Supporting Information

for

Molecular Assembling Using Axial Phenolate on Iron N-Confused Porphyrin Complex

Contents

General Information

Manipulations, reactions and transfers of samples were conducted under nitrogen in an inert atmosphere dry box or according to standard Schlenk techniques. For inert-atmosphere operation, solvents were dried, distilled, and degassed using standard techniques. Pyrrole was fresh distilled from calcium hydride before use. Otherwise all starting materials were obtained commercially and used without further purification. UV-Vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer. Analysis of carbon, hydrogen and nitrogen were obtained with a CHN analyzer (Heraeus). Magnetic susceptibility data were recorded on a Quantum Design MPMS5 5 T SQUID magnetometer. The SQUID results were obtained with a field of 10000 G.

Preparation of [Fe(*H*CTPP*H*)(OPh)] (2) and [Fe(CTPP)(OPh)•Na(THF)$_2$]$_2$ (3)

A 100 mL vessel charged with a THF (30 mL) solution of Fe(NCTPP)Br (50 mg, 0.067 mmol) was added with NaOPh (60 mg, 0.52 mmol) in an inner atmosphere dry box. The solution was heated to 65° C and continuously stirred under nitrogen. The tracing of the Uvvis spectra of reaction observed the shift of the *Soret* band to 465 nm and *Q* band to 676 nm. The reaction was discontinuous after 3 hours and the solvent was evaporated under vacuum. The resulted solid was then dissolved in about 20 mL CH_2Cl_2 and the undissolved solid and excess sodium phenolate was filtered off with the assistance of a Celite plugged filter. Hexane was then added slowly into the filtrate until the solid precipitate out from the solution to obtain green solid of **2**. (43 mg, 77 % yield) The sample for elemental analysis was obtained from the recrystallization of crude product from CH_2Cl_2/hexane. The dissolving of the crude product in a mixture solvent of THF/CH_2Cl_2 (1:1) and slowly diffused with hexane in the anaerobic dry box obtained the crystal of **3** after two weeks. Alternatively, **3** can be obtained from dissolving the crude product of **2** (35 mg) in THF/CH_2Cl_2 (1:1) and briefly introduced dioxygen gas into the solution. The completion of the reaction was confirmed from the absorption maximum shifted from 465 nm to 414 nm. The solvent was then removed under vacuum and stored under nitrogen. The crystalline form of **3** (21 mg) can be obtained from the diffusion of hexane into a CH_2Cl_2 solution of crude sample of **3** under anaerobic conditions.

2: Absorption spectrum (CH_2Cl_2) [λ_{max}, nm (log ε, $M^{-1}cm^{-1}$)]: 466 (4.64), 676 (3.74). Anal. Calcd. for $FeC_{50}H_{33}N_4O \cdot C_6H_{14} \cdot CH_2Cl_2$: N,6.01; C, 73.39; H, 5.29. Found: N,5.69; C, 72.93; H,5.03.; δ_H (300 MHz; d_8-THF) -31.18 (1 H, br s, phenolate), -27.45 (2 H, s, phenolate), -8.50 (1 H, s, NH), -6.20 (1 H, s, *β*-pyrrole), -2.23 (1 H, s, *β*-pyrrole), -0.86 (1 H, s, *β*-pyrrole), 3.0-11.0 (20 H, m, phenyl), 30.51(2 H, s, phenolate), 37.33 (1 H, s, *β*-pyrrole), 39.75 (1 H, s, *β*-pyrrole), 41.40 (1 H, s, *β*-pyrrole), 47.05 (1 H, s, *β*-pyrrole).

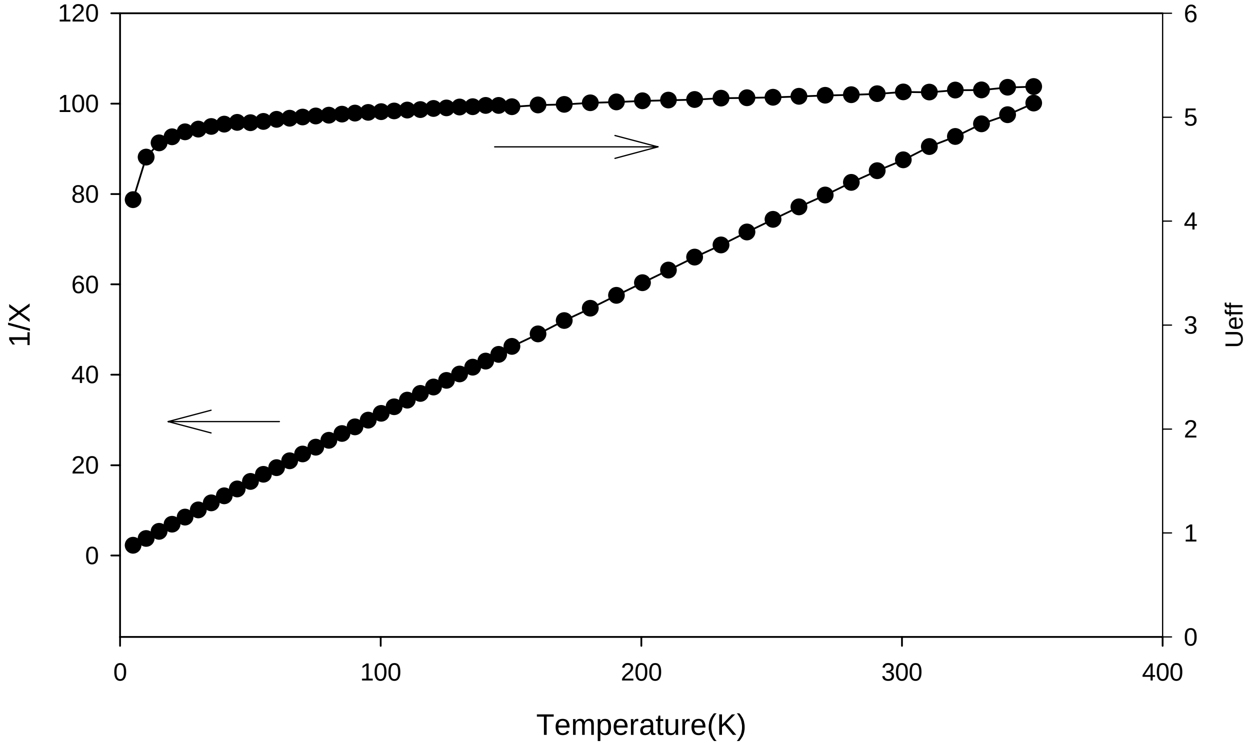
3: Absorption spectrum (CH_2Cl_2) [λ_{max}, nm (log ε, $M^{-1}cm^{-1}$)]: 416 (4.40), 538 (3.79,sh). Anal. Calcd for $Fe_2C_{116}H_{92}N_8O_6Na_2 \cdot C_6H_{14} \cdot 1.5CH_2Cl_2$: N, 5.42; C,71.82; H,5.32. Found: N,5.35; C, 71.61; H, 5.32.

X-ray Analysis of the Structures of 3

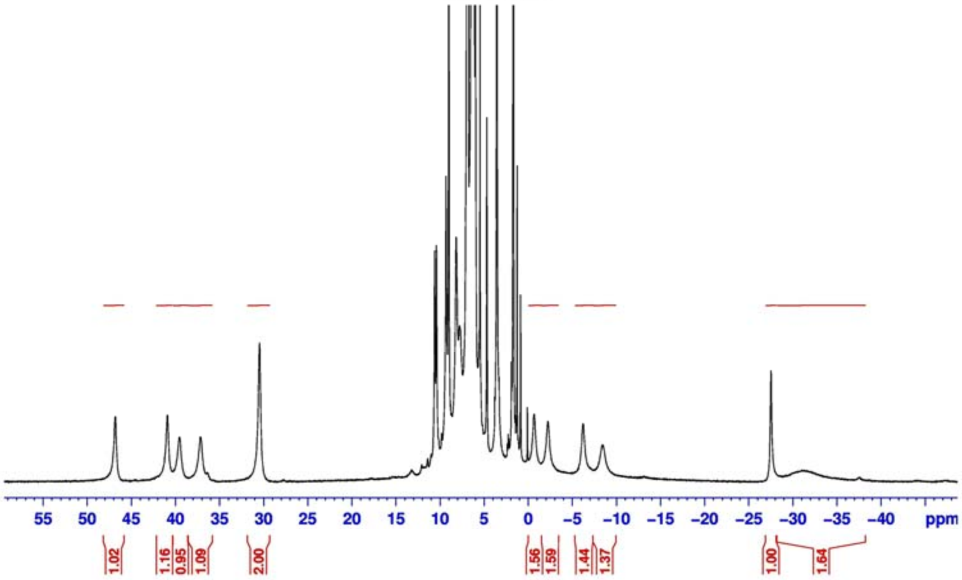
Diffraction measurements were carried out at 150(2) K on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Least-squares refinement of the positional and anisotropic thermal parameters for the contribution of all non-hydrogen atoms and fixed hydrogen atoms was based on F^2. A SADABS absorption correction was made. The SHELXTL structural refinement program was employed.

3: The crystal suits for structure analysis measured 0.15 x 0.12 x 0.10 mm^3 which was grown from a slow diffusion of hexane into the CH_2Cl_2 solution of **3** in an inert-atmosphere dry box. **3** crystallized in triclinic unit cell, space group P-1, a =13.2565 (14) Å, b = 13.3978 (14) Å, c = 14.8122 (16) Å,α=90°, α = 75.423 (2)°, β = 87.871 (2)°, γ= 88.046 (2)° V = 2543.5(5) $Å^3$, Z = 2, D_c = 1.322 Mg/m^{-3}, λ = 0.71073 Å, μ = 0.460 mm^{-1}, $F(000)$ = 1054. Data were collected for 1.42 < θ < 27.55°. The structure was solved by direct method and refined by least square against F^2 to $R1$ = 0.0656 (w$R2$ = 0.1102) and S_{goof} = 0.976. The residue largest peak and hole are 0.480 and -0.458 e $Å^3$, respectively.

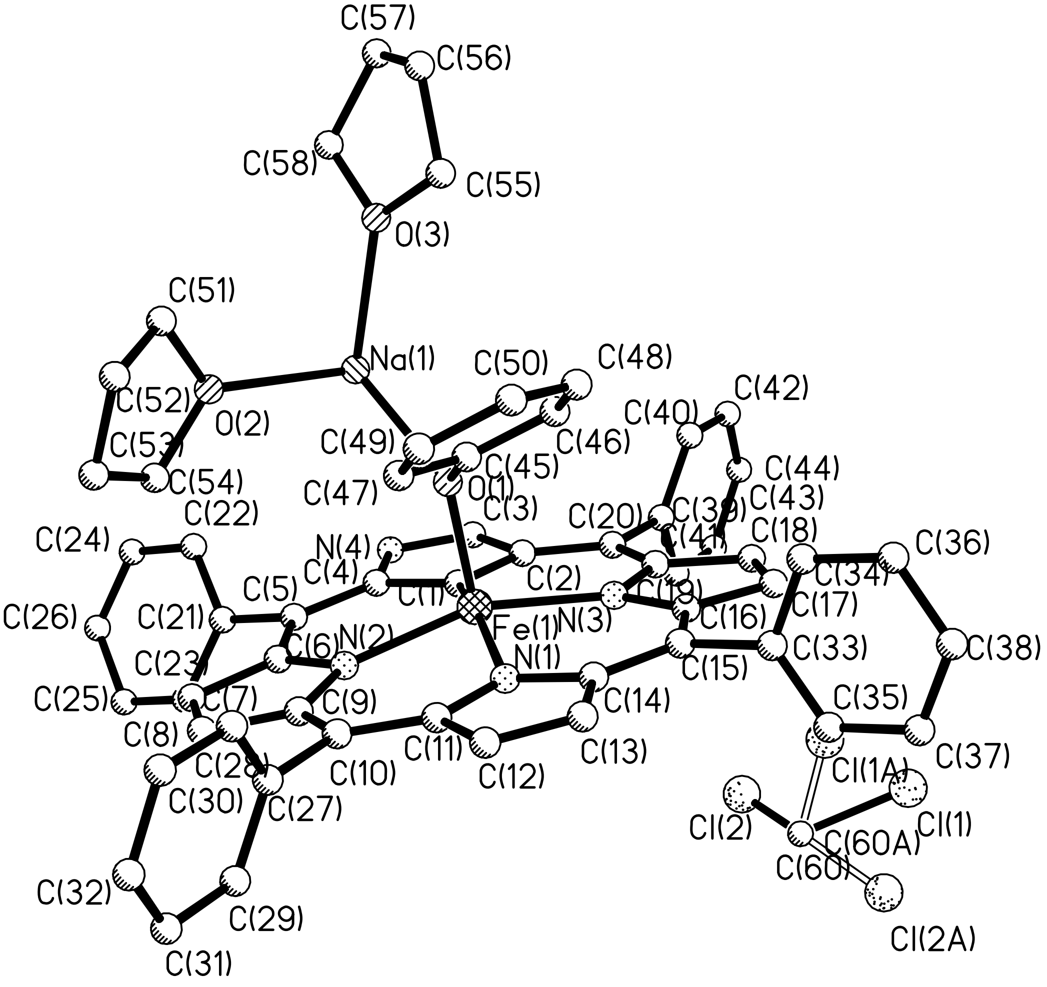
Supporting Figure 1. SQUID magnetic susceptibility data for [Fe(*H*CTPP*H*)(OPh)], (**2**)



Supporting Figure 2. ^{1}H NMR spectrum of [Fe(*H*CTPP*H*)(OPh)], (**2**) in D$_8$-THF.



Supporting Figure 3. Full atomic labeling in the crystal structure of [Fe(CTPP)(OPh)•Na(THF)$_2$]$_2$ (**3**)



Note: (1). For clarity only half of the molecule is shown here. The second half of molecule is generated through symmetry. (2) Solvation methylene chloride is omitted for clarity.