Molecular Recognizable Cucurbituril/Silica Hybrids

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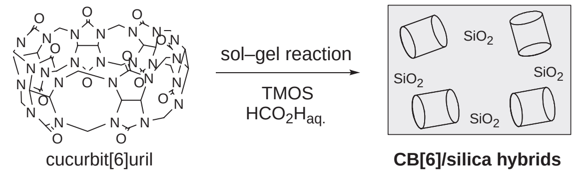
The preparation of molecular recognizable hybrid materials with cucurbituril was achieved by applying sol–gel reaction in an aqueous formic acid without any functionalization of cucurbituril moieties. The hybrid materials obtained showed good film forming properties and benzene recognition abilities.

Cucurbit[*n*]uril derivatives (CB[*n*], $n = 5–10$) are a new family of molecular hosts comprising *n* glycoluril units, and have a hydrophobic cavity that is accessible through two identical carbonyl-fringed portals.[1] Similarly to cyclodextrins (CDs), the hydrophobic interior of CB[*n*] provides a potential site for inclusion of various small molecules. The unique structures and recognition properties make CB[*n*] attractive not only as a synthetic receptor but also as a building block for the construction of supramolecular architectures. Although CB[*n*] are potentially useful as well-known host molecules such as crown ethers and CDs, their practical applications are still limited because of their poor solubility, and difficulty in introducing functional groups on their surfaces. Very recently, the discovery of a direct functionalization method of CB[*n*][2] makes it possible to synthesize a wide variety of CB derivatives and to study many applications such as ion channels, vesicles, and polymers.[3] Those functionalized CBs were also anchored on the surface of silica gel by normal organic reactions, resulting in novel potential materials for separation.[4] The incorporation of CBs into inorganic matrix can broaden the scope of the cucurbituril chemistry, but few reports are known until now. In this study, we describe a novel synthetic method for CB/silica hybrids by sol–gel reaction without any functionalization of CB moieties, and then show the molecular recognition properties of CB/silica hybrids. This is the first example that optically transparent and homogeneous hybrid materials with cucurbituril derivatives based on the sol–gel technique could be prepared.

It is known that cucurbit[6]uril (CB[6]) is a weak base (The pK_a value of the conjugate acid of CB[6] is 3.02) so that the solubility of CB[6] increases dramatically in an aqueous acid (61 mM for CB[6] in H_2O/formic acid (1:1, v/v)). Therefore in this paper, CB[6]/silica hybrids were prepared by sol–gel reaction in an aqueous formic acid (Scheme 1).

A typical preparation method of CB[6]/silica hybrids is as follows. CB[6] (50 mg) was dissolved in 5 mL of H_2O/HCO_2H (1:1, v/v). To the mixture, prescribe amount of TMOS was added. The resulting solution was stirred for 1 h in a sealed bottle. Then, the resulting solution was placed in a polypropylene container covered with a paper towel and left at room temperature for 3 h. The formation of silica gel took place. The container was placed in a 60-°C oven to evaporate the solvent. Finally, the resulting hybrids were heated under reduced pressure at 80 °C for 6 h to remove the remaining solvents and to complete the sol–gel reaction. The results of hybridization are shown in Table 1.



Scheme 1. Cucurbit[6]uril/silica hybrids in an aqueous formic acid.

Table 1. Cucurbit[6]uril/silica hybrids in an aqueous formic acid

Run	TMOS /mg	CB[6]/silica (wt/wt)	Appearance	Ceramic yield/wt %	
				calcd.	obsd.[a]
1	—	—	turbid	0	0
2	25	5/1	turbid	16.7	16.1
3	63	2/1	turbid	33.3	34.0
4	130	1/1	transparent	50.0	49.9
5	250	1/2	transparent	66.7	63.1
6	630	1/5	transparent	83.3	76.6

[a]Determined by TGA.

The obtained CB[6]/silica composites with less than 33.3 wt % of silica were turbid and heterogeneous (Runs 2 and 3). On the other hand, in the samples with more than 50.0 wt % of silica (Runs 4–6), transparent and homogeneous CB[6]/silica hybrids could be easily obtained via the hydrogen-bonding interaction between ureido carbonyl groups of CB[6] and residual silanol groups of siliceous phase, as described in the previous papers.[5] In addition, the original CB[6] film without silica was turbid and heterogeneous, suggesting the poor film forming property of CB[6] (Run 1). These observations are explained by the crystallinity of CB[6] in hybrids. The crystallinity of CB[6] in silica gel matrix was investigated by X-ray diffraction patterns (Figure 1).

The pristine CB[6] exhibited high crystallinity as shown in Figure 1a. But the crystallinity of CB[6] was gradually decreasing with increasing of silica gel contained (Runs 2 and 3, Figures 1b and 1c). In the transparent hybrids (Runs 4–6, Figures 1d–1f), the characteristic peaks of CB[6] clearly disappeared and the single broadening halo peak around 22° resulting

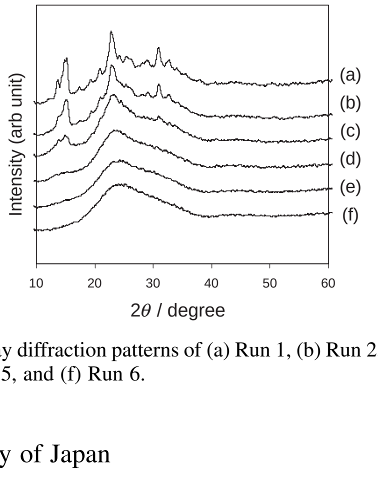
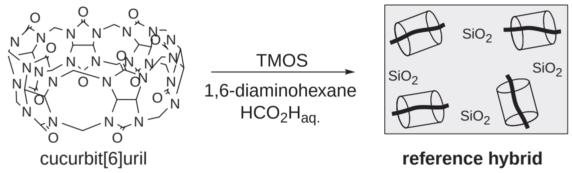


Figure 1. X-ray diffraction patterns of (a) Run 1, (b) Run 2, (c) Run 3, (d) Run 4, (e) Run 5, and (f) Run 6.



Scheme 2. CB[6] pseudo[2]rotaxane/silica hybrid as a reference hybrid.

Table 2. Synthesis of cucurbit[6]uril pseudo[2]rotaxane/silica hybrid[a]

Run	1,6-Diaminohexane /mg	CB[6]/silica (wt/wt)	Ceramic yield/wt %	
			calcd.	obsd.[b]
6	—	1/5	83.3	76.6
7	5	1/5	81.8	79.6

[a] CB[6] (50 mg), 5 mL of H_2O/formic acid (1:1, v/v), and TMOS (530 mg) were used. [b] Determined by TGA.

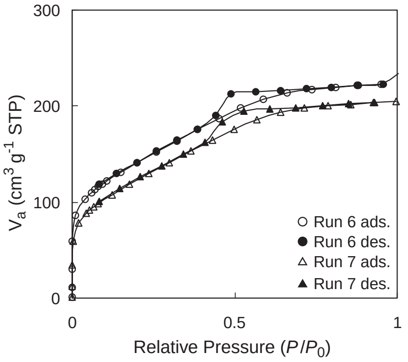


Figure 2. Nitrogen adsorption/desorption isotherm curves of Run 6 original hybrid (circles) and Run 7 reference hybrid (triangles).

from amorphous silica was observed. These results clearly indicate that the crystallization of CB[6] in silica gel matrix is inhibited by the amorphous reticular silica network in case of the high silica ratio. In addition, solid-state ^{29}Si NMR spectrum of Run 6 hybrid showed completely the same as that of silica gel without CB[6], indicating the absence of the siliceous segments inside the cavity of CB[6].

As a reference, CB[6] pseudo[2]rotaxane/silica hybrid was also prepared (Scheme 2). It is known that CB[6] forms stable inclusion complex with 1,6-diaminohexane (mole ratio = 1:1, $K_a > 10^5$).[6] We expected the included guest molecules might change the molecular recognition abilities of hybrids.

The preparation method of reference hybrid is as follows. CB[6] and 1,6-diaminohexane (1:1, mole ratio) were dissolved in H_2O/HCO_2H (1:1, v/v). To the mixture, prescribed amount of TMOS was added after confirming the formation of inclusion complex by ^{1}H NMR. The workup procedure is the same as that of CB[6]/silica hybrid (Run 6), and the result of hybridization is shown in Table 2 (Run 7).

The obtained hybrids were crushed into powders, then nitrogen sorption porosimetry measurements were conducted (Figure 2). Both hybrids (Runs 6 and 7) showed type IV curves, indicating that these hybrids had nano-pores. Expectedly, the surface area (calculated by BET[7] method) of reference hybrid (Run 7) was smaller than that of original hybrid (Run 6) due to the existence of the included guest molecules.

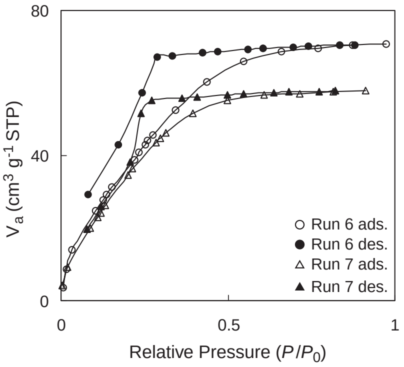


Figure 3. Benzene vapor adsorption/desorption isotherm curves of Run 6 original hybrid (circles) and Run 7 reference hybrid (triangles).

It is known that CB[6] can encapsulate neutral molecules such as benzene, furan, and tetrahydrofuran (THF) in aqueous solution.[8] To confirm the molecular recognition behavior of the obtained hybrids, benzene vapor adsorption study was conducted. Benzene vapor adsorption studies were carried out at 25 °C from 0 to 0.99 (P/P_0, P_0 = saturated benzene vapor pressure) for adsorption process and from 0.99 to 0.10 (P/P_0) for desorption process. As shown in Figure 3, low-pressure hysterisis can be seen in original hybrid (Run 6) due to the benzene recognition ability of CB[6]. On the other hand, in reference hybrid (Run 7), the correct amount of the adsorbed benzene vapor was released at low-pressure region, and no low-pressure hysterisis exists. This result clearly indicates that the benzene recognizable CB[6] cavities were filled with the included 1,6-diaminohexanes, consequently reference hybrid lost the benzene recognition ability. From these observations, in original hybrid, CB[6] retains both the structure and the molecular recognition property even after hybridization.

In conclusion, organic–inorganic hybrid materials with CB[6] were prepared by sol–gel process in an aqueous formic acid. The transparency and homogeneity of the obtained CB[6]/silica hybrids were gradually improved according to the increase of silica gel segment. The optically transparent CB[6]/silica hybrids containing up to 50 wt % silica components could be obtained. The obtained hybrids showed film forming properties which can not be achieved from the original CB[6] themselves. Furthermore, the CB[6]/silica hybrids showed benzene recognition property as CB[6] itself. Therefore, they will be promisingly applied for various fields such as sensors, membranes, and separations.

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