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Unique 2D metalloporphyrin networks constructed from iron(II) and *meso*-tetra(4-pyridyl)porphyrin

Long Pan, Sean Kelly, Xiaoying Huang and Jing Li*
Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ 08854, USA.
E-mail: jingli@rutchem.rutgers.edu

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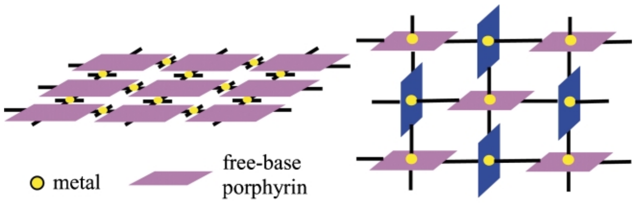
A one-pot solvothermal reaction of iron(II) with *meso*-tetra(4-pyridyl)porphyrin (TPyP) leads to two novel layered structures with an unprecedented two-dimensional paddle-wheel-like pattern; the two structures have the same composition Fe(TPyP) but a different packing sequence, namely ···ABAB··· and ···ABCDABCD···.

The interest in extended networks of coordination complexes has increased exponentially during the past decade, due to their fascinating structures and promising applications in practical areas such as catalysis, magnetism, nonlinear optics, sensors, and separation.[1] Rational design and synthesis of organic–inorganic materials with unusual structures often lead to unprecedented chemical/physical phenomena and applications.[2] Highly organized multiporphyrin structures are especially attractive because of their superb electron charge and energy transfer properties, and potential as functional materials by self-assembly.[3] Recently, an amazing porphyrin tape has been reported to possess an absorption band in the near-IR region,[4] in great contrast with most of the known porphyrins whose absorption bands are in the ultraviolet-to-visible region. In addition to their important optical properties, some porphyrin compounds also exhibit interesting magnetic behavior. For example, one-dimensional metal TCNE porphyrin compounds represent a new family of organic-based magnetic materials.[5] In attempts to construct metalloporphyrin network structures that possess useful properties, we have developed a synthetic strategy that focuses on particular systems with specific topologies. Free-base *meso*-tetra(4-pyridyl)porphyrin (H_2TPyP) has been selectively employed in our synthesis. H_2TPyP contains a rigid plane and four pendant pyridine arms opposite from each other, measuring nearly 15 Å apart. Generally, deprotonation of pyrrole hydrogens takes place fairly easily under hydro(solvo)thermal conditions,[6] thus metals would bind directly to the porphyrin center rather than to pyridine N atoms. This would lead to a structure in which neighboring porphyrins are mutually perpendicular to each other, rather than to a free-base porphyrin or a tessellated network.[7] In Scheme 1, a non-tessellated structure with metal centered porphyrins (right) is shown in comparison with a tessellated structure having free-base porphyrins (left).

The actual solvothermal synthesis was carried out using ferrocene as a metal source. A typical reaction involved mixing of 0.54 mmol (150 mg) of ferrocene and 0.24 mmol (150 mg) of H_2TPyP in 3 mL of DMF solvent. The sample was placed in a 23 mL Teflon lined acid-digestion bomb and heated at 150 °C for 5 days. The product was treated with ethanol and diethyl ether, followed by drying for ~30 min at 80 °C. It contained two phases, with the main phase being dark-red cubic crystals of Fe(TPyP)(**1**), and the minor phase being red plate-like crystals of Fe(TpyP)(**2**) (150 mg, 92% total yield). Both crystals were insoluble in common solvents, and showed no structural change after refluxing in distilled water, organic polar and non-polar solvents such as DMF, CH_3CN, $CHCl_3$ and toluene. X-ray diffraction analyses were performed† on single crystals of **1** and **2**, and the results revealed that both are layered structures with similar building blocks but different packing sequences.

The coordination geometry around each iron(II) ion in both **1** and **2** is octahedral (Fig. 1). The equatorial positions located in the porphyrin plane are occupied by four N donor atoms from four pyrrole moieties of the porphine ligand. The axial positions are occupied by two pyridine nitrogen atoms coming from the two adjacent porphine molecules with an identical Fe–N bond length of 2.009 Å for **1** and 2.010 Å for **2**. The average Fe–N_{eq}/N_{ax} distance of 1.998 Å for **1** and 1.995 Å for **2** are consistent with a similar Fe porphyrin complex previously reported.[6a] The metal center may be regarded as having a nearly D_2 symmetry and all metals are located in the same plane. The dihedral angles between the porphyrin plane and the four attached pyridine rings are 90.1, 89.9, 114.4 and 65.6° for **1**, and 101.5, 78.5, 114.0, 66.0° for **2**, respectively, and are similar to those reported.[6b] All neighboring porphyrins are mutually perpendicular to each other. Such an arrangement gives rise to an unprecedented two-dimensional paddle-wheel-like pattern with a 'paddle' depth of 15.6 Å. This unique geometry also leads to a metal–metal distance of 9.74 Å in **1** and 9.73 Å in **2**, respectively, significantly shorter than that found in tessellated structures (15.5 Å). Upon stacking, the adjacent layers in **1** are shifted by $\frac{1}{2}b$, resulting in an alternating ···ABAB··· packing sequence as shown in Fig. 2. Alternatively, the layers in **2** are shifted by $\frac{1}{2}a$, $\frac{1}{2}(a + b)$ and $\frac{1}{2}b$, *respectively*, to generate an ···ABCDABCD··· sequence (see Fig. 2). The pendant pyridine arms from the porphyrins in each layer effectively occupy the interporphyrin cavities in the adjacent layers, thus resulting in a structure excluding any solvent molecules, a feature different from any known porphyrin networks. To the best of our knowledge, such a 2D network of 4^4 topology with perpendicu-



Scheme 1

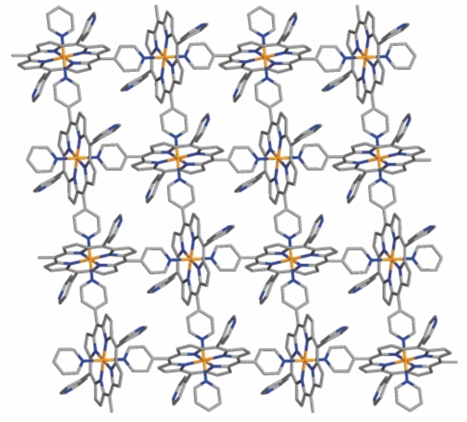


Fig. 1 View of structure **1** shown along the *a*-axis.

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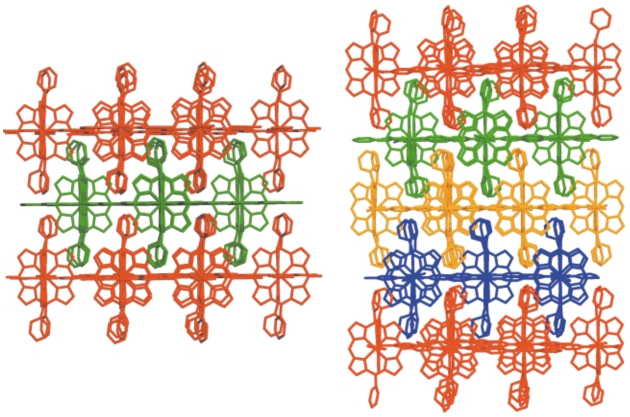

Fig. 2 View of **1** along [011] and **2** along [110], respectively.The packing sequence is indicated by different colors: Red–A, green–B, gold–C and blue–D.

larly arranged porphyrin molecular planes has not been reported previously.

Thermogravimetric (TG) experiments showed an unusually high thermal stability of these compounds. The structures remain intact up to 550 °C under a nitrogen atmosphere. Fig. 3 depicts photographs of crystals of **1** taken at room temperature and after being heated at 430 °C. The unit cell data, obtained after the crystals were heated to 400, 500 and 550 °C, shows negligible changes compared with the room temperature data.[8] Powder X-ray diffraction (PXRD) analysis generated identical patterns for a room temperature sample and samples after being heated at 500 °C for 30 min. In air, the compound was stable up to 330 °C. The TG analysis performed between 20 and 1000 °C showed a very sharp, but single peak associated with a weight loss occurring between 330 and 340 °C. This weight loss of 1.227 mg corresponds to 91.3% of the sample (1.344 mg), and is in excellent agreement with the calculated weight percentage of porphyrins (91.7%). Powder PXRD analysis immediately following the TG experiments shows only Fe_2O_3 as the residue.

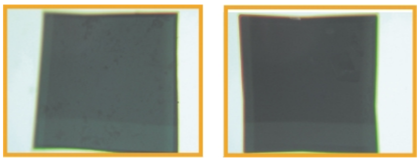

Fig. 3 Photographs of crystals of **1** taken (a) at room temperature and (b) after being heated at 430 °C.

The room temperature fluorescence spectra were measured using a Fluorolog-3 modular spectrofluorometer with 5 × 5 nm bandpass, on both the emission and excitation monochrometer, with an excitation of 410 nm. The spectrum of the sample, in the solid state, is plotted in Fig. 4. Two fluorescence bands were observed at 667.5 and 715.7 nm, which are similar but different from those of the free-base ligand, and in accordance with a number of other porphyrin systems.[9]

In summary, a new type of layered metalloporphyrin–iron(II) structures has been synthesized and characterized. These structures possess an interesting topology of alternately perpendicular porphyrins that leads to a novel 2D paddle-wheel-like network. The high thermal stability of these compounds is promising for high temperature applications. The compounds exhibit characteristic fluorescence functionality.

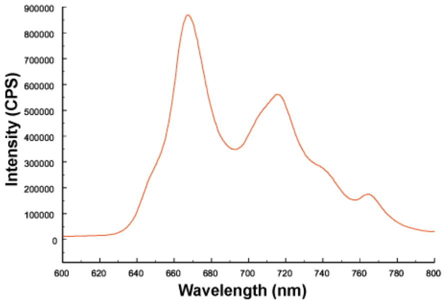

Fig. 4 Fluorescence spectrum of **1** in solid state.

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Notes and references

† *Crystal data for* **1**: space group *Cmca* (no.64) with $a = 18.178(11)$, $b = 13.7783(8)$, $c = 13.7565(8)$ Å, $V = 3445.5(4)$ Å^3, $Z = 4$, $D_c = 1.296$ g cm^{-3} and μ(Mo-Kα) = 0.479 cm^{-1}. All measurements were made on a SMART CCD area detector with graphite-monochromated MoKα radiation; $R_1 = 0.042$ and $R_w = 0.096$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.50 and −0.32 e$^-$ Å^{-3}.

Crystal data for **2**: space group $I4_1/acd$ (no.142) with $a = 13.758(2)$, $b = 13.758(2)$, $c = 36.606(7)$ Å, $V = 6928.9(19)$ Å^3, $Z = 8$, $D_c = 1.289$ g cm^{-3} and μ(Mo-Kα) = 0.476 cm^{-1}. All measurements were made on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation; $R_1 = 0.067$ and $R_w = 0.107$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.56 and −0.35 e$^-$ Å^{-3}.

CCDC 179299 and 190853. See http://www.rsc.org/suppdata/cc/b2/b207855d/ for crystallogaphic data in CIF or other electronic format.

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