

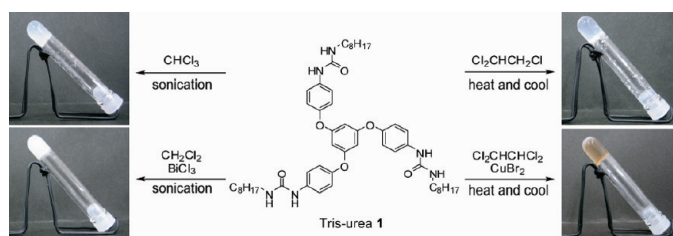
Chloroalkane Gel Formations by Tris-urea Low Molecular Weight Gelator under Various Conditions

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C_3 -symmetrical tris-urea low molecular weight gelator **1** was synthesized in three steps from phloroglucin. The gelation ability of **1** in four chloroalkanes, i.e., CH_2Cl_2 , $CHCl_3$, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane, was investigated under various conditions. Thermal treatment was effective in gelating 1,1,2-trichloroethane. In the presence of equimolar **1** and $CuBr_2$, 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane formed gels. Mixtures of **1** and $CHCl_3$ or 1,1,2,2-tetrachloroethane gave gels after ultrasound irradiation. CH_2Cl_2 changed into a gel in the presence of equimolar **1** and $BiCl_3$ after sonication. Spherical particles with rough surfaces were found by SEM observation of $CHCl_3$ gel prepared from ultrasound irradiation of **1** and $Y(NO_3)_3$.

Introduction

Regulated assembly of a low molecular weight compound builds up a supramolecular gel. Many low molecular weight

gelators (LMWGs) have been reported.^{1–9} The ability to use several stimuli for the sol–gel phase transition based on the rational design of LMWGs is a remarkable advantage of supramolecular gels.^{10–14} These reversible conversions of rheology have potential as future materials with wide application in

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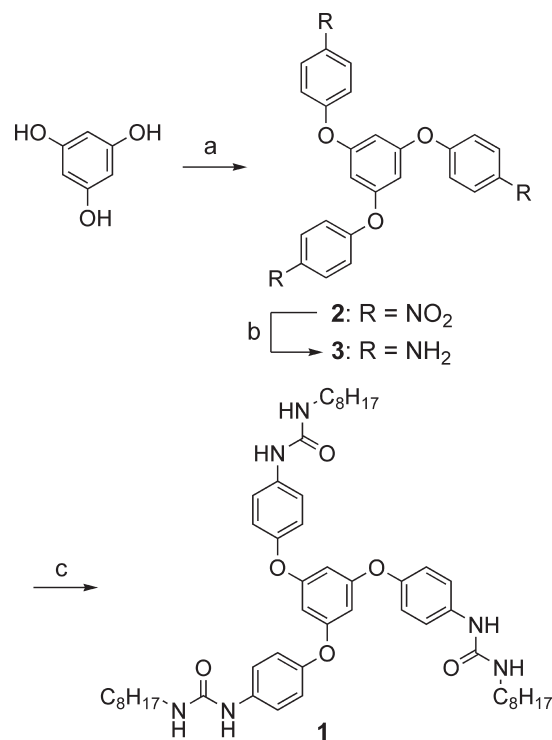
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material separations, sensors, drug delivery systems, cosmetics, etc. One general method for supramolecular gel formation is the thermal dissolution of LMWG into a solvent and cooling the mixture. Ultrasound irradiation-induced supramolecular gel formations have also been reported lately.¹⁵ Gel formation by the cooperative work of two chemicals, i.e., two-component gels, is another topic of LMWG research.^{16–18} Ideas of metal–ligand coordination or host–guest chemistry were adopted in these two-component gels. Generally, an LMWG gels solvents under one specific condition. Multifunctional LMWGs, for instance, an LMWG gelled by different stimuli depending on the solvents, are hardly known. Recently, we have developed tris-urea LMWGs that enable reversible sol–gel phase transitions in response to chemical stimuli.¹⁹ Our tris-urea gelator has a highly symmetrical and readily divisible structure; therefore, it is easy to synthesize various derivatives using similar procedures.²⁰ In the course of this study, we designed C_3 -symmetrical tris-urea **1** as a derivative. Synthesized tris-urea **1** acted as a talented LMWG beyond expectations. In this paper, we would like to report that a tris-urea LMWG **1** gels four chloroalkanes in different ways, i.e., by thermal dissolution and cooling or ultrasound irradiation in the presence or absence of metal salt.

Results and Discussion

Tris-urea **1** was synthesized in three steps from phloroglucin (Scheme 1). Nucleophilic aromatic substitution of

SCHEME 1. Synthesis of Tris-urea 1



- a) 4-fluoronitrobenzene, K₂CO₃, DMF, 67%.
 b) H₂, 10% palladium on carbon, EtOAc, 95%.
 c) octylisocyanate, 1,2-dichloroethane, 86%.

phloroglucin and 4-fluoronitrobenzene gave tris-nitro compound (**2**). Nitro groups of **2** were reduced to amino groups by hydrogen in the presence of palladium on carbon. Tris-amine **3** was reacted with an excess amount of octylisocyanate, and the desired tris-urea **1** was obtained as a white solid.

Gelation experiments using **1** were accomplished in four chloroalkanes: CH₂Cl₂, CHCl₃, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane. Gel formation was evaluated by the inverted tube test. A mixture remaining at the top of an inverted test tube was defined as a gel. The term “partial gel” was used when some part of a mixture remained at the top of the inverted test tube and some flowed down the tube slowly or quickly.

Thermal treatment and cooling of a mixture of **1** and chloroalkane solvents were performed (Table 1, Figure 1). Mixtures of tris-urea **1** and CH₂Cl₂ or CHCl₃ in plugged test tubes were heated up to 70 °C; however, insoluble suspensions remained unchanged. Homogeneous solutions were obtained by heating mixtures of **1** and 1,1,2-trichloroethane or 1,1,2,2-tetrachloroethane in plugged test tubes to 110 °C. A 1,1,2-trichloroethane solution of **1** was converted into a white semitransparent gel by cooling, and the critical gelation concentration (CGC) was determined to be 10 mM. A 1,1,2,2-tetrachloroethane solution of **1** gave only a partial gel even at higher concentrations (up to 25 mM). A scanning electron microscope (SEM) image of a xerogel prepared by freeze-drying a 1,1,2-trichloroethane gel with **1** showed intertwining nanofibers (Figure 2a). Freeze-drying a sample of the gelous mixture of **1** and 1,1,2,2-tetrachloroethane indicated micrometer-sized fibrous aggregates (Figure 2b).

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TABLE 1. Gelation Properties of Tris-urea 1 by Thermal Treatment and Cooling^a

additive ^b	CH ₂ Cl ₂	CHCl ₃	1,1,2-trichloroethane	1,1,2,2-tetrachloroethane
none	I	I	G (10)	PG
CuBr ₂	I	I	G (5)	G (5)

^aTris-urea **1** = up to 25 mM. Abbreviations: G, gel; PG, partial gel; I, insoluble suspension; values in parentheses refer to critical gelation concentration (mM). ^bEquimolar amount for tris-urea **1**.

It is known that some low molecular weight compounds form supramolecular gels by adding metal salt,¹⁸ and the effect of metal salts on the gelation of **1** and chloroalkane solvents was investigated (Table 1, Figure 3). The addition of CuBr₂ was effective for the gelation of **1** in 1,1,2-trichloroethane. A mixture of **1** and CuBr₂ in 1,1,2-trichloroethane gave a pale brown semitransparent gel after thermal dissolution and cooling. The CGC of **1** with 1,1,2-trichloroethane was reduced from 10 to 5 mM by adding 1 equiv of CuBr₂. A SEM image of the 1,1,2-trichloroethane gel with **1** and CuBr₂ showed spherical particles of 1–2 μm diameter (Figure 2c). These results indicated that gelation proceeds with different mechanisms in the presence or absence of CuBr₂. Similar phenomena were also observed in the gelation of **1** and metal salts with ultrasound irradiation (vide infra). A dramatic alteration in the gelation ability of **1** in 1,1,2,2-tetrachloroethane was observed by addition of CuBr₂. An equimolar mixture of **1** and CuBr₂ in 1,1,2,2-tetrachloroethane afforded a pale brown semitransparent gel, and the CGC was 5 mM; however, **1** itself only gave a partial gel in 1,1,2,2-tetrachloroethane without the metal salt. A SEM image of 1,1,2,2-tetrachloroethane gel with **1** and CuBr₂ showed fibrous aggregates that were much thinner than those prepared from **1** without the metal salt (Figure 2d). Tris-urea **1** and CH₂Cl₂ or CHCl₃ did not form gels by adding CuBr₂ or other metal salts (such as MgCl₂, LaCl₃, or BiCl₃) in thermal treatment and cooling.

Gelation of some kinds of LMWGs has been induced by ultrasound irradiation.^{15,19,20} Sonication-induced gelation of chloroalkanes by tris-urea **1** is shown in Table 2 and Figure 4. A mixture of **1** and CHCl₃ formed a semitransparent gel with ultrasound irradiation for several hours, and the CGC was determined as 15 mM. 1,1,2,2-Tetrachloroethane gave a gel with high transparency in the presence of 5 mM of **1** after sonication. Mixtures of **1** and either CH₂Cl₂ or 1,1,2-trichloroethane afforded heterogeneous suspensions even after ultrasound irradiation; however, a mixture of **1** and 1,1,2-trichloroethane formed a gel by thermal dissolution and cooling. The gelation property of tris-urea **1** was considerably altered according to the gel-forming methods. Other solvents such as methanol, acetone, and ethyl acetate were also gelled by sonication in the presence of appropriate amounts of **1**. CGCs of **1** were determined as 5 mM for methanol, 10 mM for acetone, and 15 mM for ethyl acetate (Figure S1, Supporting Information). It seems that ultrasound irradiation is generally a better procedure than thermal treatment for gelation using tris-urea **1**. A xerogel of the CHCl₃ gel with **1** showed micrometer-sized fibrous structures on SEM observation (Figure 5a). Thermal treatment of a mixture of 1,1,2,2-tetrachloroethane and **1** gave a partial gel that was constructed from micrometer-

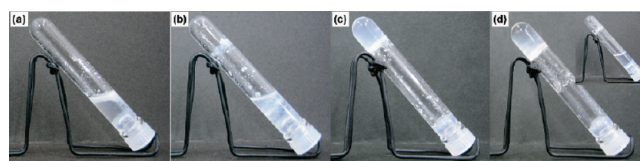


FIGURE 1. Photographs of mixtures of chloroalkanes and **1** after thermal treatment and cooling: (a) CH₂Cl₂, (b) CHCl₃, (c) 1,1,2-trichloroethane, (d) 1,1,2,2-tetrachloroethane.

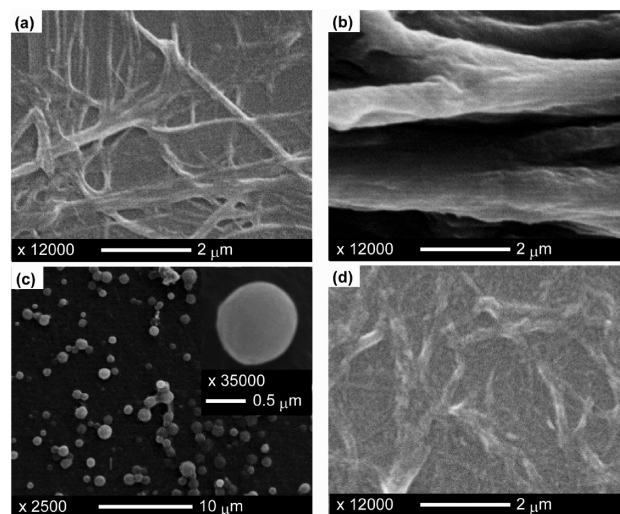


FIGURE 2. SEM images of gels (xerogels) prepared by thermal treatment and cooling: (a) 1,1,2-trichloroethane gel of **1**, (b) 1,1,2,2-tetrachloroethane partial gel of **1**, (c) 1,1,2-trichloroethane gel of **1** and CuBr₂, (d) 1,1,2,2-tetrachloroethane gel of **1** and CuBr₂.

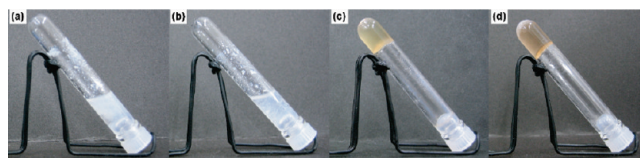


FIGURE 3. Photographs of mixtures of chloroalkanes, **1**, and CuBr₂ after thermal treatment and cooling: (a) CH₂Cl₂, (b) CHCl₃, (c) 1,1,2-trichloroethane, (d) 1,1,2,2-tetrachloroethane.

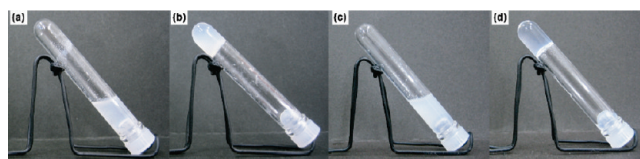


FIGURE 4. Photographs of mixtures of chloroalkanes and **1** after ultrasound irradiation: (a) CH₂Cl₂, (b) CHCl₃, (c) 1,1,2-trichloroethane, (d) 1,1,2,2-tetrachloroethane.

sized fibrous aggregates (Figure 2b). On the other hand, nano-ordered thin fibers were observed by SEM measurement of the xerogel prepared by freeze-drying the 1,1,2,2-tetrachloroethane gel with **1** (Figure 5b). SEM images of the methanol, acetone, and ethyl acetate gels with **1** showed intertwined nanofibers on SEM observation.

Gelation experiments were performed using chloroalkanes in the presence of **1** and metal salts with ultrasound irradiation (Table 2). A mixture of **1** and CuBr₂ gelled CHCl₃

TABLE 2. Gelation Properties of Tris-urea 1 by Ultrasound Irradiation^a

additive ^b	CH ₂ Cl ₂	CHCl ₃	1,1,2-trichloroethane	1,1,2,2-tetrachloroethane
none	I	G (15)	I	G (5)
CuBr ₂	I	G (5)	I	G (5)
BiCl ₃	G (15)	PG	I	G (20)
Y(NO ₃) ₃	PG	G (10)	I	I

^aTris-urea **1** = up to 25 mM. Abbreviations: G, gel; PG, partial gel; I, insoluble suspension. Values in parentheses refer to critical gelation concentration (mM). ^bEquimolar amount for tris-urea **1**.

with sonication; however, this combination did not give a gel with thermal treatment. The CGC for CHCl₃ was reduced from 15 to 5 mM by addition of CuBr₂. Tris-urea **1** and CuBr₂ also gelled 1,1,2,2-tetrachloroethane, although the CGC was unchanged. The 1,1,2,2-tetrachloroethane gel with **1** and CuBr₂ prepared by ultrasound irradiation was freeze-dried for SEM observation. The xerogel showed intertwining nanofibers that were somewhat different from the SEM image of the same component's gel prepared by thermal dissolution and cooling (Figures 2d and 5c). The difference in the two 1,1,2,2-tetrachloroethane gels with **1** and CuBr₂ also appeared in their mechanical stabilities. The gel–sol transition temperature (T_{gel}) measured by the ball-dropping method²¹ was used to estimate the mechanical stabilities of gels prepared in different ways. The T_{gel} of the gel (10 mM each of **1** and CuBr₂) prepared by thermal dissolution and cooling was 69 °C, while the T_{gel} of the gel (10 mM each of **1** and CuBr₂) prepared by ultrasound irradiation was 57 °C. The thermal dissolution and cooling method seemed to give more stable gels than those prepared using ultrasound irradiation. Mixtures of **1** and CuBr₂ in CH₂Cl₂ or 1,1,2-trichloroethane did not form gel with sonication. The addition of BiCl₃ was effective for gelation of a mixture of **1** and CH₂Cl₂ (Figure 6). Ultrasound irradiation of a mixture of **1** and BiCl₃ (each 15 mM) in CH₂Cl₂ gave an opaque gel. Adding an equimolar amount of BiCl₃ was essential to form the CH₂Cl₂ gel with **1**: a shortage or excess of BiCl₃ with **1** no longer formed gels but gave suspensions. An equimolar mixture of **1** and BiCl₃ in CHCl₃ afforded only a partial gel even at higher concentrations (< 25 mM). 1,1,2-Trichloroethane did not give a gel by mixing with **1** and BiCl₃. A mixture of **1** and BiCl₃ in 1,1,2,2-tetrachloroethane formed a gel by sonication; however, the CGC (20 mM) was higher than the CGC with tris-urea **1** alone. CH₂Cl₂ formed a partial gel by mixing with equimolar **1** and Y(NO₃)₃ after sonication. Tris-urea **1** and Y(NO₃)₃ (each 10 mM) in CHCl₃ formed a semitransparent gel after ultrasound irradiation. An SEM image of the gel showed 1 to 5 μm-sized spherical particles with rough surfaces (Figure 5d). A precipitable suspension of Y(NO₃)₃ in CHCl₃ also showed micrometer-sized spherical particles, although their sizes were smaller and their surfaces were smoother than the particles of the gel with **1** and Y(NO₃)₃ (Figure S2, Supporting Information). The explanation seems to be that micrometer-sized particles were constructed from Y(NO₃)₃ in CHCl₃ and their surfaces were covered with self-assembled tris-urea **1**. Both 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane became suspensions by mixing with **1** and Y(NO₃)₃ even after sonication.

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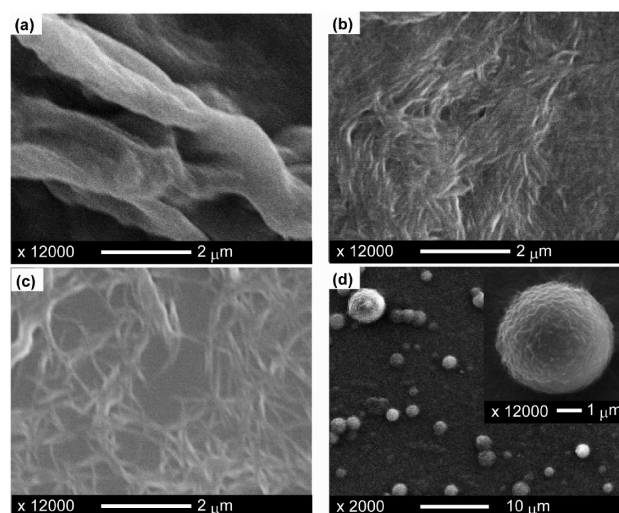


FIGURE 5. SEM images of gels (xerogels) prepared by ultrasound irradiation: (a) CHCl₃ gel of **1**, (b) 1,1,2,2-tetrachloroethane gel of **1**, (c) 1,1,2,2-tetrachloroethane gel of **1** and CuBr₂, (d) CHCl₃ gel of **1** and Y(NO₃)₃.

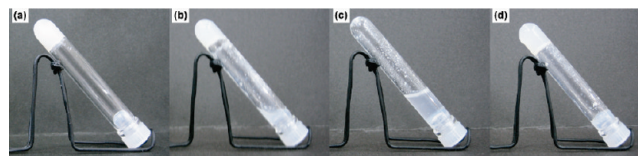


FIGURE 6. Photographs of mixtures of chloroalkanes, **1**, and BiCl₃ after ultrasound irradiation: (a) CH₂Cl₂, (b) CHCl₃, (c) 1,1,2-trichloroethane, (d) 1,1,2,2-tetrachloroethane.

Conclusion

We have synthesized tris-urea LMWG **1** from phloroglucin. Tris-urea **1** was able to gelate four chloroalkanes using several procedures. The process of thermal treatment and cooling was effective for forming 1,1,2-trichloroethane gel with **1**. 1,1,2,2-Tetrachloroethane changed into a gel in the presence of both **1** and CuBr₂ by thermal treatment and cooling. Ultrasound irradiation induced CHCl₃ gel formation with **1**. Equimolar amounts of **1** and BiCl₃ could form CH₂Cl₂ gel after ultrasound irradiation. Most gels showed fibrous structures distinctive of gels on SEM observation; however, some gels (e.g., the CHCl₃ gel with **1** and Y(NO₃)₃) exhibited spherical particles as constituents. We have demonstrated that tris-urea **1** can act as a talented LMWG.

Experimental Section

Synthesis of 1,3,5-Tris(4-nitrophenoxy)benzene (2). To a mixture of phloroglucin (3.00 g, 23.8 mmol), K₂CO₃ (65.8 g, 476 mmol), and DMF (240 mL) was added 4-fluoronitrobenzene (10.0 mL, 94.0 mmol). The reaction mixture was stirred at 100 °C for 2 days. K₂CO₃ was removed by filtration, and then the filtrate was concentrated under reduced pressure. The residue was dissolved in CH₂Cl₂ and washed with water and brine successively. The organic layer was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO₂, *n*-hexane/EtOAc 40/1). The desired product (**2**) was obtained as a yellow solid (7.76 g, 67%); mp 195–196 °C;

^1H NMR (600 MHz, CDCl_3) δ 6.65 (s, 3H), 7.13 (d, $J = 8.9$ Hz, 6H), 8.26 (d, $J = 8.9$ Hz, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 108.0, 118.6, 126.5, 144.0, 158.2, 161.7; HRMS (ESI, $\text{M} + \text{Na}^+$) calcd for $\text{C}_{24}\text{H}_{15}\text{N}_3\text{NaO}_9$ 512.0706, found 512.0698.

Synthesis of 1,3,5-Tris(4-aminophenoxy)benzene (3). A mixture of **2** (7.00 g, 14.3 mmol), 10% palladium on carbon (700 mg, 10 wt %), and EtOAc (140 mL) was stirred at ambient temperature under a hydrogen atmosphere for 16 h. The mixture was filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography (SiO_2 , EtOAc). The desired product (**3**) was obtained as a brown solid (5.43 g, 95%); mp 142–145 °C; ^1H NMR (600 MHz, CDCl_3) δ 6.15 (s, 3H), 6.64 (d, $J = 8.2$ Hz, 6H), 6.84 (d, $J = 8.2$ Hz, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 100.3, 116.5, 121.5, 143.2, 148.1, 161.1; HRMS (ESI, $\text{M} + \text{Na}^+$) calcd for $\text{C}_{24}\text{H}_{21}\text{N}_3\text{NaO}_3$ 422.1481, found 422.1498.

Synthesis of 1,3,5-Tris(4-octylureidophenoxy)benzene (1). To a mixture of **3** (1.00 g, 2.50 mmol) and $\text{ClCH}_2\text{CH}_2\text{Cl}$ (50 mL) was added octyl isocyanate (2.00 mL, 11.3 mmol). The reaction mixture was refluxed for 1 day. The mixture was cooled to ambient temperature, and the solid obtained was collected by filtration. Further washing of the solid with *n*-hexane and CH_2Cl_2 gave pure **1** as a white solid (1.87 g, 86%); mp 165–166 °C; ^1H NMR (600 MHz, CDCl_3) δ 0.84 (t, $J = 6.9$ Hz, 9H), 1.26–1.41 (m, 36H), 3.05 (dt, $J = 2.5, 6.5$ Hz, 6H), 6.06–6.08 (m, 6H), 6.94 (d, $J = 8.9$ Hz, 6H), 7.37 (d, $J = 8.9$ Hz, 6H), 8.42 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 13.9, 22.1, 26.4,

28.7, 28.8, 28.8, 29.7, 31.2, 99.9, 119.0, 120.2, 137.3, 148.6, 155.2, 160.1; HRMS (ESI, $\text{M} + \text{Na}^+$) calcd for $\text{C}_{51}\text{H}_{72}\text{N}_6\text{NaO}_6$ 887.5411, found 887.5382.

Gelation Experiments. A weighed amount of tris-urea **1** (and metal salt) was placed in test tube, and 0.3 mL of solvent was added. For the thermal treatment, mixtures of CH_2Cl_2 or CHCl_3 in closed test tubes were heated at 70 °C over 2 h, and mixtures of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane in closed test tubes were heated at 110 °C until dissolved. All heated mixtures were gradually cooled to room temperature. For ultrasound irradiation, mixtures in closed test tubes were placed in an ultrasonic cleaner and sonicated for 5 h. The bath temperature of the cleaner was maintained at approximately 25 °C. Gels were evaluated at the point of formation, and partial gels and suspensions were judged after being kept undisturbed at room temperature for 1 day.

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Supporting Information Available: Figures S1 and S2 and ^1H and ^{13}C NMR spectra of synthesized compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.