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Effective Adsorption of Chlorophyll *a* by FSM-Type Mesoporous Silica Modified with 1,4-Butanediol

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Received October 22, 1999. In Final Form: June 28, 2000

Surface silanol groups of FSM-type mesoporous silica were modified with 1,4-butanediol, and the esterified material was successfully used as the adsorbent to accommodate chlorophyll *a* molecules. Pheophytinization was effectively suppressed by the presence of the surface organic groups grafted onto the mesoporous silica, whereas pheophytinization occurred in unmodified mesoporous silica.

Ordered mesoporous silicas prepared by utilizing surfactant assemblies possess both high surface areas and large pore volumes,[1,2] and the materials are useful for catalysts, catalyst supports, and adsorbents for relatively large molecules which cannot be accommodated in micropores (<2 nm) of zeolites and related materials.[3] These applications have been extended by modification of the silanol (Si−OH) groups inside the mesopores.[4−6] For example, MCM-41, a typical mesoporous silica, was modified with aminopropylsilyl groups ($\equiv$SiCH$_2$CH$_2$CH$_2$-NH$_2$) and can functionalize a Mn(III) Schiff-base complex[7] and a Co complex[8] in the modified mesopores. Mesoporous silica grafted with 3-mercaptopropylsilyl groups ($\equiv$SiCH$_2$-CH$_2$CH$_2$SH) is extremely efficient in removing toxic metal ions even when other metal ions coexist.[9,10] Here, we report that chlorophyll *a* (Chl *a*), which plays a major role in the primary processes of photosynthesis,[11] can be successfully adsorbed onto FSM-type mesoporous silicas modified with α,ω-diols without pheophytinization. The results contribute to various fields such as porous materials design, inclusion chemistry of photoactive molecules, and photochemistry and photophysics.

Stable charge separation systems are expected to be artificially constructed for solar energy conversion and storage as in the case of photosynthesis of green plants. Porphyrin derivatives were immobilized on the surface of several porous solids such as zeolites,[12] silica gels,[12] FSM,[13]

and MCM-41.[5,14] The decrease of photoyields caused by back electron transfers was suppressed, and the lifetimes of the photogenerated radical ions increased, in comparison with those observed for homogeneous media. However, the attempts to immobilize chlorophylls into the pores of zeolites are unsuccessful, because the pores cannot be utilized due to the smaller pore sizes than kinetic diameters of chlorophylls. Although a clay-chlorophyll *a* system was reported,[15] there were no data reported on whether Chl *a* was intercalated between the layers or not. In addition, the metal center in the chlorophylls is less stable at the surface acid sites of amorphous silica. As described later, pheophytinization of Chl *a* occurs at the surface of FSM-type mesoporous silica. To incorporate Chl *a* into FSM without pheophytinization may be the first step toward the application to biomimetic devices for solar energy. Inorganic mesoporous materials are advantageous because of the mechanical strength and the thermal stability, when compared with organic matrixes.

Mesoporous silica (C$_{18}$FSM) was synthesized using an octadecyltrimethylammonium chloride[16] and was modified with 1,4-butanediol (1,4BD-C$_{18}$FSM).[17] The powder X-ray diffraction (XRD) pattern of 1,4BD-C$_{18}$FSM was quite similar to that observed for C$_{18}$FSM ($a_0 = 4.5$ nm). The porosities before and after the modification varied, as shown in Table 1.[18] All the peaks in the ^{13}C magic angle spinning (MAS) NMR spectrum (Figure 1) of 1,4BD-C$_{18}$FSM are assignable to carbon atoms in 1,4-butanediol.[19] In the IR spectrum of C$_{18}$FSM, the band

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(16) (a) Inagaki, S.; Koiwai, A.; Suzuki, N.; Fukushima, Y.; Kuroda, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1449. (b) Hata, H.; Saeki, S.; Kimura, T.; Sugahara, Y.; Kuroda, K. *Chem. Mater.* **1999**, *11*, 1110. Although the synthetic method is referred to that described in (a), the synthetic conditions were slightly changed as described in (b); kanemite was prepared by dispersing 5 g of δ-Na$_2$Si$_2$O$_5$ in 100 mL of water and by stirring for 30 min.

(17) The reaction of C$_{18}$FSM with 1,4-butanediol was performed as follows. C$_{18}$FSM was pretreated at 150 °C for 3 h in vacuo to remove adsorbed water. The dried C$_{18}$FSM (1.0 g) was dispersed in 75 mL of 1,4-butanediol, and the mixture was refluxed for 24 h at 230 °C under N$_2$ atmosphere. After the reaction, the product was washed twice with acetone to remove unreacted 1,4-butanediol and dried at room temperature in vacuo.

Table 1. Pore Characteristics of $C_{18}FSM$, 1,4BD-$C_{18}FSM$, and the Chl *a* Containing Materials

	adsorbed amt of Chl *a*/mg[a]	occupied density of Chl *a*/molecules nm⁻¹	distance between the Chl *a*/nm	BET surface area/m² g⁻¹	pore volume/ cm³ g⁻¹	pore diameter/nm
			Before Adsorption			
$C_{18}FSM$				1000	0.78	3.5
1,4BD-$C_{18}FSM$				640	0.41	2.8
			After Adsorption			
$C_{18}FSM$[b]				840	0.60	3.5
1,4BD-$C_{18}FSM$	0.19	2.0×10^{-4}	80	660	0.41	2.9
	0.52	5.6×10^{-4}	48	620	0.39	2.8
	2.3	2.4×10^{-3}	23	620	0.38	2.8
	4.5	4.8×10^{-3}	16	630	0.36	2.8
	10	1.3×10^{-2}	10	520	0.34	2.8

[a] These values are estimated as adsorbed amounts per 1.0 g of 1,4BD-$C_{18}FSM$. [b] The result in the adsorption experiment was not available because of pheophytinization of Chl *a*.
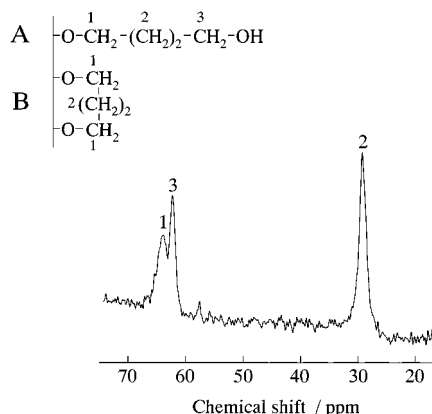

Figure 1. Solid-state ^{13}C MAS NMR spectrum of 1,4BD-C_{18}-FSM. The spectrum was obtained by using a JEOL GSX-400 spectrometer at a spinning rate of 5 kHz and a resonance frequency of 100.40 MHz with a pulse length of 5.2 μs and a recycle time of 60 s. The chemical shifts were expressed with respect to tetramethylsilane.

due to ν(OH) of Si−OH groups was observed at 3690 cm⁻¹. The peak almost disappeared after the reaction with 1,4-butanediol, and a broad peak appeared in the range 3550−3300 cm⁻¹,[20] indicating that most of the Si−OH groups reacted with 1,4-butanediol. In the differential thermal analysis (DTA) curve of 1,4BD-$C_{18}FSM$, a sharp exothermic peak was observed at around 280 °C, in accordance with the previous study on the esterification of FSM-type mesoporous silicas with *n*-alcohols.[21] All the results support that the surface of $C_{18}FSM$ was modified with 1,4-butanediol.

The grafted number of the organic groups was estimated by CHN analysis and N_2 adsorption data. The grafted number is ca. 2.2 groups nm⁻², being slightly smaller than the number of Si−OH groups of $C_{18}FSM$ (ca. 2.4 groups nm⁻², calculated from the mass loss in the range from 120 to 1100 °C by thermogravimetric analysis). The IR spectrum of 1,4BD-$C_{18}FSM$ indicated that almost all the Si−OH groups in $C_{18}FSM$ reacted with 1,4-butanediol. The reactivity of two OH groups in 1,4-butanediol with

the Si−OH groups was analyzed by ^{13}C MAS NMR. Two kinds of carbon atoms bonded to oxygen were detected at $\delta = 64$ and 62 ppm (Figure 1), showing that one or two OH groups in 1,4-butanediol were linked to the surface Si−OH groups of $C_{18}FSM$; the ratio of 1,4-butanediol with one-OH group esterified to the diol with two-OH groups esterified was roughly estimated to be 8:1. Therefore, the density of the OH groups of 1,4BD-$C_{18}FSM$ is ca. 3.0 groups nm⁻², based on the surface area of 1,4BD-$C_{18}FSM$.

The adsorption experiments of Chl *a* by 1,4BD-$C_{18}FSM$ were conducted as follows. Various amounts of Chl *a* (0.05−2.1 mg, Wako Chemical Co.) were dissolved in 10 mL of toluene, and then 0.15 g of 1,4BD-$C_{18}FSM$ was dispersed in the Chl *a* solutions (5.6×10^{-6} to 2.4×10^{-4} M). The mixtures were stirred at room temperature for 3 h in the dark and centrifuged to remove supernatants. After the adsorption, the recovered 1,4BD-$C_{18}FSMs$ were air-dried in the dark. The solid had a light green color,[22] and the green color of the starting Chl *a* solutions was substantially lightened after the adsorption.

The amounts of Chl *a* adsorbed on 1,4BD-$C_{18}FSMs$ were estimated from the difference in UV−vis absorption intensities of the toluene solutions before and after the adsorption (Table 1). The N_2 adsorption isotherms of the 1,4BD-$C_{18}FSMs$ indicated that the porosity of 1,4BD-$C_{18}FSM$ decreased after the adsorption as shown in Table 1, meaning that Chl *a* is introduced into the uniform pore system of 1,4BD-$C_{18}FSMs$. The UV−vis absorption spectra of Chl *a* in 1,4BD-$C_{18}FSMs$ are shown in Figure 2. The peaks due to the Soret band and the Q_y transition were observed at around 415 and 665 nm, respectively, and all the other observed peaks were assignable to Chl *a*, indicating that Chl *a* molecules can be successfully encapsulated into 1,4BD-$C_{18}FSM$ without pheophytinization.

In general, pheophytinization of Chl *a* readily occurs on silica surfaces, and in fact almost all the Chl *a* molecules changed to pheophytin *a* by using unmodified $C_{18}FSM$.[23] The H_0 value of the surface Si−OH groups of FSM-type mesoporous silica has been estimated to be −3.0, which is lower than that of amorphous SiO_2 (+3.0).[24] Therefore, the pheophytinization on the surface of $C_{18}FSM$ progressed

(18) Horváth, G.; Kawazoe, K. *J. Chem. Eng. Jpn.* **1983**, *16*, 470. Using N_2 adsorption−desorption measurements (BELSORP 28 (Bel Japan, Inc.) at 77 K), BET surface areas, pore volumes, and average pore diameters were determined. The average pore diameters were calculated by the Horváth−Kawazoe method.

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(20) The broad peak can be assigned to OH groups in 1,4-butanediol. Although the presence of adsorbed water molecules cannot be excluded, the amount of adsorbed water should be very small because the samples were heated at 120 °C before IR measurements.

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(22) XRD indicated that the ordered structures of $C_{18}FSM$ and 1,-4BD-$C_{18}FSM$ were retained before and after the adsorption experiments.

(23) The adsorbed amount was 0.38 mg on the $C_{18}FSM$ (0.15 g). Two peaks due to pheophytin *a* were observed at 509 and 538 nm. (Watanabe, T.; Hongu, A.; Honda, K.; Nakazato, M.; Konno, M.; Saitoh, S. *Anal. Chem.* **1984**, *56*, 251.) When the green $C_{18}FSM$ was dispersed into methanol, the adsorbed pigment was fully eluted and the resultant $C_{18}FSM$ was white in color. The ^1H NMR spectrum of the methanol solution showed the peaks due to an NH group in pheophytin *a* at −1.7 and −1.9 ppm. (Abraham, R. J.; Rowan, A. E. In *Chlorophylls*; Sheer, H., Ed.; CRC Press: Boca Raton, FL, 1991; Chapter 4.4.) In the IR spectrum of $C_{18}FSM$ after the adsorption of Chl *a*, the OH stretching band at 3690 cm⁻¹ decreased substantially.
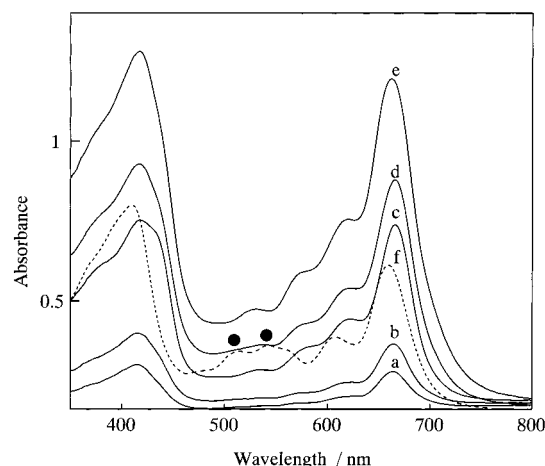
Figure 2. UV−vis absorption spectra of 1,4BD-C$_{18}$FSMs (solid line) with the adsorbed amount of Chl *a*: (a) 0.19, (b) 0.52, (c) 2.3, (d) 4.5, and (e) 10 mg per 1.0 g of 1,4BD-C$_{18}$FSM. The spectrum of C$_{18}$FSM (dotted line) after the adsorption is shown in (f); filled circles denote typical absorption bands due to pheophytin *a*. The spectra were measured by a Shimadzu UV-3100PC spectrometer.
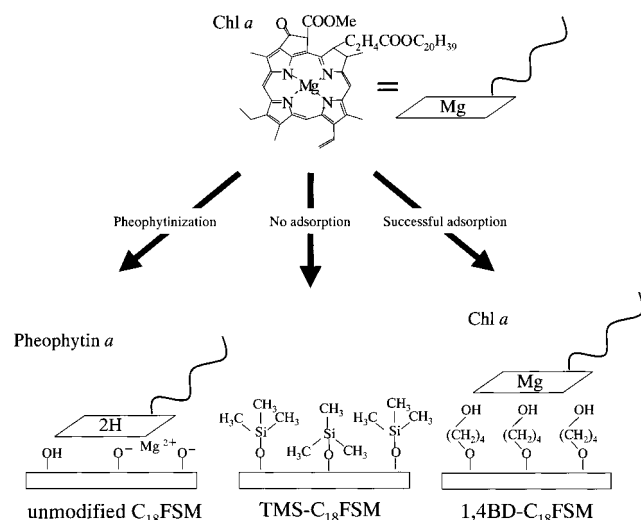

Figure 3. Schematic model for the adsorption of the Chl *a* molecules on the surface of organically modified C$_{18}$FSM.

owing to the acidic property of the surface Si−OH groups. The pheophytinization of Chl *a* during the adsorption on the surface of 1,4BD-C$_{18}$FSM is suppressed by the presence of organic groups formed through the esterification of C$_{18}$FSM with 1,4-butanediol. When trimethylsilylated C$_{18}$FSM[4b] was used as an adsorbent, Chl *a* molecules were not adsorbed on the silylated C$_{18}$FSM. This finding indicates that new OH groups generated by the modification with 1,4-butanediol play a role in the adsorption of Chl *a* molecules and a schematic model is shown in Figure 3. In fact, the adsorbed Chl *a* molecules were extracted by acetone. The UV−vis absorption spectrum of the extracted solution also showed no pheo-

phytinization of Chl *a*, though the possibility of other types of variation of the Chl *a* structure cannot be excluded completely.[11]

The peak due to the Q$_y$ transition of the Chl *a* molecules in a monomeric state is observed at 665.8 nm in methanol.[25] The peaks observed for 1,4BD-C$_{18}$FSMs after the adsorption of Chl *a* were broader than those observed for monomeric Chl *a* molecules in organic solvents, being in line with the phenomenon found for a clay−chlorophyll system.[15] The formation of aggregates of Chl *a* is explained by a considerable red-shift (observed at ca. 700−750 nm) in comparison with the monomer peak of Chl *a* molecules.[25] In the present system, the Q$_y$ transition was observed at around 665 nm, suggesting that the encapsulated Chl *a* molecules are well dispersed in the mesopores of 1,4BD-C$_{18}$FSMs. The steady-state fluorescence spectra of Chl *a* in 1,4BD-C$_{18}$FSM showed an emission peak due to Chl *a* molecules at around 660 nm. The excitation spectra monitored at 660 nm had the same profiles as the corresponding absorption spectra.

If Chl *a* molecules are homogeneously adsorbed on the surface of the pores of 1,4BD-C$_{18}$FSMs, the distances among the Chl *a* molecules are calculated to be ca. 10−80 nm, based on both the adsorbed amounts of Chl *a* (0.19−10 mg/1.0 g of 1,4BD-C$_{18}$FSM) and the BET surface area of the original 1,4BD-C$_{18}$FSM (640 m^2 g^{-1}). All the calculated results are shown in Table 1.

In the light harvesting system, the solar energy collected by antenna pigments is transferred between the antenna chlorophylls and finally trapped at the reaction center. The critical transfer distances (R_0) have been reported on various photosynthetic pigments, and the R_0 value between the Chl *a* molecules is 8−9 nm.[26] Therefore, the energy transfer between the Chl *a* molecules is likely to occur on the system presented here (especially, the system of the distance of 10 nm). Because such an energy transfer usually occurs between photosynthetic molecules, we are investigating the subsequent incorporation of photosynthetic pigments into 1,4BD-C$_{18}$FSM containing Chl *a* in order to achieve an effective energy transfer between Chl *a* and other photosynthetic pigments.

In conclusion, FSM-type mesoporous silica was modified with 1,4-butanediol and the esterified material was used as the adsorbent to encapsulate Chl *a* molecules. Pheophytinization of Chl *a* is suppressed by the presence of the surface organic groups grafted onto the mesoporous silica. Other diols such as 1,6-hexanediol and 1,8-octanediol can also be utilized as the modifying agents for successful encapsulation of Chl *a*. The UV−vis spectrum of 1,4BD-C$_{18}$FSMs containing Chl *a*, which was stored under dark and cold (0 °C) conditions for 6 months, was measured in order to estimate the stability of incorporated Chl *a*, and the spectrum showed no alteration. The results contribute to the development in the fields of photochemical and photophysical studies using chlorophylls in porous heterogeneous media and may lead to the construction of in vitro biomimetic solar energy conversion and storage systems.

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