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Accounts

Guest-Induced Assembly of Pd^{II}-Linked Coordination Nanotubes

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This article reviews a coordination approach to discrete tubular structures. Families of pyridine-based molecular strands assemble into large tubular molecules through metal-coordination. In particular, cis-protected square-planar metals, $[\mathrm{enPd^{II}}]^{2+}$ (en = ethylenediamine), are very useful building blocks to link these molecules. Pyridine-based oligo(3,5-pyridine) ligands efficiently self-assemble into well-defined tube frameworks having a variety of shapes and sizes upon treatment with $[\mathrm{enPd(NO_3)_2}]$ in the presence of rod-like organic guests as templates. The length of the tube can be strictly controlled according to the numbers of pyridine nuclei involved in the component ligand. These nanotubes collapse when the template molecule is removed. A hexapyridine ligand, in which two tripyridine units are linked by an alkyl spacer, forms a complex with the Pd^{II} building block leading to the formation of a stable nanotube with an empty cavity without templates. With the aid of a 3.0 nm template strand molecule, a hexapyridine ligand consisting of two tripyridine units and a biphenyl linker assembles into a 3.5-nm nanotube, in which the four ligands are held together by twelve Pd^{II} ions. Facile preparation as well as the stability of the tube, even after the template is removed makes possible the hollow discrete assembly of the tubes. A dodecapyridine ligand possessing four tripyridine podands on a benzenetetracarboxylate scaffold, six Pd^{II} ions, and a template molecule generate a mono end-capped tube, which converts into a double open tube upon crystallization. Once formed, there is no route back to the end-capped tube. The structures are not in rapid equilibrium and are kinetically trapped during self-assembly. These tubular structures have been confirmed by NMR, CSI-MS observations, and X-ray crystallographic analysis. Studies on the dynamic behavior of rod-like guests accommodated in the nanotubes are also discussed.

Molecular-based nanotubes with one-dimensional cavities have been providing a stimulating area of research in the field of organic/inorganic synthetic chemistry, material science, and supramolecular chemistry for the last two decades.[1] The use of these tubular molecules as synthetic transmembrane channels and pores as well as building blocks for the fabrication of nanoscale devices are subjects of considerable current interest.[2–4] Inspired by the remarkable functions of tubular structures in biology, physics, and material science, much attention has been paid to the creation of simpler molecular-based nanotubes for their potential properties, such as ion sensors, molecular sieves, gas absorption, ion exchange, size-selective separation, heterogeneous catalysis, and fluidic transport systems.[5–12] Inorganic nanotubes consisting of pure carbon,[13] boron nitride,[14] metal dichalcogenides,[15] and other layered materials[16] have been reported from many research fields. In this account, we focus on non-covalent syntheses, which have several inherent advantages over conventional covalent syntheses and have become a reliable approach to nanotube architectures. Through non-covalent interactions (hydrogen bonding, hydrophobic interaction, aromatic stacking, metal-coordination), open-ended hollow nanotubes have been constructed from cyclic peptides,[17] lipids,[18] oligocyclodextrins,[19] related organic molecules,[20] and the combination of ligands and metal ions.[21]

Conceptually, there are several possible approaches to hollow tubular structures through molecular self-assembly. Linear molecules form tubular structures by coiling into helical, folded conformations (Fig. 1a). An α-peptide chain with an alternating sequence of D- and L-α-amino acids is twisted to induce a single-stranded β-helix in the intramolecular hydrogen bonding.[22] Moore and co-workers have demonstrated that oligophenylacetylenes are spontaneously folded into a stable helical conformation having a large cavity, which could be stabilized by solvophobically driven packing between backbone phenyl rings.[23] Self-complementary macrocyclic subunits are stacked to form continuous tubular networks (Fig. 1b). Ghadiri and co-workers have shown that 24- and 30-membered-ring cyclo-α-peptides with an even number of alternating D- and L-α-amino acids stack in an antiparallel β-sheet-like arrangement to form hydrogen-bonded tubular structures denoted "peptide nanotubes."[17] The assembly of sectors and wedge-shaped subunits results in the formation of discs, followed by stacks, to form progressive cylinders (Fig. 1c). Percec and co-workers have systematically studied the assembly of amphiphilic wedge-shaped dendrons, which have lipophilic chains at the

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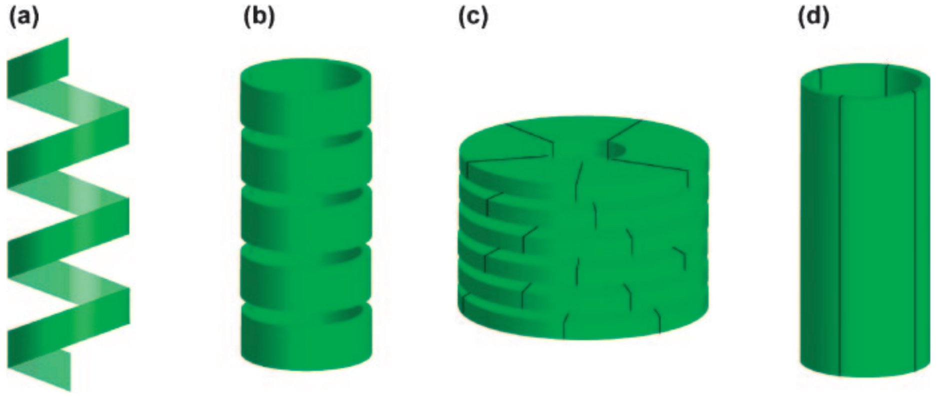


Fig. 1. Tubular structures originated from (a) linear, (b) macrocyclic, (c) wedged, and (d) rectangular motifs through molecular self-assembly.

periphery and a hydrophilic carboxylate core.[24] These molecules have discotic conformations with hydrophilic carboxylate groups pointing towards one another in the center of the disc, which subsequently induce to tubular architectures displaying a hexagonal columnar liquid-crystalline phase originated from hydrophobic interactions.

Tube Formation via Molecular Paneling

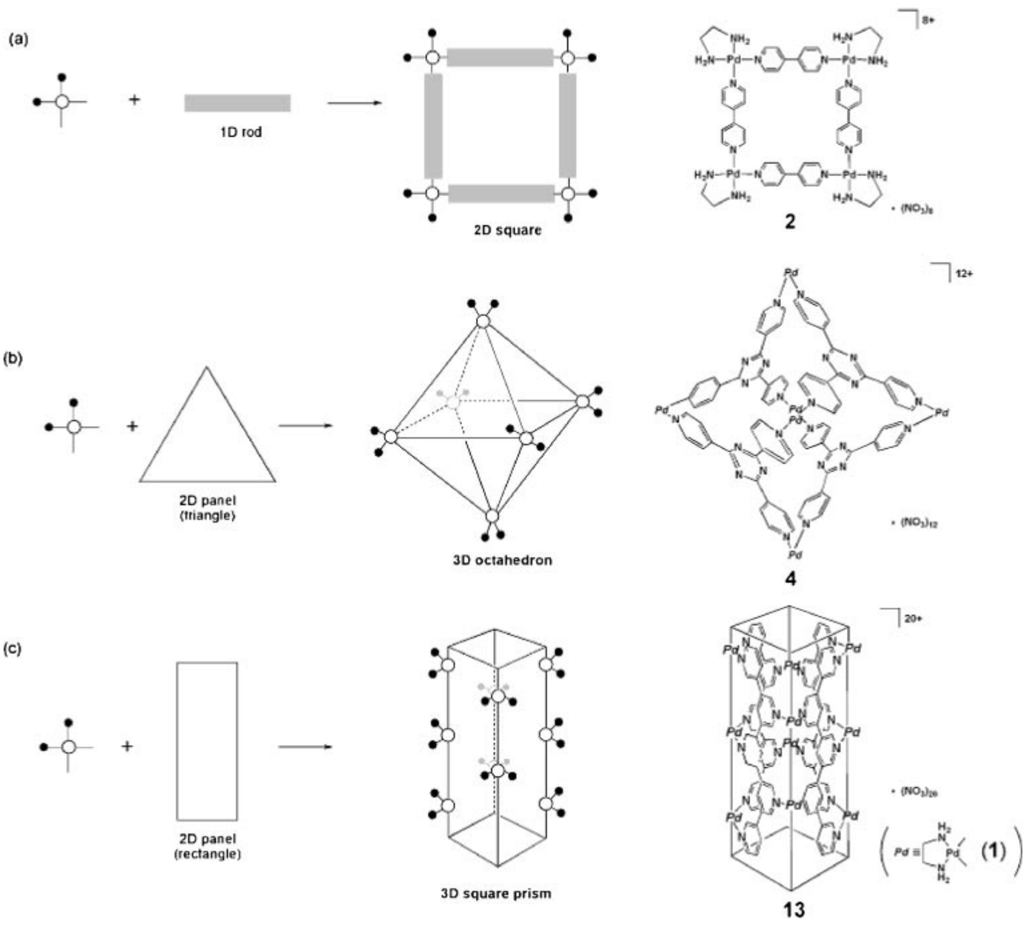
Although various promising synthetic methods to produce the motifs in Figs. 1a–1c exist in the literature, precise control of the length of self-assembled tubular objects has not yet been achieved to our knowledge. Another approach to tube structures is the self-assembly of molecular strands via non-covalent interactions (Fig. 1d). Matile and co-workers have reported that β-barrel structures form from rigid octa(p-phenylene)s conjugating short α-peptide side chains interdigitated with side chains of adjacent staves, forming antiparallel β-sheets via hydrogen bonding.[25] Our group has shown a coordination approach to nanotubes possessing very stable, well-defined frameworks. We designed an assembly of strand-like rectangular exo-multidentate ligands into nanotubes by linking them with transition-metal components. Rectangular panels should be linked with an appropriate structural turn (e.g., 90°), and thus, the use of cis coordination sites of transition metals is effective to provide such turns in the tubular structures. In this regard, $[\text{enPd}^{\text{II}}]^{2+}$ (en = ethylenediamine) (**1**) is a versatile metal component, which makes possible the design of precise tubular structures assembled from rectangular molecular panels.

Major efforts in our laboratory have been dedicated to metal-directed self-assembly of discrete two- and three-dimensional structures,[26] since we first demonstrated the spontaneous formation of a tetranuclear square framework (**2**) by the complexation of cis-protected Pd^{II} building block **1** with one of the simplest bridging ligand, 4,4′-bipyridine (Scheme 1a).[27] This molecular design has been extended to the construction of 3D structures by considering 2D molecular components. Instead of 1D rod, a 2D triangular panel (**3**) was used as an organic component. In 1995, this idea was first realized by the synthesis of an octahedral 3D structure (**4**) (Scheme 1b).[28] This example illustrates that the molecular paneling of a 2D organic component is undoubtedly an efficient method for the construction of large 3D entities. Since then, we have demonstrated that a family of molecular panels can be paneled into various 3D molecules via metal coordination.[29–35] Among the 2D panels we designed, a strand-like pentakis(3,5-pyridine) ligand (**7**) should have a planar rectangular conformation due to the dipole repulsion between the pyridine nuclei. Thus, when this ligand is linked together with **1**, which provides 90 degree turn for the assembled structure, coordination nanotube (**13**) is expected to form from four molecules of **7** and ten molecules of **1** (Scheme 1c).[36] An assembly of 3D architectures from these panels can be considered as a new concept, which we call "*molecular paneling*."[26]

Accordingly, we designed a new family of rectangular molecular panels **5**–**10** in order to assemble them into several tubular structures of a variety of sizes and shapes (Fig. 2). Oligo(3,5-pyridine) panels **5**, **6**, and **7** contain three, four, and five binding sites, respectively. Molecular panels **8** and **9** contain six binding sites, and two tripyridine units are linked by an appropriate spacer (an alkyl chain or a biphenyl unit). Molecular panel **10**, which has four tripyridine podands on a benzenetetracarboxylate scaffold, has twelve binding sites. The complexation of the cis-end-capped Pd^{II} building block with these ligands produced a variety of tubular structures, as illustrated in Fig. 3. In addition to open-ended nanotubes, highly organized tube frameworks, such as mono end-capped tube-shaped molecules bearing specific inner spaces and shapes, were also obtained, which cannot be constructed from the motifs shown in Figs. 1a–1c.

Dynamic Self-Assembly of Coordination Nanotubes

Quantitative Formation of Nanotubes Templated by Rod-Like Guests. We designed coordination nanotubes using rectangular panel-like oligo(3,5-pyridine) ligands **5**–**7** and $[\text{enPd}(\text{NO}_3)_2]$. In case of pentakis(3,5-pyridine) ligand **7**, coordination nanotube **13** should be assembled from four molecules of **7** and ten molecules of **1**.[36] However, it formed only in the presence of a rod-like template molecule, such as disodium 4,4′-biphenylenedicarboxylate (Fig. 4).[37] Similarly, coordination nanotubes **11** and **12** were also obtained with the aid of appropriate templates and were characterized by NMR and cold-spray-ionization mass spectrometry (CSI-MS).[38] In the NMR spectrum, the protons of 4,4′-biphenylenedicarboxylate were shifted upfield by up to 2.6 ppm due to shielding from the aromatic ligands, indicating its encapsulation in the nanotube. A similar template effect was also observed with two



Scheme 1. Schematic representation of molecular paneling: (a) from rods to square-molecules, (b) from triangle-panels to cage-molecules, (c) from rectangle-panels to tube-molecules.

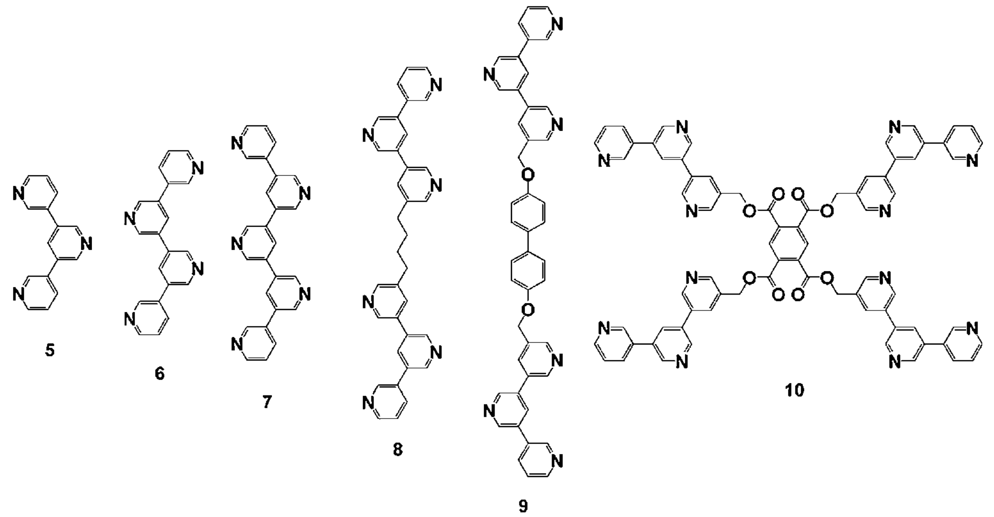


Fig. 2. Rectangular ligands **5**, **6**, **7**, **8**, **9**, and **10**.

other rod-like molecules biphenyl and *p*-terphenyl. Spherical and large molecules, such as adamantane carboxylate, failed to template the nanotubes. Interestingly, it was found that the formation of these tubes was completely reversible. In other words, the tube dissociated into its components upon removal of the guest molecule and again re-assembled by the addition of guest molecule.

We observed the formation of two isomers **12a** and **12b** for nanotube **12** in a ca 1:1 ratio, of which the symmetries were D_{2h} and C_{2h}, respectively.[39] Although both isomers of **12** contained sixteen Pd^{II}–pyridine bonds, the labile nature of Pd^{II}–pyridine interaction allowed the two isomers to interconvert

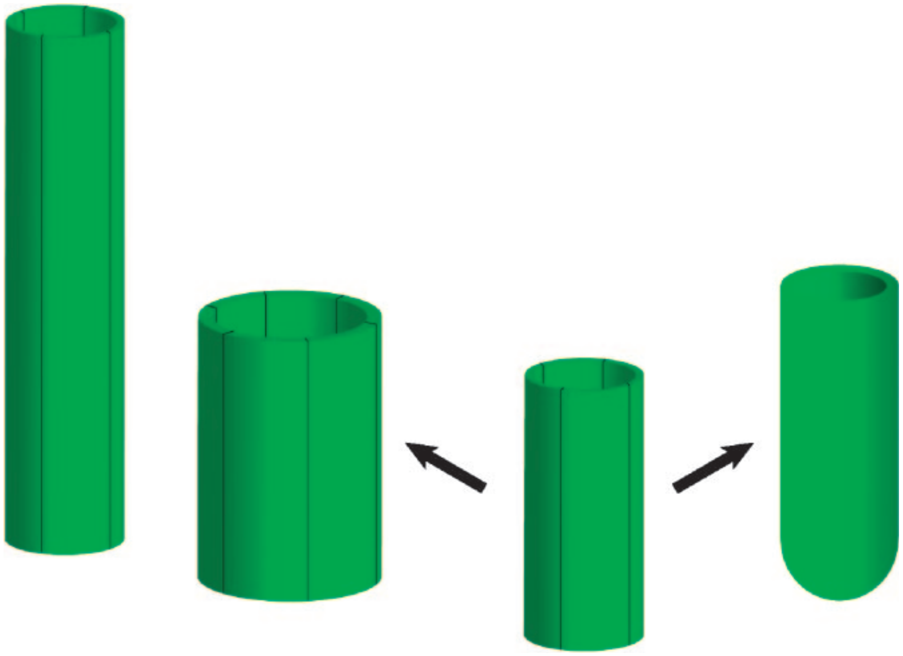


Fig. 3. Schematic representation of tubular structures with a variety of sizes and shapes.

into each other. NMR measurement showed a very slow interconversion exists between isomers **12a** and **12b**, but the tube was considerably stable on the laboratory timescale, unless the template molecule was removed. In isomer **12a**, each ligand kept its symmetry showing only seven protons, which corresponds to half of the framework. On the other hand, in isomer **12b**, each ligand was in a non-C_2-symmetric environment, and thus fourteen individual signals were observed for the ligand part in ^{1}H NMR.

The tubular structures enclathrating the template molecule were confirmed for complexes **11**, **12b**, and **13** by X-ray crystallographic analysis (Fig. 7). The crystal structures showed that tubular structures of **11** and **12b** were efficiently assembled around template 4,4′-biphenylenedicarboxylate via strong π–π and CH–π interactions. To gain a better host–guest interaction, *p*-terphenyl was selected as a template for nanotube **13**. The crystal structure of **13** again displayed good host–guest compatibility both in the width and the length. The shape of the tube, which ideally should be square, was significantly distorted in order to maximize strong aromatic interactions. That is, the two faces, which interact with template molecule via π–π interactions, were squeezed inwards, while the remaining two faces, which interact with template molecule via CH–π interactions, were pushed outwards.

Dynamic Behavior of Guest Molecules Encapsulated within Nanotubes. Studies on the dynamic behavior of the guest molecules inside the cavity of tubular assemblies are particularly important, because the guests are allowed to move only in a one-dimensional way within the tubes leading to novel functions for the tubular molecules. As mentioned above, tube complex **13** effectively encapsulates the rod-like organic guests in its cavity. This efficient guest binding is attributed to the amphiphilic nature of the tube, i.e., the inside of **13** is surrounded by twenty aromatic rings and thus hydrophobic, whereas the outside surface of the tube is hydrophilic due to the exposure of ten charged Pd^{II} centers. Consequently, the hydrophobic pocket provided by tube complex **13** is capable of efficient hydrophobic binding of organic guests, which enables the examination of biding ability and dynamic behavior toward organic compounds. For tubular assemblies developed by using the motifs in Figs. 1a–1c, the selective inclusion and specific transportation of aqueous small molecules and ions within their hydrophilic channels and pores have been discussed.

To understand the guest motion in the tube, the formation of nanotube **13** was studied by employing sodium biphenylcarboxylate (**14**) as an asymmetrical template molecule, which stayed at a fixed position or only shuttled inside the tube at room temperature, desymmetrizing the host framework.[40] At high temperature, the guest could exit from the tube, making both ends of the host equivalent. The dynamic movements of the guest molecules can occur via two possible pathways. In case of $[G]/[H] < 1$, guest molecules self-dissociate via an empty intermediate (S_N1-like pathway, Scheme 2a). When $[G]/[H] > 1$, the guest can be replaced by the second guest via S_N2-like pathway (Scheme 2b). The S_N2-like displacement is accelerated with an increase in the guest concentration. Therefore, the coalescence temperature gradually decreases upon the addition of more guest. The preferential binding of anionic guest **14** over a neutral guest, 4-methylbiphenyl, was shown by a guest-exchange experiment. Again, the desymmetrization of the host framework of complex **13** was observed showing that this guest was also trapped in the tube at room temperature. Upon the addition of **14** to this solution, however, 4-methylbiphenyl was immediately replaced by **14**. This result suggests that, in addition to the aromatic interactions, efficient electrostatic interaction between the tube and the template is also particularly important for the host–guest complexation.

Stabilization of a Nanotube by Covalent Link. When the template molecule was removed, nanotube **13** immediately

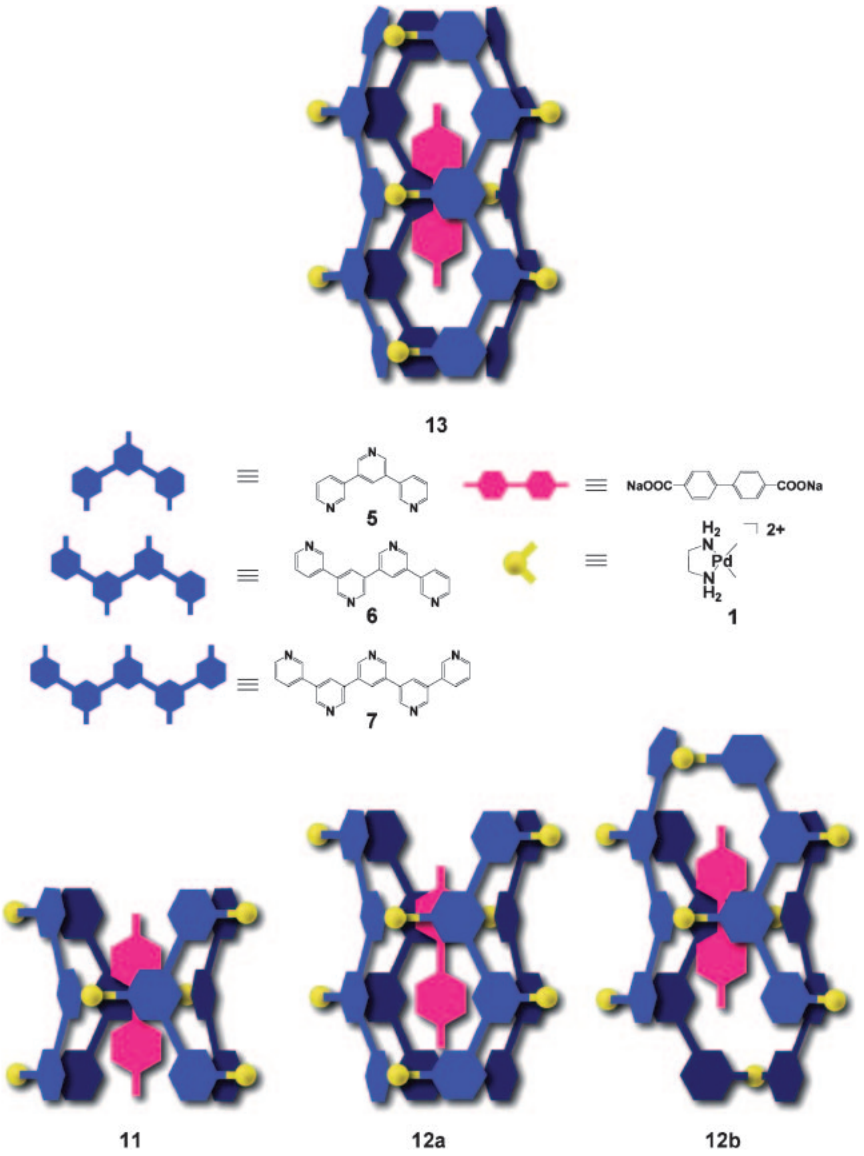
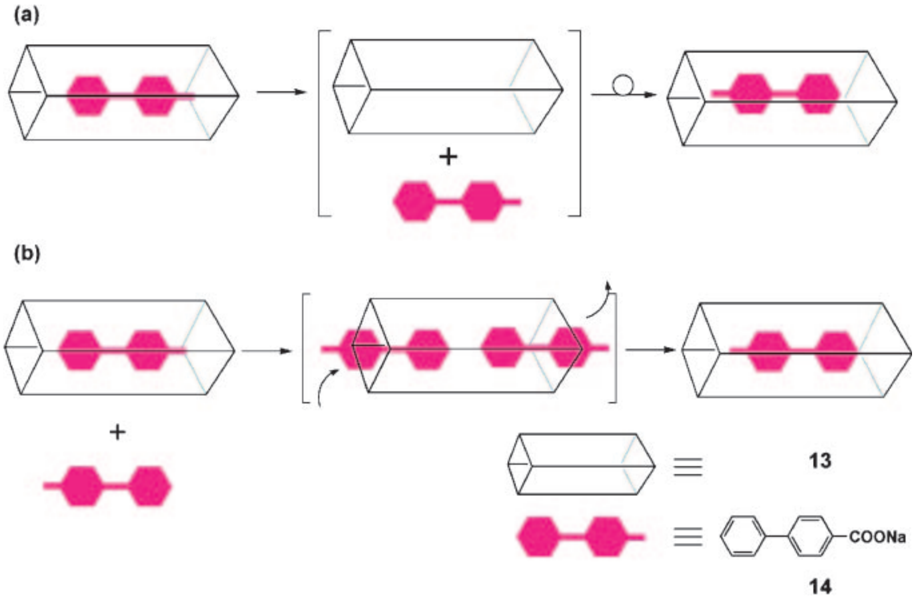


Fig. 4. Schematic representation of the structure of **11**, **12a**, **12b**, and **13**.

collapsed, indicating that the stability of the tube was due not only to the cooperation of the Pd–N bonds but also to the nonbonded interactions between the tube and the template. Therefore, we designed more stable tubes, which do not collapse even in the absence of guests. A hexapyridine ligand (**8**), in which two tris(3,5-pyridine) units are covalently linked by an alkyl (butyl) spacer, was synthesized to make the tube structure more stable. Thus, the assembly of a stable nanotube with an empty cavity (**15**) was accomplished by simply mixing [enPd(NO_3)$_2$] and ligand **8** without employing any template molecules (Fig. 5).[41] Due to the flexibility of the alkyl linker, the ligand adopted a U-shaped conformation that led to intramolecular coordination with the Pd^{II} building block. The size and the shape of nanotube **15** were almost the same as those of **11**. Nanotube **15** encapsulated aliphatic guests, which did not induce the assembly of **11**, because of insufficient stabilization. Guest encapsulation was also observed with similar aliphatic molecules, such as cyclohexane and octane. The lengths of host and guest should be compatible, since decane and dodecane were not accommodated, showing that nanotube **15** can discriminate the chain length of linear alkanes.

A 3.5-nm Nanotube. To construct a long coordination nanotube, we designed molecular tape **9**, in which two tris(3,5-pyridine) units are connected by a rigid biphenyl group in order to replace of a flexible alkyl group to avoid unfavorable intramolecular coordination. The self-assembly of a 3.5-nm nanotube (**16**) was achieved by using a 3.0-nm strand molecule (**17**) as a template (Fig. 6).[42] The length of tubular structure, determined by X-ray analysis, was quite long, meaning that this is the longest framework among structurally defined tubular host molecules reported so far (Fig. 7). Each ligand adopted the most extended conformation, whereas the tube framework was slightly helicated. Within the cavity of tube complex, two anthracene moieties of **17** are gripped by four tris(3,5-pyridine) units that are held together by six Pd^{II} ions via π–π stacking and CH–π contact. In the presence of another linear molecule (**18**), in which two biphenyl units are covalently linked by a penta(ethylene glycol) spacer, the high yield



Scheme 2. Schematic representation of the mechanism of guest exchange at (a) [H] + [G] = 1 + 1 and (b) [H] + [G] = 1 + 2.

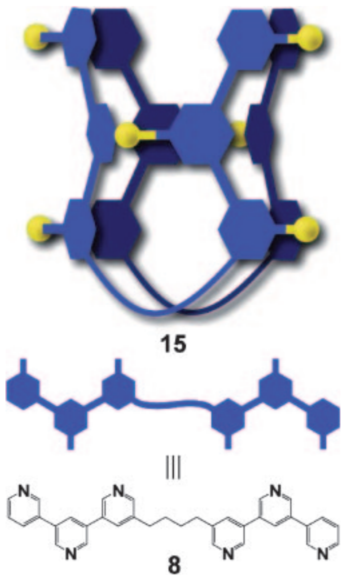


Fig. 5. Schematic representation of the structure of **15**.

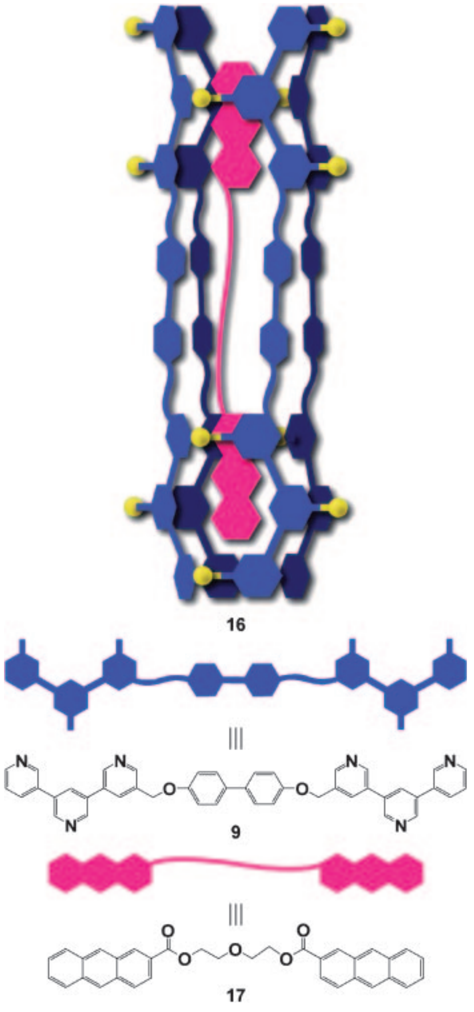


Fig. 6. Schematic representation of the structure of **16**.

formation of nanotube **16′** was also observed. After removal of the guest **18**, the framework remained unchanged at room temperature, in sharp contrast to the behavior of shorter tubes **11–13**, which immediately collapsed when the template was removed. Empty tube **16** had considerable kinetic stability due to the 24 Pd^{II}–pyridine interactions. The empty tube is capable of binding other molecules in the cavity. In addition to reentrance of long guests **17** and **18** into empty cavity, nanotube **16″**, which accommodates two molecules of biphenylcarboxylate as a small rod-like guest, was formed; however, it only formed via complex **16′**. This fact clearly demonstrated the "chaperoning effect" of **18** in the self-assembly of kinetically stabilized empty tube **16** and **16″**.[43]

Dynamic Assembly of End-Capped and Open Tubes. A mono end-capped tube bearing a specific inner cavity is ex-

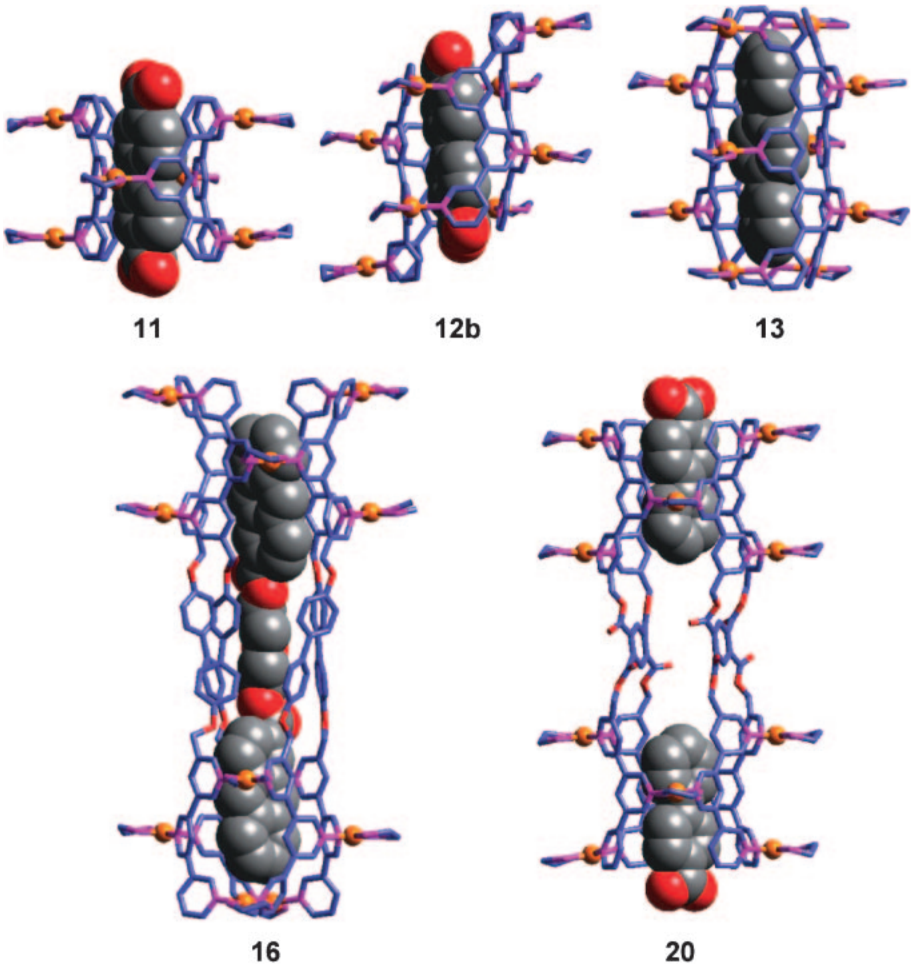
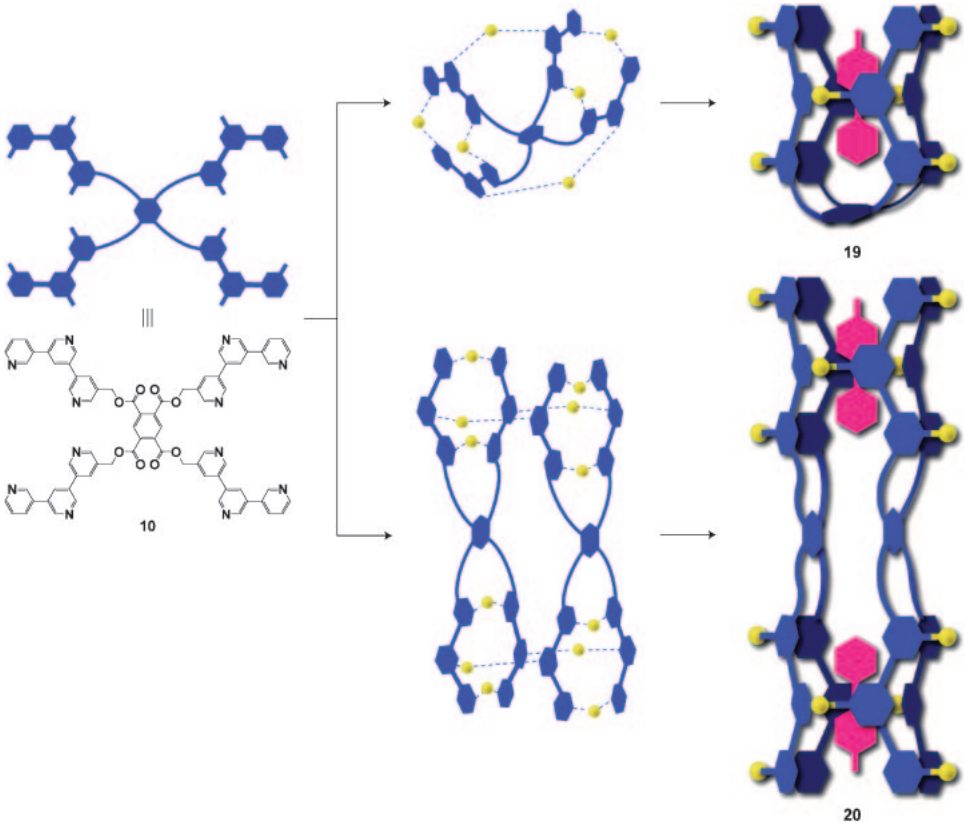


Fig. 7. X-ray crystallographic structures of self-assembled coordination nanotubes discussed in this account.

pected to discriminate the both ends of symmetrical rod-like molecules, namely, one end accommodated at the bottom of the tube should show different properties from another end. Thus, a dodecadentate ligand (**10**) was synthesized by incorporating four tripyridine podands on a benzenetetracarboxylate platform. Due to the template effect of symmetrical 4,4′-ditolyl and asymmetrical sodium biphenylcarboxylate **14**, the quantitative formation of **10** into end-capped tube (**19**) was accomplished upon treatment with [enPd$(NO_3)_2$] (Scheme 3).[44] The two methyl groups of 4,4′-ditolyl accommodated in **19** were clearly observed at δ -0.25 and 1.83. The significant upfield shift of one of the methyl groups suggests that this methyl is located on the benzene scaffold and surrounded by four pyridine rings. Asymmetric guests **14** was efficiently accommodated in a unidirectional fashion. Only one isomer, in which the hydrophobic biphenyl group was included deeply within the tube and the hydrophilic carboxylate group was exposed outside, was formed. Interestingly, disodium 4,4′-biphenylenedicarboxylate, which was bound in open tube **11**, was not included in **19**, showing that the end-capped site of **19** provides an efficient hydrophobic pocket that cannot bind the hydrophilic portion of the guest. Nanotube **19**, formed via intramolecular coordination, is in fact a kinetically favored structure. In addition to nanotube **19**, we obtained a double open tube (**20**), in which ligand **10** adopts an extended conformation. Nanotube **20** was observed only at higher concentrations as a minor component but could be isolated in a pure form through slow crystallization. X-ray crystallographic analysis showed that nanotube **20** was a double open tube, which consisted of two molecules of ligand **10** held together by twelve Pd^{II} ions (Fig. 7). Open tube **20** accommodated two molecules of biphenylcarboxylate, each of which was oriented so that its carboxylate group was exposed outside the tube. Interestingly, once isolated, **20** did not convert to **19** at lower concentrations, which indicates that both structures are kinetically trapped at local minima of the potential surface.[45] It is noteworthy that two different assemblies (i.e., **19** and **20**) were obtained under a set of identical thermodynamic conditions; the difference was only whether the assembly process involved crystallization or not.

Conclusion

This article demonstrated that the simple combination of palladium's square-planar geometry (90° coordination angle) with pyridine-based rectangular ligands leads to the quantitative self-assembly of discrete tubular structures with nanometer-order lengths. In particular, an efficient approach to tube molecules was developed by exploiting the concept of molecular paneling. This concept has some advantages in the design, preparation and functionalization of tubular structures. The



Scheme 3. Schematic representation for the molecular paneling of **10** into **19** and **20**.

facile and very efficient construction of a variety of tube molecules (shapes, sizes, etc.) can be accomplished by simply mixing the components in water, and the target molecules are isolated in quantitative yields under mild conditions. Finite one-dimensional cavities and pores created in the tube molecules are in general very large, and novel binding properties for rod-like organic molecules as well as specific transportation are anticipated.

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