

1-D Infinite Array of Metalloporphyrin Cages

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The reaction of Co(II) with 5,15-dipyridyl-10,20-diphenylporphyrin (H₂DPyP) produces the first metal-organic coordination polymer supported by a trans meso-bifunctional porphyrin ligand. Formulated empirically as [Co₃(DPyP)₃] \cdot 4DMF, this compound exhibits a ribbonlike coordination network consisting of tetranuclear metalloporphyrin cages. The DMF guest molecules fill the intra-ribbon cages as well as the inter-ribbon space. Evacuation of [Co₃(DPyP)₃] \cdot 4DMF at 130 °C generates [Co₃(DPyP)₃] that retains crystallinity, as shown by its powder X-ray diffraction pattern, which is consistent with that of [Co₃(DPyP)₃] \cdot 4DMF.

The driving force behind the recent phenomenal growth of the field of metal–organic coordination polymers is twofold: such supramolecular assemblies not only display interesting extended structures, they also exhibit useful properties such as porosity, magnetism, and nonlinear optical behavior.¹ The strategy for assembling coordination polymers is based on well-defined coordination chemistry and allows for a level of design of network structures. Within this context, several research groups, ours included, have studied the role of functionalized porphyrins in supporting infinite coordination networks.^{2,3} The large and rigid structure of

porphyrins makes them suitable for sustaining large cavities and channels that have potential adsorption and catalysis properties.

Thus far, only the readily available meso-tetrafunctional porphyrins have been employed to support infinite coordination networks, which include meso-tetra(4-pyridyl)porphyrin (H₂TPyP) and meso-tetra(4-carboxylphenyl)porphyrin (H₂-TCpP) and their metalated forms. We seek to expand the investigation of porphyrin-based supramolecular assemblies through the exploration of the coordination polymer chemistry of trans meso-bifunctional porphyrins such as 5,15-dipyridyl-10,20-diphenylporphyrin (H₂DPyP).⁴ H₂DPyP can be viewed as an analogue of 4,4'-bipyridine (bipy) with a large and rigid tether approximately 1 nm wide between the pyridyl groups. In view of the large variety of coordination networks supported by bipy,⁵ one could envision a rich coordination polymer chemistry for H₂DPyP that could lead to new porous metalloporphyrin networks having potential applications in size- and shape-selective adsorption and catalysis. In this communication, we report the synthesis and characterization of a 1-D infinite metalloporphyrin network made from H₂DPyP.

Pink crystals of [Co₃(DPyP)₃] \cdot 4DMF were obtained from a reaction of [Co(NO₃)₂] \cdot 6H₂O with H₂DPyP in *N,N*-dimethylformamide (DMF) at 130 °C. The IR spectrum of the crystalline compound shows a strong amide absorption band at 1676 cm⁻¹. The structure of [Co₃(DPyP)₃] \cdot 4DMF was determined via single-crystal X-ray diffraction analysis.⁶ The 1-D extended coordination network in [Co₃(DPyP)₃] \cdot 4DMF can be viewed as an infinite ribbon of adjoining tetranuclear metalloporphyrin cages, a structural motif that has never before been reported for porphyrin-based coordi-

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(6) Crystal data: C₁₃₈H₁₀₆Co₃N₂₂O₄, *M* = 2313.24, triclinic, space group *P*1, *Z* = 1, *a* = 11.7984(5) Å, *b* = 14.7047(6) Å, *c* = 16.5434(7) Å, α = 90.168(1)°, β = 104.665(1)°, γ = 98.719(1)°, *U* = 2697.0(2) Å³, μ (Mo K α) = 0.519 mm⁻¹, *T* = 100(1) K. Data were collected on a Bruker-AXS smart APEX CCD diffractometer. Of a total of 38630 reflections collected, 16475 were independent (*R*_{int} = 0.039). The structure was solved by direct methods and refined by full-matrix least squares on *F*². Final *R*1 [*I* > 2 σ (*I*)] = 0.0629 and *wR*2 = 0.1348 (all data).

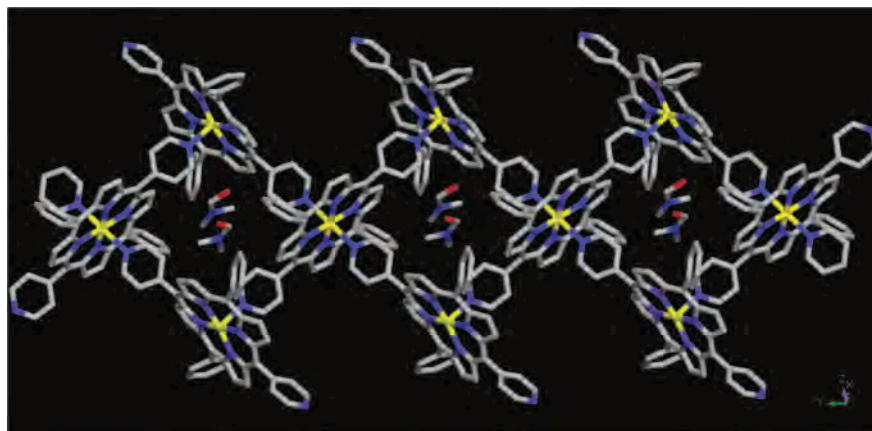


Figure 1. Cylinder representation of the 1-D coordination array in $[\text{Co}_3(\text{DPyP})_3]\cdot 4\text{DMF}$, with H atoms omitted for clarity. Color scheme: Co, yellow; N, blue; C, gray; and O, red. The Co–N (pyrrolic) bond distances range from 1.964(2) to 2.001(2) Å, and the Co–N (pyridyl) bond distances range from 2.171(2) to 2.278(2) Å.

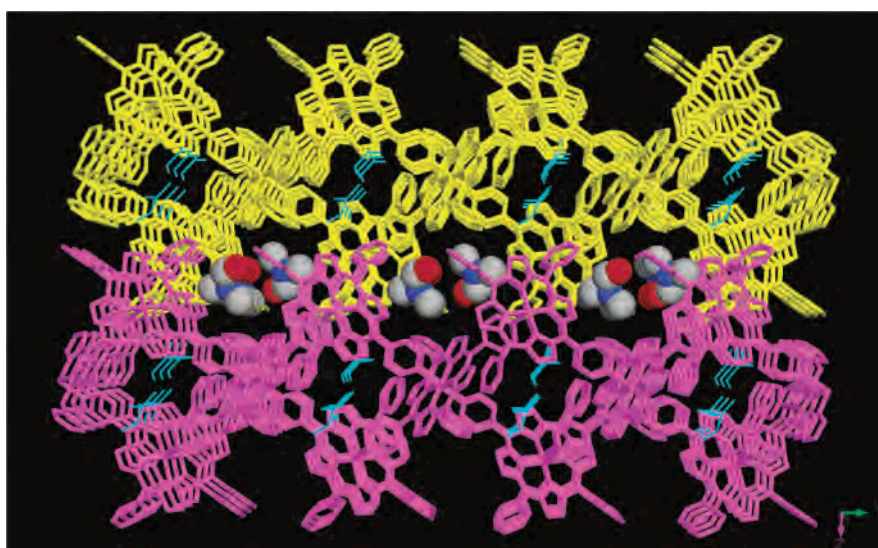


Figure 2. Crystal packing diagram of $[\text{Co}_3(\text{DPyP})_3]\cdot 4\text{DMF}$ showing two sets of 1-D arrays indicated by different colors. Intra-ribbon and inter-ribbon DMF molecules are represented by cylinder and space-filling models, respectively.

nation polymers (Figure 1). This structure suggests that metal insertion occurs first in the reaction of $[\text{Co}(\text{NO}_3)_2]\cdot 6\text{H}_2\text{O}$ with H_2DPyP , affording $[\text{Co}(\text{DPyP})]$ molecules that further self-assemble into the supramolecular aggregate. There are two types of metalloporphyrin core units, occupying the nodes and corners. A nodal unit uses both of its pyridyl groups in binding two corner units and has both of its axial coordination sites filled with the pyridyl groups of another two corner units. A corner unit uses only one pyridyl group and one axial site in coordination with two nodal units. Thus, the nodal and corner units are six-coordinate and five-coordinate, respectively. The combination of such coordination geometries leads to the unique 1-D extended structure of $[\text{Co}_3(\text{DPyP})_3]\cdot 4\text{DMF}$. We have previously reported $[\text{Fe}(\text{TPyP})]$, an infinite 2-D grid built upon topologically similar tetranuclear metalloporphyrin cages in which all $\text{Fe}(\text{TPyP})$ units are six-coordinate.^{2f} Whereas the nodal porphyrin cores of $[\text{Co}_3(\text{DPyP})_3]\cdot 4\text{DMF}$ are essentially planar and parallel to one another, those of the corner units are puckered with the pyrrole rings alternately displaced above and below the porphyrin plane. Similarly ruffled porphyrin cores have been

observed for a metalloporphyrin coordination polymer made from *meso*-tetra(4-carboxylphenyl)porphyrin.^{3b} Within a metalloporphyrin cage in $[\text{Co}_3(\text{DPyP})_3]\cdot 4\text{DMF}$, the separations between a corner $\text{Co}(\text{II})$ ion and two adjacent nodal $\text{Co}(\text{II})$ ions are measured at 9.97 and 9.63 Å, respectively. The effective dimensions of the cage are estimated at 5.7×5.7 Å from the distances between the closest van der Waals surfaces of the constituent atoms. The cage is large enough to include two DMF molecules. Figure 2 presents a crystal packing diagram of $[\text{Co}_3(\text{DPyP})_3]\cdot 4\text{DMF}$ viewed along the crystallographic *a* axis, showing two sets of 1-D metalloporphyrin arrays, as well as two series of DMF molecules—those included in the intra-ribbon cages and those filling the inter-ribbon space. The large separation between any two aryl rings indicates the absence of significant π -stacking interactions in the crystal structure of $[\text{Co}_3(\text{DPyP})_3]\cdot 4\text{DMF}$.

A thermogravimetric (TG) analysis performed on a sample of $[\text{Co}_3(\text{DPyP})_3]\cdot 4\text{DMF}$ under a flow of N_2 gas showed a 12.7% weight loss at 124 °C, which corresponded to the loss of four DMF molecules per formula unit (calcd 12.6%). No further weight loss was observed until the temperature

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reached 400 °C, at which decomposition apparently occurred. The TG results indicate the thermal stability of the metalloporphyrin network in $[\text{Co}_3(\text{DPyP})_3] \cdot 4\text{DMF}$. In view of the TG analysis, a sample of $[\text{Co}_3(\text{DPyP})_3] \cdot 4\text{DMF}$ was evacuated at 130 °C, affording the desolvated phase $[\text{Co}_3(\text{DPyP})_3]$, which showed essentially the same crystal habit as $[\text{Co}_3(\text{DPyP})_3] \cdot 4\text{DMF}$. The IR spectrum of $[\text{Co}_3(\text{DPyP})_3]$ clearly indicates the disappearance of the intense DMF absorption band at 1676 cm^{-1} . The X-ray powder diffraction (XRD) pattern of $[\text{Co}_3(\text{DPyP})_3]$ appears similar to that of as-synthesized $[\text{Co}_3(\text{DPyP})_3] \cdot 4\text{DMF}$, indicating the retention of crystalline order in $[\text{Co}_3(\text{DPyP})_3]$ in the absence of the solvent molecules. With DMF removed, the void accounts for 22.6% of the crystal volume, as estimated by the PLATON program.⁷

Preservation of crystallinity has been reported for some 2-D and 3-D metal–organic frameworks derived from removing solvent of crystallization, but it is rare for a coordination polymer network extending in only one dimension.⁸ We offer the following insight into the crystallinity of $[\text{Co}_3(\text{DPyP})_3]$. In $[\text{Co}_3(\text{DPyP})_3] \cdot 4\text{DMF}$, one-half of the DMF molecules are included in the metalloporphyrin cages and therefore should not significantly affect the packing of the 1-D coordination arrays. This inclusion leaves only two inter-ribbon DMF molecules per three porphyrin units, which appear to have little effect on the crystalline order of the 1-D coordination arrays. This insight is supported by comparing $[\text{Co}_3(\text{DPyP})_3] \cdot 4\text{DMF}$ with $[\text{Hg}(\text{H}_2\text{TPyP})_{0.5}\text{Br}_2] \cdot$

CHCl_3 , a 1-D free-base porphyrin coordination polymer that we have previously reported.^{2c} In $[\text{Hg}(\text{H}_2\text{TPyP})_{0.5}\text{Br}_2] \cdot \text{CHCl}_3$, all CHCl_3 molecules fill the interchain space, and there are six of them per three porphyrin units. These CHCl_3 molecules are essential to the ordering of the 1-D coordination arrays of $[\text{Hg}(\text{H}_2\text{TPyP})_{0.5}\text{Br}_2]$, as the crystals immediately collapse and become amorphous upon loss of CHCl_3 .

In summary, we have synthesized the first metal–organic coordination polymer supported by a trans bifunctional porphyrin ligand and formulated as $[\text{Co}_3(\text{DPyP})_3] \cdot 4\text{DMF}$. This supramolecular compound exhibits a new 1-D extended structure consisting of tetranuclear metalloporphyrin cages. The structural motif and the packing scheme of $[\text{Co}_3(\text{DPyP})_3] \cdot 4\text{DMF}$ appear to explain the retention of crystallinity in the desolvated phase $[\text{Co}_3(\text{DPyP})_3]$. Further studies will include investigation into the adsorption properties of $[\text{Co}_3(\text{DPyP})_3]$, as well as extension of the coordination polymer chemistry of H_2DPyP .

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Supporting Information Available: XRD and TGA data and a complete X-ray crystallographic file in CIF format for the title compound. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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