SUPPORTING INFORMATION

Generation and transformation of a hemi-iminal-based metal-organic Fe(II) structure obtained via subcomponent self-assembly in water

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Contents

1. NMR data

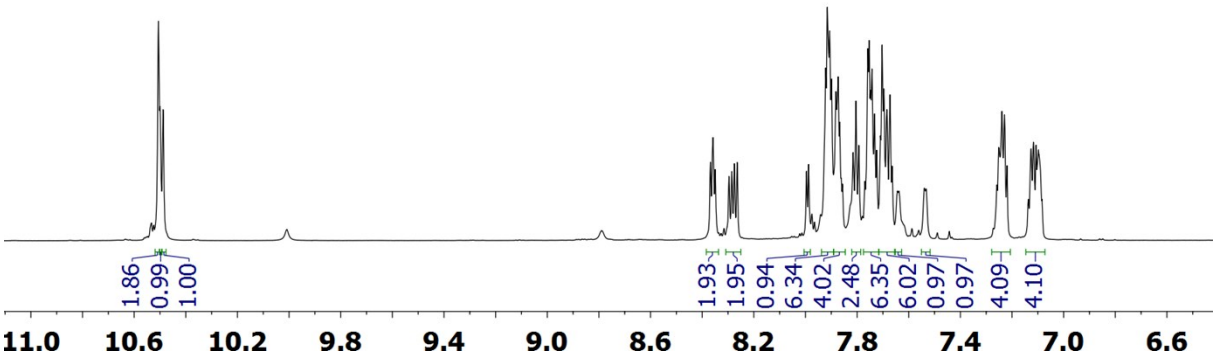


Figure S1. ^{1}H NMR (700 MHz CD_3CN) spectrum of $[Fe^{II}(\mathbf{L})_2](ClO_4)_2$.

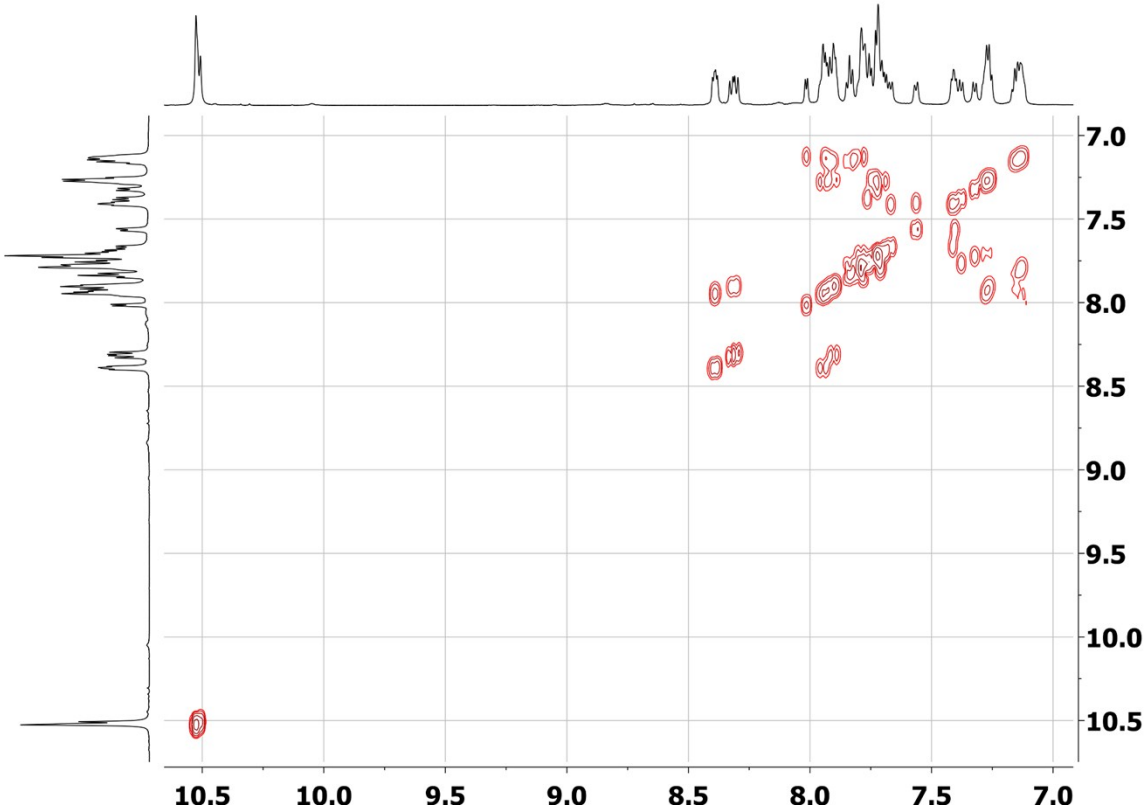


Figure S2. COSY NMR (600 MHz CD_3CN) spectrum of $[Fe^{II}(\mathbf{L})_2](ClO_4)_2$.

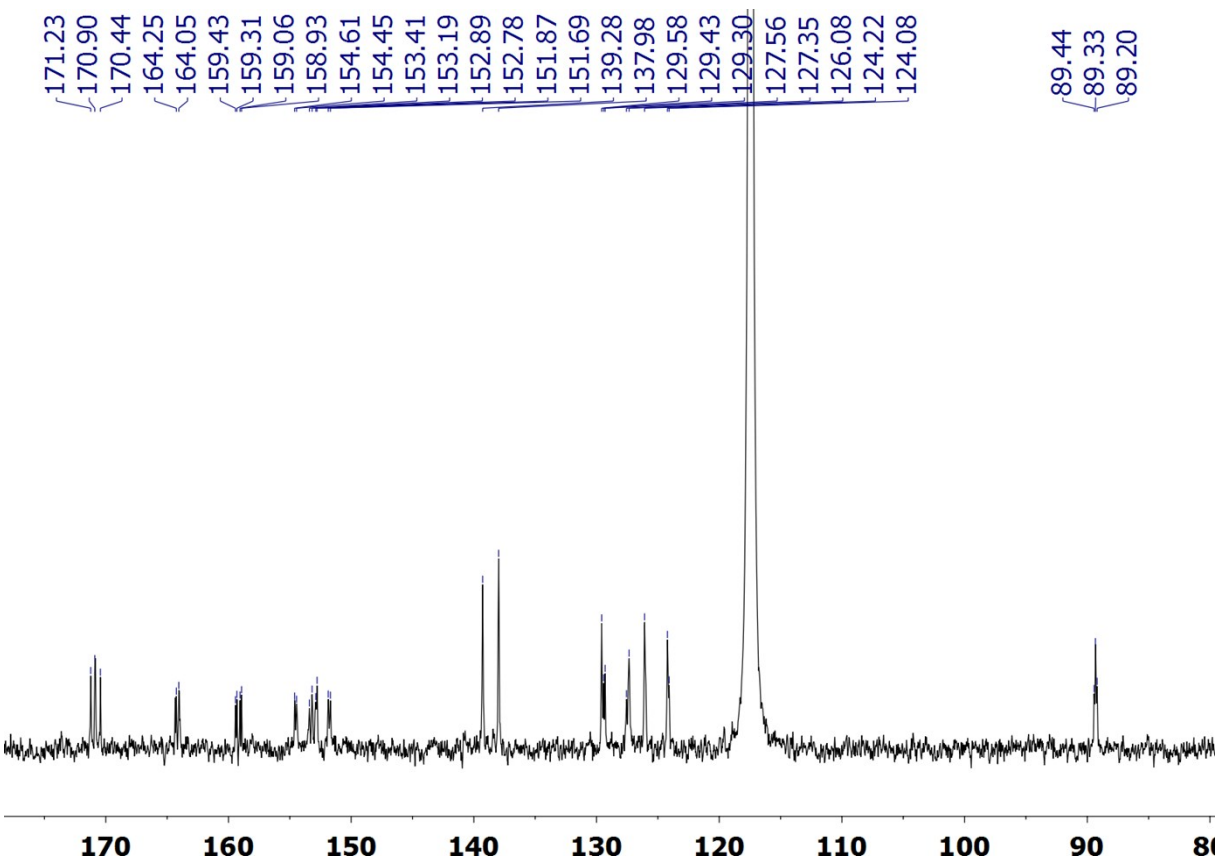


Figure S3. ^{13}C NMR (75 MHz CD_3CN) spectrum of $[Fe^{II}(\mathbf{L})_2](ClO_4)_2$.

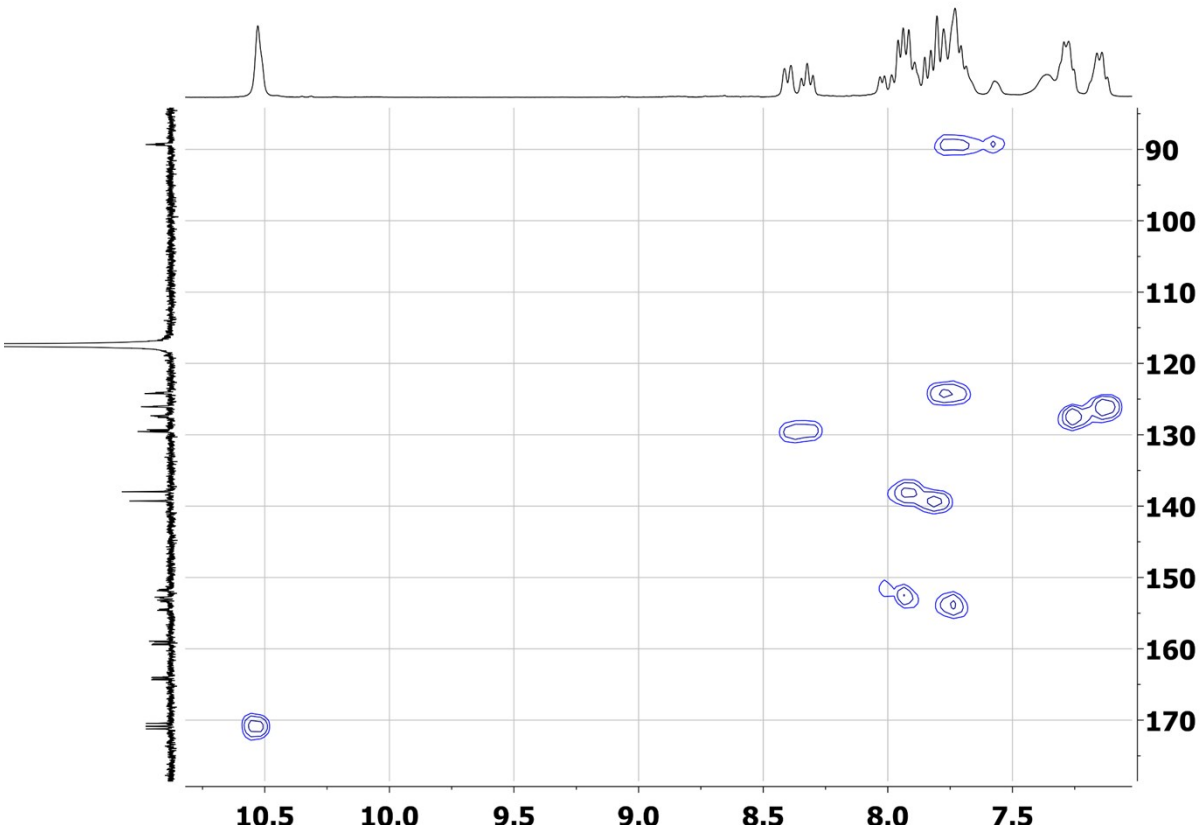


Figure S4. ^{1}H-^{13}C HSQC NMR (300/75 MHz CD_3CN) spectrum of $[Fe^{II}(\mathbf{L})_2](ClO_4)_2$

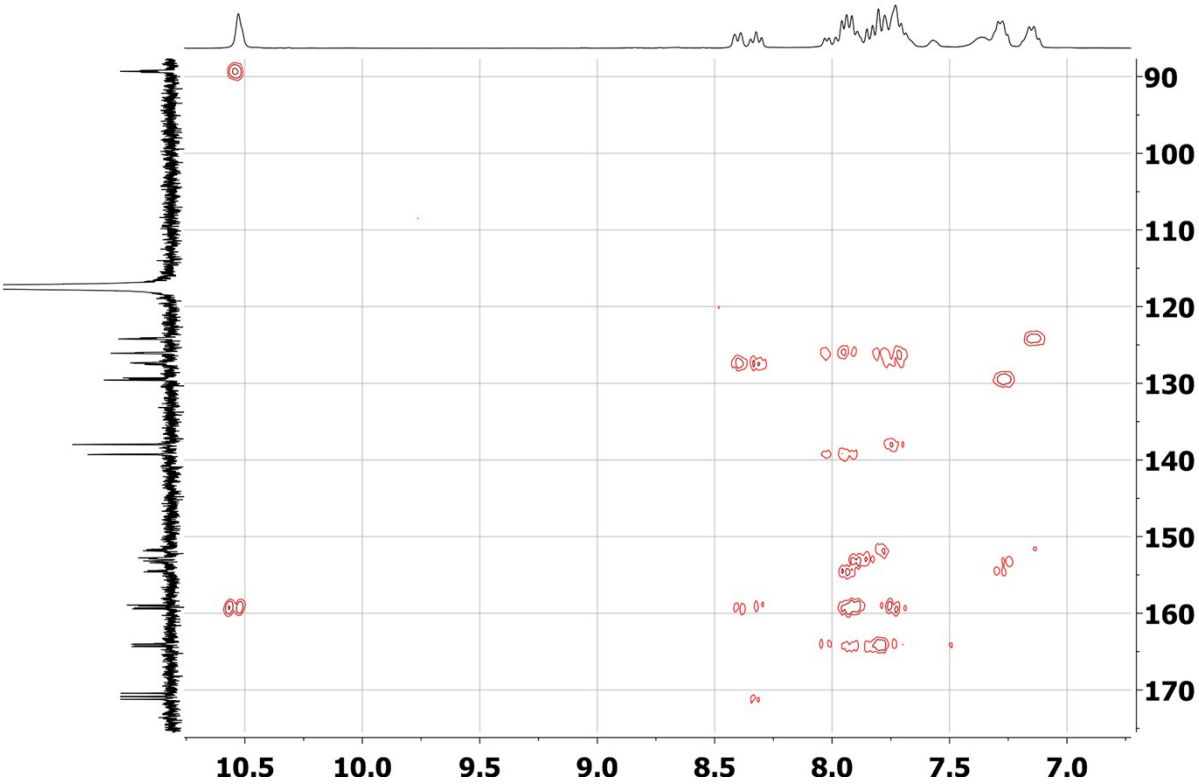


Figure S5. ^{1}H-^{13}C HMBC NMR (300/75 MHz CD_3CN) spectrum of $[Fe^{II}(\mathbf{L})_2](ClO_4)_2$

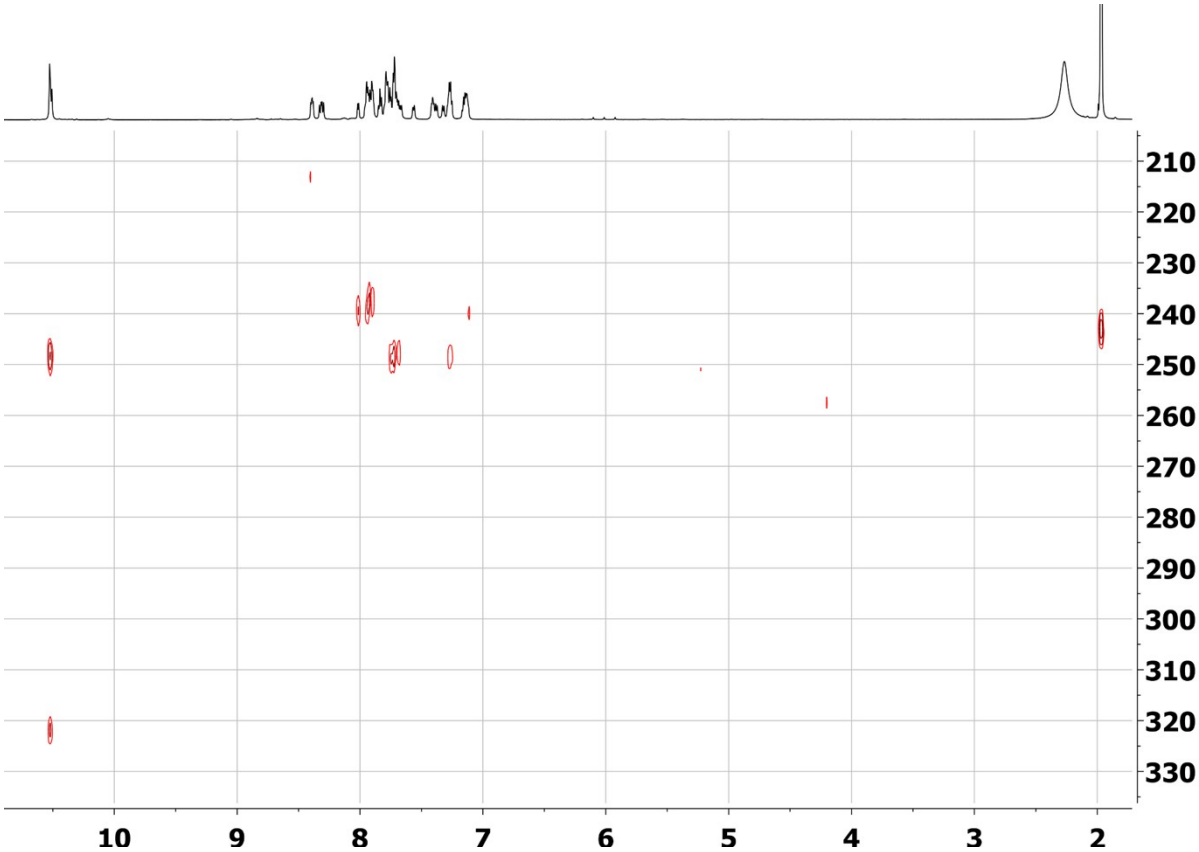


Figure S6. ^{1}H-^{15}N HMBC NMR (600/60 MHz CD_3CN) spectrum of $[Fe^{II}(\mathbf{L})_2](ClO_4)_2$

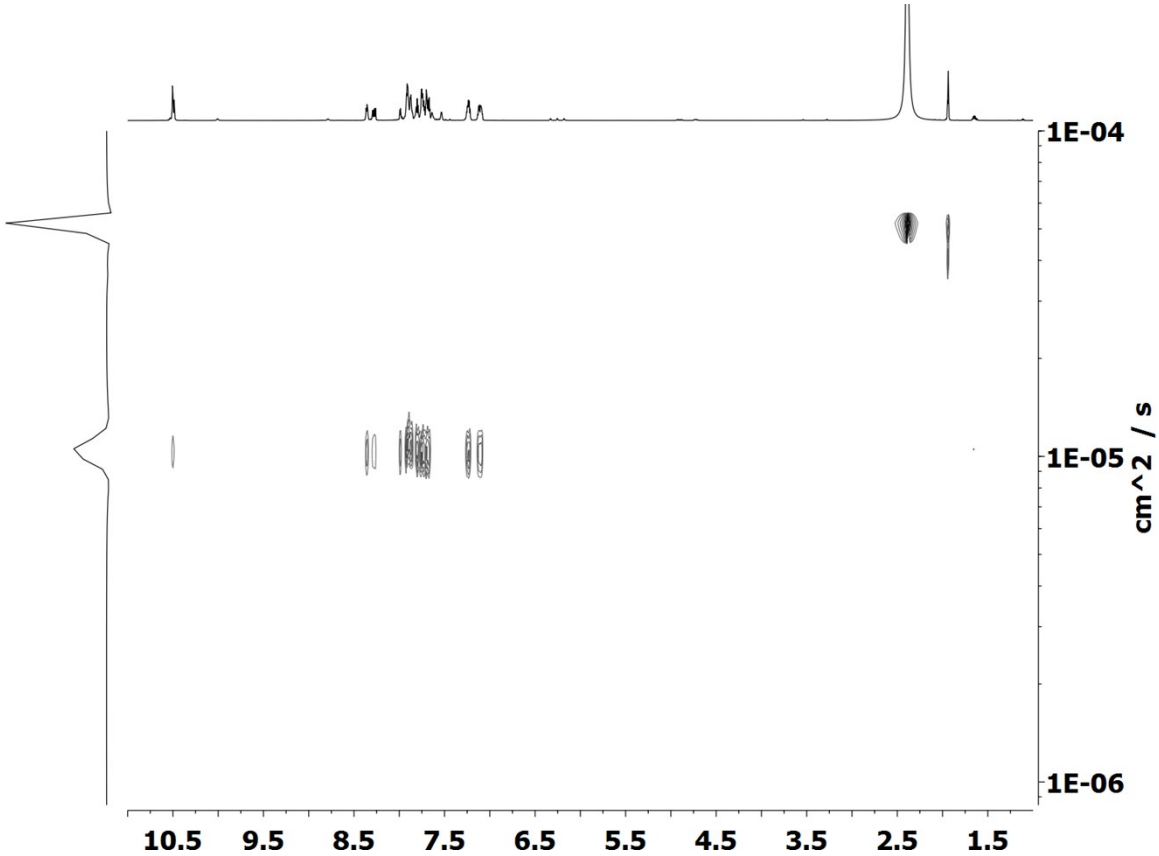


Figure S7. ^{1}H DOSY NMR (700 MHz, CD_3CN) spectrum of $[Fe^{II}(\mathbf{L})_2](ClO_4)_2$. Observed diffusion coefficient D=1.02 10^{-9} m^2/s.

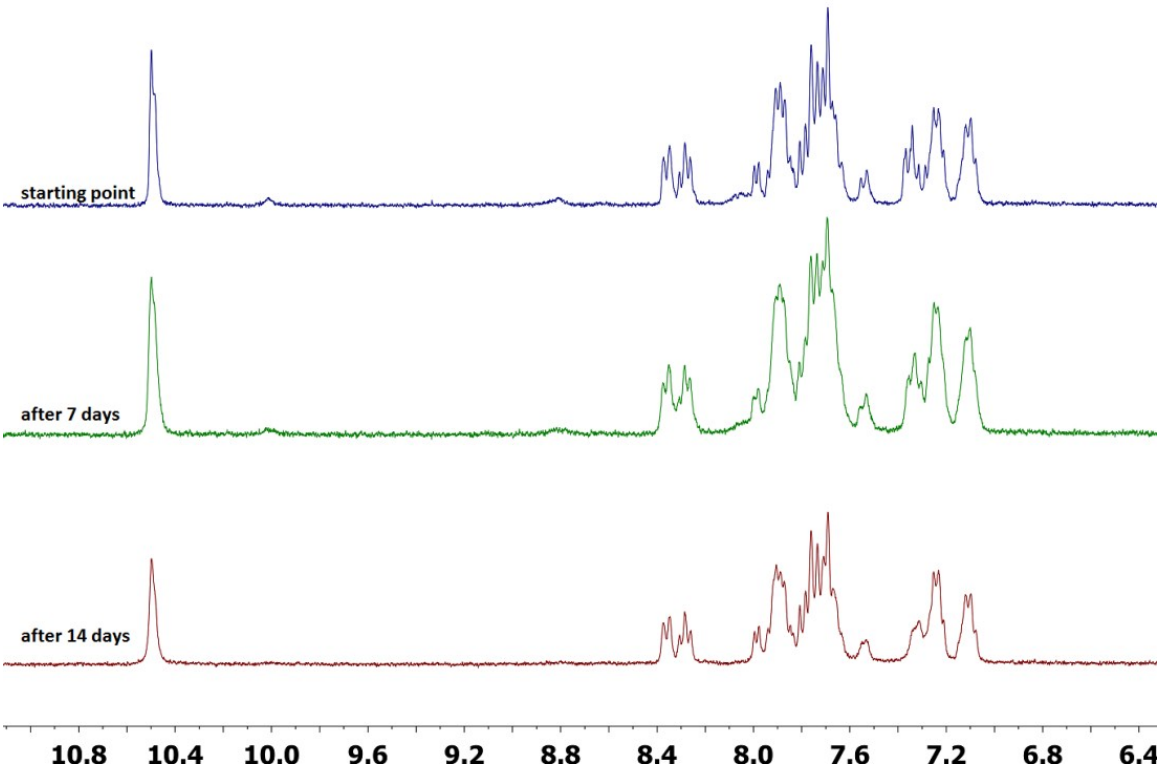


Figure S8: Long term stability of the $[Fe^{II}(\mathbf{L})_2](ClO_4)_2$ complex followed by ^1H NMR (300 MHz CD_3CN) spectra recorded in the absence of oxygen.

2. Mass Spectrometry Data

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3600 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

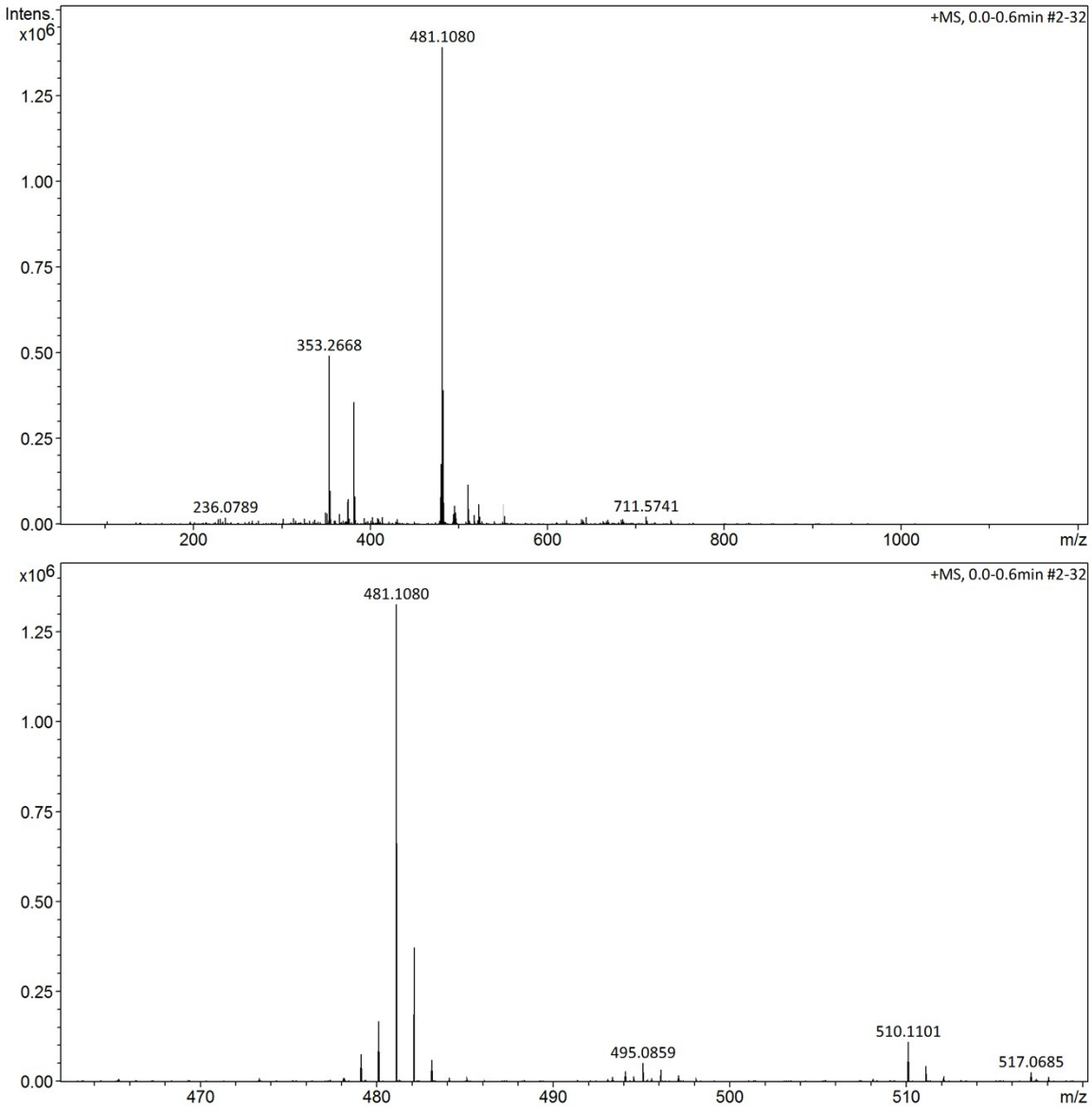
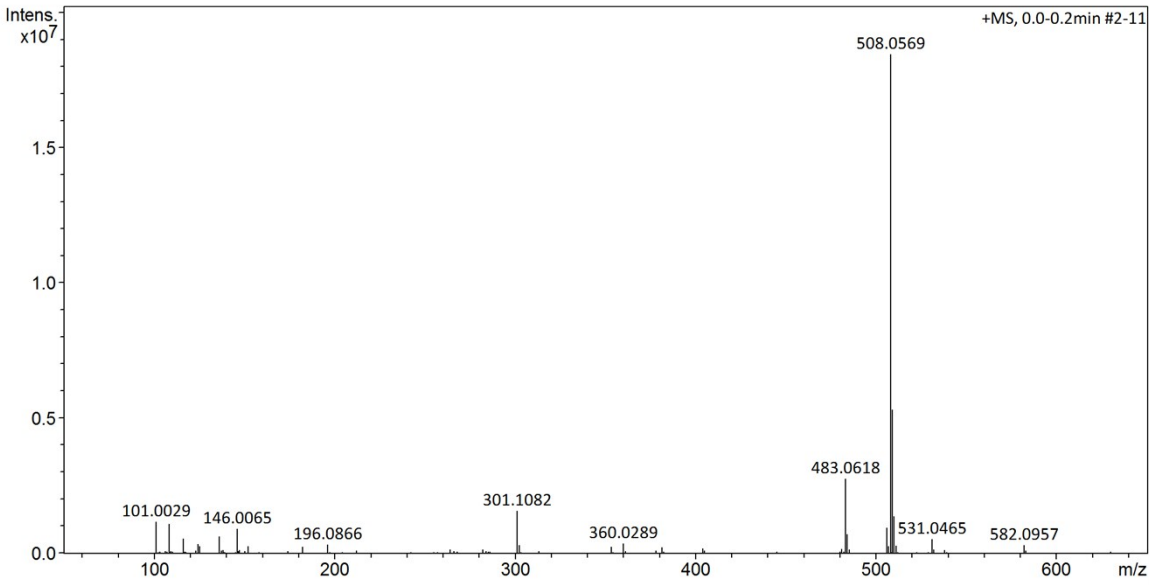


Figure S9. ESI-TOF MS spectrum of $[Fe^{II}(\mathbf{L})_2](ClO_4)_2$. Calc. $\{[Fe^{II}(\mathbf{L})_2]\text{-}H\}^+$ 481.107 m/z. Found 481.1080 m/z.

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	5500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	650 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



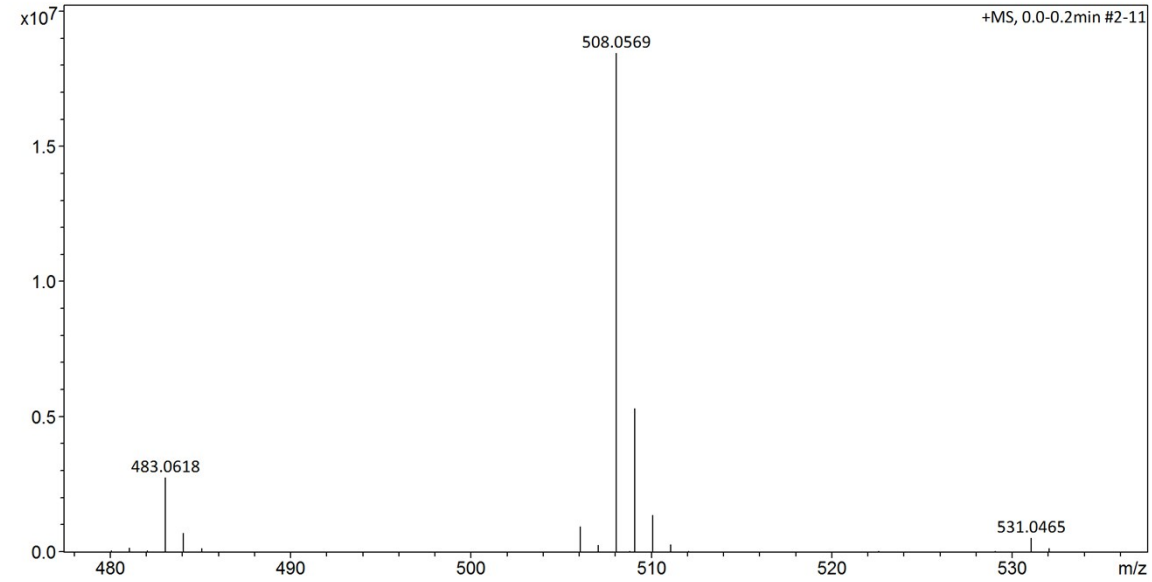


Figure 10. ESI-TOF MS spectrum of $[Fe^{III}(\mathbf{L^{ox}}\text{-H})_2]ClO_4$. Calc. $[Fe^{III}(\mathbf{L^{ox}}\text{-H})_2]^+$ 508. 058 m/z. Found 508.0569 m/z.

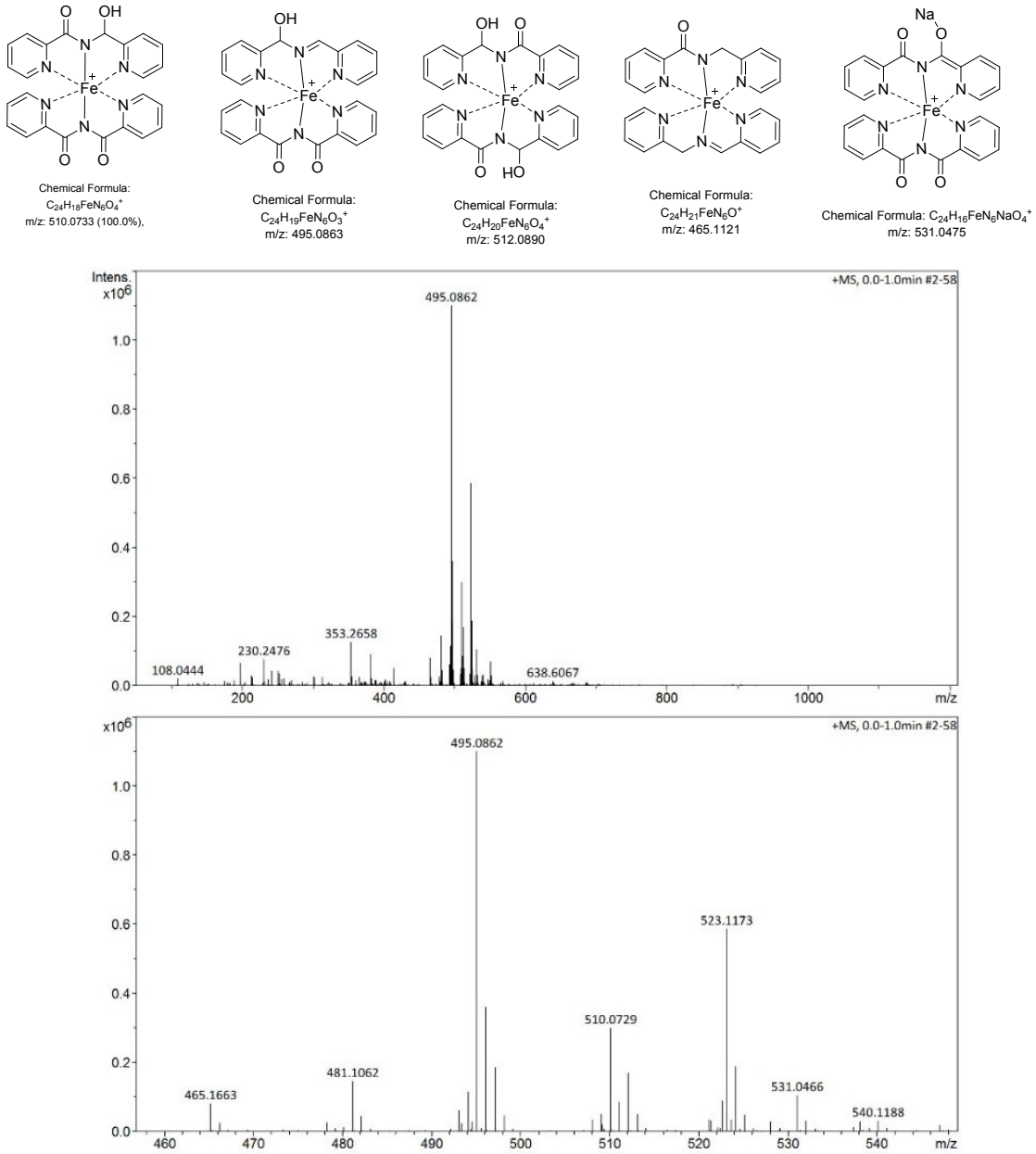


Figure S11. ESI-TOF-MS spectra of the oxidation intermediates found in crystallisation solution (ethanol) and their chemical structures.

3. UV-Vis data

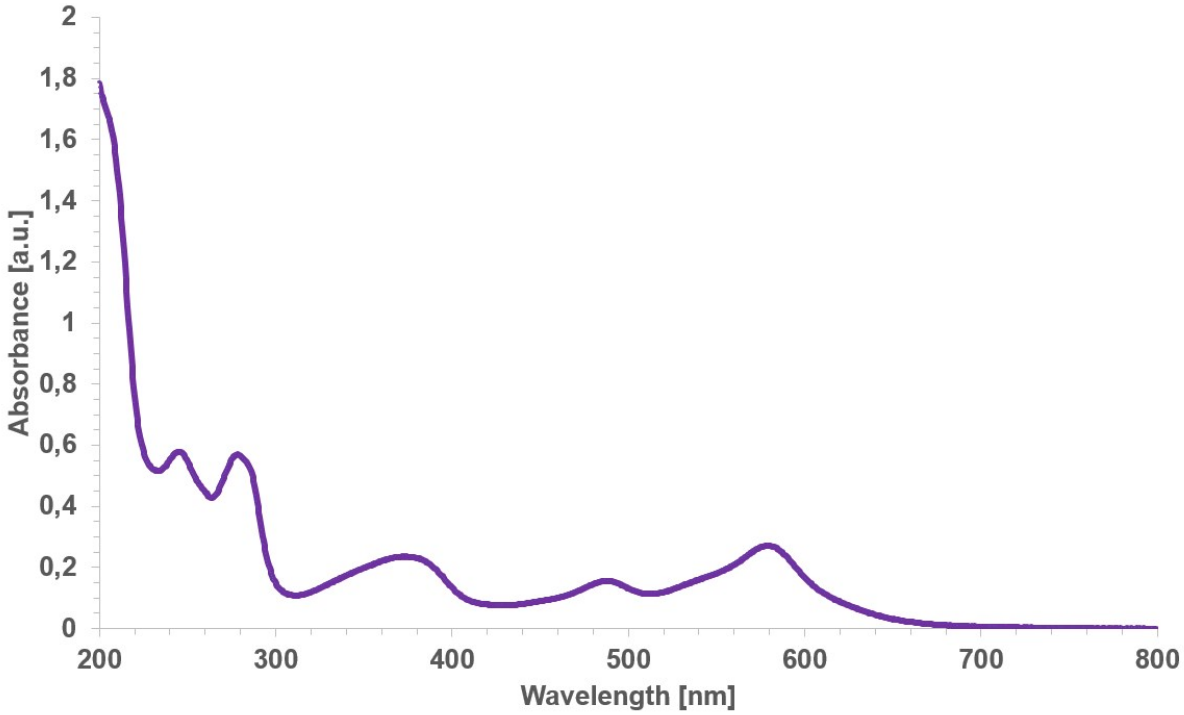


Figure S12. UV-Vis spectrum (MeCN solution) of $[Fe^{II}(\mathbf{L})_2](ClO_4)_2$.

4. Elemental Analysis data

Table S1. Elemental analysis

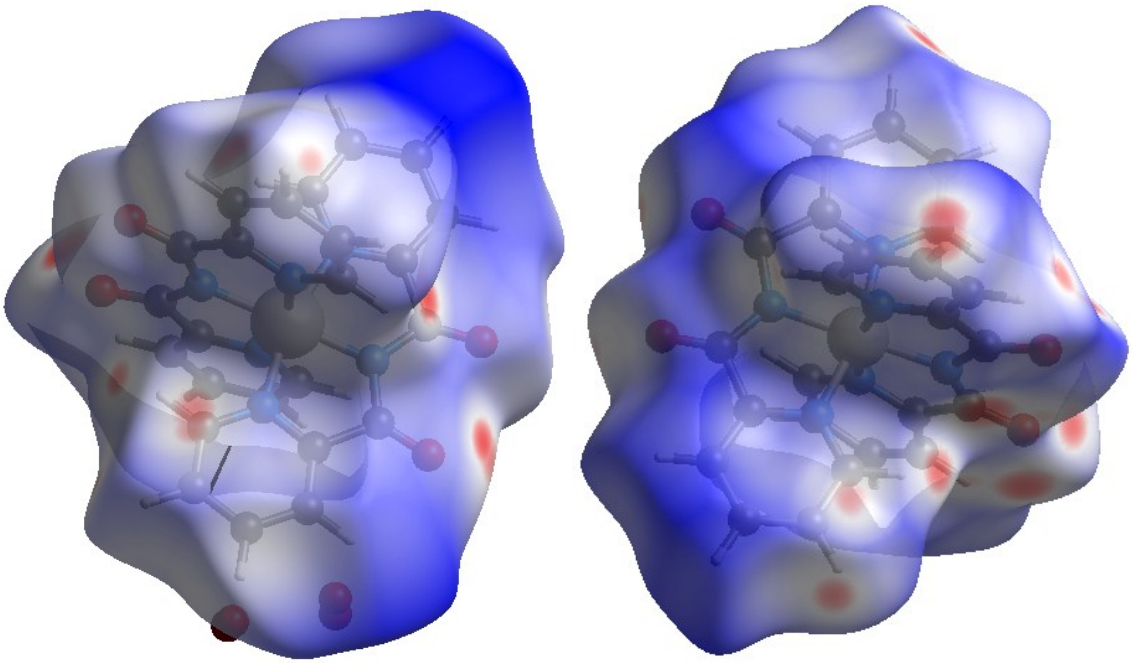
$[Fe^{II}(L)_2](ClO_4)_2 * 2H_2O$ *Calc. for $C_{24}H_{26}Cl_2FeN_6O_{12}$* C: 40.19; H: 3.65; N: 11.72; Found 1: C: 40.16; H: 3.74; N: 11.78; Found 2: C: 40.24; H: 3.64; N: 11.69; Found 3: C: 40.18; H: 3.71; N: 11.79;
$[Fe^{III}(L^{ox}\text{-}H)_2]ClO_4 * C_2H_5OH$ *Calc. for $C_{26}H_{22}ClFeN_6O_9$* C: 47.76; H: 3.39; N: 12.85; Found 1: C: 47.70; H: 3.44; N: 12.91; Found 2: C: 47.67; H: 3.58; N: 12.74; Found 3: C: 47.84; H: 3.50; N: 12.78;

5. Crystallographic data

Suitable single crystals for X-ray analysis were obtained by slow evaporation from ethanol. Data was collected on a 4-circle Xcalibur EosS2 diffractometer (Agilent Technologies) equipped with a CCD detector. X-ray data was collected at room temperature using graphite-monochromated Mo Kα radiation (λα = 0.71073 Å) with the ω-scan technique. For data reduction, UB-matrix determination and absorption correction CrysAlisPro software was used[1]. Using Olex2[2], the structure was solved by direct methods using ShelXL[3], and refined by full-matrix least-squares against F2 utilizing with the program SHELXL[4]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in idealized positions by molecular geometry and refined as rigid groups. Uiso of hydrogen atoms were set as 1.2 (for C-carries) and 1.5 (for O-carriers) times Ueq of the corresponding carrier atom. Selected structural parameters are reported in Table 1. Structure of $[Fe^{III}(\mathbf{L^{ox}}\text{-H})_2]ClO_4$.contain solvent accessible voids with small amount of solvent molecule(s) used for recrystallization. As they could not be modelled satisfactorily data were treated with the solvent mask in Olex2. Single-crystal structure analysis reveals that $[Fe^{III}(\mathbf{L^{ox}}\text{-H})_2]ClO_4$. crystallizes in the triclinic system P-1 space group. The Fe(III) ion is six-coordinated showing an almost perfected octahedral coordination geometry.

Table S2 Crystal data and structure refinement for $[Fe^{III}(\mathbf{L^{ox}}\text{-H})_2]ClO_4$.

Identification code	Radiation MoKα (λ = 0.71073)
Empirical formula C24H16ClFeN6O8	2Θ range for data collection/° 8.206 to 50.048
Formula weight 607.73	Index ranges -10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -15 ≤ l ≤ 16
Temperature/K 293(2)	Reflections collected 41842
Crystal system triclinic	Independent reflections 4442 [Rint = 0.0664, Rsigma = 0.0396]
Space group P-1	Data/restraints/parameters 4442/0/361
a/Å 8.9536(2)	Goodness-of-fit on F2 1.065
b/Å 11.9966(3)	Final R indexes [I>=2σ(I)] R1 = 0.0480, wR2 = 0.1295
c/Å 13.8709(3)	Final R indexes [all data] R1 = 0.0612, wR2 = 0.1373
α/° 107.694(2)	Largest diff. peak/hole / e Å-3 0.49/-0.43
β/° 105.087(2)	
γ/° 99.040(2)	
Volume/Å3 1324.54(6)	
Z 2	
ρcalcg/cm3 1.524	
μ/mm-1 0.730	
F(000) 618.0	
Crystal size/mm3 0.3 × 0.2 × 0.1	



(a) (b)

Figure S13 Hirshfeld surface representations (viewed down a) for (a) $[Fe^{III}(\mathbf{L^{ox}}\text{-H})_2]ClO_4$ (= $[Fe(bpca)_2]ClO_4$) and (b) $[Co(bpca)_2]ClO_4.CH_3OH$,[5] CCDC 187392. Red regions indicate points where interaction with an adjacent atom exceeds that of dispersion; in both cases, the atoms adjacent to the oxygen centres are aromatic hydrogen.

6. Supplementary References

1. Oxford Diffraction, Oxford Diffraction Ltd., Xcalibur CCD system, CrysAlis Software system, Version 1.171, **2004**.

2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339-341.

3. G. M. Sheldrick, *Acta Cryst. A* 2015, **71**, 3-8.

4. G. M. Sheldrick, *Acta Cryst. C* 2015, **71**, 3-8.

5. J. M. Rowland, M. M. Olmstead and P. K. Mascharak, *Inorg. Chem.* 2002, **41**, 2754-2760.