Supplementary Information

Design of Molecular Scaffolds Based on Unusual Geometries for Magnetic Modulation of Spin-diverse Complexes with Selective Redox Response

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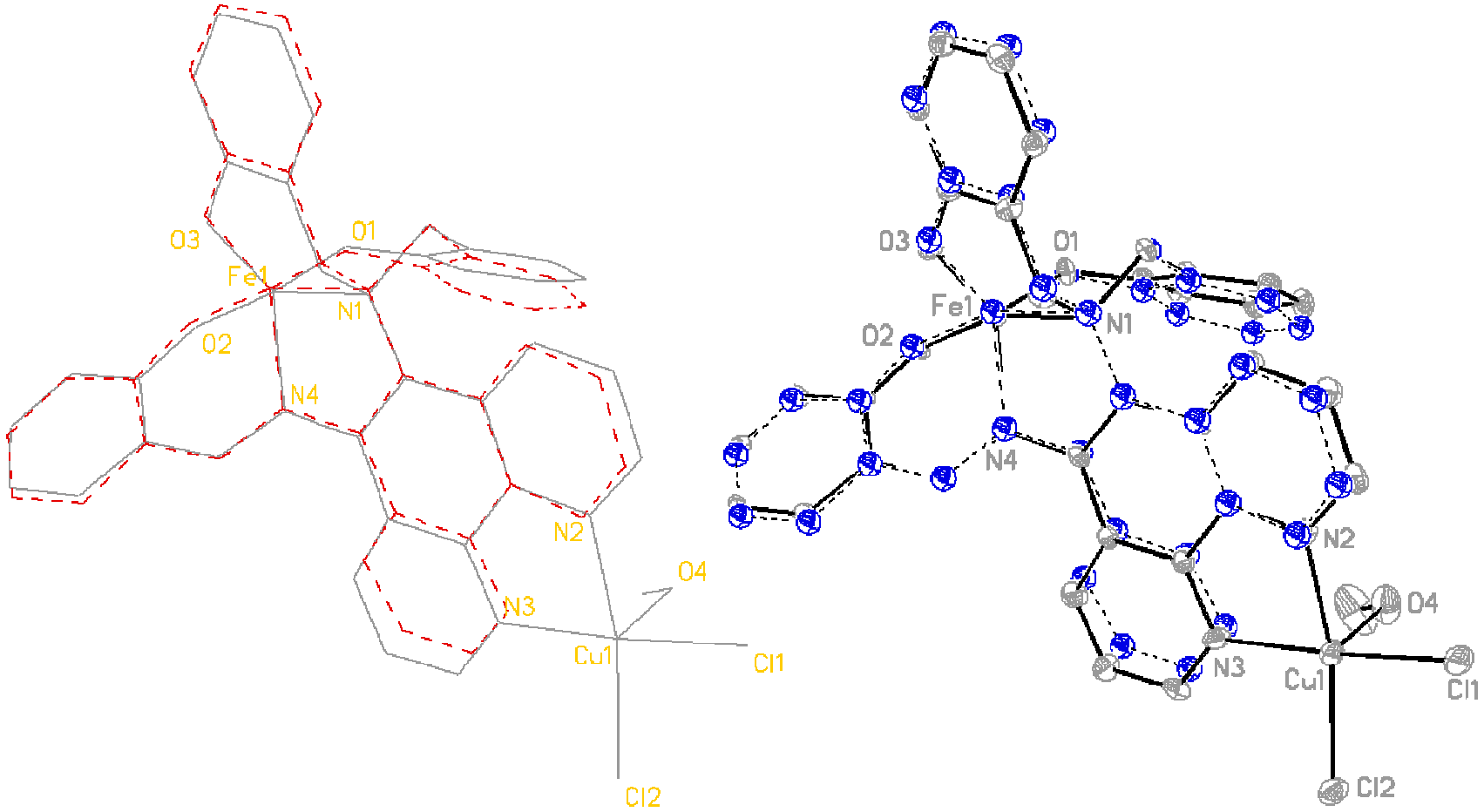
Figure S1. Two different views for the overlap of the least-squares fits for **2** and **3** Dihedral angles between the outer rings of the phenanthroline ligands are 9.5(2) ^{o} for **2** and 1.5(5) ^{o} for **3**.



Analysis of the EPR Spectrum for High Spin Fe(III) centers.

The EPR spectra of high spin Fe(III), S = 5/2, powder samples can be very complex, but become simpler when the zero field interactions have magnitudes greater than the photon energy of the EPR spectrometer. This behavior is demonstrated in **Figures 2S, 3S and 4S**, where simulations are presented for various relevant situations for an X-band EPR spectrometer. These spectra were calculated assuming using the spin Hamiltonian given in the paper with g = 2.0 and various values of D and E and a spectrometer frequency of 9.75 GHz. The fourth order spin terms were taken to be zero. The D, E values are listed in gauss and the relevant value for the photon energy in gauss is 3500, so values of D greater than 3500 gauss have zero field interactions greater than the Zeemann energy of the system.

In **Figure 2S**, we have plotted spectra for the maximum magnitude of E, which is one-third of D. Note that for D values below 3500 gauss, the spectra show many features from B = 0 to 10000 gauss but for higher D values only the peak at g = 4.3 is present. At higher gain a second turning point is noted at g = 8. This single peak at g = 4.3 has been observed frequently for biological samples containing high spin Fe(III).

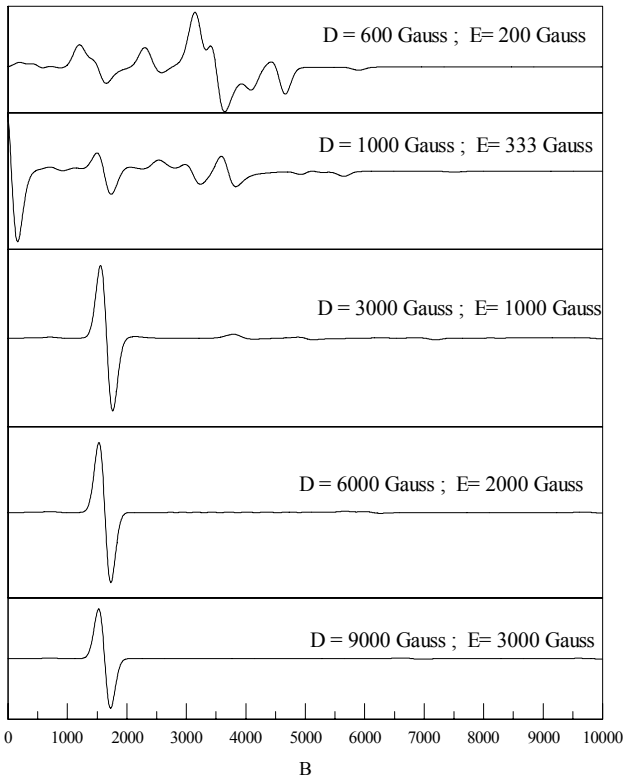


Figure S2. Fe(III) EPR spectra simulated for E = D/3 case. The peak at 1600 gauss (g ~ 4.3) persists as D increases. Notice the major changes when D is less than 3000. Simulation assumes X-band frequency of 9.75 GHz (3500 gauss).

In **Figure 3S**, we have plotted spectra for different D values but the symmetry has been taken as axial where E = 0. In this case the spectrum is dominated by one peak when D is much greater than 3500 gauss but it has a g value of 6 instead of 4.3. This spectrum is commonly observed in Fe(III) porphyrins.

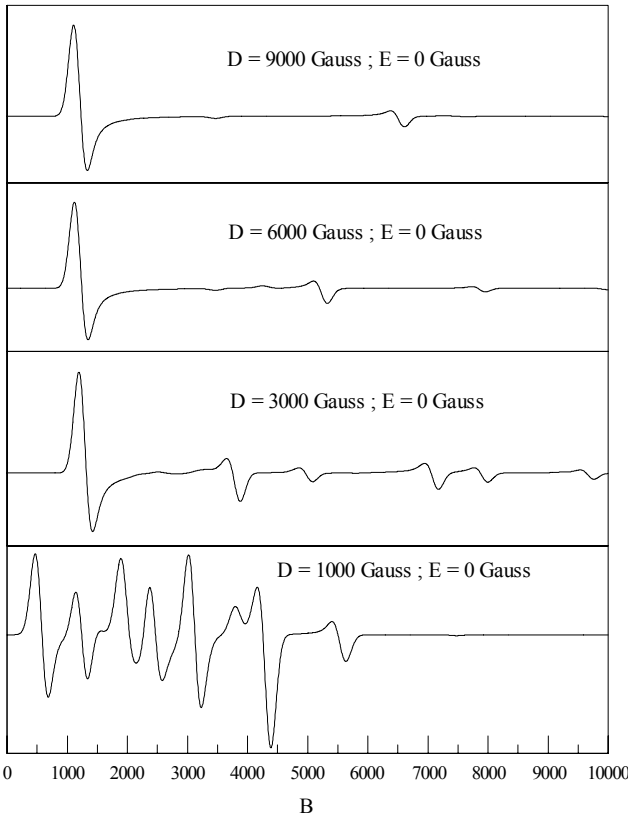


Figure S3. Figure shows how EPR spectrum of Fe(III) changes with D when E = 0. Note that the peak at 1200 gauss (g ~ 6) remains fixed above D = 3000 gauss. This continues to remain there for much larger D values. It is the only peak detected in Fe(III) porphyrins.

In **Figure 4S**, we observe the effect of varying E for a value of D = 6000 gauss, larger than 3500 gauss. It will be noted that as E is reduced from it's maximum value of D/3 the g = 4.3 line becomes asymmetric and splits into multiple lines. Also the intensity off the g = 8 turning point strengthens relative to the main peak at g = 4.3. This mainly is what we observe in our Fe(III) spectrum and thus leads us to propose that D is much greater than 0.3 cm^{-1} and that the magnitude of E is slightly less than D/3.

In this system the only way to get good values for the zero field parameters is to study the EPR spectra over a larger range of magnetic fields with spectrometer frequencies much larger than that of an X-band spectrometer.

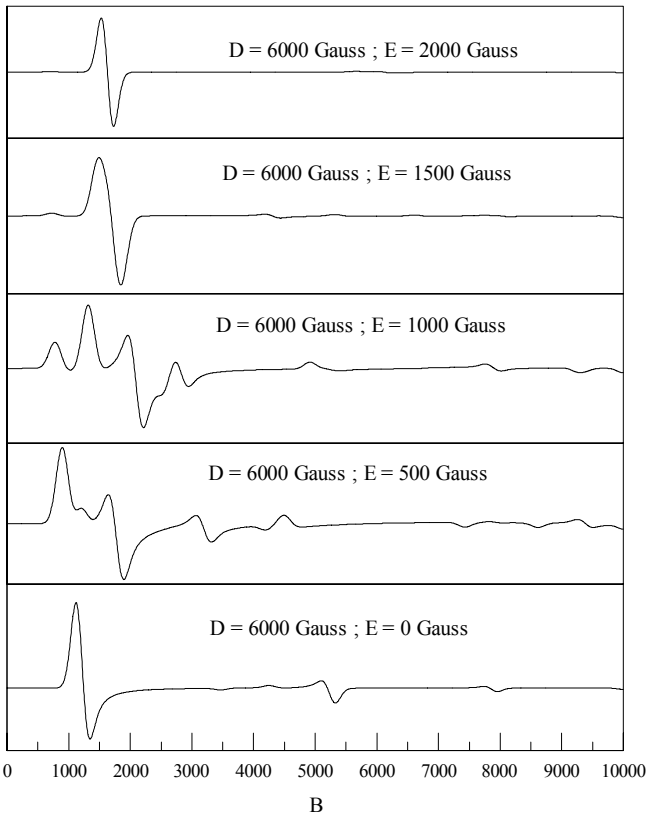
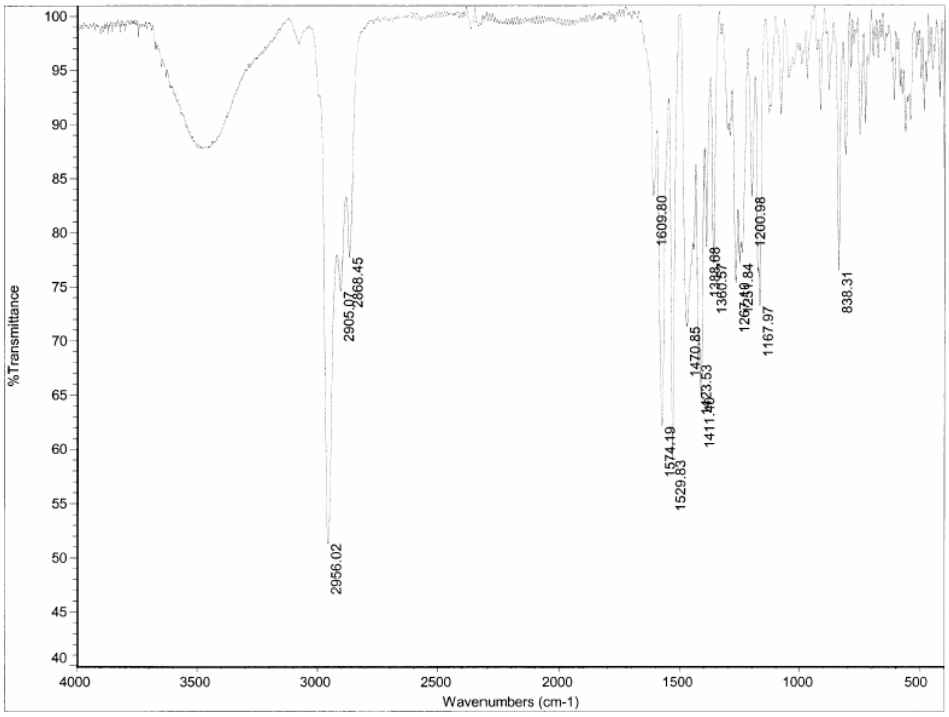


Figure S4. Figure shows simulated Fe(III) spectra for different values of E with D = 6000 gauss to maximum E value of D/3 = 2000 gauss. Note that semi peak at 800 gauss becomes more prominent at E = 1500 gauss.

Figures S5 and S6: Infrared Spectrum for 3.

From 4000 to 400 cm^{-1}



From 1800 to 400 cm^{-1}