Supplementary Information for

Oxidation triggers guest dissociation during reorganization of from an Fe$^{II}$4L₆ twisted parallelogram

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# Table of Contents

1. Materials and methods ........................................................................................................... 3
2. Synthesis and characterisation of 1 .......................................................................................... 5
   2.1 Cyclic Voltammetry of 1 ....................................................................................................... 15
   2.2 Synthesis and assembly of 1-1’-Bis(4-(2-pyridyldiazenyl)phenyl)ferrocene (L\textsuperscript{H}) .. 16
3. Oxidative disassembly into mononuclear complexes ................................................................. 19
4. Investigations of the transformation of 1 into 2 ....................................................................... 23
   4.1 NMR Titration ......................................................................................................................... 23
   4.2 Spectroelectrochemistry and optical titrations ...................................................................... 23
   4.3 Determination of the magnetic moment of 2 using Evans’ method .................................... 26
5. Synthesis and Characterization of new compounds ................................................................. 27
   5.1 Synthesis of mononuclear [FeL\textsubscript{3}](PF\textsubscript{6})\textsubscript{2} complex ........................................ 27
6. Crystallography ......................................................................................................................... 31
7. References .................................................................................................................................. 33
1. Materials and methods

All reagents were purchased from commercial sources and used as received. For electrochemical experiments, dry solvents were purchased from Sigma-Aldrich and purged with argon before use. nBu₄NPF₆ was recrystallised three times from ethanol before use. 2-Nitrosopyridine,¹ (4-aminophenylene)-ferrocene B and bis(4-aminophenylene)-ferrocene A were synthesized according literature procedures. Note that B readily oxidised in the presence of air (over the course of several weeks), and was thus stored in a glove-box when not in use.

Nuclear Magnetic Resonance (NMR): NMR spectra were recorded using a 400 MHz Avance III HD Smart Probe (routine 1H NMR), DCH 500 MHz dual cryoprobe (high-resolution 13C and 2D experiments), DPX S5 500 MHz BB ATM (variable temperature NMR) and 500 MHz TCI-ATM cryo NMR spectrometers. Chemical shifts for 1H, 13C and 19F are reported in ppm on the δ scale; 1H and 13C were referenced to the residual solvent peak. Coupling constants (J) are reported in hertz (Hz). The following abbreviations are used to describe signal multiplicity for 1H, 13C and 19F NMR spectra: s: singlet, d: doublet, t: triplet, dd: doublet of doublets; dt: doublet of triplets; m: multiplet, b: broad. 1H DOSY NMR experiments were performed on a Bruker 400 MHz Avance III HD NMR. Maximum gradient strength was 6.57 G/cm A. The standard Bruker pulse program, ledbpgp2s, employing a stimulated echo and longitudinal eddy-current delay (LED) using bipolar gradient pulses for diffusion using 2 spoiler gradients was utilised. Rectangular gradients were used with a total duration of 1.5 ms. Gradient recovery delays were 875-1400 μs. Individual rows of the S4 quasi-2D diffusion databases were phased and baseline corrected.

Mass spectrometry: Low resolution electrospray ionisation (LR-ESI) mass spectrometry was undertaken on a Micromass Quattro LC mass spectrometer (cone voltage 10-30 V; desolvation temp. 313 K; ionization temp. 313 K) infused from a Harvard syringe pump at a rate of 10 μL min⁻¹. High resolution electrospray ionisation mass spectrometry (HRMS-ESI) was performed on a Waters LCT Premier Mass Spectrometer featuring a Z spray source with electrospray ionisation and modular LockSpray interface.

UV-Vis spectroscopy: UV-Visible absorption spectroscopy was performed using a Perkin Elmer Lambda 750 UV-Vis-NIR spectrophotometer fitted with a PTP-1 Peltier temperature controller accessory. Spectra were obtained in double beam mode using only the (front) analyte beam to record spectra, with air in the (rear) reference path. A background spectrum
of the neat solvent was recorded using the analyte beam prior to each experiment and baseline correction applied using the Perkin Elmer WinLab software suite. Samples were analysed using quartz cuvettes with optical path lengths of 10 mm.

**Cyclic voltammetry**: Solution state cyclic voltammetry (CV) was performed using a BioLogic SP-150 potentiostat with ferrocene (Fc) as an internal reference. Measurements were conducted under an Ar atmosphere using a conventional three-electrode cell: a glassy carbon working electrode, a Pt wire auxiliary electrode, and a Ag/Ag⁺ quasi-reference electrode. A 0.1 M nBu₄NPF₆/CH₃CN electrolyte was used, with scan rates in the range 25-1000 mV s⁻¹.

**Spectroelectrochemistry**: Electronic spectra were obtained in situ using an Optically Semi-Transparent Thin-Layer Electrosynthetic (OTTLE) cell (path length 0.1 mm) accommodating the Pt counter and Ag/Ag⁺ reference electrodes, which were separated from the solution by salt bridges containing 0.3 M nBu₄NPF₆/CH₃CN electrolyte. A Pt gauze working electrode (70% transmittance) was located centrally in the optical beam in the lower section of the cell. All solutions were purged with Ar prior to transferral into the OTTLE cell. Potentials were controlled by a BioLogic SP-150 potentiostat, and absorption spectra recorded at regular intervals over the range 250-800 nm. The attainment of a steady-state spectrum and the decay of the current to a constant minimum were taken as being indicative of the complete conversion of the starting material.

**Molecular modelling**: Molecular model simulations (MM3 force fields) SCIGRESS version FJ 2.6 (EU 3.1.9) Build 5996.8255.20141202.
2. Synthesis and characterisation of 1

Bis(4-(aminophenylene))-ferrocene A (6.0 mg, 16 µmol), 2-pyridinecarboxaldehyde (3.5 mg, 10 µmol) and Fe(PF₆)₂(CH₃CN)₆ (6.4 mg, 10.3 µmol) were dissolved in 1 ml CH₃CN and transferred into a J. Young tube. The purple solution was subjected to three freeze-pump-thaw cycles under N₂ atmosphere and then heated at 60 °C over 16 h. After cooling to room temperature the purple solution was added to 10 ml Et₂O to precipitate the product. The precipitate was collected by centrifugation and dried in vacuo. Yield (10 mg, 85%, 2.2 µmol).

¹H NMR (CD₃CN, 700 MHz, 298K): δ[ppm] = 9.41 (s), 9.32 (s), 9.28 (s), 9.13 (s), 8.84 (s), 8.62–8.51 (m), 8.45 (d, J = 6.3 Hz), 8.39 (d, J = 5.6 Hz), 8.29 (d, J = 6.4 Hz), 8.28 -8.20 (m), 8.12 (d, J = 7.7 Hz), 8.05 (d, J = 6.4 Hz), 7.97 (d, J = 6.6 Hz), 7.95 (t, J = 5.6 Hz), 7.85 – 7.72 (m), 7.73 – 7.65 (m) 7.64 – 7.60 (m), 7.57 (s), 7.57 – 7.50 (m), 7.48 (d, J = 5.6 Hz), 7.46 – 7.42 (m), 7.42 – 7.35 (m), 7.31 (d, J = 8.2 Hz), 7.27 – 7.20 (m), 7.24 – 7.13 (m), 7.02 (d, J = 7.3 Hz), 6.96 (s), 6.75 (bs), 6.66 (d, J = 8.4 Hz), 6.57 (s), 6.48 (d, J = 9.0 Hz), 6.42 (d, J = 7.8 Hz), 6.15 (s), 6.02 (s), 5.39 (d, J = 9.0 Hz), 4.81 (s), 4.70 (s), 4.65 (s), 4.57 (d, J = 3.1 Hz), 4.38 (s), 4.35 (s), 4.25 (s), 4.22 (s), 4.19 (s), 4.16 (s), 4.10 (s), 3.91 (s), 3.75 (s), 3.71 (s), 3.43 (s), 3.30 (s), 3.13 (s), 2.53 (s), 2.48 (s); see figure below for signal assignment.

¹³C NMR (CD₃CN, 176 MHz, 298K): δ[ppm] = 175.00, 173.98, 173.14, 171.27, 169.60, 164.81, 159.55, 158.49, 158.26, 158.20, 158.12, 157.98, 157.73, 157.16, 156.91, 156.75, 156.58, 156.24, 155.17, 149.26, 148.46, 145.10, 144.89, 143.95, 141.37, 140.67, 140.63, 140.58, 140.39, 140.29, 140.12, 139.63, 139.07, 138.47, 138.44, 138.05, 131.44, 131.38, 130.64, , 129.76, 129.28, 129.09, 129.03, 128.82, 128.72, , 128.28, 128.10, 127.05, 126.89, 126.55, 126.42, 126.06, 125.79, 125.68, 125.46, 124.57, 124.22, 121.67, 121.45, 121.25, 120.89, 120.58, 85.02, 83.97, 83.75, 83.52, 82.61, 78.15, 77.96, 77.77, 76.85, 75.38, 75.19, 73.89, 72.47, 72.42, 71.87, 71.34, 71.25, 71.02, 70.84, 70.53, 70.44, 70.09, 69.76, 69.44, 68.75, 67.75, 65.97, 65.67, 65.40, 64.70, 64.37, 63.67

¹⁹F NMR (CD₃CN, 471 MHz, 298K) δ[ppm] = -70.35 (d, J = 714.7 Hz), -72.54 (d, J = 707.8 Hz).

MS (ESI-MS, positive mode): m/z [Fe₄L₆(PF₆)₅]³⁺ (calcd. 1409.16): found 1409.16, [Fe₄L₆(PF₆)₄]⁺ (calcd. 1020.63): found 1020.56, [Fe₄L₆(PF₆)₃]⁵⁺ (calcd. 787.51): found
787.40, [Fe₄L₆(PF₆)₂]⁶⁺ (calcd. 632.10): found 631.95, [Fe₄L₆(PF₆)]⁷⁺ (calcd. 521.10): found 437.83

Alternatively, the cage can be assembled through the exact same experimental procedure, substituting Fe(PF₆)₂ for Fe(OTf)₂; however, the resulting ¹H NMR spectrum of this assembly

![NMR Spectrum](image)

**Figure S1**: ¹H NMR Spectrum (CD₃CN, 700 MHz, 298K) of 1(PF₆)₈.

**Assignment comments**: Imine protons were identified by ¹H-¹³C HSQC and the absence of coupling. From there, H-4 was identified by ¹H-¹³C HMBC and ¹H-¹H NOESY spectra. The rest of the pyridine moiety was assigned through ¹H-¹H COSY correlations. Assignment of the phenylene protons is not possible due to broadening and overlap; hence, correlation between the pyridylimine and ferrocene region was not possible. However, 6-fold dessymetrization can be seen in both regions. At lower temperature (238 K), we could resolve the broad phenylene protons into distinct, individual signals.
**Figure S2:** Aromatic region of the $^1$H NMR spectrum (CD$_3$CN, 700 MHz, 298 K) of 1.

**Figure S3:** Ferrocene region of the $^1$H NMR spectrum (CD$_3$CN, 700 MHz, 298 K) of 1.
**Figure S4**: Phenylene region of the $^1$H NMR spectrum (CD$_3$CN, 500 MHz) of 1 at 238 K and 298 K showing sharpening of the phenylene resonances upon cooling.

**Figure S5**: $^{13}$C NMR spectrum (CD$_3$CN, 176 MHz, 298 K) of 1.
Figure S6: $^1$H-$^{13}$C HSQC NMR spectrum (CD$_3$CN, 176 MHz, 298K) of 1.

Figure S7: Partial $^1$H-$^{13}$C HSQC NMR spectrum (CD$_3$CN, 176 MHz, 298K) of 1 highlighting the 6 imine resonances resulting from 2 meridional coordination environments.
Figure S8: Partial $^1$H-$^{13}$C HSQC NMR spectrum (CD$_3$CN, 176 MHz, 298 K) of 1 highlighting the 24 CH ferrocene resonances resulting the restricted axial rotation in 1. 6 coordination environments and 4 ferrocene protons per linker gives 24 resonances.

Figure S9: $^1$H-$^1$H COSY NMR spectrum (CD$_3$CN, 700 MHz, 298 K) of 1.
Figure S10: $^1$H-$^1$H NOESY NMR spectrum (CD$_3$CN, 700 MHz, 298 K) of 1.

Figure S11: $^1$H-$^{13}$C HMBC NMR spectrum (CD$_3$CN, 176 MHz, 298 K) of 1.
Figure S12: $^1$H DOSY NMR spectrum (400 MHz, CD$_3$CN, 298 K) of 1.

Figure S13: $^{19}$F NMR (470 MHz, CD$_3$CN, 298 K) spectrum of 1.
Figure S14: Comparison between the $^1$H NMR spectrum (CD$_3$CN, 700 MHz top, 400 MHz bottom, 298K) of the PF$_6^-$ and OTf$^-$ salt of 1; singlet at 5.5 corresponds to residual DCM from the ligand.

Figure S15: Low resolution ESI mass spectrum of 1 in CH$_3$CN.
**Figure S16:** High resolution ESI mass spectrum (positive mode) in CH$_3$CN; zoom in on M$^{5+}$ peak of 1 in CH$_3$CN and calculated isotope pattern for M$^{5+}$ peak ion of 1 in CH$_3$CN.

**Figure S17:** Low resolution ESI mass spectrum (positive mode) derivative of 1 assembled from A, 2-pyridinecarboxaldehyde and Fe(OTf)$_2$ in CH$_3$CN.
2.1 Cyclic Voltammetry of 1

Figure S18: CV of 1 in 0.1 M nBu₄NPF₆/CH₃CN electrolyte at a scan rate of 10 mV/s.

Figure S19: CV of 1 in 0.1 M nBu₄NPF₆/CH₃CN electrolyte at a scan rate of 100 mV/s.
2.2 Synthesis and assembly of 1-1’-Bis(4-(2-pyridyl diazenyl)phenyl)ferrocene (L_{azo})

1-1’-Bis(4-aminophenyl)ferrocene (100 mg, 0.27 mmol) and 2-nitrosopyridine (59 mg, 0.54 mmol) were dissolved in CH$_2$Cl$_2$ (5 mL). Glacial AcOH (1 ml) was added, and the solution was stirred at room temperature for 16 hours. The mixture was neutralised with saturated sodium bicarbonate and diluted with 10 ml of CH$_2$Cl$_2$. The organic phase was separated and washed with brine, water and dried over magnesium sulfate. The solvent was removed and the crude product suspended in boiling water and isolated by filtration. Yield L_{azo} (76%, 0.205 mmol).

$^1$H NMR (CDCl$_3$, 400 MHz, 298K): \( \delta \text{[ppm]} = 8.70 \text{ (d, } J = 3.9 \text{ Hz, 2H)}, 7.84 \text{ (d, } J = 8.5 \text{ Hz, 4H)}, 7.82 – 7.75 \text{ (m, 2H)}, 7.72 \text{ (d, } J = 7.9 \text{ Hz, 2H)}, 7.35 \text{ (d, } J = 8.4 \text{ Hz, 6H)}, 4.65 \text{ (s, 4H)}, 4.39 \text{ (s, 4H)}. \) See figure below for assignment.

$^{13}$C NMR (CDCl$_3$, 101 MHz, 298K): \( \delta \text{[ppm]} = 163.11, 150.50, 149.38, 142.43, 138.09, 126.15, 124.70, 123.89, 115.17, 84.84, 71.30, 68.27. \)

HRMS (ESI-MS, positive mode): m/z [M+H]$^+$ (calcd. 549.1490) found 549.1510.
Figure S20: $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298K) of L$_{azo}$.

Figure S21: $^{13}$C NMR spectrum (CDCl$_3$, 101 MHz, 298K) of L$_{azo}$. 
Employing the pre-formed ligand B (in place of A and 2-pyridylcarboxaldehyde) with Fe(NTf$_2$)$_2$ likewise produced a Fe$_4$L$_6$ congener of 1 by ESI-MS, however, the $^1$H NMR signals of this derivative were likewise too broad to allow full NMR characterization.

Figure S22: Low resolution ESI mass spectrum (positive mode) the derivative in of 1 assembled from L$_{azo}$ and Fe(NTf)$_2$ in CH$_3$CN.
3. Oxidative disassembly into mononuclear complexes

To a solution of 1 (5.0 mg, 1.1 µmol) in 1 ml of CH₃CN was added NOPF₆ (1.2 mg, 6.6 µmol) in 0.5 ml inside a N₂ filled glovebox. The resulting orange solution was filtered using a syringe filter and transferred to a J. Young tube and connected to a Schlenk line. 7 ml of Et₂O were added precipitate 1. The supernatant was syringed from the flask and the solid product was washed with H₂O and THF and dried in vacuo to yield 2 as an orange powder (3.9 mg, 3.8 µmol, 86%).

The yield is given considering that 1 only provides 4 Fe(II) per 6 ligands. Thus, only 4 mononuclear complexes 2 can be generated from one equivalent of 1.

^1H NMR (400 MHz, CD₃CN, 298K) δ[ppm]= 144.84, 90.85, 58.90, 57.60, 53.20, 45.99, 35.64, 31.88,16.85, -10.70, -21.74.

^19F NMR (376 MHz, CD₃CN, 298K) δ[ppm]= -74.07 (d, J = 706.5 Hz).

MS (ESI-MS): m/z (FeL(+)PF6)_2+ (calc 899.01) found 892.12; (FeL(+)PF6)^2+ calc (373.52) found 373.40; (FeL(+)^3+) (calc 200.69) found 200.57

MS (HRESI-MS): m/z FeL(CH₃CN)_3+ (calc 214.3072) 214.3695.

Figure S23: Wide sweep ^1H NMR spectrum (CD₃CN, 400 MHz, 298 K) of 2.
Figure S24: $^{19}$F NMR spectrum (CD$_3$CN, 376.3 MHz, 298K) of 2; signals stacked for clarity.

Figure S25: LR-ESI-MS (positive mode) of the mononuclear 2 complex in MeOH.
Figure S26: LR-ESI-MS (positive mode) of the mononuclear complex 2 generated from the OTf salt of 1 in MeOH.

Figure S27: HR-ESI-MS of the +3 peak of the acetonitrile adduct of 2 in CH₃CN, indicating acetonitrile coordination in solution.
**Figure S28**: HR-ESI-MS/MS of $2(\text{OTf})_2$ showing fragmentation of the mononuclear complex in CH$_3$CN into the oxidized ligand, showing that oxidation is occurring at the ferrocene unit. No presence of protonated Fe$^{II}$-ferrocene species was observed.
4. Investigations of the transformation of 1 into 2

4.1 NMR Titration

Figure S29: Partial wide-sweep $^1$H NMR spectrum of the titration of 1 with NOPF$_6$ in CD$_3$CN showing the gradual increase of the mononuclear species upon cage oxidation.

4.2 Spectroelectrochemistry and optical titrations

Figure S30: UV-Vis spectroelectrochemistry of 1 (3 µM in CH$_3$CN) in 0.3 M nBuNPF$_6$/CH$_3$CN electrolyte upon oxidation at +0.7 V vs. Ag$^+$/Ag (quasi-reference).
Figure S31: UV-Vis spectroelectrochemistry of 1 (3µM in CH$_3$CN) in 0.3 M nBuNPF$_6$/CH$_3$CN electrolyte, following spectral changes at 0 V vs. Ag$^+$/Ag, after oxidation.

Figure S32: UV-Vis titration of 1 (3µM in CH$_3$CN) with sequential addition of NOPF$_6$. 
**Figure S33**: UV-Vis titration of 2 (12 μM in CH$_3$CN) with sequential addition of tetrakis(dimethylamine)ethylene.

**Figure S34**: Comparison of the Fe$^{II}$ MLCT bands after one cycle electrochemical and chemical oxidation and reduction (Start = 1, End = after oxidation + reduction).
4.3 Determination of the magnetic moment of 2 using Evans’ method

**Figure SS35**: Evans method using benzene as the shifted reagent by paramagnetic 2 in CD$_3$CN.

The magnetic susceptibility is calculated from:

$$\chi_M = \frac{(3\Delta f)}{(4\pi F c)}$$

with the difference between paramagnetically-shifted and unshifted benzene $\Delta f = 99.6$ Hz, the spectrometer frequency $F = 400$ MHz and the concentration of the paramagnetic complex $c = n/V = 3.6 \times 10^{-6}$ mol/ml ($n = m/M; m = 2$ mg, Fe(L(PF$_6$)$_3$(CH$_3$CN)$_2$) = 1119 g/mol, V = 0.5 ml):

$$\chi_M = 0.0165 \text{ cm}^3/\text{mol}$$

Which gives a magnetic moment of

$$\mu = \sqrt{8\chi_M T} = 6.27\mu_B$$

with $T = 298$ K. This value compares well to the magnetic moment of 5 unpaired electrons $\mu = 5.92\mu_B$. No diamagnetic correction was applied.
5. Synthesis and Characterization of new compounds

5.1 Synthesis of mononuclear [FeL₃](PF₆)₂ complex

4-(aminophenylene)-ferrocene B (2.8 mg, 10 µmol), 2-pyridinecarboxaldehyde (1.2 mg, 10 µmol) and Fe(PF₆)₂(CH₃CN)₆ (2.0 mg, 3.3 µmol) were dissolved in CD₃CN (0.5 ml) and transferred into a J-Young NMR tube. The purple solution was subjected to three freeze-pump-thaw cycles under an N₂ atmosphere, and then heated at 50 °C for 16 h. The resulting purple solution was poured into 10 ml Et₂O to precipitate the product, which was isolated through centrifugation and dried under vacuum. Yield (5.1 mg, 2.9 µmol, 87%).

¹H NMR (CD₃CN, 400 MHz, 298 K): δ[ppm] = 9.37 (s, H-5), 9.10 (s, H-5), 8.98 (s, H-5), 8.57 (m, H-1, H-4), 8.42 (d, J = 5.8 Hz, H-4), 8.30 (t, J = 7.6 Hz, H-2), 8.13 (t, J = 7.1 Hz, H-2), 8.07 (d, J = 7.6 Hz, H-1), 8.00 (d, J = 7.1 Hz, H-1), 7.90 (t, J = 7.1 Hz, H-2), 7.76 (d, J = 4.9 Hz, H-4), 7.69 (t, J = 7.1 Hz, H-3), 7.69 (d, J = 7.1 Hz, H-3), 7.56 – 7.46 (m, H-3), 7.42 (d, J = 7.3 Hz, H-7), 7.31 (d, J = 5.9 Hz, H-7), 7.13 (d, J = 8.3 Hz, H-7), 6.78 – 6.58 (pt, J = 7.1 Hz, H-6, H-6), 6.21 (d, J = 7.4 Hz, H-6), 4.85 – 4.65 (m, H-8), 4.56 (d, J = 12.4 Hz, H-8), 4.52 – 4.27 (m, H-9), 4.08 (s, H-10), 3.92 (s, H-10), 3.91 (s, H-10).

¹³C NMR (CD₃CN, 126 MHz, 298K): δ[ppm] = 174.31, 172.37, 171.19, 159.48, 158.88, 158.57, 157.08, 156.64, 155.91, 149.72, 145.46, 144.35, 141.37, 141.26, 140.83, 138.91, 138.81, 138.59, 131.60, 130.25, 129.93, 128.83, 128.70, 128.42, 126.67, 126.29, 125.99, 122.58, 122.12, 121.76, 69.75, 69.71, 69.67, 69.63, 69.60, 69.55, 66.69, 66.33, 65.86.
MS (ESI-MS, positive mode): m/z [ML$_3$PF$_6$]$^+$ (calcd. 1299.14): found 1298.93 [ML$_3$]$^{2+}$ (calcd. 577.09) found 577.06.

HRMS (ESI-MS, positive mode): m/z [ML$_3$]$^{2+}$ (calcd. 577.0901) found 577.0902.

Figure S36: $^1$H NMR spectrum (298K, CD$_3$CN, 400 MHz) of FeL$_3$(PF$_6$)$_2$; asterisks denote excess 2-pyridinecarboxaldehyde.
Figure S37: $^{13}$C NMR spectrum $^{13}$C NMR (CD$_3$CN, 126 MHz, 298K) of FeL$_3$(PF$_6$)$_2$.

Figure S38: LR-ESI (positive mode) mass spectrum of FeL$_3$(PF$_6$)$_2$. 
Figure S39: HRESI (positive mode) mass spectrum of the FeL$_3$$^{2+}$ peak.
6. Crystallography

Data were collected at Beamline I19 of Diamond Light Source employing silicon double crystal monochromated synchrotron radiation (0.6889 Å) with ω scans at 100(2) K. Data integration and reduction for were undertaken with xia2\cite{4}; multi-scan empirical absorption corrections were applied to the data using xia2\cite{4}. Subsequent computations were carried out using the WinGX-32\cite{5} graphical user interface. Structures were solved by direct methods using SHELXT-2013\cite{6} then refined and extended with SHELXL-2013\cite{6}.

Crystal structure of 1·8NTf·5MeCN

Formula $C_{218}H_{159}F_{48}Fe_{10}N_{49}O_{32}S_{16}$, $M$ 5960.39, Monoclinic, $P2_1/c$ (#16), $a$ 26.651(5), $b$ 27.050(5), $c$ 36.959(7) Å, $\beta$ 98.81(3), $V$ 26330(9) Å$^3$, $D_c$ 1.504 g cm$^{-3}$, $Z$ 4, crystal size 0.200 by 0.200 by 0.150 mm, colour purple, habit block, temperature 100(2) Kelvin, $\lambda$(Synchrotron) 0.6889 Å, $\mu$(Synchrotron) 0.767 mm$^{-1}$, $T$(Analytical)$_{\text{min,max}}$ 0.9524, 1.0, $2\theta_{\text{max}}$ 36.50, $hkl$ range -24 24 -24 24 -32 33, $N$ 98034, $N_{\text{ind}}$ 20709($R_{\text{merge}}$ 0.1258), $N_{\text{obs}}$ 12914($I > 2\sigma(I)$), $N_{\text{var}}$ 3364, residuals * $R_1(F)$ 0.1492, $wR_2(F^2)$ 0.3409, GoF(all) 1.059, $\Delta\rho_{\text{min,max}}$ -0.548, 1.085 e$^-$/Å$^3$, CCDC 2006764.

* $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2)/\Sigma(wF_c^2)^2)^{1/2}$ all reflections $w=1/[\sigma^2(F_o^2)+(0.0500P)^2+400.0000P]$ where $P=(F_o^2+2F_c^2)/3$

Specific refinement details

Crystals of Fe4L$^\text{azo}$·8NTf·5MeCN were grown by slow diffusion of diethyl ether into a CD3CN solution of Fe4L$^\text{azo}$·(NTf)8. Despite the use of synchrotron radiation, few reflections at greater than 1.1 Å resolution were observed. Nevertheless, the quality of the data is more than sufficient to establish the connectivity of the structure.

The crystals employed in this study rapidly lost solvent after removal from the mother liquor and rapid handling prior to flash cooling in the cryostream was required to collect data. Due to the less than ideal resolution, bond lengths and angles within pairs of organic
ligands were restrained to be similar to each other (SAME) and thermal parameter restraints (SIMU, DELU) were applied to all non-metal atoms to facilitate anisotropic refinement. Ligand-based atoms that still displayed thermal parameters greater than 0.4 were further refined to approximate isotropic behavior (ISOR). Four triflimide anions were modelled as disordered over two positions.

In general, non-hydrogen atoms with occupancies greater than 0.5 were refined anisotropically. Carbon-bound hydrogen atoms were included in idealized positions and refined using a riding model. Disorder was modelled using standard crystallographic methods including constraints, restraints and rigid bodies where necessary. The amount of solvent quoted in the molecular formula is only that which could be assigned directly from the electron density map.

The SQUEEZE-d portion of the cell totals 856 electrons per unit cell, with a solvent accessible void volume of 2,917 Å³ per unit cell. This equates to 214 electrons per structure, where \(Z = 4\). As all NTf₂⁻ molecules were resolved, we attribute this excess electron density to unresolved solvent molecules (Et₂O and MeCN).

CheckCIF produces 1 Level A and 4 Level B alerts. These alerts are due to the high thermal motion of some atoms in the crystal (particularly the sulfur atoms of the triflimide anions), leading to the less than ideal resolution of the data.
7. References


