

Multicomponent metal–ligand self-assembly

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Self-assembly of pre-designed organic ligands with transition metal atoms is a powerful method for construction of novel supramolecular architectures. Particularly, various discrete 3-D hollow structures such as cages, cones, capsules and boxes have been obtained by multicomponent self-assembly of exo-multidentate ligands with *cis*-protected square planar metal complexes, [(L)M](NO₃)₂ (where L is ethylenediamine or 2,2'-bipyridine and M is Pd or Pt). Furthermore, these hollow structures act as molecular flasks to encapsulate guest molecules and regulate/promote specific reactions; for example, oligomerization of silanetriols and [2+2] intermolecular photodimerization of olefins.

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Abbreviations

bpy 2,2'-bipyridine
en ethylenediamine
ESI-MS electrospray ionization mass spectrometry

Introduction

In contrast to traditional synthesis by stepwise formation of covalent bonds, non-covalent synthesis by the simultaneous assembly of multicomponents has been proved to be a very useful method in construction of well-defined supramolecular architectures with specific topology and functionality [1]. Nature utilizes the principles of non-covalent interactions for the organization of simple units into various intricate structures with complex and efficient functions. For example, closed-shell virions comprise smaller proteins that assemble by non-covalent interactions to form a spherical capsid around the nucleic acid [2]. Taking inspiration from the examples of biological systems, efforts are underway to synthesize artificial models with biomimetic functions using self-assembly processes [3]. Several excellent reviews about molecular assembly by coordination and/or hydrogen bonding appeared up to 2000 [1,4,5]. This review focuses on the work accomplished in the past year. Particularly, multicomponent self-assembly of discrete 3-D hollow structures (cages, cones, capsules, boxes, etc.) mediated by *cis*-protected square-planar metals, [(L)M]²⁺ (where L is en or bpy and M is Pd or Pt) are described. The rationally designed exo-multidentate ligands combine to form various hollow structures with nanometer-sized inner cavities, in which specific reactions can be regulated or promoted.

Self-assembly of discrete three-dimensional hollow structures

In recent years, interest has grown in the chemistry of molecular container compounds because of their inner cavity, which can, for example, encapsulate guests and stabilize reactive species [6•]. The great progress in non-covalent synthesis has enabled the efficient construction of molecular containers with large cavities by the assembly of predetermined building blocks [7]. In particular, metal-mediated self-assembly of molecular containers have been extensively studied [4].

Several years ago, we initiated a systematic study of self-assembly of pre-designed organic ligands with transition metals having 90° coordination angles. We successfully incorporated *cis*-protected square planar metals, [(L)M]²⁺, into metal-organic frameworks such as cages, cones, capsules and boxes [8••]. Some typical examples are illustrated in Figure 1. Octahedral M₆L₄ type cage **6** is readily available from self-assembly of six *cis*-protected Pd(II) complexes, [Pd(en)](NO₃)₂, and four tridentate ligands **1** [9]. Interestingly, cage **6** can strongly bind a variety of anionic and neutral guest molecules in aqueous solution because of the hydrophobic environment inside the cage [9,10]. The large inner cavity (diameter ~2 nm) of **6** allows encapsulation of one to four guest molecules per cage, depending on the size of the guest. However, no encapsulation was observed for electron-deficient compounds (e.g. 1,4-dibromobenzene, 1,3,5-tribromobenzene and perfluorobenzene), which implies that the interior cavity is not only a hydrophobic but also an electrophilic microspace [10].

A detailed analysis by NMR of the host framework revealed the inclusion geometry and dynamics of guest molecules inside the cage [11]. For example, two guest molecules of 4,4'-dimethoxydibenzoyl inside the cavity of **6** were predicted from NMR results and confirmed by X-ray crystallography to aggregate orthogonally and adopt a chiral, twisted conformation with opposite screw senses. Such inclusion geometry of guest molecules induces the desymmetrization of the host **6** from T_d (empty) to an S₄ symmetry. The results demonstrate that host–guest interactions are remarkably strong and that the conformations of enclathrated guest molecules are completely frozen at room temperature.

Several M₄L₂-type coordination cages have been recently synthesized by self-assembly of pre-organized tetradentate cavitand ligands using cyano (-CN) as the coordination group with *cis*-protected Pd or Pt complexes [12]. The self-assembly process and the encapsulation of anions inside the cage were studied. It was found that the formation of such coordination cages is extremely sensitive to the structure of the metal precursor. In addition, M₃L₂-type metallocages have also been obtained by assembly of organic ligands with

Figure 1

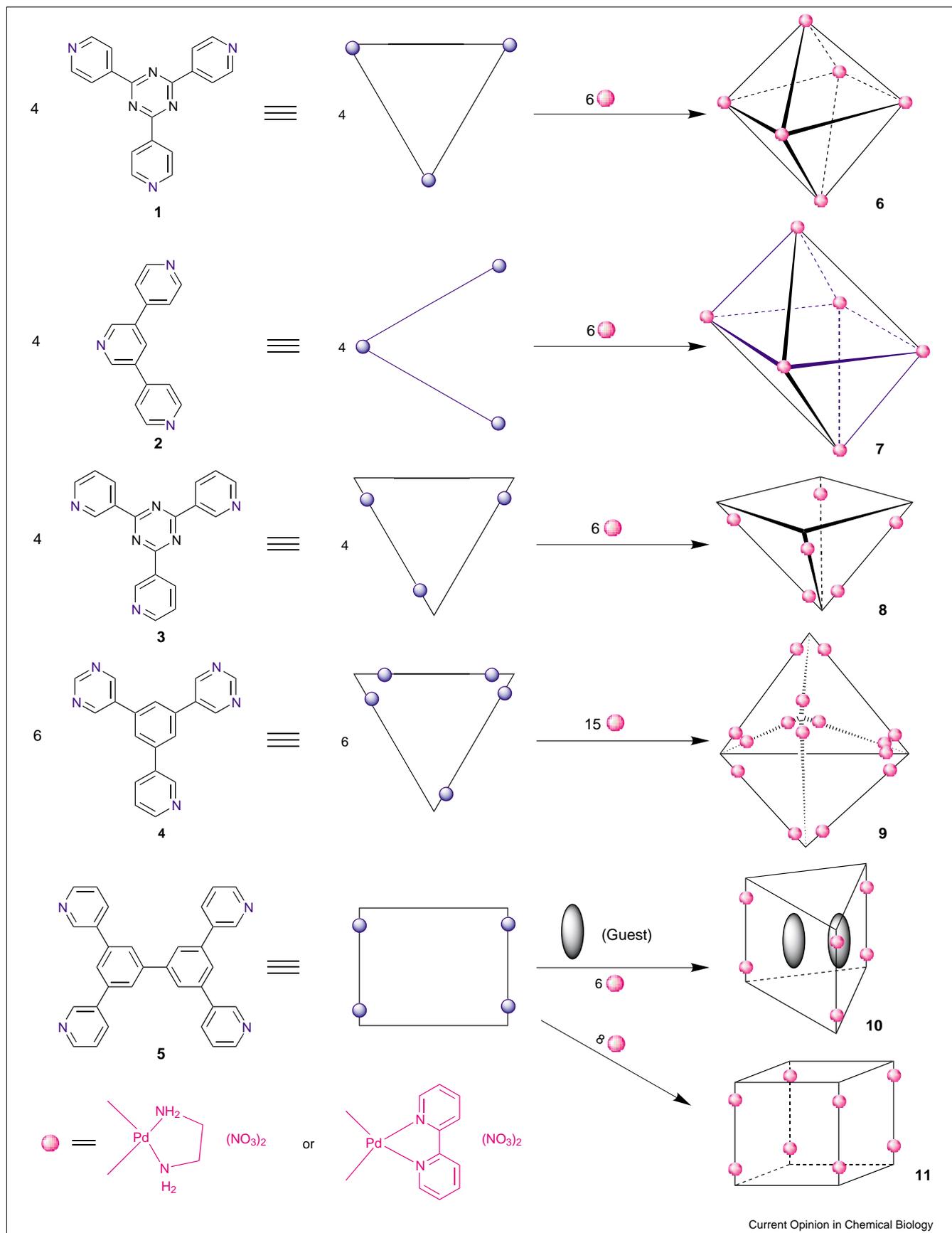


Figure 1 legend

Schematic drawings of self-assembly of various hollow structures from pyridine- and pyrimidyl-based organic ligands and *cis*-protected square planar metal complex.

transition metal atoms, and their guest inclusion and anion exchange properties have been reported recently [13–15].

The above-mentioned organic ligands used for self-assembly all have high symmetry, which limits the formation of structural isomers caused by the different orientations of the same ligands in the self-assembly process. The tridentate ligand **1** (D_{3h} symmetry), when assembled with metal ions, generates cage **6** with the highest class of T_d symmetry. As a result of desymmetrization of ligands, less-symmetric cages, possibly with site-specific functionalization of the cavities, can be formed by self-assembly with metal ions. In addition, the construction of chiral cages from less symmetric achiral components is possible [16–20]. Modification of ligand **1** by eliminating one pyridine ring leads to a terpyridine ligand (**2**) with D_{2h} symmetry. A C_2 chiral M_6L_4 type cage (**7**) was obtained by self-assembly of achiral ligand **2** with *cis*-protected Pd complexes in the presence of an aromatic template molecule (e.g. *p*-dichlorobenzene, *p*-xylene or *p*-diethylbenzene) [21]. In the solid state, the X-ray analysis confirmed the formation of the cage with simultaneous encapsulation of one template molecule and one nitrate anion inside the cavity of **7**. The molecular chirality in solution was observed by circular dichroism and NMR spectral measurements using (*R,R*)-1,2-diaminocyclohexane- or (*S,S*)-1,2-diaminocyclohexane- (instead of ethylenediamine) protected Pd complex. The results provide an example of chiral assemblies obtained by introducing a chiral source and less symmetric ligand, and open a new route for preparation of chiral compounds.

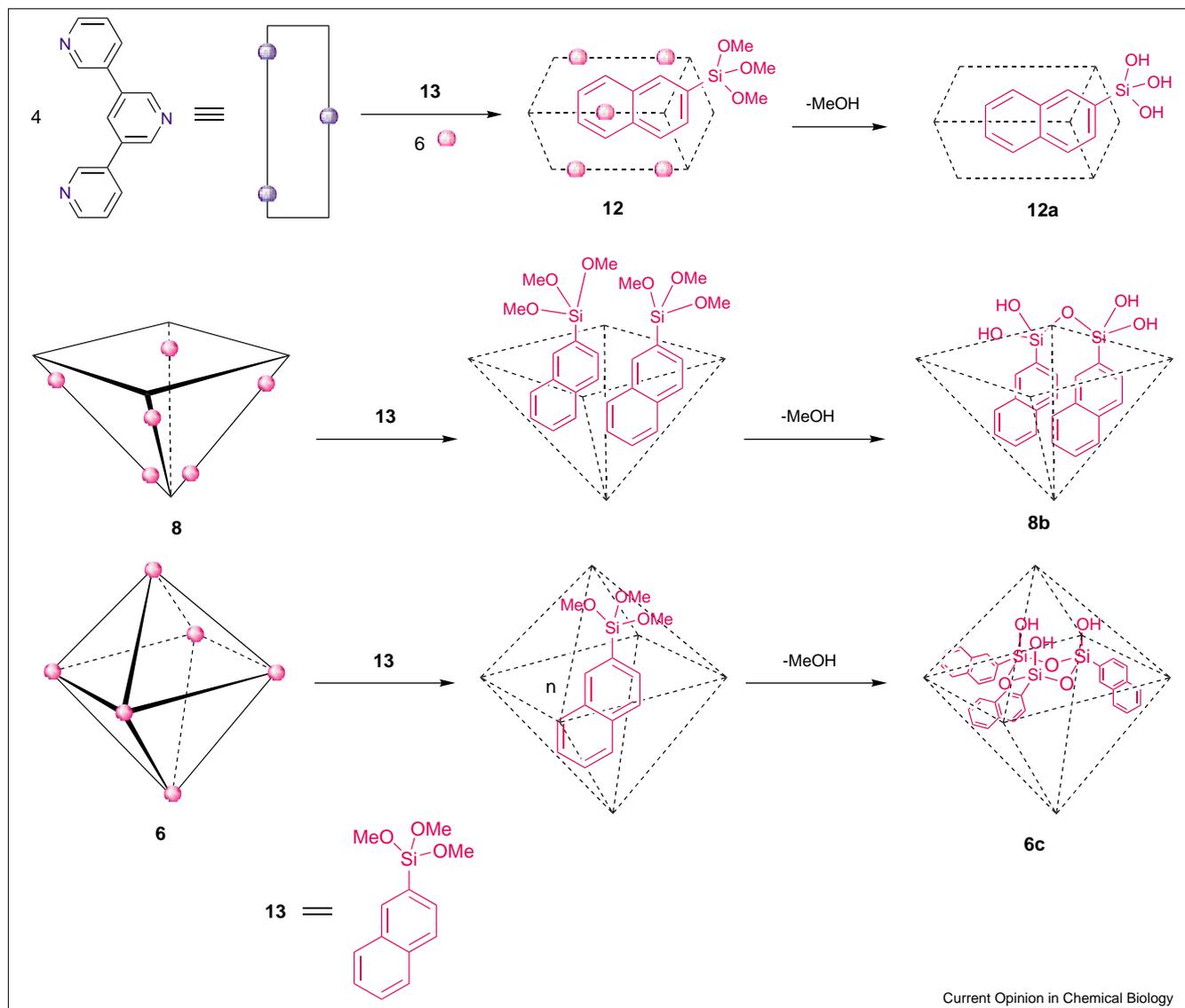
Using a 3-pyridyl instead of a 4-pyridyl group in ligand **1** results in another tridentate ligand (**3**). A M_6L_4 framework (**8**) was obtained by self-assembly of **3** with the *cis*-protected Pd complex [22]. **6** and **8** have similar components but different topologies. **8** is a cone-shaped (or bowl-shaped) square-pyramid, which looks like the cyclodextrin with larger dimensions (approximately $3 \times 2 \times 2$ nm), whereas **6** is an octahedral cage (Figure 1). The topology of **8** determines its inclusion properties, which are different from those of **6**. In contrast to the almost spherical cage of **6**, **8** has an open pocket. Thus, it can be expected that such cone-shaped molecules dimerize to give a molecular capsule by non-covalent binding of guest molecules [23]. The host–guest interactions were investigated by NMR spectroscopy in aqueous solution and X-ray crystallography in solid state [24]. The crystal analysis unambiguously showed the formation of a dimer capsule $(\mathbf{8})_2 \bullet (\text{guest})_4$ (where the guest is *m*- or *o*-terphenyl) and $(\mathbf{8})_2 \bullet (\text{guest})_6$ (where the guest is *cis*-stilbene). The difference between **6** and **8** is also apparent in the regulation/promotion of specific reactions (see below).

The above pyridine-based ligands have been shown to provide novel and unique discrete 3-D hollow structures by multicomponent metal–ligand self-assembly. Further modification was successfully carried out by incorporation of a 3,5-pyrimidyl group (instead of a pyridyl group) into ligands [25*,26,27]. Accordingly, derivation from ligands **1** and **3** yielded **4** with five binding sites [25*]. Strikingly, NMR studies showed that the assembly product of ligand **4** with *cis*-protected Pd complex is a unique $M_{15}L_6$ hexahedral capsule (**9**), which was further confirmed by X-ray crystallography, without the formation of any other structural isomers. Interestingly, capsule **9** has more flexibility than the $M_{18}L_6$ hexahedral capsule, assembled from an exohexadentate ligand (1,3,5-tris(3,5-pyrimidyl)benzene) and *cis*-protected Pd complex [26]. This is due to one binding site fewer in **4** than in the exohexadentate ligand. In contrast to the closed-shell $M_{18}L_6$ capsule, there are three clefts with size 3.5–5.0 Å at the non-binding sites of the $M_{15}L_6$ capsule **9** (Figure 1). Therefore, **9** can be expected to encapsulate and release small guest molecules reversibly through these clefts. In fact, the encapsulation of CBr_4 in aqueous solution of **9** was observed to form a $\mathbf{9} \bullet (\text{CBr}_4)_2$ complex, and decapsulation occurred on addition of ethanol to the aqueous solution. Molecular capsules with nanometer dimensions obtained by the self-assembly method via coordination and/or hydrogen bonds have also been reported to have guest-encapsulation properties [28,29].

In addition to the triangular ligands, square-panel-like ligands are also very useful building blocks for construction of supramolecular frameworks. Among them, porphyrin-based ligands, echoing the importance of porphyrin assemblies in biological system, are the most common and well studied [30]. Assembly of porphyrin-based ligands with metal ions offered coordination polymers and molecular cages [31,32]. Formation of a 3-D discrete molecular prism [33] was achieved by assembly of tetrakis(3-pyridyl)porphyrin with *cis*-protected Pd complex [34]. The assembly process, anion exchange and guest inclusion were investigated in detail by cold electrospray ionization mass spectrometry (ESI-MS), NMR spectroscopies and model calculations, and the structure of the molecular prism was confirmed by X-ray analysis. Interestingly, the conformation of empty prism changed greatly by encapsulation of guest molecule such as pyrene, and a host–guest complex with 1:1 ratio was formed. The NMR analysis revealed that the binding of guest molecule to the prism triggered the conformational change from a D_{3h} symmetry to a C_2 symmetry.

Another square-panel-like ligand (**5**) was designed by expansion of the well-known bridging ligand 4,4'-bipyridine. A doubly ligating 3,5-bis(3-pyridyl)phenyl unit was

Figure 2



Selective oligomerization of trialkoxysilanes to prepare silanetriol in tube-like framework **12**, its dimer in the cone-shaped structure **8** and cyclic trimer in the cage **6**.

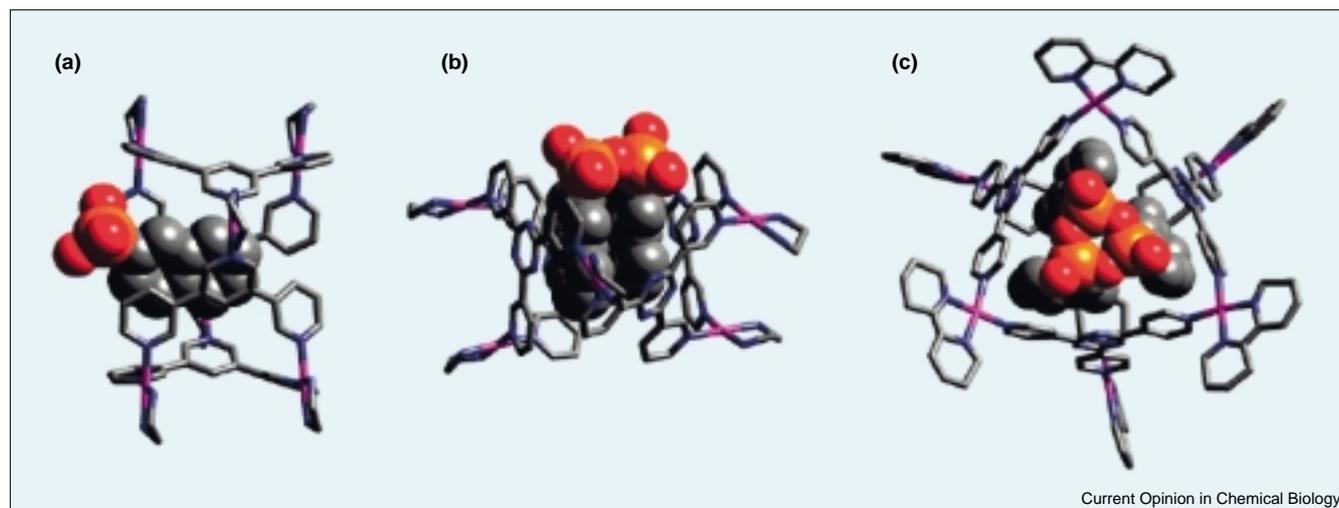
used to replace the mono-coordinating 4-pyridyl group of 4,4'-bipyridine to give **5** [35^{*}]. Treatment of **5** with *cis*-protected Pd complex provided a dynamic library consisting of several box structures that are in equilibrium and interconvertible. Notably, trimeric and tetrameric boxes **10** and **11** were successfully isolated using a template or by changing the reaction conditions. The trimeric box **10** was formed quantitatively in aqueous solution in the presence of biphenyl template as a complex of **10**•(biphenyl)₂, as determined by NMR and cold ESI-MS spectral measurements. However, when the assembly reaction was carried out in water:methanol (1:1) solution, tetrameric box **11** was obtained as a major product. Attempts to crystallize the assembly products by diffusion of tetrahydrofuran vapor into the reaction mixture in water:acetonitrile solution led

to the finding of a structural isomer of **11** that has the same component, but with a different conformation of **5**. Further studies on dynamic process monitored by NMR and cold ESI-MS revealed that the trimeric box **10**•(biphenyl)₂ in acetonitrile solution favored tetrameric box **11** via a pentameric box as a kinetic intermediate.

Regulation oligomerization reactions of alkoxy-silanes within self-assembled metal-organic frameworks with hollow structures

Functions, properties and stability of molecules may significantly be changed when they are encapsulated into the cavities of hollow structures as a result of the conformational restriction within the limited interior space of the cavities [36]. Organic capsules linked by covalent bonds

Figure 3



Crystal structures of host–guest complexes of hollow structure (host) with the products of oligomerization of trialkoxysilanes. (a) **12**•**13a**; (b) **8**•**13b**; (c) **6**•**13c'**.

such as hemicarcerands [37] or by hydrogen bonds [38] have been demonstrated to stabilize reactive species. Recently, we succeeded in selective oligomerization of trialkoxysilanes, $\text{RSi}(\text{OMe})_3$, in self-assembled hollow structures by introducing the concept of cavity-directed synthesis [39,40].

Three discrete 3-D hollow compounds **6** [9], **8** [22] and **12** (Figure 2) [41], which have the same M_6L_4 stoichiometry but differ in the sizes of their inner cavities, were employed to study the selective oligomerization of 2-naphthyltrimethoxysilane (**13**) in aqueous solution. Tube-like compound **12** has the smallest cavity and has been shown to include only one rod-like guest molecule [41]. The coordination tube **12** was synthesized in the presence of **13** as a template. The reaction monitored by NMR occurred first by formation of **12**•**13** complex followed by hydrolysis of trialkoxysilanes to give a complex of **12**•**13a** (where **13a** is 2-naphthylsilanetriol) (Figure 2) [40]. Finally, pure **12**•**13a** complex was formed and can be isolated by recrystallization in over 90% yield. Further structural analysis by X-ray crystallography clearly indicated that the hydrophobic 2-naphthyl group was deeply encapsulated in the cavity of **12**, whereas the hydrophilic silanetriol, $\text{Si}(\text{OH})_3$ group was exposed outside (Figure 3). The results show that the very labile silanetriol monomer is stabilized by **12**, which prevents further condensation reaction.

Regulation of the hydrolysis and condensation of trialkoxysilanes to form a silanol dimer was achieved by utilizing the cone-shaped framework **8** with a middle-size cavity among **6**, **8** and **12**. The NMR measurements demonstrated that the cavity of **8** can accommodate two molecules of **13** to form a complex of **8**•(**13**)₂ at room temperature. Hydrolysis and condensation of **13** was

completed in 1 h at 100°C to generate a silanol dimer (**13b**) (Figure 2). The dimer structure was further confirmed by cold ESI-MS and X-ray analysis. Interestingly, the crystal structure of the complex of **8**•**13b** showed that the conformation of **8** varied from cone-shape to box-like by flipping of the two Pd(en) hinges after binding of the silanol dimer (Figure 3).

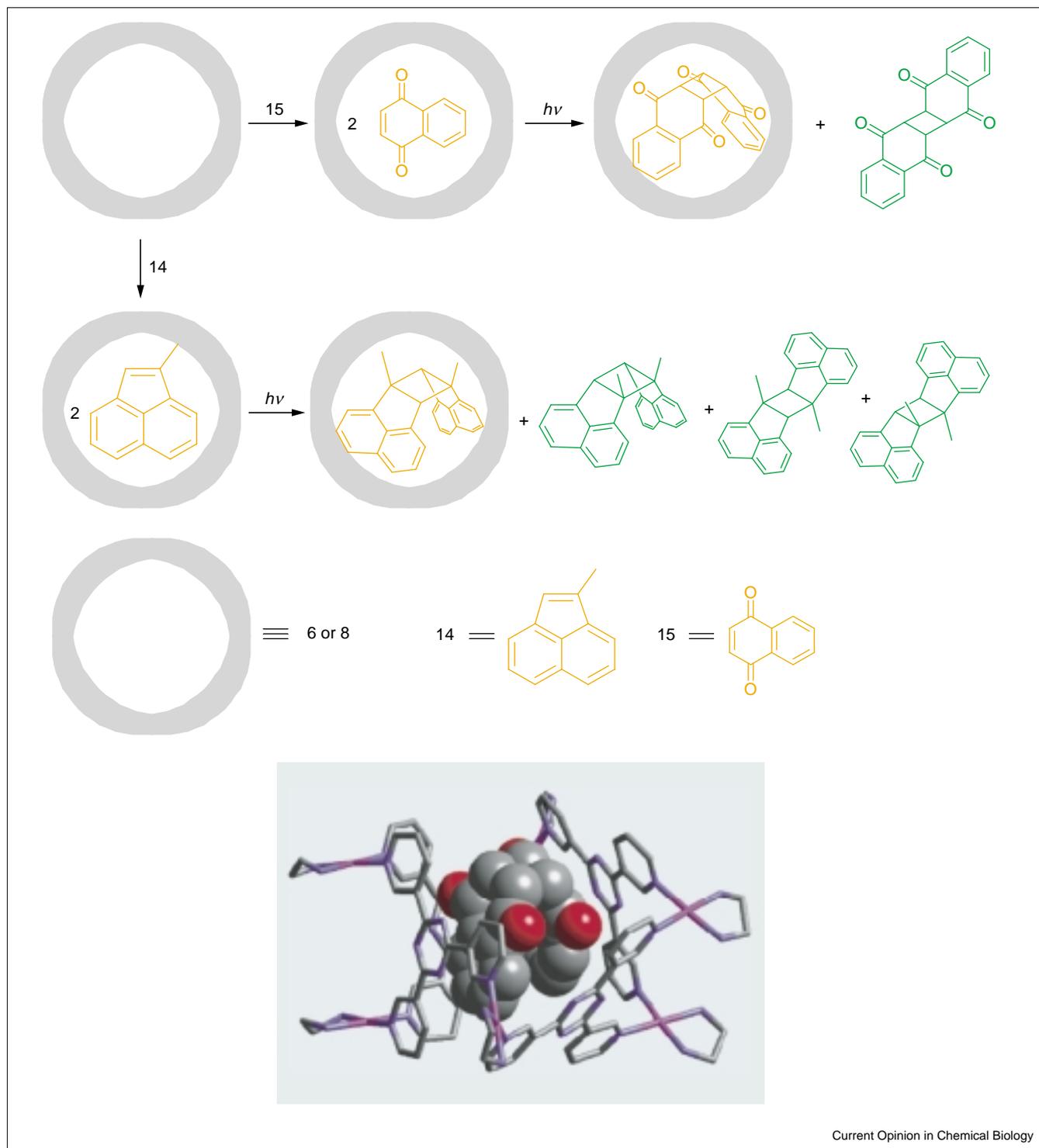
Hydrolysis and condensation of **13** in the cavity of cage-like complex **6** led to the formation of a silanol cyclic trimer (**13c**) (Figure 2). The crystal structure of **8**•**13c'** with the *m*-tolyl group as an analogue of **13**, illustrated in Figure 3, confirms the formation of the cyclic trimer with all *cis* conformation. The reactive Si-OH was insulated by the cavity and thus further condensation was stopped.

The above study clearly indicates that the formation of silanetriol, its dimer and cyclic trimer can be regulated by the size and shape of the cavities provided by the hollow structures. It can be expected in future that the oligomerizations of reactive monomers could be controlled at the desired degree by selection of hollow structures with different cavity size and shape, prepared by self-assembly of appropriate organic ligands with transition metals.

Highly stereoselective [2+2] photodimerization of olefins within self-assembled coordination cages

In addition to the stabilization of reactive species by cavities in aqueous medium as described above, promotion of specific reactions with high regioselectivity and/or stereoselectivity is expected because of the proximity and the strictly determined orientation of reactants inside the cavities of hollow structures. Further, reactions occurring within the hydrophobic cavities can be considered as

Figure 4



Stereoselective [2+2] photodimerization of large substituted olefins within self-assembled hollow structures **6** and **8**; crystal structure of the photodimerization product of naphthoquinone within the hollow structure **8**.

models for mimicking enzymatic reactions in biological system, as many enzymatic reactions occur in hydrophobic environments (though the bulk aqueous medium is hydrophilic) with high efficiency and regioselectivity and

stereoselectivity. In fact, photodimerization and cycloaddition have been successfully carried out within organic hosts such as hemicarcerand [42], cucurbituril [43] and self-assembled capsule [44].

Most recently, we studied the [2+2] photodimerization of olefins within the cavities of self-assembled hollow structures **6** and **8** [45[•]]. In the aqueous medium, the photodimerization reactions of 1-methylacetylene (**14**) and naphthoquinone (**15**) (Figure 4) were greatly promoted and the stereochemistry of the product was strictly controlled in the presence of **6** or **8**. NMR spectral measurements revealed that the substrate **14** was first encapsulated into the cavity of **6** and dimerization was completed in 3 h by photoirradiation (400 W) at room temperature. Furthermore, only the head-to-tail *syn* isomer was obtained and no head-to-head and *anti* isomers were formed (Figure 4). No photodimerization of the same substrate (**14**) was observed in benzene in the absence of cage **6** even at a very high concentration of the substrate.

The formation of *syn* isomer (**15a**) was also observed in photodimerization of **15** in the presence of cone-shaped host **8**. Further X-ray crystal analysis of **8**•**15a** confirmed the formation and encapsulation of the *syn* dimer within the cavity of **8** (Figure 4). To elucidate the effect of hollow structures on the photodimerization, 2-methylnaphthoquinone was photoirradiated in the presence of **6** and **8**. Interestingly, the regioselectivity was higher within cage **6** (96% head-to-tail) than within cone **8** (78% head-to-tail). Photodimerization of 2-methylnaphthoquinone did not occur without the hollow structures in benzene.

Conclusions

Discrete 3-D molecules with very large (nanometer-order size) cavities can be prepared readily by multicomponent self-assembly by incorporating transition metal atoms [46]. The localized microspace interior of the cavity provides a specific environment (e.g. hydrophobic) for stabilization of labile species and promotion of reactions. In the former case, the discrete molecules can be considered as *molecular safety boxes*, in which reactive species can be stabilized. Generally, molecules encapsulated within the cavities were placed in an isolated and shielded state and thus may have different properties/reactivities to those in the bulk phase. Generally, stabilization of labile reaction intermediates by hollow structures can be expected, as in the case of silanetriol oligomers described in this review. Alternatively, in the latter case, the discrete molecules with large cavities can be regarded as *molecular flasks* in which the reactions actually occur. In a chemistry context, encapsulation of two or more reactant molecules within the same cavity markedly increases the concentration, bringing the reactants in close proximity and regulated orientation. As a result, greatly accelerated and regioselective and/or stereoselective intermolecular reactions can be expected. In a biological context, where reactions occurred efficiently and selectively, it is important and interesting to regulate reactions properly as mimics of enzymatic reactions. Further studies of these molecular containers are thus expected in the near future.

Update

Recent work appearing after submission of this manuscript showed that the cavity of the cage **6** can encapsulate four

ferrocene molecules per cage [47]. The interactions of ferrocene, its derivatives and their corresponding ferrocenium ions with cage **6** were studied by electrochemistry. The clathrated ferrocene molecules within the cavity of the cage go outside when they are electrochemically oxidized to ferrocenium ions. The clathration and declathration were confirmed by NMR and crystal structure analysis. The result provides a nice example of a molecular-based switching system.

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