Molecular paneling *via* coordination

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This article deals with a coordination approach to three-dimensional assemblies *via* '*molecular paneling*'. Families of planar exo-multidentate organic ligands (molecular panels) are found to assemble into large three-dimensional assemblies through metal-coordination. In particular, *cis*-protected square planar metals, (en)Pd^{2+} or (en)Pt^{2+} (en = ethylenediamine), are shown to be very useful to panel the molecules. Metal-assembled cages, bowls, tubes, capsules, and polyhedra are efficiently constructed by this approach.

Introduction

The last decade has witnessed the syntheses of several complex 3D-molecules that are assembled by linking molecules *via* non-covalent bonds such as coordination and/or hydrogen bonds and has led to the development of a new paradigm denoted *non-covalent synthesis*.[1] This non-covalent synthesis has become a reliable approach to prepare 3D-complex molecules and has been considered as an alternative approach to organic synthesis. Earlier the important examples of metal-directed assembly of 3D structures, for example Saalfrank's M_4L_6 cages and Lehn's cylindrical cages, have been well documented.[2,3] Remarkable progress in the construction of 3D structures *via* metal coordination has been made by the groups of Raymond, Stang, Steels, Robson, Shinkai and others.[4–8] The focus of this article will be on our efforts in the construction of three-dimensional (3D) structures by linking two-dimensional (2D) planar organic components *via* metal-coordination. Before going into the main topic, we would like to brief the basic concept of the present study that prompted us to develop a concept of *molecular paneling* which points to a highly efficient approach for constructing large 3D molecules.

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A basic concept

It was more than a decade ago when we first had the idea to incorporate 90° coordination angles of transition metals into metal–organic frameworks.[9] We paid special attention to the geometry of square-planar metals since non-distorted 90° bond angles can not be afforded by the hybridization of organic elements. To exploit this angle, we designed a *cis*-protected square-planar metal as illustrated in Fig. 1. Accordingly, an

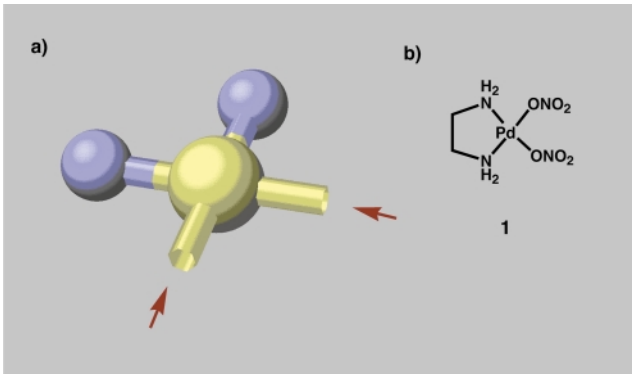


Fig. 1 (a) Cartoon representation of the *cis*-protected Pd(II) building block **1** and (b) structural drawing of **1**.

ethylenediamine-protected Pd(II) complex was prepared and successfully incorporated into a tetranuclear square framework by complexation with one of the simplest bridging ligands: 4,4′-bipyridine (Fig. 2). The design of the *cis*-protected Pd(II) as well as the formation of the square complex **1** cultivated the basic concept of our study which has been carried out over the last decade and can be dictated as follows:

Upon *cis*-protection, the coordination nature of the metal ion changes from divergent to convergent. Owing to the convergent nature, the discrete framework **1** was efficiently generated without formation of any oligomeric products, in striking contrast to the previous coordination chemistry of 4,4′-

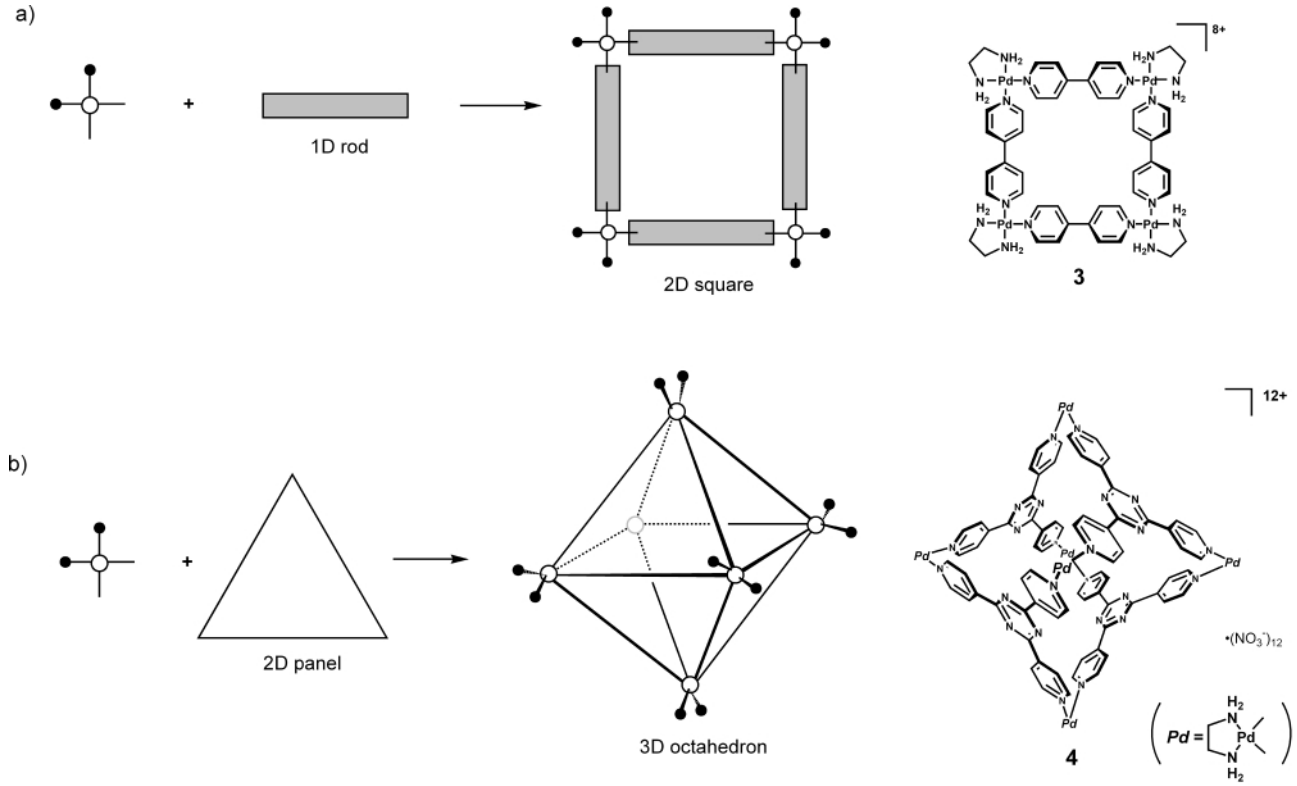
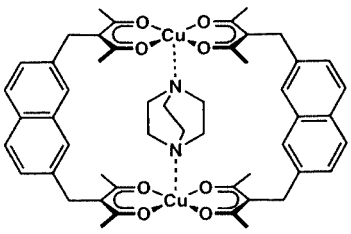


Fig. 2 (a) Schematic representation of molecular paneling: (a) from 1D-rods to 2D-molecules and (b) from 2D-panels to 3D-molecules.

bipyridine where infinite complexes were afforded in most cases.[10] The Pd(II)–pyridine coordination bond is labile and hence the product is formed under thermodynamic control. Thus, under a set of appropriate conditions, the square molecule is spontaneously generated in quantitative yield.

A square molecule in which the transition metal provides a 90° angle at each corner of the square has been recently termed as a 'molecular square' by Stang.[11] The extensive studies by Stang and others stirred considerable current interest in such square molecules. Prior to our study, there have been some important studies on the synthesis of metal-linked macrocycles. One of the excellent examples is the Cu(II)-linked dinuclear complex **2** synthesised by Maverick *et al.*[12]



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From 2D to 3D structures

A 1D molecular rod, 4,4′-bipyridine, upon linking with 90° coordination block **1** was assembled into a 2D square as discussed above. This molecular design was extended to the construction of 3D structures by considering 2D molecular components. Namely, instead of 1D rod, a 2D triangular panel was used as an organic component (Fig. 2). In 1995 this idea was first realized by the synthesis of an octahedral 3D structure **4** (Fig. 2b).[13] This example illustrates that the molecular paneling of a 2D organic component is undoubtedly an efficient method for the construction of large 3D entities. In the following sections, we will show a family of molecular panels that are successfully paneled into various 3D molecules *via* metal coordination. In addition to the coordination approach, 3D molecules are also accessible by hydrogen-bond directed self-assembly. The groups of Rebek[14] and Atwood[15] have demonstrated the efficient self-assembly of capsules through hydrogen bonding. The cavity volumes of these capsules range from 0.3 to 1.7 nm^3.[14,15]

Molecular panels

3D-molecular structures can be well designed by deducing the molecular components from polyhedra. For example, the basic components (polygons) to construct Platonic solids are equilateral triangles, squares and pentagons.[16] The common feature in these solids is that they are made up of regular polygons which are arranged in space such that the edges, vertices and three coordinate directions of each solid are equivalent. Here we have designed several molecular panels with the basic shapes of triangle, square and rectangle (Fig. 3). The assembling of these panels with the 90° *cis*-protected coordination block **1** can be considered as a new concept that we term as '*molecular paneling*'.

Paneling triangles

An important aspect of regular polygons is that they enclose space. In particular, four triangles enclose space, without the use of curved surface, and this is the lowest number of polygons which will do so.[16] Thus we first deal with a triangle which is a very basic building block of several polyhedra. For example out of five Platonic solids, three (tetrahedron, octahedron and icosahedron) are originated from equilateral triangles indicating the importance of triangular panels in the construction of polyhedra (Fig. 4). Accordingly we designed triangular molecular panels **5**–**9** to assemble them into several 3D-structures (polyhedra). The differences between these triangular panels is the number (varying from three to six) and position of the binding sites. Molecular panels **5** and **6** contain three binding

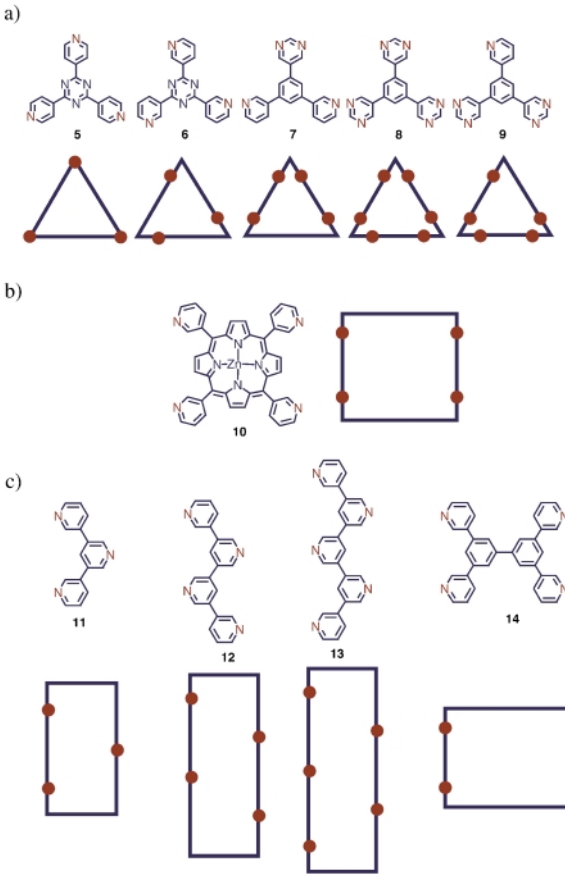


Fig. 3 Structural and cartoon representation of molecular panels: (a) triangular, (b) square and (c) rectangular. The filled circles represent the binding sites.

sites each but the position of the sites differs, whereas molecular panels **7**, **8** and **9** contain four, six and five binding sites each, respectively. The assembled architectures from these molecular panels include octahedra, square pyramids, tetrahedra and hexahedra.

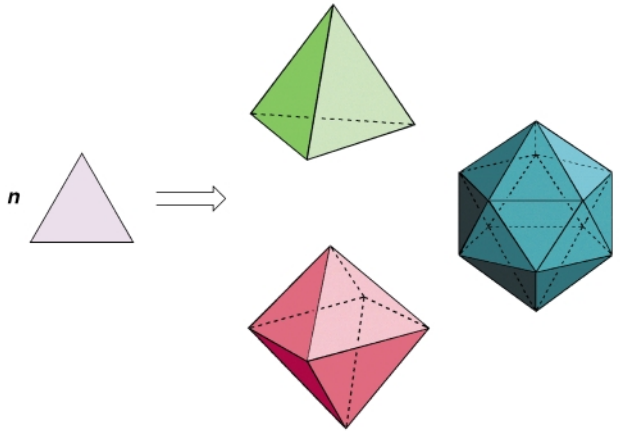


Fig. 4 Schematic representation of assembling of three types of Platonic solids from a triangular unit.

M_6L_4 octahedral cage

As discussed above, the first example of using the molecular panel approach to obtain a 3D discrete structure is an M_6L_4 octahedral assembly **4**, reported in 1995.[13] By treating **1** with **5** in 3:2 ratio, the octahedral complex **4** is assembled in quantitative yield (Fig. 5). In this complex, the four triangular panels are linked together at the corners of the triangles such that every alternate face of the octahedron contains either molecular panel or portal. Complex **4** is a thermodynamically stable product because the formation of the product is not affected by the presence of an excess of **1**. The synthetic procedure is so simple that a 10–50 g scale synthesis can be carried out in a laboratory.

It has been shown that the cage complex **4** effectively binds various organic guest molecules in its cavity. The structure of the clathrate complex of **4** with the adamantane carboxylate ion has been determined by X-ray crystallography (Fig. 5c), which showed that four guest molecules are tightly encapsulated inside the nano-sized cavity of **4**. The inclusion geometry of the guest in the cavity is interesting as the hydrophobic and hydrophilic groups (CO_2^-) are located inside and outside of the cavity, respectively. A space filling presentation of **4** shows that the

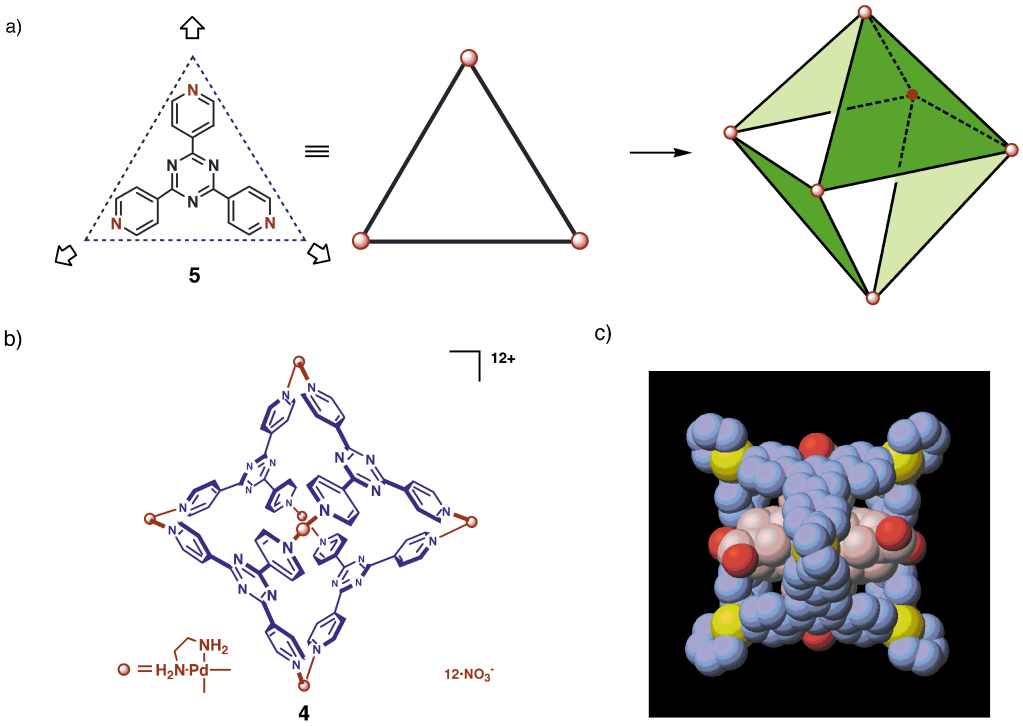


Fig. 5 (a) Schematic representation of molecular paneling of **5** to form **4**, (b) structural drawing of **4** and (c) X-ray structure of **4** with adamantane carboxylates in the cavity.

dimension of the portal of the cage is comparable to that of adamantane, whereas the interior space can hold as many as four guest molecules. The ^{1}H NMR study showed that the same host–guest aggregation was retained even in aqueous media.

A kinetically stable octahedral M_6L_4 cage

The Pd(II) self-assembly described above is a result of thermodynamical equilibration and the product is not stable under extreme conditions (*e.g.* acidic, basic or nucleophilic). In order to prepare a kinetically stable M_6L_4 complex, a Pt(II) analogue of **4**, **15** was used instead of **1**. In contrast to the Pd cage, the formation of Pt cage was quite slow to form in a reasonable yield. However, heating the solution and adding a guest molecule, adamantanecarboxylate, dramatically improved the reaction rate as well as the yield. The host–guest ratio and the guest inclusion geometry were found to be similar to those of Pd structure **4**. Usually, a receptor framework organized by guest induced fit will be lost when the guest is removed. In contrast, the assembled Pt cage did not lose its cage structure even after removal of the guest because of the locking, irreversible nature of Pt(II)–pyridine bond. As anticipated, the Pt(II) complex was very stable and did not decompose even in the presence of an acid (HNO_3), a base (K_2CO_3) or a nucleophile (NEt_3) owing to the inertness of a Pt(II)–pyridine coordinate bond.[17]

M_6L_4 square-pyramidal cone

The triangular molecular panel **6** was used to assemble a bowl-like M_6L_4 square-pyramidal cone. Although **6** has a similar structure as **5**, due to the different placement of N-atoms in the ligand this component formed a square-pyramidal cone **16** upon treatment with **1** (Fig. 6).[18a] The structure of **16** was characterized in solution by ^{1}H NMR spectroscopy and in the solid state by X-ray crystallography. The framework is held together by 10 molecular components (six metal ions and four ligands) having nanometer dimensions (*ca.* 3 × 2 × 2 nm) in spite of the small size of the molecular components.

In aqueous media the square-pyramidal cone **16** is expected to assemble into a dimeric capsule that contains a large hydrophobic pocket inside the framework because of its amphiphilic properties: hydrophobic inside and hydrophilic outside. In fact, such a dimeric structure does assemble in the solid state. That is, X-ray structures have been obtained for host–guest complexes with large guest molecules, all of which showed the dimeric capsule structure of the host accommodating as many as six neutral organic molecules.[18b] The solid structure of the complex with *o*-terphenyl (Fig. 7a) is recognized as a dimer of 1:2 host–guest complexes because the whole structure can be divided into two identical 1:2 complexes. On the other hand, the solid structure of the complex with *m*-terphenyl (Fig. 7b) can not be divided into two halves and thus the whole structure is regarded as a 2:4 complex rather than a dimer of 1:2 complex. With *cis*-stilbene, 1:6 complexation has been confirmed by X-ray analysis.

Dynamic assembly of an M_8L_4 cone and tetrahedron

Whilst molecular panels **5** and **6** contain C_3-symmetry, molecular panel **7** has C_2-symmetry, and therefore is expected to link in two different ways upon treatment with **1**: parallel and antiparallel fashions. Linking in parallel fashion is expected to generate the square-pyramidal cone **17** whereas linking in antiparallel fashion is expected to generate a closed tetrahedron **18** (Fig. 8). Interestingly, these two routes are found to be controlled effectively by the guest molecules.[19] Larger guest molecules such as dibenzoyl templated formation of the square-pyramidal cone **17** while small tetrahedral guests like CBr_4 templated formation of the closed tetrahedron **18**. Ligand **7** and dibenzoyl were suspended in aqueous solution of **1** and stirred for 24 h. The ^{1}H NMR spectra and ESI-MS of this solution revealed the formation of **17** which accommodated one molecule of dibenzoyl. In the ESI-MS, major peaks corresponding to $\{[\mathbf{17}(\text{dibenzoyl})_m\cdot(NO_3)_{16-n}]^{n+}$ (m = 0–2, n = 3, 4)$\}$ were observed suggesting the formation of a cone structure. In ^{1}H NMR spectra eight signals appeared corresponding to the C_2-symmetric environment of **7**. The signals of dibenzoyl were substantially upfield shifted suggesting its inclusion in the cone-shaped cavity. Other bulky guest molecules such as 1,2-dibenzoyl, ethane-1,2-diol and 1,1′-ferrocenedicarboxylic acid were also found to template the same square pyramidal cone **17**.

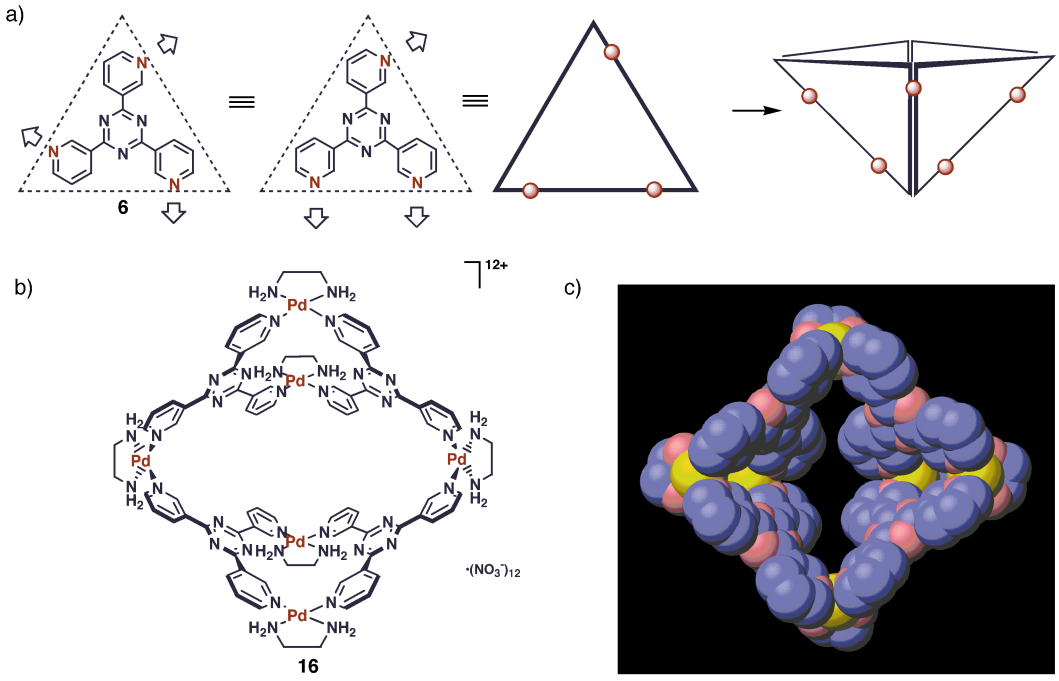


Fig. 6 (a) Schematic representation of molecular paneling of **6** to form **16**, (b) structural drawing of **16** and (c) space-filling representation of **16** exhibited in its crystal structure.

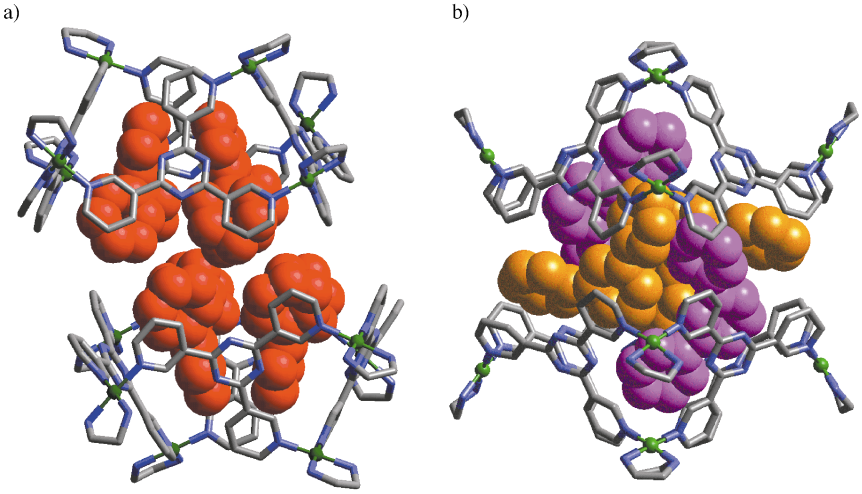


Fig. 7 Dimeric capsules of **16** accommodating (a) *o*-terphenyl and (b) *m*-terphenyl exhibited in their crystal structures.

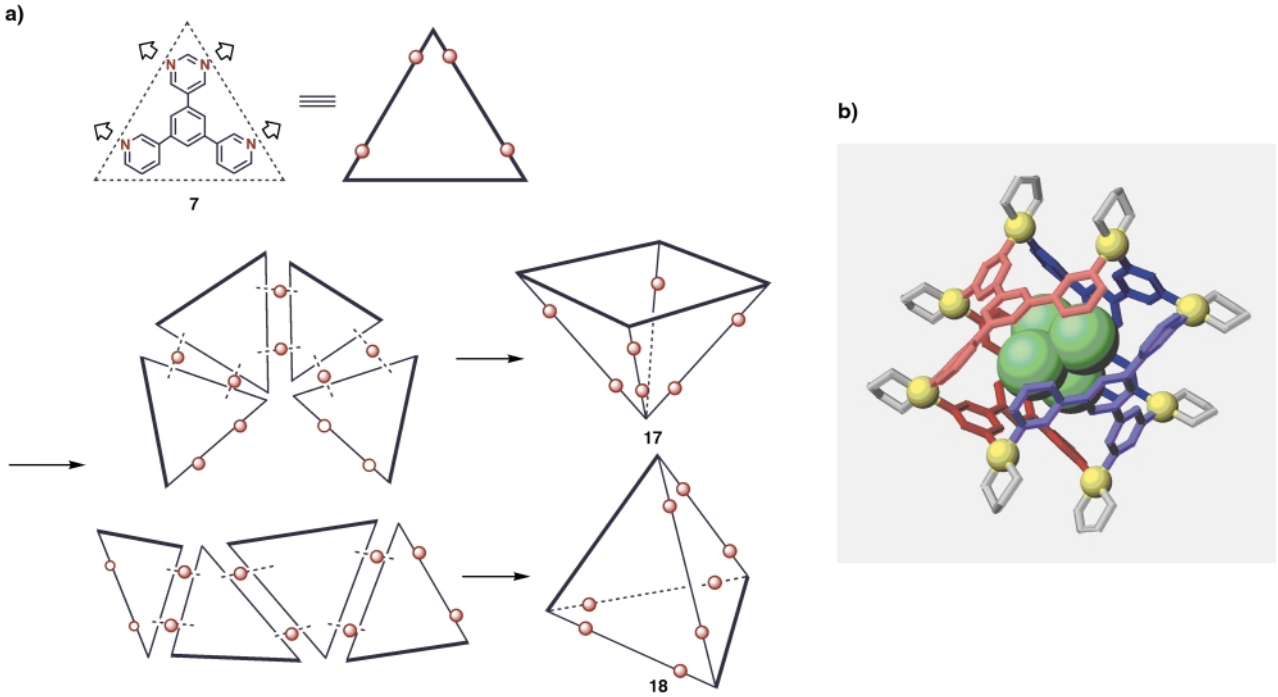


Fig. 8 (a) Schematic representation of molecular paneling of **7** to form **17** and **18** and (b) X-ray structure of the tetrahedron **18** (cylinder mode) with CBr_4 (space filling) in its cavity.

The closed tetrahedron structure **18** resulted when **1** and **7** were allowed to react in the presence of CBr_4 in D_2O. The antiparallel linking of the ligands was strongly supported by the observation of NOE between adjacent ligands. The complex was precipitated in 93% yield after adding an excess of EtOH and an elemental analysis supported a 1:1 host–guest ratio. Similarly $CHCl_3$ and $CBrCl_3$ were also found to template a similar type of structure. Further the assigned structure was supported by the single-crystal X-ray structure which showed the complete entrapment of CBr_4 in its closed tetrahedral cavity (Fig. 8b).

In the absence of guest molecules at 25 mM concentration, **1** and **7** were found to assemble into a 3:2 mixture of two products. According to ^{1}H NMR spectroscopy the minor product was identified as square-pyramidal cone **17** whereas an increase in the percentage of the major product was observed when the reaction was conducted at lower concentrations. This fact indicates that the major component could be a trimeric open-cone structure assembled from a lower number of molecular components than the tetrameric cone. These assembled trimeric and tetrameric cones and tetrahedron were found to reorganize from one structure to the other by the guest addition/exchange.

$M_{18}L_6$ hexahedron

Following the exotridentate ligands **5** and **6**, an exohexadentate ligand, 1,3,5-tris(3,5-pyrimidyl)benzene **8** was also designed as a triangular unit. As already discussed, the triangle is a basic unit for the self-assembly of polyhedra. Ligand **8** is an almost coplanar triangle and is expected to give an edge-sharing polyhedron when it is self-assembled with **1**. When ligand **8** is treated with **1** in D_2O, the predominant formation of a single component was observed, the ^{1}H NMR spectrum of which showed seven singlet-like signals in an integral ratio of 2:2:2:2:2:1:1. Of several possibilities, the assembly of the molecular hexahedron **19** was strongly suggested by ^{1}H NMR spectroscopy (Fig. 9).[20] This observation confirms that, after complexation, ligand **8** is placed in a less-symmetrical environment with one symmetry axis passing through a 3,5-pyramidyl (pym) ring and a core benzene ring. This symmetry is in good agreement with the trigonal-bipyramidyl structure of the

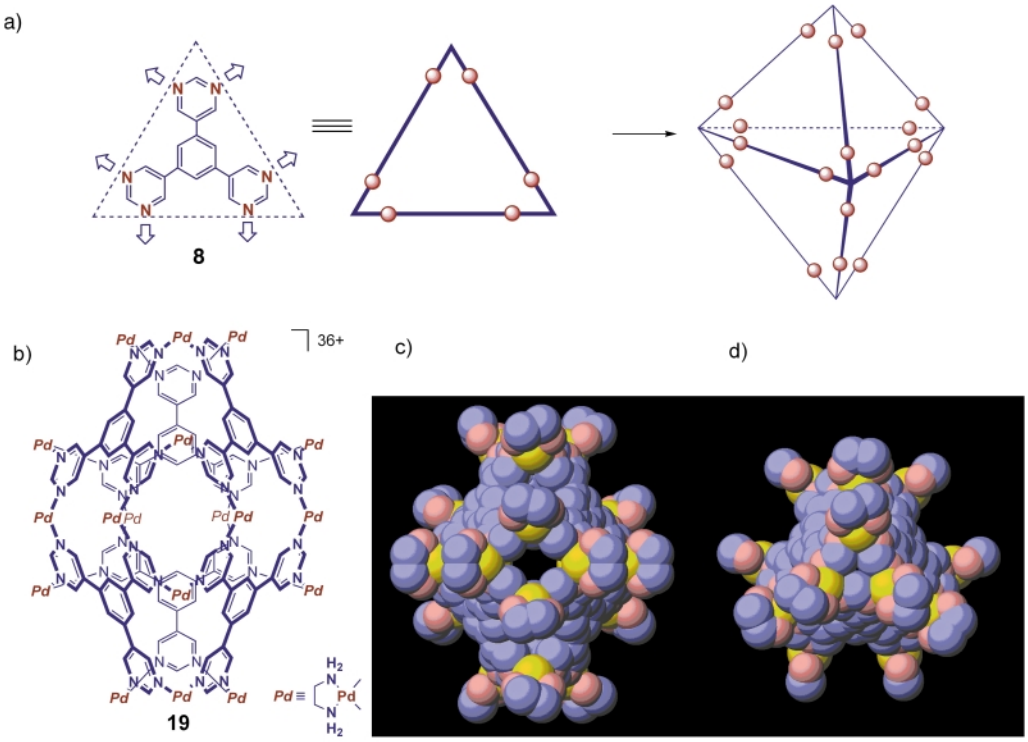


Fig. 9 Schematic representation of molecular paneling of **8** to form hexahedron **19**, (b) structural drawing of **19** and space filling representation of the X-ray structure of **19**: (c) equatorial and (d) apical views.

molecular hexahedron **19** in which the pym groups at the apical corners are not equivalent to those at equatorial corners. The metal-linked dimer and trimer of **8**, which are the possible intermediates for assembly process of **19**, were observed when ligand **8** was treated with **1** in D_2O in 1:1 and 3:4 ratios, respectively.

Reliable evidence for the hexahedron structure of **19** was provided by X-ray crystallography (Fig. 9c and d). The crystal structure clearly demonstrates that the assembly is a trigonal-bipyramidal capsule with a chemical formula of $C_{144}H_{216}N_{108}Pd_{18}$, a molecular mass of 7103 Da, and dimensions of 3 × 2.5 × 2.5 nm. Each equatorial corner of the hexahedron is the assembly of four triangle units, where [Pd(II)–pym]$_4$ leads to a small pinhole (2 × 2 Å). Only small molecules such as water and molecular oxygen may pass through these holes, whereas, ordinary organic molecules cannot enter or escape. The free volume inside the capsule, into which guests can be accommodated, is *ca.* 900 Å^3.

$M_{15}L_6$ hexahedron: reversible guest inclusion

As described above hexahedron **19** is a very closed and rigid structure making it difficult to encapsulate/exchange guest molecules. To prepare a hexahedron that has more flexibility to encapsulate/exchange guest molecules we designed another molecular panel **9**, which is similar to **8**, but has one binding site less than **8**. We found that the treatment of **9** with **1** in D_2O affords hexahedron **20** (Fig. 10). Interestingly as anticipated molecules of **20** can exchange the encapsulated encapsulates and small guest molecules.[21]

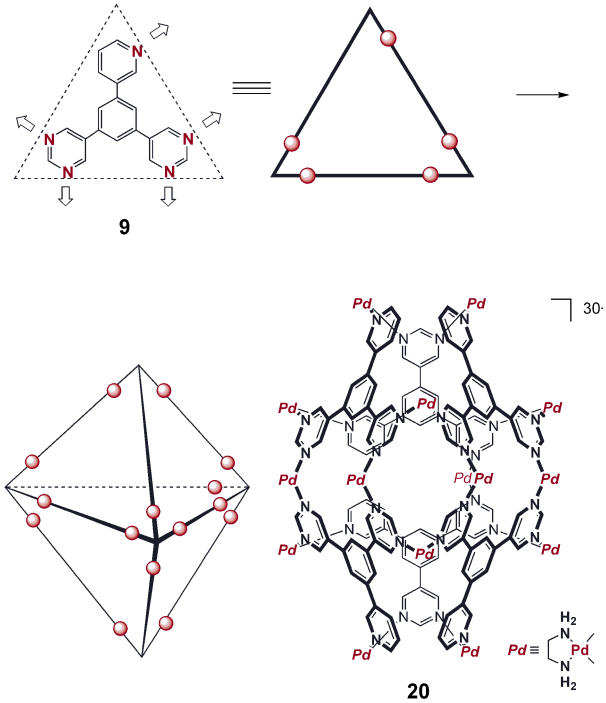


Fig. 10 Molecular paneling of **9** to form **20**.

Some functions of M_6L_4 octahedral cages

Cage compounds prepared by conventional covalent synthesis usually contain small cavities and can encapsulate only one or two small molecules. The *molecular paneling* approach gives us an opportunity to construct larger frameworks containing relatively large cavities. For example, the octahedral cage compound **4** has a very large cavity with a diameter of 1 nm and exhibited a remarkable ability to encapsulate large and neutral molecules. In the following sections we describe its abilities in molecular recognition, catalysis and condensation of trialkoxysilanes.

Molecular recognition

It has been already described that M_6L_4 can bind four molecules of aqueous guest such as adamantanecarboxylate. Further, it efficiently encapsulates neutral and spherical guest molecules such as adamantane, 1- and 2-adamantanol, *o*-carborane, and aromatic compounds such as 1,3,5-trimethoxybenzene, anisole and toluene in the cavity.[22] Interestingly, adamantane was found to transfer into the aqueous phase even in a solid–liquid

two-phase system. The very efficient guest binding by **4** can be ascribed to the amphiphilic nature of the cage: *i.e.* the inside of **4** is surrounded by 16 aromatic rings and thus hydrophobic, whereas the outside surface of the cage is hydrophilic due to the exposure of six charged Pd(II) centers.

Notably, complexation is faster with smaller guest molecules and slower with larger guest molecules. For example 1,3,5-tri-*tert*-butylbenzene which is slightly larger than the portal of **4**, was encapsulated very slowly. Tetrabenzylsilane required a few hours to be completely encapsulated by **4′** which is the 2,2′-bipyridine protected analogue of **4**. Crystallographic analysis showed a good fit for the tetrahedral symmetry of the guest in the octahedral cage (Fig. 11).[23]

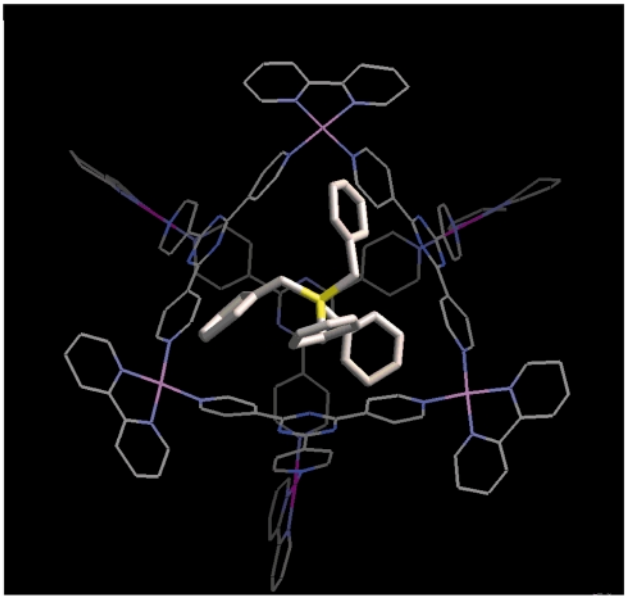


Fig. 11 X-Ray crystallographic structure of **4′** (stick mode) enclathrating tetrabenzylsilane (cylinder mode).

Compound **4** also exhibited a remarkable ability to encapsulate C-shaped molecules such as *cis*-azobenzene **21** and *cis*-stilbene **22**, derivatives.[24] These guest molecules are enclathrated in the cavity *via* the formation of a hydrophobic dimer with a topology reminiscent of a hydrogen-bonded tennis ball (Fig. 12a).[24] The formation of a hydrophobic dimer was

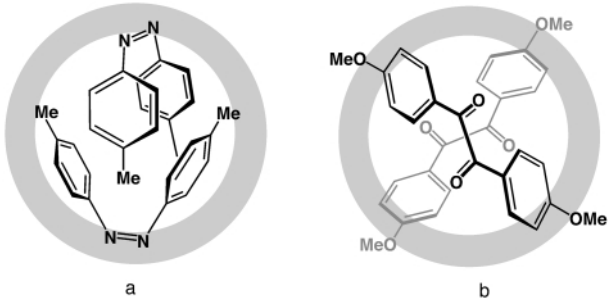


Fig. 12 Schematic drawing of formation of a hydrophobic dimer of (a) *cis*-stilbene and (b) 4,4′-dimethoxydibenzoyl within the cavity of **4** (shown as circle).

suggested by NOE and also by molecular dynamic simulation. Further the selective enclathration of only the *cis* isomer was observed when *cis–trans* mixtures of either **21** or **22** in hexane were stirred in a D_2O solution of **4**. The NMR spectra confirm the encapsulation of dimers of *cis*-isomers in the cavity. Notably, the *cis* isomer of **21** was significantly stabilized in the cavity and not isomerised to the *trans* isomer even after allowing the solution to stand for a few weeks under visible light at room temperature. Molecular modeling calculations suggest that the hydrophobic dimers are a perfect fit for cavity of **4**. Dimerization of the guests prior to enclathration is unlikely because the dimension of the spherical dimer (*ca.* 11 Å in diameter) is larger than that of the portals of **4** (*ca.* 7 Å diameter). Therefore, two guest molecules can subsequently, but not simultaneously, be enclathrated in the cavity leading *in situ* into the stable hydrophobic dimer.

A similar dimer formation was observed when 1,2-diketone **23** was employed as a guest (Fig. 12b). In the 1:2 complex, dissymmetrization of the host structure was observed by NMR spectroscopy: that is, before addition of guest the four ligands in host are equivalent, but after addition of guest, 12 protons on each ligand were observed independently. This observation was clearly revealed by X-ray crystallographic analysis. As shown in Fig. 13, two guest molecules are assembled in a similar way

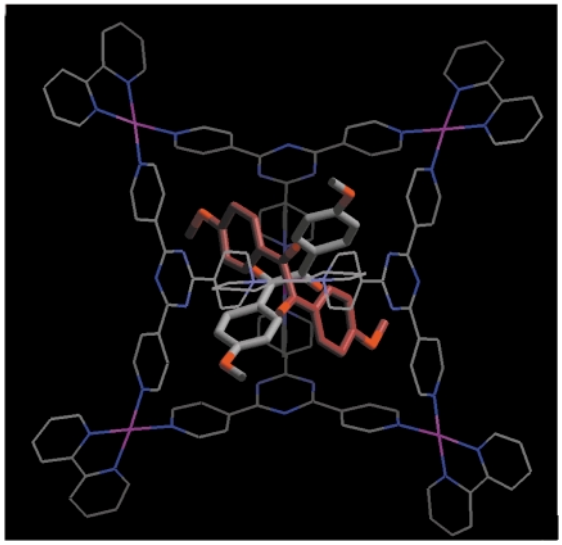
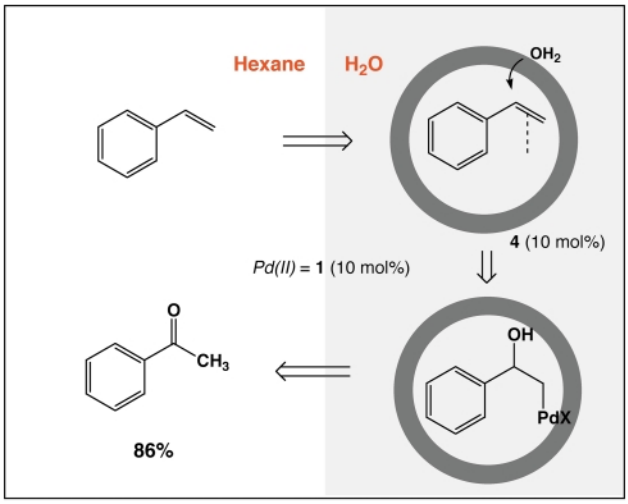


Fig. 13 X-Ray crystallographic structure of **4′** (stick mode) enclathrating the hydrophobic dimer of 4,4′-dimethoxydibenzoyl (cylinder mode).

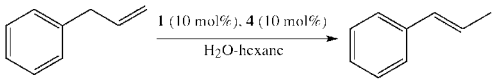
to that of **21** and **22**. However, each guest adapts a twisted conformation: one is *P*-form and another is *M*-form. As a consequence, the formed dimer has a *meso* configuration with no centrosymmetry making all protons on each ligand inequivalent.[22]

Catalysis in the cavity of M_6L_4 cage

Reactivity and catalysis represent one of the most important features of the functional properties of self-assembled molecular systems.[25] The existence of a large cavity in **4** motivated us to test its ability to catalyze the oxidation of styrene and isomerization of allylbenzene.[26] When **1** and **5** were mixed in D_2O in 2:1 ratio, formation of only **4** was observed and excess of **1** remained in the solution. Our strategy was to use the remaining amount of **1** as a mediator between organic and aqueous phases: that is to use **1** to transfer the substrate, cyclically and continuously, into a aqueous phase that contains **4** and then the formed product into the organic phase (Scheme 1). It was observed that **4** can accommodate nearly three molecules of styrene in its cavity. The oxidation of styrene at 80 °C in an aqueous solution of either **1** or **4** gave acetophenone only in 4% yield. Importantly, the presence of both **1** and **4** in an aqueous solution increased the yield of the reaction up to 86%. Similarly, the isomerization of allylbenzenes catalyzed by the presence of **1** and **4** in aqueous solution gave β-methylstyrene in 50% yield, whereas the reaction did not occur in the absence of either **1** or **4** (Scheme 2). The presence of trimethoxybenzene in the reaction media inhibited these reactions because the cavity of **4** was strongly occupied by this molecule. The yields of these reactions reveal that as the size and electron deficiency of the substrate increases the yield of the reaction decreases. These are



Scheme 1 Schematic representation of reversed phase-transfer catalysis of **4**. Wacker oxidation is promoted by a slight excess of **1**.

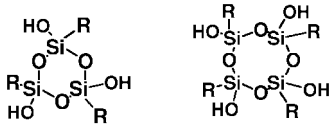


Scheme 2 Olefin isomerization in an aqueous phase with the aid of **1** (10 mol%) and **4** (10 mol%).

good examples of organic reactions in solutions but in the absence of organic solvents.

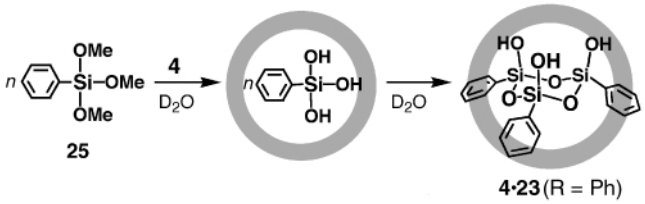
Condensation of trialkoxysilanes

Isolated cavities in molecular capsules are well known to stabilize labile molecules formed *in situ* by the reaction of smaller molecular components.[27] These components, being smaller in size, can enter into the cavity through the portals and react with each other to form a larger molecule that can not leave the cavity since it is larger than the portal. By using the same principles here we studied the condensation reaction of trialkoxysilanes in the cavity of an M_6L_4 cage.[28] Cyclic oligomers of silanols **23** and **24** are considered to be ephemeral



23 **24**

intermediates in the poly-condensation of trialkoxysilanes.[29] Cyclic tetramer **24** has been isolated in moderate yields whereas cyclic trimer **23** has never been isolated in a pure and stable form. Interestingly, when we conducted the condensation of trialkoxysilanes in the M_6L_4 cavity we observed the exclusive formation of cyclic trimer **23** as a stable form. In a typical reaction, phenyltrimethoxysilane **25** was suspended in D_2O solution of **4** at 100 °C. The ^{1}H NMR of the solution after 5 min showed the formation of complexes **4**·(**25**)$_3$ and **4**·(**25**)$_4$. After 1 h, the ^{1}H NMR spectrum showed the presence of only one complex **4**·**A**. The formation **4**·**A** was also evidenced by ESI-MS and single crystal X-ray crystallography (Scheme 3). We note the following important features of this reaction. First, the cyclic trimers are formed in a *ship-in-a-bottle* fashion. Secondly, the formed cyclic trimers, which are protected by the cavity, are very stable even in acidic aqueous solutions and isolable as pure clatharate compounds. Lastly, the stereochemistry of the condensation is highly controlled within the cage giving only all-*cis* isomers.



Scheme 3 Schematic representation of trimer formation in the cavity of **4** (shown as circle).

Paneling squares

The square is a basic unit for the construction of cubes and prisms (trigonal, square, pentagonal, hexagonal, *etc.*) Tetrakis(pyridyl)porphyrins are the most common and easily available square panels. Indeed tetrakis(4-pyridyl)porphyrin is already known to form coordination polymers and also some 2D-molecular squares with transition metal atoms.[30] However, 3D-discrete molecules using porphyrin molecular panels have not yet reported. We found the formation of a triangular prism **26** by the self-assembly of tetrakis(3-pyridyl)porphyrin **10** (Fig. 14).[31] The formation of the prism structure was confirmed by ^{1}H NMR ESI-MS and X-ray analyses.

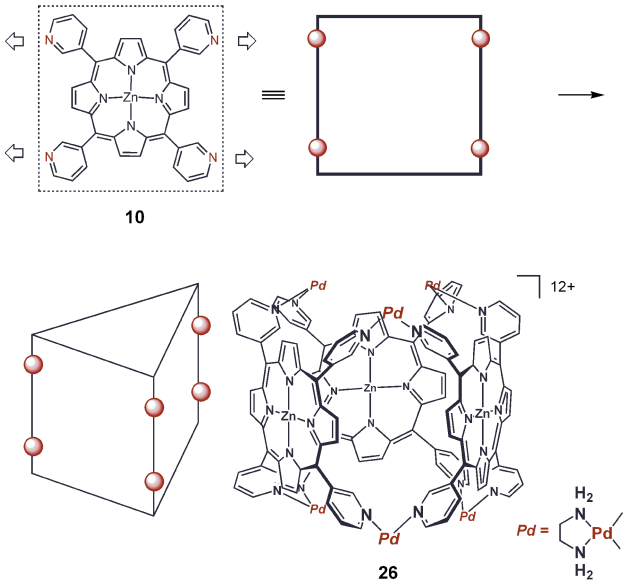


Fig. 14 Schematic representation of molecular paneling of **10** to form **26**.

Paneling rectangles

Similar to square panels, rectangular panels can also be used to construct prismatic structures of (triangles, squares, pentagonal, hexagonal *etc.*) However, depending on the length and width of the rectangular panel the assembled structures can be denoted as either tubes or boxes. Further a number of important topological surfaces such as torus, Möbius strip, Klein bottle and projective plane can also be constructed from rectangular panels. Here, we describe the self-assembly of a family of rectangular panels **11**–**13** to form molecular tubes, and that of **14** to form a molecular nano-box.

Coordination nanotubes

Molecular-based tubular structures have attracted considerable current interest because of their potential abilities for selective inclusion and transportation of ions and molecules and catalysis of specific chemical transformations.[32] Rectangular panels **11**–**13** were designed in anticipation of such tubular structures upon treatment with **1**.[33] For **13**, a coordination nanotube **27** is

expected from four molecules of **13** and 10 molecules of **1** (Fig. 15). However, the formation of coordination nanotubes were observed only in the presence of a rod-like template molecule

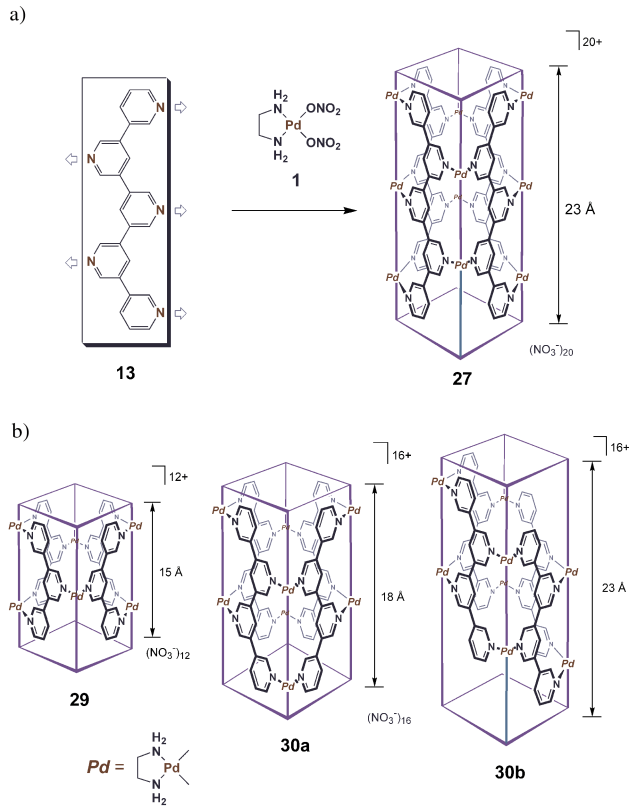


Fig. 15 (a) Schematic representation of molecular paneling of **13** and (b) structural drawings of **29**, **30a** and **30b**.

such as sodium 4,4′-biphenylenedicarboxylate **28**. Similarly, coordination nanotubes **29** and **30** were also obtained and characterized using NMR and ESI-MS. According to NMR spectroscopy, the protons of **28** were up-field shifted by up to 2.6 ppm indicating its encapsulation in the nanotube. A similar template effect was observed with two other rod-like molecules biphenyl and *p*-terphenyl. Spherical and large molecules such as adamantane carboxylate failed to template the nanotubes. Interestingly, it is found that the formation of these tubes is a completely reversible process. That is, the tube dissociates into its components by the removal of the guest molecule and again associates by the addition of guest molecule.

Shuttle movements of guest molecules were observed: at low temperatures the guest stays at a fixed position of the tube, shuttles on the NMR time scale at 60 °C, and rapidly moves or partially goes out at above 60 °C. NMR studies of nanotube **30** revealed that it is a 1 : 1 mixture of structural isomers **30a** and **30b**. In isomer **30a**, each ligand is placed on a C_2-symmetry site and only seven protons corresponding to half of **30a** were observed. On the other hand, in isomer **30b**, all 14 protons were observed as the C_2-symmetry of the ligands was removed. Tubes **29** and **30b** were characterized by X-ray crystallography. The crystal structures display tubular structures of **29** and **30b** efficiently assembled around template **28** *via* strong π–π and CH–π interactions (Fig. 16). The shape of the tube, which ideally should be square, is significantly distorted in order to maximize strong aromatic interactions. That is, the two faces which are interacting with **28** *via* π–π interactions, are squeezed towards the inside, while the remaining two faces, which interact with **28** *via* CH–π interactions, are pushed outwards. Another interesting feature of this crystal structure is the presence of a second molecule of **28** which is enclathrated between the nanotubes.

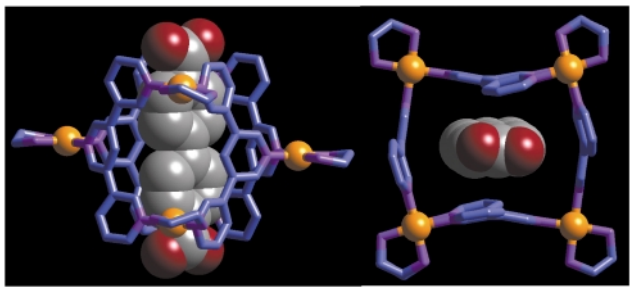


Fig. 16 The X-ray structure of **29**, side view (left) and top view (right).

Coordination box with dynamic property

A 1D rod-like ligand, such as biphenyl, upon treatment with **1** is known to be in equilibrium with two types of two-dimensional structures, namely square **3** and a triangle.[9] In order to extend this property into 3D structures we designed a rectangular molecular panel **14** which has four exodentate coordination sites. As anticipated the molecular panel **14** upon treatment with **1** was found to be in rapid equilibrium with several products which constitute a dynamic library of box structures. From the library we were able to isolate two box structures: namely trimeric box **31** and tetrameric box **32** which are minor products under normal conditions (Fig. 17).[34]

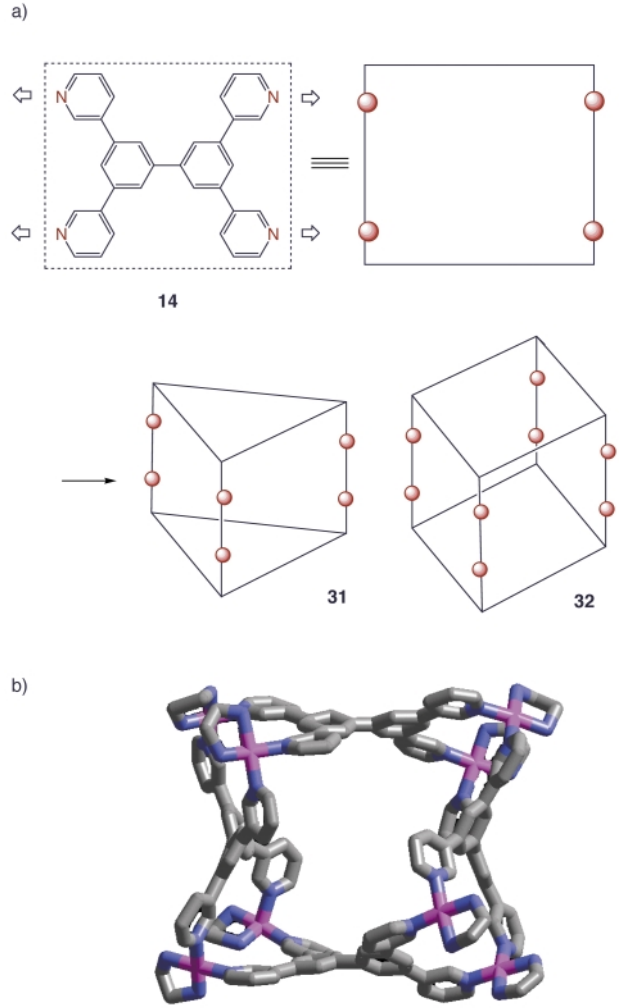


Fig. 17 Schematic representation of molecular paneling of **14** to form **31** and **32** and (b) X-ray crystal structure of an isomer of **32**.

The trimeric molecular box **31** was isolated quantitatively when a template such as biphenyl was suspended in a D_2O solution of **1** and **14** at 80 °C. The ^{1}H NMR of the solution showed two sets of signals: one set corresponds to triangular box **31** (δ 7–10) while the other set corresponds to biphenyl (δ

4.8–6.5). The biphenyl protons were significantly up-field shifted due to the inclusion in the box and the integration of the signals suggests that there are two biphenyl molecules per box. Moreover the proposed formula is in agreement with ESI-MS which shows five peaks at *m/z* 1502.9{[**31**·10NO_3]$^{2+}$}, 982.1{[**31**·9NO_3]$^{3+}$},720.8{[**31**·8NO_3]$^{4+}$},564.3{[**31**·7NO_3]$^{5+}$} and 460.3 {[**31**·6NO_3]$^{6+}$}.

Tetrameric box **32** was isolated as the major product when ligand **14** was treated with **1** at 50 °C for four days in D_2O–CD_3OD. In its ^{1}H NMR spectrum a set of six signals were observed in accord with D_{4h} symmetry of **32**, while CSI-MS of its PF_6 salt also supported the tetrameric box structure (*m/z* 1688.8 [**32**·13PF_6]$^{3+}$ and 1230.8 [**32**·12PF_6]$^{4+}$). Slow diffusion of THF vapor into an H_2O–CH_3CN solution of **1** and **14** for a few weeks resulted in single crystals suitable for X-ray analysis. The crystal structure revealed the formation of an unexpected structure that has the same composition as **32** but is composed of two structural isomers of **14**. The differences between solution and solid-state structures could be due to the presence of THF vapor that possibly shifted the equilibrium during the crystallization. However, the formation of a similar box structure in solution was not observed as it is rapidly isomerizes into box structure **32**.

The dynamic behavior of these box structures in solution was studied by ^{1}H NMR and CSI-MS. When the PF_6 salt of trimeric box **31**·2(biphenyl) was dissolved in CD_3CN the guest was liberated immediately leaving empty **31**. Interestingly monitoring of this solution by ^{1}H NMR and CSI-MS showed the reorganization of trimeric box **31** into tetrameric box **32** in 24 h and also revealed the presence of a pentameric box as a kinetic intermediate during the reorganization process.

Conclusions

Here we have described a highly successful strategy, which we term as *molecular paneling*, to construct various 3D-molecules that resembles several existing polyhedra. We note the following as advantages of using the concept of *molecular paneling* to construct 3D-architectures.

The syntheses are very facile: most of the compounds described here can be synthesized on a several gram scale in the laboratory simply by mixing the components in water, and the yield is quantitative in most cases.

This method provides the opportunity for the construction of larger cage-like molecules with larger cavities. Such larger cavities allow for the existence of isolated spaces which can be used for chemical transformations as described for octahedral cage **4**.

The involvement of transition metals in the molecular frameworks may lead to new properties (photo, redox, magnetic and/or thermal).

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