Sol–Gel Transcription of Sugar-Appended Porphyrin Assemblies into Fibrous Silica: Unimolecular Stacks versus Helical Bundles as Templates

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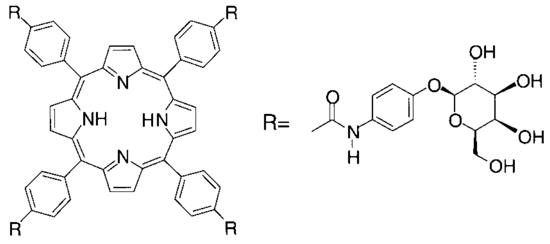
A diverse range of supramolecular structures can be created, not only in nature but also in an artificial system, by self-assembly of designed organic building blocks. In general, the creation of such diverse supramolecular structures seems to be very difficult or nearly impossible in inorganic materials. Is there any innovative method by which ordered supramolecular structures can be created from inorganic materials? The sole method is to transcribe the supramolecular structures of organic molecular assemblies into inorganic materials. It is known that amphiphilic organic molecules are self-assembled into various supramolecular structures,[1] which can be utilized as templates to create novel mesophasic inorganic materials in mesoporous materials,[2] vesicles,[3] ultrathin membranes,[4] etc.[5] As natural examples of these processes, one can prepare inorganic microfibers by mineralization of bacterial fibers[6] or of self-assembled lipid tubules of a galactocerebroside and a phosphate.[7] Since in these attempts it is very important to "design" the different size and shape of the inorganic materials (in the same way that organic compounds and assemblies are "designed"), it has been desirable to explore the use of various organic materials as templates and elucidate the mechanism of the template effect.[8] Thus, it is now possible to "design" the inorganic catalysts, electrodevices, etc. at a micrometer level.[9]

Increasing attention has been paid to low molecular mass compounds that can efficiently gelate various organic solvents.[10–21] These phenomena are interesting in that the fibrous aggregates formed by noncovalent interactions are responsible for the gelation. We have shown that these "organic" superstructures can be elaborately transcribed into "inorganic" silica materials by utilizing template–silanol interactions.[22] Recently, we found that an amphiphilic porphyrin (**1**) bearing four β-D-galactopyranoside groups at its periphery tends to aggregate in a one-dimensional direction, which results in very robust gels in DMF/alcohol mixed solvents.[23, 24] Interestingly, we noticed that the speed of bundle growth of this gelator is relatively slow, which would provide us with a greater chance to transcribe nanosized incipient fibers into silica. Here, we report that the sol–gel transcription of this gel system with tetraethoxysilane (TEOS) results in hollow fiber silica with a 4–5-nm inner diameter, which is comparable to the length of the long axis in **1**. This is a rare example of a unimolecular stack immobilized in an inorganic material.



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Sol–gel polycondensation of TEOS was carried out using a gel of **1** and DMF/benzyl alcohol (BnOH) according to the method described previously.[22] For example, **1** was dissolved in a mixture of DMF, BnOH, and TEOS at 80 °C. This solution gelled when cooled to room temperature. Before the gel was formed, however, benzylamine ($BnNH_2$) and water were added. In Method A, the mixture was heated at 80 °C again and then left at room temperature for 2 weeks. However, in Method B the mixture was just left at room temperature without the heating treatment. The silica gel thus obtained was washed with methanol to remove organic compounds adsorbed on the outer surface of the silica. After this treatment, the sample (obtained by Method A) was subjected to X-ray photoelectron spectroscopy (XPS) analysis to obtain some information on the outer surface of the silica. The peak corresponding to N atoms at 409 eV (which should result from **1** or benzylamine) was very weak, with the relative intensity of 8:92 to the peak corresponding to Si atoms at 112 eV. This result shows that **1** is scarcely adsorbed on the outer surface of the silica.

The absorption spectrum of **1** (2.3×10^{-6} M) in DMF shows the Soret band at 422 nm and the Q bands at 517, 553, 593, and 647 nm (Figure 1 A). When **1** (3.3×10^{-3} M) forms a gel in $DMF{:}BnOH{:}BnNH_2 = 40{:}120{:}3$, the spectral shape is significantly broadened and the Soret band shifts to shorter wavelength (397 nm), whereas the Q bands shift to longer wavelength (524, 559, 600, and 656 nm). This spectral change supports the porphyrin–porphyrin stacking interaction in the assembly of **1**.[25] Interestingly, the absorption spectrum after sol–gel polycondensation (Method A) shows that both the Soret band and the Q bands appear at nearly the same wavelengths as those of the organogel phase. This result implies that the stacked porphyrin structure is still retained in the silica gel phase. This view is further supported by the CD spectra (Figure 1 B): the CD spectrum obtained after sol–gel polycondensation is very similar to that of the organogel phase.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) pictures before and after calcination were used to obtain visual insights into the silica structure. The silica before calcination shows a fibrous structure with an approximate 50-nm outer diameter (Fig-

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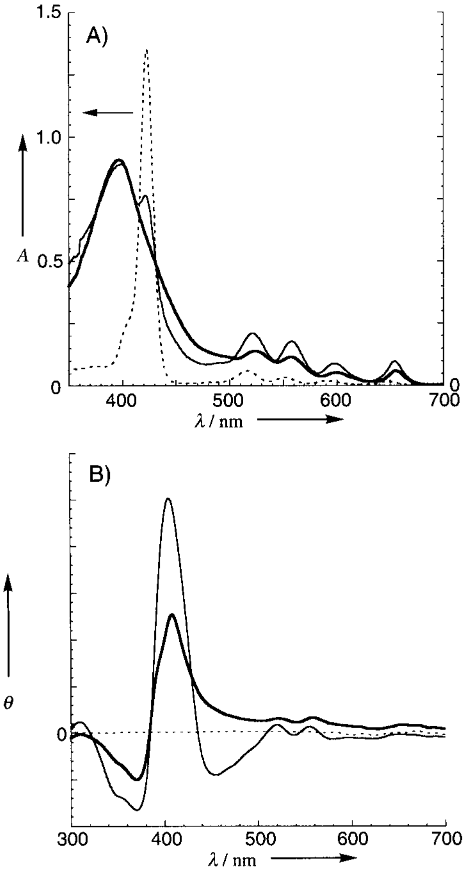

Figure 1. Absorption (A) and CD (B) spectra of silica-coated porphyrin arrays (bold line), organogel of **1** (thin line), and homogeneous solution of **1** (broken line; [**1**] = 2.3×10^{-6} M).

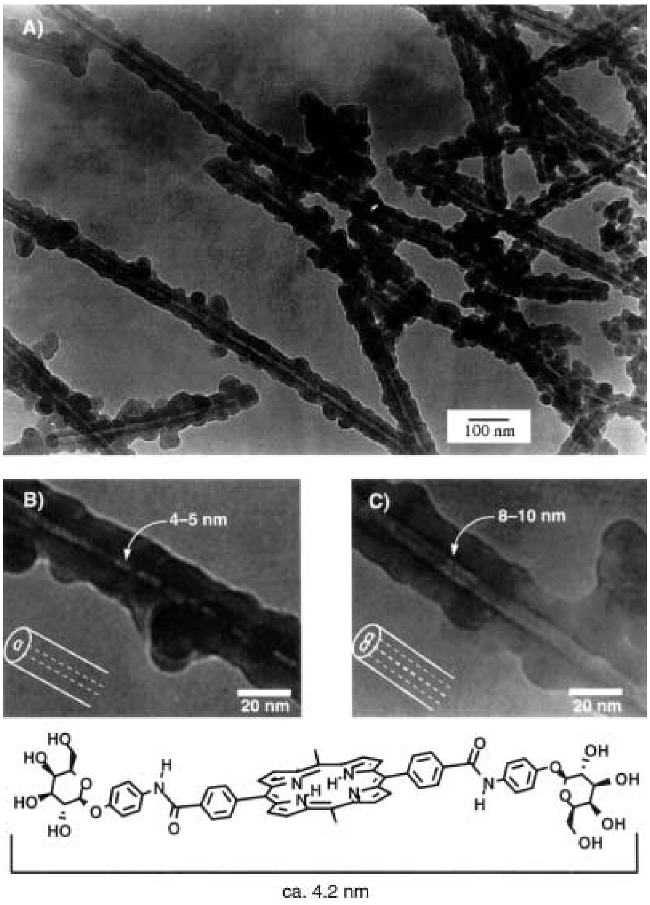

Figure 3. TEM images of silica-coated porphyrin arrays.

ure 2). This morphology scarcely changed, even after calcination (at 500 °C; see Supporting Information). It is clearly seen from the TEM image (Figure 3) that these silica fibers have an inner hollow with 4–12-nm diameters. Careful examination reveals that there are two different hollow diameters: one about 5 nm, which is comparable with the length of the long axis in **1** (4.2 nm: Figure 3B), and another about 9 nm, which is comparable to twice the length of the long axis, and bearing a stripe in the center (Figure 3C). The TEM image scarcely changed, even after calcination, but the central stripe in Figure 3C disappeared (see Supporting Information).

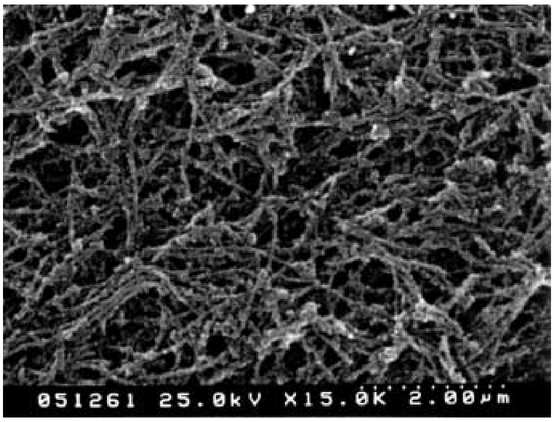

Figure 2. SEM image of silica-coated porphyrin arrays.

In Method A, the solution containing $BnNH_2$ (polycondensation catalyst)[22] was heated so that the formation of bundles of organogel fibers would be suppressed while the rate of sol–gel polycondensation of TEOS would be accelerated. Clearly, this condition facilitates the entrapment of incipient organogel fibers comprised of a unimolecular stack or a bimolecular stack. In the absence of heating after $BnNH_2$ addition (Method B), the bundle growth of organogel fibers can compete with sol–gel polycondensation to give a helically bundled silica structure from transcription of well-grown, helically bundled organogel fibers (Figure 4).

The results obtained consistently support the view that **1** aggregates into a one-dimensional stack, along which sol–gel polycondensation of TEOS proceeds in the gel phase. The size of the inner hollow obtained in Method A suggests that the incipient organogel fibers are encapsulated in these silica hollow fibers. The disappearance of the central stripe upon calcination is rationalized in terms of the disappearance of stacked **1** molecules by pyrolysis.

In conclusion, we have demonstrated that the elaborate, nanometer-level sol–gel transcription of organic assemblies is possible when the incipient organic assembly can exist stably in the gel phase and when the sol–gel reaction conditions are appropriately selected. Until now, the silica superstructures obtained by template transcription of organic assemblies have

Figure 4. SEM image of the silica structure prepared by transcription of helically bundled **1** as a template (before calcination).

been characterized by the broad size distribution. This polydispersed nature has made their chemical applications difficult. We thus believe that the creation of the new silica fiber structure with the nearly monodispersed hollow size is essential and applicable to other related transcription systems. For example, the nanosized hollow will be useful as a host cavity to enforce molecules to orientate into a one-dimensional direction. This possibility suggests the future possibility of creating various nanosized cavities by designing various sizes of "organic" template molecules.

Experimental Section

Sol–gel polycondensation: Method A: Gelator **1** (4.0 mg) was added to a mixed solvent of DMF (160 µL) and BnOH (480 µL) and the mixture was heated until the precipitate was dissolved completely. Tetraethoxysilane (TEOS, 35 µL), BnNH$_2$ (10 µL), and water (10 µL) were then added to this mixture. The reaction mixture was then reheated until it became homogeneous, and then it was placed at room temperature in the dark for 2 weeks. The product was washed with methanol and dried in vacuo to give the organic–inorganic composite as a purple solid. This sample was calcinated at 150 °C for 2 h, at 500 °C for 5 h under a nitrogen stream, and then at 500 °C for 5 h under an aerobic stream to remove the gelators. The silica thus obtained was colorless.

Method B: Gelator **1** (1.0 mg) was added to a mixture of DMF (40 µL), BnOH (120 µL), and TEOS (10 µL) and the resultant mixture was heated until the precipitate had dissolved completely. The mixture was then cooled to room temperature and BzlNH$_2$ (3 µL) and water (3 µL) were added. Without the heating process, this reaction mixture was placed at room temperature in the dark for 2 weeks. The product was washed with methanol and dried in vacuo to give the organic–inorganic composite as a purple solid.

UV/Vis, CD, and X-ray photoelectron spectra were recorded on a Shimadzu UV-2500PC spectrophotometer, a JASCO J-720 spectrometer, and a Perkin–Elmer ESCA 5300 spectrometer, respectively. The SEM and TEM pictures were taken on a Hitachi S-5000 scanning electron microscope and a Hitachi H-600 transmission electron microscope, respectively.

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Intramolecular 1,8-Hydrogen Abstraction Between Glucopyranose Units in a Disaccharide Model Promoted by Alkoxy Radicals**

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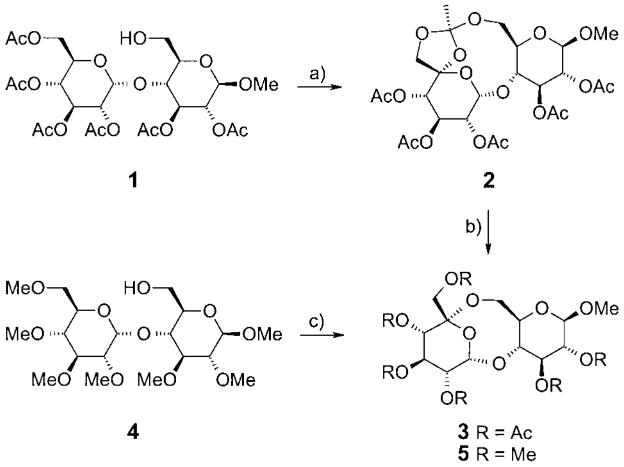
The use of radical reactions in carbohydrate chemistry has recently attracted considerable attention in the synthetic community.[1] Among free radical reactions intramolecular hydrogen abstraction (IHA) has been comparatively less studied in these systems.[2] Although 1,*n*-hydrogen transfer has been observed from C_{sp^3}–H to alkyl and aryl C radicals for $n = 4-7$,[3] 1,5-hydrogen transfer is by far the most common IHA reaction when promoted by alkoxy radicals.[4] In some cases, 1,6-hydrogen transfer from unactivated carbon atoms to alkoxy radicals has been observed, usually in low yield.[5] Only when the hydrogen atom to be removed is bonded to an oxygen-substituted carbon atom the yield of this last process could be considered to be of synthetic interest.[6] IHA reactions through eight- or higher membered transition states are practically unknown; entropic effects are probably responsible for the failure of these processes.[7]

With this in mind, we reasoned that an IHA reaction through an eight- or even higher membered transition state might be possible in a model with a restricted conformational mobility to avoid the entropic penalty. Two other conditions should be fulfilled: a low-energy transition state and a distance of around 3 Å between the O radical and the hydrogen atom to be abstracted.[8] It soon became evident that the Glc-α1→4-Glc unit in compound **1** (see Scheme 1)[9, 10] has a preferred *syn* conformation of the glycosidic bond ($\Phi = -34.2°$, $\Psi = -28.3°$) and a $C_6O\cdots HC_{5'}$ distance of 2.5 Å in accord with previously reported X-ray crystallographic[11] and molecular mechanics[12] analyses of β-D-maltose octaacetate and methyl β-D-maltoside, respectively. A study of the transition state of the C_6-O$\cdots$H-$C_{5'}$ IHA reaction gave a similar situation for the glycosidic torsion angles ($\Phi = -32.7°$, $\Psi = -37.3°$) and a distance of 3.14 Å between the O radical and H-$C_{5'}$.[13]

In order to substantiate our assumption the C_6 alkoxy radical was generated by reaction of the D-maltose derivative **1**[14] with (diacetoxyiodo)benzene and iodine under irradiation with two 100 W tungsten filament lamps (Scheme 1). The reaction, which proceeds presumably through an alkyl hypoiodite intermediate,[15] gave orthoacetate **2** in 62 % yield. Compound **2** is a moderately stable crystalline solid with an unprecedented 1,3,5,7-tetraoxecane ring system whose structure was elucidated by extensive NMR studies including COSY, TOCSY, DEPT, and HMQC experiments and confirmed by X-ray crystallographic analysis.[16] The orthoacetate group is hydrolyzed under very mild acidic conditions with concomitant ring contraction to give the 1,3,5-trioxocane derivative **3** in excellent yield. The trioxocane ring adopts a constrained, highly stable boat–chair conformation.[17] The reaction of the DIB/I_2 system with D-manoside **4**[18] gave directly the $C_{5'}$-functionalized disaccharide **5** through a nine-membered transition state (Scheme 1).



Scheme 1. IHA under oxidative conditions. a) DIB (1.5 equiv), iodine (0.7 equiv), CH_2Cl_2, $h\nu$, 25 °C, 90 min, 62 %; b) $CDCl_3$, RT, 60 h, 100 %; c) DIB (1.7 equiv), iodine (0.5 equiv), CH_2Cl_2, 25 °C, 90 min, 56 %. DIB = (diacetoxyiodo)benzene.

The IHA reaction between the two glucopyranose units can also be realized under reductive conditions. In our experience, one of the best methods to generate alkoxy radicals under reductive conditions is by reaction of *N*-hydroxyphthalimide

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