

Self-assembly of free-base tetrapyrrolylporphyrin units by metal ion coordination

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The first free-base *meso*-tetraarylporphyrin coordination polymer is assembled from *meso*-tetrapyrrolylporphyrin and HgBr₂ via 4-connected peripheral ligation, and it possesses a novel one-dimensional structural motif with large interporphyrin cavities.

There has been recent research interest in crystal engineering supramolecular architectures assembled from metal ions and polydentate ligands by coordinate covalent bonding.¹ Functionalized *meso*-tetraarylporphyrin ligands have been employed to ligate metal ions using the donor atoms (*e.g.* N) on the four *meso*-aryl substituents.² Incorporation of such tetraarylporphyrin units into supramolecular oligomers or polymers via peripheral ligation is attractive for several reasons. Tetraarylporphyrin molecules are robust, rigid and highly symmetrical and thus serve as desirable, slab-like building blocks for synthesizing microporous materials with large cavities and channels that have potential catalytic activity.³ Supramolecular systems containing multiporphyrin units have applications as biomimetic models for the study of energy/electron transfer processes in photosynthesis.^{4–7} Understanding such processes is fundamental for developing molecule-based opto-electronic materials.⁸

However, investigations of the aforementioned *meso*-tetraarylporphyrin coordination polymers are still lacking in scope. To our knowledge, only three infinite network structures have been reported by Robson and coworkers,² which contain metalloporphyrin units connected by additional metal ions via all four *meso*-peripheral functions on each metalloporphyrin molecule. Also noteworthy are the structures of several coordination polymers obtained by recrystallization of Zn- or Cu-*meso*-tetraarylporphyrins from certain organic solvents without additional metal ions.⁹ In these materials, it is the ligation of two of the functionalized aryls on each metalloporphyrin molecule to the metal centers of two adjacent metalloporphyrins that forms the infinite structures. Although several groups have described the use of free-base *meso*-tetrapyrrolylporphyrin in assembling porphyrin oligomers,^{6,10} no *coordination polymers* built upon free-base *meso*-tetraarylporphyrin units have been reported in the literature. We are interested in exploring self-assembly of free-base *meso*-tetraarylporphyrin building blocks and metal ions of various coordination environments. Our strategy involves using functionalized *meso*-aryl groups to ligate metal ions. These porphyrins are readily available commercially or synthetically.^{9b} The use of unmetallated porphyrins avoids the possible ligation of the metal center in the cavity of one metalloporphyrin molecule to the periphery of another metalloporphyrin molecule. Such additional linkages could complicate the design and engineering of solid state structures. In this communication, we report the synthesis and X-ray crystal structure of a novel one-dimensional infinite polymer in which free-base *meso*-tetrapyrrolylporphyrin (hereafter H₂TPyP) units are interconnected by mercury(II) centers via peripheral pyridyl ligation.

Under ambient conditions, a methanol solution (50 mL) of HgBr₂ (0.111 mg, 0.31 mmol) was added to a chloroform solution (50 mL) of H₂TPyP (0.047 mg, 0.076 mmol), leading to the precipitation of a purple, microcrystalline solid. This solid was isolated by filtration, washed thoroughly with methanol and then chloroform, and dried under vacuum for 12 h to give 0.071 g of product (70% yield based on H₂TPyP). As shown in the IR spectra (KBr), the pyridine ring vibrational band of H₂TPyP (1629 cm⁻¹) is significantly shifted to 1600 cm⁻¹ upon pyridyl N-coordination to mercury. A combustion analysis (for C, H and N) of the product supports an empirical formula of Hg(H₂TPyP)_{0.5}Br₂ (C₂₀H₁₃N₄Br₂Hg)[†] that is further confirmed by single crystal X-ray analysis (see below). This material is insoluble in common solvents. Moreover, it is air- and moisture-stable, exhibiting no sign of decomposition or degradation in the EA and IR analyses after being exposed in air for weeks. The air and moisture stability of Hg(H₂TPyP)_{0.5}Br₂ is as expected for Hg(II) complexes with pyridine-type ligands.¹¹

Crystals suitable for single crystal X-ray analysis were obtained by layering a dilute methanol solution of HgBr₂ (0.01 M, 4 mL) over a dilute chloroform solution of H₂TPyP (0.0025 M, 4 mL). Platelike red-purple crystals were formed as the solvate of empirical formula Hg(H₂TPyP)_{0.5}Br₂·CHCl₃ as revealed by X-ray crystallography.[‡] The infinite solid state structure may be viewed as composed of the building-block unit Hg₂(H₂TPyP)Br₄·2CHCl₃ shown in Fig. 1. In the extended one-dimensional motif shown in Fig. 2, the Hg(II) center is ligated to two bromides and two pyridyl nitrogens, thereby adopting a distorted tetrahedral geometry. This is a rare example of a crystallographically characterized tetrahedral mercury(II)–

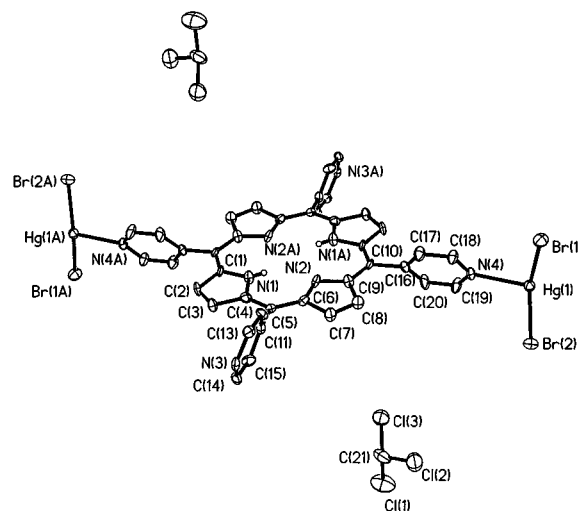


Fig. 1 Molecular structure of the building-block unit Hg₂(H₂TPyP)Br₄·2CHCl₃, with all hydrogen atoms omitted except the two in the porphyrin cavity. Atoms labeled with A are related to atoms without this letter by an inversion symmetry operation.

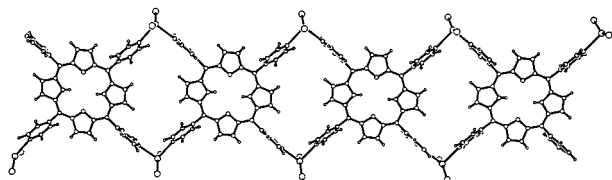


Fig. 2 View of the extended one-dimensional motif in $\text{Hg}(\text{H}_2\text{TPyP})_{0.5}\text{Br}_2\cdot\text{CHCl}_3$. H_2TPyP molecules are bridged by HgBr_2 moieties through pyridyl ligation, forming interporphyrin cavities. Solvent molecules (CHCl_3) are not shown.

nitrogen complex of general formula HgL_2X_2 , where L = pyridine or its derivatives and X = halide.¹¹ In addition, the four pyridyl rings are twisted with respect to the plane of the parent porphyrin ring. The N(3)- and N(3A)-containing pyridyl rings each form a dihedral angle with the porphyrin ring at 73.2° . The corresponding dihedral angles for N(4)- and N(4A)-containing pyridyl rings are 67.8° each. The $\text{Hg}(1)\text{--Br}(1)$ and $\text{Hg}(1)\text{--Br}(2)$ bond distances are 2.4671(10) and 2.4770(10) Å respectively; the average of 2.472 Å is close to the average shortest $\text{Hg}\text{--Br}$ distance (2.48 Å) in HgBr_2 .¹² The $\text{Hg}\text{--N}$ distances range from 2.482(6) to 2.410(6) Å.

The one-dimensional structural motif shown in Fig. 2 is unprecedented in porphyrin- or metalloporphyrin-based *coordination polymers*. In this framework HgBr_2 moieties act as linkers to bridge the H_2TPyP molecules with each $\text{Hg}(\text{II})$ center connecting two pyridyls from adjacent porphyrins. This results in relatively large interporphyrin cavities in the extended chain. The size of the cavity is measured by the $\text{Hg}\cdots\text{Hg}$ distance (14.2 Å) and the shortest distance between the two *meso*-carbons of two adjacent porphyrins (9.72 Å). Inside the cavity, the distances between the van der Waals surfaces are estimated at 8.4 Å between the diagonal pyridyls and 3.7 Å between the β -hydrogens of the two adjacent porphyrin molecules. The two neighboring porphyrin ring planes within a chain are parallel but are canted by *ca.* 1.60 Å. Solvent (CHCl_3) molecules (not shown) partially fill the interchain space, and they are not included in the interporphyrin cavities. When removed from the mother liquor, crystals of $\text{Hg}(\text{H}_2\text{TPyP})_{0.5}\text{Br}_2\cdot\text{CHCl}_3$ lose CHCl_3 and collapse rapidly, showing no sharp peaks in X-ray powder diffraction patterns. The resultant solid does not absorb CH_2Cl_2 , CHCl_3 , CH_3OH or benzene to form inclusion compounds. It seems that crystallinity of the one-dimensional $\text{Hg}(\text{H}_2\text{TPyP})_{0.5}\text{Br}_2\cdot\text{CHCl}_3$ cannot be sustained after loss of interchain space-filling solvent of crystallization. Networks of

higher dimensionalities may be required for porphyrin coordination polymers to function like porous materials.

Currently, we are studying the physical properties of $\text{Hg}(\text{H}_2\text{TPyP})_{0.5}\text{Br}_2$ using a combination of photoacoustic, reflection UV-VIS and fluorescent spectrometries. Additionally, we are examining different metal ions as potential linkers to assemble porphyrin coordination polymers of higher dimensionalities, including 2-D sheets and 3-D networks.

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Notes and references

† Calc. (found) for $\text{C}_{20}\text{H}_{13}\text{N}_4\text{Br}_2\text{Hg}$: C, 35.87 (36.15); H, 1.96 (2.08); N, 8.37 (8.31)%.

‡ *Crystal data* for $\text{Hg}(\text{H}_2\text{TPyP})_{0.5}\text{Br}_2\cdot\text{CHCl}_3$: $M = 1578.24$, space group $P1$, $a = 9.507(3)$, $b = 11.641(2)$, $c = 12.732(4)$ Å, $\alpha = 73.418(9)$, $\beta = 80.316(16)$, $\gamma = 66.294(7)^\circ$, $U = 1234.2(6)$ Å³, $Z = 1$, $D_c = 2.123$ Mg m⁻³, $F(000) = 738$, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, crystal size = $0.11 \times 0.05 \times 0.02$ mm, 16409 reflections collected on a Siemens SMART CCD diffractometer at 171 K, 6489 independent reflections, final $R1 = 0.0548$ for 4487 reflections with $I > 2\sigma(I)$, $wR2 = 0.0831$, GOF = 1.032. The structure was solved by using Patterson heavy atom method. CCDC 182/1104. See <http://www.rsc.org/suppdata/cc/1999/157/> for crystallographic files in .cif format.

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