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Supporting Information for

A Three-Coordinate Fe(II) Center within a [3Fe–(μ_3-S)] Cluster That Provides an Accessible Coordination Site

Yousoon Lee,[a] Khalil A. Abboud,[a] Ricardo García-Serres,[b] and Leslie J. Murray*,[a]
[a] Center for Catalysis and Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States
[b] Univ. Grenoble Alpes, LCBM/PMB and CEA, IRTSV/CBM/PMB and CNRS, LCBM UMR 5249, PMB, 38000 Grenoble, France

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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. Infrared spectra were 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 spectra (HR ESI-MS) were 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). Solution samples were prepared in anhydrous tetrahydrofuran (THF) and loaded into Hamilton Gastight Sample Lock syringes in an N_2-filled glove box. Samples were introduced into the MS by direct infusion concurrent with a continuous flow of the 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. Complete Analysis Laboratories, Inc. (Parsippany, NJ) conducted elemental analyses on samples prepared and shipped in ampoules sealed under vacuum. THF, toluene, and hexanes were purified using either a GlassContour or Innovative Technologies solvent purification system, and stored over 3Å molecular sieves prior to use. 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. $NaSCPh_3$,[1] KC_8,[2] and $Fe_3Br_3\mathbf{L}$ (**1**)[3] were prepared according to published procedures. All other reagents were purchased from Sigma-Aldrich and used without further purification.

Fe_3Br_2SL (2). A light yellow solution of $NaSCPh_3$ (85.8 mg, 0.288 mmol) in cold THF (3.5 mL, -34°C) was slowly added to a stirred red solution of $Fe_3Br_3\mathbf{L}$ (299.4 mg, 0.2734 mmol) in cold THF (13.5 mL, -34°C), causing an immediate color change to dark green. The reaction mixture was stirred at -34°C overnight and then was brought to dryness under reduced pressure at room temperature. 6 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 (3 x 20 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 (8 mL) at 60°C, and slow evaporation of THF to toluene at r.t. afforded black-green crystals of the desired triiron dibromide mono(μ_3-sulfide) complex (135.0 mg, 0.1289 mmol, 47.1%). Crystals suitable for single-crystal X-ray analysis can be obtained from a vapor diffusion of hexanes to a solution of the crude product in THF at room temperature. IR: 2922, 1515, 1429, 1389, 1372, 1323, 1256, 1067, 1013, 939, 892, 730, 465 cm^{-1}. ESI(+)-HRMS ($[M]^+$) m/z calcd. for $C_{45}H_{63}N_6Br_2S_1Fe_3$: 1047.1234. Found: 1047.1228. Anal. Calcd. for $C_{45}H_{63}N_6Br_2S_1Fe_3$: C, 51.60; H, 6.06; N, 8.02; S, 3.06. Found: C, 51.75; H, 6.18; N, 7.82; S, 2.95.

$Fe_3BrSL\cdot0.5THF$ (3). *Method A.* $Fe_3Br_2S\mathbf{L}$ (40.0 mg, 0.0382 mmol) was added as a solid to Na/Hg amalgam (0.5 wt% Na, 365.7 mg, 0.07859 mmol) in cold THF (10 mL, -34°C). The dark green slurry was stirred with a glass stir bar at -34°C overnight over which time the reaction became clearer with a color change to dark red-brown. The resulting mixture was filtered through a plug of THF-rinsed Celite, and the red-brown filtrate was brought to dryness under reduced pressure at room temperature. The crude product was extracted with toluene (4 mL) at r.t., filtered through a plug of toluene-rinsed Celite, and dried under vacuum. The red-brown solid residue was then dissolved in THF (3 mL) at r.t., and a vapor diffusion of hexanes to the THF solution at r.t. afforded red-brown single-crystals of the triiron monobromide mono(μ_3-sulfide) complex solvated with 0.5 THF (20.0 mg, 0.0199 mmol, 52.2%). IR: 2863, 1510, 1426, 1389, 1371, 1323, 1260, 1069, 1013, 941, 892, 767, 739, 489, 438 cm^{-1}.

Method B. Fe_3Br_2S**L** (10.6 mg, 10.1 μmol) and KC_8 (1.6 mg, 12 μmol) were combined as solids to which cold THF (3 mL, -34°C) was added. Stirring the reaction slurry with a glass stir bar at -34°C led to an immediate color change from dark green to dark brown. The dark brown reaction mixture was allowed to stir overnight at -34°C, and then solvent was removed under reduced pressure at r.t. The crude product was extracted with toluene (1.6 mL) at r.t., filtered through a plug of toluene-rinsed Celite, and dried under vacuum. The red-brown solid residue was dissolved in THF (0.6 mL) at r.t., and a vapor diffusion of hexanes to the THF solution at r.t. afforded red-brown single-crystals of **3** (6.5 mg, 6.5 μmol, 64%). The single-crystal had the same unit-cell as the one from *Method A* within error. IR: identical to the product from *Method A*. Anal. Calcd. for $C_{47}H_{67}N_6O_{0.5}Br_1S_1Fe_3$: C, 56.25; H, 6.73; N, 8.37. Found: C, 56.12; H, 6.93; N, 8.18.

X-ray Crystallography. 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[1] 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 structures were solved and refined in *SHELXTL2014*, 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.

*Fe_3Br_2S**L*** (**2**). The asymmetric unit consists of the Fe_3 complex and a THF solvent molecule. The latter is disordered and is refined in two positions with their site occupation factors refined until the last refinement cycles when they were fixed at 0.85/0.15 ratio. The core of the complex molecule is also disordered with two configurations of the Fe and Br atoms. They were refined with an occupation ratio of 0.95/0.05 for the major and minor products, respectively. In the final cycle of refinement, 11145 reflections (of which 7854 are observed with $I > 2\sigma(I)$) were used to refine 603 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 3.68%, 8.40% and 0.958, 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.

*Fe_3BrS**L**·0.5THF* (**3**). The asymmetric unit consists of the Fe_3 cluster, one THF molecule in general position and another one at an inversion center. The latter half molecule is disordered with traces of Br that is part of the core. On the other hand, we have a disorder in the core where the major part consists of a full Br, a 97% Fe1, a 100% Fe2 and a disorder of the third position as Fe3/Fe3′ with occupancies refining to 0.93/0.07. There is a THF molecule disordered around an inversion center and against traces (0.03%) of Br(2). In the final cycle of refinement, 11378 reflections (of which 9547 are observed with $I > 2\sigma(I)$) were used to refine 588 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 2.94%, 7.96% and 1.077, 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).

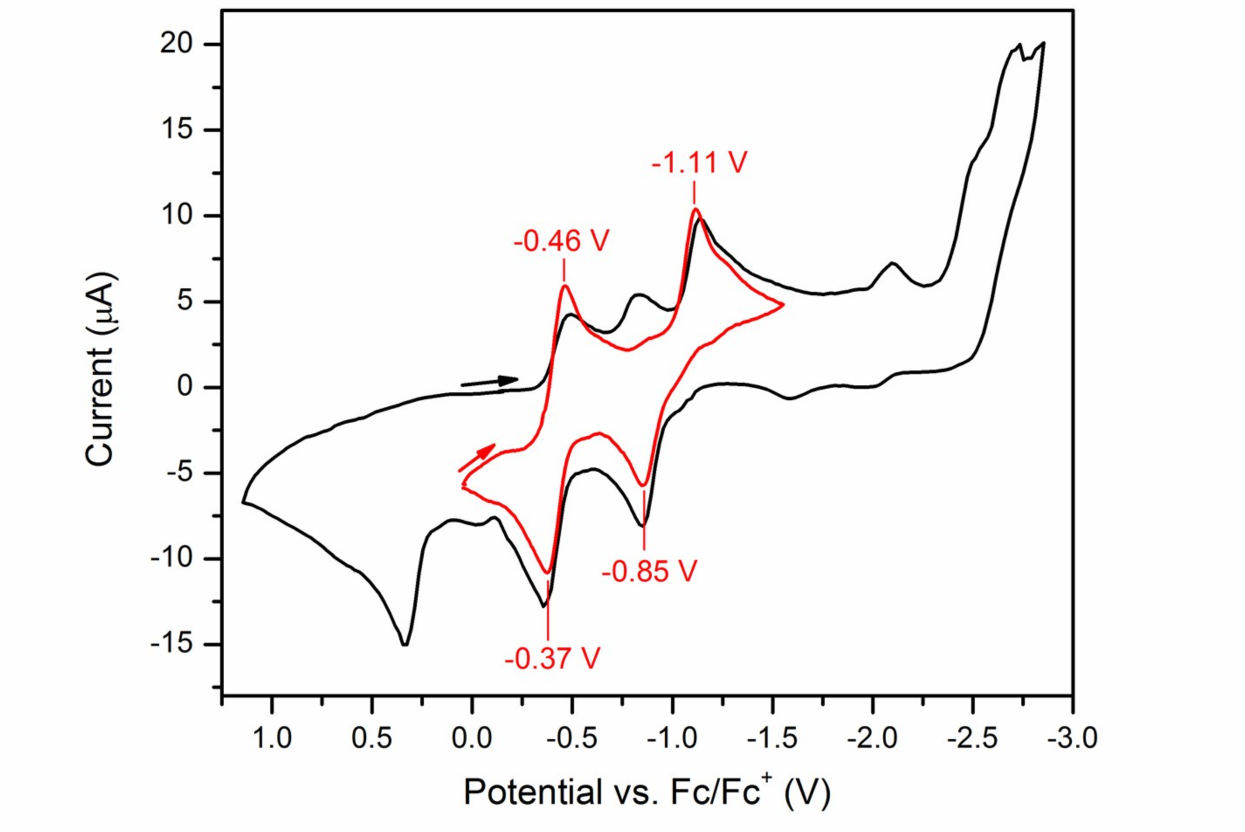

Figure S1. Cyclic voltammograms of Fe_3Br_2S**L** (**2**) in isobutyronitrile using 0.3 M $[Bu_4N]PF_6$ as a supporting electrolyte. Working electrode: 1 mm Pt button; reference electrode: $Ag/AgNO_3$; counter electrode: Au coil; scan rate: 200 mV/s.

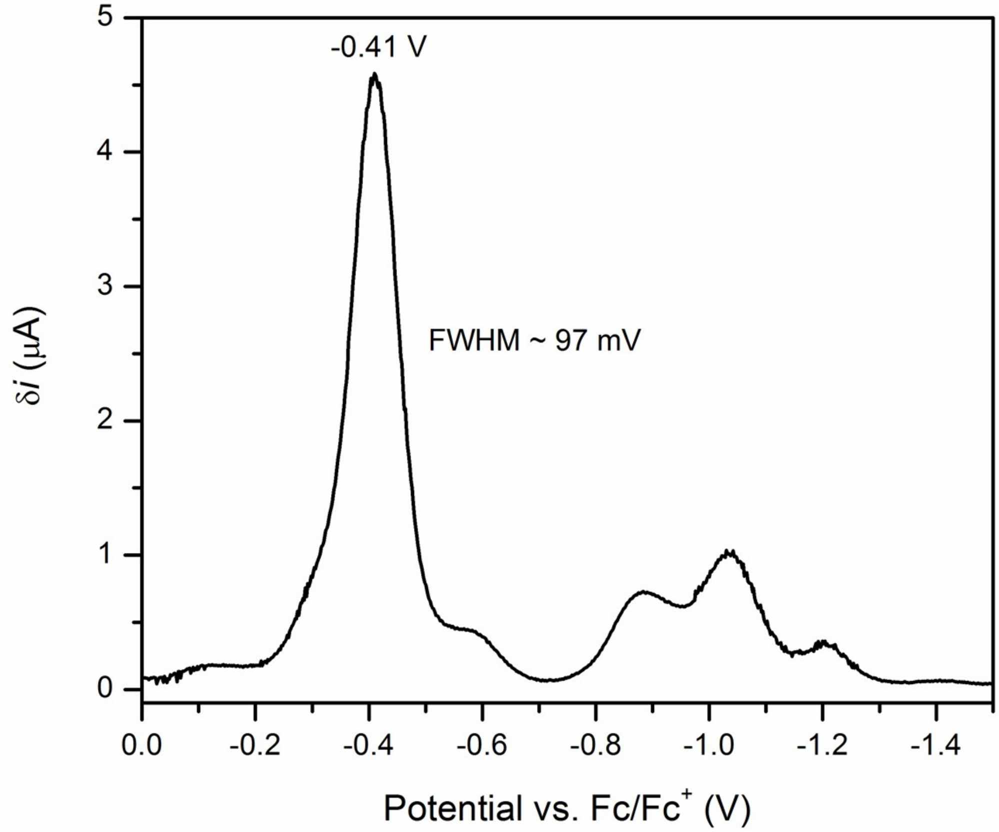

Figure S2. Differential pulse voltammogram of Fe_3Br_2S**L** (**2**) in isobutyronitrile using 0.3 M $[Bu_4N]PF_6$ as a supporting electrolyte. Working electrode: 1 mm Pt button; reference electrode: $Ag/AgNO_3$; counter electrode: Au coil; scan rate: 5 mV/s; pulse height: 25 mV.

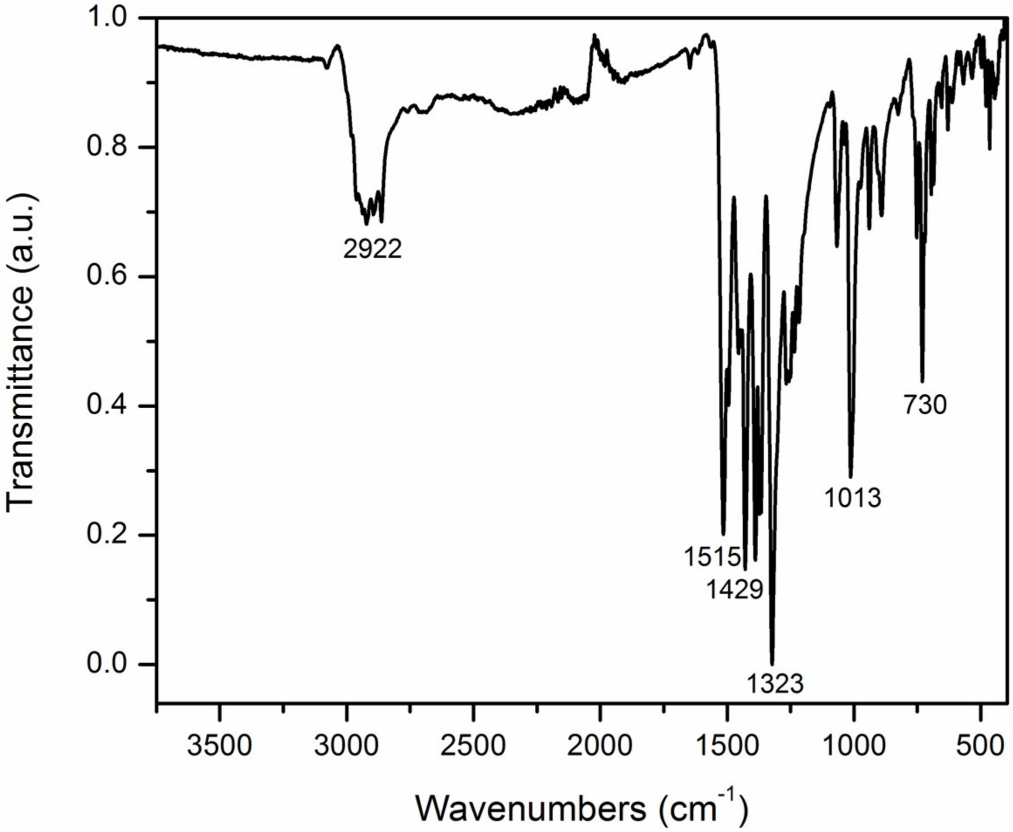

Figure S3. Infrared spectrum of Fe_3Br_2S**L** (**2**).

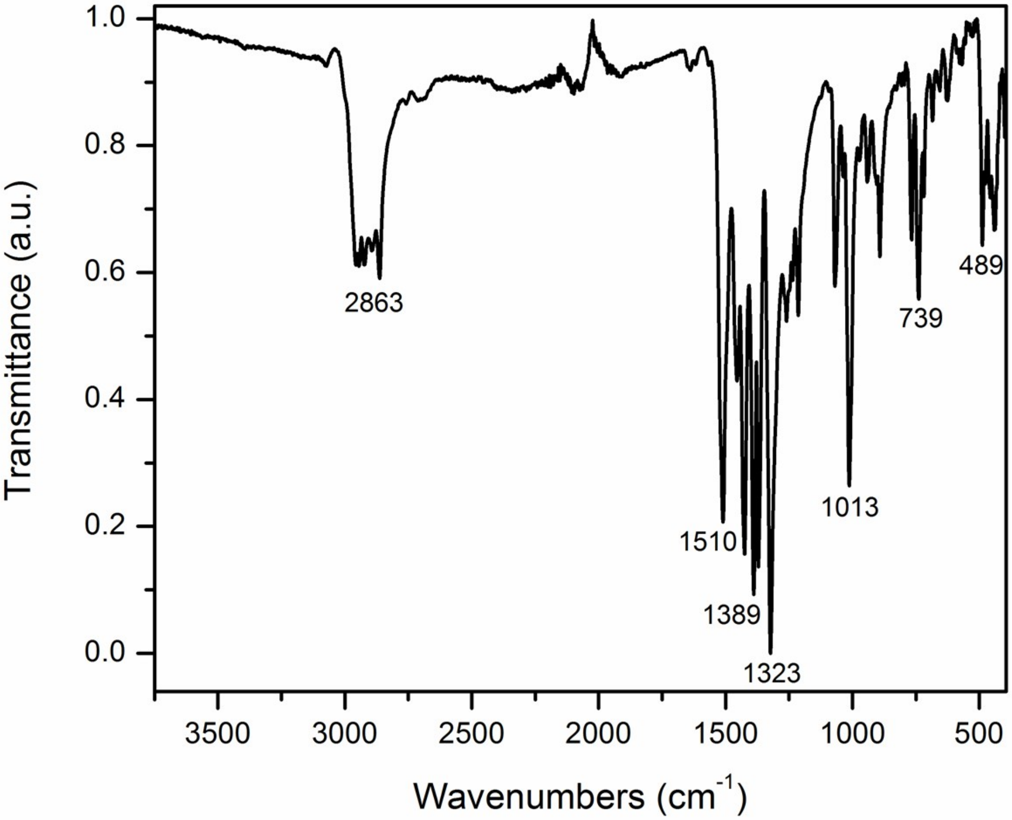

Figure S4. Infrared spectrum of $Fe_3BrS\mathbf{L}\cdot0.5THF$ (**3**).

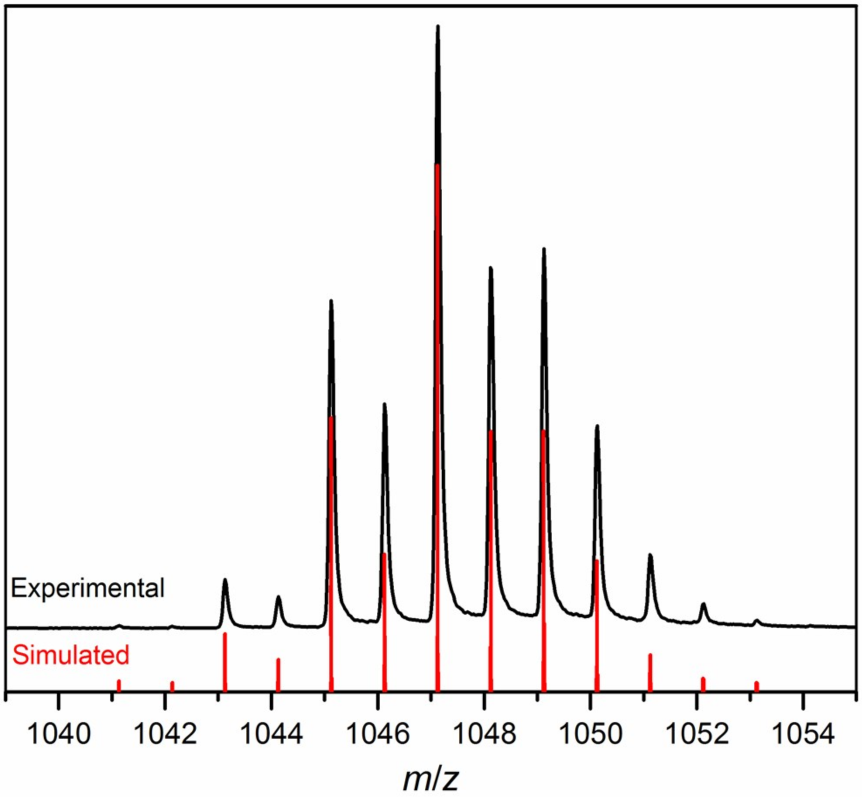

Figure S5. ESI/MS(+) data for Fe_3Br_2S**L** (**2**) in THF. Capillary voltage: 4000 V. Fragmentation voltage: 120 V. Desolvation temperature: 350°C.

Table S1. Selected bond distances and angles from Fe_3Br_2SL (2) and $Fe_3BrSL·0.5THF$ (3).

	$Fe_3Br_2S\mathbf{L}$ (**2**)	$Fe_3BrS\mathbf{L}·0.5THF$ (**3**)
Fe1–N_L (Å)	2.001(2), 2.008(2)	2.008(2), 2.013(2)
Fe2–N_L (Å)	2.003(2), 2.011(2)	2.002(2), 2.007(2)
Fe3–N_L (Å)	1.992(2), 1.994(2)	2.002(2), 2.012(2)
Fe3′–N_L (Å)	-	1.975(2), 1.979(2)
Fe1–S (Å)	2.2918(8)	2.2677(6)
Fe2–S (Å)	2.2915(8)	2.2528(5)
Fe3–S (Å)	2.1722(8)	2.238(1)
Fe3′–S (Å)	-	2.1148(9)
$\angle N_L$–Fe1–N_L	101.1(1)	100.31(6)
$\angle N_L$–Fe2–N_L	96.1(1)	97.59(6)
$\angle N_L$–Fe3–N_L	96.8(1)	98.29(8)
$\angle N_L$–Fe3′–N_L	-	100.33(8)
Fe1···NCCCN plane (Å)	0.20	0.14
Fe2···NCCCN plane (Å)	0.25	0.30
Fe3···NCCCN plane (Å)	0.63	0.55
Fe3′···NCCCN plane (Å)	-	0.11
dihedral angle of Ar···Ar (°)	8.3	6.2

Table S2. Crystal data and structure refinement for Fe_3Br_2SL (2).

Identification code	ylee94	
Empirical formula	C49 H71 Br2 Fe3 N6 O S	
Formula weight	1119.54	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 11.9958(6) Å	α = 104.697(1)°
	b = 12.5852(7) Å	β = 102.692(1)°
	c = 17.0913(9) Å	γ = 91.246(1)°
Volume	2426.6(2) $Å^3$	
Z	2	
Density (calculated)	1.532 Mg/m^3	
Absorption coefficient	2.618 mm^{-1}	
F(000)	1158	
Crystal size	0.176 x 0.118 x 0.041 mm^3	
Theta range for data collection	1.678 to 27.500°.	
Index ranges	$-15\leq h\leq 15$, $-16\leq k\leq 16$, $-22\leq l\leq 22$	
Reflections collected	54540	
Independent reflections	11145 [R(int) = 0.0539]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Analytical	
Max. and min. transmission	0.9418 and 0.7776	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11145 / 10 / 603	
Goodness-of-fit on F^2	0.958	
Final R indices [I>2sigma(I)]	R1 = 0.0368, wR2 = 0.0840 [7854]	
R indices (all data)	R1 = 0.0660, wR2 = 0.0918	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.839 and -0.968 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.

Table S3. Crystal data and structure refinement for $Fe_3BrSL{\cdot}0.5THF$ (3).

Identification code	ylee99	
Empirical formula	C50.88 H74.76 Br1.03 Fe3 N6 O1.47 S	
Formula weight	1075.92	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P$\bar{1}$	
Unit cell dimensions	a = 11.6510(3) Å	α = 94.401(1)°
	b = 12.6465(4) Å	β = 95.909(1)°
	c = 17.0493(5) Å	γ = 96.266(1)°
Volume	2474.0(1) Å^3	
Z	2	
Density (calculated)	1.444 Mg/m^3	
Absorption coefficient	1.787 mm^{-1}	
F(000)	1128	
Crystal size	0.237 x 0.201 x 0.060 mm^3	
Theta range for data collection	1.205 to 27.500°.	
Index ranges	-15≤h≤15, -16≤k≤16, -22≤l≤22	
Reflections collected	62395	
Independent reflections	11378 [R(int) = 0.0313]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Analytical	
Max. and min. transmission	0.3074 and 0.2523	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11378 / 0 / 588	
Goodness-of-fit on F^2	1.077	
Final R indices [I>2sigma(I)]	R1 = 0.0294, wR2 = 0.0796 [9547]	
R indices (all data)	R1 = 0.0376, wR2 = 0.0843	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.931 and -0.544 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.

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