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Stabilization of Crown-Based Organogelators by Charge-Transfer Interaction

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Molecular self-assembly and network formation by gelators have stimulated related research studies intensively to answer the fundamental questions on the nature of this fascinating phenomenon.[1−8] Due to their potential applications to template materials synthesis, drug delivery, separations, and biomimetics, gels formed by molecular agents (gelators) were constituted an important class of functional materials. The aggregation of gelator molecules into fibrous networks is driven by multiple noncovalent interactions such as dipole−dipole, van der Waals, and H-bonding interac-

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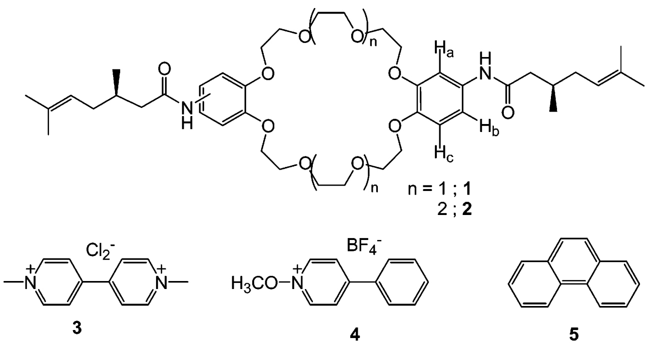
tions.[1−7] Therefore, the gelators are generally classified into two categories: H-bond based gelators[4,5] and non-H-bond based ones[1,2] Amide-, urea-, and saccharide-based compounds are examples of the former, while cholesterol derivatives fall into the latter.

Since the organogels stability is closely related to their superstructures to be formed, we have considered that it would be sensitively affected by modification of the superstructures by additives, which can interact with the gelators (e.g., by the host−guest interaction). If the additives can enhance the sol−gel phase-transition temperature ($T_{\rm gel}$), the fragility, a common drawback of organogels, may be rectified to some extent. Very recently, the validity of this idea was demonstrated in a few limited systems.[8] For example, cholesterol-based gelators having an aza-crown moiety are efficiently gelated in organic solvents mainly by the van der Waals force between cholesterol groups. We also reported an intermolecular H-bonding between crown-appended cholesterol gelators and diamine.[8a] By the way, Stoddart[9] has demonstrated that bipyridinium-based ions can form complex with larger dibenzo-crown rings by the charge-transfer interaction. Thus, one can expect that the organogelator bearing the larger dibenzo-crown moiety also can form the complex with the bipyridinium-based ions in a same manner and this result may induce the enhancement of the gelation stability of the corresponding organogels.

Since the cholesterol moiety in crown-based gelators play a critical role to stabilize in any solvents, we became interested in the cholesterol-free crown-based gelators, which has selective gelation ability in aromatic solvents because they would be useful as a separator or an extractant to purify and collec solvent or waste in a mixed medium. As a part of our continuing studies involving crown-based gelators, new crown-appended organogelators **1** and **2** were designed and synthesized by keeping this aspect in mind. In fact, the dibenzo-crown and citrolloyl moieties were introduced for the charge-transfer and hydrophobic interaction as well as the chiral molecular packing.

Compounds **1** and **2** were synthesized by treating citrolloyl chloride with diaminodibenzo-24-crown-8 and diaminodibenzo-30-crown-10, respectively, in refluxing THF for 24 h. The products were purified by an alumina column, which turned out as a mixture of cis (30%) and trans (70%) isomers (confirmed by ^{1}H NMR). The purity was ascertained by HPLC and elemental analyses.[11]



Chemical structures of **1-5**

Table 1. Gelation Abilities of 1 and 2 in the Presence of Additives (3 and 4) at 25 °C[a]

	1	1+3	1+4	2	2+3	2+4
methanol	S	S	S	S	S	S
1-butanol	S	S	S	S	S	S
THF	S	S	S	S	S	S
DMF	S	S	I	S	S	S
n-hexane	I	I	I	I	I	I
cyclohexane	I	I	I	I	I	I
benzene	G	G	G	PG	G	G
toluene	PG	G	PG	G	G	G
p-xylene	PG	G	G	PG	G	PG
m-xylene	G	G	G	G	G	G
acetic acid	S	S	S	S	S	S

[a] [gelator] = 5.0 wt %, G: stable gel; PG: partially gel, I: insoluble, S: soluble.

The gelation abilities of **1** and **2** without and with the additives were examined for 11 different solvent systems and the results are summarized in Table 1. Commonly, **1** and **2** showed two 'G' (stable gel) marks, two 'PG' (partially gel) marks, and five 'S' (soluble) marks, indicating that their gelation ability is not so high due to the relatively high solubility (mainly in polar solvents). Interestingly, **1** and **2** can gelate only aromatic solvents. With the additives, the gel stabilities were intensified especially in aromatic solvents. Interestingly, guest **3** exhibited higher gelation ability than that of **4**. As far as we are aware, this is a very rare example of the organogel being stabilized by a host−guest type interaction.[8a,10]

To explore the interaction of gelator with guest in gel state, the experiments for sol−gel phase transition were carried out. The $T_{\rm gel}$ values were measured as a function of mole ratio of guest to gelator. The curves for **1**+**3** and **2**+**3** indicate the formations of 1:2 (guest/gelator) complexes through the charge-transfer interaction (Figure 1a). Accordingly, the $T_{\rm gel}$ values beyond mole ratio = 0.5 are nearly constant, suggesting the complexes with this stoichiometry are quite stable. The maximum values of $\Delta T_{\rm gel}$ for **1** and **2** by addition of **3** were approximately 15 °C and 20 °C, respectively. This result strongly suggests that the binding ability of **2** (30-crown-10) toward **3** is higher than that of **1** (24-crown-8).

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(11) For **1**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.33 (d, $J = 12$ Hz, 2H), 6.88 (d, $J = 12$ Hz, 2H), 6.83 (d, $J = 12$ Hz, 2H), 5.12 (m, 2H), 4.71 (b, 2H), 4.15 (d, $J = 3$ Hz, 8H), 3.89 (m, 8H), 3.81 (m, 8H), 2.35 (m, 2H), 2.08 (m, 8H), 1.94 (d, $J = 9$ Hz, 4H), 1.64 (m, 12H), 1.02 (d, $J = 8$ Hz, 6H); IR (KBr, cm^{-1}): 3282.8, 3026.3, 2918.3, 2866.2, 2364.7, 1649.1, 1604.7, 1494.8, 1454.3, 1375.2, 1226.7, 1134.1, 1080.1, 1030.0. Anal. Calcd for $C_{44}H_{66}N_2O_{10}$: C, 67.49; H, 8.50; N, 3.58; Found: C, 66.52; H, 8.30; N, 3.50. For **2**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51 (d, $J = 12$ Hz, 2H), 6.88 (d, $J = 9$ Hz, 2H), 6.79 (d, $J = 9$ Hz, 2H), 5.11 (m, 2H), 4.41 (b, 2H), 4.11 (d, $J = 3$ Hz, 8H), 3.85 (t, $J = 3$ Hz, 8H), 3.73 (t, $J = 3$ Hz, 8H), 3.68 (t, $J = 3$ Hz, 8H), 2.35 (m, 2H), 2.12 (m, 8H), 1.94 (d, $J = 9$ Hz, 4H), 1.64 (m, 12H), 1.00 (d, $J = 8$ Hz, 6H); IR (KBr, cm^{-1}): 3280.9, 2922.1, 2864.1, 2358.9, 1649.1, 1604.7, 1514.1, 1452.4, 1377.2, 1228.7, 1138.0, 1041.6. Anal. Calcd for $C_{48}H_{74}N_2O_{12}$: C, 66.18; H, 8.56; N, 3.22. Found: C, 67.05; H, 8.52; N, 3.15.

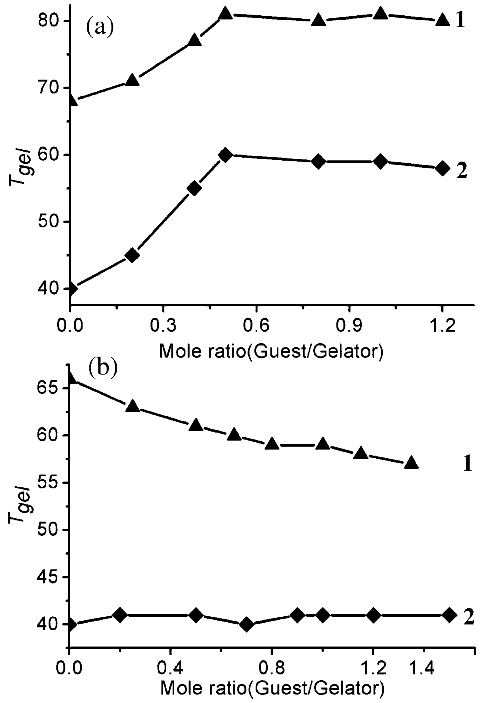

Figure 1. The T_{gel} of **1** and **2** in the presence of (a) **3** and (b) **4**.

By addition of **4**, however, no such significant change of T_{gel} values between **1** and **2** was observed (Figure 1b). This also supports the belief that the bridging effect of **3** could be an additional driving force for stabilization of the organogel.

^{1}H NMR titrations were carried out to explore the interactions of **2** with guests in the sol state because of broadening of the corresponding resonance lines in the gel state (Figure 2). The bipyridinium of guest **3** forms a 2:1 (host:guest) complex with host **2** by charge-transfer interaction (Figure 2a,b). Guest **4** forms also a 2:1 (host:guest) complex with host **2** (Figure 2c). But the binding force is different. For example, the pyridinium part has interaction with host **2** by charge transfer. Otherwise, the phenyl part forms $\pi-\pi$ interaction with the aromatic groups of host **2**. Once again, this result coincides with the stoichiometry obtained from the phase transition temperature (T_{gel}) induced by addition of **3**. The larger shifts were observed by **3** than those of **4** due to the higher binding strength of **3** with **2**. No remarkable interaction was observed by **5** (Figure 2d). Furthermore, according to curve-fitting results,[12] as we expected, the K values (overall binding constants) for **2**,**3** are approximately ($K = 420 \pm 50$) 2 times larger than that of **2**−**4** ($K = 150 \pm 50$).

According to FT-IR experiment, the amide carbonyl band of the gels **1** and **2** formed in toluene appeared at 1637 cm^{-1} due to the strong intermolecular hydrogen-bonding interaction between amide carbonyl groups, which is almost identical to that of the solid-state one (1640 cm^{-1}). The same band for the gelators **1** and **2** dissolved in methanol, however, appeared at 1658 cm^{-1} due to the weak H-bonding networks in solution.

The SEM pictures of the xerogels prepared from the frozen samples of the *p*-xylene gels were obtained (Figure 3). The xerogels **1** and **2** without guest show well-developed network structures of the fibrils with 50−100 nm diameters and several hundred μm lengths, respectively. After addition of guest **3** or **4**, however, no significant difference was found in their visual morphology of **1** or **2**. Hence, the influence induced by **3** or **4** is not so large as to change the superstructure.

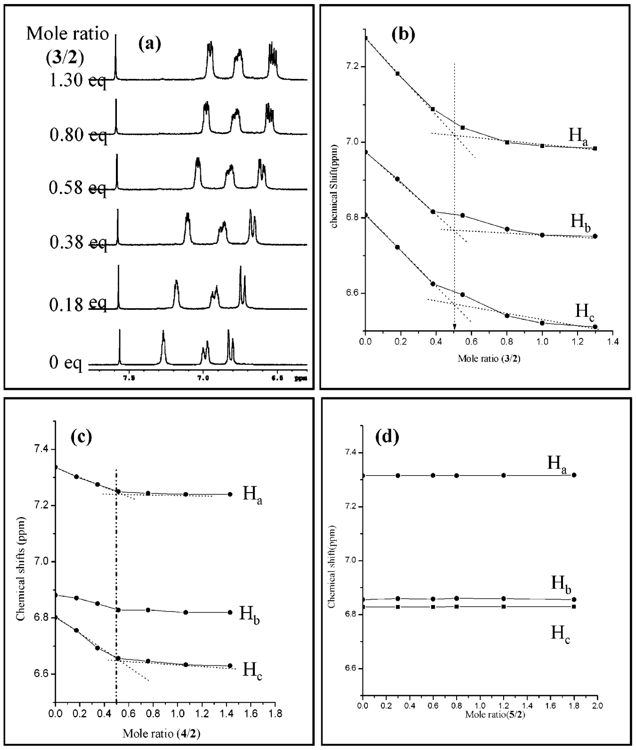

Figure 2. (a) Aromatic region of ^{1}H NMR spectra of **2** by stepwise addition of **3** (0−1.3 equiv) in $CDCl_3$−CD_3CN (1:2 v/v). The signal labeled with an asterisk presents $CHCl_3$. The ^{1}H NMR titration curves for binding of **2** with (b) **3**, (c) **4**, and (d) **5**. For labeling of protons in **2**, see chemical structure **2**.

Additionally, by the X-ray diffraction pattern we obtained mechanistic information[13] on the molecular packing of the gelators in a neat gel. The xerogel **2** obtained from benzene by the freezing method resulted in the spongelike aggregate, but not the typical crystal. The small-angle diffraction patterns of **2** showed at least four ordered reflection peaks with a long period of 2.70 nm, which is smaller than the extended length of one molecule **2** (3.5 nm the CPK molecular modeling). On the other hand, the **2**+**3** complex gave a long period of 4.83 nm, which is larger than the length of one molecule **2**. These results strongly suggest that the **2**+**3** complex forms a bilayered structure by the charge-transfer interaction.

In summary, we demonstrate the remarkable stabilization of the crown-based organogels **1** or **2** in the presence of bipyridinium-based ion **3** as a guest. On the basis of the sol−gel phase transition, NMR, IR, and XRD results, the host−guest type interaction stabilizes the proposed organogels by synergic effect of H-bonding, hydrophobic, and charge-

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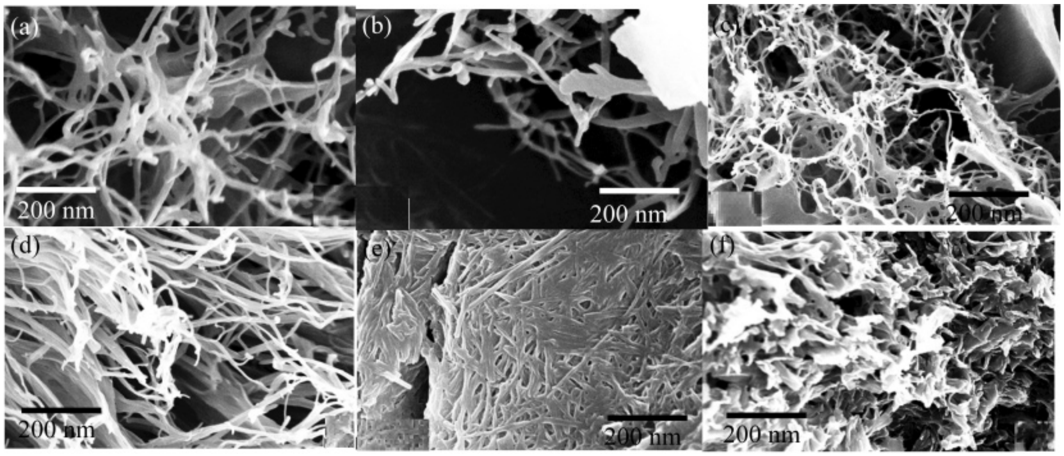

Figure 3. SEM images of (a) **1**, (b) **1**+**3**, (c) **1**+**4**, (d) **2**, (e) **2**+**3**, and (f) **2**+**4** in toluene.

transfer interactions. Furthermore, the proposed organogelators can gelate the aromatic solvents selectively. To the best of our knowledge, this is a rare example exhibiting the large gelation ability controlled by the host−guest type molecular recognition. This finding suggests that the phase transition of the gels induced by the host−guest interaction could be applicable to drug delivery systems, collection of waste materials, pollutants, recovery of precious bioactive compounds, etc.

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