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A new urea gelator: incorporation of intra- and intermolecular hydrogen bonding for stable 1D self-assembly

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A new bisurea gelator derived from 2,6-diaminopyridine has been developed. It efficiently gelates common organic and liquid crystalline (LC) solvents by forming elongated self-assembled fibres in solvents. X-Ray crystallography and ^{1}H NMR measurements reveal that two urea groups in pyridine-based bisurea compounds form different hydrogen bonding patterns. One of two urea units is involved in intramolecular hydrogen bonding with the pyridyl nitrogen, while the other urea unit forms bifurcated intermolecular hydrogen bonding. This hydrogen-bonded structure is key for the fibrous self-assembly along with the efficient gelation. In addition, LC gels based on the pyridine-based gelator exhibit good electrooptic properties. These results indicate that the pyridine-based bisurea compound is a good gelator not only effective in gelation but also useful as a component of functional soft materials.

Introduction

Recently, fibrous self-assembly of low-molecular-weight gelators on the nanometer-scale in various organic and aqueous solvents has attracted attention because of the potential for functional materials.[1–16] For example, self-assembled fibres of gelators have been used as templates for porous inorganic[10] and polymeric[11] materials. Electrolyte gels are applicable to batteries.[12] Liquid crystalline (LC) gels have shown excellent electrooptic[13,14] and electronic[15] properties, while anisotropically oriented self-assembled fibres have been obtained in aligned LC states.[16] In these gelators, hydrogen bonding,[2–6] π–π aromatic stacking,[7] lipophilic,[8] and dipolar[9] interactions have been used to drive one-dimensional (1D) fibrous self-assembly. Among these interactions, hydrogen bonding is one of the most frequently used interactions for the design of gelators.

For example, amide,[2] hydroxyl,[2d,3] and urea[4–6] groups have been incorporated into the structures of gelators for the formation of one-dimensional self-associated chains. Here, we focus on urea compounds having a pyridyl moiety. Urea groups have one-dimensional molecular assembling properties. X-Ray analyses of urea compounds in the crystalline state have shown that urea groups form bifurcated hydrogen bonds.[17] Several urea gelators have been prepared by Hanabusa,[4] Feringa,[5] and Hamilton[6] and their coworkers. Urea gelators are useful for the spatial organization of functional entities such as electroactive moieties[5c] and polymerizable groups[6c] due to the high directionality of bifurcated hydrogen bonds. On the other hand, pyridyl moieties have been used for the formation of supramolecular materials.[13b,18] Our intention here is to develop new urea-based gelators by introducing a pyridyl moiety to urea compounds. Recently, Meijer[19] and Zimmermann[20] and their coworkers have reported that a variety of inter- and intramolecular hydrogen bonds are formed in heterocyclic ureas. Thus, new assembled patterns of molecules are expected by the connection of a pyridyl moiety with the urea groups. Moreover, bis(acylamino)pyridine units are widely used as components for molecular recognition.[21] We report here that a pyridine-based bisurea compound acts as a gelator, and how the combination of intra- and intermolecular hydrogen bonds can contribute to fibrous self-assembly.

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Results and discussion

Formation of physical gels

Four aromatic bisurea compounds **1**, **2**, **3** and **4** (Chart 1) were easily prepared by a one step reaction with amines and isocyanates. Table 1 shows the results of the gelation test of these compounds having dodecyl chains. A pyridine-based bisurea compound **1** exhibits good gelation abilities for common organic solvents such as halogenated and aromatic solvents. For example, minimum gel concentration of **1** for benzene is 9 g L^{-1}. In contrast, benzene-based bisurea compounds **2** and **3** have poor gelation abilities for common organic solvents. No gelation is observed for compound **5** in which the urea groups of **1** were replaced by amide groups. These results show that the

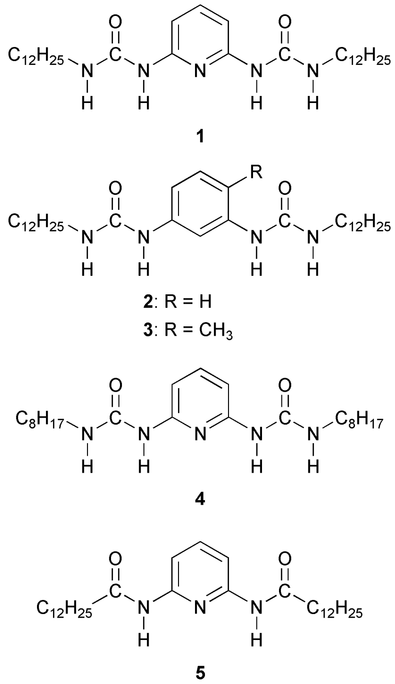


Chart 1 Bisurea compounds and a diamide compound used in this study.

Table 1 Gelation properties and minimum gel concentrations of aromatic bisurea compounds[a]

Solvent	**1**	**2**[b]	**3**
Acetone	P	I	I
Chloroform	G[c] (40)	P	P
Dichloromethane	G (25)	I	P
Tetrachloromethane	G (16)	I	V
Ethyl acetate	P	I	I
DMF	G[c] (19)	P	P
Hexane	I	I	I
Methanol	P	P	P
Ethanol	P	P	P
Benzene	G (9)	P	P
Toluene	G (10)	P	G[d]
Pyridine	G[c] (33)	P	P
5CB	G	G	G

[a] Minimum gel concentrations are in parentheses (given in g L^{-1}). The following abbreviations are used: P, precipitate; I, insoluble; G, gel; V, increasing viscosity. [b] **2** was reported to gelate *n*-hexadecane.[5b] [c] Gelation occurred below room temperature. [d] Gel collapsed within a few hours.

incorporation of the pyridyl moiety and the urea groups plays an important role in gelation.

Microscopic observation reveals that compound **1** forms elongated fibrous aggregates in organic solvents. A SEM image of self-assembled fibres of **1** formed in pyridine is shown in Fig. 1.

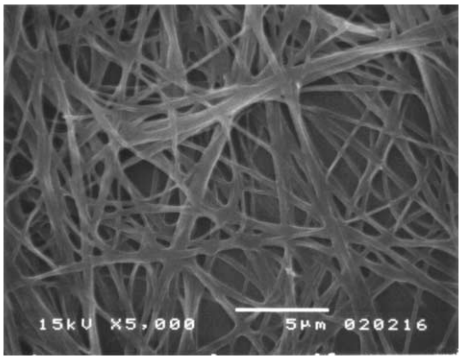


Fig. 1 SEM image of self-assembled fibres of **1** formed in pyridine.

Fig. 2 shows the melting temperatures (T_m) of toluene gels based on **1** as a function of concentration. T_ms are determined by the dropping-ball method.[22] The T_m increases from 53 °C to 68 °C as the concentration of **1** increases from 10 g L^{-1} to 50 g L^{-1}. The T_ms are dependent on the solvents. For apolar solvents such as benzene, toluene, and tetrachloromethane, the gels containing 40 g L^{-1} of **1** are stable around 65 °C on heating, while the gels of pyridine and chloroform with the same amount of **1** melt around 35 °C. These T_ms are relatively low in comparison to those of other bisurea gelators reported previously.[4–6] The T_ms are sensitive to the self-assembled structures of gelators and solvents. Generally, urea compounds form bifurcated hydrogen bonds with thermal stability. It is expected that the nitrogen of the pyridyl unit affects the hydrogen bonding pattern of the urea groups of **1**.

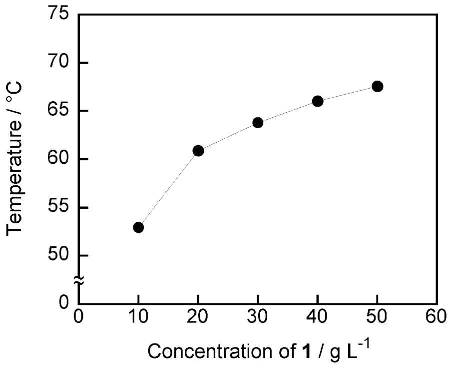


Fig. 2 Melting temperatures of toluene gels based on **1**.

Self-assembled structures of a pyridine-based gelator

The X-ray crystallographic study has shown that the pyridine-based bisurea compounds form unusual self-assembled structures for urea compounds. Though no single crystal of gelator **1** suitable for X-ray analysis was obtained, the crystal structure of an analogous compound **4** with shorter alkyl chains was determined. Compound **4** loses gelation ability. Molecules of **4** form a zigzag layered structure in the crystal as shown in Fig. 3a. Details of the hydrogen-bonded structure are shown in Fig. 3b. One of two urea units in molecule **4** is involved in bifurcated intermolecular hydrogen bonds, leading to the formation of 1D molecular arrays.

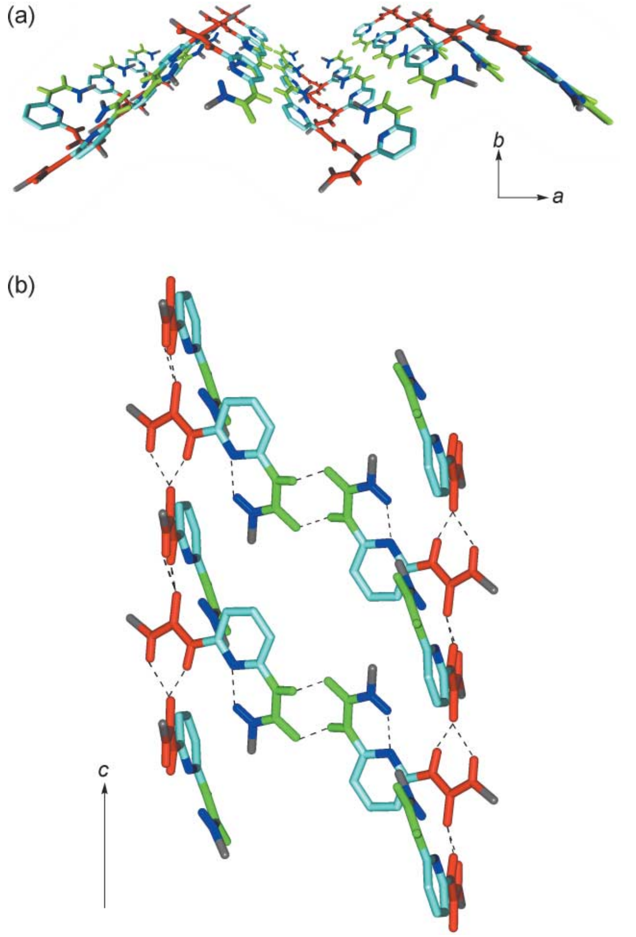


Fig. 3 Layered structure (a) and hydrogen-bonding pattern (b) in the crystal of **4**. Hydrogen atoms and alkyl chains are omitted for clarity.

As expected, another urea unit forms intramolecular hydrogen bonds with the pyridyl nitrogen. It induces the formation of new intermolecular hydrogen bonds which act as linkers of these 1D molecular arrays as shown in Fig. 3b. The formation of intramolecular hydrogen bonds is entropically favorable process compared with intermolecular hydrogen bonds. In addition, 6-membered ring structures are formed by these intramolecular hydrogen bonds. Therefore, this self-assembled structure is stable. X-Ray studies on other analogous compounds of **1** with shorter alkyl chains show similar trends to **4**, in that they form intramolecular hydrogen bonds as well as bifurcated hydrogen bonds. Similar hydrogen bonding patterns were reported for *N*-methyl-*N′*-pyridylurea and naphthyridine derivatives.[20] The formation of intramolecular hydrogen bonds between nitrogen atoms on heterocycles and the N–H of urea groups was also seen in 2-ureido-4[1*H*]-pyrimidinones.[19] Concentration-dependent ^{1}H NMR measurements of **1** convince us that the hydrogen bonding pattern of **1** is similar to that of **4**. Changes in the spectral positions of urea N–H protons were traced. As shown in Fig. 4, spectral positions of the proton of N–H adjacent to the alkyl chain are around 7 ppm even in lower concentration ranges for pyridine-based **1**. This spectral position is much downfield shifted than that of **3** (5.7 ppm) which forms only bifurcated hydrogen bonds. In addition, only small shifts are observed for the proton of N–H adjacent to the alkyl chain in **1**, while the protons of N–H adjacent to the pyridyl unit show downfield shifts as the concentration increases. In the case of **3**, both urea N–H protons show downfield shifts. These results indicate that the urea N–H adjacent to the alkyl chain is involved in intramolecular hydrogen bonds in the molecules of **1**. Though it is difficult to compare **1** and **4** directly due to the lack of solubility of **4** to chloroform at 25 °C, small concentration-dependence is attributable to intramolecular interactions. Therefore, a hydrogen-bonded structure of **1** in the self-assembled fibres can be described as shown in Fig. 5a. 1D molecular arrays of **1** are formed through intermolecular bifurcated hydrogen bonds with one urea group of molecule **1**. These molecular arrays are linked by intermolecular hydrogen bonds with the other urea group which is involved in intramolecular hydrogen bonds with a pyridyl nitrogen. This leads to the formation of bundles of molecular arrays. Self-assembled fibres of **1** consist of these bundles. Relatively low T_ms of **1** as mentioned above can be explained by this hydrogen bonding pattern in which intramolecular hydrogen bonds partially disturb the formation of stable bifurcated hydrogen bonds. In addition, this hydrogen bonding pattern cannot be achieved by bisurea compounds **2** and **3** with a benzene core, as well as diamide compound **5** derived from 2,6-diaminopyridine which has poor gelation ability. Based on previous studies of urea gelators[4–6] and other crystallographic studies,[17] it is reasonable to consider benzene-based bisurea compounds form two bifurcated hydrogen bonds as shown in Fig. 5b. It seems that the existence of a pyridyl moiety and two urea groups located adjacent to each other plays a key role for effective gelation. Gelator **1** is the first example to exploit incorporation of intra- and intermolecular hydrogen bonding.

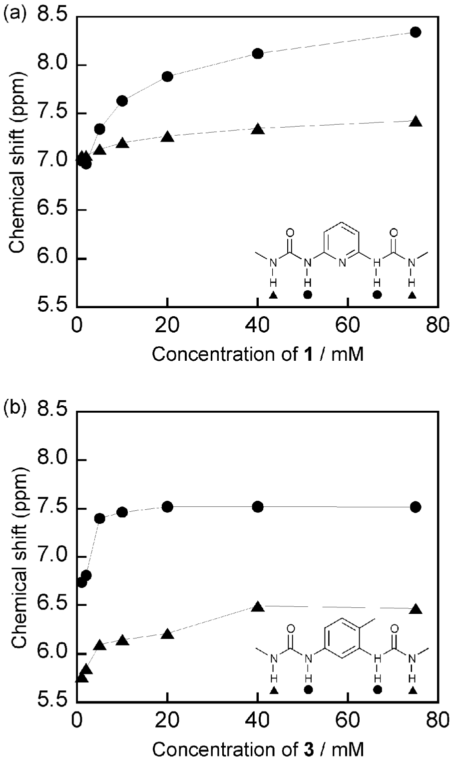


Fig. 4 Concentration-dependent ^{1}H NMR shifts of **1** (a) and **3** (b) in $CDCl_3$ at 25 °C.

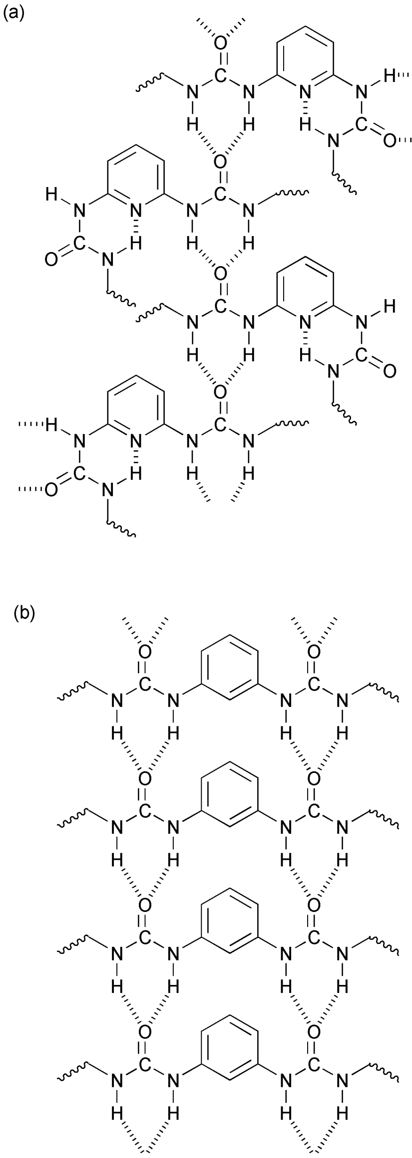
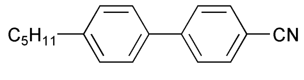


Fig. 5 Hydrogen-bonded structures of pyridine-based **1** (a) and benzene-based **2** (b).

Self-assembly in liquid crystals

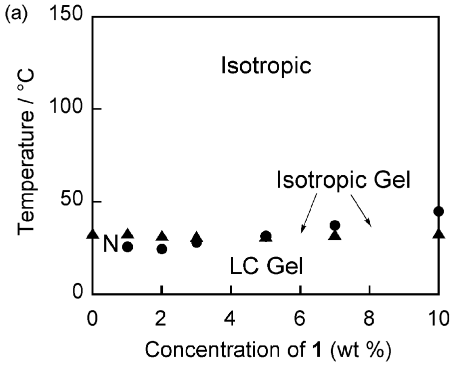
The effects of incorporation of intra- and intermolecular hydrogen bonding are more distinct when gelation occurs in LC solvents. As shown in Table 1, bisurea compounds **1**, **2**, and **3** can successfully gelate room temperature nematic liquid crystal **5CB**, which exhibits a nematic phase below 34 °C (Chart 2).



5CB

Chart 2 Chemical structure of 5CB.

It is noted that compounds **2** and **3** which have poor gelation ability for common organic solvents can specifically gelate LC solvents. Phase transition behavior of the mixtures of **5CB** and bisurea gelators changes drastically with aromatic cores as shown in Fig. 6. Benzene-based gelators **2** and **3** exhibit high sol-gel transition temperatures due to the formation of thermally stable bifurcated hydrogen bonds. For example, the



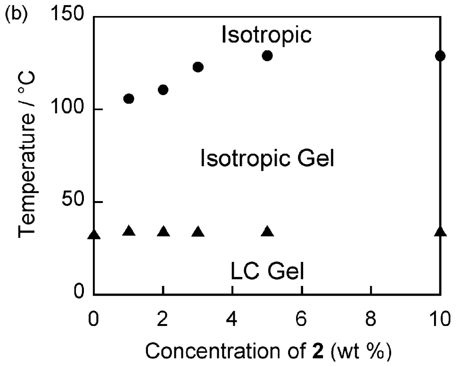


Fig. 6 Phase diagrams of the mixtures of **5CB** with **1** (a) and **2** (b). N: nematic.

sol-gel transition temperatures of the mixtures of **5CB** with 10 wt% of **2** and **3** are 129 and 124 °C, respectively. On the other hand, the sol-gel temperatures of the mixtures with pyridine-based gelator **1** are much lower. Even the mixture of **5CB** with 10 wt% of **1** exhibits a sol-gel transition at 45 °C which is lower by about 85 °C than the mixture with **2**. This is due to the partial deformation of the bifurcated hydrogen bonds, which agrees with the results of the X-ray crystallography and NMR experiments mentioned above. The isotropic-nematic transition temperatures of **5CB** are not affected by the addition of gelators. The morphologies of the self-assembled fibres of pyridine-based gelator **1** are also different from benzene-based gelators as shown in Fig. 7. Benzene-based gelator **2** forms short and thick fibres similar to needle-like crystals. Thick aggregates are formed for gelator **3**. These are due to the formation of strong bifurcated hydrogen bonds between urea groups. In contrast to **2** and **3**, pyridine-based gelator **1** forms elongated thin fibres. These fibres are finely dispersed in the solvents. It is considered that the partial deformation of bifurcated hydrogen bonds in molecule **1** prevents thick aggregation. One of the interesting properties of LC gels is electrooptic effects resulting from LC components.[13,14] Response behavior to electric fields can be tuned by the choice of liquid crystals and gelators. Differences between pyridine-based **1** and benzene-based **2** and **3** are also observed in electrooptic effects of LC gels in TN cells. For example, a faster response is observed for the **5CB** gel with **1**. The response time is 4 ms for the **5CB** gel with 1 wt% of **1**, while that of the single component of **5CB** is 12 ms. We previously reported faster responses of LC gels based on an amino acid gelator.[13,14*b*,*c*] The response time of the gel based on **1** is shorter than that of the gel based on the amino acid gelator. A faster response is not observed for **5CB** gels with **2** or **3**. This difference in electrooptic effect arises from the difference in the self-assembled fibres and their network structures as shown in Fig. 7.

Conclusion

We have reported here unusual self-assembling behavior of pyridine-containing bisurea compound **1**. The pyridyl unit acts as a hydrogen bond acceptor and forms intramolecular hydrogen bonds with urea N–H. This leads to the partial deformation of bifurcated hydrogen bonding between urea groups which is typical for urea compounds. This hydrogen-bonded structure is key for the fibrous self-assembly along with efficient gelation. This is the first example of a low-molecular-weight gelator efficiently incorporating intra- and intermolecular hydrogen bonding for self-assembly. In addition, LC gels based on this gelator exhibit good electrooptic properties. Thus, pyridine-based bisurea compound **1** is not only effective in gelation but also useful as a component of functional soft materials. This molecular design toward the control of hydrogen-bonded structures would serve a new approach for the development of low-molecular-weight gelators and various functional molecular materials.

Experimental

General method

Unless otherwise noted, chemical reagents and solvents were used without further purification. As for tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and dichloromethane, commercially available anhydrous solvents were used for reaction. Aromatic diamines such as 1,3-phenylenediamine and 2,6-diaminopyridine were purified with active charcoal followed by recrystallization from methanol. All reactions were carried out under an argon atmosphere. ^{1}H NMR 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 2,6-di(3-(1-dodecyl)ureido)pyridine (1). To a solution of 2,6-diaminopyridine (1.20 g, 11.0 mmol) in dichloromethane (50 mL), a solution of dodecylisocyanate (4.88 g, 23.1 mmol) in dichloromethane (30 mL) was slowly added at 0 °C. The reaction mixture was stirred for 3 days at room temperature. Then the solution was extracted with chloroform. The organic layer was washed with water and brine followed by drying on anhydrous $MgSO_4$. After filtration the solvent was

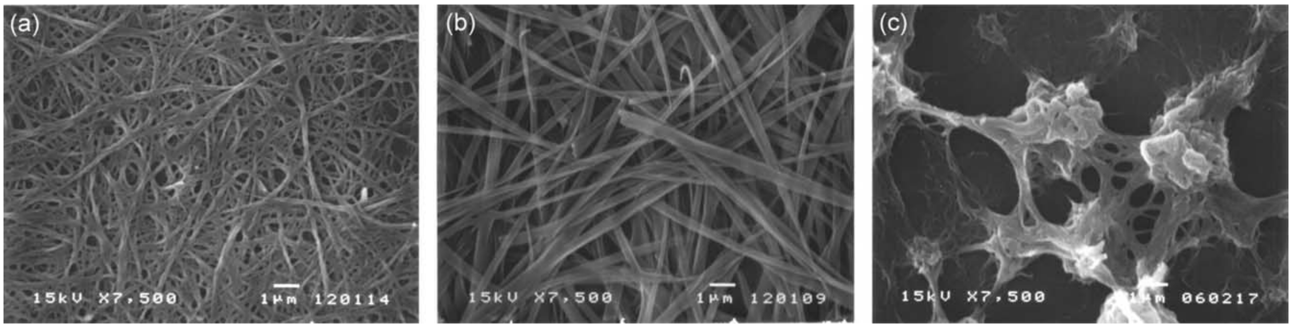


Fig. 7 SEM images of self-assembled fibres of **1** (a), **2** (b) and **3** (c) formed in **5CB** after the extraction of **5CB**.

removed under reduced pressure. The residue was purified by column chromatography first with chloroform and then with chloroform–methanol (40 : 1) as eluent to afford **1** (4.85 g, 83%) as a white solid (Found: C, 69.74; H, 10.63; N, 13.41. Calc. for $C_{31}H_{57}N_5O_2$: C, 70.01; H, 10.80; N, 13.17%); mp 130 °C (from chloroform–hexane); IR (KBr): ν 3334 cm^{-1} (N–H), 1636 cm^{-1} (amide I), 1571 cm^{-1} (amide II); ^1H NMR: (d_6-DMSO, 400 MHz) δ 8.87 (s, 2H, ArN*H*), 7.57 (m, 2H, N*H*CH$_2$), 7.48 (t, J = 8.8 Hz, 1H, Ar*H*), 6.87 (d, J = 8.1 Hz, 2H, Ar*H*), 3.11 (q, J = 6.6 Hz, 4H, NHC*H*$_2$), 1.46–1.43 (m, 4H, NHCH$_2$C*H*$_2$), 1.25–1.22 (m, 36H, C*H*$_2$), 0.84 (t, J = 6.4 Hz, 6H, C*H*$_3$); ^{13}C NMR (d_6-DMSO, 100 MHz): δ 154.46, 151.25, 139.71, 103.29, 31.31, 29.66, 29.04, 28.80, 28.74, 26.44, 22.11, 13.96.

Synthesis of 1,3-di(3-(1-dodecyl)ureido)benzene (2). Starting from 1,3-phenylenediamine (0.43 g, 4 mmol) and dodecylisocyanate (1.69 g, 8 mmol), the procedure reported by van Esch *et al.*[5b] afforded **2** (1.46 g, 69%) as a white solid; mp 178 °C; ^1H NMR (d_6-DMSO, 400 MHz) δ 8.28 (s, 2H, ArN*H*), 7.44 (s, 1H, Ar*H*), 6.95 (t, J = 1.6 Hz, 1H, Ar*H*), 6.90 (d, J = 2.2 Hz, 2H, Ar*H*), 5.98 (t, J = 0.54 Hz, 2H, N*H*CH$_2$), 3.30–3.24 (m, 4H, NHC*H*$_2$), 1.41–1.35 (m, 4H, NHCH$_2$C*H*$_2$), 1.33–1.23 (m, 36H, C*H*$_2$), 0.84 (t, J = 6.5 Hz, 6H, C*H*$_3$).

Synthesis of 1-methyl-2,4-di(3-(1-dodecyl)ureido)benzene (3). To a solution of dodecylamine (4.63 g, 25 mmol) in THF (40 mL), a solution of 2,4-diisocyanato-1-methylbenzene (0.87 g, 5 mmol) in THF (30 mL) was slowly added at 0 °C. The reaction mixture was stirred for 4 h at room temperature. The resultant mixture was filtered to give a white solid. This solid was stirred with diethyl ether for 4 h at room temperature and was collected by filtration to afford **3** (2.66 g, 98%) as a white solid (Found: C, 72.41; H, 10.87; N, 10.49. Calc. for $C_{33}H_{60}N_4O_2$: C, 72.74; H, 11.10; N, 10.28%); mp 187 °C; IR (KBr): ν 3308 cm^{-1} (N–H), 1633 cm^{-1} (amide I), 1585 cm^{-1} (amide II); ^1H NMR (d_6-DMSO, 400 MHz) δ 8.33 (s, 1H, ArN*H*), 7.78 (s, 1H, ArN*H*), 7.54 (s, 1H, Ar*H*), 7.18 (d, J = 7.6 Hz, 1H, Ar*H*), 6.98 (d, J = 7.6 Hz, 1H, Ar*H*), 6.57 (m, 1H, N*H*CH$_2$), 6.01 (m, 1H, N*H*CH$_2$), 3.11 (q, J = 5.6 Hz, 4H, NHC*H*$_2$), 2.14 (s, 3H, ArC*H*$_3$), 1.53–1.40 (m, 4H, NHCH$_2$-C*H*$_2$), 1.39–1.23 (m, 36H, C*H*$_2$), 0.92 (t, J = 6.4 Hz, 6H, CH$_2$C*H*$_3$); ^{13}C NMR (d_6-DMSO, 100 MHz, 60 °C) : δ 155.41, 148.09, 138.64, 138.24, 129.85, 119.65, 112.00, 110.84, 31.25, 29.80, 28.98, 28.76, 28.63, 26.42, 22.01, 17.06, 13.82.

Synthesis of 2,6-di(3-(1-octyl)ureido)pyridine (4). This compound was synthesized as described above for **1**, starting from 2,6-diaminopyridine (0.49 g, 4.5 mmol) and octylisocyanate (1.47 g, 9.5 mmol). The crude product was purified by column chromatography first with chloroform and then with chloroform–methanol (40 : 1) as eluent to afford **4** (1.34 g, 71%) as a white solid (Found: C, 65.60; H, 9.71; N, 16.71. Calc. for $C_{23}H_{41}N_5O_2$: C, 65.83; H, 9.85; N, 16.69%); mp 177 °C (from chloroform–hexane); IR (KBr): ν 3367 cm^{-1} (N–H), 1644 cm^{-1} (amide I), 1566 cm^{-1} (amide II); ^1H NMR: (d_6-DMSO, 400 MHz) δ 8.87 (s, 2H, ArN*H*), 7.55 (m, 2H, N*H*CH$_2$), 7.48 (t, J = 8.4 Hz, 1H, Ar*H*), 6.90 (d, J = 8.0 Hz, 2H, Ar*H*), 3.11 (q, J = 6.8 Hz, 4H, NHC*H*$_2$), 1.47–1.43 (m, 4H, NHCH$_2$C*H*$_2$), 1.26–1.24 (m, 20H, C*H*$_2$), 0.84 (t, J = 6.8 Hz, 6H, C*H*$_3$); ^{13}C NMR (d_6-DMSO, 100 MHz): δ 154.24, 151.08, 139.34, 103.27, 30.93, 29.40, 28.44, 28.34, 26.17, 21.74, 13.55.

Synthesis of 2,6-di(tridecanoylamino)pyridine (5). To a solution of 2,6-diaminopyridine (0.327 g, 3.0 mmol) and triethylamine (0.85 ml) in dichloromethane (10 mL), a solution of tridecanoyl chloride (1.54 g, 6.6 mmol) in dichloromethane (5 mL) was slowly added at 0 °C. The reaction mixture was stirred for 12 h at room temperature. Then the solution was extracted with chloroform. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine followed by drying on anhydrous $MgSO_4$. After filtration the solvent was removed under reduced pressure to afford **4** (1.26 g, 83%) as a white solid (Found: C, 74.39; H, 11.23; N, 8.94. Calc. for $C_{31}H_{55}N_3O_2$: C, 74.20; H, 11.05; N, 8.37%); mp 122 °C (from hexane–ethanol); IR (KBr): ν 3308 cm^{-1} (N–H), 1637 cm^{-1} (amide I), 1569 cm^{-1} (amide II); ^1H-NMR: (CDCl$_3$, 400 MHz) δ 7.90 (d, J = 8.8 Hz, 2H, Ar*H*), 7.65 (t, J = 7.2 Hz, 1H, Ar*H*), 7.53 (s, 2H, N*H*), 2.37 (t, J = 7.3 Hz, 4H, COC*H*$_2$), 1.72 (t, J = 7.7 Hz, 4H, COCH$_2$C*H*$_2$), 1.37–1.22 (m, 36H, C*H*$_2$), 0.88 (t, J = 6.8 Hz, 6H, C*H*$_3$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 171.53, 149.35, 140.88, 109.30, 37.87, 31.90, 29.62, 29.44, 29.33, 29.18, 25.33, 22.68, 14.13.

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. As for the gelation of liquid crystals, both a liquid crystal and a gelator were weighed and mixed at various ratios 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 and 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 a minimum gel concentration (MGC) was determined. MGC is the minimum concentration of a gelator necessary for gelation. When the mixture remained as a 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. In some cases, a solution with high viscosity was obtained without gelation or precipitation. It was distinguished from a gel, and considered as a "viscous solution".

Determination of the melting temperatures of organogels

For the determination of the melting temperatures of organogels, the "dropping-ball" method[22] was used. A steel ball was placed on top of the gel in a test tube. Then the tube was sealed and heated in a stirred oil bath with a thermometer. As the temperature gradually increased, the position of the ball was monitored as well as the temperature of the bath. The temperature at which the steel ball reached the bottom of the tube was taken as the melting temperature.

Crystal structure determination of compound 4

Suitable colorless single crystals of **4** were grown from dimethylformamide solution by a slow evaporation method. Data collection was performed on a MacScience DIP 2000 Image Plate System using MoK$_\alpha$ radiation (λ = 0.7107 Å) operating at 40 kV and 200 mA.†

Crystal data for **4**: $C_{23}H_{41}N_5O_2$, M = 419.6, colorless, 0.92 × 0.49 × 0.28 mm^3, orthorhombic, *Pccn* (no. 56), Z = 8, a = 21.200(3) Å, b = 26.956(6) Å, c = 9.2050(11) Å, V = 5260(2) Å^3, μ(MoK$_\alpha$) = 0.07 mm^{-1}, ρ_{calcd} = 1.06 g cm^{-3}, 11982 reflections measured, 4736 unique (R_{int} = 0.045) reflections. The final R = 0.094, R_w = 0.162 for 2441 reflections with [$I > 1.0\sigma(I)$], 271 parameters, GOF = 0.814.

Scanning electron microscopic (SEM) observation

For the SEM observation of self-assembled fibres of **1** formed in organic solvents, **1** was dissolved in pyridine 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. As for self-assembled fibres

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† CCDC reference number 213793. See http://www.rsc.org/suppdata/ob/b3/b307149a/ for crystallographic data in .cif or other electronic format.

of **1** formed in liquid crystals, SEM samples were prepared differently. The mixture of **5CB** and **1** in isotropic states were placed between glass slides. This glass cell was cooled to room temperature to form self-assembled fibres of **1**. SEM samples were prepared by immersing the glass cell in hexane for 12 h to extract the LC solvent followed by drying at room temperature. All the samples were shaded with gold and used for SEM observation. SEM observation was performed with a Jeol JSM-5400/LV. The accelerating voltage was 15 kV.

Determination of phase transition behavior of liquid crystalline gels

Phase transition behavior of the samples with a liquid crystal was determined by DSC measurements and microscopic observation. Heating and cooling rates were 5 °C min^{-1} in all cases. Transition temperatures were taken at the maximum of transition peaks. A polarizing microscope, Olympus BH2 equipped with a Mettler FP82HT hot stage was used for visual observation.

Measurement of electrooptic effects of liquid crystalline gels

Measurements of electrooptic effects in the liquid crystalline gels were performed with twisted nematic (TN) cells 16 μm thick. The cell contained sandwiched ITO (indium tin oxide) glasses coated with polyimide (JSR AL1254) layers, in which the rubbing direction of the two surfaces was perpendicular. The response time was measured at 10 V. Alternating current (AC) fields (300 Hz) were applied to the cells. A He–Ne laser (633 nm) was used as a light source.

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