

## Supporting Information

### A Four-Coordinate Fe(III) Porphyrin Cation

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#### Experimental Section:

##### Synthesis of 5,10,15,20-tetrakis(2',6'-dihydroxyphenyl)-porphyrinatoiron(III) chloride

The precursor, 5,10,15,20-tetrakis(2',6'-dihydroxyphenyl)-porphyrin, was synthesized according to the literature procedures.<sup>1</sup> 5,10,15,20-tetrakis(2',6'-dihydroxyphenyl)porphyrin (5 g, 6.7 mmol) was dissolved in 250 mL methanol along with iron(II) chloride (15 g, 118 mmol) and 2,6-lutidine (2 mL, 17 mmol). The resulting solution was warmed up to 50 °C and then stirred for 3 hours. After methanol was removed, the resulting solid was dissolved in ethyl acetate, washed with 1.2 M HCl solution, and then washed with water until pH was neutral. The crude product was purified by column chromatography (1:1 mixture of methanol / ethyl acetate) to give 5,10,15,20-tetrakis(2',6'-dihydroxyphenyl)porphyrinatoiron(III) chloride as a purple solid. (5.5g, yield 98%)

<sup>1</sup>H-NMR (CD<sub>3</sub>OD, 500 MHz): δ = 79.5(s, 8H, β-pyrrole H), 9.02(t, 4H, *p*-H hydroxyphenyl), 9.51(d, 8H, *m*-H hydroxyphenyl). MALDI-TOF calcd. for [FeC<sub>44</sub>H<sub>28</sub>N<sub>4</sub>O<sub>8</sub>]<sup>+</sup> = 796. Found 796.

##### Synthesis of 5,10,15,20-tetrakis(2',6'-bis(triisopropylsiloxy)-phenyl)porphyrinatoiron(III) chloride

5,10,15,20-tetrakis(2',6'-dihydroxyphenyl)porphyrinatoiron(III) chloride (1g, 1.2 mmol) was dissolved in 10g, 3.26 mmol triisopropylsilyl chloride along with imidazole (10g, 147 mmol). The mixture was heated up to 250 °C and then stirred for 1.5 hours under Ar. The high boiling point starting material and by products were removed by vacuum distillation. The resulting solid was dissolved in dichloromethane, washed with 3M HCl solution and then washed with water until pH was neutral. The crude product was purified by column chromatography (1:50 mixture of ethyl acetate / hexane) to give 5,10,15,20-tetrakis(2',6'-bis(triisopropylsiloxy)phenyl)porphyrinatoiron(III) chloride as a dark brown solid. (500 mg, yield 20%). The yield can be further improved by using triisopropylsilyl triflate as the starting material. After the reaction, the raw product was washed with 3M HCl(aq.) to obtain the pure products.

<sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): δ = 81.4(s, 8H, β-pyrrole H), 7.2(t, 4H, *p*-H phenyl), 14.6, 13.1(d, 8H, *m*-H phenyl), 2.2 to -5.1(m, 168H, *isopropyl*-H). Elemental analysis, calcd. for FeC<sub>116</sub>H<sub>188</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>8</sub>Cl: C=66.9, H=9.1, N=2.7%. Found C=66.9, H=9.1, N=2.8%. MALDI-TOF calcd. for FeC<sub>116</sub>H<sub>188</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>8</sub>Cl = 2083. Found 2081.

##### Synthesis of 5,10,15,20-tetrakis(2',6'-bis(triisopropylsiloxy)-phenyl)porphyrinatoiron(III) hexabromocborane

5,10,15,20-tetrakis(2',6'-bis(triisopropylsiloxy)phenyl)porphyrinatoiron(III) chloride (500mg, 0.24 mmol) was dissolved in 5mL dry CH<sub>2</sub>Cl<sub>2</sub> along with 173 mg AgCB<sub>11</sub>H<sub>6</sub>Br<sub>6</sub> (1:1 molar ratio, 0.24 mmol). After overnight reaction, the white AgCl precipitate was removed by filtration with a medium frit inside the inert atmosphere box. The raw product was purified by recrystallization with 1:1 CH<sub>2</sub>Cl<sub>2</sub>/heptane to give 5,10,15,20-tetrakis(2',6'-bis(triisopropylsiloxy)phenyl)porphyrinatoiron(III) hexabromocborane as a red-brown solid. (546 mg, yield 80%).

<sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): δ = -81.3(s, 8H, β-pyrrole H), 8.7(t, 4H, *p*-H phenyl), 9.2(d, 8H, *m*-H phenyl), -0.8(s, 144H, isopropyl CH<sub>3</sub>), -0.2(s, 24H, isopropyl CH). 2.7(b, 6H, *carborane*-H). Elemental analysis, calcd. for FeC<sub>116</sub>H<sub>188</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>8</sub>CB<sub>11</sub>H<sub>6</sub>Br<sub>6</sub>: C=52.8, H=7.3, N=2.1%. Found: C=50.5, H=7.2, N=2.1%. MALDI-TOF calcd. for [FeC<sub>116</sub>H<sub>188</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>8</sub>]<sup>+</sup> = 2047. Found 2047.

##### Synthesis of 5,10,15,20-tetrakis(2',6'-bis(triisopropylsiloxy)-phenyl)porphyrinatoiron(III) triflate

5,10,15,20-tetrakis(2',6'-bis(triisopropylsiloxy)phenyl)porphyrinatoiron(III) chloride (500mg, 0.24 mmol) was dissolved in 5mL dry CH<sub>2</sub>Cl<sub>2</sub> along with 61.7 mg AgCF<sub>3</sub>SO<sub>3</sub> (1:1 molar ratio, 0.24 mmol). After overnight reaction, the white AgCl precipitate was removed by filtration with a medium frit inside the inert atmosphere box. The raw product was purified by recrystallization with 1:1 CH<sub>2</sub>Cl<sub>2</sub>/Heptane to give 5,10,15,20-tetrakis(2',6'-bis(triisopropylsiloxy)phenyl)porphyrinatoiron(III) triflate as a red-brown solid. (421 mg, yield 80%).

<sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): δ = -81.2(s, 8H, β-pyrrole H), 8.7(t, 4H, *p*-H phenyl), 9.2(d, 8H, *m*-H phenyl), -0.8(s, 144H, isopropyl CH<sub>3</sub>), -0.2(s, 24H, isopropyl CH). Elemental analysis, calcd. for FeC<sub>116</sub>H<sub>188</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>8</sub>CF<sub>3</sub>SO<sub>3</sub>: C=64.0, H=8.6, N=2.6%. Found: C=61.7, H=8.6, N=2.6%. MALDI-TOF calcd. for [FeC<sub>116</sub>H<sub>188</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>8</sub>]<sup>+</sup> = 2047. Found 2047.

X-band EPR was measured on a Varian E-122 spectrometer at near liquid helium temperature. For both Evan's method and SQUID analysis, the magnetic susceptibility was adjusted for diamagnetic contributions by measuring the diamagnetic susceptibility of the free base porphyrin. The diamagnetic susceptibility of the counter ion was calculated with Pascal's constants.<sup>2,3</sup>

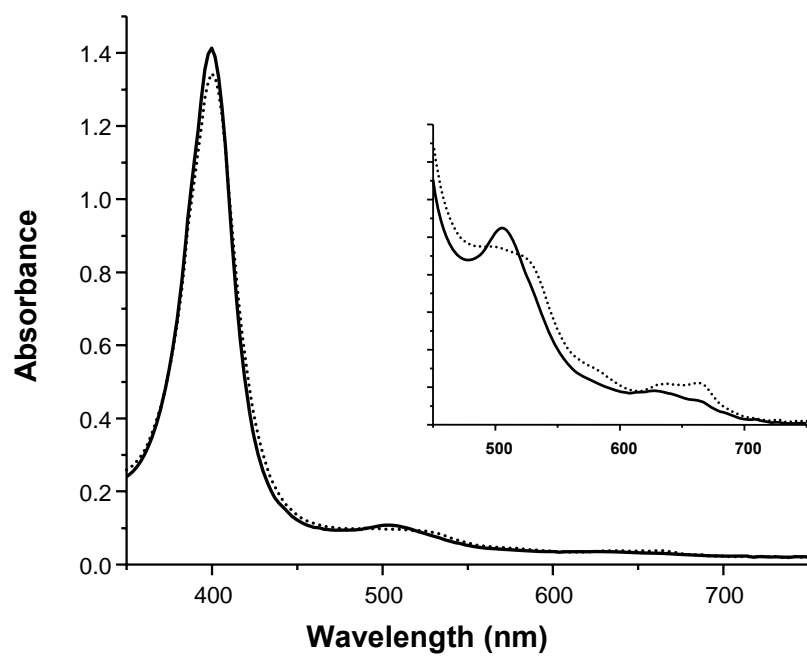
- (1) Bhyrappa, P.; Vaijayanthimala, G.; Suslick, K. S. *J. Am. Chem. Soc.* **1999**, *121*, 262-263
- (2) Evans, D. F. *J. Chem. Soc.* **1959**, 2003-2005
- (3) Yatsunyk, L. A., Walker, F. A. *Inorg. Chem.* **2004**, *43*, 757-77
- (4) Evans, D. R., Reed, C. A. *J. Am. Chem. Soc.* **2000**, *122*, 4660-4667

**Table S1. Crystal data and structure refinement for [Fe(TipsiPP)]<sup>+</sup>[CB<sub>11</sub>H<sub>6</sub>Br<sub>6</sub>]<sup>-</sup>**

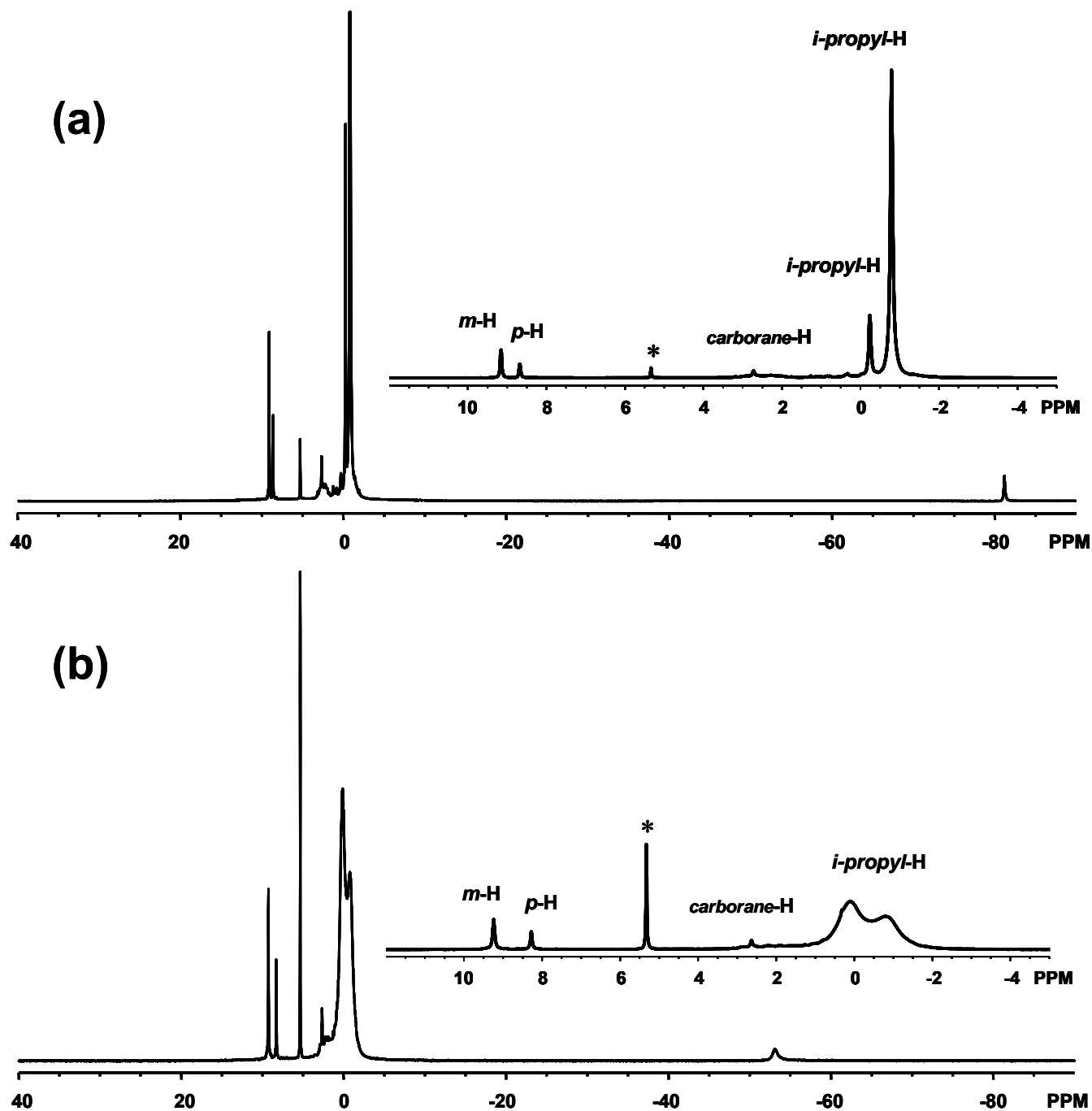
Identification code	ga92ttapanis	
Empirical formula	C <sub>116</sub> H <sub>188</sub> FeN <sub>4</sub> O <sub>8</sub> Si <sub>8</sub> , 0.6894(CH <sub>6</sub> B <sub>11</sub> Br <sub>6</sub> ), 0.3106(C <sub>2</sub> H <sub>12</sub> B <sub>22</sub> Br <sub>12</sub> Ag), 0.5(CH <sub>2</sub> Cl <sub>2</sub> ), C <sub>7</sub> H <sub>16</sub>	
Formula weight	24248.19	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	C m c 21	
Unit cell dimensions	a = 37.028(2) Å	α = 90°.
	b = 29.3262(19) Å	β = 90°.
	c = 29.3677(18) Å	γ = 90°.
Volume	31890(3) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.263 Mg/m <sup>3</sup>	
Absorption coefficient	2.226 mm <sup>-1</sup>	
F(000)	12564	
Crystal size	0.53 x 0.25 x 0.05 mm <sup>3</sup>	
Theta range for data collection	1.10 to 26.01°	
Index ranges	-32<=h<=45, -35<=k<=26, -36<=l<=31	
Reflections collected	65276	
Independent reflections	27861 [R(int) = 0.1379]	
Completeness to theta = 26.01°	98.0 %	
Absorption correction	Integration	
Max. and min. transmission	0.9000 and 0.5429	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	27861 / 4123 / 1939	
Goodness-of-fit on F <sup>2</sup>	1.289	
Final R indices [I>2σ(I)]	R1 = 0.0986, wR2 = 0.2398	
R indices (all data)	R1 = 0.3398, wR2 = 0.2824	
Absolute structure parameter	0.03(2)	
Largest diff. peak and hole	0.883 and -0.487 e.Å <sup>-3</sup>	

**Table S2. Crystal data and structure refinement for Fe(TipsiPP)(CF<sub>3</sub>SO<sub>3</sub>).**

Identification code	g53oas	
Empirical formula	C <sub>117</sub> H <sub>188</sub> F <sub>3</sub> Fe N <sub>4</sub> O <sub>11</sub> S Si <sub>8</sub>	
Formula weight	2196.34	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 35.42(2) Å	α = 90°.
	b = 14.532(8) Å	β = 124.497(8)°.
	c = 29.733(17) Å	γ = 90°.
Volume	12613(12) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.157 Mg/m <sup>3</sup>	
Absorption coefficient	0.271 mm <sup>-1</sup>	
F(000)	4748	
Crystal size	0.72 x 0.56 x 0.32 mm <sup>3</sup>	
Theta range for data collection	1.95 to 25.39°	
Index ranges	-42<=h<=42, -17<=k<=17, -35<=l<=35	
Reflections collected	65286	
Independent reflections	11563 [R(int) = 0.0540]	
Completeness to theta = 25.39°	99.7 %	
Absorption correction	Integration	
Max. and min. transmission	0.8981 and 0.8537	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	11563 / 487 / 798	
Goodness-of-fit on F <sup>2</sup>	1.025	
Final R indices [I>2σ(I)]	R1 = 0.0573, wR2 = 0.1486	
R indices (all data)	R1 = 0.0896, wR2 = 0.1717	
Largest diff. peak and hole	0.692 and -0.509 e.Å <sup>-3</sup>	

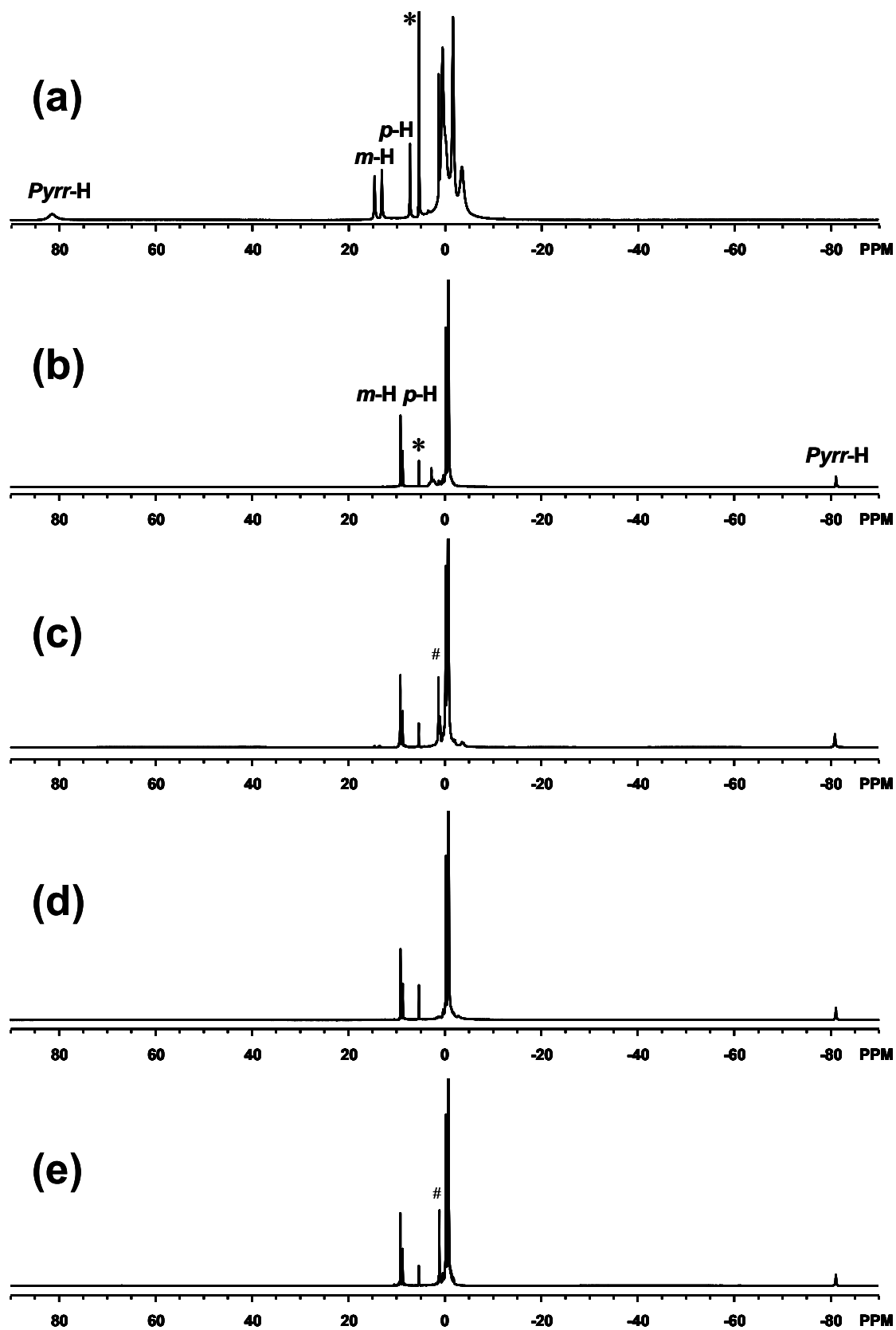


**Figure S1.** UV-Visible spectrum of  $[\text{Fe}^{\text{III}}(\text{TipsiPP})]^+[\text{CB}_{11}\text{H}_6\text{Br}_6]^- \cdot (\text{H}_2\text{O})$  (dotted line) and four coordinate  $[\text{Fe}^{\text{III}}(\text{TipsiPP})]^+[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$  (solid line). Absorbance of the insert is 5X expanded.

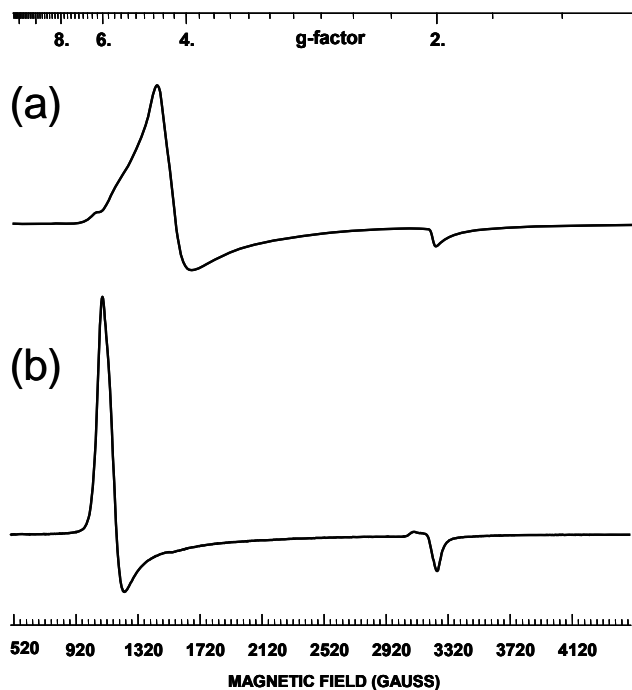


**Figure S2.** NMR spectra of (a)  $[\text{Fe}^{\text{III}}(\text{TipsiPP})]^+[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$  (b)  $[\text{Fe}^{\text{III}}(\text{TipsiPP})]^+[\text{CB}_{11}\text{H}_6\text{Br}_6]^- \cdot (\text{H}_2\text{O})$  in  $\text{CD}_2\text{Cl}_2$  at 290K. Inserts: enlarged view of the 12 to -4 ppm region. \*NMR solvent peak

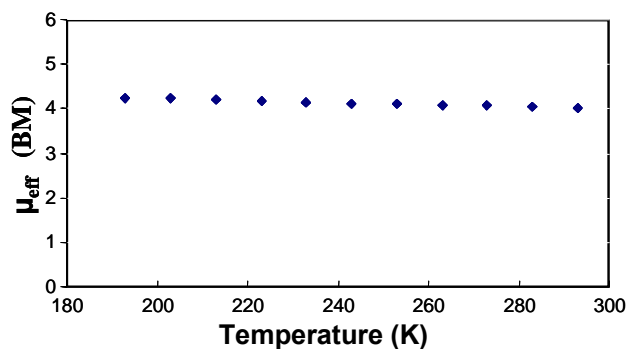
Note: The downfield shift of the porphyrin pyrrole signal from -82ppm to -53ppm is due to the coordination of water molecule to iron, which changes the spin state of iron from intermediate to the admixed spin state. The downfield shift is characteristic of a 5/2 high spin component in the spin state of iron.<sup>4</sup>



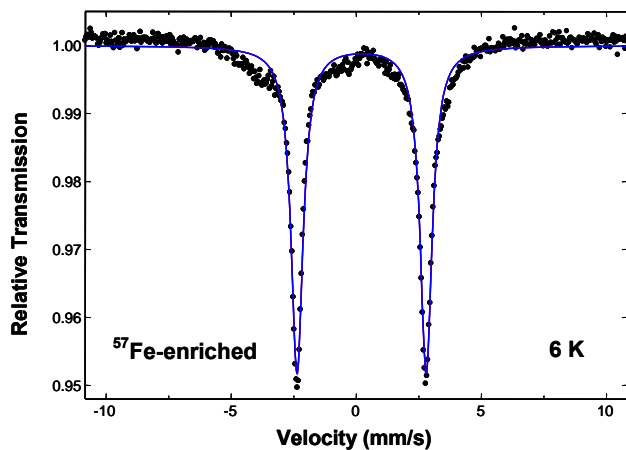
**Figure S3.** NMR spectra of (a)  $\text{Fe}^{\text{III}}(\text{TipsiPP})(\text{Cl})$ , (b)  $[\text{Fe}^{\text{III}}(\text{TipsiPP})]^+[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ , (c)  $[\text{Fe}^{\text{III}}(\text{TipsiPP})]^+[\text{CF}_3\text{SO}_3]^-$ , (d)  $[\text{Fe}^{\text{III}}(\text{TipsiPP})]^+[\text{ClO}_4]^-$ , (e)  $[\text{Fe}^{\text{III}}(\text{TipsiPP})]^+[\text{AsF}_6]^-$  in  $\text{CD}_2\text{Cl}_2$  at 290K. See the S3(a) insert for an enlarged view of the 12 to -4 ppm region of S4(b). \*NMR solvent peaks #vacuum grease contamination



**Figure S4.** EPR spectrum of (a)  $[\text{Fe}^{\text{III}}(\text{TipsiPP})]^+[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$  powder sample and (b)  $\text{Fe}^{\text{III}}(\text{TipsiPP})(\text{CF}_3\text{SO}_3)$  powder sample at 15K.

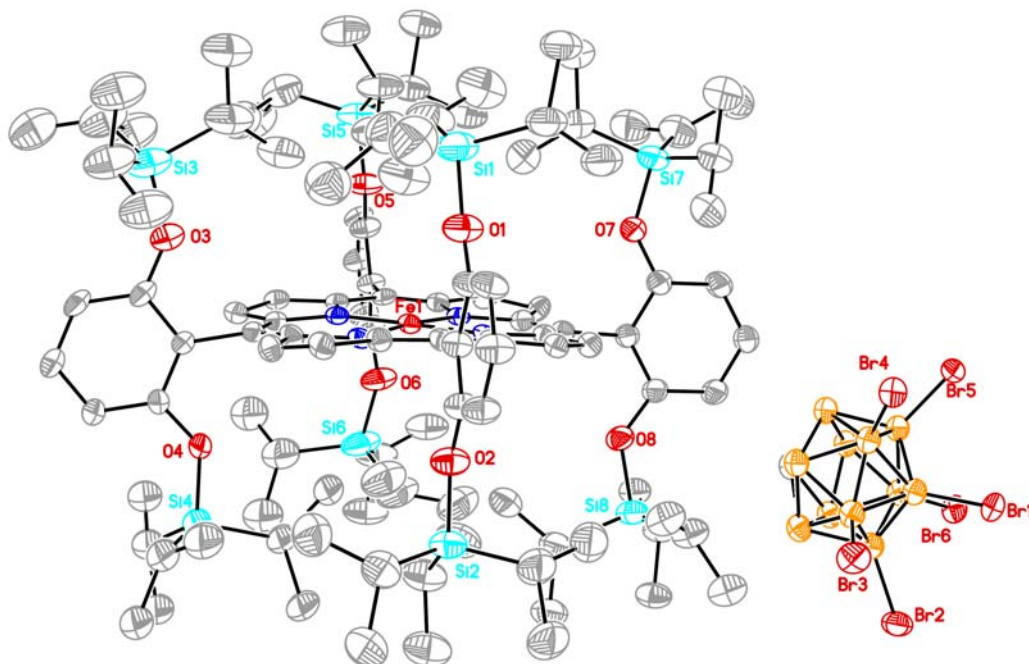


**Figure S5.** Magnetic moment of  $[\text{Fe}^{\text{III}}(\text{TipsiPP})]^+[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$  in  $\text{CD}_2\text{Cl}_2$  determined by Evan's method.

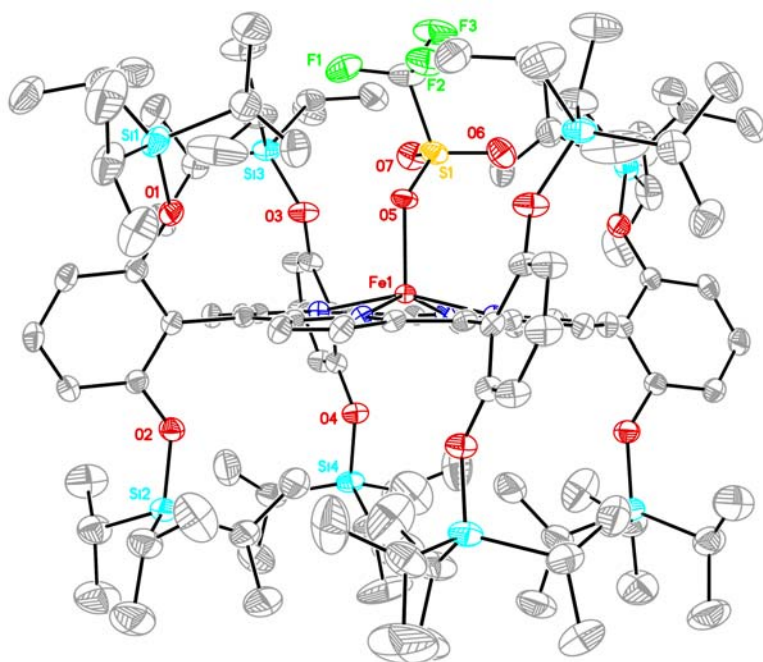


**Figure S6.** Mossbauer spectrum of  $[\text{Fe}^{57}(\text{TipsiPP})]^+[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$  at 6K.

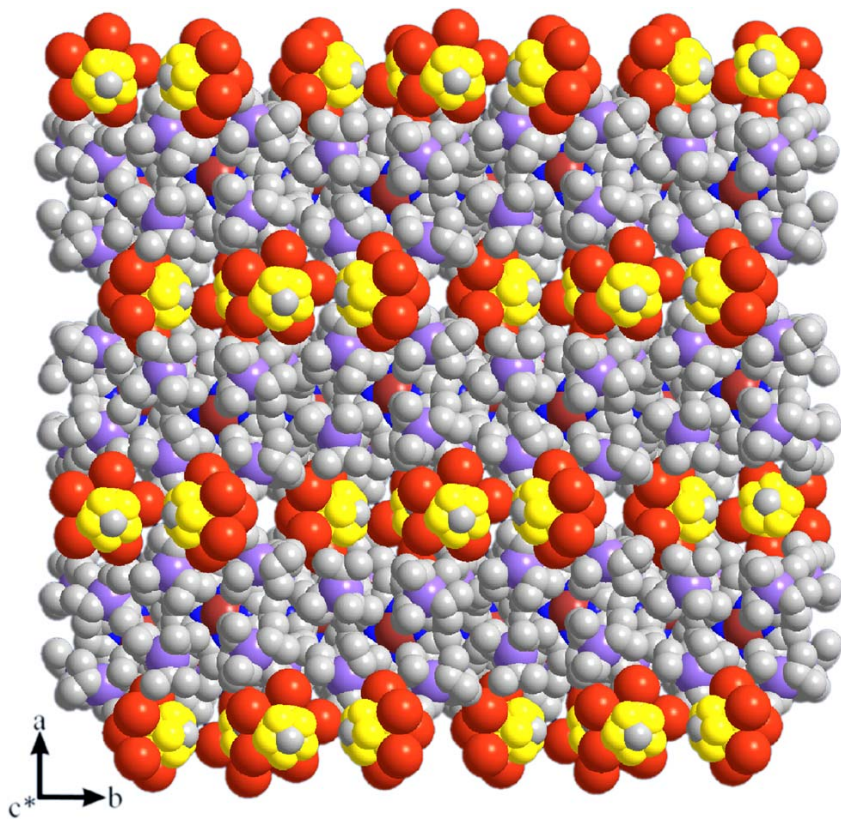
Isomer Shift (relative to  $\alpha$ -iron coil) = 0.33 mm/s, Quadrupole Splitting = 5.16 mm/s



**Figure S7.** SHELXTL (Bruker, 2005) plot of the porphyrin cation and hexabromocarborane anion showing 20% probability ellipsoids for non-H atoms. Hexabromocarborane atoms were generated by the symmetry operator  $(1/2-x, 1/2-y, -1/2+z)$ . H atoms and disordered sites for the anion, three independent heptane solvates, and a methylene chloride solvate were omitted for clarity.



**Figure S8.** SHELXTL (Bruker, 2001) plot showing 25% probability ellipsoids for non-H atoms; H atoms and disordered triflate sites were omitted for clarity. The unlabeled atoms are related by the symmetry operator  $(-x, y, 0.5-z)$ .



**Figure S9.** Packing diagram of the layered salt  $[\text{Fe}^{\text{III}}(\text{TipsiPP})]^+[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$  showing 1.5x2x1 unit cells. The bis-pocket metalloporphyrin cations are in blue/gray and the carborane anions are in orange-yellow. Solvents and disordered anions are omitted for clarity. The view is along  $c^*$ .