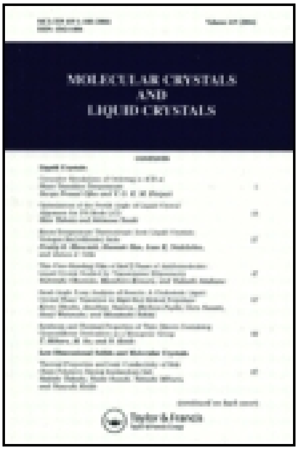

Molecular Crystals and Liquid Crystals

Self-Assembly of a Pyridyl Derivative and its Silver Complex: Formation of a Liquid Crystalline Phase and Organogels

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Self-Assembly of a Pyridyl Derivative and its Silver Complex: Formation of a Liquid Crystalline Phase and Organogels

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Self-assembling behavior of N,N′-didodecyl-3,5-pyridinedicarboxamide and its silver complex has been studied. They act as gelators in solution and gelate a variety of organic solvents. Though the silver complex exhibits lower gelation abilities for halogenated and aromatic solvents, long-term stability is achieved for ethanol and acetone gels. Moreover, the silver complex exhibits a smectic A phase on cooling while a single component of N,N′-didodecyl-3,5-pyridinedicarboxamide exhibits no mesomorphic behavior. The XRD pattern for the complex shows that the layer spacing of the S_A *phase is 37Å.*

Keywords: hydrogen bonding; liquid crystal; metal coordination; organogel; pyridine derivative; self-assembly

INTRODUCTION

Self-assembly is one of promising processes for the development of functional molecular materials [1]. In this process, specific molecular

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interactions such as hydrogen bonding, π-π interactions, and dipole interactions often play important roles. On the other hand, metal coordination is also useful for self-assembly [2]. The combination of these interactions may yield elaborate assembled structures and induce dynamic functions. From this point of view, pyridyl derivatives are useful components for the construction of functional molecular materials because of their attractive self-assembling behavior as a hydrogen bond acceptor [3] and a metal ligand [2b,c,4]. In the field of liquid crystalline materials, supramolecular liquid crystals have been developed using a pyridyl unit as a hydrogen bond acceptor [3].

Pyridyl derivatives are also useful for the construction of self-assembled fibers and physical gels based on low molecular weight gelators [5]. Low molecular weight gelators have attracted much attention due to their potential for functional molecular materials [6]. These gelators form self-assembled fibers consisting of bundles of one-dimensional molecular aggregates through noncovalent interactions in solvents. Formation of a three-dimensional network of these self-assembled fibers results in physical gelation of solvents. We recently reported on a new low molecular weight gelator having

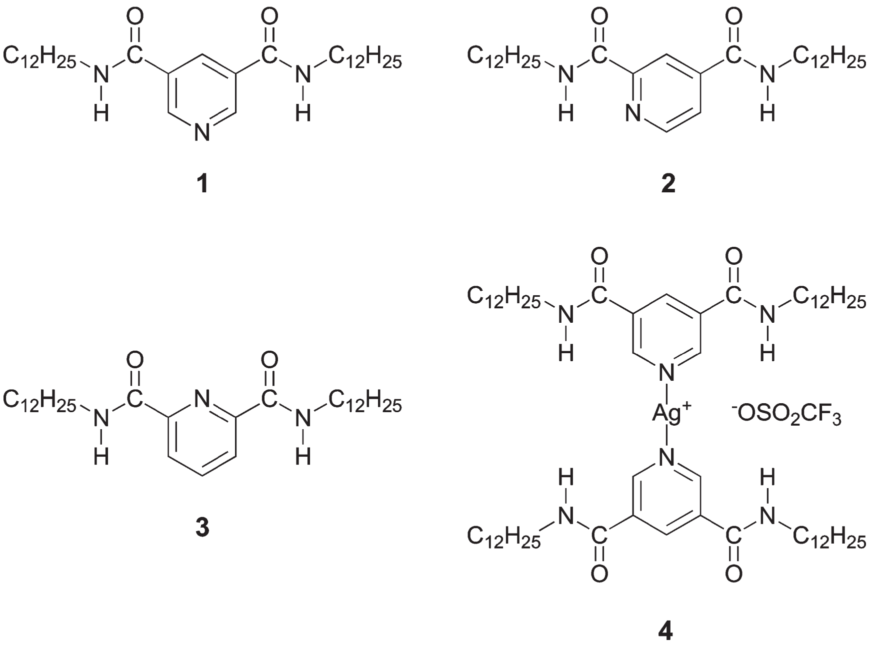

FIGURE 1 Molecular structures of pyridinedicarboxamide derivatives.

a pyridyl unit as a hydrogen bond acceptor [5]. For this gelator, the incorporation of intra- and intermolecular hydrogen bonding leads to efficient gelation. As for gelators containing ligand groups, only a few examples have been reported [7]. Utilization of metal coordination has not yet been developed extensively in the field of physical gels.

Here we report self-assembly of pyridyl derivatives **1–3** and metal complex **4** (Fig. 1). We have examined the liquid crystalline properties and gelation abilities of **1–4**.

RESULTS AND DISCUSSION

Self-Assembling Behavior in Solution: Formation of Organogels

We have found that *N*,*N*′-didodecyl-3,5-pyridinedicarboxamide **1** acts as an efficient gelator for common organic solvents among pyridinedicarboxamide derivatives **1–3** (Fig. 1). Compound **1** was prepared from 3,5-pyridine dicarboxylic acid. It gelates a wide range of solvents as shown in Table 1. For example, 4 g of **1** can gelate 1 L of toluene. A network of self-assembled fibers is formed in the gels as shown in Figure 2a. It should be noted that the position of amide moieties on a pyridine ring affects self-assembling behavior of pyridinedicarboxamide derivatives. No gelation ability is observed for compound **2** due to its high solubility. As for 2,4-disubstituted compound **3**, crystallization occurs without gelation. Only 3,5-disubstituted compound **1** forms organogels. It is expected that a nitrogen atom on the pyridyl unit is

TABLE 1 Comparison of the Gelation Ability of Pyridinedicarboxamide Derivatives and Metal Complex **4**[a]

Solvent	**1**	**2**	**3**	**4**
Acetone	G (9)	S	C	G (5)
Ethanol	G (18)	S	C	G (22)
Dichloromethane	G (14)	S	S	G[b]
Tetrachloromethane	G (13)	S	C	G[b]
Ethyl acetate	G (5)	S	C	G[b]
Hexane	I	C	C	I
Benzene	G (9)	S	C	C
Toluene	G (4)	S	C	G[b]
Pyridine	C	S	C	C

[a] Minimum gel concentrations are in parentheses (given in g L^{-1}). The following abbreviations are used: C, crystallization; I, insoluble; S, solution; G, gel.

[b] Gelation occurred below room temperature.

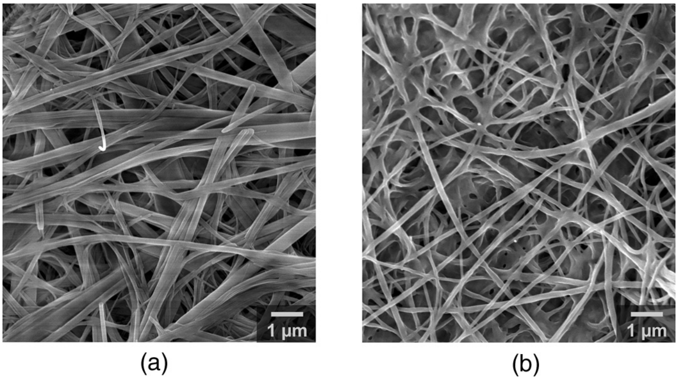

FIGURE 2 SEM images of the self-assembled fibers of **1** (a) and **4** (b) formed in ethanol.

involved in the fibrous self-assembly process of these compounds as a hydrogen bond acceptor. We previously reported on this behavior for the organogels based on a 2,6-disubstituted bisurea compound [5].

We have also examined gelation abilities of the metal complexes of pyridinedicarboxamide derivatives. Silver trifluoromethane sulfonate was chosen as a metal salt because it is soluble in many organic solvents and often used for a component of metallomesogens [2b,c,4]. Complex **4** was simply obtained in a high yield from compound **1** and silver trifluoromethane sulfonate in a molar ratio 2:1. Complex **4** also acts as a gelator as shown in Table 1. No gelation is observed for metal complexes of other pyridinedicarboxamide derivatives. For only ethanol and acetone, compound **4** shows good gelation abilities at room temperature. The morphologies of self-assembled fibers are slightly changed by the addition of silver trifluoromethane sulfonate as shown in Figure 2b. The fibers of complex **4** seem to be rounded and elongated compared to those of **1** as shown in Figure 2a.

Metal coordination improves thermal stability of the gels based on **1**. In the case of ethanol gels containing $25\,\mathrm{g\ L^{-1}}$ of gelators, the gel-sol transition temperature increases from 52°C for **1** to 72°C for **4**. Moreover, the addition of silver trifluoromethane sulfonate to **1** affords long-term stability of self-assembled fibers. Though compound **1** gelates various organic solvents, some of these gels lack long-term stability. Figure 3 shows changes in appearance of ethanol gels with time. There is little difference in appearance between two gels shortly after the preparation. Both gels are turbid. The gel containing $20\,\mathrm{g\ L^{-1}}$ of **1** collapses and crystallization occurs in ten days. On the other

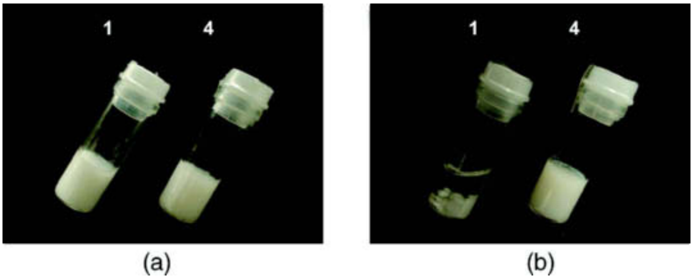

FIGURE 3 Comparison of the appearance of gels based on **1** and **4** shortly after the preparation of the samples (a) and after 10 days (b).

hand, the gel containing 20 g L^{-1} of **1** with 5.1 g L^{-1} of silver trifluoromethane sulfonate which is equivalent to 25 g L^{-1} of complex **4** seems to be unchanged. This silver-containing gel is stable even for months. A similar trend is observed for acetone gels based on **4**. Figure 4 shows the SEM images of self-assembled fibers of **1** and **4** taken from the samples left for two weeks after the preparation. The collapse of a network of self-assembled fibers is observed for the gels based on **1**, while a network of elongated fibers is maintained for the gels based on complex **4**. This observation agrees with macroscopic observation as shown in Figure 3. These results indicate that assembled structures of pyridinedicarboxamides are changed by metal coordination.

^{1}H NMR measurements have been performed to examine the effects of metal coordination on hydrogen-bonded structures of **1** (Fig. 5). The downfield shifts of the N-H protons are observed by metal

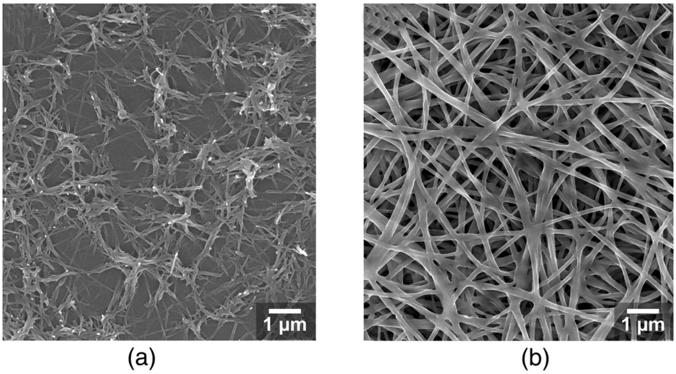

FIGURE 4 SEM images of the self-assembled fibers of **1** (a) and **4** (b) left for two weeks after the preparation of gels.

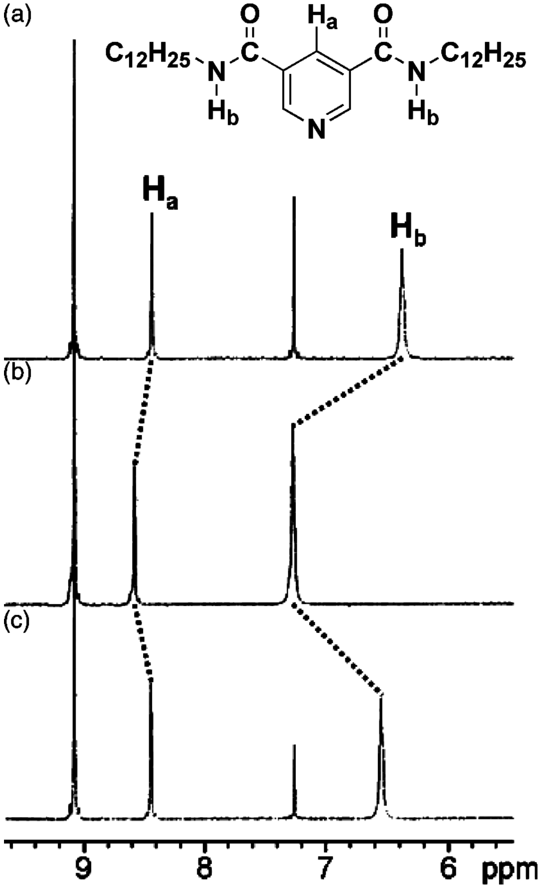

FIGURE 5 Comparison of the chemical shifts of ^1H NMR measurements in $CDCl_3$. (a) **1** (10 mM); (b) complex **4** (10 mM); (c) **1** (20 mM).

coordination. The range of the shifts on coordination is larger than that on a concentration change. When the concentration of **1** increases from 10 mM to 20 mM, the chemical shift of N-H protons moves from 6.38 to 6.56 ppm. On the other hand, the addition of silver trifluoromethane sulfonate to 10 mM of **1** induces downfield shifts from 6.38 to 7.25 ppm. In addition, the downfield shifts of the proton at the C_4 position of a pyridine ring are also observed. These shifts are attributable to ionic interactions with counter anions. A similar trend was observed for the anion-templated rotaxane formation [9]. The incorporation of ionic interactions and hydrogen bonding may lead to the stabilization of the self-assembled fibers of **4**.

Self-Assembling Behavior in Bulk States: Mesomorphic Behavior

The mesomorphic behavior of pyridinedicarboxamide derivatives and their metal complexes has also been studied. As for pyridinedicarboxamide derivatives without metal salts, no mesomorphic behavior is observed. Melting temperatures of **1**, **2**, and **3** are 153, 91, and 94°C, respectively. Compound **1** exhibits the highest melting temperature, which also indicates that a nitrogen atom on the pyridyl unit plays an important role for the self-assembly process of these compounds as a hydrogen bond acceptor.

The addition of silver trifluoromethane sulfonate to **1** induces mesomorphic behavior along with distinct changes in thermal properties. The melting point increases from 150°C for **1** to 187°C for **4** by metal complexation. DSC measurements (Fig. 6) and microscopic observation (Fig. 7) reveal that complex **4** exhibits a smectic A phase between 173 and 160°C on cooling. These results indicate that the metal coordination affects the molecular packing of **4**. Figure 8 shows the XRD pattern for complex **4** at 160°C. The layer spacing of the S_A phase is 37 Å. The sharp peaks are attributable to the layered structure of silver atoms. Considering that the distance between a silver atom and the alkyl terminal group of **1** in complex **4** can be estimated about 20 Å, the alkyl chains are expected to interdigitate one another as shown in Figure 9.

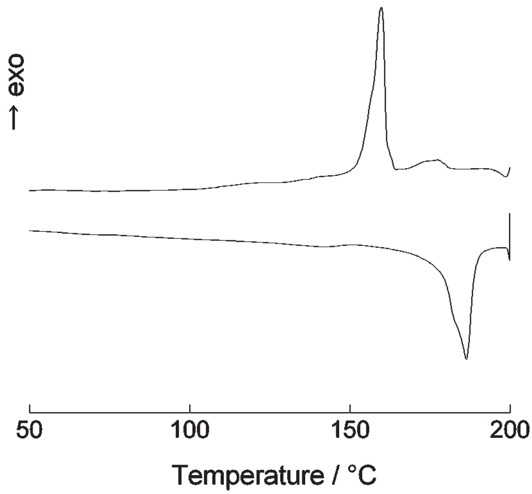

FIGURE 6 DSC thermogram of complex **4**.

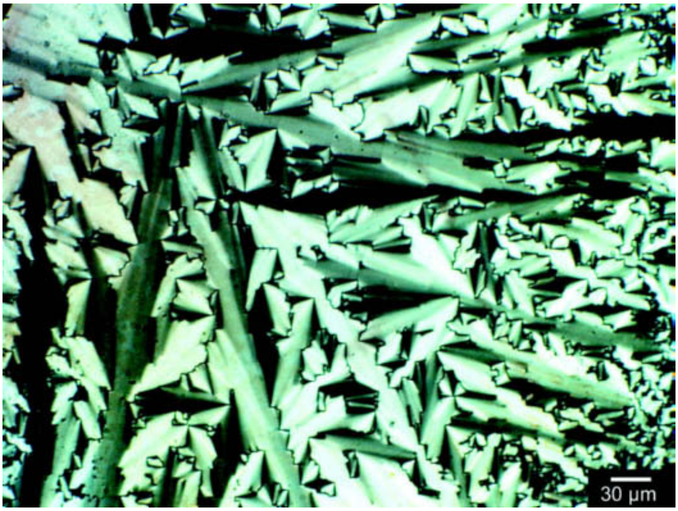

FIGURE 7 Polarized optical micrograph of complex **4** at 160°C.

There are only a few examples of low molecular weight gelators which exhibit mesomorphic behavior [8]. Recently, Mori and coworkers reported troponoid-based gelators with hexagonal columnar phases [8a]. Mesomorphic properties and gelation abilities seem to be closely related since non-mesomorphic tropones do not act as

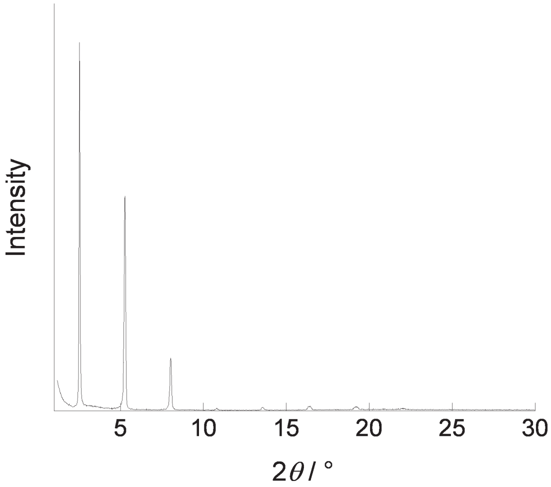

FIGURE 8 XRD pattern of complex **4** at 160°C.

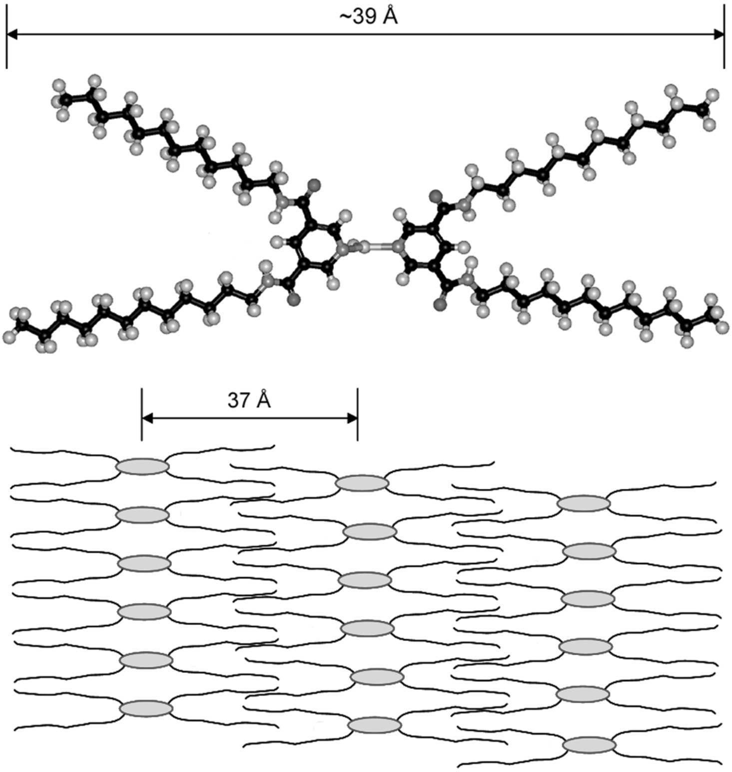

FIGURE 9 Schematic illustration of layered structure of **4**. Triflate anions are omitted for clarity.

gelators. In our case, it is expected that a smectic layered structure is closely related to the formation of stable self-assembled fibers in solvents mentioned above.

CONCLUSION

We have developed a pyridine-based diamide gelator that can form metal complexes. Metal coordination to a pyridyl unit induces the stabilization of assembled structures leading to the exhibition of mesomorphic behavior and the formation of organogels with long-term stability. Here, the incorporation of hydrogen bonding and metal coordination plays an important role for the self-assembly. Such molecular design would serve a new approach not only for the development of low molecular weight gelators and liquid crystalline materials but also for other organic/inorganic hybrid materials.

EXPERIMENTAL

General Method

Unless otherwise noted, chemical reagents and solvents were used without further purification. As for dichloromethane, a commercially available anhydrous solvent was used for reactions. All reactions were carried out under argon atmosphere. ^{1}H and ^{13}C NMR spectra were determined with a Jeol JNM-400EX. Infrared spectra were recorded on a Jasco FT-IR 8900 μ spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400II CHNS/O elemental analyzer. DSC measurements were performed with a Mettler DSC 30.

Synthesis of N,N′-Didodecyl-3,5-Pyridinedicarboxamide (1)

Thionyl chloride 20 mL was added to 3,5-pyridine dicarboxylic acid (0.334 g, 2.0 mmol) and the reaction mixture was stirred for 6 h under reflux condition. Unreacted thionyl chloride was removed under reduced pressure. The residual needle crystals were dissolved in 10 mL of dichloromethane. This solution was slowly added to a solution of dodecylamine (0.927 g, 5.0 mmol) and 1.0 mL of triethylamine in dichloromethane (10 mL) at 0°C. The reaction mixture was stirred for 8 h at room temperature. The resultant mixture was filtered to give a white solid. The solid was recrystallized from hexane/ethyl acetate to afford **1** (0.685 g, 68%) as a white solid (Found: C, 74.25; H, 11.07; N, 8.57. Calc. for $C_{31}H_{55}N_3O_2$: C, 74.20; H, 11.05; N, 8.37%); mp 153°C (from hexane/ethyl acetate); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.10 (s, 2H, Ar*H*), 8.44 (s, 1H, Ar*H*), 6.25 (m, 2H, N*H*), 3.50 (q, $J = 6.6$ Hz, 4H, $NHCH_2$), 1.67 – 1.61 (m, 4H, $NHCH_2CH_2$), 1.35 – 1.26 (m, 36H, CH_2), 0.88 (t, $J = 6.6$ Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.77, 150.28, 133.35, 130.08, 40.38, 31.89, 29.63, 29.61, 29.58, 29.53, 29.34, 29.30, 26.98, 22.68, 14.12.

Synthesis of N,N′-Didodecyl-2,6-Pyridinedicarboxamide (2)

This compound was synthesized as described above for **1**, starting from 2,6-pyridine dicarboxylic acid (3.27 g, 19.6 mmol). The reaction mixture was extracted with chloroform. The organic layer was washed with saturated aqueous $NaHCO_3$ followed by drying on anhydrous $MgSO_4$. After filtration the solvent was removed under reduced pressure. The crude product was purified by column chromatography with chloroform as eluent followed by recrystallization from hexane/ethyl acetate to afford **2** (7.42 g, 75%) as a white solid (Found: C, 74.76; H, 11.99; N, 8.58. Calc. for $C_{31}H_{55}N_3O_2$: C, 74.20; H, 11.05; N, 8.37%); mp 91°C (from hexane/ethyl acetate); ^{1}H NMR ($CDCl_3$, 400 MHz): δ

8.36 (d, $J = 8.0$ Hz, 2H, Ar*H*), 8.03 (t, $J = 7.8$ Hz, 1H, Ar*H*), 7.69 (m, 2H, N*H*), 3.52 (q, $J = 6.8$ Hz, 4H, NHCH_2), 1.69 – 1.62 (m, 4H, NHCH$_2$CH_2), 1.39 – 1.26 (m, 36H, CH_2), 0.88 (t, $J = 6.4$ Hz, 6H, CH_3); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 163.37, 148.88, 138.97, 124.92, 39.65, 31.89, 29.74, 29.65, 29.62, 29.60, 29.59, 29.34, 27.06, 22.67, 14.11.

Synthesis of N,N′-Didodecyl-2,4-Pyridinedicarboxamide (3)

This compound was synthesized as described above for **1** (2.51 g, 15 mmol), starting from 2,4-pyridine dicarboxylic acid. The crude product was purified by recrystallization from hexane/ethyl acetate to afford **3** (6.78 g, 90%) as a white solid (Found: C, 74.26; H, 11.13; N, 8.57. Calc. for $C_{31}H_{55}N_3O_2$: C, 74.20; H, 11.05; N, 8.37%); mp 94°C (from hexane/ethyl acetate); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.69 (d, $J = 4.8$ Hz, 1H, Ar*H*), 8.35 (s, 1H, Ar*H*), 8.06 (t, $J = 5.2$ Hz, 1H, N*H*), 7.95 (d, $J = 4.8$ Hz, 1H, Ar*H*), 6.39 (t, 1H, $J = 5.0$ Hz, N*H*), 3.50 (q, $J = 5.9$ Hz, 4H, NHCH_2), 1.66–1.62 (m, 4H, NHCH$_2$CH_2), 1.34 – 1.26 (m, 36H, CH_2), 0.88 (t, $J = 7.0$ Hz, 6H, CH_3); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 164.61, 163.60, 150.63, 149.19, 143.14, 124.65, 118.03, 40.38, 39.62, 31.91, 29.63, 29.59, 29.54, 29.45, 29.35, 29.33, 29.28, 26.99, 22.70, 14.14.

Preparation of a Silver Complex (4)

Weighed silver trifluoromethane sulfonate was dissolved in ethanol (or acetone, THF). Weighed gelator **1** was added to this solution followed by heating until a homogeneous solution was obtained. Molar ratio of silver trifluoromethane sulfonate to **1** is fixed at 0.5. Then the solvent was removed by evaporation and the resultant solid was dried *in vacuo* to afford silver complex **4** as a white solid.

Gelation Test

In a typical gelation experiment, an organic solvent (0.2 mL) was added to a weighed sample (20 mg) in a test tube. The tube was sealed and heated until a clear solution was obtained. The resultant solution was allowed to cool to room temperature. Then gelation was checked visually. When the tube could be inverted without any flow, it was considered as "gel." In this case, more solvent was added to the sample and minimum gel concentration (MGC) was determined. MGC is the minimum concentration of a gelator necessary for gelation. When the mixture remained solution at room temperature, it was further cooled in a refrigerator to check whether gelation occurred at lower temperature. When the gel formed at lower temperature was stable even at room temperature, it was also considered as gel.

Determination of Melting Temperatures of Organogels

For the determination of melting temperatures of organogels, "dropping-ball" method [10] was used. A steel ball was placed on top of the gel in a test tube. The tube was sealed and wrapped in aluminum foil, and then it was heated on a hot stage. As the temperature was elevated at a $10^\circ\mathrm{C\,min^{-1}}$, the position of the ball was monitored. The temperature at which the steel ball reached the bottom of the tube was taken as the melting temperature.

Scanning Electron Microscopic (SEM) Observation

For the SEM observation of the self-assembled fibers of gelators formed in organic solvents, a gelator was dissolved in solvents at the concentration of MGC. A droplet of the solution was placed on a glass slide (8 mm × 8 mm) and frozen by immersion in liquid nitrogen. Then the solvent was removed *in vacuo*. The glass was attached to the SEM sample stage. SEM observation was performed with a Hitachi S-900S. The accelerating voltage was 10 kV. All the samples were shaded with platinum.

Long-Term Stability Test

For the test of long-term stability of gels, fresh gels were prepared in a sealed test tube. These gels were left in the dark under argon atmosphere. Changes of appearance of the gels were checked visually. After two weeks, some of the samples were picked up and used for SEM observation.

XRD Measurement

X-ray diffraction (WAXD) patterns were obtained using a Rigaku RINT-2100 system with monochromated CuK_α radiation (12.5 kW). Samples were placed on a glass plate and heated to appropriate temperatures with a PTC-20L temperature controller.

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