Molecular assembling using axial phenolate on an iron N-confused porphyrin complex†

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The reaction of sodium phenolate and Fe(*H*CTPP*H*)Br assembles a dimeric iron(III) complex with a channel-like solid state packing; the intramolecular iron-to-iron distance of 8.864 Å is the longest among the available N-confused porphyrin dimeric complexes.

The inverted pyrrole ring inside the N-confused porphyrin (NCP) constructs a three-nitrogen–one-carbon inner coordination environment and a peripheral pyrrolic nitrogen.[1,2] The unique inner-core environment on NCP furnishes rich and unusual coordination chemistry.[3–5] Versatile coordination modes such as agostic type interactions between metal and inner C–H and a direct metal–carbon bond have been reported.[6–9] Moreover, the peripheral nitrogen provides a potential site for intermolecular linkages and NCPs have been suggested as new scaffolds for supramolecular architecture.[10] Earlier results coordinated Rh or Pt metal ion to the peripheral nitrogen and revealed the coordination ability of the peripheral nitrogen.[11–13] Shortly, several face-to-face dimers or tetramers with a central metal ion coordinated to their three inner core nitrogens and to the peripheral nitrogen on the paired NCP were reported.[14–16] The rates of monomer exchange reaction as well as metal dissociation have been evaluated.[17] Alkylation of the peripheral nitrogen to construct more complicated polymeric NCPs has been demonstrated in the recent reports.[18,19] However, new approaches are awaited to fully utilize the unique molecular shape. Herein we report the synthesis of monomeric and dimeric iron NCP complexes with a bio-related phenolate as the axial ligand. The dimeric NCP complex exhibits a novel NCP architecture with sodium ions bridging in between the axial phenolate oxygen and peripheral nitrogen on the paired NCP complexes to give a rectangular type shape. Importantly, the dimer assembles into a channel-like geometry in the crystal lattice to form a rare well-organized architecture in the NCP complexes.

As shown in Scheme 1, the starting NCP iron complex [Fe(*H*CTPP*H*)Br], **1**,[7] was reacted with an excess amount of NaOPh in THF to give a monomeric iron NCP phenolate complex **2**.‡ As shown in Fig. 1, the UV-vis spectrum of the product changed slightly to have a Soret band at 466 nm and a broad Q band at 676 nm. Comparing with the starting compound, the Soret band of **2** is slightly red-shifted while the Q band is significantly blue-shifted. The pattern of the UV-vis spectrum suggests a square pyramidal iron(II) complex with a three coordinated non-planar NCP ring similar to the staring compound **1**.[7] The ^{1}H NMR chemical shifts of **2**, spread within the range of 47 to −31 ppm with downfield shifted β-pyrrolic protons, suggest a high spin monomeric iron(II) NCP complex.[20,21] The chemical shifts for axial phenolate confirmed by an isotope labeling study give upfield resonances at −27.44 and −31.30 ppm for *ortho* and *para* protons and a downfield resonance at 30.48 ppm for *meta* protons. The pattern of phenolate resonances resembles that for [Fe(TTP)(OPh)] with corresponding shifts three times smaller for the high spin iron(II) complex of **2** compared with the iron(III) high spin complex of [Fe(TTP)(OPh)].[22] The integrated values of phenolate resonances in **2** confirm one phenolate in an axial position. The SQUID magnetic susceptibility measurement using a solid sample of **2** gave a temperature independent curve above 15 K. The effective magnetic moment of 5.24 μ_B at room temperature is in the range of a high spin iron(II) metal center.

Compound **2** is stable in the solid state under anaerobic conditions but extremely unstable under aerobic conditions. Its stability in solution is solvent dependent. The toluene solution of **2** is stable under anaerobic conditions but the UV-vis spectrum for a CH_2Cl_2 solution of **2** changes slowly in an N_2 dry box to give a new compound with a Soret band at 416 nm. Presumably, trace oxygen and slightly acidic conditions might slowly promote the oxidation of **2** in dry box to form an iron(III) complex with the three-nitrogen–one-carbon four coordinated planar iron NCP core. When the CH_2Cl_2 solution of **2** was exposed to air, the UV-vis spectrum changed immediately to have a Soret band at 416 nm identical to the slow oxidation reaction product of **2** in a dry box. The ^{1}H NMR spectrum of the oxidation product exhibits β-pyrrole resonances in the upfield region with the most shielded pyrrolic proton resonance located at −54.13 ppm. Although further studies are required to confirm the spin state, the spreading of β-pyrrole chemical shifts of 62.1 ppm and the upfield shifted resonances resemble those reported for Fe(CTPP)Br and suggest that an intermediate spin state is likely.[20] A much slower second oxidation reaction was observed with the Soret band shifted further from 416 nm to a broad absorption band around 390 nm. The absorption spectrum of the second oxidation product resembles those of products with oxygen insertion to the inner iron–carbon bond as in the case of [Fe(CTPPO)Br].[20]

Crystals of **3** suitable for single crystal X-ray diffraction study were obtained from a slow diffusion of hexane vapor into a CH_2Cl_2–THF solution of **2**. The solution of the obtained crystals

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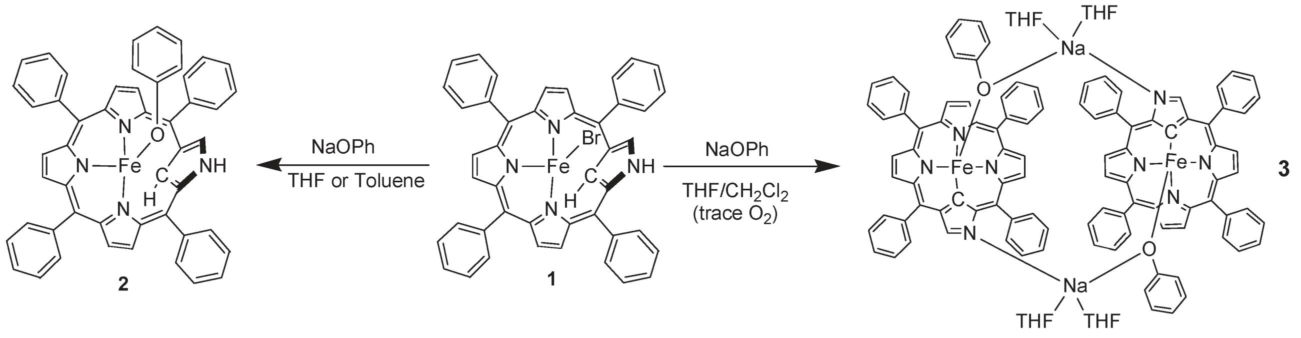

Scheme 1

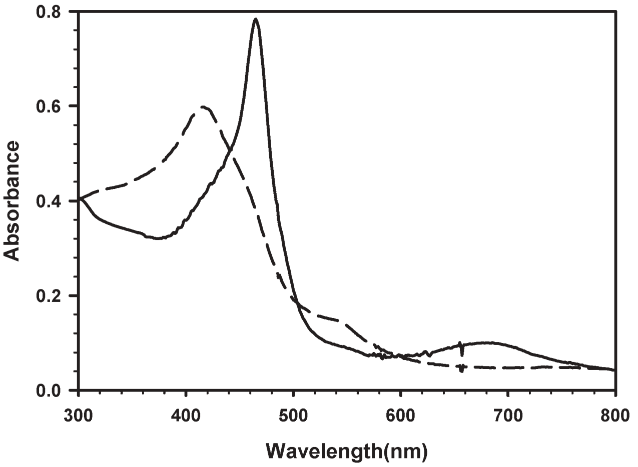

Fig. 1 The UV-vis spectra of [Fe(*H*CTPP*H*)(OPh)] (**2**) (—) and $[Fe(CTPP)(OPh)\cdot Na(THF)_2]_2$ (**3**) (– – –).

exhibited a UV-vis spectrum identical to that of **3** and suggests the oxidation of **2** during the crystal growth.

The dimeric $[Fe(CTPP)(OPh)\cdot Na(THF)_2]_2$, **3**, was crystallized in a triclinic $P\bar{1}$ space group with a disordered CH_2Cl_2 as a solvated molecule.§ The dimeric porphyrin complex lies about an inversion centre with half of the molecule generated from symmetry. As shown in Fig. 2, a face-to-face dimer constructed from two five coordinated NCP iron(III) complexes linked with sodium ions in between the axial phenolate oxygen and NCP peripheral nitrogen was obtained. Two THF molecules on each sodium were located to stabilize the sodium ions. The distances between sodium and oxygens on THFs of 2.327(5) and 2.372(4) Å as well as the Na–N distance of 2.417(4) Å are near identical to those in a previously reported iron(III) hydroxyl bridged NCP dimer.[14] The distance of 2.274(4) Å between sodium and phenolate oxygen is slightly shorter than the corresponding distance in other phenolate bridging complexes.[23]

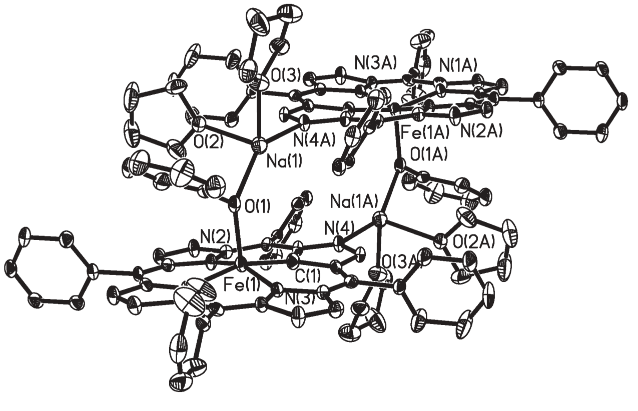

Fig. 2 The structure of $[Fe(CTPP)(OPh)\cdot Na(THF)_2]_2$, **3**, in 50% ellipsoids. Additional "A" letters in the atom labels denote atoms at equivalent positions (1 − *x*, 2 − *y*, 1 − *z*). Hydrogens are omitted for clarity.

As expected for an iron(III) NCP complex, the NCP ring has a near planar conformation. Unlike most face-to-face dimers with a tilted inverted pyrrole ring, **3** represents a unique NCP dimer constructed from a planar NCP ring with a direct iron–carbon bond. A slightly saddle shaped distorted porphyrin core is observable with an average deviation of 0.0716 Å for atoms deviating from the 24 atoms mean plane. The central iron deviates by 0.4034 Å from the mean plane toward the axial phenolate. In the dimeric central core, the intramolecular iron-to-iron separation of 8.864 Å is much longer than the value of 5.008 Å found in the direct linkage NCP dimer, $[Fe(CTPPH)]_2$.[14] The surrounded porphyrins, phenolates and sodium ions link together to form a

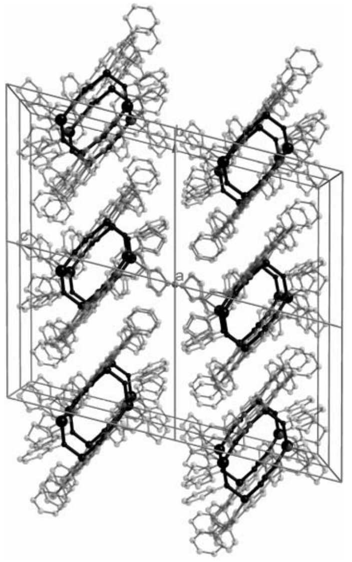

Fig. 3 The packing diagram of $[Fe(CTPP)(OPh)\cdot Na(THF)_2]_2$ with ordered arrays of rectangle-like structures highlighted viewed down the *a* axis.

rectangle-like structure with an 8.39 Å wide and 4.22 Å thick central core. As shown in Fig. 3, in the crystal lattice the complexes aligned into a channel-like array. The average distance of 11.65 Å between rectangles along a channel is relatively long. The porphyrin-to-porphyrin distance of 4.696 Å between layers of porphyrins is longer than the ideal distance of 3.4 Å for π–π interactions but a weak π–π interaction between layers can not be ruled out.[24,25]

In summary, novel iron NCP phenolate complexes have been prepared. The data of the monomeric complex **2** are in agreement with a high spin iron(II) center. The dimeric iron(III) complex obtained from the oxidation of the monomer demonstrates a new method to create a central core within a hydrophobic porphyrinic environment taking advantage of the peripheral nitrogen and axial ligand. The use of other axial ligands to construct large core NCP dimers, locating the proton resonance of the porphyrinic internal C–H in **2**, as well as understanding the electronic interaction between irons in the dimeric structure are under investigation.

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Notes and references

‡ *Characterisation data*. **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%; **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%.

§ *Crystal data*. $[Fe(CTPP)(OPh){\cdot}Na(THF)_2]_2{\cdot}CH_2Cl_2$, **3**, $C_{59}H_{50}Cl_2FeN_4NaO_3$, M = 2025.54, monoclinic, a = 13.2565(14), b = 13.3978(14), c = 14.8122(16), α = 75.423(2)°, β = 87.871(2)°, γ = 88.046(2)°, V = 2543.5(5) Å^3, T = 150 K, space group $P\bar{1}$, Z = 1, μ = 0.460 mm^{-1}, ρ_c = 1.322 Mg m^{-3}, crystal size = 0.15 × 0.12 × 0.10 mm^3, 11302 independent data with $I > 2\sigma(I)$, S_{gof} = 0.976, $R1$ = 6.59%, $wR2$ = 11.02%. CCDC 295479. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600423g

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