Immobilization of a Two-dimensional Porphyrin Assembly by Sol–Gel Polycondensation in the Gel Phase

Takanori Kishida, Norifumi Fujita, Kazuki Sada, and Seiji Shinkai*
Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka, Fukuoka 812-8581

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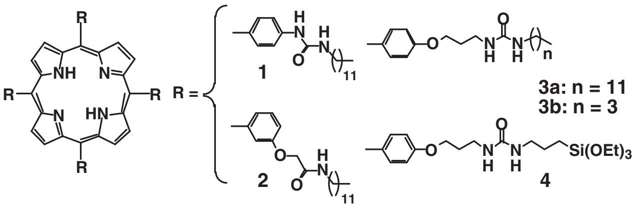
A porphyrin which assembles into a two-dimensional sheet structure by the hydrogen-bonding interaction among the peripheral urea groups has been designed. Introduction of triethoxysilyl groups into the terminal groups has enabled us to immobilize this novel porphyrin-based cluster by sol–gel polycondensation.

It is well known that porphyrins and phthalocyanines tend to align into one-dimensional (1-D) aggregates and therefore are of much concern in relation to creation of novel supramolecular architectures such as nanowires, discotic liquid crystals, helical ribbon structures, etc.[1–5] The major driving forces operating in these architectures are considered to be π–π stacking and/or van der Waals interactions. It is possible to fabricate these 1-D aggregates by inorganic materials to produce fibrous organic–inorganic hybrid materials.[4,6,7] More recently, another supramolecular architectures constructed in organogels attract broad attention of supramolecular chemists: the origin of organogel formation is considered to be 1-D alignment of gelator molecules supported by these interactions and/or hydrogen-bonding interactions.[8,9] Through these studies, we found that porphyrin rings can be arranged not only in a 1-D fashion but also in a two-dimensional (2-D) fashion by adjusting the structure of the peripheral hydrogen-bonding network: for example, **1** tends to assemble into a 1-D aggregate whereas **2** tends to assemble into a 2-D aggregate.[10,11] These findings encouraged us to challenge the fabrication of two-dimensionally arranged "porphyrin sheets" by sol–gel polycondensation. We thus designed in situ polymerizable porphyrin **4** and its reference porphyrins **3a** and **3b**.



The gelation properties of **3a** have been tested for 20 different solvents and compared with those of **1**.[10] The gelation test was carried out as follows: the gelator was mixed in a capped test tube with the appropriate amount of solvent and the mixture was heated until the solid was dissolved. The sample vial was cooled in air to 25 °C, left for 1 h at this temperature, and then turned upside down. When the gelator formed a clear or slightly opaque gel by immobilizing the solvent at this stage, it was denoted by a "G" mark in Table 1. It is seen from Table 1 that **3a**, in which the urea groups are located somewhat away from the porphyrin nucleus, shows better gelation ability than **1**, gelating 11 solvents among 20 solvents tested herein. In **1**, the *meso*-phenyl groups favorably adopt a conformation perpendicular to the porphyrin plane, so that it is energetically unfavorable for the urea groups directly connected to the *meso*-phenyl groups to form hydrogen-bonding arrays in the same direction as a 1-D stacking array of the porphyrin rings. Introduction of four $O(CH_2)_3$ spacers into **1** enables these two groups to stack into the same direction and improves gelation ability. It is also worthy to mention that the lowest gelation concentrations for **3a** are relatively low: e.g., $5.0\,g\,dm^{-3}$ ($2.9\,mmol\,dm^{-3}$) for benzene and $2.5\,g\,dm^{-3}$ ($1.4\,mmol\,dm^{-3}$) for diphenyl ether.

Table 1. Gelation properties of compounds **1** and **3a**

Solvent	State	
	1	**3a**
Benzene	I	G (5.0)
Toluene	I	G (15)
p-Xylene	I	G (15)
Anisole	G (1.25)	G (10)
Diphenyl ether	G (1.25)	G (2.5)
Chloroform	I	G (15)
1,1,2,2-Tetrachloroethane		G (30)
THF	P	G (30)
1,4-Dioxane		G (10)
Acetone	I	G (30)
DMSO		G (25)
Other solvents[a]		S, I, or P

G, P, I, and S denote gelation, precipitation, insoluble, and soluble, respectively. The critical gelation concentration is showed in a parenthesis. The unit is $g\,dm^{-3}$. [a]**3a**: soluble (pyridine and DMF), insoluble (methanol, ethanol, hexane, and cyclohexane), precipitation (tetrachloromethane, ethyl acetate, and acetonitrile) at [**3a**] = $30\,g\,dm^{-3}$.

Compound **4** (4.0 mg) was dissolved in benzene ($200\,\mu dm^3$) by heating. After cooling, TFA (0.2 equiv. with respect to **4**) and water ($1.0\,\mu dm^3$) were added and the resultant mixture was left at room temperature for 3 days. The purple precipitates thus obtained were isolated by centrifugation and washed with benzene. This operation was repeated with chloroform/ethanol (1:1 v/v) and with ethanol to remove TFA and unreacted **4**. After drying in vacuo, the sample was subjected to spectral and microscopic analyses. The FT-IR spectrum (KBr) shows that 1101 and $1076\,cm^{-1}$ peaks assignable to the Si–OEt groups disappear, while a broad $1044\,cm^{-1}$ peak assignable to the Si–O–Si group newly appears, indicating that sol–gel polycondensation proceeds successfully. The peaks assignable to the urea groups are scarcely changed before and after the reaction ($1627 \rightarrow 1633\,cm^{-1}$, $1572 \rightarrow 1564\,cm^{-1}$, and $3319 \rightarrow 3318\,cm^{-1}$). This result suggests that the hydrogen-bonding network is scarcely damaged by the reaction. UV–vis spectra of **3a** and **4** before and after sol–gel polycondensation were measured. Both in **3a**

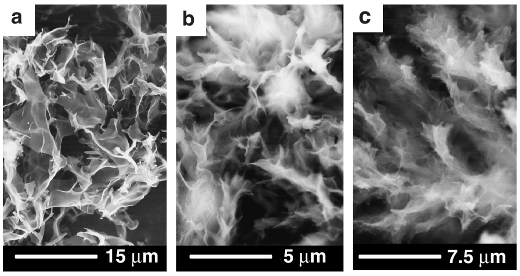


Figure 1. SEM images of the xerogel of (a) **3a** gel (benzene, [**3a**] = 20 g dm^{-3}) and self-assembled **4** (benzene, [**4**] = 20 g dm^{-3}) (b) before and (c) after sol–gel polycondensation.

and **4**, the Soret band in the gel phase ($\lambda_{max} = 428$ and 426 nm, respectively) shifts to longer wavelength region ($\Delta\lambda = 5$ and 3 nm, respectively) than that in the solution phase ($\lambda_{max} =$ 423 nm). The finding implies that both **3a** and **4** tend to assemble according to a J-aggregate fashion. The similar red-shifted Soret band ($\Delta\lambda = 5$ nm) is also recognized for the sample after sol–gel polycondensation. This result is in line with that obtained from the FT-IR measurements.

To obtain visual images of the gel structure and the organic–inorganic hybrid structure we took SEM and TEM pictures of the xerogels. We previously found that the H-aggregated porphyrins tend to grow up to a fibrous structure whereas the J-aggregated porphyrins tend to grow up to a sheet structure.[11] As expected, the SEM images of **3a** and **4** appear as the 2-D sheet structure (Figure 1). Even after sol–gel polycondensation, hybrid **4** keeps the sheet structure. This morphological invariability is compatible with the spectroscopic data obtained above. Very interestingly, the TEM picture shows a fine striped structure, the periodical distance of which is ca. 4.0 nm (Figure 2). The result is another evidence that hybrid **4** firmly maintains the 2-D sheet structure.

We are now attempting X-ray analysis of the single crystal grown up from **3b**. Although the quality is not satisfactorily high at present ($R_1 = 0.24$), one can visualize how the porphyrin rings are arranged in the crystal: that is, (1) in fact, they adopt a columnar J-aggregate, (2) these columns are assembled into a two-dimensional sheet structure, and (3) looking at the plane angle of the porphyrins in the column, they are tilted by ca. 90° alternately from one column to the neighboring column. On the basis of these lines of X-ray information, one can reasonably explain the TEM image and the XRD data. The distance of 4.0 nm in Figure 2 corresponds to that of two porphyrin columns. As the porphyrin planes in one column are tilted, it cannot clearly appear as a stripe. The XRD peaks at $2\theta = 20.4^\circ$ ($d = 0.44$ nm), 10.5° ($d = 0.85$ nm), and 6.6° ($d = 1.34$ nm) obtained from the xerogel of **3a** can be assigned to the distance between the hydrogen-bonding urea groups, that between the porphyrin planes, and that between the 2-D sheets. In **4** the latter two peaks become broad but the main peak still appears clearly at $2\theta = 20.6^\circ$ ($d = 0.43$ nm).

In conclusion, the present study demonstrated that the porphyrin rings can be arranged in a 2-D sheet structure by the hydrogen-bonding interaction among the peripheral urea groups and introduction of triethoxysilyl groups into the terminal groups enables us to immobilize this novel 2-D structure by in situ sol–gel polycondensation. To the best of our knowledge, this is the first example that the sheet structure of porphyrins is immobilized. We are now extending this novel hybridized assembly to chemical and physical studies of porphyrin-based clusters.

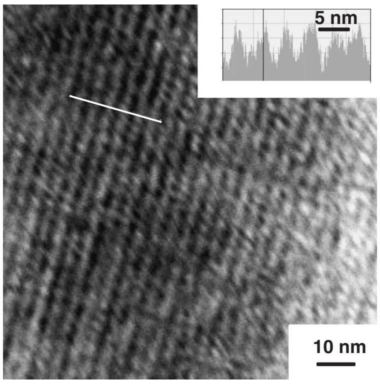


Figure 2. TEM image of self-assembled **4** (benzene, [**4**] = 20 g dm^{-3}) after sol–gel polycondensation. Inset shows the periodicity of a fine striped structure. White line in figure represents the place scanned.

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