

Supporting Information
Nucleophilic Ring-opening of Iron(III)-hydroxy-isoporphyrin

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Synthesis:

Synthesis of chloro[5-(hydroxy)-5,10,15,20-tetrakis(4-methyl)-5,21H-porphinato]iron(III) [Fe(4-Me-HTPI)(Cl)]⁻ (**1**)

Nitrogen dioxide (NO + O₂) gas was passed through a dichloromethane solution of 100 mg (0.13 mmol) *meso*-tetrakis (4-methylphenyl)porphyriniron(III) chloride for 45 seconds. The solution was layered with three times petroleum ether (60-80 C°) and collected the crystalline product after three days. Yield 50 mg (51%) Molecular Formula: C₄₈H₃₇ClFeN₄O; Molecular Weight: 776.200; UV/Vis (CH₂Cl₂) λ_{max}(ε/ mol⁻¹dm³cm⁻¹): 430 (65121), 820 (8511), 905 (11871) nm. FTIR (cm⁻¹); 1518 [ν_a NO₃⁻], 1258 [ν_s NO₃⁻], 1026 [ν NO₃⁻].

Synthesis of chloro[5-(hydroxy)-5,10,15,20-tetrakis(4-methoxy)-5,21H-porphinato]iron(III) [Fe(4-Me-HTPI)(Cl)]⁻ (**2**)

To a dichloromethane solution of 100 mg (0.12 mmol) *meso*-tetrakis (4-methoxyphenyl)porphyriniron(III) chloride nitrogen dioxide gas (NO + O₂) was passed for 45 seconds. The solution was layered with three times petroleum ether (60-80 C°) and collected the precipitate after three days. Yield 55 mg (56%) Molecular Formula: C₄₈H₃₇ClFeN₄O₅; Molecular Weight: 840.180; UV/Vis (CH₂Cl₂) λ_{max}(ε/ mol⁻¹dm³cm⁻¹): 342 (59161), 425 (66134), 805 (8823), 912 (11456) nm); FTIR (cm⁻¹); 1512 [ν_a NO₃⁻], 1252 [ν_s NO₃⁻], 1026 [ν NO₃⁻].

Reaction with alcohols (methanol):

A sample of 2 mg (2 X 10⁻⁵ mol) of isoporphyrin **1** was dissolved in methanol and the spectral changes were observed by electronic spectroscopy. The resulting reaction mixture was analysed for ESI-mass analysis.

Reactions with N-nucleophiles:

A sample of 0.05 mL pyridine was added to a 5 mL dichloromethane solution of iron(III) hydroxy-isoporphyrin **1** (2 X 10⁻⁵ mol) under argon atmosphere. The solution turned into greenish colour due to the formation of iron benzoyl bilinone.

Reactions with S-nucleophiles:

A sample of 0.1 mL thiophenol was added to a 10 mL dichloromethane solution of iron(III) hydroxy-isoporphyrin **1** and **2** (2×10^{-5} mol) with trace pyridine under argon atmosphere and the electronic spectral changes was observed.

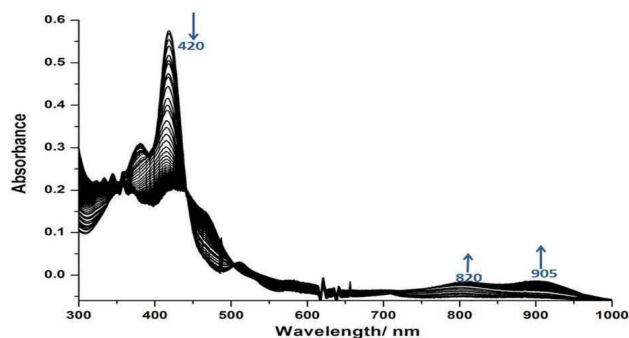


Figure S1. Spectral changes of meso-tetrakis(4-methylphenyl)porphyriniron(III) chloride [Fe(4-Me-TPP)Cl] in chloroform on passing NO₂ gas for 30 seconds. The appearance of new peaks at 820 and 905 nm and decrease in intensity of the Soret band supports the formation of iron isoporphyrin.

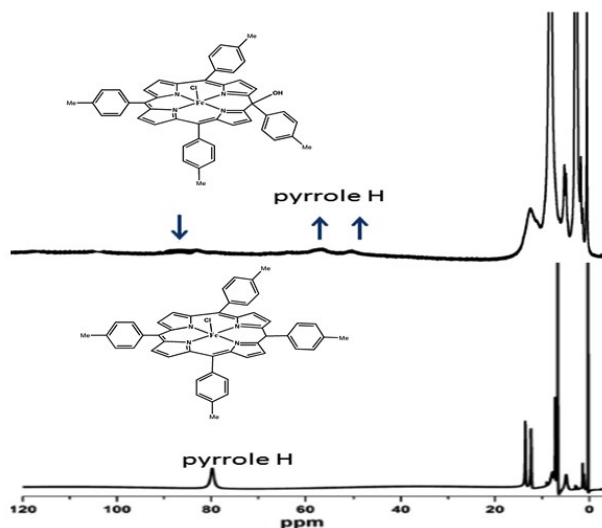


Figure S2. ¹H NMR spectra of meso-tetrakis(4-methoxyphenyl)porphyriniron(III) chloride [Fe(4-Me-TPP)Cl] and hydroxy-isoporphyrin **1** in CD₃Cl.

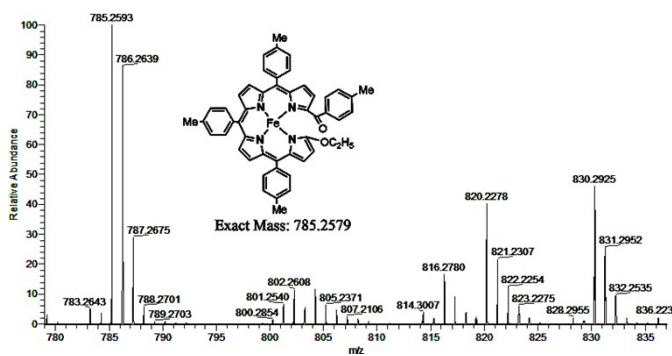


Figure S3. Positive mode ESI-mass spectrum of ring opened 19-benzoyl-1ethoxy-bilin iron complex formed in the reaction of isoporphyrin **1** with ethanol.

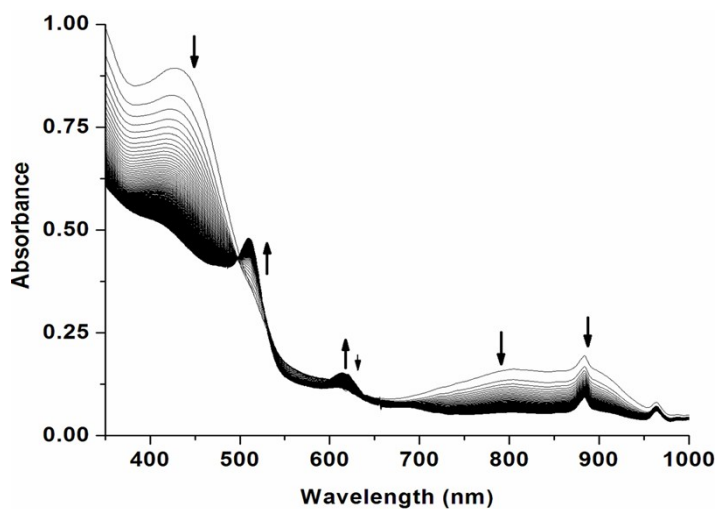


Figure S4. Spectral changes of iron isoporphyrin **1** in dichloromethane on addition of 100 times CAN.

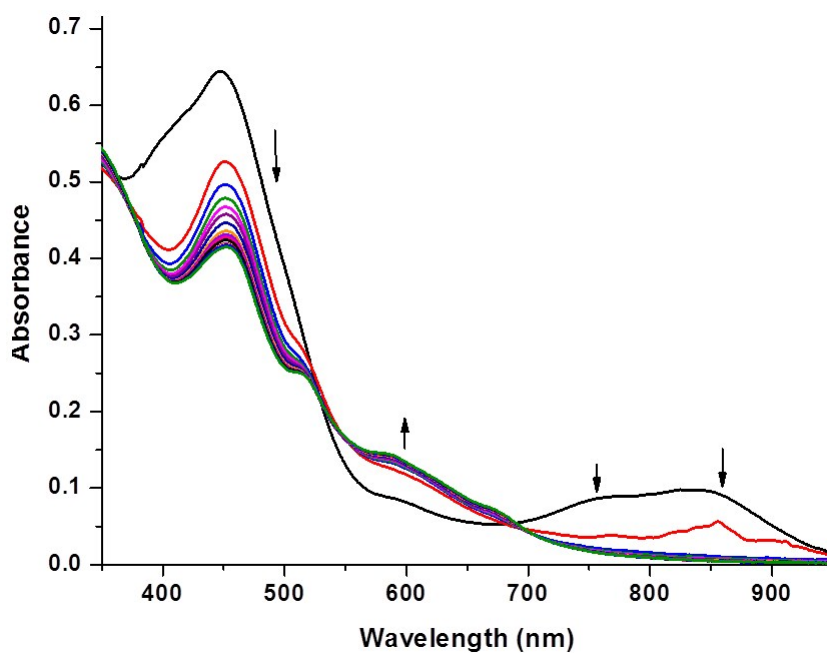


Figure S5. Spectral changes of iron isoporphyrin **1** in dichloromethane on addition of excess n-octylamine.

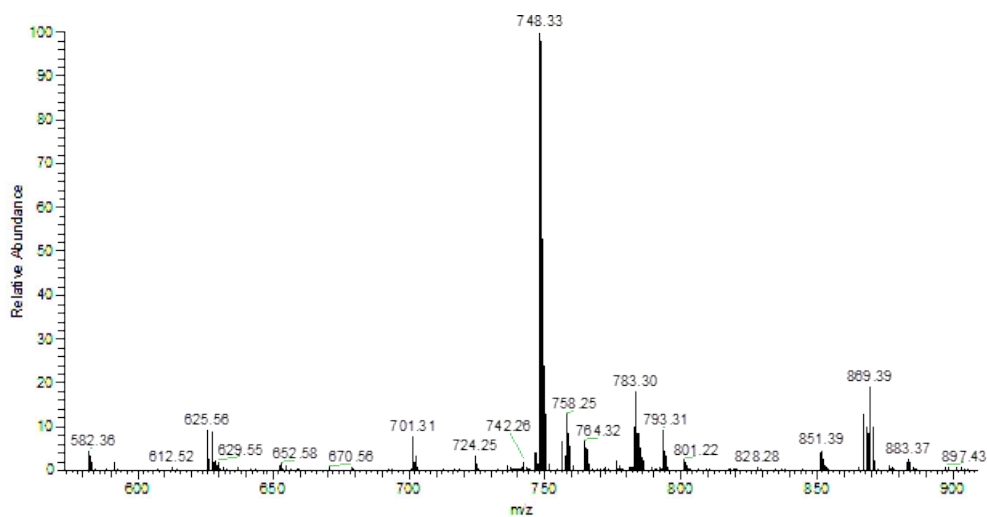


Figure S6. Part of the ESI Mass spectrum of ring opened 19-benzyl-1-octylamin-bilin iron complex formed in the reaction of isoporphyrin **1** with n-octylamine. Parent ion, $[C_{56}H_{54}FeN_5O + H]^+$ is identified.

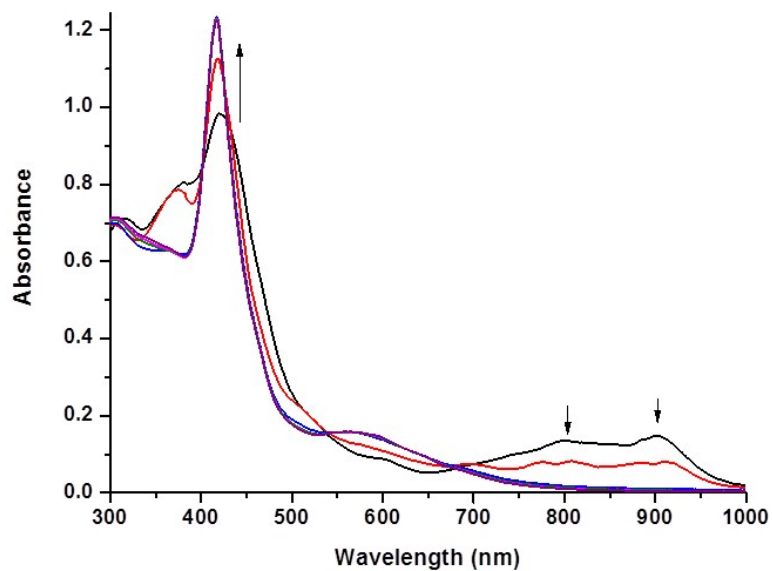


Figure S7. Reduction of iron hydroxy isoporphyrin **2** to parent iron tetraphenyl porphyrin by thiophenol, trace pyridine. (Total time 15 minutes).

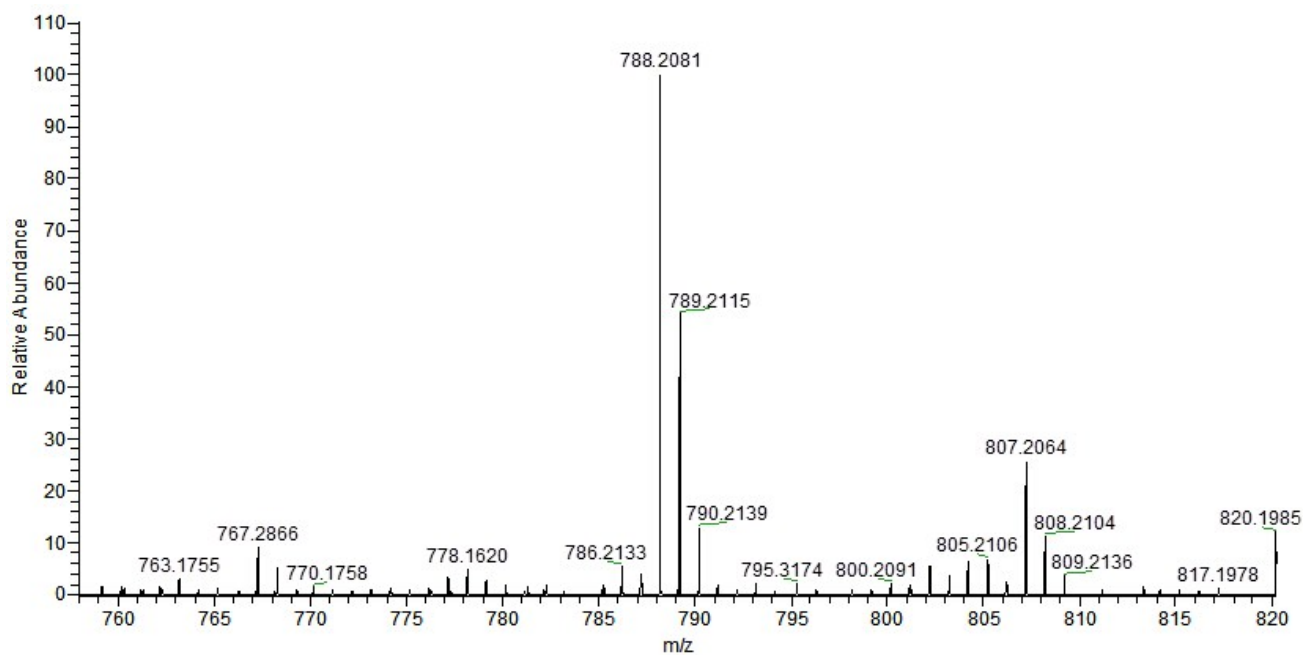


Figure S8. Positive mode ESI-mass spectrum of meso-tetrakis(4-methoxyphenyl)porphyriniron(III) complex ($m/z = 788.20$) formed in the reaction of isoporphyrin **2** with thiophenol.

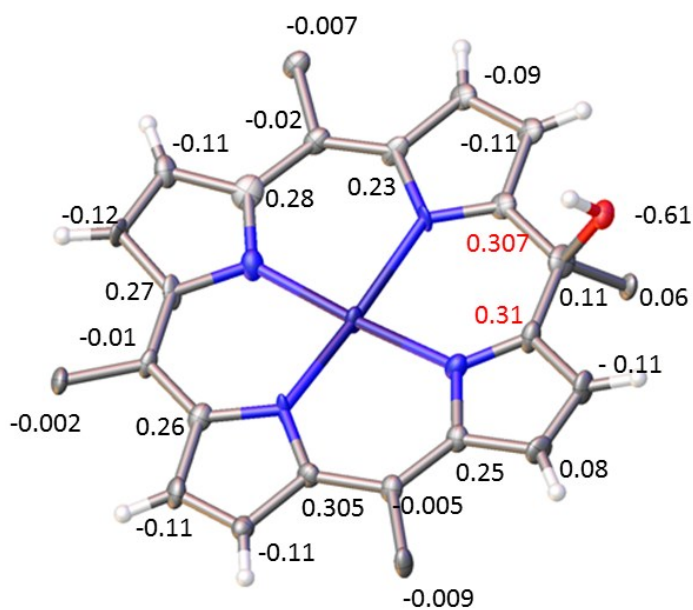


Figure S9. Mulliken atomic charges for atoms of the iron hydroxy isoporphyrin **3**. The neighboring two carbon atoms of the saturated meso carbon atom (displayed as red in colour) have higher positive charges than other carbon atoms, which suggest the nucleophilic attack at the adjacent carbon atom of the saturated *meso* carbon atom.