Electronic Supplementary Material (ESI) for Dalton Transactions.

Energy Storage Inspired by Nature – Ionic Liquid Iron-Sulfur Clusters as Electrolytes for Redox Flow Batteries

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1. Experimental Procedures

1.1. General

All manipulations were carried out using standard Schlenk, glovebox, and high-vacuum manifold techniques under an atmosphere of high-purity nitrogen. Tetrahydrofuran (THF) and diethylether (Et_2O) were distilled over sodium benzophenone ketyl, acetonitrile was distilled over CaH_2 and methanol was distilled over magnesium. $NaSCH_3$[1] and CF_3CH_2SH[2] were prepared according to literature procedures. Ionic liquids were obtained from IoLiTec. All other reagents were purchased from ABCR, Acros Chemical Co. and Apollo Scientific and used as received.

^1H, ^{13}C, ^{19}F NMR spectra were recorded on Bruker 300 MHz magnet equipped with a RS^{2}D NMR Cube console. The ^1H and ^{13}C NMR spectra are referenced to the residual resonances of the solvent. ^{19}F NMR spectra were referenced against trifluoroacetic acid as external standard with a shift of -76.55 ppm. Elemental analyses were performed by Zentrale Elementaranalyse, Universität Hamburg. DSC measurements were performed on a Netzsch DSC 204 F1 with a heating rate of 10 K min^{-1} in broached aluminium pans in a nitrogen atmosphere. The instrument was calibrated against the melting enthalpy of indium. DTA/TG-MS measurements were recorded on a Netzsch STA/TG 449F3 coupled with a Netzsch QMS 403 C Aëolos quadrupole mass spectrometer with a heating rate of 10 K min^{-1} in an argon atmosphere. Conductivity was measured with a Knick Konduktometer 702 with an electrode from Ingold (C = 10.5). Rheological measurements were performed on an AR-G2 controlled stress rheometer (TA Instruments) with cone-plate geometry. Cyclic voltammograms were recorded with a BAS100BW potentiostat with IR-compensation using a glassy carbon working electrode, a Pt-wire auxiliary electrode and a Ag-wire as pseudo-reference electrode. The potentials were referenced vs. the ferrocene/ferrocenium couple as internal reference. Impedance measurements were performed with a SP-150 potentiostat from BioLogic and were conducted at the open circuit potential with an amplitude of 10 mV.

Flow cell measurements were conducted in a thermostated flow cell from ElectroCell using 0.1 M solutions of $(EMIm)_2[Fe_4S_4(Stfe)_4]$ and 0.15 M solutions of EMImBr both in $EMImNTf_2$ at a flow rate of approximately 1 L/h. SGL carbon felt electrodes (KFD 2.5 EA) were used, contacted by graphite plates. As separator a FuMATech F-14100 membrane was applied after pre-treatment by impregnation with $EMImNTf_2$ in MeOH (v/v = 1:3) for 18 h and consecutive evaporation of MeOH in a nitrogen stream. Flow cell measurements with 1.0 M solutions of $(EMIm)_2[Fe_4S_4(Stfe)_4]$ and 1.5 M solutions of EMImBr in $EMImNTf_2$ were conducted at 50 °C by heating the electrolyte tanks to 50 °C with a heating bath and the cell with a stream of preheated nitrogen through separate compartments in the cell on the back side of the graphite plates.

For NMR measurements of the 0.1 M aliquots of approximately 10 µL of the electrolyte solution were taken from the anolyte tank and were dissolved in CD_3CN. The assignment to the corresponding clusters was based on data for ehanthiolato-clusters.[3]

1.2. Synthesis

$(Me_4N)_2[Fe_4S_4(SMe)_4]$: In analogy to known procedures[4] $NaSCH_3$ (28.4 g, 400 mmol) was dissolved in 400 mL MeOH followed by the addition of a solution of $FeCl_3$ (16.2 g, 100 mmol) in 100 mL MeOH and sulfur (3.20 g, 100 mmol). The brown, heterogeneous reaction mixture was stirred for 16 h at room temperature and then filtered. To the filtrate a solution of Me_4NBr (11.6 g, 75.0 mmol) in 200 mL MeOH was added resulting in the precipitation of black needles of the crude product, which was recrystallized at -30 °C from hot acetonitrile yielding 7.7 g (39 %). Crystals suitable for x-ray diffraction were obtained by recrystallization from hot MeCN. ^1H NMR (300 MHz, CD_3CN): δ = 14.95 (s, 12H, SCH_3) 3.14 (s, 24H, Me_4N) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ = 64.32 (s, Me_4N) ppm. (The methanethiolato ^{13}C resonance cannot be detected due to the low solubility and paramagnetic line broadening)

$(Me_4N)_2[Fe_4S_4(Stfe)_4]$:) $(Me_4N)_2[Fe_4S_4(SMe)_4]$ (10.3 g 10.0 mmol) was suspended in 50 mL THF and CF_3CH_2SH (8.71 g, 75.0 mmol) were added. The reaction mixture was then refluxed for 16 h, filtered and the solvent was removed *in vacuo* yielding 13.7 g (89 %). Crystals suitable for x-ray diffraction were obtained by recrystallization from hot THF. ^1H NMR (300 MHz, CD_3CN: δ = 12.11 (s, 8H, SCH_2), 3.08 (s, 24H, Me_4N) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ = 163.4 (q, ($^1J(^{19}F,^{13}C)$=278 Hz), CF_3), 114.9 (s, SCH_2), 59.3 (s, Me_4N) ppm. ^{19}F NMR (282 MHz, CD_3CN): δ = -59.0 ppm. Elemental analysis calc. for $C_{16}H_{32}F_{12}Fe_4N_2S_8$: C 20.01; H 3.36; N 2.92; S 26.71, found: C 20.01; H 3.44; N 2.98; S 26.83.

$(EMIm)_2[Fe_4S_4(Stfe)_4]$: $(Me_4N)_2[Fe_4S_4(Stfe)_4]$ (41.9 g 43.6 mmol) and EMImBr (16.7 g, 87.2 mmol) were dissolved in 100 mL MeCN, stirred for 15 min and the precipitated Me_4NBr was removed by filtration. The residue was washed three times with 1 mL MeCN and the combined filtrates were dried in high vacuum. The residue was extracted into 50 mL THF and the solution was dried *in vacuo* to yield 37.8 g (84 %). ^1H NMR (300 MHz, CD_3CN) δ = 12.14 (s, 8H, SCH_2), 8.50 (s, 2H, C_{2Im}-H), 7.37 (s, 2H, C_{4Im}-H), 7.32 (s, 2H, C_{5Im}-H), 4.16 (q, *J* = 7.1 Hz, 2H, NCH_2), 3.83 (s, 6H, NCH_3), 1.47 (t, ^3J(H,H)=7.0 Hz, 6H, $CH_2\mathbf{CH_3}$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ = 163.1 (q ($^1J(^{19}F,^{13}C)$=267 Hz), CF_3), 139.4 (C_{Im}-2), 126.6 (C_{Im}-4), 124.9 (C_{Im}-5), 113.9 (s, SCH_2), 49.1 (NCH_2), 41.4 (NCH_3), 18.0 ($CH_2\mathbf{C}H_3$) ppm. ^{19}F NMR (282 MHz, CD_3CN): δ = -59.0 ppm. Elemental analysis calc. for $C_{16}H_{32}F_{12}Fe_4N_2S_8$: C 23.22; H 2.92; N 5.42; S 24.80, found: C 23.44; H 2.94; N 5.80; S 24.61.

General procedure for **$(IL)_2[Fe_4S_4(Stfe)_4]$:** $(Me_4N)_2[Fe_4S_4(Stfe)_4]$ (1 mmol) and the appropriate IL halide salt were dissolved in ca. 5 mL of MeCN, stirred for 15 min. and the resulting precipitate was removed by filtration. The residue was washed three times with 1 mL MeCN and the combined filtrates were dried *in vacuo*. The obtained residue was extracted in 3 mL THF and washed with small portions of THF until an off-white residue remains. The combined filtrates were dried in vacuo to yield $(IL)_2[Fe_4S_4(Stfe)_4]$.

$(BMIm)_2[Fe_4S_4(Stfe)_4]$: Yield: 90 %. ^1H NMR (300 MHz, CD_3CN) δ = 12.06 (s, 8H, SCH_2), 8.50 (s, 2H, C_{2Im}-H), 7.35 (s, 2H, C_{4Im}-H), 7.32 (s, 2H, C_{5Im}-H), 4.12 (q, *J* = 7.1 Hz, 4H, NCH_2), 3.83 (s, 6H, NCH_3), 1.82 (m, 4H, $NCH_2C\mathbf{H}_2$), 1.32 (m, 4H, $N(CH_2)_2C\mathbf{H}_2$), 0.94 (t, ^3J(H,H)=7.0 Hz, 6H, $CH_2C\mathbf{H}_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ = 163.2 (q ($^1J(^{19}F,^{13}C)$=267 Hz), CF_3), 141.5 (C_{Im}-2), 127.7 (C_{Im}-4), 126.2 (C_{Im}-5), 114.8 (SCH_2), 55.2 (NCH_2), 44.0 (NCH_3), 34.8 ($NCH_2\mathbf{C}H_2$), 21.7 $N(CH_2)_2\mathbf{C}H_2$), 15.3 ($CH_2\mathbf{C}H_3$) ppm. ^{19}F NMR (282 MHz, CD_3CN): δ = -58.3 ppm.

$(HMIm)_2[Fe_4S_4(Stfe)_4]$: Yield: 86 %. ^{1}H NMR (300 MHz, CD_3CN) δ = 12.11 (s, 8H, SCH_2), 8.46 (s, 2H, C_{2Im}-H), 7.36 (s, 2H, C_{4Im}-H), 7.32 (s, 2H, C_{5Im}-H), 4.11 (q, *J* = 6.6 Hz, 4H, NCH_2), 3.83 (s, 6H, NCH_3), 1.83 (m, 4H, $NCH_2C\mathbf{H}_2$), 1.31 (m, 12H, $N(CH_2)_2(C\mathbf{H}_2)_3$), 0.89 (t, ^3J(H,H)=6.1 Hz, 6H, $CH_2C\mathbf{H}_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ = 163.0 (q ($^1J(^{19}F,^{13}C)$=268 Hz), CF_3), 139.6 (C_{Im}-2), 126.7 (C_{Im}-4), 125.3 (C_{Im}-5), 114.2 (SCH_2), 53.6 (NCH_2), 41.4 (NCH_3), 32.5 ($NCH_2\mathbf{C}H_2$), 32.1 $N(CH_2)_2C\mathbf{H}_2$), 27.5 $N(CH_2)_3C\mathbf{H}_2$), 23.8 $N(CH_2)_4C\mathbf{H}_2$), 15.1 ($CH_2\mathbf{C}H_3$) ppm. ^{19}F NMR (282 MHz, CD_3CN): δ = -59.0 ppm.

$(HDMIm)_2[Fe_4S_4(Stfe)_4]$: Yield: 97 %. ^{1}H NMR (300 MHz, CD_3CN) δ = 12.06 (s, 8H, SCH_2), 7.24 (s, 2H, C_{4Im}-H), 7.24 (s, 2H, C_{5Im}-H), 4.02 (q, *J* = 7.1 Hz, 4H, NCH_2), 3.70 (s, 6H, NCH_3), 2.51 (s, 6H, $C_{2Im}CH_3$), 1.76 (m, 4H, $NCH_2C\mathbf{H}_2$), 1.32 (m, 12H, $N(CH_2)_2(C\mathbf{H}_2)_3$), 0.90 (t, ^3J(H,H)=6.2 Hz, 6H, $CH_2C\mathbf{H}_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ = 163.0 (q ($^1J(^{19}F,^{13}C)$=274 Hz), CF_3), 145.6 (C_{Im}-2), 125.6 (C_{Im}-4), 124.1 (C_{Im}-5), 114.1 (SCH_2), 51.9 (NCH_2), 40.0 (NCH_3), 32.7 ($NCH_2\mathbf{C}H_2$), 31.7 $N(CH_2)_2Cz\mathbf{H}_2$), 27.6 $N(CH_2)_3C\mathbf{H}_2$), 23.9 $N(CH_2)_4C\mathbf{H}_2$), 15.3 ($CH_2\mathbf{C}H_3$), 14.3 ($C_{2Im}\mathbf{C}H_3$), ppm. ^{19}F NMR (282 MHz, CD_3CN): δ = -59.0 ppm.

For **$(IL)_2[Fe_4S_4(SMe)_4]$** the procedure is the same as above, starting with $(Me_4N)_2[Fe_4S_4(SMe)_4]$, with the exception that the extraction with THF requires the addition of a minimum amount MeCN to extract the product (ca. 1:2 – 1:5 MeCN/THF, depending on the cation).

$(EMIm)_2[Fe_4S_4(SMe)_4]$: Yield: 97 %. ^{1}H NMR (300 MHz, CD_3CN) δ = 15.47 (s, 12H, SCH_3), 8.79 (s, 2H, C_{2Im}-H), 7.41 (s, 2H, C_{4Im}-H), 7.36 (s, 2H, C_{5Im}-H), 4.19 (m, 4H, NCH_2), 3.87 (s, 6H, NCH_3), 1.51 (m, 6H, $CH_2C\mathbf{H}_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ = 143.4 (C_{Im}-2), 128.6 (C_{Im}-4), 126.8 (C_{Im}-5), 105.8 (s, SCH_3),52.2 (NCH_2), 46.0 (NCH_3), 20.2 ($CH_2\mathbf{C}H_3$) ppm.

$(BMIm)_2[Fe_4S_4(SMe)_4]$: Yield: 90 %. ^{1}H NMR (300 MHz, CD_3CN) δ = 14.95 (s, 12H, SCH_3), 8.66 (s, 2H, C_{2Im}-H), 7.37 (s, 2H, C_{4Im}-H), 7.34 (s, 2H, C_{5Im}-H), 4.14 (m, 4H, NCH_2), 3.86 (s, 6H, NCH_3), 1.84 (m, 4H, $NCH_2C\mathbf{H}_2$), 1.36 (m, 4H, $N(CH_2)_2C\mathbf{H}_2$), 0.95 (t, ^3J(H,H)=7.3 Hz, 6H, $CH_2C\mathbf{H}_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ = 143.1 (C_{Im}-2), 128.2 (C_{Im}-4), 126.7 (C_{Im}-5), 102.8 (SCH_3), 55.7 (NCH_2), 45.2 (NCH_3), 35.2 ($NCH_2\mathbf{C}H_2$), 21.9 $N(CH_2)_2C\mathbf{H}_2$), 15.5 ($CH_2\mathbf{C}H_3$) ppm.

$(HMIm)_2[Fe_4S_4(SMe)_4]$: Yield: 96 %. ^{1}H NMR (300 MHz, CD_3CN) δ = 15.22 (s, 12H, SCH_3), 8.64 (s, 2H, C_{2Im}-H), 7.37 (s, 2H, C_{4Im}-H), 7.34 (s, 2H, C_{5Im}-H), 4.12 (m, NCH_2), 3.86 (s, 6H, NCH_3), 1.87 (m, 4H, $NCH_2C\mathbf{H}_2$), 1.33 (m, 12H, $N(CH_2)_2(C\mathbf{H}_2)_3$), 0.89 (m, 6H, $CH_2C\mathbf{H}_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ = 144.7 (C_{Im}-2), 129.5 (C_{Im}-4), 128.0 (C_{Im}-5), 103.4 (SCH_3), 57.8 (NCH_2), 48.1 (NCH_3), 34.0 ($NCH_2\mathbf{C}H_2$), 33.2 $N(CH_2)_2C\mathbf{H}_2$), 28.6 $N(CH_2)_3C\mathbf{H}_2$), 24.2 $N(CH_2)_4C\mathbf{H}_2$), 15.7 ($CH_2\mathbf{C}H_3$) ppm.

$(HDMIm)_2[Fe_4S_4(SMe)_4]$: Yield: 91 %. ^{1}H NMR (300 MHz, CD_3CN) δ = 15.04 (s, 12H, SCH_3), 7.27 (m, 4H, C_{4Im}-H, C_{5Im}-H), 4.03 (m, 4H, NCH_2), 3.71 (s, 6H, NCH_3), 2.53 (s, 6H, $C_{2Im}CH_3$), 1.80 (m, 4H, $NCH_2C\mathbf{H}_2$), 1.32 (m, 12H, $N(CH_2)_2(C\mathbf{H}_2)_3$), 0.90 (m, 6H, $CH_2C\mathbf{H}_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ = 145.8 (C_{Im}-2), 127.8 (C_{Im}-4), 125.8 (C_{Im}-5), 103.8 (SCH_3), 53.5 (NCH_2), 42.9 (NCH_3), 32.8 ($NCH_2\mathbf{C}H_2$), 32.4 $N(CH_2)_2C\mathbf{H}_2$), 28.0 $N(CH_2)_3C\mathbf{H}_2$), 24.0 $N(CH_2)_4C\mathbf{H}_2$), 16.6 ($CH_2\mathbf{C}H_3$), 15.3 ($C_{2Im}\mathbf{C}H_3$), ppm.

$(Bu_4N)_3[Fe_4S_4(Stfe)_4]$: Electrochemical reduction: In a typical electrochemical cell with two compartments separated by a porous glass frit and carbon felt electrodes $(Me_4N)_2[Fe_4S_4(Stfe)_4]$ (260 mg, 200 µmol) were dissolved in 20 mL of acetonitrile containing a 0.1 M concentration of Bu_4NPF_6 as supporting electrolyte. The solution was reduced with a potential of 1.7 V (vs. Ag/Ag^+). After transferring a charge of 22.3 C the solution was filtered reduced to a third of its original volume. Subsequently it was cooled to -35 °C. After 18 h a black solid was obtained that was dried *in vacuo* yielding 150 mg. ^{1}H NMR (300 MHz, CD_3CN): *δ* = 31.44 (s, 8H, SCH_2), 3.05 (s, 24H, NCH_2), 1.69 (s, 24H, $NCH_2C\mathbf{H}_2$), 1.40 (s, 24H, $N(CH_2)_2C\mathbf{H}_2$), 1.02 (s, 36H, $N(CH_2)_3C\mathbf{H}_3$), ppm. ^{19}F NMR (282 MHz, CD_3CN): *δ* = -37.7 ppm.

2. Energy Density

For two electrolytes that undergo electron transfers at a single potential and have the same concentration the theoretical energy density ED can be calculated according to eq. (1)

$$ED = F \cdot \Delta E \cdot n \cdot \frac{c}{2} \quad (1)$$

Where *F* is the Faraday constant, *ΔE* is the difference between the redox potentials of the electrolytes, *n* is the number of transferred electrons at this potential and *c* is the concentration of the electrolytes. If the electrolytes are used in different concentrations and one electrolyte can transfer two electrons at different potential as for the iron-sulfur cluster electrolyte *ED* can be calaculated according to eq. (2):

$$ED = F \cdot \frac{1}{2}(\Delta E_1 + \Delta E_2) \cdot \frac{2c_{FeS}}{1 + \frac{2c_{FeS}}{c_{Br}}} \quad (2)$$

For ΔE_1 = 1.55 V and ΔE_2 = 2.23 V and a concentration of the iron-sulfur cluster of 1.5 mol/L, which is the concentration of the neat ionic liquid $(EMIm)_2[Fe_4S_4(Stfe)_4]$ and with a bromide concentration bromide is 5.0 mol/L, i.e. the concentration of the neat ionic liquid HMImBr, a theoretical energy density of 88 Wh/L is obtained.

The practical energy density will always be lower since the energy efficiency will never be near 100 % due to overpotentials and internal cell resistance thereby not even considering the energy requirement of the electrolyte pumps. Therefore, in general the theoretical energy densities of different RFB systems are compared.

3. Cyclic voltammetry

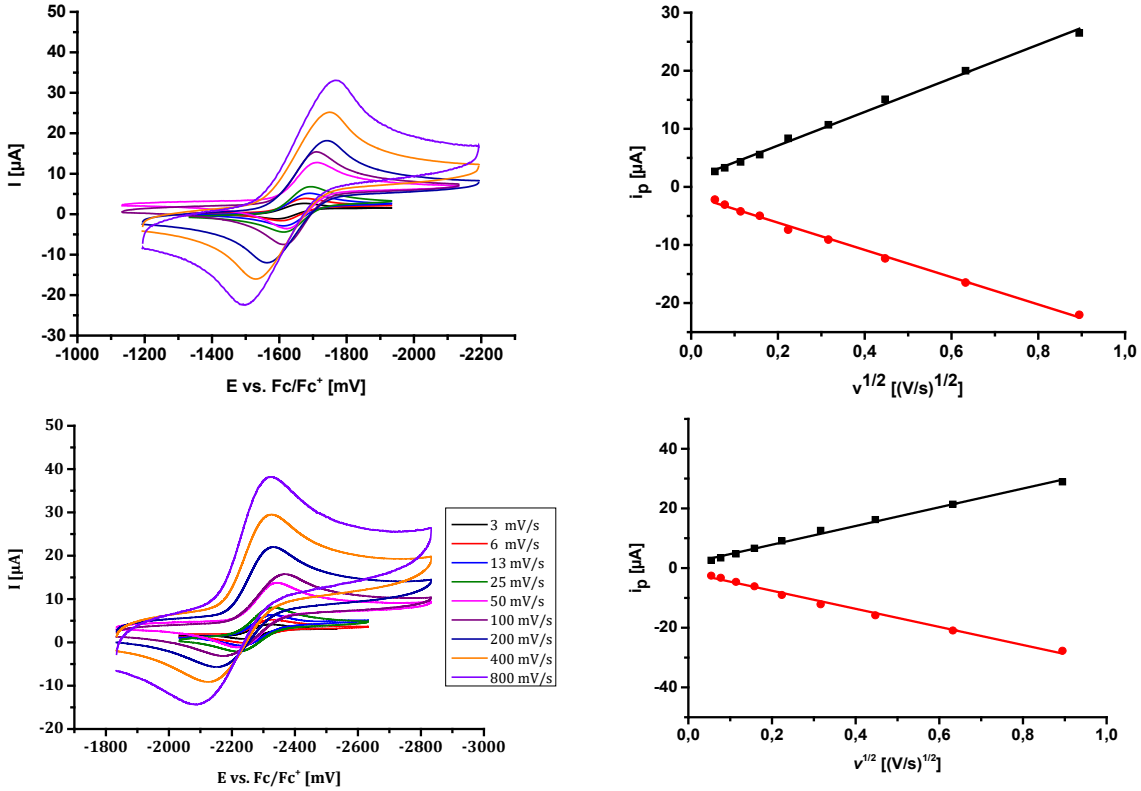


Figure S1: Randles-Sevcik-plot of 1 mM $(Me_4N)_2[Fe_4S_4(Stfe)_4]$ in 0.1 M nBu$_4$NPF$_6$ in THF.

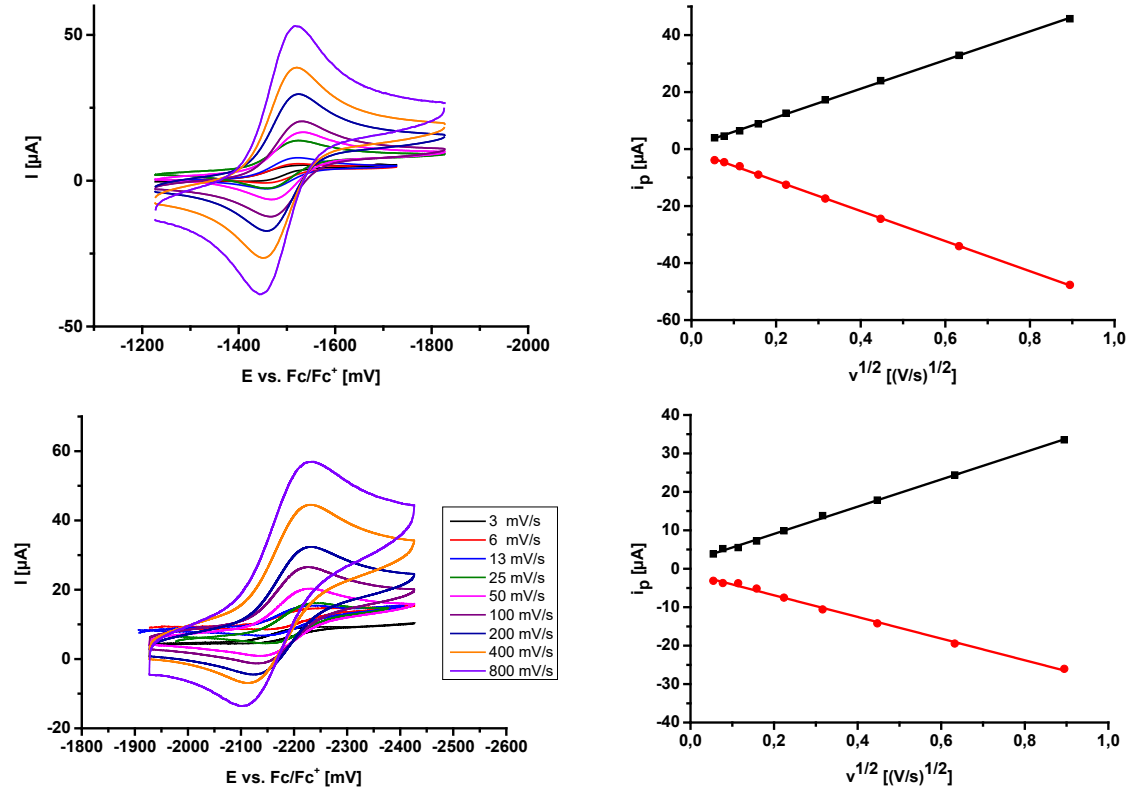


Figure S2: CV and Randles-Sevcik-plot of 1 mM $(n$Bu$_4$N$)_2[Fe_4S_4(Stfe)_4]$ in 0.1 M nBu$_4$NPF$_6$ in MeCN.

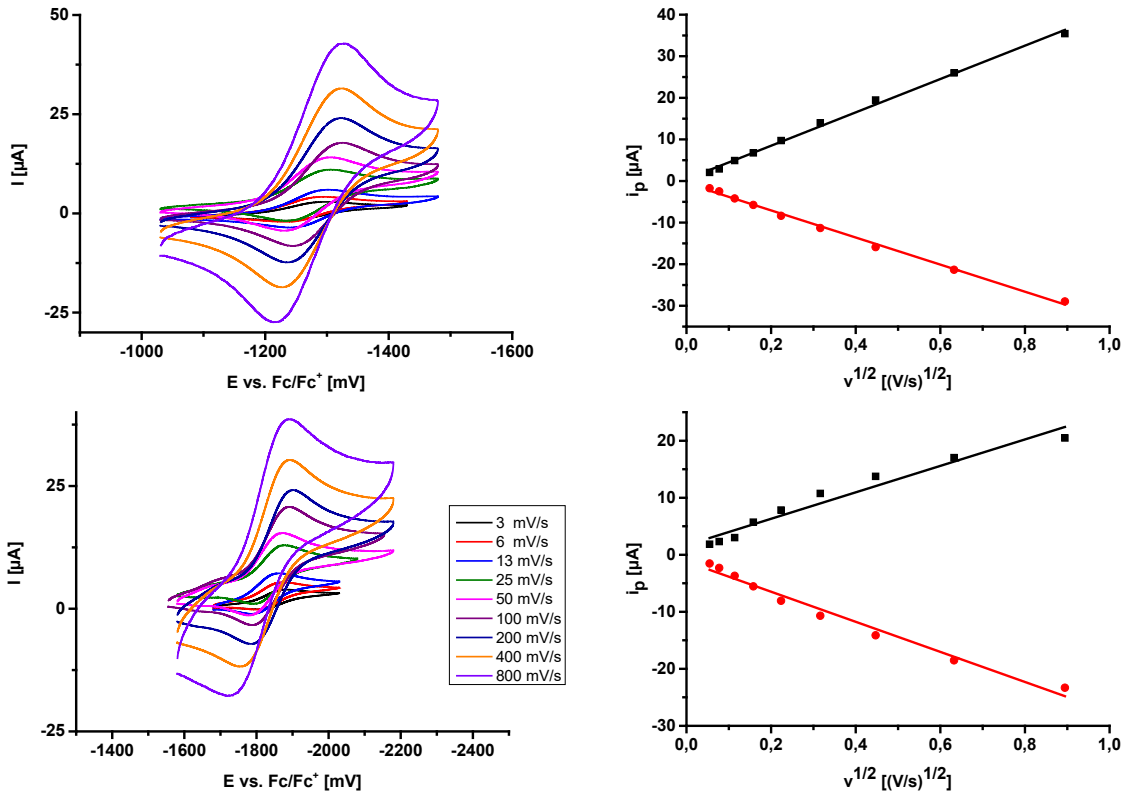


Figure S3: CV and Randles-Sevcik-plot of 13 mM $(EMIm)_2[Fe_4S_4(Stfe)_4]$ in $EMImNTf_2$.

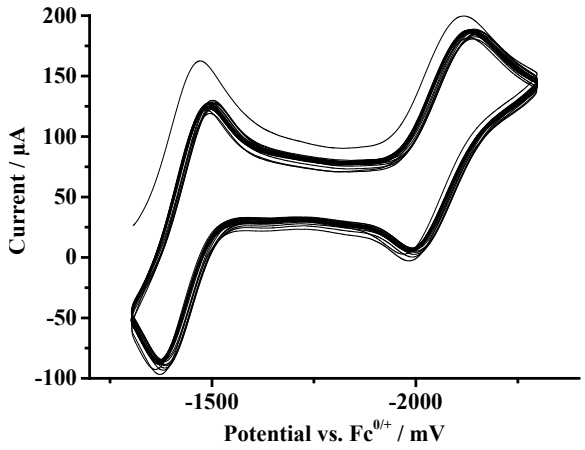


Figure S4: CV with 50 cycles at 100 mV/s of 10 mM $(EMIm)_2[Fe_4S_4(Stfe)_4]$ in 0.1 M $n Bu_4NPF_6$ in MeCN.

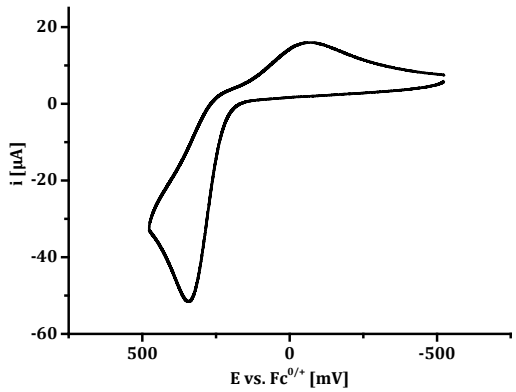


Figure S5: CV at 100 mV/s of 10 mM EMImBr in $EMImNTf_2$.

4. Additional battery data

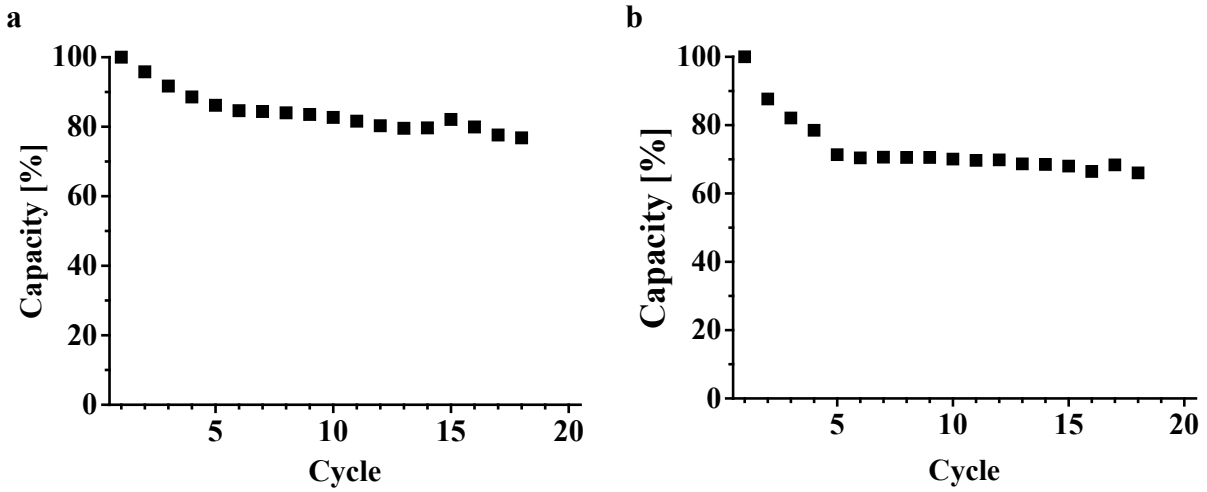


Figure S6: (a) Capacity with 0.1 M $(EMIm)_2[Fe_4S_4(Stfe)_4]$ and 0.15 M EMImBr and (b) 1 M $(EMIm)_2[Fe_4S_4(Stfe)_4]$ and 1.5 EMImBr M in $EMImNTf_2$ at 1 mA/cm^2.

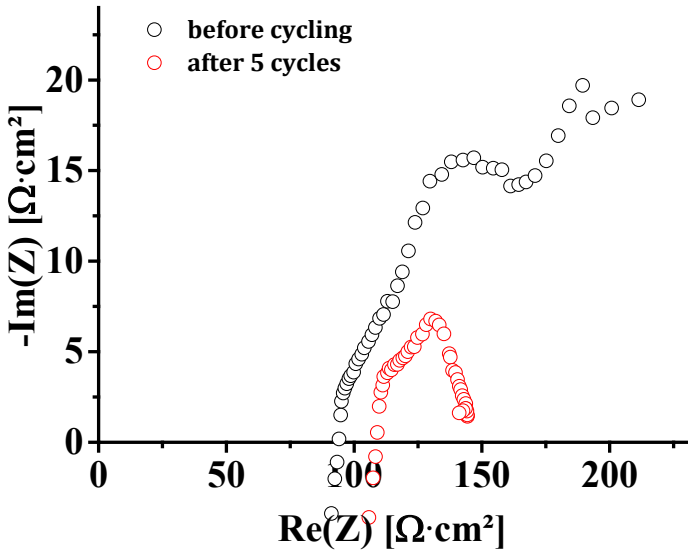
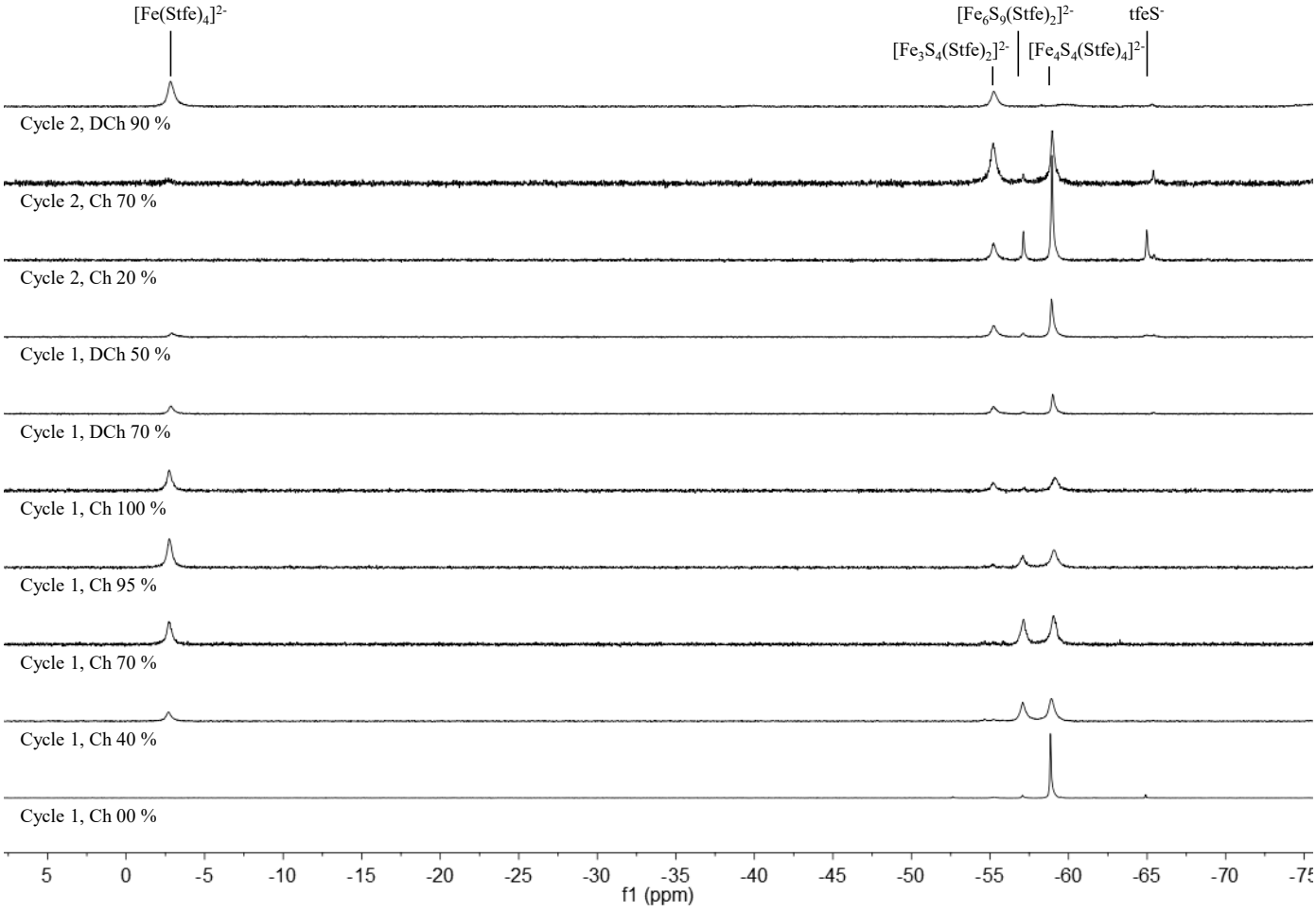


Figure S7: Impedance measurement of the 1 M cell at 50 °C before cycling and after 5 cycles in the range of 10^{-2}-10^6 Hz.

5. NMR-study during charging/discharging



6. Thermogravimetric analysis

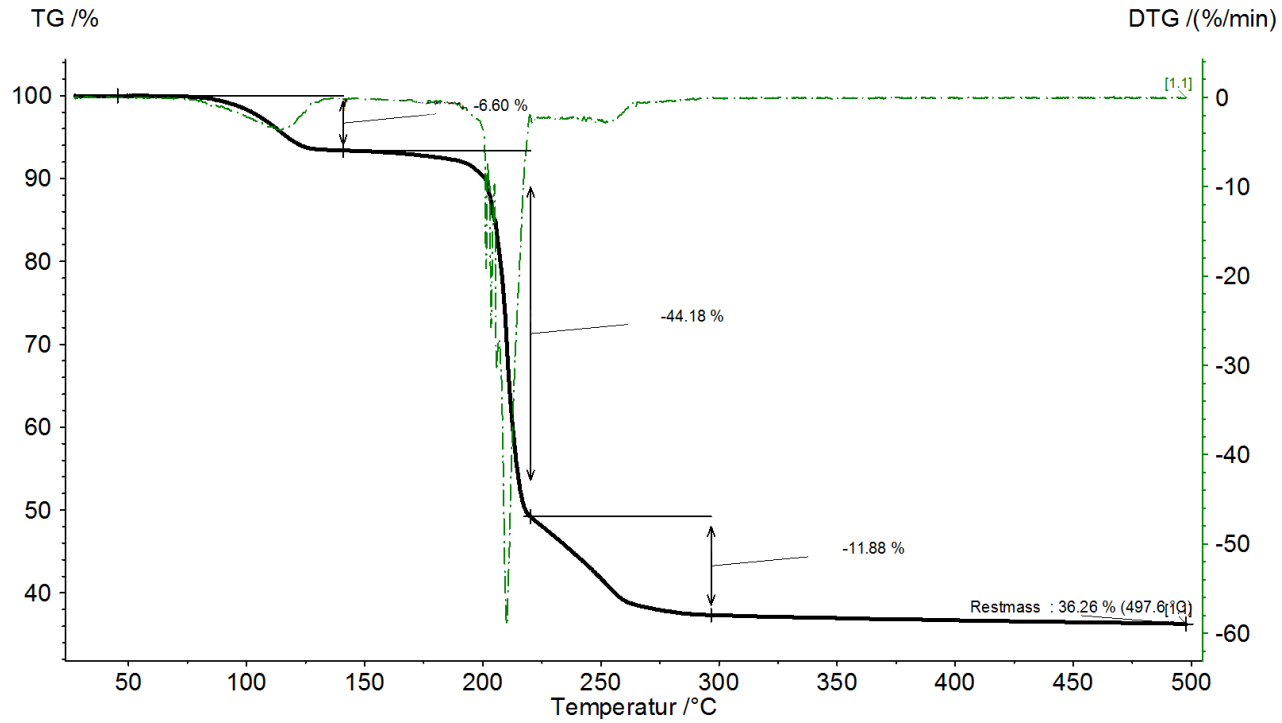


Figure S8: TGA of $(Me_4N)_2[Fe_4S_4(Stfe)_4]$, first mass loss correlates to one cocrystalized THF-molecule.

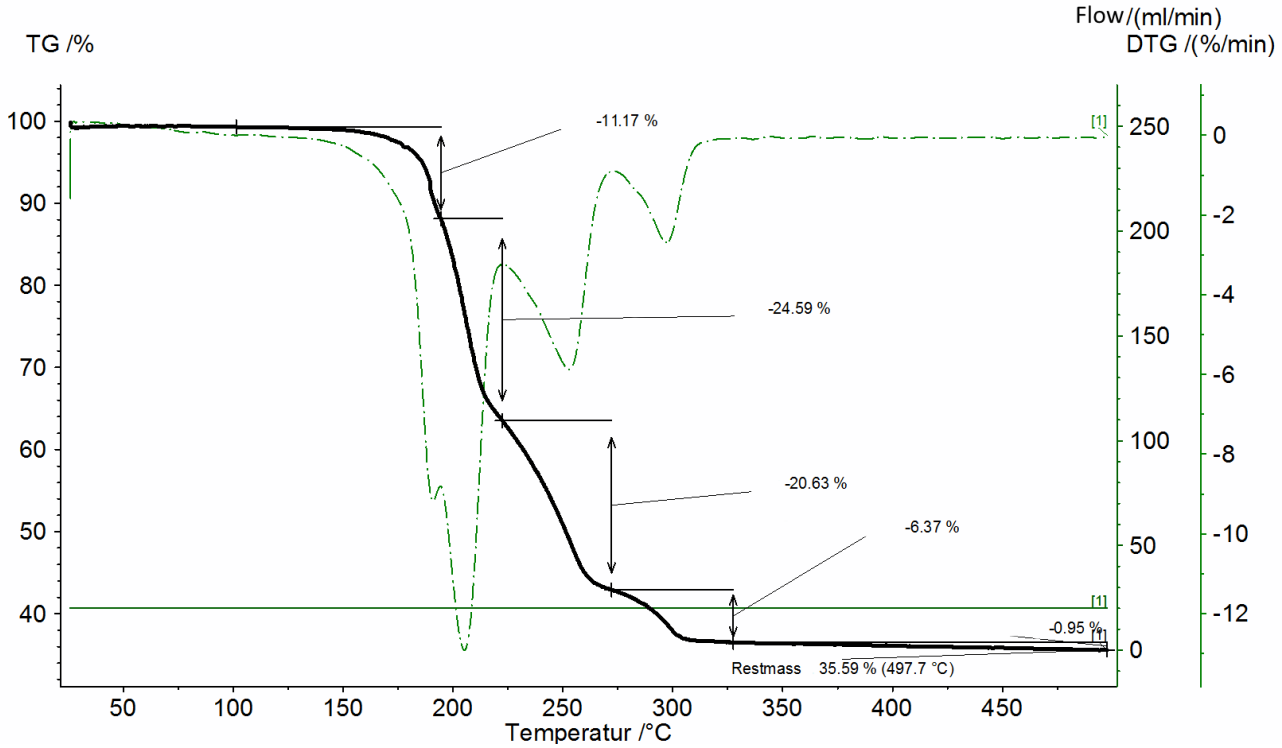


Figure S9: TGA of $(EMIm)_2[Fe_4S_4(Stfe)_4]$.

7. Viscosity and conductivity

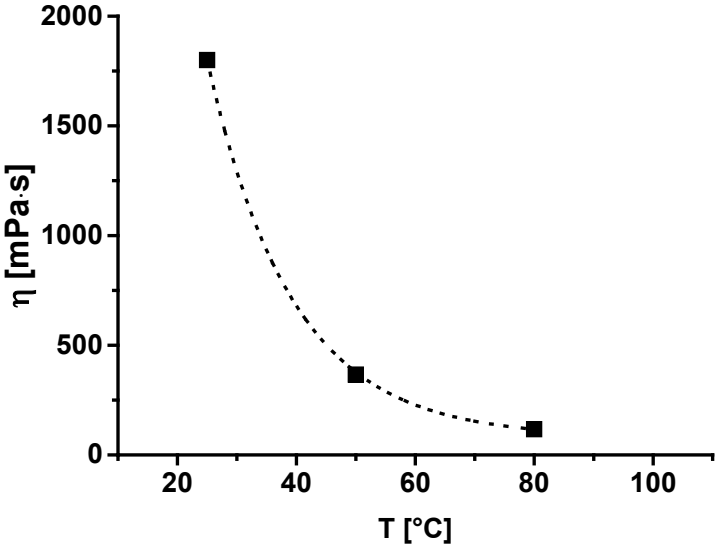


Figure S10: Viscosity of $(EMIm)_2[Fe_4S_4(Stfe)_4]$.

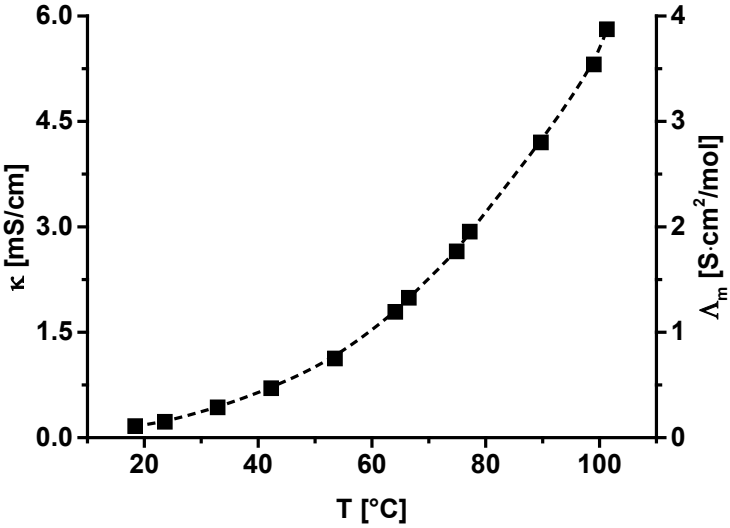
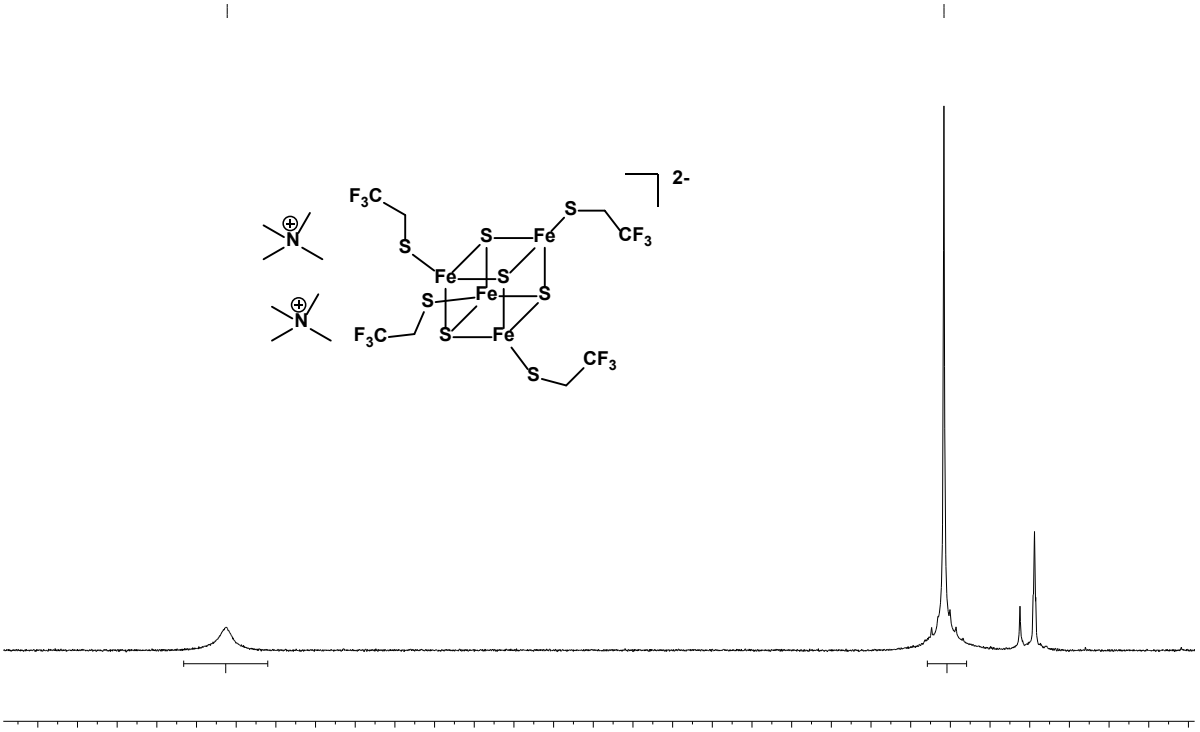


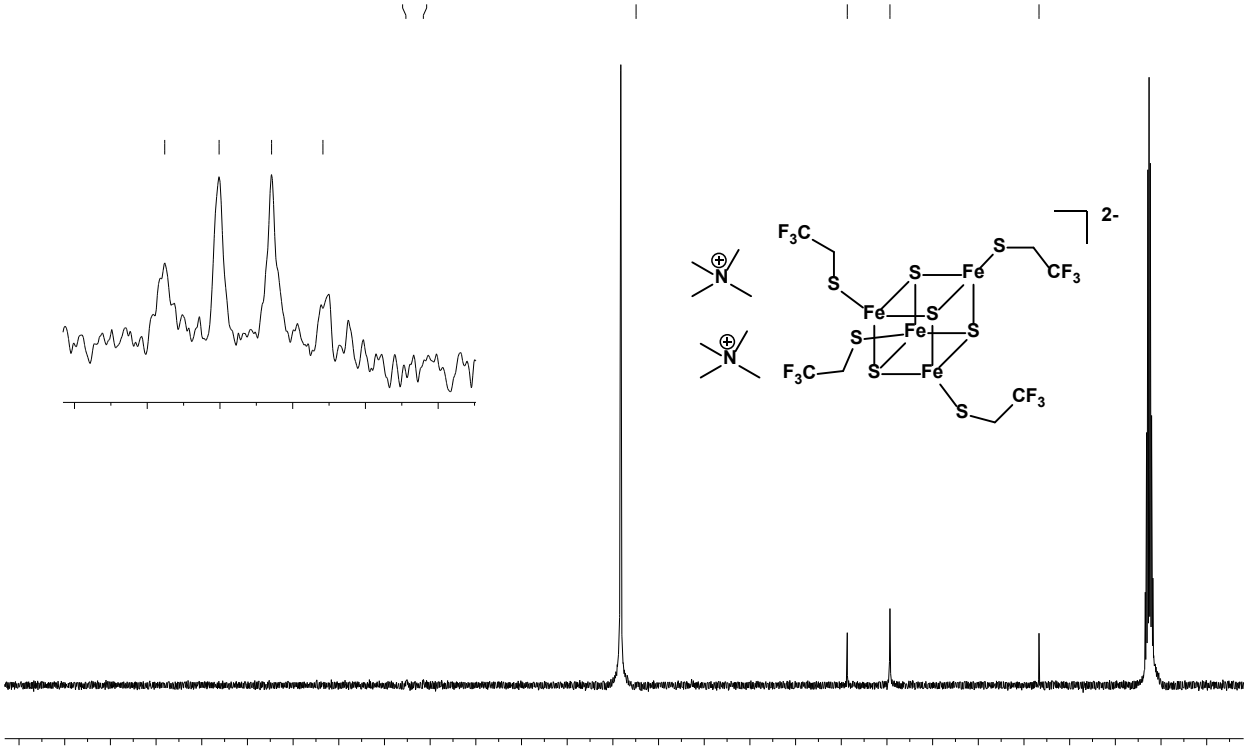
Figure S11: Electrical and molar conductivity of $(EMIm)_2[Fe_4S_4(Stfe)_4]$.

8. NMR-Spectra

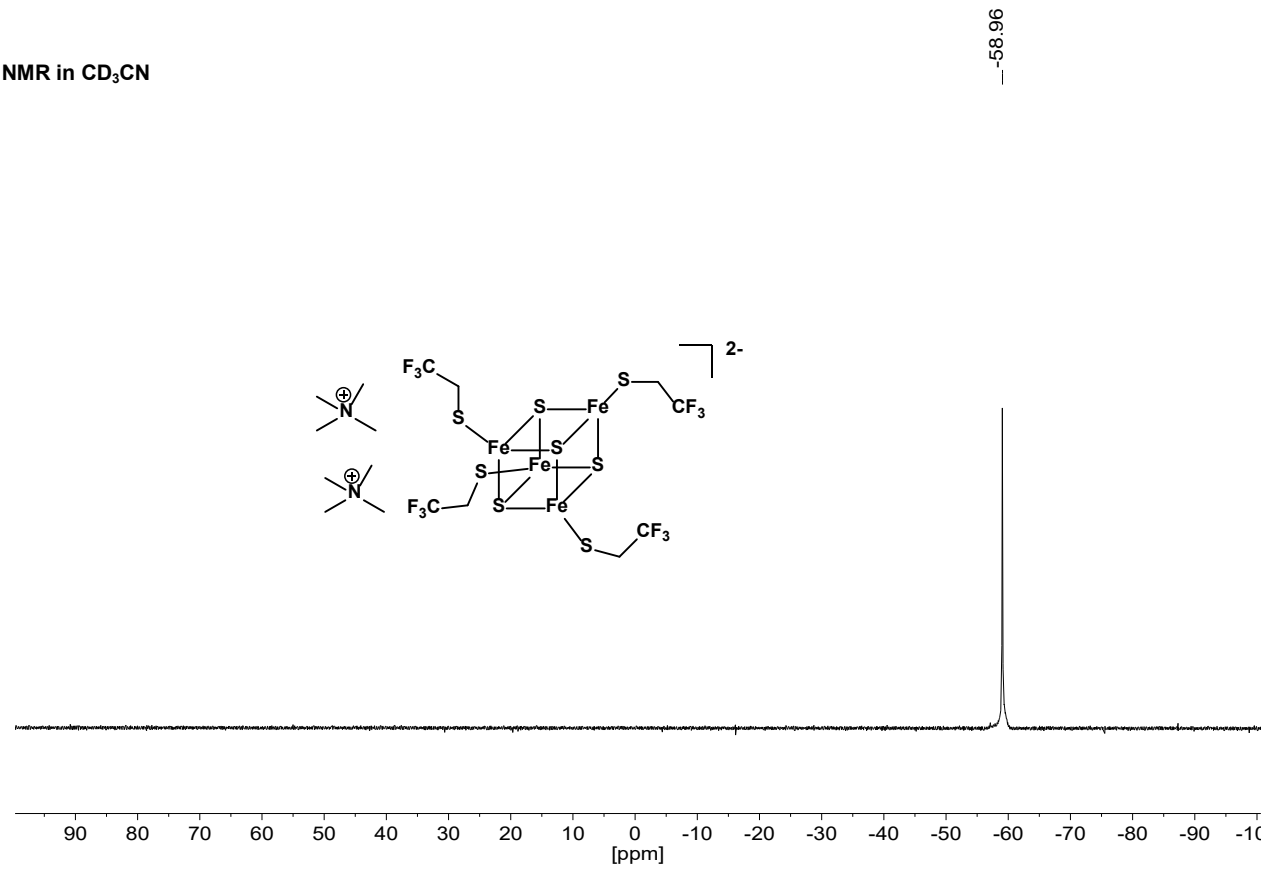
^{1}H NMR in CD_3CN



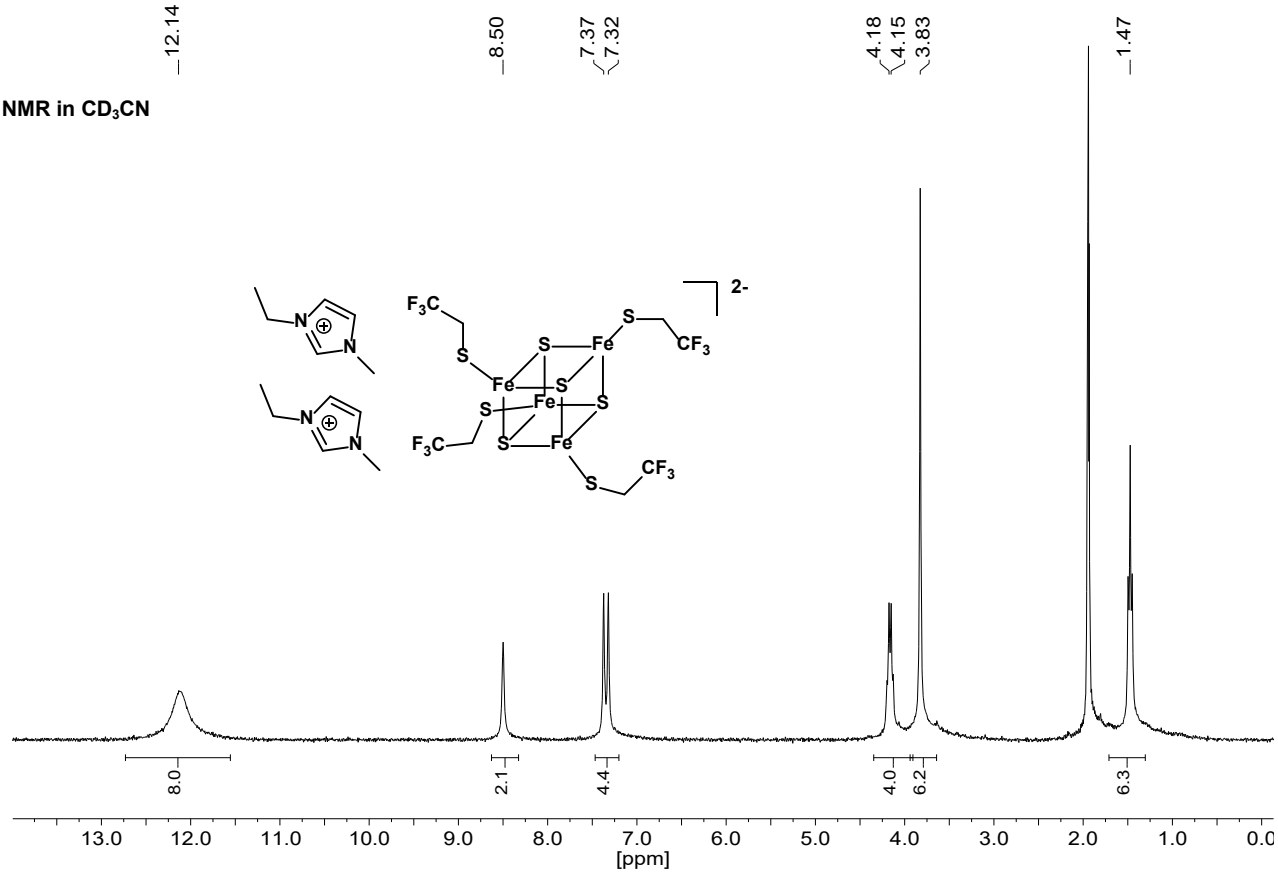
^{13}C NMR in CD_3CN



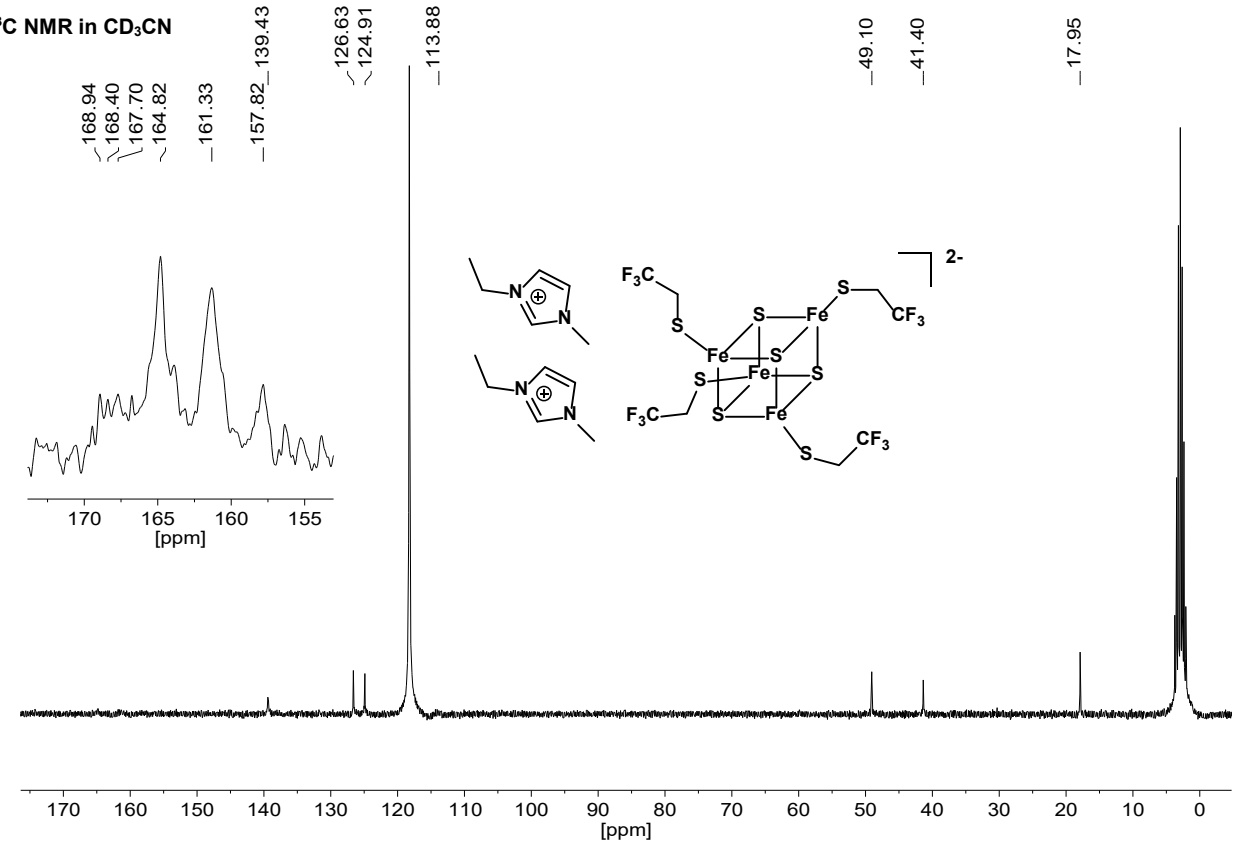
^{19}F NMR in CD_3CN



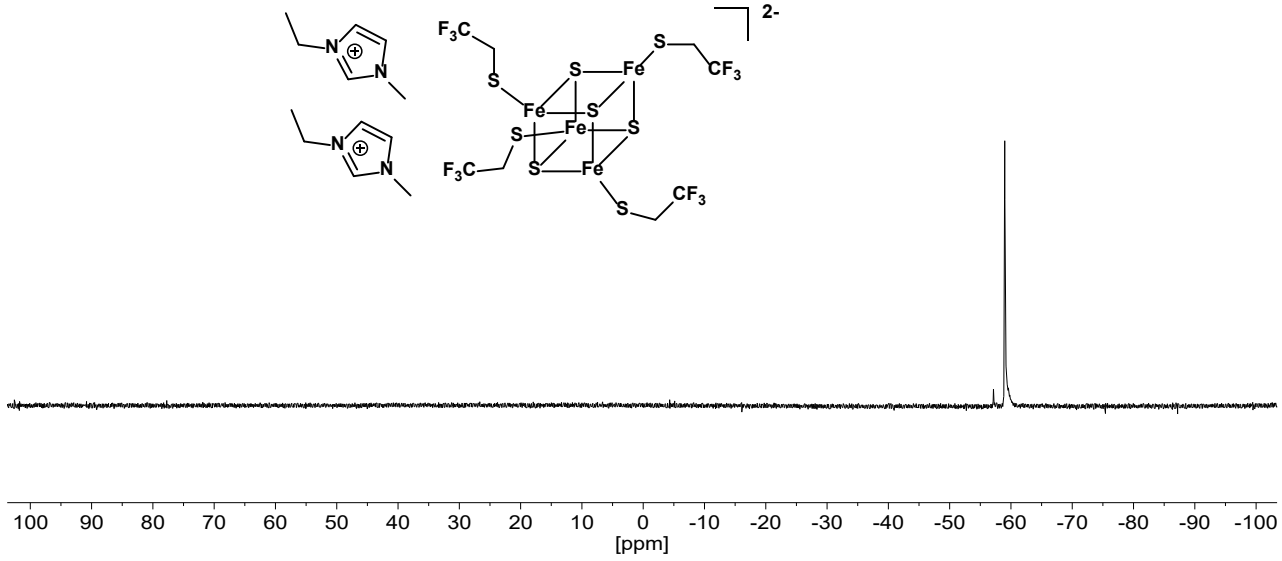
^{1}H NMR in CD_3CN

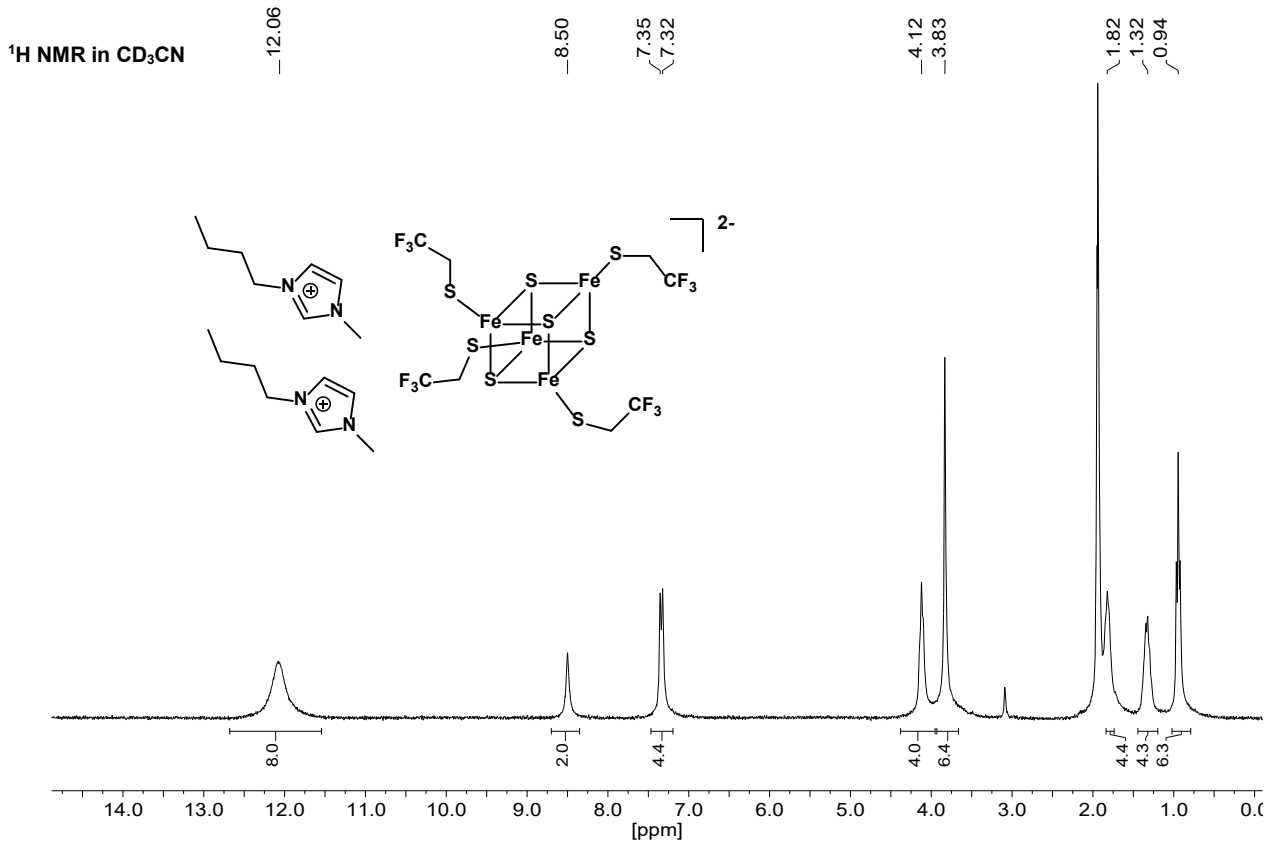


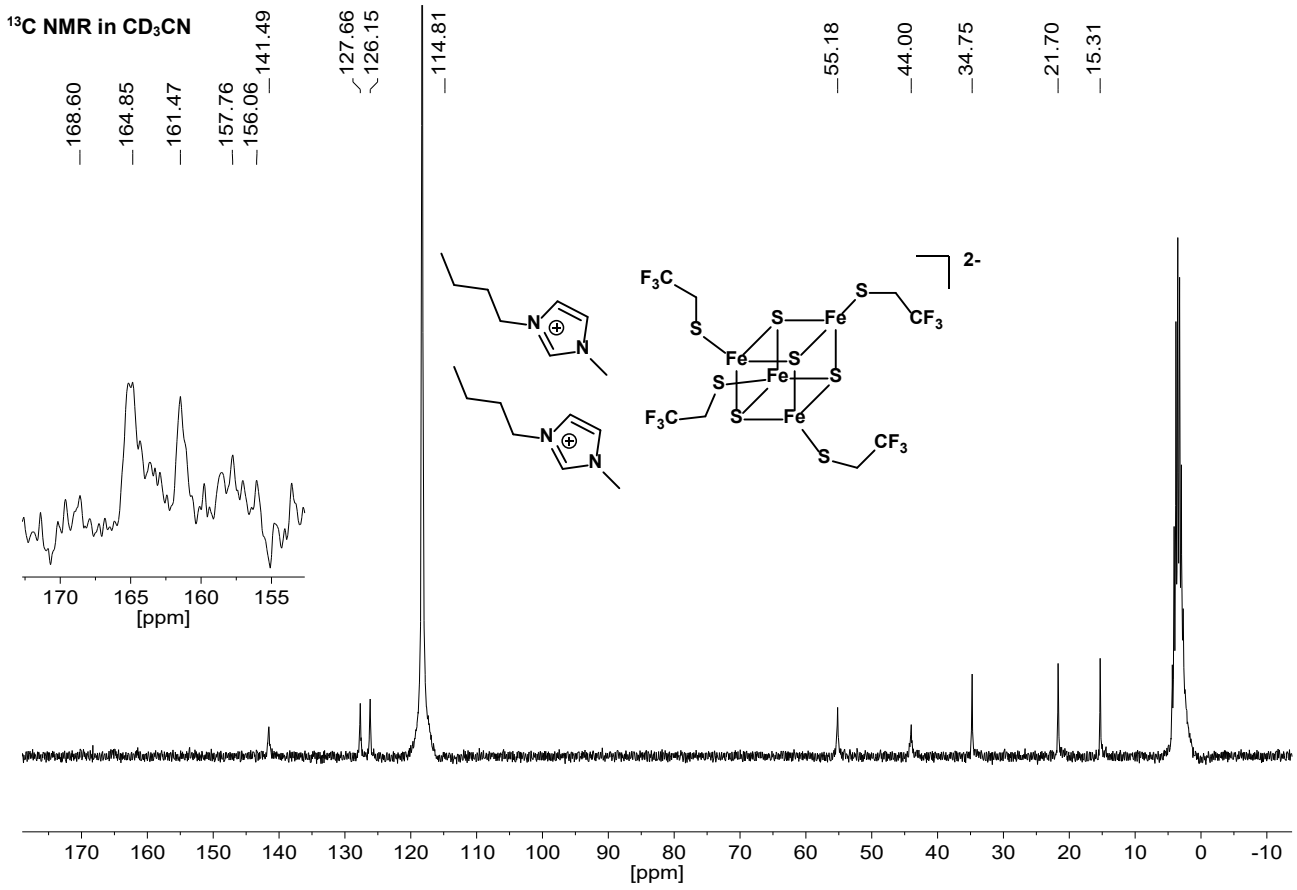
^{13}C NMR in CD_3CN



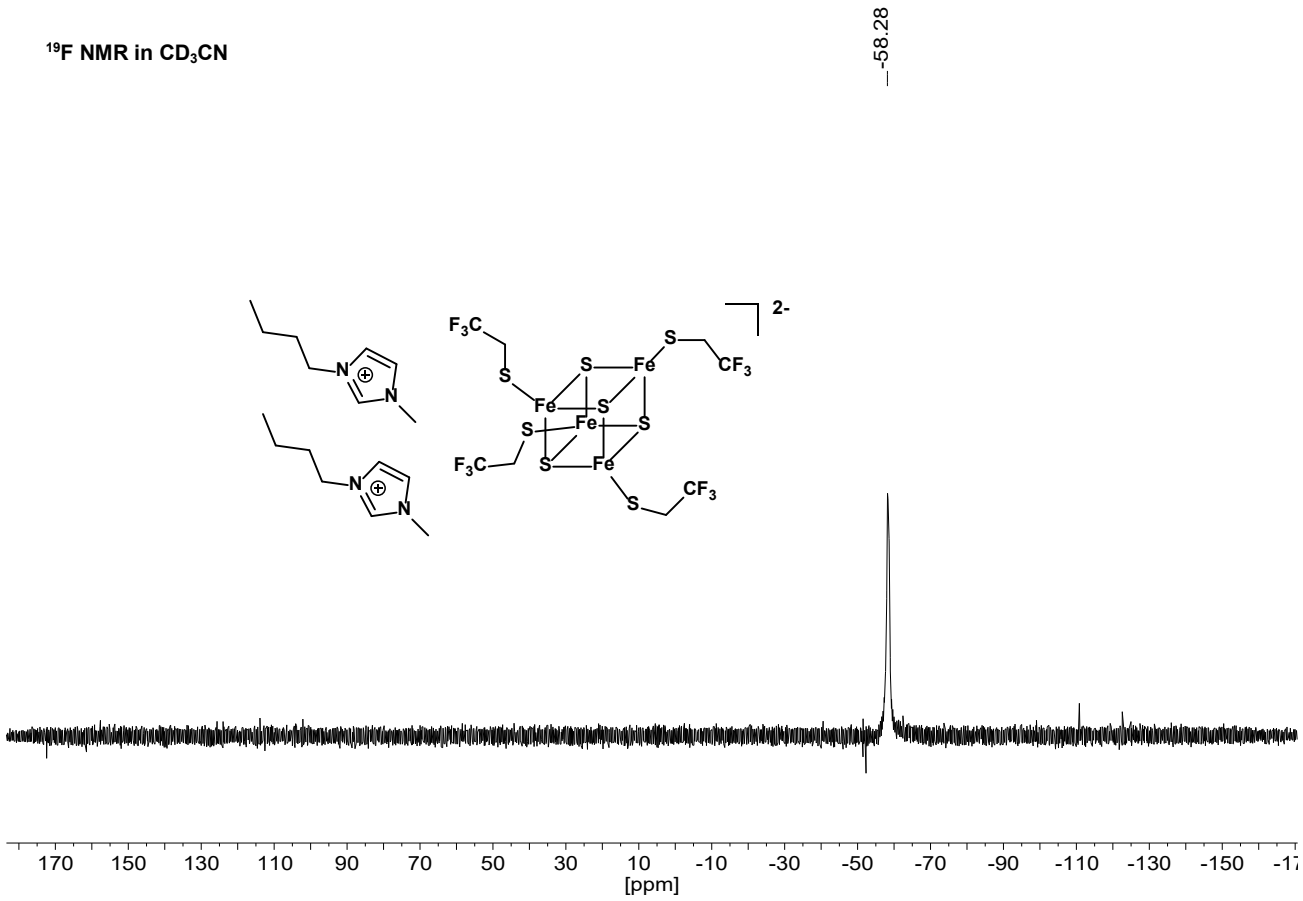
^{19}F NMR in CD_3CN



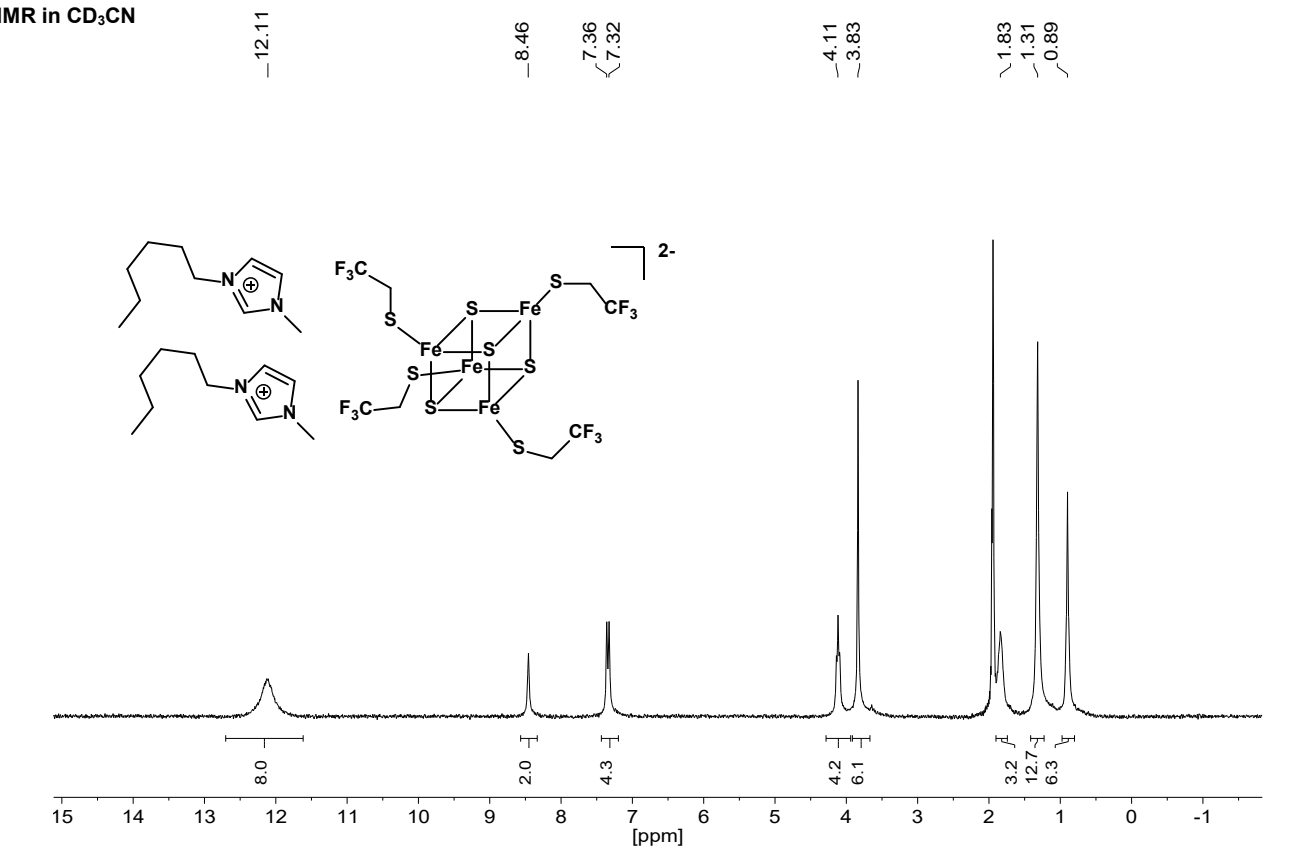

^{1}H NMR in CD_3CN
12.06
8.50
7.35
7.32
4.12
3.83
1.82
1.32
0.94
2-
8.0
2.0
4.4
4.0
6.4
4.4
4.3
6.3
14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
[ppm]


^{13}C NMR in CD_3CN
168.60
164.85
161.47
157.76
156.06
141.49
127.66
126.15
114.81
55.18
44.00
34.75
21.70
15.31
2-
170 165 160 155
[ppm]
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]

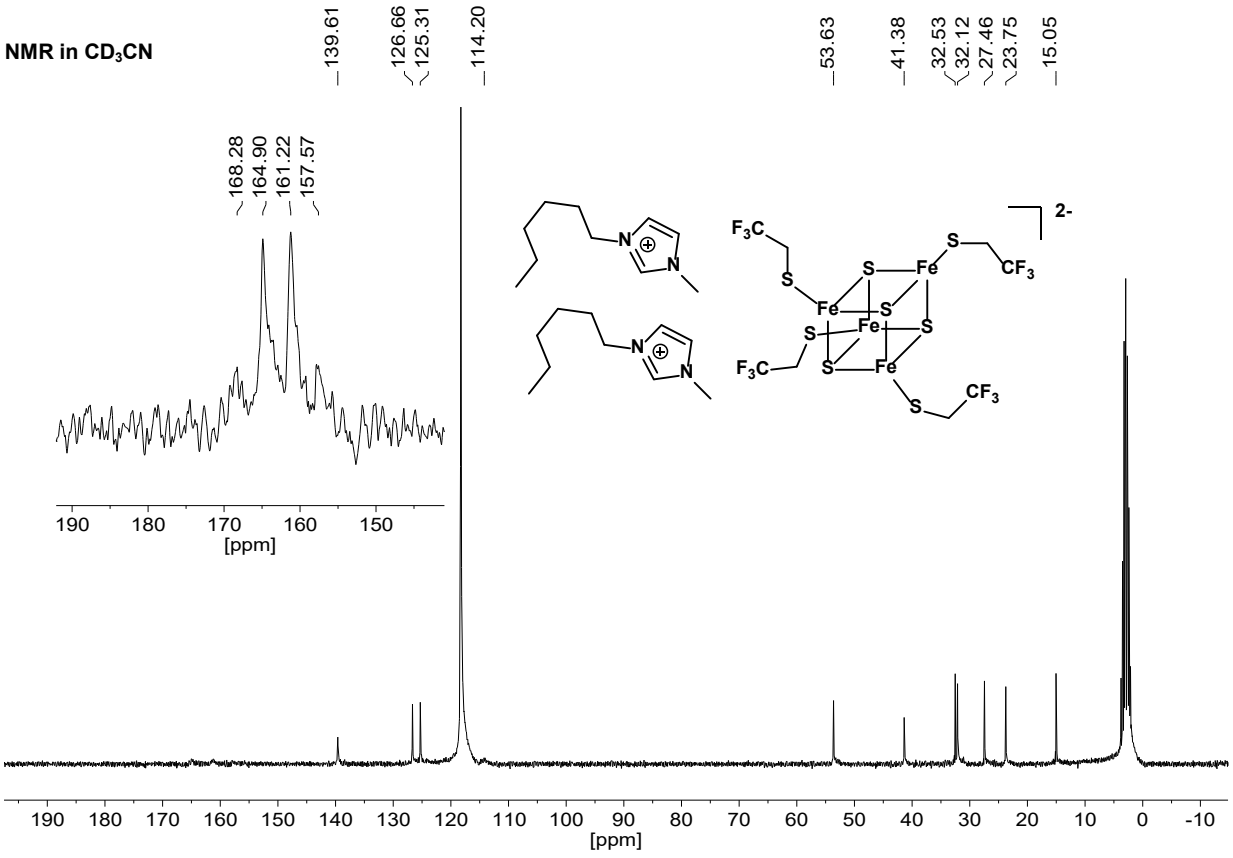
^{19}F NMR in CD_3CN



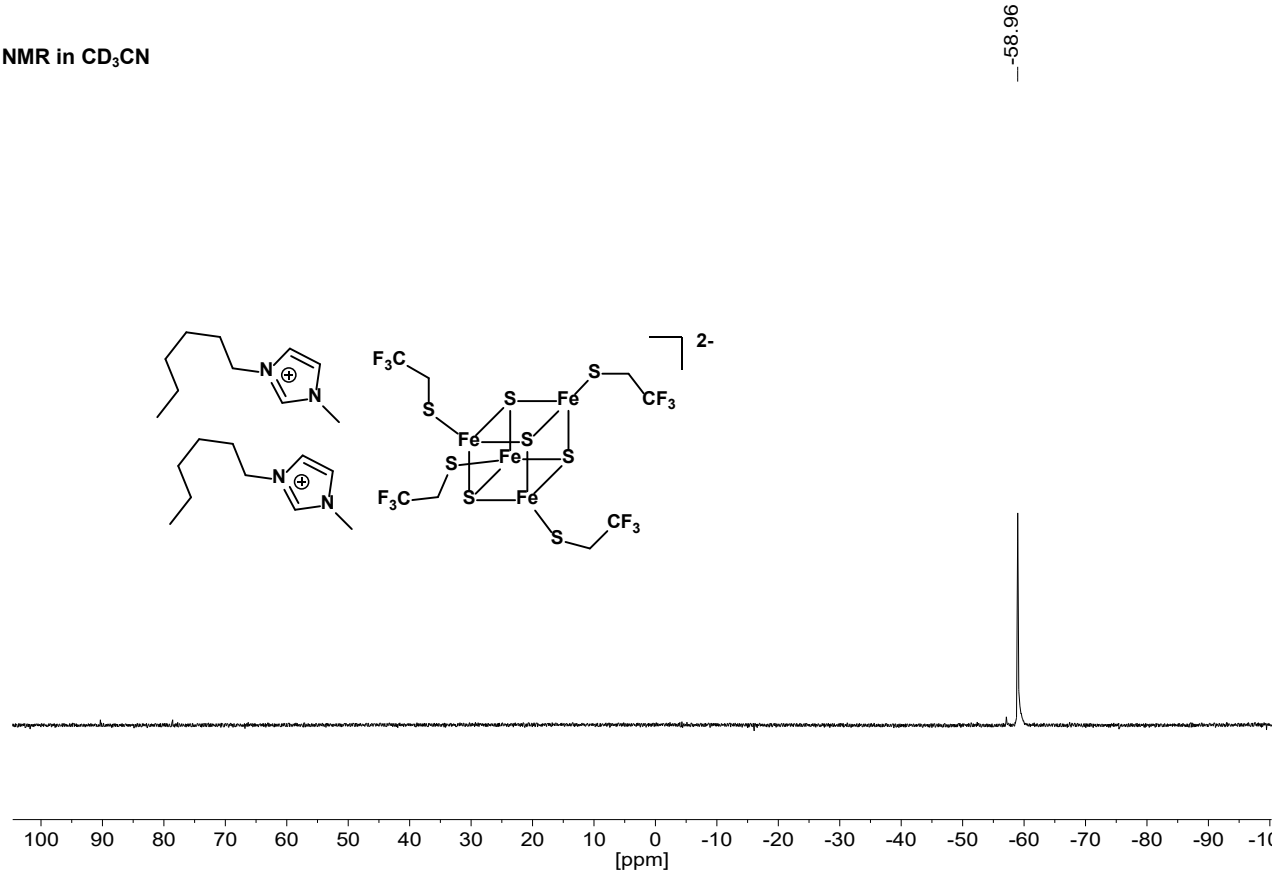
^{1}H NMR in CD_3CN



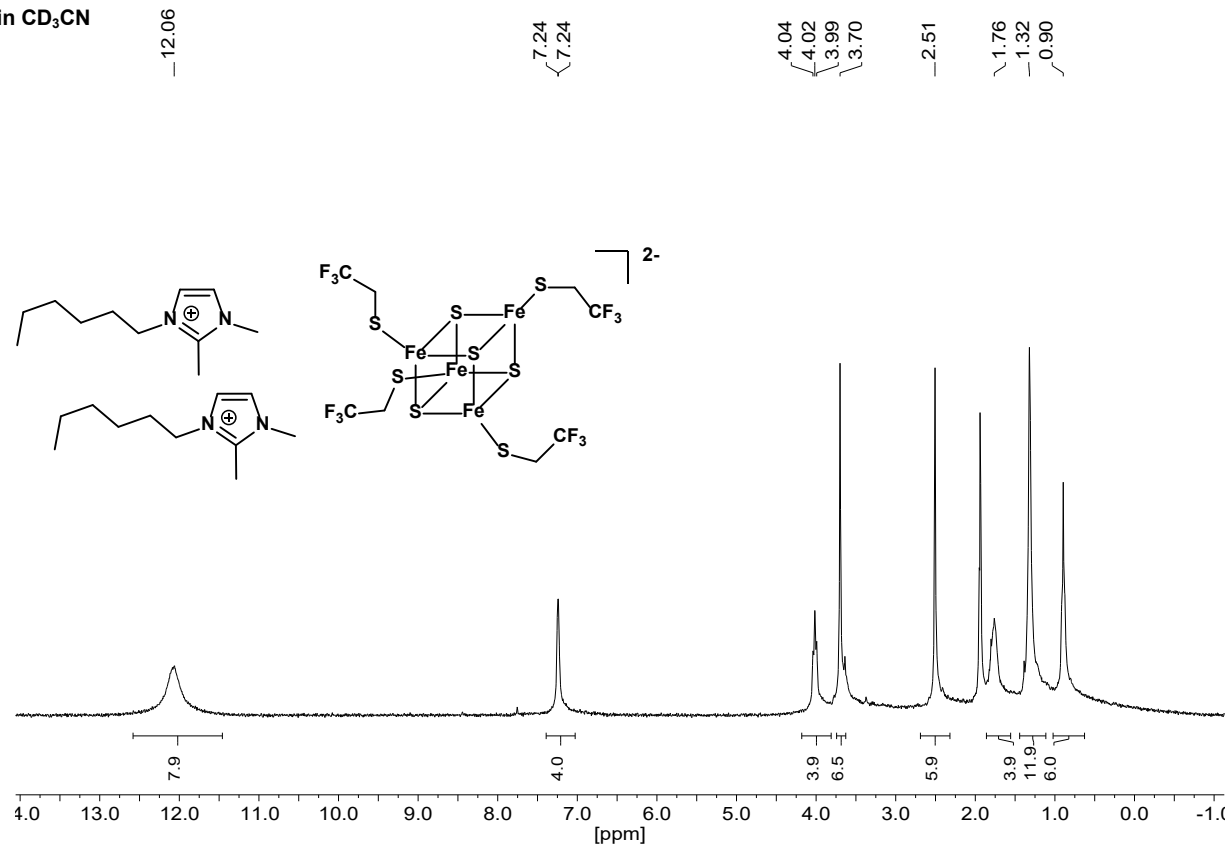
^{13}C NMR in CD_3CN

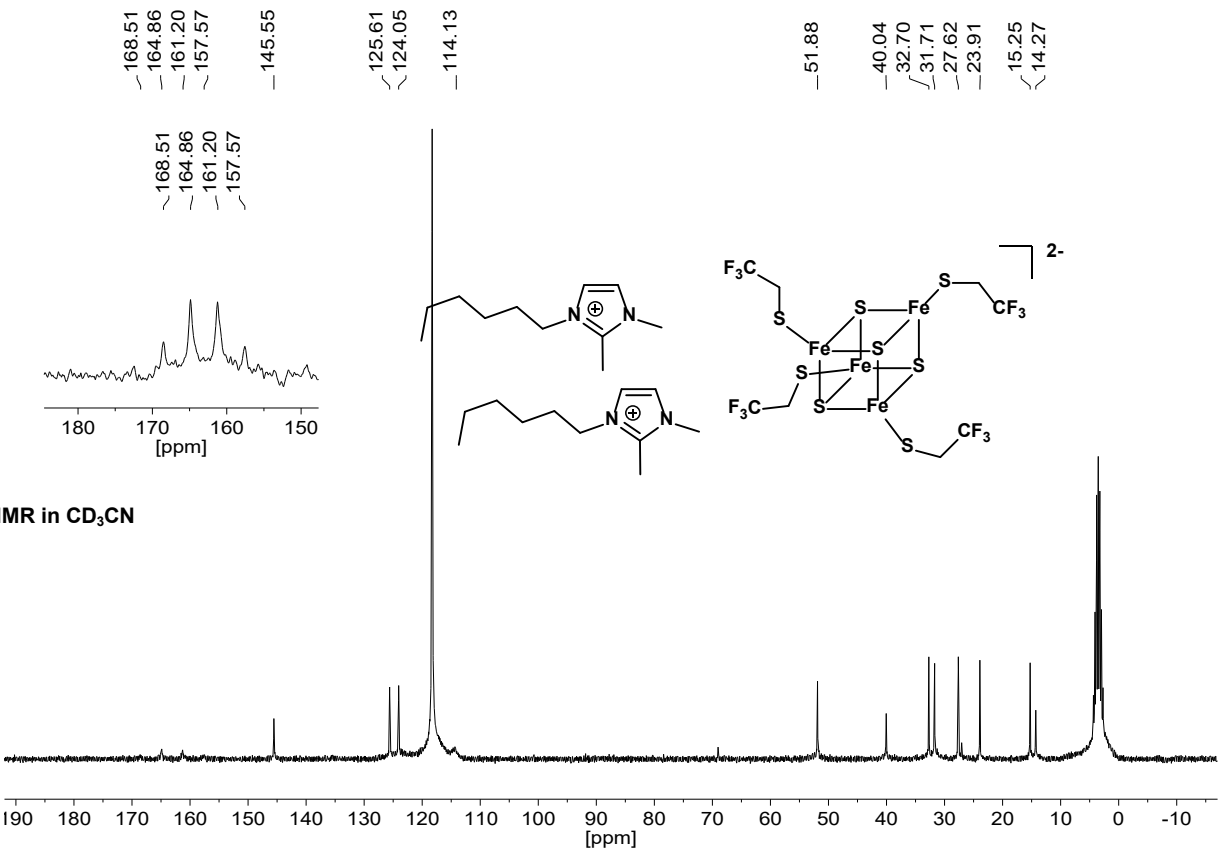


^{19}F NMR in CD_3CN



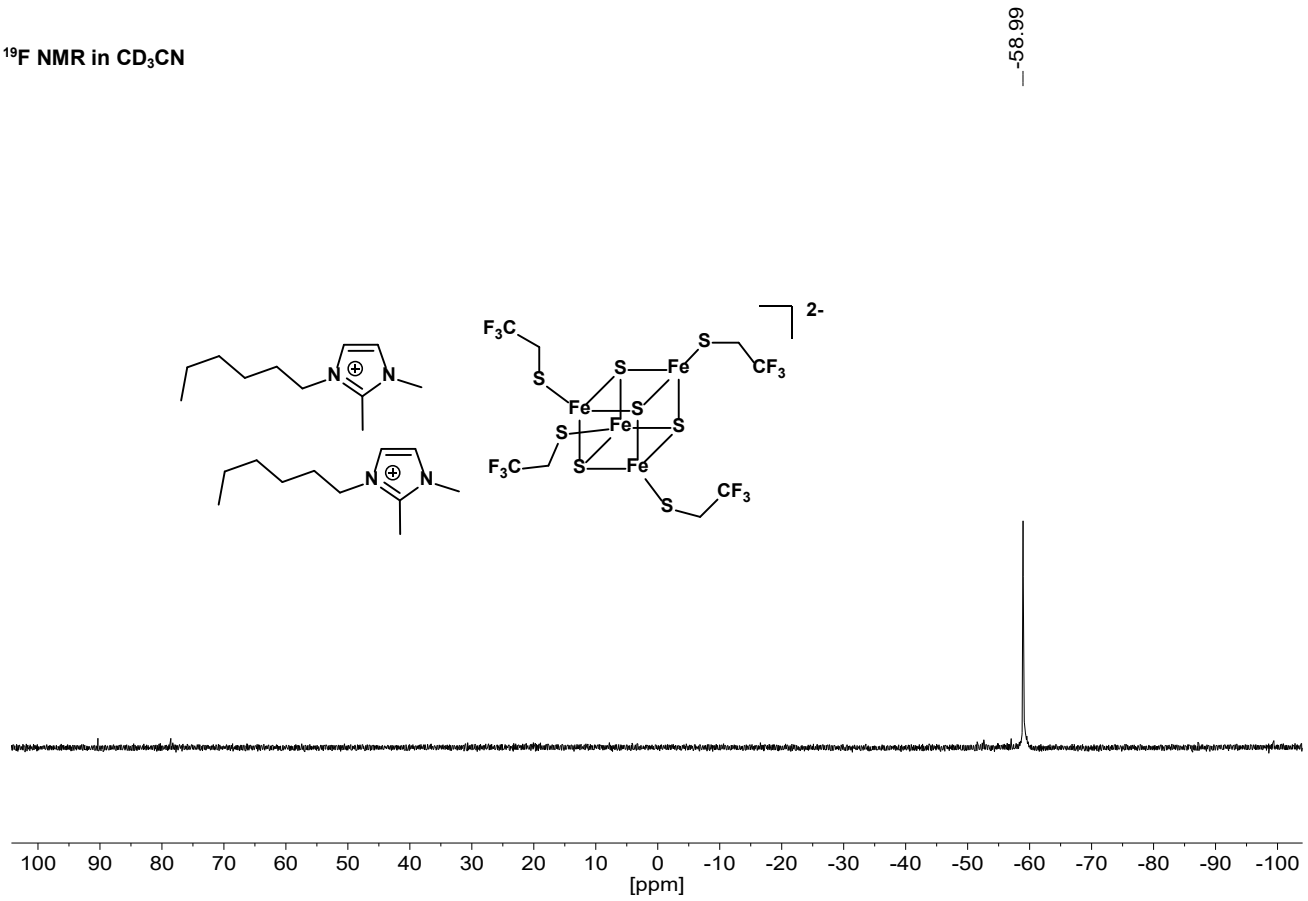
^{1}H NMR in CD_3CN



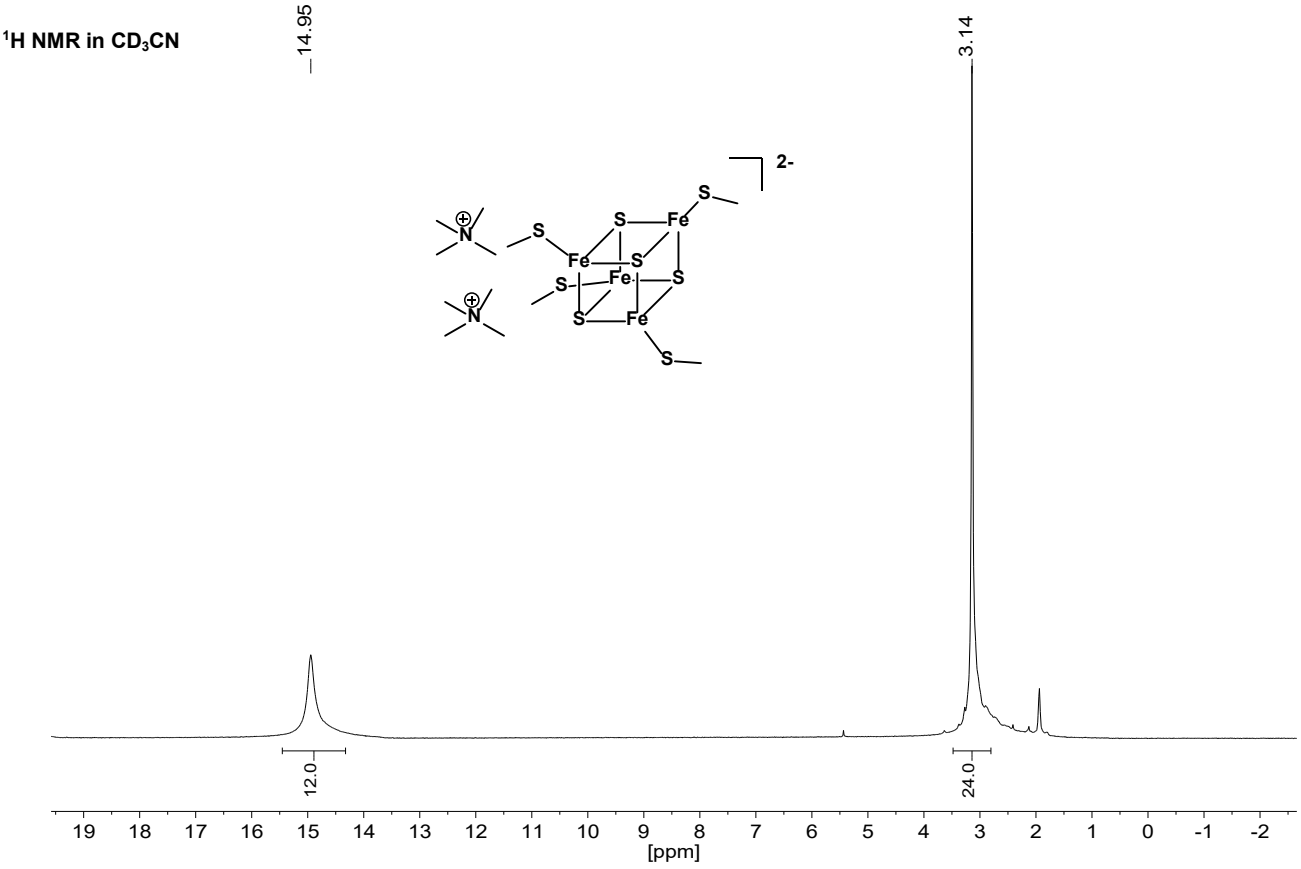


^{13}C NMR in CD_3CN

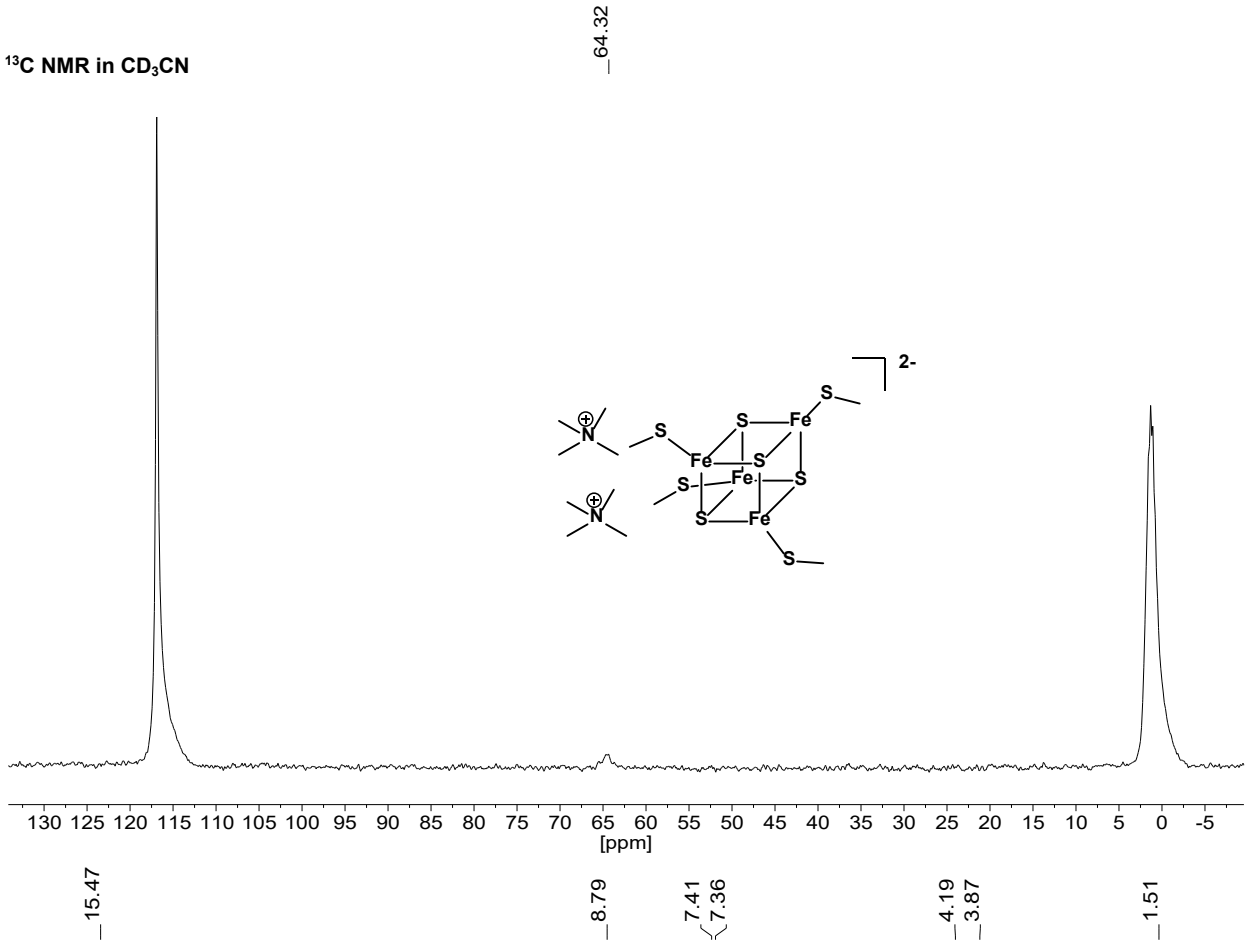
^{19}F NMR in CD_3CN



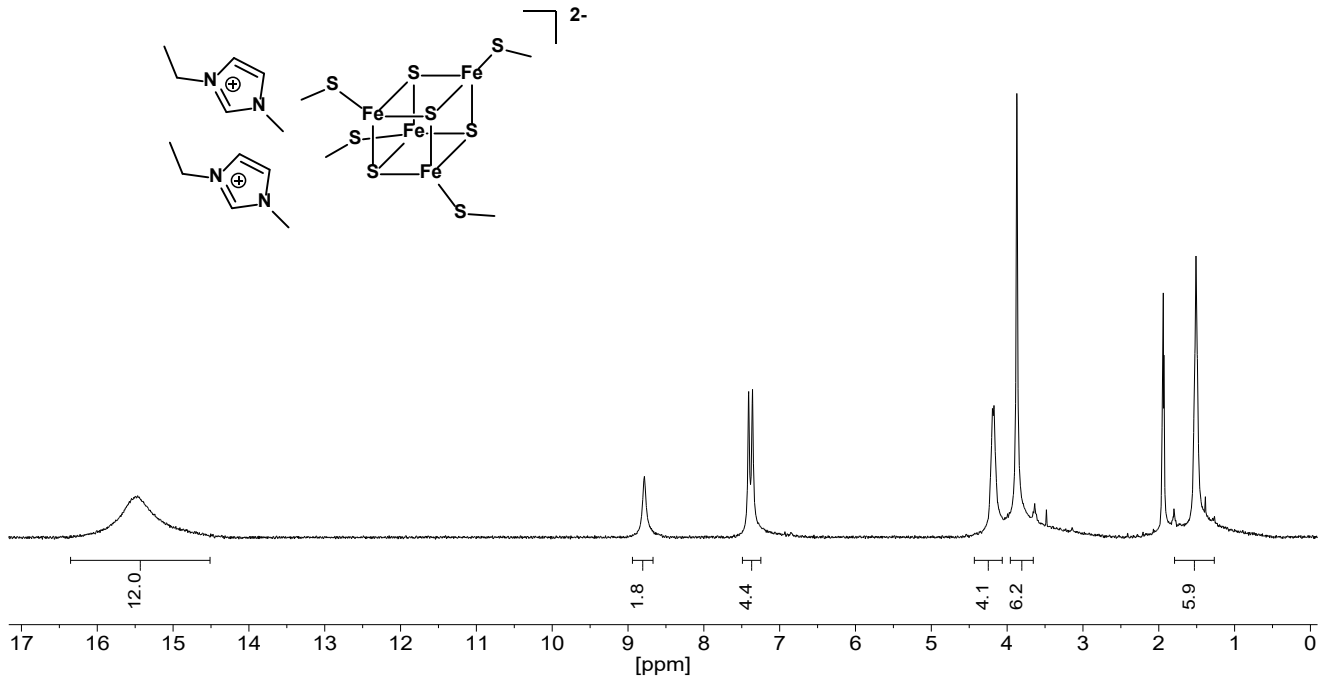
^{1}H NMR in CD_3CN

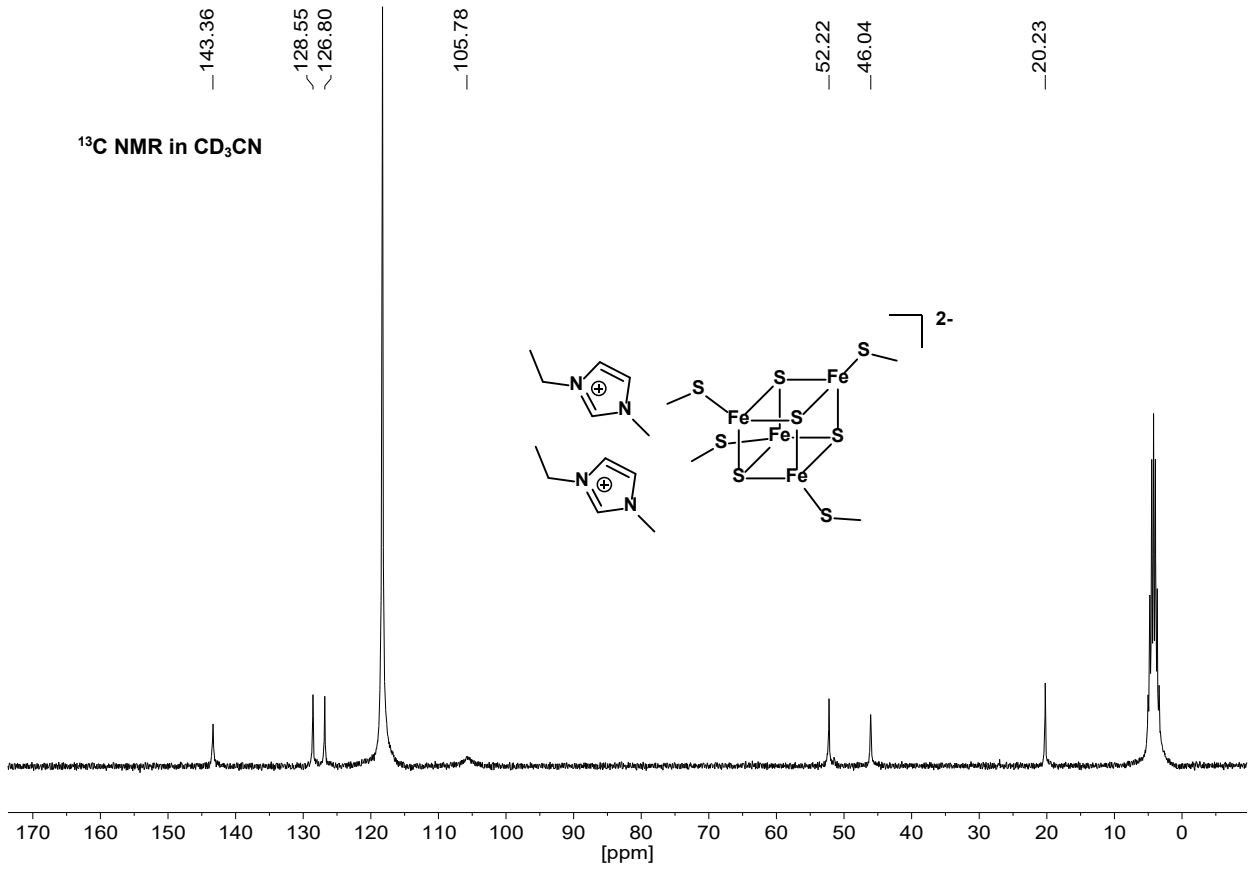


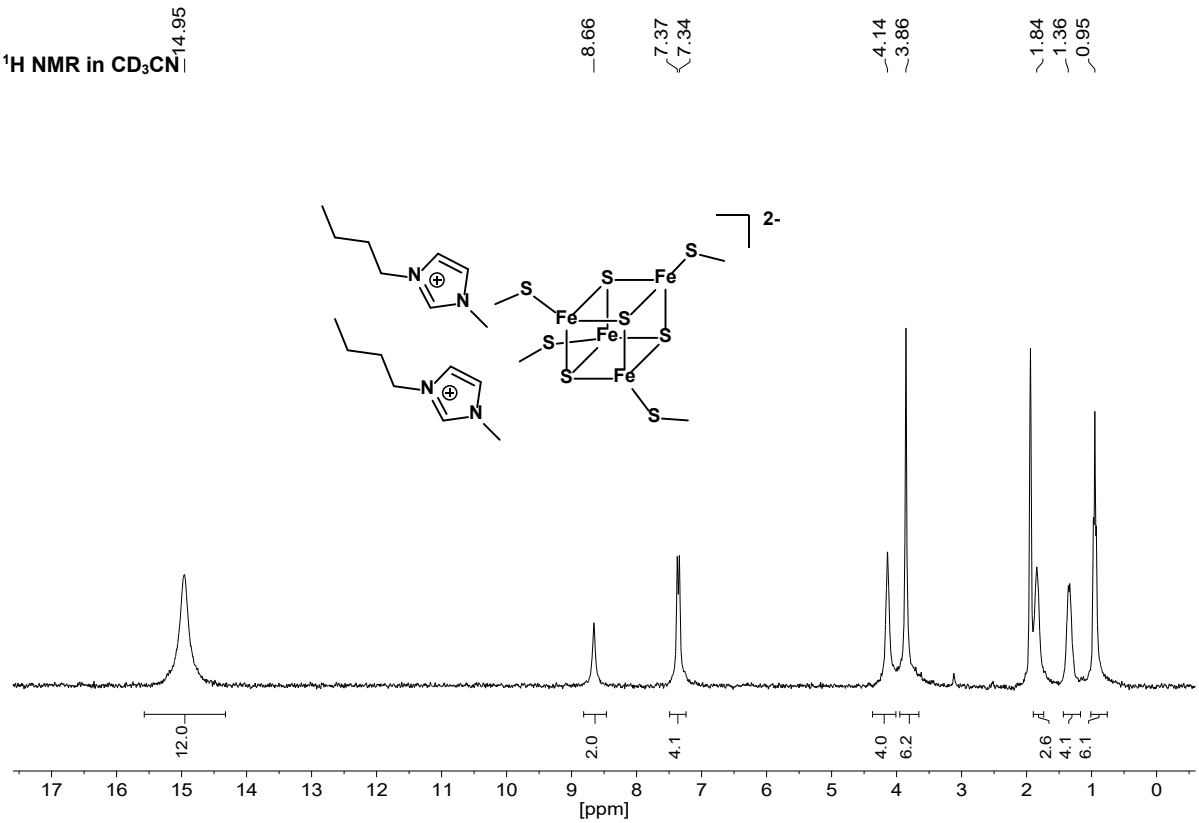
^{13}C NMR in CD_3CN

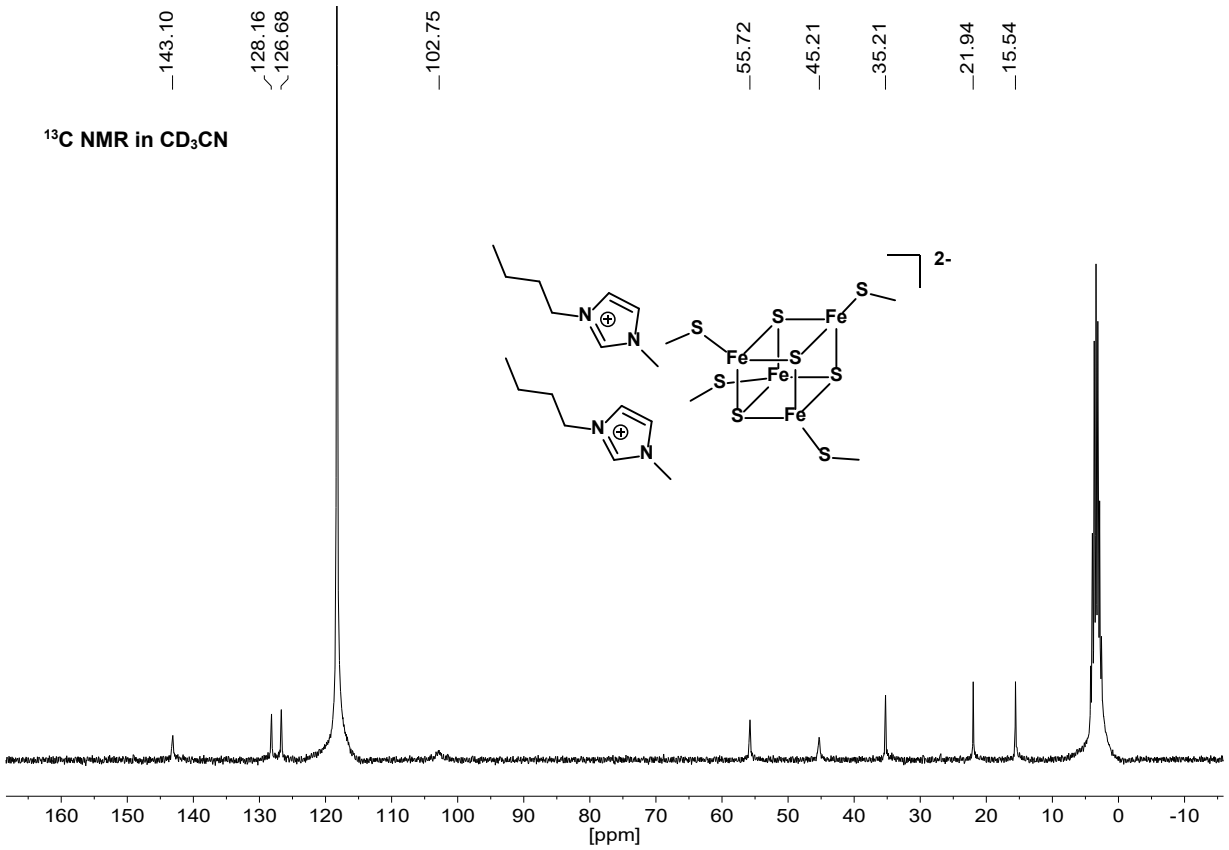


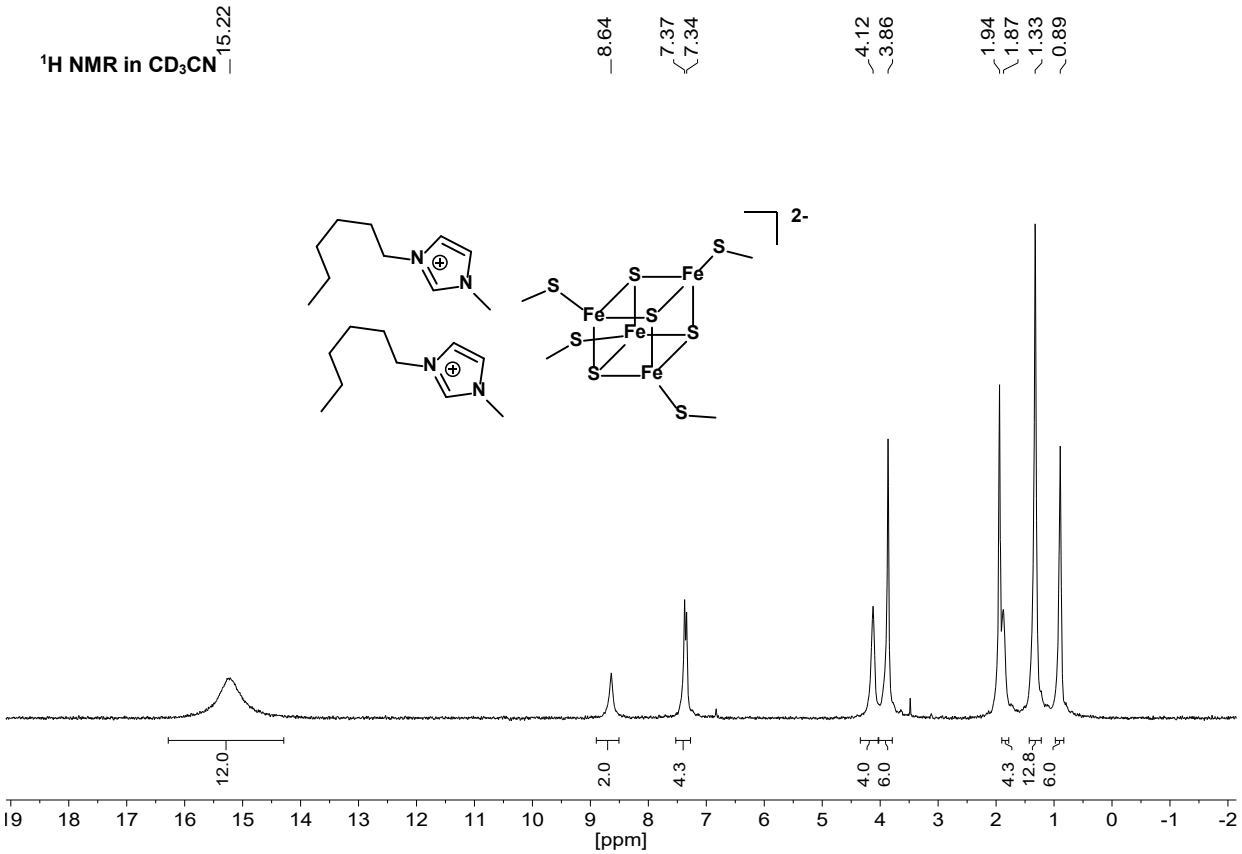
^{1}H NMR in CD_3CN

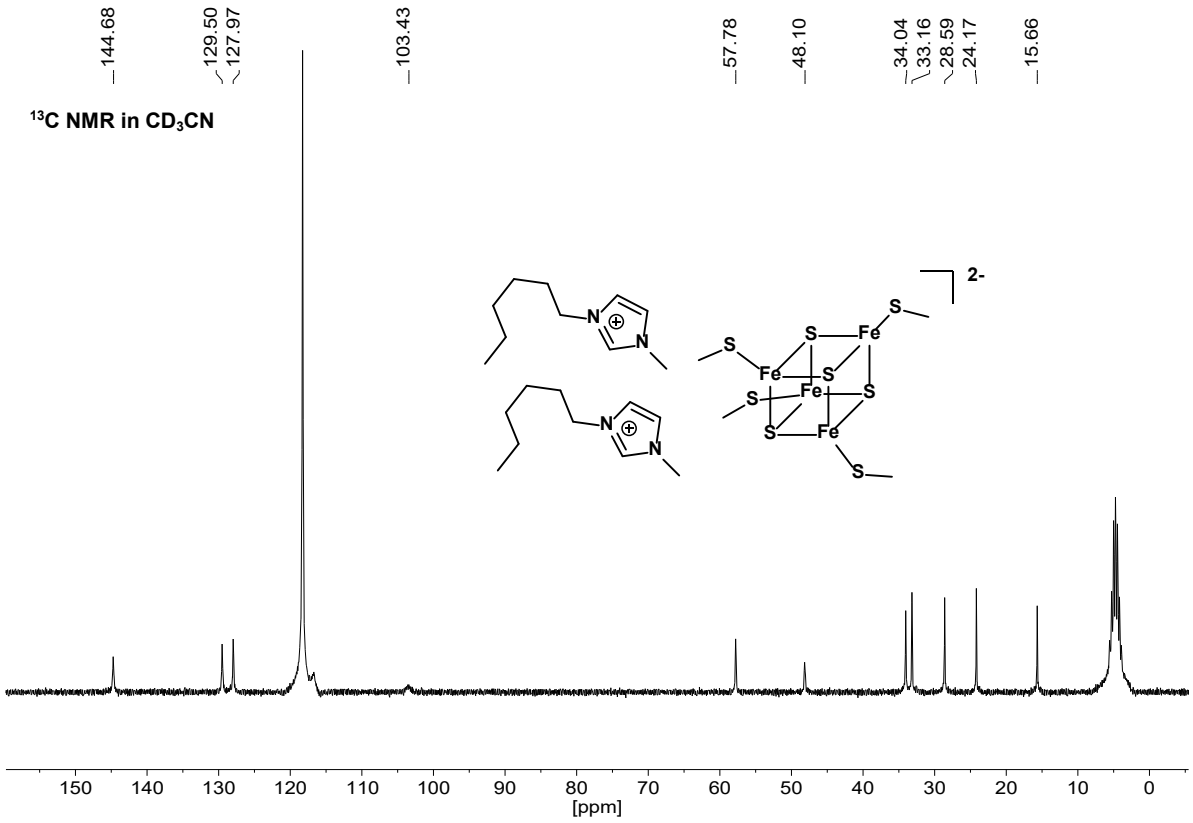


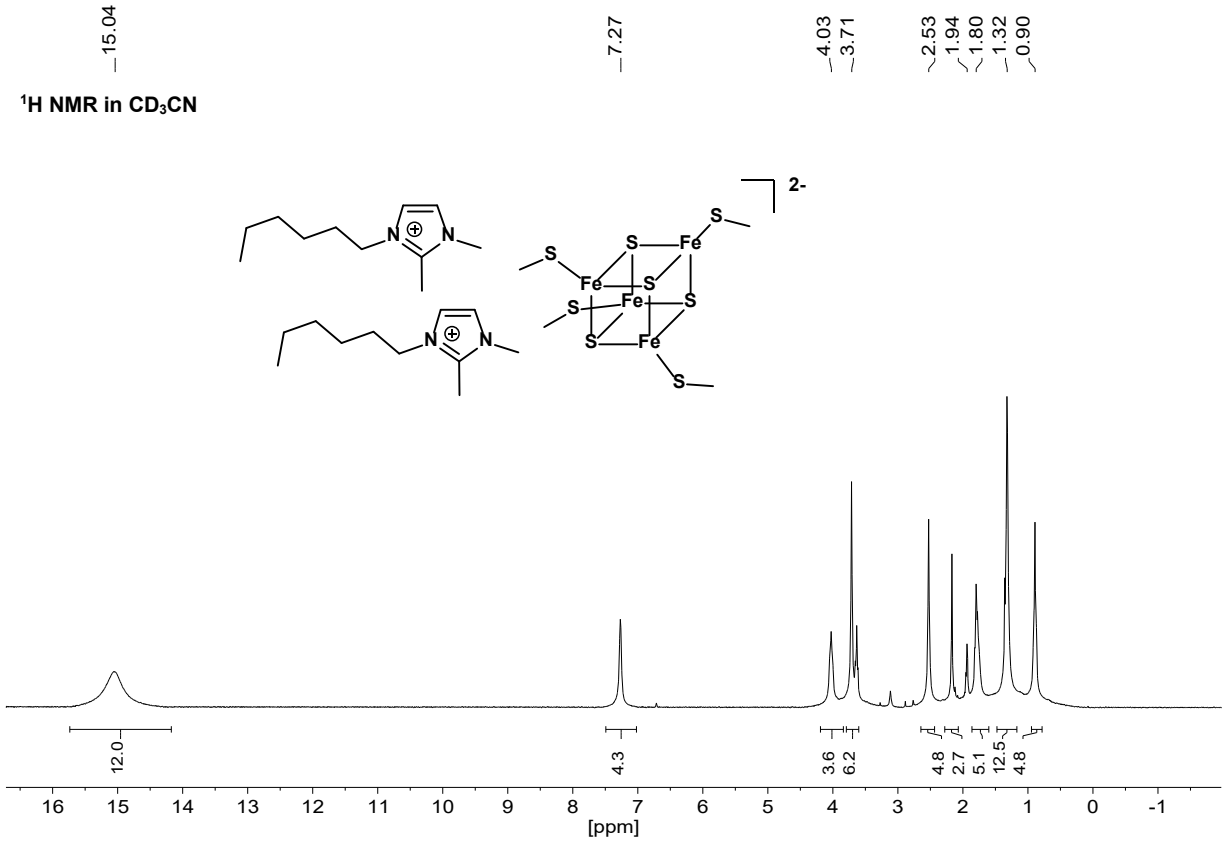

143.36
128.55
126.80
105.78
52.22
46.04
20.23
13C NMR in CD3CN
2-
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
[ppm]

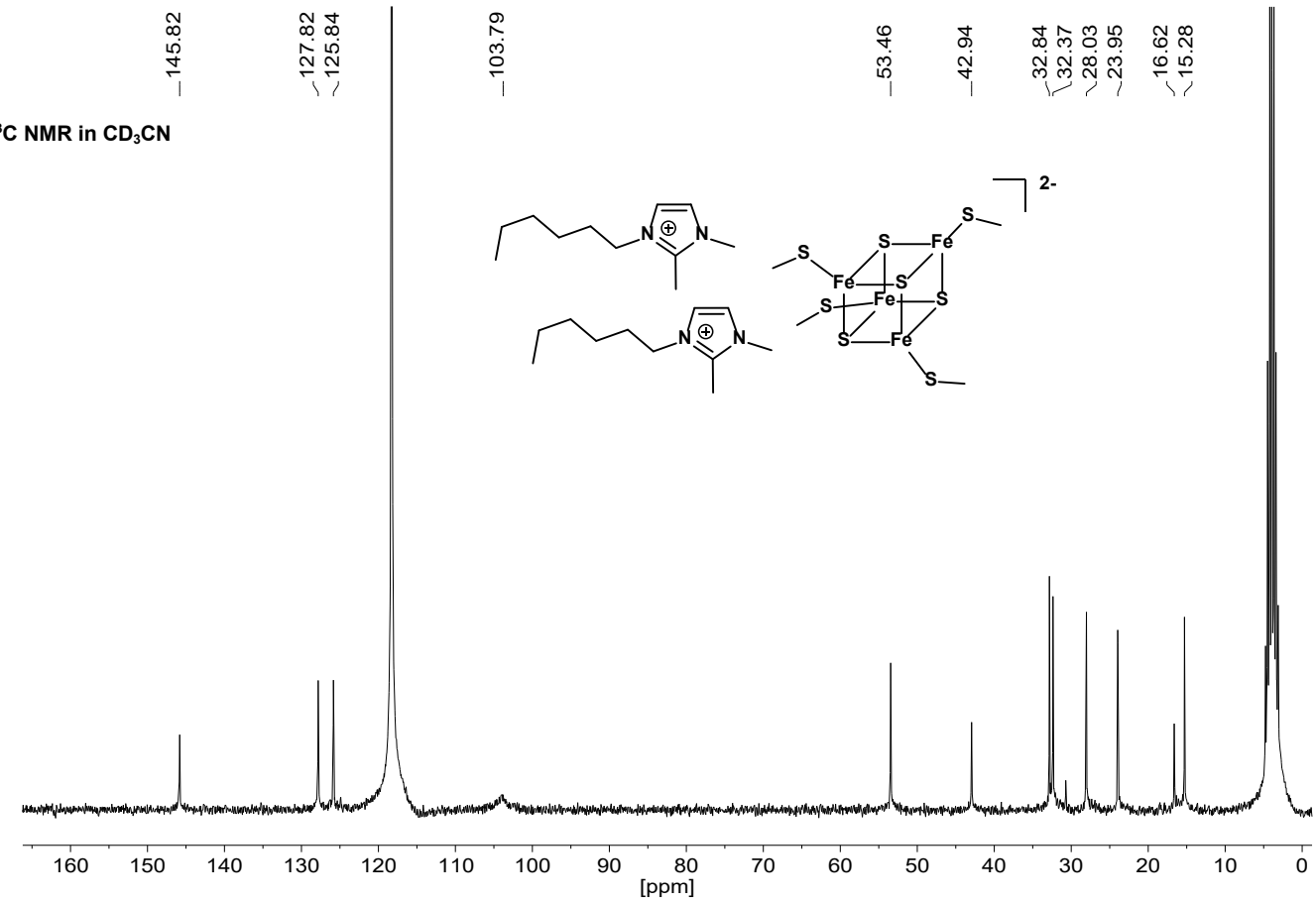

14.95
8.66
7.37
7.34
4.14
3.86
1.84
1.36
0.95
1H NMR in CD3CN
2-
12.0
2.0
4.1
4.0
6.2
2.6
4.1
6.1
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
[ppm]

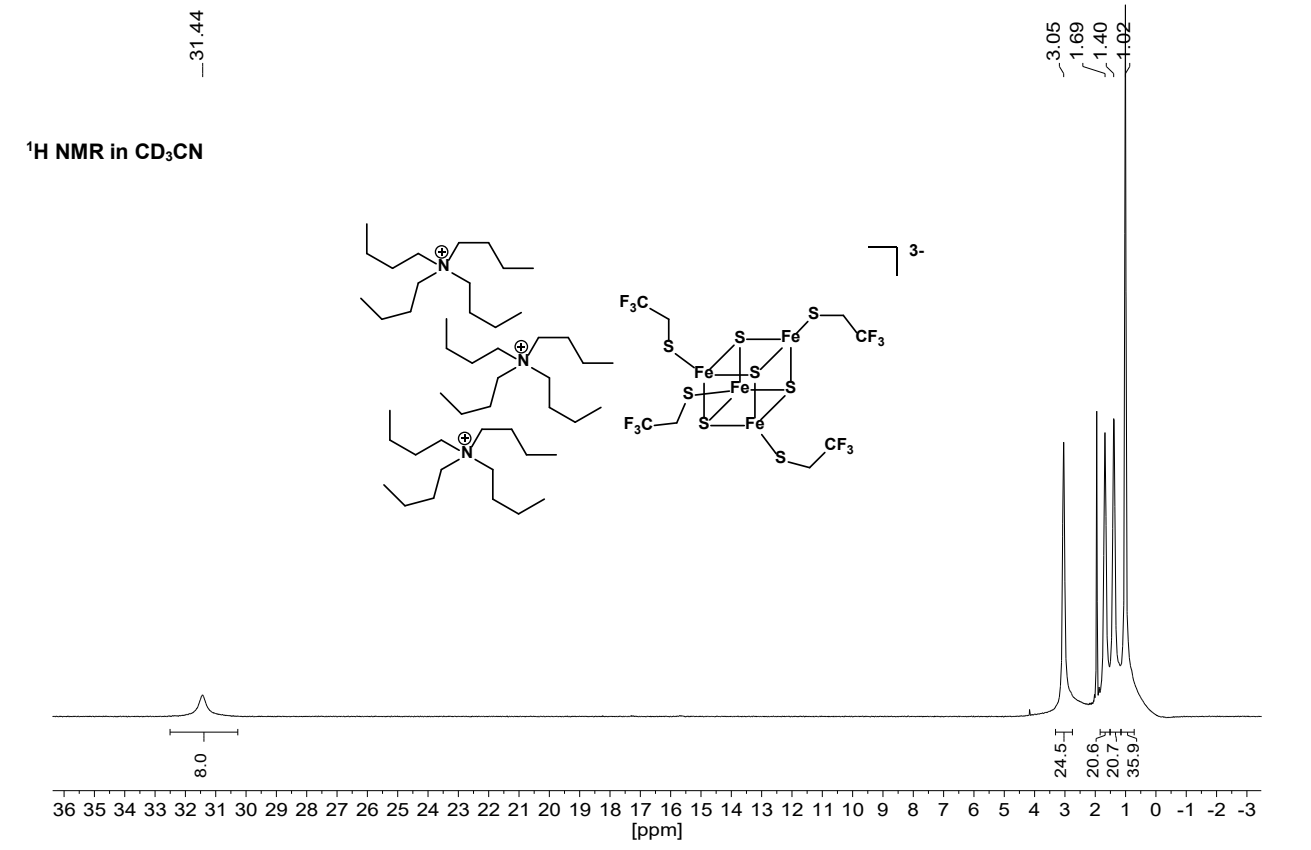

143.10
128.16
126.68
102.75
55.72
45.21
35.21
21.94
15.54
13C NMR in CD3CN
2-
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


15.22
8.64
7.37
7.34
4.12
3.86
1.94
1.87
1.33
0.89
1H NMR in CD3CN
2-
12.0
2.0
4.3
4.0
6.0
4.3
12.8
6.0
19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
[ppm]


144.68
129.50
127.97
103.43
57.78
48.10
34.04
33.16
28.59
24.17
15.66
13C NMR in CD3CN
2-
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
[ppm]


15.04
7.27
4.03
3.71
2.53
1.94
1.80
1.32
0.90
1H NMR in CD3CN
2-
12.0
4.3
3.6
6.2
4.8
2.7
5.1
12.5
4.8
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
[ppm]


145.82
127.82
125.84
103.79
53.46
42.94
32.84
32.37
28.03
23.95
16.62
15.28
13C NMR in CD3CN
2-
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
[ppm]


31.44
3.05
1.69
1.40
1.02
1H NMR in CD3CN
3-
8.0
24.5
20.6
20.7
35.9
36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
[ppm]

9. Crystallographic data

Crystallographic measurements were carried out with Mo-K_α radiation at 100 K on a SuperNova single crystal diffractometer from Oxford Diffraction (Agilent Technologies). The structures were solved by direct methods and refined against F^2 by full matrix least squares (SHELXL).[5] All non-hydrogen atoms were anisotropically refined unless otherwise reported; the H-atoms were included in calculated positions as riding model in the refinement. For $(Me_4N)_2[Fe_4S_4(Stfe)_4]\cdot THF$ the structure was disordered and was refined with two positions with an occupancy of 87 % for the atoms Fe1, Fe3, S1, S5, S7, S8, C1, C2, F1, F2, F3.
CCDC 1573434 and 1573435 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Table S1: Crystal data for $(Me_4N)_2[Fe_4S_4(Stfe)_4]\cdot THF$ and $(Me_4N)_2[Fe_4S_4(SMe)_4]$

	$(Me_4N)_2[Fe_4S_4(Stfe)_4]\cdot THF$	**$(Me_4N)_2[Fe_4S_4(SMe)_4]$**
Empirical formula	$C_{20}H_{40}F_{12}Fe_4N_2OS_8$	$C_{12}H_{36}N_2S_8Fe_4$
Formula weight	1032.42	688.31
Temperature/K	100.0(1)	100.0(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	13.4591(4)	10.8738(6)
b/Å	21.7890(5)	18.0751(10)
c/Å	13.3532(3)	14.0504(8)
β/°	90.297(2)	97.3330(10)
Volume/Å^3	3915.91(15)	2738.9(3)
Z	4	4
ρ_{calc}g/cm^3	1.751	1.669
μ/mm^{-1}	1.957	2.689
F(000)	2088.0	1416.0
Crystal size/mm^3	0.36 × 0.2 × 0.16	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.102 to 65.236	3.69 to 57.878
Index ranges	-20 ≤ h ≤ 20, -32 ≤ k ≤ 32, -20 ≤ l ≤ 20	-14 ≤ h ≤ 14, -24 ≤ k ≤ 24, -18 ≤ l ≤ 19
Reflections collected	75982	40909
Independent reflections	13502 [R_{int} = 0.0483, R_{sigma} = 0.0382]	6821 [R_{int} = 0.0210, R_{sigma} = 0.0124]
Data/restraints/parameters	13502/0/466	6821/0/247
Goodness-of-fit on F^2	1.250	1.242
Final R indexes [I>=2σ (I)]	R_1 = 0.0724, wR_2 = 0.1487	R_1 = 0.0168, wR_2 = 0.0404
Final R indexes [all data]	R_1 = 0.0945, wR_2 = 0.1573	R_1 = 0.0172, wR_2 = 0.0405
Largest diff. peak/hole / e Å^{-3}	1.11/-1.04	0.43/-0.28

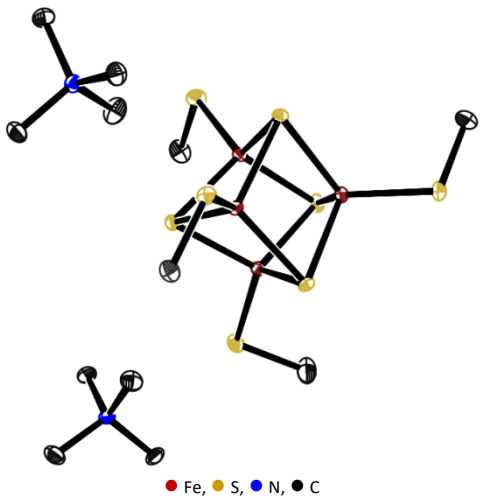


Figure S12: ORTEP-plot (50 %) of $[Me_4N]_2[Fe_4S_4(SMe)_4]$. Hydrogen atoms are omitted for clarity.

10. References

1 T. A. Wark, D. W. Stephan, *Organometallics*, 1989, **8**, 2836.
2 A. Y. Sizov, A. N. Kovregin, R. N. Serdyuk, M. V. Vorob'ev, V. A. Porosyatnikov, A. A. Tsvetkov, D. O. Korneev, A. F. Ermolov, *Russ. Chem. Bull.*, 2006, **55**, 1200.
3 K. S. Hagen, A. D. Watson, R. H. Holm, *J. Am. Chem. Soc.*, 1983, **105**, 3905.
4 G. Christou, C. D. Garner, *J. Chem. Soc., Dalton Trans.*, 1979, 1093.
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