

Design Strategies for Solid-State Supramolecular Arrays Containing Both Mixed-Metalated and Freebase Porphyrins

C. V. Krishnamohan Sharma, Grant A. Broker, Jonathan G. Huddleston, Jeffrey W. Baldwin, Robert M. Metzger, and Robin D. Rogers*

Contribution from the Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487

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Abstract: The design of predictable multichromophoric supramolecular arrays of freebase and metallo porphyrins constitutes an essential first step toward the synthesis of light-harvesting complexes. We now report crystal engineering strategies to achieve the synthesis of controllable and predictable porphyrinic multichromophores in the solid state. The coordination complexes of metal halides, MX_2 ($\text{M} = \text{Cd}, \text{Hg}, \text{Pb}$; $\text{X} = \text{Br}, \text{I}$), with freebase tetrapyrrolylporphyrin (TPyP) form either 1D, $[(\text{HgX}_2)_2\text{TPyP}] \cdot 2\text{TCE}$, **1**, or 2D, $[(\text{MX}_2)\text{TPyP}] \cdot 4\text{TCE}$, ($\text{M} = \text{Pb}$, **2**; Cd , **3**) polymeric networks. The porphyrin cavities in these crystalline networks can be selectively populated with various metal cations to generate ordered multiporphyrinic supramolecular arrays without distorting the coordination networks, either by (a) crystallizing the metal halides and TPyP in the presence of suitable metal salts or by (b) reacting metal halides with a mixture of freebase and metallo porphyrins in specific stoichiometric ratios. A design limit has been reached following approach b, synthesis of the complexes using 100% metalated TPyP results in a change in structure due to intermolecular MTPyP coordination. The UV/vis and fluorescence spectra recorded on partially metalated complexes indicate the presence of the expected absorption and emission bands. Additionally, complex **1** reveals an unusual clathration behavior, wherein the stacking features perpendicular to the porphyrin plane adjust to allow inclusion of variable amounts of identical guest solvent molecules without modification of the layered structure.

Introduction

Nature uses multiple chromophoric assemblies (light-harvesting complexes) to capture sunlight and transfer the energy/electrons into the photosynthetic reaction centers of green plants and bacteria.^{1–10} We could mimic the functional properties of such natural systems, if we could develop a viable design strategy for the construction of well-defined polymeric multichromophoric arrays.^{2,3} We now report a novel crystal-engineering strategy to imbed virtually unlimited numbers of porphyrin chromophores in desirable, controlled metalation states (including mixed metallo porphyrins and freebase porphyrins) into highly organized, rigid one-dimensional and/or two-dimensional crystalline, supramolecular arrays.^{11–13}

Tetraarylporphyrins (TAPs) have been widely studied in solution and in the solid state for a variety of purposes, but in general the solution studies have focused on electron and energy transfer, while the solid-state studies have discussed the importance of TAPs as host materials based on the shape of the porphyrin or based on networks formed by intermolecular hydrogen bonding or coordination.^{1–10,14–17} Multiple TAPs have been linked in solution through covalent bonds, hydrogen bonds, and coordination bonds, or even mechanically (rotaxane-type).^{18–24} However, no attempts have been made to link

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multiple porphyrins (i.e., network structures of both freebase porphyrin and metallo porphyrins) through noncovalent bonds in the solid state.

Solid-state multichromophoric assemblies have an advantage over solution species because with a suitable design strategy, one could interlink an unlimited number of metallo and metal-free porphyrins, either through hydrogen bonding or coordination bonds, into rigid and highly organized supramolecular arrays.^{11–13} Indeed, such rationally designed solids may reveal interesting optoelectronic, magnetic, catalytic, and photosensitizing properties, thus leading quickly to practical applications.^{5,24,25}

Various metalated TAP coordination polymers have been reported, using either bifunctional bridging ligands or coordinating groups built into the aryl periphery (e.g., tetrapyrrolylporphyrin (TPyP)). While these designs are suitable for building in certain functional properties, in general, any design strategy which requires use of a metalated porphyrin to maintain the supramolecular structure is automatically limited in scope: further metalation is not possible because the cavities are occupied and, thus, may not be useful for electron- or energy-transfer studies. Demetalation of such polymers based on coordination to the metal in the porphyrin cavity will lead to loss of supramolecular structure.

Robson has published two important papers utilizing exterior functionality of metalated TPyP to create novel 3D and large open channel networks by coordination with Cd²⁺ or Cu⁺ to the pyridyl ligands.¹⁷ Despite these and other efforts directed toward TAP compounds; however, coordination polymers based on freebase porphyrins or porphyrins with variable metalation seem to be unknown. Now, however, we report a novel crystal-engineering design strategy, wherein metalated and metal-free tetrapyrrolylporphyrins coordinate with metal halides and form highly organized, reproducible 2D supramolecular arrays which can be selectively metalated without disrupting the supramolecular structures.

Experimental Section

Synthesis. All of the chemicals except metalated TPyPs were purchased from Aldrich (Milwaukee, WI). The TPyP was metalated with Zn²⁺, Cu²⁺, and Ni²⁺ using well-established literature procedures.²⁶ The single crystals of TPyP coordination polymers (freebase, partially, and fully metalated) were grown using a layering technique at ambient temperatures in which TPyP was dissolved in 3:1 solution mixtures of 1,1,2,2-tetrachloroethane (TCE) and MeOH and then layered with metal salts dissolved in MeOH.

TPyP (0.031 g, 0.5 mmol) dissolved in TCE–MeOH (20 mL) was layered with a methanolic solution of HgI₂ (0.045 g, 1 mmol, 10 mL) to form [(HgI₂)₂TPyP]·2TCE, **1**. The same reaction with PbI₂ (0.070 g, 1 mmol, 20 mL) or CdI₂ (0.055 g, 1 mmol, 10 mL) produced the isostructural complexes [(PbI₂)TPyP]·4TCE, **2**, and [(CdI₂)TPyP]·4TCE, **3**, respectively. Our attempts to crystallize TPyP·HgX₂ complexes in the presence of Co, Ni, and Zn metal nitrates resulted in either partially metalated or clathrated complexes with varying number of solvent guest molecules.

Addition of Zn(NO₃)₂·6H₂O (0.015 g, 0.5 mmol) to the methanolic solution of HgI₂ (0.045 g, 1 mmol) layered with TPyP (0.031 g, 0.5 mmol) resulted in the 30% Zn-metalated compound, [(HgI₂)₂Zn_{0.3}TPyP]·4TCE, **4**. When Co(NO₃)₂·6H₂O or Ni(NO₃)₂·6H₂O were added to methanolic solution of HgBr₂ or HgI₂, only freebase porphyrin coordination polymers, [(HgBr₂)₂TPyP]·6TCE, **5**, and [(HgI₂)₂TPyP]·

4TCE, **6**, were isolated. The latter, **6**, is crystallographically isostructural with the 30% Zn-metalated compound, **4**. Thermogravimetric analysis on all of these complexes suggested the loss of TCE from the crystalline compounds at the boiling point of TCE (147 °C).

We have also synthesized coordination complexes of ZnTPyP with HgI₂ using the layering technique, but the resultant crystals are of poor quality. ZnTPyP (0.034 g, 0.5 mmol) dissolved in TCE–MeOH (20 mL) was layered with methanolic solutions of HgI₂ (0.045 g, 1 mmol, 10 mL) and (0.068 g, 1.5 mmol, 10 mL) to form complexes [(HgI₂)₂ZnTPyP]·xTCE, **7**, and [(HgI₂)₃(ZnTPyP)₂]·xTCE, **8**, respectively.

X-ray Crystallography. Data (4 < θ < 56°) on complexes **1–8** were collected on a Siemens CCD area detector-equipped diffractometer with Mo Kα (λ = 0.710 73 Å) radiation at –100 °C using a stream of nitrogen gas. The crystal structures of **1–8** were solved by direct methods using the SHELXTL package. All nonhydrogen atoms were anisotropically refined and aromatic hydrogen atoms were calculated (d_{C–H} = 0.95 Å) and fixed with the thermal parameters based upon the carbon atom to which they are bonded. Summaries of the crystallographic parameters of **1–8** are reported in Tables 1 and 2.

The TPyP molecules in complexes **1–3** and **5** are located on a crystallographic inversion center, and the asymmetric unit contains only half of the formula unit. The Cd and Pb metal centers in **2** and **3** are also located on special positions. The TCE molecules in the majority of the complexes are disordered with Cl atoms exhibiting high thermal parameters. The site occupancy factors for the metal centers in the partially metalated (Zn, Cu, and Ni) porphyrins of **1–3** were determined by identifying reasonable temperature factors and accompanying low R-factors during least-squares refinements. The occupancy factors obtained from least-squares refinements were later confirmed by UV/vis spectra.

Single crystals of **7** and **8** were of poor quality, and the X-ray data obtained was useful only for determination of gross structural features. Full crystallographic details of these complexes are not discussed here.

Distribution Ratios. We have calculated the uptake of Cd²⁺ and Ni²⁺ from aqueous solution into the crystalline networks of **1**. Single crystals of complex **1** were suspended in 1 mL of water containing trace quantities of ⁶³NiCl₂ and ¹⁰⁹CdCl₂ and stirred for 1 h. The radioactivity of the solution was significantly reduced, and the weight distribution ratios (D_w) for uptake of Cd²⁺ and Ni²⁺ were calculated from the following equation:

$$D_w = \left(\frac{A_i - A_f}{A_i} \right) \left(\frac{\text{contact volume}}{\text{mass of crystals}} \right)$$

where A_i is the activity in counts per minute in the initial sample and A_f is the activity in counts per minute after contact with the crystals. The contact volume is the total volume of the adsorbate.

Spectroscopy. The titration curves for the freebase and metallo porphyrins have been developed to estimate the unknown composition of metallo porphyrins in the freebase porphyrin networks. The titration curves were recorded for solution mixtures of TPyP (λ = 514 nm) and ZnTPyP (λ = 561 nm) by systematically varying the percentage of metallo porphyrins (0 to 100%) in TCE at a concentration of 2.5 × 10^{–4} M. The single crystals of partially metalated complexes **1–4**, containing unknown compositions of freebase and metalated porphyrins, were collected, dried, and redissolved in TCE whereupon their absorption spectra were compared with the titration curves.

The solid-state fluorescence spectra of partially metalated porphyrins were recorded by making a Nujol mull of finely grounded single crystals of complexes **1–3**. Quartz glass plates were used to mount the sample. The fluorescence emission spectra were measured for the 420 nm excitation wavelength. The absolute intensities of the fluorescence spectra for freebase and partially metalated complexes of **1** vary depending upon the amount of porphyrin sample used. We were not able to quantify the energy transfer in these systems.

Results and Discussion

In our efforts to design multiporphyrin arrays in the solid state, we found that the design of rigid coordination polymers of freebase porphyrins is an essential first step. Construction

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Table 1. Comparison of Unit Cell Parameters and Metalation Ratios

compd	initial ratio TPyP–MTPyP (%)	MTPyP from UV/vis (%)	MTPyP from X-ray (%)	space group	cell data						cell vol. (Å ³)	density (g cm ⁻³)	interplanar angles of pyridyl groups (deg)
					<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	α (deg)	β (deg)	γ (deg)			
freebase, 1				<i>P</i> -1	10.0350(7)	11.9656(8)	12.9198(8)	98.935(1)	101.752(1)	113.669(1)	1342	2.306	82.7, 72.8
50% Zn, 1	50:50	51.4	50	<i>P</i> -1	10.130(1)	11.842(2)	12.861(2)	98.112(3)	102.129(3)	113.638(3)	1337	2.352	81.8, 71.3
75% Zn, 1	25:75	73.5	75	<i>P</i> -1	10.1734(6)	11.7880(7)	12.8166(6)	97.884(1)	102.216(1)	113.594(2)	1334	2.378	84.4, 72.6
freebase, 2				<i>C2/c</i>	20.8977(1)	20.8623(1)	15.0090(1)	90	112.458(1)	90	6047	1.919	70.7, 60.8
30% Ni, 2	70:30		30	<i>C2/c</i>	20.864(1)	20.837(1)	14.9387(8)	90	112.220(1)	90	6012	1.949	70.0, 60.7
50% Zn, 2	50:50	51.8	20 ^c	<i>C2/c</i>	20.8693(1)	20.8536(3)	14.8930(2)	90	111.933(1)	90	6012	1.952	70.7, 62.3
freebase, 3				<i>C2/c</i>	20.467(2)	20.406(2)	15.167(1)	90	112.787(1)	90	5840	1.884	69.1, 62.8
20% Zn, 3	80:20	19.6	15	<i>C2/c</i>	20.5045(3)	20.4417(4)	15.1418(2)	90	112.629(1)	90	5858	1.887	69.6, 65.3
10% Cu, 3	90:10		6–8	<i>C2/c</i>	20.4965(5)	20.4356(5)	15.1562(3)	90	112.777(2)	90	5853	1.883	70.2, 60.6
30% Zn, 4	<i>a</i>	55.6 ^b	30	<i>P</i> -1	14.6129(5)	16.2090(5)	16.3263(5)	62.053(1)	80.372(1)	73.281(1)	3269	2.252	84.3, 78.3, 76.1
freebase, 6				<i>P</i> -1	14.6094(3)	16.2154(2)	16.3862(2)	61.984(1)	80.733(1)	73.365(1)	3282	2.243	82.3, 79.3, 74.8
5				<i>P</i> -1	10.8167(6)	11.6757(7)	16.1584(9)	104.591(1)	95.899(2)	101.073(1)	1913	2.036	82.6, 68.4
7^d				<i>P</i> -1	15.5961(9)	16.7186(9)	16.7390(9)	102.237(1)	90.550(1)	90.203(1)	4265		
8^d					24.625(2)	14.008(1)	31.970(2)	90	94.527(3)	90	10867		

^a Metalated through diffusion of Zn(NO₃)₂. ^b The UV spectra were recorded 4 mo. after single-crystal data was collected by freshly collecting crystals from the mother liquor. It is assumed that the enhanced metal content is a result of continued slow diffusion of the metal ions into the crystalline lattice. Atomic absorption spectroscopy indicated 58% zinc metalation. ^c Crystallographic data quality is poor; high *R* values. ^d These structures suffer from small crystal size and poor quality data. Preliminary structure solution has revealed the major structural features of the coordination polymer only.

Table 2. Summary of Additional Crystallographic Parameters^a

cryst data	1	1·75% Zn	2	3	4·30% Zn	5
formula	C ₄₄ H ₃₀ Cl ₈ Hg ₂ I ₄ N ₈	C ₄₄ H _{28.5} Cl ₈ Hg ₂ I ₄ N ₈ Zn _{0.75}	C ₄₈ H ₃₄ Cl ₁₆ PbI ₂ N ₈	C ₄₈ H ₃₄ Cl ₁₆ CdI ₂ N ₈	C ₄₈ H _{33.4} Cl ₁₆ Hg ₂ I ₄ N ₈ Zn _{0.30}	C ₅₂ H ₃₈ Cl ₂₄ Hg ₂ Br ₄ N ₈
formula wt	1863.14	1910.15	1750.99	1656.23	2216.41	2346.52
cryst size (mm)	0.38 × 0.20 × 0.18	0.22 × 0.20 × 0.12	0.54 × 0.20 × 0.14	0.30 × 0.18 × 0.08	0.20 × 0.20 × 0.10	0.45 × 0.30 × 0.25
cryst syst	triclinic	triclinic	monoclinic	monoclinic	triclinic	triclinic
color of cryst	violet	violet	violet	violet	violet	violet
<i>Z</i>	1	1	4	4	2	1
GOF on <i>F</i> ²	0.960	1.051	1.023	0.965	0.935	0.851
final <i>R</i> values, ^b <i>R</i> , w <i>R</i>	0.0516, 0.1206	0.0873, 0.1487	0.0333, 0.0740	0.1029, 0.2225	0.0496, 0.0958	0.0655, 0.1249

^a Cell parameters, volumes, densities, and space groups are located in Table 1; data collected at 173 K. ^b Refinements on *F*² carried out on all data; conventional *R* values quoted for [*I* > 2σ(*I*)] data.

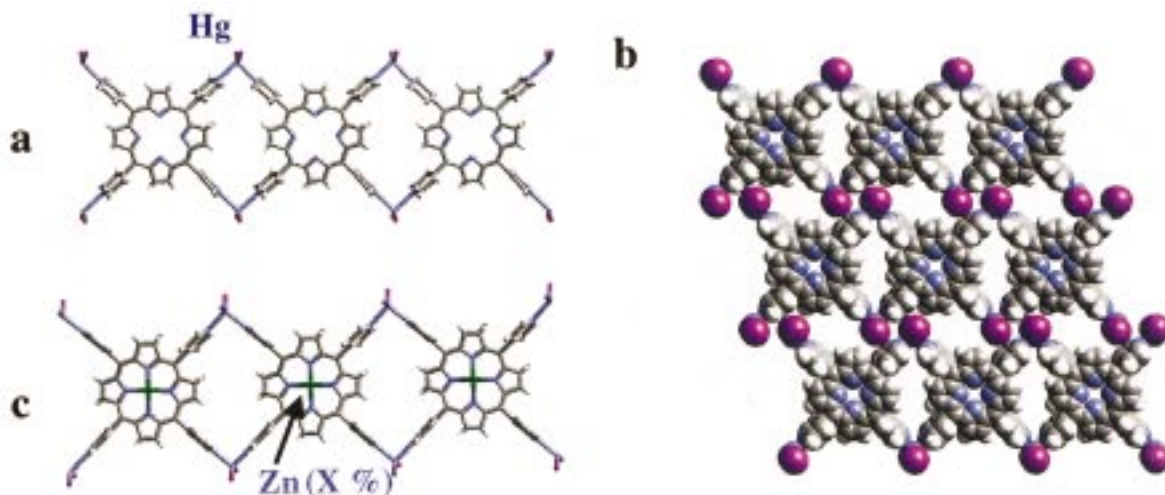
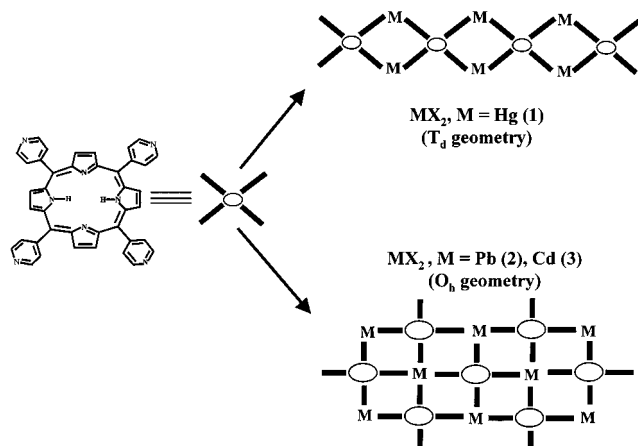


Figure 1. (a) Nanoporous 1D coordination polymers of freebase porphyrin **1** produce one type of supramolecular cavity. (b) The 1D polymers are arranged in a layered fashion inducing a second cavity. (In the space-filling model, the H atoms of the NH groups are not shown to highlight the porphyrin cavity.) (c) Partially metalated coordination polymers of **1** (Zn^{2+} occupancy is either 30, 50, or 75% in the complexes characterized).

of the supramolecular polymer or sheet with the freebase porphyrin utilizing functionality external to the cavity may allow selective metalation and demetalation of the cavity without disturbing the overall crystalline architecture. The coordination complexes of metal halides, MX_2 ($\text{M} = \text{Cd}, \text{Hg}, \text{Pb}$; $\text{X} = \text{Br}, \text{I}$), with freebase TPyP form predictable 1D (HgX_2) or 2D ($\text{CdX}_2, \text{PbX}_2$) nanoporous coordination networks depending upon the coordination geometry of the metal (Scheme 1). The

Scheme 1



porphyrin cavities in these supramolecular arrays can be selectively populated with various metal cations to generate ordered multiporphyrin arrays without distorting the coordination networks, either by crystallizing them in the presence of suitable metal salts or by reacting metal halides with a mixture of porphyrins comprising varying compositions of metallo porphyrins and freebase porphyrin(s) as discussed below. This strategy provides the distinct ability to fine-tune the metalation and to include functionality into the porphyrin itself, thus offering further control of spectroscopic properties. In addition, the crystalline freebase-coordination polymers may selectively remove metal ions directly from aqueous solution in an ion exchange mechanism directed by the selectivity of the porphyrin cavity.

Crystal Structures of 1–3. The crystal structure of complex **1** has a nanoporous 1D polymeric architecture with each HgI_2 tetrahedrally coordinated with a pyridyl moiety of two TPyP

molecules. While the Hg atoms in each polymeric chain are coplanar, each TPyP molecule is tilted ca. 10° with respect to this plane (the interplanar angles of the pyridyl moieties with respect to the porphyrin core in **1–5** are listed in Table 1). A supramolecular cavity is formed between the linked porphyrins with an effective cavity size of $2.5 \times 7.7 \text{ \AA}$ (Scheme 1, Figure 1a). The 1D coordination polymers are arranged in layers inducing another supramolecular cavity (effective cavity size, $2.4 \times 3.0 \text{ \AA}$, Figure 1b). The 2D layers are offset stacked at 5.5 \AA and form a partially open porous network. The TCE molecules are sandwiched between the layers and cap the supramolecular cavities.

The Pb and Cd centers in **2** and **3** adopt octahedral geometry with trans-halides and coordination of four pyridyl moieties to form isostructural nanoporous 2D coordination polymers (Scheme 1, Figure 2a). The TPyP molecules are decidedly nonplanar and adopt a butterfly configuration, presumably due to the additional structural rigidity of the 2D polymer sheet. The TCE molecules are sandwiched between the layers, and the 2D sheets are offset stacked at ca. 6.9 \AA such that a portion of the porphyrin cavity resides over the supramolecular pore (Figure 3).

Partial Metalation of 1–3. We have successfully introduced varying compositions of Zn^{2+} , Cu^{2+} , Ni^{2+} , and mixed metallo porphyrins into 1D and 2D networks isostructural with **1–3** to generate solid-state multiporphyrin arrays (Table 1, Figures 1c and 2b). Metalation may be obtained through two independent routes. Initially, we added $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to the methanolic solution of HgI_2 and layered this with TPyP, which resulted in the 30% Zn-metalated single crystals, **4**, $[(\text{HgI}_2)_2\text{Zn}_x\text{TPyP}] \cdot 4\text{TCE}$. Interestingly, the crystals collected from the same reaction mixture after a 3 mo. period revealed an enhanced percentage of ZnTPyP (55.6% from UV/vis absorption spectra, 58.0% from atomic absorption spectra). Complex **4** has a 1D polymer and layer-like structure identical to **1**, but is solvated with four TCE molecules per formula rather than two as in **1**.

The ability of single crystals of the freebase porphyrin **1** to directly remove metal cations from aqueous solution was investigated using radioactive tracers of ^{63}Ni and ^{109}Cd . When crystals of **1** were suspended in 1 mL of water containing tracer quantities of $^{63}\text{NiCl}_2$ or $^{109}\text{CdCl}_2$, a significant uptake of the metal ions was observed as measured by the reduction in activity of the solution (75% for Ni, 95% for Cd). Weight distribution

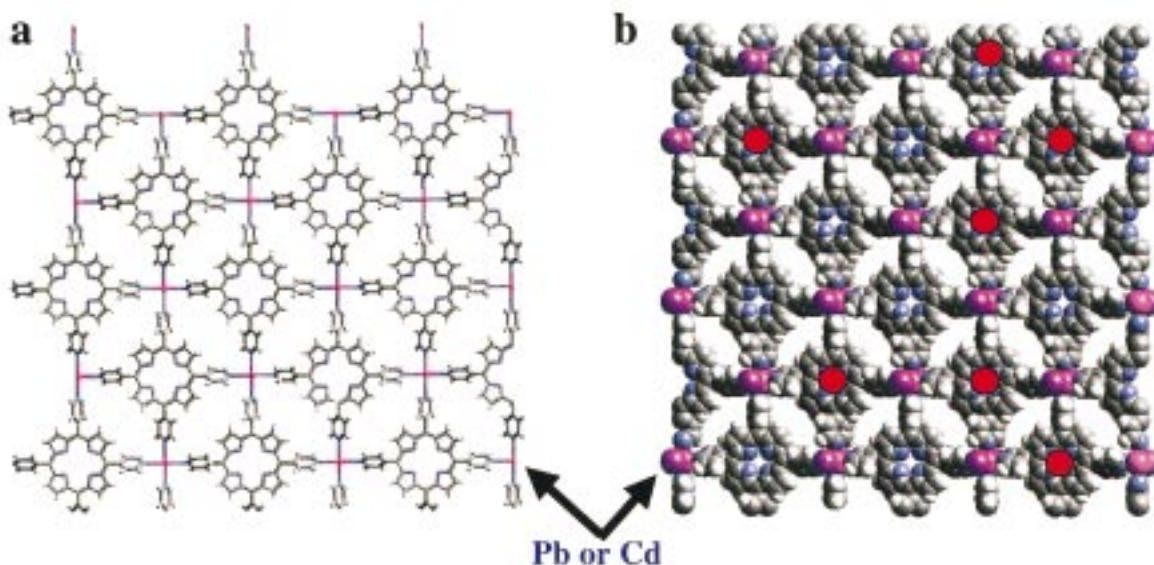


Figure 2. (a) The 2D coordination polymers obtained for **2** and **3**. The iodides are perpendicular to the 2D layer. (b) Space-filling model of **2** or **3** with the H atoms of the NH groups omitted to highlight the porphyrin cavities. The partial metalation of the porphyrin cavities is represented with random placement of red spheres.

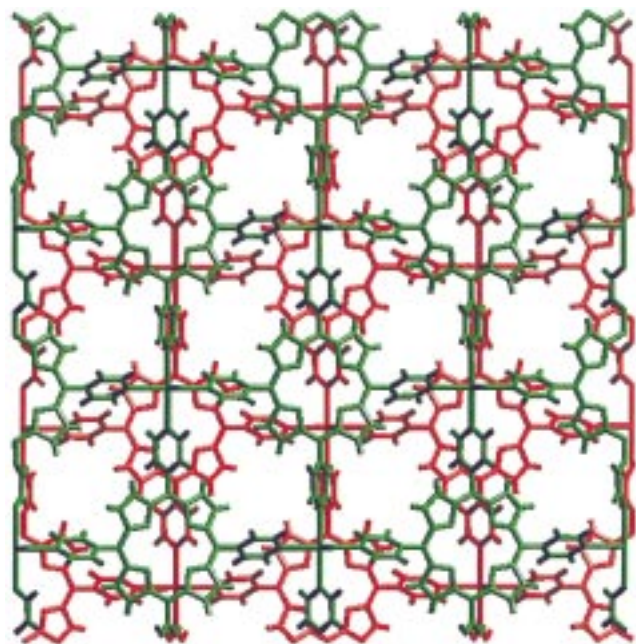


Figure 3. The stacking of polymeric sheets in **2** and **3** with green and red representing adjacent layers. For clarity, the solvent layer is not shown.

ratios of 12 000 for Cd and 1600 for Ni were calculated. Although the mechanism for uptake of these metal ions is not yet clear, the potential for direct uptake into the solid state was clearly demonstrated.

The crystal structures of **1** and **4** indicate that it is possible to selectively populate freebase porphyrin networks with metal cations and neutral molecules without distorting the polymeric structure in the presence of suitable metal salts. These two approaches, however, lack the control necessary to fine-tune the metalation, and thus, a new strategy was adopted in which both freebase TPyP and Zn-metalated (ZnTPyP) tetrapyrrolylporphyrins were mixed and then reacted with MI_2 ($M = \text{Hg}, \text{Pb}, \text{Cd}$) in controlled stoichiometries. This synthetic strategy provides greater control over the introduction of various porphyrin chromophores and their integration in the solid state.

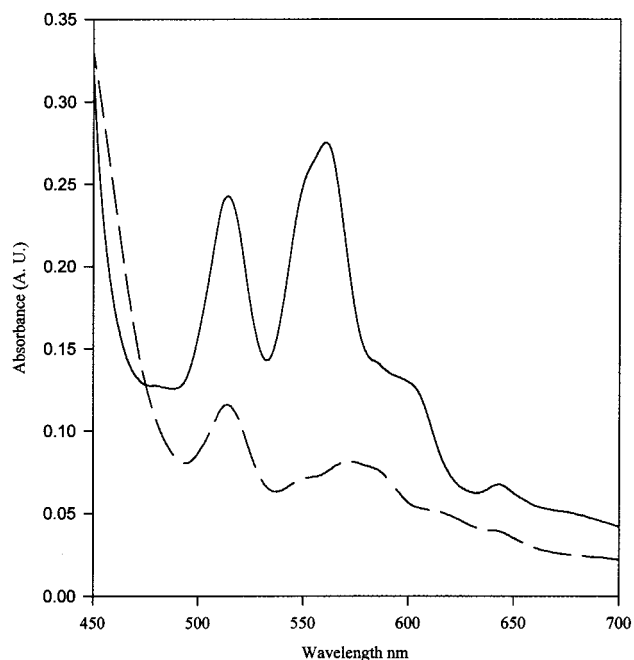


Figure 4. The UV/vis absorption spectra of 75% Zn- (solid line) and 50% Zn- (broken line) metalated-**1**, dissolved in TCE. The percentage of ZnTPyP was estimated by comparing these spectra with the titration curves recorded for solution mixtures of TPyP ($\lambda = 514 \text{ nm}$) and ZnTPyP ($\lambda = 561 \text{ nm}$) at $2.5 \times 10^{-4} \text{ M}$ concentration.

To test this route, mixtures of Zn and freebase TPyP (ZnTPyP content, 50% or 75%) were reacted with HgI_2 or PbI_2 in 1:2 molar ratios using the layering technique as described above. The crystals of the resulting complexes are isostructural with **1–3** (Figures 1c and 2b, Table 1). The presence and percentage of ZnTPyP was determined by spectroscopic and crystallographic methods, and the metal contents determined match the ratio of ZnTPyP utilized in the reactions. Figure 4 shows the UV/vis absorption spectra of 75% and 50% Zn-metalated single crystals of **1**. In similar reactions we were able to introduce Ni^{2+} and Cu^{2+} into the crystalline lattices of **1–3** in controlled ratios (Table 1).

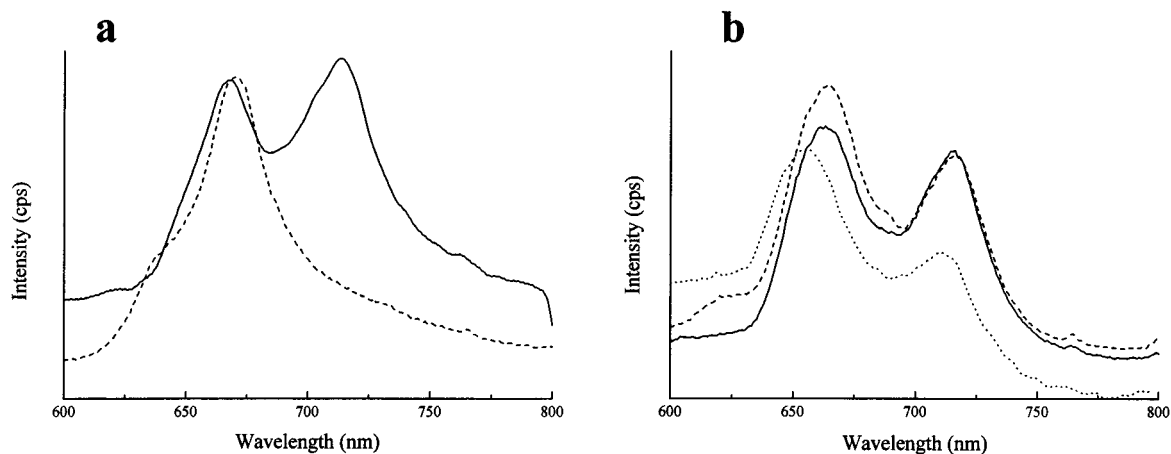


Figure 5. The solid-state fluorescence spectra of (a) TPyP (—) and ZnTPyP (---) and (b) freebase porphyrin crystals **1** (—), **1**·50% Zn (---), and **1**·75% Zn (···). The spectra of the metallo porphyrins were arbitrarily multiplied to compare with emission spectra of **1**. Notice that the enhanced intensity around 660 nm is due to the partial overlap of ZnTPyP and TPyP emission bands.

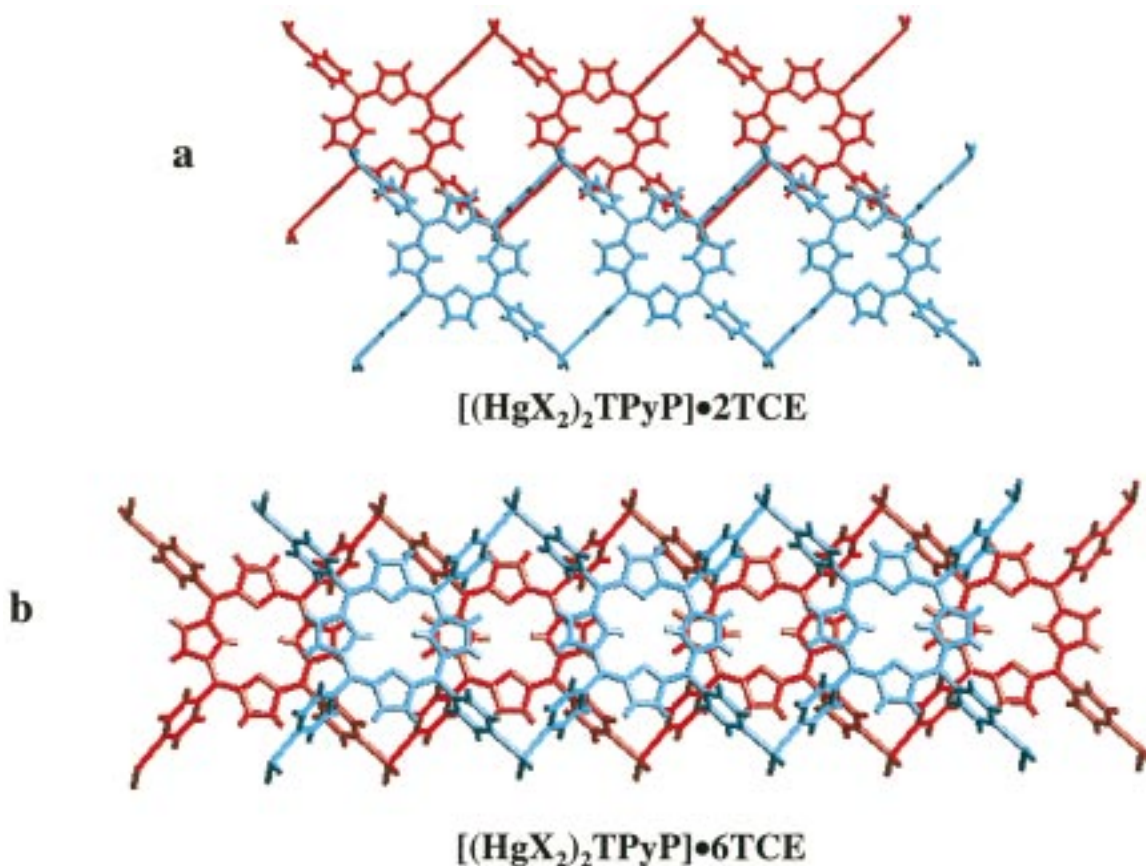


Figure 6. Two types of stacking patterns are observed for the 1D polymers in **1** and **4–6**: (a) offset stacking (**1**, solvated with two TCE per formula unit) and (b) overlap stacking (**5**, solvated with six TCE per formula unit). Complexes **4** and **6** (isostructural complexes solvated with four TCE per formula unit) exhibit both types of stacking with the number of TCE molecules sandwiched between the layers corresponding to the type of stacking (two in a and three in b). Solvent molecules are not shown.

The solid-state fluorescence spectra were recorded for free-base complex **1** and its 50% and 75% Zn^{2+} -metalated analogues to compare their emission spectra. The fluorescence spectra of TPyP (λ 667 nm (s), 713 nm (s)) and ZnTPyP (λ 642 nm (w), 670 nm (s)) in comparison with **1** and its analogues, **1**·50%Zn and **1**·75%Zn, revealed that while the fluorescence spectrum of **1** is similar to TPyP, the spectra of **1**·50%Zn and **1**·75%Zn show an enhanced intensity around λ 660 nm due to the partial overlap of ZnTPyP and TPyP emission bands (Figure 5).

Although, the fluorescence intensities for **1**·50%Zn and **1**·75%Zn are very weak compared to their parent chromophores for approximately the same amount of sample, we are not yet able to quantify the energy transfer in the solid state because of limitations in preparing solid samples with accurate concentrations.

Controlled Inclusion of TCE Molecules. Interestingly, our attempts to metalate 1D or 2D networks with the addition of Ni^{2+} and Co^{2+} metal nitrates during the synthesis of **1–3**,

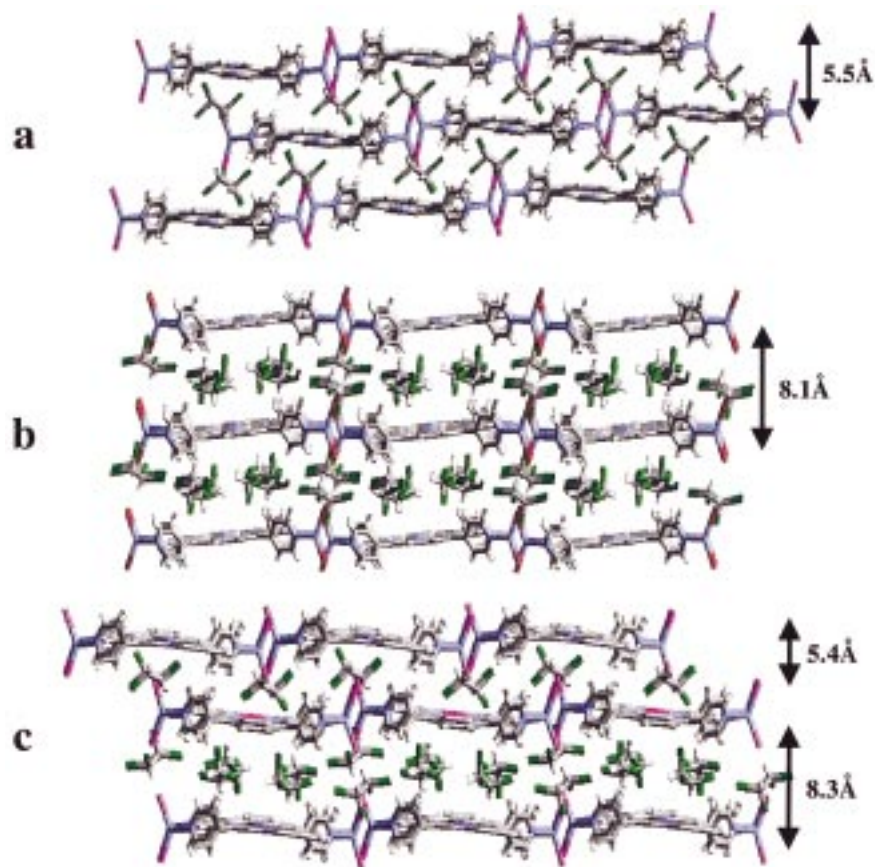
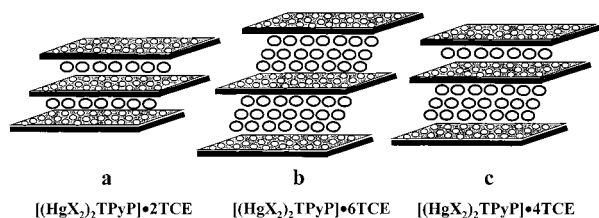


Figure 7. Intercalation of TCE molecules between the 2D layers of **1** and **4–6**: (a) **1**, intercalated with two TCE molecules (Scheme 2a), (b) **5**, intercalated with six TCE molecules (Scheme 2b), and (c) **4** and **6**, intercalated with four TCE molecules (Scheme 2c).

uncovered unusual inclusion behavior for these complexes. Variable amounts of identical guest solvent molecules are incorporated into the crystal lattices simply by adjusting their stacking features without modification of the overall 1D or 2D frameworks.

Addition of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to methanolic solution of HgBr_2 or HgI_2 while layering with TPyP solution resulted in only freebase porphyrin coordination polymers, $[(\text{HgBr}_2)_2\text{TPyP}] \cdot 6\text{TCE}$, **5**, and $[(\text{HgI}_2)_2\text{TPyP}] \cdot 4\text{TCE}$, **6**. The latter, **6**, is crystallographically isostructural with the 30% Zn-metalated compound, **4**. The crystal structures of **1** and **4–6** demonstrate an interesting ability to include variable numbers of identical neutral guest molecules by subtle rearrangement of the stacking of layers (Scheme 2).²⁷

Scheme 2



In complex **5**, there are three TCE molecules per TPyP between the layers, and the 1D polymers stack (porphyrin cavity directly over supramolecular cavity) at an 8.1 Å separation (Figure 6). The isostructural complexes **4** and **6** have bilayer structures (Figure 7) which exhibit solvation and stacking

features of both **1** and **5**. Alternating layers have either one (between offset stacked layers as in **1**) or three (between stacked layers as in **5**) TCE molecules per TPyP with interlayer separations of 5.4 and 8.3 Å, respectively (Scheme 2, Figure 7). Indeed, these two stacking distances correspond to the interlayer stacking distances of **1** (5.5 Å) and **5** (8.1 Å). Few if any crystalline TAP compounds have been reported that bind identical guest molecules at different levels of inclusion.

Limitations of the Design Strategy. Our strategy for the synthesis of metalated-porphyrin coordination polymers does have a design limit: *the 1D and 2D polymeric networks cannot be prepared by reaction with 100% ZnTPyP*. Our attempts to synthesize completely metallated analogues of **1** and **4–6** by reacting HgI_2 exclusively with ZnTPyP in 2:1 and 3:1 molar ratios resulted in the partially characterized complexes $[(\text{HgI}_2)\text{-ZnTPyP}] \cdot x\text{TCE}$, **7**, and $[(\text{HgI}_2)_3(\text{ZnTPyP})_2] \cdot x\text{TCE}$, **8**. The crystal structures of **7** and **8** indicate that preferential coordination of the TPyP to Zn^{2+} in the porphyrin cavity interferes with the formation of the 1D structures observed in **1** and **4–6**. The structures reveal combinations of coordination polymers generated by Zn and by Hg coordination to the exterior pyridyl groups. One structural feature of this mode of polymer generation which needs to be further examined, is the fact that *polymers generated by Zn coordination must contain both parallel and perpendicular porphyrin cavities*. The structures of **1–6** all have the porphyrin molecules in parallel orientations.

Conclusions

The design strategies reported here lead to multichromophoric arrays of defined rigidity, dimensionality, porosity, and selectivity. A virtually unlimited number of metal ions can be inserted

(27) Russell, V. A.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575.

into the polymeric porphyrin arrays, thus features that are relevant to the design of light harvesting model systems, and sensors can be fine-tuned. (i) One can design a highly organized supramolecular array of numerous porphyrin chromophores in the solid state such that the constituent chromophores exhibit significant overlap in their absorption and emission bands to generate various light-harvesting model systems. (ii) The metal cations can be directly inserted into 1D/2D arrays of **1–6** to generate multiporphyrin arrays and may also be selectively stripped by exploiting the discrepancies in their acid stability constants. (Such a property may be used to design sensors and optical switches.) (iii) Complexes **1–4** with nanopores and layered structures have the propensity to function either like zeolites or clays to accommodate guest molecules into the crystal lattice which may allow fine-tuning of electronic properties. (iv) The level of solvent inclusion in crystals of **1** seems to be controlled by additives or impurities. This interesting property may be exploited to control the interlayer separations of the 2D layers or the host–guest properties of these networks.

Further, the exchange of solvent molecules with suitable quenchers may be used for sensing applications.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1–5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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