SUPPORTING INFORMATION
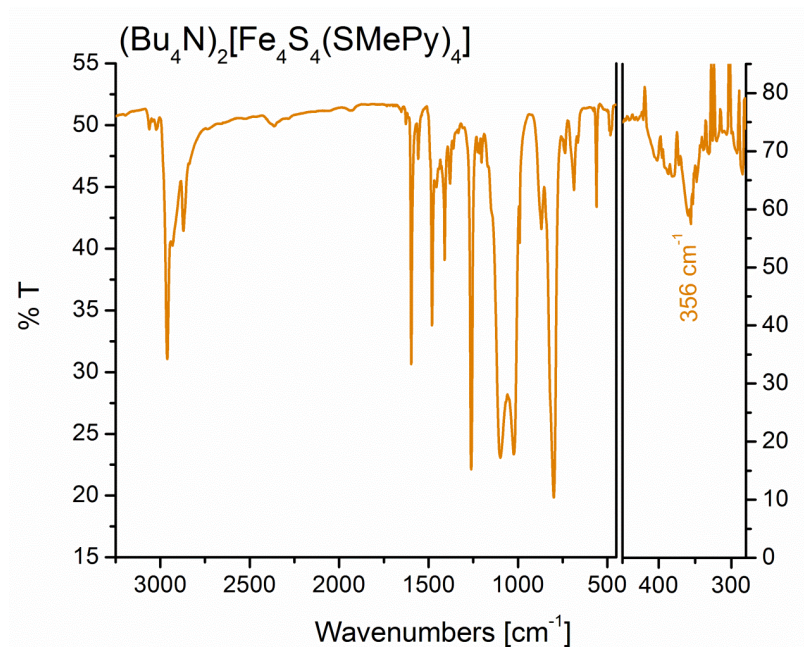
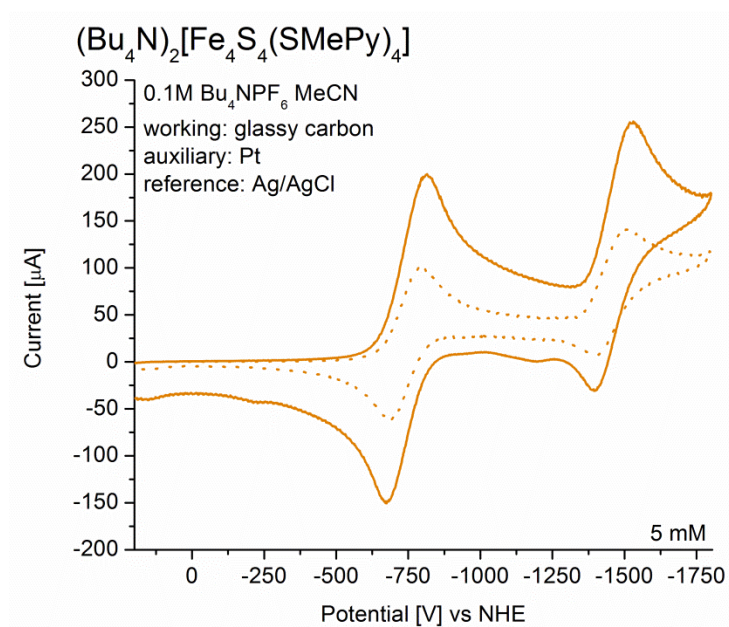**Title:** Isolation and Characterization of Single and Sulfide-Bridged Double [4Fe–4S] Cubane Clusters with 4-Pyridinethiolato Ligands

Author(s): Deidra L. Gerlach, Dimitri Coucouvanis,* Jeff Kampf, Nicolai Lehnert*

Figure S1. Mid- (left) and Far-IR (right) spectra of $(Bu_4N)_2[Fe_4S_4(SMePy)_4]$.

Figure S2. Cyclovoltammetry of $(Bu_4N)_2[Fe_4S_4(SMePy)_4]$ in MeCN at scan rates: 200 mV/s (solid) and 50 mV/s (dotted).

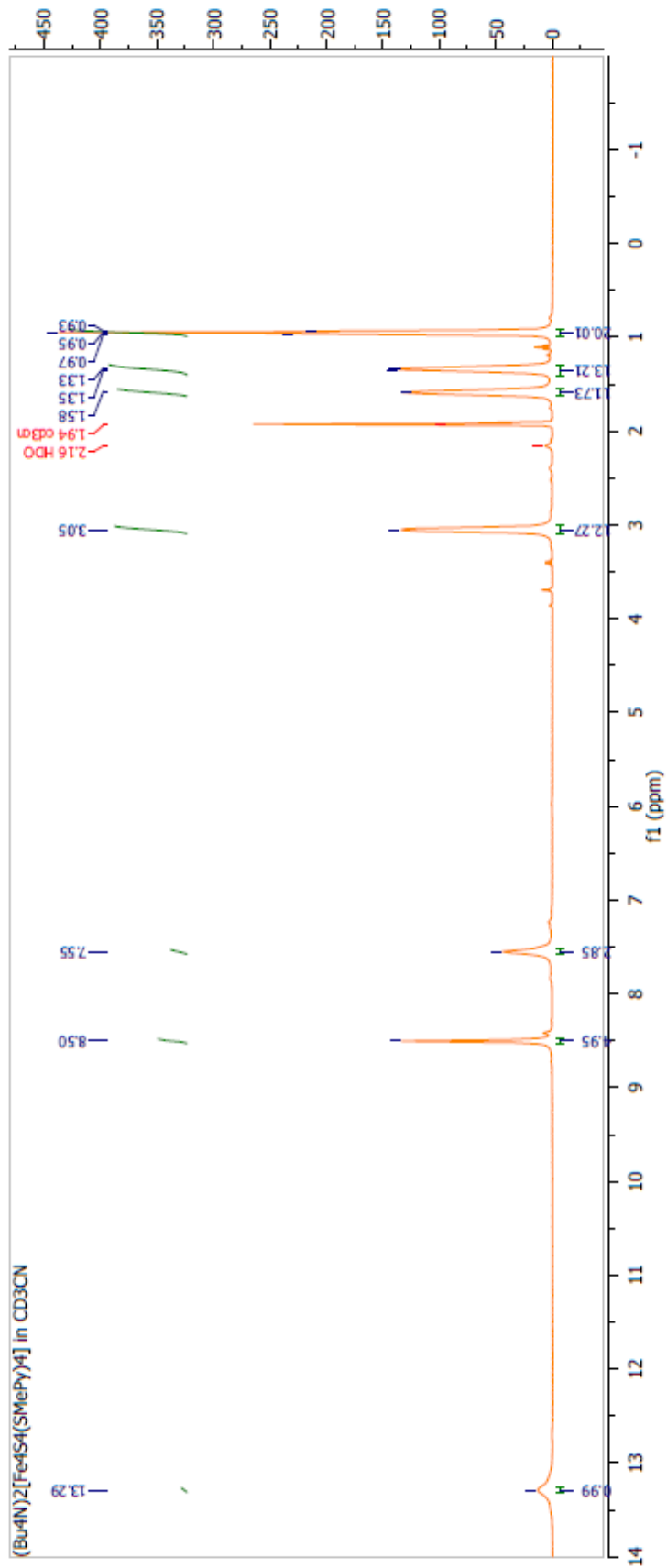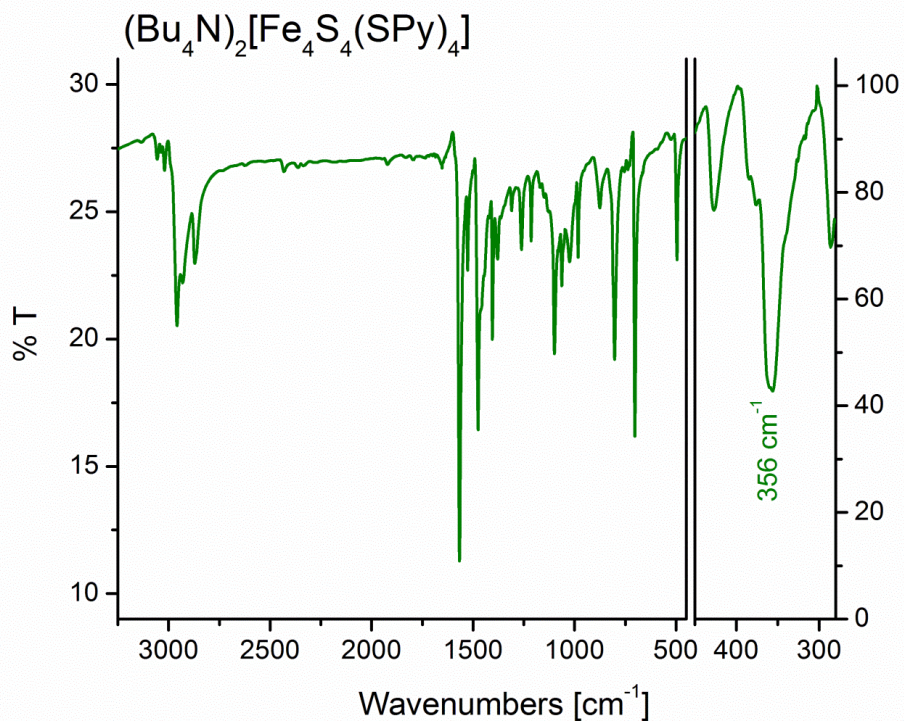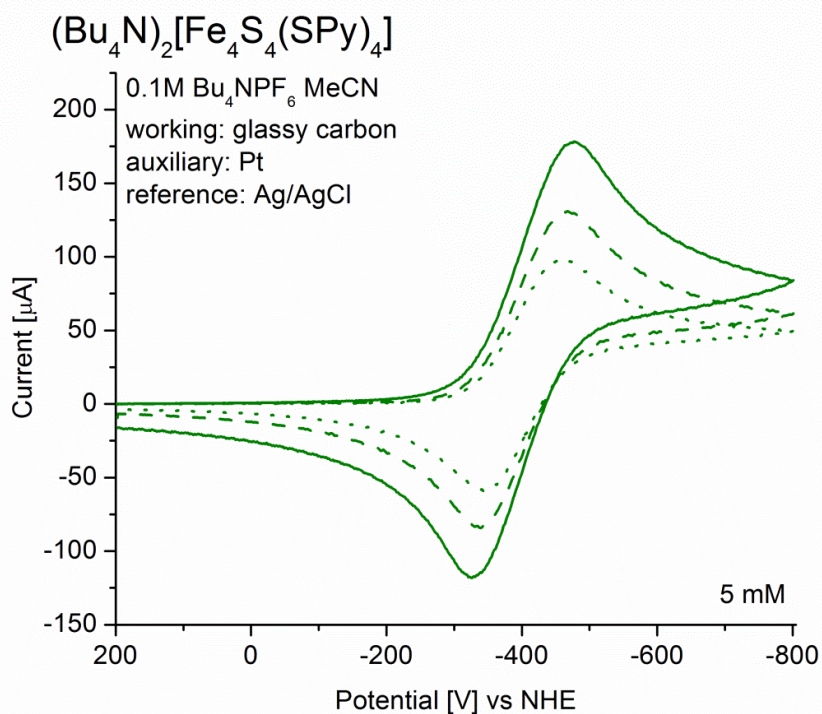**Figure S3.** ^{1}H-NMR spectrum of $(Bu_4N)_2[Fe_4S_4(SMePy)_4]$ in CD_3CN.

2

(Bu₄N)₂[Fe₄S₄(SPy)₄]

% T

356 cm⁻¹

Wavenumbers [cm⁻¹]

Figure S4. Mid- (left) and Far-IR (right) spectra of (Bu$_4$N)$_2$[Fe$_4$S$_4$(SPy)$_4$].

(Bu₄N)₂[Fe₄S₄(SPy)₄]

0.1M Bu$_4$NPF$_6$ MeCN

working: glassy carbon
auxiliary: Pt
reference: Ag/AgCl

Current [μA]

5 mM

Potential [V] vs NHE

Figure S5. Cyclovoltammetry of (Bu$_4$N)$_2$[Fe$_4$S$_4$(SPy)$_4$] in MeCN at scan rates: 200 mV/s (solid), 100 mV/s (dashed), and 50 mV/s (dotted).

Figure S6. ^{1}H-NMR spectrum of $(Bu_4N)_2[Fe_4S_4(SPy)_4]$ in CD_3CN.

4
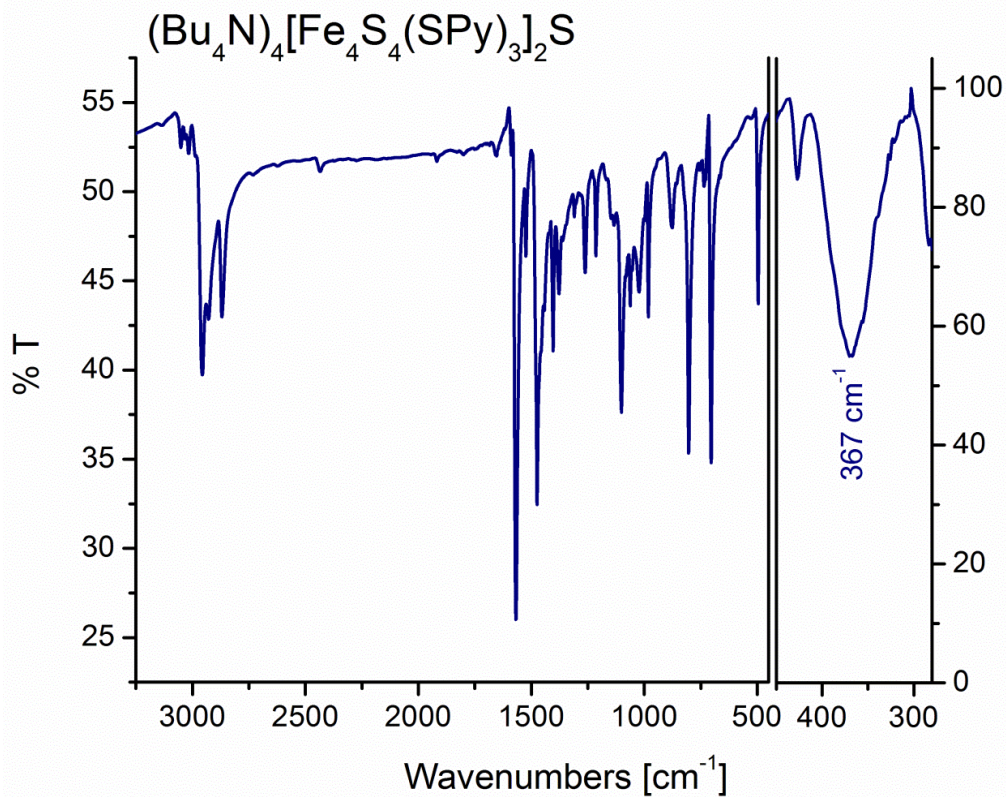
Figure S7. Mid- (left) and Far-IR (right) spectra of $(Bu_4N)_4[(Fe_4S_4(SPy)_3)_2S]$.

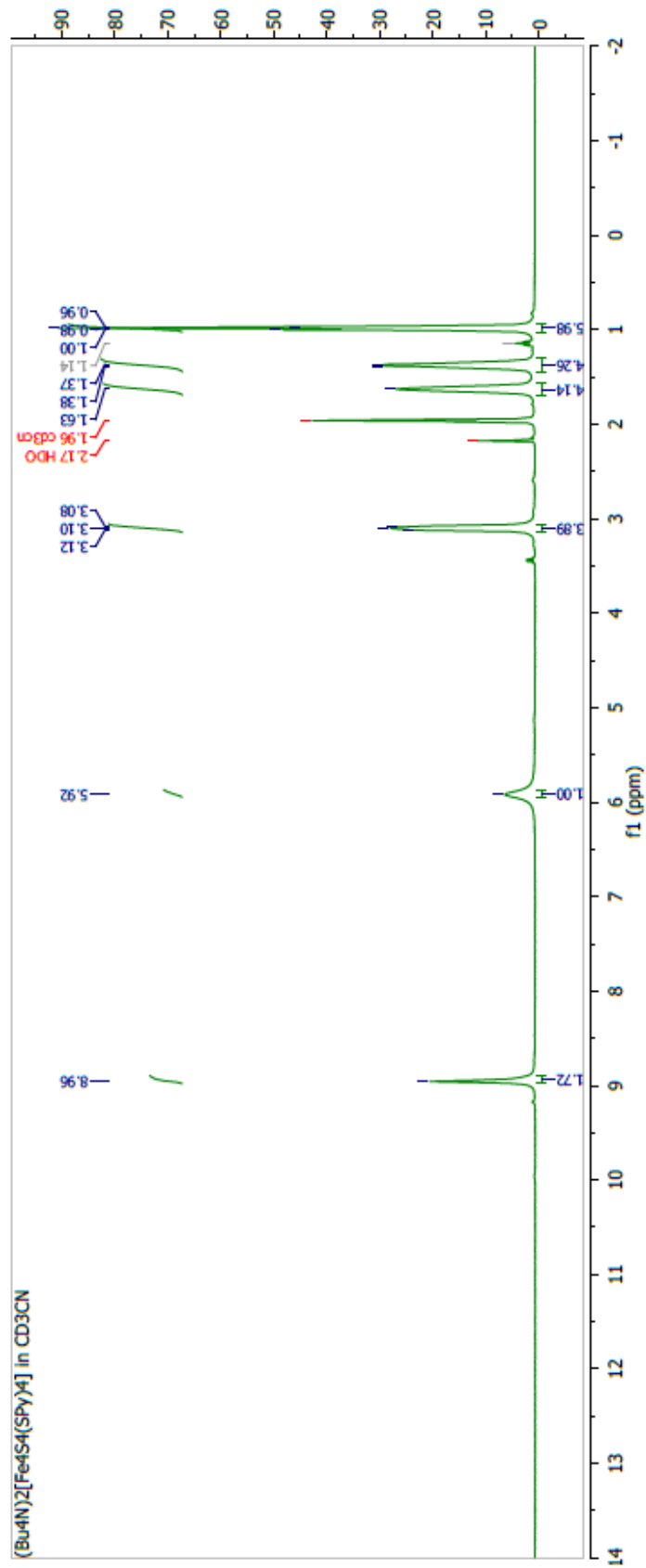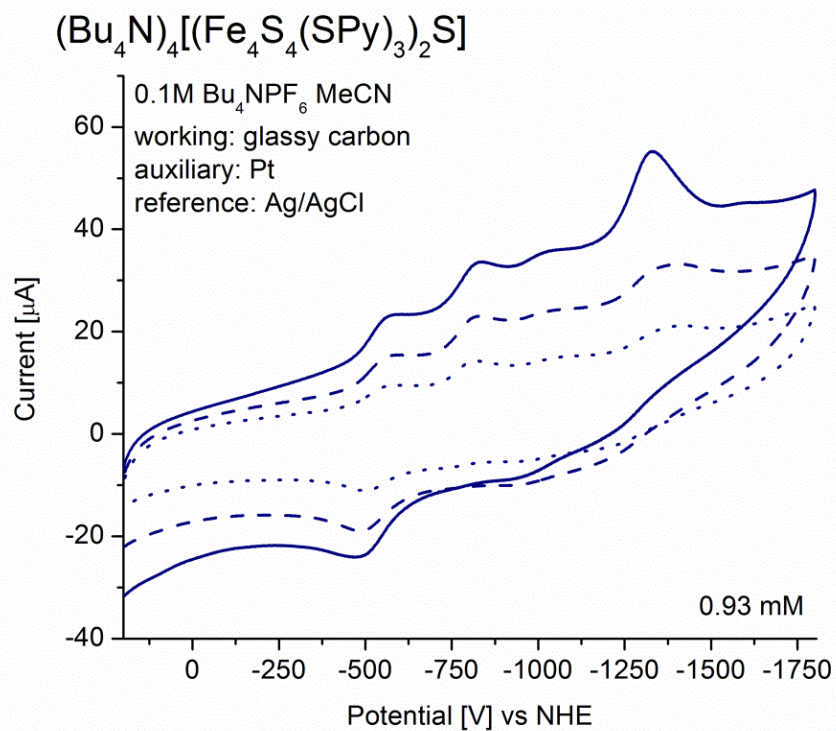**Figure S8.** Cyclovoltammetry of $(Bu_4N)_4[(Fe_4S_4(SPy)_3)_2S]$ in MeCN at scan rates: 200 mV/s (solid), 100 mV/s (dashed), and 50 mV/s (dotted).

Figure S9. ^{1}H-NMR spectrum of $(Bu_4N)_4[(Fe_4S_4(SPy)_3)_2S]$ in CD$_3$CN.

6
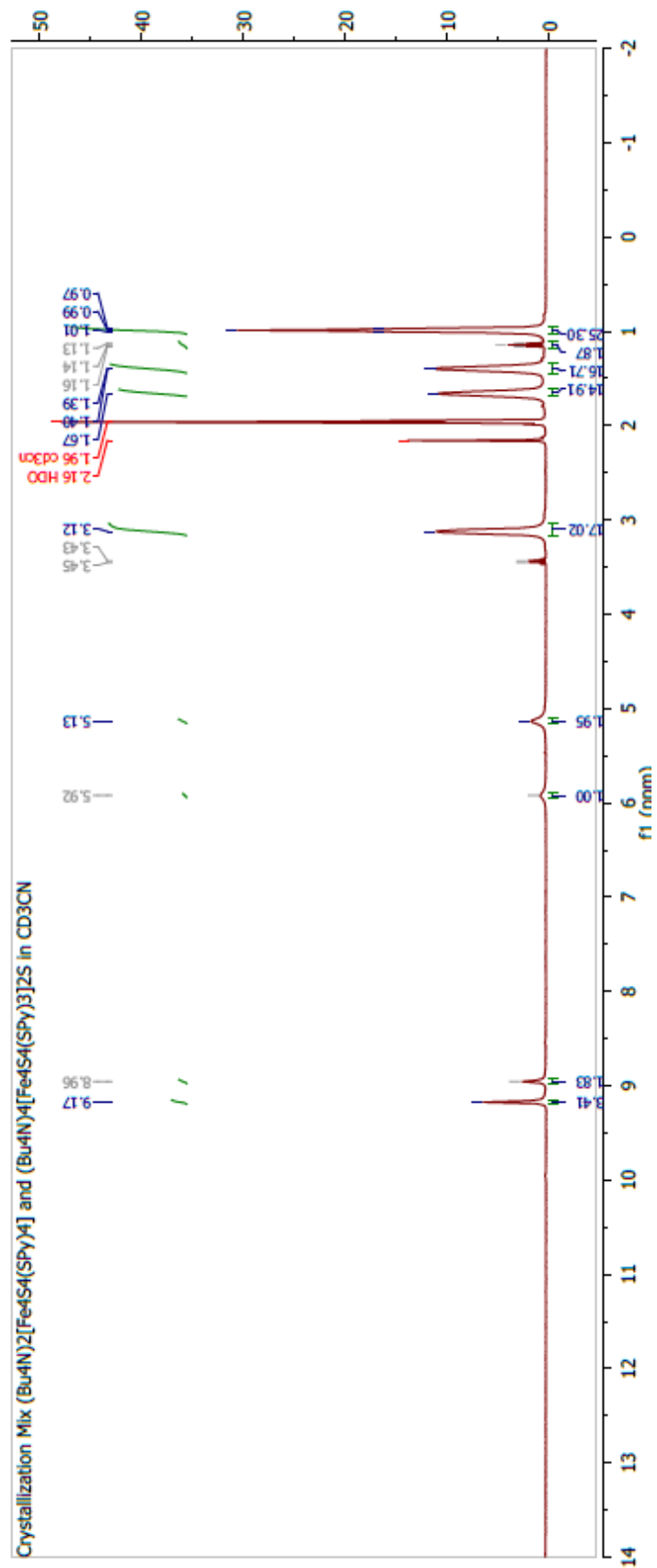
Figure S10. ^{1}H-NMR spectrum of a mixture of $(Bu_4N)_4[(Fe_4S_4(SPy)_3)_2S]$ and $(Bu_4N)_2[Fe_4S_4(SPy)_4]$ in CD$_3$CN.

Crystallization Mix (Bu4N)2[Fe4S4(SPy)4] and (Bu4N)4[Fe4S4(SPy)3]2S in CD3CN

7
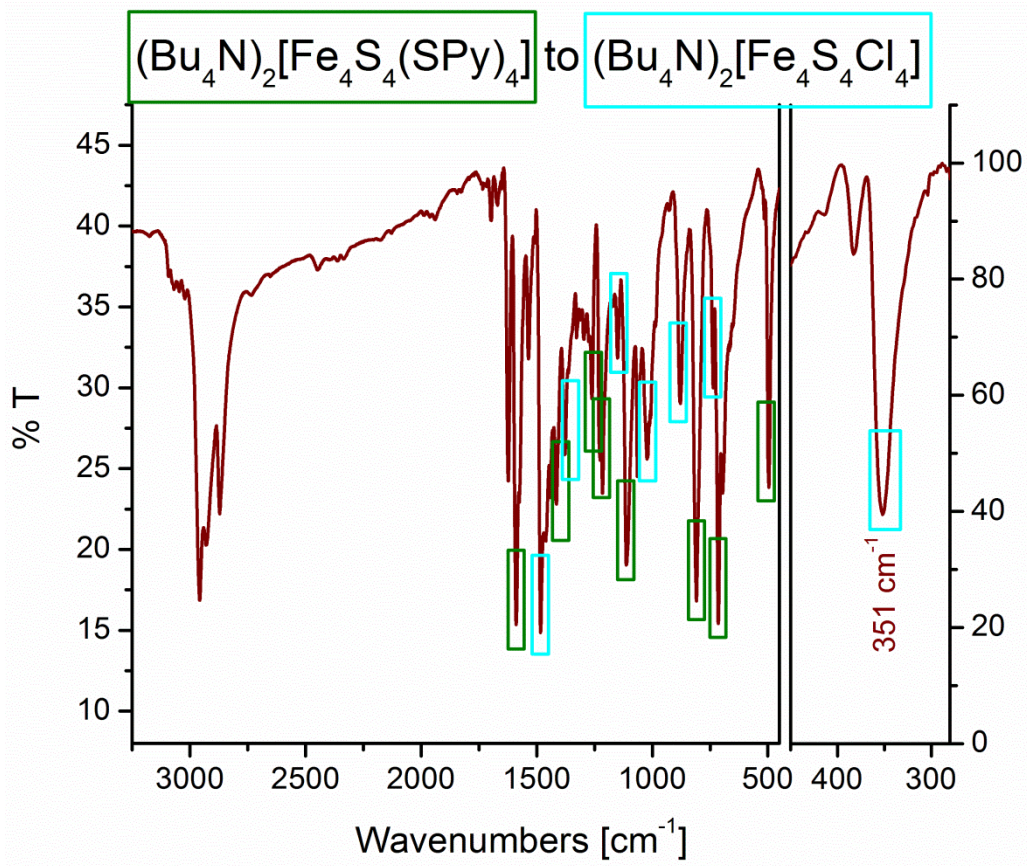
Figure S11. Mid- (left) and Far-IR (right) spectra of solid isolated after $(Bu_4N)_2[Fe_4S_4(SPy)_4]$ was dissolved in 1,2 dichloroethane for several days and recollected by precipitation. The boxes in green indicate signals assigned to $(Bu_4N)_2[Fe_4S_4(SPy)_4]$ and boxes in teal indicate signals assigned to $(Bu_4N)_2[Fe_4S_4Cl_4]$.

Statement for structure determination of (Bu$_4$N)$_2$[Fe$_4$S$_4$(SPy)$_4$].

Although the GooF and R-factors are high but not severe for the preliminary structure for (Bu$_4$N)$_2$[Fe$_4$S$_4$(SPy)$_4$], the connectivity and chemical identity of the crystal components are readily confirmed for the anion and the two ammonium counter ions. Unfortunately, even though sharp diffraction signals were collected, some unresolved problem (possibly twinning or pseudo-symmetry in the crystal) exists which prevents the determination of a final model and is evident in the number of A- and B-alerts in the checkcif file seen in the excerpt included here:

```
Bond precision:   C-C = 0.0118 A           Wavelength=0.71073

Cell:             a=36.861(3)    b=31.236(2)         c=22.5729(15)
                  alpha=90       beta=108.690(1)     gamma=90
Temperature:      85 K

                  Calculated              Reported
Volume            24620(3)                24619(3)
Space group       C 2/c                   ?
Hall group        -C 2yc                  ?
Moiety formula    C24 H20 Fe4 S8, 2(C16 H36  ?
                  N)
Sum formula       C56 H92 Fe4 N2 S8       C56 H92 Fe4 N2 S8
Mr                1273.28                 1273.20
Dx,g cm-3         1.374                   1.374
Z                 16                      16
Mu (mm-1)         1.232                   1.232
F000              10784.0                 10784.0
F000'             10823.90
h,k,lmax          49,41,30                49,41,30
Nref              30873                   30717
Tmin,Tmax         0.673,0.831             0.687,0.837
Tmin'             0.659

Correction method= ?

Data completeness= 0.995            Theta(max)= 28.380

R(reflections)= 0.1072( 26739)     wR2(reflections)= 0.2349( 30717)

S = 1.198                   Npar= 1845
```

Alert level A
```
PLAT122_ALERT_1_A No _symmetry_space_group_name_H-M Given ........      ? Do !
PLAT213_ALERT_2_A Atom C89           has ADP max/min Ratio .....      6.2 prola
PLAT411_ALERT_2_A Short Inter H...H Contact   H4A   ..  H55B   ..     1.62 Ang.
PLAT411_ALERT_2_A Short Inter H...H Contact   H10A  ..  H61A   ..     1.51 Ang.
PLAT411_ALERT_2_A Short Inter H...H Contact   H16A  ..  H57A   ..     1.65 Ang.
PLAT411_ALERT_2_A Short Inter H...H Contact   H70A  ..  H44A   ..     1.79 Ang.
PLAT411_ALERT_2_A Short Inter H...H Contact   H57A  ..  H16B   ..     1.77 Ang.
PLAT411_ALERT_2_A Short Inter H...H Contact   H10F  ..  H34A   ..     1.76 Ang.
PLAT411_ALERT_2_A Short Inter H...H Contact   H10W  ..  H40A   ..     1.77 Ang.
PLAT413_ALERT_2_A Short Inter XH3 .. XHn     H10U  ..  H60A   ..     1.87 Ang.
PLAT413_ALERT_2_A Short Inter XH3 .. XHn     H10U  ..  H60C   ..     1.18 Ang.
PLAT413_ALERT_2_A Short Inter XH3 .. XHn     H10V  ..  H60A   ..     1.76 Ang.
```

Alert level B
```
PLAT057_ALERT_3_B Correction for Absorption Required   RT(exp) ...      1.24
PLAT411_ALERT_2_B Short Inter H...H Contact   H10S  ..  H46B   ..     1.89 Ang.
PLAT411_ALERT_2_B Short Inter H...H Contact   H10W  ..  H40B   ..     1.94 Ang.
PLAT411_ALERT_2_B Short Inter H...H Contact   H11B  ..  H40A   ..     1.86 Ang.
PLAT413_ALERT_2_B Short Inter XH3 .. XHn     H5A   ..  H56A   ..     2.04 Ang.
PLAT413_ALERT_2_B Short Inter XH3 .. XHn     H10B  ..  H28A   ..     1.93 Ang.
PLAT413_ALERT_2_B Short Inter XH3 .. XHn     H10U  ..  H60B   ..     2.02 Ang.
PLAT413_ALERT_2_B Short Inter XH3 .. XHn     H11D  ..  H52B   ..     1.92 Ang.
PLAT413_ALERT_2_B Short Inter XH3 .. XHn     H11F  ..  H40B   ..     1.99 Ang.
PLAT413_ALERT_2_B Short Inter XH3 .. XHn     H11G  ..  H87B   ..     2.01 Ang.
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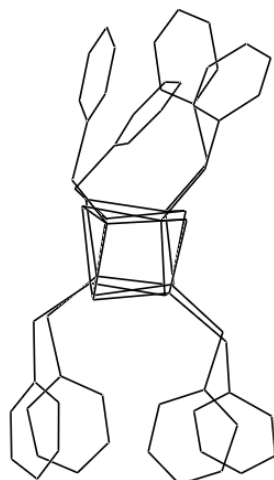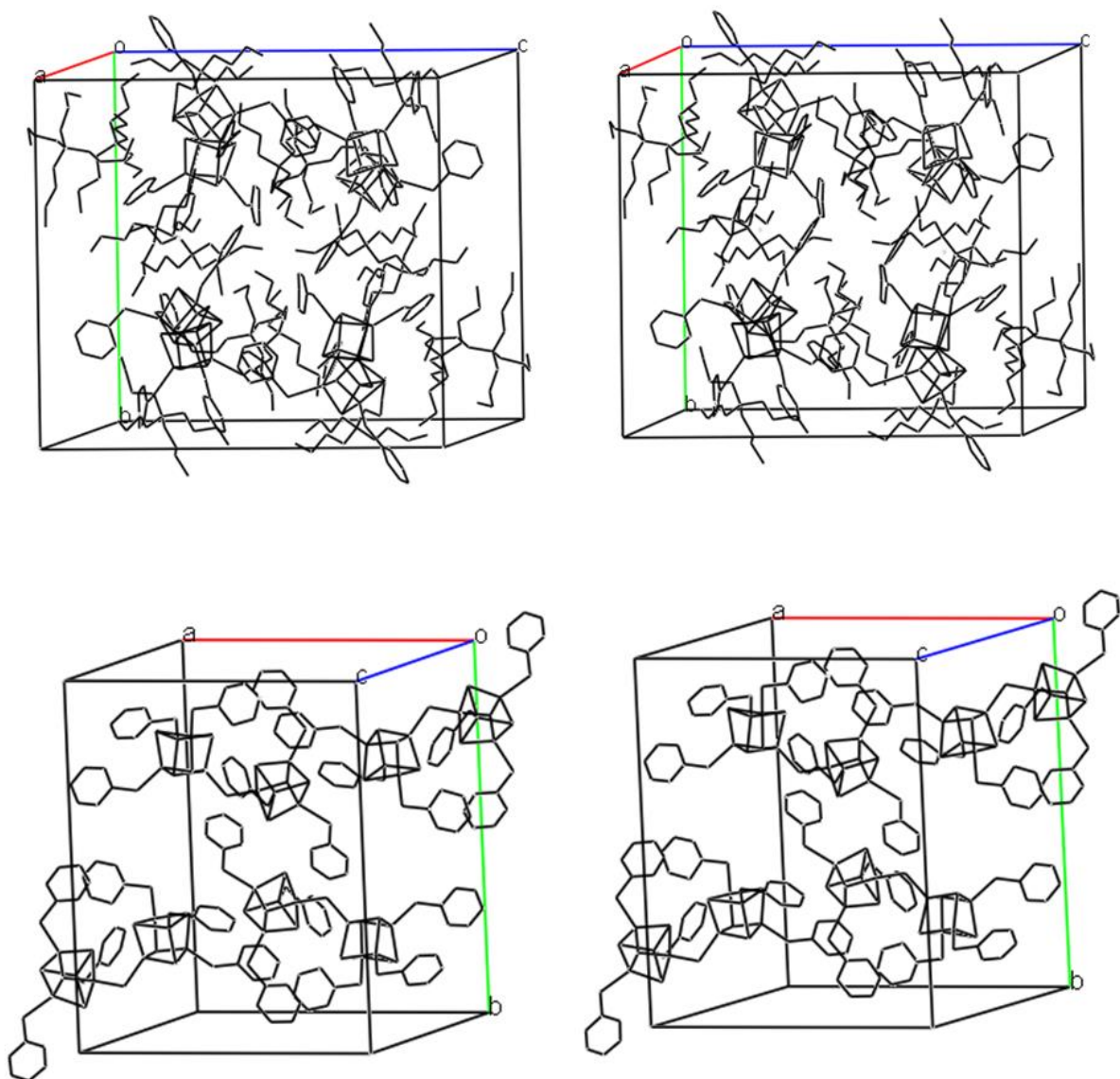
Figure S12. Wireframe overlay of the two symmetry unique anions in the crystal structure of $(Bu_4N)_2[Fe_4S_4(SPy)_4]$ (hydrogen atoms, disordered ligands, and counter-ions are omitted for clarity).
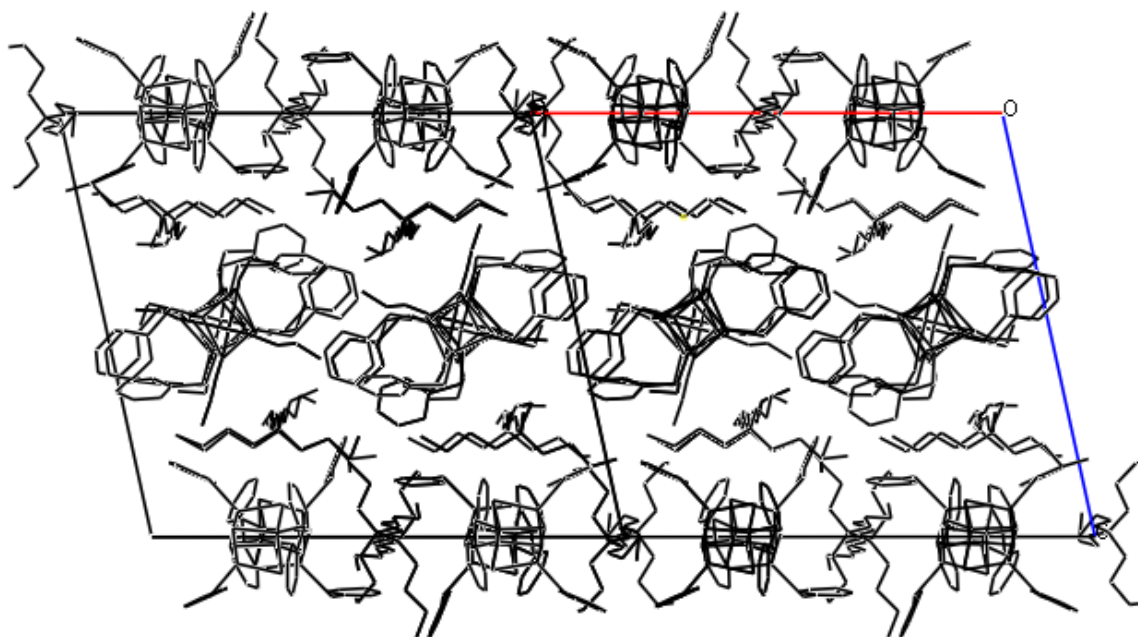
Figure S13. Wireframe crystal packing of $(Bu_4N)_2[Fe_4S_4(SPy)_4]$ (hydrogen atoms and disordered ligands are omitted for clarity).

Figure S14. Wireframe stereo view of the crystal packing of $(Bu_4N)_4[(Fe_4S_4(SPy)_3)_2S]$ with hydrogen atoms and disordered ligands omitted for clarity (top) and counter-ions, hydrogen atoms and disordered ligands omitted for clarity (bottom).
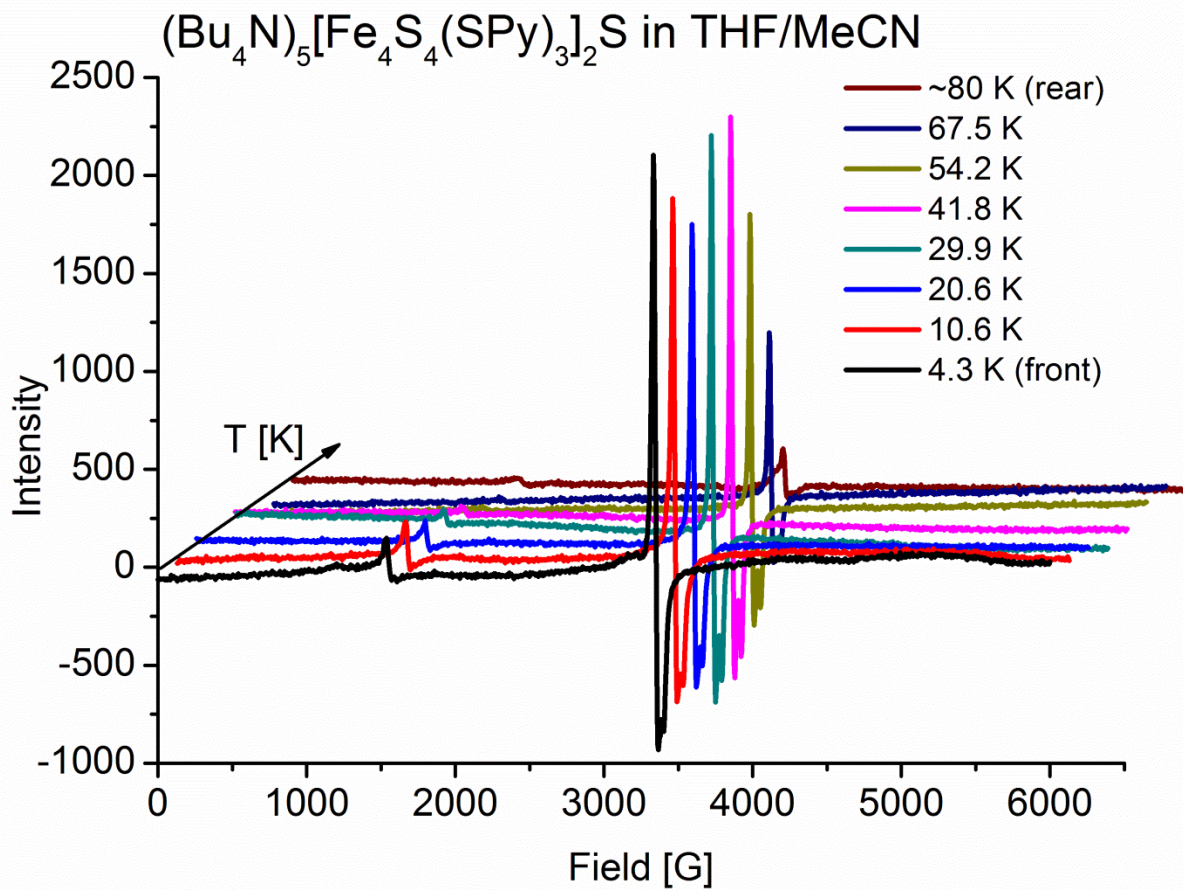
Figure S15. EPR spectra for the one electron reduced cluster $(Bu_4N)_5[(Fe_4S_4(SPy)_3)_2S]$ at varying temperatures.

Table S1. Crystal data and structure refinement for $(Bu_4N)_4[(Fe_4S_4(SPy)_3)_2S]$.

Empirical formula $C_{94} H_{168} Fe_8 N_{10} S_{15}$

Formula weight   2366.08

Temperature   85(2) K

Wavelength   0.71073 Å

Crystal system, space group   Monoclinic, P2(1)/n

Unit cell dimensions $a = 19.807(2)$ Å $\alpha = 90\ °$

                                     $b = 23.032(3)$ Å $\beta = 97.860(2)\ °$

                                     $c = 25.315(3)$ Å $\gamma = 90\ °$

Volume $11440(2)$ Å^3

Z, Calculated density   4, 1.374 Mg/m^3

Absorption coefficient   1.304 mm^{-1}

F(000)   5000

Crystal size   0.47 x 0.22 x 0.01 mm

Theta range for data collection   1.85 to 24.39 °

Limiting indices $-22 \le h \le 22, -26 \le k \le 26, -29 \le l \le 29$

Reflections collected / unique   164432 / 18681 [R(int) = 0.1135]

Completeness to theta = 24.39   99.4 %

Absorption correction   Semi-empirical from equivalents

Max. and min. transmission   0.9935 and 0.5794

Refinement method   Full-matrix least-squares on F^2

Data / restraints / parameters   18681 / 266 / 1244

Goodness-of-fit on F^2 1.055

Final R indices [I>2sigma(I)]   R1 = 0.0562, wR2 = 0.1280

R indices (all data)   R1 = 0.1009, wR2 = 0.1476

Largest diff. peak and hole   1.333 and -0.843 e. Å^{-3}