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Chemically Responsive Supramolecular Structural Change of Pillar[5]arene Nanotubes

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We prepared organo-nanotubes from pillar[5]arene molecules via intermolecular hydrogen bonding between the molecules. In the absence of guest molecules, formation of the nanotubes was observed simply by heating a solution of pillar[5]arene in a suitable solvent. In contrast, formation of the nanotubes did not occur in the presence of guest molecules.

The construction of supramolecular architectures is currently a subject of great interest in chemistry, biology, physics, and materials science.[1–17] For this purpose, self-assembly of new angstrom- and nanoscale building blocks is a useful approach. Supramolecular architectures constructed from these building blocks have a close relationship with their shapes. For example, disk-shaped molecules such as triphenylene, coronene, porphyrin, and metallophthalocyanine form nanoscale wire structures by π–π stacking.[11] The self-assembly of nanoscale ring-shaped molecules has also been of interest. Since calixarenes are vase-shaped nanostructures, self-assembly of two calixarene molecules affords a molecular capsule by facing the upper rims of the calixarene molecules toward each other.[12] Kim et al. reported that four calixarenes assemblies led to nanowire structure.[13] Supramolecular self-assembled architectures of cyclodextrins have also been investigated. Depending on conditions for self-assembly of cyclodextrins, gelation took place by formation of a network or to cubic structures.[14,15] Moreover, dynamic change in the supramolecular architecture in response to stimuli such as pH, temperature, redox state, light, and chemicals is also a challenge and opens the way for new applications such as storage and sensors.[16,17]

We synthesized a new type of macrocyclic host for the first time and named it "pillar[5]arene" (Figure 1a).[18–26] Pillar[5]arene is a cyclic pentamer composed of phenolic units, and its composition is analogous to that of typical calixarenes.[27–29] However, because the repeating units are connected by methylene bridges at the *para*-position, pillar[5]arene has a unique symmetric pillar architecture that is quite different from the basket-shaped structure of the *meta*-bridged calixarenes. Due to the pillar-shape structure, self-assembly of pillar[5]arene molecules should afford tubular architectures. Accordingly, in this communication we report formation of a nanotube structure by self-assembly of pillar[5]arene molecules. Moreover, based on host–guest properties of pillar[5]arene, a chemically responsive supramolecular structural change of the pillar[5]arene nanotubes is demonstrated.

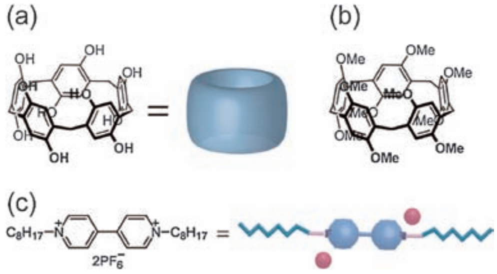

Figure 1. Chemical structures of (a) pillar[5]arene, (b) permethylated pillar[5]arene, and (c) C8Bpy.

Intermolecular hydrogen bonding between pillar[5]arene molecules was employed to form the self-assembled tubular structures. Hydrogen bonding is strong in nonpolar solvents but weak in polar solvents; however, pillar[5]arene is soluble in polar solvents such as acetone, methanol, and DMSO but insoluble in nonpolar solvents such as chloroform and hexane. Consequently, in the first step pillar[5]arene was dissolved (20 mM) in acetone (1 mL) to form the intermolecular hydrogen bonds, the nonpolar poor solvent chloroform (1 mL) was added to the mixture. At this stage the solution was transparent. To enhance intermolecular hydrogen bonding, the proportion of chloroform in the mixture was increased by heating. Since the boiling point of acetone (56 °C) was lower than that of chloroform (61 °C), acetone evaporated more rapidly than chloroform, the proportion of chloroform relative to acetone increased in the solution, and a wisteria violet precipitate appeared.

The structure of the precipitate was investigated by scanning electron microscopy (SEM) (Figure 2a). Uniform tubular structures were observed with average width of about 150 nm. Figure 2a (inset) shows the ends of the nanotubes in a nanotube bundle. Figure 2b shows a transmission electron microscopy (TEM) image of the edge of a nanotube. Lines were observed along the long axis of the nanotube, as indicated by the white arrow, confirming formation of a bundle of pillar[5]arene molecular tubes.

We investigated the role of the cosolvent chloroform in formation of the nanotubes. In the absence of cosolvent chloroform, even on heating, a precipitate was not formed and SEM image of the residue after solvent evaporation did not show tubular structures (Figure 2c). These observations indicate that the presence of chloroform is necessary for formation of the tubular-shaped architectures. Formation of the tubes was examined using permethylated pillar[5]arene (Figure 1b). Even in the same mixed solvent (acetone:chloroform = 1:1), a precipitate was not observed. It was thus found that intermolecular hydrogen bonding between OH groups of pillar[5]arene is the driving force for formation of the tubular-shaped structures.

Pillar[5]arene is able to capture electron-accepting octyl viologen (C8Bpy, Figure 1c) as a guest,[8,21] and we investigated the effect of inclusion of C8Bpy in the pillar[5]arene cavity on self-assembly of pillar[5]arene. To a solution of pillar[5]arene (10 mM) in the mixed solvent (acetone:chloroform = 1:1), C8Bpy (10 mM) was added. Formation of the pillar[5]arene–

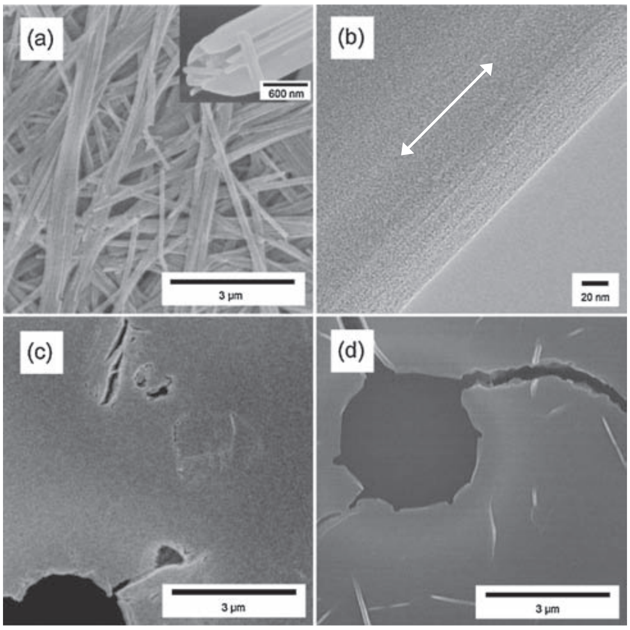

Figure 2. (a) SEM image of nanotubes of pillar[5]arene (Inset: the end of the nanotube prepared from mixed solvent). (b) TEM image of the edge of the nanotube. SEM images of (c) pillar[5]arene from acetone solution without chloroform and (d) the complex between pillar[5]arene and C8Bpy from the mixed solvent.

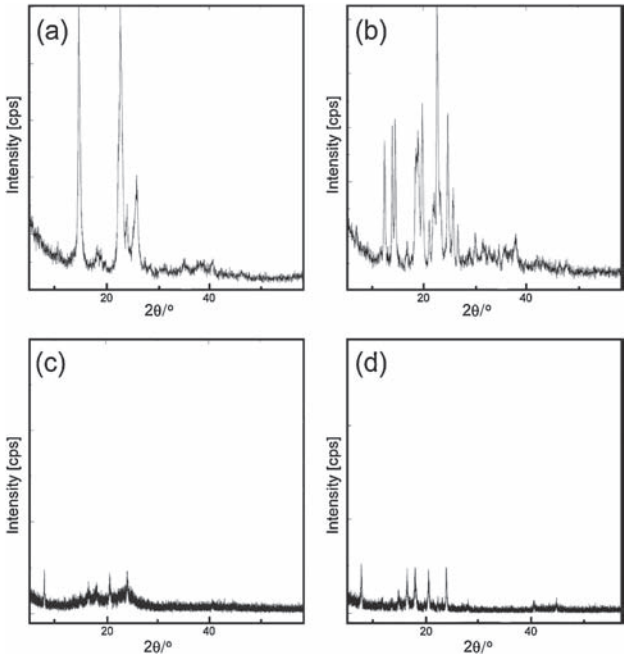

Figure 3. XRD patterns of (a) pillar[5]arene nanotube, (b) crystal of pillar[5]arene from acetone solution, (c) the complex between pillar[5]arene and C8Bpy, and (d) C8Bpy.

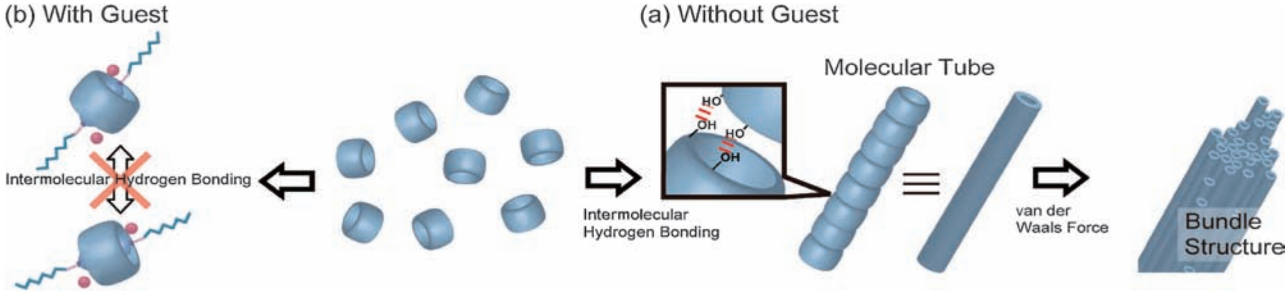

Figure 4. Proposed chemically responsive supramolecular structural change of pillar[5]arene nanotubes.

C8Bpy complex in the mixed solvent was confirmed by ^{1}H NMR measurements (ESI[32]). In a similar manner to the procedure for formation of the nanotubes, solution was heated, but the residue did not show characteristic tubular-shaped structures (Figure 2d), showing that inclusion of C8Bpy into the pillar[5]arene cavity inhibited self-assembly of pillar[5]arene.

Figure 3 shows X-ray diffraction (XRD) patterns. Simple diffraction patterns were observed in the nanotubes (Figure 3a), whereas complicated peaks were observed for the residue from the solution of pillar[5]arene in acetone (Figure 3b). These observations indicate that pillar[5]arene molecules formed a regular arrangement in the nanotube structure. Weak diffraction patterns were observed for the solid complex between pillar[5]-arene and C8Bpy (Figure 3c). Similar diffraction patterns were observed in C8Bpy (Figure 3d); thus, the patterns in the complex are ascribed to C8Bpy. Inclusion of C8Bpy in the pillar[5]arene cavity apparently disturbed the arrangement of the pillar[5]arene molecules.

From these results, the chemically responsive self-assembly of pillar[5]arene shown in Figure 4 is proposed. In the absence of C8Bpy (Figure 4a), one-dimensional molecular tubes were formed by intermolecular hydrogen bonding. These molecular tubes subsequently assembled to form a bundle by van der Waals interaction, similar to the behavior of carbon nanotubes.[30,31] When C8Bpy (Figure 4b) was present as an inclusion in the pillar[5]arene cavity, intermolecular hydrogen bonding was inhibited and tubular structures were not formed.

In conclusion, a pillar[5]arene-based nanotubular structure was prepared by a facile heating process. Surprisingly, addition of the guest molecule C8Bpy inhibited nanotube formation, and it is interesting to note that inclusion of C8Bpy into the pillar[5]arene cavity drastically changes the tubular assembly of pillar[5]arene. Thus, microscale molecular recognition events are reflected in the macromolecular self-assembly architectures of pillar[5]arene. This suggests that the length and diameter of the nanotubes may be controllable by tuning the amount of guest additive. Since the process of formation of the pillar[5]arene nanotubes is very straightforward, large scale synthesis of the pillar[5]arene nanotubes is possible. We anticipate that as for carbon nanotubes the pillar[5]arene nanotubes will be applied for storage, reaction media, filler for hybrid materials, and starting materials for nanoscale carbon fibers.

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