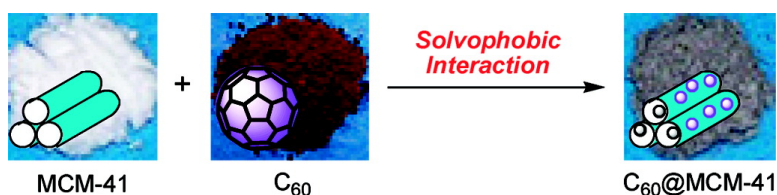


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Inclusion of C₆₀ into MCM-41 by Solvophobic Nature

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A new class of mesoporous, silica-based, organic–inorganic hybrid composites has been developed.¹ Control of the one-dimensional arrangement of fullerene [C₆₀]² was expected to induce unprecedented physical and/or chemical properties. It was expected that if C₆₀ was combined with periodic mesoporous hosts in high density, such as MCM-41³ and FSM-16,⁴ the resulting organic–inorganic composites would be new and potent functional materials. Although some progress has been made in attempts to combine C₆₀ with mesoporous materials,^{5–9} the methods used required high temperature (600 °C) and highly reduced pressure and the resulting yields of C₆₀ embedded in the materials were low—clearly, a reliable process has not been established. A novel silica–water reaction medium based on the adsorptive nature of silica gel was recently discovered, which provided a potential method for synthesis of aziridines from olefins in water.¹⁰ Silica is effective as an organic reaction medium in water since the organic substrate would be adsorbed to the silica by hydrophobic interaction between the surface of the silica and the organic molecule. On the basis of this concept, a novel process for inclusion chemistry in periodic mesoporous hosts was devised. Taking advantage of the fact that C₆₀ is not easily soluble by organic solvents, solvophobic interaction between the internal surface of MCM-41 and C₆₀ was induced, which resulted in an organic–inorganic nanocomposite of highly concentrated C₆₀ in MCM-41 (Figure 1).

Commercially produced crystalline C₆₀ (36 mg) was first dissolved in toluene, and then MCM-41 (100 mg) was added to the solution (Figure 2). Toluene was slowly removed from the suspension using a rotary evaporator. To facilitate the efficient inclusion of C₆₀ into MCM-41, the aggregation of the C₆₀ molecule was unbound by dissolving it in toluene. In order to find media to induce a solvophobic interaction that would facilitate the efficient incorporation of C₆₀ into MCM-41, several organic solvents, each of which minimally dissolves C₆₀, were evaluated: benzene, methylene chloride, chloroform (sample A), diethyl ether (sample B), and ethanol. Only chloroform was found to achieve efficient incorporation. Recently, Yadasaka et al. reported a method for incorporation of C₆₀ into single-wall carbon nanotubes in liquid phase, to prepare “peapods”.¹¹ The following experiment was carried out to evaluate the method. The suspension of MCM-41 and C₆₀ in chloroform was left to stand for 1 day. The insoluble material was then filtered off and dried to yield a brindle solid (sample C). To investigate whether this method incorporated C₆₀ into MCM-41, a control sample was prepared by grinding and mixing a mixture of C₆₀ and MCM-41 in a mortar (sample D).

The color of sample A is clearly distinct from that of samples B, C, and D by visual observation. For example, when the color of these samples is described in terms of the *L* a* b** color space, MCM-41 by itself is white (*L** = 97.99, *a** = 0.07, *b** = 0.24), sample A is gray (*L** = 42.30, *a** = 3.64, *b** = 2.12), and sample D is brown (*L** = 39.86, *a** = 5.61, *b** = 20.50). In contrast to the specific surface area of MCM-41 (1060 m² g⁻¹), the surface area of sample A decreased to 670 m² g⁻¹. The X-ray powder diffraction patterns of samples A, B, C, and D and the patterns of

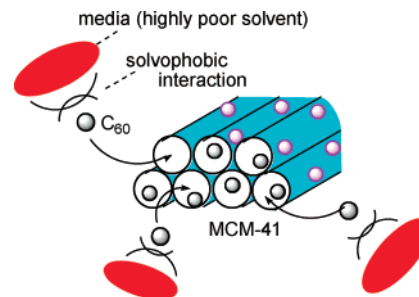
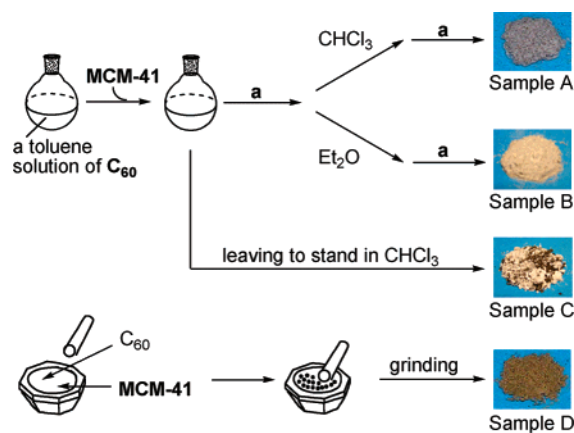


Figure 1. Schematic illustration of the concept of inclusion of C₆₀ into MCM-41 based on solvophobic interaction.



(a) Evaporation of the solvent by rotary evaporator.

Figure 2. Inclusion methods of C₆₀ into MCM-41 and grinding and mixing of these two materials in a mortar as a control sample.

C₆₀ and MCM-41 are shown in Figure 3. The sharp peaks at approximately 11, 18, and 21° (derived from C₆₀) and the typical halo pattern of SiO₂ around 22° were observed in samples B, C, and D. The three sharp peaks, however, did not appear in sample A. These results suggest that C₆₀ was completely incorporated into MCM-41 in sample A but was not incorporated into the mesopore and C₆₀ remained in samples B, C, and D. One major peak at around 2°, which is not shown in Figure 3, was observed in samples A–D, indicating that the hexagonal pore structure of MCM-41 was retained in sample A after the incorporation of C₆₀. The evaporation of the solvent from the suspension of C₆₀ and MCM-41 in chloroform accelerated the inclusion of C₆₀ into the mesopore and also led to its homogeneous dispersion. Moreover, the relationship between XRD patterns and various amounts of C₆₀ included into MCM-41 by the method presented here was investigated.¹² The XRD patterns of C₆₀ were observed in composites that contain more than 40 mg of C₆₀. Therefore, the maximum allowable amount of C₆₀ into MCM-41 (100 mg) was found to be between 36 and 40 mg, and the phenomenon also should strongly support the inclusion of C₆₀ into the mesopore.

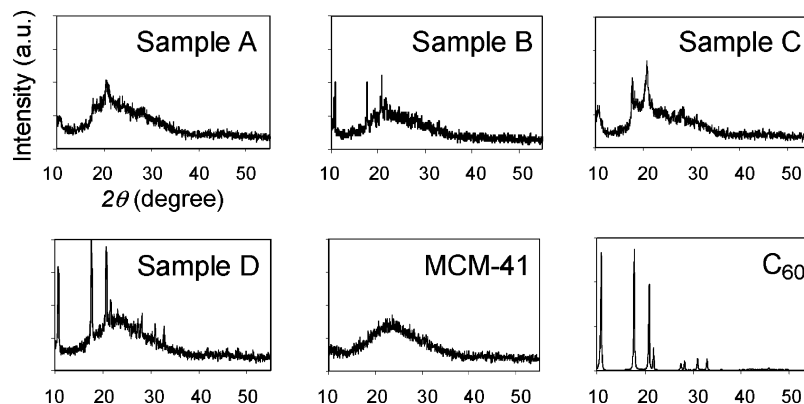


Figure 3. XRD patterns of samples A–D, MCM-41, and C₆₀.

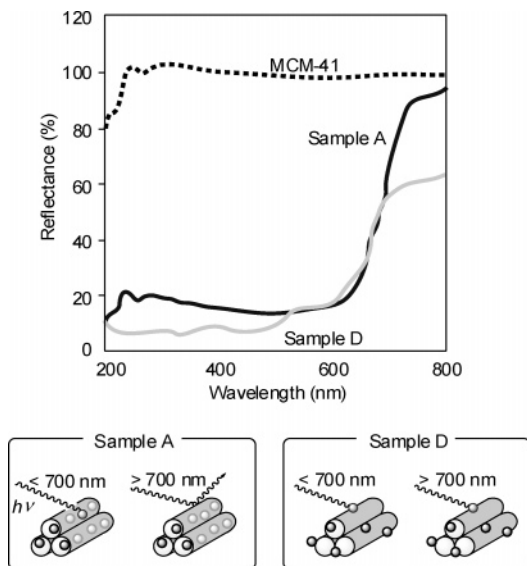


Figure 4. UV–vis reflection spectra of MCM-41, samples A and D, and schematic illustration for the spectra.

The reflectance spectra of samples A, D, and MCM-41 were measured. While samples A and D both absorbed light of less than 700 nm—a high penetration power—sample A reflected light of lower penetration (>700 nm), at a level similar to that of MCM-41 and comparable with that of sample D (Figure 4). The reflectance of long wavelength light by sample A indicates that C₆₀ was incorporated into MCM-41.

Observation of thermogravimetric analysis (TGA) of sample A in a stream of air revealed that the charged sample lost a considerable amount of its mass (charged, 26 wt %; lost on heating, 27 wt %). The curving lines of differential thermal analysis (DTA) for sample A and crystalline C₆₀ were quite different. The curve of sample A was very sharp—in the temperature range of 420–570 °C—and that of C₆₀ was broad (400–700 °C).¹² These results indicate that the C₆₀ incorporated into sample A was homogeneously distributed in the MCM-41. In contrast, bulk C₆₀ and charged C₆₀ incorporated into MCM-41 did not bind to the surface of MCM-41 with a covalent bond. In fact, all of the C₆₀ could be extracted by washing sample A with toluene.

High-resolution electron microscopy images of MCM-41, sample A, and sample D are shown in Figure 5. The TEM images provide evidence that C₆₀ was incorporated into the mesopore. While a black object derived from C₆₀ was observed in the TEM image of sample D, no object on the exterior of the mesopore was observed in sample A. The TEM image of sample A reveals the same hexagonal pore structure as MCM-41.

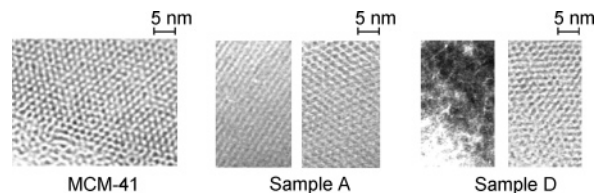


Figure 5. TEM images of MCM-41 and samples A and D.

A previous study reported C₆₀ encapsulated in cubic mesoporous silica (MCM-48),¹³ and this method was also used with MCM-41. However, C₆₀ was not incorporated into MCM-41, and 99% of the C₆₀ was recovered.

The method described above is a new concept for incorporation of C₆₀ into a periodic mesoporous material, utilizing solvophobic interaction between the surface of the mesopore and C₆₀. This process may also provide a potential new methodology¹⁴ for incorporation of organic molecules into inorganic fine pores. The resulting organic–inorganic composites could potentially be used to create versatile hybrid materials.

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Supporting Information Available: Experimental details, the XRD data for various amounts of C₆₀ included into MCM-41, and TGA and DTA data of sample A. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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