Supporting Information

Control of Spins by Ring Deformation in a Diiron(III)bisporphyrin: Reversal of ClO$_4^-$ and CF$_3$SO$_3^-$ 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-$\mu$s 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 ($\chi$) of the paramagnetic compound was calculated from the following equation.

$$\chi = \chi_0 + 3000\Delta\nu/4\pi\nu_0\kappa M$$

where, $\chi_0$ is the volume magnetic susceptibility of the pure solvent; $\Delta\nu$ (Hz) is the separation of the reference solvent peaks from the inner and outer tubes; $\nu_0$ 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 (\( \chi_M \)) and the magnetic moment (\( \mu_{\text{eff}} \)) at a particular temperature were then calculated usual way from \( \chi \), 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 K\( \alpha \) radiation (\( \lambda = 0.71073 \) 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[\( \mu \)-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\(_2\)SO\(_4\) 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) [\( \lambda_{\text{max}}, \text{nm} (\varepsilon, \text{M}^{-1} \text{cm}^{-1}) \)]: 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, CH\(_3\): 2.6, 2.8, 2.9, CH\(_2\): 16.0, 16.7, 17.2, 18.1, 18.2, 18.8, 19.3, 21.6; CH\(_3\)(b): 33.5 ppm.
Table S1: Normal-coordinate structural decomposition (NSD)\textsuperscript{8} analysis of the complexes

<table>
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<tr>
<th>Complex</th>
<th>Core</th>
<th>B2u, saddle</th>
<th>B1u, ruffle</th>
<th>A2u, dome</th>
<th>Eg(x), wave(x)</th>
<th>Eg(y), wave(y)</th>
<th>A1u, propeller</th>
<th>sum</th>
<th>ruf/sum (%)</th>
<th>Sad/sum (%)</th>
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<tbody>
<tr>
<td>2a</td>
<td>core-I</td>
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<td>-0.3928</td>
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<td>26.66</td>
<td>25.99</td>
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<tr>
<td></td>
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<td>2b</td>
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<td>-0.0091</td>
<td>1.7651</td>
<td>68.83</td>
<td>7.38</td>
</tr>
</tbody>
</table>

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 CH₂Cl₂ using modified Evans method.

References: