

Supporting Information

•NO₂ -mediated meso-hydroxylation of Fe (III) porphyrin

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Experimental Methods:

Solvents like chloroform, ethyl acetate, dichloromethane, petroleum ether and pyrrole were obtained from S. D. Fine-Chem Ltd. purified and dried before use by standard methods. 3, 4, 5-trimethoxybenzaldehyde was procured from Acros Organics and dimethylformamide (DMF) from Thomas Baker. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was synthesized by literature procedure. Electronic absorption spectral measurements were carried out by USB 2000 (Ocean Optics Inc.) equipped with fiber optics with a *D2 Lite*TM light source. Infrared spectra were recorded on a Bruker Vertex 70, FT-IR spectrophotometer as pressed KBr disks in the IR region. The ESI mass spectra (positive mode) were recorded on a Waters Micromass Q TOF Premier Mass Spectrometer. The sample (dissolved in acetonitrile) was introduced into the ESI source through a syringe pump at the rate of 5 $\mu\text{l}/\text{min}$. The ESI capillary was set at 2.3 kV and voltage was 36 V. Elemental analysis for carbon, hydrogen and nitrogen were analyzed with Perkin-Elmer 2400 microanalyser. Magnetic susceptibilities were measured at 0.5T as powder packed in gelatin capsules using a Quantum Design MPMSR2 SQUID susceptometer. The data were corrected for diamagnetism of the sample holder and the diamagnetic component of the samples was evaluated from Pascal's constants. X-band EPR measurements were carried out on solid samples at RT on a Bruker EMX spectrometer.

The crystal used was glued to a glass fiber and mounted on BRUKER SMART APEX diffractometer. Cell constant was obtained from the least-squares refinement of three-dimensional centroids through the use of CCD recording of narrow ω rotation frames, completing almost all-reciprocal space in the stated θ range. The instrument was equipped with CCD area detector and data were collected using graphite-monochromated

Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$) at low temperature (100K). All empirical absorption correction were applied using the SADABS program.¹ All data were collected with SMART 5.628 (BRUKER, 2003), and were integrated with the BRUKER SAINT program.² The structure was solved using SIR97 and refined using SHELXL-97.³ The space group of the compound was determined based on the lack of systematic absence and intensity statistics. Full matrix least squares / difference Fourier cycles were performed which located the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Synthesis:

Synthesis of *meso*-tetrakis(3,4,5-trimethoxyphenyl)porphyriniron(III) chloride (**1**):

1.0 g (5.1 mmol) 3, 4, 5-trimethoxybenzaldehyde was dissolved in 50 ml of argon-purged dimethylformamide. 0.5 ml conc. HCl was added into it followed by drop wise addition of 0.35 ml (5.1 mmol) of freshly distilled pyrrole. The mixture was stirred under argon for 1 hr. and then ~ 2.5 equivalent of ferrous chloride was added and the final reaction mixture was refluxed for 8hr. in air. The solvent was evaporated under vacuum and the solid was washed with hot water. The crude product was extracted by flash chromatography over basic alumina using 5% methanol-chloroform. Compound **1** was finally purified by column chromatography over basic alumina using 2% methanol-chloroform mixture. The yield of the purple crystalline solid of **1** was 19%.

Molecular Formula: C₅₆H₅₂N₄O₁₂FeCl; Molecular Weight: 1063.26; UV-Vis λ_{max} (CHCl₃, log ϵ); 424 (5.08), 512 (4.21), 580 (3.59), 680 (3.52); ESR at RT solid: $g_{\parallel} = 1.97$,

$g_{\perp}=5.17$; Elemental analysis calculated (found) in % for $C_{56}H_{52}N_4O_{12}FeCl$; C, 63.19 (63.07); H, 4.92 (4.85); N, 5.26 (5.17).

Synthesis of aquachloro*meso*-hydroxy-tetrakis(3,4,5-trimethoxyphenyl)porphyrinato iron(III) nitrate (**2**):

50 mg (0.05 mmol) of **1** was dissolved in 20 ml argon purged DCM containing pre-bubbled nitric oxide for a minute under normal pressure. This solution was layered with air purged hexane and the flask was allowed to stand for a week. Compound **2** was precipitated out as dark red solid in 45% yield along with some X-ray diffraction quality crystals appeared on the wall of the vessel which were separated out and analyzed as **2**.

Molecular Formula: $C_{57}H_{57}Cl_3FeN_5O_{17}$; Molecular Weight: 1246.28; UV-Vis λ_{max} ($CHCl_3$, log ϵ); 350 (4.75), 432 (4.82), 820 (3.94), 920 (4.06); ESR at RT solid: $g_{\parallel}=1.96$, $g_{\perp}=5.52$; FTIR (cm^{-1}); 1503 [$\nu_a NO_3^-$], 1237 [$\nu_s NO_3^-$], 1023 [νNO_3^-] Elemental analysis calculated (found) in % for $C_{57}H_{57}Cl_3FeN_5O_{17}$; C, 54.93 (54.87); H, 4.61 (4.53); N, 5.62 (5.64). Magnetic moment, $\mu_{eff} = 5.8$ BM.

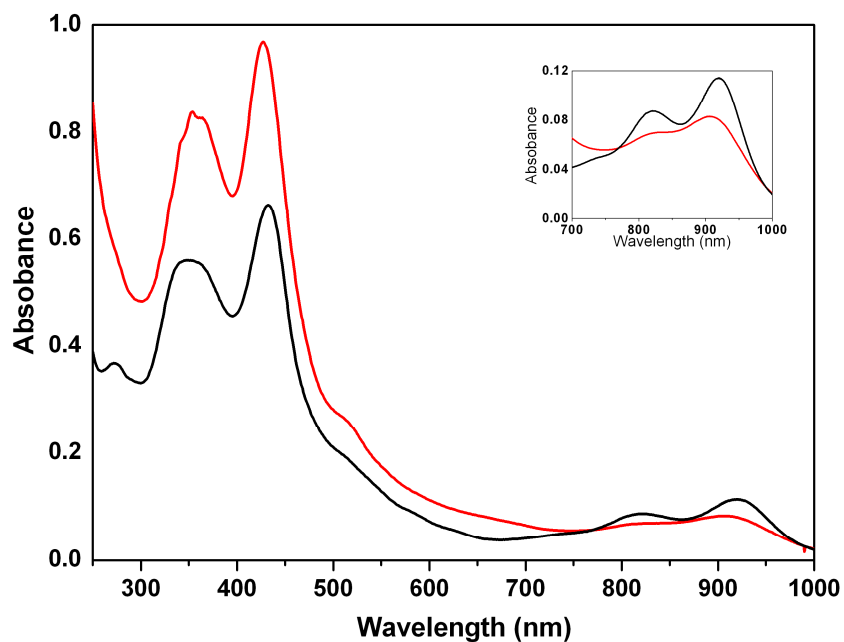


Figure1. Electronic spectrum of **1** (1×10^{-5} M) in DCM containing dissolved $\bullet\text{NO}_2$ (red trace). Electronic spectrum of **2** (1×10^{-5} M) (black) for comparison. Inset : Enlarge spectral features in the 700-1000nm region.

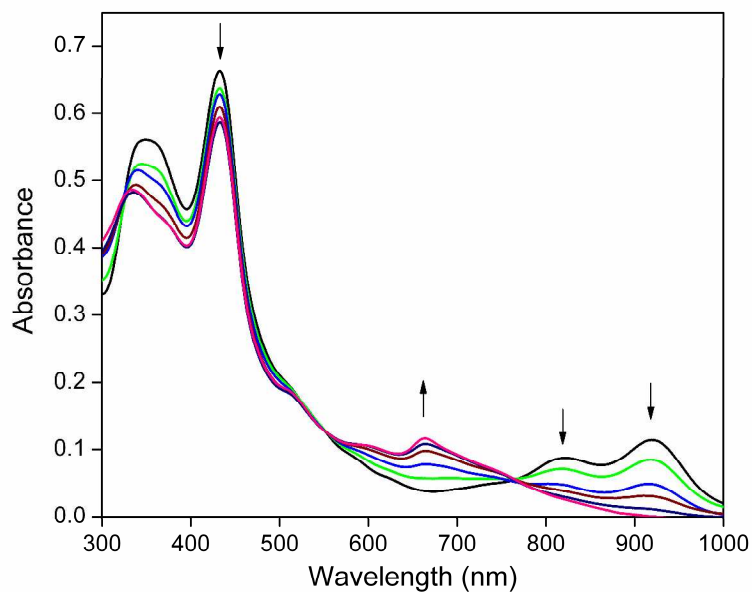


Figure 2. **2** in DCM slowly changed to a green species (pink trace after 24 hours) resembling verdoheme type species.

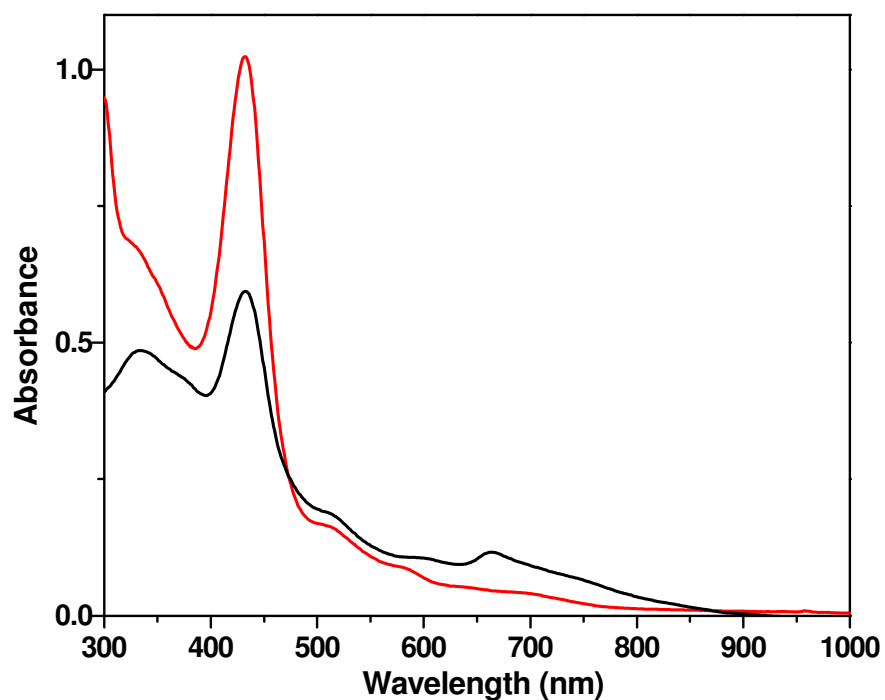


Figure 3. The electronic spectrum of the green verdoheme type product (black) and its demetallation using EDTA to produce yellow orange color similar to bilverdin (red).

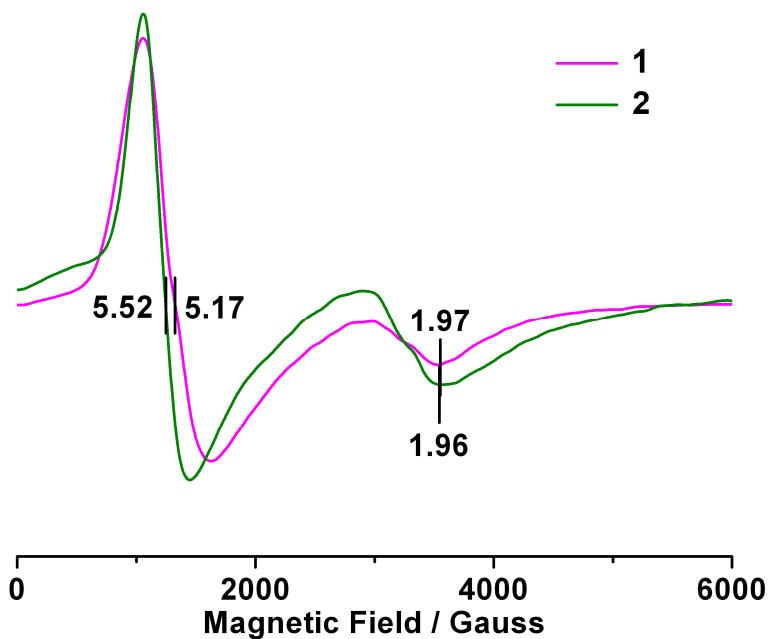


Figure 4. Solid state EPR spectra of **1** and **2** at RT.

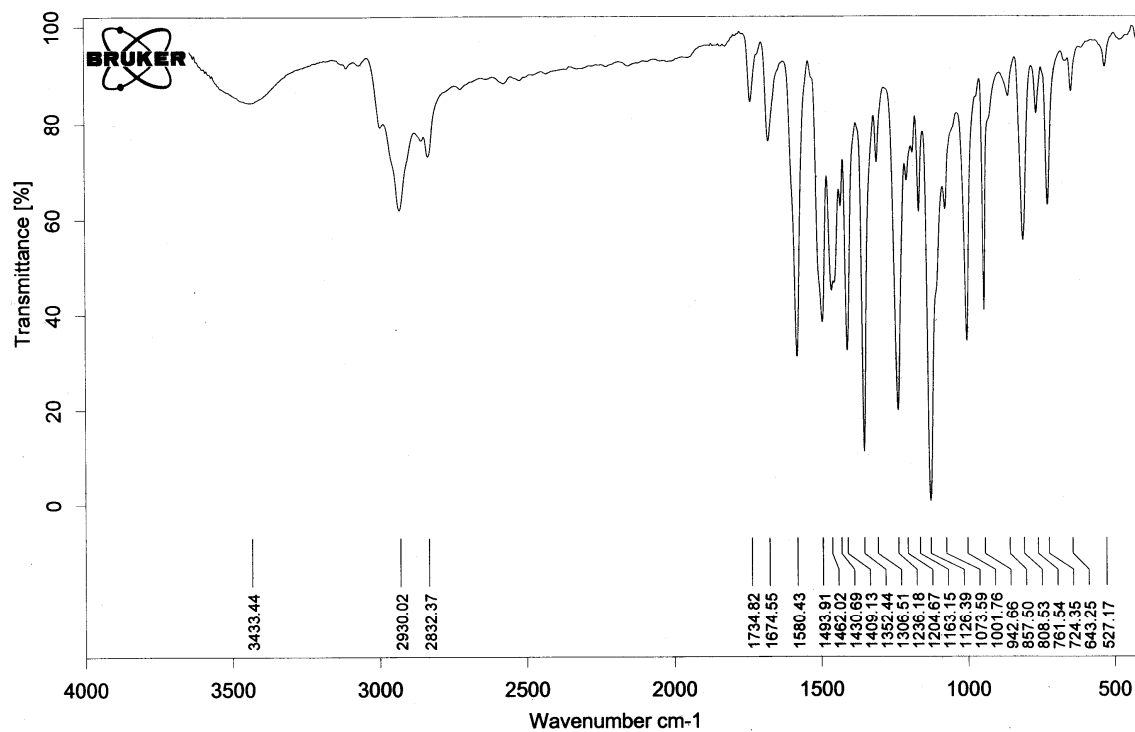


Figure 5. IR spectra of **1** in KBr disc

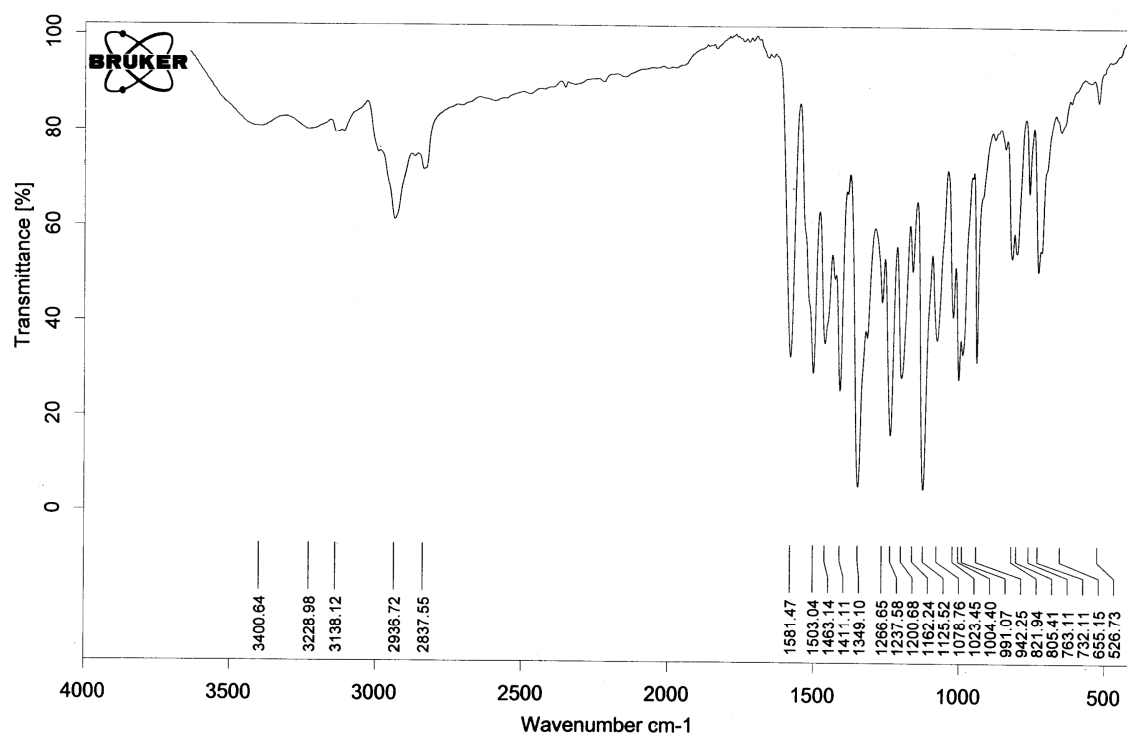


Figure 6. IR spectra of **2** in KBr disc

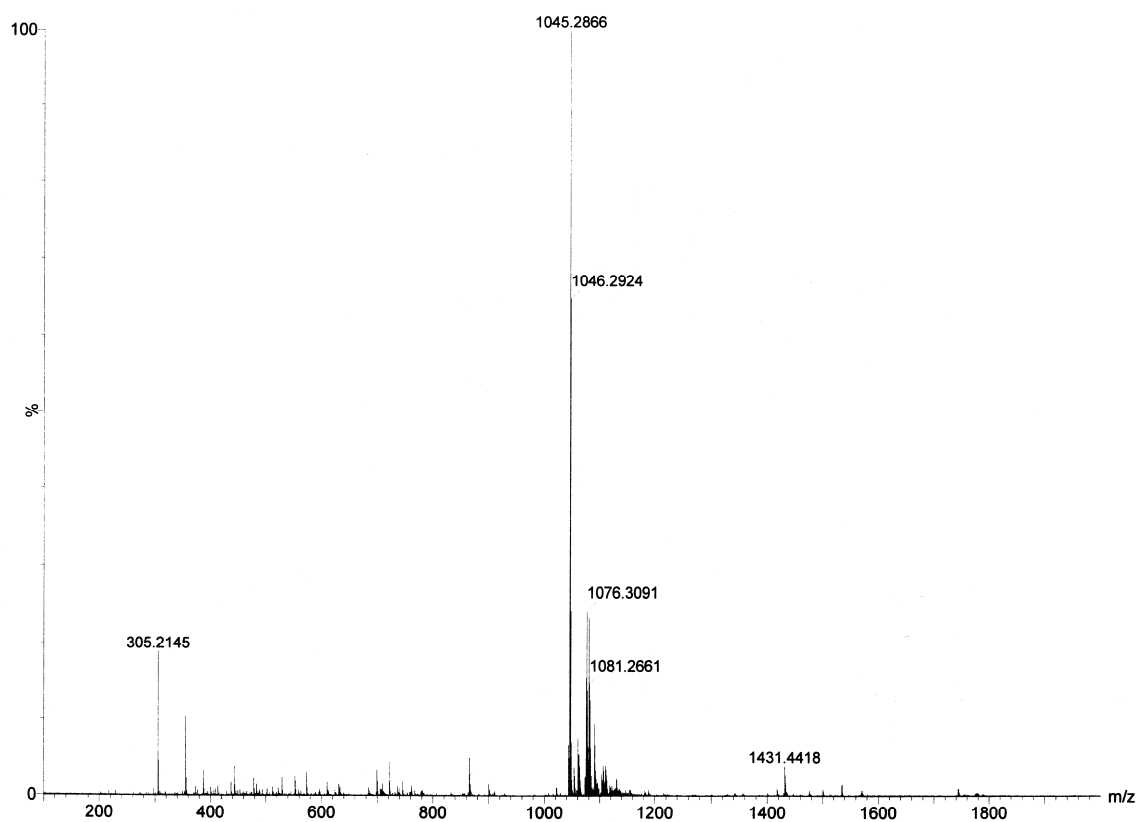


Figure 7. ESI Mass spectra of **2** in acetonitrile positive scan.

Parent ion, $[\text{C}_{56}\text{H}_{53}\text{N}_4\text{O}_{13}\text{FeCl}]^+$ at 1081.266 and $[\text{M}-35]^+$ peaks at 1046.292 are identified

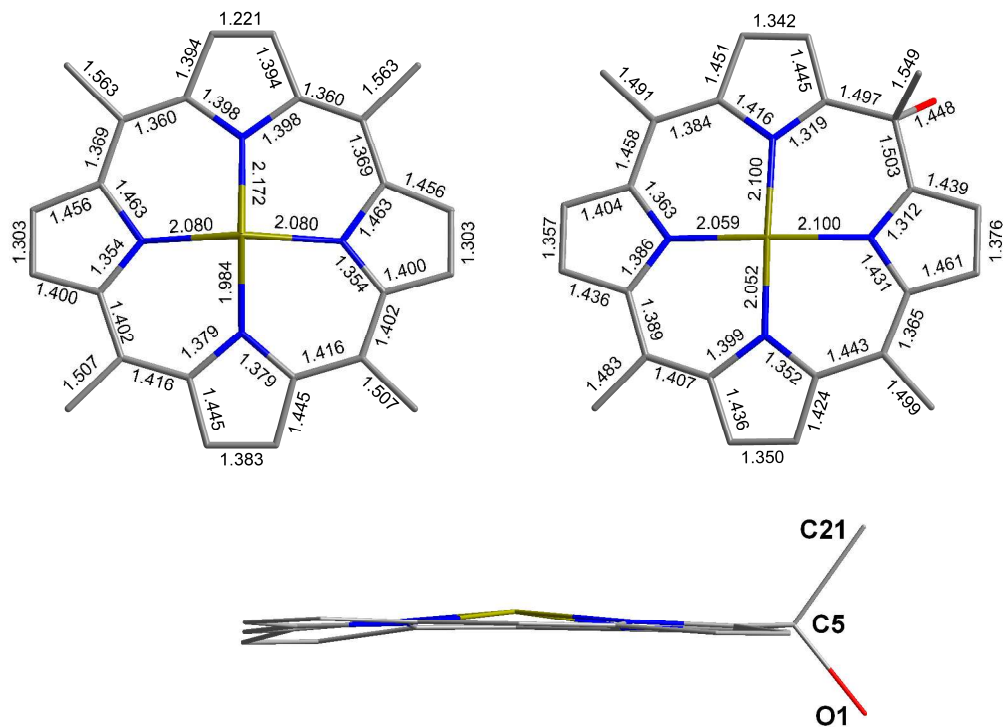


Figure 8. X-ray crystal structure of **1** (above left) (structure taken from ref.13 of the manuscript) and **2** (above right) present study showing the elongation of the bond lengths on hydroxylation. Puckering of FeN1N2C4C6C5 plane due to sp^3 hybridization of C5 in **2** (below). (grey-carbon; blue-nitrogen; red-oxygen; yellow-iron).