Electronic Supplementary Information

Reversible conversion between the pleated oligo-Tetrathiafulvalene radical foldamer and folded donor-acceptor [3]pseudorotaxane under redox condition

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Contents

General Methods

All the chemical reagents were obtained from commercial sources and used without further purification unless otherwise noted, and the solvents for synthesis have been purified by standard procedures before use.

Cyclic voltammetry (CV) experiments: ^{n}-Bu_4NPF_6 (0.1M) was used as the supporting electrolyte and saturated calomel electrode (SCE) as the reference electrode. The internal resistances of the TTF solutions were measured and the IR compensation was considered before CV scanning. The CV diagrams were recorded at the scan rate of 0.1 V/S in $CHCl_3$ at ambient temperature. 4.0 mL of each sample was used and bubbling with argon gas for 30 seconds before CV scanning.

UV-*vis*-NIR Experiments: absorption spectra were recorded with Agilent Technologies Cary 60 UV-Vis spectrometer at 25 ^{o}C. The solutions of TTF oligomers samples and $Fe(ClO_4)_3$ were freshly prepared, and 2.5 mL of each TTF sample was used.

EPR experiments: TTF samples were prepared by carefully injecting the corresponding solution of an as-prepared radical solution into a capillaron, respectively, and then submitted to an electron paramagnetic resonance spectrometer at 25 ^{o}C.

NMR Experiments: ^{1}H NMR and ^{13}C NMR spectra of the TTF oligomers and intermediates were recorded with a Bruker Advance 400 MHz and 600 MHz spectrometer at 25 ^{o}C, respectively. **Me-4TTF** was firstly dissolved in acetone-d_6 with a concentration of 2.0 mM, and then two equivalent of $CBPQT^{4+}$ ring was added into the NMR tube, which was mixed well before submit to the NMR spectrometer.

DFT Calculation: All computations were carried out with GAUSSIAN 09 program [1]. The initial complex structure was modified from the crystallographic data CCDC 946414 [2] in Cambridge Structural Database (CSD). Molecular geometries were optimized with B3LYP/6-31G method [3-4]. To hold the flexible complex structure, the **$CBPQT^{4+}$** moieties were firstly kept frozen during the optimization and then released to a further optimization. The optimized complex structure was shown in Fig.S5 and the [C−H···O] interactions in optimized complex structure were

analyzed and depicted by MOE 2014 program.

Synthesis

Compound 4 and Me-2TTF. Compound **2** (0.414 g, 1.31 mmol) was dissolved in 10 mL anhydrous DMF, which was then degassed by Ar bubbling for 2 min and poured into a 50 mL flask under Ar protection. $CsOH•H_2O$ (0.26 g, 1.55 mmol) was dissolved in 1 mL CH_3OH (degassed by Ar bubbling) and added to the above solution of compound **2** and the resulting mixture was stirred for another 2 hours at room temperature. 3 mL degassed DMF solution containing (0.86 g, 2.08 mmol) compound **3** was added and the resulting mixture was stirred overnight. After the reaction was completed (monitered by TLC), 5 mL ethyl acetate was added and the mixture was poured into 15 mL water, the water phase was extracted by ethyl acetate (25 mL×2), organic phase was combined and washed with brine, dryed by Na_2SO_4 and purified by column chromatogram (PE/EA = 4:1), compound **4** was obtained as yellow oil (0.22 g, 30%); **Me-2TTF** was also isolated as yellow oil (0.13 g, 14%).

Me-2TTF: ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 6.89 (s, 2H), 6.74 (s, 2H), 3.59 (t, J_1 = 4.0 Hz, J_2 = 4.0 Hz, 4H), 3.52 (s, 8H), 2.97 (t, J_1 = 4.0 Hz, J_2 = 4.0 Hz, 4H), 2.43 (s, 6H). ^{13}C NMR (150MHz, $CDCl_3$): δ (ppm) 129.15, 126.87, 123.32, 119.83, 119.76, 70.96, 70.85, 70.02, 35.50, 30.01 and 19.76. MS (ESI): *m/z* 722 $[M + H]^+$. HRMS (MALDI-TOF) Calcd. for $C_{22}H_{26}O_3S_{12}Na$ $[M + Na]^+$ 744.8428, Found: 744.8422.

Compound 4: ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 6.90 (s, 1H), 6.75 (s, 1H), 3.66 (t, J_1 = 4.0 Hz, J_2 = 4.0 Hz, 2H), 3.59 (t, J_1 = 4.0 Hz, J_2 = 4.0 Hz, 2H), 3.56-3.53 (m, 8H), 3.31(t, J_1 = 4.0 Hz, J_2 = 4.0 Hz, 2H), 2.97 (t, J_1 = 4.0 Hz, J_2 = 4.0 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (150MHz, $CDCl_3$): δ (ppm) 129.01 (128.95), 126.67, 123.25 (123.21), 119.66 (119.54), 112.51 (112.37), 72.13, 70.84, 70.80, 70.69, 70.41, 69.88, 35.34, 19.64 and 3.37. MS (ESI): *m/z* 568 $[M + H]^+$. HRMS (ESI) Calcd. for $C_{15}H_{21}IO_3S_6Na$ $[M + Na]^+$ 590.8757, Found: 590.7850.

Compound 5. Compound **1** (0.176 g, 0.47 mmol) was dissolved in 8 mL degassed anhydrous DMF under Ar protection, and 0.5 mL CH_3OH solution of $CsOH•H_2O$ (0.095 g, 0.57 mmol) was then added. The resulting mixture was stirred for 2 hours at room temperature, 3.0 mL degassed anhydrous DMF solution of compound **4** (0.22 g, 0.38 mmol) was added and the resulting mixture was stirred overnight. After the reaction was completed (monitered by TLC), 10 mL ethyl acetate was added and the mixture was poured into 15 mL water, the water phase was extracted by ethyl acetate (50 mL×2), organic phase was combined and washed with brine, dryed by Na_2SO_4 and purified by column chromatogram (PE/EA = 3:2), compound **5** was obtained as brown oil (0.114 g, 40%).

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.00 (s, 1H), 6.89 (s, 2H), 6.74 (s, 1H), 3.59 (t, J_1 = 4.0 Hz, J_2 = 4.0 Hz, 4H),, 3.52 (s, 8H), 3.06 (t, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 2H), 2.97 (t, J_1 = 8.0 Hz, J_2 = 8.0 Hz, 4H), 2.83 (t, J_1 = 8.0 Hz, J_2 = 8.0 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 129.13, 126.96, 126.67, 126.55, 124.18, 124.10, 123.39, 123.33, 123.30, 119.71, 117.79, 70.94, 70.85, 69.99, 60.71, 35.52, 30.90, 28.28, 19.41, 18.82 and 14.52. MS (ESI): *m/z* 761 $[M + H]^+$. HRMS (ESI) Calcd. for $C_{24}H_{27}NO_3S_{12}Na$ $[M + Na]^+$ 783.8537, Found: 783.8506.

Me-4TTF. Compound **5** (0.114 g, 0.15 mmol) was dissolved in 8 mL degassed anhydrous DMF under Ar protection, and 1.0 mL CH_3OH solution of $CsOH•H_2O$ (0.72 g, 4.3 mmol) was then added. The resulting mixture was stirred for 2 hours at room temperature, 3.0 mL degassed anhydrous DMF solution of compound **3** (0.035 g, 0.084 mmol) was added and the resulting mixture was stirred overnight. After the reaction was completed (monitered by TLC), 15 mL ethyl acetate was added and the mixture was poured into 15 mL water, the water phase was extracted by ethyl acetate (50 mL×2), organic phase was combined and washed with brine, dryed by Na_2SO_4 and purified by column chromatogram (PE/EA = 3:1), **Me-4TTF** was obtained as brown oil (0.065 g, 28%).

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 6.87 (s, 6H), 6.73 (s, 2H), 3.59 (t, J_1 = 8.0 Hz, J_2 = 8.0 Hz, 12H), 3.52 (s, 24H), 2.97 (t, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 12H), 2.43 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 129.16, 126.85, 123.30, 119.82, 119.69, 112.53, 70.96, 70.86, 70.01, 35.50 and 19.75. MS (ESI): *m/z* 1574 $[M + H]^+$. HRMS (MALDI-TOF) Calcd. for $C_{50}H_{63}O_9S_{24}$ $[M + H]^+$1574.7699, Found 1574.7685.

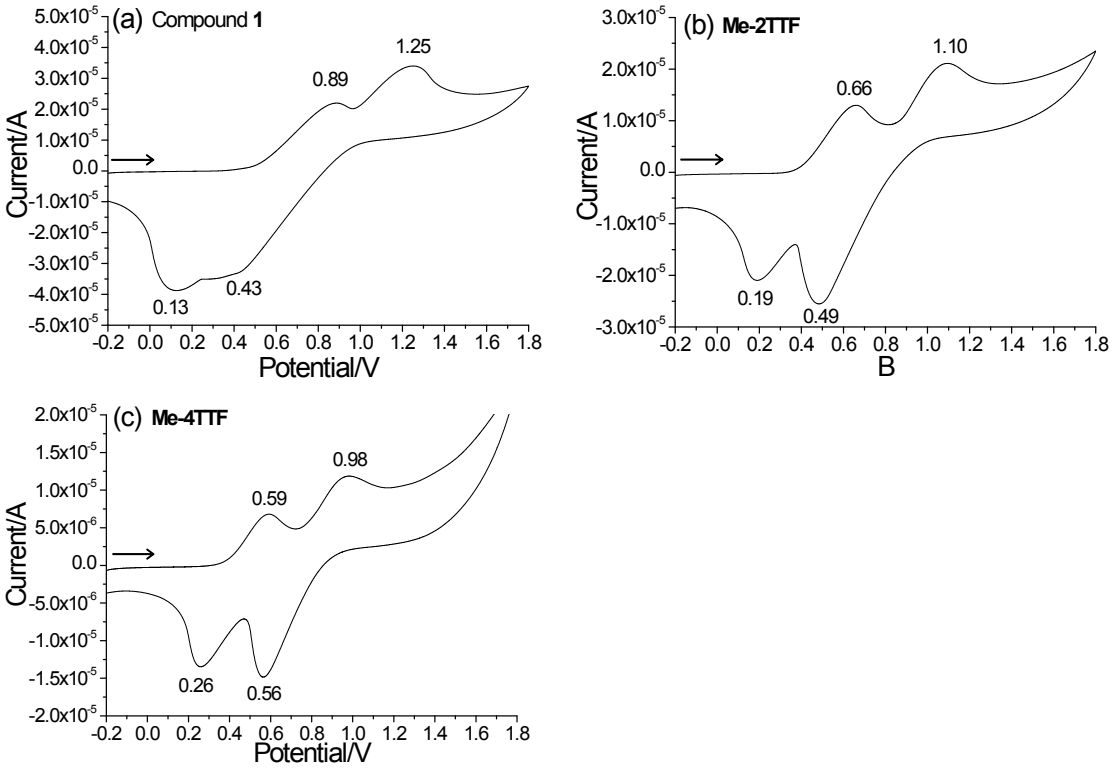

Fig. S1 The cyclic voltammograms of (a) compound **1**; (b) **Me-2TTF** and (c) **Me-4TTF** recorded at a scan rate of 0.1 V/S in $CHCl_3$ at 25 ^{o}C, the total TTF unit concentration is 2.0 mM, n-Bu_4NPF_6 (0.1 M) was used as the supporting electrolyte and saturated calomel electrode (SCE) as the reference electrode.

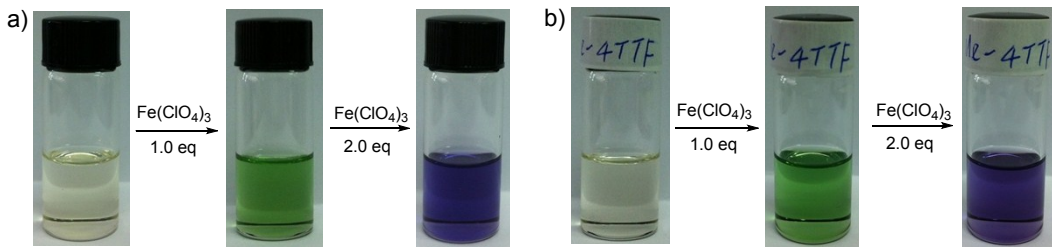

Fig. S2 The solution color of (a) **Me-2TTF** and (b) **Me-4TTF** in $CHCl_3$ with 0, 1.0 and 2.0 equiv of $Fe(ClO_4)_3$ respected to the total TTF concentration.

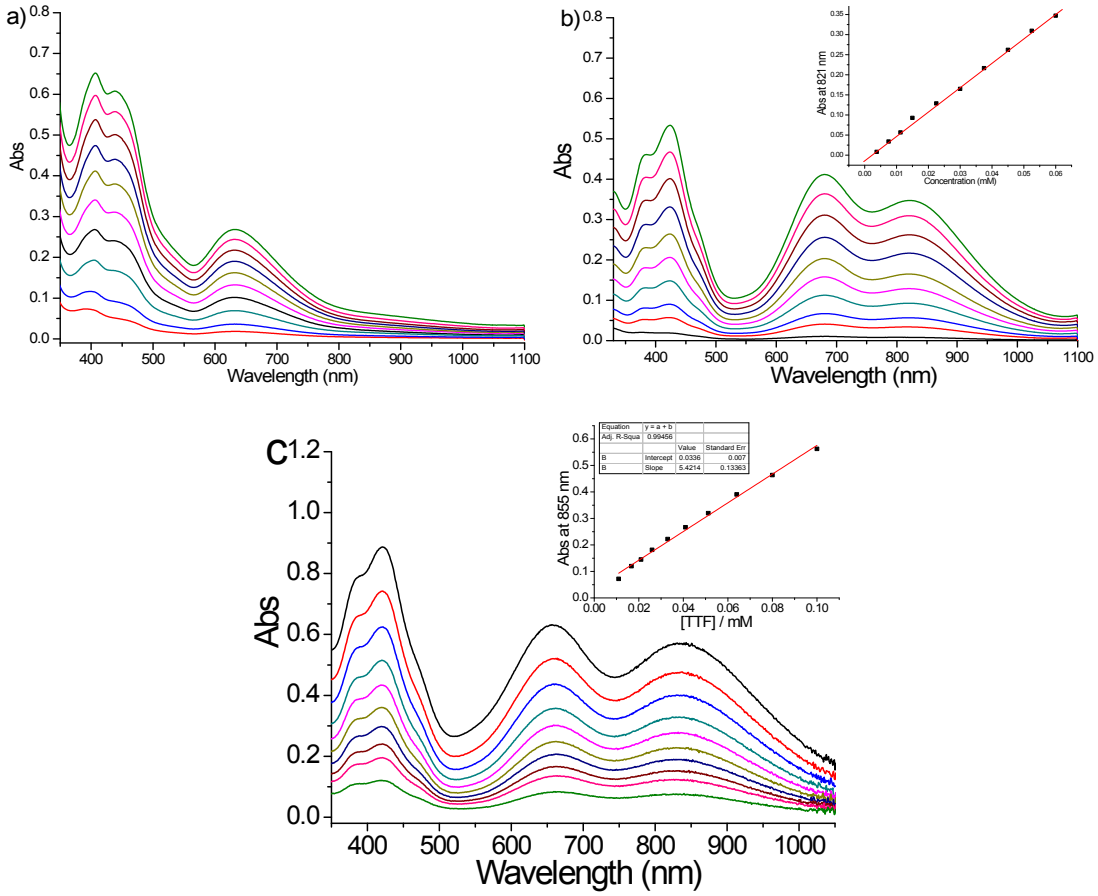

Fig. S3 The UV-vis-NIR dilution absorption spectra of (a) **1** in $CHCl_3$; (b) **Me-2TTF** in $CHCl_3$ (inset: absorption changes vs concentration recorded at 821 nm); (c) **Me-4TTF** in $CHCl_3$ (inset: absorption changes vs concentration recorded at 855 nm)

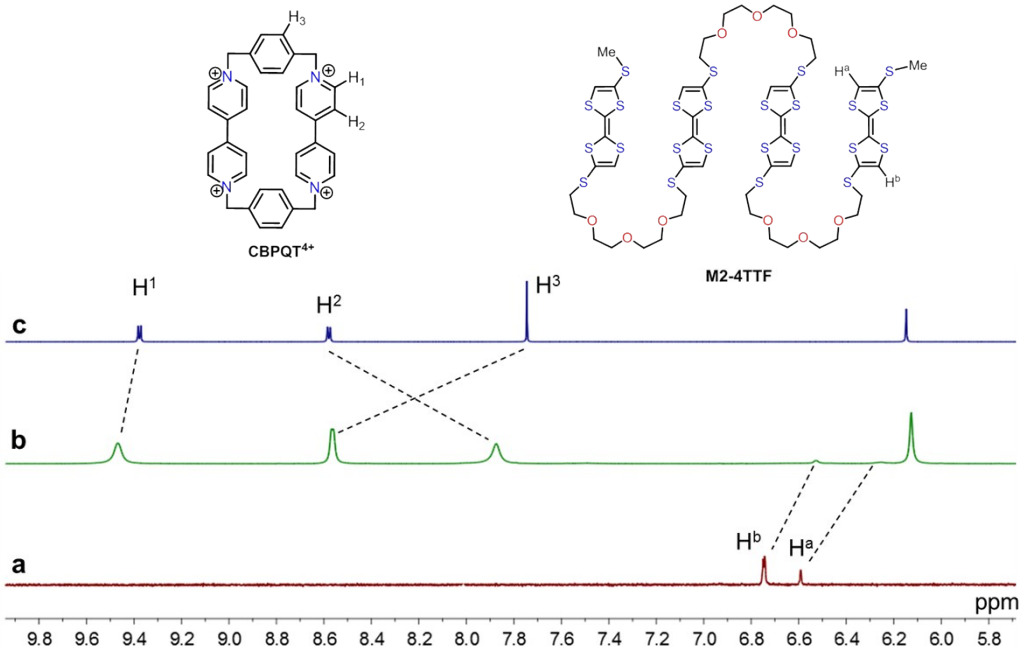

Fig. S4 (a) The UV-vis-NIR titration absorption spectra of **Me-4TTF** (2 mM) with $CBPQT^{4+}$ (0 to

1.0 equiv) in acetone-d_6 at 20°C.

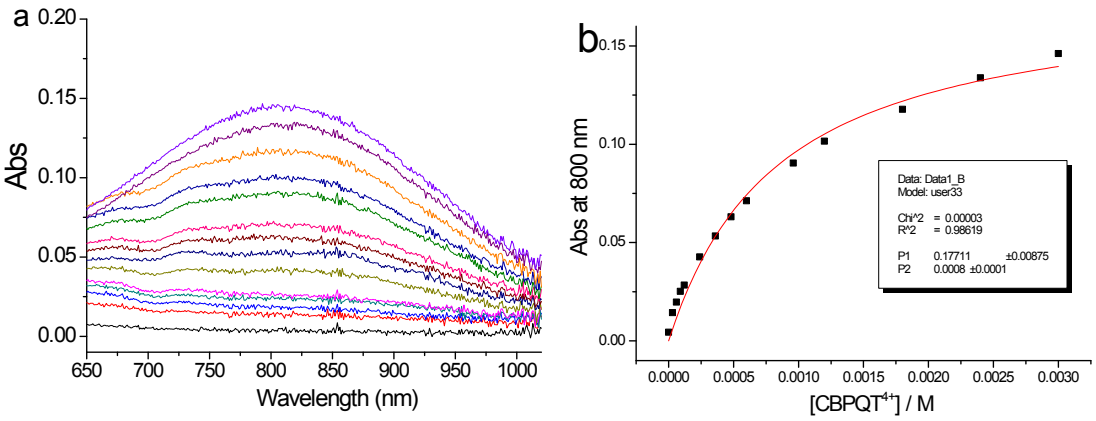

Fig. S5 (a) The UV-vis-NIR titration absorption spectra of **Me-4TTF** (0.02 mM) with $CBPQT^{4+}$ (0 to 4.0 equiv) in acetone at 25°C; (b) Fitting plot of the maximum CT absorption band at 800 nm of **Me-4TTF** with $CBPQT^{4+}$ ring to a nonlinear self-binding equation.

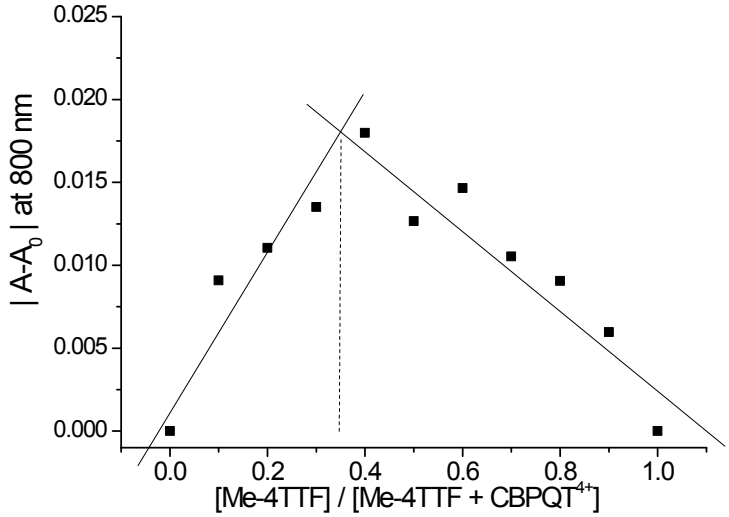

Fig. S6 Job's plot of **Me-4TTF** with $CBPQT^{4+}$ (total concentration was 0.06 mM) in acetone at 25°C.

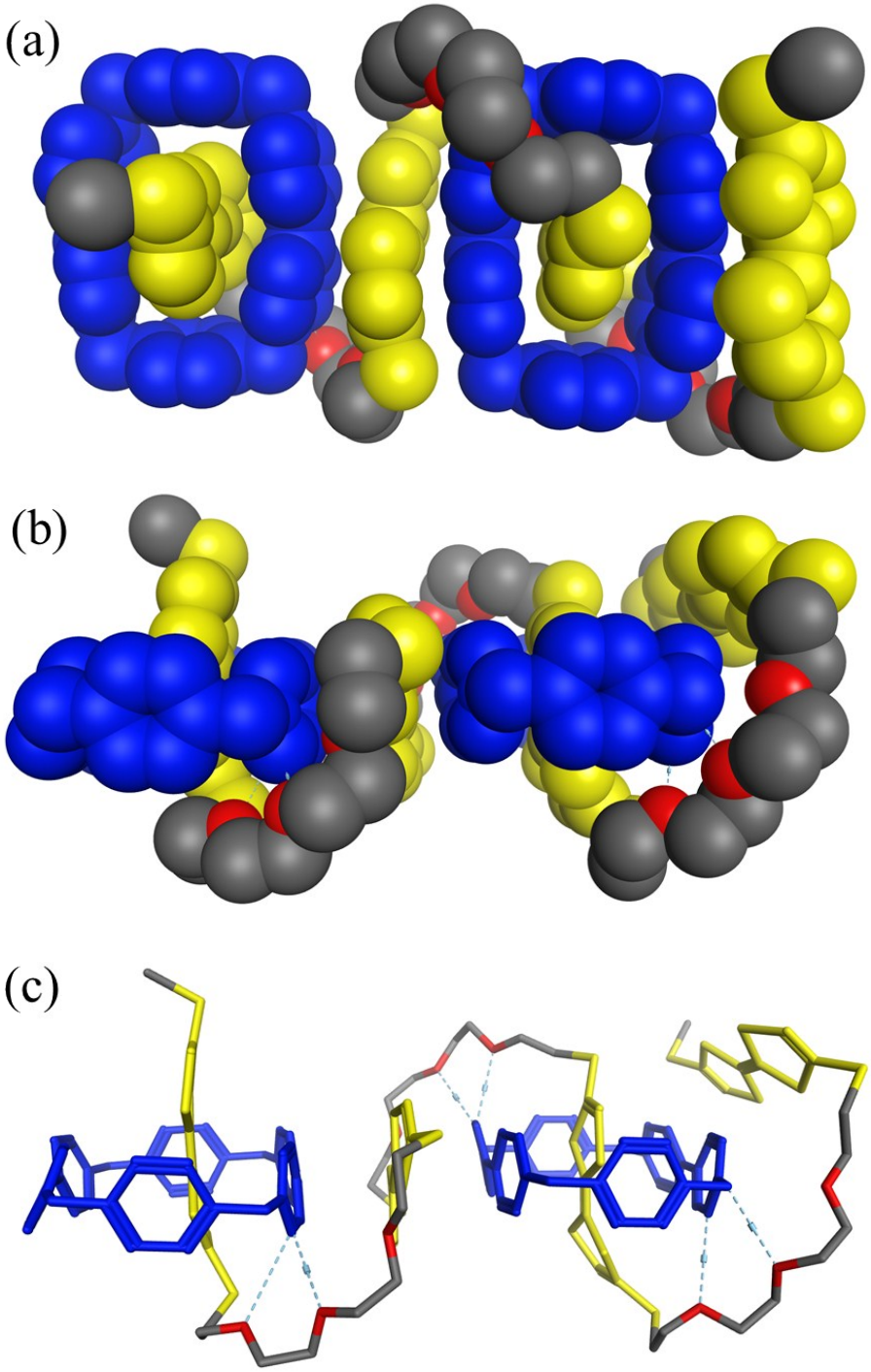

Fig. S7 The top view (a) and the side view (b) of the optimized folded donor-acceptor [3]pseudorotaxane in space-filling mode (75% atomic van der Waals radii). The **TTF** and **CBPQT**$^{4+}$ moieties were colored by yellow and blue, respectively. The view (c) in stick mode showed the [C−H···O] interactions (depicted by dash line) between the hydrogens α to pyridinium nitrogens in **CBPQT**$^{4+}$ and glycol oxygens in **Me-4TTF**.

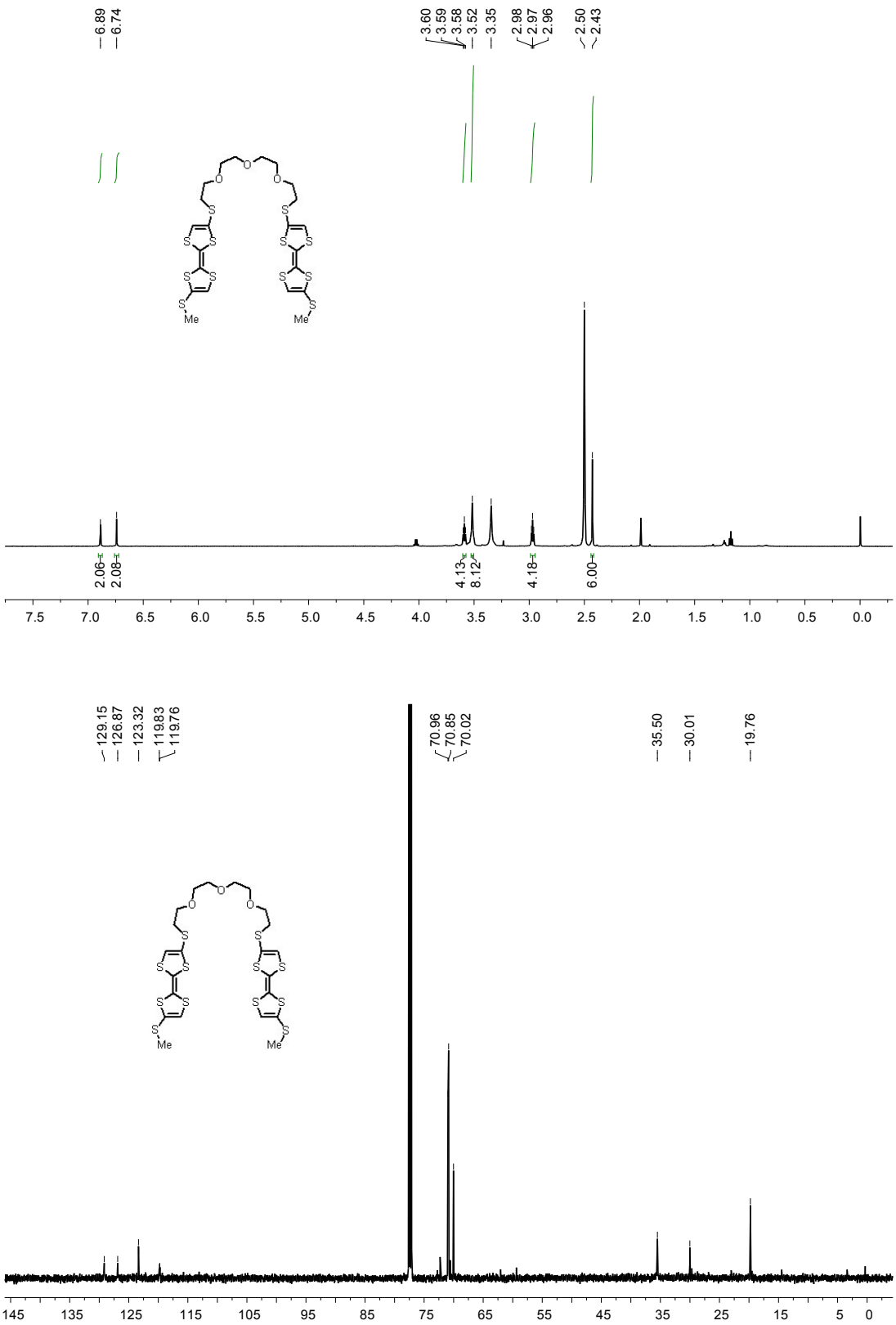

Fig. S8 The ^{1}H NMR (DMSO-d_6, 400 MHz, 298K) and ^{13}C NMR ($CDCl_3$, 150 MHz, 298K) spectra of **Me-2TTF**.

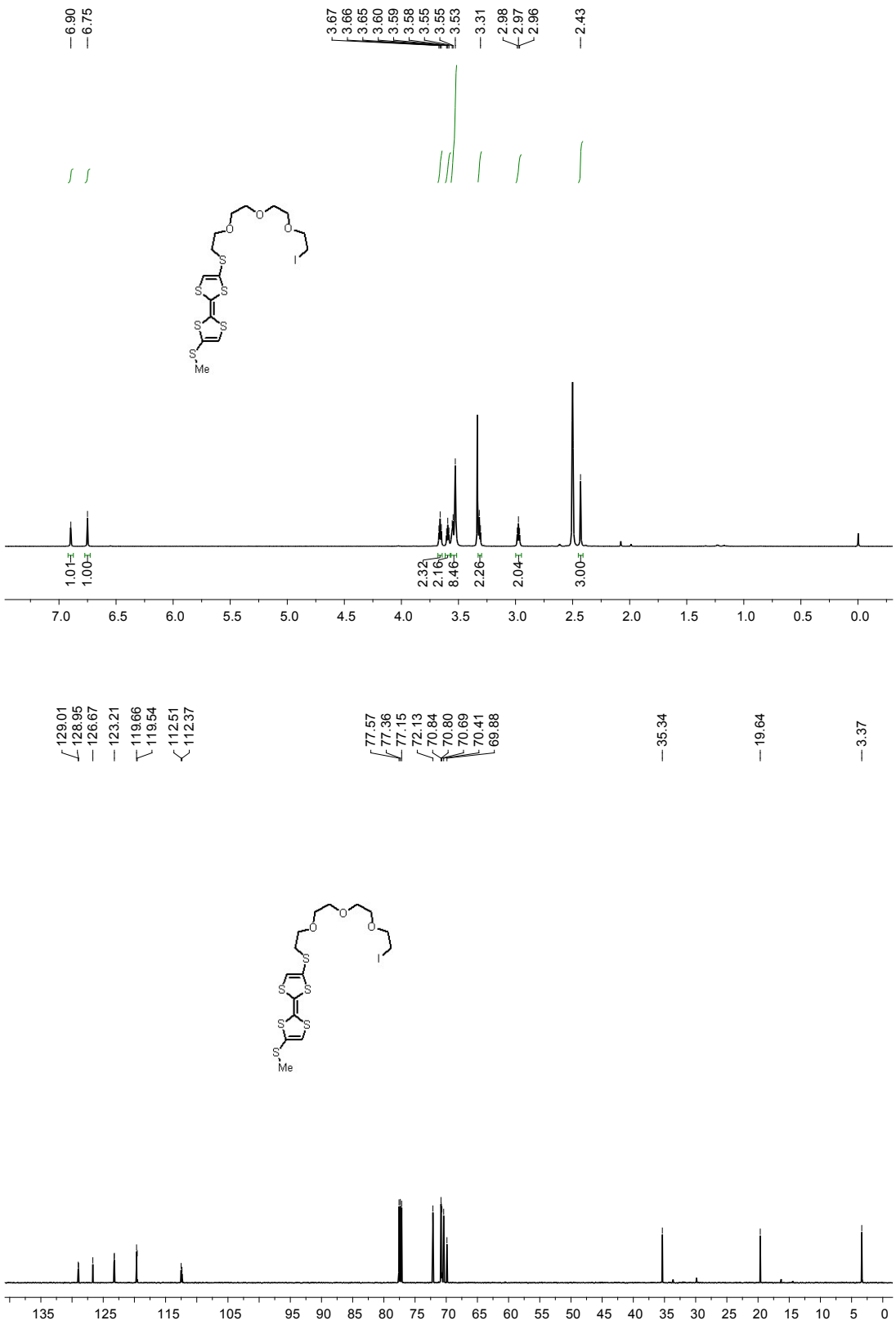

Fig. S9 The ^{1}H NMR (DMSO-d_6, 400 MHz, 298K) and ^{13}C NMR ($CDCl_3$, 150 MHz, 298K) spectra of compound **4**.

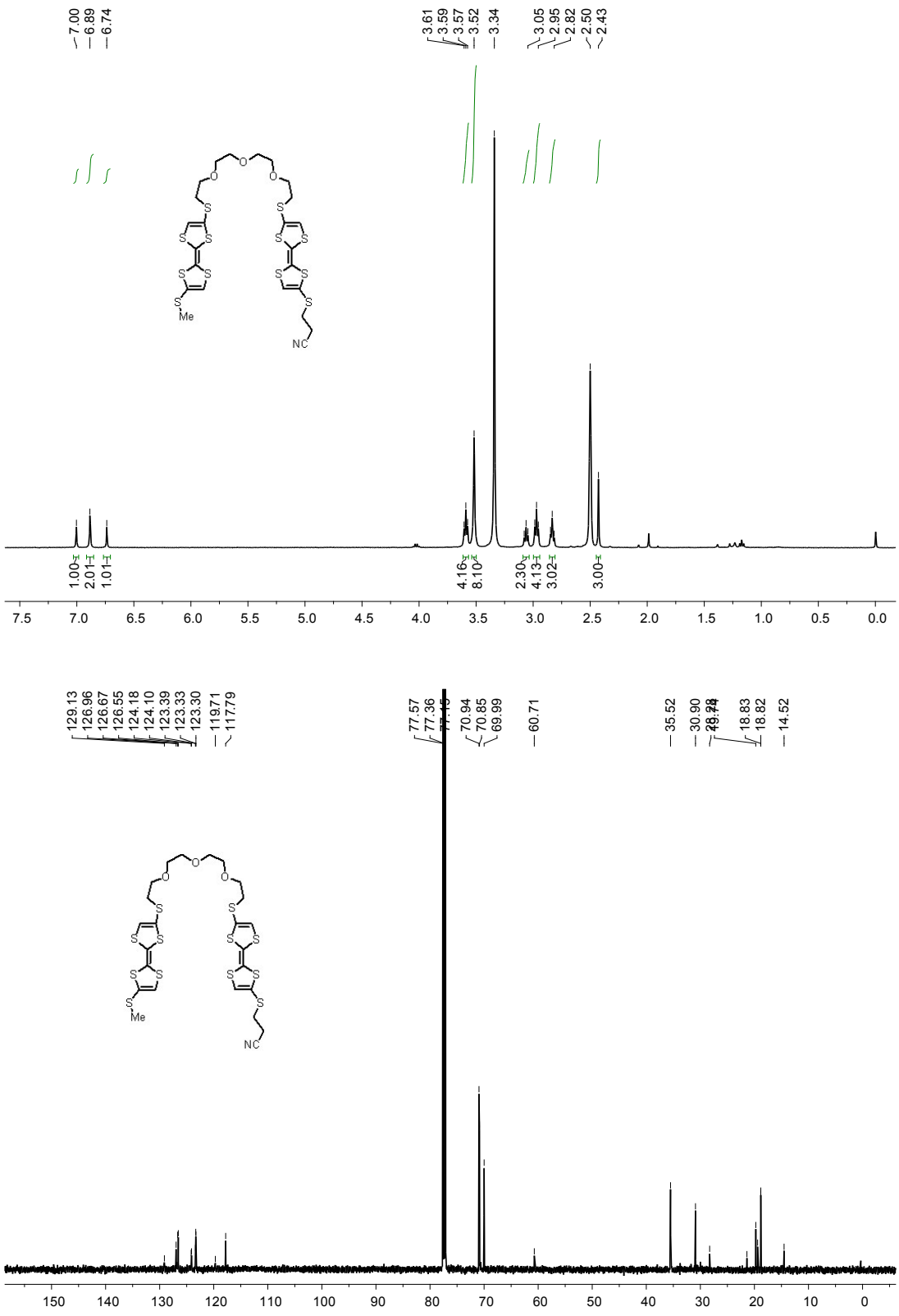

Fig. S10 The ^{1}H NMR (DMSO-d_6, 400 MHz, 298K) and ^{13}C NMR ($CDCl_3$, 150 MHz, 298K) of compound **5**.

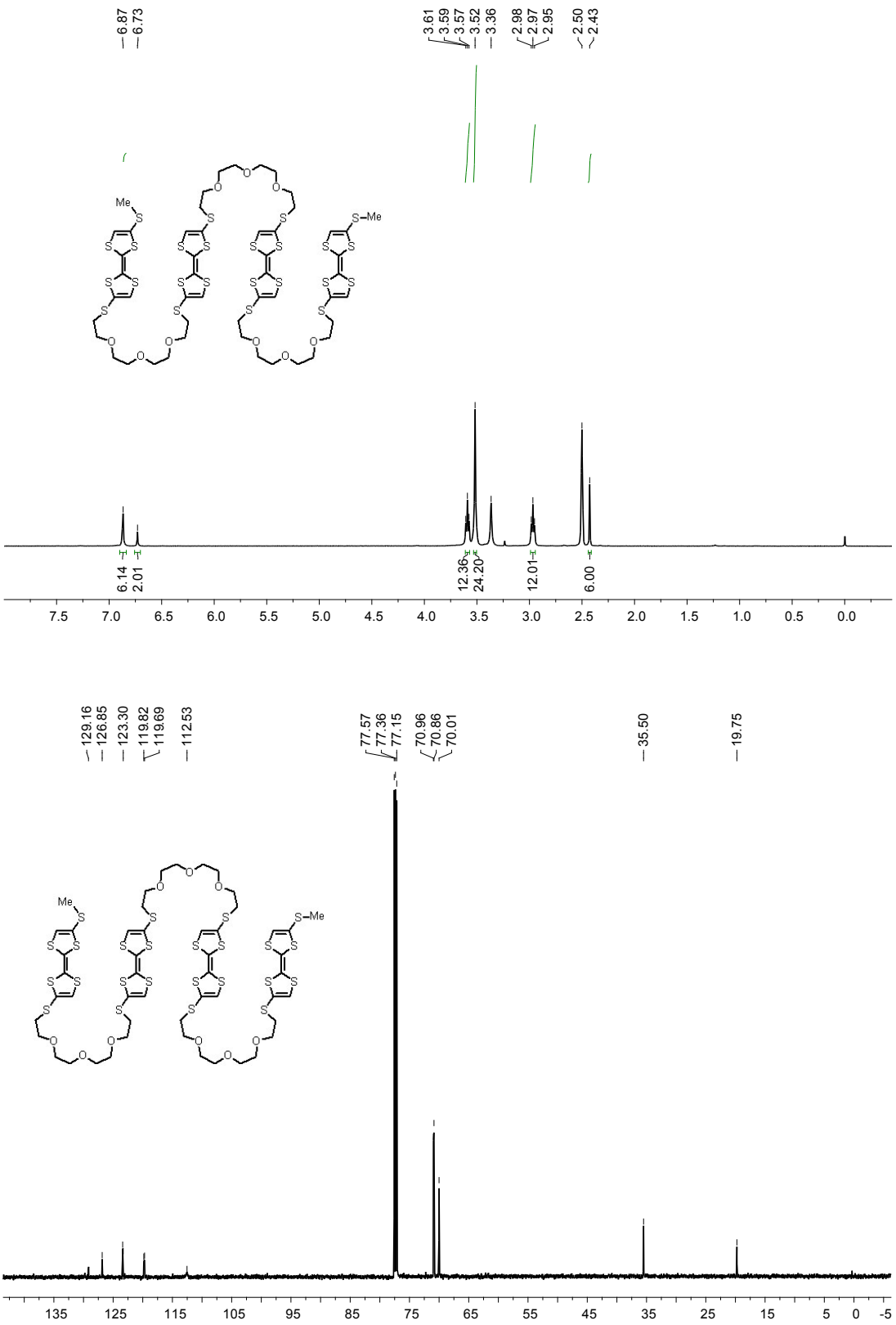

Fig. S11 The ^{1}H NMR (DMSO-d_6, 400 MHz, 298K) and ^{13}C NMR ($CDCl_3$, 150 MHz, 298K) of **Me-4TTF**.

References

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