One-, Two-, and Three-Dimensional Supramolecular Assemblies Based on Tubular and Regular Polygonal Structures of Pillar\([n]\)arenes

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Pillar\([n]\)arenes, which were first reported by our group in 2008, are promising macrocyclic compounds in supramolecular chemistry. The simple, tubular, and highly symmetrical shape of pillar\([n]\)arenes has allowed various supramolecular assemblies with well-defined structures to be constructed. The pillar-shaped structures of pillar\([n]\)arenes are suitable for surface modification and formation of one-dimensional (1D) channels. The regular polygonal prism shape of organized pillar\([n]\)arenes contributes to the construction of highly assembled structures such as two-dimensional (2D) sheets and three-dimensional (3D) spheres. In this minireview, we describe supramolecular assemblies with various dimensions. First, we discuss 1D supramolecular assemblies based on tubular structures of pillar\([n]\)arenes. Second, 2D supramolecular sheet formation based on regular polygonal structures is described. Finally, 3D supramolecular assemblies such as vesicles and 3D frameworks constructed from pillar\([n]\)arenes are discussed.

Keywords: macrocyclic compounds, supramolecular assembly, host-guest interaction

Introduction

Macrocyclic compounds, including crown ethers,\(^1\) cyclodextrins,\(^2,4\) calix\([n]\)arenes,\(^5\) and cucurbit\([n]\)urils,\(^6,8\) are important building blocks for the construction of supramolecular assemblies because they are highly symmetrical at the nanometer scale. Macrocyclic compounds can capture guest molecules in their cavities, and thus, supramolecular assemblies constructed from macrocyclic compounds can bind guest molecules at multiple points. Formation of continuous porous structures via self-assembly of macrocyclic compounds can not only result in cooperative binding of guest molecules, but also bring about new advantages, which are different from simple 1:1 host-guest complex formation in solution. For instance, one-dimensional (1D) channels constructed by connecting macrocyclic compounds may be employed as transmembrane channels for water, ions, or neutral...
small molecules, taking advantage of the continuous tubular/hollow structures. Moreover, higher-dimensional \([i.e., \text{two-dimensional (2D) and three-dimensional (3D)}]\) assemblies can provide new voids in the networks and spaces, which will not only help to construct complex structures, but also provide new binding sites for new guest molecules.

Among all macrocyclic compounds, those possessing a highly symmetrical property along the transverse direction are naturally perfect building blocks of \(1\text{D channels}\) and \(2\text{D and 3D self-assembly structures}\), owing to the possibility and potential of lateral interaction. In particular, macrocyclic molecules owning regular polygonal structures can perform close packing laterally, which will afford regular dense \(2\text{D structures}\), whereas the assembly of pentagonal structures results in irregular structures.

Pillar\([n]\)arenes are composed of electron-donating \(1,4\text{-dialkoxybenzene units}\). Therefore, their cavities are electron-rich spaces. Because the cavities of pillar\([n]\)arenes are electron rich, molecules with cationic moieties and electron-withdrawing groups are good guest molecules. The cavity sizes of pillar\([5]\)arenes and pillar\([6]\)arenes are approximately 4.7 and 6.7 Å, respectively. Therefore, linear alkanes with cationic groups, such as pyridinium and trimethyl ammonium cations, and electron-withdrawing groups, such as cyano, halogen, and triazole groups, are good guest molecules for pillar\([5]\)arenes. In particular, linear C4 alkanes possessing electron-withdrawing groups at both ends form very stable host–guest complexes with pillar\([5]\)arenes because the C4 length fits well into the height of pillar\([5]\)arenes (Figure 1e). Bulky hydrocarbons with cationic groups are good guest molecules for pillar\([6]\)arenes (Figure 1f).

In this minireview, we describe supramolecular assemblies with various dimensions. First, we discuss \(1\text{D supramolecular assemblies based on tubular structures of pillar}\([n]\)arenes\). Second, \(2\text{D supramolecular sheet formation based on regular polygonal structures is described}\). Finally, \(3\text{D supramolecular assemblies such as vesicles and 3D frameworks are discussed}\).

1D Supramolecular Assemblies

Pillar\([n]\)arene monolayer formation on surfaces

The installation of macrocyclic molecules on surfaces can lead to the creation of new materials owing to the host–guest properties of the installed macrocycles. Applying a force in one direction will lead to a specific response in that dimension. The highly symmetrical pillar-shaped structures of pillar\([n]\)arenes are more suitable for surface modification than nonsymmetrical macrocyclic compounds such as calix\([n]\)arenes and cyclodextrins. Yang and co-workers reported the
formation of a pillar[n]arene monolayer on a silica support. First, tetrachlorosilane (SiCl₄) was reacted with silanol groups on the silica surface to introduce reactive O-SiCl₃ groups. Reaction of phenolic groups on both rims of pillar[n]arenes (Figure 2; P[5]₁ and P[6]₁) with the O-SiCl₃ groups enabled immobilization of pillar[n]arenes on the silica supports through Si-O-C linkages.

The pillar[n]arene-immobilized silica took up paraquat, which indicated that the pillar[n]arene cavities on the surface worked as recognition sites for paraquat. The pillar[n]arene-modified silica showed higher adsorption ability than that of the pillar[5]arene-modified silica. This is related to the different binding mode depending on the cavity size of the pillar[n]arene.

Li and co-workers constructed a pillar[n]arene monolayer via a copper(I)-catalyzed alkynyl-azole cycloaddition (CuAAC) “click” reaction for controlled dynamic self-assembly of paraquat droplets. A pillar[5]arene with five alkynyl groups on one rim and five n-butyl groups on the other rim (Figure 3; P[5]₂) was synthesized. A silicon surface was functionalized with azide groups.

The same group formed pillar[5]arene monolayers on the surface of a nanochannel using host–guest interactions, providing a Hg²⁺ responsive nanochannel (Figure 4a). First, 1,6-hexanediamine molecules, which are good guests for pillar[5]arenes, were immobilized on a surface. The surface of the nanochannel was positively charged, so potassium cation transport was suppressed (in the “off” state) even when an electrical voltage was applied. The surface charge was changed from positive to negative by host–guest complexation between 1,6-hexanediamine guest molecules and water-soluble mercaptoacetic acid-pillar[5]arene host molecules (P[5]₃).

In this state (denoted as the “on” state), potassium cation transport was enabled. After immersing the film in a solution containing Hg²⁺, the potassium cation transport changed to the “off” state because Hg²⁺ competed with 1,6-hexanediamine to form complexes with P[5]₃. The water-soluble potassium cation transport was maintained in the “off” state by exposure to electrolytes containing other metal cations because P[5]₃ only forms complexes with Hg²⁺, not with other metal cations. The same group reported a photoregulated ion nanochannel using a photoresponsive host–guest system (Figure 4b). First, a positively charged trans-azobenzene-modified nanochannel was prepared. In this state (denoted as the “off” state), potassium cation transport was suppressed because of the positive surface. Ultraviolet (UV) light irradiation converted trans-azobenzene to cis-azobenzene. In the cis state, potassium cation transport was also suppressed because the surface was still positively charged. A photoresponsive host–guest system was then used to construct photoregulated ion nanochannels as follows. Pillar[6]arenes form host–guest complexes with trans-azobenzene guest molecules. Thus, formation of host–guest complexes of the catonic trans-azobenzene guest molecules on the surface and water-soluble anionic pillar[6]arene (P[6]₂) caused the CuAAC reaction between the azide groups on the surface and five alkynyl groups of P[5]₂ afforded a pillar[5]arene monolayer film. There was no clear difference between the static contact angles of pure water and the paraquat droplets on the P[5]₂-modified surface. In contrast, the dynamic contact angles of pure water and the paraquat droplets on the modified surface exhibited clear differences: the sliding angles using pure water and paraquat droplets were about 7° and 56°, respectively. The sliding angle using droplets containing other viologen salts and 4,4′-dipyridyl was almost the same as that using a pure water droplet because the host pillar[5]arene formed the most stable host–guest complex with paraquat. Pure water and droplets containing other viologen salts and 4,4′-dipyridyl slid quickly off a surface tilted to 45°. Conversely, the paraquat droplet stayed on the surface because of the host–guest interaction between the pillar[5]arenes on the surface and paraquat-related derivatives in the paraquat droplet.

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surface charge to change from positive to negative, promoting potassium cation transport (denoted as the “on” state). Under UV light irradiation, trans-azobenzene isomerized to cis-azobenzene, which induced the dissociation of the host-guest complex because of the size mismatch between the pillar[6]arene cavity and cis-azo-benzene. Therefore, positively charged cis-azobenzene species were exposed to the surface, and the potassium cation transport changed from the “on” state to the “off” state. The photoinduced trans–cis isomerization process was completely reversible by alternating UV and visible light irradiation, allowing potassium cation transport to be photoregulated. Based on a temperature-responsive host-guest system, a temperature-regulated ion nanochannel was constructed (Figure 4c). The host-guest interaction between an ionic liquid guest and water-soluble anionic pillar[5]arene host P[5]4 was thermally responsive. The complexion occurred at 25 °C, but dissociation took place upon heating to 55 °C. By immobilization of the temperature-responsive host-guest system, a temperature-regulated ion nanochannel was constructed. At 25 °C, the potassium cation transport was facilitated (in the “on” state) because the surface possessed anionic charges resulting from the host-guest complexion. During heating at 55 °C, the potassium cation transport was switched to the “off” state because the surface was positively charged after the dissociation of the complex. This temperature-regulated ion–channel system also displayed reversible cation transport behavior.

**Pillar[5]arene multilayer formation on surfaces**

The tubular structure of pillar[n]arenes and the presence of functional groups on both rims make it suitable for the construction of 1D tubular assemblies on surfaces via a layer-by-layer strategy. Our group successfully constructed multilayer pillar[5]arene films by alternating adsorption of a pillar[5]arene with 10 cationic groups (Figure 5a; P[5]5) and a pillar[5]arene with 10 anionic groups (P[5]4). The multilayer film contained the original pores of the pillar[5]arene cavities, allowing the film to selectively take up guest molecules. The cavity size of pillar[5]arene is ca. 4.7 Å, which is larger than the size of para-dinitrobenzene (DNB) (ca. 4.3 Å), but smaller than the sizes of ortho-DNB (ca. 5.9 Å) and meta-DNB (ca. 5.9 Å). Thus, the film took up para-DNB, but did not take up ortho- or meta-DNB.
By introducing a photosresponsive azobenzene cap on the pore outlets, we also regulated access of the guest molecules using photostimulation (Figure 5b). A pillar[5]arene bearing nine cationic groups and one azobenzene group (P[5]6) was synthesized. P[5]6 was immobilized on a surface with anionic charges, produced by the alternating adsorption of cationic and anionic pillar[5]arenes P[5]4 and P[5]5 on the surface. In the trans state, para-DNB guest molecules can access the tubular assemblies of pillar[5]arenes on the surface. Photoisomerization of the azobenzene group from trans to cis form was induced by UV light irradiation. In the cis state, access of para-DNB was completely inhibited. After uptake of the para-DNB guest molecules, 1,4-dicyanobutane was added to the solution as a competitive guest. In the trans state, release of para-DNB was observed. In contrast, para-DNB located inside the channels after photoconversion to the cis form was not released. Access of para-DNB guest molecules was completely regulated by light using the azobenzene gates.

Yang and co-workers reported the electrochemical recognition of guest molecules using multilayer pillar[5]arene films (Figure 5c). To achieve electrochemical recognition, multilayer films were constructed on a glassy carbon electrode (GCE). Various redox reactions were carried out using the GCE coated with the...
multilayer film. When ortho-nitrophenol was added, the intensity of the redox peak corresponding to the reduction of nitryl groups decreased as the number of multilayers increased because ortho-nitrophenol is not a good guest for pillar[5]arene and thus could not access the GCE surface as the pillar[5]arene film became thicker. In contrast, the intensities of the redox peaks related to the reduction reactions of para- and meta-nitrophenols increased with the number of multilayers because para- and meta-nitrophenol guests can enter the cavity of pillar[5]arene. The pillar[5]arene multilayer-immobilized GCE was also used for the chiral recognition of D/L-tryptophan. No chiral recognition ability was found for a bare GCE. However, a considerable difference between the peak currents of D- and L-tryptophan was observed as the number of pillar[5]arene multilayers increased. Pillar[5]arene forms a more stable host-guest complex with L-tryptophan than with D-tryptophan. Thus, L-tryptophan could access the 1D channels of the multilayer more readily than D-tryptophan.

Wang and co-workers constructed photoregulated 1D channels using pillar[n]arene-based azobenzene liquid crystals. A pillar[5]arene bearing 10 mesogenic azobenzene groups was synthesized (Figure 6).

Casting a solution of pillar[5]arene onto a quartz substrate formed a film with random arrangement. Irradiation with 450 nm visible light or annealing at 100 °C caused the azobenzene groups to isomerize from trans to cis form. The isomerization destroyed the homeotropic arrangement of the bent core of azobenzene. Exposure to 450 nm visible light triggered photoisomerization from cis- to trans-azobenzene, converting the film back to a random orientation. This process was completely reversible.

1D tubular arrays
The most direct strategy to construct 1D tubular structures is to connect both rims of pillar[n]arenes through a covalent bond. Recently, 1D tubular arrays have been synthesized by incorporating pillar[5]arenes into rigid polymer main chains. Stoddart and co-workers reported the formation of 1D pillar[5]arene arrays by polymerization of an AB-type monomer (Figure 7a). Müllen and co-workers synthesized a rod-like conjugated polymer by copolymerization of a pillar[5]arene containing two ethynyl groups with a diiodoaromatic monomer (Figure 7b). Our group synthesized rod-like π-conjugated polymers containing pillar[5]arenes in the main chain by Pd-catalyzed copolymerization of pillar[5]arene ditriflate and 4,4′-biphenyldiboronic acid (Figure 7c). These rod-like π-conjugated polymers containing pillar[5]arenes showed fluorescence in solution and the solid state.

Coskun and co-workers synthesized a π-conjugated microporous polymer incorporating pillar[5]arenes by a Pd-catalyzed Sonogashira–Hagihara coupling reaction of pillar[5]arene bearing 10 triflate groups with 1,4-diethynylbenzene. The pillar[5]arene-based π-conjugated microporous polymer was amorphous but possessed high thermal stability up to 350 °C in air and a high surface area of up to 400 m²/g. Furthermore, the polymer was able to separate methane from a simulated natural gas mixture (methane/propane = 9:1) at 25 °C.
because the polymer showed a high affinity for propane owing to the size match between the kinetic diameter of propane and the cavity of the pillar[5]arene.

2D Supramolecular Assemblies

2D sheet formation induced by intermolecular charge-transfer and π-π interactions of pillar[6]arenes

As previously mentioned, the aromatic ring-rich and regular polygonal structure of pillar[n]arenes makes them ideal building elements of 2D assemblies via charge-transfer and π-π interactions in the lateral direction, which leads to the formation of lamellar structures. In particular, the hexagonal symmetry of pillar[6]arene can even provide long-range ordered structures owing to the dense packing between adjacent pillar structures. Our group reported the formation of a porous carbon material PC[6] with controlled angstrom-level pore sizes using a two-step strategy in which the charge-transfer (CT) interaction between hydroquinone and benzoquinone (quinhydrone) was the driving force for the original assembly in the first step (Figure 8a).34 By treatment of a homogeneous solution of pillar[6]arene P[6]1 with oxidant, some hydroquinone units of P[6]1 were oxidized to benzoquinones. As a result of the ready formation of intermolecular CT complexes, 2D supramolecular assemblies (CT[6]) with a side-by-side arrangement of P[6]1 molecules were immediately afforded. The hexagonal symmetric structure of P[6]1 led to a CT[6] assembly consisting of 2D porous sheets with hexagonal packing of P[6]1 (Figure 8b). The powder X-ray diffraction (PXRD) pattern of CT[6] showed diffraction peaks consistent with the hexagonal phase with a lattice parameter a of 8.32 Å. In contrast, the assembly of P[5]1 obtained by oxidation was amorphous because of the lack of long-range order in the assembly of molecules with pentagonal symmetry. The pore size of CT[6] was almost the same as the cavity size of P[6]1, which suggested the dense packing of P[6]1 within the 2D supramolecular layer. The 2D porous sheets of CT[6] were easily carbonized at 900 °C for 2 h under an inert gas atmosphere to afford porous carbon materials PC[6] with the same pore size and at char yield of 54%.

Thereafter, we realized controlled synthesis of hexagonal structures on an electrode surface via electrochemical oxidation of the hydroquinone units of P[6]1.35 Cyclic voltammetry measurements of P[6]1 were carried out using an indium-tin-oxide (ITO) working electrode. A thin film of white deposits of the P[6]1 CT complex was observed on the electrode after repeated potential
sweep cycles. After 100 cycles, dense cylindrical deposits were observed on the surface of the electrode by scanning electron microscopy measurements. The diameter and length of the cylinders formed by potentiostatic electrolysis on an ITO working electrode at 50 mC depended on the applied potential. For example, fine hexagonal cylindrical structures with a uniform diameter of ca. 1.6 mm were obtained by electrolysis at 1.0 V.

Figure 8 | (a) 2D supramolecular polymerization by oxidation of hydroquinone units, and porous carbon (PC[6]) prepared by carbonization of CT[6]. (b) Hexagonal packing of CT[6].

Figure 9 | Construction of 2D hybrid nanosheets consisting of P[6]3 and POM.
Liu and co-workers prepared 2D organic–inorganic nanosheets via self-assembly of an imidazolium-functionalized pillar[6]arene (P[6]3) and polyoxometalate (POM), as shown in Figure 9.36

Upon mixing aqueous solutions of P[6]3 and POM at room temperature, the supramolecular assembly was observed as a cloudy suspension, which was confirmed by transmission electron microscopy as 2D nanosheets with curled and folded edges. PXRD diffraction measurements indicated that the thickness of these sheets was around 1.03 nm, which was consistent with a single-layer 2D structure because the diameter of a POM molecule is around 1 nm. The supramolecular assembly was found to be able to enhance the efficiency of dye degradation. In contrast, mixing P1, the building block of P[6]3, with POM did not provide ordered assemblies or enhancement of dye degradation, which suggested that the macrocyclic cavity of P[6]3 played an important role in building the 2D nanosheet structure.

2D supramolecular assemblies formed by interactions of side chains

Compared with the dense structures constructed from the lateral packing of pillar[n]arenes through interactions between the hard-core parts, the connections on both rims can provide looser assembly. Taking advantage of the recognition ability of the cavity of pillar[n]arenes in regard to linear alkyl chains, the installation of aliphatic groups on the rims of pillar[n]arenes can form inclusive networks. Lin, Liu, Wei, and co-workers reported a 2D supramolecular organic framework based on the host–guest interactions between a bis-thioacetylhydrazine functionalized pillar[5]arene (Figure 10; P[5]8) and a bis-bromohexane-functionalized pillar[5]arene (P[5]9).37

By mixing the host P[5]8 and guest P[5]9 molecules in cyclohexanol, a supramolecular assembled gel with a critical gelation concentration of 47.5 mM and gel–sol transition temperature at 43–47 °C was formed. The 1H NMR titration of P[5]9 to P[5]8 and concentration-dependent 1H NMR spectra of P[5]8 revealed that the alkyl chains of P[5]9 threaded into the cavity of P[5]8 via C–H⋯π interactions, and intermolecular hydrogen bonds formed between the –NH and –C=O groups on the side chains of adjacent molecules of P[5]8. The two orthogonal interactions induced the formation of a 2D network, which then stacked into multilayered 3D structures via π–π interactions between neighboring pillar[5]arenes. This assembled material displayed excellent recyclable absorption ability for Hg2+, Cr3+, Cu2+, and Fe3+ and detection of F−, Br−, and L-cysteine because of its sensitive fluorescent response. The reason for this absorption behavior was the ability of the hydrazide groups to coordinate with the metal ions. This process could be reversed by the addition of F−, Br−, or L-cysteine because of the stronger binding ability of these anions and

Figure 10 | The chemical structures of P[5]8 and P[5]9 and a cartoon representation of the formation of their supramolecular organic framework designed for adsorption of Hg2+, Cr3+, Cu2+, and Fe3+.
sulfhydryl groups to the abovementioned metal cations than that of the supramolecular assembly.

In addition to the noncovalent interactions that can drive the supramolecular assembly of pillar[n]arene derivatives, formation of carbon metal bonds is another strategy to induce their assembly. Shi and co-workers synthesized a pillar[5]arene-based organometallic cross-linked polymer (Figure 11; P[5]-OCP) by vigorously stirring a solution of P[5]10 and Pd(OAc)2 with a 1:5 stoichiometric ratio in DMF at 110 °C under argon for 48 h.38

The obtained polymer P[5]-OCP has a 2D network structure in which every palladium center is coordinated with an average of two imidazolium groups. The Pd species in P[5]-OCP were found to be only in the +2 state. P[5]-OCP was then used as the catalyst in the Suzuki–Miyaura coupling reaction. Excellent activity and substrate scope were observed in a series of

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**Figure 11** | Fabrication of P[5]-OCP through the complexation of P[5]10 and Pd(OAc)2 and a cartoon representation of the cross-linked structure of the P[5]-OCP.

**Figure 12** | Schematic representation of (a) the conjugated macrocycle polymer (P[5]-TPE-CMP) constructed from pillar[5]arene P[5]11 and TPE and (b and c) its two-photon fluorescence-based sensing.
Suzuki–Miyaura coupling reactions even when using aryl chlorides, which display low reactivity toward most of the present heterogeneous palladium catalysts. The highly catalytic activity of P[5]-OCP was attributed to the encapsulation of the aryl halide in the cavity of P[5]10, which enhanced the interaction between the reagents and palladium.

Irreversible covalent self-assembly by copolymerizing pillar[n]arenes with small organic molecules is another efficient strategy to obtain polymers with high stability. Yang and co-workers reported a novel fluorescent conjugated macrocycle polymer (CMP) displaying two-photon fluorescence (TPF) behavior using this strategy. As illustrated in Figure 12, the CMP denoted as P[5]-TPE-CMP was synthesized by coupling the ditriolate pillar[5]arene P[5]11 with 1,1,2,2-tetrakis(4-ethynylphenyl)ethane (TPE), a moiety that displays aggregation-induced emission (AIE).

Although the cross-coupling reaction in solution produced different sizes of spherical and/or rod-like microstructures, the obtained CMP tended to polymerize into 2D porous rectangular assemblies in the first stage, because of the relatively planar and rigid structure of TPE. P[5]-TPE-CMP showed TPF displaying a consistent emission wavelength at 537 nm upon excitation at 300–400 nm or 650–800 nm. Moreover, P[5]-TPE-CMP exhibited a highly selective sensing capability toward Fe³⁺ and 4-aminoazobenzene out of 39 different cations and a group of common organic compounds. Fe³⁺ and 4-aminoazobenzene quenched the fluorescence intensity of P[5]-TPE-CMP by 92.9% and 98.5%, respectively. When P[5]11 was replaced by 1,4-diiodobenzene or TPE by the non-AIE-active compound 2,4,6-tris(4-ethynylphenyl)-1,3,5-triazine in the polymerization reaction, no TPF (in the former case) or fluorescence (in the latter case) was observed for the obtained polymers. These results suggested that both the pillar[5]arene macrocycles and AIE-active TPE linker contributed to the unique optical properties of this 2D assembled microporous CMP.

3D Supramolecular Assemblies

3D vesicle assemblies

Planar 2D assemblies can be constructed based on hexagonal pillar[6]arene structures. However, introduction of a curved structure is necessary for the formation of 3D vesicle assemblies. Liu and co-workers fabricated a series of high-performance 2D and 3D polymers by cross-reacting the laterally functionalized bromopillar[5]arene P[5]12 with diamines (Figure 13a). When stirring P[5]12 with a slight excess of a long diamine (e.g., hexanediame), well-defined nanocapsules with a shell thickness of only 1.2 ± 0.2 nm, consistent with one molecular layer, were generated. Other relatively long
amines, such as cystamine and 1,4-butanediamine, also produced similar nanocapsules under the same conditions. The diameters of these nanocapsules strongly depended on the length of the diamine. Conversely, using shorter diamines, such as ethanediame, resulted in micrometer-thick films. Thus, the length of the alkyldiamines determined the resulting assembled structure. This was because of the variable rigidity and curvature of the formed oligomeric patches depending on the length of the diamine linker. Thereafter, the same group used cystamine-linked nanocapsules as an anticancer drug delivery vehicle. The disulfide bonds of cystamine can be easily cleaved by reducing agents such as glutathione, which is present in high concentration in tumor cells. The nanocapsules containing an anticancer drug were found to display low cytotoxicity, excellent target recognition, high penetration of tumor cells, and inhibition of tumor cell growth.41

Our group constructed 3D vesicle assemblies by coassembly of pentagonal pillar[5]arenes and hexagonal pillar[6]arenes (Figure 13b).42 Pillar[5]quinone P[5]13, which contains five benzoquinone groups, was used as the pillar[5]arene because hydroquinone selectively forms a CT complex with benzoquinone. Pillar[6]arene P[6]1 assembles to form 2D sheet structures because of their highly symmetrical hexagonal structures. However, as the ratio of low-symmetry pentagonal pillar[5]quinone in the system was increased, the 2D sheets converted to 3D vesicle assemblies. A ratio of pillar[5]quinone to pillar[6]arene of 12:20 provided uniform vesicles with smooth surfaces. A coassembled structure with a 12:20 ratio of five- to six-membered rings is also observed in fullerene. The five-membered rings in fullerene provide the curvature required to form its spherical structure. Thus, pentagonal pillar[5]quinone provided curvature to form a vesicle structure.

3D metal–organic frameworks containing pillar[5]arenes

Metal–organic frameworks are 3D network structures consisting of metal–ligand complexes. Stoddart and co-workers reported metal–organic frameworks containing pillar[5]arene domains. First, a pillar[5]arene with two carboxylic acid groups as ligands (P[5]14, Figure 14a) was synthesized.43 Cubic and transparent crystals of metal–organic frameworks containing pillar[5]arenes were obtained by heating a mixture of P[5]14 and Zn(NO3)2·6H2O. The color of metal–organic framework crystals changed upon immersing the crystals in a solution containing guest molecules. The yellow crystals immediately changed to orange upon addition of a viologen salt or 1,4-dinitrobenzene because of the formation of CT complexes between these electron-poor guests and pillar[5]arene domains in the metal–organic frameworks.

Yang and co-workers constructed nanosized metal–organic frameworks with surfaces that were coated...
with pillar[5]arenes (Figure 14b).\textsuperscript{44} First, a nanosized metal-organic framework bearing pyridinium guest groups on its surface was constructed. Host-guest complexation between the pyridinium groups and pillar[5]arenes was carried out after loading drug molecules into the 3D metal-organic framework. The host-guest complexes on the framework surface worked as caps to securely store the drug molecules. Addition of competitive guests or changing pH induced the dissociation of the host-guest complexes, which contributed to the drug release.

### Summary and Outlook

In this minireview, we described supramolecular assemblies with various dimensions, that is, 1D, 2D, and 3D, constructed from pillar[n]arenes as the building blocks. The simple, tubular, and highly symmetrical shape of pillar[n]arenes has allowed various supramolecular assemblies with well-defined structures to be constructed. The pillar-shaped structures of pillar[n]arenes are suitable for surface modification and creation of ID channels. The regular polygonal prism shape of pillar[n]arenes also aids the construction of highly assembled structures such as 2D sheets and 3D spheres. Because of the cavity-dependent host-guest interaction ability of pillar[n]arenes, pillar[n]arene assemblies can bind guest molecules at multiple points. Pillar[n]arenes have unlimited potential and serve as ideal building blocks to create various supramolecular assemblies that cannot be produced using other host molecules. The year “2018” marks one decade of research on pillar[n]arenes; we eagerly anticipate the development of new supramolecular assemblies using pillar[n]arenes in the future.

### Conflicts of Interest

The authors declare no conflict of interest.

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