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Coordination-Driven Self-Assembly: Solids with Bidirectional Porosity

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Coordination driven self-assembly reactions have been used in the preparation of a variety of discrete supramolecular species featuring transition metals bridged by organic ligands,[1] some of which have shown promise as synthetic receptors.[2] Likewise, many highly ordered coordination polymers[3] and porous networks[4] have also been prepared by simple self-assembly reactions. While a few of these solids are capable of the uptake of small organic molecules in the resultant molecular channels, the formation of truly porous structures has frequently been thwarted by lattice interpenetration, thereby precluding their potential utility. A strategy for the formation of porous solids that may circumvent this problem is based on the covalent construction of nanoscale macrocycles,[5] which are subsequently allowed to crystallize. In these systems, the possibility of interpenetration is prevented, and tubular assemblies are achieved by simply eclipsing the macrocyclic building blocks.

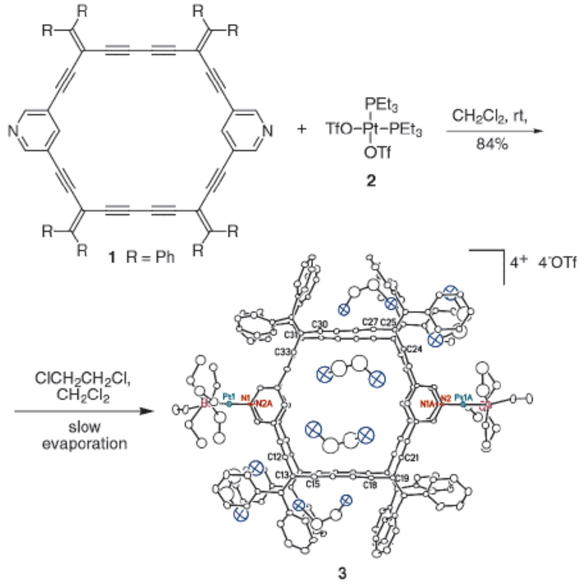
Our strategy toward the realization of multidimensional, porous networks incorporates both of these concepts. Conjugated macrocycle **1** contains two pyridine moieties that direct its participation in self-assembly reactions.[6] In this report, we show that, in the presence of the metal species, **2**, macrocycle **1** self-assembles in solution to provide a discrete supramolecular species, which subsequently crystallizes to give a solid with bidirectional porosity.

A solution of macrocycle **1**[6] (CH_2Cl_2) was added portion-wise to *cis*-$(TfO)_2Pt(PEt_3)_2$[7] in CH_2Cl_2 over a period of 2 days.[8] Slow evaporation of the solvent yielded assembly **3** as bright orange crystals (Scheme 1). This material is thermally very stable, decomposing only at temperatures greater than 245 °C.

Single crystals for X-ray analysis[9] were grown by slow evaporation from a solution of **3** in $CH_2Cl_2/ClCH_2CH_2Cl$. The representation of assembly **3** in Figure 1 shows how the remarkably flexible building block **1** has adopted a boatlike conformation, presumably to reduce steric interactions between the pendant diphenyl vinylidene groups and adjacent ligands. The macrocycle is relatively free from strain as reflected in the alkyne bond angles, which depart from the ideal value of 180° by a maximum of 7.7°, with a mean deviation of 4.8°. Furthermore, the vinylidene bond angles are comparable to those of similar acyclic systems.[10] The N−Pt−N bond angle of 83.3° is also consistent with that observed in unstrained molecular squares constructed from bipyridine and related *cis*-Pt complexes (see Scheme 1 for atom numbering).[11]

The six dihedral angles of the boatlike conformation of the macrocycle approximate the degree of distortion of the macrocyclic core. Using dummy atoms generated at the center of the pyridine rings as two centroids (cen) of the hexagon and the alkylidene carbons C(31), C(25), C(19), and C(13), the following dihedral angles are obtained: (1) 23.7° [(cen1)−C(31)−C(25)−(cen2)], (2) 49.5° [C(31)−C(25)−(cen2)−C(19)], (3) 34.9° [C(25)−(cen2)−C(19)−C(13)], (4) 8.8° [(cen2)−C(19)−C(13)−(cen1)], (5) 30.3° [C(19)−C(13)−(cen1)−C(31)], and (6) 14.2° [C(13)−(cen1)−C(31)−C(25)].[12]

Scheme 1



The solid-state structure of **3** possesses two sets of perpendicular channels that result from the combined attributes of the macrocyclic building block and the supramolecular assembly. When viewed along the *c*-axis (Figure 2, bottom), the channels resulting from the boatlike conformation of the macrocycle are clearly evident. This cavity is 7.5 Å across by 16.3 Å (Pt−Pt). When viewed along the *a*-axis (Figure 2, top), stacking of the macrocyclic portion of the assembly provides a second set of perpendicular channels, with smaller internal dimensions as circumscribed by the enyne scaffold of the macrocycle at 6.6 by 9.7 Å. Noteworthy is the selective uptake of $ClCH_2CH_2Cl$ from the solvent mixture into the crystal lattice; the unit cell of **3** incorporates a total of eight solvent molecules. Two molecules are located within the channel defined by the conjugated macrocyclic core, as viewed down the *a*-axis (Scheme 1). These two molecules also occupy space in the perpendicular channel circumscribed by the supramolecular assembly. Four additional solvent molecules are also present in this channel, for a total of six when viewed along the *c*-axis (four of which are shown in Figure 1). Two of the associated triflate ions are also present in this channel (not shown). The remaining two solvent molecules and two triflate ions occupy positions peripheral to the assembly. Overall, there is a significant proportion of void

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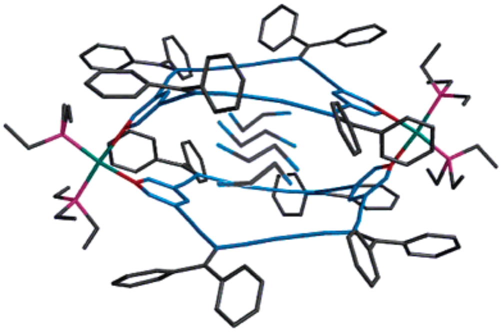

Figure 1. Representation of complex **3** highlighting the boat conformation of ligand **1** (shown in blue). Triflate anions and four of eight solvent molecules are omitted for clarity.

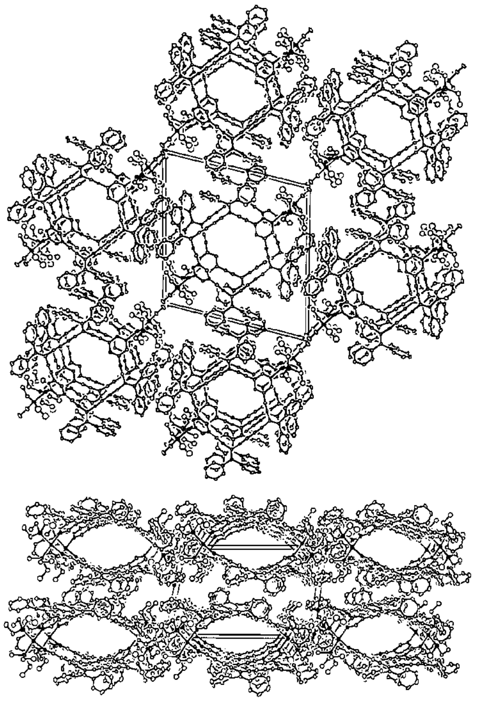

Figure 2. Crystal packing of supramolecular assembly **3**. (Top) View down the crystallographic *a*-axis. (Bottom) Side view down the *c*-axis (triflate anions and solvent molecules removed for clarity).

space in the structure, calculated at 13%, when the cocrystallized solvent is excluded.

Evidence for the presence of the assembly **3** in solution comes from NMR spectroscopic analysis. The ^{1}H NMR spectrum of **1** shows signals of the ortho and para pyridyl protons as a doublet and triplet at δ 8.13 and 7.83, respectively. These same resonances appear as a second-order multiplet at δ 8.42 and a triplet at δ 7.95, respectively, in the ^{1}H NMR spectrum of complex **3**. ^{1}H- and ^{31}P NMR decoupling experiments establish that the splitting pattern for the ortho protons of **3** is due to long-range coupling to the two phosphorus atoms (which are not magnetically equivalent) and confirm the association of **1** to the platinum center in solution.[8] The ^{31}P- and ^{19}F NMR spectra each show only a single resonance at -1.3 and -78.2 ppm, respectively. The ^{13}C NMR spectrum for **3** also suggests the presence of a distinct symmetrical species, with sharp well-resolved resonances observed for all unique carbons.

ESI mass spectral analysis for complex **3** was acquired by slow infusion of a solution of **3** in CH_2Cl_2/CH_3NO_2 and supports the existence of assembly **3** in solution. Specifically, a prominent signal at *m*/*z* 745 (24%) is assigned to $[M - 4^-OTf]^{4+}$. In addition, several mass peaks consistent with the fragmentation of **3** are observed.[8]

In conclusion, we have demonstrated the value of utilizing both the covalent and dative bond approach toward the realization of porous materials. The metal-directed, self-assembly of macrocycle **1** provides assembly **3**. X-ray crystallographic analysis establishes that assembly **3** packs such that bidirectional channels are realized, and the incorporation of only $ClCH_2CH_2Cl$ into the crystal lattice demonstrates that these channels are potentially suitable for the selective uptake of small organic guests.

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Supporting Information Available: Synthetic, spectral, ESI MS, and X-ray crystallographic details for complex **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Compound **3** ($C_{192}H_{152}F_{12}N_4O_{12}P_4Pt_2S_4{\cdot}C_{16}H_{32}Cl_{16}$; $M_r = 4369.09$) crystallized in the triclinic space group $P\bar{1}$ with $a = 13.252$ (2) Å, $b = 20.821$ (3) Å, $c = 21.983$ (3) Å; $\alpha = 102.407$ (3)°, $\beta = 102.973$ (3)°, $\gamma = 95.742$ (3)°; $V = 5701.9$ (15) Å^3, $Z = 1$; $R_1 = 0.12$ (15230 reflections with $F_o^2 \geq 2\sigma(F_o^2)$), $wR_2 = 0.36$ for 878 variables and 23153 unique reflections with $F_o^2 \geq -3\sigma(F_o^2)$; $T = -80$ °C; $GOF = 1.299$.

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