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[7] Potentials for the one-electron oxidation of **1-Zn**, **1-Ni**, **1-H$_2$**, and zinc 5,15-bis(3,5-di-*tert*-butyl-phenyl)porphyrin were measured by cyclic voltammetry in $CHCl_3$ to be 0.17, 0.32, 0.40, and 0.31 V, respectively, versus ferrocene/ferrocenium ion.

[8] All new porphyrin compounds reported here were fully characterized by $^1$H NMR spectroscopy (500 MHz) as well as FAB and MALDI-TOF mass spectrometry.

[9] In the analytical SEC, **7-Ni** and **10-Ni** eluted after 20.1 and 18.9 min, respectively, while the porphyrin 15-mer eluted after 18.1 min. The reaction of **10-Ni** with excess $AgPF_6$ afforded the porphyrin 20-mer, as judged by SEC (retention time: 17.9 min) and MALDI-TOF-MS ($m/z$ = 16666; calcd for $C_{1064}H_{1274}N_{80}Ni_{16}O_{16}Zn_4$: 16640), in 20–30% yield. However, the very broad signals in the $^1$H NMR spectra of the 15-mer and 20-mer precluded their full characterization. These results may imply that not only the linear porphyrin arrays but also the windmill-like orthogonal porphyrin arrays are useful building blocks.

[10] Since the energy difference between the singlet excited state of the *meso–meso* diporphyrin and the peripheral porphyrin rings is small (0.07 eV), the energy transfer may be reversible and the dynamics of the photoexcited state of the windmill-like porphyrin arrays are very complicated.

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# Supramolecular Assembly of Heterogeneous Multiporphyrin Arrays—Structures of $[\{Zn^{II}(tpp)\}_2(tpyp)]$ and the Coordination Polymer $[\{[Mn^{III}(tpp)]_2(tpyp)(ClO_4)_2\}_\infty]$[**]

R. Krishna Kumar and Israel Goldberg*

Multiporphyrin architectures have diverse potential for applications as biomimetic models or functional materials for the transport of energy, charge, molecules, and ions.[1, 2] The formulations of light-harvesting porphyrin arrays and new receptors for selective catalysis has relied mostly on covalent synthesis of oligomeric arrays.[3, 4] For many years the construction of stable multiporphyrin arrays by supramolecular aggregation has remained relatively unexplored, in spite of the diverse molecular recognition algorithm that can be incorporated into the porphyrin building blocks. Recent investigations have shown, however, that predictable architectures of oligomers and polymers from metallomacrocyclic building blocks can be rationally designed by selection of the coordination geometry of metals and the structure of multitopic ligands involved in the supramolecular synthesis.

Examples of successful attempts to assemble supramolecular porphyrin structures, in solution as well as in the solid state, include the generation of patterns stabilized by external metal centers[5] or multidentate bridging ligands,[6] and the construction of aggregates by self-coordination of suitably functionalized lateral substituents of a given porphyrin entity directly to the metal center of an adjacent unit.[7] In the latter context, we have described the assembly of one-, two-, and three-dimensional homogeneous coordination polymers consisting of the $Zn^{II}$ tetra(4-pyridyl)porphyrin [Zn(tpyp)] or $Zn^{II}$ tetra(4-cyanophenyl)porphyrin moieties.[8] Self-assembly of hydrogen-bonded arrays of porphyrin molecules that are peripherally substituted with molecular recognition groups has also been reported.[9]

The *meso*-tetrapyridylporphyrin free base is representative of square-shaped building blocks containing symmetrically disposed ligating sites. This is thus an excellent ligand for tetrametalloporphyrin assemblies[4b, 10] and a potentially excellent building block for the generation of heterogeneous supramolecular networks in combination with other metalloporphyrin units. We report here on the assembly and structural characterization of the supramolecular oligomer $[\{Zn^{II}(tpp)\}_2(tpyp)]$ (**1**) and the uniquely architectured coordination polymer $[\{[Mn^{III}(tpp)]_2(tpyp)(ClO_4)_2\}_\infty]$ (**2**; tpp = tetraphenylphorphyrin). To our knowledge, the latter represents the first example of a well-defined two-dimensional coordination polymer incorporating at least two different porphyrin entities.

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The tpp and tpyp building blocks were synthesized from the corresponding aldehyde and pyrrole, and tpp was metalated with $Zn(OAc)_2$ or $Mn(OAc)_2$ by standard procedures.[8a, 11] The axial ligation of the metal ion inserted into the porphyrin center provides an important element in the construction of multiporphyrin assemblies. The $Zn^{II}$ ion has a strong affinity for a five-coordinate environment, which favors axial ligation of only one ligand to the {Zn(tpp)} moiety. On the other hand, the paramagnetic $Mn^{III}$ ion tends to adopt a six-coordinate structure.[12] This should facilitate the formation of coordination polymers with suitable multidentate ligands which might have significant potential as molecular magnetic materials.[2b, 6a–c] These preferences of the two metal ions are best illustrated by the different aggregation modes of $[Zn^{II}(tpp)]$ and $[Mn^{III}(tpp)]\cdot ClO_4$ with tpyp.

The reaction of $[Zn^{II}(tpp)]$ with tpyp in chloroform followed by recrystallization from nitrobenzene yields the 2:1 coordination oligomer **1**. Its structure consists of a tetrapyridyl unit which coordinates to, and effectively bridges, two centrosymmetrically related [Zn(tpp)] molecules (Figure 1). The zinc ions typically deviate inward from the porphyrin plane (by 0.27 Å) towards the axially coordinated pyridyl groups ($Zn\cdots N_{py}$ 2.197(7) Å). The three-porphyrin oligomer is capped from both sides by nitrobenzene molecules. The latter lie approximately parallel to the porphyrin frameworks at an average distance of 3.3 Å, which is indicative of significant $\pi-\pi$ interaction between the two aromatic systems. Formation in solution of similar supramolecular trimers consisting of one dipyridyldiphenylporphyrin and two {Zn(tpp)} moieties has been proposed earlier on the basis of NMR data.[7f] In accordance with the previous observations, $^1H$ NMR study of the dissolved crystals of **1** provides clear evidence that the coordination of [Zn(tpp)] to tpyp is present in this case as well. In chloroform, the signals of the 2,6-pyridyl ($\alpha$ to N), 3,5-pyridyl ($\beta$ to N), and pyrrole N protons are shifted upfield by $\Delta\delta = 2.88$, 1.07, and 0.80, respectively in relation to those of uncoordinated tpyp (see the Experimental Section and related NMR data in references [4b] and [7f]). These values along with the broad nature of the signals and the absence of signals corresponding to uncoordinated pyridyl rings indicate that there is a rapid exchange of [Zn(tpp)] between the four pyridyl sites of tpyp. A solution of a 1:4 mixture of tpyp and [Zn(tpp)] in chloroform shows even higher upfield shifts of the tpyp protons, suggesting possible formation of a pentameric assembly $[\{Zn^{II}(tpp)\}_4(tpyp)]$ in which all pyridyl sites are involved in the coordination. No such complexes could be obtained as yet, however, in the crystalline form, which can be attributed to inefficient crystal packing of such pentameric porphyrin entities (in relation to the arrangement of the trimeric oligomers, which is more effective and of lower free energy).

The engineering of more extended heterogeneous arrays was made possible by the reaction of $[Mn^{III}(tpp)]\cdot ClO_4$ with neutral tpyp in chloroform. Detailed analysis of the resulting material reveals an unprecedented square-grid architecture of these assemblies (Figure 2). They represent heterogeneous coordination polymers made up of a single framework in which each tpyp unit is surrounded by, and coordinated to, four [Mn(tpp)] molecules and each [Mn(tpp)] molecule is coordinated to two neighboring tpyp units. Thus, the coordination potential of the two porphyrin building blocks involved in this structure is utilized to capacity in an exceptionally well-defined manner. In the two-dimensional polymers, which are roughly planar, the alternating metalloporphyrin and tetrapyridyl units are linked to each other by metal–ligand coordination; the $Mn\cdots N_{py}$ distances range from 2.34 to 2.37 Å. The polymeric layers are stacked in the crystal along the $b+2c$ direction (the average interlayer distance is about 10.2 Å) with an offset overlap to effectively accommodate the [Mn(tpp)] frameworks, which are aligned perpendicular to the polymeric networks and the tpyp molecules. This essentially docks one layer into the other, yielding a stable crystalline solid.

Figure 3 shows the relative disposition of, and the packing interactions between, two adjacent layers in the crystal. The open nature of the polymeric layers gives rise to the formation of channels in the crystals which penetrate through the stacked layers. Thus, four small channels centered approximately at ¼,¼,*z*, ¼,¾,*z*, ¾,¼,*z*, and ¾,¾,*z* run along the *c* axis of the crystal. In addition, two wider channels centered at ¼,*y*,¾ and ¾,*y*,¼ propagate in the *b* direction; the smallest cross-section distance between van der Waals surfaces of the channels is about 4.5 Å. These tubularly

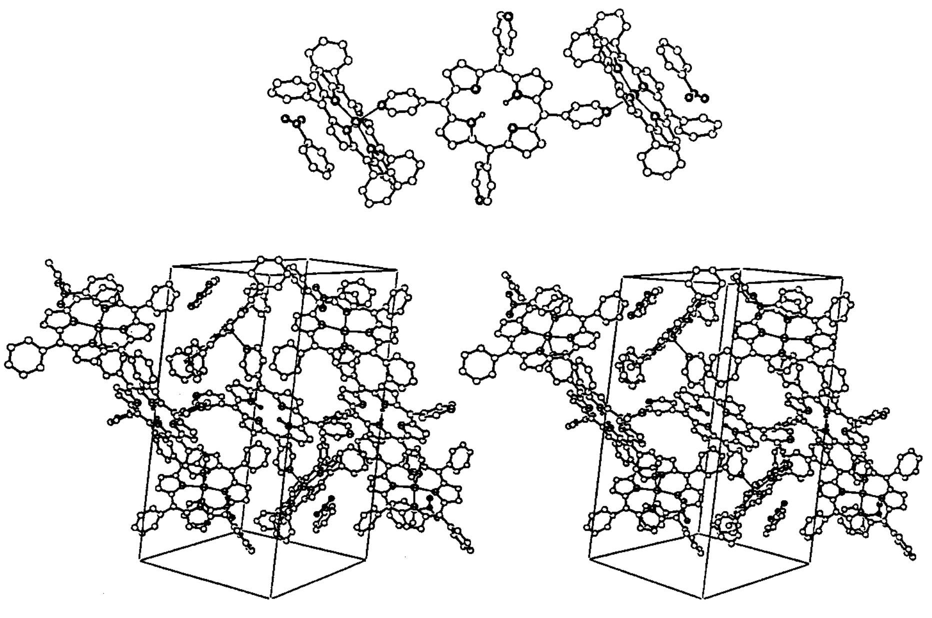

Figure 1. Structure of the trimeric $[\{Zn^{II}(tpp)\}_2(tpyp)]$ aggregate in **1** and stereoview of its crystal packing approximately along $b+c$ (the *a* axis is vertical). The tpyp molecules are located on centers of inversion. Noteworthy is the effective packing of the tpyp moieties along the direction of the noncoordinated pyridyl groups and the capping of the concave side of the [Zn(tpp)] unit by nitrobenzene.

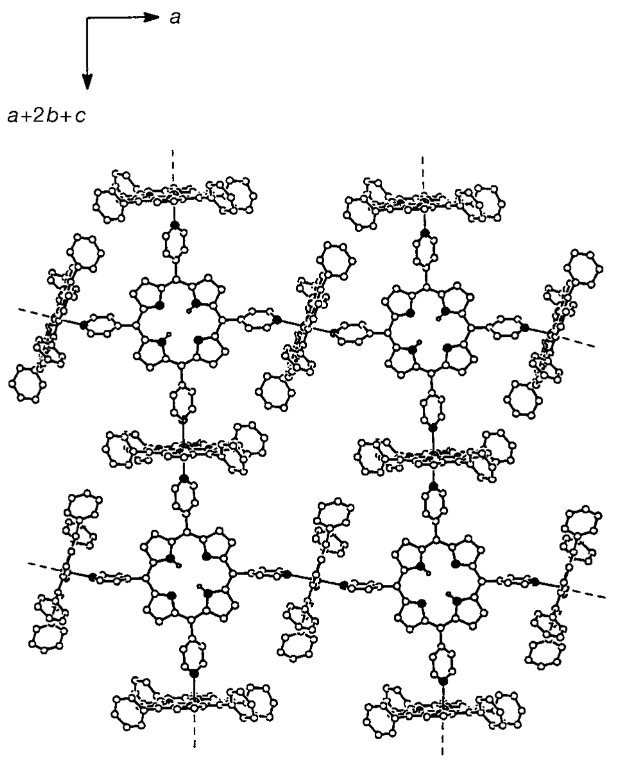

Figure 2. Structure of the heterogeneous coordination polymer in **2**. The Mn and N atoms are represented by partially darkened circles.

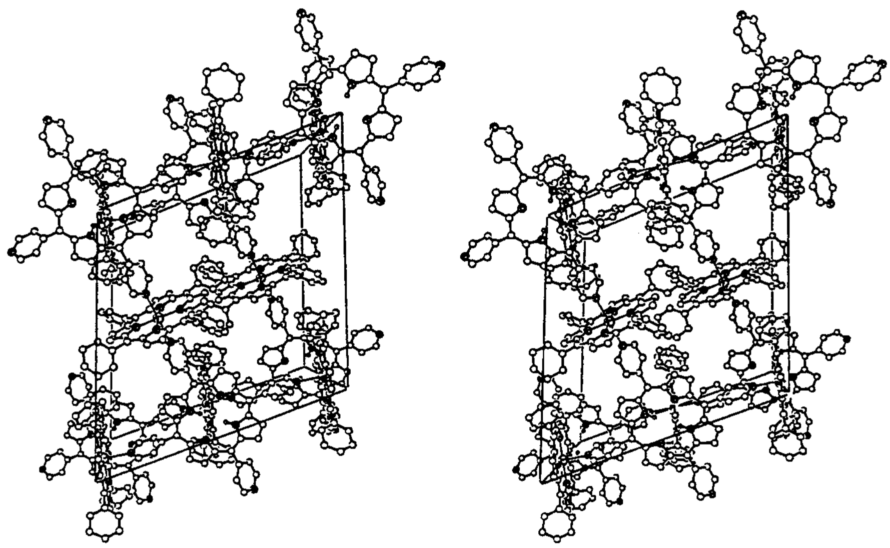

Figure 3. Stereoview of the crystal structure of **2** approximately along the *c* axis (*a* is nearly horizontal, and *b* is vertical). The relative displacement of, and steric fit between, two neighboring polymeric layers is depicted. Note the open channels which run through the polymeric layers along the *b* and *c* axes (see text). The perchlorate ions and nitrobenzene molecules which occupy these channels are omitted for clarity.

shaped voids that criss-cross the porphyrin structure are occupied by perchlorate counterions and nitrobenzene solvent molecules. Some of the latter access, and form π–π interactions with, the open faces of the tpyp moieties. Various experimental results indicate that there are about twenty nitrobenzene molecules per unit cell, which occupy 46% (!) of the crystal volume. Their positions have all been determined reasonably well based on diffraction data. Thermogravimetric analysis (TGA) shows that the onset of solvent loss occurs in these crystals at 80°C and is completed by 150°C, and that no other phase transition of the solid occurs until 300°C. The observed weight loss of about 32.5% of the nitrobenzene further confirms the high content of this solvent in the structure. It should be possible to fine-tune the solvent-accessible space within the lattice by introduction of small alkyl groups on the pyrrole rings of tpp and tpyp. These groups might also enhance the solubility of the material in organic solvents. Another variation involves utilizing negatively charged tpyp units, by incorporating neutral metal atoms into the porphyrin,[13] in order to balance the formal charge of the $[\mathrm{Mn^{III}(tpp)}]$ moiety and maintain a lipophilic environment within the channels.

The ability to generate homogeneous as well as heterogeneous multiporphyrin coordination polymers of varying dimensionality by design provides a promising perspective for new molecular solids with interesting and useful properties. Their potential application in different areas of materials science, including formulation of new molecular magnetic materials and zeolite mimics, is also in sight.

## *Experimental Section*

The analyzed materials were obtained by adding stoichiometric amounts of $[\mathrm{Zn^{II}(tpp)}]$ or $[\mathrm{Mn^{III}(tpp)}]\cdot\mathrm{ClO_4}$ to a solution of tpyp in chloroform and stirring the resulting mixtures for 24 h. Single crystals of **1** and **2** suitable for X-ray diffraction analysis were obtained by dissolving the solids thus formed in hot nitrobenzene and allowing the solution to cool very slowly.

**1** ($2\,\mathrm{C_{44}H_{28}N_4Zn}\cdot\mathrm{C_{40}H_{26}N_8}\cdot 2\,\mathrm{C_6H_5NO_2}$): Elemental analysis: calcd: C 75.7, H 4.2, N 11.4; found: C 75.2, H 4.4, N 11.2; UV/Vis ($\mathrm{CHCl_3}$): $\lambda_{\max} = 421$, 476, 513, 551, 591, 642 nm; $^1$H NMR ($\mathrm{CDCl_3}$, 360 MHz): $\delta = 8.95$ (16H, s, β-pyrrole of [Zn(tpp)]), 8.25 (20H, m, *o*-phenyl of [Zn(tpp)] and *o*-nitrobenzene), 7.97 (8H, s, β-pyrrole of tpyp), 7.75 (26H, m, *m*- and *p*-phenyl of [Zn(tpp)], *p*-nitrobenzene), 7.54 (4H, t, *m*-nitrobenzene), 7.11 (8H, br d, β-H of tpyp), 6.16 (8H, br, α-H of tpyp), −3.7 (2H, s, N-pyrrole); IR (KBr): $\tilde{\nu} = 1590$, 796 (tpyp), 1590, 1068, 1002, 992, 796, 752 ([Zn(tpp)]), 1523, 1343, 699 cm$^{-1}$ (nitrobenzene).

**2** ($2\,\mathrm{C_{44}H_{28}N_4Mn}\cdot 2\,\mathrm{ClO_4}\cdot\mathrm{C_{40}H_{26}N_8}\cdot 10\,\mathrm{C_6H_5NO_2}$): Elemental analysis: calcd: C 66.7, H 3.9, N 10.8; found: C 65.9, H 3.9, N 10.3; UV/Vis ($\mathrm{CHCl_3}$): $\lambda_{\max} = 417$, 477, 513, 585, 614 nm; IR (KBr): $\tilde{\nu} =$ 1599, 803 (tpyp), 1599, 1012, 803, 755, 701 ($[\mathrm{Mn(tpp)}]^+$), 1522, 1345, 703 (nitrobenzene), 1087 cm$^{-1}$ ($\mathrm{ClO_4^-}$).

Crystal structure analyses: Data for **1** and **2** were collected on a standard Enraf-Nonius CAD4 diffractometer with $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.7107$ Å) and $\omega$-$2\theta$ scans. In view of the very large unit cell of **2** and the high content of partially disordered solvent molecules, the measurements for this crystal were conducted at low temperature. The two crystals did not show significant diffraction beyond $2\theta = 42.0°$. The crystal structures were solved by direct methods and Fourier techniques, and then refined by least squares employing the SHELXS and SHELXL program suite.[14] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101400. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for **1** (at ca. 298 K): $C_{44}H_{28}N_4Zn \cdot 0.5\,(C_{40}H_{26}N_8) \cdot C_6H_5NO_2$, $M_r = 1110.6$, monoclinic, space group $P2_1/c$, $a = 26.125(7)$, $b = 15.132(3)$, $c = 13.780(3)$ Å, $\beta = 98.57(2)^\circ$, $V = 5386.7$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.369\ g\,cm^{-3}$, $F(000) = 2300$, $\mu(Mo_{K\alpha}) = 5.15\ cm^{-1}$, crystal size $\approx 0.45 \times 0.40 \times 0.30$ mm, $2\theta_{max} = 42.0^\circ$, 5040 unique reflections, final $R1 = 0.069$ for 3541 reflections with $F > 4\sigma(F)$, $R1 = 0.101$, $wR2 = 0.187$, and GoF = 1.109 for all 5040 data. The noncoordinated nitro group of the solvent molecules exhibits a considerable "wagging" motion out of the plane of the aromatic ring. All non-hydrogen atoms (except for those of the disordered nitro group) were refined anisotropically, and hydrogen atoms were placed in calculated positions.

Crystal data for **2** (at ca. 150 K): $2\,(C_{44}H_{28}N_4Mn \cdot ClO_4) \cdot C_{40}H_{26}N_8 \cdot 10\,C_6H_5NO_2$, $M_r = 3384.0$, triclinic, space group $P\bar{1}$, $a = 19.944(8)$, $b = 20.615(8)$, $c = 21.334(6)$ Å, $\alpha = 97.33(3)$, $\beta = 98.59(3)$, $\gamma = 109.77(3)^\circ$, $V = 8011$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.403\ g\,cm^{-3}$, $\rho_{obs.} = 1.39\ g\,cm^{-3}$, $F(000) = 3500$, $\mu(Mo_{K\alpha}) = 2.76\ cm^{-1}$, crystal size $\approx 0.30 \times 0.15 \times 0.10$ mm, $2\theta_{max} = 42.0^\circ$, 13749 unique reflections. The considerable crystallographic complexity of this structure can be appreciated from the size of the asymmetric unit: It contains one [Mn(tpp)] unit in a general position, two additional [Mn(tpp)] units on centers of inversion, two tpyp units on other centers of inversion, and two perchlorate anions as well as ten nitrobenzene molecules in general positions. Although the porphyrin lattice itself, which consists of centrosymmetric molecules, appears to have much simpler periodicity characteristics (Figure 2), lack of inversion in the tetrahedral perchlorate anions and somewhat random distribution of the numerous nitrobenzene molecules provide a plausible cause for the large unit cell identified from the diffraction data. Isotropic refinement (only the three Mn and two Cl atoms of the asymmetric unit were refined anisotropically) of the full structure with approximate positions of the ten partly disordered nitrobenzene molecules (of which at least six could not be modeled precisely) converged at final $R1 = 0.19$ for 7439 reflections with $F > 4\sigma(F)$ and 694 refined parameters, $R1 = 0.25$, $wR2 = 0.44$, and GoF = 1.99 for all 13 749 data. The large size of the asymmetric unit (246 non-hydrogen atoms), the limited resolution of the diffraction data, and the partial disorder of the solvent molecules did not allow an anisotropic refinement of the full structure. Correspondingly, the correctness of the interporphyrin organization and interaction scheme was confirmed by further refinement calculations of the $[Mn(tpp)] \cdot ClO_4$ and tpyp fragments only by using the "bypass" technique in which the overall contribution of all the nitrobenzene solvent molecules (located in the channel-type voids of the lattice) to the diffraction pattern is substracted from the observed data.[15] The reduction in the number of atoms and the improved quality of the resulting ("noise-free") data allowed an anisotropic refinement of a much larger portion of the structure (only the phenyl carbon atoms of the [Mn(tpp)] residues and the oxygen atoms of the perchlorate anions remained isotropic), and led to considerably more precise results. This refinement converged smoothly at $R1 = 0.078$ for 6139 reflections with $F > 4\sigma(F)$ and 1128 refined parameters, $R1 = 0.117$ and $wR2 = 0.20$ for all 13 749 data; min./max. residual electron density $0.614/-0.425\ e\,Å^{-3}$. The residual electron density for the solvent molecules in the interporphyrin voids of the unit cell was assessed by the "bypass" method to be 1212*e*, which is reasonably close to the calculated value of 1280*e* for twenty nitrobenzene molecules. In all calculations, the hydrogen atoms were placed in calculated positions and added as fixed contributions to the structure factors.

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