

Supporting Informations

Axial Thiophenolate Coordination on Diiron(III)bisporphyrin: Influence of Heme-Heme Interactions on Structure, Function and Electrochemical Properties of the Individual Heme Center

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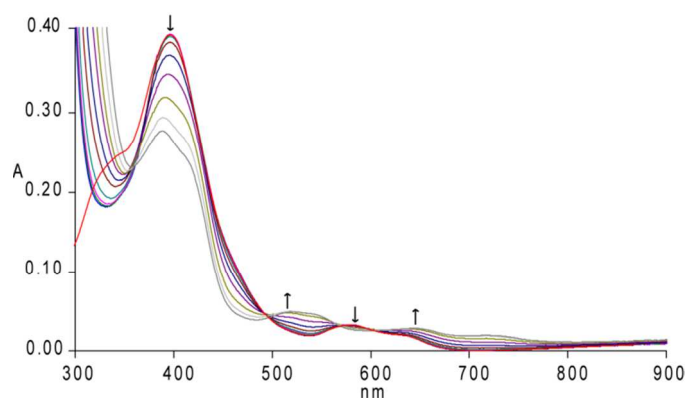


Figure S1. Time resolved UV-vis spectral changes upon gradual addition of thiophenol to a solution of **1** ($\sim 10^{-6}$ M) in DCM at 298K, as the host:guest ratio changes from 1:0 to 1:5. Arrows indicate an increase or decrease of band intensity.

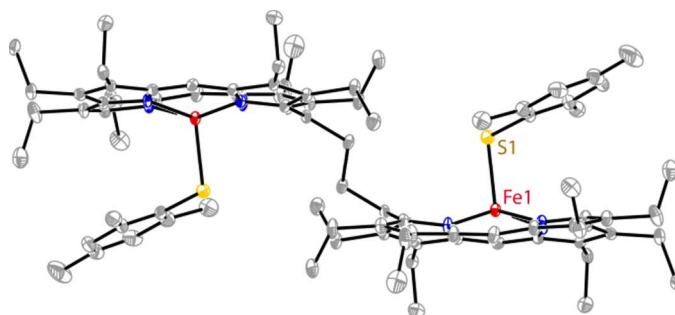


Figure S2. A perspective view of **2b** showing 50% thermal contours for all non-hydrogen atoms at 100 K (H atoms have been omitted for clarity).

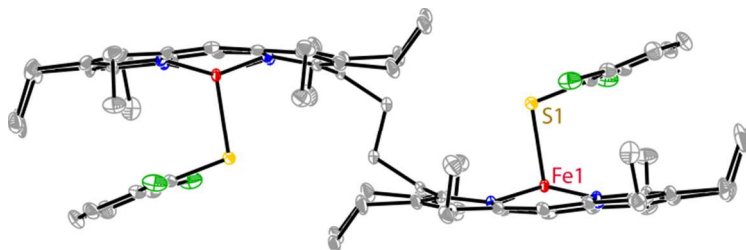


Figure S3. A perspective view of **2c** showing 50% thermal contours for all non-hydrogen atoms at 100 K (H atoms have been omitted for clarity).

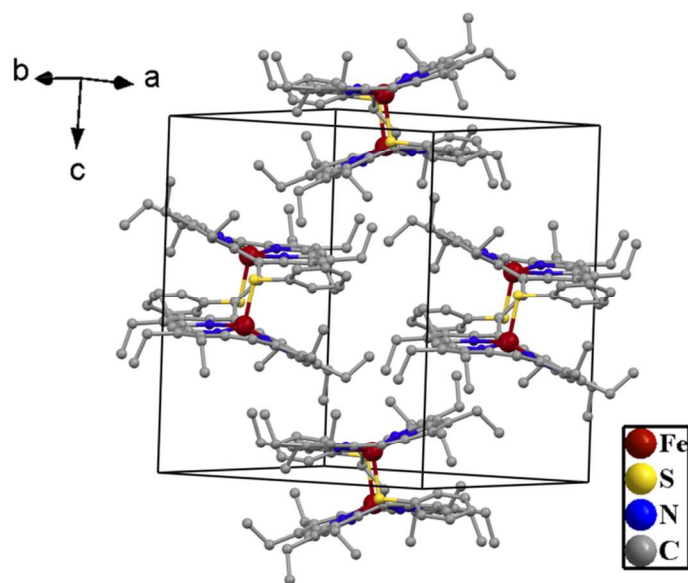


Figure S4. Diagram illustrating the packing of the **2a** in the unit cell (H-atoms and uncoordinated phenol have been omitted for clarity).

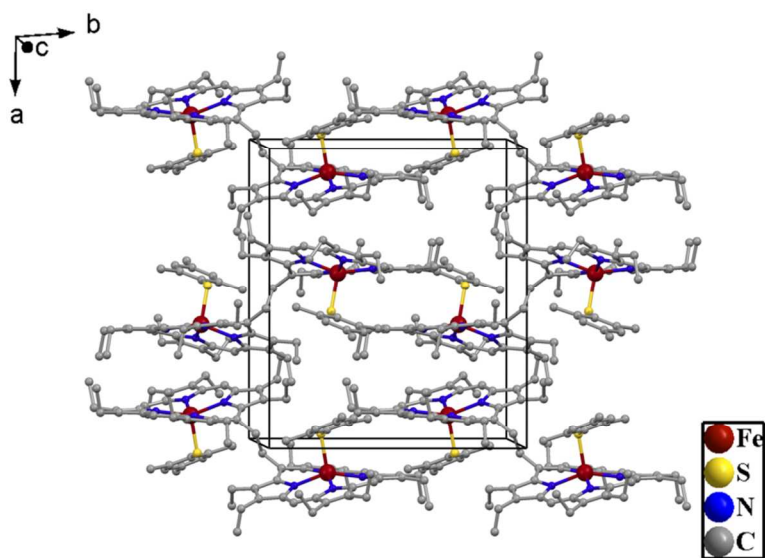


Figure S5. Diagram illustrating the packing of **2b** in the unit cell (H-atoms have been omitted for clarity).

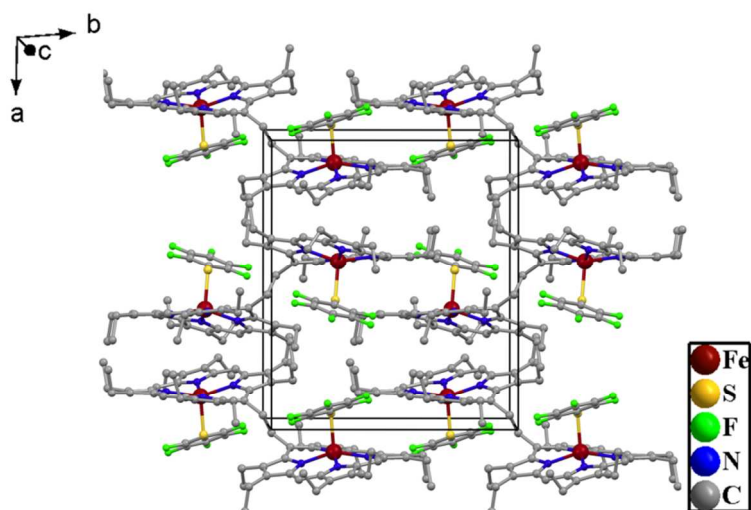


Figure S6. Diagram illustrating the packing of **2d** in the unit cell (H-atoms have been omitted for clarity).

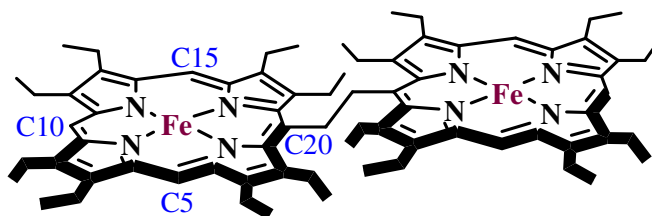


Figure S7. Atom numbering scheme used for the out-of-plane displacement plot of the porphyrin macrocycle.

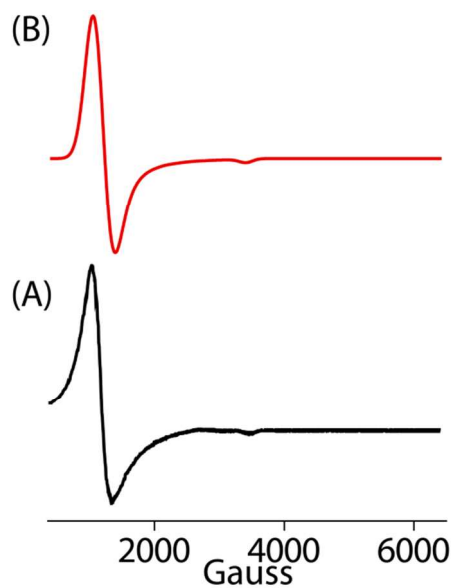


Figure S8. X-band EPR spectra of **2b** in CH_2Cl_2 (at 120 K) (A) experimental and (B) simulated spectra.

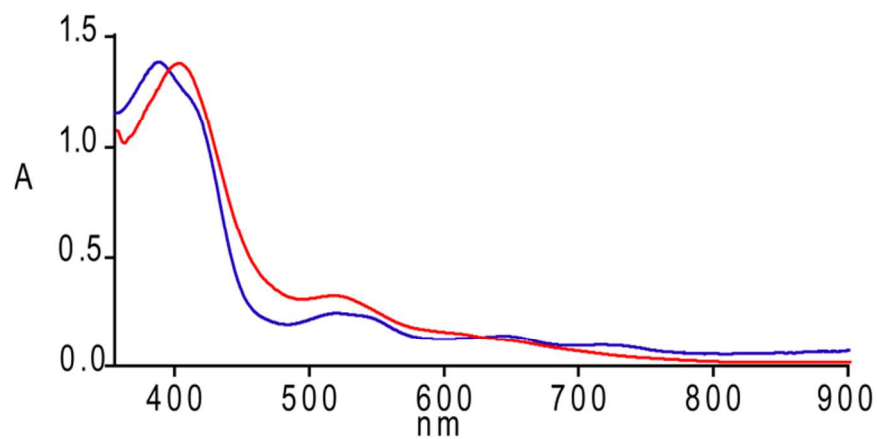


Figure S9. UV-visible spectra (at 298K) of **2a** (blue line) and **6a** (red line) in dichloromethane.

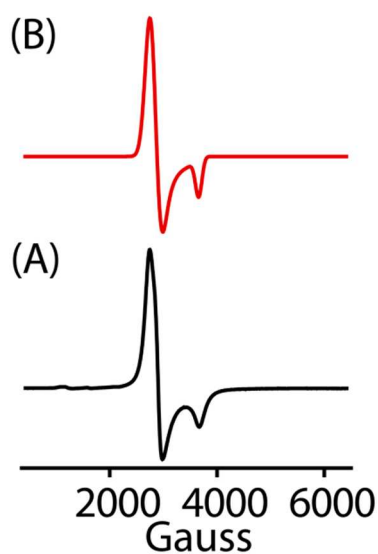


Figure S10. X-band EPR spectra of **6b** in CH_2Cl_2 (at 120 K) (A) experimental and (B) simulated spectra.

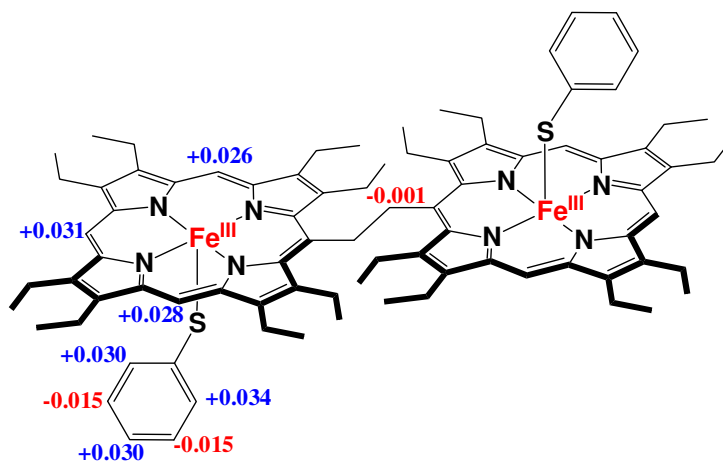


Figure S11. Mulliken spin densities on thiophenolato carbons and porphyrin *meso*- and bridging carbons for **2a**.

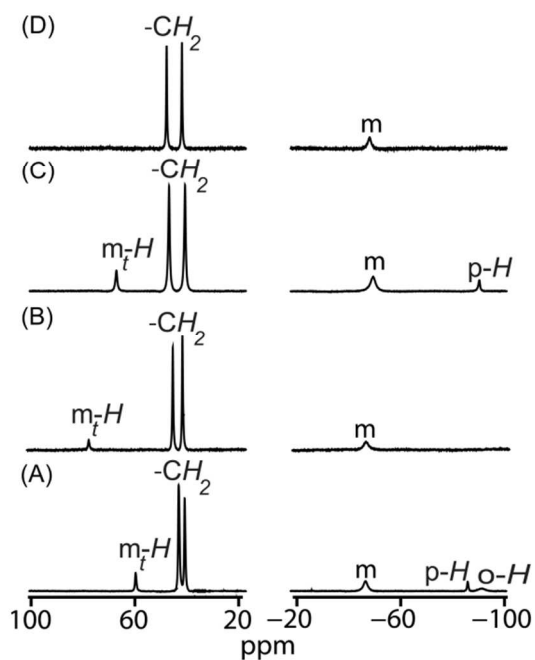


Figure S12. ^1H NMR spectra (at 298 K in CDCl_3) of (A) **4a**, (B) **4b**, (C) **4c** and (D) **4d**.

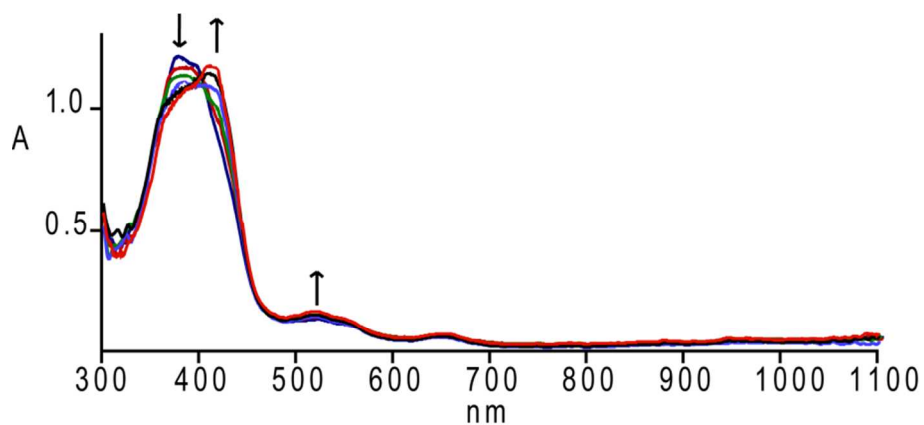


Figure S13. UV-visible spectral change in CH_2Cl_2 during $1e$ -reduction of **2c** at a constant potential of -0.75 V under nitrogen at 298 K. Arrows indicate an increase or decrease of band intensity.