Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2015

Supporting Information for

A [3Fe–3S] cluster with exclusively μ-sulfide donors

Yousoon Lee,[a] Ie-Rang Jeon,[b] Khalil A. Abboud,[a] Ricardo García-Serres,*,[c] Jason Shearer,[d] and Leslie J. Murray*,[a]

[a] Center for Catalysis and Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States

[b] Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, United States

[c] Université Grenoble Alpes, LCBM/PMB and CEA, iRTSV/CBM/PMB and CNRS, UMR 5249, LCBM/PMB, 38000 Grenoble, France

[d] Department of Chemistry, University of Nevada, Reno, Reno, Nevada 89557, United states

Table of Contents

Experimental Details

General Considerations. Unless specified otherwise, all operations were performed under a dry, air-free atmosphere using a dinitrogen-filled MBraun Unilab glove box. Solution magnetic susceptibility was determined by Evans' method[1] based on the ^{1}H NMR spectrum recorded on a Varian Unity Inova 500 MHz spectrometer at room temperature. Infrared spectrum was recorded in a nitrogen-filled glovebox as solids on a Bruker Alpha FTIR with an ATR diamond crystal stage using the Opus 7.0 software package. High resolution electrospray ionization mass spectrum (HR ESI-MS) was recorded on an Agilent 6200 TOF-MS by the Mass Spectrometry Core Laboratory of University of Florida, and are reported as *m/z* (relative ratio). A solution sample was prepared in anhydrous tetrahydrofuran (THF) and loaded into Hamilton Gastight Sample Lock syringes in an N_2-filled glove box. The sample was introduced into the MS by direct infusion concurrent with a continuous flow of anhydrous THF. Cyclic voltammetry and differential pulse voltammetry experiments were performed in an N_2-filled glovebox using a Princeton Applied Research Versastat II potentiostat and a three-electrode setup (1 mm Pt button working, Au coil counter, and $Ag/AgNO_3$ reference) with electrodes purchased from BASi, Inc. and/or CH Instruments, Inc. EPR measurement was recorded on a Bruker Elexsys E580 with a Bruker 4116DM resonator. Data were collected at 5 K in the field from 50 to 7050 G with the following parameters: power = 6 μW; frequency = 9.48 GHz; modulation frequency = 100.00 kHz; modulation amplitude = 10 G; and gain = 60 dB. Complete Analysis Laboratories, Inc. (Parsippany, NJ) conducted elemental analysis on a sample prepared and shipped in an ampoule sealed under vacuum. THF, toluene, benzene, and hexanes were purified using either a GlassContour or Innovative Technologies solvent purification system, and stored over 3Å molecular sieves prior to use. THF-d_8 (Cambridge Isotope Laboratories) was dried over Na/benzophenone, distilled, and stored over 3Å molecular sieves. The water content of each solvent was measured using a Mettler Toledo C20 Coulometric Karl-Fischer Titrator prior to use and, in all cases, were below 1 ppm. Celite and 3Å molecular sieves were dried at 220°C under vacuum overnight. $NaSCPh_3$[2] and Fe_3Br_3**L** (**1**)[3] were prepared according to published procedures. All other reagents were purchased from Sigma-Aldrich and used without further purification.

Fe_3S_3L (2). A light yellow solution of $NaSCPh_3$ (347.2 mg, 1.164 mmol) in THF (20 mL) was slowly added dropwise to a stirred red solution of Fe_3Br_3**L** (403.0 mg, 0.3679 mmol) in THF (20 mL) at room temperature, which immediately yielded a dark green mixture. The reaction mixture was stirred overnight and then filtered through a 0.2 μm nylon filter paper. The dark green filtrate was brought to dryness under reduced pressure, to which 18 mL hexanes was added and vigorously stirred at r.t. for 3 hrs. The dark green solid residue was isolated through filtration of the slurry in hexanes and rinsed with copious amounts of hexanes. The crude product was extracted with toluene (75 mL) at r.t., filtered through a plug of toluene-rinsed Celite, and dried under vacuum. The dark green solid residue was then dissolved in THF (20 mL), and a vapor diffusion of benzene into the THF solution at r.t. afforded black-green crystals of the desired triiron(III) tri(μ-sulfide) complex (265.0 mg, 0.2784 mmol, 75.7%) IR: 2926, 1518, 1428, 1385, 1371, 1316, 1010, 738, 686, 472, 419 cm^{-1}. μ_{eff} (THF-d_8, 298K): 3.8 μ_B. ESI(+)-HRMS ($[M]^+$) m/z calcd. for $C_{45}H_{63}N_6S_3Fe_3$: 951.2322. Found: 951.2338. Anal. Calcd. for $C_{45}H_{63}N_6S_3Fe_3$: C, 56.79; H, 6.67; N, 8.83; S, 10.11. Found: C, 56.70; H, 6.82; N, 8.76; S, 9.98.

X-ray Crystallography. *Fe_3S_3L* (**2**). X-Ray Intensity data were collected at 100 K on a Bruker DUO diffractometer using MoKα radiation (λ = 0.71073 Å) and an APEXII CCD area detector. Raw data frames were read by program SAINT[4] and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structure was solved and refined in SHELXTL6.1,[5] using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The asymmetric unit consists of a 1/6 Fe3 complex located on a -6 symmetry element, a 1/6 benzene solvent molecule also located on a -6 symmetry element and another benzene molecule located on a mirror plane. The solvent molecule located on a -6 symmetry was significantly disordered and could not be modelled properly, thus program SQUEEZE,[6] a part of the PLATON[7] package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. All displacement ellipsoids seem to have elongated in the c-axis direction. As a result, a lower symmetry model in space group $P6_3$ was refined but it showed the same characteristic. There is a good possibility that we have a whole molecule disorder but it is not enough to resolve into two parts. Thus our reported model is that of the higher symmetry $P6_3/m$ and the complex refined in one part. In the final cycle of refinement, 2495 reflections (of which 1938 are observed with $I > 2\sigma(I)$) were used to refine 129 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 4.44%, 12.18% and 1.041, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

Mössbauer Spectroscopy. Mössbauer spectra were measured either on a low-field Mössbauer spectrometer equipped with a closed-cycle SHI-850-5 cryostat from Janis and SHI or an Oxford Instruments Spectromag 4000 cryostat containing an 8T split-pair superconducting magnet. Both spectrometers were operated in constant acceleration mode in transmission geometry. The isomer shifts are referenced against a room temperature metallic iron foil. Analysis of the data was performed using the program WMOSS (WEB Research).

Magnetic Measurements. Magnetic measurements of **2** were performed on polycrystalline samples sealed in a polyethylene bag under a dinitrogen atmosphere. All data were collected using a Quantum Design MPMS-XL SQUID magnetometer from 1.8 to 300 K at applied dc fields ranging from 0 to +7 T. Dc susceptibility data were corrected for diamagnetic contributions from the sample holder and for the core diamagnetism of each sample.

Magnetometry Data Analysis. The data were fit to the Van Vleck equation according to spin Hamiltonian $H_{ex} = J_{12}\boldsymbol{S_1} \cdot \boldsymbol{S_2} + J_{23}\boldsymbol{S_2} \cdot \boldsymbol{S_3} + J_{13}\boldsymbol{S_1} \cdot \boldsymbol{S_3}$ with the constraint $J_{12} = J_{23}$ in the temperature range between 2 and 300 K, considering intermolecular interactions treated in the mean-field approximation according to the following equation:[8]

$1/\chi = 1/\chi_{[\mathrm{Fe3}]} + zJ'/(N\mu_B^2 g^2)$ where z = number of the nearest neighbours.

The exchange constants were estimated at $J_{12} = J_{23} = +\ 158.4\ \mathrm{cm}^{-1}$, $J_{13} = +\ 187.4\ \mathrm{cm}^{-1}$, and $zJ' = +3.16\ \mathrm{cm}^{-1}$ with fixed $g = 2$. Although the compound has D_{3h} symmetry, no satisfactory fitting was obtained by assuming $J_{12} = J_{23} = J_{13}$ due to nonpreferred spin vector alignment.

Electronic Structure Calculations. All electronic structure calculations were performed using *ORCA* v. 3.0.[9] Alrichs' tzvp basis set was employed for all atoms. Owing to the size of the system and high level of theory required to accurately describe the electronic structure geometry optimizations were not performed; the crystallographic coordinates for **2** were employed for single point calculations. The *ORCA* verytightscf convergence criteria were used for the SCF cycles along with the *ORCA* integration Grid4. All other program defaults were used. Initial calculations were performed at the BP86, PBE0, B3LYP, mPWPW91 (both with and without the use of the broken symmetry approximation), and B2PLYP levels. The broken symmetry calculation considered a variety of different numbers of unpaired spins per center, and in each case yielded a wave function containing only one localized unpaired spin (all other spins were strongly coupled resulting in quasi closed shell orbitals). NEVPT2 calculations utilized a CAS-SCF(5,6) active-space. Natural orbitals from MP2 level calculations were used as input orbitals for the NEVPT2 calculations. Iso-surface plots were generated using the program *Molekel* v 5.4.[10]

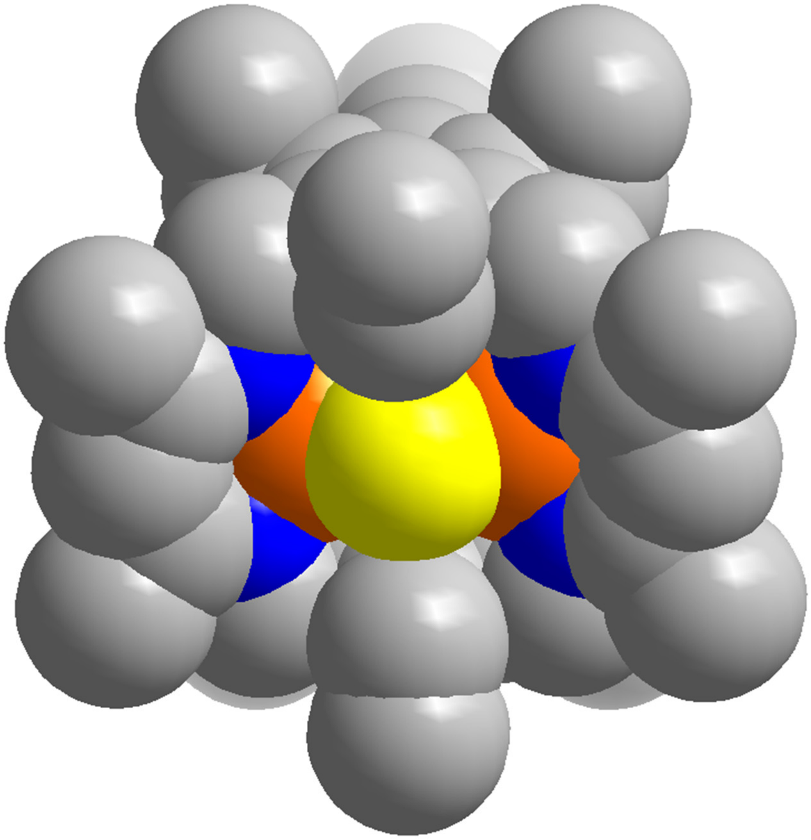

Figure S1. Space-filling representation of the molecular structure of **2**. Hydrogen atoms have been omitted for clarity, and C, N, S, and Fe are represented as grey, blue, yellow, and orange spheres, respectively.

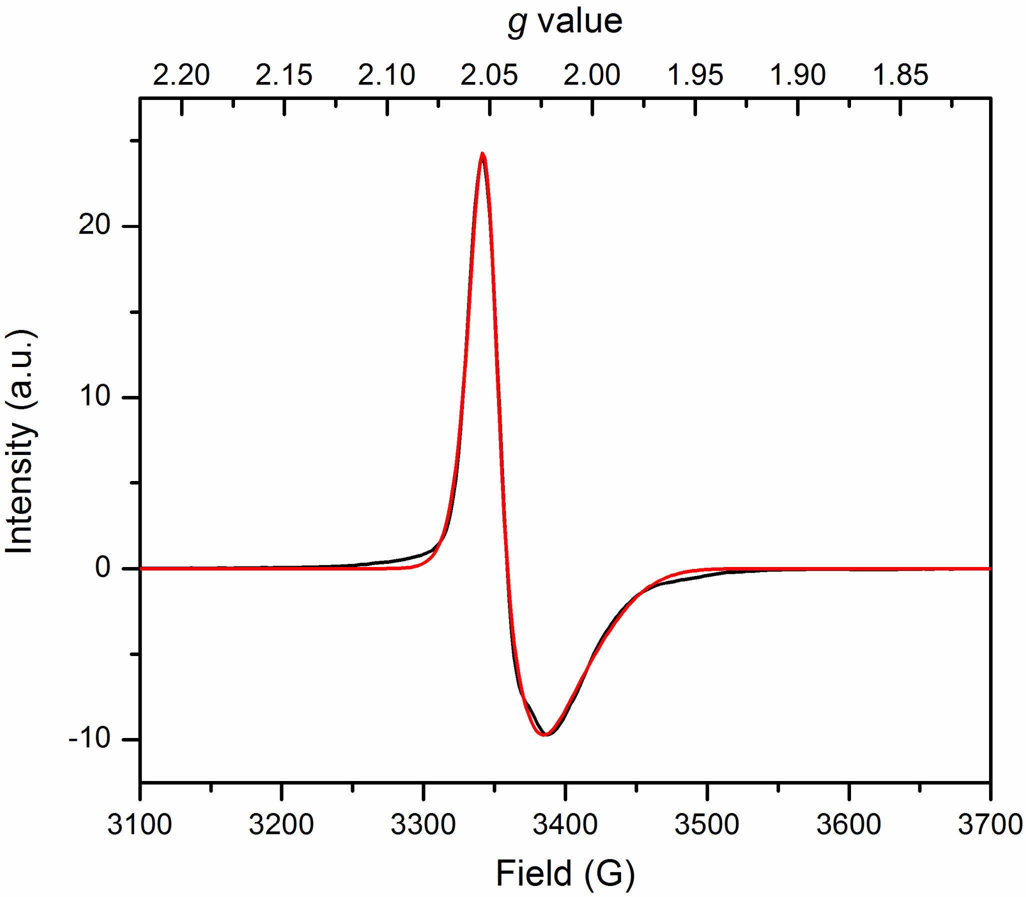

Figure S2. X-band EPR spectrum of **2** was recorded in toluene at 5 K (black line), and its rhombic signal could be simulated with *g* = 1.989, 2.006, and 2.013 (red line), gStrain = 0.0291, 0.0177, 0.004 and lw (full width at half height) = 0.9833. Frequency = 9.48 GHz; power: 6 µW; attenuation = 45 dB.

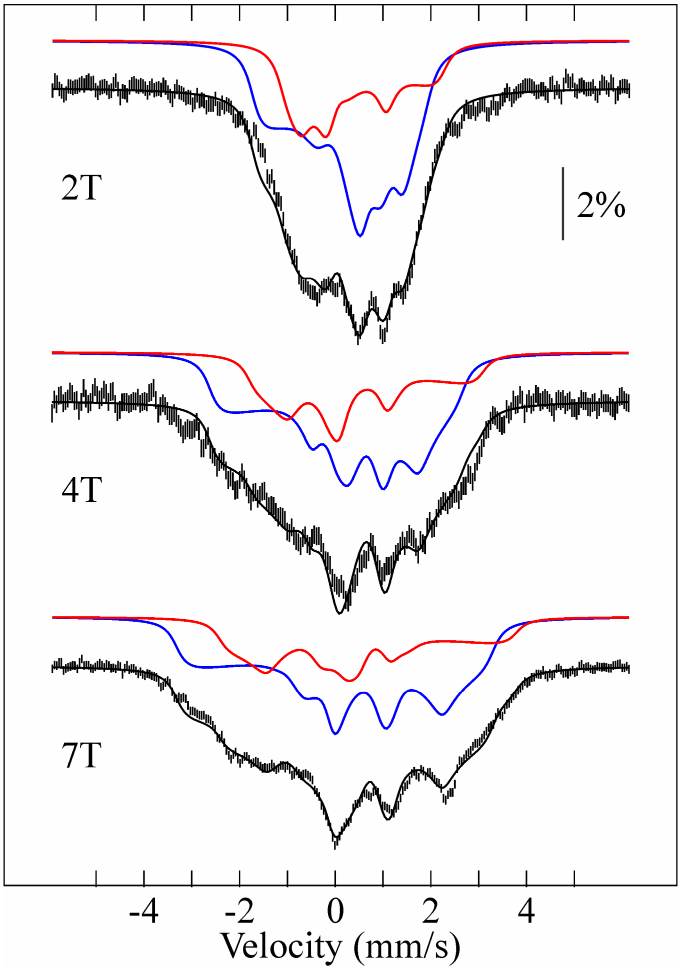

Figure S3. Mössbauer spectra of **2** measured at 2.1 K in different parallel applied magnetic fields**.** The vertical bars are the experimental points. The spectra were simulated with the usual S = ½ spin-Hamiltonian (g-values taken from EPR), as two components, one (blue line) accounting for two equivalent Fe sites and having double the intensity of the other (red line). The black lines overlaid with the experimental data are the composite theoretical spectra. Simulation parameters are given in Table S1.

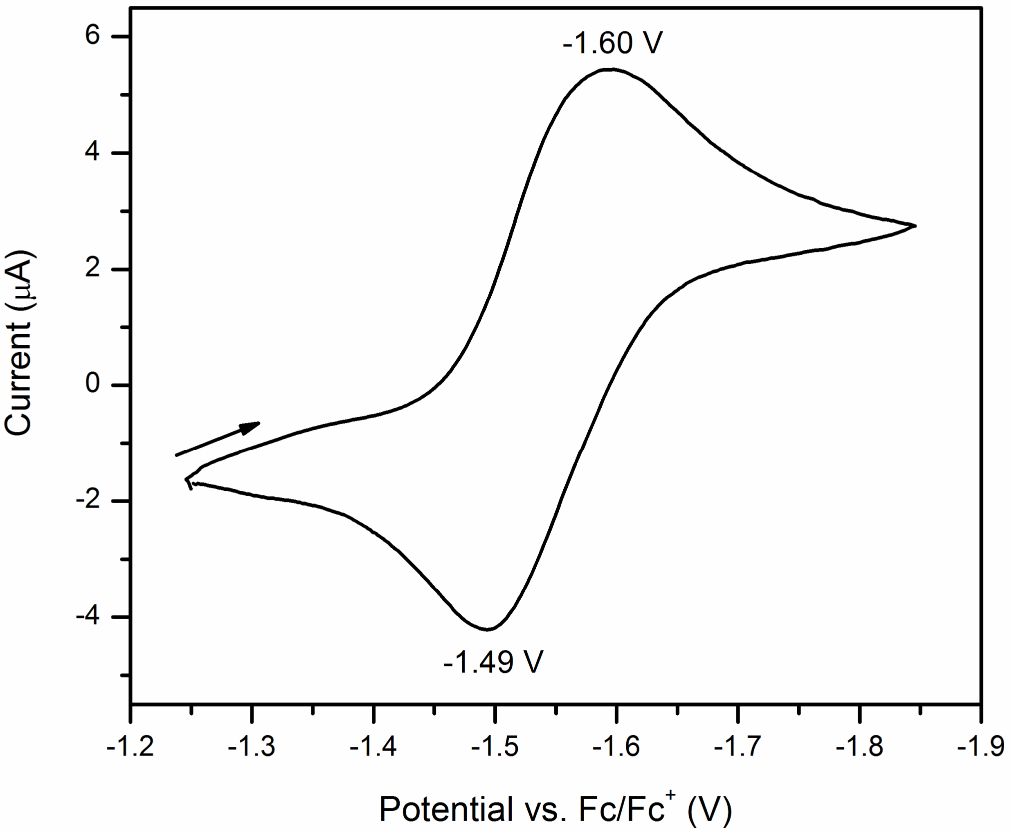

Figure S4. Cyclic voltammogram of **2** in isobutyronitrile using 0.3 M [Bu_4N]PF_6 as a supporting electrolyte. Working electrode: 1 mm Pt button; reference electrode: Ag/$AgNO_3$; counter electrode: Au coil; scan rate: 100 mV/s.

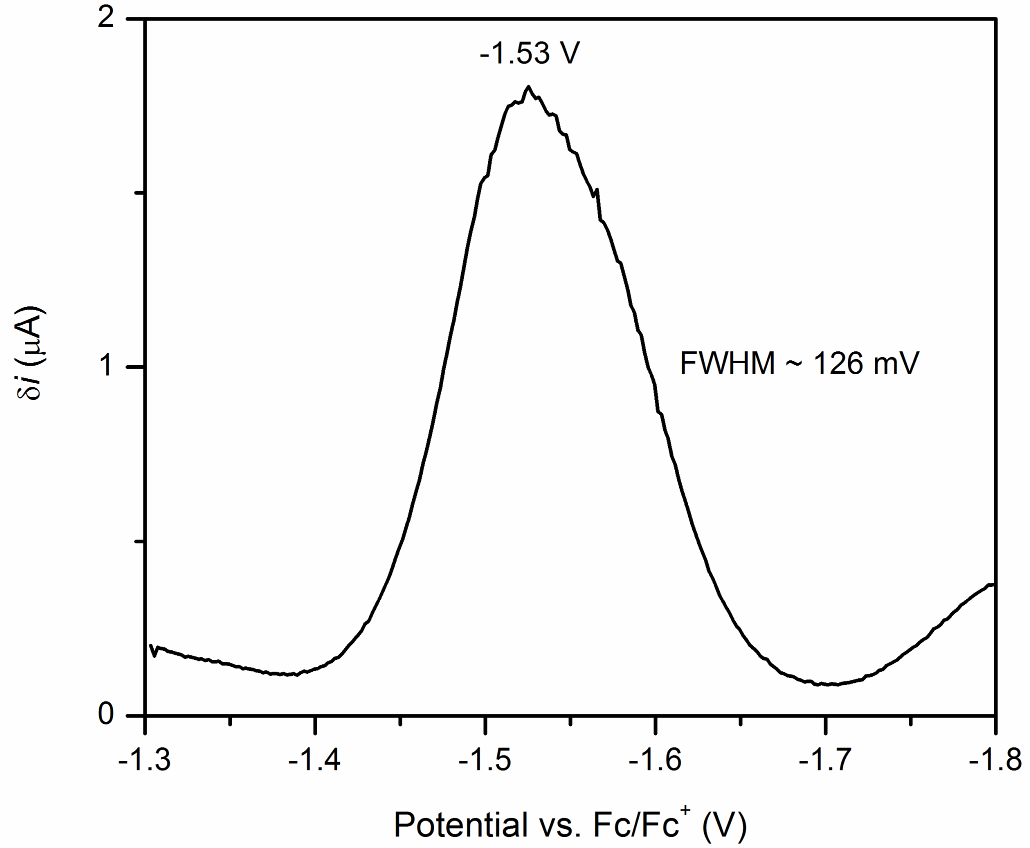

Figure S5. Differential pulse voltammogram of **2** in isobutyronitrile using 0.3 M $[Bu_4N]PF_6$ as a supporting electrolyte. Working electrode: 1 mm Pt button; reference electrode: $Ag/AgNO_3$; counter electrode: Au coil; scan rate: 5 mV/s; pulse height: 25 mV.

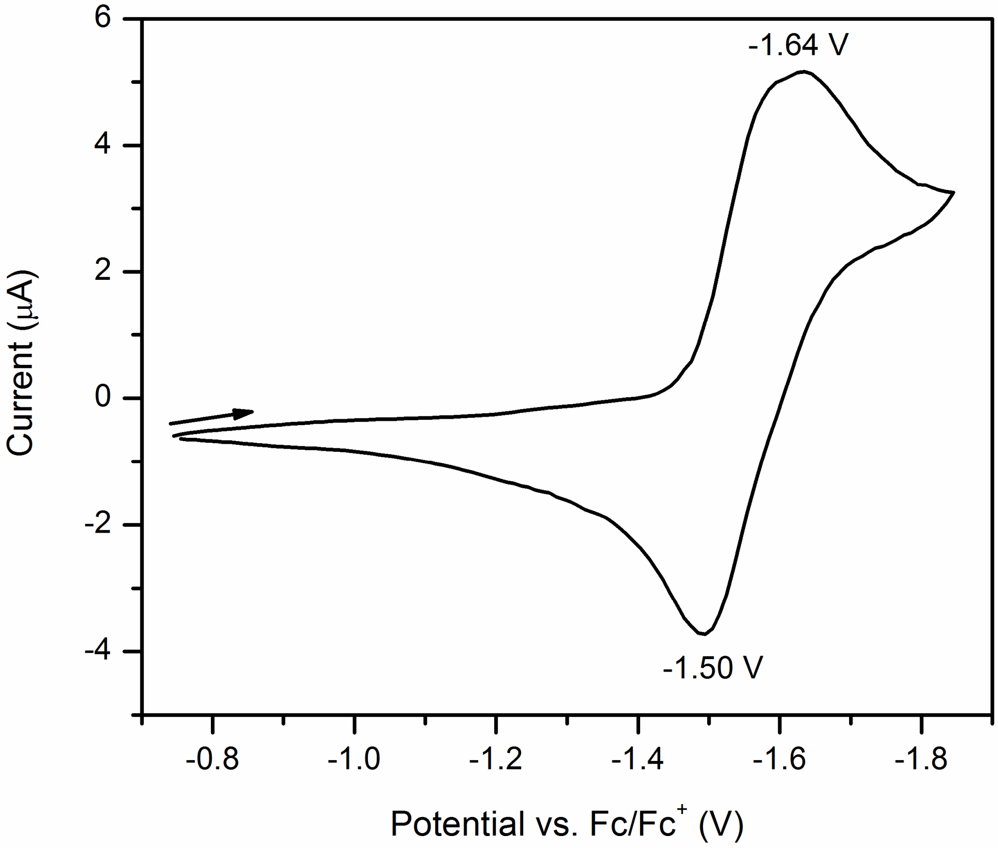

Figure S6. Cyclic voltammogram of **2** in dimethoxyethane using 0.3 M $[Bu_4N]PF_6$ as a supporting electrolyte. Working electrode: 1 mm Pt button; reference electrode: $Ag/AgNO_3$; counter electrode: Au coil; scan rate: 200 mV/s.

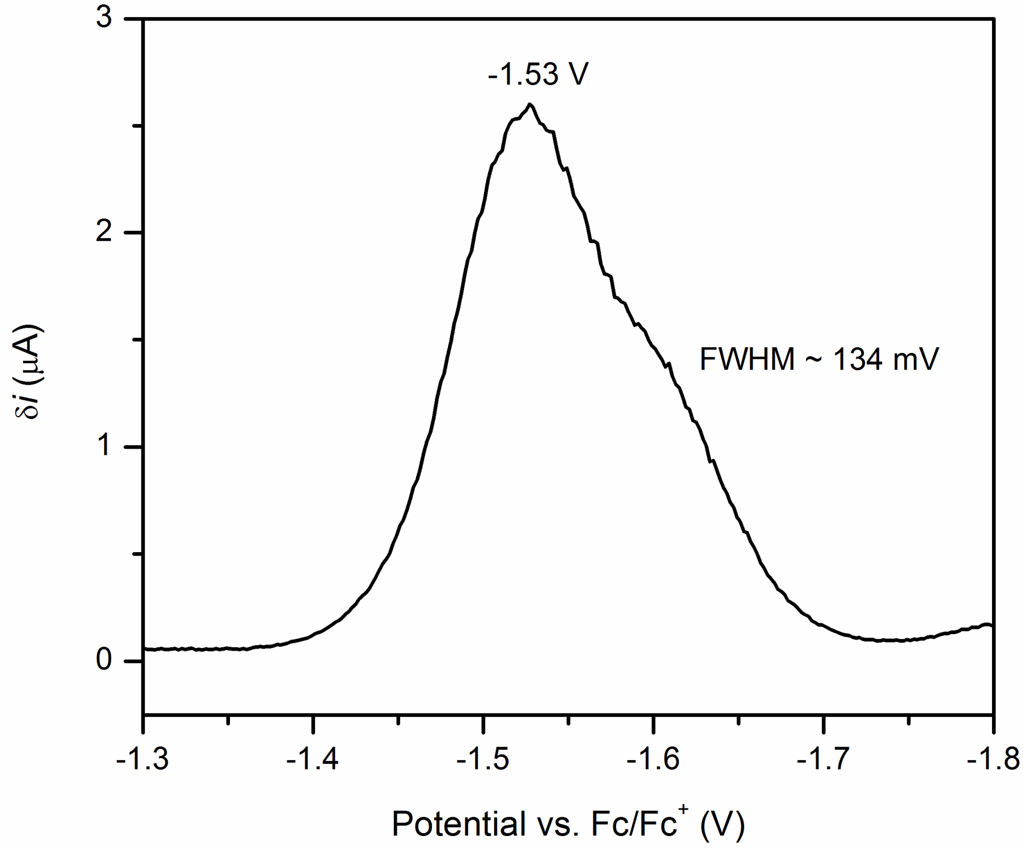

Figure S7. Differential pulse voltammogram of **2** in dimethoxyethane using 0.3 M $[Bu_4N]PF_6$ as a supporting electrolyte. Working electrode: 1 mm Pt button; reference electrode: $Ag/AgNO_3$; counter electrode: Au coil; scan rate: 5 mV/s; pulse height: 25 mV.

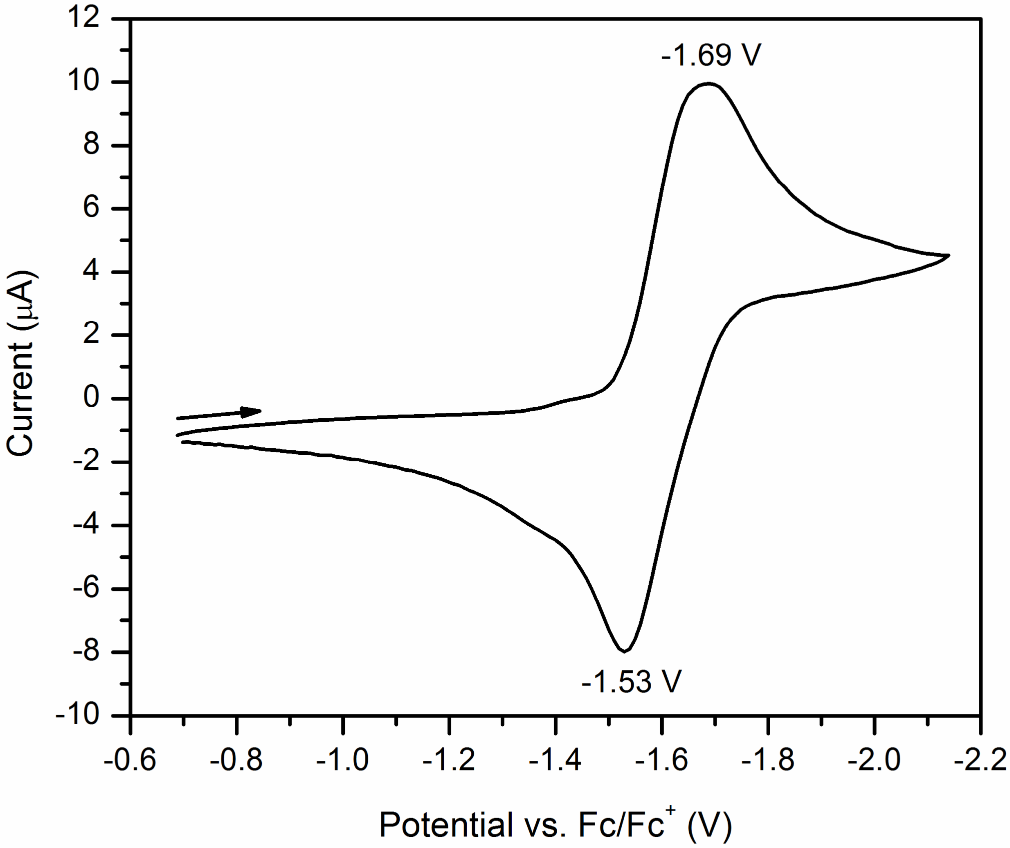

Figure S8. Cyclic voltammogram of **2** in THF using 0.3 M $[Bu_4N]PF_6$ as a supporting electrolyte. Working electrode: 1 mm Pt button; reference electrode: $Ag/AgNO_3$; counter electrode: Au coil; scan rate: 200 mV/s.

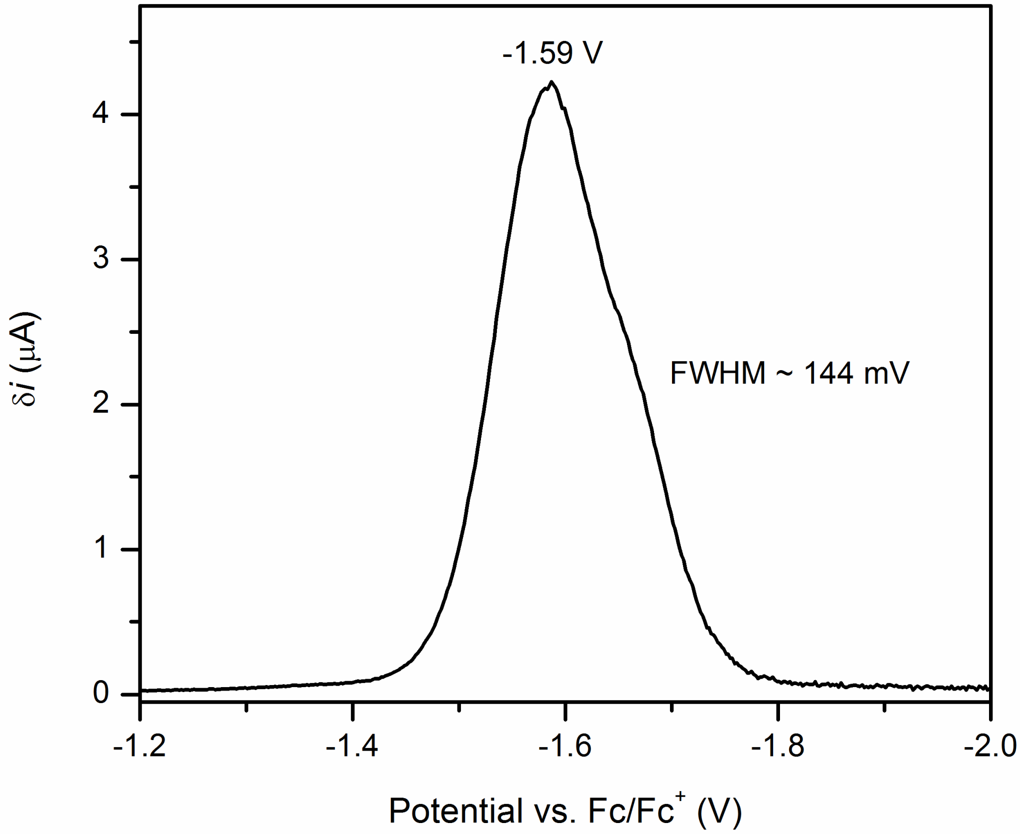

Figure S9. Differential pulse voltammogram of **2** in THF using 0.3 M $[Bu_4N]PF_6$ as a supporting electrolyte. Working electrode: 1 mm Pt button; reference electrode: $Ag/AgNO_3$; counter electrode: Au coil; scan rate: 5 mV/s; pulse height: 25 mV.

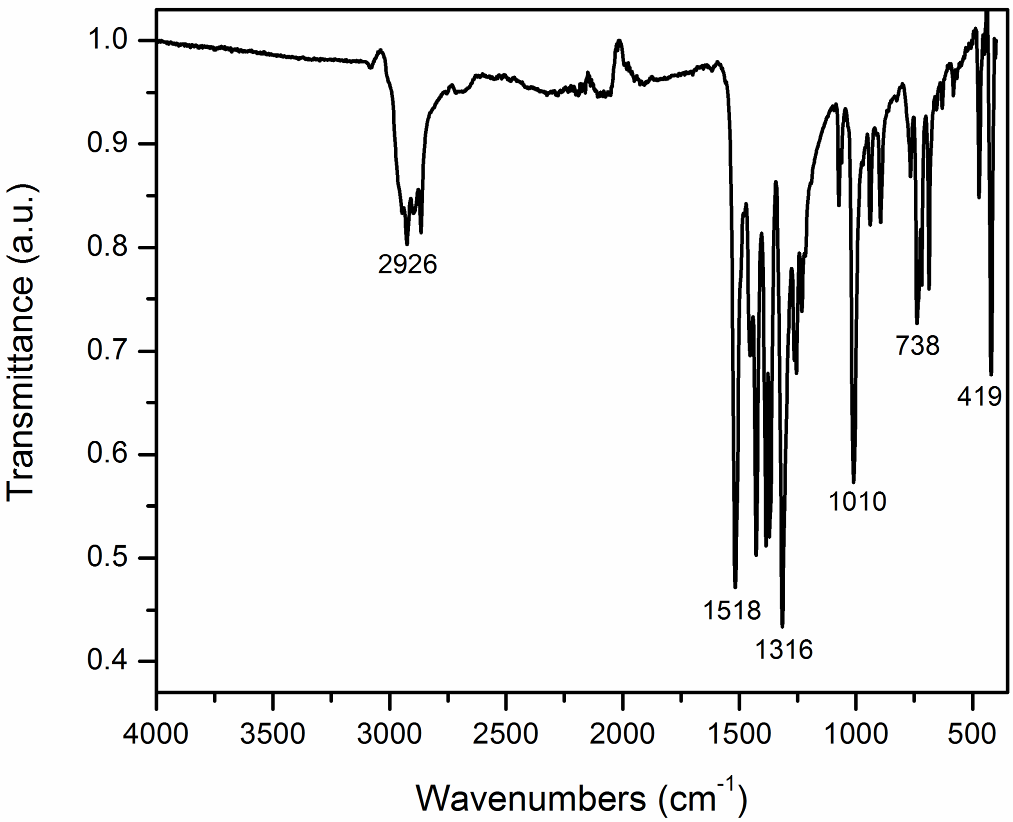

Figure S10. Infrared spectrum of **2**.

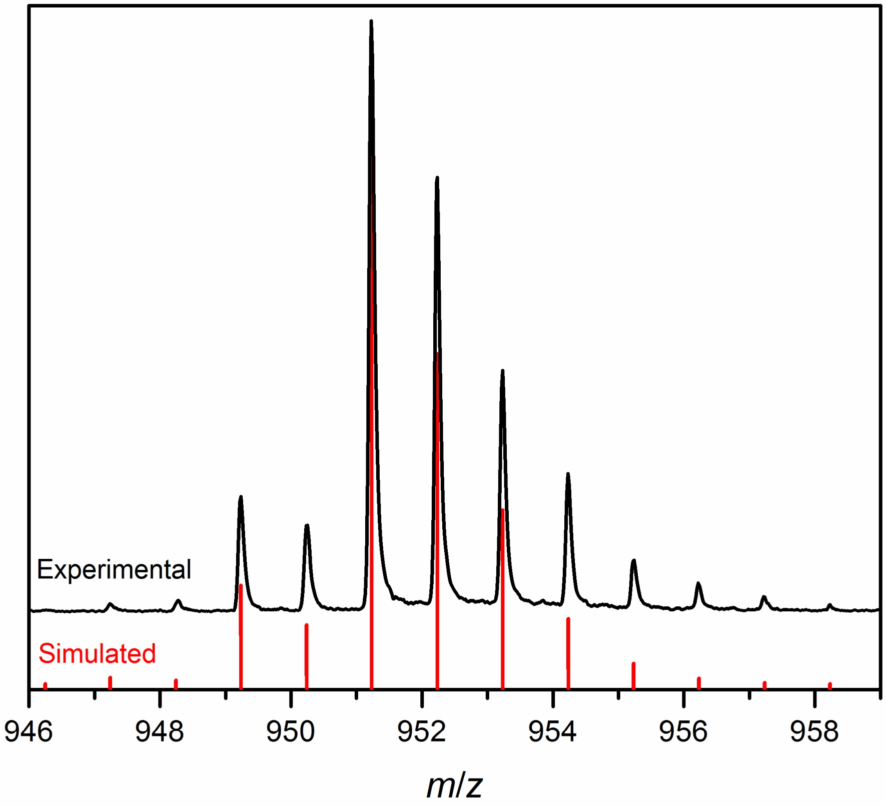

Figure S11. ESI/MS(+) data for **2** in THF. Capillary voltage: 4000 V. Fragmentation voltage: 120 V. Desolvation temperature: 350°C.

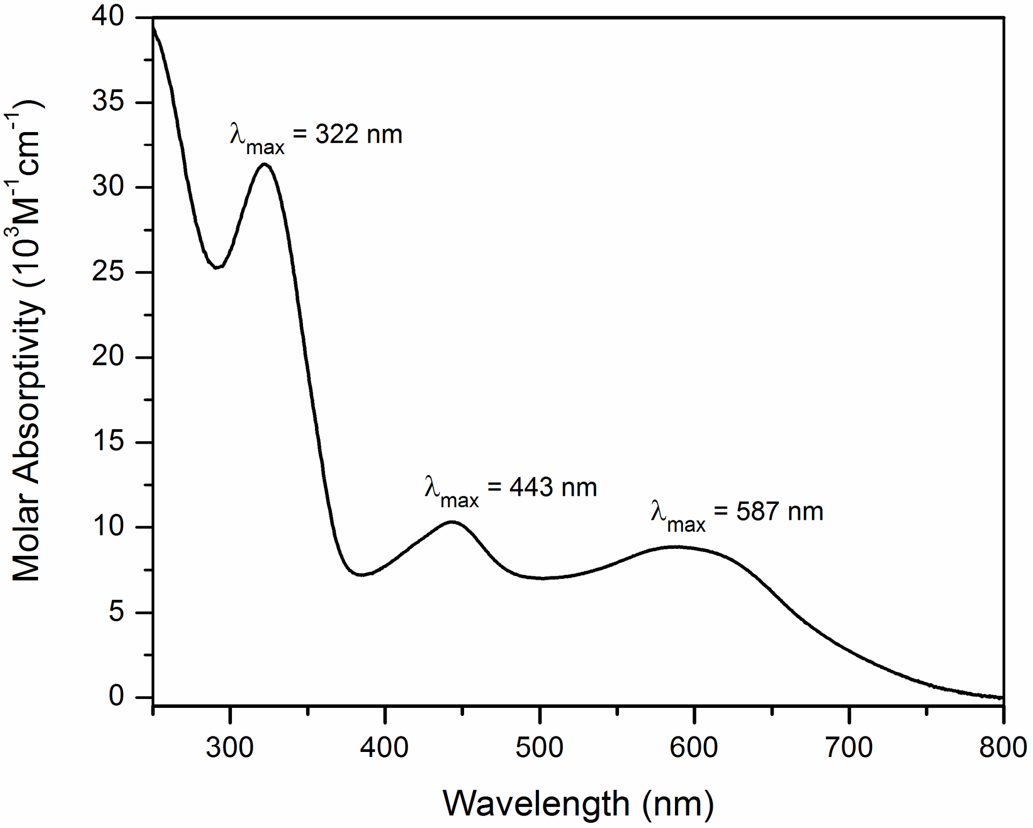

Figure S12. UV-vis spectrum of **2** in THF.

Table S1. Simulation parameters for Mössbauer spectra of **2** measured at 2.1 K in different parallel applied magnetic fields.

Fe(III) site	δ (mm/s)	ΔE_Q (mm/s)	η	A_{xx}, A_{yy}, A_{zz} (T)	A_{iso} (T)	integration
a (blue)	0.30	-1.28	0.1	25.3, 4.4, -16.3[α]	+4.5	2/3
b (red)	0.30	-1.48	0.16	-8.7, 23.2, -1.7	+4.3	1/3

[α] The A tensor was rotated by an angle of 120º respect to the y axis of the molecular frame.

Table S2. Crystal data and structure refinement for Fe_3S_3L (2).

Identification code	ylee71	
Empirical formula	C69 H87 Fe3 N6 S3	
Formula weight	1264.17	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	P 6_3/m	
Unit cell dimensions	a = 16.8444(10) Å	α = 90°
	b = 16.8444(10) Å	β = 90°
	c = 12.6713(8) Å	γ = 120°
Volume	3113.6(4) $Å^3$	
Z	2	
Density (calculated)	1.348 Mg/m^3	
Absorption coefficient	0.837 mm^{-1}	
F(000)	1338	
Crystal size	0.392 x 0.075 x 0.069 mm^3	
Theta range for data collection	1.396 to 27.497°.	
Index ranges	$-21 \le h \le 21$, $-21 \le k \le 21$, $-16 \le l \le 16$	
Reflections collected	48177	
Independent reflections	2495 [R(int) = 0.0508]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Analytical	
Max. and min. transmission	0.9618 and 0.8578	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2495 / 0 / 129	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.1218 [1938]	
R indices (all data)	R1 = 0.0591, wR2 = 0.1284	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.608 and -0.614 $e.Å^{-3}$	

$R_1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w = 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

References

[1] a) D. F. Evans, *J. Chem. Soc. Resumed* **1959**, 2003–2005; b) G. A. Bain, J. F. Berry, *J. Chem. Educ.* **2008**, *85*, 532; c) S. K. Sur, *J. Magn. Reson. 1969* **1989**, *82*, 169–173; d) E. M. Schubert, *J. Chem. Educ.* **1992**, *69*, 62.

[2] a) P. L. Holland, W. B. Tolman, *J. Am. Chem. Soc.* **1999**, *121*, 7270–7271; b) L. Yang, W. B. Tolman, *JBIC J. Biol. Inorg. Chem.* **2012**, *17*, 285–291.

[3] G. L. Guillet, F. T. Sloane, D. M. Ermert, M. W. Calkins, M. K. Peprah, E. S. Knowles, E. Čižmár, K. A. Abboud, M. W. Meisel, L. J. Murray, *Chem. Commun.* **2013**, *49*, 6635–6637.

[4] Bruker AXS (2013) Apex II. Bruker AXS, Madision, Wisconsion, USA.

[5] G. M. Sheldrick, *SHELXTL-Plus Structure Determination Software Programs* (2013).

[6] P. van der Sluis, A. L. Spek, *Acta Crystallogr. A* **1990**, *46*, 194–201.

[7] A. L. Spek, *Acta Cryst.* **2009**, *D65*, 148.

[8] a) B. E. Myers, L. Berger, S. Friedberg, *J. Appl. Phys.* **1969**, *40*, 1149; b) C. J. O'Connor, *Prog. Inorg. Chem.* **1982**, *29*, 203.

[9] F. Neese Wiley Interdisciplinary Reviews: Computational Molecular Science 2012, **2**, 73.

[10] U. Varetto, Molkel, version 5.4.0.8, Swiss National Supercomputing Center, Manno, Switzerland, 2009.