A New Class of Low-Molecular-Weight Amphiphilic Gelators

Nils Mohmeyer and Hans-Werner Schmidt*[a]

Abstract: A new powerful class of low-molecular-weight amphiphilic compounds has been synthesized and their structure–property relationships with respect to their gelation ability of organic solvents have been investigated. These compounds are able to gel organic solvents over a broad range of polarity. Especially polar solvents such as valeronitrile and γ-butyrolactone can be gelled even at concentrations far below 1 wt %. It was found that the gelation ability of these asymmetrically substituted *p*-phenylendiamines depends on a well-balanced relation of the terminal head group, the units involved in hydrogen bonding (amide or urea groups), and on the length of the alkyl chain. With this class of new gelators it is possible to tailor thermal and mechanical properties in different organic solvents and open various application possibilities.

Keywords: amphiphiles · amphiphilic gelators · gels · self-assembly · supramolecular chemistry

Introduction

Organogelators are a family of low-molecular-weight organic molecules that can gel organic solvents at low concentrations. The subject of organogels has generated enormous interest due to industrial potential in different areas ranging from cosmetics to advanced materials.[1–16] The process of self-assembly of these small organic molecules into supramolecular structures is complex and different for each individual compound. However, although the sequence of the gelation process is understood, up to now it has been impossible to predict from the molecular structure the gelation efficiency in a given solvent. Low-molecular-weight organic gelator molecules are capable of self-organizing into finely dispersed anisotropic structures within the organic solvent, forming a three-dimensional network resulting in gelation. Specific noncovalent interactions of gelator molecules such as hydrogen bonding, hydrophobic interactions, π–π interactions, electrostatic interactions, and metal-ion coordination can be employed and are required to form the supramolecular aggregates and subsequently the three-dimensional network structure. These structures are thermoreversible, destroyed upon heating and reformed during cooling. In the literature 1,3:2,4-di-*O*-benzylidene-D-sorbitol (DBS),[17] cholesterol derivatives,[18] bolaform amides,[19] symmetrical dialkylamides,[20] symmetrical bisureas,[3,4,21] and *N*-*n*-octyl-D-gluconamide[22,23] are examples of investigated organogelators. An analysis of the utilized building blocks of gelator molecules indicates that an efficient organogelator must contain defined molecular units. Important factors are geometrically defined ring systems, functional groups like amides or urea units to form hydrogen bonds, and long alkyl chains to tune the melting point and the solubility.[4]

The various combinations of these molecular units motivated us to synthesize a new class of asymmetrical substituted *para*-phenylendiamines based on readily available starting materials and simple organic reactions. The different structural units were varied in order to systematically explore their influence on the gelation ability, especially with regard to the sol–gel phase-transition temperature and the mechanical properties. In the literature the gelation ability of most gelators is examined, in addition to apolar solvents, in polar solvents like THF, acetone, or methanol. Of special interest to us is the gelation of polar solvents such as γ-butyrolactone and valeronitrile with respect to their application possibilities as solvents in dye-sensitized solar cells.[24–27]

Results and Discussion

The gelation ability of the synthesized low-molecular-weight compounds in organic solvents depends strongly on the

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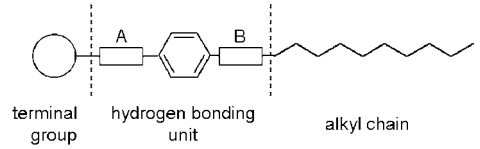
structural fragments of the molecules. Therefore we have varied systematically the different units within the amphiphilic molecule. The investigated molecules consist of three different structural units, shown here: an apolar terminal head group, a hydrogen-bonding segment based on *p*-phenylendiamines, and a long alkyl chain with more than eight carbon atoms.



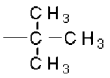
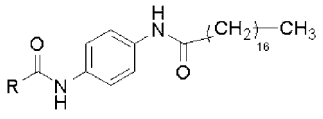
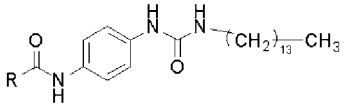
In this work we selected as terminal head group an aromatic phenyl, a cycloaliphatic cyclohexyl, and a bulky *tert*-butyl group. Within the hydrogen-bonding segment amide and urea units were selected.

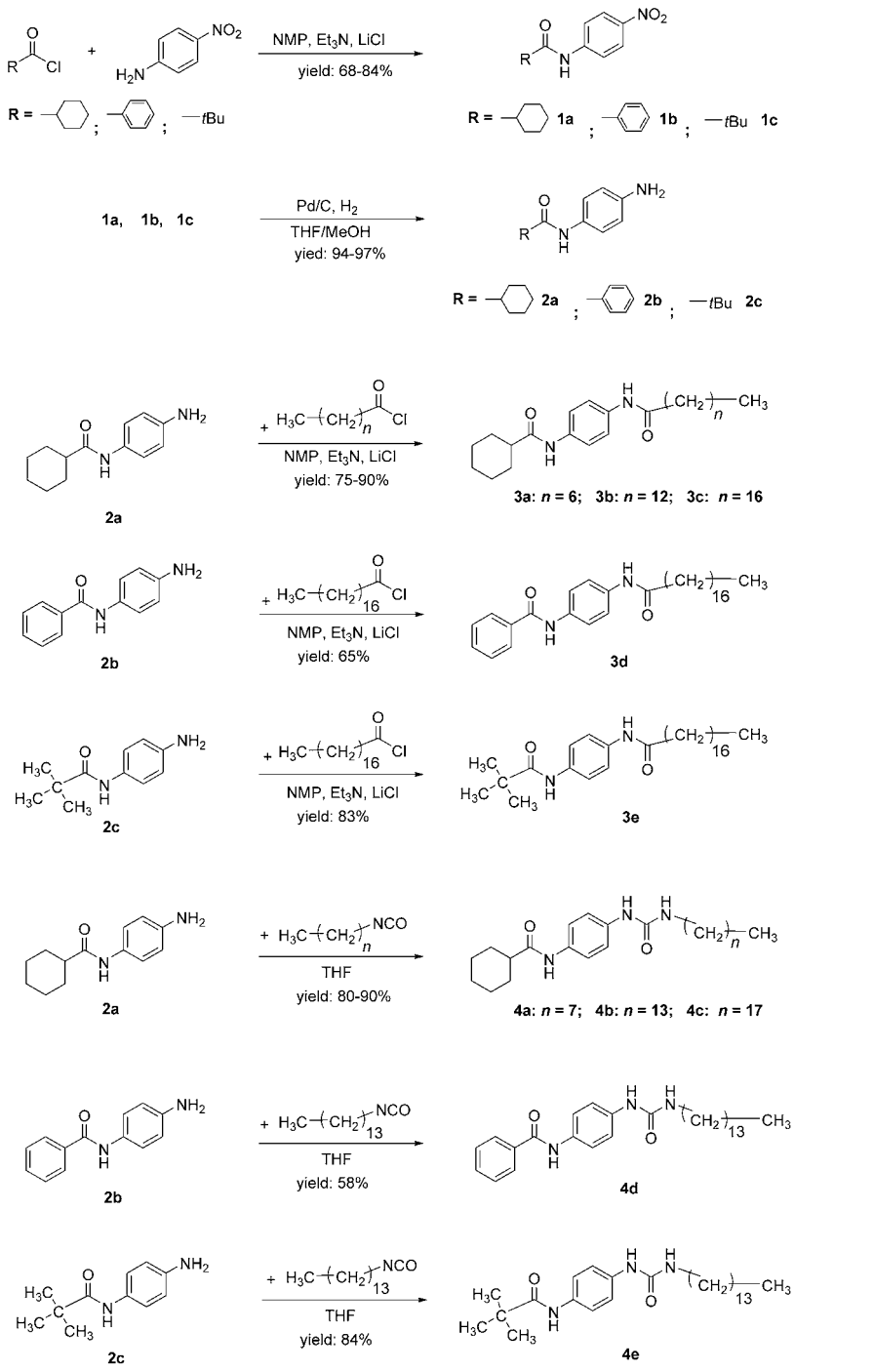
Synthesis of the amphiphilic molecules: The synthetic routes to the asymmetrically substituted *p*-phenylendiamine-based bisamide derivatives **3a–e** and amide/urea functionalized derivatives **4a–e** are shown in Scheme 1. In the first step 4-nitroaniline was treated in dry *N*-methyl-2-pyrrolidone (NMP) and triethylamine with the different acid chlorides, benzoyl chloride, cyclohexane carboxylic acid chloride, and pivaloyl chloride. These acid chlorides were selected to represent aromatic, flexible cycloaliphatic, and bulky aliphatic end groups. The resulting nitro compounds **1a–c** were reduced with hydrogen, using palladium on activated carbon as catalyst, to the corresponding amine derivatives **2a–c**. These different amines were treated with aliphatic acid chlorides of different chain lengths resulting in a series of asymmetrically substituted *p*-phenylendiamine-based bisamide derivatives **3a–e**. For cyclohexane-based derivatives **3a–c** we chose octanoyl chloride (**3a**), tetradecanoyl chloride (**3b**), and octadecanoyl chloride (**3c**) in order to discuss the influence of the chain length on the gelation ability. To discuss the influence of the terminal head group we treated the phenyl- (**2b**) and *tert*-butyl-terminated amines (**2c**) to the octadecanoyl chloride to obtain bisamides **3d** and **3e**. The amide/urea-functionalized compounds **4a–e** were synthesized by the addition of amino compounds **2a–c** to the different isocyanates (-C_8, -C_{14}, and -C_{18} chain length). This resulted in the amide/urea-functionalized derivates **4a–e**, which can be compared with the bisamides **3a–e** to discuss the influence of the type of hydrogen-bonding unit on the gelation ability.

The synthetic route to obtain the urea/amide-functionalized derivatives **7a–c** and the bisureas **8a–c** (Scheme 2) starts with the reaction of cyclohexylamine with nitrophenyleneisocyanate. The resulting nitro compound **5** was reduced to amino compound **6** in a procedure similar to that used in the synthesis of compounds **2a–c** by using palladium on activated carbon. To retrieve the urea/amide-functionalized derivatives **7a–c**, the amino compound **6** was subsequently treated with three different aliphatic acid chlorides. These urea/amide-functionalized derivatives **7a–c** are isomeric structures of compounds **4a–c**. Only the position of the amide and the urea unit are changed. The corresponding bisureas **8a–c** to the bisamides **3a–c** were synthesized by the addition of amino compound **6** to the three different isocyanates. With the synthesized amphiphilic molecules we want to investigate the structure–property relationships with respect to their gelation ability in organic solvents. Especially the well-balanced interactions of the terminal head group, the hydrogen-bonding unit, and the alkyl chain are the major factors to tailor efficient organogelators.

Structure–property relationships on the gelation ability: In the following we would like to discuss the influence of the different structural units on the gelation behavior. The aim is to find a well-balanced situation of attractive and repulsive forces and to optimize the gelation efficiency. First, the influence of the terminal head group of the asymmetrically substituted *p*-phenylendiamines on the capability to gel organic solvents is discussed. We compared the gelation ability in *p*-xylene of two series of compounds at a concentration of 1 wt%. For this purpose, mixtures of each compound in *p*-xylene were heated until the solid was completely dissolved. The resulting solution was slowly allowed to cool to room temperature and gelation was visually observed. Gelation was considered to have occurred when a homogenous sample was obtained that exhibited no gravitational flow. This process was repeated many times, demonstrating the thermoreversibility of the gelation and dissolution process. The molecules of the first series were the asymmetrically substituted *p*-phenylendiamine-based bisamide derivatives **3c–e**. They all have an alkyl chain with seventeen carbon atoms and the same hydrogen bonding unit, but have different terminal head groups. Compound **3c** has a flexible cyclohexane ring, **3d** an aromatic phenyl ring, and **3e** a bulky *tert*-butyl group. The derivatives **4c–e** were used as a comparison; they have the same terminal groups but one of the amide groups has been replaced by a urea group with a -C_{14} moiety. Table 1 shows the initial trend of the gelation ability of these kinds of molecules in *p*-xylene. Within both the bisamide derivatives **3c–e** and the amide/urea-functionalized

Table 1. Comparison of different terminal groups with respect to the ability to gelate *p*-xylene at a concentration of 1 wt%.

			
	**3c** gel	**3d** no gel	**3e** no gel
	**4c** gel	**4d** no gel	**4e** no gel

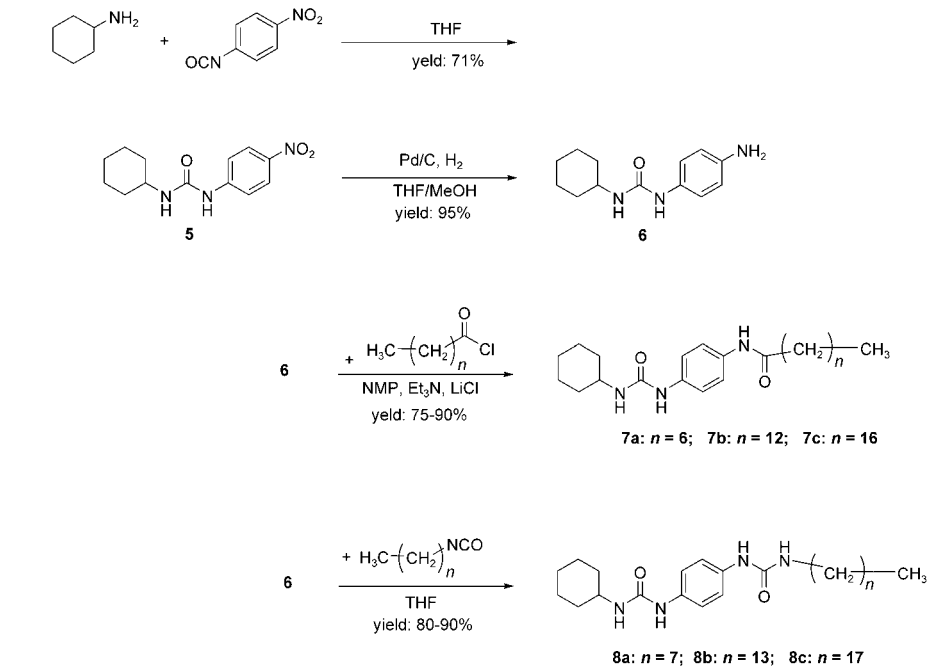


Scheme 1. Synthesis of asymmetrically substituted *p*-phenylendiamine-based bisamide derivatives **3a–e** and amide/urea-functionalized derivatives **4a–e**.

derivatives **4c–e**, the cyclohexyl-terminated derivatives **3c** and **4c** are the only ones to gel *p*-xylene at a concentration of 1 wt%. In both cases transparent stable gels were obtained. The derivatives with phenyl (**3d**, **4d**) or *tert*-butyl (**3e**, **4e**) groups exhibit no gelation ability. The molecules precipitated during cooling from solution. These results show that in *p*-xylene the terminal head group of this class of molecules greatly affects the gelation ability. The gelation ability depends strongly on the balanced intermolecular interactions of the hydrogen-bond-forming units. In these cases, the bulky *tert*-butyl group could disturb the intermolecular interactions of the adjacent amide group so much that the gel state cannot be reached. Also, the derivatives with a terminal phenyl group as a conjugated planar rigid unit are not able to form gels. As a result it seems that the flexible cyclohexane ring as a terminal head group in this class of molecules promotes the intermolecular interactions of the hydrogen-bonding unit for *p*-xylene in the required way.

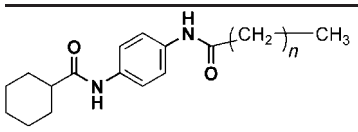
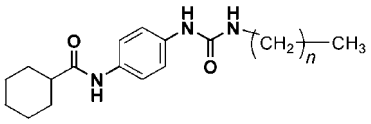
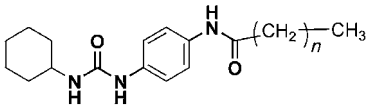
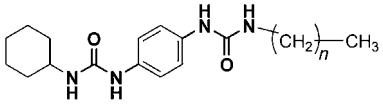
The second comparison discusses the structure–property relationship of the gelation ability with respect to the influence of different hydrogen-bonding units in combination with the length of the pendent alkyl chain. We investigated the gelation ability of selected molecules in *p*-xylene as an apolar hydrocarbon, and in valeronitrile and γ-butyrolactone as more polar solvents. The last two solvents are of immense interest with regard to their potential application in dye-sensitized solar cells.

Table 2 summarizes the minimum required additive concentration necessary to form a stable gel. If a gel is not formed the molecules are either insoluble (insol) at the boiling point of the solvent or they precipitate (ppt) during the cooling process. The structure of the hydrogen-bonding unit was systematically varied. Starting from the bisamides **3a–c**, the amide groups were successively replaced by one urea group yielding amide/urea- and urea/amide-functionalized derivatives **4a–c** and **7a–c**, respectively, and subsequently the bisurea series **8a–c**. In addition, the length of the aliphatic chain was increased within each of these four classes from 7 (**a**), to 13 (**b**) and to 17 carbon atoms (**c**). Although the chemical structures of the presented molecules are rather similar, only selected compounds are efficient gelators. Most



Scheme 2. Synthesis of asymmetrically substituted *p*-phenylendiamine-based urea/amide-functionalized derivatives **7a–c** and bisurea derivatives **8a–c**.

Table 2. Minimum required concentration given in wt% of the compounds **3a–c**, **4a–c**, **7a–c**, and **8a–c** to form a stable gel in different solvents (insol: compound is not completely soluble at the boiling temperature of the solvent; ppt: additive precipitates during the cooling process).

		n	*p*-xylene	valeronitrile	γ-butyrolactone
	**3a**	6	1.1	ppt	ppt
	3b	12	1.5	ppt	ppt
	3c	16	1.5	ppt	0.5
	**4a**	7	0.3	0.5	ppt
	4b	13	0.25	0.25	1.0
	4c	17	0.2	0.05	0.75
	**7a**	6	insol	insol	insol
	7b	12	0.8	insol	insol
	7c	16	0.6	insol	insol
	**8a**	7	insol	insol	insol
	8b	13	insol	insol	insol
	8c	17	insol	0.2	insol

of the investigated compounds show good gelation efficiency in the nonpolar solvent *p*-xylene. The minimum required concentration of the bisamides **3a–c** in *p*-xylene is about 1–1.5 wt%. However, the amide/urea-functionalized derivatives **4a–c** are able to gel *p*-xylene at much lower concentrations, that is, 0.2–0.3 wt%. This more efficient gelation is caused by increasing the intermolecular interactions through the replacement of the amide moiety with a urea group and by the additional asymmetry. By changing the position of the amide and urea groups in the molecule (**7a–c**) the gelation efficiency decreases. The minimum required additive concentration in *p*-xylene is in the range of 0.6–0.8 wt%. Compound **7a**, with the shortest (octyl) alkyl chain is not soluble in boiling *p*-xylene. The replacement of the second amide group by a urea leads to the obtained bisureas **8a–c**, which are completely insoluble in boiling *p*-xylene. These results indicate that the intermolecular interactions increase proportional to the number of introduced urea groups, at the expense of solubility in boiling *p*-xylene.

This trend was also observed in the two investigated polar solvents, valeronitrile and γ-butyrolactone. The amide/urea-functionalized class of compounds **4a–c** are by far the best gelators and are able to gel these polar solvents. For valeronitrile the most efficient organogelator is compound **4c**. Gels were obtained at a concentration as low as 0.05 wt%. By decreasing the length of the alkyl chain the gelation efficiency in valeronitrile decreases. The required concentration is 0.25 wt% for **4b** and 0.5 wt% for **4a**. The bisamide derivatives **3a–c** precipitate in valeronitrile upon cooling, whereas the amide/ureas **7a–c** and bisureas **8a–c** are, with the exception of **8c**, not completely soluble in valeronitrile even at boiling point. Surprisingly, compound **8c** with the longest alkyl chain is able to form a gel at a concentration of 0.2 wt%. The results in γ-butyrolactone are similar to those in valeronitrile. From the amide/urea series, compounds **4b** and **4c** form stable gels at 1.0 and 0.75 wt% respectively, whereas compound **4a** precipitates during cooling. The urea/amides **7a–c** and the bisureas **8a–c** are not soluble enough in γ-butyrolactone. Surprisingly, an efficient gelator was found in compound **3c**, the bisamide with the longest alkyl chain. Gelation occurs readily at 0.5 wt%. The derivatives **3a** and **3b**

precipitate during cooling and do not form a gel. The optical appearance of the gels is also different. All *p*-xylene gels are transparent, whereas the gels of γ-butyrolactone are opaque. The transparency of valeronitrile gels increases with decreasing gelator concentration with all investigated compounds. The differences in the optical appearance of the gels can result either from differences in refractive indices or from differences in the width of the fibres forming the gel.

The morphology of the different organogelators was investigated by transmission electron microscopy after evaporation of the solvent. Figure 1 shows the transmission electron microscopy pictures of the dried three-dimensional network of amide/urea-functionalized derivatives **4c**, **4c**, and the bisurea **8c** gelled at 0.5 wt% in valeronitrile. The electron micrographs show differences in the morphology of the different compounds. Compound **4b** forms fine cylindrical fibrils in valeronitrile with a diameter of 100–150 nm; compound **4c** also forms these fine cylindrical fibrils, but with lower diameters of 50–70 nm. However, bisurea **8c** forms a more twisted ribbonlike structure with an average width of 100–300 nm. These different morphological structures and dimensions show the strong influence of the hydrogen bonding and packing in the formation of the supramolecular structures.

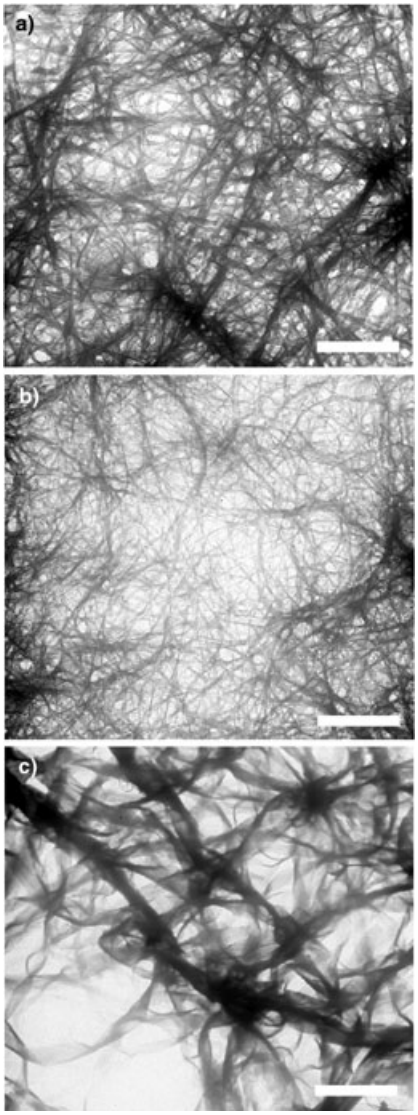


Figure 1. TEM pictures of network structures a) **4b**, b) **4c**, and c) **8c** after evaporation of valeronitrile (initial concentrations: 0,5 wt%). Scale bars are 1 μm.

Concentration dependence of gel formation: For selected compounds the concentration dependence of gel formation and sol–gel transition was studied in more detail. The thermal behavior of **3c**, **4b**, **4c**, and **8c** gels with, in order, γ-butyrolactone, valeronitrile, and *p*-xylene were investigated by the dropping ball method to determine the sol–gel transition temperature (T_{gel}) of the gels dependent on the additive concentration. As shown in Figure 2 the T_{gel} value is dependant on the concentration of the gelator. As expected, in all investigated gels the sol–gel transition temperatures increase with increasing gelator concentration. Figure 2 displays comparisons of the sol–gel transition temperatures at different gelator concentrations of the gels of **4b** and **4c** in *p*-xylene, valeronitrile, and γ-butyrolactone. In all cases the maximum investigated additive concentration was about 3 wt%. The transition temperature T_{gel} depends on the alkyl chain length of the gelator. Increasing the alkyl chain length from derivative **4b** to **4c** increases the T_{gel}in all three cases. At a first look this is unexpected, since generally the melting point of amphiphilic molecules and liquid crystals is lowered with increasing chain length.[28,29] However, it seems that in the supramolecular aggregates of the present amphiphilic molecules the packing and the formation of the intermolecular hydrogen bonds is stabilized with increasing chain length. The transition temperatures decrease with increasing polarity of the solvent. For example at a concentration of 1 wt% of **4c** in *p*-xylene a T_{gel} value of 107°C was obtained. With increasing polarity of the solvent, the transition temperature in valeronitrile decreases to 100°C and in γ-butyrolactone to 84°C. Also, the maximum concentration needed to dissolve these two derivatives is much lower in *p*-xylene than in both polar solvents. In summary it was found that the amide/urea derivatives in particular are efficient gelators for organic solvents and that the transition temperature can be tuned by changing the concentration and the chain length of the alkyl substituent.

In the following we would like to compare the structural variations of the hydrogen-bonding unit from selected examples. For this comparison the bisamide **3c**, the amide/urea-functionalized derivative **4c**, and the corresponding bisurea **8c** were selected. The dependence of the concentration on the sol–gel transition temperature of bisamide **3c** and of derivative **4c** in *p*-xylene is shown in Figure 3 (top). In both cases the T_{gel} values increase with increasing gelator concentration. However, the concentration range in which stable gels are reached differs immensely. With bisamide **3c**, a con-

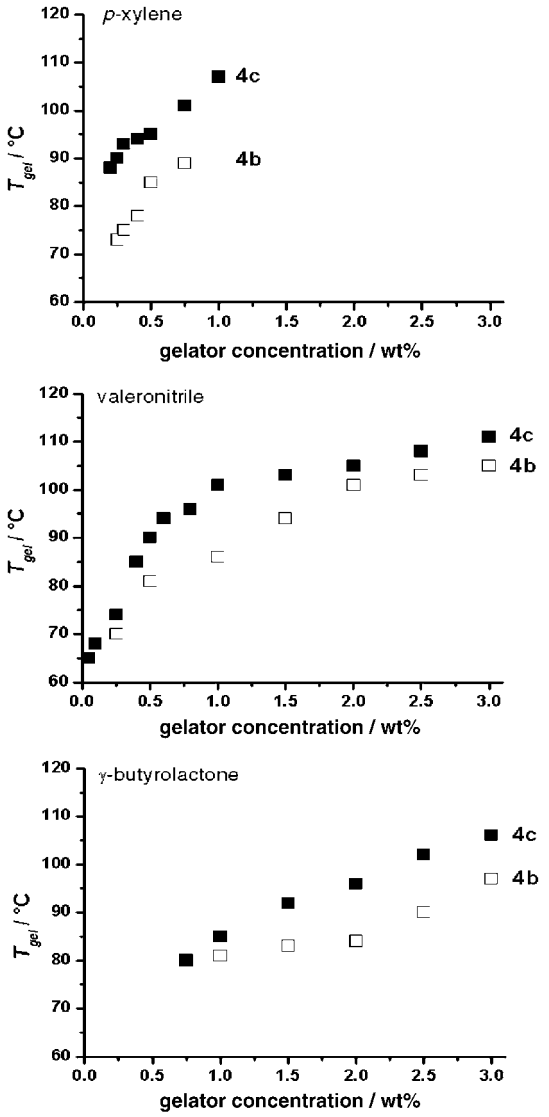


Figure 2. Sol–gel transition temperature as a function of the gelator concentration of compounds **4b** (open squares) and **4c** (filled squares) in *p*-xylene (top), valeronitrile (middle) and in γ-butyrolactone (bottom) determined by the dropping ball method.

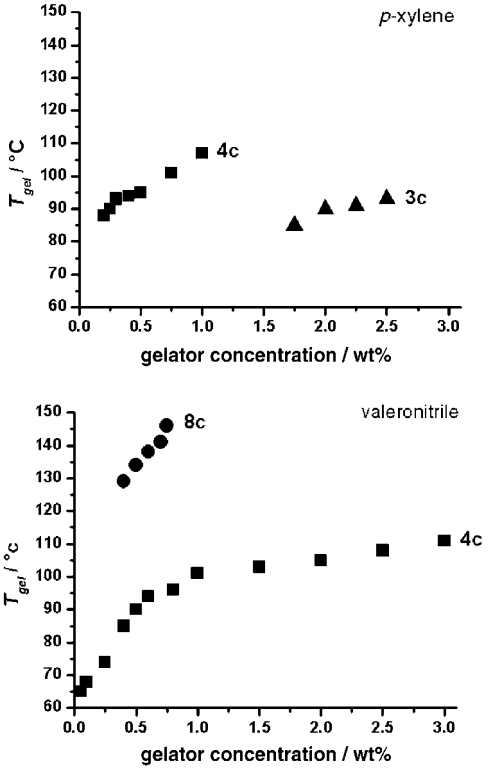


Figure 3. Sol–gel transition temperature as a function of the gelator concentration of bisamide **3c** (triangles) and the amide/urea-derivative **4c** (squares) in *p*-xylene (top) and of the amide/urea-derivative **4c** (squares) and the bisurea derivative **8c** (circles) in valeronitrile (bottom) determined by the dropping ball method.

centration range of 1.75–2.5 wt% is required to obtain a stable gel with *p*-xylene. In comparison, the amide/urea-functionalized derivative **4c** gels *p*-xylene at a lower concentration range from 0.2 to 1 wt%. It seems that this behavior and also the higher T_{gel} values achieved for derivative **4c** are due to the increased intermolecular interaction of the hydrogen-bonding unit. Additionally, we examined the sol–gel transition temperatures of **4c** and the bisurea **8c** in valeronitrile. The effect is even more pronounced. The **4c**/valeronitrile forms, over a broad concentration range, a gel with T_{gel} starting at 65°C and levelling off between 105 and 110°C. However, the T_{gel} values of **8c** in valeronitrile are 40°C higher than that of **4c**. At the gelator concentration of 0.5 wt% the transition temperature of **8c**/valeronitrile is about 132°C and increases to almost 150°C at 0.75 wt%. Higher concentrations are not possible due to the limited solubility of gelator **8c** up to 0.75 wt%.

Rheology measurements were carried out on the selected examples of the best gels. Figure 4 shows a rheology measurement of amide/urea compound **4b** in γ-butyrolactone ($c = 2$ wt%) at different frequencies. The viscoelastic behavior of the gels is characterized by the storage (G') and loss

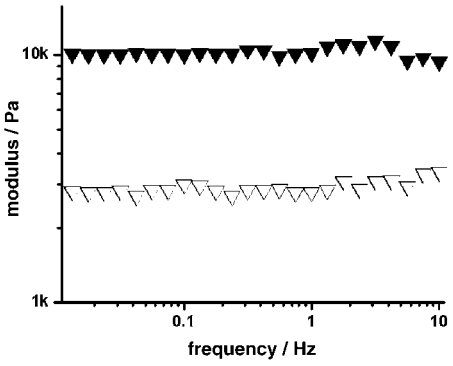


Figure 4. Dynamic rheological behavior of **4b** in γ-butyrolactone at a concentration of 2 wt%. The plot shows the storage modulus G' (filled triangle) and loss modulus G'' (open triangle) versus frequency.

(G'') moduli, which are independent of frequency over the range from 0.01–10 Hz. At this concentration the storage modulus G' is about 10 kPa. The value indicates a good resistance against mechanical stress.

Derivative **4c** forms stable and transparent gels in valeronitrile between concentrations of 0.5 to 2 wt%. Figure 5 shows the different storage moduli of **4c**/valeronitrile gels at

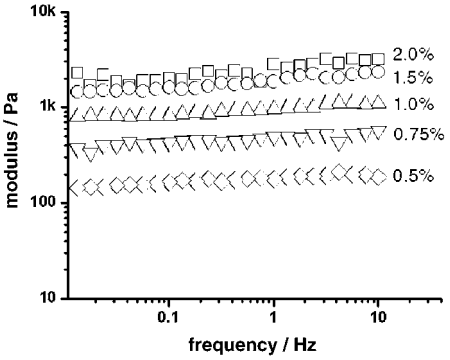


Figure 5. Comparison of the elastic storage modulus G' values versus frequency at different concentrations of gelator **4c** in valeronitrile.

the different investigated concentrations. The moduli are also independent of the frequency. It was found that by increasing the gelator concentration from 0.5 to 2.0 wt%, the storage moduli increase from 150 to 1200 Pa. However, the storage modulus of the **4c**/valeronitrile gel at a concentration of 2 wt% is about 2.5 kPa and four times lower that of the **4b**/valeronitrile gel (10 kPa).

Figure 6 compares the influence of gelator concentration on storage and loss moduli of the two amide/urea-functionalized compounds **4b** and **4c** in valeronitrile. In both cases the storage modulus G' and the loss modulus G'' increase, as expected, with increasing gelator concentration from 0.5 to 2 wt%. The stability of the gel network and the elastic behavior both increase with increasing gelator concentration and thus form a denser network structure. The mechanical properties of the resulting gels from **4b** are substantially higher than those of **4c**. As shown in the transmission electron microscopy pictures from valeronitrile (Figure 1) the network structure of compound **4b** consists of thicker fibres that are well interconnected. In contrast, **4c** has a finer network structure. This difference may contribute to the higher values of G' and G'' for gels with compound **4b**. The same trend was observed in γ-butyrolactone. The storage moduli of **4b**/γ-butyrolactone gels are higher than those of **4c** in γ-butyrolactone at the same concentration. Compared to the bisamide **3c** gels, both storage moduli of the gels of **4b** and **4c** are much higher.

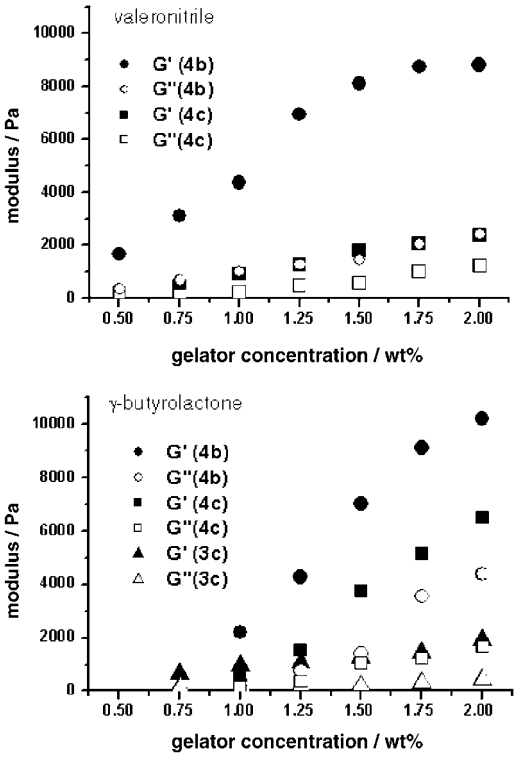


Figure 6. Influence of the concentration of the amide/urea-functionalized derivatives **4b** (circles) and the **4c** (squares) and bisamide **3c** (triangle) in valeronitrile (top) and in γ-butyrolactone (bottom) on storage modulus G' (filled symbols) and on loss modulus G'' (open symbols) at a frequency of 1 Hz.

Conclusion

In the present work the influence of the chemical structure on the gelation ability of a new class of amphiphilic compounds is described. It was demonstrated that a well-balanced relationship between the terminal head group, the groups involved in hydrogen bonding (amide or urea groups, or combination of both), and the length of the alkyl chain is required to optimize the gelation ability in organic solvents. It was possible to find candidates that were able to gel even polar solvents such as valeronitrile and γ-butyrolactone at concentrations far below 1 wt%. Depending on the employed gelator and the concentration, the thermal and mechanical properties can be adjusted.

Experimental Section

Materials and methods: Solvents for synthesis were purified and dried when necessary according to standard procedures. The used amines and isocyanates were obtained from Aldrich and Fluka and purified by distillation or recrystallization. Solvents for gelation tests were obtained from Merck-Suchardt and Fluka and used as received. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AC 250 instrument. IR spectra were recorded on a BIO-RAD Digilab FTS-40 (FT-IR) as thin films on an Si-Wafer (after evaporation of the solvent on hotstage) or as KBr pellets. Mass spectra were recorded on a VARIAN MAT CH-

7-instrument (direct probe inlet, electron impact ionization) at the central analytic laboratories of the University of Bayreuth. Elemental analysis was carried out with a EA 3000 (HEKAtech) at the department of chemical engineering laboratory (Prof. A. Jess) of the University of Bayreuth.

***N*-(4-Nitrophenyl)cyclohexanecarboxamide (1a)**: 4-Nitroaniline (22.61 g, 163.7 mmol) was dissolved in *N*-methyl-2-pyrrolidone (180 mL) and added to triethylamine (30 mL) and a spatula-point of LiCl. Cyclohexane carboxylic acid chloride (18 mL, 136.4 mmol) was added and the mixture was stirred for 2 h at 80 °C. After cooling to room temperature, the mixture was precipitated in ice water (500 mL). The mixture was filtered (glassfilter G3), and the residue was washed with water and dried. Chromatography (3:1 hexane/EtOAc) provided the nitro-compound **1** as an orange–yellow solid (28.6 g, 84 %). R_f = 0.55 (3:1 hexane/EtOAc); ^{1}H NMR ([D$_6$]DMSO, 250 MHz): δ = 1.51 (m, 10H),, 2.35 (m, 1H), 7.83 (d, J = 9.2 Hz, 2H), 8.17 (d, J = 9.2 Hz, 2H), 10.43 ppm (s, 1H); ^{13}C NMR ([D$_6$]DMSO, 62.5 MHz): δ = 175.5, 146, 142.1, 125.3, 125, 119, 118.8, 45.3, 29.3, 26.7, 25.4 ppm.

***N*-(4-Nitrophenyl)benzamide (1b)**: This compound was prepared as described for **1a**, starting from 4-nitroaniline (6.0 g, 43.4 mmol) and benzoyl chloride (5.04 mL, 43.4 mmol). The product was purified by recrystallization from acetone/water. Yield: (8.17 g, 78 %). R_f = 0.27 (3:1 hexane/THF); ^{1}H NMR ([D$_6$]DMSO, 250 MHz): δ = 7.59 (m, 3H), 8.00 (d, J = 6.8 Hz, 2H), 8.06 (d, J = 9.3 Hz, 2H), 8.27 (d, J = 9.3 Hz, 2H), 10.80 ppm (s, 1H).

2,2-Dimethyl-*N*-(4-nitrophenyl)propionamide (1c): This compound was prepared as described for **1a**, starting from 4-nitroaniline (27.63 g, 0.2 mol) and 2,2-dimethylpropionyl chloride (29.53 mL, 0.24 mol). The product was purified by recrystallization from methanol. Yield: (37.3 g, 85 %); ^{1}H NMR ([D$_6$]DMSO, 250 MHz): δ = 1.24 (s, 9H), 7.94 (d, J = 9.3 Hz, 2H), 8.20 (d, J = 9.3 Hz, 2H), 9.77 ppm (s, 1H).

***N*-(4-Aminophenyl)cyclohexanecarboxamide (2a)**: Compound **1a** (25 g, 100.7 mmol) was dissolved in a mixture of THF (200 mL) and methanol (40 mL) and Pd/C (0.6 g; 10 wt % Pd on activated carbon) was added. This mixture was stirred in an autoclave for 24 h at 40 °C with H_2 pressure of 3.5 bar. The colorless mixture was filtered (Alox N) and the solvents were evaporated. The solid was subjected to chromatography on silica gel (1:1 hexane/EtOAc) to give the slightly magenta amino compound **2a** (21.32 g, (97 %). R_f = 0.25 (1:1 hexane/EtOAc); ^{1}H NMR ([D$_6$]DMSO, 250 MHz): δ = 1.51 (m, 10H), 2.24 (m, 1H), 4.75 (s, 2H), 5.83 (s, 1H) 6.67 (d, J = 8.7 Hz, 2H), 7.05 ppm (d, J = 8.7 Hz, 2H).

***N*-(4-Aminophenyl)benzamide (2b)**: This compound was prepared as described for **2a** starting from compound **1b** (7.94 g, 32.8 mmol). The product was purified by recrystallization from methanol/water. Yield: (6.9 g, 99 %); R_f = 0.2 (1:1 hexane/THF); ^{1}H NMR ([D$_6$]DMSO, 250 MHz): δ = 4.91 (s, NH$_2$, 2H), 6.54 (d, J = 8.9 Hz, 2H), 7.38 (d, J = 8.7 Hz, 2H), 7.52 (m, 3H), 7.90 (d, J = 7.3 Hz, 2H), 9.86 ppm (s, 1H).

2,2-Dimethyl-*N*-(4-aminophenyl)propionamide (2c): This compound was prepared as described for **2a** starting from compound **1c** (30.0 g, 0.147 mol). Yield: (24.25 g, 94 %); ^{1}H NMR ([D$_6$]DMSO, 250 MHz): δ = 1.24 (s, 9H), 4.69 (s, 2H), 6.82 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H), 9.62 ppm (s, 1H).

***N*-(4-Octoylaminophenyl)cyclohexanecarboxamide (3a)**: This compound was prepared as described for **1a**, starting from compound **2a** (1.09 g, 5.0 mmol) and octanoyl chloride (1.07 mL, 6.6 mmol). The product was purified by recrystallization from EtOAc. Yield 1.3 g of a white powder (76 %, 3.7 mmol); m.p. 225 °C; R_f = 0.8 (1:1 hexane/THF); ^{1}H NMR (5:1, CDCl$_3$, CF$_3$COOD, 250 MHz): δ = 0.85 (t, J = 6.9 Hz, 3H), 1.31 (m, 14H), 1.73 (m, 3H), 1.87 (m, 2H), 2.00 (m 2H), 2.36 (m, 1H), 2.53 (t, J = 8.1 Hz, 2H), 7.40 pm (s, 4H); MS: m/z (%): 344 (95) [M^+]; elemental analysis calcd (%) for $C_{21}H_{32}N_2O_2$ (344.25): C 73.22, H 9.36, N 8.13; found: C 73.23, H 9.41, N 8.12.

***N*-(4-Tetradecoylaminophenyl)cyclohexanecarboxamide (3b)**: This compound was prepared as described for **1a**, starting from compound **2a** (1.09 g, 5.0 mmol) and tetradecoyl chloride (1.7 mL, 6.25 mmol). The product was purified by recrystallization from EtOAc. Yield 0.85 g of a white powder (40 %, 2.0 mmol); m.p. 215 °C; R_f = 0.85 (1:1 hexane/THF); ^{1}H NMR (5:1, CDCl$_3$, CF$_3$COOD, 250 MHz): δ = 0.85 (t, 3H), 1.31 (m, 25H), 1.71 (m, 3H), 1.87 (m, 2H), 2.00 (m, 2H), 2.36 (m, 1H), 2.51 (t, 2H), 7.40 ppm (s, 4H); MS: m/z (%): 428 (100) [M^+]; elemental analysis calcd (%) for $C_{27}H_{44}N_2O_2$ (428.34): C 75.65, H 10.35, N 6.54; found: C 75.45, H 10.37, N 6.49.

***N*-(4-Octadecoylaminophenyl)cyclohexanecarboxamide (3c)**: This compound was prepared as described for **1a**, starting from compound **2a** (1.09 g, 5.0 mmol) and octadecoyl chloride (1.51 g, 5 mmol). The product was purified by recrystallization from methanol. Yield 2.1 g of a white powder (87 %, 4.3 mmol); m.p. 211 °C; R_f = 0.9 (1:1 hexane/THF); ^{1}H NMR (5:1, CDCl$_3$, CF$_3$COOD, 250 MHz): δ = 0.85 (t, J = 6.9 Hz, 3H), 1.25 (m, 33H), 1.73 (m, 3H), 1.87 (m, 2H), 2.00 (m, 2H), 2.37 (m, 1H), 2.50 (t, 2H), 7.40 (s, 4H); MS: m/z (%): 484 (100) [M^+]; elemental analysis calcd (%) for $C_{31}H_{52}N_2O_2$ (484.4): C 76.81, H 10.81, N 5.78; found: C 76.82, H 10.89, N 5.74.

***N*-(4-Octadecoylaminophenyl)benzamide (3d)**: This compound was prepared as described for **1a**, starting from compound **2b** (1.0 g, 4.7 mmol) and octadecoyl chloride (1.42 g, 4.7 mmol). The product was purified by recrystallization from THF. Yield 1.46 g of a white powder (65 %, 3.1 mmol); m.p. 216 °C; R_f = 0.7 (1:1 hexane/THF); ^{1}H NMR (5:1, CDCl$_3$, CF$_3$COOD, 250 MHz): δ = 0.87 (t, J = 7.0 Hz, 3H), 1.27 (m, 28H), 1.77 (m, 2H), 2.56 (t, J = 7.4 Hz, 2H), 7.54 (m, 7H), 7.81 ppm (d, J = 7.5 Hz, 2H); MS: m/z (%): 478 (38) [M^+]; elemental analysis calcd (%) for $C_{31}H_{46}N_2O_2$ (478.72): C 77.78, H 9.69, N 5.85; found: C 77.21, H 9.86, N 5.85.

2,2-Dimethyl-*N*-(4-octadecylaminophenyl)propionamide (3e): This compound was prepared as described for **1a**, starting from compound **2c** (1.1 g, 7.8 mmol) and octadecoyl chloride (2.84 g, 9.4 mmol). The product was purified by recrystallization from methanol. Yield 2.8 g of a white powder (83 %, 6.1 mmol); m.p. 196 °C; R_f = 0.8 (1:1 hexane/THF); ^{1}H NMR (5:1, CDCl$_3$, CF$_3$COOD, 250 MHz): δ = 0.86 (t, J = 7.0 Hz, 3H), 1.23 (m, 22H), 1.35 (s, 9H), 1.52 (m, 2H), 3.29 (t, J = 7.8 Hz, 2H), 7.29 (d, J = 7.4 Hz, 2H), 7.46 ppm (d, J = 7.4 Hz, 2H); MS: m/z (%): 458 (49) [M^+]; elemental analysis calcd (%) for $C_{29}H_{50}N_2O_2$ (458.73): C 75.93, H 10.99, N 6.11; found: C 76.22, H 11.13, N 6.05.

***N*-[4-(3-Octylureido)phenyl]cyclohexanecarboxamide (4a)**: A solution of compound **2a** (1.2 g, 5.5 mmol) in THF (40 mL) was added to a solution of octylisocyanate (1.06 mL, 6.0 mmol) in THF (40 mL). The reaction mixture was heated under reflux for 2 h. After cooling to room temperature, the mixture was added to methanol (80 mL) and evaporated to half its original volume. The precipitation began while cooling to room temperature. After 2 h the mixture was filtered (glassfilter G3), and the residue was washed with water and dried. The product was purified by recrystallization from THF. Yield 1.83 g of a white powder (86 %, 4.7 mmol); m.p. >232 °C (decomp); R_f = 0.7 (1:1 hexane/THF); ^{1}H NMR (5:1, CDCl$_3$, CF$_3$COOD, 250 MHz): δ = 0.82 (t, J = 6.8 Hz, 3H), 1.31 (m, 17H), 1.71 (m, 1H), 1.87 (m, 2H), 1.98 (m, 2H), 2.38 (m, 1H), 3.28 (t, J = 7.4 Hz, 2H), 7.21 (d, J = 8.9 Hz, 2H), 7.45 ppm (d, J = 8.9 Hz, 2H); MS: m/z (%): 373 (40) [M^+]; elemental analysis calcd (%) for $C_{22}H_{35}N_3O_2$ (372.27): C 70.74, H 9.44, N 11.25; found: C 70.79, H 9.50, N 11.12.

***N*-[4-(3-Tetradecylureido)phenyl]cyclohexanecarboxamide (4b)**: This compound was prepared as described for **4a**, starting from compound **2a** (0.74 g, 3.4 mmol) and tetradecylisocyanate (1 mL, 3.6 mmol). The product was purified by recrystallization from THF. Yield 1.22 g of a white powder (79 %, 2.7 mmol); m.p. >230 °C (decomp); R_f = 0.75 (1:1 hexane/THF); ^{1}H NMR (5:1, CDCl$_3$, CF$_3$COOD, 250 MHz): δ = 0.86 (t, J = 6.8 Hz, 3H), 1.33 (m, 20H), 1.75 (m, 1H), 1.89 (m, 2H), 2.03 (m, 2H), 2.41 (m, 1H), 3.30 (t, J = 7.6 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 7.48 ppm (d, J = 8.7 Hz, 2H); MS: m/z (%): 457 (25) [M^+]; elemental analysis calcd (%) for $C_{28}H_{47}N_3O_2$ (457.37): C 73.48, H 10.39, N 9.18; found: C 73.89, H 10.35, N 9.19.

***N*-[4-(3-Octadecylureido)phenyl]cyclohexanecarboxamide (4c)**: This compound was prepared as described for **4a**, starting from compound **2a** (0.66 g, 3 mmol) and octadecylisocyanate (0.97 g, 3.3 mmol). The product was purified by recrystallization from THF. Yield 1.26 g of a white powder (82 %, 2.5 mmol); m.p. >215 °C (decomp); R_f = 0.8 (1:1 hexane/THF); ^{1}H NMR (5:1, CDCl$_3$, CF$_3$COOD, 250 MHz): δ = 0.86 (t, J = 6.8 Hz, 3H), 1.33 (m, 37H), 1.77 (m, 1H), 1.89 (m, 2H), 2.01 (m,

2H),2.41 (m, 1H), 3.30 (t, $J=7.6$ Hz, 2H), 7.23 (d, $J=8.7$ Hz, 2H), 7.48 ppm (d, $J=8.7$ Hz, 2H); MS: m/z (%): 513 (28) [M^+]; elemental analysis calcd (%) for $C_{32}H_{55}N_3O_2$ (513.43): C 74.80, H 10.79, N 8.18; found: C 72.46, H 10.53, N 7.85.

***N*-[4-(Tetradecylureido)phenyl]benzamide (4d)**: This compound was prepared as described for **4a**, starting from compound **2b** (1.0 g, 4.7 mmol) and tetradecylisocyanate (1.29 mL, 4.7 mmol). The product was purified by recrystallization from THF. Yield 1.2 g of a white powder (58%, 2.5 mmol); m.p. 183°C; $R_f=0.55$ (1:1 hexane/THF); ^{1}H NMR (5:1, $CDCl_3$, CF_3COOD, 250 MHz): $\delta=0.86$ (t, $J=6.9$ Hz, 3H), 1.31 (m, 22H), 1.77 (m, 1H), 1.58 (m, 2H), 3.35 (t, $J=7.4$ Hz, 2H), 7.34 (d, $J=8.9$ Hz, 2H), 7.63 (m, 5H), 7.84 ppm (d, $J=8.9$ Hz, 2H); MS: m/z (%): 452 (30) [M^++H]; elemental analysis calcd (%) for $C_{28}H_{41}N_3O_2$ (451.66): C 74.46, H 9.15, N 9.30; found: C 74.07, H 9.33, N 9.35.

2,2-Dimethyl-*N*-[4-(3-tetradecylureido)phenyl]propionamide (4e): This compound was prepared as described for **4a**, starting from compound **2c** (1.1 g, 7.8 mmol) and tetradecylisocyanate (2.6 mL, 9.4 mmol). The product was purified by recrystallization from methanol. Yield 2 g of a white powder (84%, 5.0 mmol); no melting point (decomp); $\underline{R}_f=0.6$ (1:1 hexane/THF); ^{1}H NMR (5:1, $CDCl_3$, CF_3COOD, 250 MHz): $\delta=0.85$ (t, $J=7.0$ Hz, 3H), 1.24 (m, 22H), 1.37 (s, 9H), 1.55 (m, 2H), 2.59 (t, $J=7.8$ Hz, 2H), 7.31 (d, $J=8.7$ Hz, 2H), 7.49 ppm (d, $J=8.7$ Hz, 2H); MS: m/z (%): 431 (7) [M^+]; elemental analysis calcd (%) for $C_{26}H_{45}N_3O_2$ (431.67): C 72.35, H 10.51, N 9.73; found: C 71.82, H 10.83, N 9.79.

1-(4-Nitrophenyl)-3-cyclohexylurea (5): This compound was prepared as described for **4a**, starting from cyclohexylamine (3,99 mL, 35 mmol) and nitrophenyleneisocyanate (5.74 g, 35 mmol). The product was purified by recrystallization from methanol. Yield 6.3 g of a yellow solid (71%, 23.9 mmol); $R_f=0.6$ (1:1 hexane/THF); ^{1}H NMR ([D_6]DMSO, 250 MHz): $\delta=1.49$ (m, 10H), 3.48 (m, 1H), 6.31 (d, $J=7.9$ Hz, 1H), 7.58 (d, $J=9.0$ Hz, 2H), 8.11 (d, $J=9.0$ Hz, 2H), 9.11 ppm (s, 1H).

1-(4-Aminophenyl)-3-cyclohexylurea (6): The nitro-compound **5** (6.3 g, 23.9 mmol) was dissolved in a mixture of THF (200 mL) and methanol (40 mL) and Pd on activated carbon (0.6 g of 10 wt%) was added. This mixture was stirred in an autoclave for 24 h at 40°C with an H_2 pressure of 3.5 bar. The colorless mixture was filtered (Alox N) and the solvents were evaporated. Yield 5.1 g (90%, 21.5 mmol); $R_f=0.2$ (1:1 hexane/THF); ^{1}H NMR ([D_6]DMSO, 250 MHz): $\delta=1.49$ (m, 10H), 3.48 (m, 1H), 4.66 (s, 2H), 6.87 (d, $J=7.9$ Hz, 1H), 6.48 (d, $J=8.7$ Hz, 2H), 7.03 (d, $J=8.7$ Hz, 2H), 7.76 ppm (s, 1H); IR (Si-Wafer): $\nu=3322$, 2928, 2852, 1623, 1566, 1518 cm^{-1}.

***N*-[4-(Cyclohexylureido)phenyl]octanamide (7a)**: This compound was prepared as described for **1**, starting from compound **6** (0.6 g, 2.6 mmol) and octanoyl chloride (0.54 mL, 3.0 mmol). The product was purified by recrystallization from methanol. Yield 0.7 g of a white powder (75%, 1.9 mmol); m.p. >192°C (decomp); $R_f=0.7$ (1:1 hexane/THF); ^{1}H NMR (5:1, $CDCl_3$, CF_3COOD, 250 MHz): $\delta=0.85$ (t, $J=6.8$ Hz, 3H), 1.27 (m, 15H), 1.72 (m, 5H), 1.93 (m, 2H), 2.51 (t, $J=8.1$ Hz, 2H), 3.67 (m, 1H), 7.25 (d, $J=8.7$ Hz, 2H), 7.50 ppm (d, $J=8.7$ Hz, 2H); MS: m/z (%): 359 (25) [M^+]; elemental analysis calcd (%) for $C_{21}H_{33}N_3O_2$ (359.26): C 70.16, H 9.25, N 11.69; found: C 69.94, H 9.12, N 11.07.

***N*-[4-(Cyclohexylureido)phenyl]tetradecanamide (7b)**: This compound was prepared as described for **1**, starting from compound **6** (0.5 g, 2.1 mmol) and tetradecoyl chloride (0.68 mL, 2.5 mmol). The product was purified by recrystallization from methanol. Yield 0.95 g of a white powder (85%, 1.8 mmol); m.p. >198°C (decomp); $R_f=0.76$ (1:1 hexane/THF); ^{1}H NMR (5:1, $CDCl_3$, CF_3COOD, 250 MHz): $\delta=0.85$ (t, 3H), 1.25 (m, 27H), 1.59 (m, 5H), 1.95 (m, 2H), 2.52 (t, $J=8.1$ Hz, 2H), 3.68 (m, 1H), 7.23 (d, $J=8.7$ Hz, 2H), 7.49 ppm (d, $J=8.7$ Hz, 2H); MS: m/z (%): 443 (8) [M^+]; $C_{27}H_{45}N_3O_2$ (443.35): C 73.09, H 10.22, N 9.47; found: C 73.02, H 10.23, N 9.31.

***N*-[4-(Cyclohexylureido)phenyl]octadecanamide (7c)**: This compound was prepared as described for **1**, starting from compound **6** (0.93 g, 4.0 mmol) and octadecoyl chloride (1.3 g, 4.3 mmol). The product was purified by recrystallization from methanol. Yield 1.7 g of a white powder (84%, 3.4 mmol); m.p. >200°C (decomp); $R_f=0.8$ (1:1 hexane/THF); ^{1}H NMR (5:1, $CDCl_3$, CF_3COOD, 250 MHz): $\delta=0.85$ (t, $J=6.8$ Hz, 3H), 1.25 (m, 35H), 1.73 (m, 5H), 1.95 (m, 2H), 2.52 (t, $J=7.4$ Hz, 2H), 3.69 (m, 1H), 7.24 (d $J=8.7$ Hz, H), 7.50 ppm (d, $J=8.7$ Hz, 2H); elemental analysis calcd (%) for $C_{31}H_{53}N_3O_2$ (499.41): C 74.50, H 10.69, N 8.41; found: C 73.95, H 10.62, N 8.16.

1-[4-(Cyclohexylureido)phenyl]-3-octylurea (8a): This compound was prepared as described for **4a**, starting from compound **6** (0.8 g, 3.4 mmol) and octylisocyanate (0.67 mL, 3.8 mmol). The product was purified by recrystallization from DMF. Yield 0.9 g of a white powder (64%, 2.2 mmol); m.p. >209°C (decomp); $R_f=0.5$ (1:1 hexane/THF); ^{1}H NMR (5:1, $CDCl_3$, CF_3COOD, 250 MHz): $\delta=0.87$ (t, $J=6.9$ Hz, 3H), 1.27 (m, 15H), 1.56 (m, 3H), 1.75 (m, 2H), 1.94 (m, 2H), 3.30 (t, $J=7.3$ Hz, 2H), 3.64 (m, 1H), 7.31 ppm (s, 4H); MS: m/z (%): 388 (14) [M^+]; elemental analysis calcd (%) for $C_{22}H_{36}N_4O_2$ (388.23): C 68.01, H 9.34, N 14.42; found C 68.04, H 9.38, N 14.23.

1-[4-(Cyclohexylureido)phenyl]-3-tetradecylurea (8b): This compound was prepared as described for **4a**, starting from compound **6** (0.3 g, 1.3 mmol) and tetradecylisocyanate (0.4 mL, 1.5 mmol). The product was purified by recrystallization from DMF. Yield 0.5 g of a white powder (78%, 1.0 mmol); m.p. >219°C (decomp); $R_f=0.6$ (1:1 hexane/THF); ^{1}H NMR (5:1, $CDCl_3$, CF_3COOD, 250 MHz): δ 0.85 (t, $J=6.8$ Hz, 3H), 1.24 (m, 27H), 1.57 (m, 3H), 1.74 (m, 2H), 1.94 (m, 2H), 3.30 (t, $J=7.3$ Hz, 2H), 3.65 (m, 1H), 7.31 ppm (s, 4H); MS: m/z (%): 472 (6) [M^+]; elemental analysis calcd (%) for $C_{28}H_{48}N_4O_2$ (472.38): C 71.14, H 10.23, N 11.85; found: C 70.63, H 10.17, N 11.65.

1-[4-(Cyclohexylureido)phenyl]-3-octadecylurea (8c): This compound was prepared as described for **4a**, starting from compound **6** (0.93 g, 4.0 mmol) and octadecylisocyanate (1.28 g, 4.3 mmol). The product was purified by recrystallization from DMF. Yield 1.7 g of a white powder (81%, 3.2 mmol); m.p. >214°C (decomp); $R_f=0.68$ (1:1 hexane/THF); ^{1}H NMR (5:1, $CDCl_3$, CF_3COOD, 250 MHz): δ 0.85 (t, $J=6.8$ Hz, 3H), 1.25 (m, 35H), 1.56 (m, 3H), 1.74 (m, 2H), 1.94 (m, 2H), 3.30 (t, $J=7.3$ Hz, 2H), 3.65 (m, 1H), 7.31 ppm (s, 4H); MS: m/z (%): 528 (6) [M^+]; elemental analysis calcd (%) for $C_{32}H_{56}N_4O_2$ (528.44): C 72.68, H 10.67, N 10.59; found: C 72.68, H 10.63, N 10.57.

Gelation tests: In a typical gelation test a weighed amount of the compound was mixed with 2 mL of solvent in a test tube with a screw cap, and then the mixture was heated until the solid was completely dissolved. The resulting solution was slowly allowed to cool to room temperature. Gelation was considered to have occurred when a homogenous substance was obtained which exhibited no gravitational flow.

For the determination of the sol–gel transition temperature (T_{gel}) of the gels the steel ball method was used.[4] A steel ball (260 mg) with a diameter of 4.5 mm was placed on the top of the gel and the vial was sealed. The samples were placed in a heating system, which was slowly heated, typically 5°C min^{-1}, while the temperature was determined with a temperature sensor that was dipped in a separate vial containing solvent. The T_{gel} of the gel was defined as the temperature when the steel ball hit the bottom of the vial.

Electron microscopy: For the transmission electron microscopy a formar/carbon-coated copper grid (300 mesh) was dipped for a very short time ($t<1$ s) into the solution of the gelator in the organic solvent and put on a weighing paper to become a gel. After 1 h the grid was placed in a round-bottomed flask and dried at low pressure ($<10^{-2}$ mbar). The grids were examined in a Zeiss CEM 902 electron microscope, operating at 80 kV.

Rheology: Rheological measurements were carried out with a stress rheometer Haake RS600 with a cone-plate (60 mm diameter). The width of the gap was 0.052 mm. Oscillatory experiments were performed in a 0.001–100 Hz frequency range at constant stress in the linear regime of deformation (1 Pa for a gel at 0.5 wt% and about 5 Pa for a gel at 2 wt%). The following procedure was used to load the sample: 1.5 mL of solvent solution containing gelator was placed on the plate that was about 95°C and closed by a cone. The system was cooled down to 25°C at a rate of 20°C min^{-1} as soon as the gap was totally filled with the gel; the measurements were started after 30 minutes.

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