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ARTICLE

Pillar[5]- and pillar[6]arene-based supramolecular assemblies built by using their cavity-size-depending host-guest interactions

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Pillar[n]arenes, which we first synthesized and named in 2008, are new pillar-shaped macrocyclic hosts. Pillar[n]arene homologues with $n = 5-10$ have already been synthesized, but the cyclic pentamers, i.e., pillar[5]arenes, and cyclic hexamers, i.e., pillar[6]arenes, have been most widely used because these can be obtained in good yields. To date, nearly all pillar[n]arene-based supramolecular assemblies have been constructed using pillar[5]- and pillar[6]arene scaffolds. In this *feature article*, we describe supramolecular assemblies built with host-guest interactions depending on the cavity sizes of pillar[5]- and pillar[6]arenes. We first discuss the effects of the type of substituents at the rims of pillar[5]- and pillar[6]arenes on their solubilities, functionalities and host-guest properties. We then discuss supramolecular assemblies based on their host-guest properties and pillar-shaped architectures.

1. Introduction

Supramolecular assembly of well-defined molecules is a useful approach to the creation of functional materials.¹⁻¹⁰ Macrocyclic compounds, such as cyclodextrins (CDs),¹¹⁻¹⁶ cucurbit[n]urils (CB[n]s),¹⁷⁻¹⁹ calix[n]arenes,²⁰⁻²⁴ and crown ethers,²⁵ are candidates for well-defined molecules and play a major role in supramolecular chemistry, based on their host-guest interactions depending on their cavity sizes.¹¹⁻³¹ For example, the cavity sizes of α -CD and cucurbit[6]uril are ca. 4.7 Å and 5.8 Å, respectively, and accommodate linear alkanes and simple aromatic compounds. In contrast, the cavity sizes of β -CD (ca. 6.0 Å) and CB[7] (ca. 7.3 Å) are larger than those of α -CD and CB[6]. Thus, β -CD and CB[7] bind various bulky hydrocarbons and polyaromatic compounds. Numerous supramolecular assemblies have been constructed using different host-guest properties depending on cavity sizes.

Pillar[n]arenes, which we introduced in 2008,³² are new macrocyclic compounds and are at the core of supramolecular chemistry.³³⁻³⁸ Pillar[n]arene homologues ($n = 5-10$) have already been synthesized, but pillar[5]arenes, which contain five repeating units, have been most widely used because they can be obtained in high yields. We reported a general high-yield synthetic procedure for pillar[5]arenes in 2011,³⁹ and this has accelerated pillar[5]arene chemistry. Pillar[6]arenes, consisting of six repeating units, have also been widely used since 2011 because of the developing of a moderate-yield synthesis of pillar[6]arenes by Cao and coworkers.⁴⁰ To date, nearly all pillar[n]arene-based supramolecular assemblies have been constructed from pillar[5]- and pillar[6]arene scaffolds. In

this *feature article*, we describe supramolecular assemblies built on the basis of the host-guest properties of pillar[5]- and pillar[6]arenes. First, we compare the chemical and X-ray crystalline structures and calculated electrostatic potential profiles of pillar[5]- and pillar[6]arenes with those of calix[5]arene, which is composed of similar phenolic units. The different chemical structures of pillar[n]arenes and calix[n]arenes greatly affect their shapes and electrostatic potential profiles. Second, we discuss the effect of the types of substituents on the rims of pillar[n]arenes on their solubilities, host-guest properties and functionalities. Based on these properties, which reflect substituent types, we discuss various supramolecular assemblies such as micelles, vesicles, tubes, self-inclusion complexes, supramolecular dimers and polymers, and mechanically interlocked molecules (MIMs) containing rotaxanes, polyrotaxanes and catenanes.

2. Structures and electrostatic potential profiles of pillar[5]- and pillar[6]arenes

Fig. 1 shows the chemical and X-ray crystal structures and calculated electrostatic potential profiles of (a) perpropylated pillar[5]arene **H1**,⁴¹ (b) perpropylated pillar[6]arene **H2**⁴¹ and (c) calix[5]arene **H3**.⁴² The most important point regarding the chemical structures of pillar[n]arenes is the position of the methylene bridges connecting the units. Pillar[n]arenes are composed of 1,4-dialkoxybenzene units, which are connected

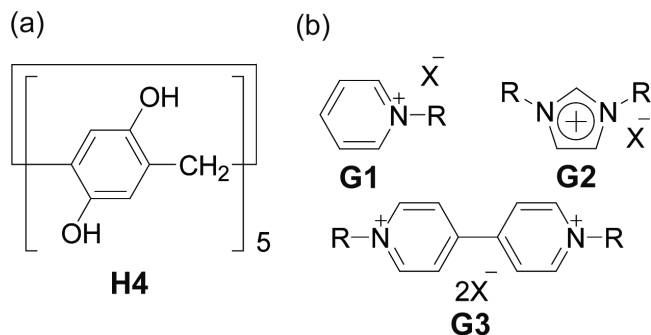


Fig. 2 Chemical structures of (a) perhydroxylated pillar[5]arene (**H4**) and (b) electron accepting cationic guests (**G1-G3**).

Perhydroxylated pillar[5]arene **H4** (Fig. 2a),³² which contains five hydroquinone units, is soluble in polar solvents such as acetone, DMSO and methanol, but insoluble in alkanes, halogenated, and aromatic solvents. This is the result of the high polarity of the five hydroquinone units. Hydroquinone is a strong electron donor, and forms charge-transfer complexes with electron acceptors. **H4** forms moderately stable host-guest complexes with electron acceptors such as pyridinium,^{32,43} imidazolium,^{44,45} and viologen cations^{32,43,46} (**G1-G3**, Fig. 2b) in acetone, DMSO, and methanol ($K = 10^2 - 10^3 \text{ M}^{-1}$).

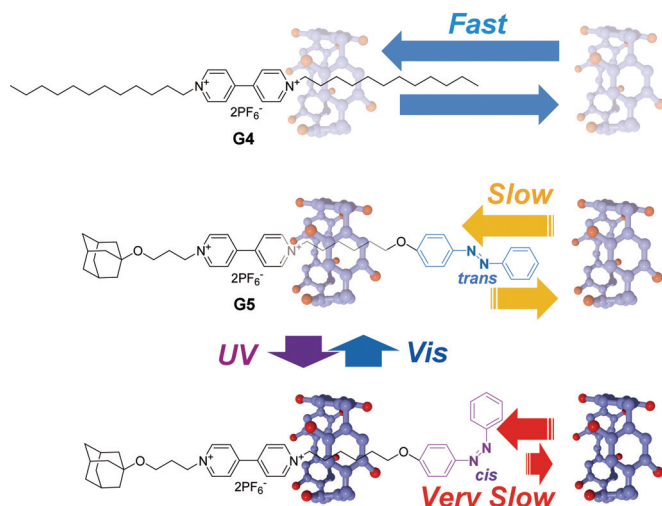


Fig. 3 Photo-switching transformation between second and hour time-scales: threading of **H4** onto azobenzene end of viologen derivative (**G5**).

Various supramolecular assemblies have been constructed based on host-guest complexes between **H4** and viologen cations. We investigated the shuttling behaviour of **H4** onto viologen axes containing different end moieties.⁴⁷ The threading of **H4** onto a viologen axle without bulky ends (**G4**) was very quick and could not be monitored directly. The half-life, determined using variable temperature ¹H NMR spectroscopy, was $1.44 \pm 0.03 \times 10^{-5} \text{ s}$ at 25 °C. We synthesized a viologen axle containing a bulky adamantyl moiety at one end and a photoresponsive azobenzene moiety at the other (**G5**, Fig. 3). The adamantyl moiety is too bulky to slip over the pillar[5]arene cavity; therefore **H4** forms a host-guest complex with **G5** from the azobenzene end. For the *trans*

form of **G5**, the half-life for complexation was $3.33 \pm 0.21 \text{ s}$ at 25 °C, but, the *cis* form of **G5**, induced by UV irradiation, took a very long time to form a complex. The complexation was directly monitored and the half-life, determined by monitoring ¹H NMR spectroscopic changes, was $9.13 \pm 1.2 \text{ h}$ at 25 °C, which is approximately 9770 times slower than that for the *trans* form. Photoisomerization from the *trans* to the *cis* form generated an increase in the activation free energy at 25 °C ($22.8 \pm 0.24 \text{ kJ/mol}$). The increased activation free energy results in very slow host-guest complexation. The azobenzene end-group therefore acts as a gate, controlling the rate of complexation with **H4**.

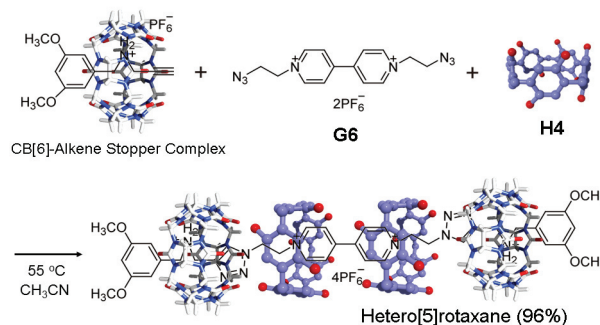


Fig. 4 High-yield synthesis of hetero[5]rotaxane containing two pillar[5]arenes (**H4**) and two CB[6] wheels.

A high-yield synthesis of rotaxanes, using the hydrogen bonding between the hydroxyl moieties of **H4** and urea moieties of CB[6], was recently reported by Stoddart and coworkers (Fig. 4).⁴⁸ An axle containing a viologen guest part and reactive azido end moieties was mixed with **H4**. The click reaction between the azido ends of the complex and a CB[6]-alkene stopper complex afforded a hetero[5]rotaxane containing two **H4** and two CB[6] wheels and one axle, in high yield (96%). The hydroxyl groups on **H4** form multiple hydrogen bonds with the carbonyl groups on the rim of CB[6], therefore these two macrocycles work together cooperatively to give the hetero[5]rotaxane in high yield.

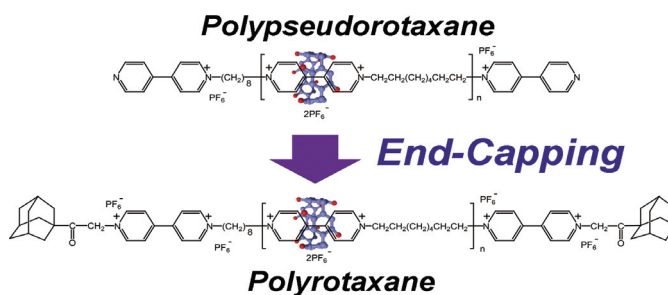


Fig. 5 Synthesis of perhydroxylated pillar[5]arene (**H4**)-based polyrotaxane by end-capping method.

The first pillar[*n*]arene-based polypseudorotaxane and polyrotaxane were synthesized by us, using a viologen polymer chain and **H4** wheels (Fig. 5).^{49,50} The shuttling movement of **H4** on the polymeric viologen chain in acetone-*d*₆/acetonitrile-*d*₃ (1:1 v/v) was fast on the NMR timescale, whereas the shuttling motion was slow in DMSO-*d*₆. A new polyrotaxane

composed of **H4** wheels and a viologen polymer was successfully synthesized by capping the chain ends with bulky adamantyl moieties; these are too bulky to slip over the pillar[5]arene cavity. Both the starting components, i.e., **H4**, the adamantyl stopper, and the viologen polymer, are soluble in acetone, acetonitrile, methanol, DMF, and DMSO, but the polyrotaxane is only soluble in DMF and DMSO. The polyrotaxane can therefore be isolated in high yield (93%) by washing with acetonitrile. The formation of *inter*-molecular hydrogen bonds between the hydroxyl moieties reduced the solubility of the polyrotaxane. This method of reducing the solubility by formation of polyrotaxanes is the same as that used for CD-based polyrotaxanes, which form *inter*-molecular hydrogen bonds between the CDs on the polymer chain.⁵¹

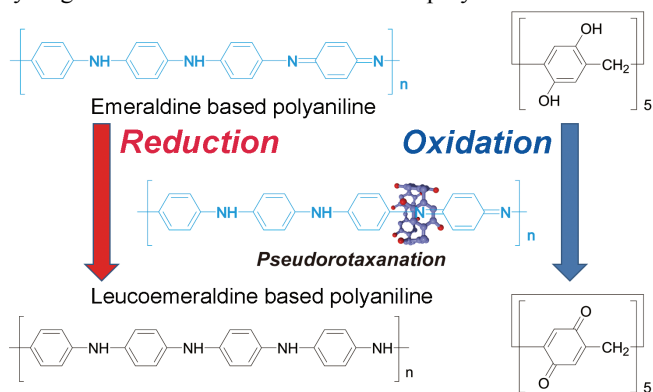


Fig. 6 Proposed structure in mechanism of emeraldine-base polyaniline reduction using macrocyclic reducing agent **H4**.

Hydroquinone is easily oxidized and converted to *p*-benzoquinone, and has therefore been used as a reducing agent.⁵² We used perhydroxylated pillar[5]arene **H4** containing five *p*-benzoquinone units as a macrocyclic reducing agent for emeraldine-base polyaniline, which is half-oxidized polyaniline (**Fig. 6**). When **H4** was mixed with emeraldine-base polyaniline, the blue solution colour of emeraldine-base polyaniline became completely colourless. This indicates reduction of the emeraldine-base polyaniline. The emeraldine-base polyaniline was converted to leucoemeraldine-base polyaniline, which is fully oxidized form. **H4** acts as a reducing agent for emeraldine based polyaniline. In addition, **H4** shows a stronger reducing ability than the unit model of hydroquinone. Pseudorotaxanation between polyaniline chains and **H4** wheels was the main reason for the strong reducing ability. Entrapment of **H4** wheels is ideal for moving the reducing agent **H4** close to the polyaniline chain.⁵³

Perhydroxylated pillar[5]arene **H4** itself forms supramolecular tubular assemblies as a result of *inter*-molecular hydrogen bonding between hydroxyl groups on the rims of **H4** molecules (**Fig. 7a**). **H4** is soluble in acetone, but insoluble in chloroform. Hydrogen bonding is effective in the non-polar solvent chloroform, so addition of chloroform to a homogeneous **H4** solution in acetone led to formation of tubular-shaped assemblies (**Fig. 7b**). **Fig. 7c** shows a TEM image of the nanotubes. Lines can be detected along the long axis of the nanotube, indicating formation of a bundle of molecular tubes

consisting of **H4**. In contrast, in the presence of viologen guest, nanotube formation did not occur, even in suitable mixed solvents. The formation of host-guest complexes should inhibit nanotube formation by *inter*-molecular hydrogen bonding.⁵⁴ The nanotube formation leads to a sol to gel transition.⁵⁵

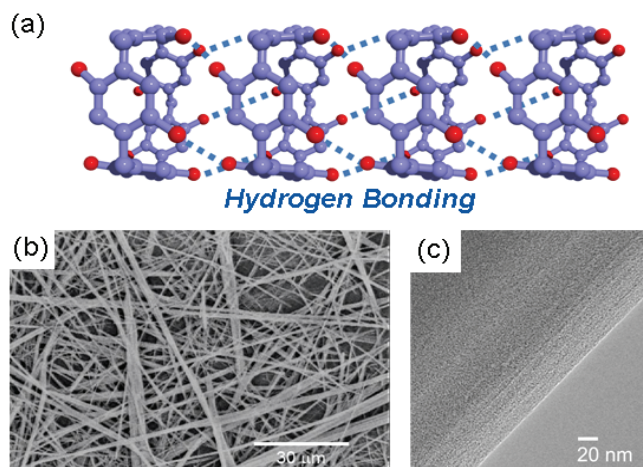


Fig. 7 Formation of nanotube assemblies from **H4**. (a) Schematic mechanism of formation of tubular assemblies by intermolecular hydrogen bonding between pillar[5]arenes, and (b) SEM and (c) TEM images of nanotubes.

3.2 Peralkylated pillar[5]arenes

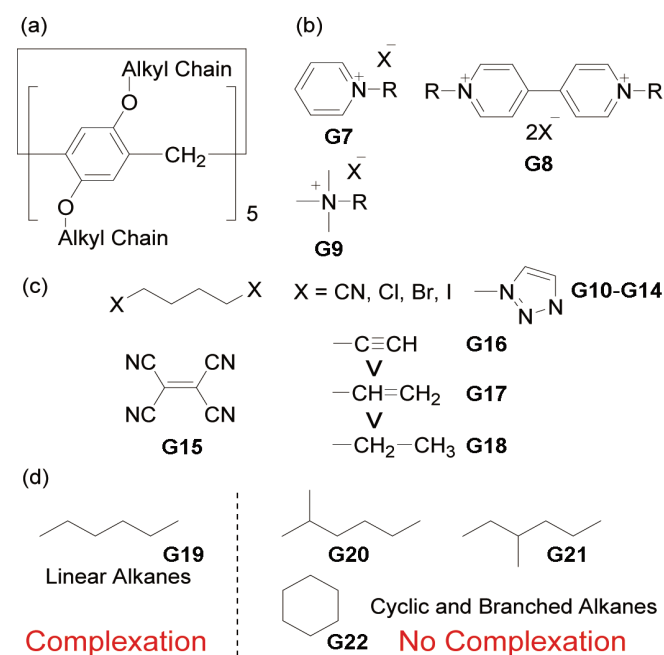
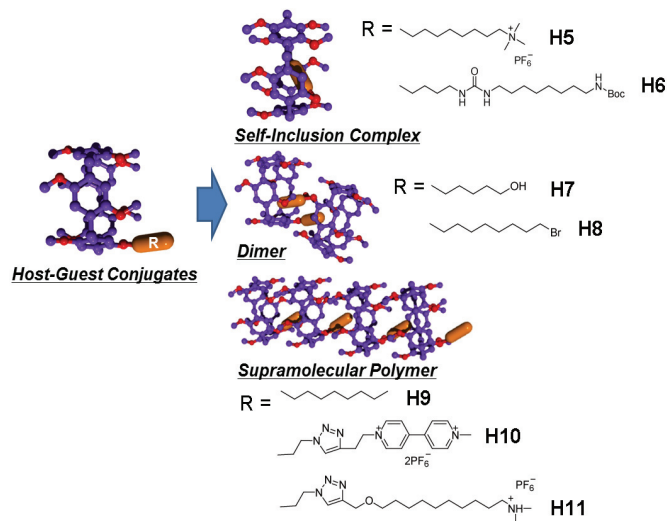


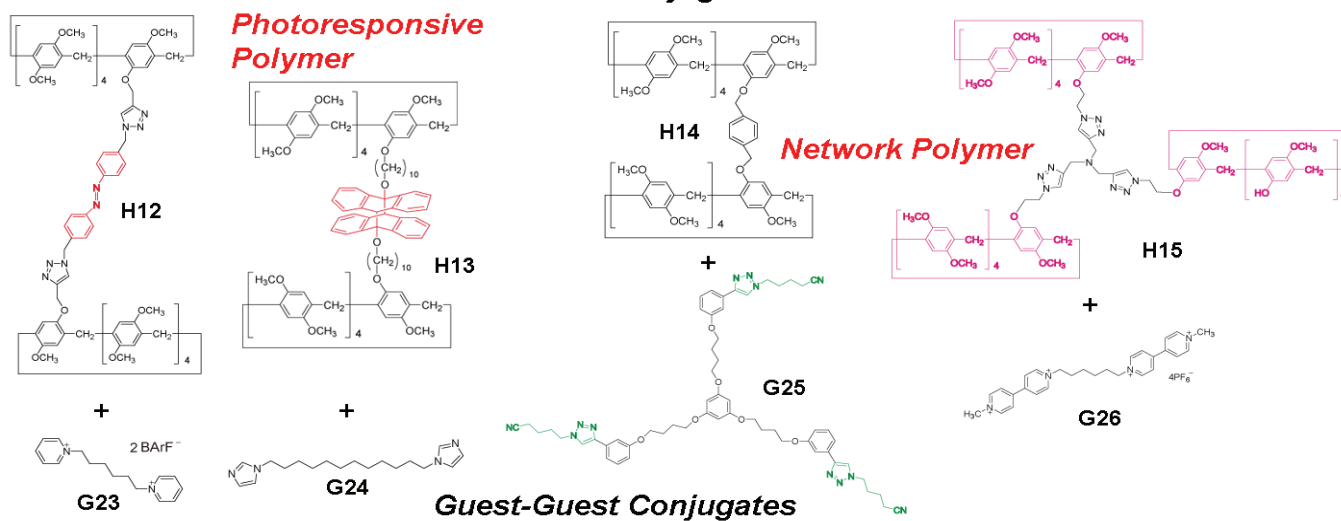
Fig. 8 Chemical structures of (a) peralkylated pillar[5]arenes and guest molecules containing (b) cationic (**G7-G9**) and (c) electron-withdrawing groups (**G10-G15**). (d) Size selective host-guest complexation between hydrocarbons (**G19-G22**) and peralkylated pillar[5]arenes.

Peralkylated pillar[5]arenes are soluble in non-polar solvents such as hexane, chloroform, and toluene. Chloroform is therefore mainly used for host-guest complexation between peralkylated pillar[5]arenes and guest molecules. The main driving forces of host-guest complexation are mainly cation- π and CH- π interactions. **Fig. 8** shows guest molecules for

peralkylated pillar[5]arenes. Cationic molecules containing pyridinium (**G7**)⁵⁶⁻⁶⁰, viologen (**G8**),^{61,62} amine⁶³ and ammonium (**G9**)⁶⁴⁻⁷² cations formed relatively strong complexes with peralkylated pillar[5]arenes ($K = 10^3 - 10^4 \text{ M}^{-1}$). Linear molecules containing cyano (**G10** and **G15**),^{73, 74} halogen (**G11-G13**),⁷⁵⁻⁷⁷ imidazole,⁷⁸ and triazole⁷⁹ (**G14**) groups were also included in peralkylated pillar[5]arenes ($K = 10^2 - 10^4 \text{ M}^{-1}$). Linear hydrocarbons also formed host-guest complexes with peralkylated pillar[5]arenes.⁸⁰⁻⁸² The host-guest complexation between peralkylated pillar[5]arenes and hydrocarbons increased in the following order: alkyne **G16** > alkene **G17** > alkane **G18**.⁸³ This is reasonable, because the relatively high electro-negativities of sp- and sp²-hybridized carbon atoms results in methylenes being better hydrogen bond donors, whereas these complexes are relatively weak ($K = 10 - 10^2 \text{ M}^{-1}$). Peralkylated pillar[5]arenes formed complexes with linear alkane **G19**, but not with bulky branched alkenes **G20**



Host-Host Conjugates



and **G21** and cyclic alkane **G22**.⁸⁰ Since bulky cyclic and branched alkanes hardly interacted with peralkylated pillar[5]arenes, the compact linear shape of *n*-alkanes is favourable for complexation. This is because the pillar[5]arene cavity is very narrow and has a well-defined cylindrical architecture.

Host-guest conjugates consisting of pillar[5]arene host and guest parts formed various supramolecular assemblies (Fig. 9). Pillar[5]arenes containing octatrimethylammonium (**H5**)⁶⁷ and urea moieties (**H6**)⁸⁴ mainly formed self-inclusion complexes. Pillar[5]arenes carrying a hydroxyl (**H7**)⁸⁵ and bromo (**H8**)⁷⁶ group at the end of the alkyl guest formed double-threaded supramolecular dimers. Monofunctionalized pillar[5]arenes carrying octyl (**H9**),⁸² viologen (**H10**),⁶¹ and di-alkyl ammonium (**H11**) at the end of the chain formed supramolecular daisy-chain polymers as the concentration increased.

Fig. 9 Self-inclusion complexes, supramolecular dimers and polymers, constructed from host-guest conjugates (**H5-H11**).

Fig. 10 Formation of photoresponsive and network supramolecular polymers constructed from homoditopic and homotripic host-host (**H12-H15**) and guest-guest (**G23-G26**) conjugates.

Another method for the formation of supramolecular polymers is mixing homoditopic monomers between host-host and guest-guest conjugates. We constructed a photoresponsive supramolecular polymer by mixing azobenzene-bridged pillar[5]arene dimer (**H12**) and dipyridinium guest (**G23**).⁵⁶ The assembly and disassembly of the supramolecular polymer switched completely under alternating UV- and visible-light irradiation. Yang and coworkers reported switchable supramolecular assemblies formed using pillar[5]arene dimers connected by reversible [4+4] photocycloaddition of anthracene.⁸⁶ A supramolecular gel was formed by mixing **H13** and **G24** under UV irradiation. Dissociation of the anthracene dimer, induced by heating, triggered a gel-sol transition. Mixing ditopic host **H14** and tritopic guest **G25**,⁸⁷ or tritopic host **H15** and ditopic guest **G26**,⁸⁸ resulted in formation of supramolecular network polymers.

Various peralkylated pillar[5]arene-based MIMs have been constructed based on host-guest complexes. A pillar[5]arene-based [2]rotaxane, using 1,8-diaminooctane as an axle, was reported by Stoddart and coworkers.⁶³ However, the yield of the [2]rotaxane was quite low (7%).⁶³ [2]Rotaxanes consisting of an alkane axle were also synthesized, but their yields were also low (20% and 35%).^{89,90} The low yields are resulted of weak association constants between these axles and pillar[5]arenes ($K = 10 - 10^2 \text{ M}^{-1}$).

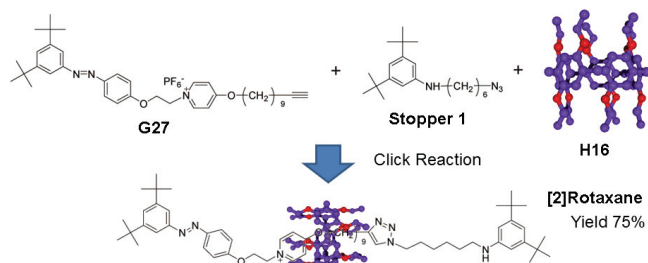


Fig. 11 High-yield synthesis of pillar[5]arene-based [2]rotaxane using Sharpless alkyne-azido click reaction.

To overcome this problem, we used the stable host-guest complex between pyridinium guest **G27** and perethylated pillar[5]arene **H16** [Fig. 11, $K = (7.6 \pm 1.1) \times 10^4 \text{ M}^{-1}$].⁵⁸ The main driving force of host-guest complexation is cation- π interaction. We successfully synthesized a [2]rotaxane in high yield (75%) using the stable host-guest complex and a click reaction to introduce bulky stopper **1**, even in a [3]rotaxane consisting of two pillar[5]arene **H16** wheels and one axle; the yield was moderate (45%). Various cationic axles, which can form stable host-guest complexes with peralkylated pillar[5]arenes, were used to form [2]rotaxanes with efficient Förster resonance energy transfer,⁹¹ and solvent-/thermo-responsive property.⁹²

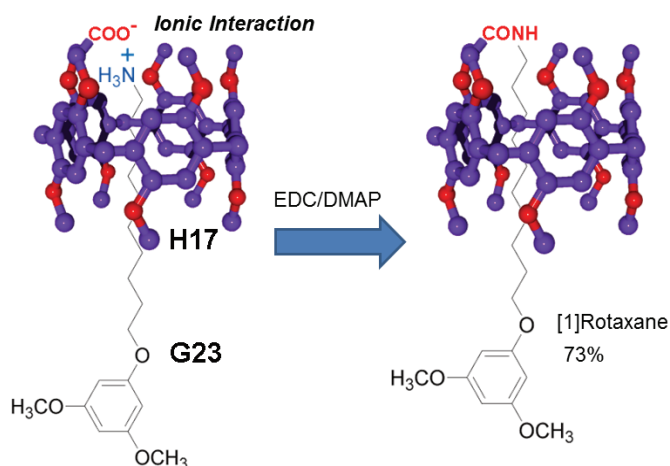


Fig. 12 High-yield synthesis of pillar[5]arene-based [1]rotaxane by preorganization using ionic interactions between pillar[5]arene (**H17**) and guest (**G23**).

Xue and Xia synthesized pillar[5]arene-based [1]rotaxane by pre-organization of a pseudo[1]rotaxane structure between host **H17** and guest **G23** containing a bulky stopper at the end, based

on cation- π and ionic interactions.⁹³ Formation of an amide bond between the primary amine and the carboxylic acid groups then afforded the [1]rotaxane in high yield (73%). A double-threaded [2]rotaxane was also synthesized by capping the end group of the double-threaded preorganized supramolecular dimer.⁹⁴ A pseudo[1]catenane in which the guest was an alkyl chain connected to one pillar[5]arene unit was also synthesized by a Sharpless click reaction between a pillar[5]arene containing two alkyne moieties (**H18**) and alkane with two azido moieties at the ends (**G24**, Fig. 13a).⁶⁴ The capture and release of achiral guests and solvents trigger the inclusion and dethreading of the alkyl chain, causing inversion of the planar chirality.

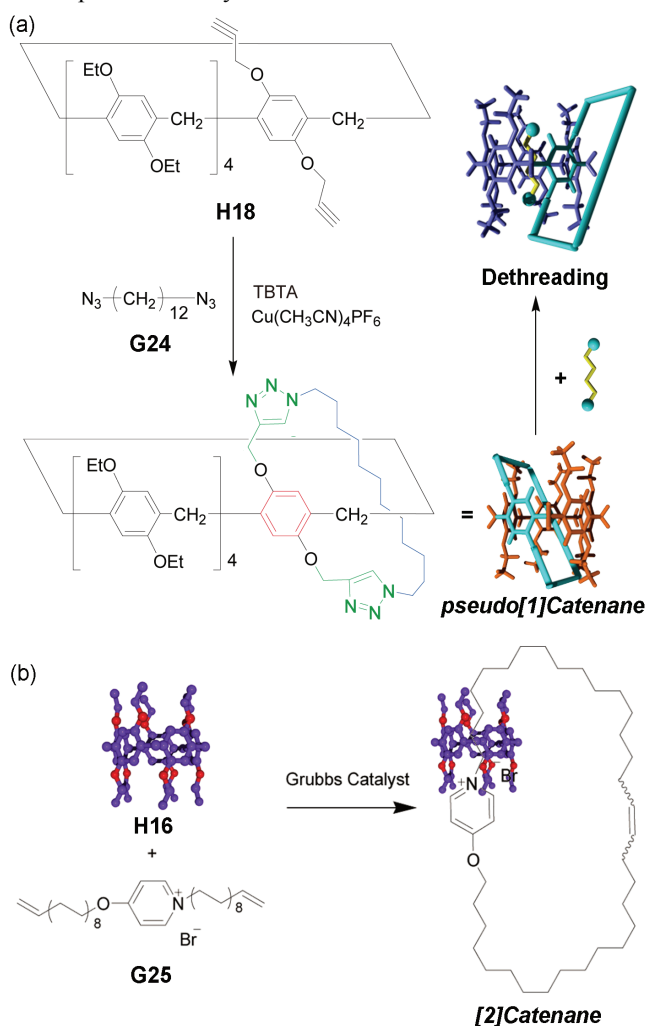


Fig. 13 Synthesis of (a) pseudo[1]catenane by Sharpless azido-alkyne click reaction and (b) [2]catenane by ring-closing metathesis reaction.

The first pillar[5]arene-based [2]catenane was synthesized in moderate yield (24%) by a ring-closing metathesis reaction between perethylated pillar[5]arene **H16** and a pyridinium molecule **G25** bearing an alkene at both ends (Fig. 13b).⁶⁰

3.3 Ionic and non-ionic pillar[5]arenes

Pillar[5]arenes containing ionic and non-ionic moieties are soluble in aqueous media. Host-guest complexation is therefore carried out in aqueous media. We first synthesized a water-soluble pillar[5]arene by modification of carboxylate anion moiety **H19** (Fig. 14a).⁹⁵ **H19** forms stable complexes with cationic molecules such as pyridinium **G26** and viologen salts **G27** ($K = 10^3 - 10^6 \text{ M}^{-1}$).^{95,96} Li, Jia, and coworkers investigated the inclusion complexation behaviour of 20 naturally occurring amino acids with **H19**.⁹⁷ **H19** shows strong binding towards basic acids such as L-lysine, L-arginine and L-histidine ($K = 10^3 \text{ M}^{-1}$), compared with other α -amino acids ($K = 20 \text{ M}^{-1}$). Cationic pillar[5]arenes containing ammonium (**H20**, Fig. 14b) and imidazolium (**H21**)⁹⁸ cations strongly accommodate sodium dodecyl sulfonate **G28** [$K = (1.3 \pm 0.9) \times 10^4 \text{ M}^{-1}$].⁹⁹ In these ionic pillar[5]arenes, electrostatic interactions are the dominants driving forces. Hydrophilic-hydrophobic, CH- π and hydrogen bond interactions also support host-guest binding. We also first synthesized a non-ionic pillar[5]arenes containing oligo(ethylene oxide) **H22** and **H23** (Fig. 14c).¹⁰⁰ **H23** is soluble in aqueous media, but **H22**, with short ethylene oxide chains, is insoluble in water. **H23** forms complexes with cationic viologen moieties [$K = (4.3 \pm 0.5) \times 10^3 \text{ M}^{-1}$].¹⁰⁰

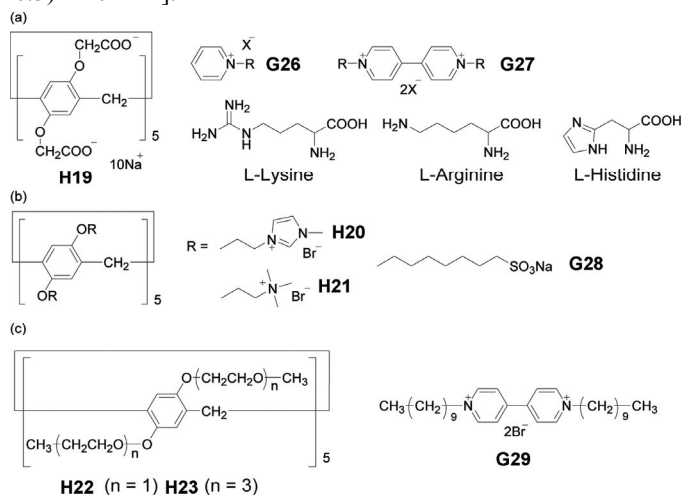


Fig. 14 Chemical structures of water-soluble pillar[5]arenes. (a) Anionic pillar[5]arene (**H19**) and its guests (**G26**, **G27**, and α -amino acids). (b) Cationic pillar[5]arenes (**H20** and **H21**) and their guest (**G28**). (c) Non-ionic pillar[5]arenes (**H22** and **H23**) and their guest (**G29**).

H23 showed a lower critical solution temperature (LCST). The LCST behaviour can be attributed to the combination of hydrophilic tri(ethylene oxide) moieties with the hydrophobic pillar[5]arene core. At room temperature, water molecules solvate tri(ethylene oxide) chains. However, at temperatures above the cloud point, desolvation of water molecules takes place and interactions of the hydrophobic groups cause aggregation and then separation from water. The cloud point was determined from the UV-vis transmission changes, observed using a temperature-controlled spectrometer. On heating, the cloud point of **H23** was 42 °C, and easily controlled from 42 to 60 °C (Fig. 15a) using viologen guest **G29** (Fig. 14c). Repulsive forces between the complexed

cations can prevent aggregation of **H23**; therefore, heating at high temperature is needed to aggregate **H23-G29** complexes. The cloud point was reversed to that of the pristine state by addition of competitive host CB[7] (Fig. 15b). Viologen derivatives form highly stable 1:1 host-guest complexes with CB[7] (over 10^5 M^{-1}) and therefore can dissociate **H23-G29** complexes. The dissociation of the complex resulted in a decrease in the cloud point from 60 to 47 °C. We demonstrated reversible cloud point changes using the host-guest system.¹⁰⁰

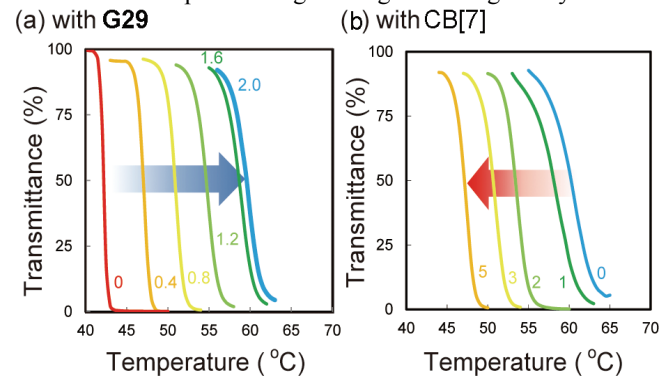


Fig. 15 (a) Temperature dependence of light transmittance of aqueous solution of **H23** (2 mM) on addition of **G29** (0-2 mM) and heating. (b) Temperature dependence of light transmittance of mixture of **H23** (2 mM) and **G29** (2 mM) in aqueous solution on addition of CB[7] (0-5 mM) and heating. Reprinted with permission from ref 100. Copyright 2012, American Chemical Society.

The pillar[5]arene with 10 tri(ethylene oxide) chains (**H23**) can also be used as the solvent because **H23** is a liquid at room temperature. This is because tri(ethylene oxide) chains are soft segments and reduce the crystallinity of pillar[5]arene. Using the liquid pillar[5]arene **H23** as a solvent for the synthesis of MIMs, liquid [2]rotaxanes consisting of solid axle molecules covered with the liquid host were obtained with 97% conversion in a solvent-free reaction. In contrast, the conversion was very low (8%) in the normal solvent system in chloroform because of the low association constant ($K = \text{ca. } 10 \text{ M}^{-1}$) in the presence of CDCl₃. The solvent-free reaction system is a new powerful method for the synthesis of MIMs because the Sharpless alkyne-azido click reaction, which has been used for the synthesis of various MIMs, can also be used in the solvent-free reaction system.¹⁰¹

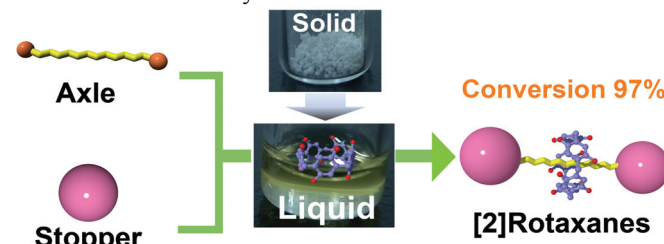


Fig. 16 High-yield syntheses of pillar[5]arene-based [2]rotaxanes using cyclic host liquid as the solvent. Reprinted with permission from ref. 101 Copyright 2012, American Chemical Society.

3.4 Amphiphilic pillar[5]arene

We synthesized an amphiphilic pillar[5]arene carrying 10 tetra-alkyl phosphonium bromide groups **H24**. **H24** was formed with linear alkenes **G30** but not with branched alkenes **G31**, which is the same trend as that for peralkylated pillar[5]arenes. **H24** is soluble in aqueous and organic media, and can therefore be used as a phase-transfer catalyst. In the presence of **H24**, oxidation of the linear alkene 1-hexene **G30** and 1-heptene with KMnO_4 proceeded to completion, but that of the branched alkene 4-methyl-1-hexene **G31** did not (conversion 31%). These results indicate that inclusion of the substrate in the cavity of **H24** brings the phosphonium salts and the substrates into close contact, leading to efficient oxidation of alkenes.¹⁰²

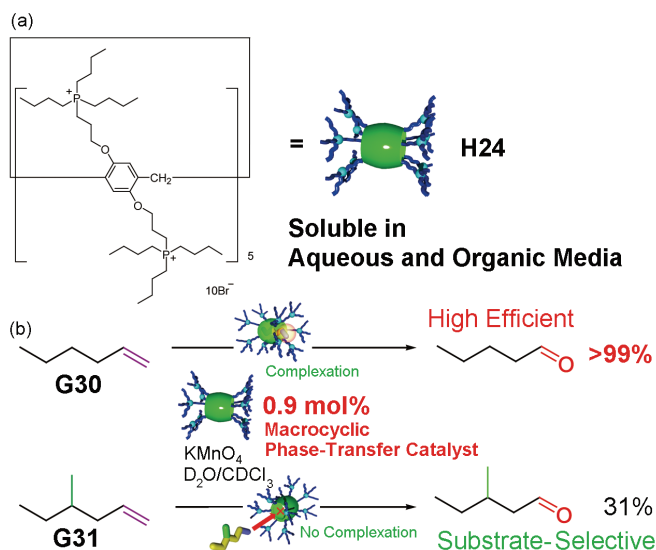


Fig. 17 (a) Amphiphilic pillar[5]arene (**H24**) and (b) oxidation reactions of alkenes (**G30**) and (**G31**) based on host-guest complexation. Reprinted with permission from ref 102. Copyright 2012 American Chemical Society.

3.5 Non-symmetric pillar[5]arenes

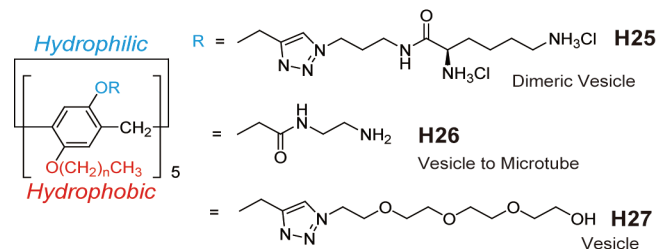


Fig. 18 Non-symmetric pillar[5]arenes (**H25-H27**) consisting of hydrophobic and hydrophilic rims.

Amphiphilic molecules containing hydrophilic and hydrophobic segments undergo supramolecular assembly in aqueous media to produce micelles, vesicles, layers, and tubes. Pillar[5]arene has two rims and 10 arms (five arms at each rim), so introduction of five hydrophilic arms at one rim and five hydrophobic arms at the other rim affords amphiphilic molecules. The self-assembly of an amphiphilic pillar[5]arene composed of hydrophilic ammonium arms and hydrophobic

alkyl arms (**H25**) afforded dimeric spherical micelles.¹⁰³ An amphiphilic pillar[5]arene **H26** consisting of five amino groups (hydrophilic head) and five alkyl chains (hydrophobic tail) assembled in water to form vesicles and multi-walled microtubes.¹⁰⁴ Vesicles consisting of amphiphilic pillar[5]arenes **H27** containing hydrophilic oligo(ethylene oxide) arms of different lengths are non-toxic, and can encapsulate and deliver dyes.¹⁰⁵

4. Pillar[6]arene-based supramolecular assemblies built with host-guest interactions

The cavities of pillar[6]arenes are negatively charged electron-rich spaces (**Fig. 1**). Pillar[6]arenes can therefore form host-guest complexes with electron-poor guests. The cavity size of a pillar[6]arene is ca. 7.5 Å, which is almost equal to those of CB[7] (ca. 7.3 Å) and β -CD (ca. 6.0 Å). Like CB[7] and β -CD, pillar[6]arenes also form host-guest complexes with various positively charged polyaromatic compounds and bulky hydrocarbons. The formation of host-guest complexes of pillar[6]arenes with photo-responsive azobenzene and redox-responsive ferrocenium moieties is particularly useful for constructing stimuli-responsive supramolecular assemblies. Pillar[6]arenes have 12 substituents, and the properties of these substituents affect the solubilities and host-guest properties of pillar[6]arenes. As in the case of pillar[5]arenes, we classify pillar[6]arenes based on their solubility and discuss the relationship between their host-guest properties and supramolecular assemblies using pillar[6]arene scaffolds.

4.1 Perhydroxylated pillar[6]arene

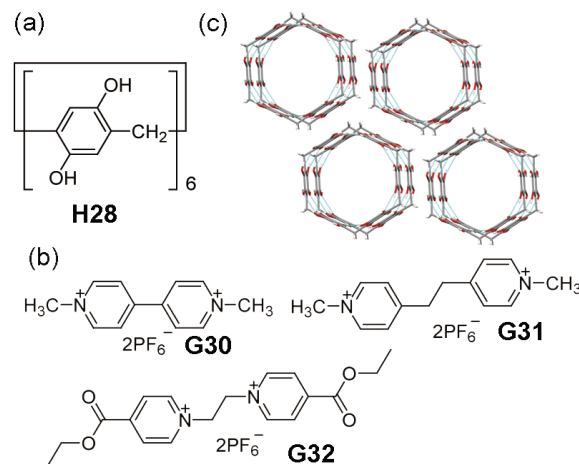


Fig. 19 Chemical structures of (a) perhydroxylated pillar[6]arene (**H28**) and (b) cationic guests (**G30-G32**) for **H28**. (c) Crystal structure (packing mode) of **H28**.

Huang and coworkers synthesized perhydroxylated pillar[6]arene **H28** containing 12 phenol moieties.¹⁰⁶ However, **H28** forms intramolecular hydrogen bonds in an alternating up-and-down manner as a result of the even number of benzene rings in the cyclic hexagonal structure. **Fig19c** shows the packing mode of **H28**. A close-packed arrangement of **H28** is

stacked in an up-to-down manner to form infinite channels. Due to the up-and-down hydrogen bonding, the solubility of perhydroxylated pillar[6]arene **H28** is low compared with that of perhydroxylated pillar[5]arene **H4**. **H28** forms host-guest complexes with viologen **G30** and pyridinium derivatives **G31** and **G32**. However, their association constants are relatively low ($K = 10 - 10^2 \text{ M}^{-1}$). New suitable guests for **H28** are needed for the construction of perhydroxylated pillar[6]arene-based supramolecular assemblies.

4.2 Peralkylated pillar[6]arenes

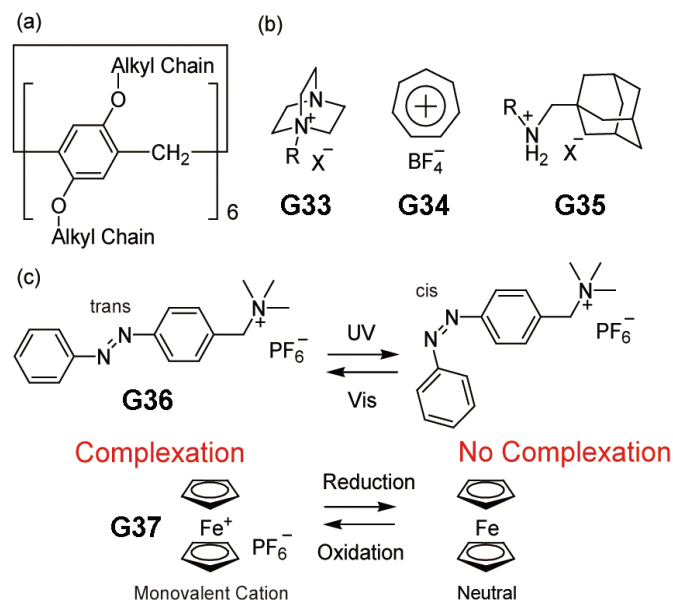


Fig. 20 Chemical structures of (a) peralkylated pillar[6]arene and (b) cationic guests (**G33-G35**) for peralkylated pillar[6]arenes. (c) Photo- (**G36**) and redox- (**G37**) responsive guests for peralkylated pillar[6]arenes.

The solubility of peralkylated pillar[6]arenes (**Fig. 20**) are the same as those of peralkylated pillar[5]arenes: peralkylated pillar[6]arenes are soluble in non-polar solvents such as hexane, chloroform and toluene. Chloroform is therefore mainly used in host-guest complexation. As with peralkylated pillar[5]arenes, the main driving force of host-guest complexation is cation- π interaction. A simple aromatic compound, i.e., the pyridinium cation, which is a good guest for peralkylated pillar[5]arenes, shows extremely weak binding affinity with peralkylated pillar[6]arenes ($K = 19.1 \pm 2.2 \text{ M}^{-1}$)⁵⁷ because the pyridinium cation is too small to fit the cavities of pillar[6]arenes. Peralkylated pillar[6]arenes form stable complexes with bulky hydrocarbons containing cations such as 1,4-diazabicyclo[2.2.2]octane (**G33**, $K = 552 \pm 65 \text{ M}^{-1}$)⁵⁹ adamantyl cations [**G35**, $K = (3.4 \pm 0.2) \times 10^3 \text{ M}^{-1}$]⁷¹ and carbonium ion tropylium tetrafluoroborate [**G34**, $K = (1.8 \pm 0.3) \times 10^3 \text{ M}^{-1}$]¹⁰⁷. The trans form of azobenzene containing cations can complex with pillar[6]arenes [**G36**, $K = (2.2 \pm 0.3) \times 10^3 \text{ M}^{-1}$], but the cis form of the azobenzene guest forms very weak host-guest complexes with peralkylated pillar[6]arenes [$K = (2.6 \pm 0.3) \times 10^2 \text{ M}^{-1}$]⁴¹. Pillar[6]arenes can form host-guest complexes with the oxidized form of the ferrocenium cation

[**G37**, $K = (2.0 \pm 0.1) \times 10^4 \text{ M}^{-1}$], but hardly complexes with the reduced form ($K = 18 \pm 0.5 \text{ M}^{-1}$)¹⁰⁸.

Perethylated pillar[5]- and pillar[6]arenes were used to synthesize pillararene-based rotaxanes (**Fig. 21**). In the case of pillar[5]arene-based [2]rotaxane (**Fig. 21a**), the pillar[5]arene wheel is located on the pyridinium moiety. In contrast, when pillar[6]arene is used as the wheel (**Fig. 21b**), the pillar[6]arene wheel can freely move along long linear alkyl chains between the pyridinium and triazole moieties and short linker alkyl chains between the pyridinium and trityl moieties, because of the large pillar[6]arene cavities. The pillar[6]arene wheel moves from the short alkyl chain to the long alkyl chain as a result of thermal stimuli. The movement of the pillar[6]arene wheel is favourable in terms of entropy dominance.⁵⁷

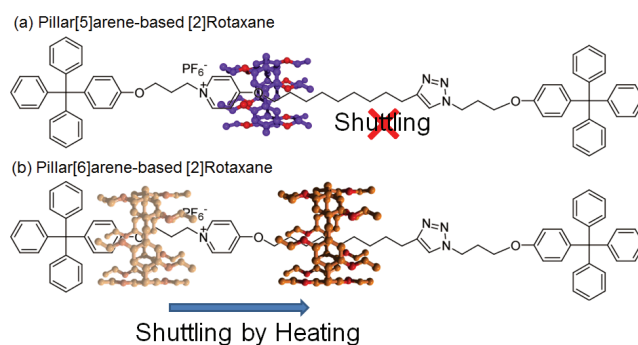


Fig. 21 Thermo-responsive shuttling behaviour of pillar[6]arene-based [2]rotaxane.

Huang and coworkers used photoresponsive host-guest complexation between pillar[6]arenes and azobenzene guests to demonstrate switching of supramolecular assemblies. Assemblies of host-guest complexes between the trans-form of azobenzene **G36** and a pillar[6]arene result in irregular aggregates. On irradiation with UV light, photoisomerization from the trans to the cis form occurs, which triggers formation of vesicle-like aggregates. Alternate irradiation with UV and visible light can therefore reversibly switch the supramolecular assembly state between irregular and vesicle-like aggregates.⁴¹

4.3 Ionic and non-ionic pillar[6]arenes

As in the cases of ionic and anionic pillar[5]arenes, pillar[6]arenes carrying ionic and non-ionic moieties are soluble in aqueous media. Complexation of these pillar[6]arenes with guest molecules is therefore mainly investigated in aqueous media. An anionic pillar[6]arene **H29** (**Fig. 22a**) carrying 12 carboxylate anions forms very stable host-guest complex with viologen cation **G38** [$K = (1.0 \pm 0.1) \times 10^8 \text{ M}^{-1}$]¹⁰⁹ its association constant is much higher than that of anionic pillar[5]arene **H19** [$K = (8.2 \pm 1.7) \times 10^4 \text{ M}^{-1}$]⁹⁵. This is because viologen is the best size to fit the internal cavities of the pillar[6]arene. A cationic pillar[6]arene **H30** (**Fig. 22b**) containing 12 pyridinium cations formed host-guest complexes with water-soluble naphthalene molecules **G39** and **G40**. The association constants were $(2.1 \pm 0.3) \times 10^5 \text{ M}^{-1}$ and (3.8 ± 0.2)

$\times 10^4 \text{ M}^{-1}$ for **G39** and **G40**, respectively.¹¹⁰ The cooperative ionic interactions between two the sulfonate anions of guest **G39** and the two cationic rims of **H30** enhanced the stability of the host-guest complex. A non-ionic pillar[6]arene **H31** (Fig. 22c) with 12 tri(ethylene oxide) chains formed complexes with the trans-form of azobenzene derivative **G40** [$K = (1.0 \pm 0.003) \times 10^3 \text{ M}^{-1}$], but the non-ionic pillar[5]arene **H23** containing 10 tri(ethylene oxide) chains did not. The trans form of **G40** fits the cavity of **H31**, but is too bulky to form a complex with **H23**. Photoisomerization of **G40** from the trans to the cis form induced dissociation of the complex. This photoresponsive host-guest system can therefore be used to control the LCST of **H31**.¹¹¹

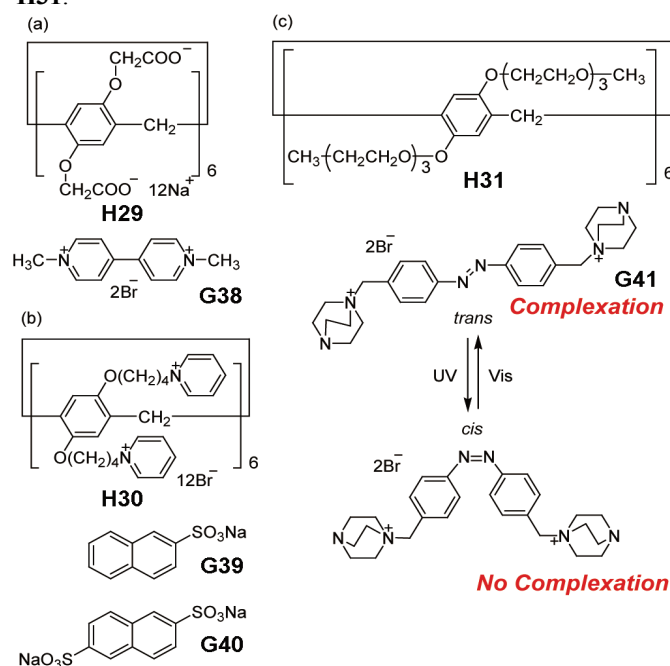


Fig. 22 Water-soluble pillar[6]arenes: (a) anionic pillar[6]arene (**H29**) and its guest (**G38**), (b) cationic pillar[6]arene (**H30**) and its guests (**G39** and **G40**), and (c) non-ionic pillar[6]arene (**H31**) and its photoresponsive guest (**G41**).

5. Summary and outlook

In this *feature article*, we described the host-guest interactions of pillar[5]- and pillar[6]arenes in terms of the cavity size and types of substituents at the rims, and supramolecular assemblies produced using the host-guest interactions. The substituents on the rims of pillar[5]- and pillar[6]arenes affect their solubilities and give new functionalities. For example, a combination of a hydrophobic pillar[n]arene core and hydrophilic tri(ethylene oxide) chains leads to LCST behaviour,^{100,111} and a pillar[5]arene carrying phase-transfer catalyst moieties acts as a substance-selective supramolecular catalyst.¹⁰² The introduction of various functional groups at the rims of pillar[5]- and pillar[6]arenes is a useful way of the creating pillar[n]arene-based supramolecular assemblies with new functionalities. Photo- and redox-responsive host-guest systems based on pillar[6]arenes enabled us to build various stimuli-responsive supramolecular assemblies.

In view of the differences between the host-guest properties of pillar[5]- and pillar[6]arenes, pillar[n]arene homologues ($n > 7$) with large cavities should be interesting and expand the potential of the pillar[n]arene chemistry. However, compared with other well-known macrocyclic hosts, one of the problems in pillar[n]arene chemistry is that preparation of pillar[n]arene homologues is different. Recently, new pillar[n]arene homologues, i.e., pillar[7-10]arenes, were reported by Cao and Hou, but the yields were quite low.¹¹² To date, pillar[n]arene chemistry using large pillar[n]arene homologues ($n > 7$) has not been investigated because of their low yields. New synthetic methodologies for new pillar[n]arene homologues and construction of supramolecular assemblies using pillar[n]arene homologues with large cavities would be a breakthrough in pillar[n]arene chemistry.

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Notes and references

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