

Supporting Information

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**A Tetrathiafulvalene-Functionalized Radiannulene with Multiple Redox States\*\***

*Kasper Lincke, Anders Floor Frelsen, Christian Richard Parker, Andrew D. Bond, Ole Hammerich, and Mogens Brøndsted Nielsen\**

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# Supporting Information

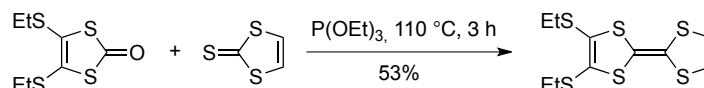
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## General Methods

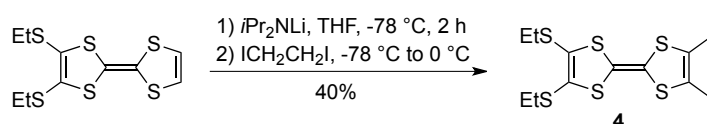
Chemicals were purchased from Aldrich, Merck, and GFS Chemicals and used as received. 4,5-Bis(ethylthio)-1,3-dithiol-2-one was prepared according to literature [R. Schulz, A. Schweig, K. Hartke, J. Kosterzb, *J. Am. Chem. Soc.* **1983**, *105*, 4519]. TEE **3** was prepared according to literature [J. Anthony, A. M. Boldi, Y. Rubin, M. Hobi, V. Gramlich, C. B. Knobler, P. Seiler, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 13]. Dry solvents were obtained from a Solvent Purification System, Innovative Technology, Inc. All reactions were performed under an inert atmosphere of argon. Lithium diisopropylamide was prepared by adding BuLi (2.65 mL, 4.24 mmol, 2.5 M in hexanes) dropwise to a solution of *i*Pr<sub>2</sub>NH (0.6 mL, 4.25 mmol) in dry THF (4 mL) at -78 °C. The mixture was stirred for 15 min before use. Purification of products was carried out either by flash chromatography on silica gel (ROCC 40-63 micron) or by size exclusion chromatography (Bio-Rad Biobeads, SX-3). Thin-layer chromatography (TLC) was carried out using aluminum sheets pre-coated with silica gel 60F (Merck 5554). The plates were inspected under UV light. <sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C NMR (125 MHz) spectra were recorded on a Bruker instrument with cryoprobe using the residual solvent as the internal standard. All chemical shifts are quoted on the  $\delta$  scale (ppm), and all coupling constants (*J*) are expressed in Hz. In APT spectra, CH and CH<sub>3</sub> correspond to negative signals and C and CH<sub>2</sub> correspond to positive signals. High Resolution Electrospray Ionization (HRMS ESI) mass spectra were recorded on a Bruker Micro-TOF Q II spectrometer and Matrix Assisted Laser Desorption Ionization (MALDI) mass spectra were recorded on a Bruker Daltonix Autoflex time-of-flight apparatus. IR Spectra was obtained using a Bruker ALPHA-P spectrometer using the 'ATR platinum Diamond 1 Refl' accessory. Melting points are uncorrected. UV-Vis spectroscopic measurements on neutral compounds (not for spectroelectrochemistry) were performed in a 1-cm path length quartz cuvette. Cyclic voltammograms (CVs) were recorded using a CH Instruments Model CHI630B potentiostat. Electrochemical samples (1-2 x 10<sup>-3</sup> M) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>] as the supporting electrolyte. External reference: FeCp<sub>2</sub> / [FeCp<sub>2</sub>]<sup>+</sup> (*E* = 0.00 V) scanned at 100 mV/s. Electrodes: glassy carbon disk electrode (working), silver (reference), and platinum (counter). Spectroelectrochemical experiments were carried out at room temperature, using an optically transparent thin-layer electrochemical (OTTLE) cell equipped with a Pt mini grid working electrode (32 wires cm<sup>-1</sup>) and CaF<sub>2</sub> windows [Ref. M. Krejčík, M. Daněk, F. Hartl, *J. Electroanal. Chem.* **1991**, *317*, 179]. The cell was positioned in the sample compartment so the photon source passed through the working electrode mini grid. IR (400-9000 cm<sup>-1</sup>) spectra were obtained using a Bruker ALPHA-P T Transmission accessory under an atmosphere of N<sub>2</sub> and UV-Vis-NIR (200-1100 nm; 50000 – 9090 cm<sup>-1</sup>) spectra using a Cary 50 Bio spectrophotometer. The controlled-potential electrolyses were carried out using a CH Instruments Model CHI630B potentiostat.

#### 4,5-Bis(ethylthio)tetrathiafulvalene



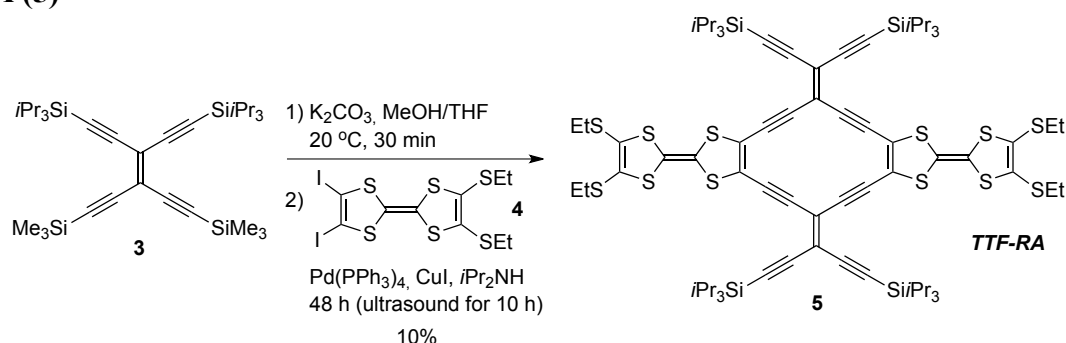
To a mixture of 4,5-bis(ethylthio)-1,3-dithiol-2-one (2.33 g, 9.8 mmol) and 1,3-dithiol-2-thione (3.28 g, 24.5 mmol) was added dry degassed  $\text{P}(\text{OEt})_3$  (6 mL) and the mixture was heated to  $110\text{ }^\circ\text{C}$  for 3 h. The solution was then cooled to rt and concentrated *in vacuo*. The residue was purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CS}_2$ ); the first yellow band was discarded, while the following red band was collected. The solvent was removed under reduced pressure to give the title compound as a dark red oil. Yield: 1.69 g (53%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 6.29$  (s, 2H), 2.81 (q,  $J = 7.4$  Hz, 4 H), 1.27 (t,  $J = 7.4$  Hz, 6 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 127.8, 118.9, 114.6, 105.9, 30.4, 15.1$ . MS (MALDI-TOF):  $m/z$  323.6 [ $\text{M}^+$ ]. HRMS (ESI):  $m/z$  323.9258 [ $\text{M}^+$ ] (calcd. for  $\text{C}_{10}\text{H}_{12}\text{S}_6^+$ : 323.9258).

#### 4,5-Bis(ethylthio)-4',5'-diiodotetrathiafulvalene (4)



A freshly prepared solution of lithium diisopropylamide (16.7 mL, 0.59 M in THF, 9.7 mmol) was added to a solution of 4,5-bis(ethylthio)tetrathiafulvalene (1.50 g, 4.6 mmol) in dry THF (50 mL) cooled to  $-78\text{ }^\circ\text{C}$ . The mixture was stirred at  $-78\text{ }^\circ\text{C}$  for 2 h, whereupon 1,2-diiodoethane (2.77 g, 9.8 mmol) was added in one portion. Stirring was continued for 1 h at  $-78\text{ }^\circ\text{C}$  and the mixture was then allowed to slowly reach  $0\text{ }^\circ\text{C}$  using an ice/water bath and was then allowed to reach room temperature and stirred for an additional 30 min at this temperature. The mixture was partitioned between saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{Et}_2\text{O}$  (200 mL). The aqueous phase was extracted with  $\text{Et}_2\text{O}$  (200 mL) and the combined organic phases were washed with  $\text{H}_2\text{O}$  (200 mL), dried with  $\text{MgSO}_4$ , filtered and concentrated *in vacuo*. Column chromatography ( $\text{SiO}_2$ , pentane/ $\text{CH}_2\text{Cl}_2$  9:1) gave **4** as an orange crystalline solid. Yield: 1.06 g (40%). M.p.  $95\text{--}98\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.84$  (q,  $J = 7.4$  Hz, 4 H), 1.32 (t,  $J = 7.4$  Hz, 6 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 128.1, 117.3, 111.7, 77.0, 30.8, 15.2$ . MS (MALDI-TOF):  $m/z$  575.7 [ $\text{M}^+$ ]. HRMS (ESI):  $m/z$  575.7174 [ $\text{M}^+$ ] (calcd. for  $\text{C}_{10}\text{H}_{10}\text{I}_2\text{S}_6^+$ : 575.7191).

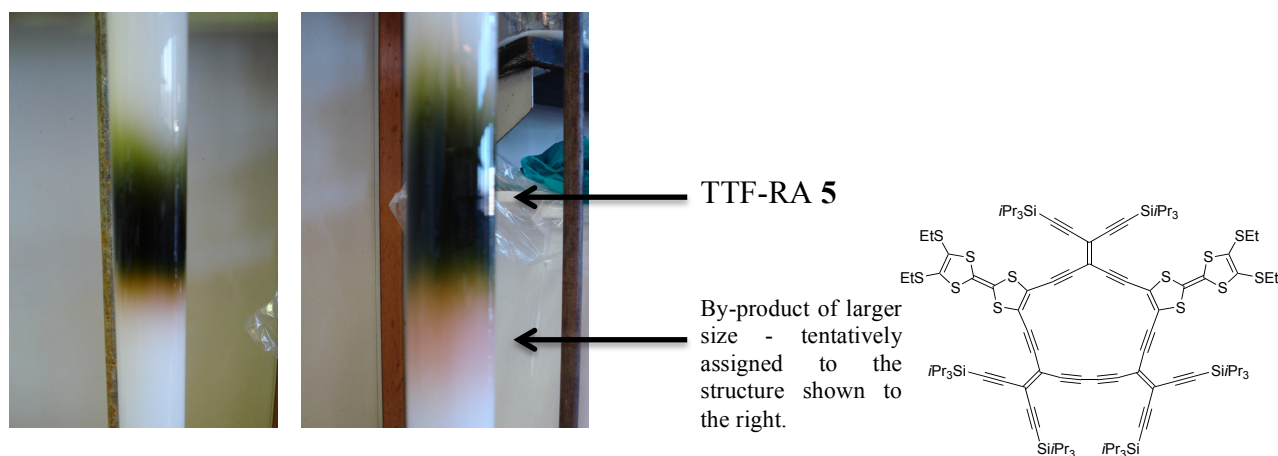
#### TTF-RA (5)



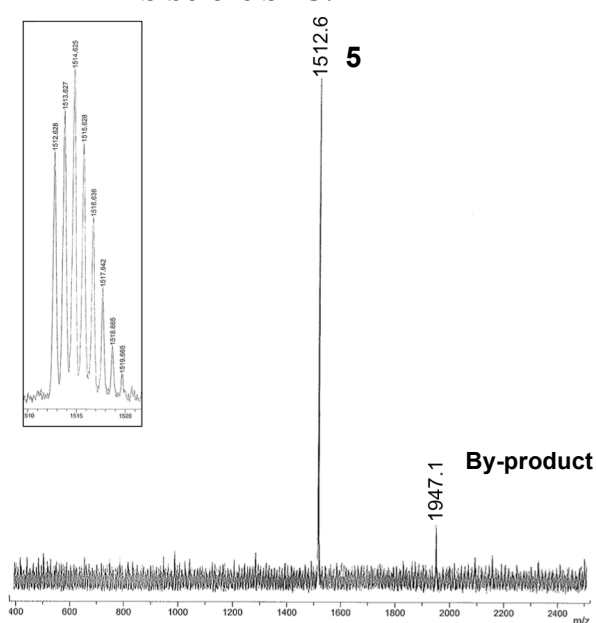
A solution of TEE **3** (101 mg, 0.17 mmol) in THF (5 mL) was added to a solution of  $\text{K}_2\text{CO}_3$  (96 mg, 0.69 mmol) in MeOH (10 mL). The mixture was stirred for 30 min; complete desilylation was confirmed by TLC (heptane/ $\text{CH}_2\text{Cl}_2$  1:1). Then the solution was filtered through a plug ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ) and partly concentrated *in vacuo* to near dryness. Due to the instability of this desilylated

TEE, it was immediately subjected to the next step. To a solution of **4** (100 mg, 0.17 mmol) in argon-degassed *i*Pr<sub>2</sub>NH (10 mL) were added Pd(PPh<sub>3</sub>)<sub>4</sub> (42 mg, 0.036 mmol) and CuI (3.3 mg, 0.018 mmol), followed by the desilylated TEE (0.17 mmol) in argon-degassed *i*Pr<sub>2</sub>NH (8 mL). The reaction mixture was stirred for 48 h, during which it was exposed to ultrasound for 10 h, whereupon heptane (50 mL) was added and the solution was filtered through a plug (SiO<sub>2</sub>, heptane/CH<sub>2</sub>Cl<sub>2</sub> 1:1) and concentrated *in vacuo*. Column chromatography (SiO<sub>2</sub>, CS<sub>2</sub>) afforded a mixture of **5** and a by-product (suspected structure shown below), which could be separated by repeated size exclusion chromatography (Biobeads SX-3, CH<sub>2</sub>Cl<sub>2</sub>) affording the product **5** as a red, glass-like solid. Yield: 14 mg (10%). Dark green colored crystals suitable for X-ray diffraction were grown from CH<sub>2</sub>Cl<sub>2</sub> / MeOH by slow diffusion at about 5 °C. M.p. > 230 °C. IR (ART): 2941s, 2925s, 2891m, 2864s, 2198vw (νC≡C), 2154vw (νC≡C), 2135w (νC≡C), 1595m, 1461w, 1381w, 1239m, 1073w, 1015m, 999m, 919w, 882m, 774w, 728w, 680m, 576w cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 2.85 (q, *J* = 7.4 Hz, 8 H), 1.33 (t, *J* = 7.4 Hz, 12 H), 1.15 (s, 84 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 128.1, 122.7, 117.7, 114.8, 113.5, 109.8, 106.1, 104.1, 97.9, 90.3, 30.9, 19.0, 15.3, 11.5. MS (MALDI-TOF): *m/z* 1512.6 [M<sup>+</sup>]. HRMS (ESI): *m/z* 1512.3821 [M<sup>+</sup>] (calcd. for C<sub>76</sub>H<sub>104</sub>S<sub>12</sub>Si<sub>4</sub><sup>+</sup>: 1512.3858).

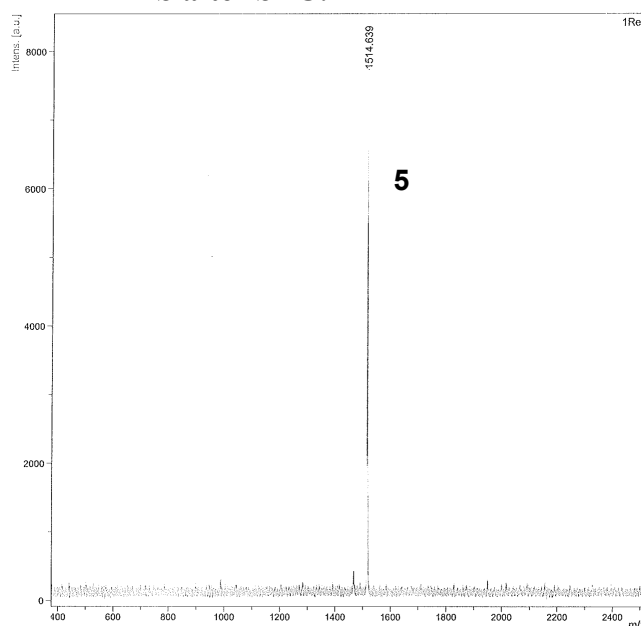
Photos showing the separation of **5** from a by-product by size exclusion chromatography (SEC):



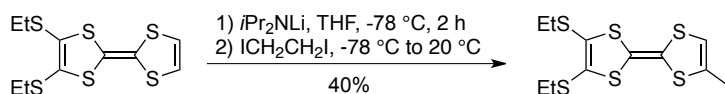
MALDI-MS before SEC:



MALDI-MS after SEC:

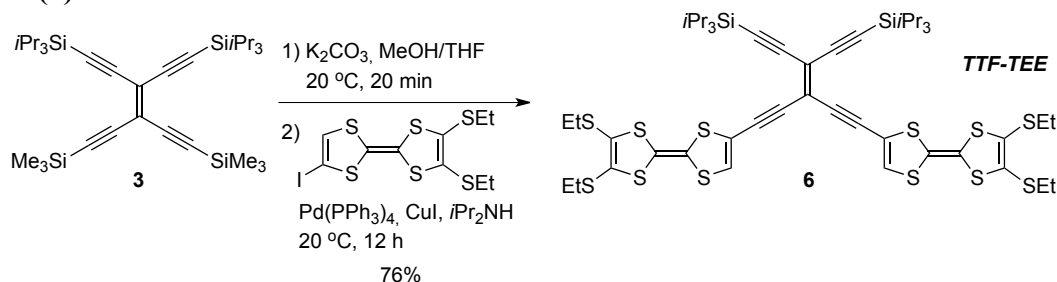


#### 4,5-Bis(ethylthio)-4'-iodotetrathiafulvalene



A freshly prepared solution of lithium diisopropylamide (3.6 mL, 0.59 M in THF, 2.1 mmol) was added dropwise to a solution of 4,5-bis(ethylthio)tetrathiafulvalene (591 mg, 1.82 mmol) in dry THF (40 mL) cooled to  $-78\text{ }^\circ\text{C}$ . The mixture was stirred at  $-78\text{ }^\circ\text{C}$  for 2 h, whereupon 1,2-diiodoethane (583 mg, 2.1 mmol) was added in one portion. Stirring was continued for 2 h at  $-78\text{ }^\circ\text{C}$  and the mixture was then allowed to heat to  $20\text{ }^\circ\text{C}$  and stirred for an additional 10 min at this temperature. The reaction mixture was partitioned between saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  (10 mL) and  $\text{Et}_2\text{O}$  (150 mL). The aqueous phase was extracted with  $\text{Et}_2\text{O}$  (100 mL) and the combined organic phases were washed with  $\text{H}_2\text{O}$  (100 mL), dried with  $\text{MgSO}_4$ , filtered and concentrated *in vacuo*. Column chromatography ( $\text{SiO}_2$ ,  $\text{CS}_2$ ) afforded the title compound as a dark yellow oil. Yield: 330 mg (40%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.43 (s, 1 H), 2.85 (2 x q,  $J$  = 7.3 Hz, 4 H), 1.31 (2 x t,  $J$  = 7.3 Hz, 6 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 128.0, 127.9, 124.1, 115.5, 108.8, 63.6, 30.6 (2 x S- $\text{CH}_2$ ), 15.1, 15.0. MS (MALDI-TOF):  $m/z$  449.6 [ $\text{M}^{++}$ ]. HRMS (ESI):  $m/z$  449.8210 [ $\text{M}^{++}$ ] (calcd. for  $\text{C}_{10}\text{H}_{11}\text{IS}_6^+$ : 449.8224).

#### TTF-TEE (6)

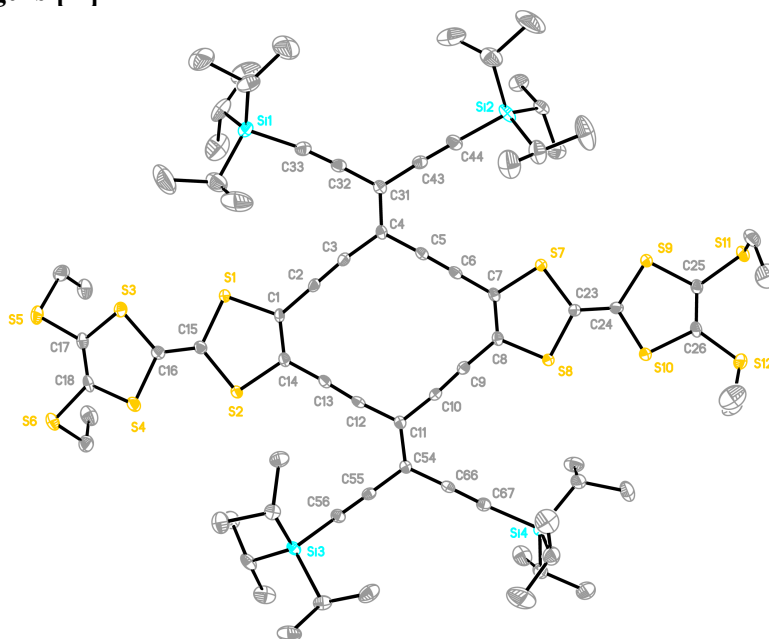


To a solution of  $\text{K}_2\text{CO}_3$  (79 mg, 0.57 mmol) in MeOH (10 mL), TEE **3** (84 mg, 0.14 mmol) dissolved in THF (2 mL) was added, and the mixture was stirred at rt for 20 min, whereupon the solution was filtered through a short plug of silica ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ). Due to the instability of the dsilylated TEE, it was directly subjected to the next step. A solution of 4,5-bis(ethylthio)-4'-iodotetrathiafulvalene (165 mg, 0.37 mmol) in  $i\text{Pr}_2\text{NH}$  (8 mL) was argon-degassed on an ultrasound bath for 30 min, whereupon  $\text{Pd}(\text{PPh}_3)_4$  (34 mg, 0.029 mmol) and  $\text{CuI}$  (3.3 mg, 0.017 mmol) were added followed by a solution of the desilylated TEE (0.14 mmol) in argon-degassed  $i\text{Pr}_2\text{NH}$  (3 mL). The reaction mixture was stirred at  $20\text{ }^\circ\text{C}$  under argon for 12 h, whereupon heptane (10 mL) was added and the mixture was passed through a plug ( $\text{SiO}_2$ , heptane/ $\text{CH}_2\text{Cl}_2$  1:1) and concentrated *in vacuo*. Column chromatography ( $\text{SiO}_2$ , heptane/ $\text{EtOAc}$  8:2) afforded the product **6** as a purple glass-like solid. Yield: 118 mg (76%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.58 (s, 2 H), 2.85 (q,  $J$  = 7.4 Hz, 8 H), 1.32 (t,  $J$  = 7.4 Hz, 12 H), 1.12 (s, 42 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 128.4, 127.8, 126.7, 118.9, 115.6, 114.9, 112.6, 109.8, 104.6, 103.6, 90.6, 89.6, 30.7 (2 x S- $\text{CH}_2$ ), 18.9, 15.24, 15.20, 11.4. MS (MALDI-TOF):  $m/z$  1080.5 ( $\text{M}^+$ ). HRMS (ESI):  $m/z$  1080.1138 [ $\text{M}^{++}$ ] (calcd. for  $\text{C}_{48}\text{H}_{64}\text{S}_{12}\text{Si}_2^+$ : 1080.1190).

## X-Ray Crystal Data for TTF-RA 5

The 14 C atoms of the RA core are close to planar (RMS deviation from mean plane 0.28 Å), and the first five-membered ring of one of the TTF units lies essentially within the plane of this core. The second five-membered ring of the same TTF unit bends at the S atoms, forming an angle of *ca* 11° to the RA ring plane. The other TTF unit bends significantly at the S atoms of both rings, forming angles of *ca* 13° and 29° between the successive planar sections and the plane of the RA core.

### Selected bond lengths [Å]

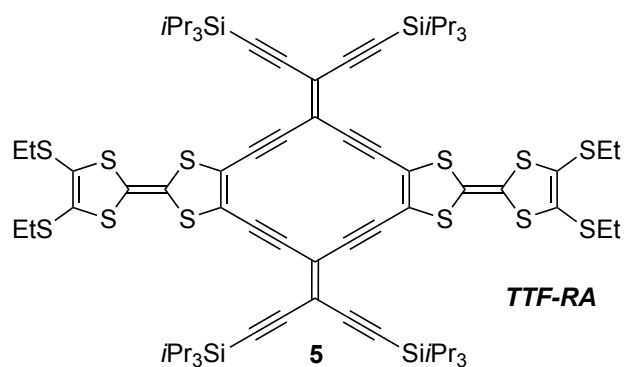


Radiannulene core		TTF		TTF	
C1—C2	1.408(4)	C1—S1	1.766(3)	C7—S7	1.754(3)
C2—C3	1.204(4)	C14—S2	1.755(3)	C8—S8	1.749(3)
C3—C4	1.422(4)	S1—C15	1.756(3)	S7—C23	1.762(3)
C4—C5	1.418(4)	S2—C15	1.755(3)	S8—C23	1.754(3)
C5—C6	1.206(4)	C15—C16	1.333(4)	C23—C24	1.331(4)
C6—C7	1.401(4)	C16—S3	1.755(3)	C24—S9	1.751(3)
C7—C8	1.361(4)	C16—S4	1.757(3)	C24—S10	1.761(3)
C8—C9	1.406(4)	S3—C17	1.765(3)	S9—C25	1.765(3)
C9—C10	1.198(4)	S4—C18	1.761(3)	S10—C26	1.756(3)
C10—C11	1.418(4)	C17—C18	1.337(4)	C25—C26	1.339(4)
C11—C12	1.420(4)	S5—C17	1.746(3)	S11—C25	1.750(3)
C12—C13	1.205(4)	S6—C18	1.751(3)	S12—C26	1.745(3)
C13—C14	1.405(4)				
C14—C1	1.357(4)				

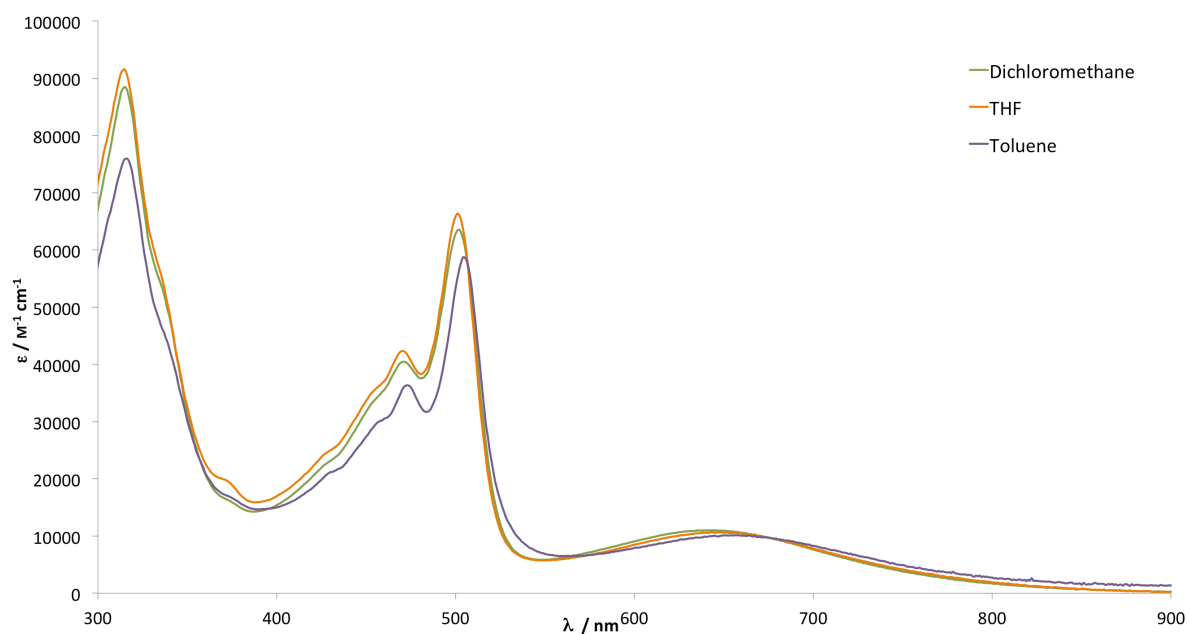
  

Ethynyl		Ethynyl	
C4—C31	1.380(4)	C11—C54	1.381(4)
C31—C32	1.427(4)	C54—C55	1.426(4)
C32—C33	1.205(4)	C55—C56	1.209(4)
C33—Si1	1.852(3)	C56—Si3	1.845(3)
C31—C43	1.432(4)	C54—C66	1.430(4)
C43—C44	1.206(4)	C66—C67	1.209(4)
C44—Si2	1.855(3)	C67—Si4	1.852(3)

## UV-Vis Absorption Spectra of TTF-RA 5



TTF-RA **5** exhibits a small degree of solvatochromism:

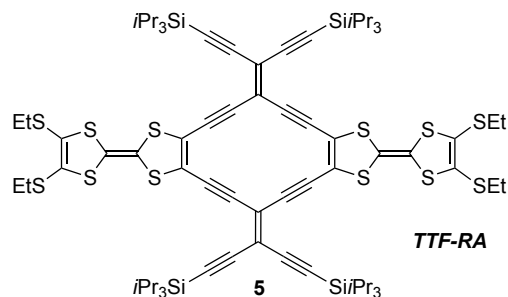


TTF-RA **5** forms a red solid film (photo to the left below), but is green in solution ( $CH_2Cl_2$ , photo to the right below). When crystallized by slow diffusion of methanol into  $CH_2Cl_2$ , TTF-RA **5** forms dark green crystals.

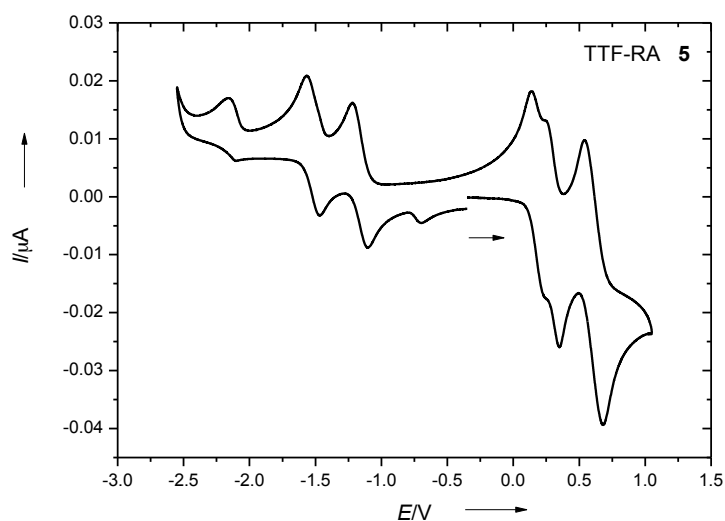




## Electrochemistry



### Cyclic voltammogram of TTF-RA **5**:

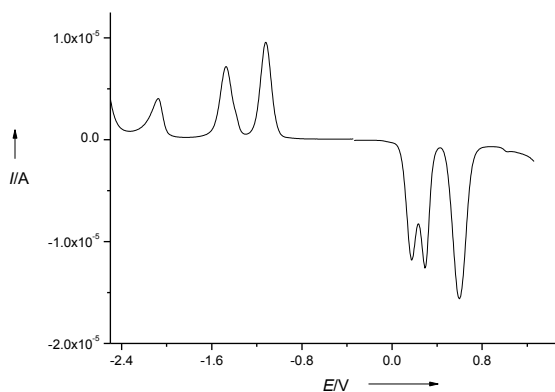


Half-wave potentials vs  $\text{FeCp}_2^+/\text{FeCp}_2$ : +0.20 (1e), +0.29 (1e), +0.61 (2e), -1.16 (1e), -1.52 (1e)<sup>a)</sup>.

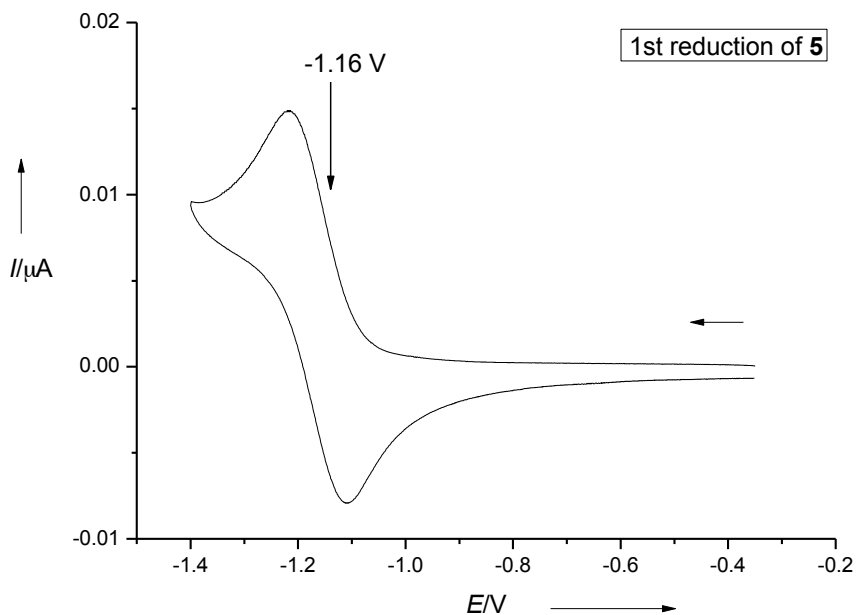
<sup>a)</sup> Partially reversible; a third less intense partially reversible wave was observed at -2.13 V and an oxidation wave associated with the  $E_{\text{red}2}$  at  $E_{\text{pa}} = -0.70$  V.

The voltammogram of **5** shows a set of reduction and oxidation peaks in which the heights of the two closely spaced oxidation peaks are nearly the same as those for the two one-electron reduction peaks and in addition the peak for the third oxidation process is roughly twice this height. Thus, from the relative peak heights alone it can be deduced that the oxidation of **5** includes two closely spaced one-electron processes followed by a two-electron process.

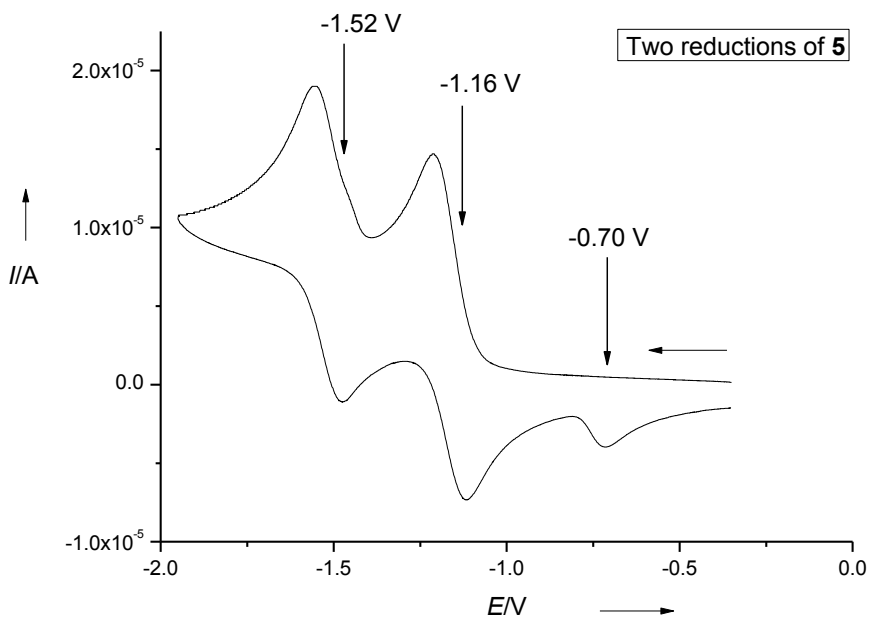
### Differential-pulse voltammogram of TTF-RA **5**:



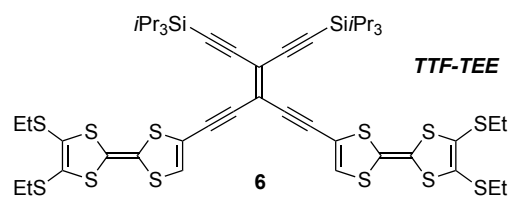
**Cyclic voltammogram showing the fully reversible, first one-electron reduction of TTF-RA 5:**



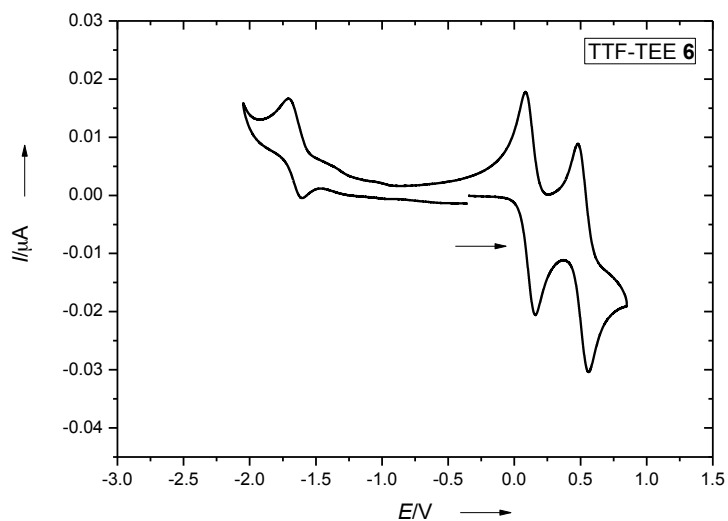
**Cyclic voltammogram showing the first two one-electron reductions of TTF-RA 5:**



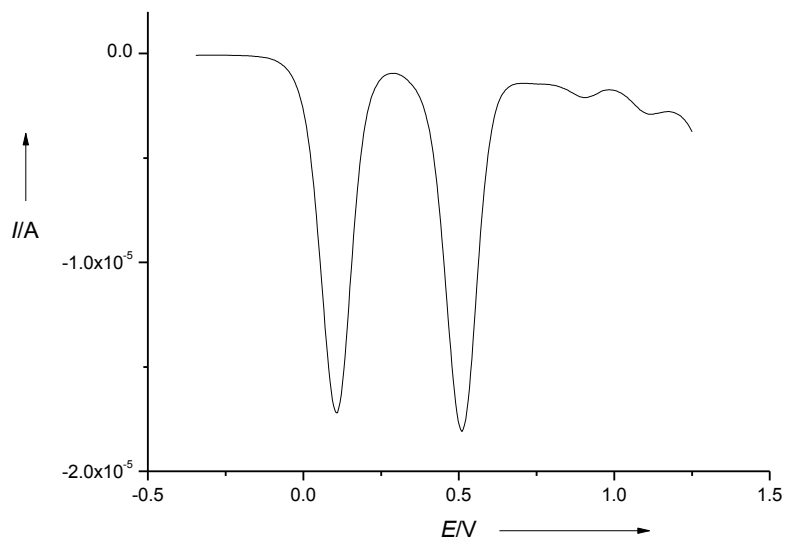
The 2nd reduction at -1.52 V was not fully reversible and gave the corresponding oxidation wave at -0.70 V, which could be the oxidation of the protonated dianion.



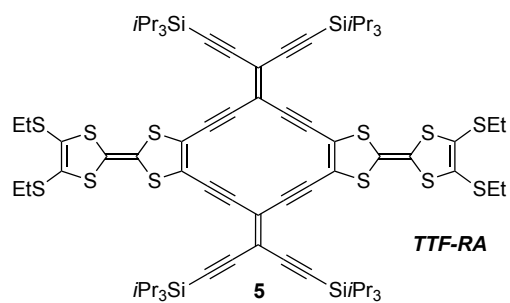
**Cyclic voltammogram of TTF-TEE 6:**



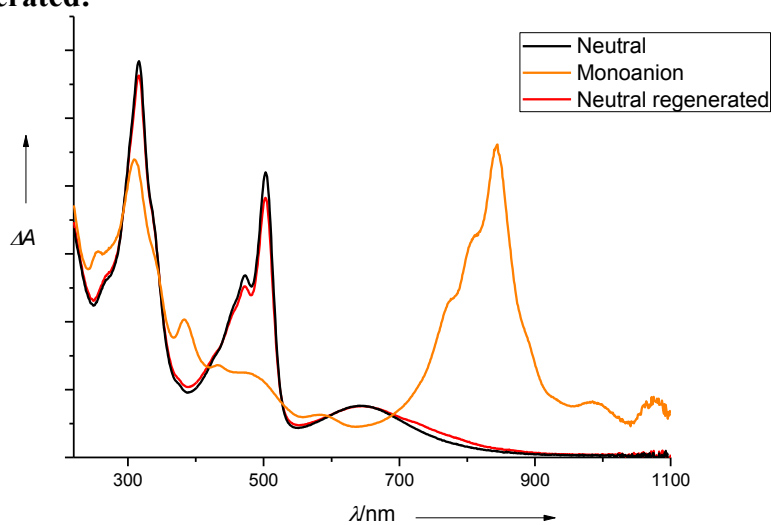
**Differential-pulse voltammogram showing the two two-electron oxidations of TTF-TEE 6:**



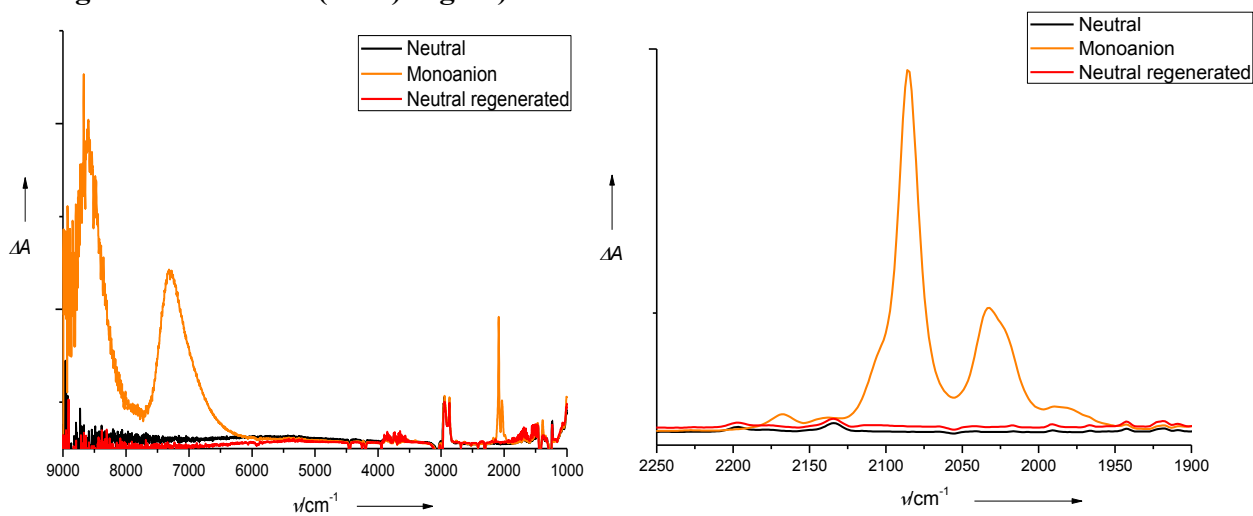
## Spectroelectrochemistry of TTF-RA 5 (UV-Vis-NIR and NIR-IR)



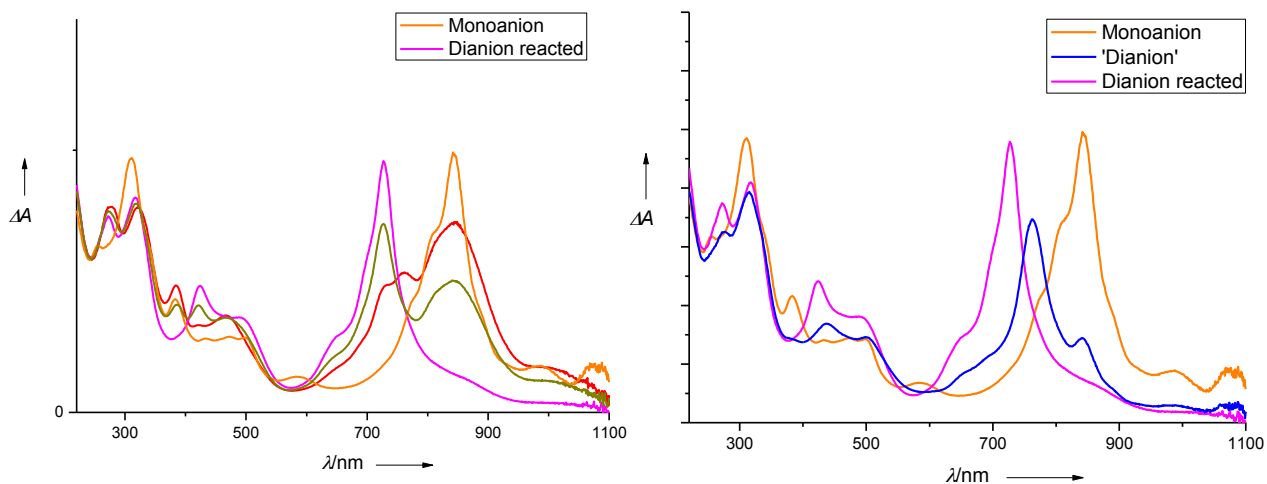
UV-Vis-NIR spectra of neutral TTF-RA 5, its monoanion, and the neutral species regenerated:



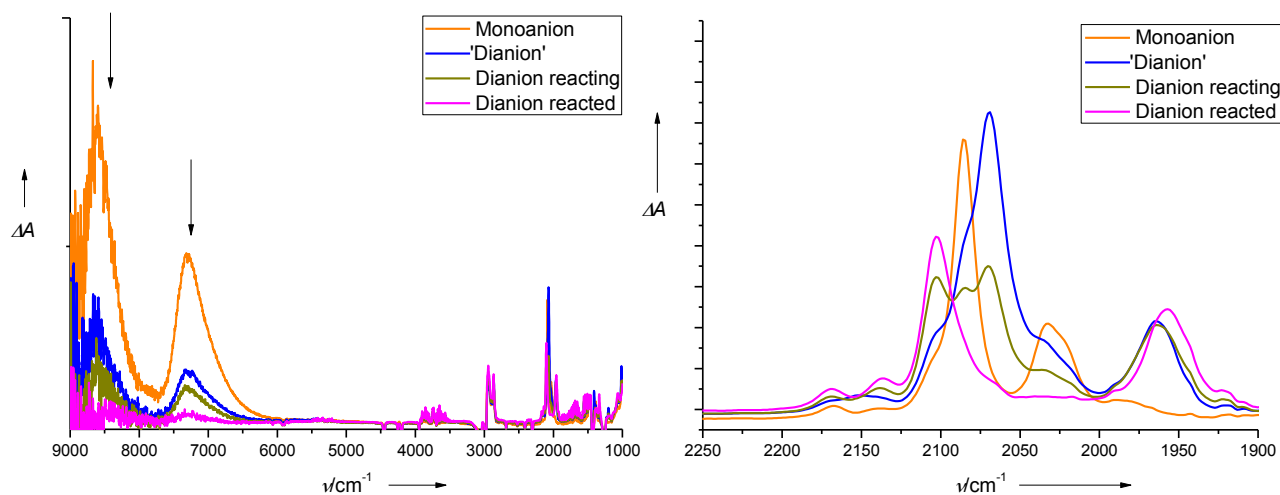
NIR-IR Spectra of neutral TTF-RA 5, its monoanion, and the neutral species regenerated (to the right is shown the  $\nu(\text{C}\equiv\text{C})$  region):



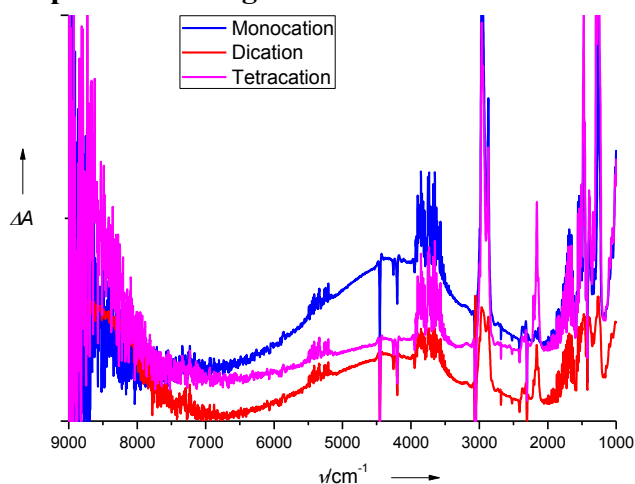
### UV-Vis-NIR spectra of the reduction of the monoanion 5<sup>-</sup> to the 'dianion':



### NIR-IR spectra showing reduction of the monoanion 5<sup>-</sup> to the 'dianion' which reacts further (to the right is shown the $\nu(\text{C}\equiv\text{C})$ region):

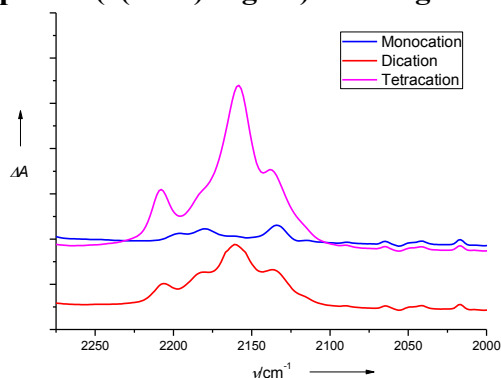


### NIR-IR spectra showing the oxidation of the monocation $5^+$ to the di- and tetracations:



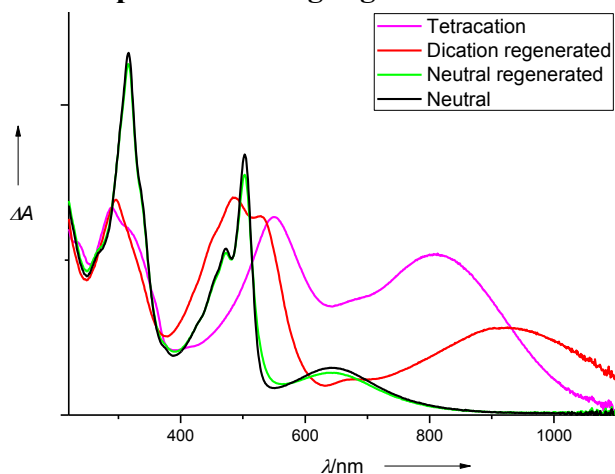
NB: An intervalence CT band is seen at 4431  $\text{cm}^{-1}$  for the monocation (mixed valence state). For the dication the band is still visible, albeit of lower intensity, due to dis/comproportionation reactions. Moreover, exhaustive oxidation may not have been achieved in the cell, and the band has therefore not disappeared completely in the spectrum of the tetracation. It should be noted also that the baseline fluctuated somewhat during the experiment.

### IR spectra ( $\nu(\text{C}\equiv\text{C})$ region) showing the oxidation of the monocation $5^+$ to the tetracation:



NB: The baseline fluctuated during the experiment.

### UV-Vis-NIR spectra showing regeneration of neutral 5 from the tetracation:



UV-Vis-NIR spectroelectrochemical data (220-1100 nm / 45454-9090 cm<sup>-1</sup>) of TTF-RA **5** (0.6 x 10<sup>-3</sup> M in CH<sub>2</sub>Cl<sub>2</sub> + 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>]).

Redox State of <b>5</b>	Peak values in nm/cm <sup>-1</sup> (relative Absorbance)								
+4	289/34602 (0.668)	550/ 18182 (0.639)	813/ 12300 (0.521)						
+2	295/ 33898 (0.696)	484/ 20661 (0.721)	525/ 19047 (0.635)	676/ 14793 (0.110)	930/ 10753 (0.295)				
+1	315/ 31746 (0.863)	502/ 19920 (0.623)	690/ 14493 (0.104)	930/ 10753 (0.108)					
neutral	316/ 31646 (1.169)	473/ 21142 (0.533)	503/ 19881 (0.829)	646/ 15480 (0.148)					
-1	256/ 39063 (0.607)	309/ 32362 (0.878)	383/ 26110 (0.467)	433/ 23095 (0.273)	585/ 17094 (0.126)	815/ 12270 (0.659)	845/ 11834 (0.923)	985/ 10152 (0.166)	1080/ 9259 (0.174)
'-2'*	766/ 13055 (0.461)								
-2 react	272/ 36765 (0.673)	317/ 31546 (0.739)	424/ 23585 (0.433)	492/ 20325 (0.317)	727/ 13755 (0.812)				

\*The suspected dianion was unstable but had one peak that clearly belonged only to it.

NIR-IR spectroelectrochemical data (1000-9000 cm<sup>-1</sup> / 10000-1111 nm) of TTF-RA **5** (0.6 x 10<sup>-3</sup> M in CH<sub>2</sub>Cl<sub>2</sub> + 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>]).

Redox State of <b>5</b>	NIR peak values: cm <sup>-1</sup> (range) / nm	ν (C≡C) in cm <sup>-1</sup>					
+4	7750-9000 <sup>#</sup> m / 1290-1111 <sup>#</sup>		2208vw	2180sh vw	2158w	2138vw	
+2	7500-9000 <sup>#</sup> s / 1333-1111 <sup>#</sup>	4431br w / 2257	2206vw	2180vw	2161w	2137vw	
+1	8000-9000 <sup>#</sup> w / 1250-1111 <sup>#</sup>	4431br s (7000-2000) / 2257 (1429-5000)		2180vw	2161vw	2133vw	
neutral				2197vw		2134vw	
-1	8597vs (7850- 9000 <sup>#</sup> ) / 1163 (1274-1111 <sup>#</sup> )	7308br s (6250-7700) / 1368 (1600-1299)	2167vw	2138vw	2085s	2033m	1989w
'-2'*			2153w	2069s		1964m	
-2 react			2169w	2137w	2103m	1957m	1921sh w

Relative intensity abbreviations vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, br = broad. # continueing > 9000 cm<sup>-1</sup> or < 1111 nm. \*The suspected dianion was unstable but had peaks that clearly belonged only to it.

## Calculations - Complete Gaussian References

In general, calculations were performed with the following version of Gaussian:

*Gaussian 09*, EM64L-G09RevB.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

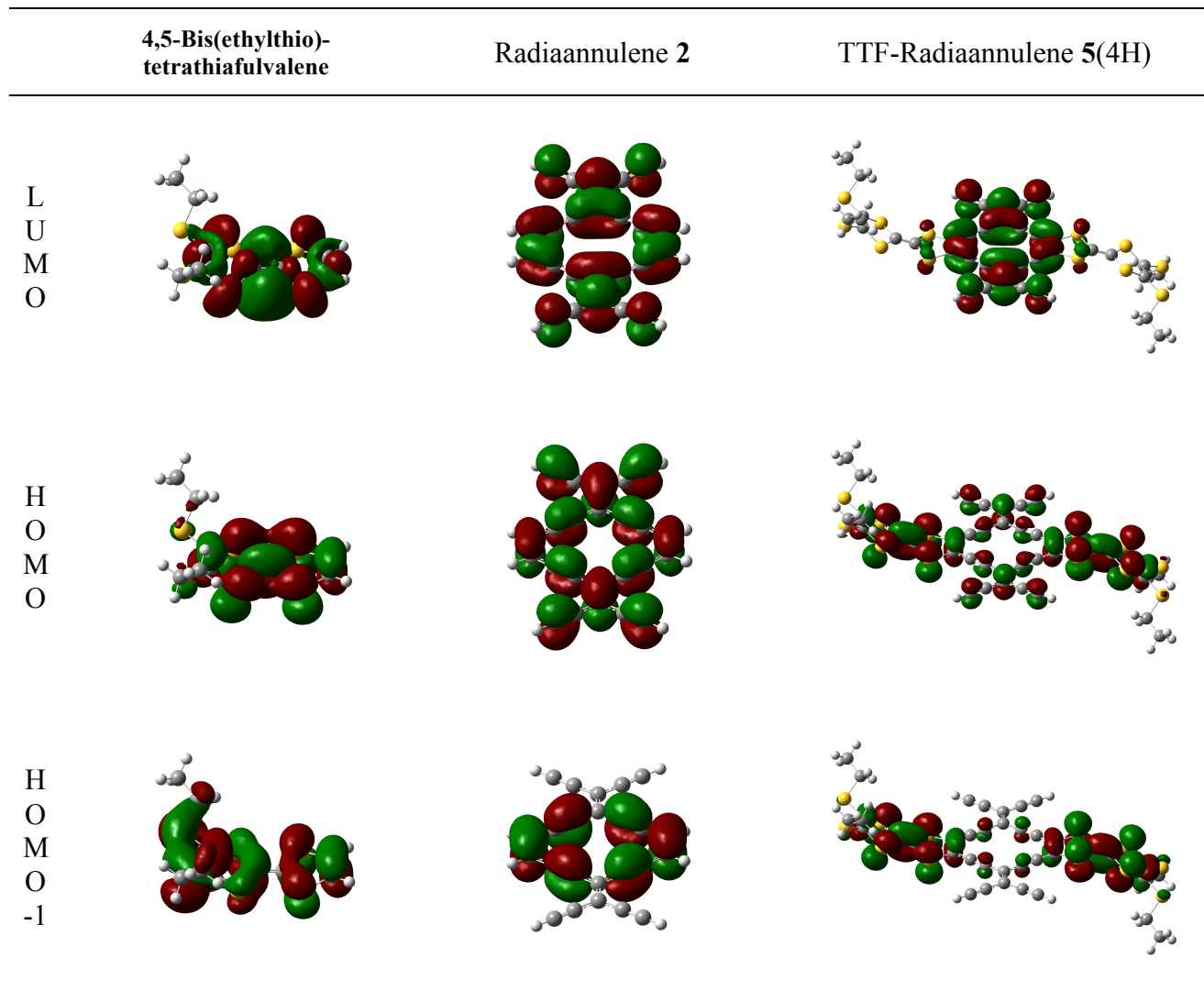
IR spectra were calculated using this version of Gaussian:

*Gaussian 03*, Revision B.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.



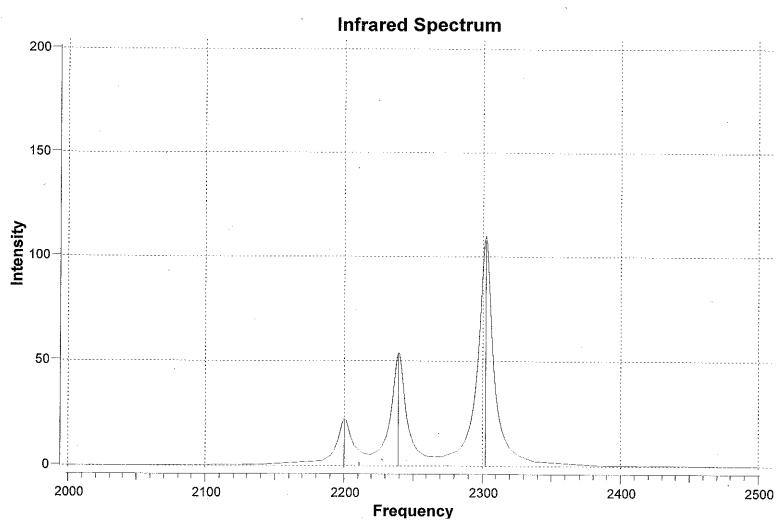
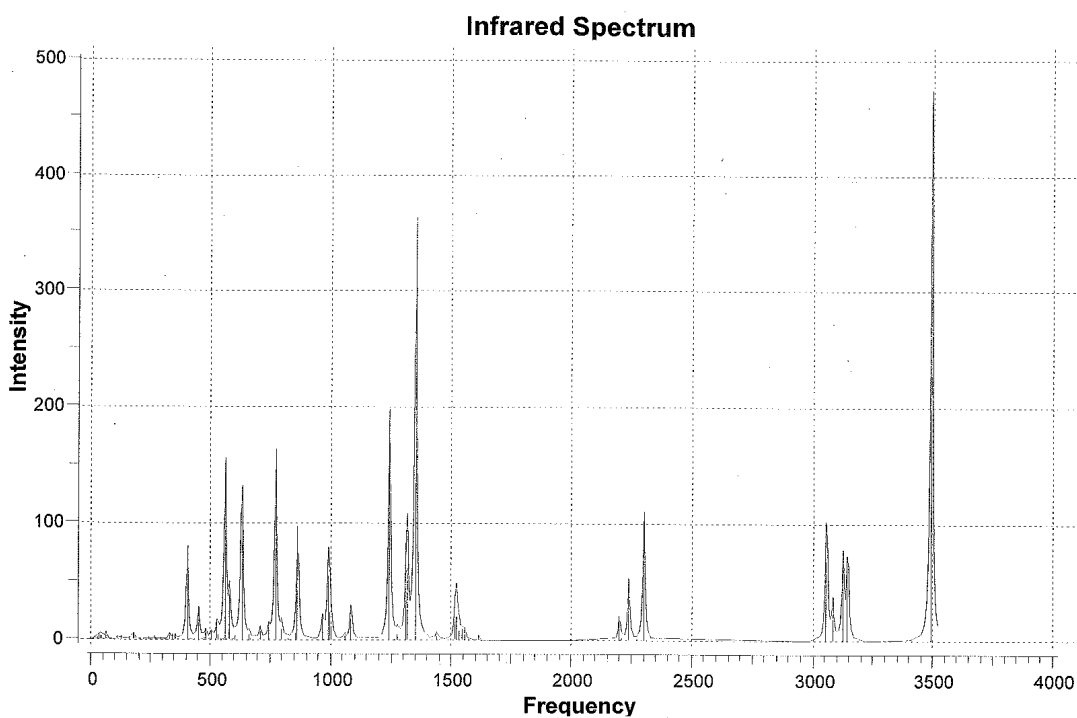
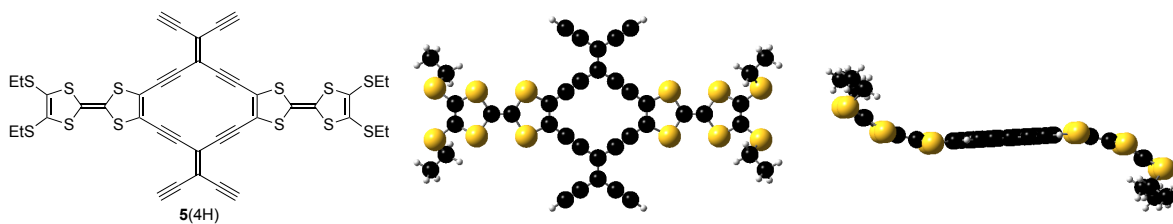
## Calculations - Orbital plots, Geometries and IR Spectra

### Frontier Orbitals (B3LYP/6-31G(d))

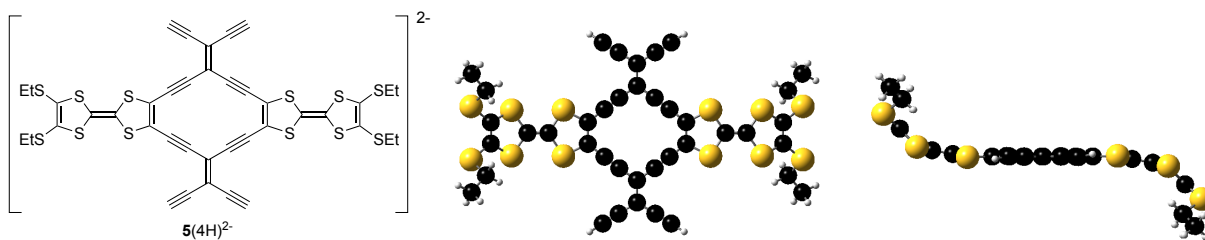


*Calculated Geometries and IR Spectra (frequencies in  $\text{cm}^{-1}$ )*

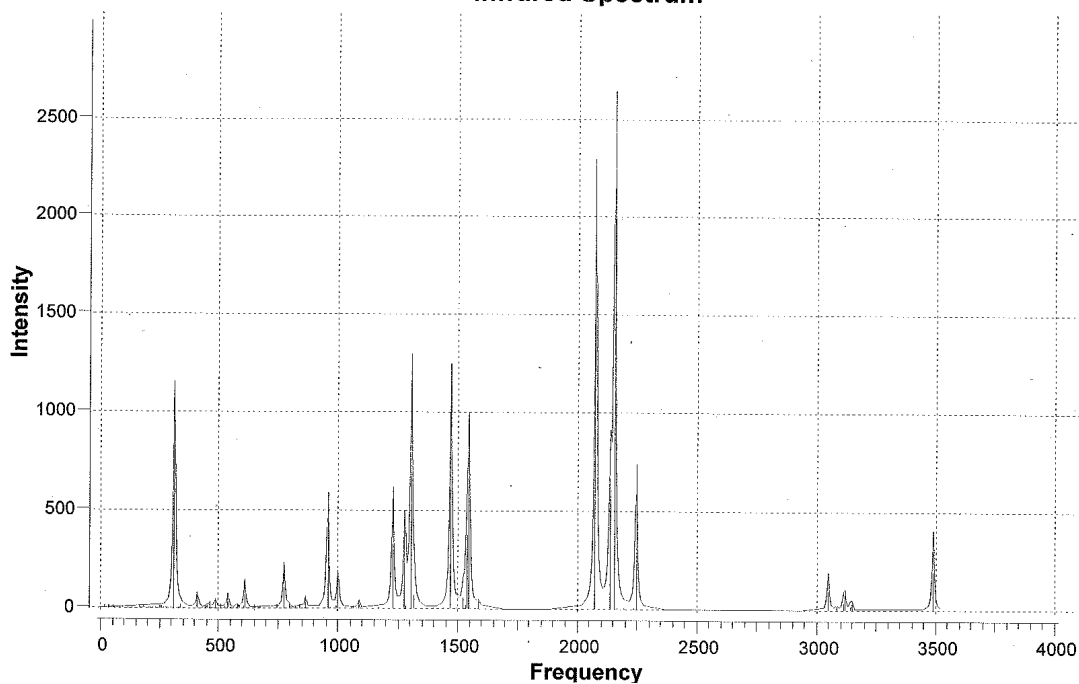
**TTF-Radiaannulene 5(4H) – Neutral (B3LYP/6-31G(d))**



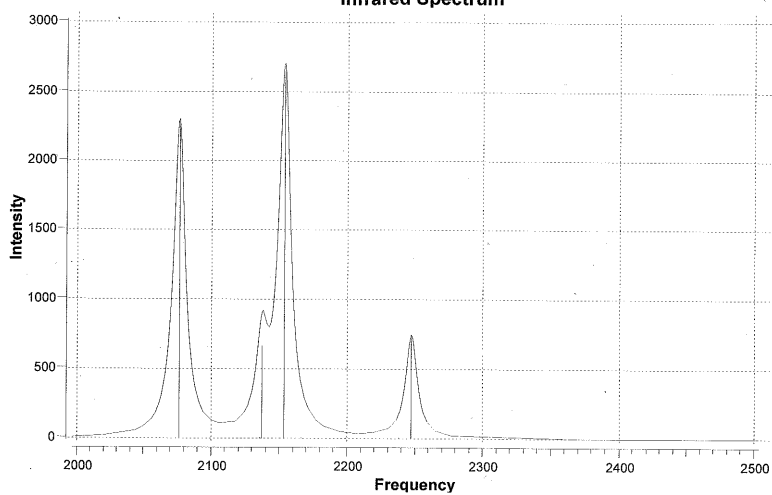
# TTF-Radiaannulene 5(4H) – Dianion (B3LYP/6-31G(d))



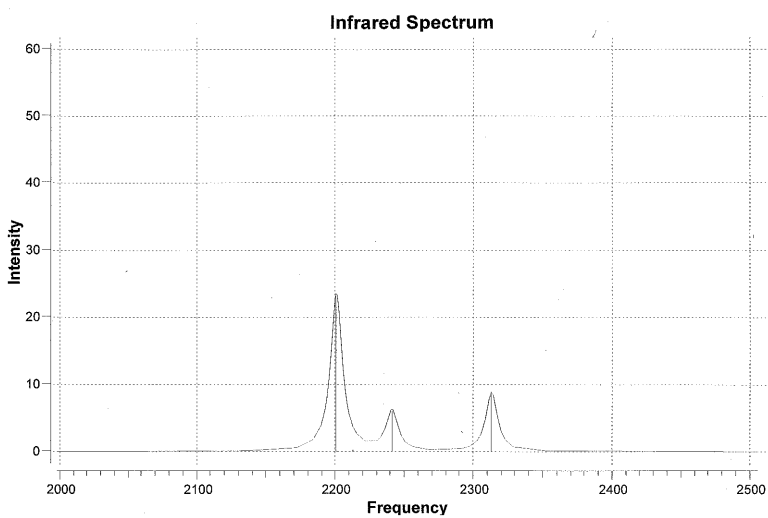
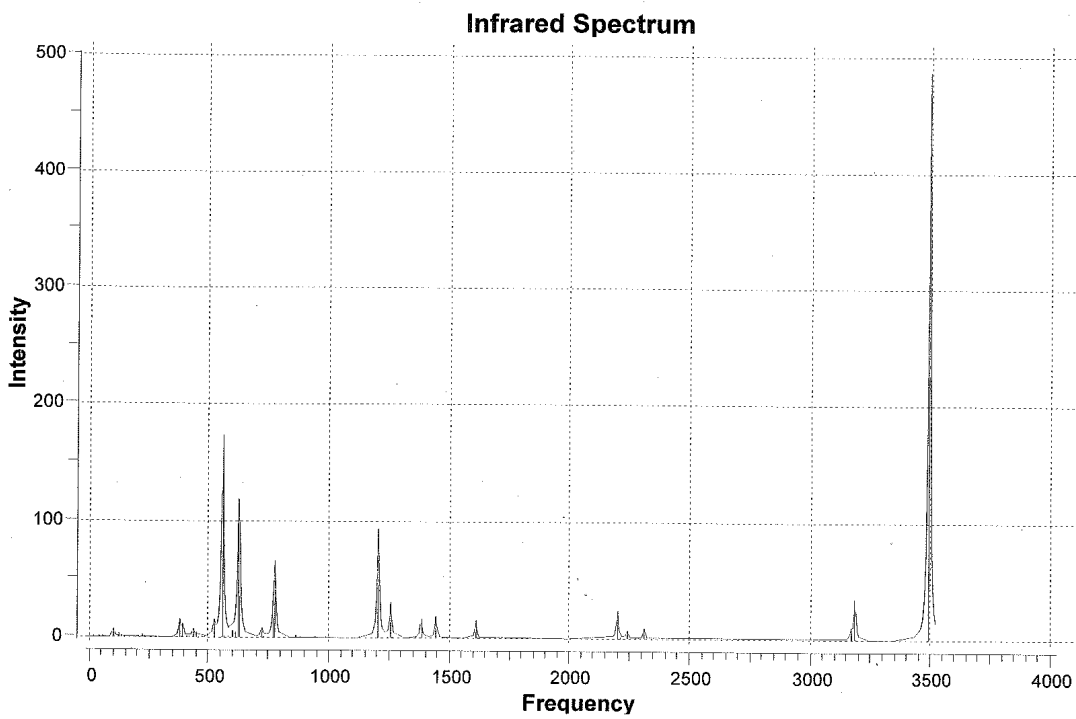
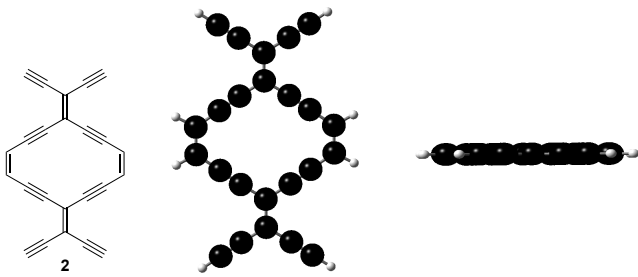
### Infrared Spectrum



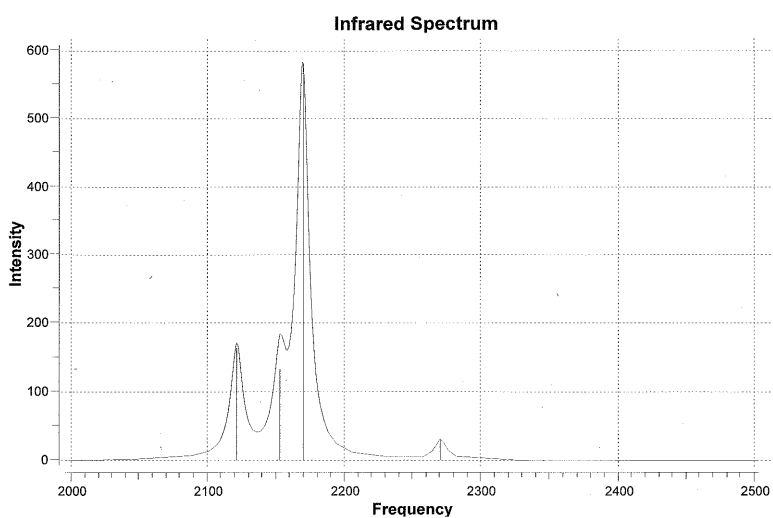
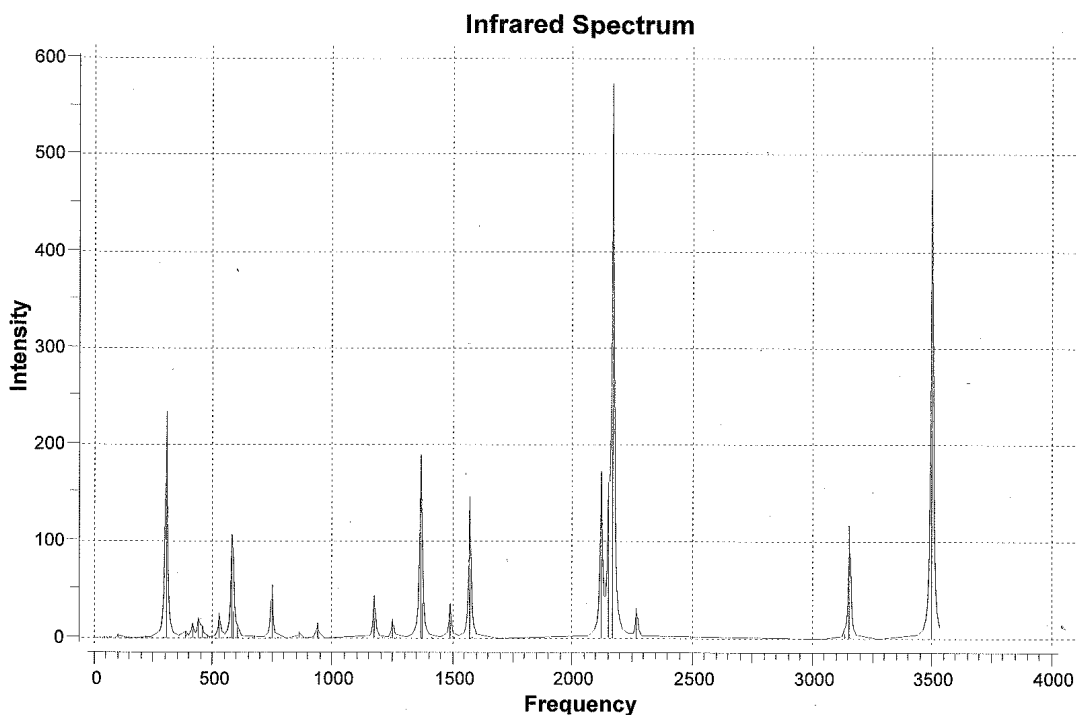
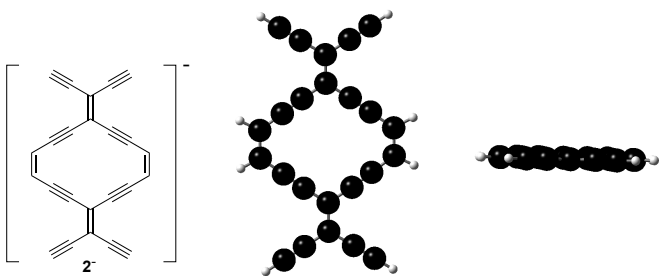
### Infrared Spectrum



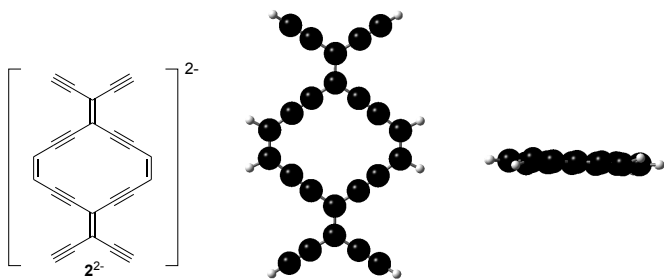
# Radiaannulene 2 – Neutral



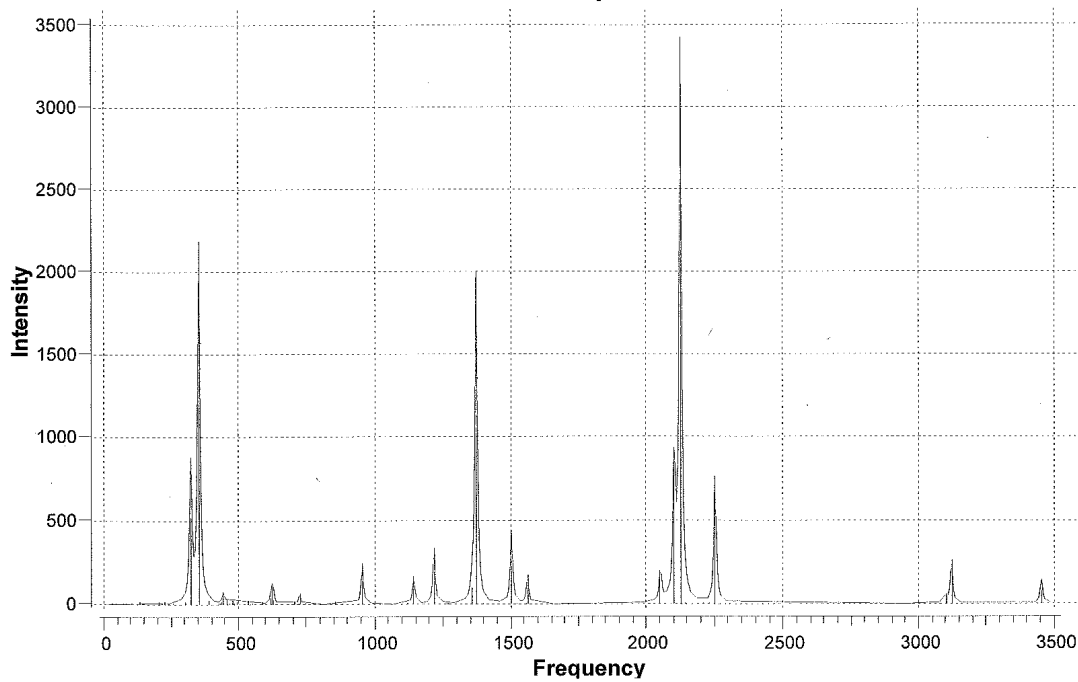
# Radiaannulene 2 – Monoanion



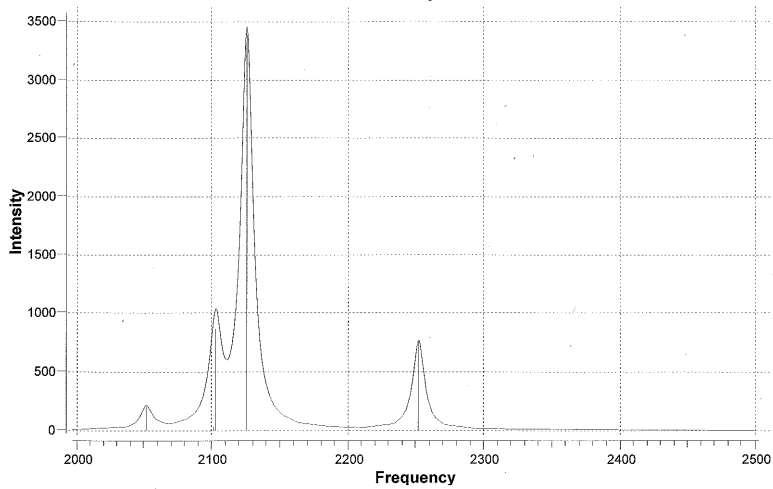
# Radiaannulene 2 – Dianion



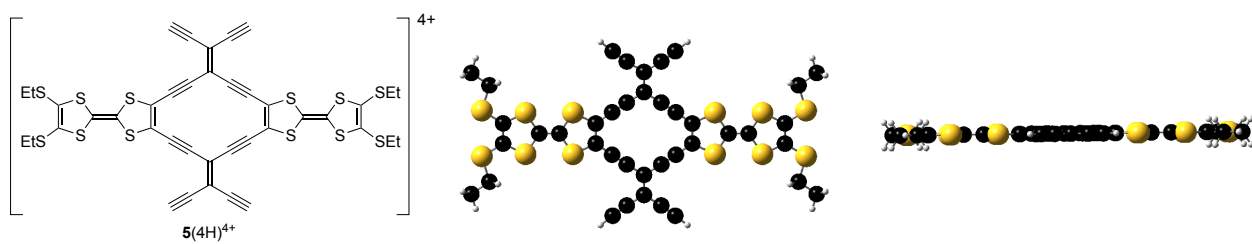
### Infrared Spectrum



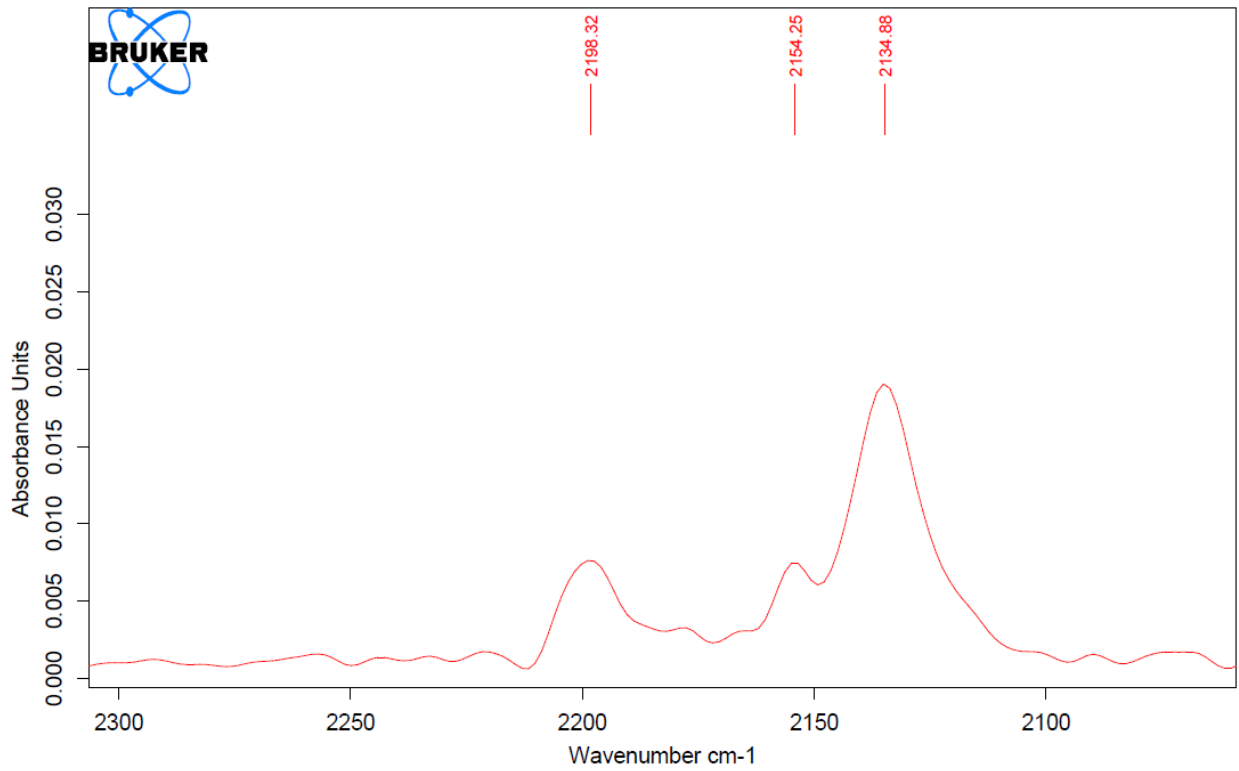
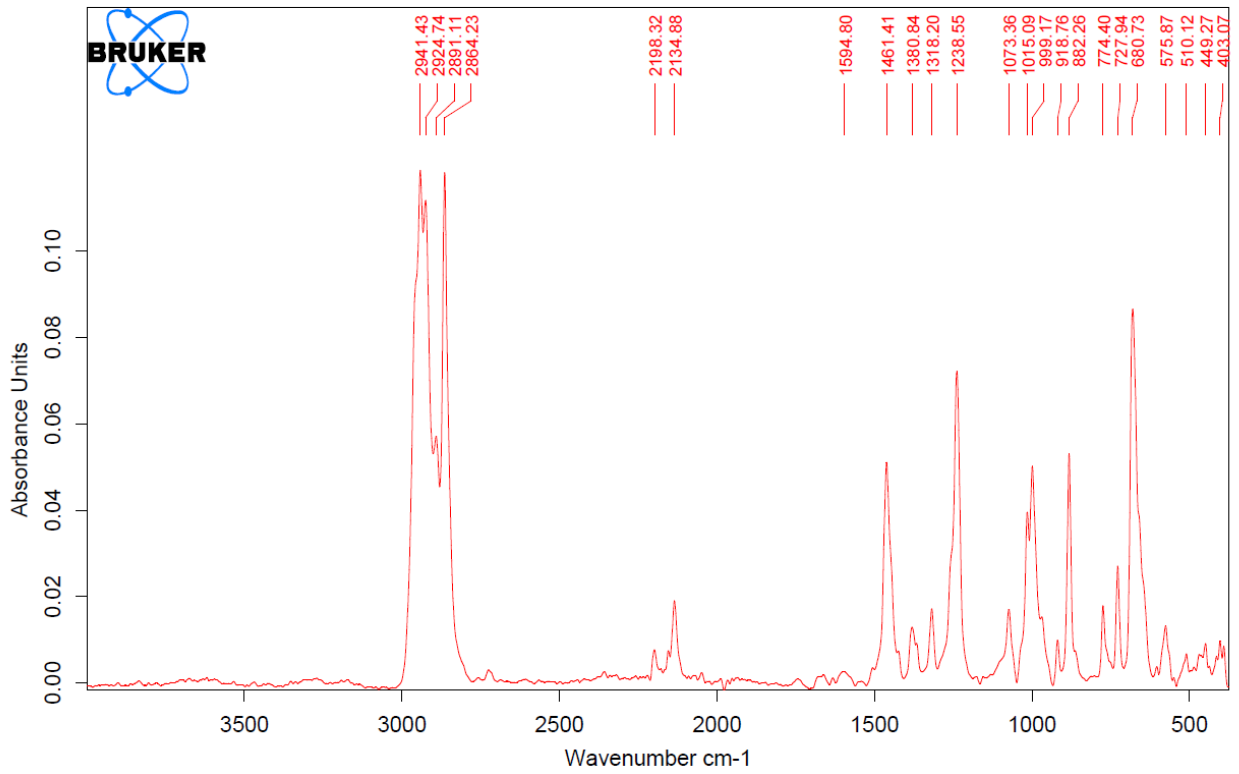
### Infrared Spectrum



## Geometry of $5(4H)^{4+}$ (B3LYP/6-31G(d))

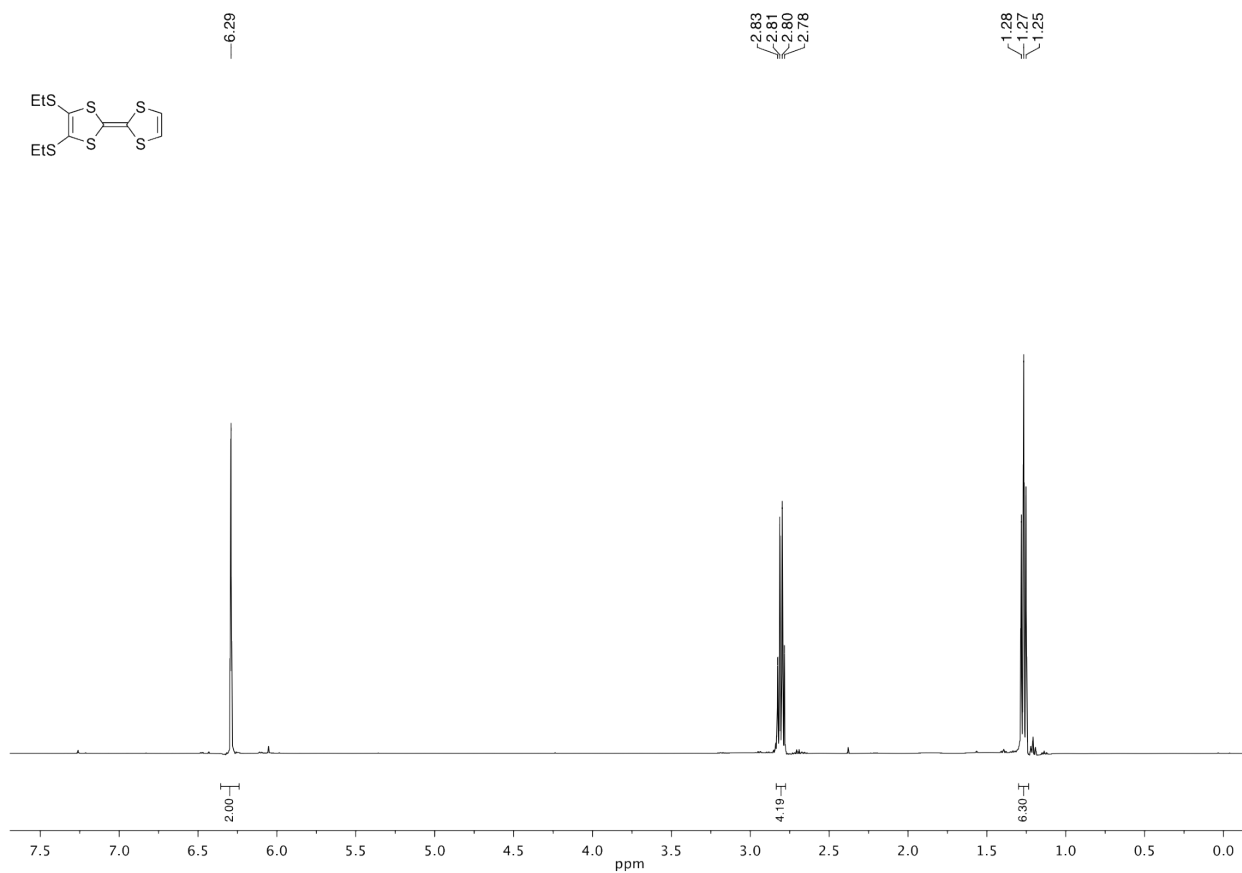


# IR Spectra of TTF-RA 5 (Experimental)

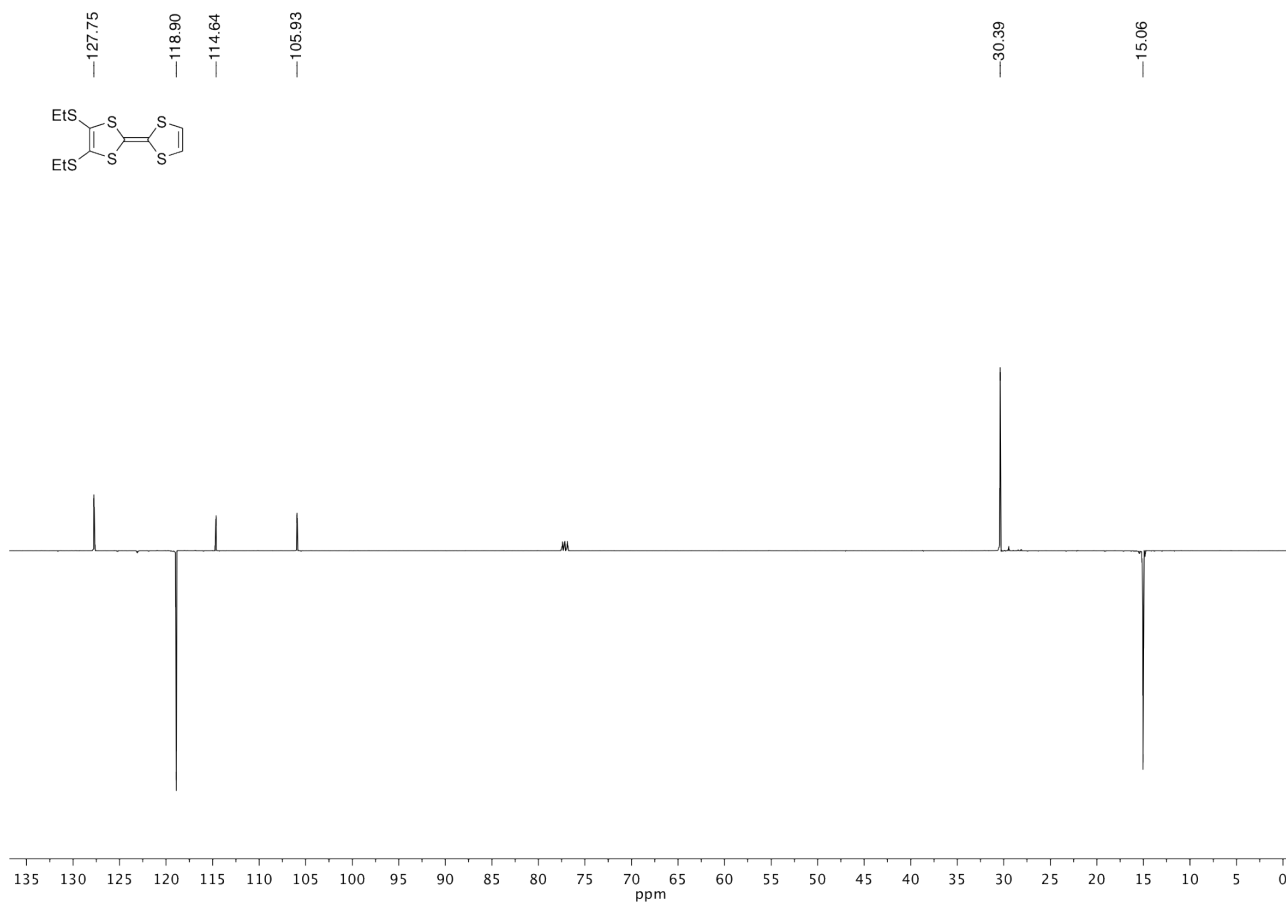




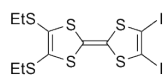
# NMR Spectra



$^1\text{H}$  NMR spectrum of compound 4,5-bis(ethylthio)tetrathiafulvalene ( $\text{CDCl}_3$ ).



$^{13}\text{C}$  APT NMR spectrum of 4,5-bis(ethylthio)tetrathiafulvalene ( $\text{CDCl}_3$ ).

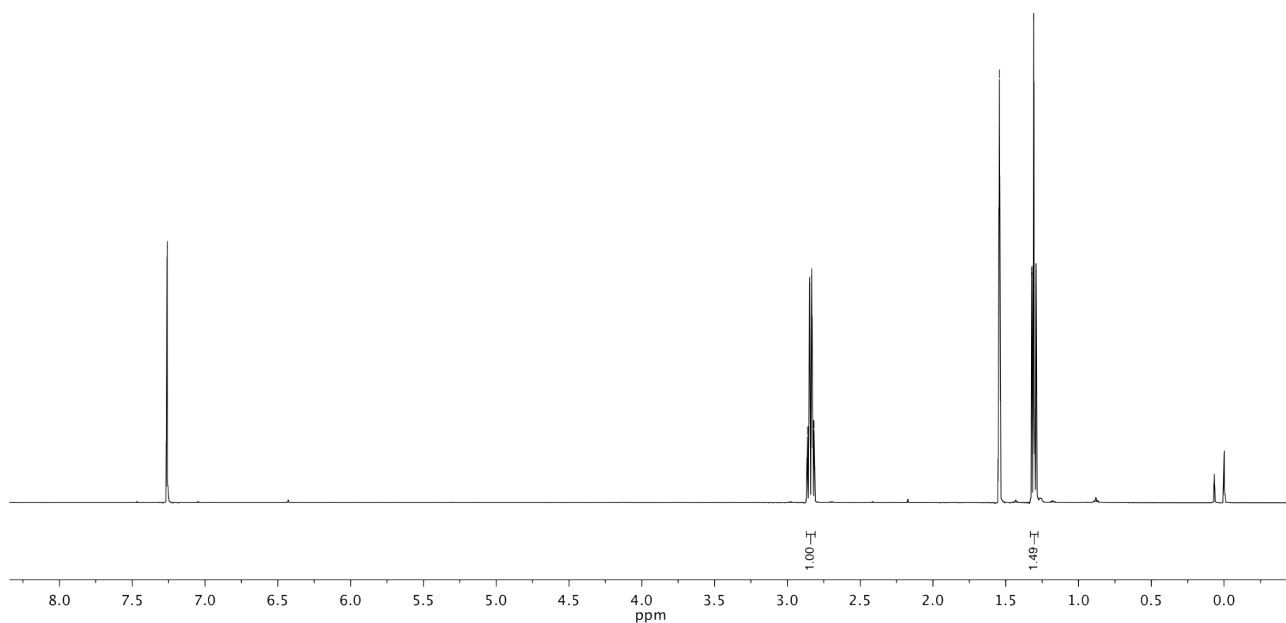


4

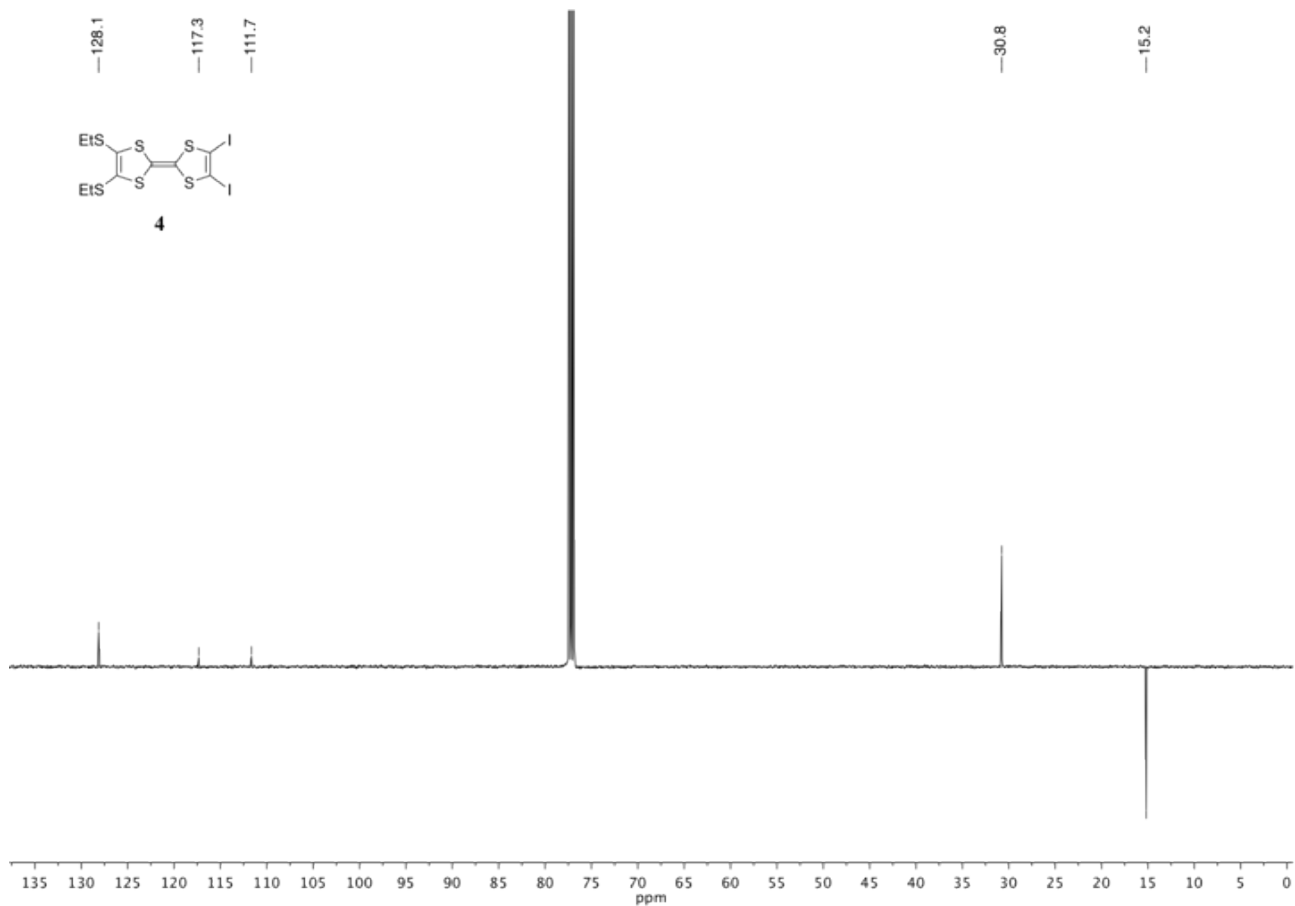
7.26

2.86  
2.85  
2.83  
2.82

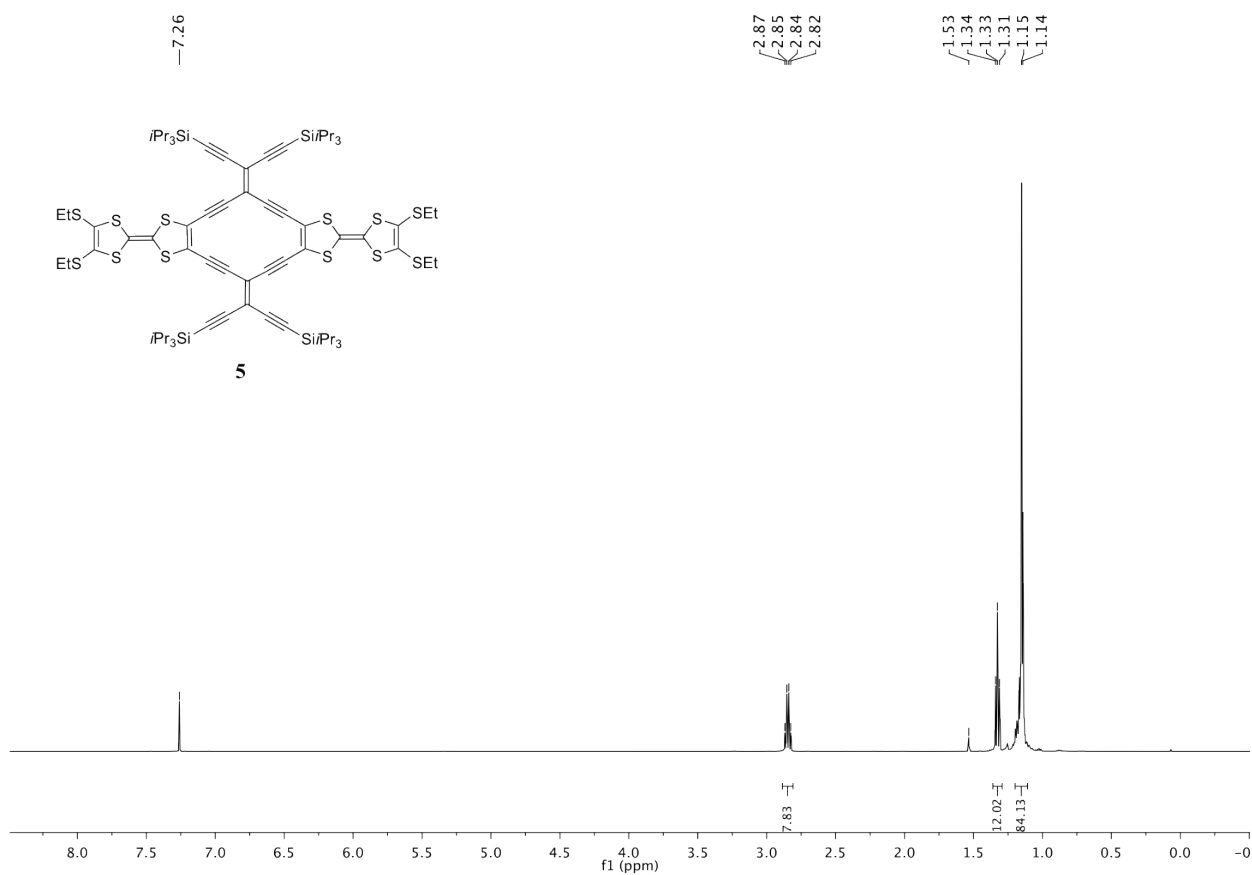
1.54  
1.32  
1.31  
1.29



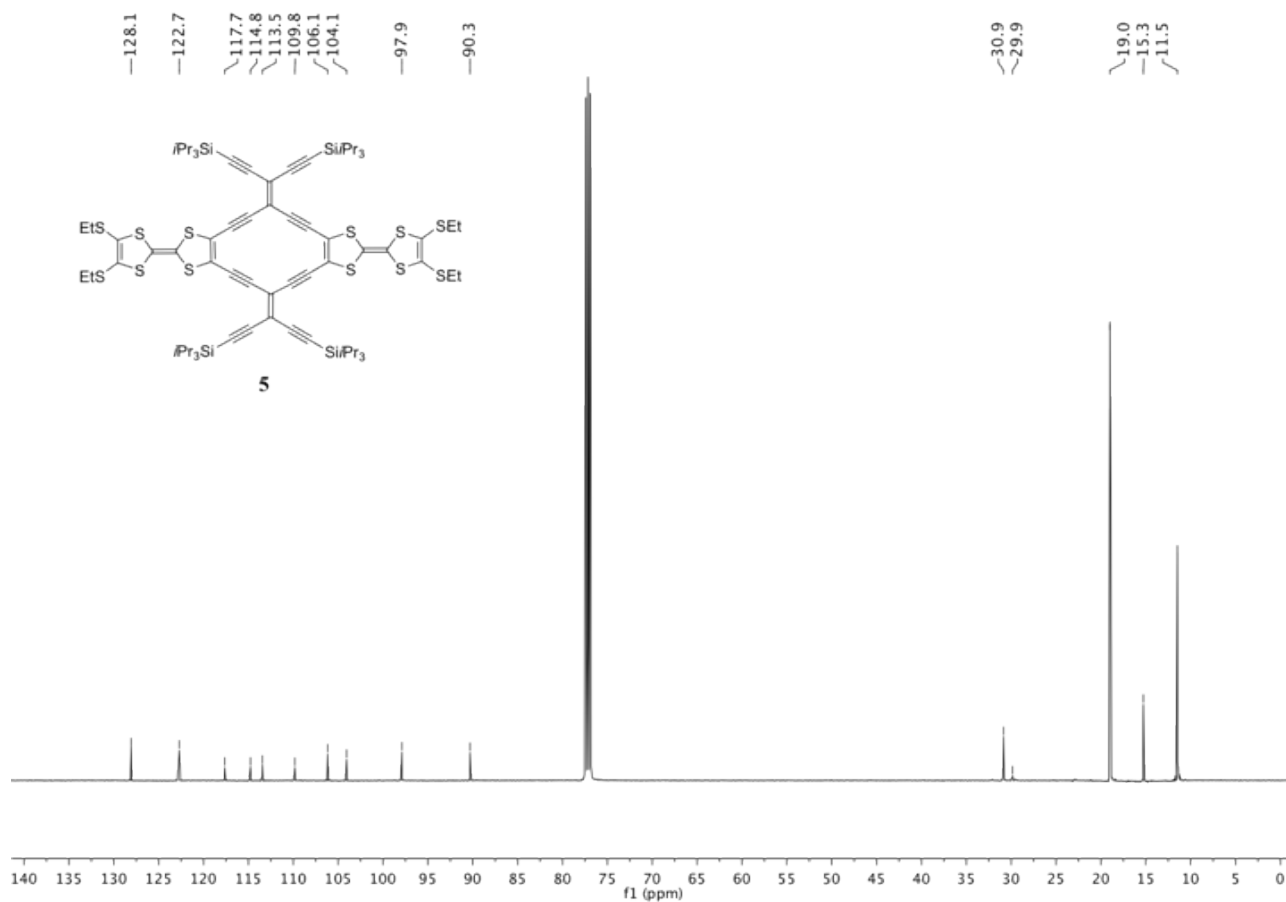
$^1\text{H}$  NMR spectrum of compound 4 ( $\text{CDCl}_3$ ).



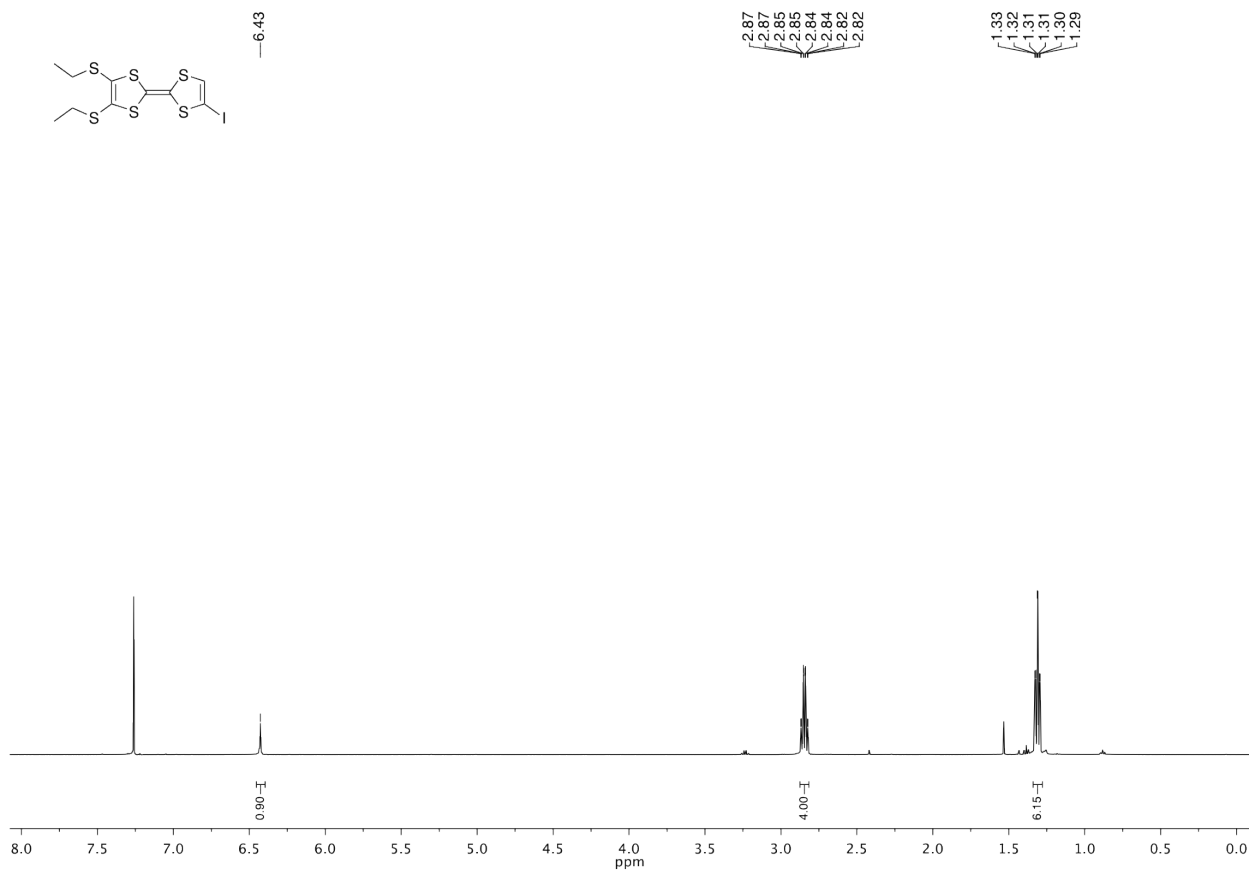
<sup>13</sup>C APT NMR spectrum of compound 4 (CDCl<sub>3</sub>).



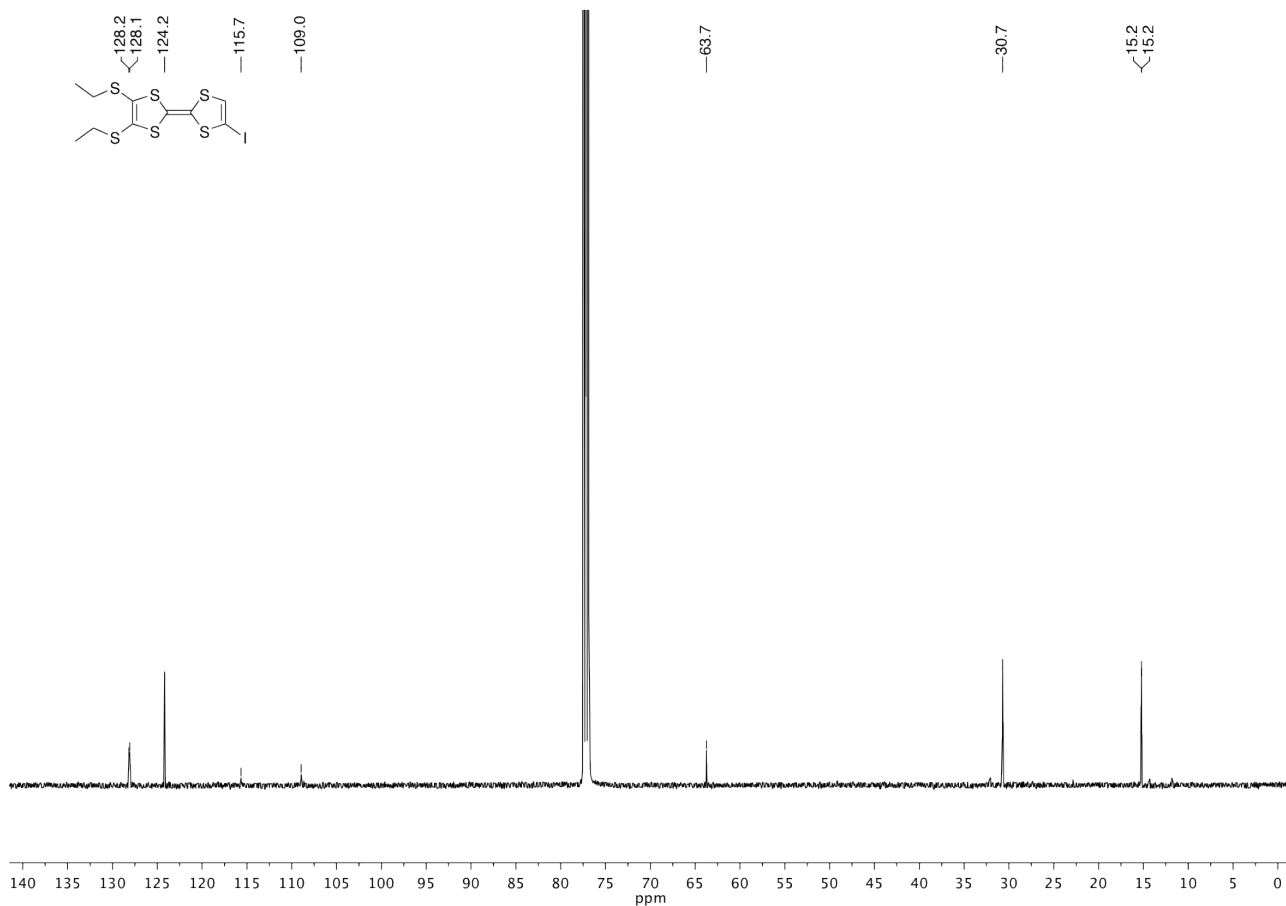
$^1\text{H}$  NMR spectrum of TTF-RA **5** (CDCl<sub>3</sub>).



<sup>13</sup>C NMR spectrum of TTF-RA **5** (CDCl<sub>3</sub>). Signal at 29.9 ppm corresponds to grease.

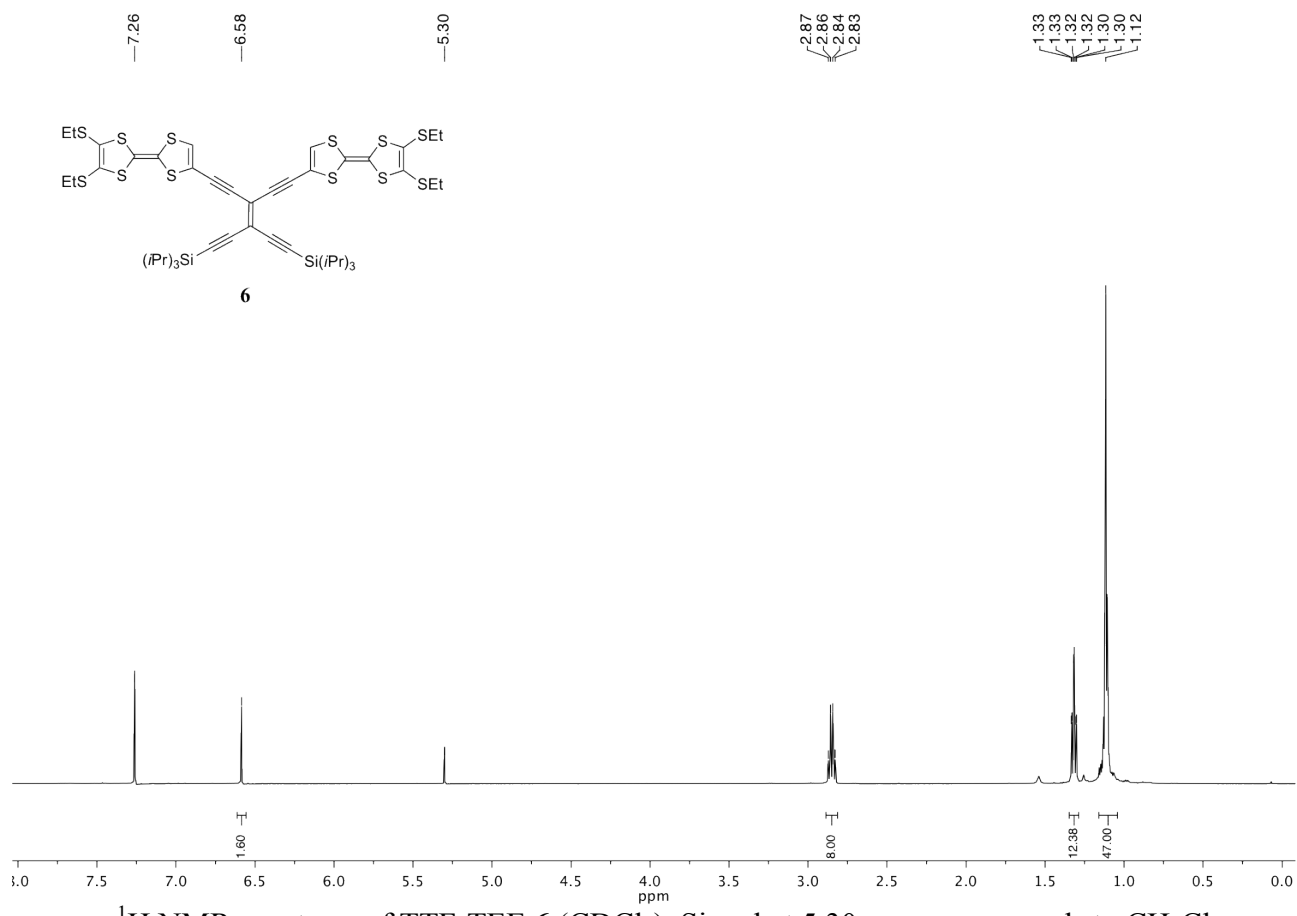


$^1\text{H}$  NMR spectrum of 4,5-bis(ethylthio)-4'-iodotetrathiafulvalene ( $\text{CDCl}_3$ ).

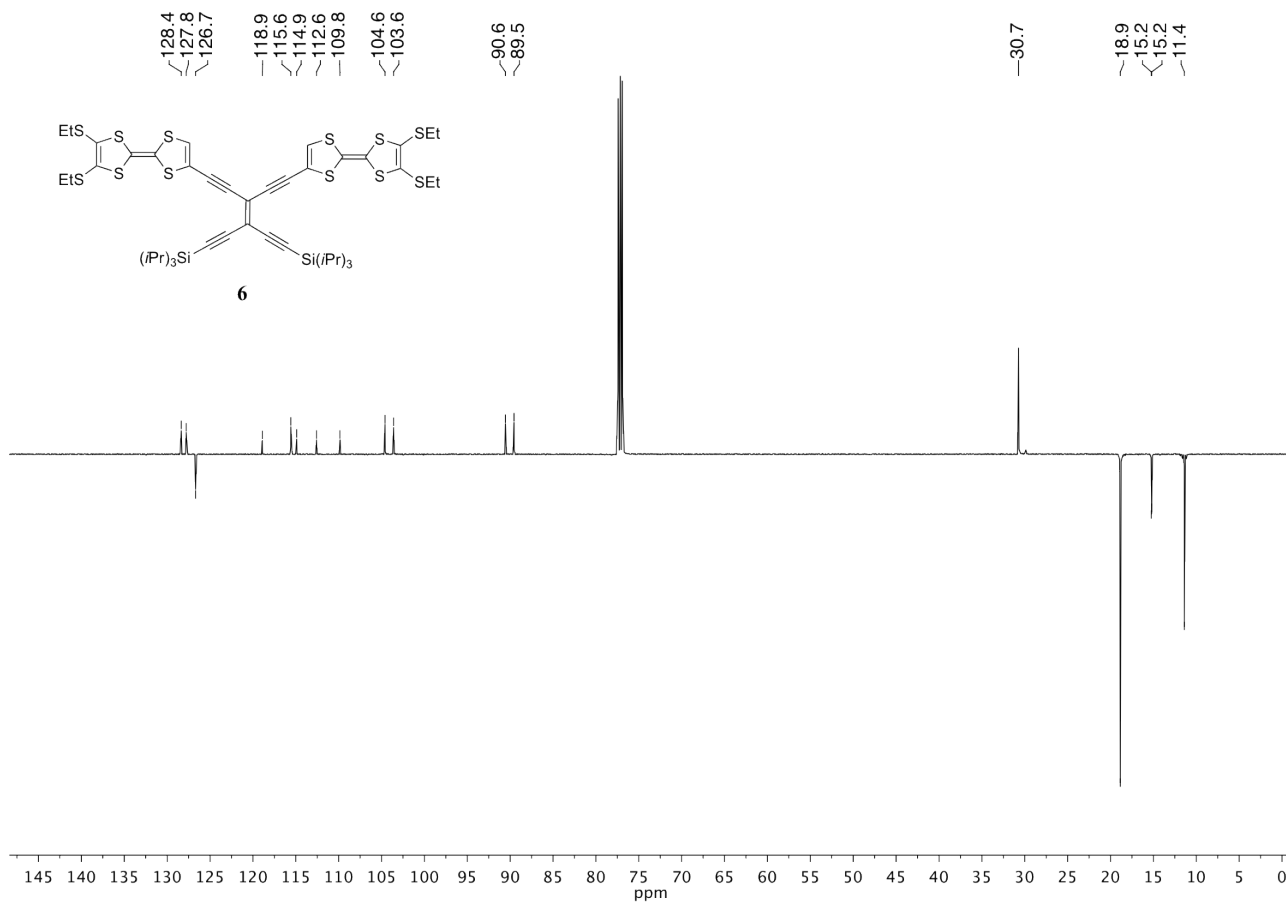


$^{13}\text{C}$  APT NMR spectrum of 4,5-bis(ethylthio)-4'-iodotetrathiafulvalene ( $\text{CDCl}_3$ ).





$^1H$  NMR spectrum of TTF-TEE **6** ( $CDCl_3$ ). Signal at 5.30 ppm corresponds to  $CH_2Cl_2$ .



$^{13}\text{C}$  APT NMR spectrum of TFF-TEE **6** ( $\text{CDCl}_3$ ).