parameters with all 9299 unique reflections converged at $R_1 = 0.0824$ (for $F_o > 4\sigma(F_o)$). Hydrogen atoms were included in calculated positions; max./min. residual electron density $1.06/-0.89\,e\,\AA^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115498. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

A Novel Layered Silicate with a Helical Morphology

Yoshikatsu Akiyama, Fujio Mizukami,*
Yoshimichi Kiyozumi, Kazuyuki Maeda,
Hiroyuki Izutsu, and Kengo Sakaguchi

Some layered silicate materials such as kanemite and magadiite (a mineral clay) are formed from silica under hydrothermal conditions.[1] Various silicate phases can be formed only by calcination.[2] When small amounts of aluminum hydroxide and tetramethylammonium hydroxide (TMA-OH) are added to a silica source and treated under hydrothermal conditions, high-silica zeolites such as Nu-1[3], Fu-1,[4] (Na, TMA)-E,[5] and sodalite[6] are formed. Furthermore, it was reported recently that the TMA ion is a template for the formation of the zeolite precursor RUB-15,[7, 8] in which hemihedral cavities constitute a layered structure; however, the precise role of the TMA ions is still obscure. We considered that comparing products obtained with and without TMA or an aluminum component in organic or aqueous solution under hydrothermal conditions might give insights into this subject, and also provide an opportunity to elucidate the difference between the transformation of amorphous silica into layered and microporous structures. In the course of our investigations, under aluminum-free conditions, we found a novel silicate phase, the scanning electron micrograph of which (Figure 1) showed a helical morphology consisting of stacked layers. This morphology differs strongly from those of traditional layered silicates such as kanemite and magadiite[1, 2] and from those of more recently reported layered silicates.[7, 8]

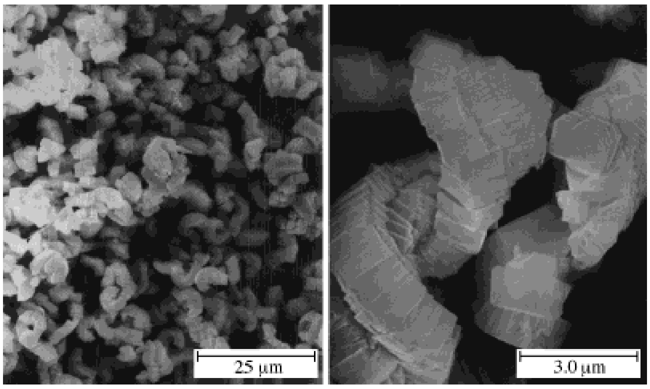

Figure 1. Two scanning electron micrographs of the novel silicate material obtained from run 1 (Table 1).

Table 1. Products obtained under different reaction conditions.[a]

Run	Composition of the reaction mixture				Product[c]
	SiO_2 [10^{-2} mol]	TMA-OH [10^{-3} mol]	NaOH [10^{-3} mol]	H_2O:1,4-dioxane[b]	
1	3.60	4.80	3.00	2.20	HLS
2	3.60	4.80	3.00	3.77	HLS
3	3.60	4.80	3.00	4.46	HLS
4	3.60	4.80	3.00	6.61	Amo
5	3.60	4.80	3.00	9.71	Amo
6	3.60	4.80	3.00	34.3	Amo
7	3.60	4.80	3.00	∞	Amo
8	3.60	0	3.00	2.45	Mag
9	3.60	4.80	0	34.3	Amo

[a] The reaction was carried out at 150 °C for 10 d. [b] In all runs, the total amount of 1,4-dioxane and H_2O was 18.0 g. [c] HLS = helix layered silicate, Amo = amorphous silica, Mag = magadiite. These phases were evaluated by means of XRD patterns.

Table 1 lists the reaction conditions under which the helix layered silicate (HLS) was formed. As indicated in runs 1–3 and 7–9, besides silica, NaOH, TMA-OH, and 1,4-dioxane are essential for the formation of HLS, which is also favored by low H_2O:1,4-dioxane ratios. Under the conditions investigated here, TMA-OH did not transform silica into a layered silicate, whereas NaOH transformed silica into a magadiite phase. Consequently, it can be concluded that silica sol is transformed into the HLS by the cooperative action of both TMA-OH and NaOH. The elemental analysis of the HLS gave a TMA content of 13.2 wt%, consistent with the value obtained by thermogravimetric differential thermal analysis (TG-DTA), and the water content as determined by TG-DTA was 10.8 wt%. The silicon and sodium contents calculated from elemental analysis and energy dispersive analysis of X rays (EDAX) were 30.4 and 0.48 wt%, respectively. When a 0.1-g sample of the HLS was treated with 30 mL of 0.05 N HCl in aqueous solution, the EDAX peak of sodium disappeared completely, and the TMA content by elemental analysis decreased to 4.2 wt%. This indicates that both TMA and sodium ions in the HLS are easily replaced with protons.

We then investigated whether the HLS is a single phase or a mixture of different layered silicates. Figure 2 shows the ^{29}Si MAS NMR and ^{13}C CP-MAS NMR spectra of the HLS. The ^{29}Si MAS NMR contains a strong signal at $\delta = -104.4$, which can be assigned to $-Si(OSi)_3$ (Q^3) units, and weak broad signals, probably due to unchanged amorphous silica. This Q^3 connectivity is characteristic of layered silicates. The ^{13}C CP-MAS NMR spectrum displays a strong signal for TMA at $\delta = 57.9$. When TMA is trapped in a confined space, its ^{13}C NMR

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[*] Dr. F. Mizukami, Y. Akiyama, Dr. Y. Kiyozumi, Dr. K. Maeda, Dr. H. Izutsu
National Institute of Material and Chemical Research
1-1, Higashi, Tsukuba, Ibaraki 305-8565 (Japan)
Fax: (+81) 298-54-4487
E-mail: mizukami@home.nimc.go.jp

Prof. Dr. K. Sakaguchi
Faculty of Science and Technology, Science University of Tokyo
2641 Yamazaki, Noda, Chiba 278-0022 (Japan)

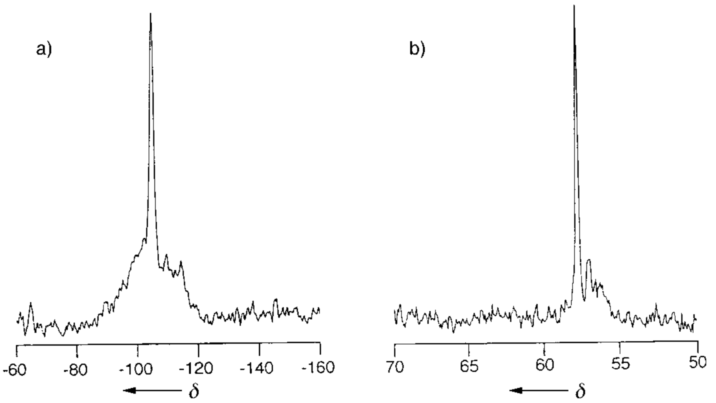

Figure 2. a) ^{29}Si MAS NMR and b) ^{13}C CP-MAS NMR spectra of the helix layered silicate shown in Figure 1.

signal of shifts from $\delta = 56.0$ (for free TMA) to 59.0.[9] In RUB-15[7] TMA has a ^{13}C chemical shift of $\delta = 56.4$. Therefore, in the HLS prepared the TMA ions are located in a confined space, that is, between the anionic silicate sheets. There is no signal for 1,4-dioxane, and therefore it is not present in the HLS. This suggests that 1,4-dioxane may contribute to the formation of the sheet silicate, but is not a template for the helical layered structure. This is in contrast to silica sodalite, for which 1,3,5-trioxane and 1,3-dioxolane can act as templates.[10]

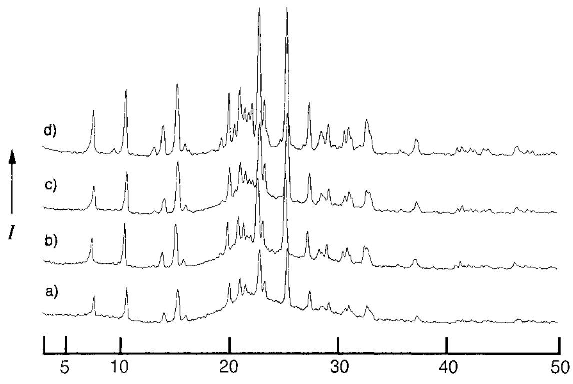

Figure 3. X-ray diffraction patterns of the helix layered silicate after a reaction time of a) 96, b) 119, c) 262, and d) 383 h. The reaction conditions are as for run 1 (Table 1).

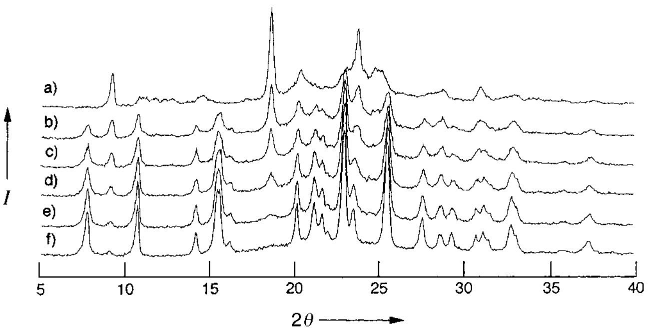

Figure 4. X-ray diffraction patterns of the HLS silicate a) 0, b) 20, c) 40, d) 60, e) 80, f) 100 min after calcination at 200 °C. The sample from Figure 3c was used here.

Figure 3 shows the X-ray diffraction (XRD) pattern of the HLS after different reaction times. The diffraction pattern is characteristic of a layered structure and is the same for all four samples. However, the crystallinity increases with increasing reaction time, and the diffraction pattern differs from those of all silicate phases reported so far.[2, 7, 8] When the HLS was heated to 200 °C, the XRD pattern was changed drastically, but the original XRD pattern was completely restored when the product was left at room temperature in air (Figure 4). The HLS still contains TMA ions even at 200 °C. A typical property of mineral clays is reversible adsorption and desorption of H_2O molecules between the layers,[1, 11] and the restoration of the XRD pattern is due to the readsorption of H_2O molecules into the silicate layer structure. This reversible change in the XRD pattern suggests that the HLS is a single phase, because such a smooth and simple reversible transition is regarded as being difficult for a mixture of different layered structures. When the HLS was heated to above 300 °C in air, the XRD pattern showed formation of an amorphous phase. At this temperature, the TMA ions were lost from the silicate (TG-DTA). Likewise, after removal of TMA and sodium ions by the treatment with 0.05 N HCl, the HLS showed a similar change in the XRD pattern (drastic lowering of crystallinity). However, the morphology in the SEM images did not show so drastic a change as the XRD patterns.

The transformation of amorphous silica into layered crystalline helix silicate is believed to occur as follows: Firstly, NaOH plays a role in converting the silica sol into the layer structure (see run 8 in Table 1), and then TMA ions are incorporated and stabilize the layered structure. During formation of the the layered structure, 1,4-dioxane could induce a helical morphology, because a low H_2O:1,4-dioxane molar ratio or a high 1,4-dioxane concentration is an important factor for the formation of HLS. Since 1,4-dioxane molecules break hydrogen bonds between water molecules,[12] they can also be expected to disrupt the hydration sphere around TMA ions. Hence, the hydration structure of TMA ions at low H_2O:1,4-dioxane ratios should be different from that of TMA ions in aqueous solution, and TMA ions in a solution with a low H_2O:1,4-dioxane ratio would interact with silicates in a different manner from those in aqueous solution and could induce the formation of HLS. This consideration may be supported by our finding that the helix silicate is also formed in H_2O/pyridine system at low H_2O:pyridine ratios.

Experimental Section

SiO_2 was synthesized by hydrolysis of tetraethyl orthosilicate (TEOS) at a TEOS:H_2O:ethanol molar ratio of 0.3:20:1 at 70 °C for 24 h. The resulting gel was dried at 70 °C under vacuum.

The novel silicate phase was obtained as follows: SiO_2 (3.60×10^{-2} mol), 1,4-dioxane (0.11 mol), TMA-OH (4.80×10^{-3} mol), NaOH (3.00×10^{-3} mol), and H_2O (0.37 mol) were mixed in a teflon-lined autoclave (Table 1, run 2). The mixture was heated to 150 °C for 10 d. After the reaction was complete, the resulting powder was recovered by filtration, washed with acetone, and dried at 90 °C for 1 d. When this hydrothemal synthesis was carried out at 170 °C, the HLS was not obtained, and only amorphous silica powder was recovered.

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Light Harvesting and Energy Transfer in Novel Convergently Constructed Dendrimers**

Sylvain L. Gilat, Alex Adronov, and
Jean M. J. Fréchet*

A characteristic of dendritic macromolecules is the presence of numerous peripheral chain ends that all surround a single core.[1] If a long-range interaction could be introduced between these multiple chain ends and the focal point it would then be possible to influence the core of the macromolecule by events that initially occur with a higher probability on the dendrimer periphery.[2] Following this rationale we report that it is possible to essentially create a light-harvesting antenna by functionalizing a dendrimer with suitable interacting chromophores.[3] In these dye-labeled dendrimers light absorbed by the numerous peripheral chromophores is funneled to a central fluorescent core with a remarkably high efficiency and by a mechanism that is independent of the dendritic architecture. Hence, this new strategy is different from all the previous approaches to energy or electron transfer within dendritic architectures,[4] where the transfer was achieved by through-bond or “hopping” processes.

The array of terminal chromophores in the present macromolecules provides a large overall cross-section for collecting energy and plays the role of an antenna for light harvesting, while the focal dye (Figure 1) plays the role of a fluorescent probe whose emission signals that energy is actually received at a single localized site. Furthermore, both the peripheral chromophores and the focal dye contribute to the absorption of the entire macromolecule. Since their individual absorptions each cover a different wavelength range, the absorption of the whole macromolecule is particularly broad and provides a larger spectral coverage than the focal dye alone. The energy transfer process converts this broad absorption into the narrow emission of the central laser dye. Therefore, such a dye-labeled dendrimer represents both a spatial and spectral light concentrator: the energy of any photon of any wavelength absorbed anywhere in this ensemble of chromophores is transferred to a single point and converted into a relatively narrow emission spectrum.

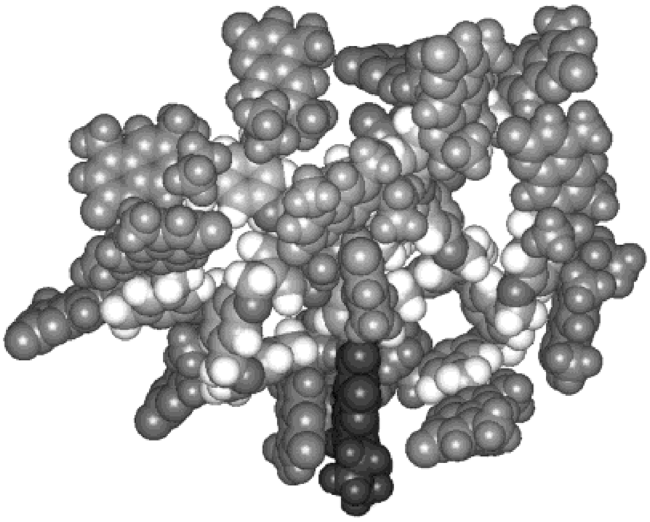

Figure 1. Molecular model (MM3) of the G-4 dendron showing peripheral donor chromophores surrounding the core acceptor (indicated in dark gray).

This scheme is indeed reminiscent of the primary event of photosynthesis, where solar energy absorbed anywhere in an array of hundreds of chlorophyll molecules is efficiently transferred to a single reaction center.[5] The higher the dendrimer generation number, the higher the number of terminal groups that surround the core,[1] and the larger the cross-section for energy collection. However, the average distance between the core and the peripheral groups also increases as the generation number G-x ($x = 1-4$) increases. By considering the size of dendritic macromolecules,[1] energy transfer from the periphery to the core would most likely take place through a dipole–dipole interaction. According to Förster theory[6, 7] the efficiency of energy transfer decreases as the inverse sixth power of the interchromophoric distance. Clearly, it was necessary to determine whether this dipole–dipole interaction would be strong enough to achieve an efficient energy transfer, even at high generations.

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[*] Prof. J. M. J. Fréchet, A. Adronov
Department of Chemistry, 718 Latimer Hall
University of California at Berkeley
Berkeley, CA 94720-1460 (USA)
Fax: (+1) 510-643-3079
E-mail: frechet@cchem.berkeley.edu

S. L. Gilat
Bell Laboratories
Murray Hill, NJ 07974 (USA)

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