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Construction of Two- or Three-Component Low Molecular Weight Gel Systems

Masamichi Yamanaka* and Ryohei Aoyama

Department of Chemistry, Faculty of Science, Shizuoka University, 836 Ohya, Suruga-ku, Shizuoka 422-8529

Received May 7, 2010; E-mail: smyaman@ipc.shizuoka.ac.jp

Pyridyl group-bound tris-urea **2**, whose structure is similar to the tris-urea low molecular weight gelator (LMWG) **1**, was synthesized. Addition of a trace amount of **2** and $Pd(OAc)_2$ to **1** resulted in a reduction in the critical gelation concentration (CGC) in acetone. Metal–ligand interaction between $Pd(OAc)_2$ and the pyridyl group of **2** assist the gelation. Assistance by intermolecular hydrogen bonding was also effective for gelation of acetone. An acetone gel of **1** was formed at half the value of the CGC of **1** alone by adding a trace amount of **2** and isophthalic acid. Scanning electron microscopy (SEM) measurements of these aggregates showed structural alterations caused by the additive. A mixture of **1** and a trace amount of **2** in EtOAc gave a gel. Addition of **2** was essential to form the gel, because **1** alone did not gel EtOAc. SEM measurements indicated that **2** produced extension of the fibrous aggregates.

Directional regulated self-assembly of preorganized small molecules enables construction of supramolecular polymers.[1] One of the attractive manifestations of these supramolecular polymers is the supramolecular gel.[2] Principally, a fibrous aggregate composed of a one-dimensional assembly of small molecules, called a low molecular weight gelator (LMWG), is the unit constituent. Several types of single-component LMWGs have been reported, their gelations being achieved through a variety of interactions, such as hydrogen bonding,[3] π–π,[4] dipole–dipole,[5] etc. Some of them showed a gel–sol phase transition responsive to photo-,[6] chemo-,[7] or other[8] stimuli in addition to the thermo-responsiveness that is potentially provided in supramolecular gels. Supramolecular gel formation as a result of multicomponent assembly of small molecules has also been achieved.[9] Formation of a fibrous aggregate via complementary hydrogen bonding pairs,[10] metal–ligand coordination bond,[11] and other interactions[12] has been reported. As a pioneering work, Hanabusa et al., reported a two-component gelling system using an equimolar mixture of 5-alkyl-2,4,6-triaminopyrimidine and 5,5-dialkylbarbituric acid.[10a] Beck and Rowan developed a metallo-supramolecular gelling system that was based on a metal–ligand interaction between a bis-ligand monomer and a combination of metal ions (transition-metal ion and lanthanoid metal ion).[11b] Multicomponent supramolecular gels usually mix each component in the ratio of appropriate whole numbers. In contrast, a supramolecular gel composed of a main ingredient and a small quantity of accessory ingredient is hardly known. A supramolecular gel formed from a small quantity of additive has the potential to be a smart material, because its rheology enables it to be converted by a trace amount of chemical. As a unique conception, Lee and co-worker reported that addition of a small quantity of rod–coil–rod molecule to a cylindrical object that was composed of a coil–rod–coil molecule induced gelation.[13] Partial introduction of ligand or hydrogen bonding acceptor to a fibrous aggregate of LMWG would alter the gelation ability by adding a multidentate metal ion or hydrogen bonding donor, depending on the type of interaction between the fibrous aggregates (Figure 1). In this paper, we report multicomponent supramolecular gel formation involving increase in gelation ability by addition of trace amounts of molecule(s). Previously, we found that C_3-symmetric tris-urea molecule **1** and derivatives act as LMWGs for a variety of organic solvents.[14] For the purpose of making part of a multicomponent supramolecular gel, we designed tris-urea **2** with 4-pyridyl groups as the ligand or hydrogen-bonding unit (Figure 2). The gelation ability of tris-urea **1** was dramatically improved by the addition of a trace amount of **2** with or without metal salt or dicarboxylic acid.

Results and Discussion

Synthesis of Pyridyl-Substituted Tris-Urea 2. Tris-urea **2** was synthesized by a condensation reaction of triamine **3** and 4-pyridyl isocyanate (Scheme 1). Triamine **3** was prepared from 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene by etherification with 3-nitrophenol and reduction of the nitro groups in the presence of tin(II) chloride.[14] The obtained triamine **3** was reacted with in situ prepared 4-pyridyl isocyanate; 64% yield of the desired tris-urea **2** being obtained after purification. The structure of tris-urea **2** was confirmed by ^{1}H and ^{13}C NMR spectroscopy and electrospray ionization (ESI) mass spectrometry.

Three-Component LMWG Systems Using Metal–Ligand Interaction. Tris-urea **1** gelled acetone upon ultrasound irradiation, the critical gelation concentration (CGC) being 1.5 wt % (Table 1, Entry 1 and Figure 3a). The gelation of acetone was not complete at a lower concentration of **1** than the CGC. For example, a 0.75 wt % mixture of **1** in acetone gave a partial gel (Table 1, Entry 2 and Figure 3b). Scanning electron microscopy (SEM) images of xerogels prepared from the acetone gel of **1** and the partial gel of acetone and **1** showed structures resembling nanosized fibers (Figures 3a and 3b). These results indicate that conduction of intertwining of the

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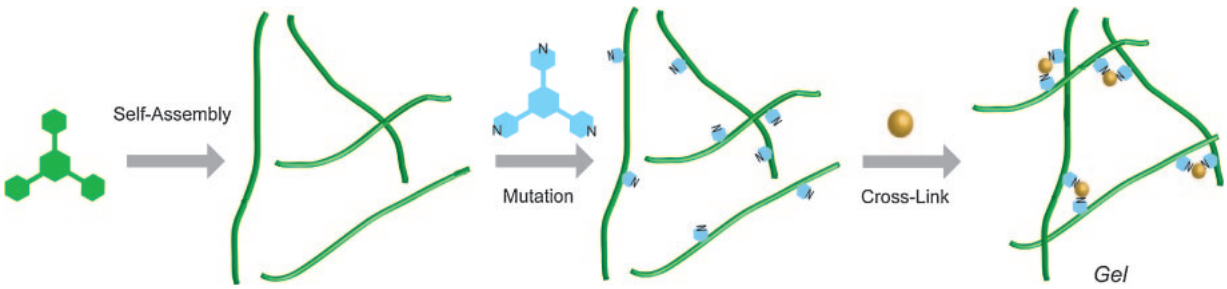


Figure 1. Schematic representation of three-component gelation system.

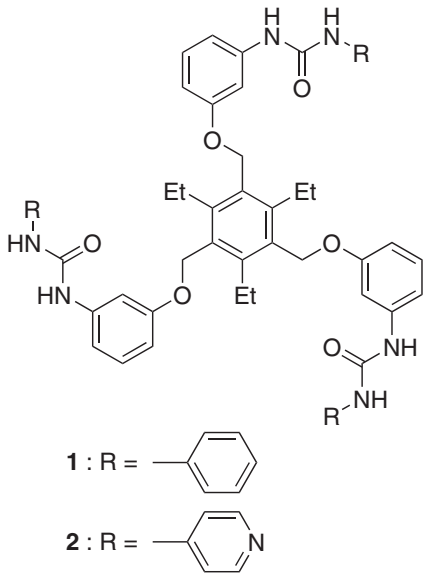
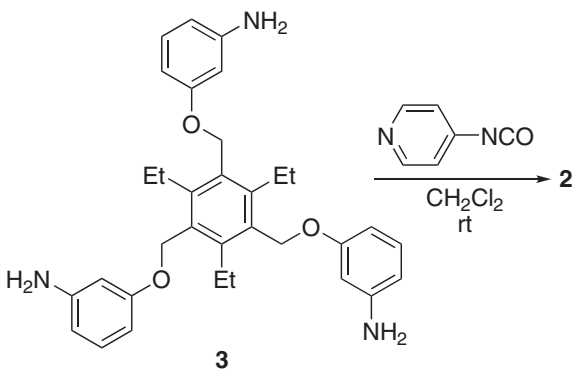


Figure 2. Chemical structures of tris-urea **1** and **2**.



Scheme 1. Synthesis of tris-urea **2**.

fibers of **1** may enable formation of a gel at a lower concentration than the present CGC. Partial variation of the fibrous aggregate of **1** with coordination sites should promote an intertwining of the fibers in the presence of an appropriate metal complex. Pyridyl groups introduced in tris-urea **2**, which resembles **1** in structure, seemed an adequate analog for partial mutation of the fibrous aggregate of **1**. A transition-metal complex, which is able to interact bidentately with pyridyl groups, should act as a glue for the fibers. A broad survey to find a suitable metal salt was carried out and $Pd(OAc)_2$ was identified as an effective salt. A mixture of **1**, **2** (1.0 mol % for **1**), and $Pd(OAc)_2$ (1.5 mol % for **1**) in acetone formed an opaque gel after ultrasound irradiation, and the CGC of **1** + **2** was estimated at 0.75 wt % (Table 1, Entry 3 and Figure 3c). The gelation completed with half the CGC by adding just trace amounts of **2** and $Pd(OAc)_2$. Neither 0.75 wt % mixtures of **1** and **2** (1.0 mol % for **1**) nor **1** and $Pd(OAc)_2$ (1.5 mol % for **1**) in acetone formed a gel (Table 1, Entries 4 and 5, and Figures 3d and 3e). This means that both **2** and $Pd(OAc)_2$ worked cooperatively to produce gelation. An SEM image of the xerogel prepared from 0.75 wt % acetone gel of **1**, **2**, and $Pd(OAc)_2$ (Table 1, Entry 3) showed moderately flexible and intertwined nanosized fibers (Figure 3c). In contrast, the SEM images of insoluble suspensions (Table 1, Entries 4 and 5) displayed different morphologies (Figures 3d and 3e). SEM observations of a sample prepared from a mixture of **1** and a small quantity of **2** showed more upright fibrous structures than the $Pd(OAc)_2$-containing three-component gel (Figure 3c vs. 3d). Short curved objects were observed by the SEM measurement of a mixture of **1** and $Pd(OAc)_2$ in comparison with the three-component gel (Figure 3c vs. 3e). Homogeneous nanosized fibers, as shown in Figure 3d, would indicate that partial mutation of the fibrous aggregate of **1** was attained by adding a trace amount of **2**. Crosslinking of the pyridyl group of **2** and $Pd(OAc)_2$ might help the intertwinement of fibers and promote gelation. $Pd(OAc)_2$ itself would obstruct the one-dimensional extension of **1** (and **2**) and proper connection between fibers. The following result supports this idea; a 0.75 wt % mixture of **1**, **2** (1.0 mol % for **1**), and $Pd(OAc)_2$ (10 mol % for **1**) in acetone gave an insoluble suspension and more curled fibers than the xerogel shown in Figure 3c, as observed by SEM (Table 1 Entry 6 and Figure 3f). The amount of **2** was not critical for gelation, and a mixture of **1**, **2** (10 mol % for **1**), and

Table 1. Gelation Properties of Mixtures of **1**, **2**, and $Pd(OAc)_2$ in Acetone

Entry	Components			State[a)]
	1/wt %	**2**/mol % for **1**	$Pd(OAc)_2$/mol % for **1**	
1	1.5	—	—	G
2	0.75	—	—	PG
3	0.75	1.0	1.5	G
4	0.75	1.0	—	I
5	0.75	—	1.5	I
6	0.75	1.0	10	I
7	0.75[b)]	10	1.5	G
8	0.75	0.5	0.75	G

a) G: gel, PG: partial gel, I: insoluble suspension. b) Total amount of **1** and **2**.

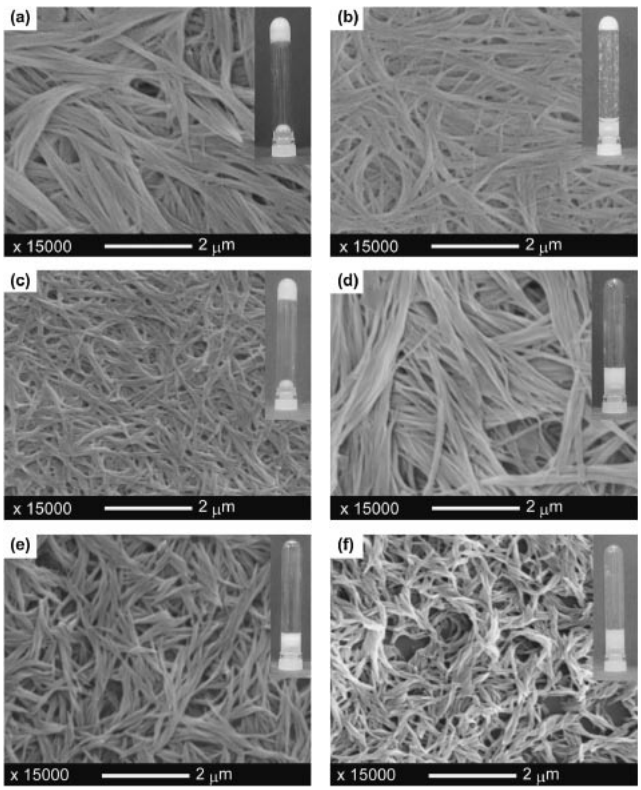


Figure 3. SEM images of dried samples and photographs of samples (inset): (a) **1** (1.5 wt %) in acetone; (b) **1** (0.75 wt %) in acetone; (c) **1** (0.75 wt %), **2** (1.0 mol % for **1**), and $Pd(OAc)_2$ (1.5 mol % for **1**) in acetone; (d) **1** (0.75 wt %) and **2** (1.0 mol % for **1**) in acetone; (e) **1** (0.75 wt %) and $Pd(OAc)_2$ (1.5 mol % for **1**) in acetone; and (f) **1** (0.75 wt %), **2** (1.0 mol % for **1**), and $Pd(OAc)_2$ (10 mol % for **1**) in acetone.

$Pd(OAc)_2$ (1.5 mol % for **1**) in acetone afforded an opaque gel after ultrasound irradiation (Table 1, Entry 7). The amounts of **2** and $Pd(OAc)_2$ could be reduced to 0.5 and 0.75 mol %, respectively, maintaining the CGC of **1** + **2** (Table 1, Entry 8).

Three-Component LMWG Systems Using Hydrogen-Bonding Interaction. A bidentate hydrogen bonding donor can be employed instead of a metal complex in this gelling system; therefore, it is possible for the pyridyl group to act as a hydrogen bonding acceptor. A dicarboxylic acid should be suitable as the bidentate hydrogen bonding donor. A mixture of **1**, **2** (1.0 mol % for **1**), and isophthalic acid (1.5 mol % for **1**) in acetone formed an opaque gel after sonication, the CGC being 0.75 wt % (Table 2, Entry 1 and Figure 4a). The SEM image of this xerogel showed intertwined nanosized fibers (Figure 4a). Crosslinking hydrogen bonds between the pyridyl groups of **2** and the carboxy groups of isophthalic acid were essential to improve the gelation ability. A 0.75 wt % mixture of **1** and isophthalic acid (1.5 mol % for **1**) in acetone gave an insoluble suspension (Table 2, Entry 2). Phthalic acid was not effective for gelation; a mixture of **1**, **2** (1.0 mol % for **1**), and phthalic acid (1.5 mol % for **1**) in acetone gave an insoluble suspension (Table 2, Entry 3 and Figure 4b). A sterically crowded dicarboxylic acid might cause excess cohesion of fibrous aggregates. The insoluble suspension containing **1**, **2**, and

Table 2. Gelation Properties of Mixtures of **1**, **2**, and Carboxylic Acid in Acetone

Entry	Components			
	1/wt %	**2**/mol % for **1**	Additive/mol % for **1**	State[a)]
1	0.75	1.0	isophthalic acid (1.5)	G
2	0.75	—	isophthalic acid (1.5)	I
3	0.75	1.0	phthalic acid (1.5)	I
4	0.75	1.0	terephthalic acid (1.5)	PG
5	0.75	1.0	terephthalic acid (3.0)	G
6	0.75	1.0	dimethyl isophthalate (1.5)	I
7	0.75	1.0	benzoic acid (1.5)	I
8	0.75	1.0	benzoic acid (3.0)	I

a) G: gel, PG: partial gel, I: insoluble suspension.

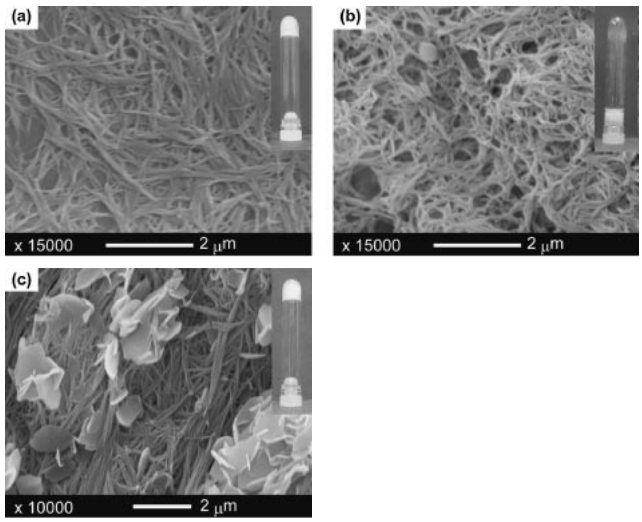


Figure 4. SEM images of dried samples and photographs of samples (inset): (a) **1** (0.75 wt %), **2** (1.0 mol % for **1**), and isophthalic acid (1.5 mol % for **1**) in acetone; (b) **1** (0.75 wt %), **2** (1.0 mol % for **1**), and phthalic acid (1.5 mol % for **1**) in acetone; and (c) **1** (0.75 wt %), **2** (1.0 mol % for **1**), and terephthalic acid (3.0 mol % for **1**) in acetone.

phthalic acid showed thin curled fibers (Figure 4b). A mixture of **1**, **2** (1.0 mol % for **1**), and terephthalic acid (1.5 mol % for **1**) in acetone (0.75 wt %) afforded a partial gel (Table 2, Entry 4). Crosslinking with terephthalic acid might cause a decrease in entropy because of the remote arrangement of the two hydrogen bonding carboxy groups. In fact, a 0.75 wt % mixture of **1**, **2** (1.0 mol % for **1**), and terephthalic acid (3.0 mol % for **1**) in acetone formed an opaque gel (Table 2, Entry 5 and Figure 4c). Sheet-shaped structures were intermingled with fibrous structures on SEM observation of the gel composed of **1**, **2**, and terephthalic acid (Figure 4c). Crosslink between fibrous aggregates (**1** and **2**) and para disubstituted terephthalic acid might promote two-dimensional assembly to form sheet-shaped structures. A gelation experiment of acetone with **1**, **2** (1.0 mol % for **1**), and dimethyl isophthalate (1.5 mol % for **1**), the dimethyl ester of isophthalic acid, did not succeed, and an insoluble suspension was obtained (Table 2, Entry 6). These results indicate that the hydrogen-bonding interaction between

Table 3. Gelation Properties of Mixtures of **1** and **2** in MeOH and EtOAc

Entry	Solvent	Components			
		1/wt %	**2**/mol % for **1**	Additive/mol % for **1**	State[a)]
1	MeOH	2.0	—	—	G
2	MeOH	0.50	—	—	PG
3	MeOH	0.50	1.0	—	G
4	MeOH	0.50	1.0	$Pd(OAc)_2$ (1.5)	PG
5	MeOH	0.50	1.0	isophthalic acid (1.5)	I
6	EtOAc	5.0	—	—	I
7	EtOAc	1.5	1.0	—	G
8	EtOAc	1.5	1.0	$Pd(OAc)_2$ (1.5)	PG
9	EtOAc	1.5	1.0	isophthalic acid (1.5)	I

a) G: gel, PG: partial gel, I: insoluble suspension.

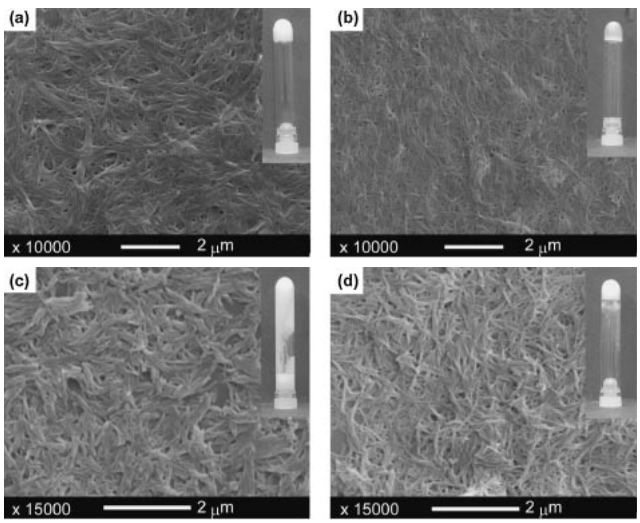


Figure 5. SEM images of dried samples and photographs of samples (inset): (a) **1** (2.0 wt %) in MeOH, (b) **1** (0.50 wt %) and **2** (1.0 mol % for **1**) in MeOH, (c) **1** (5.0 wt %) in EtOAc, and (d) **1** (1.5 wt %) and **2** (1.0 mol % for **1**) in EtOAc.

the pyridyl groups of **2** and the carboxy groups of isophthalic acid is indispensable to form a gel. The bidentate nature of the hydrogen bonding donor was essential in this gelation, and consequently a mixture of **1**, **2** (1.0 mol % for **1**), and benzoic acid (1.5 or 3.0 mol % for **1**), a monodentate hydrogen bonding donor, in acetone gave only an insoluble suspension (Table 2, Entries 7 and 8).

Two-Component LMWG System. In the course of investigating the three-component gelling system (vide ante), it was clear that the gelation ability of **1** was dramatically improved by adding a trace amount of **2** in some solvents. Tris-urea **1** itself gelled MeOH upon ultrasound irradiation, the CGC being 2.0 wt % (Table 3, Entry 1 and Figure 5a).[14] A partial gel was observed for a 0.50 wt % mixture of **1** in MeOH (Table 3, Entry 2). A mixture of **1** and **2** (1.0 mol % for **1**) gelled MeOH at 0.50 wt % after ultrasound irradiation (Table 3, Entry 3 and Figure 5b). The CGC in MeOH decreased by a factor of four upon adding 1.0 mol % of **2**. Both SEM images of the xerogels prepared from the MeOH gel of **1** (2.0 wt %) and the MeOH gel of **1** and **2** (0.50 wt %) showed similar morphologies (Figures 5a and 5b). However, the three-component systems, i.e., **1**, **2**, and $Pd(OAc)_2$ or isophthalic acid, were not effective for gelation of MeOH (Table 3, Entries 4 and 5). A dramatic change was observed on gelation of EtOAc with **1** and a trace amount of **2**. An insoluble suspension was obtained by mixing **1** and EtOAc in any concentration (Table 3, Entry 6 and Figure 5c). A mixture of **1** and **2** (1.0 mol % for **1**) in EtOAc formed an opaque gel, the CGC being estimated at 1.5 wt % (Table 3, Entry 7 and Figure 5d). A suspended mixture of **1** and EtOAc showed fragmentary objects on SEM measurement (Figure 5c). In contrast, the EtOAc gel of **1** and **2** was composed of intertwined nanosized fibers (Figure 5d). A trace amount of **2** assists the one-dimensional extension of **1** in some manner. The three-component systems were also not effective for gelation of EtOAc (Table 3, Entries 8 and 9).

Conclusion

In conclusion, we have designed and synthesized a pyridyl-substituted tris-urea **2** as a structurally similar analog of tris-urea LMWG **1**. The gelation ability of **1** in acetone was dramatically improved by the presence of trace amounts of **2** and $Pd(OAc)_2$. Crosslinking of nanosized fibers composed of **1** and **2** through the metal–ligand coordination bond of **2** and $Pd(OAc)_2$ plays an important role in the gelation. Isophthalic acid was also an effective crosslinker of the fibers in acetone. The hydrogen-bonding interaction between **2** and isophthalic acid was an essential force to achieve the gelation. In MeOH and EtOAc, addition of a trace amount of **2** was effective in improving the gelation ability of **1**. A one-dimensional extension of **1** would be caused by **2**.

Experimental

^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECA600 spectrometer. Mass spectra were measured on a JEOL JMS-T100LC AccTOF spectrometer. Ultrasound irradiation was performed using a BRANSON B2510J ultrasonic cleaner. SEM studies were carried out on a JEOL JSM-6300 spectrometer.

Synthesis of 1,3,5-Triethyl-2,4,6-tris[3-(4-pyridylureido)-phenoxymethyl]benzene (2). To a solution of 4-pyridylamine (72 mg, 0.77 mmol) in CH_2Cl_2 (7.6 mL) was added triphosgene (75 mg, 0.25 mmol) and Et_3N (0.21 mL, 1.5 mmol) under argon atmosphere at 0 °C. The mixture was stirred at room temperature for 30 min (CH_2Cl_2 solution of 4-pyridyl isocyanate). Triamine **3** (100 mg, 0.19 mmol) was added to the solution and stirred at room temperature for 21 h. Saturated sodium hydrogen carbonate solution was poured into the reaction mixture, and the precipitate was filtered off. The precipitate was added to a CH_2Cl_2 solution of 4-pyridyl isocyanate which was prepared from the same procedure and amounts with mentioned above. The mixture was stirred at room temperature for 12 h. Saturated sodium hydrogen carbonate solution was poured into the reaction mixture, and the precipitate was filtered off. The crude product was purified by reprecipitation from THF–Et_2O and MeOH–Et_2O successively to give **2** as a white solid (107 mg, 64%): mp >250 °C; ^1H NMR (600 MHz, DMSO-d_6): δ 1.20 (t, $J = 7.6$ Hz, 9H), 2.77 (q, $J = 7.6$ Hz, 6H), 5.08 (s, 6H), 6.79 (dd, $J = 8.2$, 2.1 Hz, 3H), 7.05 (dd, $J = 8.2$, 1.4 Hz,

3H), 7.25 (t, $J = 2.1$ Hz, 3H), 7.26 (t, $J = 8.2$ Hz, 3H), 7.43 (d, $J = 6.2$ Hz, 6H), 8.35 (d, $J = 6.2$ Hz, 6H), 8.91 (s, 3H), 9.12 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 16.3, 22.5, 64.0, 104.9, 108.3, 111.3, 112.3, 129.8, 130.8, 140.4, 145.5, 146.4, 150.1, 152.0, 159.1; HRMS (ESI, $M + Na^+$) calcd for $C_{51}H_{51}N_9NaO_6$ 908.3860, found 908.3837.

General Procedure of Gelation Experiments. A weighed amount of tris-ureas **1** and **2** were placed in test tube, and acetone was added. The closed test tube was sonicated for a few minutes. An acetone solution of crosslinker (e.g., $Pd(OAc)_2$ or isophthalic acid) was added to the test tube. The mixture was sonicated for 20 min, and the gelation was confirmed by the inverted test tube method.

The research was partially carried out using an instrument at the Center for Instrumental Analysis of Shizuoka University.

Supporting Information

^{1}H and ^{13}C NMR spectra of tris-urea **2**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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