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Periodic Mesoporous Organosilica with Molecular-Scale Ordering Self-Assembled by Hydrogen Bonds

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Abstract: *Nanoporous materials with functional frameworks have attracted attention because of their potential for various applications. Silica-based mesoporous materials generally consist of amorphous frameworks, whereas a molecular-scale lamellar ordering within the pore wall has been found for periodic mesoporous organosilicas (PMOs) prepared from bridged organosilane precursors. Formation of a "crystal-like" framework has been expected to significantly change the physical and chemical properties of PMOs. However, until now, there has been no report on other crystal-like arrangements. Here, we report a new molecular-scale ordering induced for a PMO. Our strategy is to form pore walls from precursors exhibiting directional H-bonding interaction. We demonstrate that the H-bonded organosilica columns are hexagonally packed within the pore walls. We also show that the H-bonded pore walls can stably accommodate H-bonding guest molecules, which represents a new method of modifying the PMO framework.*

Periodic mesoporous organosilicas (PMOs) are inorganic–organic hybrid porous materials prepared by surfactant-directed polycondensation of bridged organosilane precursors ($R[Si(OR')_3]_n$; $n \geq 2$, R = organic bridging group, R′ = Me, Et, etc.).[1] They are promising for various functional applications such as adsorbents,[2] solid catalysts,[3] luminescent materials,[4] and nano-vessels for biological applications,[5] because of their high surface areas, mesoscale porous structures enabling easy molecular diffusion, diversity of framework components, and light-harvesting properties of the frameworks.[6,7]

One of the most remarkable structural features of PMOs is the molecular-scale ordering of their pore walls achieved by the introduction of appropriate organic bridging groups.[8–15] The periodic arrangement of organic groups is expected to enable tuning and enhancement of the physical and chemical properties of the frameworks.[16] The first example was reported for a benzene-bridged PMO in 2002,[8] which possessed alternating benzene–silica lamellar structures. A similar "crystal-like" lamellar ordering for pore walls has been found in PMOs prepared from organosilane precursors with various hydrophobic bridging R groups, such as biphenyl, 1,4-divinylbenzene, naphthalene, and 2,2′-bipyridine.[2b,9–15] Such organosilane molecules tend to self-assemble into lamellar structures in water, owing to the hydrophobic and hydrophilic interactions of hydrolyzed organosilane species.[17] However, since the above-mentioned first report in 2002, there have been no studies on other types of crystal-like PMOs showing molecular-scale ordering of pore walls except for the lamellar ordering. Although we reported electroactive PMOs containing π-stacked columns of perylenebisimide within the pore wall in 2012, regular packing or long-range ordering of the columnar assemblies was not confirmed.[18]

In this study, we present a novel approach to achieving a crystal-like arrangement in the pore wall of PMOs. We reasoned that if an organosilane precursor has H-bonding components within its molecule, a new type of molecular-scale ordering can be induced in the pore walls of that PMO. Thus, we designed cyclohexane triamide derivative **1** (Figure 1 a), because the cyclohexane triamide moiety is known as a strong H-bonding component and has been applied to functional supramolecular materials such as low-molecular-weight gelators, thickeners, and stimuli-responsive nanofibers.[19] Here, we report that the use of the cyclohexane

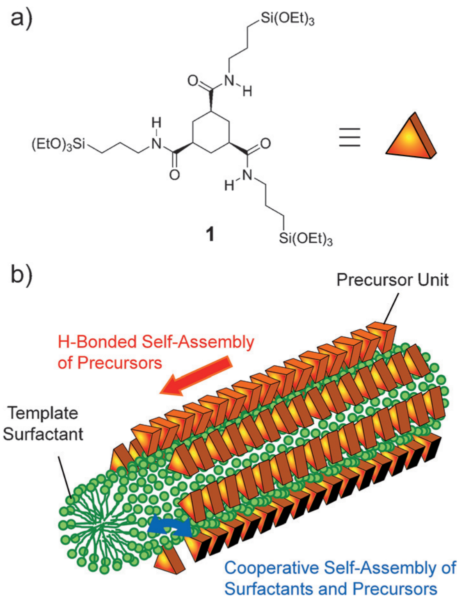

Figure 1. a) Chemical structure of H-bonding organosilane precursor **1**. b) Schematic illustration of cooperative self-assembly of surfactant micelles and organosilane precursors, combined with directional molecular self-assembly of the precursors.

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triamide moiety as a bridging R group realizes a new type of molecular-scale ordering within the framework of PMOs by the formation of H-bonded columns (Figure 1 b). PMOs with H-bonded columns have great merit for the incorporation of guest molecules within their walls by H-bonded interactions. For example, easy embedding of guest molecules within the framework will facilitate tuning of its photo- and electroactive properties toward the formation of well-designed reaction fields. We show that silane-free triamide guest molecules can be stably fixed within the pore walls of the **1**-based PMO by H-bonded intercalation, which can be regarded as a new method for structural modification of organosilica hybrids.

Precursor **1** was synthesized by reacting a 2,2,2-trifluoroethyl ester[20] of *cis*,*cis*-1,3,5-cyclohexanetricarboxylic acid with 3-aminopropyltriethoxysilane. In contrast to other synthetic routes of amides by common active esters or acid chloride, the present reaction proceeded without detectable byproducts and the resulting trifluoroethanol could be removed by filtration and drying under reduced pressure; therefore, several grams of high-purity precursor **1** could easily be obtained.

Polycondensation of **1** was carried out under basic hydrolytic conditions in the presence of a cationic template surfactant (trimethyloctadecylammonium chloride, $C_{18}TMACl$). Typically, a 1:1 (w/w) mixture of **1** and $C_{18}TMACl$ ($Si/C_{18}TMACl = 1:0.79$, molar ratio) was stirred in a 0.15 M aqueous NaOH solution at room temperature for 24 h, and heated at 95 °C for 24 h to afford a white precipitate. The surfactant-containing as-prepared precipitate was washed with a 0.6 wt% NH_4NO_3 solution in ethanol to extract the surfactant. IR absorption spectra for the as-prepared and extracted samples showed that the C=O and N−H stretching bands of cyclohexane triamide moieties were observed at 1639 and 3286 cm^{-1}, respectively, indicative of the formation of hydrogen bonds (see Figure S5 in the Supporting Information).[19a] Absorption bands corresponding to amides that were free of H-bonds (1660–1680 cm^{-1} for the C=O stretching band) were not found for any sample. Figure 2 a shows a SEM image of the organosilica powder after extraction of the surfactant. The white powder mainly consisted of roughly spherical primary particles with diameters of 1–2 µm. Solid-state ^{13}C and ^{29}Si MAS NMR measurements revealed that the organic bridging moieties could withstand the present reaction conditions and the triethoxysilyl groups of **1** efficiently condensed into well-crosslinked siloxanes (Figure S6).

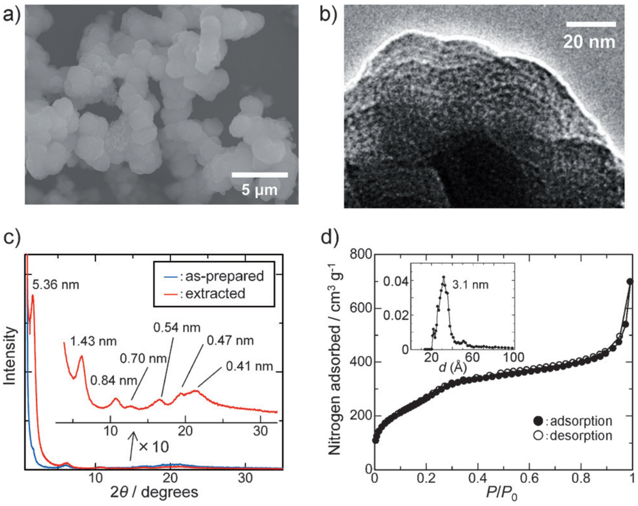

Figure 2. a) SEM and b) TEM images, c) XRD patterns, and d) nitrogen adsorption–desorption isotherm of the PMO based on **1**. The inset of (d) shows a DFT pore-size distribution.

The meso- and molecular-scale periodic structures of the organosilicas based on **1** were examined by XRD measurements, TEM observations, and nitrogen adsorption–desorption isotherm measurements. Figure 2 c shows XRD patterns for the as-prepared and extracted organosilica samples. In the small-angle region, a strong diffraction peak associated with $d = 5.36$ nm corresponding to a periodic mesostructure was observed for the extracted sample. Interestingly, several small peaks appeared at $2\theta = 6–22°$ for the as-prepared and extracted samples; these were attributed to molecular-scale ordering of the organosilica framework. The reciprocals of the *d*-spacing values (1.43, 0.84, 0.70, 0.54, 0.47, and 0.41 nm) are in the ratios $1:1/\sqrt{3}:1/2:1/\sqrt{7}:1/3:1/\sqrt{12}$. This is typical of 2D hexagonal packing with a lattice constant of 1.65 nm (Table S1). TEM images of the extracted sample indicated the formation of periodic mesoporous structures with columnar channels (Figure 2 b). The periodicities were about 5–6 nm, which agreed with the *d* value for the main XRD peak. In addition, stripe patterns with a periodicity of about 2 nm were partially observed in the TEM images (Figure S7). Although hexagonal structures were not evident, the 2 nm pattern might correspond to the ordered organosilica framework with H-bonded chains. Figure 2 d shows a nitrogen adsorption–desorption isotherm of the extracted sample; this is a type-IV isotherm typical of mesoporous materials. The Brunauer–Emmett–Teller (BET) surface area, pore volume, and DFT pore diameter were calculated to be 1079 $m^2 g^{-1}$, 0.46 $cm^3 g^{-1}$, and 3.1 nm, respectively. These results indicate that surfactant-directed polycondensation of **1** leads to the formation of PMOs with a molecularly ordered H-bonded framework.

Figure 3 shows a structural model of the PMO synthesized using **1**. The proper development of H-bonded chains of cyclohexane triamide moieties suggests that the pore walls consist of H-bonded organosilica columns with 2D hexagonal packing. The diameter of the H-bonded organosilica column is estimated to be about 1.7 nm by molecular modeling, which agrees with the lattice constant (1.65 nm) of the molecular-scale 2D hexagonal packing obtained by XRD. Comparing the mesoscale periodicity of the PMO (5–6 nm) with the DFT pore diameter (3.1 nm), the thickness of the pore wall is thought to be 3 nm. Therefore, the pore walls between mesopores presumably consist of two columns of H-bonded organosilica. When the H-bonded columns are packed in a 2D hexagonal arrangement in the pore wall, the structural periodicities of the PMO are consistent with the XRD results as shown in Figure 3. This is the first example of a crystal-like PMO with 2D hexagonal packing of organic bridging groups. This new molecular order was realized through a combination of the cooperative self-assembly of **1** and $C_{18}TMACl$, and H-

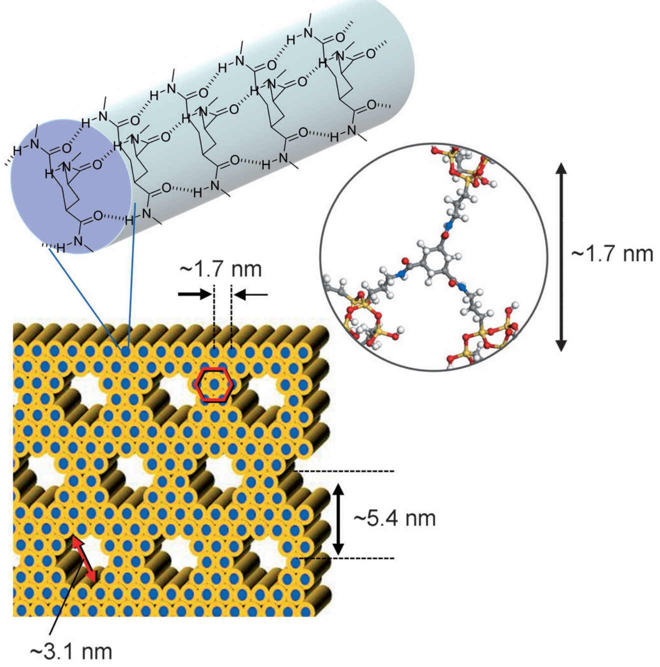

Figure 3. Schematic illustration of the hierarchical nanostructure of the PMO synthesized using **1**.

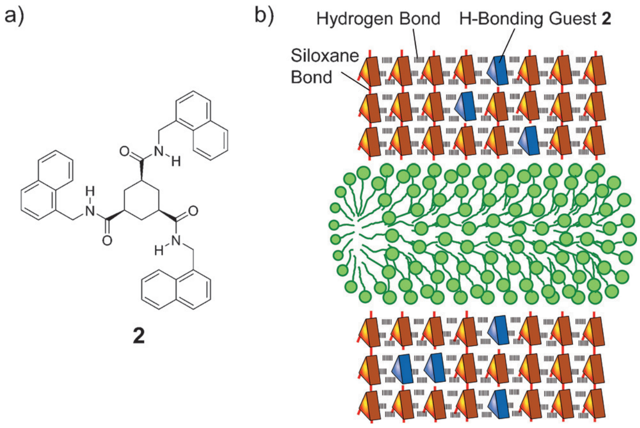

Figure 4. a) Chemical structure of the H-bonding guest **2**. b) Schematic illustration of the co-assembly of **1** and **2** in the pore walls of H-bonded PMO.

bonded self-assembly of precursor **1** itself (Figure 1 b). The pore walls formed by a three-armed organosilica network can have molecular-level roughness on the surface due to the restricted molecular packing, which may be a cause of a relatively large surface area of the PMO.

We found that PMOs based on **1** could stably hold H-bonding guest molecules within their pore walls (Figure 4). As a guest molecule, cyclohexane triamide derivative **2** with naphthyl groups was selected because i) its molecular size is close to that of **1** and 2) it functions as a fluorescent probe. To examine the incorporation of **2** into the H-bonded framework, PMOs were synthesized using **1**/**2** mixtures containing 0–10 mol % **2**, yielding white powders, as shown in Figure 5 a. The loading of **2** in the powder was confirmed by the presence of IR absorption peaks at 773 and 795 cm^{-1}, corresponding to C−H vibrations of naphthyl groups (Figure S8). IR spectra also indicated that the cyclohexane triamide moieties formed H-bonded chains without H-bond-free defects. SEM observation of the PMO revealed that the morphology changed to small rod-like nanoparticles upon the addition of **2** (inset of Figure 5 a and Figure S9). The incorporation of **2**, which is insoluble in water and has a high affinity for **1**, may promote the 1D growth of H-bonded organosilica columns, resulting in elongated nanoparticles. The white powder showed blue fluorescence under UV irradiation, owing to the naphthyl moieties of **2**. Figure 5 b shows a fluorescence micrograph of the powder. The blue-fluorescent pattern is in good agreement with the optical image shown in Figure 5 a, which suggests homogeneous dispersion of guest molecule **2** in the PMO at the micrometer scale at least.

The location of **2** in the PMO was examined by structural and spectroscopic analyses. XRD patterns for the **2**-doped PMOs showed a broad peak corresponding to a periodic mesostructure at $d = 5.4$ nm. Molecular-scale 2D hexagonal ordering was observed within the framework, similar to that observed in the PMO synthesized from **1** alone (Figure S10). Nitrogen adsorption-desorption isotherms of the **2**-doped PMOs indicated the formation of mesopores with diameters of 3.2–3.3 nm and high BET surface areas of over 700 $m^2 g^{-1}$ (Figure S11). Fluorescence spectra of the PMOs are shown in Figure 5 c. A solution of **2** in dimethyl sulfoxide (DMSO) showed a monomer band emission around $\lambda = 340$ nm, with a fluorescence quantum yield (QY) of 0.160 upon excitation at $\lambda = 290$ nm. In contrast, the neat solid of **2** showed a broad and weak emission (QY = 0.015) at wavelengths longer than 350 nm. Long-wavelength emissions above $\lambda = 500$ nm are thought to contain fluorescence from aggregates of naphthyl moieties, because excimer band emission of naphthalene derivatives is generally centered at $\lambda \approx 400$ nm.[21] Compared to the neat solid of **2**, PMOs doped with 3–10 mol % **2** exhibited relatively narrow emissions with peaks at $\lambda = 345$–347 nm and QYs of 0.046–0.058. The fluorescence spectra seem to be a superposition of monomer and excimer band emissions. Thus, guest molecule **2** is presumably fixed as a monomeric or dimeric species in the H-bonded organosilica framework.

In order to confirm the intercalation and fixation of **2** within the pore walls, an extraction test was conducted on **2**-doped PMOs. If H-bonded aggregates of **2** are physically adsorbed onto the surface of the PMOs, they should be removable by good solvents of **2**. In contrast, when the guest molecules of **2** are incorporated within the pore wall as shown in Figure 4 b, it is difficult to elute them because they are entrapped by the 3D organosilica network. We selected tetrahydrofuran (THF) as a solvent because it can dissolve **2** but has no significant effect on the PMO framework. Figure 5 d shows photographs of **2**-doped PMO immersed in THF under UV irradiation. We can see strong blue fluorescence from the powders, but not from the supernatant solution. The amount of **2** extracted into THF from 20 mg of PMO synthesized using 10 mol % **2** was calculated to be 0.19 mg on the basis of UV/Vis spectroscopy (Figure S12). On

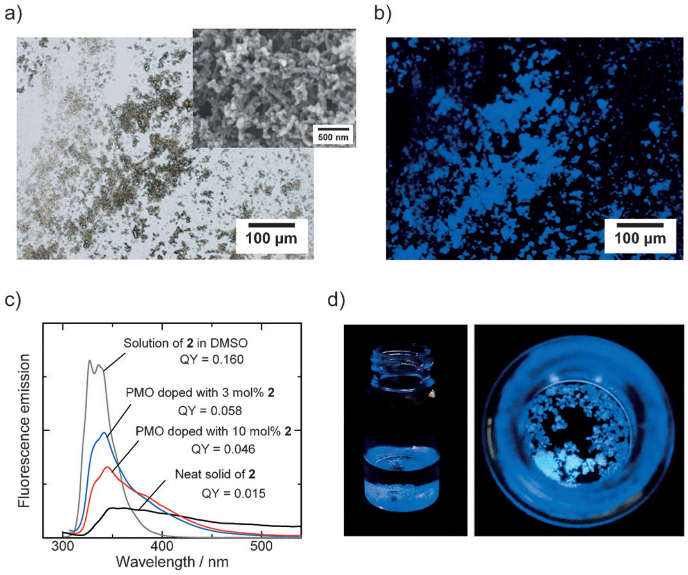

Figure 5. a) Optical photomicrograph of PMO prepared in the presence of 10 mol% **2** (Inset: SEM image; scale bar = 500 nm). b) Fluorescence micrograph of the **2**-doped PMO. c) Fluorescence spectra of **2** and **2**-doped PMOs upon excitation at 290 nm. d) Photographs of the **2**-doped PMO powders immersed in THF under UV irradiation.

the other hand, the actual amount of **2** initially contained in the PMO turned out to be 16.6 mol% (3.8 mg in 20 mg of PMO).[22] Thus, 95% of the molecules of **2** were stably fixed within the PMO pore walls. We also confirmed that no elution of **2** was observed for other organic solvents except for DMSO, such as methanol, ethanol, chloroform, acetone, and toluene.

In conclusion, a new class of PMOs with molecular-scale ordering was fabricated by selecting organosilane precursors with strong self-assembling properties. PMOs based on **1** had hexagonally packed H-bonded columns within their pore walls. Moreover, we found that silane-free guest molecules could be fixed stably within the pore walls by H-bonded intercalation. This suggests that PMOs can function as a versatile platform for the incorporation of various organic components into pore walls. The combination of H-bonded intercalation and chemical modification using silanol groups may lead to the construction of multifunctional PMOs applicable to multistep reaction fields and biomimetic systems.

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[22] Immersion of the **2**-doped PMOs in DMSO at 80 °C resulted in collapse of the periodic mesostructures presumably due to the dissociation of hydrogen bonds within the framework. In this case, guest molecule **2** was completely extracted into DMSO. The amount of extracted **2** was quantified by UV/Vis spectroscopy and direct measurements of the weight loss of the powders. Both measurements indicated that 3.8 mg of **2** was contained in 20 mg of the PMO synthesized using 10 mol % **2**.

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