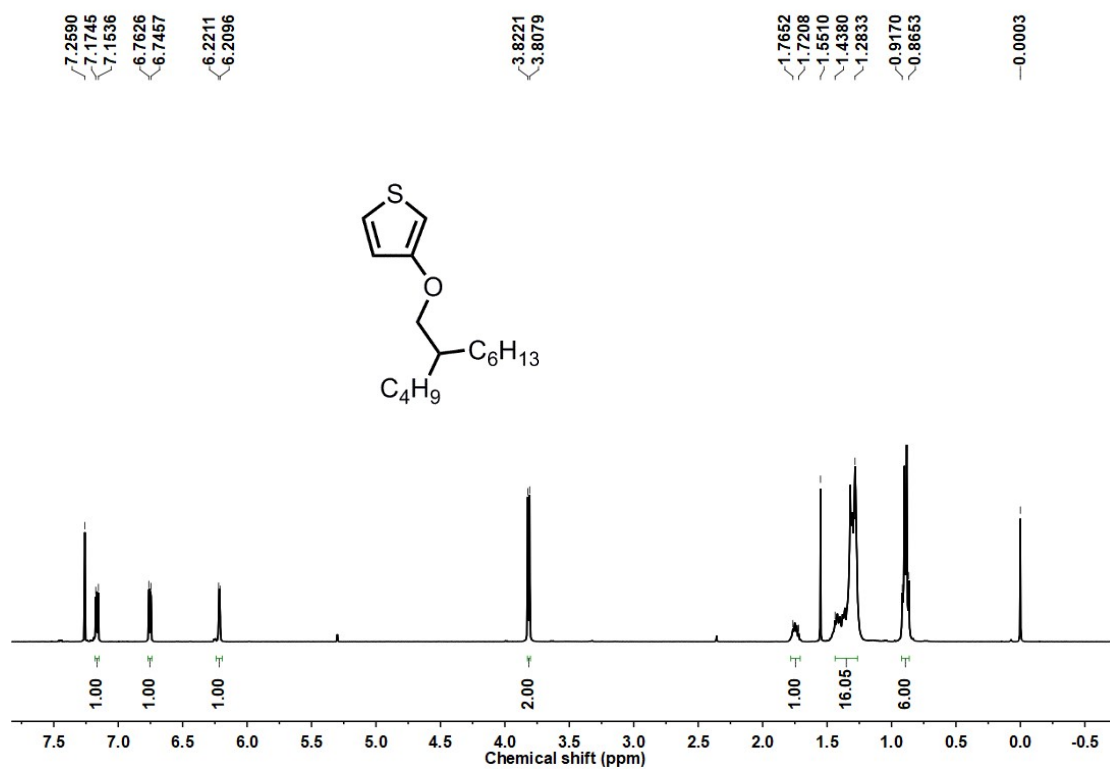


Figure S2. ¹H NMR plot of compound 2-C4C6.

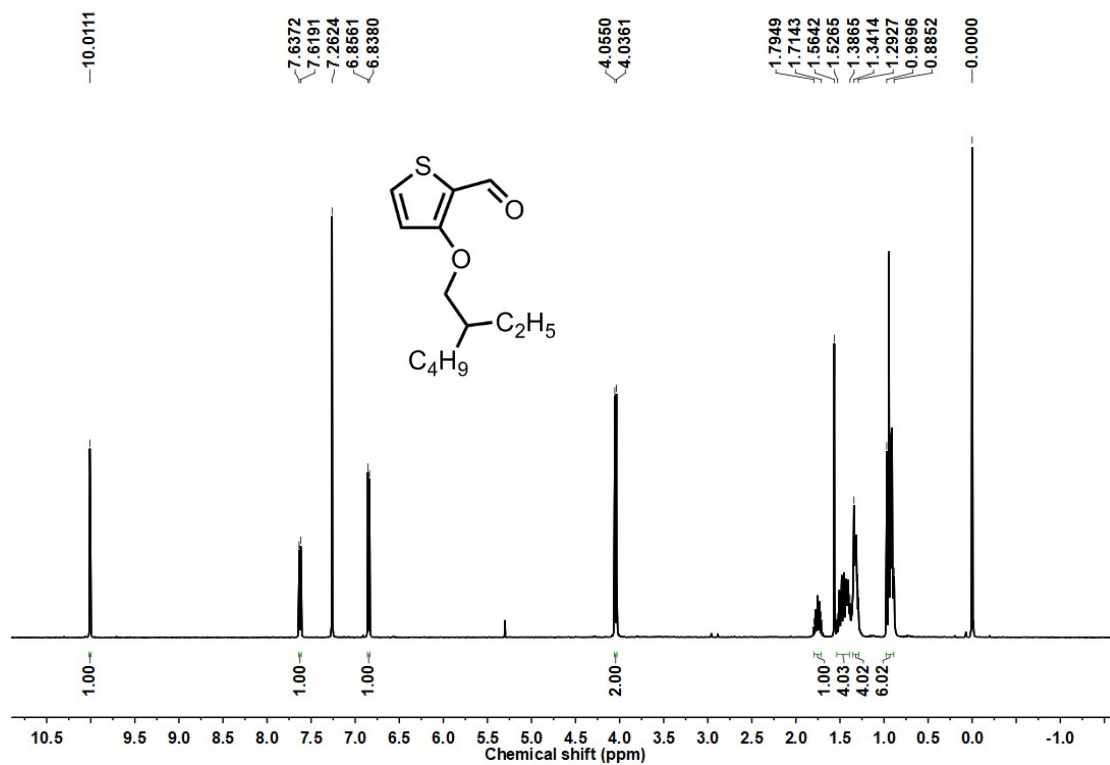


Figure S3. ¹H NMR plot of compound 3-C2C4.

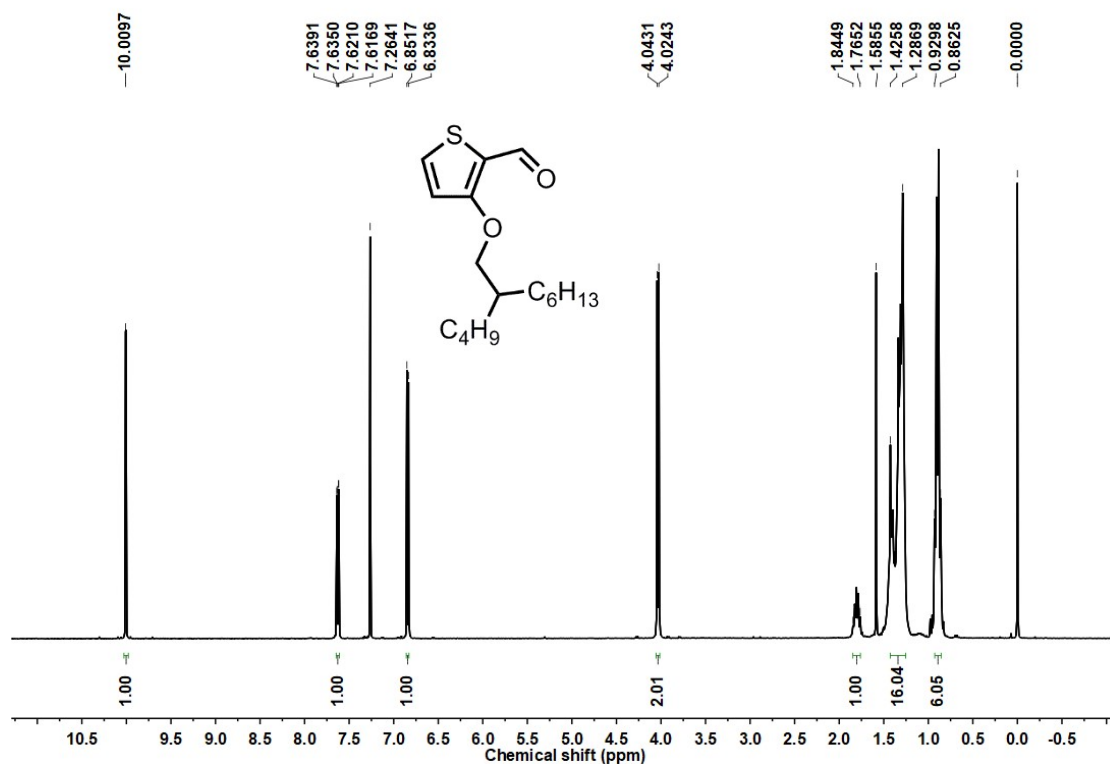


Figure S4. ¹H NMR plot of compound 3-C4C6.

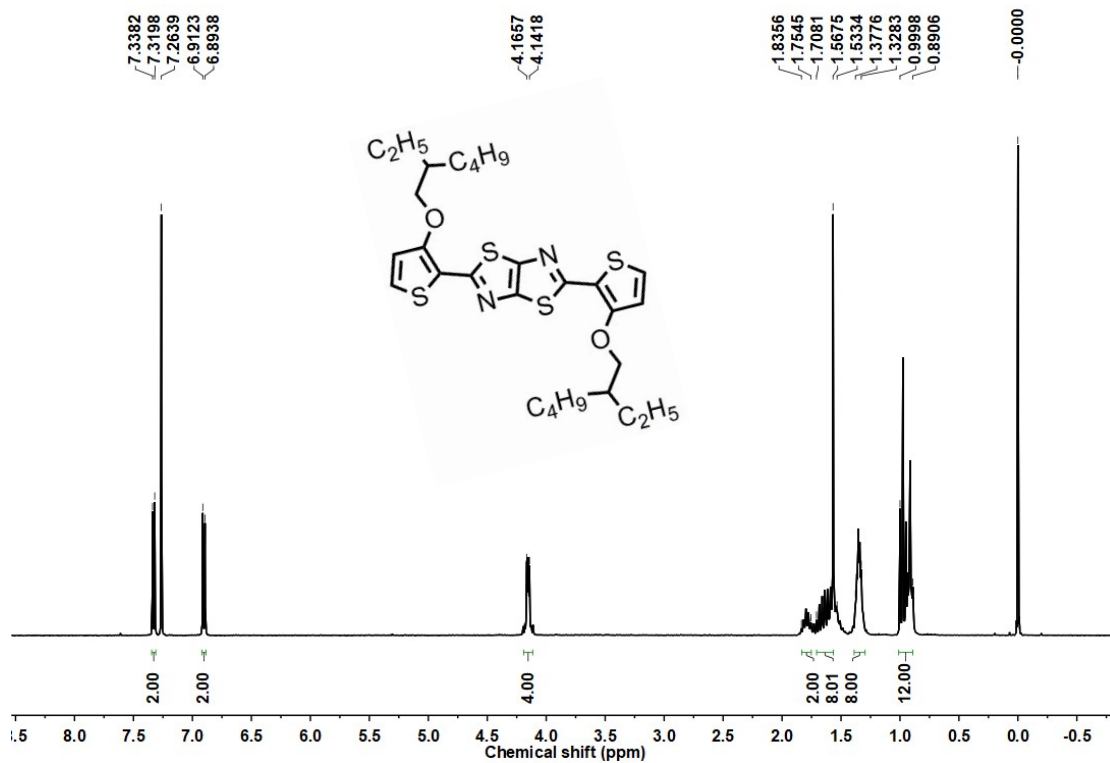


Figure 5. ^1H NMR plot of compound 4-C2C4.

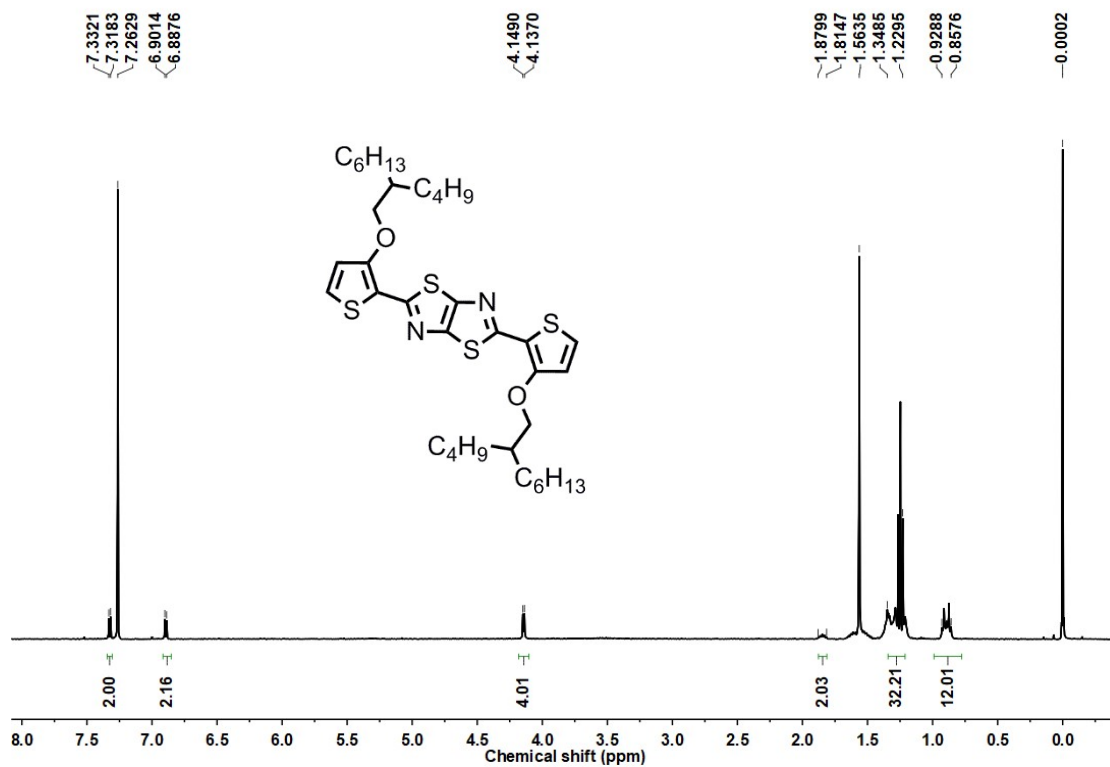


Figure S6. ^1H NMR plot of compound 4-C4C6.

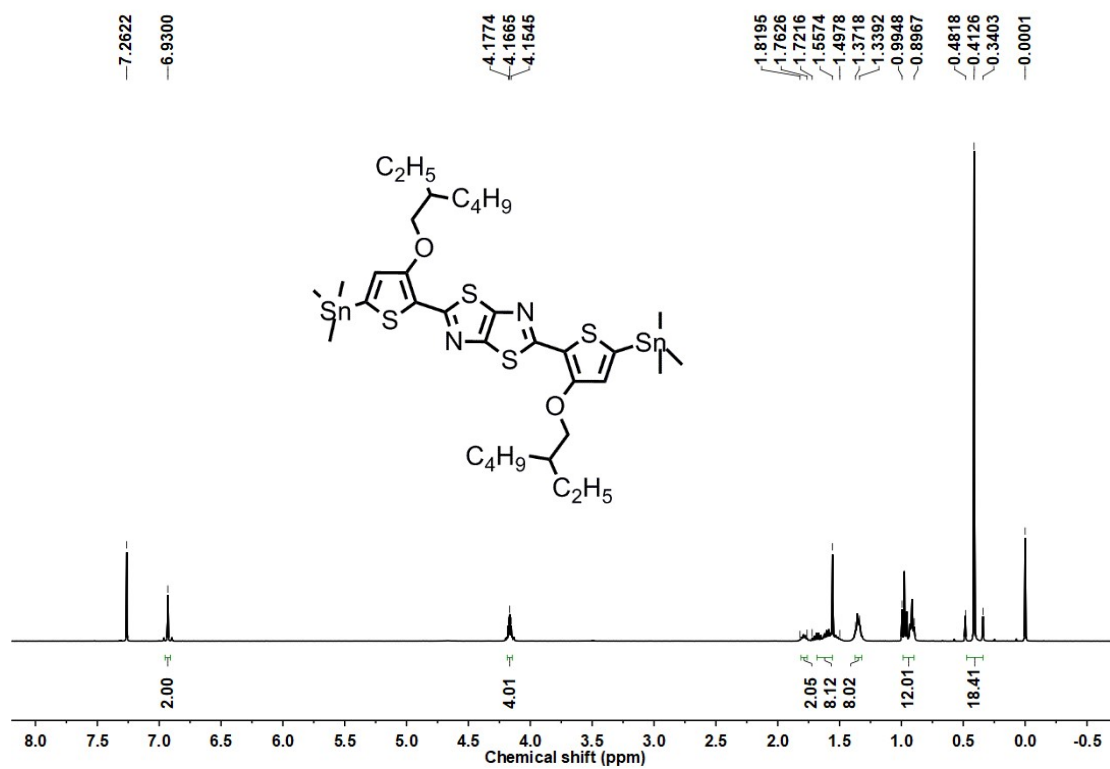


Figure 7. ¹H NMR plot of compound 5-C2C4.

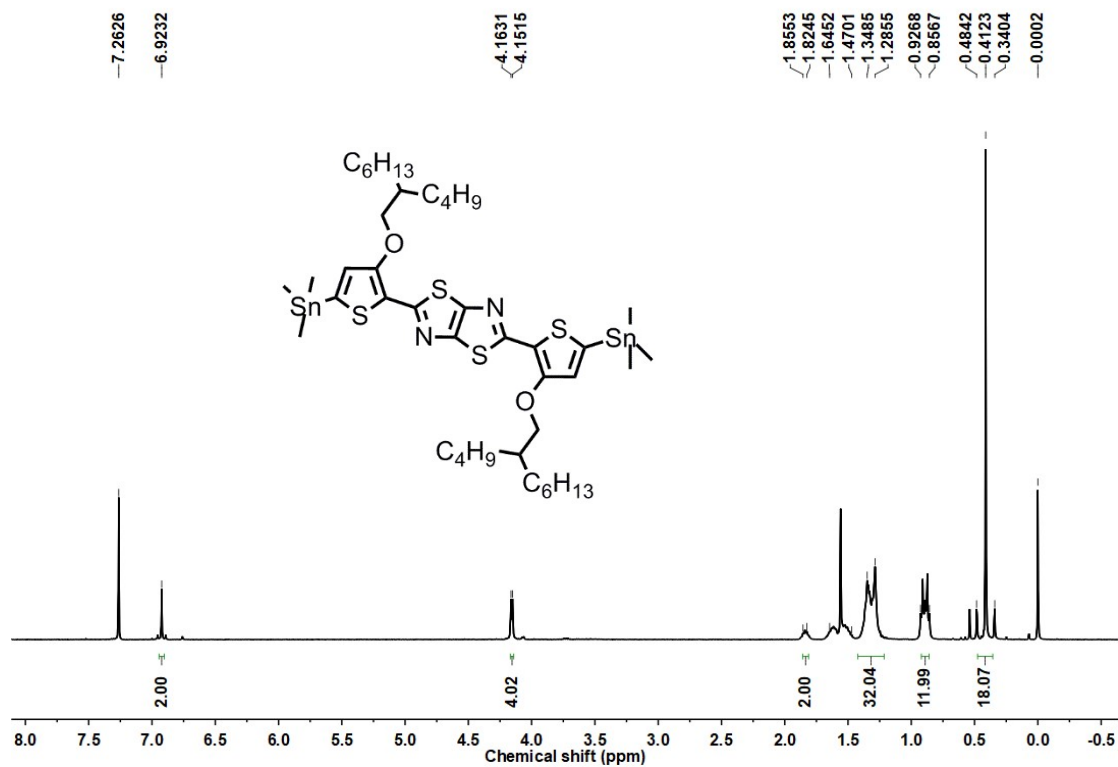


Figure S8. ¹H NMR plot of compound 5-C4C6.

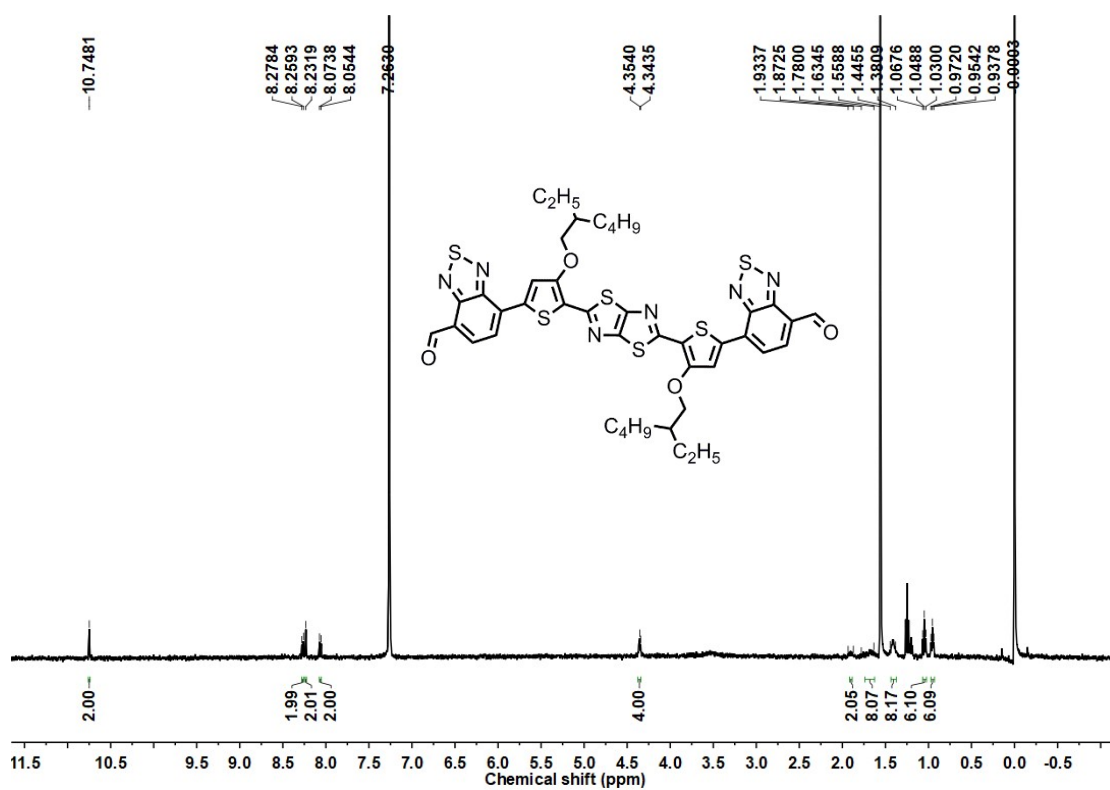


Figure 9. ¹H NMR plot of compound 7-C2C4.

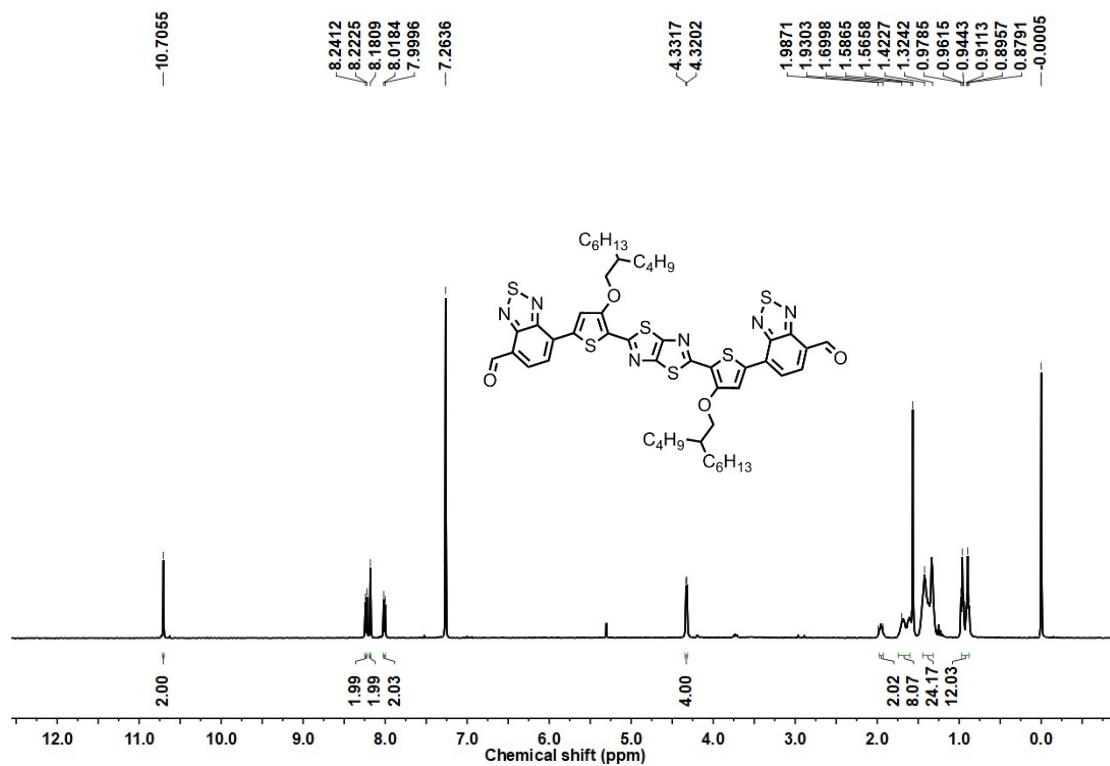


Figure S10. ¹H NMR plot of compound 7-C4C6.

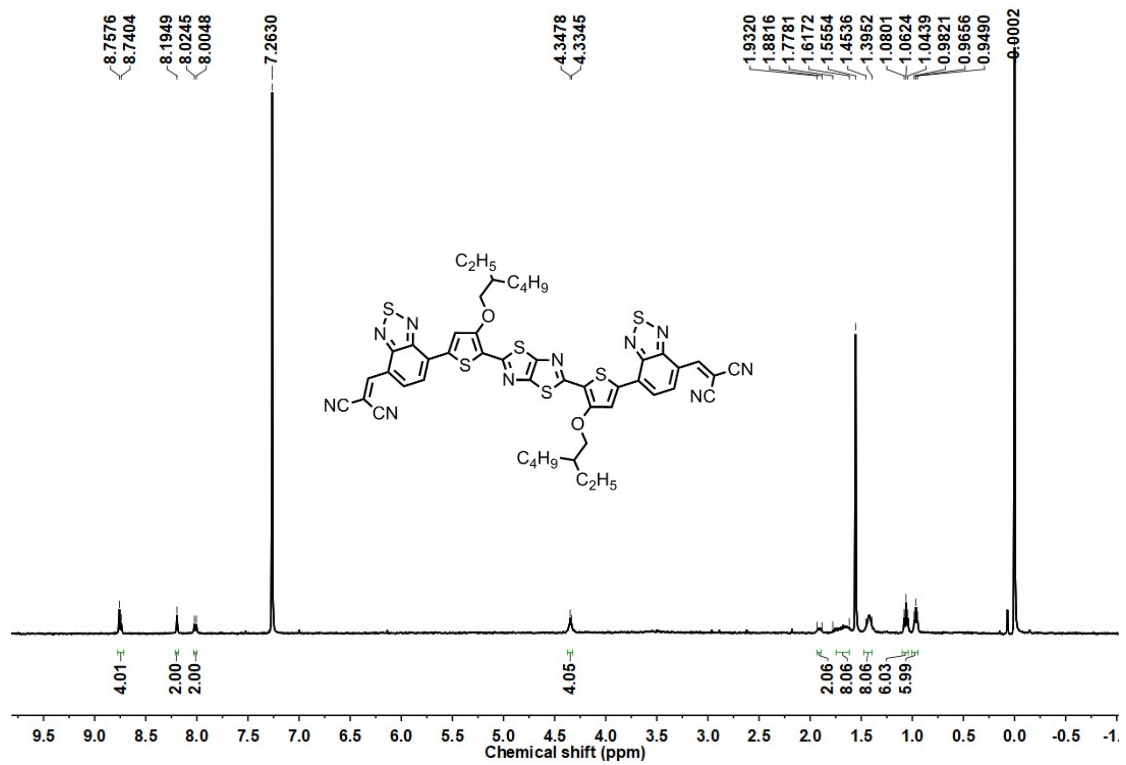


Figure S11. ¹H NMR plot of TTz3(C2C4).

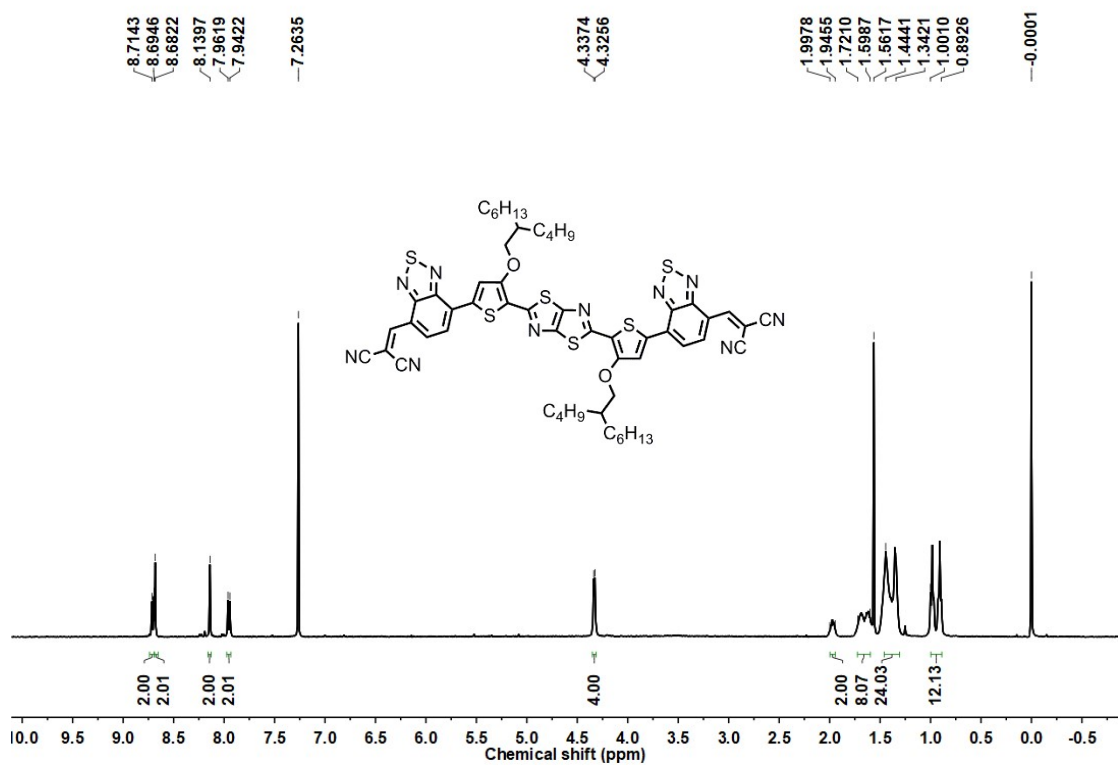


Figure S12. ¹H NMR plot of TTz3(C4C6).

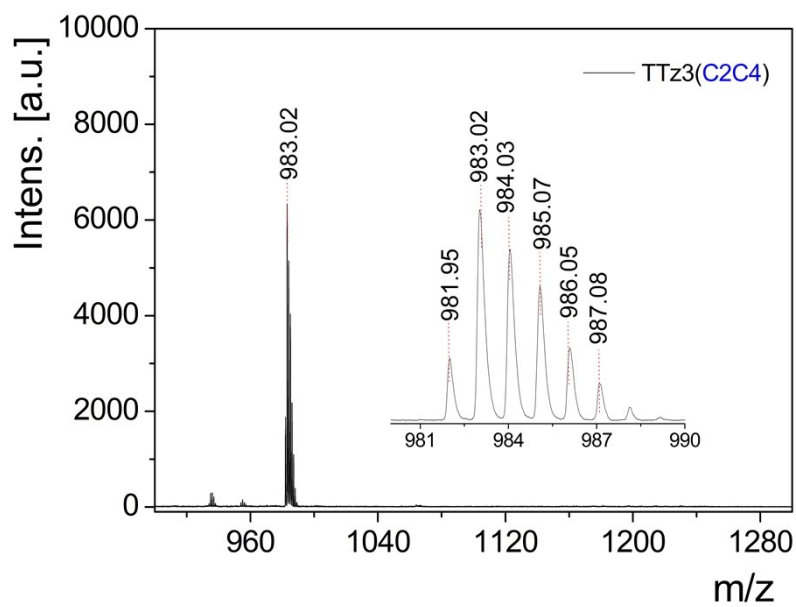


Figure S13. MS plot of TTz3(C2C4).

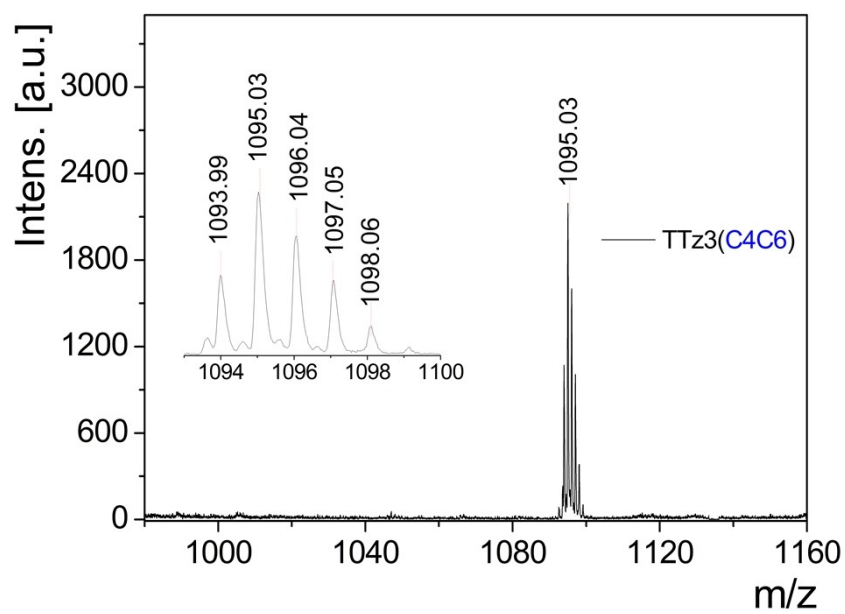


Figure S14. MS plot of TTz3(C4C6).

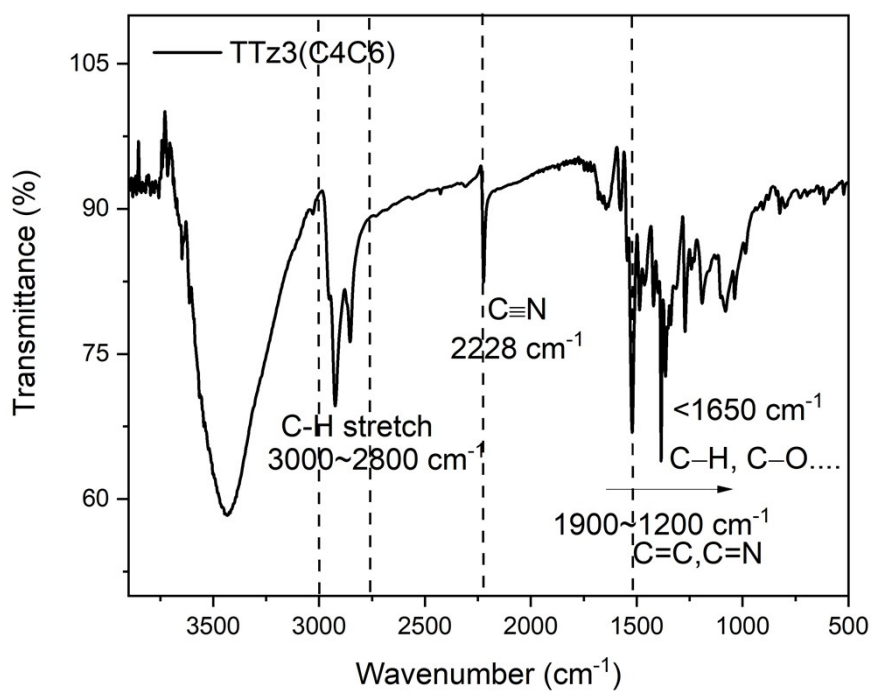


Figure S15. FT-IR spectra of small molecule acceptor TTz3(C4C6).

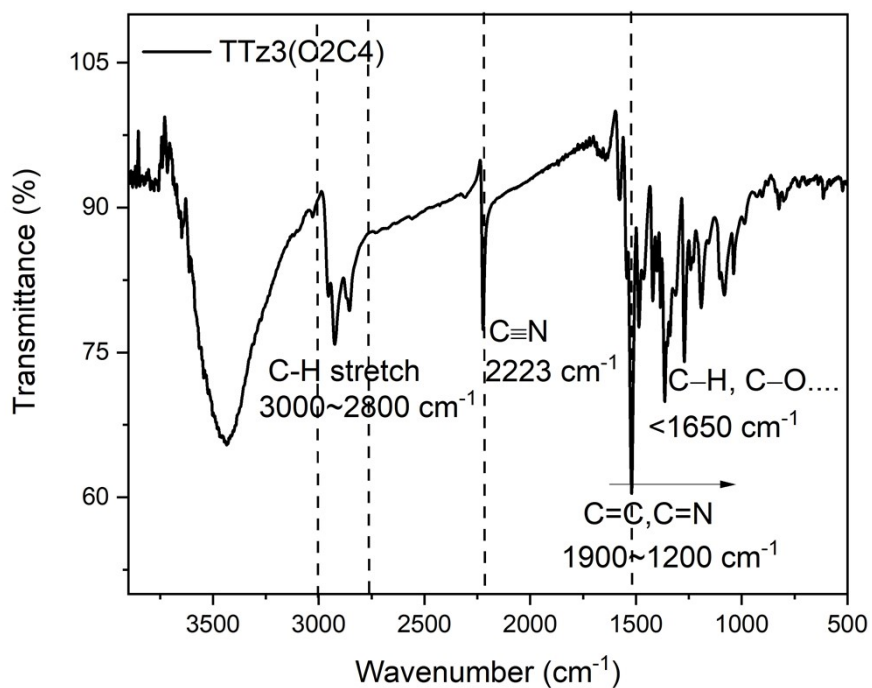


Figure S16. FT-IR spectra of small molecule acceptor TTz3(C2C4).

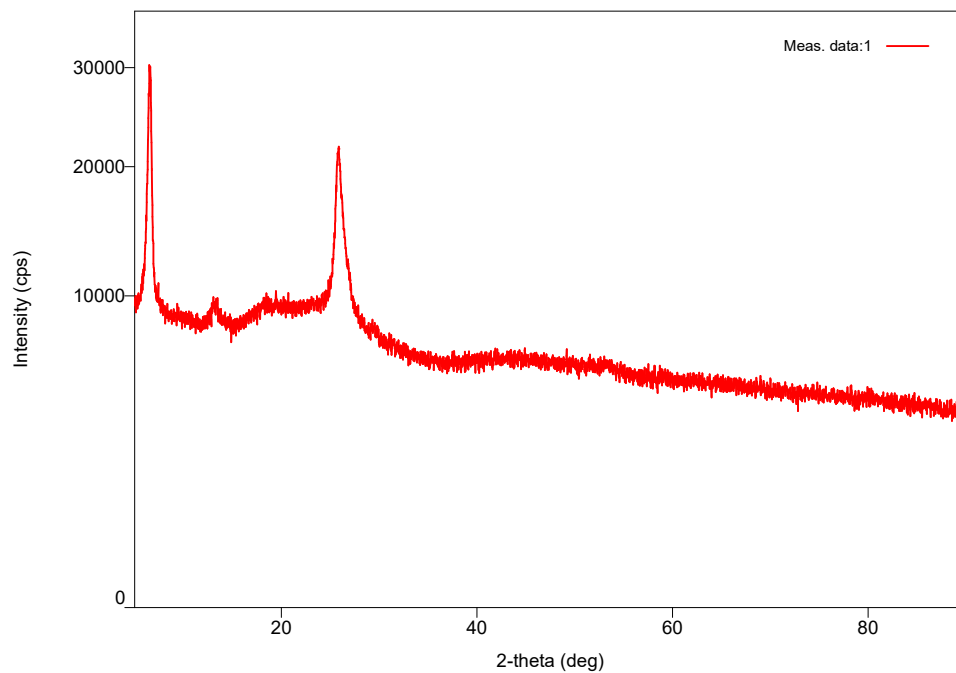


Figure S17. PXRD patterns of the TTz3(C4C6) pristine solid powders.

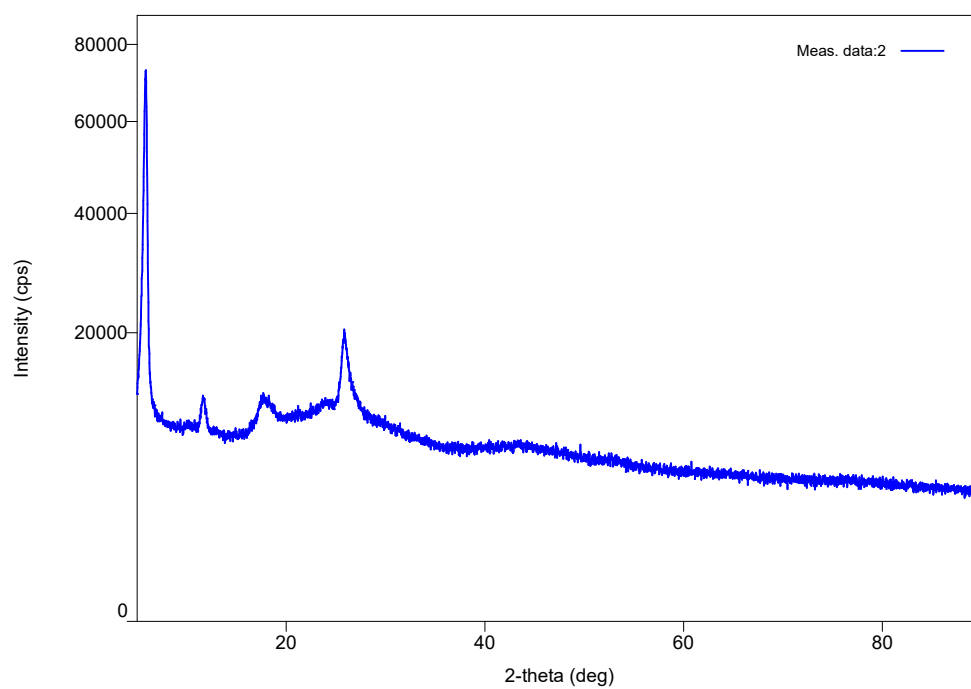


Figure S18. PXRD patterns of the TTz3(C2C4) pristine solid powders.

3. Supplementary Table S1-2

Table S1. 2θ and d -spacings calculated from XRD patterns.

Acceptors	$2\theta_1$ ($^\circ$)	$d(100)$ - spacing (\AA)	$2\theta_2$ ($^\circ$)	$d(200)$ - spacing (\AA)	$2\theta_3$ ($^\circ$)	$d(300)$ - spacing (\AA)	$2\theta_4$ ($^\circ$)	$d(010)$ - spacing (\AA)
TTz3(C6C8)	5.07	17.42	9.86	8.97	/	/	25.78	3.45
TTz3(C4C6)	6.59	13.41	13.41	6.60	/	/	25.85	3.44
TTz3(C2C4)	5.91	14.93	11.73	7.54	17.83	4.97	25.85	3.44

Table S2. Charge mobilities and AFM of the J71: TTz(R) blends.

Active layer	μ_h ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_e ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_h/μ_e	RMS (nm)
J71: TTz3(C6C8)	5.25×10^{-4}	2.50×10^{-4}	2.10	1.35
J71: TTz3(C4C6)	1.61×10^{-4}	6.18×10^{-5}	2.61	1.75
J71: TTz3(C2C4)	1.10×10^{-4}	3.29×10^{-5}	3.34	4.65

4. Reference

- 1 W. Peng, G. Zhang, L. Shao, C. Ma, B. Zhang, W. Chi, Q. Peng, W. Zhu, *J. Mater. Chem. A*, 2018, **6**, 24267-24276.
- 2 W. Peng, G. Zhang, M. Zhu, H. Xia, Y. Zhang, H. Tan, Y. Liu, W. Chi, Q. Peng, W. Zhu. *ACS Appl. Mater. Interfaces*, 2019, **11**, 48128-48133.