

## **A Strong-Field Pentadentate Ligand in Iron-based Oxidation Catalysis and Implications for Iron(IV) Oxo Intermediates**

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### **Supporting Information**

#### **X-Ray Crystallography**

##### **The X-ray crystal structure of [Fe(1)(CH<sub>3</sub>CN)](ClO<sub>4</sub>)<sub>2</sub>**

The crystals of [Fe(1)(CH<sub>3</sub>CN)](ClO<sub>4</sub>)<sub>2</sub> were found to contain two independent cationic complexes (A and B) shown in Figs. 1 and S2 respectively.

The coordinated acetonitrile ligand in molecule B was found to be disordered. Two orientations were identified of ca. 77 and 23% occupancy, their geometries optimised, the thermal parameters of adjacent chemically equivalent atoms restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically.

All four of the perchlorate anions were found to be disordered. For the Cl(1)-based anion three orientations were identified of ca. 37, 35 and 28% occupancy, their geometries optimised, the thermal parameters of adjacent chemically equivalent atoms restrained to be similar, and only the chlorine atoms of each orientation were refined anisotropically. For each of the Cl(2)-, Cl(3) and Cl(4)-based anions two orientations were identified of ca. 88:12, 83:17 and 71:29% occupancy, their geometries optimised, the thermal parameters of adjacent chemically equivalent atoms restrained to be similar, and only the chlorine atoms of each orientation and the oxygen atoms of the major occupancy orientation were refined anisotropically.

The included dichloromethane solvent was found to be distributed across two discrete sites, one in a general position [based on C(50)] and one adjacent to a centre of symmetry [based on C(60)] which consequently could not be more than 50% occupancy. The solvent in the general position was found to be disordered. Three orientations were identified of ca. 36, 23 and 16% occupancy; inspection of the thermal parameters suggested that this site was only ca. 75% occupied, and so the sum of the occupancies of the three identified orientations was fixed at this value. The geometries of all three orientations were optimised, the thermal parameters of adjacent chemically equivalent atoms were restrained to be similar, and only the chlorine atoms of each orientation were refined anisotropically.

### **The X-ray crystal structure of [ $\{\text{Fe}(\mathbf{1})\}_2\text{O}\}(\text{ClO}_4)_4$**

The crystals of [ $\{\text{Fe}(\mathbf{1})\}_2\text{O}\}(\text{ClO}_4)_4$ , which grew as very thin plates, were badly twinned and of low quality, and were found to be very weak scatterers of X-rays; despite a ca. 70 hour data collection the mean  $I/\sigma$  is only ca. 3.5. The primitive monoclinic cell given above transforms to a *C*-face centred orthorhombic cell of double the volume [12.908, 21.150, 38.877, 90.00, 90.00, 89.84]. Initially this orthorhombic cell had been thought to be the correct one and so, given the already apparent very weak nature of the scattering, the data collection was designed on the assumption of *mmm* symmetry. Unfortunately, this resulted in an incomplete data set. Despite this issue, however, this structure still has value as the identity of the species present is clear even if the details are less than ideal.

The structure of [ $\{\text{Fe}(\mathbf{1})\}_2\text{O}\}(\text{ClO}_4)_4$  was found to contain an oxygen bridged dimeric tetracation, four perchlorate anions, and included acetonitrile and water solvent molecules (one of each). The Cl(3)-based perchlorate anion was found to be disordered. Two orientations were identified of ca. 69 and 31% occupancy, their geometries optimised, the thermal parameters of adjacent atoms restrained to be similar, and only the chlorine atoms of each orientation and the oxygen atoms of the major occupancy orientation were refined anisotropically. The hydrogen atoms of the included water molecule could not be located, and so the asymmetric unit is low by  $\text{H}_2$  and the unit cell by  $\text{H}_8$ .

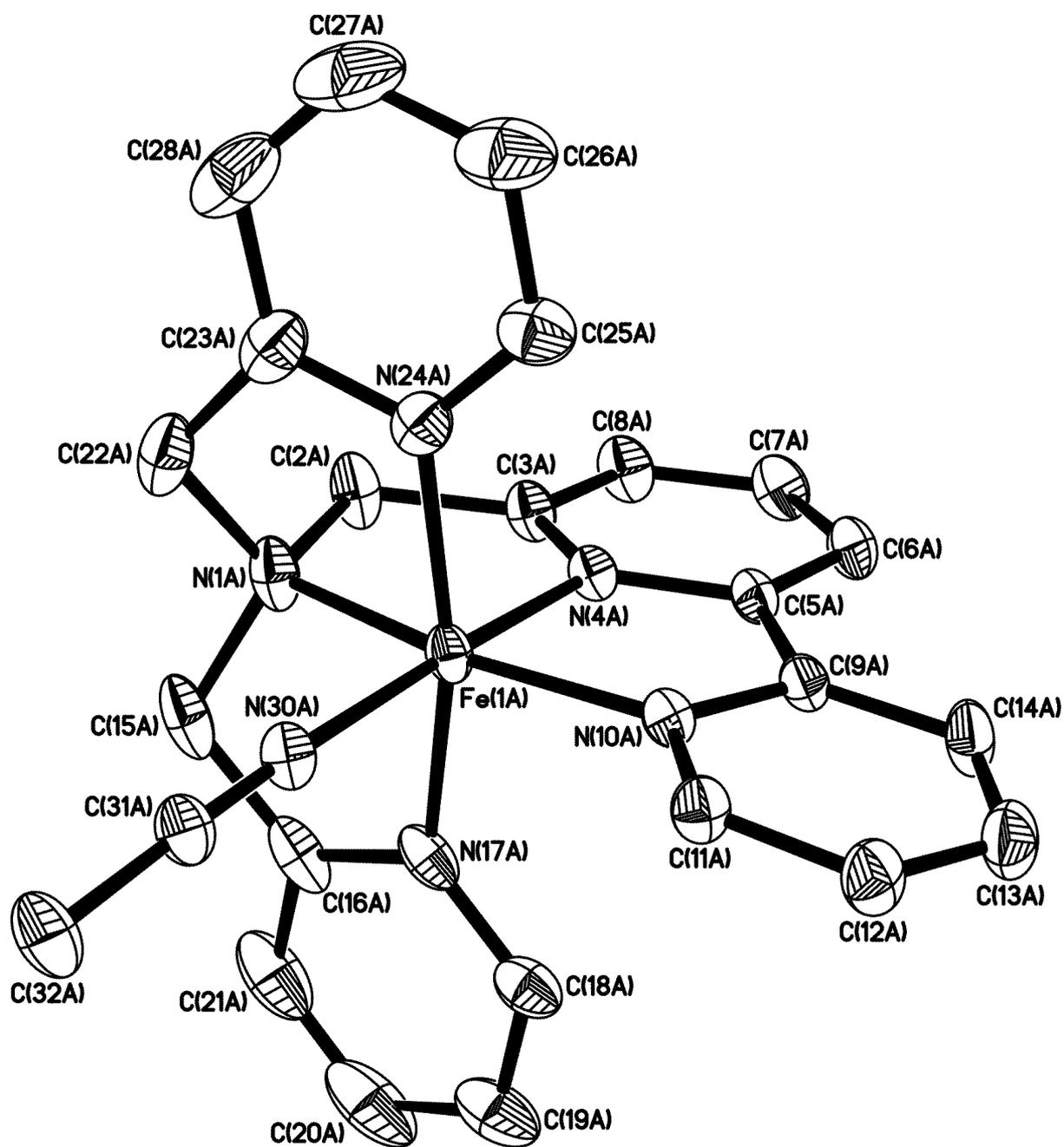


Fig. S1 The molecular structure of one (A) of the two independent cationic complexes present in the crystals of  $[\text{Fe}(\mathbf{1})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$  (30% probability ellipsoids).

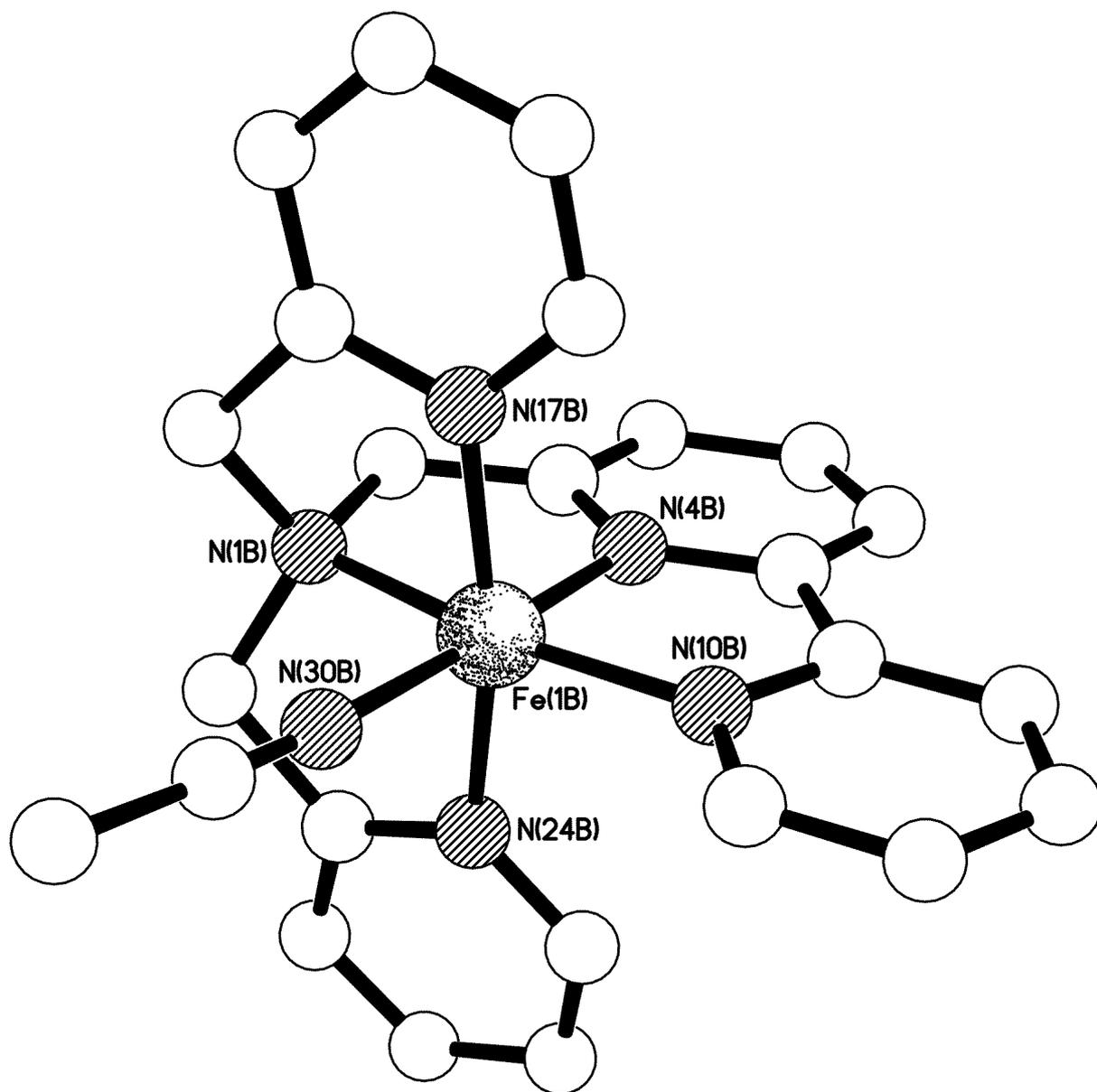


Fig. S2 The molecular structure of one (B) of the two independent cationic complexes present in the crystals of  $[\text{Fe}(\mathbf{1})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$ .

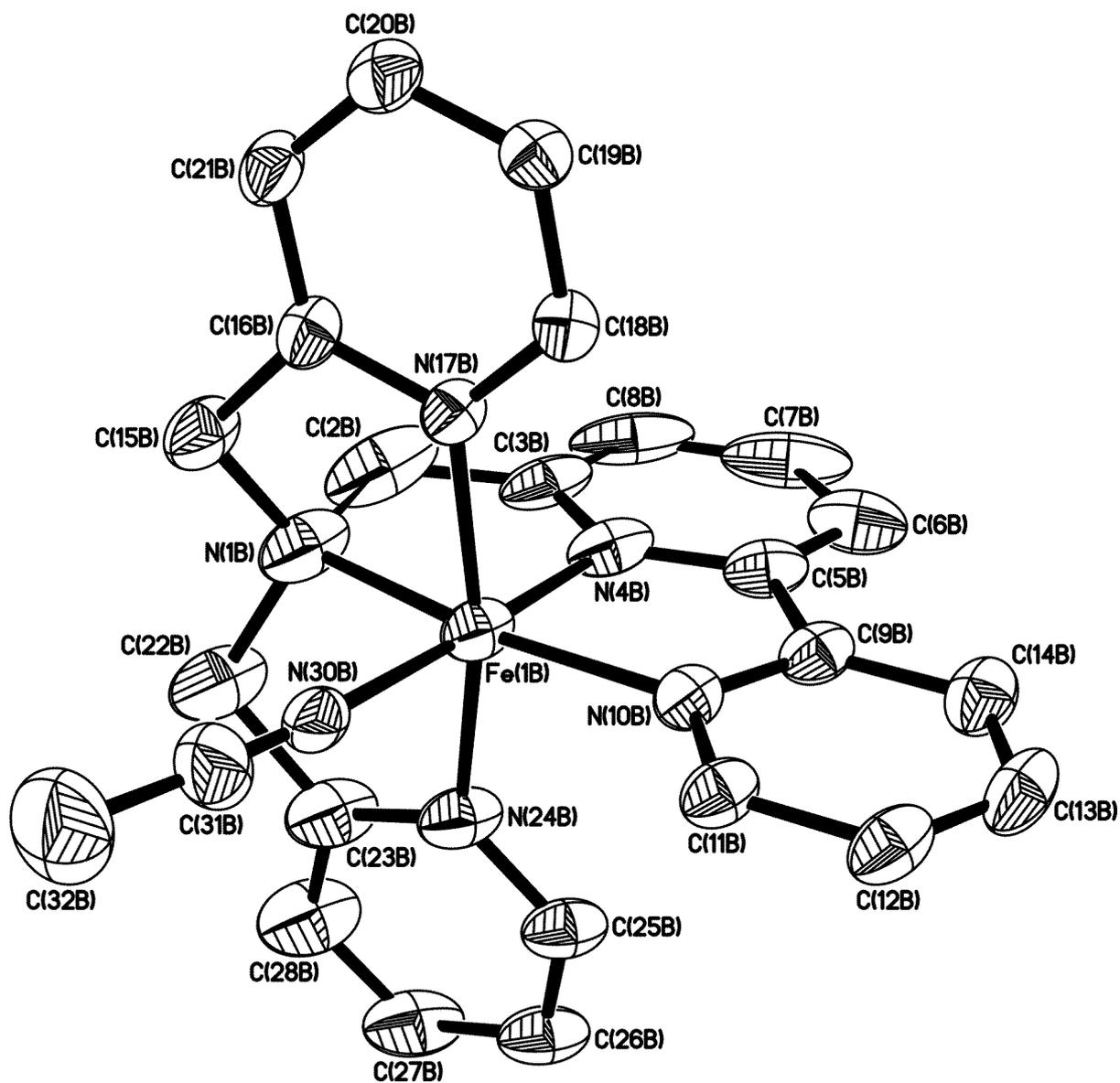


Fig. S3 The molecular structure of one (B) of the two independent cationic complexes present in the crystals of  $[\text{Fe}(\mathbf{1})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$  (30% probability ellipsoids).

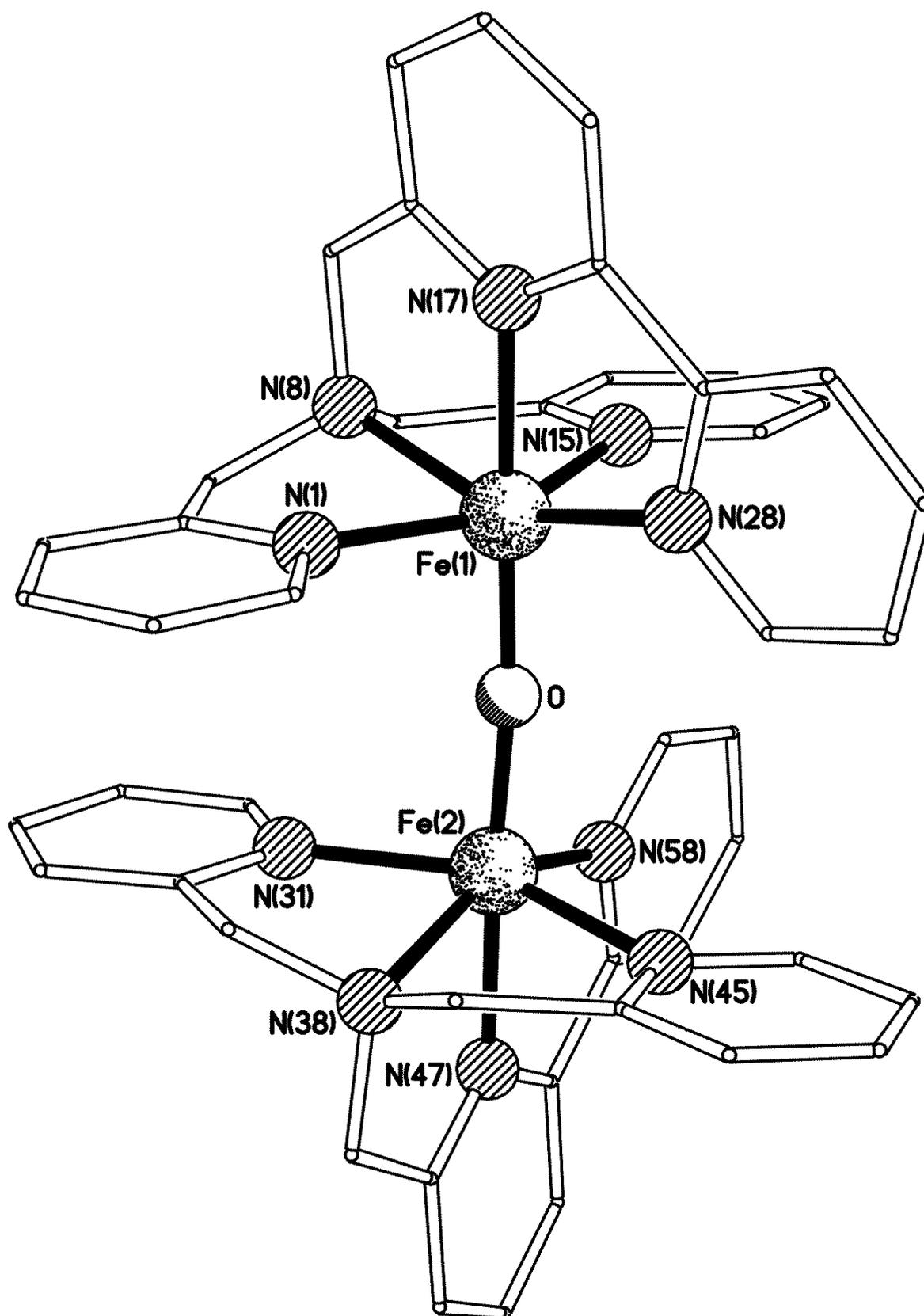


Fig. S4 The molecular structure of the cation in complex  $[\{\text{Fe}(\mathbf{1})\}_2\text{O}](\text{ClO}_4)_4$ .

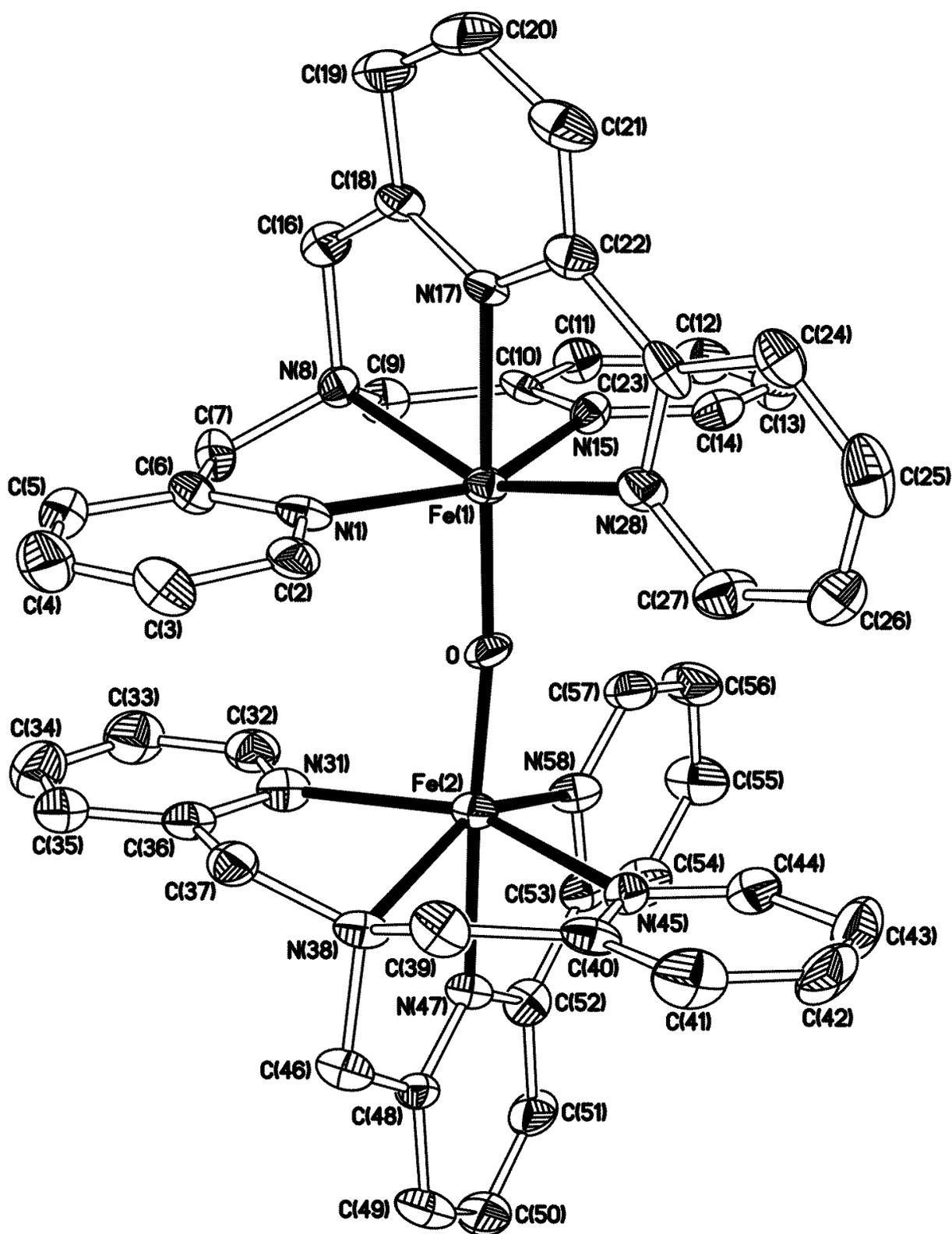


Fig. S5 The molecular structure of the cation in complex  $[\{\text{Fe}(\mathbf{1})\}_2\text{O}](\text{ClO}_4)_4$  (50% probability ellipsoids).

## NMR Spectroscopy

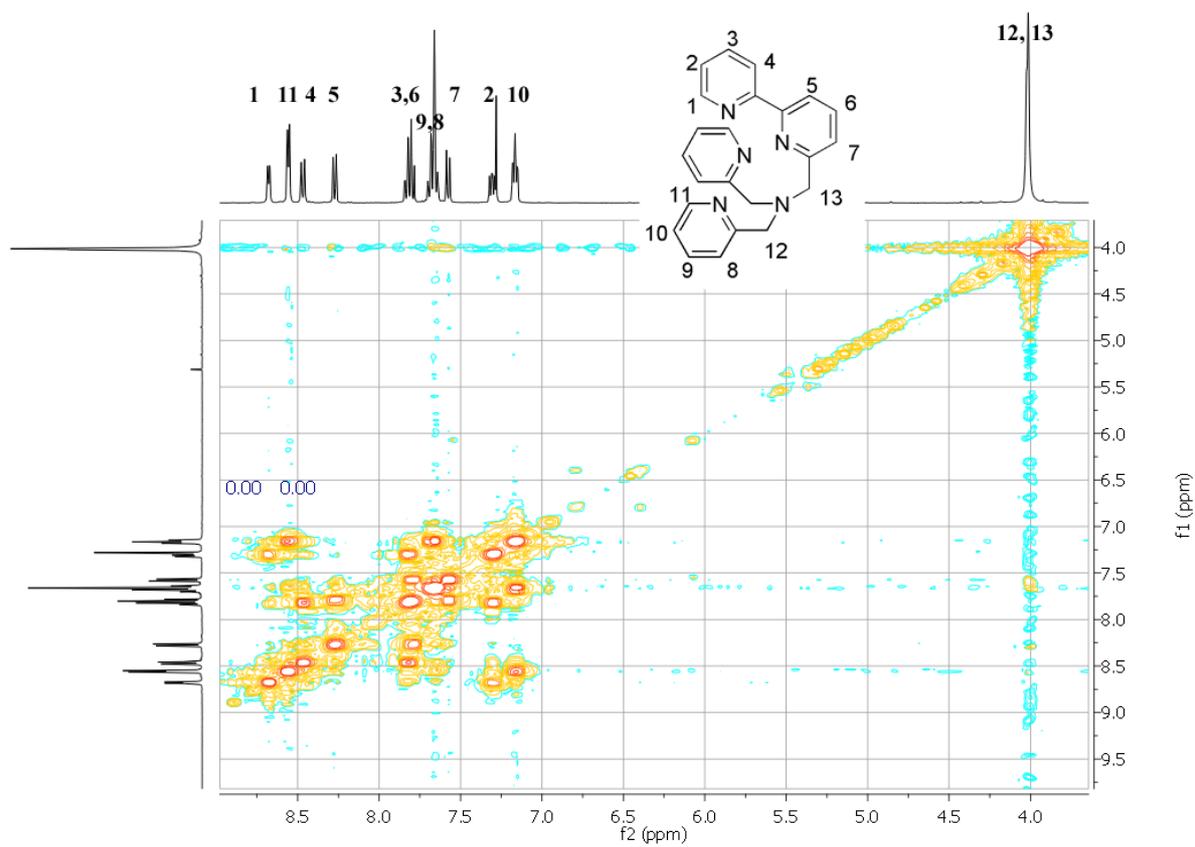


Figure S6. COSY NMR spectrum of the ligand BPABIPY (1) and peak assignment.

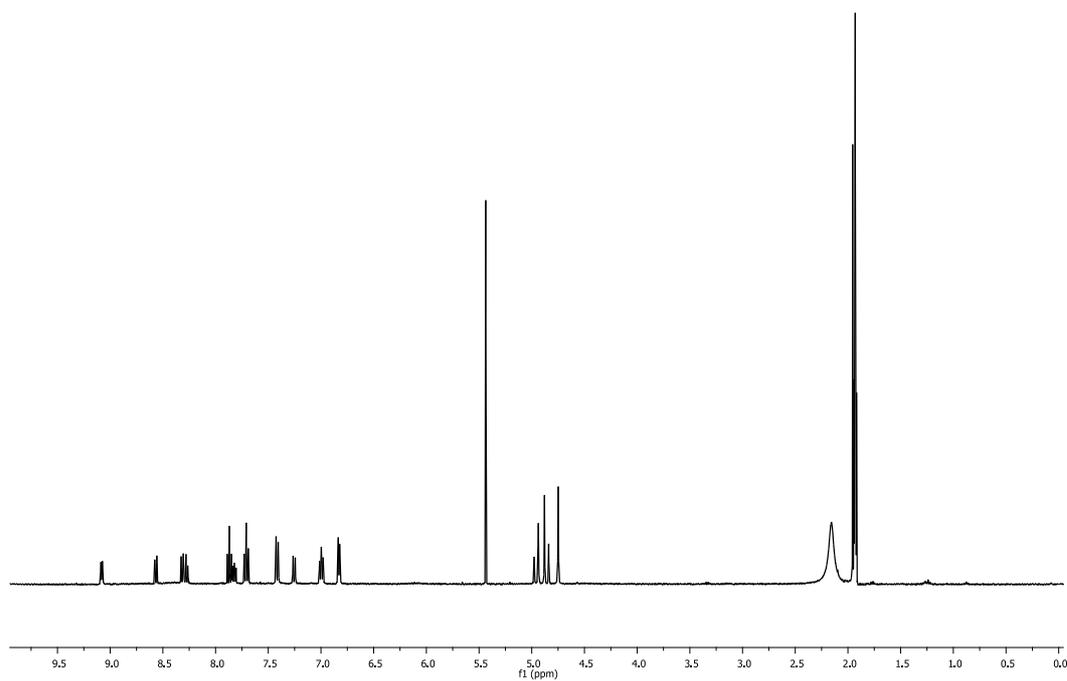


Figure S7. <sup>1</sup>H NMR spectrum of [Fe(**1**)(CH<sub>3</sub>CN)](ClO<sub>4</sub>)<sub>2</sub> in CD<sub>3</sub>CN at 298 K.

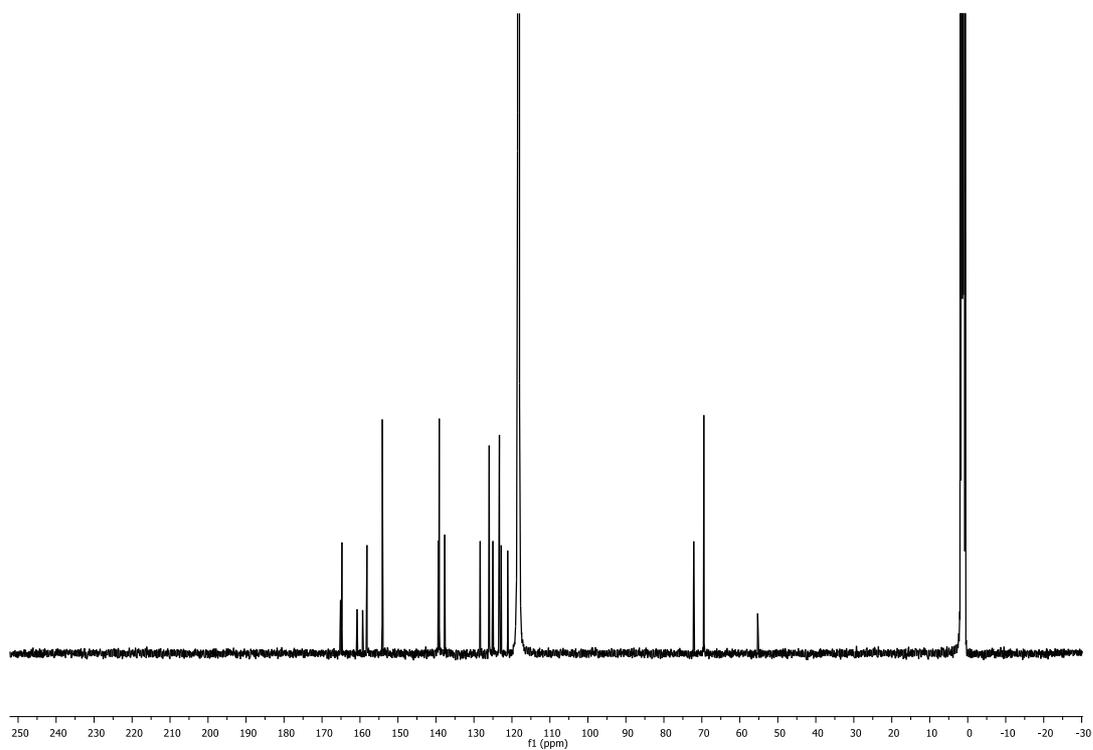


Figure S8. <sup>13</sup>C NMR spectrum of [Fe(**1**)(CH<sub>3</sub>CN)](ClO<sub>4</sub>)<sub>2</sub> in CD<sub>3</sub>CN at 298 K.

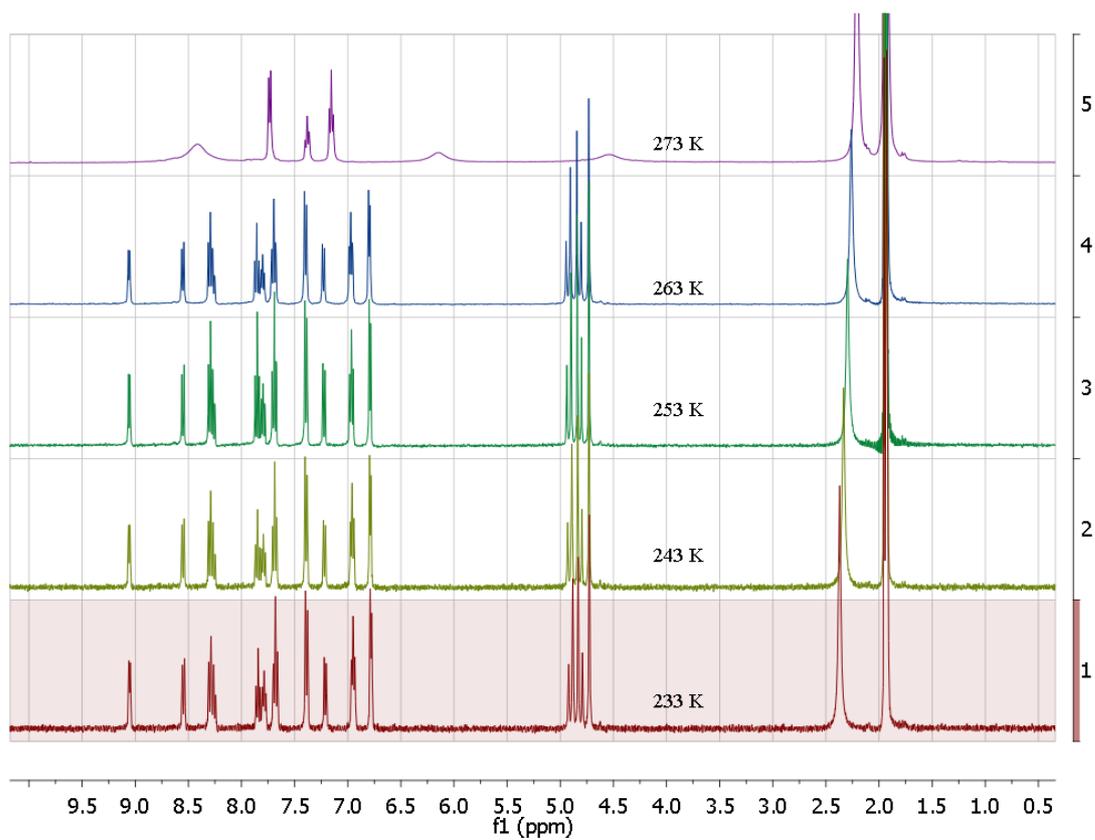


Figure S9: VT <sup>1</sup>H NMR spectra of the reaction between [Fe(1)(CH<sub>3</sub>CN)](ClO<sub>4</sub>)<sub>2</sub> and PhIO in acetonitrile from 233 K to 273 K.

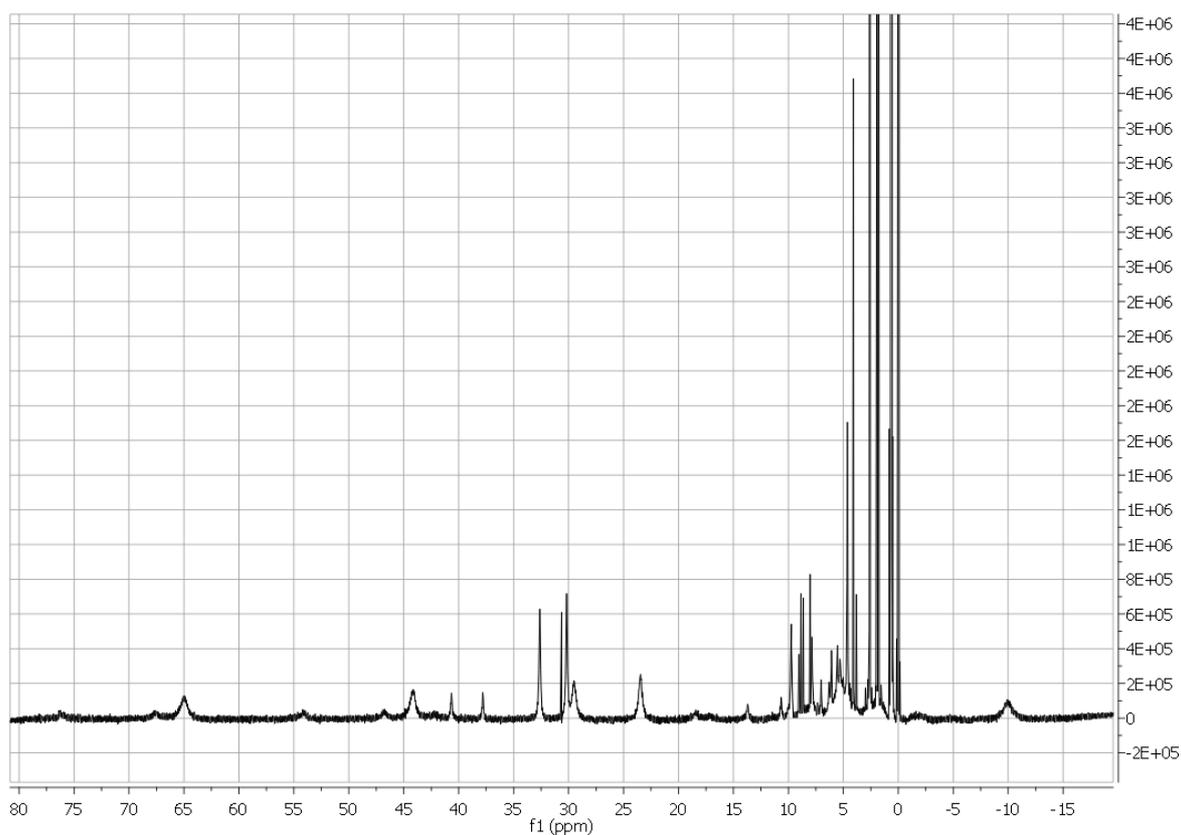


Figure S10:  $^1\text{H}$  NMR spectrum of  $[\text{Fe}(\mathbf{1})(\text{CH}_3\text{CN})(\text{ClO}_4)_2]$  in  $\text{CD}_3\text{CN}$  at 343 K after reaction with PhIO.

### UV-vis spectroscopy

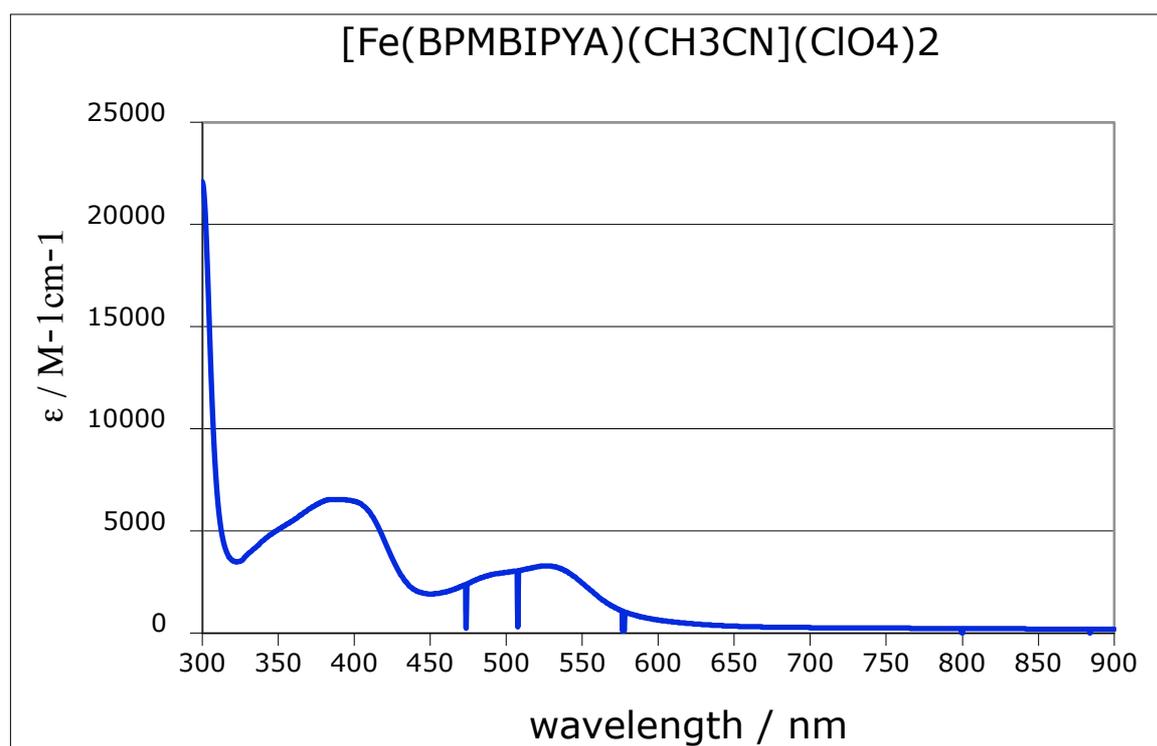


Figure S11. UV/VIS spectrum of [Fe(1)(CH<sub>3</sub>CN)](ClO<sub>4</sub>)<sub>2</sub> in acetonitrile at 298 K.

## Cyclic voltammetry

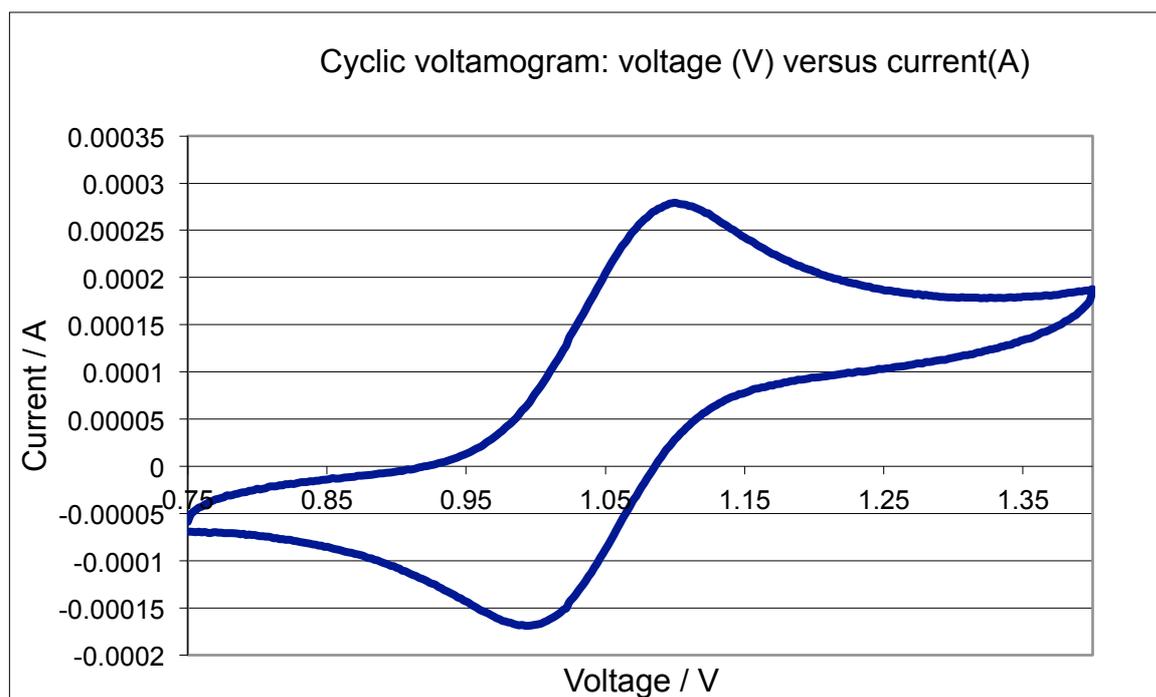


Figure S12. Cyclic voltammogram of  $[\text{Fe}(\mathbf{1})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$ , 1 mM in 0.1 M solution of  ${}^n\text{Bu}_4\text{NPF}_6$  in acetonitrile at a scan rate of 100 mV/s.