Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Monopyrrolotetrathiafulvalene and their TCNQ charge-transfer complex based supramolecular gels with multiple stimulus responsiveness

Supporting Information

*Yucun Liu, Ningjuan Zheng, Tie Chen, Longyi Jin and Bingzhu Yin**

zqcong@ybu.edu.cn

Key Laboratory for Natural Resources of Changbai Mountain & Functional Molecules of Ministry of Education and Department of Chemistry, Yanbian University, Yanji, Jilin 133002 (China)
Fax: +86 433 2732456; Tel: +86 433 2732298

1. Instrumentation

Gelation study

A weight amount of the gelator **1** with or without TCNQ adding a measured volume of the solvent were placed in a sealed test tube and made a clear solution by heating. And then, the system left at room temperature. The transition temperatures (T_{gel}) were determined by ball-drop method.

NMR experiments

All solution state NMR studies were carried out on Bruker AV-300 Spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) and chemical shifts were referenced relative to tetramethylsilane (δ_H/δ_C=0).

FT-IR spectroscopy

IR spectra were recorded on a Shimadzu FT-IR Prestige-21 instrument with the KBr disk technique.

MALDI-TOF-MS spectrometry

Mass spectra were performed on a Shimadzu Axima CFR^{TM} Plus using a 1,8,9-anthracenetriol (DITH) and β-phenylacrylic acid (CHCA) matrix.

ESI-MS spectrometry

The high-resolution mass spectra were obtained using a Bruker microTOF II focus spectrometer (ESI).

Cyclic voltametry

Cyclic voltammetry was performed with CHI660D instruments in a mixture of CH_3CN/CH_2Cl_2 (1:1, 1 mM) with 0.1 M Bu_4NPF_6 as the supporting electrolyte and a scan rate of 100 mVs^{-1}. Counter and working electrodes were made of Pt and glass carbon, respectively, and an Ag/AgCl was used as the reference electrode. A small amount of the gel or CT gel was carefully put on the glass carbon electrode, which was left in air for 24h.

UV-vis spectroscopy

UV-vis spectra were recorded on a Hitachi U-3010 spectrophotometer.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) curve was measured by DTG60 at a heating rate of 10 ºC min^{-1} under N_2 atmosphere.

Field emission scanning electron microscopy

The gel samples were placed on silicon wafer, and dried for 24h under room temperature before imaging. A layer of gold was sputtered on top to form a conducting surface and finally the specimen was transferred into the Field Emission Scanning Electron Microscope (FE-SEM, Joel Scanning Microscope-JSM-6700F and Hitachi Scanning Microscope-3500N).

Small-angle X-ray scattering

Small-angle X-ray scattering (SAXS) measurements were carried out at 298 K on a beamline 1W2A synchrotron radiation X-ray small angle system at Beijing Synchrotron Radiation Facility(λ =1.54Å).

Electron paramagnetic resonance (EPR) spectroscopy

The EPR spectra were obtained on a JES-FA 200 EPR spectrometer. The instrumental parameters were as follows: scanning frequency, 9.45 GHz; central field, 3371.44 G; scanning width, 8000 G; scanning power, 0.998 mW; scanning temperature, 25℃.

2. Synthesis and characterization of organic compounds

All solvents were purified and dried according to literature methods. The compound **6** was synthesized according to the literature procedure. [1]

2-(4,5-bis(butylthio)-1,3-dithiol-2-ylidene)-5-(3-bromopropyl)-5*H*-[1,3]d-ithiolo[4,5-*c*]pyrrole (5): Compound **6** (311.3 mg, 0.7417 mmol) and NaH (106.8 mg, 4.4502 mmol) were suspended in anhyd DMF (8.0 mL) and degassed (N_2, 20 min). Then, 1, 3-Dibromopropane was added in one portion. The reaction mixture was stirred for 3.0 h at room temperature. After addition of saturated brine (20 mL), the mixture was extracted with CH_2Cl_2, and the extract was washed with brine and dried ($MgSO_4$). After concentration, the resulting crude product was purified through flash column chromatography (silica gel, dichloromethane/ petroleum ether, v: v=1:6) to give 337.2 mg (84.0%) of **5** as yellow oil. ^{1}H NMR (300MHz, $CDCl_3$) δ0.92 (t, J = 6.0Hz, 6H), 1.37-1.49 (m, 4H), 1.57-1.67 (m, 4H), 2.17-2.25 (m, 2H), 2.83 (t, J = 6.0Hz, 4H), 3.31 (t, J = 6.0Hz, 2H), 4.04 (br, 2H), 6.50 (s, 2H); ^{13}C NMR(75MHz, $CDCl_3$) δ128.35, 127.48, 119.33, 112.56, 48.13, 35.98, 33.94,

31.80, 30.01, 21.69, 13.66; MALDI-TOF MS *m/z* Calcd for $C_{21}H_{30}BrNS_6$: 538.96. Found: 538.52 ($[M]^+$, 100).

5-(3-azidopropyl)-2-(4,5-bis(butylthio)-1,3-dithiol-2-ylidene)-5*H*-[1,3]d-ith-iolo[4,5-*c*]pyrrole (4): Compound **5** (337.2 mg, 0.6236 mmol) and NaN_3 (608.2 mg, 9.39 mmol) were suspended in anhyd DMF (11.0 mL), then stirred and heated to 90 ºC react for 12.0 h. After addition of saturated brine (50 mL), the mixture was extracted with CH_2Cl_2, and the extract was washed with brine and dried ($MgSO_4$). After concentration, the resulting crude product was purified through flash column chromatography (silica gel, dichloromethane/ petroleum ether, v: v=1:3) to give 286.2 mg (91.0%) of **4** as yellow oil. ^{1}H NMR (300MHz, $CDCl_3$) δ0.92 (t, *J* = 6.0Hz, 6H), 1.37-1.49 (m, 4H), 1.56-1.66 (m, 4H), 1.90-1.99 (m, 2H), 2.82 (t, *J* = 6.0Hz, 4H), 3.26 (t, *J* = 6.0Hz, 2H), 3.94 (br, 2H), 6.50 (s, 2H); ^{13}C NMR(75MHz, $CDCl_3$) δ127.47, 119.65, 119.31, 112.51, 111.14, 47.97, 47.33, 35.96, 31.80, 30.60, 21.68, 13.64; MALDI-TOF MS *m/z* Calcd for $C_{19}H_{26}N_4S_6$: 502.05. Found: 501.65 ($[M]^+$, 100).

3-(2-(4,5-bis(butylthio)-1,3-dithiol-2-ylidene)-5*H*[1,3]dithiolo[4,5-*c*]pyr-rol-5-yl)propan-1-amine (3): Compound **4** (286.2 mg, 0.5692 mmol) and PPh_3 (328.4 mg, 1.1384 mmol) were dissolved in THF (14.0 mL), H_2O (102.5 μL, 5.6920 mmol) was added to this solution. The mixture was stirred and heated to 45 ºC react, after 17.0 h the reaction mixture was concentrated. Purification of the product was conducted by flash column chromatography (silica gel, dichloromethane/ methanol, v: v=20:1) to give 255.7 mg (94.2%) of **3** as orange-yellow solid. ^{1}H NMR (300MHz, $CDCl_3$)□δ0.92 (t, *J* = 6.0Hz, 6H), 1.37-1.49 (m, 4H), 1.56-1.66 (m, 4H), 1.90-1.99 (m, 2H), 2.74 (t, *J* = 6.0Hz, 2H), 2.82 (t, *J* = 6.0Hz, 4H), 3.21 (br, 2H), 3.94 (br, 2H), 6.50 (s, 2H); ^{13}C NMR(75MHz, $CDCl_3$) δ127.45, 119.69, 118.85, 112.56, 110.82, 48.03, 38.53, 35.95, 33.71, 31.71, 21.68, 13.58. MALDI-TOF MS *m/z* Calcd for $C_{19}H_{28}N_2S_6$: 476.06. Found: 476.03 ($[M]^+$, 100).

4-((3-(2-(4,5-bis(butylthio)-1,3-dithiol-2-ylidene)-5*H*-[1,3]dithiolo[4,5-*c*]pyrrol-5- yl)propyl)a-mino)-4-oxobutanoic acid (2): Compound **3** (189.4 mg, 0.3972 mmol) and N,N- Diisopropyl-ethylamine (138.3 μL, 0.7944 mmol) were dissolved in CH_2Cl_2 (10.0 mL). Under stirring, Succinic anhydride (198.6 mg, 1.9860 mmol) was dropped in the solution, overnight. The reaction mixture was concentrated, and Purification of the product was conducted by flash column chromatography (silica gel, dichloromethane/ methanol, v: v=20:1) to give 181.7 mg (81.3%) of **2** as yellow solid. ^{1}H NMR (300MHz, $CDCl_3$)□δ0.92 (t, *J* = 6.0Hz, 6H), 1.37-1.49 (m, 4H), 1.63 (br, 4H), 1.86 (br, 2H), 2.42 (br, 2H), 2.64 (br, 2H), 2.90 (br, 4H), 3.20 (br, 2H), 6.16 (br, 1H), 6.50 (br, 2H), 8.83 (br, 1H); ^{13}C NMR(75MHz, $CDCl_3$) δ176.74, 172.94, 37.12, 31.98, 31.71,

30.60, 29.58, 21.71, 13.67; MALDI-TOF MS *m/z* Calcd for $C_{23}H_{32}N_2O_3S_6$: 576.07. Found: 575.73 ($[M]^+$, 100).

***N*^{1}-(3-(2-(4,5-bis(butylthio)-1,3-dithiol-2-ylidene)-5*H*-[1,3]dithiolo[4,5-*c*]pyrrol-5-yl) propyl)-*N*^{4}-butylsuccinamide (1a):** Compound **2** (181.7 mg, 0.3230 mmol), EDCI (120.8 mg, 0.6460 mmol), HOBt (85.2 mg, 0.6460 mmol) and *n*-Butylamine (61.4 μL, 0.6460 mmol) were dissolved in CH_2Cl_2 (10.0 mL) and stirred for 8.0 h at room temperature. The reaction mixture was poured into 50 mL water. The organic layer was dried with $MgSO_4$. After concentration, the crude product was purified through flash column chromatography (silica gel, dichloromethane/methanol, v: v=100:1) to give 158.5 mg (77.7%) of **1a** as yellow solid. m.p.: 142.5 ºC; ^{1}H NMR (300MHz, $CDCl_3$) δ0.89-0.94 (m, 9H), 1.25-1.52 (m, 10H), 1.57-1.67 (m, 4H), 1.87-1.96 (m, 2H), 2.46 (br, 4H), 2.83 (br, 4H), 3.23 (q, *J* = 6.0Hz, 4H), 5.85 (br, 1H), 6.33 (br, 1H), 6.50 (s, 2H); ^{13}C NMR(75MHz, $CDCl_3$) δ172.70, 172.25, 127.52, 119.09, 112.50, 48.10, 39.84, 36.75, 36.02, 31.84, 29.71, 29.42, 27.05, 22.75, 21.72, 14.18, 13.66; MALDI-TOF MS *m/z* Calcd for $C_{27}H_{41}N_3O_2S_6$: 631.15. Found: 630.79 ($[M]^+$, 100).

***N*^{1}-(3-(2-(4,5-bis(butylthio)-1,3-dithiol-2-ylidene)-5*H*-[1,3]dithiolo[4,5-*c*]pyrr-ol- 5-yl)propyl) -*N*^{4}-octylsuccinamide (1b):** This compound was prepared in a fashion similar to **1a**. Yield: 58.6%. m.p.: 131.4 ºC; ^{1}H NMR (300MHz, $CDCl_3$) δ0.86-0.94 (m, 9H), 1.27 (br, 10H), 1.40-1.49 (m, 6H), 1.58-1.68 (m, 6H), 1.88-1.96 (m, 2H), 2.50 (br, 4H), 2.84 (br, 4H), 3.22 (q, *J* = 6.0Hz, 4H), 5.84 (br, 1H), 6.32 (br, 1H), 6.51 (s, 2H); ^{13}C NMR(75MHz, $CDCl_3$) δ172.74, 172.22, 39.92, 36.76, 31.94, 31.73, 29.72, 29.58, 29.37, 29.32, 26.95, 22.70, 21.82, 14.13, 13.63; MALDI-TOF MS *m/z* Calcd for $C_{27}H_{41}N_3O_2S_6$: 687.40. Found: 687.21 ($[M]^+$, 100).

***N*^{1}-(3-(2-(4,5-bis(butylthio)-1,3-dithiol-2-ylidene)-5*H*-[1,3]dithiolo[4,5-*c*]pyrr-ol-5-yl)propyl)-*N*^{4}-dodecylsuccinamide (1c):** This compound was prepared in a fashion similar to **1a**. Yield: 83.4%. m.p.: 130.7 ºC; ^{1}H NMR (300MHz, $CDCl_3$) δ0.86-0.94 (m, 9H), 1.25 (br, 20H), 1.37-1.49 (m, 6H), 1.60-1.64 (m,4H), 1.89-1.97 (m, 2H), 2.50 (br, 4H), 2.84 (t, *J* = 3.0Hz, 4H), 3.21 (q, *J* = 6.0Hz, 4H), 5.95 (br, 1H), 6.12 (br, 1H), 6.51(s, 2H); ^{13}C NMR(75MHz, $CDCl_3$) δ172.84, 172.38, 127.65, 119.22, 112.63, 48.23, 39.98, 36.88, 36.15, 32.11, 31.98, 31.92, 29.87, 29.84, 29.79, 29.55, 27.18, 22.88, 21.85, 14.32, 13.79; MALDI-TOF MS *m/z* Calcd for $C_{27}H_{41}N_3O_2S_6$: 743.5. Found: 744.2 ($[M]^+$, 100).

***N*^{1}-(3-(2-(4,5-bis(butylthio)-1,3-dithiol-2-ylidene)-5*H*-[1,3]dithiolo[4,5-*c*]pyrr-ol-5-yl)propyl)-*N*^{4}-hexadecylsuccinamide (1d):** This compound was prepared in a fashion similar to **1a**. Yield: 64.8%. m.p.: 130.1 ºC; ^{1}H NMR (300MHz, $CDCl_3$) δ0.87-0.96 (m, 9H), 1.26 (br, 28H), 1.39-1.48 (m, 6H), 1.63 (br, 4H), 1.93 (br, 2H), 2.52 (br, 4H), 2.88 (br, 2H), 3.14-3.27 (m, 4H), 5.79 (br, 1H), 6.29 (br, 1H), 6.54 (s, 2H); ^{13}C NMR(75MHz, $CDCl_3$) δ172.76, 172.24, 48.44, 39.98, 36.83, 31.98,

29.76, 29.67, 29.63, 29.58, 29.41, 29.37, 26.99, 22.74, 21.76, 14.17, 13.66; MALDI-TOF MS *m/z* Calcd for $C_{27}H_{41}N_3O_2S_6$: 799.7. Found: 800.3 ([M]$^+$, 100).

***N*^{1}-(3-(2-(4,5-bis(butylthio)-1,3-dithiol-2-ylidene)-5*H*-[1,3]dithiolo[4,5-*c*]pyrr-ol-5-yl)propyl)-*N*^{4}-octadecylsuccinamide (1e):** This compound was prepared in a fashion similar to **1a**. Yield: 71.4%. m.p.:129.9 ºC; ^{1}H NMR (300MHz, $CDCl_3$) δ 0.86-0.94 (m, 9H), 1.25 (br, 30H), 1.37-1.40 (m, 6H), 1.60-1.67 (m, 6H), 1.89-1.96 (m, 2H), 2.49 (br, 4H), 2.85 (br, 4H), 3.21 (q, J = 6.0Hz, 4H), 5.80 (br, 1H), 6.31 (br, 1H), 6.51 (s, 2H); ^{13}C NMR(75MHz, $CDCl_3$) δ 172.88, 172.33, 127.26, 118.20, 108.67, 43.15, 40.03, 36.98, 36.05, 32.05, 31.84, 31.70, 29.83, 29.70, 29.64, 29.48, 29.43, 27.05, 22.81, 21.91, 14.25, 13.75; MALDI-TOF MS *m/z* Calcd for $C_{27}H_{41}N_3O_2S_6$: 827.6. Found: 828.4 ([M]$^+$, 100).

3. Gelation tests

Table S1 Gelation properties of **1** in various solvents.

Solvents	**1a**[a]	CGC[b]	**1b**	CGC	**1c**	CGC	**1d**	CGC	**1e**	CGC
Cyclohexane	TG	1.0	OG	2.5	P	—	P	—	P	—
MCH	OG	1.1	P	—	PG	—	P	—	P	—
n-Hexane	IS	—	IS	—	IS	—	IS	—	IS	—
n-Octane	IS	—	IS	—	P	—	P	—	P	—
EtOAc	S	—	S	—	P	—	P	—	P	—
CH_2Cl_2	S	—	S	—	S	—	S	—	S	—
$CHCl_3$	S	—	S	—	S	—	S	—	S	—
CCl_4	S	—	S	—	S	—	S	—	S	—
Benzene	S	—	S	—	S	—	S	—	S	—
Toluene	S	—	S	—	P	—	P	—	P	—
DMSO	S	—	S	—	S	—	P	—	P	—
DMF	S	—	S	—	S	—	S	—	S	—
THF	S	—	S	—	S	—	S	—	S	—
Methanol	P	—	P	—	P	—	P	—	P	—
Ethanol	S	—	S	—	P	—	P	—	P	—
CH_3CN	P	—	P	—	P	—	P	—	P	—

[a]TG = transparent gel; OG = opaque gel; P = precipitation; S = soluble; IS = insoluble; PG = partial gel

[b]CGC = the critical gelation concentrations (mg/mL) at room temperature.

4. Image of gel-sol transition

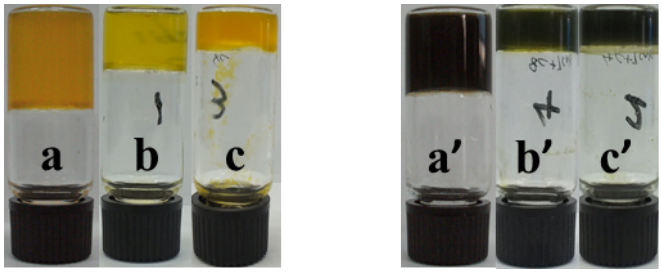


Figure S1 The photographs of gelators (a) **1a** in cyclohexane, (b) **1a** in MCH, (c) **1b** in cyclohexane and corresponding to the CT complex gels a', b' and c', respectively.

5. T_{gel} of CT complex gel

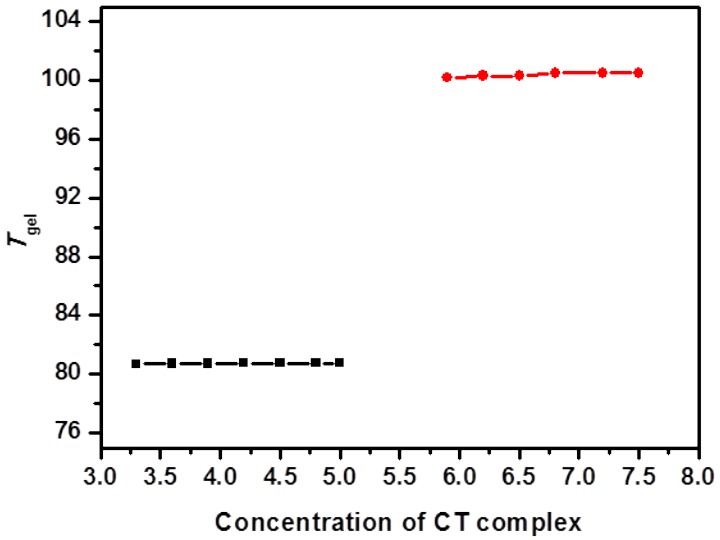


Figure S2 Plots of T_{gel} versus the concentration of CT complex (**1a** : TCNQ = 1： 1, mole ratio) in cyclohexane (■) and MCH (●).

6. TGA curves

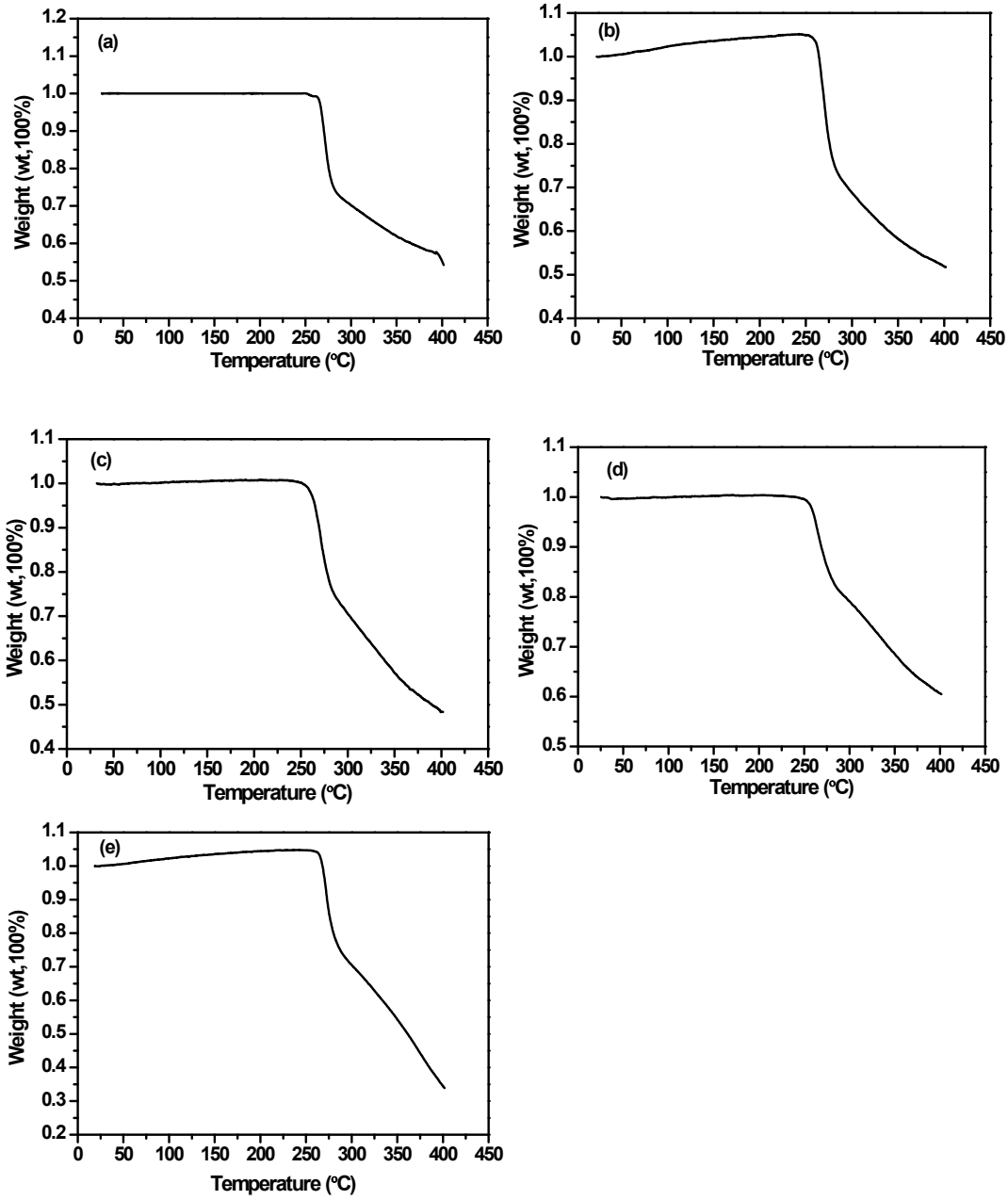


Figure S3 TGA curve of **1b** (a), **1c** (b), **1d** (c) and **1e** (d) with a heating rate of 10 ºC min^{-1} under N_2.

Table S2 Thermal properties of molecules.

Temperature	**1a**	**1b**	**1c**	**1d**	**1e**
T_m (°C)	142.5	131.4	130.7	130.1	129.9
T_d (°C)	252.6	251.7	249.4	248.3	247.9

7. SAXS analysis

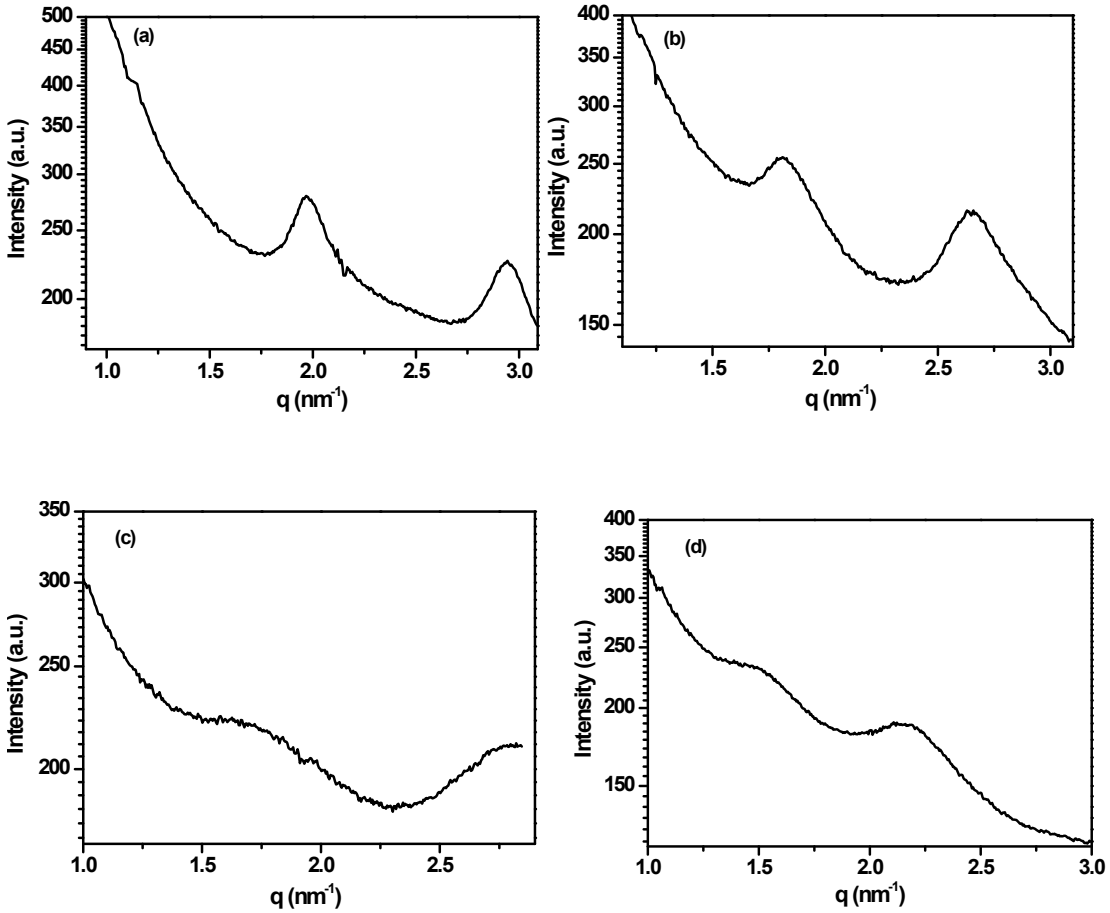
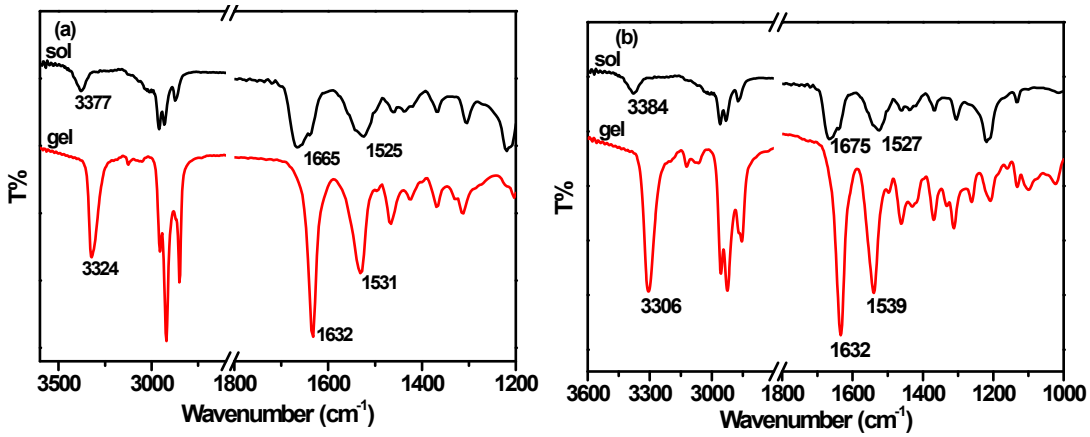


Figure S4 SAXS patterns of xerogel **1a** (a) and **1a**/TCNQ (mole ratio = 1:1, b) from MCH; xerogel **1b** (c) and **1b**/TCNQ (mole ratio = 1:1, d) from cyclohexane.

8. FT-IR Spectra



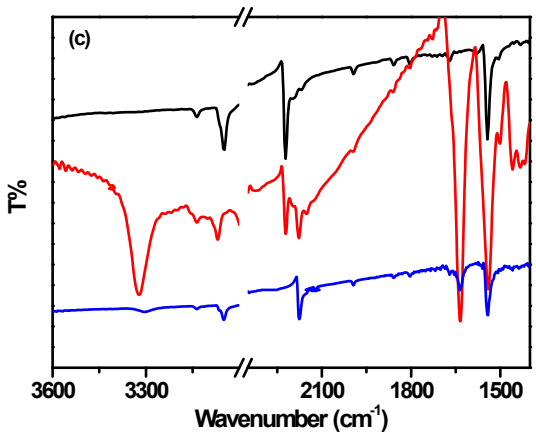


Figure S5 FT-IR spectra of (a) **1a** in $CHCl_3$ solution (black) and xerogel from MCH (red); (b) **1b** in $CHCl_3$ solution (black) and xerogel from cyclohexane (red); (c) the CT complex xerogel of **1a** with TCNQ (1: 1) from MCH (red) and **1b** with TCNQ (1: 1) from cyclohexane (blue).

9. ^{1}H NMR spectra of 1a

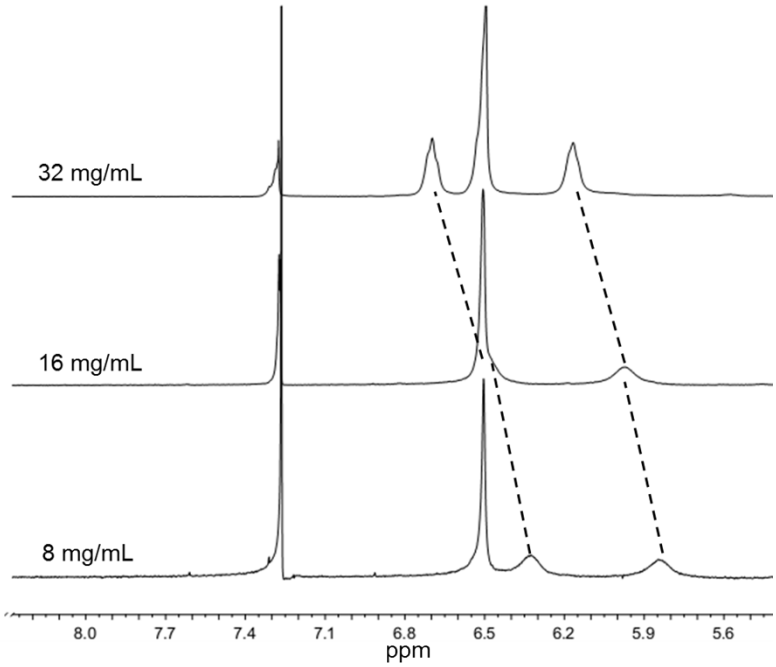


Figure S6 Variable-concentration ^{1}H-NMR spectra of **1a** in $CDCl_3$.

10. Oxidation Potentials

Table S3 Half-Wave Oxidation Potentials (V).

Properties	TCNQ			TTF	
	E^{ox}_1 (V)	E^{ox}_2 (V)	E^{ox}_3 (V)	E^{ox}_1 (V)	E^{ox}_2 (V)
1a in cyclohexane	——	——	——	0.564	0.931
Cyclohexane gel	——	——	——	0.513	0.885
CT complex gel	-0.713	-0.206	0.355	0.524	0.837
Solution of TCNQ	-0.767	-0.3	0.269	——	——

11. CV curves

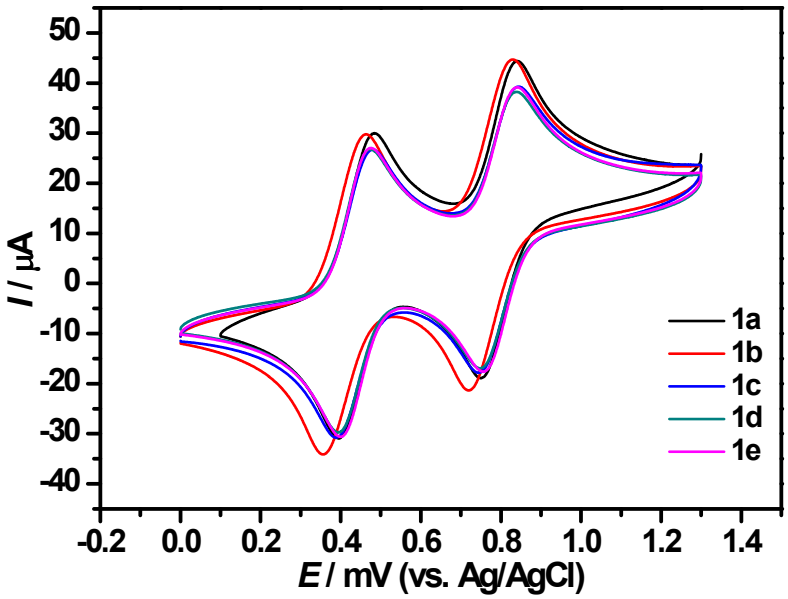


Figure S7 Cyclic voltammograms and differential pulse voltammetry (inset) of compounds **1a-c** (1×10^{-3} M) in CH_2Cl_2-CH_3CN (1:1, v/v) containing 0.1 M Bu_4NPF_6. Scan rate was 100 mV s^{-1}.

12. FT-IR spectra of addition of I_2

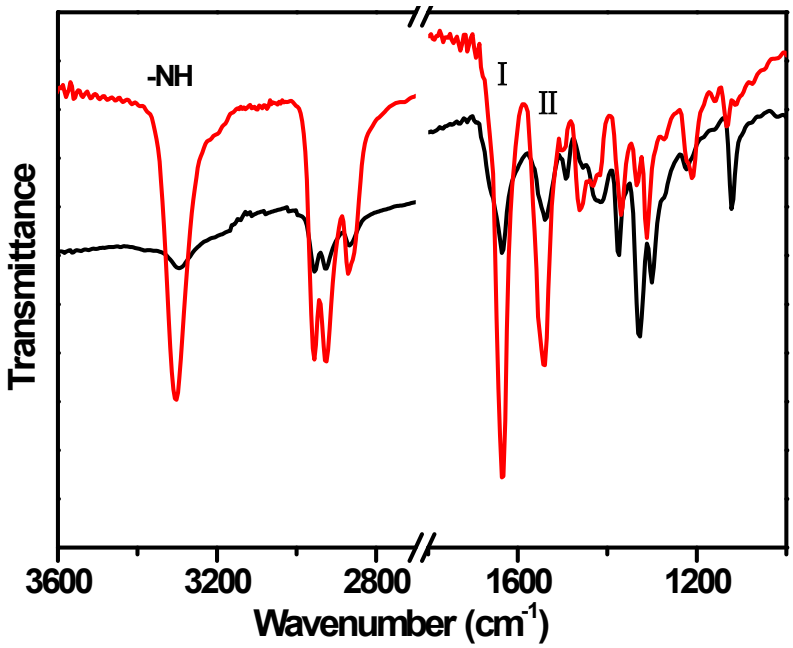


Figure S8 FT-IR spectra of xerogel **1a** (red line) and after addition of iodine (black line).

13. Colorimetric changes of redox reactions

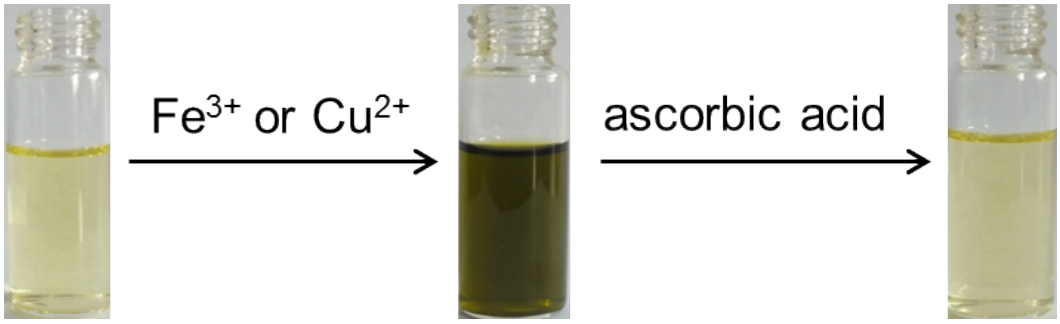


Figure S9 Colorimetric changes of **1a** (10^{-4} M) in ethanol by chemical redox process.

14. oxidants-responsive properties of CT complex gel

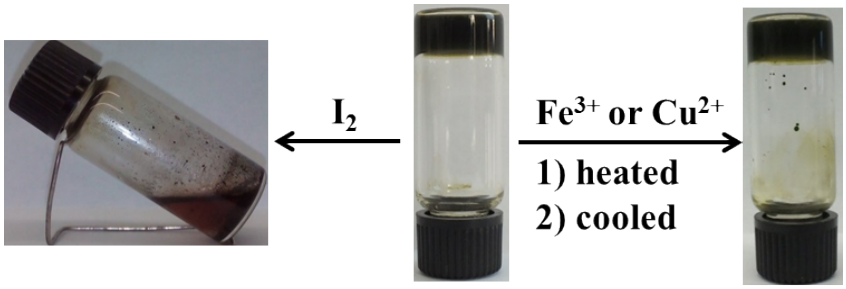
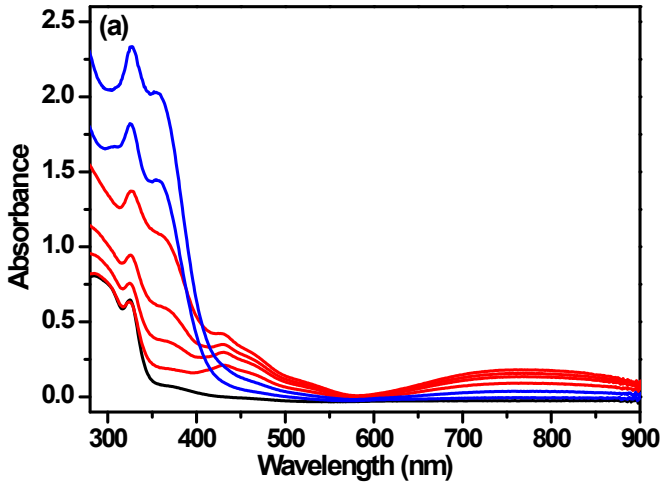


Figure S10 oxidants-responsive properties of CT complex gel of **1a** and TCNQ.

15. UV-vis spectra of Fe^{3+}/Cu^{2+}—Vc Sensitive



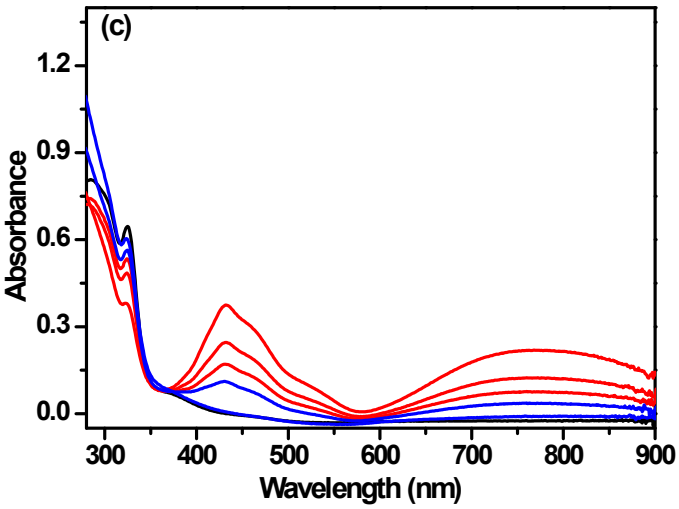


Figure S11 UV-vis absorption spectra of **1a** (5×10^{-5}M) during chemical oxidation by successive addition of (a) $FeCl_3$ (0~6 eq. red line) (b) $Cu(ClO_4)_2$ (0~8 eq. red line) and reduction by addition of ascorbic acid (2~6 eq. and 2~100 eq., respectively, blue line) in ethanol.

16. Gel-sol transition by adding TFA

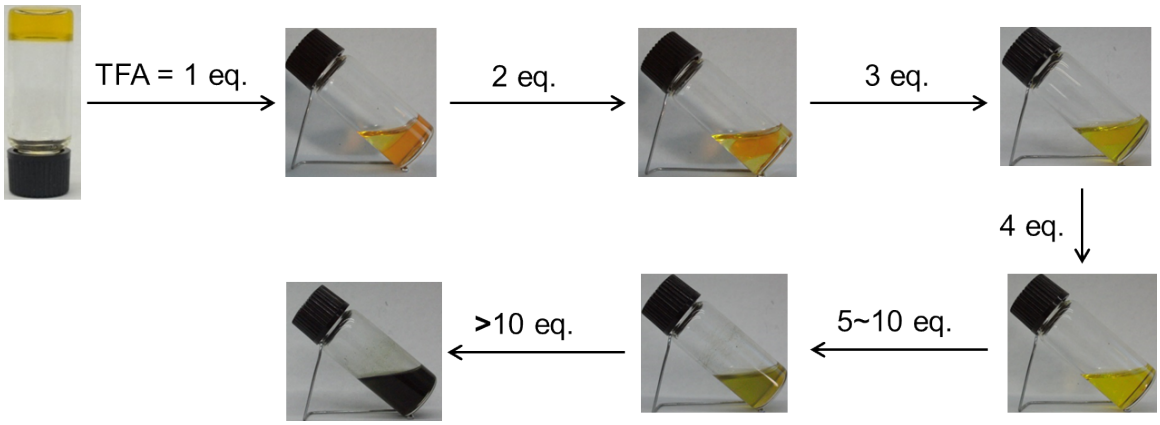


Figure S12 Schematic of gel transformation after addition of TFA (0~3 eq.) in cyclohexane.

17. Gel-sol transition by CH_3COOH/HCOOH-TEA stimuli

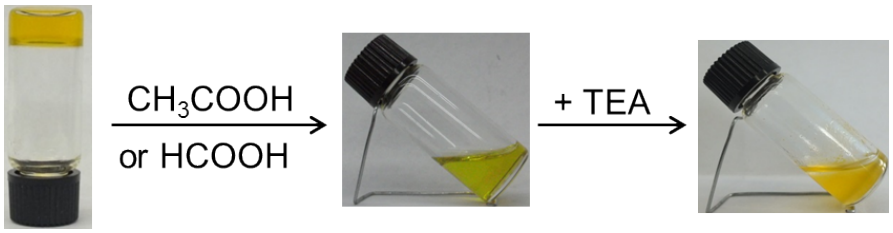


Figure S13 The irreversible gel-sol transitions of organogel (**1a**/cyclohexane) triggered by CH_3COOH/HCOOH-TEA stimuli.

18. ESI-MS spectra of TFA with 1a

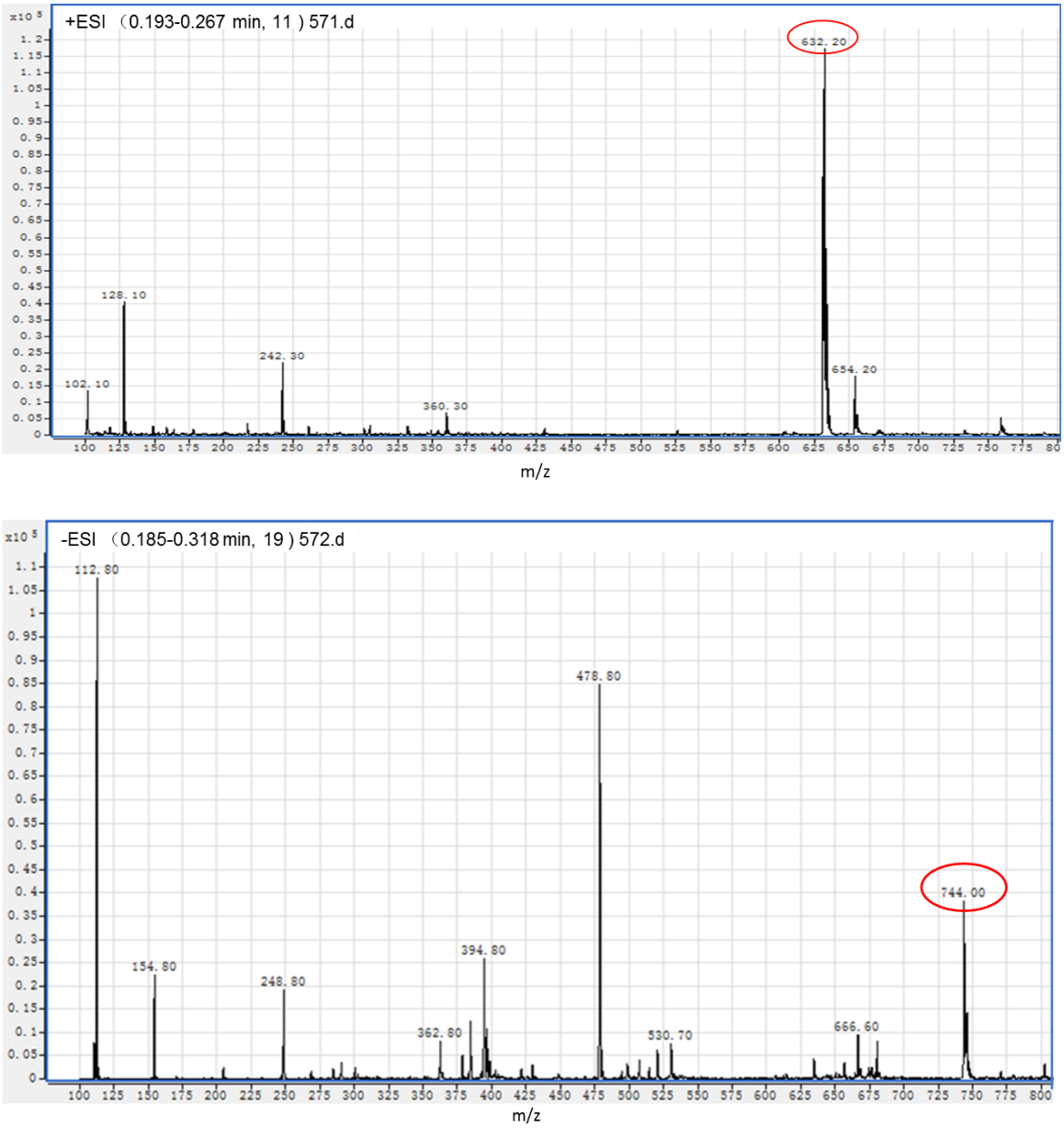


Figure S14 ESI-MS spectra of **1a** after addition of 10 equiv. TFA in $CHCl_3$.

19. UV-vis spectra of TFA-TEA Sensitive

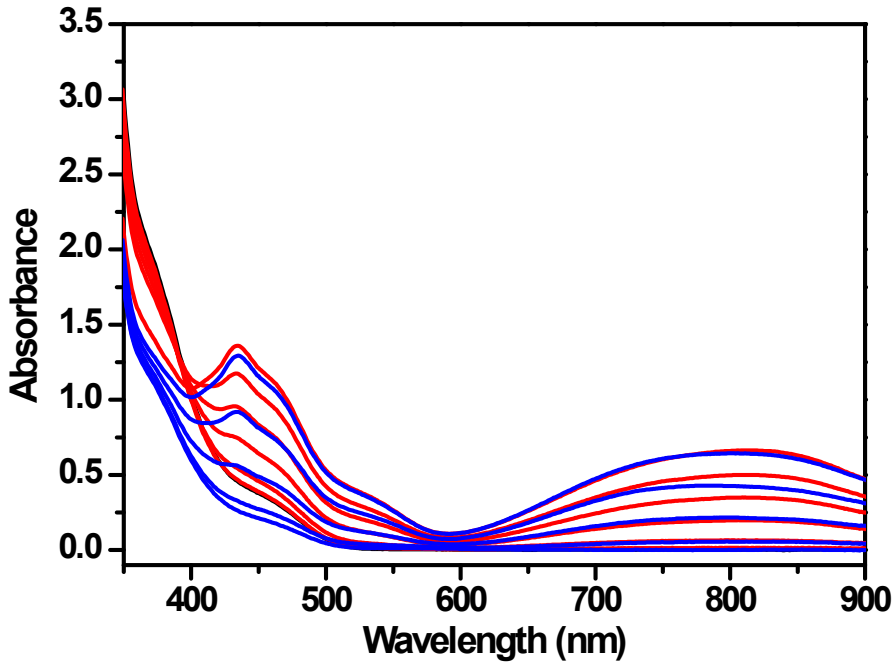


Figure S15 UV-vis absorption spectra of **1a** (10^{-4} M) before (black line) and after successive addition of TFA (1~20 eq. red line), then titration TEA (1~ 60 eq. blue line) in $CHCl_3$ solution.

20. Gel-sol transition of CT complex gel by adding TFA-TEA

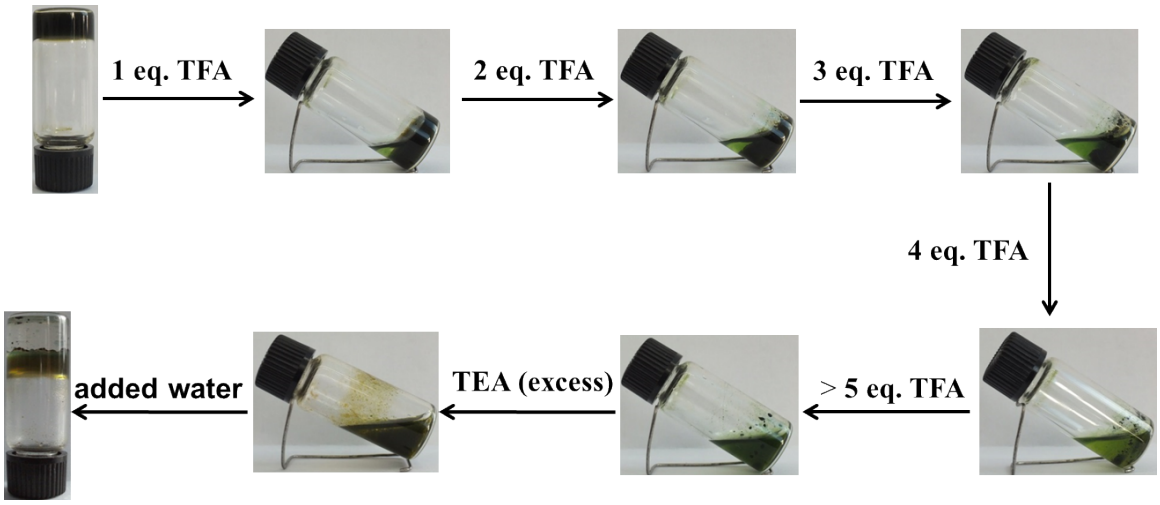


Figure S16 Schematic of CT complex gel of **1a** and TCNQ transformation after addition of TFA and TEA in cyclohexane.

21. Colorimetric changes by TFA-TEA stimuli

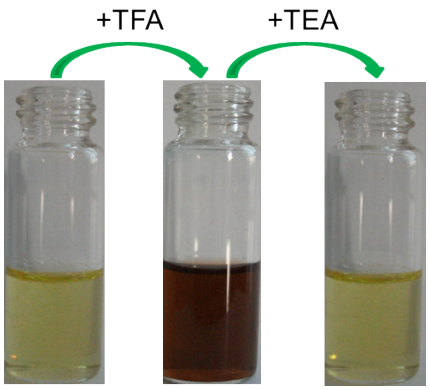


Figure S17 Colorimetric changes of **1a** (10^{-4} M) in $CHCl_3$ by TFA-TEA stimuli.

22. ^{1}H, ^{13}C NMR and MALDI-TOF-MS Spectra

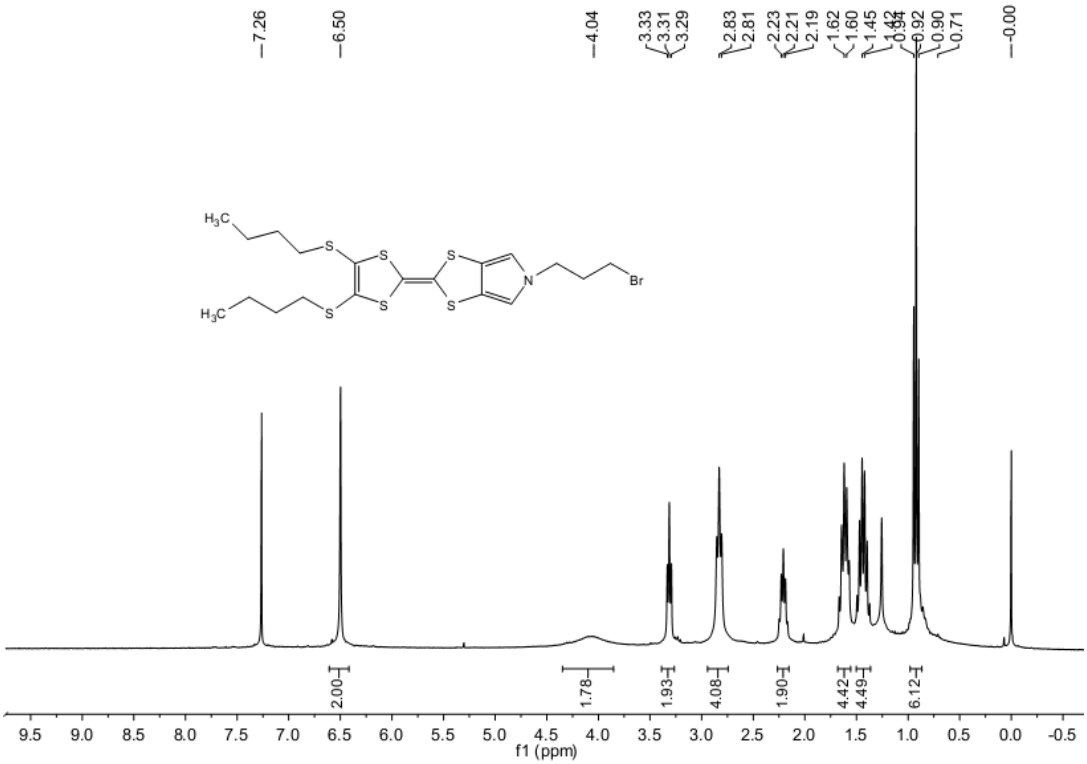


Figure S18 ^{1}H NMR spectra of compound **5**

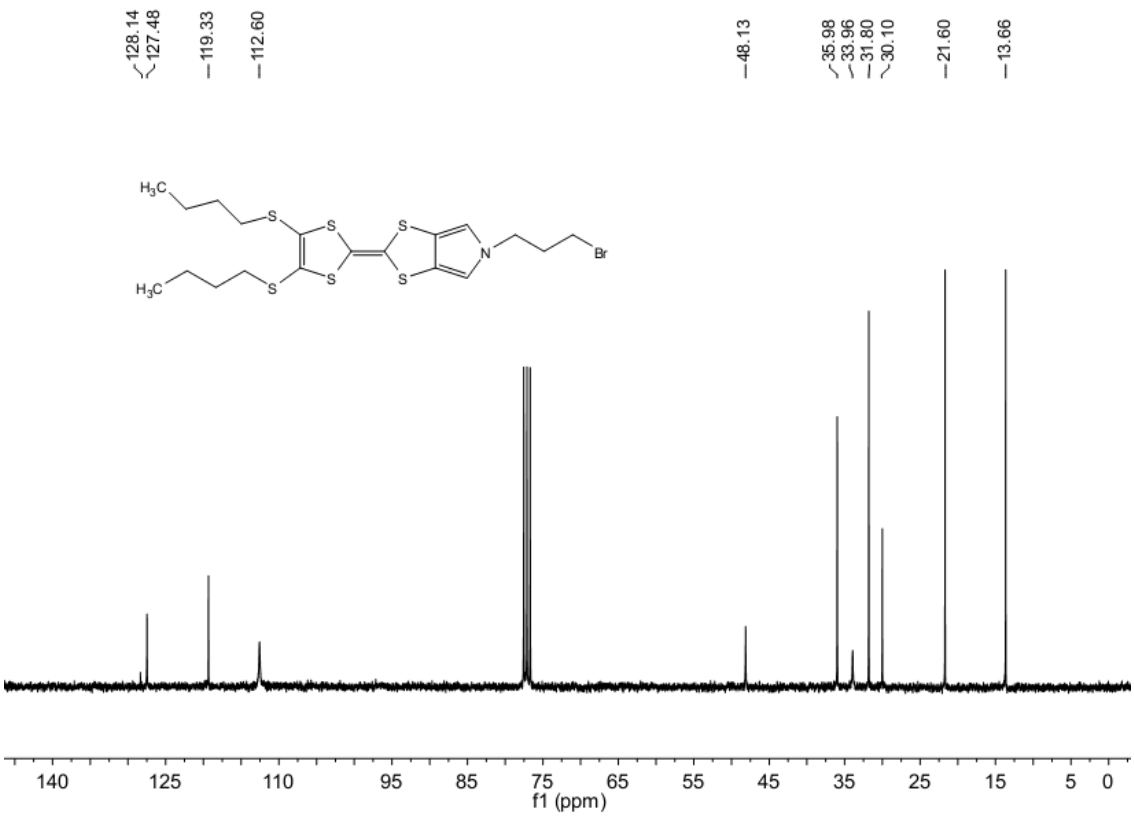


Figure S19 ^{13}C NMR spectra of compound **5**

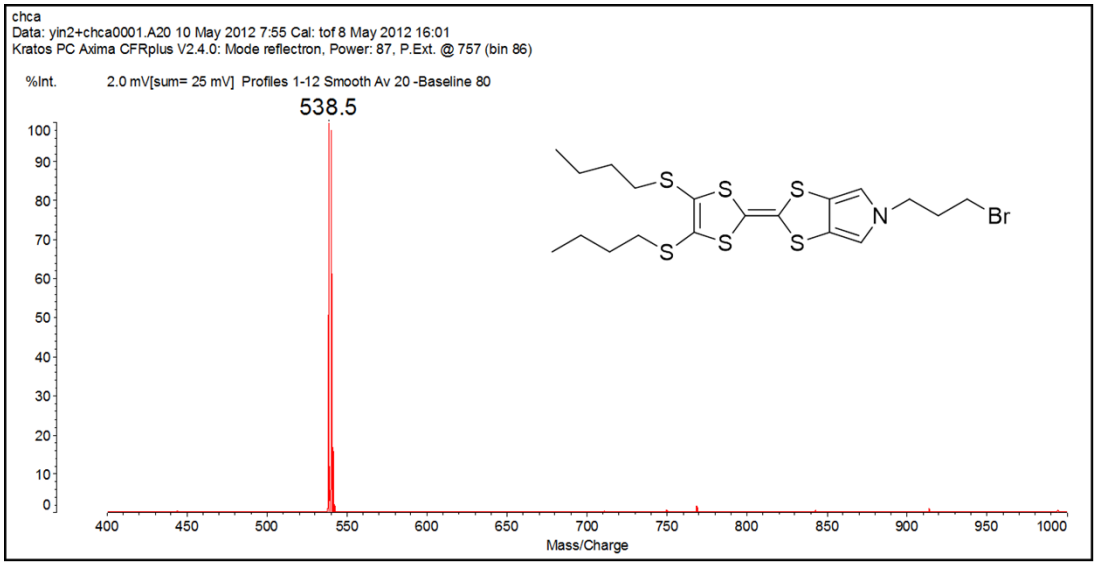


Figure S20 MALDI-TOF-MS spectra of compound **5**

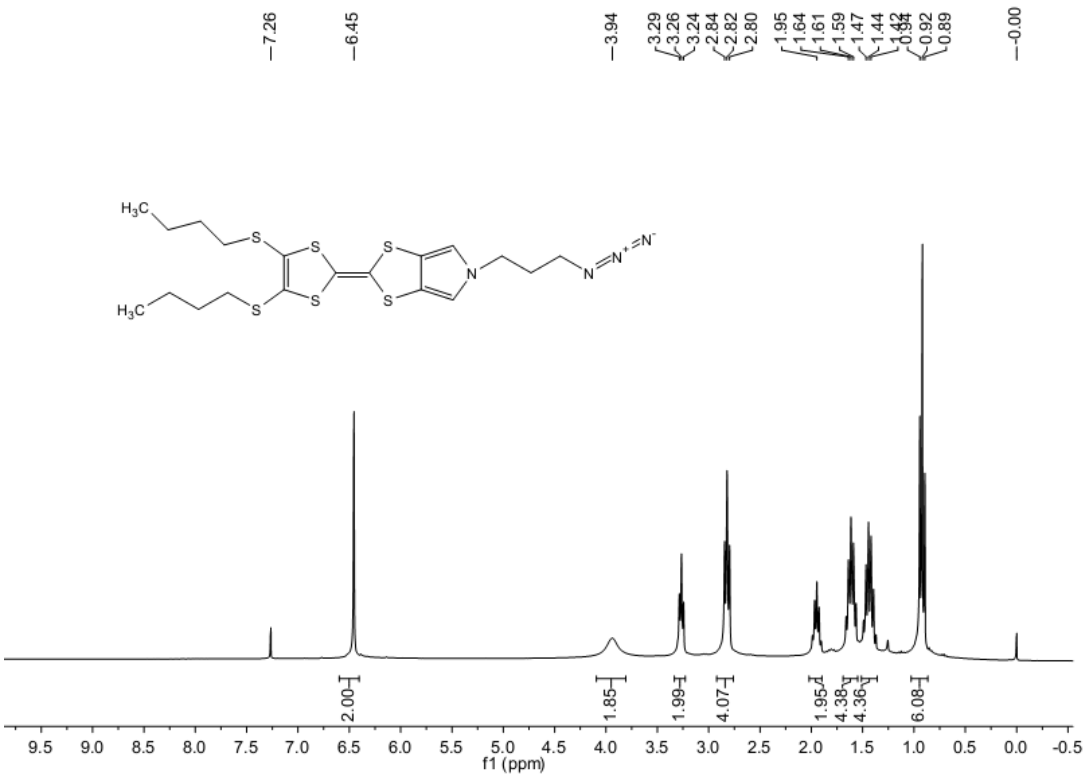


Figure S21 ^{1}H NMR spectra of compound **4**

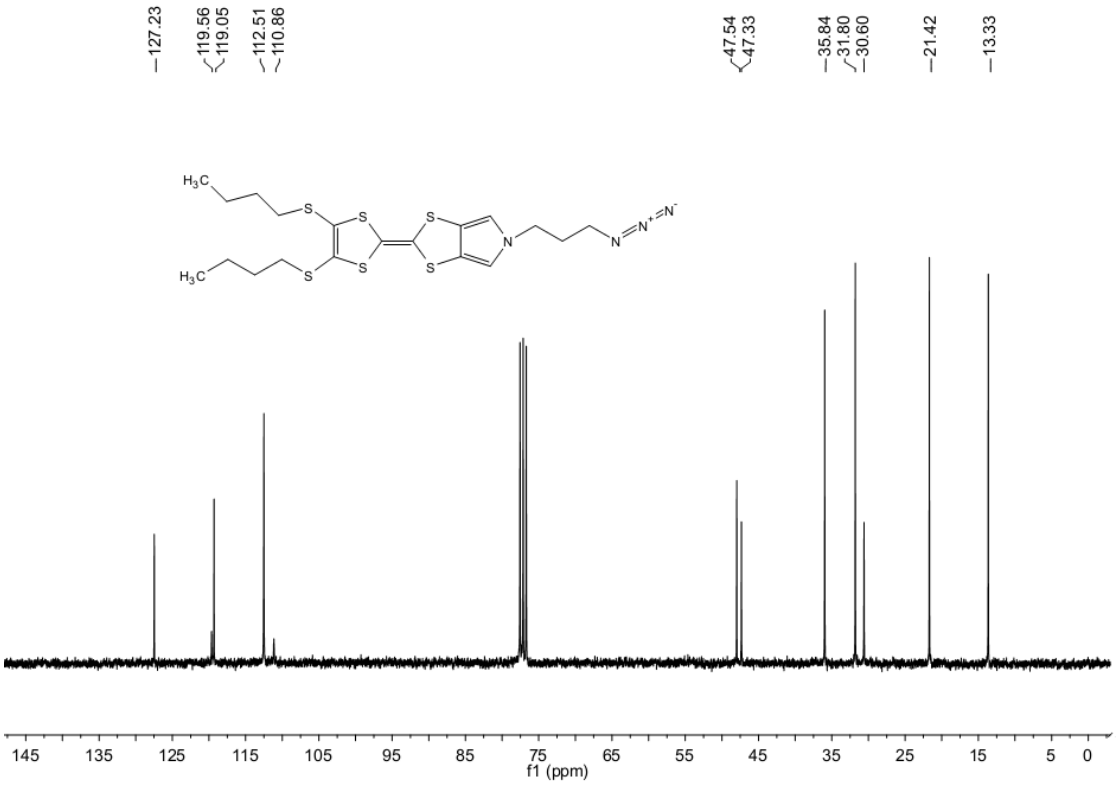


Figure S22 ^{13}C NMR spectra of compound **4**

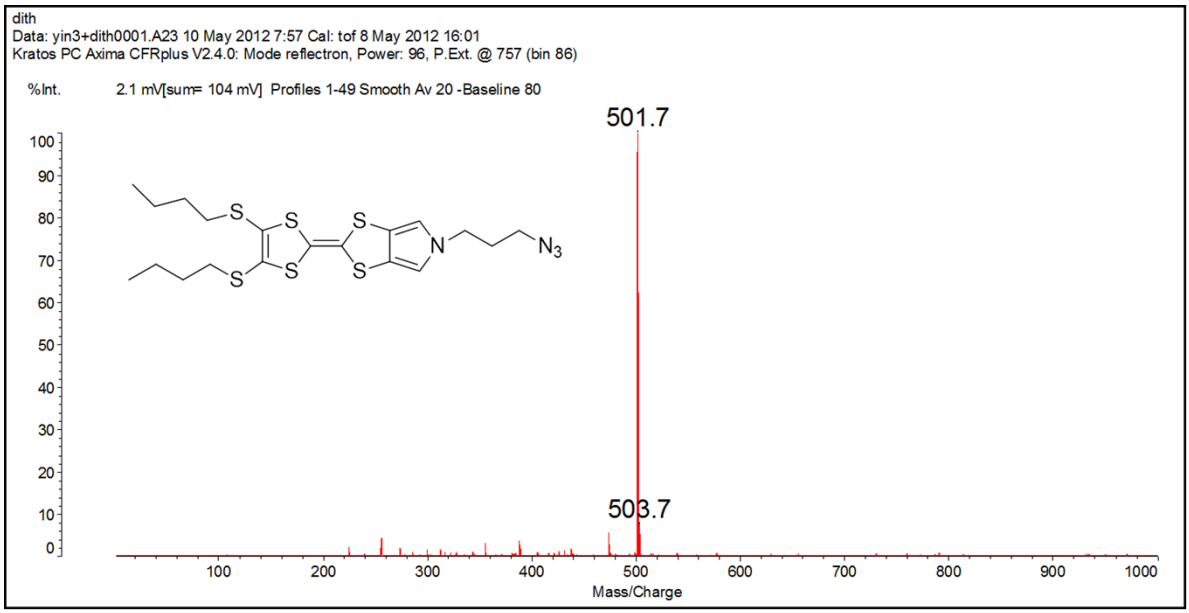


Figure S23 MALDI-TOF-MS spectra of compound **4**

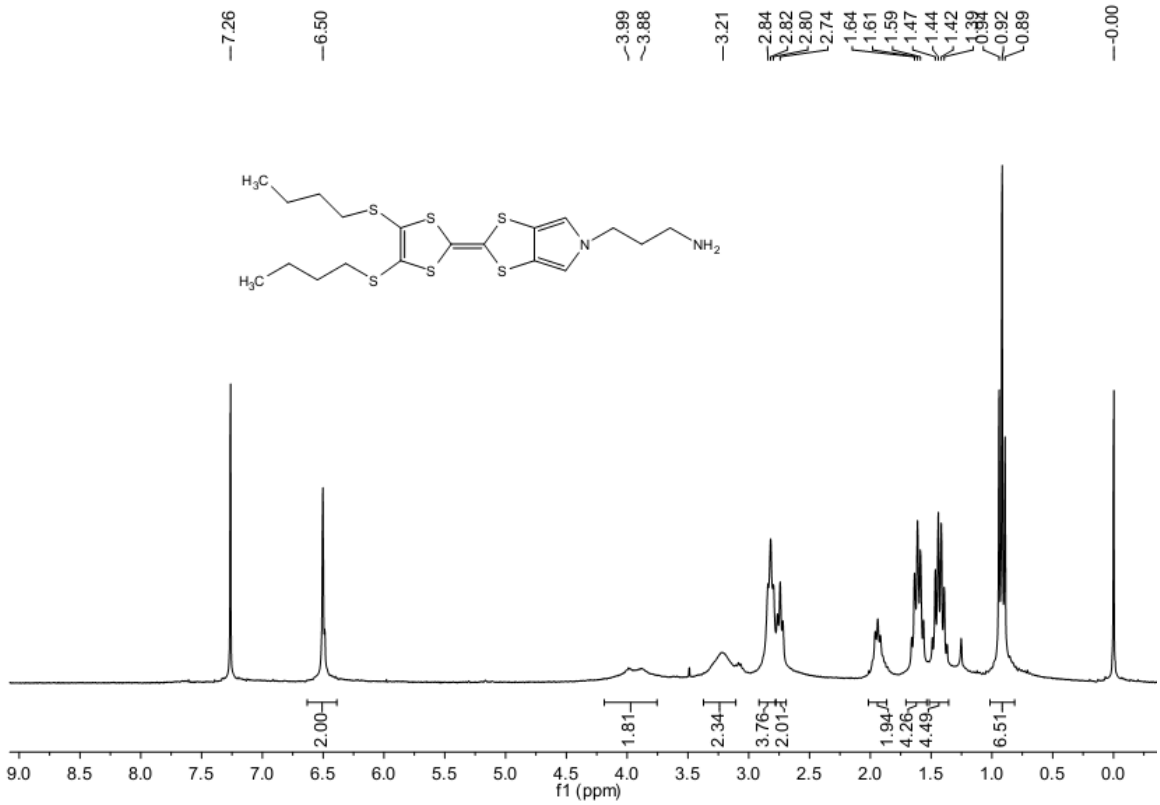


Figure S24 ^{1}H NMR spectra of compound **3**

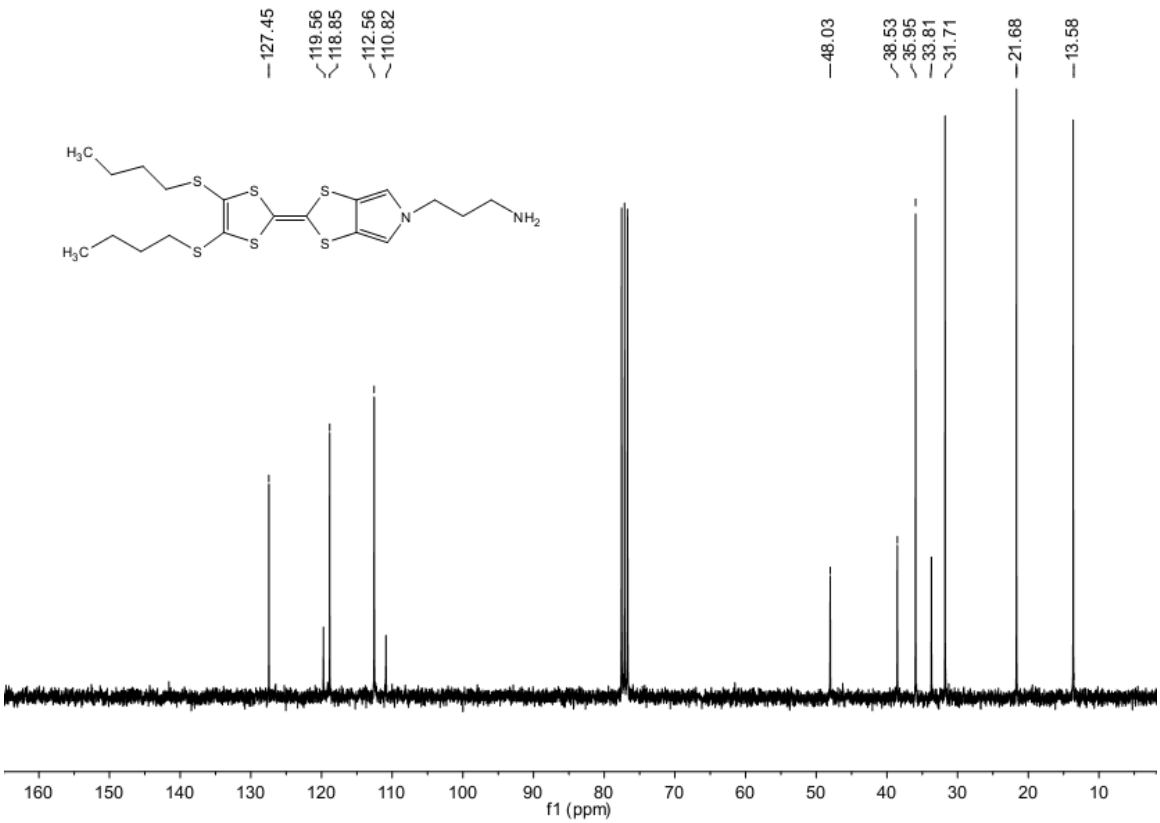


Figure S25 ^{13}C NMR spectra of compound **3**

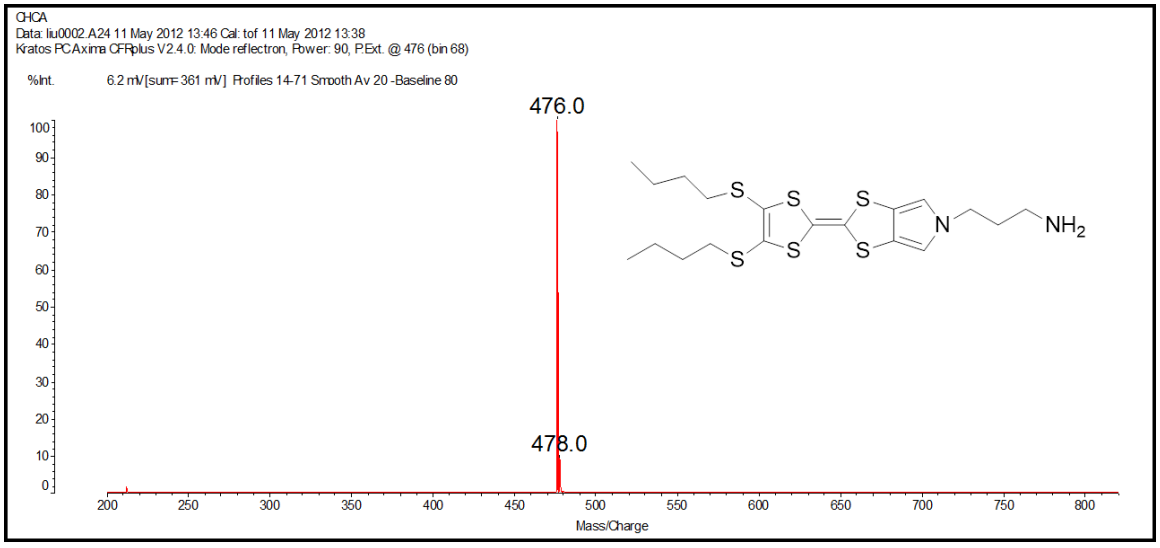


Figure S26 MALDI-TOF-MS spectra of compound **3**

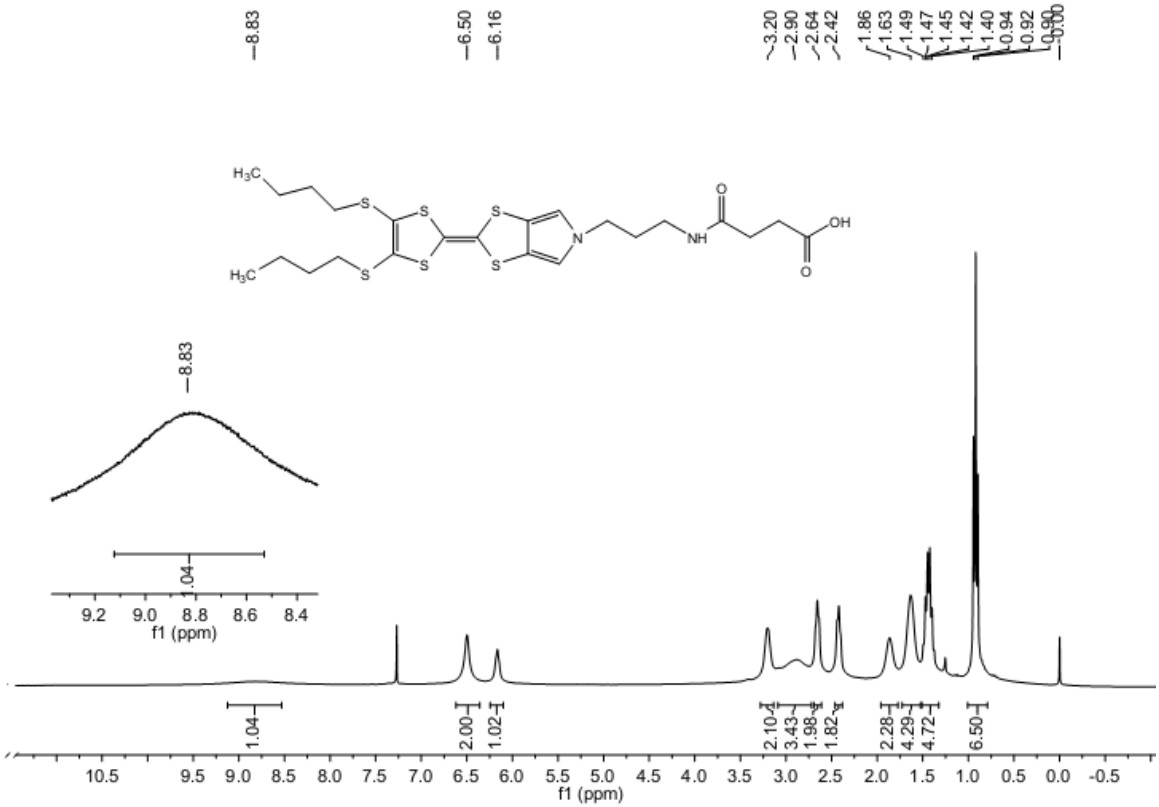


Figure S27 ^{1}H NMR spectra of compound **2**

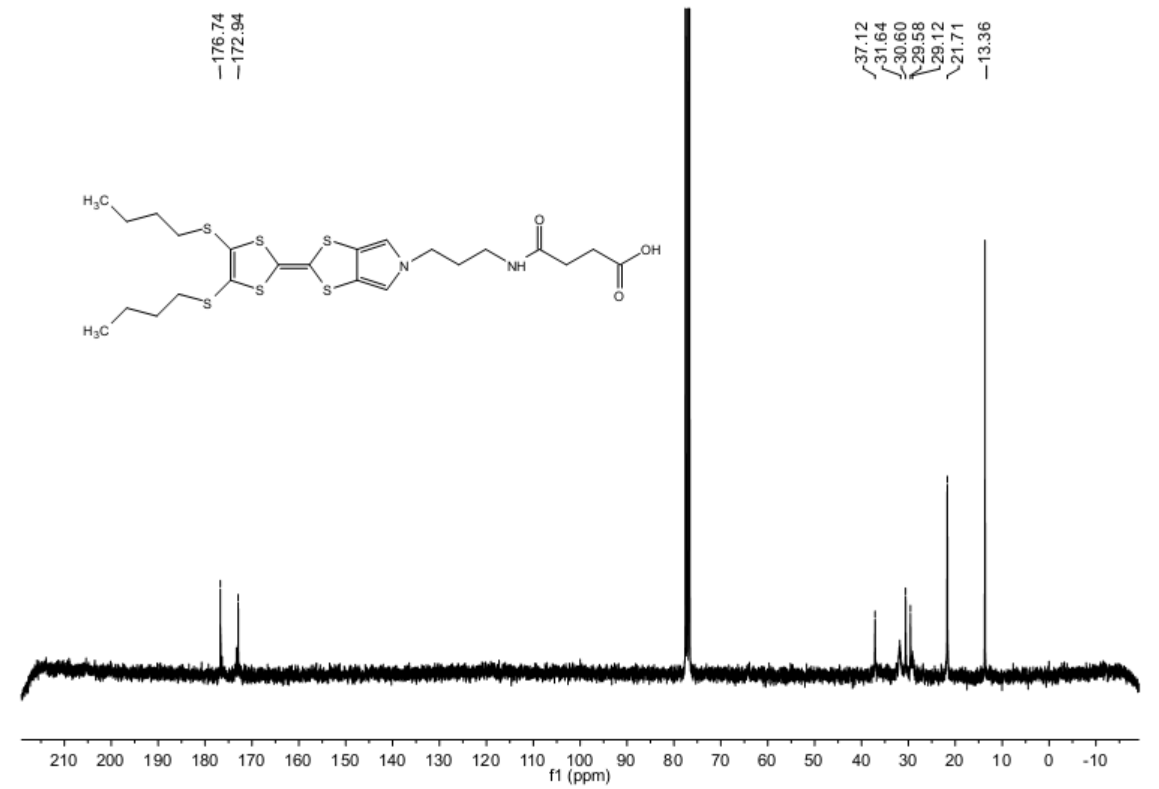


Figure S28 ^{13}C NMR spectra of compound **2**

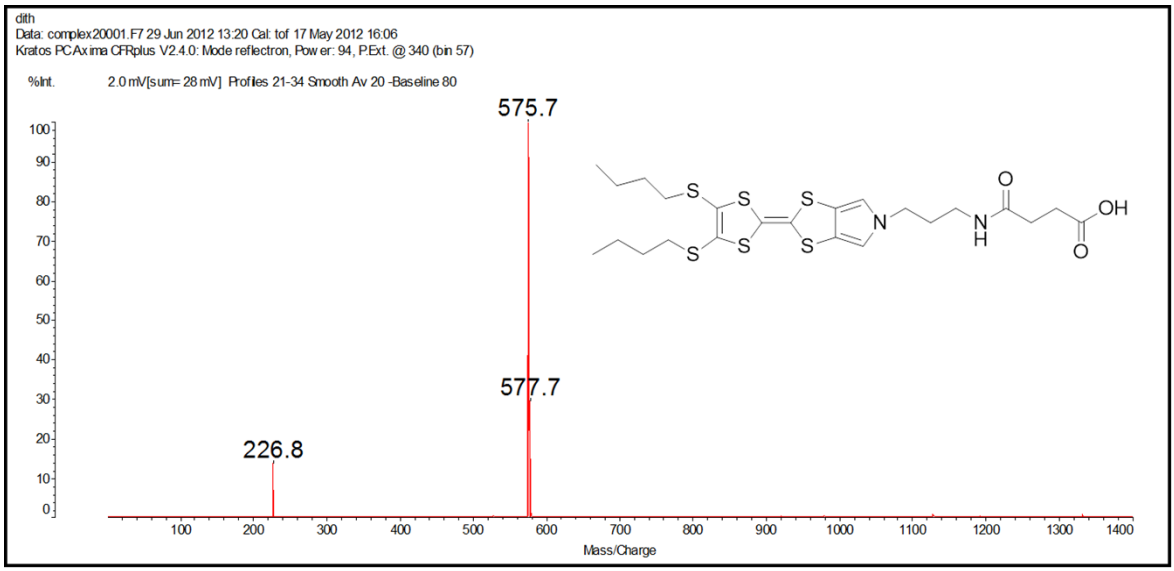


Figure S29 MALDI-TOF-MS spectra of compound **2**

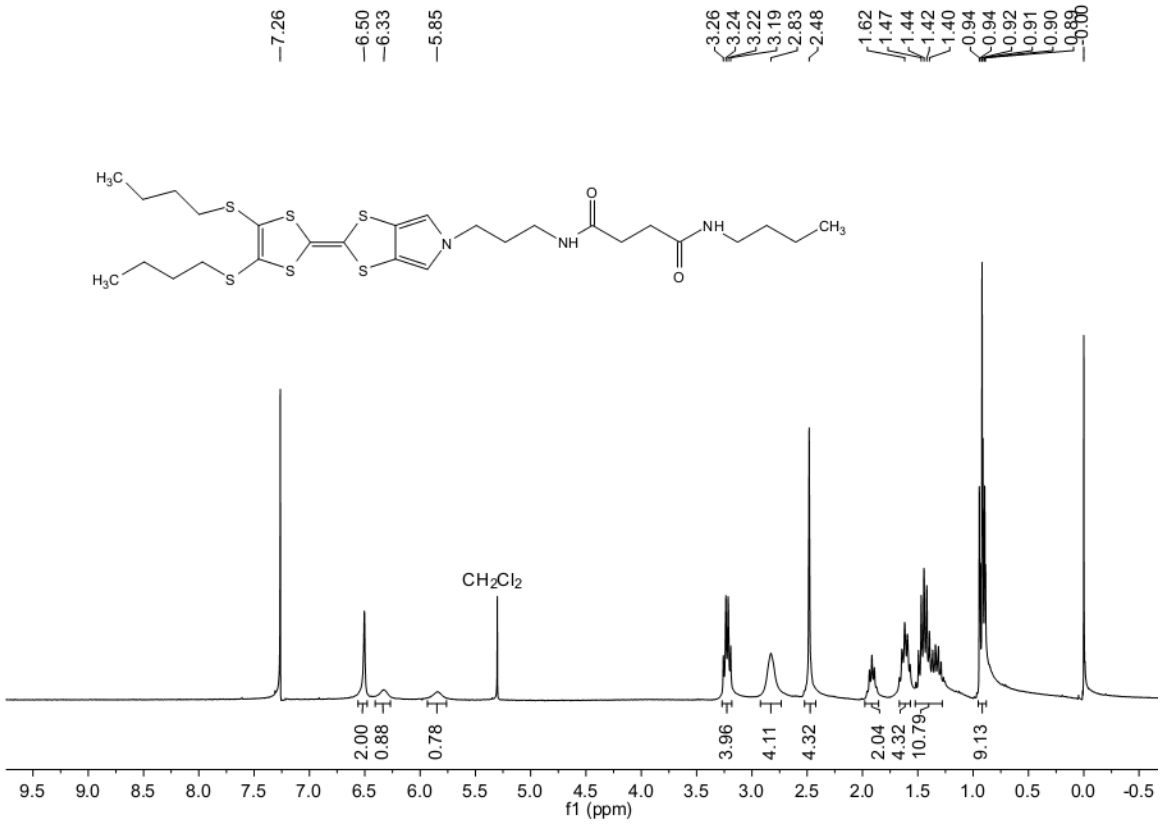


Figure S30 ^{1}H NMR spectra of compound **1a**

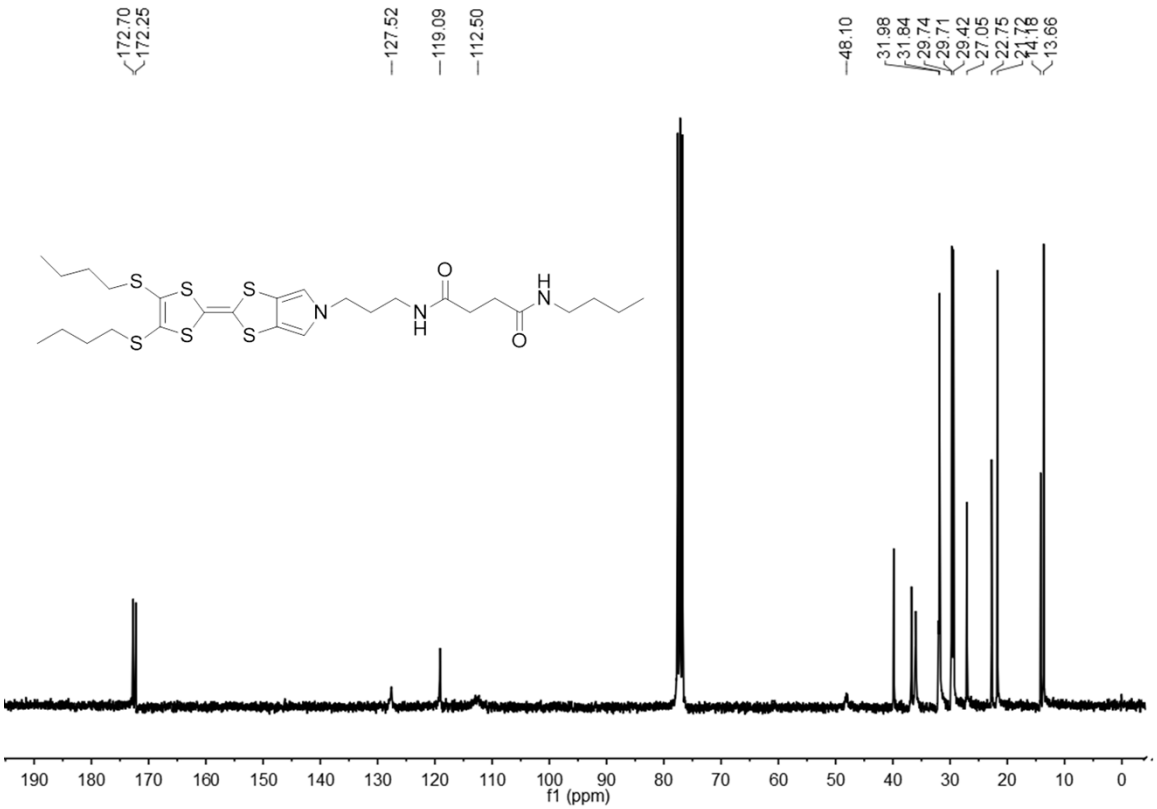


Figure S31 ^{13}C NMR spectra of compound **1a**

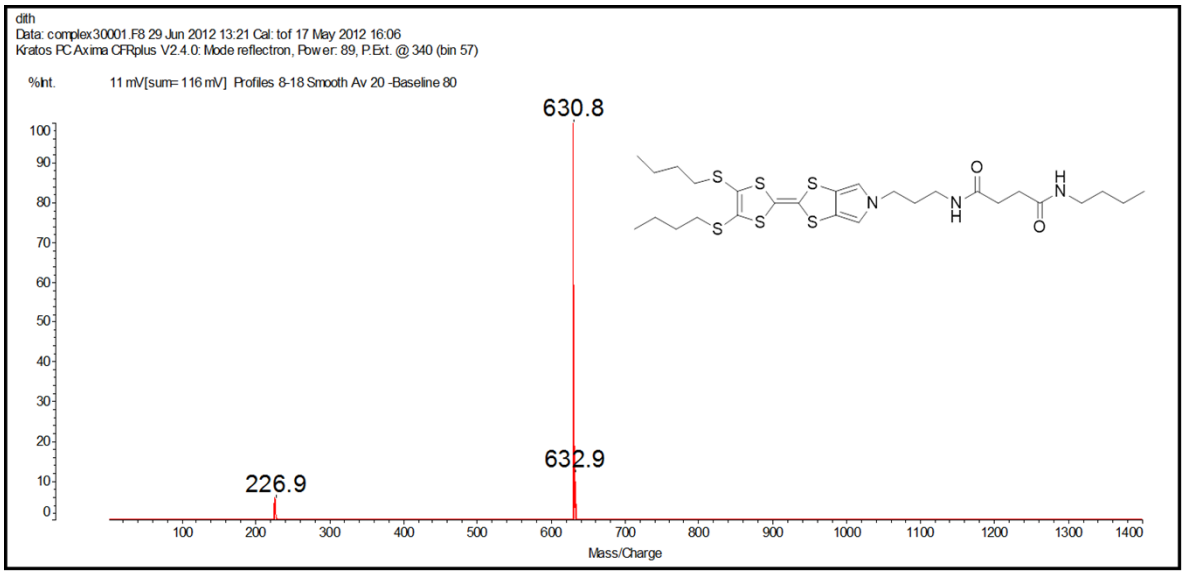


Figure S32 MALDI-TOF-MS spectra of compound **1a**

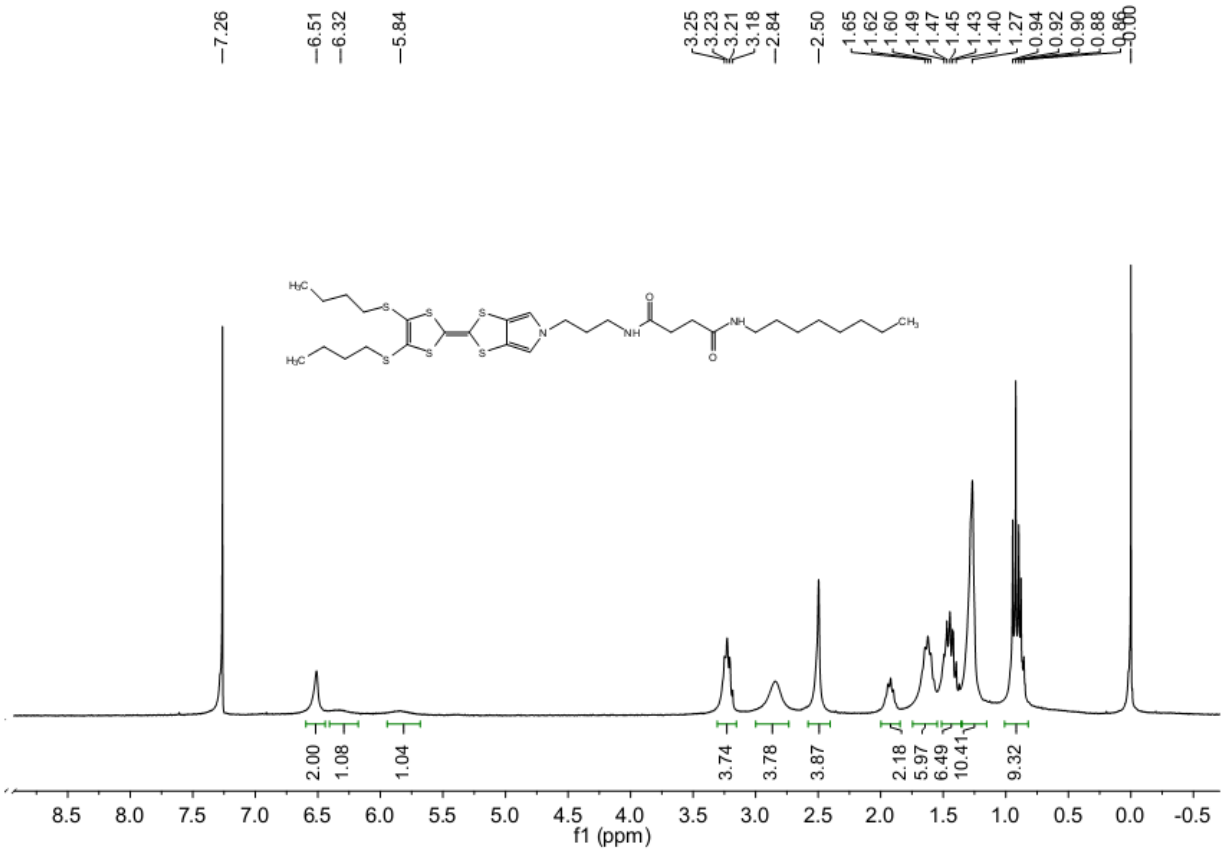


Figure S33 [1]H NMR spectra of compound **1b**

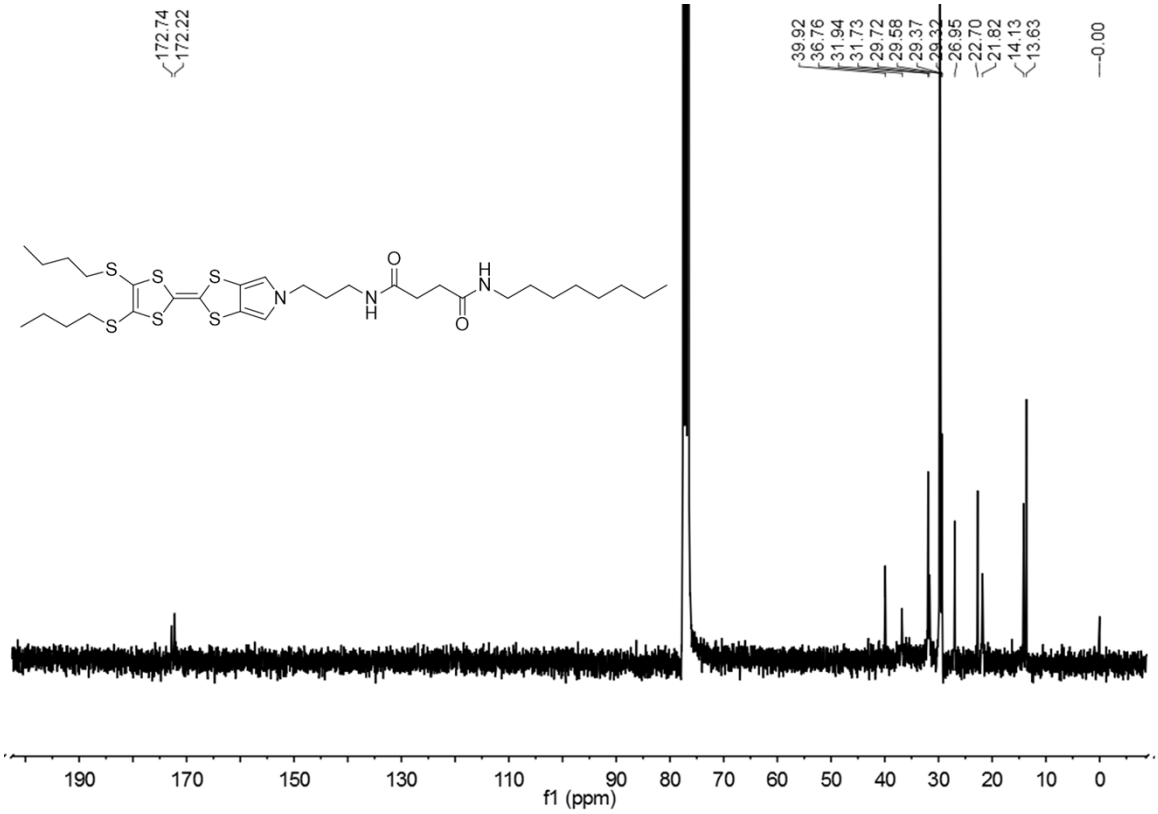


Figure S34 [13]C NMR spectra of compound **1b**

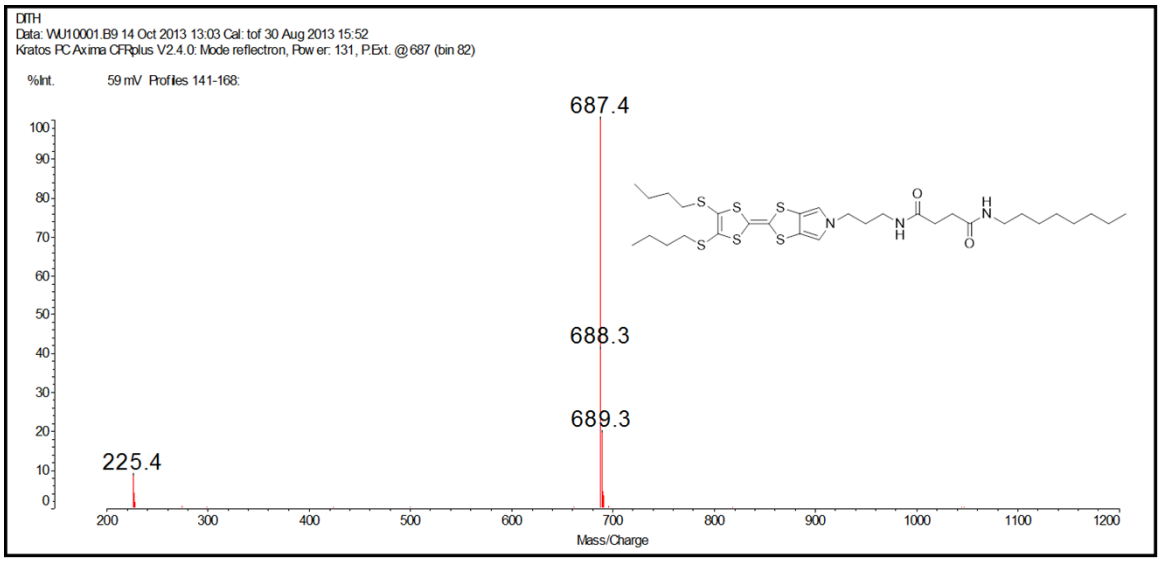


Figure S35 MALDI-TOF-MS spectra of compound **1b**

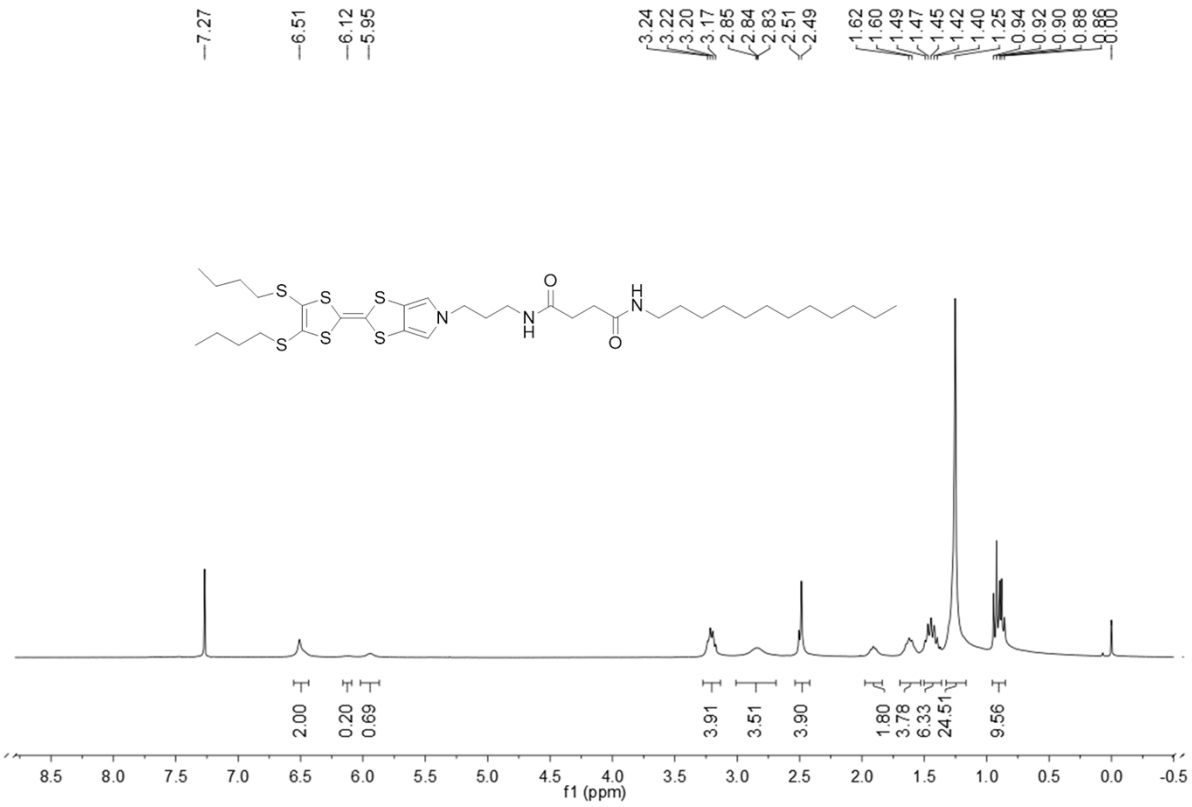


Figure S36 ^{1}H NMR spectra of compound **1c**

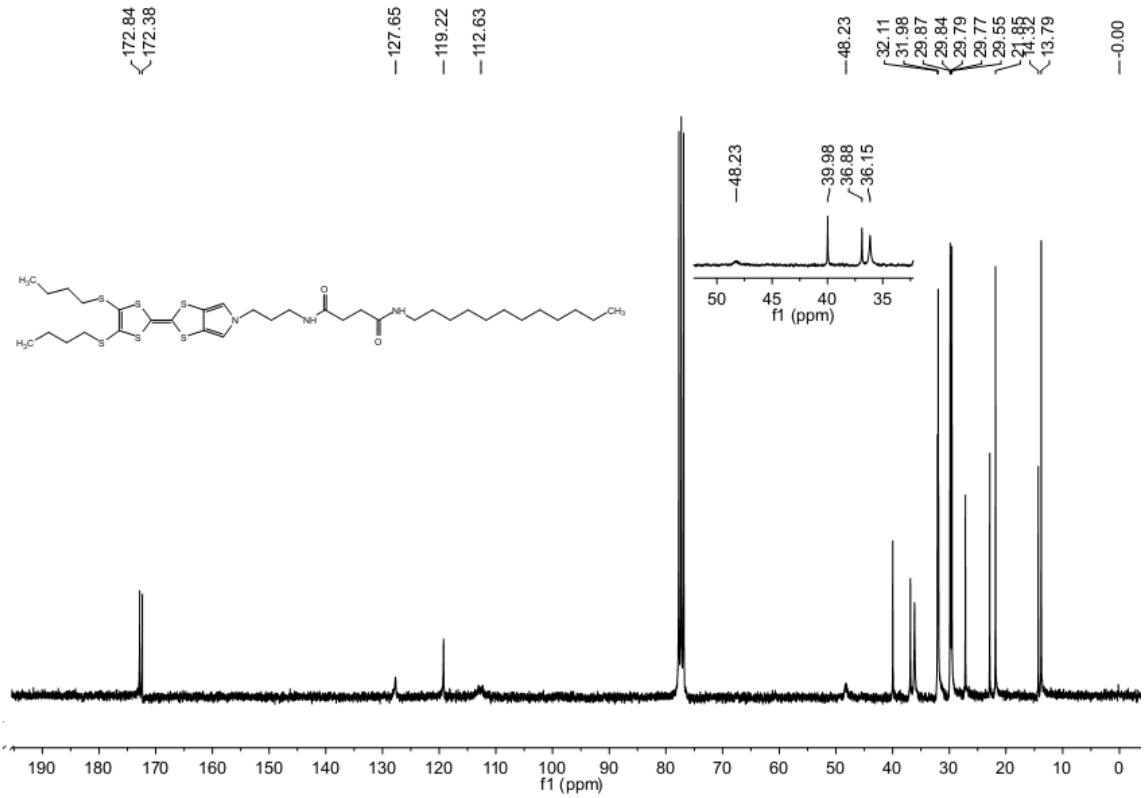


Figure S37 ^{13}C NMR spectra of compound **1c**

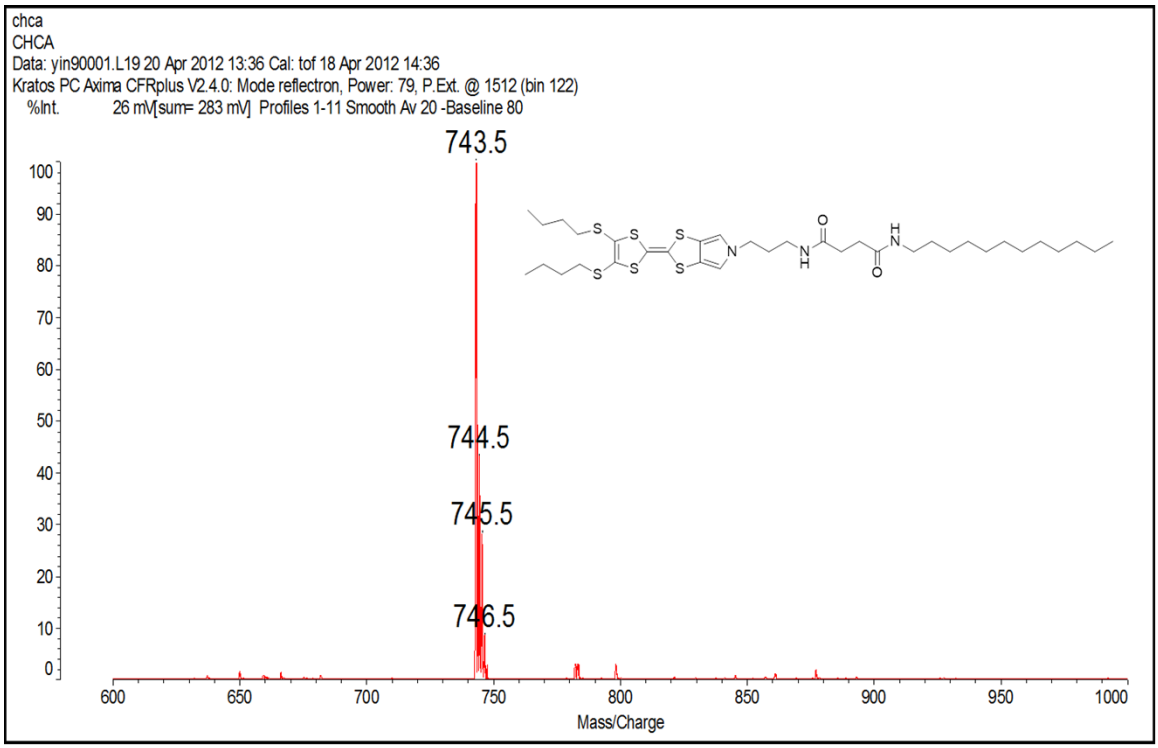


Figure S38 MALDI-TOF-MS spectra of compound **1c**

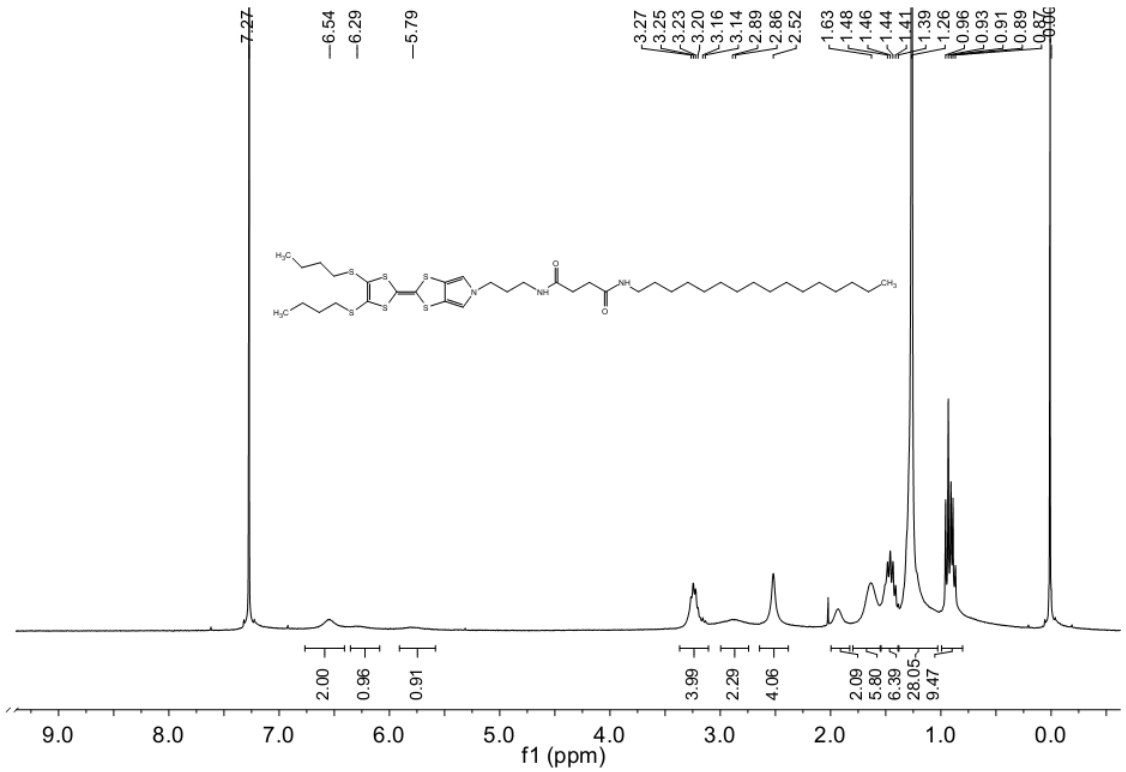


Figure S39 ^{1}H NMR spectra of compound **1d**

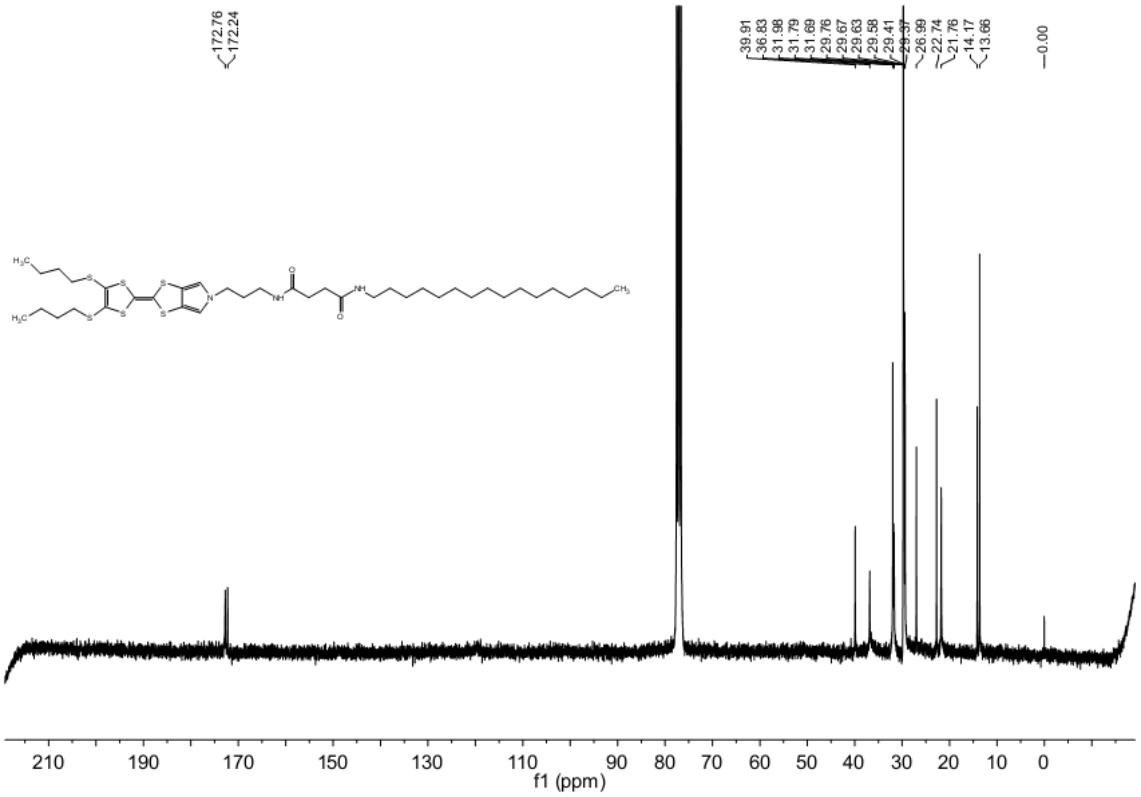


Figure S40 ^{13}C NMR spectra of compound **1d**

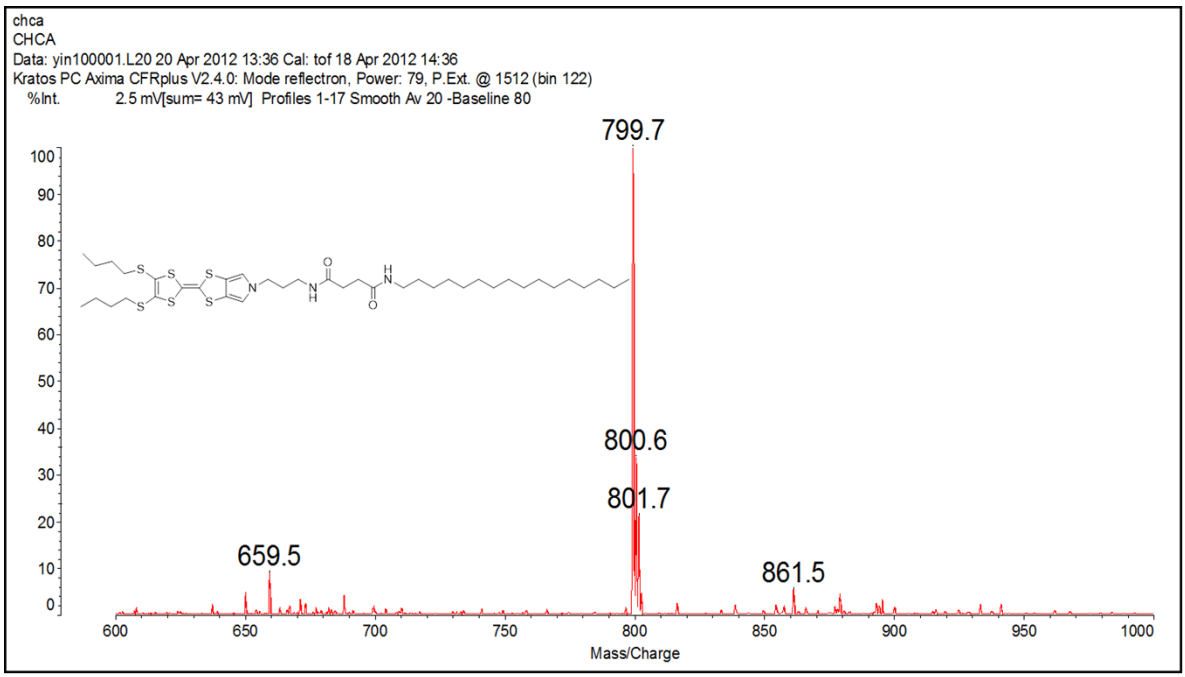


Figure S41 MALDI-TOF-MS spectra of compound **1d**

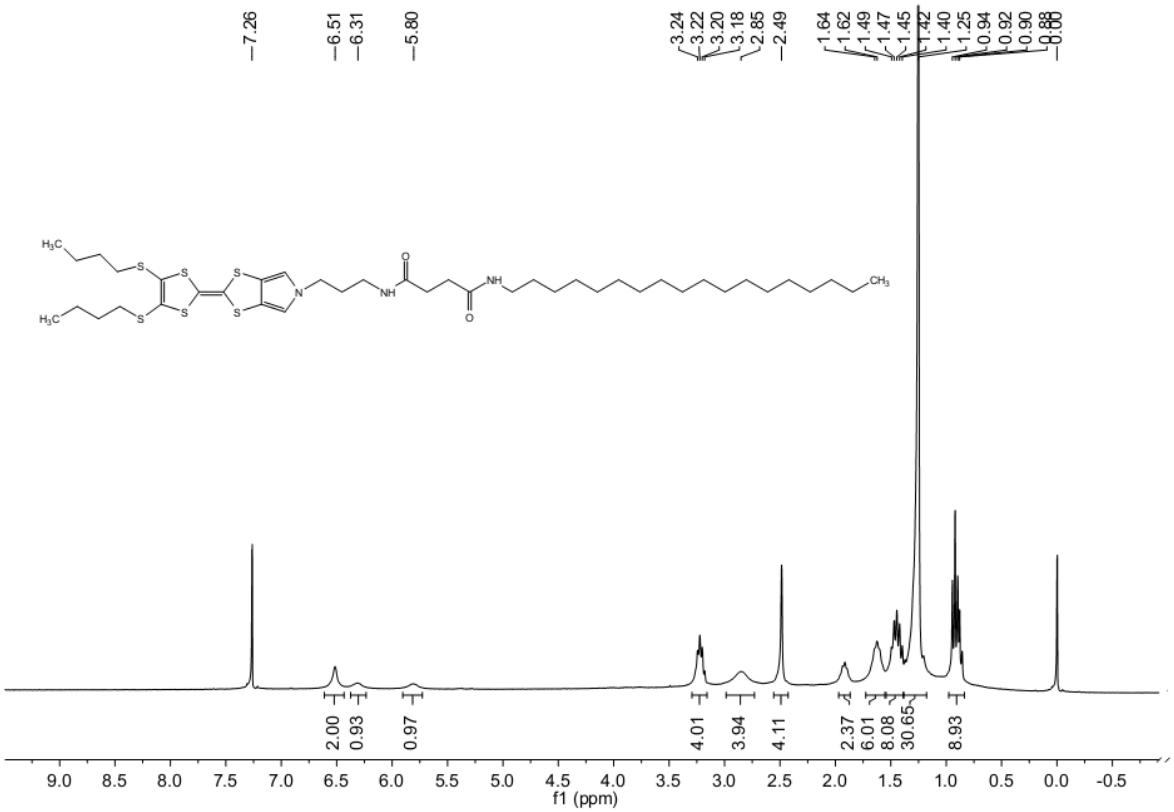


Figure S42 ^{1}H NMR spectra of compound **1e**

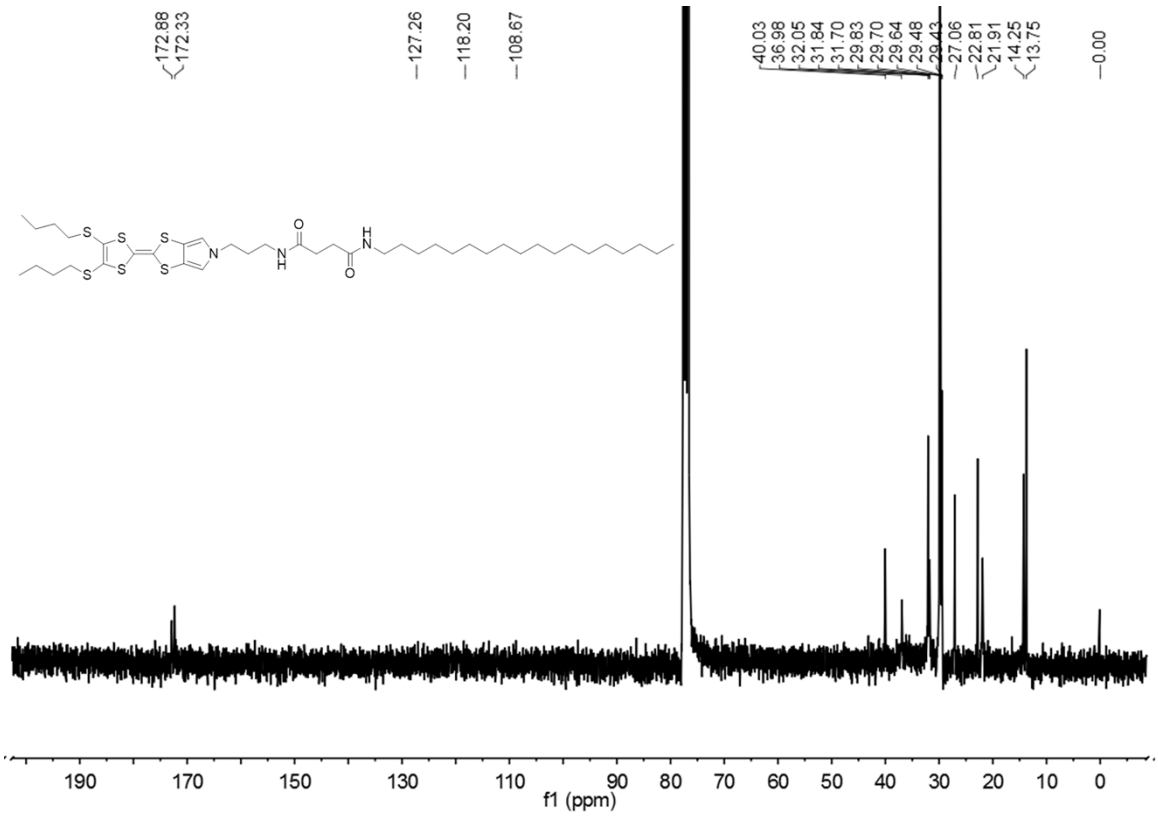


Figure S43 ^{13}C NMR spectra of compound **1e**

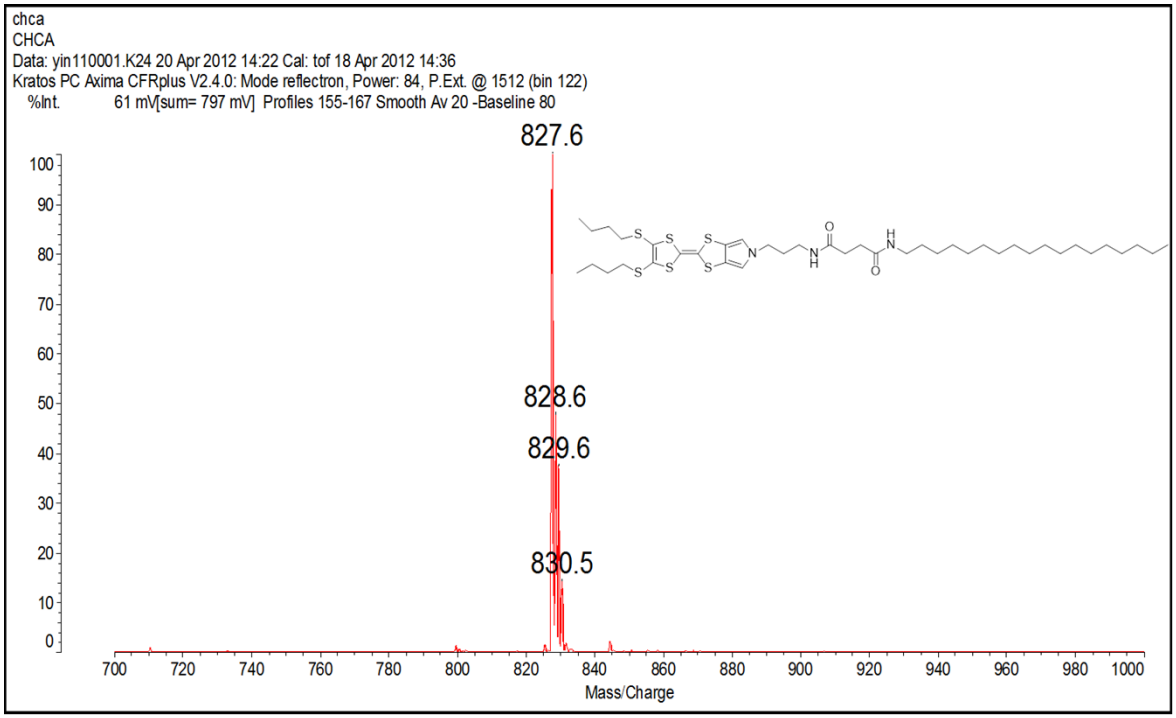


Figure S44 MALDI-TOF-MS spectra of compound **1e**