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[7] Racemic **1** was prepared by the lithiation of 2-alkynyl-5-bromopyrimidine followed by treatment with 2-methylpropanal.

[8] Preparation of (*S*)-**1** with ca. 0.00005 % *ee*. Pyrimidyl alkanol (*S*)-**1** (1.5 mg, > 99.5 % *ee*) was dissolved in ethyl acetate (or benzene) to make a standardized solution of (*S*)-**1** (3.2×10^{-6} mol L^{-1}). The solution (50 µL) was added to a solution of racemic **1** (75.1 mg) in ethyl acetate (or benzene). Then, a part of the solution was transferred to another flask, and the removal of solvent gave (*S*)-**1** with ca. 0.00005 % *ee* (9.9 mg). Dissolution of the whole (*S*)-**1** in 4.3 mL of cumene produced a 9.9×10^{-3} M solution of (*S*)-**1** with ca. 0.00005 % *ee*.

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[10] After our experiments were completed, Singleton and Vo reported asymmetric autocatalysis using (*R*)-(2-methylpyrimidyl)alkanol[5b] with the order of 10^{-5} % *ee* [a) D. A. Singleton, L. K. Vo, *J. Am. Chem. Soc.* **2002**, *124*, 10010 – 10011]. However, they used only the catalyst with the *R* configuration. We believe that it is essentially important to examine the asymmetric autocatalysts of both configurations. The reasons are as follows: 1) The chirality level of the catalyst on the order of 10^{-5} % *ee* is

below the detection level of the instruments typically used, for example, HPLC, CD, polarimeter etc. (for recent advances in the measurement of enantiomeric excesses, see: b) M. Tsukamoto, H. B. Kagan, *Adv. Synth. Catal.* **2002**, *344*, 453 – 463). 2) Only after obtaining results that the asymmetric autocatalyst with *S* configuration affords itself with *S* configuration and the asymmetric autocatalyst with *R* configuration affords itself with *R* configuration one can judge that the autocatalyst works.

[11] Autocatalyst **1** on the order of 10^{-9} % *ee* has been employed, but we have not yet received reproducible results probably because of the effect of some unexpected and unknown chiral factor.

[12] The reaction of 2-methylpyrimidine-5-carbaldehyde with *i*Pr$_2$Zn without any added chiral substance had been examined in 100 experiments. After repeated asymmetric autocatalysis, (2-methylpyrimidyl)alkanol with a chirality level above the detection level formed [K. Soai, T. Shibata, Y. Kowata, *Japan Kokai Tokkyo Koho JP*, 9-268179 **1997**]. However, the probability of the formation of *S* and *R* enantiomers in toluene was not equal, which indicates an unexpected and unknown chiral factor affects the asymmetric induction. Similar observations have been reported by Singleton and Vo.[10a]

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Coordination Networks

Open Network Architectures from the Self-Assembly of AgNO$_3$ and 5,10,15,20-Tetra(4-pyridyl)porphyrin (H$_2$tpyp) Building Blocks: The Exceptional Self-Penetrating Topology of the 3D Network of [Ag$_8$(Zn^{II}tpyp)$_7$(H$_2$O)$_2$](NO$_3$)$_8$**

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The use of suitable predetermined building blocks has assumed an increasing relevance in recent times in the crystal engineering of coordination frameworks[1] that have potential interest as zeolite-like materials.[2] In this regard, much

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attention has been devoted to the networking ability of tetra-substituted porphyrins and metalloporphyrins,[3] which are potentially able to act as tetradentate planar donor groups and to produce open lattice species with large void volumes. Moreover, the nature of such building blocks can lead to synthetic supramolecular arrays with potential applications in materials chemistry as photonic devices, conductive polymers, chemical sensors, and receptors for selective catalysis. Examples of multiporphyrin architectures constructed by supramolecular interactions include species controlled by the variation of the peripheral substituent groups and/or the encapsulated metals, and those assembled through hydrogen-bonding bridges[3] or coordinative bonds to the metals of identical neighboring metalloporphyrin units[4] or to external metal centers.[5–8] The synthetic strategy based on coordinative interactions seems quite promising for the crystal engineering of robust open networks, whose structures can, in principle, be programmed by using appropriate substituents on the porphyrin groups (which are considered as large square-planar donor ligands) and external metal units with suitable coordination geometries. The pioneering work of Robson and co-workers in this area has, indeed, shown that metalloporphyrins can give coordination networks with the $CdSO_4$[5a] or the PtS topology[5b] by using Cd^{II} centers (acting as linear spacers) or tetrahedral Cu^I centers, respectively. Most of the reported frameworks contain external divalent metal ions, while species with trivalent[6e, 8] or monovalent[6a–d] metal ions are more rare.

We are currently investigating the reactions of different silver(I) salts with the free-base 5,10,15,20-tetra(4-pyridyl)-porphyrin (H_2tpyp) and with its Zn^{II}-metalated derivative (Zntpyp). To our knowledge, only one previous example of a multiporphyrin species assembled with Ag^I ions, that is, $[Ag(H_2tpyp)]PF_6 \cdot 1.5 TCE \cdot MeOH \cdot H_2O$ (TCE = tetrachloroethane), has been reported which consists of polymeric linear chains.[9] The versatility of silver cations can afford a variety of coordination geometries, but mainly gives the digonal and the tetrahedral ones. Digonal coordination affords not only 1D linear chains, but gives access to target structures comprised of 2D square grids (Ag:porphyrin 2:1) and 3D nets with the $CdSO_4$ or NbO topologies (Ag:porphyrin 2:1), while the tetrahedral geometry would only be expected to give a 3D structure of the PtS type (Ag:porphyrin 1:1), as previously found with Cu^I ions.[5b] We report here novel polymeric frameworks obtained from the self-assembly of $AgNO_3$ with H_2tpyp or Zntpyp, namely, the 2D species $[Ag_4(H_2tpyp)_3]$-$(NO_3)_4 \cdot x$ solv (1) and $[Ag_2(H_2tpyp)(NO_3)](NO_3) \cdot x$ solv (2) as well as the 3D network $[Ag_8(Zntpyp)_7(H_2O)_2](NO_3)_8 \cdot x$ solv (3). Only compound 2 contains one of the expected structural motifs (2D square-grid layers), as also observed by us with other silver salts (such as triflate and tosylate) and which will be reported elsewhere.[10] The topologies of compounds 1 and 3 are unprecedented and the latter one is a rare case of a 3D self-penetrating net. As desired, these networks are robust and exhibit large free voids (> 50%) full of removable guest solvent molecules.

The self-assembly processes of these species were carried out by slow diffusion of solutions containing a large stoichiometric excess (up to fivefold) of $AgNO_3$ into solutions of

H_2tpyp or Zntpyp in TCE/MeOH. The solvent system plays a fundamental role in driving the processes. Compound 1 was isolated in good yield on layering a solution of $AgNO_3$ in N,N'-dimethylacetamide (DMA) over a solution of H_2tpyp in TCE/MeOH, after interposing a small volume of pure 3-chloroaniline between the two phases. Brown crystals formed within a few days. We have also observed the formation of variable amounts of smaller crystals of compound 2 under these conditions. However, the main product obtained on changing the solvents for the silver salt (for example, by using EtOH/H_2O/CH_3CN or DMSO/CH_3CN mixtures) is a different species, namely, $[Ag(H_2tpyp)](NO_3) \cdot x$ solv,[11] containing simple linear chains similar to those already reported.[9] Similarly, compound 3 was obtained in good yield upon layering a solution of $AgNO_3$ in DMA over a solution of Zntpyp in TCE/MeOH, after interposition of a small volume of pure DMA between the two phases. Dark-red crystals formed within a few days, which grew bigger and of better quality on keeping the reaction vessel at low temperature. This species can also be obtained in high yields (ca. 97%) as polycrystalline samples by adding over 1 h, under stirring, a solution of $AgNO_3$ in DMA to a solution of Zntpyp in TCE/
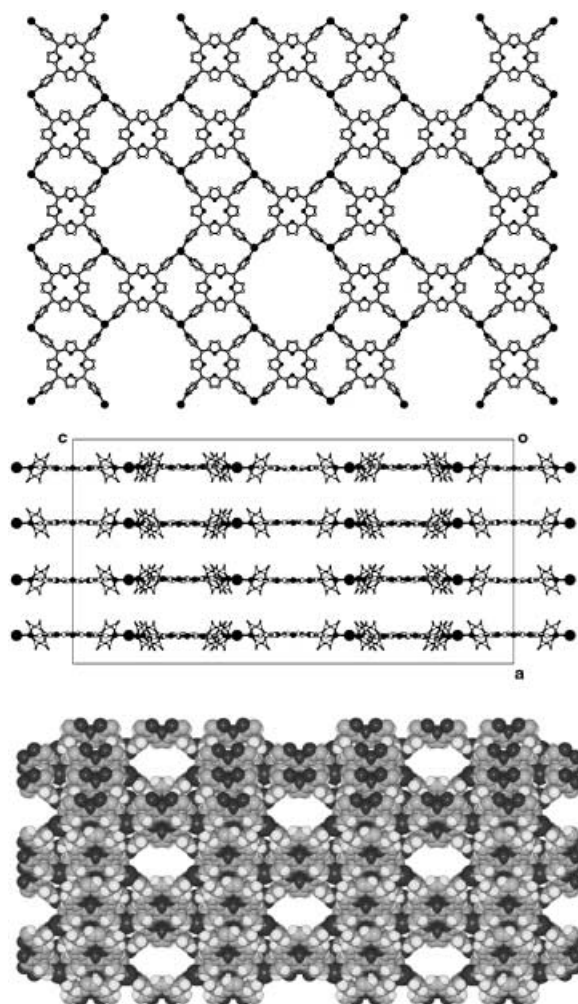

Figure 1. Structure of 1. A single 2D layer (top), a side view of the stacked layers (middle), and a view of the packing with the channels running along [110] (bottom).

MeOH in a reaction flask placed in an ice bath. All compounds were characterized by single-crystal X-ray analyses.[12]

The structure of **1** consists of two-dimensional flat layers comprised of tetracoordinate H_2tpyp centers and tricoordinate Ag^+ ions in the ratio 3:4 (Figure 1, top). This 2D net contains two types of rings: four- and eight-membered squares of alternating centers[13] with approximate edge dimensions of 10.0 × 10.2 and 19.9 × 19.9 Å, respectively. The topology is novel and can be related to the more usual square grid of (4,4) type (I in Scheme 1), as observed, for example, in the [$MCl_2(H_2$tpyp)] (M = Pb, Cd) species.[7a] The 2D layer of larger square meshes II, which contain digonal metal centers as in compound **2**, can be obtained by eliminating one half of the H_2tpyp centers from I (see below), while the elimination of only one quarter of the H_2tpyp centers can give either the layer of type III shown in Scheme 1 or that actually observed in **1**. The coordination of the metal centers in both III and compound **1** gives a tricoordinate T-shaped geometry, which is rather common for silver cations. However, the reason is not clear why the actual structure is preferred out of the two possibilities. The arms within the T-shaped coordination of the Ag^+ ions are shorter than the third Ag–N bond (2.263(3)–2.241(4) versus 2.427(3) Å) and the corresponding bond angle is larger than the other two (156.5(1) versus 101.3(1)–102.0(1)°). The 2D layers stack along the *a* axis, with an interlayer separation of 1/4 *a* (ca. 7.19 Å) and in an ABCD sequence (Figure 1, middle). The structure does not show wide channels when viewed down the stacking direction, since the larger squares of adjacent layers are not aligned. However, channels can be observed that run with an orientation inclined with respect to the planes of the layers, that is, along [110], and show an elliptical cross-section of about 6.0 × 14.5 Å (when the van der Waals radii are considered; Figure 1, bottom). The framework represents only approximate-

ly 35% of the cell volume and the interlayer regions and the channels contain disordered nitrate anions and many solvent molecules, for which a reasonable refinement was not possible. It is also difficult to establish the nature and amounts of these solvents by noncrystallographic methods because of the unavoidable formation of mixtures of crystals of **1** and **2**. Solid, air-dried samples of these mixtures were suspended in deuterated dichloromethane; ^1H NMR analyses performed on these solutions after a few hours revealed the presence of 3-chloroaniline, TCE, and DMA in a ratio of 1:2.3:1.7, similar to the composition of the reaction mother liquor.

Compound **2** contains a more usual type of 2D layers of (4,4) topology (Figure 2, top; II in Scheme 1), with large squares of edge dimensions 19.1 × 19.9 Å. This structural motif was previously observed in multiporphyrin systems connected through (−COOH)$_2$ hydrogen-bond pairs,[14] instead of the pyridyl-Ag-pyridyl synthons.

In contrast to **1**, the layers of **2** are slightly undulated (Figure 2, middle) because one of the two independent Ag^I ions exhibits a nonlinear coordination geometry as a
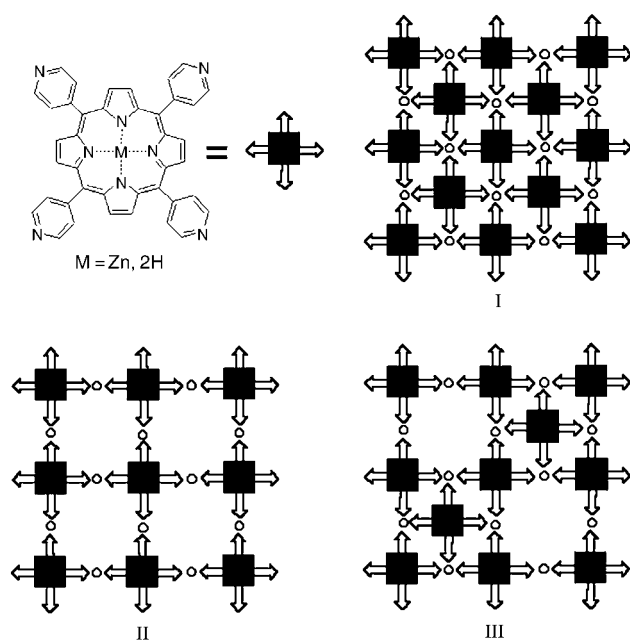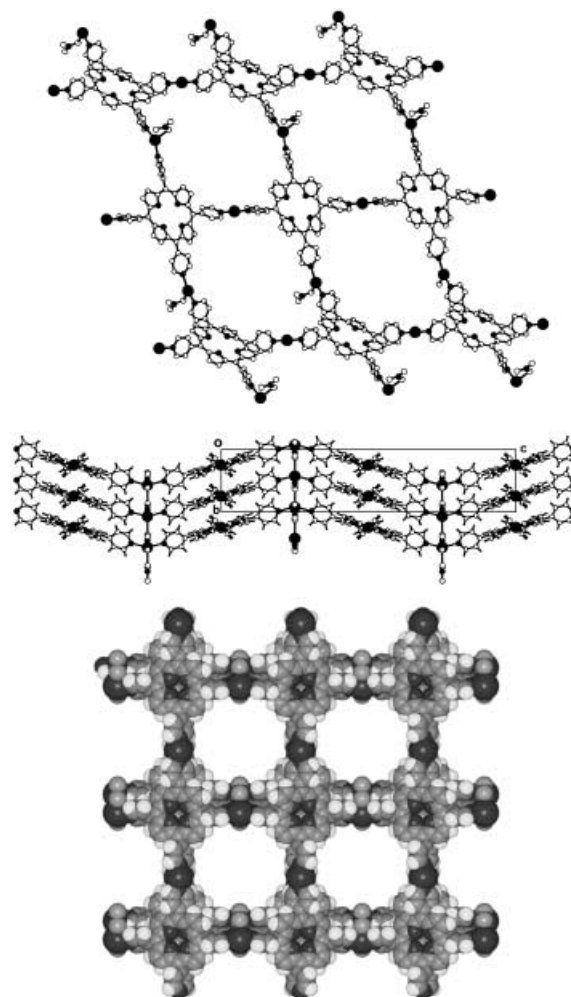

Figure 2. Structure of **2**. A single 2D layer (top), a side view of the stacked undulated layers (middle), and a view of the packing down the *b* axis showing the large square channels (bottom).

M = Zn, 2H

Scheme 1.

result of the asymmetric interactions with two oxygen atoms of two μ-η^1 nitrate anions that bridge adjacent layers (Ag$-$O 2.48(2), 2.74(2) Å). These interactions generate an overall 3D network with the CdSO$_4$-type topology. The stacking of the layers occurs down the *b* axis with a separation of 1/2 *b* (ca. 4.0 Å). The sequence is ABAB because of the presence of a small offset of adjacent sheets. This arrangement creates large channels of rectangular cross-section (ca. 12.0 × 15.0 Å, when the van der Waals radii are considered) running along the *b* direction (Figure 2, bottom). Large free voids (ca. 50 % of the cell volume) are thus associated with these regions, and this contrasts with **1**, in which free voids are mainly localized in the interlayer spaces.

The structure of compound **3** is influenced by the presence of the Zntpyp versus the H$_2$tpyp building blocks in that the Zn^{2+} ions enclosed in the porphyrin macrocycles essentially show a high tendency to increase their coordination number to five or six by axial bonding.[3] This species contains a complex 3D tetragonal open network (Figure 3), whose rationalization can be described stepwise. First of all,
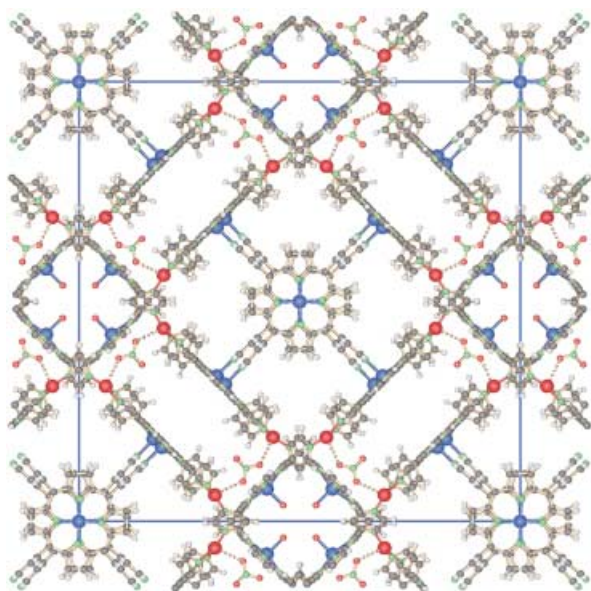

Figure 4. Portion of a 2D layer (top) and two views of the inclined interpenetration of two pairs of layers (bottom) in **3**.

Figure 3. A view of the overall network in **3** down the tetragonal *c* axis.

it is comprised of 2D layers of composition [Ag$_4$(Zntpyp)$_3$(H$_2$O)]$^{4+}$ that exhibit the same topology observed in compound **1** (Figure 4, top). Second, these layers are all parallel to the tetragonal *c* axis and are disposed in two sets of pairs (average interplanar separations: within the pairs approximately 7.3 Å, and between different pairs approximately 20.5 Å) that span two mutually perpendicular directions and interpenetrate in the "so-called" inclined fashion[1c] through all the pairs of large facing windows in the paired layers (Figure 4, bottom). Third, these sets of layers are interconnected by Zntpyp units whose macrocyclic planes are perpendicular to the tetragonal *c* axis (Figure 3). The four pyridyl groups of each of these units form axial bonds towards the metalloporphyrin Zn centers in four different surrounding layers (2/3 of the Zn centers on each layer are involved). The
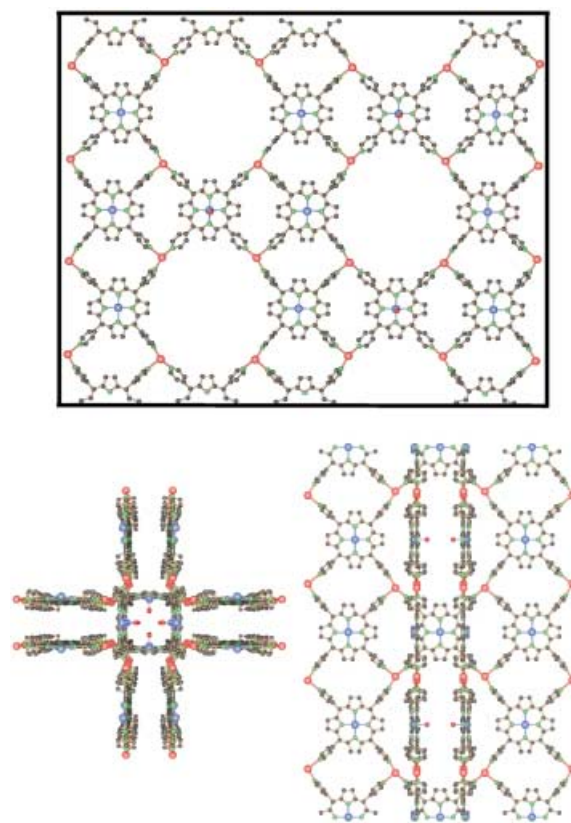
overall resulting network is therefore a unique 3D self-penetrating (or polyknotted) architecture.[15] The coordination geometries of the different metal centers are as follows: within the layers the Ag centers show T-shaped tricoordinate geometry as in **1** (Ag$-$N 2.161(9),2.195(9), 2.389(10) Å; N-Ag-N 98.5(3), 101.7(3), 157.2(3)°), while all the Zn centers are five-coordinate square pyramidal (2/3 with axial pyridyl groups, Zn$-$N 2.134(8) Å, and 1/3 with axial water molecules, Zn$-$O 2.098(16) Å); the Zn centers in the remaining Zntpyp "bridging" groups show the less-usual square-planar coordination geometry.[16] The network contains large free volumes that are populated by many disordered solvent molecules and one half of the nitrate anions. The remaining NO$_3^-$ ions are anchored to the framework and show weak interactions (2.751(11) Å) with pairs of silver centers (Figure 3). As illustrated in Figure 3, there are channels running along the *c* axis with square and rectangular cross-sections (with inter-wall distances of about 9.2 × 9.2 Å and 7.3 × 18.5 Å, respectively). The major voids, however, are enclosed within the large chambers delimited by the "horizontal" metalloporphyrin groups (ca. 20.5 × 20.5 × 14.5 Å; Figure 5). The overall free voids are 55 % of the cell volume. These are full of a mixture of solvent molecules that have been identified (by IR and NMR methods) to be TCE, DMA, and water. The composition is rather variable, as also evidenced by elemental analyses. NMR analyses of suspensions of **3** in CDCl$_3$ after one day revealed relative molar ratios of TCE:DMA:H$_2$O of

crystallinity. Thus, the network of **3** is maintained along the process, as confirmed by comparing the XRPD patterns with the calculated one.[17]

Experimental Section

1 and **2**: These two species were obtained as a mixture; attempts to get pure samples of **1** and/or **2** were unsuccessful. Pure 3-chloroaniline (2 mL) was layered onto a solution of H_2tpyp dissolved in a 3:1 mixture of TCE:MeOH (5 mL, 5×10^{-3} M) and then $AgNO_3$ dissolved in DMA (3 mL, 3×10^{-2} M) was layered on top. The mixture was left at room temperature for several days. The formation of a silver mirror with crystals of **1** and **2** on the walls and on the bottom of the vessel was noted. The crystals were recovered by filtration, washed with a mixture of TCE:DMA (1:1), and dried in the air (yield: 5–6 mg). ^{1}H NMR (17.4 mg, 1 mL CD_2Cl_2, at RT for 4 h): $\delta = 7.09$ (1 H, t), 6.71 (1 H, d), 6.70 (1 H, s), 6.58 ppm (1 H, d) for 3-chloroaniline; 6.07 ppm (2 H, s) for TCE; 3.01 (3 H, s), 2.91 (3 H, s), 2.05 ppm (3 H, s) for DMA; 1.3 ppm (2 H, br s) for H_2O. The relative ratio for these solvents was 1:2.17:1.61:2.42. The elemental analyses were rather variable, depending on the composition of the mixtures. Thermal gravimetric analyses (nitrogen, 10 °C min^{-1}) showed a continuous weight loss in the range 40–400 °C (overall ca. 30 %) attributed to the removal of the guest solvents. A weight loss of about 21 % was then observed in the range 450–630 °C which can be attributed to the dissociation of the pyridyl groups. IR spectroscopy on a single crystal of **1**: $\tilde{\nu} = 3332, 3076, 2976, 1605, 1483, 1363, 1219, 1070, 976, 787, 674$ cm^{-1}.

3: Pure DMA (1.5 mL) was layered onto a solution of ZnTpyP dissolved in a 3:1 mixture of TCE:MeOH (5 mL, 1.5×10^{-3} M) and a solution of $AgNO_3$ dissolved in DMA (3.2 mL, 7.26×10^{-3} M) then layered on top. The mixture was left at -20 °C, and after five days crystals of **3** that were suitable for the diffraction analyses were grown. Compound **3** was prepared in bulk by adding a solution of $AgNO_3$ (51.8 mg; 0.305 mmol) dissolved in DMA (28 mL) to a solution of ZnTpyP (42 mg, 0.0616 mmol) dissolved in a mixture of TCE:MeOH (3:1, 30 mL). After stirring the reaction mixture for 1 h at 0 °C a polycrystalline violet powder was formed, which was recovered by filtration through a teflon membrane, washed with a mixture of TCE:DMA (1:1) and dried in the air (yield: ca. 97 %). The XRPD analysis performed on this sample confirmed the pure nature of the powder as **3**. The ^{1}H NMR experiment was performed on 15.8 mg of **3** (the purity was checked by XRPD analysis) isolated from the reaction mixture, dried in the air with the use of adsorbent paper, and suspended in $CDCl_3$ (1 mL). The spectra were acquired after leaving the sample at room temperature for one day and showed signals at $\delta = 5.96$ ppm (2 H, s) attributed to TCE; 3.01 (3 H, s), 2.95 (3 H, s), 2.09 ppm (3 H, s) attributed to DMA; and at 1.73 ppm (2 H, s) attributed to H_2O. The absolute amounts of solvents have been calculated by the addition of naphthalene as an internal standard. Elemental analysis calcd (%) for $C_{372}H_{375.5}Ag_8Cl_{44}N_{81.5}O_{55.5}Zn_7$: C 45.86, H 3.86, N 11.72; found: C 46.82, H 3.64, N 10.64. thermal gravimetric analyses (nitrogen, 10 °C min^{-1}) were carried out on freshly prepared crystalline or polycrystalline samples. UV/Vis (solid): $\lambda_{max} = 392, 561, 607$ nm. IR (KBr pellets): $\tilde{\nu} = 1596, 1383, 1205, 1071, 923, 789, 671$ cm^{-1}.

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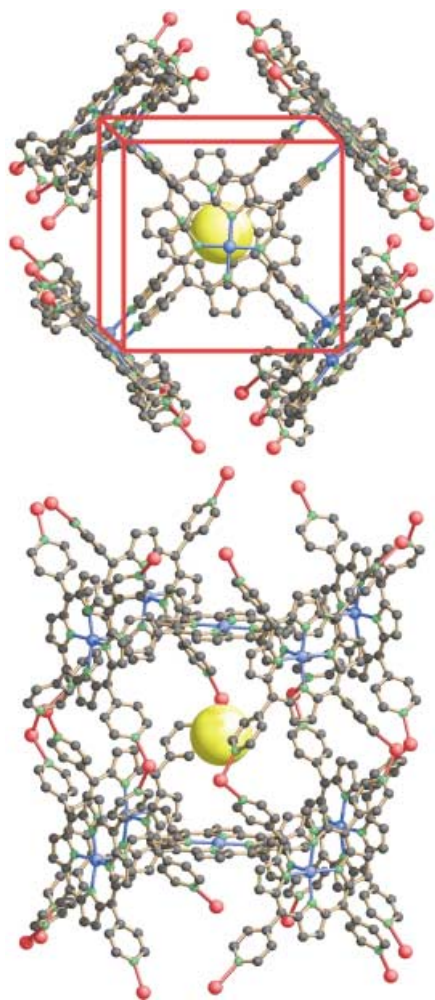

Figure 5. Two views of a large chamber between two Zn-porphyrin units perpendicular to the tetragonal axis. The central sphere (4 Å diameter) indicates the baricenter. The top view also shows an enclosed cube (having eight Zn corners) with edges of about 14 Å.

approximately 1:1.6:1.3. Compound **3** can be formulated as $[Ag_8(Zntpyp)_7(H_2O)_2](NO_3)_8 \cdot 11\,TCE \cdot 17.5\,DMA \cdot 12\,H_2O$, which is in agreement also with the residual volumes and electron densities obtained from the SQUEEZE-Bypass refinements.[12]

Thermal gravimetric (TG) analyses reveal an almost continuous loss of solvents in the range 40–400 °C; three overlapping steps are evident which can be attributed to the sequential loss of water, TCE, and DMA. The total solvent weight loss is about 35 % (calculated: 36.7 %). No further weight loss could be observed upon heating up to approximately 500 °C and, at this point, the compound starts to decompose, probably by dissociation of the pyridyl groups. Slow heating of samples of **3** in an oven up to 130 °C shows that the weight loss (solvent removal) is accompanied by a progressive loss of crystallinity (monitored by X-ray powder diffraction (XRPD)). Successive immersion of these depleted samples overnight in a solution having the same composition as the reaction mixture reveals that the process is reversible and that the solvent uptake is accompanied by a recovery of

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[12] Crystal data for **1**, C₁₂₀H₇₈Ag₄N₂₈O₁₂·x solv: orthorhombic, space group *Fmmm* (no. 69), $a = 28.770(13)$, $b = 29.035(13)$, $c = 56.46(3)$ Å, $V = 47130(37)$ Å³, $Z = 8$, final $R1$ value 0.1836 (0.0548 after SQUEEZE, see below) for 3972 independent reflections $[I > 2\sigma(I)]$. Crystal data for **2**, C₄₀H₂₆Ag₂N₁₀O₁₀·x solv: orthorhombic, space group *Pbcm* (no. 57), $a = 19.861(7)$, $b = 8.077(3)$, $c = 38.220(13)$ Å, $V = 6131(4)$ Å³, $Z = 8$, final $R1$ value 0.1455 (0.0870 after SQUEEZE, see below) for 1426 independ-

ent reflections $[I > 2\sigma(I)]$. Crystal data for **3**, C₂₈₀H₁₇₂Ag₈N₆₃O₂₆Zn₇·x solv: tetragonal, space group *I4/mcm* (no. 140), $a = b = 39.169(2)$, $c = 28.991(2)$ Å, $V = 44478(4)$ Å³, $Z = 4$, final $R1$ value 0.1577 (0.0774 after SQUEEZE, see below) for 3021 independent reflections $[I > 2\sigma(I)]$. The data collections were performed at room temperature on a Bruker SMART CCD area-detector diffractometer, using Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), by the ω-scan method, within the limits $1 < \theta < 23°$ for **1**, $1 < \theta < 22°$ for **2**, and $1 < \theta < 23°$ for **3**. Empirical absorption corrections (SADABS) were applied. The structures were solved by direct methods (SIR97) and refined by full-matrix least-squares on F^2 (SHELX-97). Anisotropic thermal factors were assigned to all the non-hydrogen atoms in **1** and **3** and to the silver atoms only in **2**. The solvent-accessible volume was assessed in these structures using the PLATON software (A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34) and the contribution of the disordered solvent (located in the voids of the interporphyrin channel of the lattice) to the diffraction pattern is subtracted from the observed data by the "Squeeze" method as implemented in PLATON (P. Van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194: The SQUEEZE-Bypass method referred therein is widely used in crystallographic analysis of compounds containing substantial amounts of disordered solvent that cannot be located precisely from diffraction data.) All the diagrams were generated using the SCHAKAL 97 program. CCDC-194964–194967 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[16] Long axial interactions with disordered solvent molecules cannot be excluded; indeed we observed small residual electron densities in the axial direction at about 2.75 Å which are difficult to rationalize and to refine.

[17] Preliminary results of an investigation on the possibility of exchanging the nitrate anions seem encouraging. A polycrystalline sample of **3** suspended overnight in an aqueous solution of (NEt₄)PF₆, recovered by filtration, washed several times with water, and dried in the air, showed IR signals typical of the PF₆⁻ ions. However, further studies are needed to establish the exact nature of the process and the fraction of exchanged anions. Indeed, the exchange may occur by a crystal-to-crystal solvent-mediated process as recently described in: A. N. Khlobystov, N. R. Champness, C. J. Roberts, S. J. B. Tendler, C. Thompson, M. Schröder, *Cryst. Eng. Comm.* **2002**, *4*, 426.