Supporting Informations

Control of Spins by Ring Deformation in a Diiron(III)bisporphyrin: Reversal of ClO_4^- and $CF_3SO_3^-$ Ligand Field Strength on the Magnetochemical Series

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Instrumentation

UV-vis spectra were recorded on a PerkinElmer UV/Vis spectrometer. Elemental (C, H, and N) analyses were performed on a Perkin-Elmer 2400II elemental analyzer. EPR spectra were obtained on a Bruker EMX EPR spectrometer. ^{1}H NMR spectra were recorded on a JEOL 500 MHz instrument. The spectra for paramagnetic molecules were recorded over a 100-kHz bandwidth with 64 K data points and a 5-ms 90° pulse. For a typical spectrum between 2000 and 3000 transients were accumulated with a 50-μs delay time. The residual ^{1}H resonances of the solvents were used as a secondary reference. Magnetic susceptibility data were collected using a Quantum Design MPMS SQUID magnetometer over the temperature range 5 to 300K. Data were collected in applied magnetic field of 0.2 T and corrected for diamagnetism using Pascal's constants.[1]

Magnetic Susceptibility Measurement in Solution:

The solution magnetic susceptibility was measured by NMR methods on a JEOL 500 MHz instrument over the temperature range 193-303K using modified Evans method.[2] In a special coaxial tube (Wilmad) the solution of the paramagnetic complex was placed in the inner narrow-bore tube, and the solvent was placed in the outer tube, which is a regular NMR tube. The volume magnetic susceptibility (χ) of the paramagnetic compound was calculated from the following equation.

$$\chi = \chi_0 + 3000\Delta v/4\pi v_0 cM$$

where, χ_0 is the volume magnetic susceptibility of the pure solvent; Δv (Hz) is the separation of the reference solvent peaks from the inner and outer tubes; v_0 is the operating RF frequency of

the spectrometer; *c* is the concentration of the complex in moles/L; and M is the molecular weight of the complex. The molar susceptibility (χ_M) and the magnetic moment (μ_{eff}) at a particular temperature were then calculated usual way from χ, after the usual diamagnetic correction from the sum of Pascal constants.[1]

X-ray Structure Solution and Refinement: Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer equipped with CRYO Industries low-temperature apparatus and intensity data were collected using graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). The data integration and reduction were processed with SAINT[3] software. An absorption correction was applied.[4] The structure was solved by the direct method using SHELXS-97 and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97[5] program package. Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using SHELXL default parameters.

Experimental Section

Materials: Syn-1,2-bis[μ-oxo iron-(III) 5-(2,3,7,8,12,13,17,18-octaethylporphyrinyl)]ethane, **1** and Anti-1,2-bis[perchloratoiron(III) 5-(2,3,7,8,12,13,17,18-octaethylporphyrinyl)]ethane, **2a** were prepared using the methods reported earlier.[6,7] Reagents and solvents were purchased from commercial sources and purified by standard procedures.

Synthesis of 2b: 100 mg of **1** (0.082 mmol) was dissolved in 100 mL dichloromethane and 100 mL 10% trifluoromethanesulfonic acid solution was added and the mixture was stirred for 15 min at room temperature. Organic layer was then separated and dried over anhydrous Na_2SO_4 which was evaporated to complete dryness. The resulting solid was then dissolved in minimum volume of benzene and then carefully layered with acetonitrile. On standing for 6-8 days, dark purple crystalline solid was formed which was collected by filtration, washed well with the mother liquor and dried in vacuum. Yield: 78 mg (63%). Anal. Calcd (found): C, 60.77 (60.69); H, 6.04 (6.12); N, 7.46 (7.40). UV-vis (dichloromethane) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 374 (1.4 x 10^5), 531 (9.9 x 10^3), 653 (5.2 x 10^2). ^{1}H NMR ($CDCl_3$, 295 K): *meso-H*: -3.7, -15.6, C*H*$_3$: 2.6, 2.8, 2.9, C*H*$_2$: 16.0, 16.7, 17.2, 18.1, 18.2, 18.8, 19.3, 21.6; C*H*$_2$(b): 33.5 ppm.

Table S1: Normal-coordinate structural decomposition (NSD)[8] analysis of the complexes

Complex	Core	B2u, saddle	B1u, ruffle	A2u, dome	Eg(x), wave(x)	Eg(y), wave(y)	A1u, propeller	sum	ruf/sum (%)	Sad/sum (%)
2a	core-I	-0.3829	-0.3928	0.2471	0.2844	-0.1538	0.0125	1.4735	26.66	25.99
	core-II	-0.3838	0.3592	0.2577	0.2347	0.2163	0.0148	1.4665	24.49	26.17
2b		-0.1303	-1.2149	0.0759	0.2705	-0.0644	-0.0091	1.7651	68.83	7.38

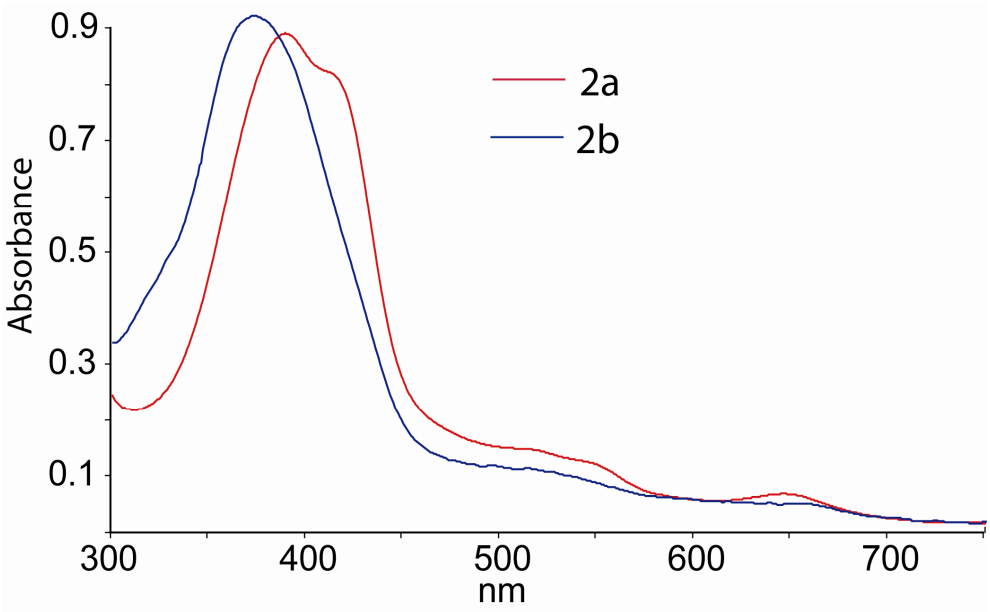

Figure S1. UV-visible spectra in dichloromethane for **2a** (red line) and **2b** (blue line) at 295K.

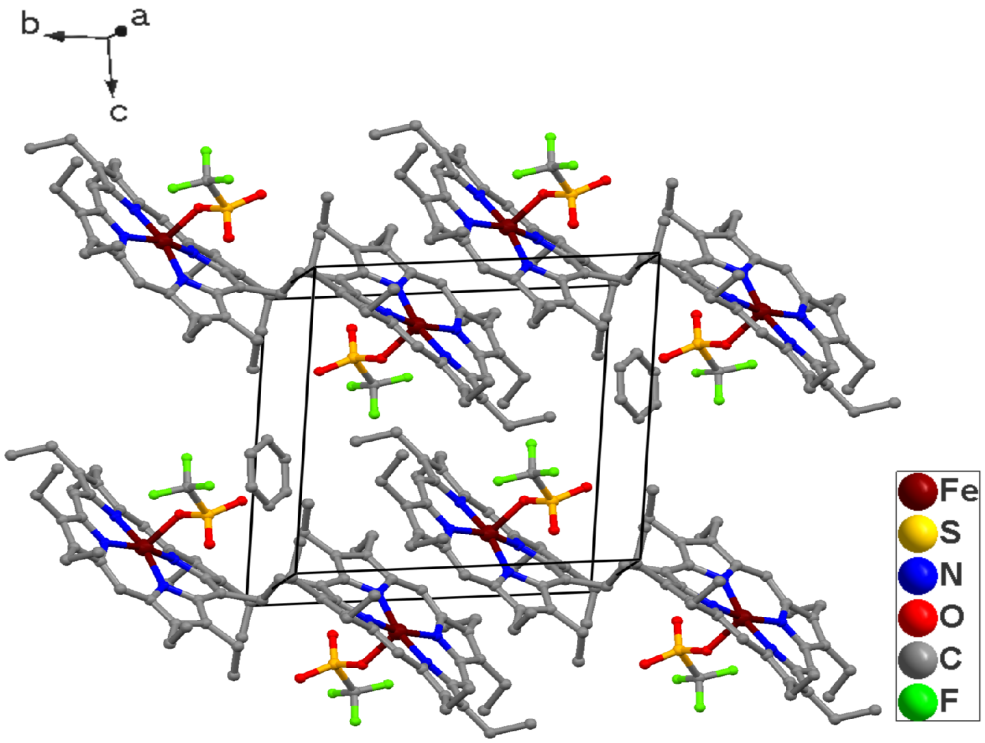

Figure S2. Diagram illustrating the packing of **2b.C_6H_6**. H-atoms have been omitted for clarity.

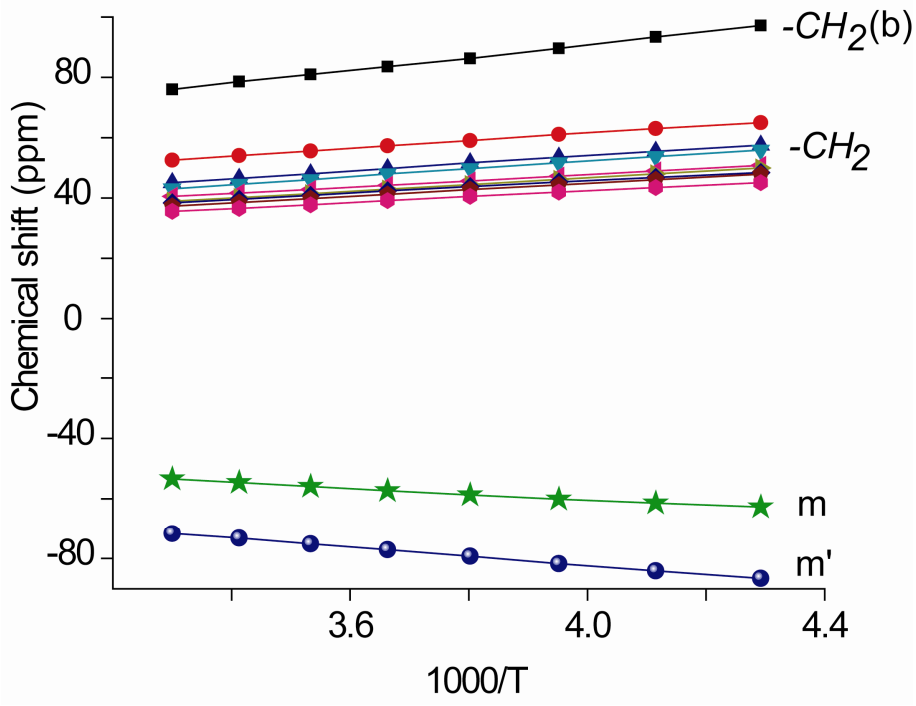

Figure S3. Curie plots (chemical shift versus 1/T) of the proton signals for **2a.**

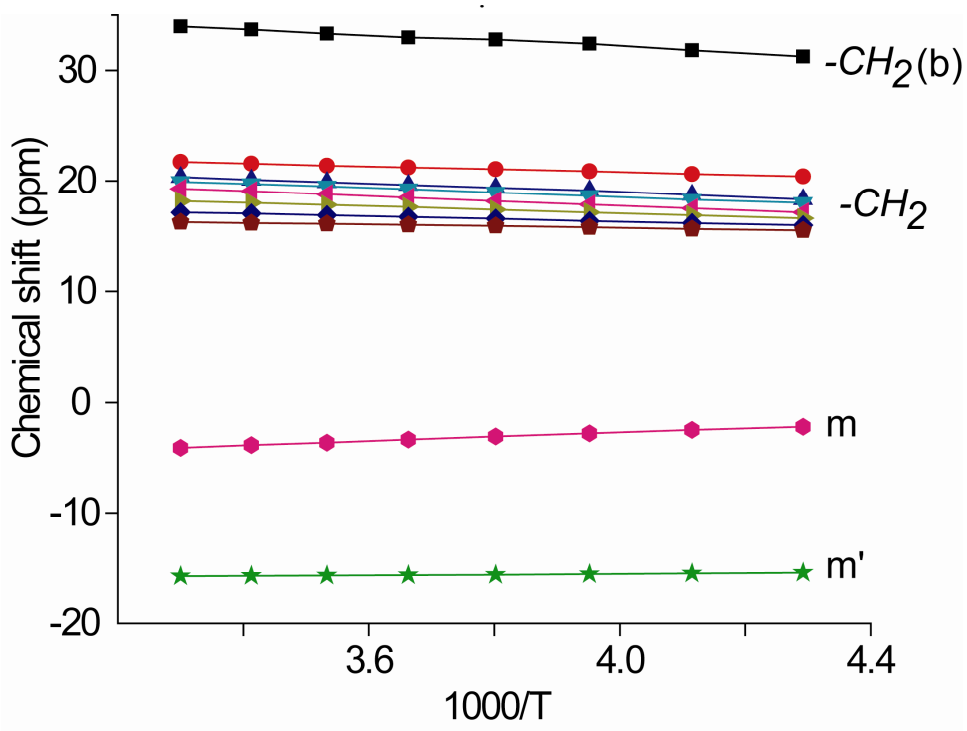

Figure S4. Curie plots (chemical shift versus 1/T) of the proton signals for **2b.**

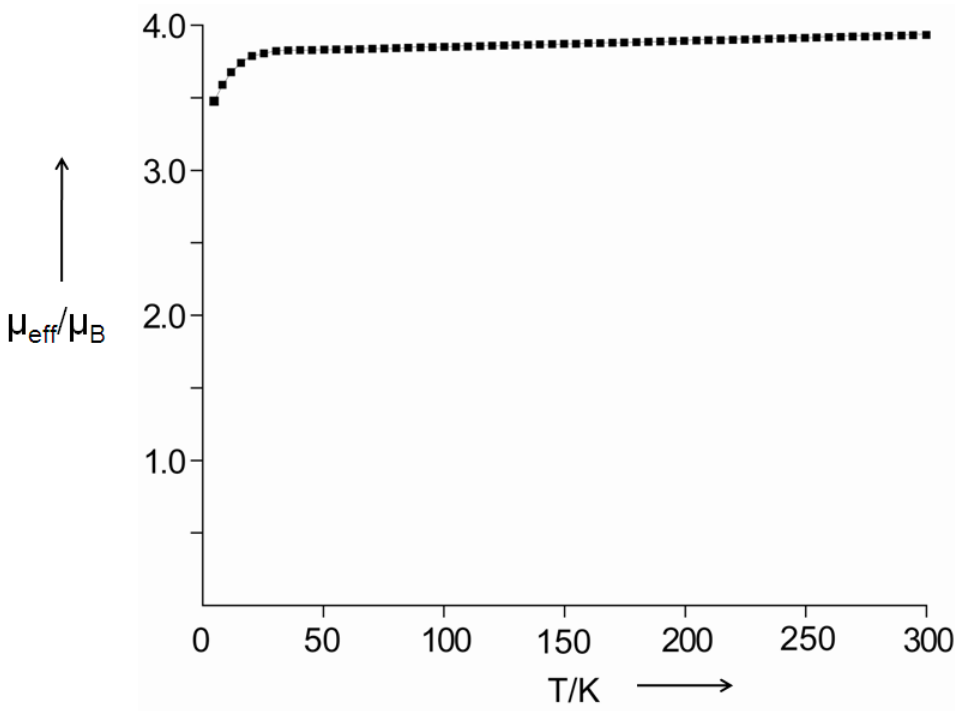

Figure S5. Magnetic moment per iron center of crystalline sample of **2b** as a function of temperature.

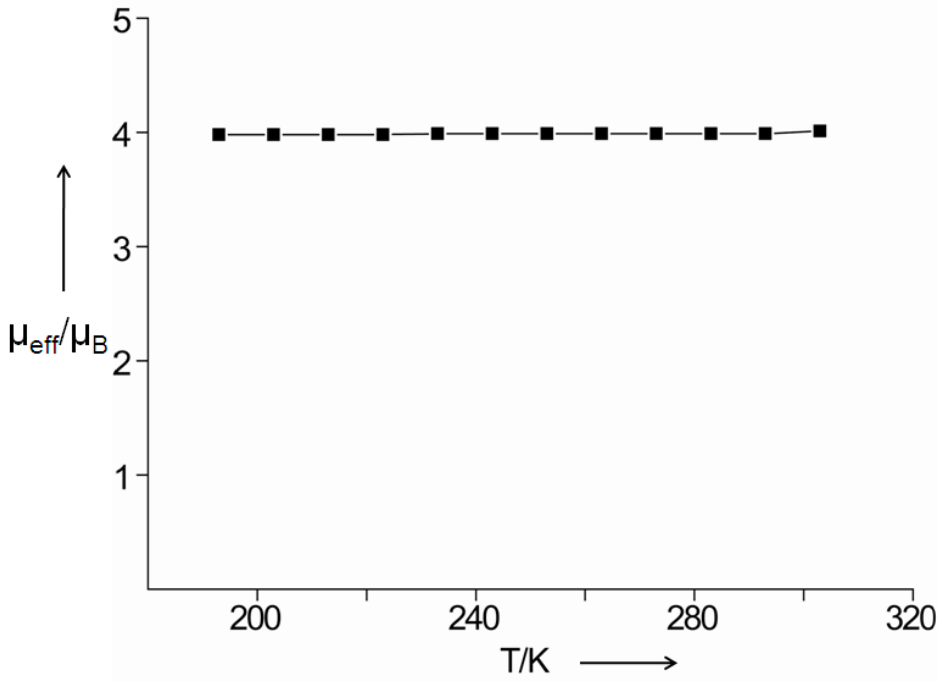

Figure S6. Magnetic moment per iron center of **2b** as a function of temperature determined in CH_2Cl_2 using modified Evans method.

References:

1. O. Kahn, *Molecular Magnetism*; VCH Publishers: Weinheim, **1993**; pp 2-4.
2. S. K, Sur, *J. Magn. Reson.* **1989**, *82*, 169.
3. *SAINT+*, 6.02 ed.; Bruker AXS, Madison, WI, **1999**.
4. G. M. Sheldrick, SADABS 2.0, **2000**.
5. G. M. Sheldrick, *SHELXL-97: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, **1997**.
6. S. K. Ghosh, R. Patra and S. P. Rath, *Inorg. Chem.* **2008**, *47*, 10196.
7. S. K. Ghosh, R. Patra and S. P. Rath, *Inorg. Chem*. **2010**, *49*, 3449.
8. (a) W. Jentzen, J. –G. Ma and J. A. Shelnutt, *Biophys. J.,* **1998**, *74*, 753; (b) W. Jentzen, X.-Z. Song and J. A. Shelnutt, *J. Phys. Chem. B.,* **1997**, *101*, 1684.