Self-Assembly of Bisurea Compounds in Organic Solvents and on Solid Substrates

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Abstract: New low molecular weight gelators based on the structure R-NHCONH-X-NHCONH-R have been synthesized and tested for their ability to cause gelation of organic solvents. Compounds **2** (R = *n*-dodecyl, X = -$(CH_2)_9$-), **3** (R = *n*-dodecyl, X = -$(CH_2)_{12}$-), **4** (R = *n*-dodecyl, X = 4,4´-biphenyl), and **5** (R = benzyl, X = -$(CH_2)_9$-) form thermoreversible gels with a wide range of organic solvents, at concentrations well below 10 mg mL^{-1}. Depending on the nature of the R and X groups, the solvents that undergo gelation include hexadecane, *p*-xylene, 1-octanol, *n*-butyl actetate, cyclohexanone, and tetralin. The gels are stable up to temperatures well above 100 °C, but are easily disrupted by mechanical agitation. Light microscopic investigations revealed that compounds **2**-**5** spontaneously aggregate to form thin flat fibers, which can be several hundreds of micrometers long and only 2-10 μm wide. Depending on the solvent, multiple twists in the fibers are observed. In the gels, these fibers form an extended three-dimensional network, which is stabilized by multiple mechanical contacts between the fibers. Electron microscopy and X-ray powder diffraction revealed that the fibers consist of stacks of sheets. The thickness of the sheets is 3.65 and 3.85 nm for **2** and **3**, respectively. Scanning tunneling microscopic investigations of **2** absorbed on graphite showed that **2** forms long ribbons with a width of 5.0 nm. In the ribbons the molecules have a parallel arrangement, with the long molecular axis perpendicular to the long ribbon axis. The two urea groups within a given molecule are each part of mutually parallel extended chains of hydrogen bonds. Based on these observations a model is proposed for the arrangement of the molecules in the fibers. In this model the bisurea molecules aggregate through hydrogen-bond formation into long ribbons, which assemble into sheets. In these sheets the ribbons are tilted. Finally, the sheets stack to form long thin fibers. This model is supported by molecular dynamics simulations.

Keywords
gels · electron microscopy · scanning tunneling microscopy · self-assembly · ureas

Introduction

Rules by which small organic molecules can be assembled into supramolecular structures of predesigned size and shape are becoming clearer.[1, 2] The same is true of some aggregation phenomena in which the associative processes can, to a certain extent, be controlled through design of the building blocks.[3] We have been interested in the gelation of organic solvents induced by small organic molecules and in the way that gelation phenomena are coupled with the formation of large supramolecular assemblies.[4] However, the structures of such gels are poorly understood, and serendipity appears to have been the major guiding principle in this particular area.[4, 5] Most of the gelating molecules known so far possess at least one moiety that can participate in highly directional noncovalent interactions with other gelator molecules. Aggregation of these molecules can, for instance, lead to extended one-dimensional arrays of hydrogen bonds. This principle has elegantly been applied in the design of new gelators for organic solvents.[6] Very recently, the capacity of urea derivatives to form extended chains of hydrogen bonds[7] has been explored by Hanabusa and coworkers[8] and our group[9] with the aim of designing new gelators[10] and of forming constructs of nanodimensions. In this study, we prepared a series of bisurea compounds that spontaneously assemble into fibers and examined their ability to induce gelation of organic solvents. Detailed information on the structure of the fibers was obtained by using a combination of electron microscopy, X-ray diffraction, and scanning tunneling microscopy.

Results and Discussion

Structures composed of two urea groups connected by a spacer group X are attractive building blocks, since they are readily

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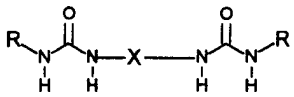
obtained from simple starting materials and can form up to eight hydrogen bonds with neighboring molecules in their aggregates. Compounds **1**-**6** (Table 1), prepared from the corresponding isocyanates and diamines, are sparingly soluble in organic solvents at room temperature (Table 2), but gradually dissolve upon heating to between 90 and 150 °C.[11] With aliphatic or aromatic hydrocarbons or cyclohexanone as the solvent, the isotropic solutions of **2** and **3** form stable gels upon cooling (Table 2). The minimum gelation concentrations for **2** are remarkably low (<3 mg mL^{-1}) and do not depend on the solvent used. When the dodecyl chain is replaced by more sterically demanding groups, as in **5** and **6**, or the long flexible linker is replaced with a shorter linker, as in **1**, or a more rigid linker, as in **4**, the gelating abilities change. For instance higher minimum gelation concentrations are found for **6** (Table 2).

Table 1. Bisurea derivatives examined in this paper.



	R	X
1	*n*-dodecyl	-$(CH_2)_6$-
2	*n*-dodecyl	-$(CH_2)_9$-
3	*n*-dodecyl	-$(CH_2)_{12}$-
4	*n*-dodecyl	4,4′-biphenyl
5	benzyl	-$(CH_2)_9$-
6	(*R*)-1-phenylethyl-	-$(CH_2)_9$-

Table 2. Ability of bisurea compounds to act as gelators [a].

	Hexadecane	*p*-Xylene	1-Octanol	*n*-Butyl acetate	Cyclohexanone	Tetralin
1	p	p	p	p	p	g
2	g(3)	g(3)	p	g(3)	g(3)	g(3)
3	g	g	p	p	g	g
4	i	g	p	p	p	g
5	i	g(10)	g(10)	p	g	g(7)
6	p	p	p	p	p	g

[a] The following abbreviations are used: gelation: g (minimum gelation concentration at 20 °C in mg compound per mL solvent); insoluble at solvent reflux temperature: i; precipitate: p.

The gels formed by these bisurea compounds are stable for months, but are irreversibly disrupted by mechanical agitation. However, they can be restored by heating above the melting temperature followed by cooling to room temperature; this indicates that gel formation is thermoreversible. The melting temperatures of the gels clearly increase with increasing concentration, but level off at higher concentrations (Figure 1 A). The melting temperature of a gel of **2** at a concentration of 12 mg mL^{-1} in tetralin is 116°C. This corresponds nicely to the onset of the melting endotherm at 117°C, measured by differential scanning calorimetry (Figure 1 B). A broad endotherm with a maximum at 125°C points to a less cooperative phase transition. The enthalpy of melting for a gel of **2** in tetralin is 160 kJ mol^{-1}. FTIR spectra of dried gels of **2** and **3** show amide I and amide II bands at 1616 and 1575 cm^{-1} and an NH stretch

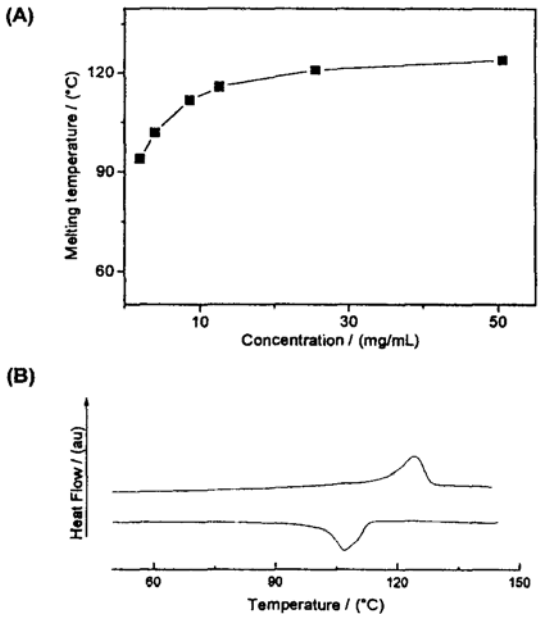


Figure 1. A) Variation of the melting temperature a gel of **2** in tetralin with the concentration of **2**. B) DSC heating (top) and cooling (bottom) traces of a gel of **2** in tetralin (10 mg mL^{-1}).

vibration at 3337 cm^{-1}. These bands are characteristic of the presence of hydrogen-bonded urea groups.[12]

With the aromatic solvents *p*-xylene and tetralin, the bisurea compounds form transparent gels, whereas with the other solvents turbidity is observed. Light microscopy reveals that the gels are strongly birefringent. In gels of **2** and **3** many small fiberlike structures are observed, and the gels appear to consist of an entangled network of such fibers (Figure 2 A and 2 B).[13, 14] These fibers are only 2-5 μm thick, but can be as long as 300-400 μm. The formation of fibers does not necessarily lead to the formation of a gel. For instance, compound **3** forms a precipitate in butyl acetate, and examination with light microscopy reveals the presence of many fibers (Figure 2 C). However, these fibers are broader (up to 10 μm) and shorter (100-200 μm) then those observed in gels. The single fibers in Figure 2 B and 2 C show repetitions of strongly birefringent regions and dark regions, indicating that the fibers are highly twisted. The thickness of the fibers cannot be determined from these micrographs. Both the width of the fibers and the degree of twisting depend on the compound as well as on the solvent. In general, fibers of compound **3** are somewhat broader than those formed by **2**, and fibers in butyl acetate are more strongly twisted than those in tetralin.

The organization in the fibers was further examined by electron microscopy (EM).[14] From the electron micrographs of a gel of **2** in tetralin, it is clear that fibers have a multilayered structure (Figure 2 D and 2 E). Typically 5 to 20 sheets are stacked in a single fiber. The thickness (d) of the fibers and sheets can be calculated from the length (l) of the shadow (applied at an angle α), by means of the equation $d = l\tan(\alpha)$. From Figure 2 E we obtained a value of 0.13 μm for the thickness of the fiber, which consists approximately of 20 sheets, giving a thickness of ± 7 nm for a single sheet. The shadow length of the top sheet in the fiber is approximately 12 nm, corresponding to a thickness of 2.2 nm. Based on these results we estimate the

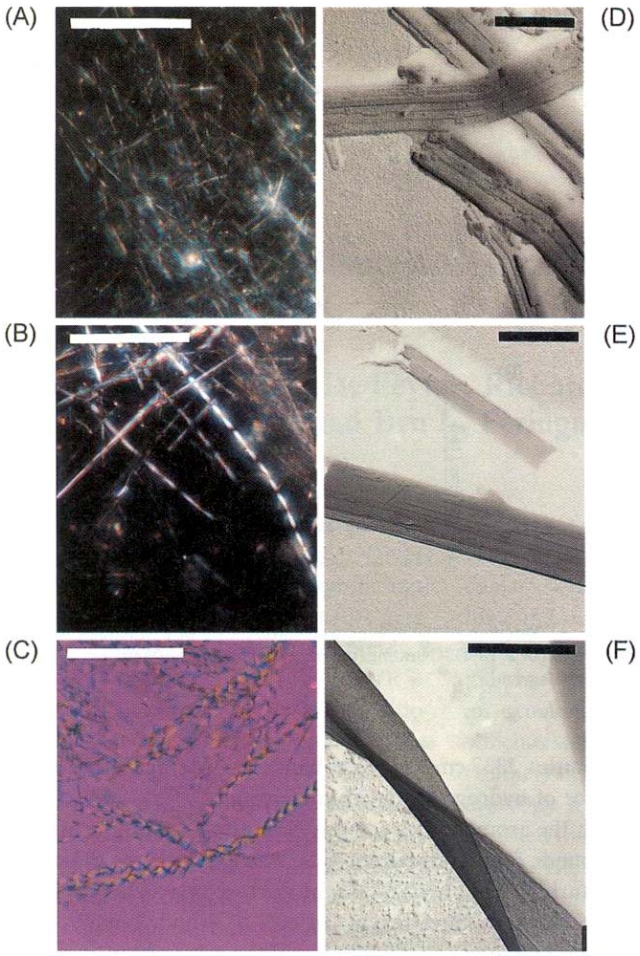


Figure 2. Photographs taken with a light microscope of a gel of **2** in tetralin (A, crossed polarizers, bar is 100 μm), in butyl acetate (B, crossed polarizers, bar is 100 μm), and of **3** in butyl acetate (C, crossed polarizers and 1/4 λ plate, bar is 100 μm), Electron micrographs of a gel of **2** in tetralin (D and E, bar is 0.5 μm), and in hexadecane (F, bar is 0.5 μm).

thickness of each sheet to be approximately 5 nm. Figure 2 F shows an EM picture of a single fiber of **2** in hexadecane. One can clearly see that the twist observed in the light micrographs is a single turn of the sheets along the long axis of the fiber, rather than multiple turns or even crumpling of the sheets. Networks of fibers from other systems are often stabilized by the presence of junction zones, which can be observed as fused or intertwined fibers.[15] However, we did not observe such structures either by EM or by light microscopy.

The strong birefringence of the fibers indicates that they consist of well-ordered arrays of molecules. Furthermore, the elongated shape of the fibers must be the result of a strong anisotropic growth, also indicative of a well-ordered molecular packing.[16] Powder diffraction[17] of the native gels did not reveal any reflections between 1.5 and 35°. After most of the solvent had been removed in the low-angle region 3 to 4 Bragg reflections were observed with a periodicity of 1/1,1/2, 1/3 and 1/4, consistent with a lamellar structure.[18] The spacings of these lamella are 3.65 and 3.89 nm for **2** and **3**, respectively, in good agreement with the thicknesses of the sheets estimated from EM. Remarkably, except for a clear reflection at 0.38 nm, we observed no other reflections in the range from 5.8 to 0.25 nm.

In order to obtain a more detailed picture of the organization at the molecular level, we investigated the structure of layers of these gelators deposited on graphite by scanning tunneling microscopy (STM). This technique provides a powerful tool in the study of the two-dimensional organisation of molecules physisorbed on a conductive surface.[19, 20] Monolayers of **2** physisorbed at the graphite/1-octanol interface were imaged by STM. A closely packed arrangement of molecules of **2** on the graphite surface with submolecular resolution can be distinguished in Figure 3 A. The darker regions in the image correspond to the location of the alkyl groups of the molecules. For the urea groups, however, two different types of contrast are observed. Some ribbons are characterized by bright spots correlated with the position of the urea groups.[21] In other ribbons the urea groups appear almost as dark as the regions correlated to the position of the alkyl groups. It is very unlikely that these differences are due to the coexistence of two different 2 D crystals. No domains are formed by only one type of ribbon. The different types of ribbons coexist randomly since the contrast of the urea groups in one ribbon is not influenced by its neighbors. The width of a ribbon (5.0±0.1 nm) and the intermolecular distance within a ribbon (0.462±0.005 nm)[22] are the same for both types of ribbon. The latter value is in very good agreement with the distances found for hydrogen-bonded urea moieties.[23]

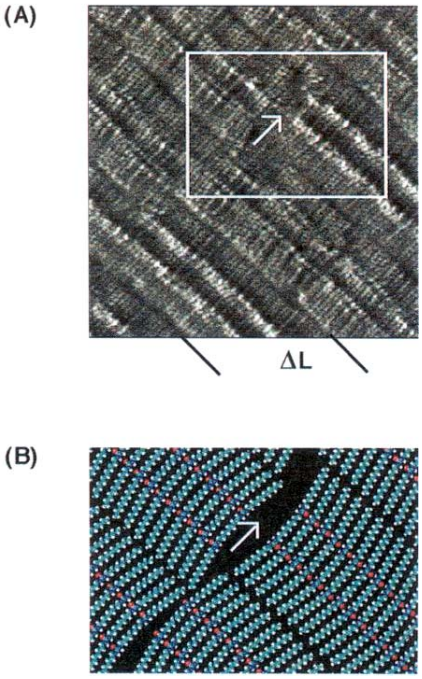


Figure 3. A) STM image of an ordered monolayer of **2** formed by physisorption from 1-octanol at a liquid/graphite interface. Image size: 13.5 × 13.5 nm^2, ΔL is the width of one ribbon of molecules of **2**. The arrow indicates the defect where hydrogen bonds are broken. B) Molecular model for the two-dimensional packing of **2**.

From molecular modeling, it is clear that for the minimum-energy conformation of **2** (all-*trans*), both carbonyl groups point almost in the same direction. Consequently, the shape of the molecule should be bent a little bit (Figure 3 B). Indeed, close inspection of high-quality images reveals such a bend. Comparison of ribbons with opposite contrast with regard to

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their urea groups shows that such ribbons are two-dimensional mirror images with the mirror plane perpendicular to the long ribbon axis. This implies that the angle between the carbonyl groups of the two ribbons is 180°. Therefore, the difference in contrast of the urea groups is correlated with the orientation of the carbonyl groups. This is also confirmed by STM imaging of bisurea compounds **1** and **3** which contain spacers with an even number of carbon atoms. In these cases, the carbonyl groups in a single molecule point in opposite directions in an all-*trans* conformation. For these molecules, the same differences with respect to the contrast of the urea groups are observed but now intramolecularly. A detailed discussion of these results will be published elsewhere.[24]

From a comparison of the thickness or width of the ribbons on graphite with the thickness of the sheets observed in gels of **2**, it becomes clear that these are related but not identical structures. The sheets most likely consist of stacks of ribbons of bisurea molecules (Figure 4A). In this arrangement the reflection at 0.381 nm observed in the powder diffractograms (vide supra) of **2** corresponds to the spacing of the ribbons within one sheet. A similar spacing has been found for the stacking of lamella in polyamide fibers.[25] Since the width of the ribbons (5.0 nm as estabished by STM) is significantly greater than the thickness of the sheets (3.65 nm), the ribbons are most probably tilted at an angle of 45° relative to the surface. Figures 4 B and 4 C show snapshots taken from a 200 ps molecular dynamics simulation of a rectangular box with 64 molecules of **2** arranged in 8 parallel stacked ribbons. Starting with tilt angles between 40 and 75° the simulations converge to a structure in which a sheet has a thickness of 4.1 nm and the ribbons make a tilt angle of ± 54° with the surface of the sheet (Figure 4 C). The spacing between successive ribbons is 0.40 nm, in good agreement with X-ray and STM data. The ribbons maintain a more or less planar structure, but in the plane of the ribbons the bisurea molecules are curved (Figure 4 B).

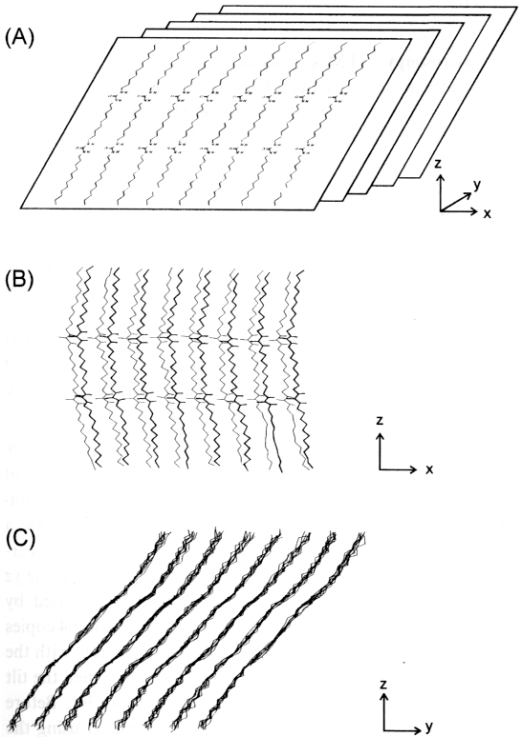

Figure 4. A) Schematic view of the arrangement of ribbons of bisurea compounds into sheets. B/C) Snapshots from a 100 ps MD simulation (300 K, NPT) of a box containing 64 molecules of **2**, showing two ribbons each consisting of 8 molecules of **2** (B, view along *y* axis; the other tapes are omitted for clarity). and a stack of 8 ribbons forming a sheet (C, view along *x* axis).

Conclusions

A new class of low molecular weight gelators comprising two urea groups connected by a spacer have been developed, which are very effective in inducing the gelation of various organic solvents at very low concentration. A notable feature of these gelators is that they are obtained from commercial starting materials (diamines and isocyanates). The simple bisurea compounds described in this paper spontaneously form highly ordered structures, namely, ribbons when absorbed on graphite and fibers in cooled homogeneous solution. These fibers form an extended three-dimensional network in solution, presumably stabilized by multiple mechanical contacts between the fibers, leading to efficient gelation of organic solvents.[26] The arrangement of the bisurea molecules within the ribbons and fibers could be elucidated in detail, and it is clear that they are aggregated through formation of multiple intermolecular hydrogen bonds between the urea moieties. The overall result is exceptionally long-term thermal stability of the structures. The well-defined molecular arrangement within the sheets and ribbons and the straightforward synthesis of the bisurea compounds offer excellent opportunities for the exploitation of this molecular architecture for the organization of other functional groups.

Experimental Procedure

Materials and methods: Solvents for synthesis were purified and dried when necessary according to standard procedures. The diamines and isocyanates were obtained form Aldrich or ACROS and purified by Kugelrohr distillation prior to use unless noted otherwise. The solvents for gelation experiments were of analytical grade and used as received. ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer (at 300 MHz), and chemical shifts are denoted in δ units relative to $CDCl_3$ or $[D_6]$DMSO and converted to the TMS scale with $\delta(CHCl_3) = 7.26$ or $\delta([D_5]DMSO) = 2.49$. ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer (at 75.48 MHz), and chemical shifts are denoted in δ units relative to $CDCl_3$ or $[D_6]$DMSO and converted to the TMS scale with $\delta(CHCl_3) = 76.91$ or $\delta(DMSO) = 39.5$. The splitting patterns in the ^{1}H NMR spectra are designated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad). Melting points were measured on a Mettler FP-2 melting point appartus equipped with a Mettler microscope. Infrared spectra were recorded on a Mattson Instruments Galaxy 4020 FTIR spectrometer. Elemental analyses were carried out in the Microanalytical Department of this laboratory.

1-Dodecyl-3-[6-(3-dodecylureido)hexyl]urea (1): Dodecylisocyanate (1.16 g, 5.5 mmol) was slowly added to a stirred solution of 1,6-diaminohexane (0.29 g, 2.5 mmol) in dichloromethane (30 mL). A gel-like precipitate was formed immediately. After stirring overnight, the crude product was collected by filtration as a white waxy solid. The product was purified by resuspending the waxy solid in dichloromethane (50 mL), stirring for 1 h, and collecting the product on a glass filter. This procedure was repeated when necessary. After drying at 60 °C under vacuum (15 mm Hg) **1** was obtained as a white solid in 87% yield. M.p. 198-199 °C; ^{1}H NMR (300 MHz, $[D_6]$DMSO, 120 °C,

TMS): δ = 5.42 (br s, 4H) 2.96 (m, 8 H) 1.35 (br, 8H) 1.26 (br, 40H) 0.85 (t, ^3J(H,H) = 6.4 Hz, 6H); ^{13}C NMR (75.48 MHz, [D$_6$]DMSO, 120 °C, TMS): δ = 157, 38.2, 38.1, 29.9, 28.7, 27.6, 27.4, 27.2, 25.1, 24.8, 20.6, 12.3, IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3335, 1614, 1574; $C_{32}H_{66}N_4O_2$ (538.90): calcd. C 71.32, H 12.34, N 10.40; found C 71.31, H 12.42, N 10.40.

1-Dodecyl-3-[9-(3-dodecylureido)nonyl]urea (2) was synthesized as described for **1**, starting from 1,9-diaminononane (0.8 g, 5 mmol) and dodecylisocyanate (2.3 g, 11 mmol). After drying at 60°C under vacuum (15 mm Hg) **2** was obtained as a white solid in 83% yield. M.p. 167-169 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 120 °C, TMS) δ = 5.4 (br s, 4H) 2.96 (m, 8 H) 1.35 (br, 8H) 1.27 (br, 46H) 0.85 (t, ^3J(H,H) = 6.5 Hz, 6H); ^{13}C NMR (75.48 MHz, [D$_6$]DMSO, 120 °C, TMS): δ = 157.6, 38.9, 30.5, 29.4, 28.2, 28.0, 27.8, 25.7, 21.2, 12.8; IR (KBr); $\tilde{\nu}$ (cm^{-1}) 3335, 1616, 1574; $C_{35}H_{72}N_4O_2$ (580.98): calcd. C 72.36, H 12.49, N 9.64, found C 72.24, H 12.42, N 9.46.

1-Dodecyl-3-[12-(3-dodecylureido)dodecyl]urea (3) was synthesized as described for **1**, starting from 1,12-diaminododecane (0.5 g, 2.5 mmol) and dodecylisocyanate (1.16 g, 5.5 mmol). After drying at 60 °C under vacuum (15 mmHg) **3** was obtained as a white solid in 90% yield. M.p. 166-167 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 120 °C, TMS): δ = 5.4 (br s, 4H) 2.96 (m, 8H) 1.38 (br s, 8H) 1.25 (s, 52H) 0.85 (t, ^3J(H,H) = 6.4 Hz, 6H); ^{13}C NMR (75.48 MHz, [D$_6$]DMSO, 120 °C, TMS): δ = 157, 38.3, 29.9, 28.8, 27.6, 27.5, 27.2, 25.1, 20.6, 12.2; IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3337, 1616, 1574; $C_{38}H_{78}N_4O_2$ (623.06): calcd. C 73.25, H 12.62, N 8.99, found C 73.21, H 12.73, N 8.98.

1-Dodecyl-3-[4′-(3-dodecylureido)biphenyl-4-yl]urea (4) was synthesized as described for **1**, starting from 4,4′-diaminobiphenyl (0.6 g, 3.3 mmol, recrystallized from water) and dodecylisocyanate (1.4 g, 6.6 mmol) using DMSO as the solvent. After drying at 60 °C under vacuum (15 mm Hg) **4** was obtained as a fine white powder in 55% yield. M.p. >260 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 120 °C, TMS): δ = 8.1 (s, 2H), 7.42 (m, 8H), 5.91 (t, ^3J(H,H) = 5.3 Hz, 2H), 3.1 (m, 4H), 1.46 (m,4H), 1.27 (s, 36H), 0.87 (t, ^3J(H,H) = 6.6 Hz, 6H); ^{13}C NMR (75.48 MHz, [D$_6$]DMSO, 120 °C, TMS): δ = 154.1, 138.3, 132.0, 124.8, 117.2, 29.9, 28.5, 27.6, 27.4, 27.2, 25.1, 20.6, 12.3; IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3335, 3302, 1631, 1556; $C_{38}H_{62}N_4O_2$ (606.94): calcd. C 75.20, H 10.30, N 9.23, found C 75.13, H 10.30, N 9.25.

1-Benzyl-3-[9-(3-benzylureido)nonyl]urea (5) was synthesized as described for **1**, starting from 1,9-diaminononane (0.8 g, 5 mmol) and benzylisocyanate (1.17 g, 10 mmol). After drying at 60°C under vacuum (15 mm Hg) **5** was obtained as a white solid in 86% yield. M.p. 194-196 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 95 °C, TMS); δ = 7.27 (m, 10H), 6.12 (br s, 2H),5.75 (br s, 2H), 4.21 (d, ^3J(H,H) = 5.9 Hz, 4H), 3.05 (m, 4H), 1.39 (m, 4H), 1.28 (s, 10H); ^{13}C NMR (75.48 MHz, [D$_6$]DMSO, 95 °C, TMS): δ = 157.8, 140.7, 127.7, 126.7, 126.1, 42.8, 39.1, 29.7, 28.6, 28.4, 26.0; IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3342, 3329, 1620, 1580; $C_{25}H_{36}N_4O_2$ (424.58): calcd. C 70.72, H 8.55, N 13.20, found C 70.37, H 8.56, N 13.06.

(R,R)-1-(1-Phenylethyl)-3-{9-[3-(1-phenylethyl)ureido]nonyl}urea (6) was synthesized as described for **1**, starting from 1,9-diaminononane (158 mg, 1 mmol) and (R)-1-phenylethylisocyanate (330 mg, 2.24 mmol). After drying at 60 °C under vacuum (15 mm Hg) **6** was obtained as a white solid in 79 % yield. M.p. 198-200 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 95 °C, TMS): δ = 7.31 (m, 10H), 6.23 (d, ^3J(H,H) = 8.4 Hz, 2H), 5.73 (t, ^3J(H,H) = 5.5 Hz, 2H), 4,70 (m, 2H), 2.94 (m, 4H), 1.35 (m, 4H), 1.31 (d, ^3J(H,H) = 7.0 Hz, 6H), 1.20 (s, 10H); ^{13}C NMR (75.48 MHz, [D$_6$]DMSO, 120 °C, TMS): δ = 157.0, 145.4, 127.6, 125.9, 125.3, 48.2, 29.5, 28.5, 28,2, 25.9, 22.7; IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3341, 3310, 1622, 1568; $C_{27}H_{40}N_4O_2$ (452.64): calcd. C 71.65, H 8.91, N 12.38, found C 71.39, H 8.91, N 12.36.

Preparation of gels: In a typical gelation experiment 10 mg of the bisurea compound and 1 mL of the solvent were placed in a test tube, which was sealed and then heated until the compound dissolved. The solution was allowed to cool to room temperature. Gelation was considered to have occurred when a homogeneous substance was obtained, which exhibited no gravitational flow. The melting points of the gels were determined by the dropping ball method.[27] A steel ball with a diameter of 1 mm was placed on the gel. The vial was closed and placed in an oil bath regulated by a thermostat. The oil bath was heated at a rate of 1-2 °Cmin^{-1}, during which time the height of the steel ball was observed. The temperature at which the ball touched the bottom of the vial was taken as the melting temperature of the gel. For light microscopy a piece of the gel was placed on a slide and covered with a cover glass. The gels were examined with a Olympus BX-60 microscope.

Differential scanning calorimetry: A given amount of gel was placed in a preweighed pan, which was sealed and weighed on a six-decimal-place balance. Heating and cooling scans were measured on a Perkin-Elmer DSC-7 instrument at a scan rate of 10 °Cmin^{-1}. After the measurements the pan was weighed again in order to check for possible leakage.

Electron microscopy: For electron microscopy a sample of the gel was placed on a formar-coated copper grid and removed after 1 min. After drying at low pressure (< 10^{-5} Torr) the specimen was shadowed at an angle of 10° with a platinum/carbon layer. The grids were examined in a Philips EM-300 electron microscope, operating at 80 kV.

X-ray diffraction: For X-ray diffraction measurements concentrated gels (100 mg bisurea compound per mL solvent) were prepared, which were deposited in a 1 mm-thick layer on a glass slide. X-ray diffractograms were recorded on a Philips powder diffractometer using $Cu_{K\alpha1/K\alpha2}$ radiation (1.54060 Å and 1.54439 Å). X-ray diffractograms were recorded from 1 to 30° with a step size of 0.02°.

Scanning tunneling microscopy: STM experiments were performed using a Discoverer scanning tunneling microscope (Topometrix Inc. Santa Barbara, CA) with an external pulse/function generator (model HP8111 A). Tips were electrochemically etched from Pt/Ir wire (80 %/20 %, diameter 0.2 mm) in 2N KOH/6N NaCN solution in water. Prior to the STM experiments, the compound under investigation was dissolved in 1-octanol. Concentrations used were typically about 1 mgmL^{-1}. Samples were prepared by spreading a drop of this solution on the basal plane of highly ordered pyrolytic graphite (HOPG) (grade ZYB, Advanced Ceramics Inc., Cleveland, OH). STM images were acquired in the variable-current mode (constant height) under ambient conditions. Typically, a tunneling current of 1 nA and a bias voltage of 0.2 V up to 0.6 V referred to the graphite surface were employed. STM images obtained at low bias voltages reliably revealed the atomic structure of HOPG providing an internal calibration standard for the monolayer studies.

Molecular dynamics simulations were performed using the GROMOS force field as implemented in GROMACS 1.31.[28] All simulations were carried out using periodic boundary conditions and a cut-off range of 1.0 nm for non-bonded interactions. The starting ensembles were constructed as follows: a molecule of **2** in the all-*trans* configuration was oriented with its urea carbonyl groups parallel to the *x* axis and with the long molecular axis in the *yz* plane. The tilt angle between the ribbons in the ensemble was varied by varying the tilt angle between the long molecular axis and the *y* axis. 64 copies of the molecule were placed on a rectangular lattice in the *xy* plane, with the size of the box ranging from (*x*,*y*,*z*) = (4.0 nm, 4.5 nm, 5.0 nm) when the tilt angle was 70° to (*x*,*y*,*z*) = (4.0, 5.6, 5.0) when the tilt angle was 30°. Before starting the MD simulations the ensemble was energy-minimized using the steepest descent method with the convergence criterion set at 0.001 kJ mol^{-1}. In a first MD run of 50 ps (step size 2 fs) the system was allowed to heat slowly from 0 to 300 K by employing a weak coupling (τ = 5 ps) to a temperature bath of 300 K, while maintaining constant pressure by coupling to a pressure bath of 1 atm and a coupling constant of 2 ps. Finally, a production run of 200 ps was carried out at 300 K (τ = 0.5 ps).

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