Design of New Organic Gelators Stabilized by a Host−Guest Interaction

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Introduction

The molecular design of organic gels is of much concern in a past decade.[1−14] Basically, gels are classified into two categories: one is a chemical gel (polymer gel) in which the three-dimensional network structure is maintained by cross-linked covalent bonds, and the other is a physical gel (low molecular gel) in which the fibrous network structure is constructed by noncovalent, intermolecular aggregation of low molecular-weight compounds: the representative noncovalent forces useful therein are the hydrogen-bonding interaction and the van der Waals interaction. As typical examples for the hydrogen-bond-based organic gels, Hanabusa et al.[2] designed cyclohexane tricarboxyamide derivatives which feature the formation of complementary intermolecular hydrogen-bonds and result in physical gelation of certain organic solvents (e.g., aprotic or apolar solvents which facilitate the hydrogen-bond formation). On the other hand, the cholesterol-based organic gels formed on the bases of the van der Waals interaction have currently been investigated by Weiss,[1,6,7] Terech,[7] and us.[1,8−10,15] It has been shown that one can create versatile gelators of organic solvents by appropriate modification of the C-3 absolute configuration and the 3-OR substituent.[1,6−10,15] In particular, when the cholesterol−cholesterol interaction can operate cooperatively with the R−R interaction in the 3-OR substituents, the gelation ability is further intensified as a super gelator.[8]

It is known that when a host and a guest form a complex on the basis of the complementary hydrogen-bonding interactions, the hydrogen-bonded planes can stack with each other like aromatic planes.[16] It thus occurs to us that if a hydrogen-bonding receptor site is appended to the cholesterol derivative, this gelator may be converted to the van der Waals-based gelator only in the presence of the complementary guest. This specific interaction would enable us to detect the guest by the sol−gel phase-transition or to selectively capture the guest in solution through the gelation. To test this working hypothesis we synthesized **1** and **2** (Scheme 1) which possess a 2,6-(dimethylamino)pyridine moiety designed by Hamilton[17,18] for the barbital guest. One can expect that they would behave as hydrogen-bond-based gelators in the absence of the guest whereas they would behave as cholesterol-based gelators in the presence of the complementary guest. We have found that the appropriate host−guest interaction can markedly change the gelation ability.

Results and Discussion

Screening of Organic Solvents. The gelation test was carried out in about 10 organic solvents in the absence and the presence of 5 different guests **3**−**7** (Scheme 1). The results are summarized in Table 1. In the absence of the guest, compound **1**, which has a $(CH_2)_3$ group and therefore is more flexible, could gelate 6 of 10 organic solvents whereas compound **2** which has a *m*-phenyl group and therefore more rigid could gelate only 3 organic solvents. Basically, when the gelators are soluble (S in Table 1), the solvation overcomes the intermolecular hydrogen-bonding or van der Waals interactions: "S" observed for chloroform and carbon tetrachloride is attributed to this case. When the gelators are insoluble or recrystallized (I or R in Table 1), the intermolecular interactions overcome the solvation: "I" observed for methanol is due to the poor solubility of the cholesterol moieties, and "I" of **1** observed for hexane is due to the strong intermolecular hydrogen-bonding interaction in this solvent. However, the origin of subtle changes between benzene (S) and toluene (R) for **2** and between hexane (I) for **1** and hexane (S) for **2** is still difficult to explain. This problem will be discussed later on the basis of the IR spectroscopic data.

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Scheme 1

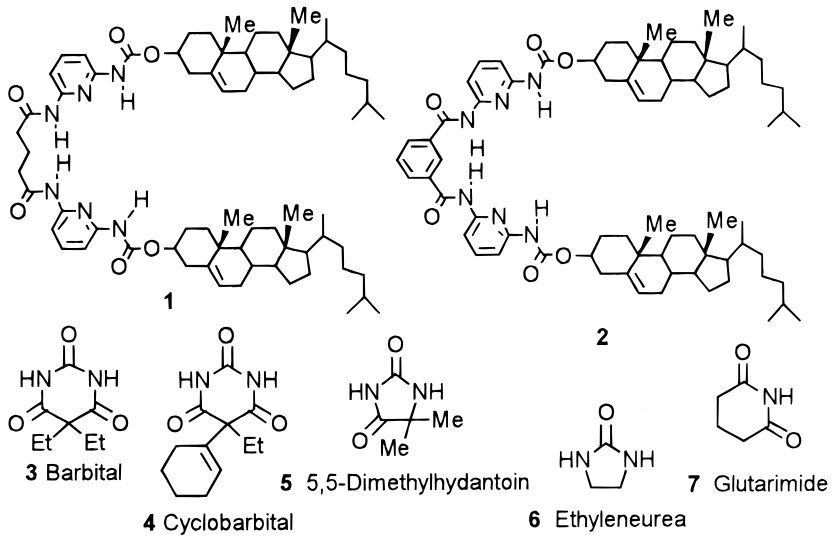
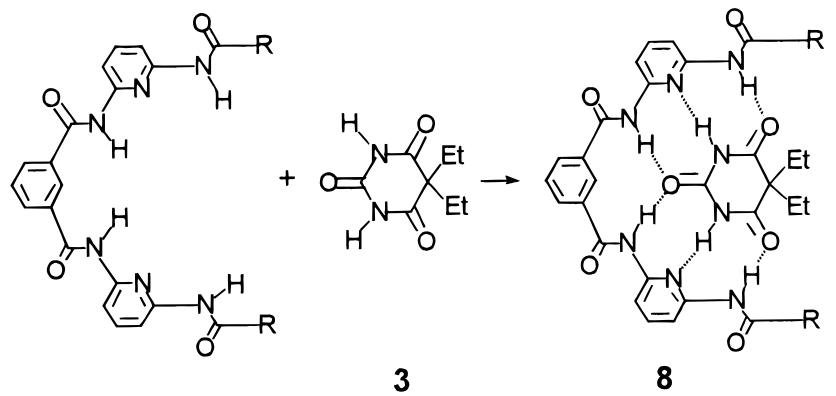


Table 1. Influence of Added Barbital and Its Analogues on the Gelation Ability[a]

		1 and guest						**2** and guest					
entry	solvent	none	**3**	**4**	**5**	**6**	**7**	none	**3**	**4**	**5**	**6**	**7**
1	benzene	G	S	S	R	G	G	S	S	S	PG	G	G
2	toluene	G	S	R	G	G	G	R	S	S	V	V	PG
3	hexane	I	I	G	I	I	I	S	G	G	I	I	I
4	cyclohexane	G	I	S	G	G	G	S	G	G	I	G	PG
5	methanol	I	I	I	I	I	I	I	I	I	I	I	I
6	*n*-butanol	G	G	G	G	G	G	G	G	G	I	I	G
7	chloroform	S	S	S	S	S	S	S	S	S	S	S	S
8	carbon tetrachloride	S	I	R	G	R	G	S	G	S	I	R	G
9	1,2-dichloroethane	G	G or R	G	G	G	G	G	I	S	G	G	I
10	1.4-dioxane	G	G	V	V	V	V	G	G	G	G	G	G

[a] [Host] = 5.00 wt%; [guest]/[host]=1/1 (mol/mol); G: gelatinize, S: soluble, R: recrystallization, I: insoluble, V: viscoelastic, PG: partially gelatinize.

Scheme 2



Influence of Added Guest Molecules. Previously, it was shown that a 2,6-diaminopyridine-type host and a barbital guest, which are poorly soluble in hexane, become very soluble in hexane when they are mixed in a 1:1 molar ratio.[19] This is due to the formation of a complementary hydrogen-bonded complex (**8** in Scheme 2) in which the NH groups unfavorable to the solubility are all shielded within the complex. The similar trend was also observed for the present system. For example, "G" for **1** in benzene and "R" for **2** in toluene become "S" in the presence of complementary guest **3** or **4**, and "I" for **1** in hexane becomes "G" in the presence of complementary guest **4**. Examination of Table 1 also reveals that extensive gelation is observed for *n*-butanol and 1,2-dichloroethane in the presence of **1** or **1**·guest complex and for 1,4-dioxane in the presence of **2** or **2**·guest complex.

We further estimated the details of the gelation properties about a **1**+**3** system in 1,2-dichloroethane (as a sample with an extensive gelation ability) and a **2**+**3** system in hexane (as a sample with a large additive effect). As shown in Figure 1, the T_{gel} values for the **1**+**3** system are always higher by 2−15 °C than those for the **1** system. Figure 2 shows the T_{gel} dependence on the **3** concentration plotted according to a molar ratio method. It is clearly seen from Figure 2 that the T_{gel} increases at

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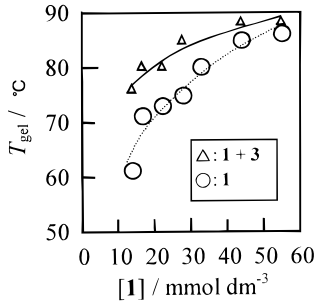

Figure 1. T_{gel} of **1** in the absence (○) and the presence (△) of **3** in 1,2-dichloroethane: the ratio of **1** and **3** is always maintained to 1:1.

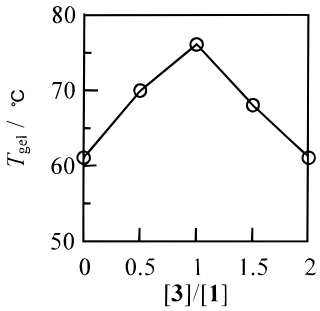

Figure 2. Influence of guest addition on T_{gel} of **1** according to a molar ratio plot: [**1**] = 1.38 × 10^{-2} mol dm^{-3} (constant), 1,2-dichloroethane.

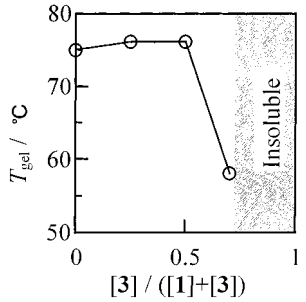

Figure 3. Influence of guest addition on T_{gel} of **1** according to a continuous variation plot: [**1**]+[**3**] = 2.76 × 10^{-2} mol dm^{-3} (constant), 1,2-dichloroethane. At [**3**]/([**1**]+[**3**]) > 0.7 the system provided the precipitate.

[**3**]/[**1**] < 1 while it decreases at [**3**]/[**1**] > 1, giving rise to a maximum at [**3**]/[**1**] = 1. Figure 3 shows the similar plot according to a continuous variation method. At [**3**]/([**1**]+[**3**]) < 0.5, the T_{gel} gradually increases, but at [**3**]/([**1**]+[**3**]) > 0.5 it drastically decreases and finally results in the precipitate. The foregoing findings consistently support the view that the most powerful gelation ability is generated from a 1:1 stoichiometric mixture of host and guest, i.e., at [**1**] = [**3**].

The plots similar to Figures 2 and 3 were also made for the **2**+**3** system in hexane (Figures 4 and 5, respectively). At a low **3** concentration region, the mixture was only soluble in hexane but above [**3**]/[**2**] = 0.6, the mixtures gelated the hexane solutions. In Figure 4, the T_{gel} drastically increases near [**3**]/[**2**] = 1.0 and then becomes nearly constant above [**3**]/[**2**] = 1.0. Figure 5 shows that a narrow plateau for the T_{gel} appears at [**3**]/([**2**]+[**3**]) = 0.5−0.7, but it decreases at [**3**]/([**2**]+[**3**]) > 0.7 (i.e., in the presence of excess **3**). These findings indicate again that the stablest gel is provided at the 1:1 host/guest.

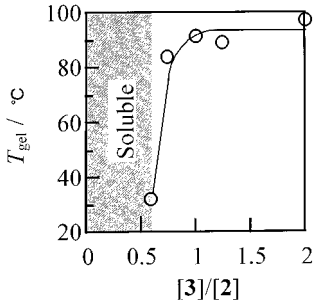

Figure 4. Influence of guest addition on T_{gel} of **2** according to a molar ration plot: [**2**] = 5.62 × 10^{-3} mol dm^{-3} (constant), hexane.

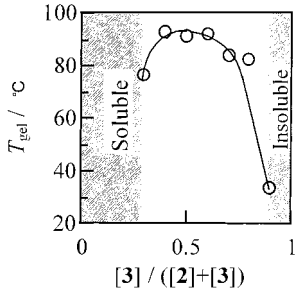

Figure 5. Influence of guest addition on T_{gel} of **2** according to a continuous variation plot: [**2**]+[**3**] = 1.13 × 10^{-2} mol dm^{-3}(constant), hexane.

SEM Pictures of the Xerogels. To obtain an insight into the influence of added guests on the gel stability, we prepared xerogels from the 1,2-dichloroethane solutions of **1** and **1·3** equimolar mixture and observed their morphology by SEM (Figure 6). It is seen from these SEM pictures that both **1** and **1·3** construct a fibrous structure with a 20−50 nm diameter. However, no significant difference was found in their visual morphology between **1** and **1·3**. It seems difficult, therefore, to obtain some useful insight into the origin of the guest addition effect from the macroscopic SEM image. Hence, we next measured the solution IR spectra (particularly, the NH vibration region) to find the possible difference from a microscopic viewpoint.

^{1}H NMR Spectral Studies. It is very difficult to obtain evidence for the formation of 1:1 complexes in the gel phase, because the concentration change affects not only the host−guest complexation but also the gel fiber structure. Hence, we measured the ^{1}H NMR spectra at 20 °C in a homogeneous $CDCl_3$ solution which can be regarded as a preliminary phase for the formation of the gel phase. The chemical shift (δ_{NH}) for the NH proton signal (8.33 ppm) in **3** moved to lower magnetic field with increasing host (**1** or **2**) concentration and was saturated at 9.85 ppm for **1** and 12.31 ppm for **2**, indicating the formation of complementary hydrogen bonds between **3** and **1** (or **2**). The larger downfield shift observed for the **2**?**3** complex implies that rigid **2** can form the stronger hydrogen bonds than flexible **3**. As expected, a sharp break point for the plots of δ_{NH} vs [**1** or **2**]/[**3**] was observed at 1.0. The results clearly establish the formation of the 1:1 complex.

We also measured the ^{1}H NMR spectra in the gel phase. However, significant spectral data were not obtained because of the serious line-broadening. Hence, we decided to collect the spectral data for the intercomplex interaction using IR spectroscopy (vide post).

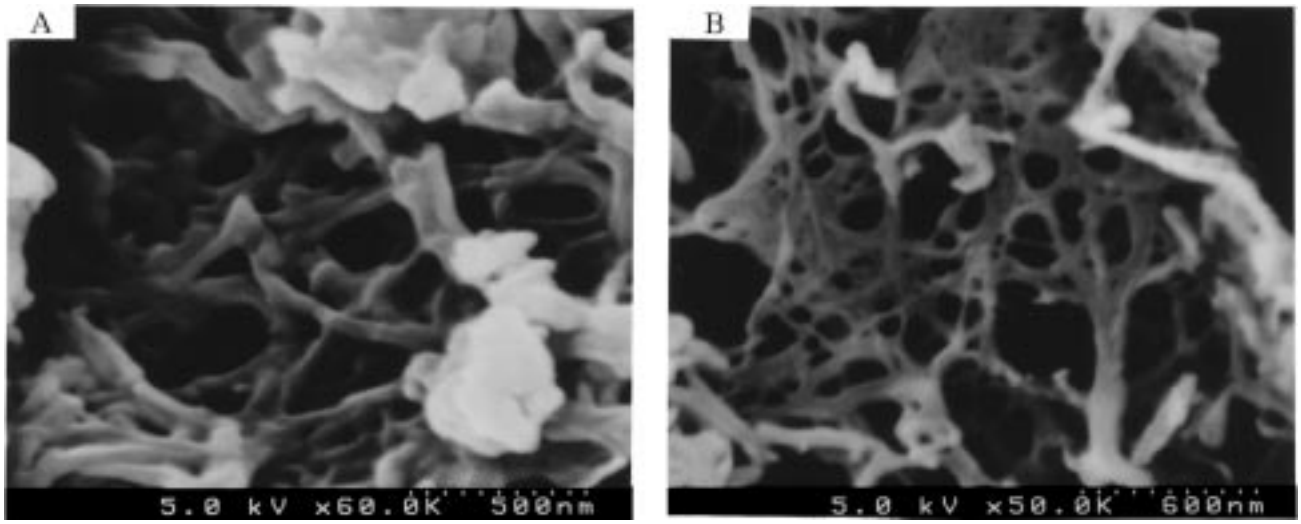

Figure 6. SEM pictures of xerogels obtained from the **1** (A) and the **1**·**3** complex (1:1 molar ratio) (B) in 1,2-dichloroethane.

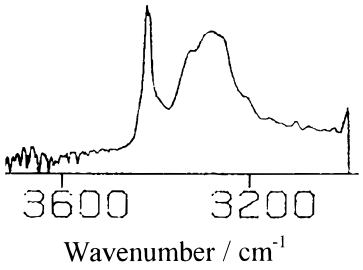

Figure 7. FT-IR spectrum of 3000 cm^{-1} region for the **1** gel (2.76×10^{-2} mol dm^{-3}) in 1,2-dichloroethane

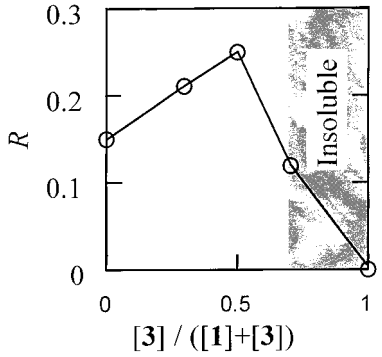

Figure 8. Plot of the peak intensity (integrated area) ratio (R) of the free NH vs the sum of free and hydrogen-bonded NH as a function of [**3**]/([**1**]+[**3**]) in 1,2-dichloroethane, where ([**1**]+[**3**]) is maintained constant (2.76×10^{-2} mol dm^{-3}). The R value at [**3**]/([**1**]+[**3**]) = 1.0 was obtained from the KBr disk of **3**.

IR Spectral Studies. The change in complementarity in the hydrogen-bonding interaction between host and guest was conveniently and sensitively monitored by FT-IR spectroscopy.[10,14] As shown in Figure 7, for example, the **1** gel prepared from 1,2-dichloroethane gave two vibration peaks for the hydrogen-bonded NH group (3300 cm^{-1}) and the free NH group (3430 cm^{-1}). These vibration peaks were not detected in **3** (KBr disk). This ratio should change with a change in the guest concentration (Figures 8 and 9), which would give some useful information on the origin of the gel stability.

As shown in Figure 9, the peak intensity ratio (R) of the free NH group to the sum of the free and hydrogen-bonded NH groups decreases with increasing guest **3** concentration up to [**3**]/([**2**]+[**3**]) = 0.3 where the system is still in the solution state. Above this concentration the free NH group is basically undetectable, indicating that the NH groups are shielded within the 1:1 host·guest complex. At [**3**]/([**2**]+[**3**]) = 0.5, one can image not only the 1:1 host·guest complex but also the 1:1 tapelike one-dimensional aggregate. As shown in Figure 4, however, the T_{gel} values are saturated at [**3**]/[**2**] >1 where the formation of the tape structure becomes difficult because of the stoichiometrical mismatch. Therefore, the intermolecular force operating for the gelation (particularly, at around [**3**]/([**2**]+[**3**]) = 0.5) cannot be the hydrogen-bonding interaction but is attributed to the van der Waals interaction. This implies that the plane composed of the complementary hydrogen-bonds can behave like an aromatic plane and stack with each other, like a cholesterol bearing a 3-OAr aromatic substituent, to form the fibrous aggregates.

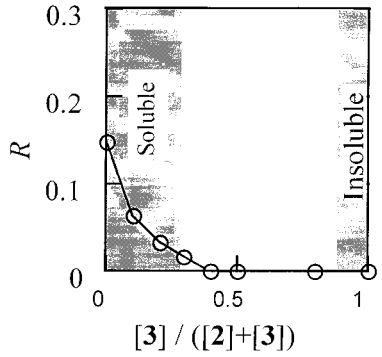

Figure 9. Plot of the peak intensity (integrated area) ratio (R) of the free NH vs the sum of free and hydrogen-bonded NH as a function of [**3**]/([**2**]+[**3**]) in 1,2-dichloroethane, where ([**2**]+[**3**]) is maintained constant (1.10×10^{-2} mol dm^{-3}). The R value at [**3**]/([**2**]+[**3**]) = 1.0 was obtained from the KBr disk of **3**.

The similar plot for the **1**+**3** system in 1,2-dichloroethane is shown in Figure 8. Surprisingly, the free NH group increases with increasing guest **3** concentration up to [**3**]/([**1**]+[**3**]) = 0.5 and then decreases above [**3**]/([**1**]+[**3**]) > 0.5. This means that **1** bearing a flexible $(CH_2)_3$ cross-link is less preorganized as a receptor than **2** bearing a rigid *m*-phenylene cross-link and tends to

aggregate more intermolecularly using the hydrogen-bonding interaction than **2** which tends to form the 1:1 host·guest complex. In Table 1, the difference related to this finding is seen between "G" for **1** and "S" for **2** in benzene and cyclohexane and between "I" for **1** and "S" for **2** in hexane. Conceivably, added **3** does not form the Hamilton-type 1:1 host·guest complex with **1** but rather bridges **1** intermolecularly to result in the hydrogen-bond-based stable gel. The plot in Figure 2 is also complementary to this proposal: that is, the gel is formed even at [**3**] = 0 mol dm^{-3}, and the T_{gel} values give a maximum at [**3**]/[**1**] = 1. One can consider, therefore, that in the **1**+**3** system the major driving-force of the gelation is the intermolecular hydrogen-bonding interaction, and the formation of the tape structure cannot be ruled out, particularly, at around [**3**]/[**1**] = 1. This would be the reason many "G" marks are observed for **1** even in the presence of noncomplementary guests **5**, **6**, and **7**. Many "G" marks observed for **2** in the presence of noncomplementary guests are also rationalized by the enhanced probability of the intermolecular hydrogen-bonding interaction.

Conclusion

The present paper demonstrated that new organic gelators can be designed by an appropriate combination of hydrogen-bonding hosts and guests. Careful examination of the gelation processes has disclosed that there exist two different gelation mechanisms: that is, the **1**+**3** system increases the free NH group and forms the gel by the intermolecular hydrogen-bonding interaction whereas the **2**+**3** system decreases the free NH group and forms the complementary host·guest complex useful for the intermolecular stacking. Although the mechanisms are different, the concept is commonly useful for selective detection and recovery of barbital through the gelation process and for molecular design of new gelators based on the host·guest binary system.

Experimental Section

Materials. Compounds **1** and **2** were synthesized in manners similar to those reported by Hamilton et al.[18]

***N*-(6-Amino-2-pyridyl)cholesteryoxyformamide (9).** To a suspension of 2,6-diaminopyridine (10.92 g, 100 mmol) and Et_3N (2.03 g, 2.80 mL, 20.1 mmol) in dry tetrahydrofurane (500 mL) was added dropwise cholesteryl chloroformate (4.50 g, 10.0 mmol) in dry tetrahydrofurane (100 mL) for 2 h at room temperature under a nitrogen atmosphere. The mixture was stirred for additional 15 h and then evaporated in vacuo. The residue was extracted with ether (500 mL), washed with water (500 mL), dried over anhydrous magnesium sulfate, and evaporated in vacuo. The residue in ether (100 mL) was acidified by treatment with 1.2 N HCl (50 mL), and then the precipitated ammonium salts were collected by filtration and washed with ether (100 mL). The ammonium salts were treated with 10% $NaHCO_3$ in $CHCl_3$. Then, the organic phase was separated, washed with water (200 mL), dried over anhydrous magnesium sulfate, and evaporated in vacuo. The residue was purified by recrystallization from MeOH to give **9** in 37% yield (1.93 g, 3.70 mmol): mp 168−169 °C; IR (KBr) ν_{max} 3567, 3478, 3434, 2950, 1740, 1717, 1622, 1539, 1464, 1300, 1211, 1046, 791 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.68 (s, 3 H, Me), 0.85−2.44 (m, 40 H), 4.10−4.50 (br-s, D_2O-exchange, 2 H, NH_2), 4.55−4.66 (m, 1 H, OCH), 5.39 (d, J = 5.1 Hz, 1 H, olefinic CH), 6.19 (d, J = 7.9 Hz, 1 H, ArH), 7.25 (d, J = 7.9 Hz, 1 H, ArH), 7.43 (t, J = 7.9 Hz, 1 H, ArH), 7.70 (br-s, D_2O-exchange, 1 H, NH). Anal. Calcd for $C_{33}H_{51}N_3O_2$: C, 75.96; H, 9.85; N, 8.05. Found: C, 75.94; H, 9.84; N, 8.03.

1,3-Bis[[(6-cholesteryloxyformamido-2-pyridyl)amino]-carbonyl]propane (1). To a solution of **9** (783 mg, 1.5 mmol) in dry toluene (60 mL) were added Et_3N (0.85 mL, 6.0 mmol) and glutaric chloride (96 μL, 0.75 mmol) at room temperature. After the mixture was refluxed for 1 h, glutaric chloride (32 μL, 0.25 mmol) was added again. After the mixture was refluxed for 2 h, the white precipitate containing the product and NEt_3·HCl was formed. This was separated by filtration, dispersed into chloroform (40 mL), washed with water (200 mL), and dried in vacuo. After the residue was dissolved in chloroform (80 mL), methanol (120 mL) was added. Afterward chloroform was removed, and pure **1** was precipitated. It was separated by filtration and evaporated in vacuo. Total yield was 35% (299 mg, 0.26 mmol): mp 259 °C (from TG-DTA); IR (KBr) ν_{max} 3429, 2950, 1740, 1701, 1590, 1505, 1456, 1381, 1296, 1200, 1157, 1082, 1011, 798, 769, 735, 623, 604 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.68 (s, 6 H, Me), 0.50−3.00 (m, 110 H), 4.50−4.80 (m, 2 H, OCH), 5.40 (d, 2 H, olefinic CH), 7.50 (br-s, 2 H, NH), 7.50−7.80 (m, 6 H, ArH), 8.04 (br-s, 2H, NH); SIMS (negative, NPOE) m/z 1137[M − H]$^-$. Anal. Calcd for $C_{71}H_{106}N_6O_6$·CH_3OH: C, 73.73; H, 9.32; N, 7.27 found: C, 73.87; H, 9.30; N, 7.25.

1,3-Bis[[(6-cholesteryloxyformamido-2-pyridyl)amino]-carbonyl]benzene (2). To a solution of **9** (1.04 g, 2.0 mmol) and Et_3N (405 mg, 0.56 mL, 4.0 mmol) in dry tetrahydrofurane (20 mL) was added portionwise isophthaloyl dichloride (244 mg, 1.2 mmol) at room temperature under nitrogen. After the mixture was stirred for 16 h, it was acidified by a treatment with 1.2 N HCl (40 mL). Then, the reaction mixture was extracted with $CHCl_3$ (200 mL), washed with water (200 mL × 10), dried over anhydrous magnesium sulfate, and evaporated in vacuo. The residue was purified by a silica gel column eluting with $CHCl_3$ and then by recrystallization from hexane/EtOH to give **2** in 49% yield (571 mg, 0.487 mmol): mp 309−310 °C; IR (KBr) ν_{max} 3436, 2950, 1742, 1682, 1590, 1497, 1455, 1381, 1300, 1196, 1078, 803, 716, 594 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.66 (s, 6 H, Me), 0.76−2.27 (m, 80 H), 4.50−4.78 (m, 2 H, OCH), 5.27 (br-s, 2 H, olefinic CH), 7.50−7.75 (m, 5 H, ArH), 7.99−8.06 (m, 4 H, ArH), 8.36 (s, 1 H, ArH), 7.40−9.50 (br-s, D_2O-exchange, 4 H, NH); SIMS (negative, NBA) m/z 1171[M − H]$^-$. Anal. Calcd for $C_{74}H_{104}N_6O_6$: C, 75.73; H, 8.93; N, 7.16. Found: C, 75.73; H, 8.93; N, 7.15.

Preparation of Organic Gels and Estimation of T_{gel}. The gelation test was carried out for 10 solvents with their 5.00 wt % solutions using a test tube-tilting method. Gelator was once dissolved in chloroform to allow the formation of hydrogen-bonding complexes with guest molecules and then dried in vacuo. The solution was sonicated or once heated until the complexes were dissolved and then cooled to 25 °C. T_{gel} was measured by the following method. A test tube containing the gel was immersed inversely in a thermostated oil bath. The temperature was raised at rate of 2 °C min^{-1}. The T_{gel} is defined as the temperature at which the gel disappears. The experimental error of T_{gel} is under ±1 °C.

Preparation of SEM Samples. Xerogels were prepared gel by a freeze-dry method.[8−10] It was coated with Pt−Pd (2−10 nm) and subjected to SEM observation. The accelerating voltage of SEM was 5 kV, and the emission current was 10 μA.

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