Photo-Switched Storage and Release of Guest Molecules in the Pore Void of Coumarin-Modified MCM-41

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A photoresponsive coumarin derivative was grafted on the pore outlet of Si−MCM-41. Irradiation of UV light longer than 310-nm wavelength to this coumarin-modified MCM-41 induced the photodimerization of coumarin to close the pore outlet with cyclobutane dimer. Guest molecules such as phenanthrene neither can enter nor escape from the one-dimensional, isolated, individual pores of MCM-41. On the other hand, the irradiation to the dimerized-coumarin-modified MCM-41 with shorter wavelength UV light around 250 nm regenerates the coumarin monomer derivative by the photocleavage of cyclobutane dimer, and guest molecules included inside are released from the pore void. For the first time, this intermolecular reversible photodimerization−cleavage cycle realized photo-switched storage and release of guest molecules from coumarin-modified MCM-41. Coumarin-modified MCM-41 prepared using tetradecyltrimethylammonium bromide as surfactant was able to store 21.6 wt % of phenanthrene as guest molecule after photodimerization and washing with *n*-hexane. Among the four different methods studied for the modification by the coumarin derivative, a grafting procedure with as-synthesized MCM-41 for short reaction time was found to be the most effective for the dense attachment of coumarin-derived monomer at the pore outlets of MCM-41, which is essential for effective storage−release controlled release.

Introduction

A large number of research studies are reported on the syntheses of hexagonal mesoporous silicas and their analogues after the discovery of MCM-41.[1,2] Recently, their applications to various fields have been actively studied using their unique pore voids in catalysis chemistry,[3] polymerization process,[4] separation process,[5,6] preparation of nanoparticles,[7] and photochemistry.[8−10] Fabrication of organic−inorganic mesoporous silica materials are also current, active subjects by direct syntheses[11] and/or post syntheses.[2,12] Recently, interesting behaviors of substrates included in the pore voids are reported.[13] On the other hand, amorphous silica materials have been well-applied to a controlled

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release system because of their high porosity suitable for the storage of molecules.[14] In the case of MCM-41, the narrow pore size distribution (ca. 2−4-nm diameter) is advantageous for including various types of compounds. The potential ability of MCM-41 as a controlled release material and drug delivery material was noted. For example, Vallet-Regi et al. presented the applications of simple calcined or modified MCM-41 for protracted release of compounds included in their pore voids.[15] Responsive release of drugs from the pore void of MCM-41 using CdS nanoparticle caps has also been claimed recently.[16] Furthermore, the sequestration and release of proteins by organically modified porous silicas are also reported.[17] Recent advances in the preparation of MCM-41 nanoparticles increase their potential for drug delivery application.[16,18]

The advantageous characteristics of MCM-41 to the utilization of controlled release are one-dimensional, isolated, and uniform size of pore void. Each isolated pore can be considered to be separated "nanosize" storage voids of guest molecules. The modification of pores in MCM-41 is a well-studied methodology[5] and recent advances are quite progressive.[19] This modification of pore voids of MCM-41 is expected to control the passage of included molecules effectively more than unmodified ones. The reversible photochromism effects, reported for diazobenzene[9] and spiropyran derivatives,[10] attached to the pore walls have a possibility to regulate pore access. Recently, Brinker and co-workers demonstrated the photo-responsive pore size control of hexagonal mesoporous silica by azobenzene modification.[9c] On the other hand, the intermolecular reversible photodimerization and photocleavage of coumarin derivatives (Figure 1) [20] well-employed in the sol−gel transition of polymers and other intelligent materials is another approach for regulating the passage of guest molecules in the pore of MCM-41. When the coumarin part is dimerized by the irradiation with UV light longer than 310 nm, the molecular "hinged double doors" of the pore in MCM-41 are closed and guest molecules are stored inside. On the other hand, the irradiation with shorter wavelength UV light around 250 nm cleaves the coumarin dimer to regenerate its monomer and opens the "double doors" of the pore in MCM-41, resulting in the release of guest molecules. We recently briefly reported that this "open−close double doors" system can be utilized in the photo-switched controlled release of included compounds.[21] In this paper, we wish to describe the details of this controlled release system using relatively smaller pores of MCM-41 and a smaller guest molecule than recently reported.[21]

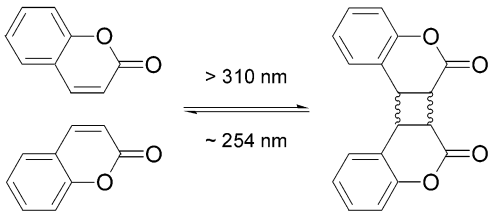

Figure 1. Reversible photodimerization and photocleavage of coumarin derivative.

Experimental Section

Synthesis. *Preparation of Si−MCM-41.* Si−MCM-41 was prepared by a modified procedure[21] using the following molar composition of the gel in the presence of tetradecyltrimethylammonium bromide (C_{14}TMABr) as surfactant: 1.0:0.50:0.67:0.39:0.57:80 SiO_2:C_{14}TMABr:TMAOH (tetramethylammonium hydroxide):Na_2O:H_2SO_4:H_2O (pH = 10.50). In a typical synthesis, 103 g of C_{14}TMABr (98%, Wako Chem.) was dissolved in 80 g of distilled H_2O and 73.28 g of TMAOH (25% aqueous, Aldrich Chem.). Then 63.13 g of tetraethoxysilane (99%, Wako Chem.) (TEOS) was added and the solution stirred for 30 min, followed by addition of 9.36 g of NaOH (Wako Chem.) in 80 g of H_2O under stirring for 1 h. Finally, 35.68 g of H_2SO_4 (47%, Wako Chem.) in 198 g of H_2O was added. A clear solution turned to homogeneous gel (precipitated) with the pH being maintained at 10.50 under stirring for 2 h. The gel was transferred into a polypropylene bottle, aged at room temperature for 1 day, and then heated at 100 °C without stirring for 3 days. The resultant product was filtered, washed, and dried at 100 °C for 1 day. This sample was an as-synthesized MCM-41 sample. Calcined MCM-41 was obtained by the calcination of this as-synthesized MCM-41 at 550 °C for 5 h.

Preparation of 7-[(3-Triethoxysilyl)propoxy]coumarin. 7-Allyloxycoumarin was obtained from umberiferon and allyl bromide in the presence of potassium carbonate and purified

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by recrystallization from ethanol. The yield was over 90%. 7-[(3-Triethoxysilyl)propoxy]coumarin was prepared as follows: after babbling of dry nitrogen to the toluene solution (100 mL) of 7-allyloxycoumarin (3.24 g, 16 mmol) and triethoxysilane (2.94 g, 17.6 mmol) for 10 min, 0.8 mL of the toluene solution (2 mM) of Pt (dvs) [platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex] (Aldrich) was added, and the resulting solution was stirred for 12 h at room temperature. After removal of the solvent under the reduced pressure, the obtained oil was used directly in the modification of MCM-41. This crude product was successfully identified as 7-[(3-triethoxysilyl)propoxy]coumarin by ^{1}H and ^{13}C NMR spectra.

Grafting Methods for Preparing Coumarin-Modified MCM-41 Samples. *(a) Method A: Grafting of 7-[(3-Triethoxysilyl)propoxy]coumarin on As-Synthesized MCM-41 for 15 min.* Two grams of as-synthesized MCM-41 was suspended in a solution containing 20 mL of *n*-hexane and 0.30 g of 7-[(3-triethoxysilyl)propoxy]coumarin under stirring at ambient temperature for 15 min. *n*-Hexane was evaporated by a rotary evaporator at 80 °C for 2 h and dried under vacuum at 150 °C for 12 h. Then 2 g of coumarin-modified as-synthesized MCM-41 with surfactant was refluxed in 100 mL of ethanol containing 4 mL of HCl (1 M) at 80 °C for 4 h. The solid was descended and washed with ethanol. This process was carried out twice to ensure the complete removal of surfactant from the pores of MCM-41. The obtained solid was filtered off, washed with ethanol and water, and finally dried at 80 °C for 12 h. This material was referred to as sample **A-1**.

(b) Method B: Grafting of 7-[(3-Triethoxysilyl)propoxy]-coumarin on As-Synthesized MCM-41 for 24 h. Sample **B-1** was prepared by the same grafting procedure as described for sample **A-1** for a 24-h duration instead of 15 min. Surfactant was extracted using the method similar to that described for sample **A-1**.

(c) Method C: Grafting of 7-[(3-Triethoxysilyl)propoxy]-coumarin on Calcined MCM-41 for 15 min. Two grams of calcined MCM-41 was suspended in a solution containing 20 mL of *n*-hexane and 0.17 g of 7-[(3-triethoxysilyl)propoxy]-coumarin under stirring at ambient temperature for 15 min. *n*-Hexane was evaporated by a rotary evaporator at 80 °C for 2 h and dried under vacuum at 150 °C for 12 h. This sample is referred to as sample **C-1**. The coumarin substituent was also grafted on silica gel (Merck Silica-Gel 60) by this procedure for comparison.

(d) Method D: Direct Hydrothermal Synthesis of Coumarin-Derived MCM-41. Sample **D-1** was synthesized from the mixed solution of tetraethoxysilane and 7-[(3-triethoxysilyl)propoxy]-coumarin (5 mol % to tetraethoxysilane) by the same procedure as described for the synthesis of as-synthesized MCM-41. The surfactant was removed as described above.

Photo-switched Controlled-Release Experiment. One gram of coumarin-modified MCM-41 (samples **A-1**, **B-1**, **C-1**, and **D-1**) was suspended in the *n*-hexane solution (20 mL) containing 1.5 g of phenanthrene at ambient temperature for 24 h. The resulting solid was filtered, washed with *n*-hexane on a filter, and dried at 60 °C for 12 h. The content of phenanthrene in filtrate was analyzed using GC in the presence of pyrene as the internal standard. The obtained solid was photodimerized by the irradiation of ultraviolet ray with wavelength longer than 310 nm for 30 min using a 450-W high-pressure mercury lamp (Ushio UM-452) through a Pyrex glass cooler. After the dimerization, the solid was suspended in *n*-hexane (100 mL) and stirred at room temperature for 48 h. Finally, it was filtered off, washed with *n*-hexane, and dried at room temperature (samples **A-2**, **B-2**, **C-2**, and **D-2**). The amounts of phenanthrene in samples **A-2**, **B-2**, **C-2**, and **D-2** were estimated from the difference between the initial and the recovered ones. The dimerized materials were subjected to the photocleavage by the irradiation around 250-nm wavelength for 2.5 min with a low-pressure mercury lamp (Ushio UL0-6DQ) through a quartz glass cooler and treated with *n*-hexane (100 mL) at room temperature under stirring for 48 h. Finally, the solid was descended, washed, and dried at room temperature (samples **A-3**, **B-3**, and **C-3**). The amounts of phenanthrene released (dissolved in *n*-hexane) were analyzed using GC and TG. The systematic scheme of these procedures is shown in Figure 2.

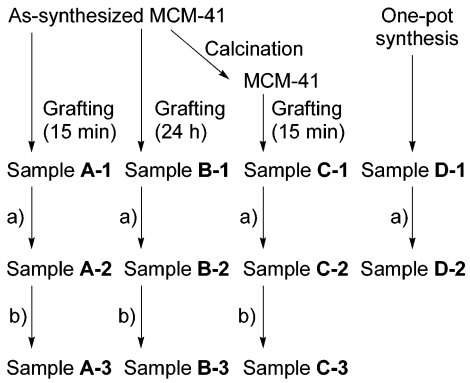

Figure 2. Systematic scheme of sample preparation and controlled release procedures. (a) Phenanthrene loading, photoirradiation (>310 nm), and *n*-hexane washing. (b) Photoirradiation (~250 nm) and *n*-hexane washing.

Product Characterizations. Si analyses of the samples were carried out using ICP (Shimadzu, ICPV-1017). CHN analyses were obtained on CE instruments EA1110. XRD patterns were recorded with MAC Science, MO3X with Ni-filtered Cu Kα radiation ($\lambda = 0.15406$ nm). BET specific surface area and pore size were obtained from nitrogen adsorption isotherms measured at −196 °C using a Bellsorp 28 instrument (BEL Japan, Inc.). Prior to nitrogen adsorption, the samples were degassed at 80 °C for 12 h. The pore size distributions were calculated from the adsorption branches of the nitrogen adsorption isotherms using the Barrett−Joyner−Halenda (BJH) method.[22] Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were performed on a Seiko SSC/5200 apparatus. All samples were held in a platinum sample holder and were heated under a nitrogen atmosphere at the rate of 5 °C/min. γ-Al_2O_3 was used as a reference for DTA measurement. UV−vis diffuse reflectance spectra were obtained with a JASCO V-570 equipped with an integrating sphere. Solid-state ^{29}Si MAS NMR spectra were collected on a JEOL, model CMX400 (9.4 T), at 79.42 MHz with 5-mm zirconia rotor (5.0-kHz rotation speed), 2.5-μs pulse width, 60-s pulse delay, and 1024 acquired length (transients). Polydimethylsilane (PDMS) was used as the external chemical shift standard. Solution ^{1}H and ^{13}C NMR spectrum measurements were performed with a JEOL ALPHA 400 spectrometer. FT-IR spectra were measured on a Perkin-Elmer Spectrum One spectrometer. The content of phenanthrene in filtrate (solution) was analyzed using GC (Shimadzu GC-17A) with a capillary column and independently verified by elemental analysis and TG. The molecular size estimation was carried out using CS ChemBats3D Pro (Cambridge Soft Corporation).

Results and Discussion

Photodimerization Behaviors of Coumarin-Modified MCM-41. As mentioned in our previous paper,[21] the grafting process of coumarin substituent on MCM-41 is an important factor in determining the performance of controlled release. Four grafting procedures were examined (Figure 2). The details of preparation methods are described in the Experimental Section. Sample **A-1** was prepared by the mixing of as-synthesized MCM-41 and the *n*-hexane solution of 7-[(3-triethoxysilyl)propoxy]coumarin for 15 min. Sample **B-1** was obtained from the same procedure as sample **A-1** for 24 h of mixing. In the preparation of sample **C-1**, calcined MCM-41 was utilized instead of the as-

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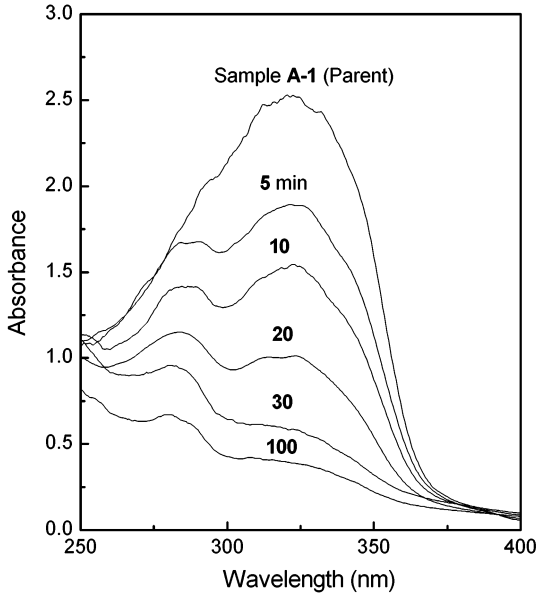

Figure 3. Change in UV−visible spectra of sample **A-1** during irradiation of UV light (>310 nm).

Table 1. Elemental Analyses Results of Coumarin-Modified MCM-41 Samples

sample	coumarin substituent (wt %)	$R-SiO_{3/2}/(R-SiO_{3/2}+SiO_2)$ (molar ratio)
sample **A-1**	4.3	0.01325
sample **B-1**	6.4	0.02014
sample **C-1**	4.3	0.01325
sample **D-1**	5.8	0.01814
coumarin-modified silica gel	4.3	0.01325

synthesized one for sample **A-1**. Sample **D-1** was synthesized from TEOS and 7-[(3-triethoxysilyl)propoxy]-coumarin directly (one-pot synthesis). Elemental analysis results of coumarin-modified samples are presented in Table 1. The contents of the coumarin substituent in samples **A-1**, **B-1**, **C-1**, **D-1**, and silica gel are in the range of 4.3−6.4 wt %. Although the sample preparation of equal quantity of grafted coumarin substituent was difficult, these differences in grafted amounts in this area (around 4−6 wt %) are unlikely to be significant. (The effect of grafted amounts on the performance of controlled release will be discussed later.) The fundamental behaviors of the photoreaction (dimerization and cleavage) were first examined using sample **A-1**, which were prepared using as-synthesized MCM-41 for short-time grafting (15 min). As shown in Figure 1, the irradiation with over 310-nm wavelength of UV light leads to the formation of a cyclobutane ring by the dimerization of coumarin monomer, and the reverse reaction occurs with around 250-nm UV light irradiation. Effect of UV light irradiation (>310 nm) on dimerization of the coumarin derivative attached on the MCM-41 surface was examined. The change in UV−vis spectra of sample **A-1** during this UV light irradiation is shown in Figure 3. Sample **A-1** without any irradiation of UV light shows an absorption band at ca. 320 nm, confirming that the coumarin substituent was in a monomer form.[20] With irradiation time, the UV band at 320 nm decreased and almost disappeared after 30 min. These results showed that the photodimerization occurred effectively, even in the coumarin grafted on the surface of MCM-41 in the case of sample **A-1**.

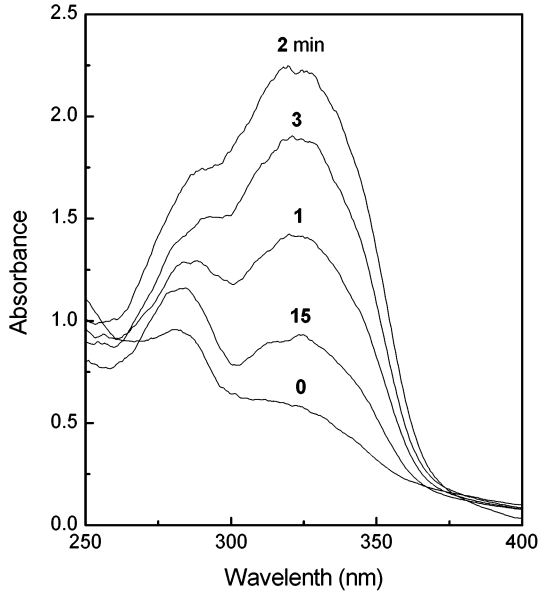

Figure 4. Change in UV−visible spectra of the sample obtained by photodimerization of sample **A-1** (analogous to sample **A-2**) during irradiation of UV light (∼250 nm).

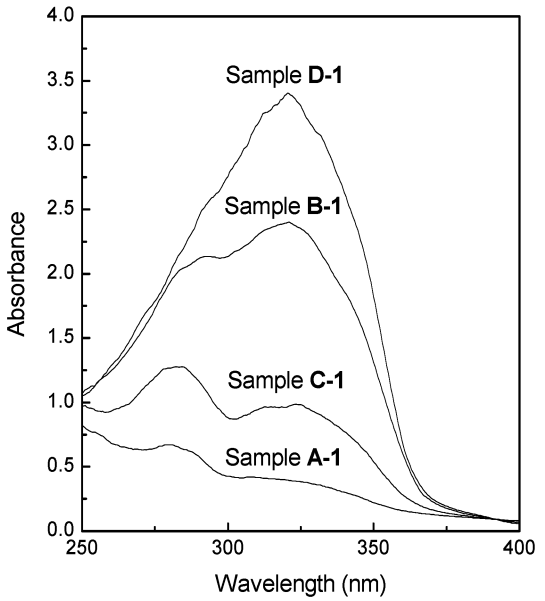

Figure 5. UV−visible spectra of various coumarin-modified MCM-41 (samples **A-1**, **B-1**, **C-1**, and **D-1**) after UV irradiation (>310 nm) for 100 min.

When the dimerized sample was irradiated with a shorter wavelength of UV light around 250 nm, the coumarin absorption band at 320 nm regenerated within 2−3 min as shown in Figure 4, owing to the photocleavage of the coumarin dimer. Thus, the reversible photoreactions (dimerization and cleavage) were verified in the coumarin substituent fixed on MCM-41 similarly to polymers.[20] Further irradiation produced the coumarin dimer again as well as in the case of the polymer,[20] suggesting that appropriate irradiation time is necessary.

In Figure 5, the effects of irradiation of UV light (>310 nm) on various coumarin-modified MCM-41 samples, samples **A-1**, **B-1**, **C-1**, and **D-1**, for 100 min are summarized (samples mentioned here after irradiation are different from samples **A-2**, **B-2**, **C-2**, and **D-2**.).

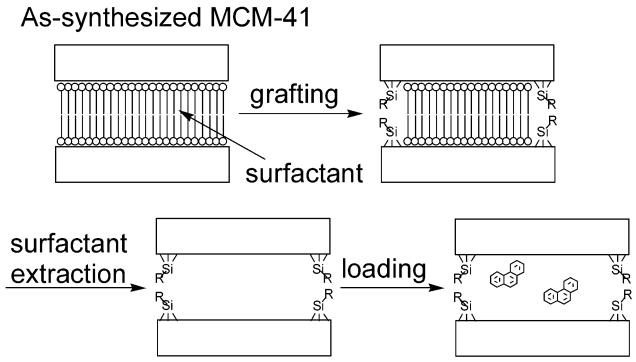

Figure 6. Conceptual scheme of preparation of sample **A-1**, where coumarin substituent is densely grafted at the pore outlet of MCM-41.

No further decrease of the UV band at 320 nm was observed after this irradiation time in all four samples. As described above (Figure 3), in the case of sample **A-1**, the absorption at 320 nm almost disappeared to indicate the complete dimerization of coumarin (>98%). On the other hand, in the cases of samples **B-1** and **C-1**, the decreases of the absorption were lower (approximately 27% and 67%, respectively). It is noteworthy that no decrease of the UV absorption was observed in the case of sample **D-1** (<1%). This means that no photodimerization of coumarin substituent occurred in this sample. The grafting methods of coumarin substituent on a MCM-41 surface determined their reactivity for this photodimerization. It is thought that the arrangement of the coumarin substituent on the pore wall of MCM-41 is the main factor. For the photodimerization of coumarin, two coumarin substituents, which are fixed on the surface of MCM-41, must be located closely enough to combine their coumarin parts. With use of our modified procedure (sample **A-1**), short-time grafting with as-synthesized MCM-41, the coumarin substituent is likely to be densely grafted. This dense arrangement of the coumarin substituent enabled complete photodimerization. The surfactant in the pore of MCM-41 depresses the permeation of 7-[(3-triethoxysilyl)propoxy]coumarin into the inner pore. The short grafting time also prevents the elimination of the surfactant from the solvent used. Therefore, it seems that the coumarin substituent is grafted around the outlet of the pore as well as the external surface (Figure 6). On the other hand, the relatively dispersed arrangement of the coumarin substituent on the surface limited the photodimerization in the cases of samples **B-1** and **C-1**. Considerable parts of this dispersed coumarin substituent cannot form the dimer because two isolated coumarin parts are far apart from each other. Longer time grafting, even using as-synthesized MCM-41, resulted in dispersed distribution of the coumarin substituent (sample **B-1**) because the surfactant used was gradually displaced during this long time process, permitting the permeation of the coumarin reagent into the inner pore. It was found that more than 90% of the surfactant was removed after the mixing process for 24 h. Grafting using calcined MCM-41 for a short time (15 min; sample **C-1**) also occurred comparatively densely.[11b,19a] The slow diffusion of coumarin−silane compound due to its considerably large size probably enhanced this tendency. However, it is convincing that the dispersed arrangement of coumarin substituent more than sample **A-1** resulted in the limited photodimerization as shown in Figure 5. In the case of coumarin-derived MCM-41 prepared by one-pot synthesis (sample **D-1**), the coumarin substituent is expected to exist randomly inside and outside the pore. This highly dispersed coumarin substituent on the surface of MCM-41 in sample **D-2** was impossible to undergo photodimerization because each coumarin group is secluded completely. These differences in photodimerization behaviors are expected to affect the performances of controlled release significantly.

Performances of Photo-switched Controlled Release. It is well-known that MCM-41 includes various kinds of molecules and materials in its comparative large pore void.[13] In our previous paper,[21] MCM-41 in larger pore size (peak pore diameter was 3.0 nm) was used for the controlled release of cholestane. In this paper, we employed narrow-pore-sized MCM-41 (peak pore diameter was 2.62 nm) using tetradecyltrimethylammonium bromide as a substitute for the hexadecyltrimethylammonium one for studying the controlled release of a smaller molecule, phenanthrene. Guest molecules were able to be loaded into the pores before the photodimerization treatment. After the mixing of sample **A-1** with *n*-hexane solution of phenanthrene and following filtration, UV light longer than 310-nm wavelength was irradiated to this solid (sample **A-2**). The amount of phenanthrene included in the pore of sample **A-2** after thorough washing with *n*-hexane was estimated to be 21.6 wt % of the solid (Table 2). Washing sample **A-1** using fresh solvent just after the absorption of phenanthrene without photodimerization resulted in no storage of phenanthrene. Unmodified MCM-41 also failed to retain phenanthrene in the solid after washing. Thus, the treatment with the fresh solvent was an effective method for removal of phenanthrene. All these observations suggest that phenanthrene was stored in sample **A-2** because the cross-linked cyclobutane coumarin dimer prevents its passage through the pore outlet from the inside to the outside. In addition, it was found that the exposure of sample **A-1** after complete photodimerization (no guest molecule in the pore) to phenanthrene solution resulted in no uptake of the guest molecule in the pore. After the irradiation of shorter wavelength UV light (∼250 nm) to sample **A-2** (to form sample **A-3**), 75% (16.2 wt %) of the guest molecule stored was released from this sample **A-3** to *n*-hexane solution with washing. This process was completed after 48 h as shown in Figure 7. Some portions of the molecule still remained in the pore (5.4 wt %). When the irradiation with ≈250-nm UV light was extended longer than 3 min, the absorption band at 320 nm decreased again (see Figure 4). Thus, the photocleavage process was not perfect and some portions of phenanthrene were still included in the pore of coumarin-modified MCM-41. This phenomenon was not unique for the coumarin derivative attached on the surface of MCM-41, but a general property of the photodimerization of coumarin-type compounds as well claimed.[20] However, the storage−release type of controlled release of the guest molecule in the pore, not slow sustained release type,[15] was first achieved using our novel modified MCM-41. Although another storage−

Table 2. Properties of Various Modified MCM-41 Samples[a]

sample	d_{100} (nm)	S_{BET} ($m^2 g^{-1}$)	S_{BJH} ($m^2 g^{-1}$)	V_P ($cm^3 g^{-1}$)	APD_{BJH} (nm)	PPD (nm)	phenanthrene[b] included (wt %)
extracted MCM-41	3.65	964	1042	0.76	2.92	2.62	0.0
sample **A-1**[c]	3.65	951	1031	0.75	2.91	2.62	0.0
sample **A-2**	3.65	250	361	0.20	2.22	1.92	21.6
sample **A-3**	3.65	728	785	0.56	2.85	2.50	5.4
sample **B-1**[d]	3.65	892	950	0.65	2.73	2.40	0.0
sample **B-2**	3.65	754	798	0.48	2.41	2.30	5.3
sample **B-3**	3.65	865	920	0.62	2.70	2.40	1.6
calcined MCM-41	3.62	946	1020	0.74	2.90	2.50	0.0
sample **C-1**[e]	3.62	903	982	0.70	2.85	2.50	0.0
sample **C-2**	3.62	602	648	0.44	2.72	1.92	11.6
sample **C-3**	3.62	870	928	0.65	2.80	2.50	2.2
sample **D-1**[f]	3.48	823	903	0.58	2.57	2.10	0.0
sample **D-2**	3.48	821	903	0.58	2.57	2.10	<0.2

[a] d_{100}: X-ray diffraction (100) interplanar spacing; S_{BET}: BET specific surface area; V_P: primary mesopore volume; $APD_{BJH} = 4V_p/S_{BJH}$, where S_{BJH} = BJH specific surface area; PPD: peak pore diameter calculated from adsorption branches of BJH pore size distribution curve. [b] Weight percent of phenanthrene stored in MCM-41 samples after thorough washing with *n*-hexane; photodimerization process for 30 min and photocleavage process for 2.5 min. [c] Samples **A**: 4.3 wt % coumarin-grafted MCM-41; grafting time, 15 min. [d] Samples **B**: 6.4 wt % coumarin-grafted MCM-41; grafting time, 24 h. [e] Samples **C**: 4.3 wt % coumarin grafted on calcined MCM-41 for 15 min. [f] Samples **D**: 5.8 wt % coumarin grafted in one-pot synthesis. This sample did not undergo photodimerization.

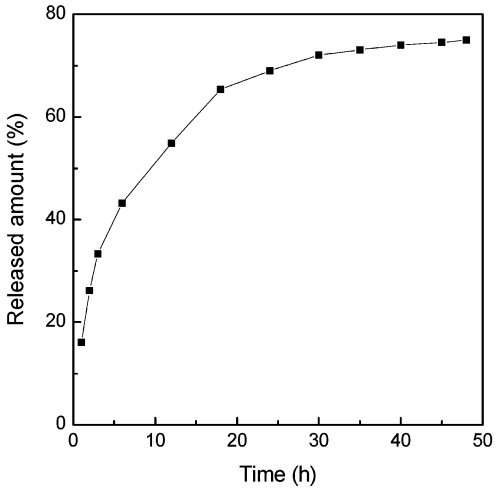

Figure 7. Time course of the release of phenanthrene from sample **A-3**.

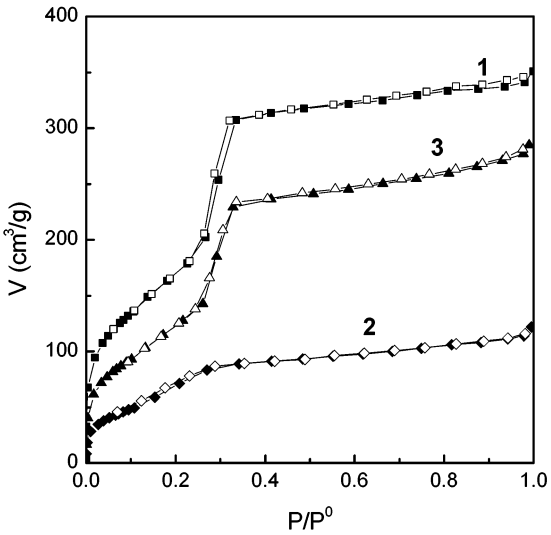

Figure 8. Effect of storage and release of phenanthrene on nitrogen adsorption−desorption isotherms in sample **A-1** (**1**), sample **A-2** (**2**), and sample **A-3** (**3**).

release type of controlled release was recently reported using MCM-41,[16] only one cycle of storage and release is expected because CdS nanoparticle used as the cap of MCM-41 pores is liberated from MCM-41 solid at the release step. On the other hand, our system can essentially perform the storage−release cycle many times by the irradiations of different wavelength UV lights.

The effect of the guest molecule on nitrogen adsorption−desorption isotherms and pore size distributions of samples **A-1**, **A-2**, and **A-3** are shown in Figure 8. As the isotherms of sample **A-1** were similar to unmodified extracted MCM-41, those of extracted MCM-41 are not shown in the figure. Therefore, the surface areas, pore volumes, pore sizes, and peak pore diameters are approximately similar between the extracted MCM-41 and sample **A-1** (see Table 2). The coumarin modification had no influence on the nitrogen sorption properties of MCM-41 in the case of sample **A-1**. On the other hand, the amount of nitrogen adsorption drastically decreased in sample **A-2** (after phenanthrene loading, photodimerization and washing) due to the inclusion of phenanthrene. The pore volume and surface area of sample **A-2** were reduced to a quarter compared with those of sample **A-1** (Figure 8 and Table 2). Pore size distribution curves showed that peak pore diameter of sample **A-2** reduced from 2.62 nm (sample **A-1**) to 1.92 nm (Figure 9). However, after photocleavage and washing with *n*-hexane (sample **A-3**), the amount of nitrogen adsorption recovered was up to 75% with respect to sample **A-1**. The release of phenanthrene stored was confirmed, even in these nitrogen sorption measurements. The peak pore diameter shifted to a higher value (2.50 nm) than that of sample **A-2**. All results shown here supported well the observations of the storage−release experiment mentioned above. The storage of phenanthrene is caused by its impoundment inside the MCM-41 pore, not by other triggers such as its strong adsorption on the surface of MCM-41. The formation of cross-linked coumarin dimer confines the guest molecule in the pore, and the photocleavage of coumarin dimer frees the molecule from the pore by opening the outlet.

The same controlled release experiments were investigated using samples **B-1**, **C-1**, and **D-1**. These results are also summarized in Table 2. The amounts of phenanthrene stored in the pores of samples **A-2**, **B-2**, **C-2**, and **D-2** were 21.6, 5.3, 11.6, and <0.2 wt %, respectively. In the case of coumarin-modified silica gel,

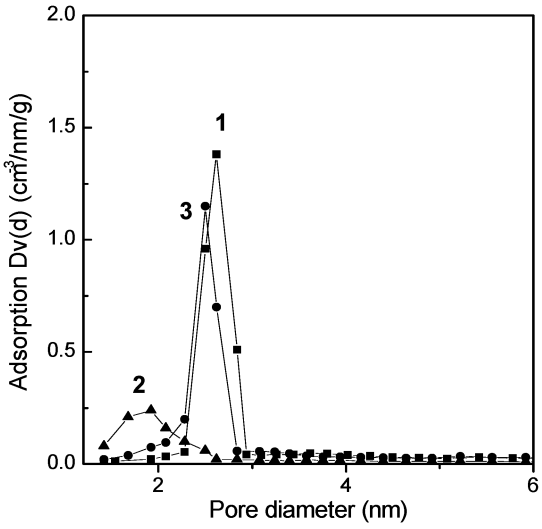

Figure 9. Pore size distributions of sample **A-1** (**1**), sample **A-2** (**2**), and sample **A-3** (**3**) calculated by the BJH method.

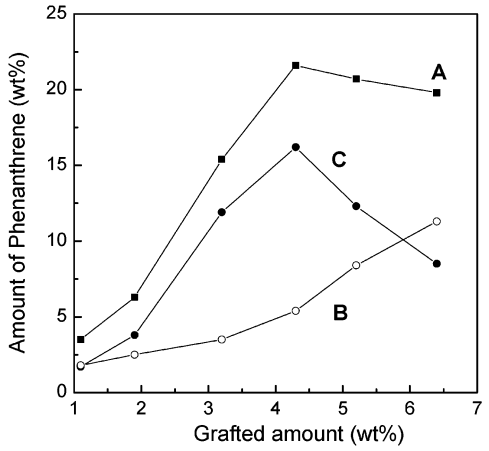

Figure 10. Effect of grafted amounts of coumarin derivative on phenanthrene storage and release. A: Stored phenanthrene after photodimerization. B: Remaining phenanthrene after photocleavage. C: Amounts of phenanthrene which were stored and released by photo-switching (A−B).

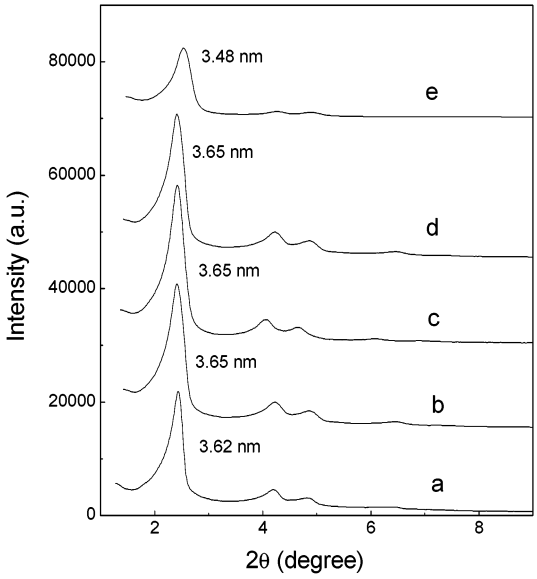

Figure 11. XRD patterns of calcined MCM-41 (a), coumarin-modified MCM-41 samples, sample **A-1** (b), sample **A-2** (c), sample **A-3** (d), and sample **D-1** (e).

no phenanthrene was stored in the pore after the same treatment. These clear differences in the storage abilities of the guest molecule are induced by the photodimerization manners of respective samples. Phenanthrene storage in sample **C-2** (11.6 wt %) was better than that in samples **B-2** (5.3 wt %) and **D-2** (<0.2 wt %), but considerably low compared with that in sample **A-2** (21.6 wt %). As mentioned above, the photodimerization behaviors of the coumarin substituent in respective samples (samples **A-1**, **B-1**, **C-1**, and **D-1**) were definitely different as shown in Figure 5. A sample that achieved complete photodimerization (sample **A-2**) stored phenanthrene at the maximum amount, and another sample that could not cause photodimerization (Sample **D-2**) preserved no phenanthrene. The coumarin substituent is regarded as molecular "hinged double doors" of MCM-41 pores. When the doors are closed (coumarin is in dimer form to cross-link), no guest molecule inside slips out of the pore, resulting in being stored (sample **A-2**). On the other hand, when the doors cannot shut, the guest molecule readily passes through the outlet of the pore, and consequently no storage of the molecule was accomplished (sample **D-2**). In the cases of samples **B-2** and **C-2**, the amounts of the molecule stored are well in agreement with the performances of the photodimerization. Samples with higher photodimerization ability can store the guest molecule more effectively. In conclusion, samples prepared by method A (samples **A-1**, **A-2**, and **A-3**) had the best performances in the photodimerization and the storage of the molecule.

The effects of grafted contents of the coumarin substituent on the performances of storage and release of phenanthrene are shown in Figure 10. All the samples were prepared by method A (for sample **A-1**). With an increase of the coumarin content from 1 to 4.3 wt %, the storage and the release of phenanthrene were gradually enhanced. However, when coumarin was loaded more than 4.3 wt %, the stored amount of phenanthrene was slightly reduced, and the release of phenanthrene stored in the pore drastically decreased after the photocleavage process. A considerable part of the guest molecule still remained in the pore of modified MCM-41, even after thorough washing. In these cases, it is likely that the pores of modified MCM-41 were mostly closed due to unsuccessful cleavage of cyclobutane coumarin dimers by the UV light irradiation (~250 nm). Thus, suitable content for a storage−release controlled release system is provided by 4−5 wt % coumarin-modified MCM-41 prepared by method A.

Characterizations of Various Coumarin-Modified MCM-41. In Figure 11, XRD patterns of calcined and coumarin-modified samples obtained using method A (for sample **A-1**) are presented. Intensities of d_{100} peaks of coumarin-modified samples were higher than that of a calcined sample, indicating that photodimerization and photocleavage, phenanthrene storage and release do not damage the hexagonal structure of modified MCM-41. TGA and DTA profiles of extracted MCM-41 and samples **A-1**, **A-2**, and **A-3** are shown in Figure 12. TGA of extracted MCM-41 shows 2.14 wt % loss between 150 and 350 °C, attributed to the removal of volatiles adsorbed during extraction, whereas 3.64 wt % loss above 350 °C resulted from loss of water during condensation of hydroxy groups. Numerical results are

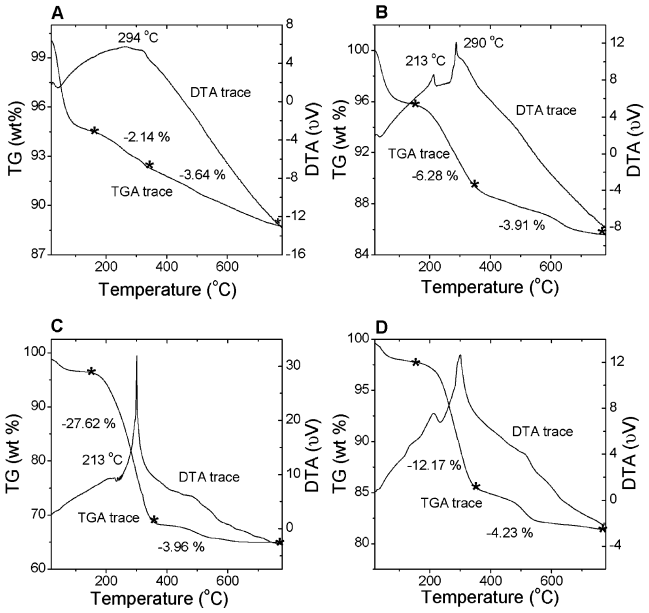

Figure 12. TGA-DTA profiles of extracted MCM-41 (A), sample **A-1** (B), sample **A-2** (C), and sample **A-3** (D).

Table 3. TGA Results of MCM-41 Samples

	wt loss (%)				
sample	<150 °C	150−350 °C	>350 °C	coumarin	phenanthrene
extracted MCM-41	5.78	2.14	3.64	0.0	0.0
sample **A-1**	10.19	6.28	3.91	4.41	0.0
sample **A-2**	31.58	27.62	3.96	4.41	21.39
sample **A-3**	16.40	12.17	4.23	4.41	6.21

also summarized in Table 3. A broad exothermic peak was observed around 294 °C in the DTA profiles of samples **A-1**, **A-2**, and **A-3** as well as extracted MCM-41 sample. In the case of sample **A-1**, coumarin substituent was probably burned below 350 °C, and the total weight loss above 150 °C was 10.19 wt %. The difference in weight loss between extracted MCM-41 and sample **A-1** was 4.41 wt %, which was close to the expected value (4.3 wt %) for the grafted amount of the coumarin substituent. Sample **A-1** showed an exothermic peak at 213 °C, probably due to the decomposition of some parts of the coumarin substituent. Samples **A-2** and **A-3** showed an additional weight loss of 21.39 and 6.21 wt %, respectively, compared with sample **A-1**, which were close to the expected value, 21.6 and 5.4 wt %, respectively, for the presence of phenanthrene stored inside the pores of coumarin-modified MCM-41.

^{29}Si MAS NMR spectra of surfactant-extracted MCM-41, samples **A-1** and **B-1**, are shown in Figure 13. Surfactant-extracted MCM-41 exhibited two resonances at −101 and −111 ppm, corresponding to HO***Si***$(OSi)_3$ (Q^3) and ***Si***$(OSi)_4$ (Q^4), respectively. Samples **A-1** and **B-1** showed two weak additional resonances at −57 and −66 ppm. As reported, in the case of mesoporous ethane silica, the resonances at −57 and −66 ppm were attributed to T^2 and T^3 species, respectively.[11f] Similarly, Pinnavaia's group[23] observed the resonances between −65 and −69 ppm assigned to fully cross-linked organosilica species (T^3) for organo-silane impregnated HMS materials. Stucky's group[24] also reported the resonances at −57 and −65 ppm corresponding to T^2 and T^3 species,

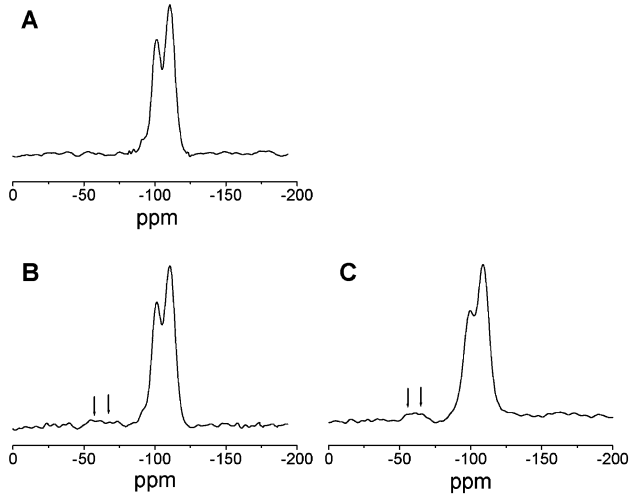

Figure 13. ^{29}Si MAS NMR spectra of surfactant-extracted MCM-41 (A), sample **A-1** (B), and sample **B-1** (C).

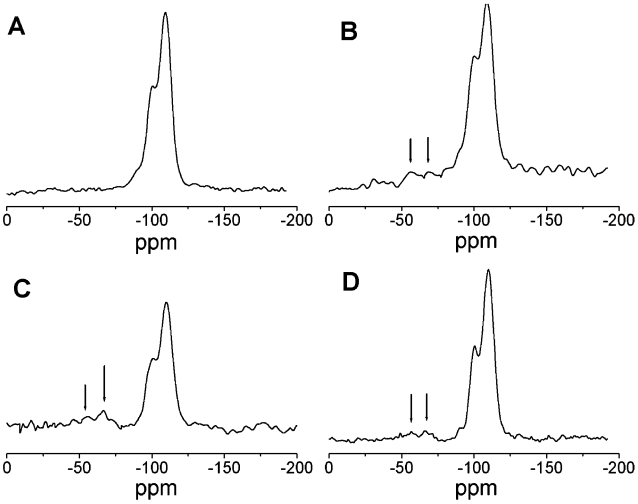

Figure 14. ^{29}Si MAS NMR spectra of calcined MCM-41 (A), sample **C-1** (B), sample **D-1** (C), and coumarin-modified silica gel (D).

respectively. Thus, these peaks at −57 and −66 ppm were assigned to R−**Si**$(OSi)_2(OH)$ (T^2) and R−**Si**$(OSi)_3$ (T^3), respectively. Intensities of T^2 and T^3 resonances in sample **B-1** were enhanced in comparison with those of sample **A-1**. The coumarin substituent was more tightly bonded to the pore wall in sample **B-1** than in sample **A-1**. In Figure 14, ^{29}Si MAS NMR spectra of calcined MCM-41, samples **C-1** and **D-1**, and coumarin-modified silica gel are shown. Calcined MCM-41 exhibited two resonances at −101 and −111 for Q^3 and Q^4 species, respectively. Samples **C-1**, **D-1**, and coumarin-grafted silica gel showed two additional resonances at ca. −55 and from −65 to −67 ppm, corresponding to T^2 and T^3 species, respectively, as expected. In the case of one-pot synthesis (sample **D-1**), most of the coumarin substituent was fully cross-linked (T^3) due to more tightly bonded organic species inside and outside the pore wall. This suggests that the condensation of silane alkoxide in TEOS and 7-[(3-triethoxysilyl)propoxy]coumarin occurs simultaneously, supporting the random distribution of the coumarin substituent as mentioned

(23) Mercier, L.; Pinnavaia, T. J. *Chem. Mater.* **2000**, *12*, 188−196.

(24) Margolese, D.; Melero, J. A.; Christiansen, S. C.; Chmelka, B. F., Stucky, G. D. *Chem. Mater.* **2000**, *12*, 2448−2459.

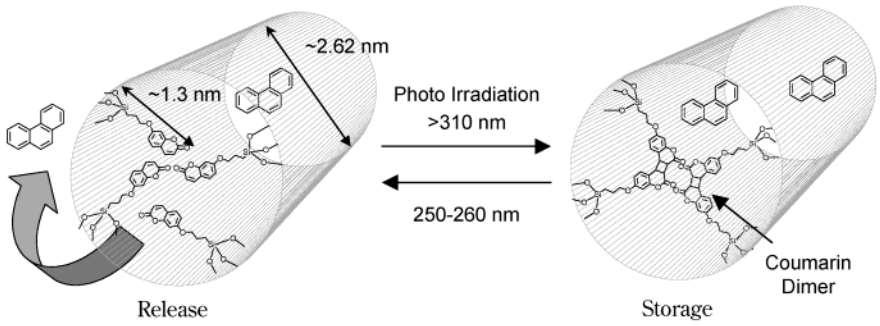

Figure 15. Conceptual scheme of photo-switched storage−release controlled release by coumarin-modified MCM-41.

before. Unexpectedly, coumarin modified on silica gel showed that the intensity of T^2 resonance was lower than T^3, although it was prepared using the method similar to that for sample **C-1**. These results indicated that the coumarin substituent was bound to the silica surface of MCM-41 through the formation of Si−O−Si bonds in all samples of coumarin-modified MCM-41 (samples **A**, **B**, **C**, and **D**). From these observations, the coumarin substituent is really compared to "molecular doors connected on the hinge".

An unclear aspect of coumarin-modified MCM-41 sample **A-1** is the real arrangement of coumarin substituent on the surface. We mentioned in the previous paragraph that the coumarin substituent is located densely on the external surface and around the outlet of the pore of MCM-41 in the case of sample **A-1**. As shown in Figure 10, the stored amount of phenanthrene was very poor in 1−2 wt % coumarin-grafted samples, and drastically increased in over 2 wt % grafted samples. It is likely that at the beginning the coumarin substituent is fixed on the outside of the pore, which does not involve the controlled release, and subsequently the inside of the pore is modified. No clear difference was observed in surface area, pore volume, pore size, and peak pore diameter between extracted MCM-41 (unmodified) and sample **A-1** (coumarin-modified) as shown in Table 2. The coumarin substituent is thought to be scarcely attached inside the pore wall or at least the amount of the coumarin substituent grafted on the inside pore of MCM-41 was so little as to be distinguished by the sorption experiment. The modification of the surface of MCM-41 by organic substituent generally affects its porosity.[2,12] Even in the cases of samples **B-1** and **C-1**, the significant decreases in surface area, pore volume, pore size, and peak pore diameter were observed compared with parent MCM-41 samples (see Table 2, for example; in specific surface area, from 964 to 892 m^2/g in sample **B-1**; from 946 to 903 m^2/g in sample **C-1**). In these cases, the coumarin substituent was obviously grafted on the inside pore wall. In the case of sample **A-1**, it is strongly suggested that the modified surface of the inside pore is only the vicinity of the outlet. The grafting process using as-synthesized MCM-41 for a short time realized this selective modification of coumarin substituent, which is an essential factor for the effective photo-switched controlled release. These explanations are very consistent with the results of UV irradiation experiments described above.

Overviews of Photo-switched Storage−Release Controlled Release. The molecular length of 7-[(3-trihydroxysilyl)propoxy]coumarin attached to silanol groups on MCM-41 is estimated to be approximately 1.3 nm.[21] After dimerization, the length of dimer in an anti head-to-head configuration[20b] is likely to be appropriate to cross-link and/or at least to be close to the center of the pore of MCM-41 (the pore diameter of MCM-41 we used was ca. 2.62 nm). Figure 15 presents a conceptual diagram of a reversible open−closed system of the pore of coumarin-modified MCM-41, where the coumarin substituent is considered to be molecular "hinged double doors". When the double doors are open without any photoirradiation or after the photocleavage (coumarin is in the monomer form), the pore void and the outer space are passable. After the photodimerization, the double doors are closed by the cyclobutane dimers. In this case, the pore void is isolated from outer space. We showed here that these double-doors-like phenomena could be applied to the photo-switched controlled release.[21] On the other hand, the intramolecular reversible photochromism of diazobenzene[9] and spiropyran derivatives[10] are not expected to regulate the access of pores like our case, although their potential ability is demonstrated.[9c] In this report, phenanthrene was used for the controlled release experiment because its molecular shape is well-defined and its diameter (about 0.57 nm) is expected to be close to cholestane. However, the molecular length of phenanthrene (0.95 nm) is considerably shorter than cholestane. Recently, molecular size of cholesterol analogous to cholestane was calculated using a cylindrical size model (diameter, 0.61 nm; length, 1.90 nm).[25] We also found that cholestane was stored in this coumarin-modified MCM-41 (after photodimerization, 22.3 wt % storage, and after photocleavage, 16.0 wt % release). Moreover, the release of progesterone as a corpus luteum hormone was controlled similarly (after photodimerization, 22.0 wt % storage, and after photocleavage, 16.2 wt % release). The potential application of modified MCM-41 to photo-switched controlled release of steroid hormones, which is probably advantageous to drug delivery system application, was found. The approximately similar results of controlled release of cholestane, progesterone, and phenanthrene indicate that this novel controlled system is dominated by the molecular diameter and not by molecular length.

It was also proved here that the combination of the utilization of as-synthesized MCM-41 and the short-time grafting method is an essential factor for preparing effective controlled release materials, where the cou-

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marin substituent attached densely around the outlet of the pore. Furthermore, we suppose that MCM-41 is a promising material for controlled release because of its one-dimensional cylinder-like pore structure. This fact is readily conceivable from recent active research studies.[9c,15,16] On the other hand, guest molecules included in other materials, where the pores are connected inside such as silica gel, are expected to escape from the inside to the outside through some unmodified (unsuccessfully grafted) outlets. The controlled release and the storage of chemicals by coumarin-modified silica gel was not successful despite progress of photodimerization, indicating the effectiveness of MCM-41 to this novel type of controlled release system.

Conclusions

In this paper, we showed that uptake, storage, and release of guest molecules in coumarin-modified MCM-41 can be regulated through the photoresponsive reversible intermolecular dimerization of coumarin derivatives attached preferentially on the pore outlets. Selective functionalization of the substituent on the outlet of MCM-41 pores requires the utilization of as-synthesized MCM-41 still filled with the surfactant (template) molecule. The short-time grafting procedure is also an essential factor for selective modification. We also found that the one-dimensional, isolated, individual pore characteristics of MCM-41 are advantageous. And 21.6 wt % of phenanthrene was stored inside the pores of coumarin-modified MCM-41 after photodimerization and washing with *n*-hexane. This included phenanthrene was released to the solution after the irradiation of shorter wavelength UV light (~250 nm), which causes the photocleavage of coumarin dimer. Our results reported here demonstrate not only that the reversible photoreaction of coumarin derivative effectively attached on a MCM-41 surface can be applied to the storage−release cycle of guest molecules but also that the fabrication of a suitable system of reversible cross-linking in the pore of MCM-41 realizes various open−closed door systems of MCM-41 pores, which are applicable to the novel types of controlled release systems including drug delivery systems (DDS).

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Supporting Information Available: Nitrogen adsorption−desorption isotherms of samples **B-1**, **C-1**, and **D-1**; BJH pore size distribution plot of samples **B-1**, **C-1**, and **D-1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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