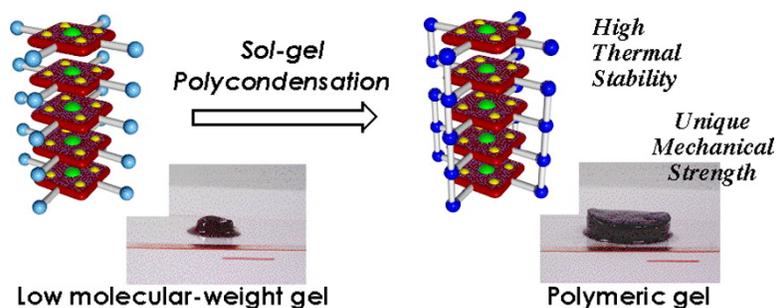


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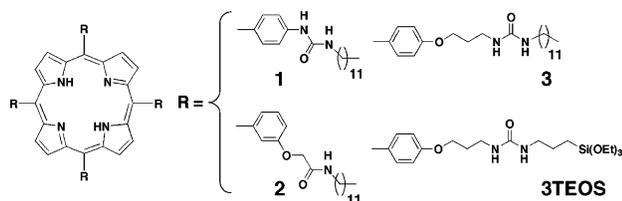
## Sol–Gel Reaction of Porphyrin-Based Superstructures in the Organogel Phase: Creation of Mechanically Reinforced Porphyrin Hybrids

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It is well-known that porphyrins and phthalocyanines tend to align into one-dimensional aggregates and, therefore, are of much concern in relation to the creation of novel supramolecular architectures, such as nanowires, discotic liquid crystals, helical ribbon structures, etc.<sup>1–6</sup> The major driving forces operating in these architectures are considered to be  $\pi$ – $\pi$  stacking and/or van der Waals interactions. It is possible to fabricate these one-dimensional aggregates by inorganic materials, utilizing electrostatic and/or hydrogen-bonding interactions, to produce novel fibrous organic–inorganic hybrid materials.<sup>4,7–9</sup> More recently, we found that the hydrogen bond forming groups introduced into the peripheral positions also play an important role in the determination of the final aggregation mode.<sup>10,11</sup> Through these studies, we learned that the aggregation mode of porphyrin rings can be tuned not only in a one-dimensional fashion but also in a two-dimensional fashion by programming the structure of these groups; for example, **1** tends to assemble into a one-dimensional aggregate, whereas **2** tends to assemble into a two-dimensional aggregate.<sup>11,12</sup> It thus occurred to us that the fabrication by sol–gel polycondensation of covalently linked triethoxysilyl groups would be useful to immobilize these different porphyrin-based superstructures and would eventually provide reinforced “porphyrin wire” and “porphyrin sheet” architectures, respectively. We previously showed that **3** and **3TEOS** assemble into a two-dimensional sheetlike structure in their gel phases, and therein, the porphyrin nuclei adopt a J-aggregation mode.<sup>13</sup> This two-dimensional structure was readily immobilized by sol–gel polycondensation of the peripheral triethoxysilyl groups.<sup>13</sup> In this work, we introduced a few kinds of metal ions into the porphyrin nuclei to seek a variety of new stacking modes and gelation properties. We have found that in the Cu(II) complex the morphology is transformed to the one-dimensional fibrous structure, which can be immobilized by sol–gel polycondensation.<sup>14d,e</sup> We report here our very interesting findings that the resultant porphyrin-based hybrid gel gains a very high thermal stability unlike low molecular weight gel and behaves as a novel “elastic” gel.



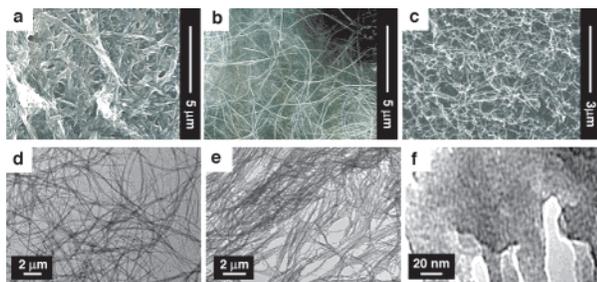
The gelation properties of **3** and its derivatives have been tested for 20 different solvents by the “stable-to-inversion of a test tube” method (Table S1). We found that **3** and its Cu(II) complex (**3·Cu**) act as good gelators which can gelatinize 11 solvents, whereas its Zn(II) complex (**3·Zn**) gelatinizes only two solvents. Introduction of triethoxysilyl groups generally enhances the solubility of gelators and frequently takes away the gelation ability. We confirmed,

however, that **3TEOS·Cu** retains the gelation ability for benzene, *p*-xylene, and anisole, whereas **3TEOS** can gelatinize only benzene. Furthermore, the critical gelation concentration for **3TEOS·Cu** is lower by about 2 orders of magnitude than that for **3TEOS**, reflecting the strong stacking property of the porphyrin·Cu(II) complex. To further characterize these gels, we mainly used benzene for **3** and **3TEOS** and anisole for **3·Cu** and **3TEOS·Cu**.

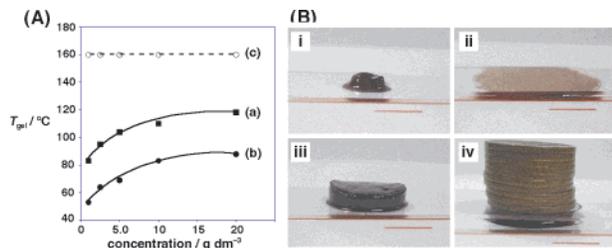
Sol–gel polycondensation of **3TEOS·Cu** + anisole gel was carried out according to our previous method, and the obtained xerogel was subjected to spectral analyses.<sup>13</sup> The FT-IR spectrum (KBr) showed that the 1101 and 1071  $\text{cm}^{-1}$  peaks assignable to the Si–OEt groups disappear, while a broad 1040  $\text{cm}^{-1}$  peak assignable to the Si–O–Si group newly appears, indicating that sol–gel polycondensation proceeds successfully. The peaks assignable to the urea groups (1568 and 1633  $\text{cm}^{-1}$ ) are scarcely changed before and after sol–gel polycondensation, indicating that the original hydrogen-bonding network is still retained (Figure S4).

The UV–vis absorption spectrum of a benzene solution of **3** ( $1.4 \times 10^{-6}$  M) gave the Soret band at 422.5 nm. In the benzene gel phase (**3** = 11.4 mM), it shifted to longer wavelength (428.0 nm), indicating that it assembles into a J-aggregate in the gel phase. On the other hand, an anisole solution of **3·Cu** ( $2.0 \times 10^{-6}$  M) gave the Soret band at 421.0 nm. In the anisole gel phase (2.8 mM), it shifted to shorter wavelength (402.5 nm), indicating that it assembles into an H-aggregate in the gel phase. As expected, the Soret band for the **3TEOS·Cu** + anisole gel also appeared in the shorter wavelength region (402.5 nm) than that in the anisole solution (421.0 nm). Interestingly, the Soret band after sol–gel polycondensation of **3TEOS·Cu** was observed at 406.5 nm, which is comparable to that of the gel phase. These results consistently support the view that introduction of Cu(II) facilitates the H-aggregation mode of porphyrin rings, which can be immobilized by in situ sol–gel polycondensation of the peripheral triethoxysilyl groups (Figures S5–S7).

This view was further confirmed by SEM observations. As shown in Figure 1a–c, both **3·Cu** and **3TEOS·Cu** construct the one-dimensional fibrous structure, and it is maintained even after sol–gel polycondensation. When sol–gel polycondensation of **3TEOS·Cu** was carried out in the solution phase, this characteristic superstructure could not be obtained at all. This difference indicates that the preorganization of porphyrin rings in the gel phase followed by sol–gel polycondensation is a convenient but indispensable process for immobilization of the organic superstructure. The better visual images of **3TEOS·Cu** before and after sol–gel polycondensation are obtained from TEM observation (Figure 1d–f). The fibers show the very uniform diameter of  $20 \pm 2$  nm and have the length reaching 15  $\mu\text{m}$ . As seen from Figure 1e, this fibrous structure is scarcely varied even after sol–gel polycondensation. Further magnification of one fiber shows the presence of a stripe



**Figure 1.** SEM (a–c) and TEM (d–f) images of xerogels prepared from the anisole gel of **3**·Cu (a) and **3TEOS**·Cu (b–f); (b), (d) before sol–gel polycondensation and (c), (e), and (f) after sol–gel polycondensation; [**3**·Cu] = 5.0 g dm<sup>-3</sup> (2.8 mM), [**3TEOS**·Cu] = 5.0 g dm<sup>-3</sup> (2.6 mM), and [HCl] = 0.2 equiv for **3TEOS**·Cu.



**Figure 2.** (A) Plots of  $T_{\text{gel}}$  versus concentration of **3**·Cu (a) and **3TEOS**·Cu (b) before and (c) after sol–gel polycondensation in anisole. (B) Photographs of the **3TEOS**·Cu + anisole gel (i) before sol–gel polycondensation, (ii) which collapses only by putting it on a glass plate, (iii) after sol–gel polycondensation, (iv) a glass plate and 10 yen coins are put on it.

structure (Figure 1f), indicating that it is a bundle of one-dimensional porphyrin aggregates.

This view is also supported by XRD data of the xerogel (Figures S8). The main XRD peaks for the **3**·Cu + anisole gel appeared at  $2\theta = 20.6^\circ$  ( $d = 0.43$  nm) and  $3.5^\circ$  ( $d = 2.5$  nm). As the intramolecular urea-to-urea distance in **3**·Cu is estimated to be 2.7 nm, the  $d = 2.5$  nm should stem from the H-aggregated porphyrin column. The  $d = 0.43$  nm is assigned to the intermolecular urea-to-urea distance. The similar peaks are also observed for the **3TEOS**·Cu + benzene gel before sol–gel polycondensation [at  $2\theta = 20.8^\circ$  ( $d = 0.43$  nm) and  $3.7^\circ$  ( $d = 2.4$  nm)], indicating that **3TEOS**·Cu also assembles into a one-dimensional column similar to **3**·Cu. After sol–gel polycondensation, these peaks became so broad that the  $d$  values could not be determined precisely.

It is known that the gel stability is sometimes enhanced by post-modification such as polymerization, cross-linking, etc.<sup>14</sup> To assess the influence of in situ sol–gel polycondensation on the gel stability, we measured  $T_{\text{gel}}$  values for the anisole gels of **3**·Cu and **3TEOS**·Cu (Figure 2A). The  $T_{\text{gel}}$  values for **3**·Cu and **3TEOS**·Cu increased with increasing gelator concentration, which is a general trend observed for low molecular weight gelators.<sup>15</sup> The  $T_{\text{gel}}$  values for **3**·Cu are somewhat higher than those for **3TEOS**·Cu, which is attributed to the enhanced solubility of **3TEOS**·Cu by introduction of the triethoxysilyl groups. Very interestingly, the  $T_{\text{gel}}$  values for **3TEOS**·Cu after sol–gel polycondensation are enhanced up to 160 °C and independent upon the concentration. At 160 °C, the solvent either oozed out or volatilized. The findings clearly support the view that to improve the gel stability by post-modification, the maintenance of the original molecular network constructed in the gel phase is very essential.

Surprisingly, the gelatinous mass obtained from **3TEOS**·Cu after sol–gel polycondensation showed the sufficient “elasticity”. To

assess its elasticity, the oscillatory shear measurement was carried out using a stress-controlled rheometer with a parallel plate-type geometry as a function of angular frequency from 100 to 0.1 rad s<sup>-1</sup> at 25 °C (Figure S9). The storage modulus  $G'$  for the **3TEOS**·Cu + anisole gel before sol–gel polycondensation (25 Pa) became larger by 14 times after sol–gel polycondensation (350 Pa), indicating that the sol–gel process enhances the elasticity of the **3TEOS**·Cu + anisole gel. Furthermore, the pictures in Figure 2B demonstrate the improved elasticity of the **3TEOS**·Cu + anisole gel after sol–gel polycondensation.

In conclusion, we have demonstrated that a one-dimensional molecular assembly created by an H-aggregated porphyrin·Cu(II) stack can be immobilized, without a morphological change, by sol–gel polycondensation of the peripheral triethoxysilyl groups. The resultant gel prepared according to this flowchart has gained a very high thermal stability as well as a unique mechanical strength. One may regard, therefore, that this is a unique polymeric gel obtainable by using the low molecular weight gel as a template.

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**Supporting Information Available:** Synthesis, <sup>1</sup>H NMR spectra, and gelation properties of **3**, **3**·M, **3TEOS**, and **3TEOS**·M (M = Cu and Zn); FT-IR and UV–vis absorption spectra, XRD diagrams, and oscillatory shear measurement for the **3** + benzene, the **3**·Cu + anisole, and the **3TEOS**·Cu + anisole gels before and after sol–gel polycondensation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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