

Spherical Vesicles Formed by Co-Assembly of Cyclic Pentagonal Pillar[5]quinone with Cyclic Hexagonal Pillar[6]arene

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S Supporting Information

ABSTRACT: Mixing cyclic pentagonal pillar[5]quinone with cyclic hexagonal pillar[6]arene in a 12:20 molar feed ratio resulted in spontaneous production of vesicles, while assembly of pillar[6]arene and pillar[5]quinone alone produced hexagonal disks and wires, respectively. Incorporation of pentagonal pillar[5]quinone rings into hexagonal pillar[6]arene sheets gave curvature and contributed to the formation of vesicles. Conventional vesicles are generally synthesized by assembly of amphiphilic molecules containing hydrophobic and hydrophilic parts. Therefore, the co-assembly of pentagonal and hexagonal molecules to obtain spherical vesicles demonstrated in this study is a new concept based on geometric design.

Fullerene (C_{60}) possesses spherical architecture, consisting of 12 five- and 20 six-membered rings.¹ The 12:20 ratio of five- to six-membered rings is optimal for constructing spherical architecture. Assembly of six-membered rings alone produces a planar hexagonal packing structure (e.g., graphene), while five-membered rings endow C_{60} with the curvature required to form a spherical structure. The spherical structure of C_{60} , composed of five- and six-membered rings, inspired us to investigate the co-assembly of highly symmetric pentagonal and hexagonal molecules in this study. Since our first report of pillar[*n*]arenes in 2008,² they have become important key players in supramolecular chemistry.³ Pillar[5]- and pillar[6]arenes are highly symmetrical pentagonal and hexagonal molecules, respectively, with their constituent hydroquinone units linked in the 2,5-positions by methylene bridges. Here, we use pillar[5]- and pillar[6]arenes as building blocks to construct spherical assemblies. Previously, we investigated 2D supramolecular polymerization using pillar[5]- and pillar[6]arenes as monomers.⁴ Oxidation of the hydroquinone pillar[*n*]arene units to benzoquinone contributed to their 2D supramolecular polymerization, due to the formation of intermolecular charge-transfer complexes between hydroquinone and benzoquinone (quinhydrone) that connected pillar[*n*]arene molecules. The 2D supramolecular polymerization of pillar[6]arene gave 2D hexagonal porous sheets (Figure 1a), while amorphous assemblies formed when pillar[5]arene was used as a monomer. The highly symmetrical hexagonal structure of pillar[6]arenes is therefore very important for formation of the 2D sheet structure. We speculated that incorporation of pentagonal

pillar[5]arene molecules into the 2D pillar[6]arene sheets would provide curvature, resulting in the formation of highly ordered spherical structures like C_{60} .

Pillar[5]arene² and pillar[6]arene⁵ were mixed in a 12:20 molar feed ratio, followed by addition of bis[(trifluoroacetoxy)iodo]benzene (oxidant) to the homogeneous solution. Addition of the oxidant immediately afforded precipitates, which were 2D sheets consisting of pillar[6]arene moieties. Since the hexagonal structure of pillar[6]arene is more symmetrical than the pentagonal structure of pillar[5]arene, only pillar[6]arene molecules assembled, even in the presence of pillar[5]arene.

To incorporate low-symmetry pillar[5]arene molecules into the 2D porous sheets constructed from pillar[6]arene, a pillar[5]quinone⁶ containing five benzoquinone units was first synthesized. The obtained pillar[5]quinone was then mixed with pillar[6]arene in different molar feed ratios (Figure 1b). The mixtures initially formed suspensions due to the low solubility of pillar[5]quinone in methanol. However, the suspensions containing pillar[6]arene more than 1 molar equiv to pillar[5]quinone changed to a light-red homogeneous solutions after stirring for 24 h (Figure 1b, photo). When the molar feed ratios of pillar[6]arene were ≤ 40 mol %, the suspensions did not change after stirring for 24 h, indicating that the amounts of pillar[6]arene are insufficient to form complex with pillar[5]quinone. These results indicate the existence of an interaction between pillar[5]quinone and pillar[6]arene. The change of color from colorless to red suggests the formation of intermolecular charge-transfer complexes between the hydroquinone moieties of pillar[5]quinone and the benzoquinone moieties of pillar[6]arene. The formation of charge-transfer complexes was checked by UV-vis absorption results (Figure S1). The 12:20 mixture of pillar[5]quinone and pillar[6]arene exhibited an obvious charge-transfer band at 430–500 nm, not found in the spectrum of either pillar[5]quinone or pillar[6]arene, suggesting the charge-transfer interaction of pillar[5]quinone with pillar[6]arene. The mixture was further characterized using Fourier transform infrared (FT-IR) spectroscopy (Figure S2), showing the appearance of new strong bands at 1645 cm^{-1} corresponding to the C=O stretch of the charge-transfer complex between hydroquinone and benzoquinone (quinhy-

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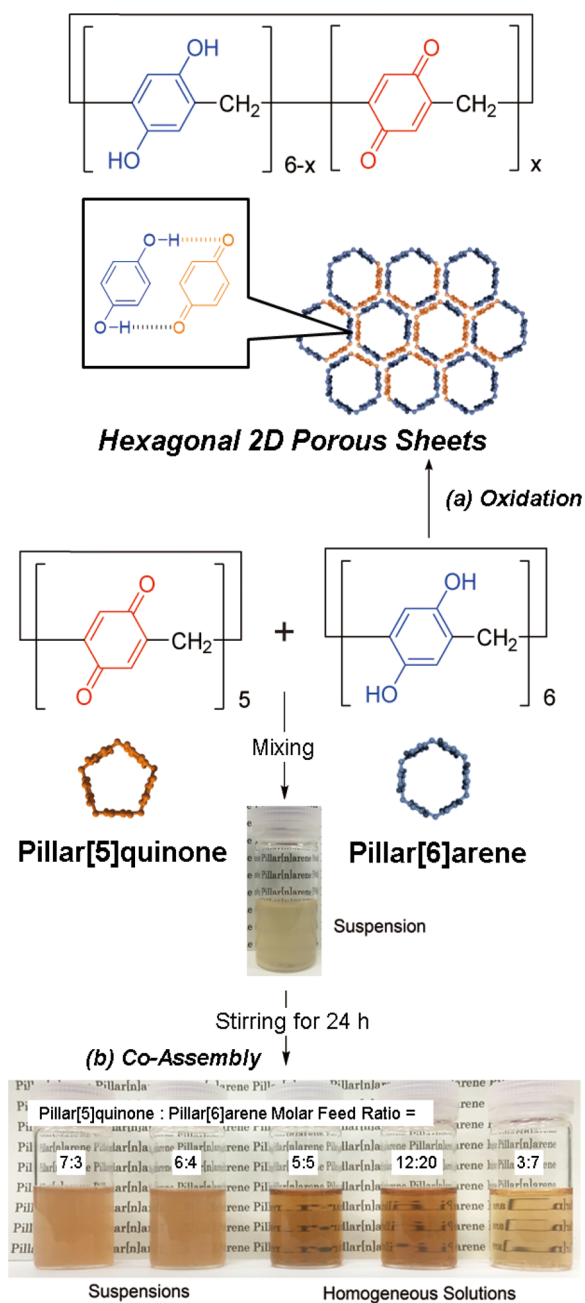


Figure 1. (a) Formation of 2D porous sheets by oxidation of the pillar[6]arene hydroquinone units. (b) Co-assembly of hexagonal pillar[6]arene and pentagonal pillar[5]quinone to form spherical vesicular assemblies.

drone).⁷ The ^1H NMR spectrum recorded after complexation in a 12:20 pillar[5]quinone:pillar[6]arene molar feed ratio (Figure S3) features broad split peaks of the phenyl and methylene bridge protons of pillar[5]quinone and pillar[6]arene, with no ^1H NMR signals of phenyl and methylene bridges of pillar[6]arene detected. Based on 2D diffusion-ordered ^1H NMR spectroscopy measurements (Table S1), the diffusion coefficient of the mixture was found to be $6.51 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, which was smaller than pillar[6]arene alone ($1.57 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$). These results suggest co-assembly of pillar[5]quinone and pillar[6]arene via formation of intermolecular charge-transfer complexes.

The assembled structure in a 12:20 pillar[5]quinone:pillar[6]arene molar feed ratio was then investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images showed spherical aggregates with diameters of 100–300 nm (Figure 2b), which

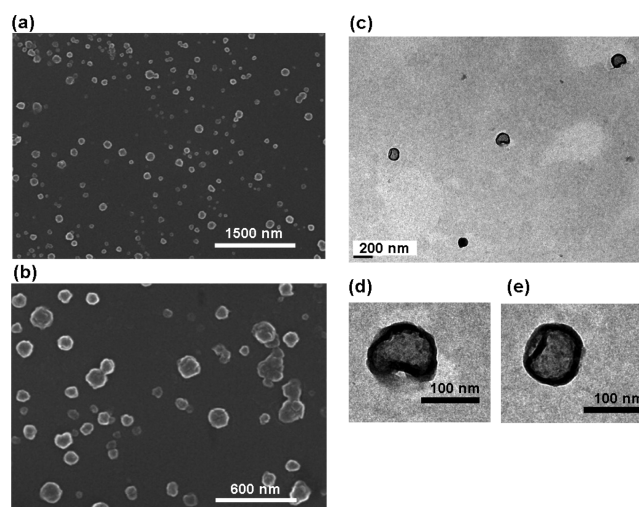


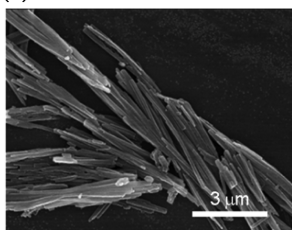
Figure 2. (a,b) SEM and (c–e) TEM images of a mixture of pillar[5]quinone and pillar[6]arene in a 12:20 molar feed ratio. (a,c) Overviews of the vesicles; (b) enlarged image of (a); (d,e) enlarged images of vesicles in (c).

greatly exceed the corresponding extended molecular length of pillar[5]quinone and pillar[6]arene (~ 2 nm), suggesting that these aggregates are vesicular entities rather than simple micelles. These vesicular assemblies were found to be uniformly distributed (Figure 2a). Further evidence for vesicle formation in the mixture of pillar[5]quinone and pillar[6]arene with a 12:20 molar feed ratio was provided by TEM measurements. Spherical aggregates (100–200 nm) with hollow cores were observed (Figure 2c), consistent with the SEM results.⁸ Enlarged TEM images (Figure 2d,e) revealed that the wall thickness of the vesicles was uniform (~ 5 –10 nm), indicating that the walls were composed of multiple layers.

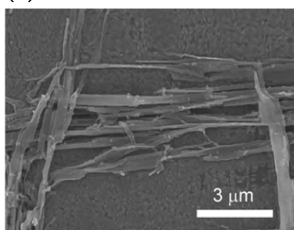
We investigated the effect of feed ratio on the morphology of assembled structures by SEM. Pillar[5]quinone alone formed tubular assemblies (Figure 3a). The formation of fiber-shaped structures by pillar[5]quinone is consistent with the findings of Harris and Sanjayan et al.⁹ Figure 3b–d depicts the fiber-shaped assemblies with spherical particles observed in co-assembled samples containing excess pillar[5]quinone (pillar[5]quinone:pillar[6]arene molar feed ratios of 5:1, 7:3, and 6:4). Spherical assembly was observed by co-assembly of pillar[5]quinone and pillar[6]arene in 5:5 and 3:7 molar feed ratios (Figure 3e,f). However, their shapes were nonhomogeneous, and aggregation of spheres was observed. Disk-shaped hexagonal assemblies were formed by pillar[6]arene alone (Figure 3h). Interestingly, the assembled structures of pillar[6]arene, which has a hexagonal structure, were themselves hexagonal. Hexagonal assemblies were also observed for a co-assembled sample containing excess pillar[6]arene (pillar[5]quinone:pillar[6]arene molar feed ratio of 1:5), as illustrated in Figure 3g. Based on these results, the 12:20 pillar[5]quinone:pillar[6]arene ratio was most suitable for constructing uniformed vesicular architecture by co-assembly of pillar[5]quinone and pillar[6]arene among the mixtures investigated.

Pillar[5]quinone : Pillar[6]arene Molar Feed Ratio =

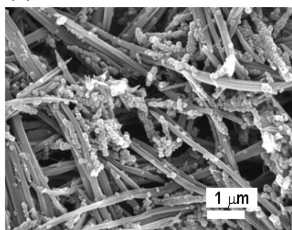
(a) 1 : 0



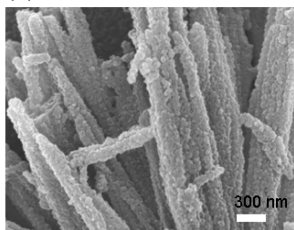
(b) 5 : 1



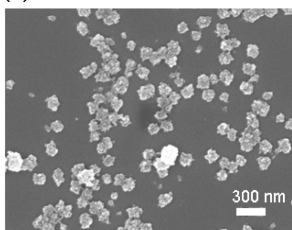
(c) 7 : 3



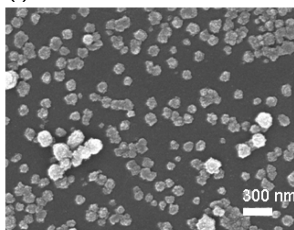
(d) 6 : 4



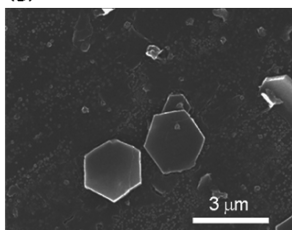
(e) 5 : 5



(f) 3 : 7



(g) 1 : 5



(h) 0 : 1

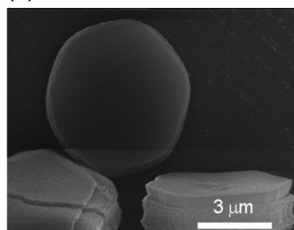


Figure 3. SEM images of (a) pillar[5]quinone, (h) pillar[6]arene, and (b–g) mixtures of pillar[5]quinone and pillar[6]arene with different molar feed ratios.

Thus, we proposed a vesicle formation mechanism by co-assembly of pillar[5]quinone with pillar[6]arene (Figure 4). Hexagonal pillar[6]arene molecules formed 2D planar sheet structures due to their hexagonal structure (Figure 4a).

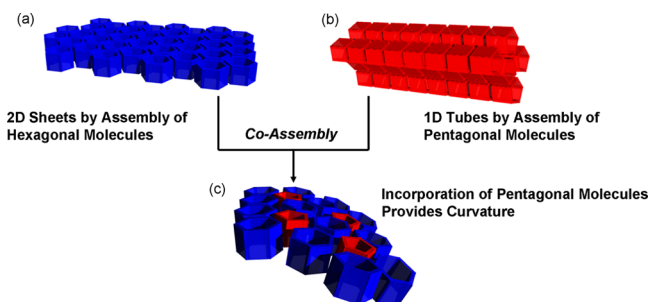


Figure 4. Proposed mechanism of (a) the 2D hexagonal sheet formation by assembly of pillar[6]arene, (b) the tube formation by pillar[5]quinone, and (c) the vesicle formation by co-assembly of cyclic pentagon pillar[5]quinones with cyclic hexagon pillar[6]arenes.

Intermolecular aromatic stacking and hydrogen bonding between pillar[6]arene molecules is one of the main driving forces for construction the 2D planar sheets. Pentagonal pillar[5]quinone molecules formed 1D channels to assemble into tubes, which was proposed by Harris and Sanjayan et al.⁹ (Figure 4b). Incorporation of pentagonal pillar[5]quinone molecules into the 2D sheets composed of pillar[6]arene molecules would provide curvature (Figure 4c), which resulted in the formation of highly ordered spherical structures. Formation of charge-transfer complexes between benzoquinone units of the pillar[5]quinone and hydroquinone units of the pillar[6]arene units is one of the main driving forces for incorporation of the cyclic pentagonal pillar[5]quinone into the 2D sheet constructed from pillar[6]arene molecules. In C_{60} , the pentagons and hexagons are positioned at an angle to each other to reduce the strain associated with curvature. In this case, the high flexibility of pillar[*n*]arenes contributes to the reduction of strain.

In conclusion, we demonstrated vesicle formation by co-assembly of pentagonal pillar[5]quinone and hexagonal pillar[6]arene molecules. As with the spherical architecture of C_{60} , a 12:20 feed ratio of cyclic pentagonal pillar[5]quinone to cyclic hexagonal pillar[6]arene was optimal for constructing spherical architectures among the mixtures investigated. Generally, spontaneous assembly of amphiphilic molecules containing hydrophobic and hydrophilic parts has been used to construct vesicular assemblies.¹⁰ In this study, we successfully constructed vesicular assemblies based on geometric considerations. Assembly of molecules composed of regular polygons, known as molecular tiling, is an attractive method to obtain well-defined 2D sheets.¹¹ Our approach should offer a new way of 3D assembly by incorporating pentagonal molecules into the 2D sheets constructed from hexagonal molecules. The geometric design of vesicle formation is a new concept to construct molecular assemblies with new dimensions. We will further investigate the formation of vesicles with uniform sizes¹² and their properties such as guest-encapsulation ability, stability, and redox-responsiveness. Furthermore, in our previous studies, we converted carbonized 2D porous sheets of pillar[6]arene molecules to obtain carbons that retained the original shapes and pores of these 2D sheets.⁴ Thus, we will now investigate the conversion of vesicles to carbons with vesicular structure.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04125.

Experimental section, ¹H NMR, FT-IR and UV-Vis spectra (PDF)

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Notes

The authors declare no competing financial interest.

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- (12) The size of vesicles composed of 12 pillar[5]quinone and 20 pillar[6]arene molecules calculated is ~3 nm. We will investigate observation of such size of the vesicles.