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# Balancing hydrogen bonding and van der Waals interactions in cyclohexane based bisamide and bisurea organogelators

*Niek Zweep, Andrew Hopkinson, Auke Meetsma, Wesley R. Browne, Ben L. Feringa, Jan H. van Esch*

## **Supporting online Information**

- 1) Experimental and spectroscopic data of compounds **a2** to **a17** and **u4** to **u18**.
- 2) Single crystal X-ray analysis of **a3**
- 3) DSC-traces of the gels in decalin, 1-propanol and DMSO and the lists of the corresponding enthalpy of the gel –sol transition
- 4) FTIR spectra of the gels and solids and the lists of selected bands
- 5) Results from the linear fitting of DSC traces

## 1) Experimental and spectroscopic data of compounds a2 till a17 and u4 till u18.

### (+)-(R,R)-Propyl-3-[2-(3-propylamido)cyclohexyl]amide (a3)<sup>1</sup>

A solution of (0.50 g, 4.4 mmol) 1,2-(R,R)-diaminocyclohexane in 20 mL of freshly distilled THF at 0 °C was added slowly to a solution of (0.94 g, 8.9 mmol) butyryl chloride in 50 mL of freshly distilled THF and a precipitation was formed immediately. After 10 min (1 g, 10 mmol) triethylamine was added and the solution was stirred for another 30 min at room temperature. Subsequently, the solution was heated at reflux for 2 h and after cooling to room temperature the precipitate was collected on a glass filter (P3) and washed with a 100 mL aqueous HCl solution (pH 2). The precipitate was collected and stirred in 100 mL of diethyl ether for 2 h followed by filtration on a glass filter (P3). Stirring the precipitate in 100 mL of CHCl<sub>3</sub> for 16 h and filtration on a glass filter (P3) gave a white precipitate which was collected and dried at 60 °C *in vacuo* for 1 h. Compound **a3** was obtained as a white solid in (0.36g, 1.42 mmol, 32.2 %). mp. 174 - 176 °C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ= 0.89 (t, J=6.6 Hz, 6H), 1.10-1.30 (m, 4H), 1.54 (m, 4H), 1.71 (m, 4H), 2.00 (d, J=9.5 Hz, 2H), 2.14 (dt, J=7.6 Hz, 4H), 3.63 (m, 2H), 5.84 (bs, 2H) ppm. <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>): δ= 13.66 (p), 19.51 (s), 24.72 (s), 32.39 (s), 38.74 (s), 53.62 (t), 173.72 (q) ppm. FTIR (KBr): ν = 3280, 2933, 1638, 1548 cm<sup>-1</sup>. MS(EI) for C<sub>14</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>: m/z 254 [M<sup>+</sup>], HRMS calcd: 254.199, found: 254.201.

### (+)-(R,R)-Pentyl-3-[2-(3-pentylamido)cyclohexyl]amide (a5)

Compound **a5** was synthesised as for **a3** starting from (1.16 g, 8.6 mmol) hexanoyl chloride, (0.5 g, 4.3 mmol) (1R,2R)-(-)-1,2-diaminocyclohexane, and (1 g, 10 mmol) triethylamine. Compound **a5** was obtained as a white solid (0.88 g, 2.8 mmol, 65.8 %). mp. 214 - 216 °C. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ= 0.89 (t, J=6.6 Hz, 6H), 1.10-1.30 (m, 12H), 1.54 (m, 4H), 1.71 (m, 2H), 2.00 (d, J=9.5 Hz, 2H), 2.14 (dt, J=7.6 Hz, 4H), 3.63 (m, 2H), 5.84 (bs, 2H) ppm. <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>): δ= 13.89 (p), 22.36 (s), 24.70 (s), 25.46 (s), 31.40 (s), 32.38 (s), 36.86 (s), 53.61 (t), 173.84 (q) ppm. FTIR (KBr): ν = 3280,

2933, 1638, 1548  $\text{cm}^{-1}$ . MS(EI) for  $\text{C}_{18}\text{H}_{34}\text{N}_2\text{O}_2$ :  $m/z$  310 [ $\text{M}^+$ ], HRMS calcd: 310.262, found: 310.267. Anal. Calc. for  $\text{C}_{18}\text{H}_{34}\text{N}_2\text{O}_2$ : C, 69.63%; H, 11.04%; N, 9.02%; found (%): C, 69.75%; H, 11.07%; N, 9.01%.

**(+)-(R,R)-Heptyl-3-[2-(3-heptylamido)cyclohexyl]amide (a7)<sup>1</sup>**

Compound **a7** was synthesised as for **a3** starting from (0.51 g, 4.3 mmol) (*1R,2R*)-(-)-1,2-diaminocyclohexane, (1.42 g, 8.6 mmol) octanoyl chloride, and (1 g, 10 mmol) triethylamine. Compound **a7** was obtained as a white solid (1.10 g, 3.0 mmol, 69.8 %). mp. 216 - 218 °C. <sup>1</sup>H-NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$ = 0.87 (t, J= 6.5 Hz, 6H), 1.10-1.25 (bs, 20H), 1.52 (bs, 4H), 1.66 (bs, 2H) 1.95 (m, 2H) 2.10-2.20 (m, 4H), 3.64 (m, 2H), 5.94 (s, 1H) 6.28 (s, 1H) ppm. <sup>13</sup>C-NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$ = 13.94 (p), 22.51 (s), 24.70 (s), 25.79 (s), 28.97(s), 29.20(s), 31.62(s), 32.23(s), 36.75(s), 53.35(t), 173.87(q) ppm. FTIR (KBr):  $\nu$  = 3284, 2926, 1637, 1546  $\text{cm}^{-1}$ . MS(EI) for  $\text{C}_{22}\text{H}_{42}\text{N}_2\text{O}_2$ :  $m/z$  366 [ $\text{M}^+$ ], HRMS calcd: 366.325, found: 366.354.

**(+)-(R,R)-Undecyl-3-[2-(3-undecylamido)cyclohexyl]amide (a11)<sup>1</sup>**

Compound **a11** was synthesised as for **a3** starting from (0.46 g, 4.0 mmol) (*1R,2R*)-(-)-1,2-diaminocyclohexane, (1.75 g, 8.0 mmol) lauroyl chloride and (1 g, 10 mmol) triethylamine. Compound **a11** was obtained as a white solid (1.49 g, 3.1 mmol, 86.0 %). mp. 175 - 178 °C. <sup>1</sup>H-NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$ = 0.86 (t, J=6.6 Hz, 6H), 1.10-1.25 (m, 36H), 1.52 (m, 4H), 1.74 (m, 2H), 2.00 (d, J=12.1 Hz, 2H), 2.08 (dt, J=7.6 Hz, 4H), 3.62 (m, 2H), 5.85 (bs, 2H) ppm. <sup>13</sup>C-NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$ = 14.08 (p), 22.66 (s), 24.70 (s), 25.82 (s), 29.32 (s), 29.38 (s), 29.51 (s), 29.62 (s), 31.88 (s), 32.36 (s), 36.91 (s), 53.58 (t), 173.85 (q) ppm. FTIR (KBr):  $\nu$  = 3276, 2919, 1637, 1549  $\text{cm}^{-1}$ . MS(EI) for  $\text{C}_{30}\text{H}_{58}\text{N}_2\text{O}_2$ :  $m/z$  479 [ $\text{M}^+$ ], HRMS calcd: 478.450, found: 478.450.

**(+)-(R,R)-Tridecyl-3-[2-(3-tridecylamido)cyclohexyl]amide (a13)**

Compound **a13** was synthesised as for **a3** starting from (1.42 g, 12.4 mmol) (*1R,2R*)-(-)-1,2-diaminocyclohexane, (6.14 g, 24.8 mmol) myristoyl chloride and (3 g, 30 mmol) triethylamine.

Compound **a13** was obtained as a white solid (2.77 g, 5.2 mmol, 41.8 %). mp. 182 - 184 °C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 50°C): δ= 0.89 (t, J=7.4 Hz, 6H), 1.25 (m, 44H), 1.53 (m, 4H), 1.74 (m, 2H), 2.00 (d, J= 12.0 Hz, 2H), 2.11 (dt, J=7.6 Hz, 4H), 3.64 (m, 2H), 5.78 (m, 2H) ppm. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, TFA): δ= 14.08 (p), 22.56 (s), 24.73 (s), 25.82 (s), 29.32 (s), 29.39 (s), 29.52 (s), 29.65 (s), 31.90 (s), 32.38 (s), 36.93 (s), 53.60 (t), 173.83 (s) ppm. FTIR (KBr): ν = 3285, 2919, 1637, 1546 cm<sup>-1</sup>. MS(EI) for C<sub>34</sub>H<sub>66</sub>N<sub>2</sub>O<sub>2</sub>: m/z 535 [M<sup>+</sup>], HRMS calcd: 534.512, found: 534.510. Anal. Calcd. for C<sub>34</sub>H<sub>66</sub>N<sub>2</sub>O<sub>2</sub>: C, 76.34%; H, 12.44%; N, 5.24%; found (%): C, 76.30%; H, 12.63%; N, 5.23%.

**(+)-(R,R)-Pentadecyl-3-[2-(3-pentadecylamido)cyclohexyl]amide (a15)**

Compound **a15** was synthesised as for **a3** starting from (1.77 g, 14.8 mmol) (*1R,2R*)-(-)-1,2-diaminocyclohexane, (8.81 g, 32.0 mmol) palmitoyl chloride and (3 g, 30 mmol) triethylamine. Compound **a15** was obtained as a white solid (4.30 g, 7.3 mmol, 49.2 %). mp. 180 - 185 °C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 50°C): δ= 0.86 (t, J=6.6 Hz, 6H), 1.20-1.30 (m, 52H), 1.57 (m, 4H), 1.71 (m, 2H), 2.00 (d, J=9.5 Hz, 2H), 2.14 (dt, J=7.6 Hz, 4H), 3.63 (m, 2H), 5.84 (bs, 2H) ppm. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, TFA): δ= 14.03 (p), 22.72 (s), 24.11 (s), 25.87 (s), 28.98 (s), 29.05 (s), 29.40 (s), 29.55 (s), 29.69 (s), 31.47 (s), 31.98 (s), 35.81 (s), 54.21 (t), 178.22 (q) ppm. FTIR (KBr): ν = 3282, 2919, 1637, 1549 cm<sup>-1</sup>. MS(EI) for C<sub>38</sub>H<sub>74</sub>N<sub>2</sub>O<sub>2</sub>: m/z 591 [M<sup>+</sup>], HRMS calcd: 590.574, found: 590.575. Anal. Calc. for C<sub>38</sub>H<sub>74</sub>N<sub>2</sub>O<sub>2</sub>: C, 77.23%; H, 12.62%; N, 4.74%; found (%): C, 77.30%; H, 12.86%; N, 4.68%.

**(+)-(R,R)-Heptadecyl-3-[2-(3-heptadecylamido)cyclohexyl]amide (a17)**

Compound **a17** was synthesised as for **a3** starting from (0.28 g, 2.4 mmol) (*1R,2R*)-(-)-1,2-diaminocyclohexane, (1.50 g, 4.9 mmol) stearoyl chloride, and (1 g, 10 mmol) triethylamine. Compound **a17** was obtained as a white solid (1.45 g, 2.2 mmol, 93.3 %). mp. 175 - 179 °C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 50°C): δ= 0.86 (t, J=6.6 Hz, 6H), 1.20-1.30 (m, 60H), 1.57 (m, 4H), 1.71 (m, 2H), 2.00 (d, J=9.5 Hz, 2H), 2.14 (dt, J=7.6 Hz, 4H), 3.63 (m, 2H), 5.84 (bs, 2H) ppm. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, TFA): δ= 13.98 (p), 22.72 (s), 24.00 (s), 25.94 (s), 29.00 (s), 29.07 (s), 29.44 (s), 29.58 (s), 29.66 (s), 29.76 (s),

31.35 (s), 31.99 (s), 35.65 (s), 54.47 (t), 178.59 (q) ppm. FTIR (KBr):  $\nu = 3280, 2919, 1637, 1548 \text{ cm}^{-1}$ . MS(EI) for  $\text{C}_{42}\text{H}_{82}\text{N}_2\text{O}_2$ :  $m/z$  647 [ $\text{M}^+$ ], HRMS calcd: 646.638, found: 646.635. Anal. Calcd. for  $\text{C}_{42}\text{H}_{82}\text{N}_2\text{O}_2$ : C, 77.95%; H, 12.77%; N, 4.33%; found (%): C, 77.61%; H, 12.82%; N, 4.19%.

#### **(+)-(R,R)-Ethyl-3-[2-(3-ethylamido)cyclohexyl]amide (a2)<sup>1</sup>**

Compound **a2** was synthesised as for **a3** starting from (0.30 g, 2.6 mmol) (*1R,2R*)-(-)-1,2-diaminocyclohexane, (0.50 g, 5.4 mmol) propionyl chloride, and (0.4 g, 4 mmol) triethylamine. Compound **a2** was obtained as white solid (0.4 g, 1.8 mmol, 68.0 %). mp. 246 - 249 °C. <sup>1</sup>H-NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.08$  (t,  $J=7.6$  Hz, 6H), 1.20-1.30 (m, 4H), 1.73 (m, 2H), 1.99 (d,  $J=11.2$  Hz, 2H), 2.10 (m, 4H), 3.68 (m, 2H), 5.90 (bs, 2H) ppm. <sup>13</sup>C-NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta = 9.93$  (p), 24.71 (s), 29.86 (s), 32.34 (s), 53.64 (t), 174.50 (q) ppm. FTIR (KBr):  $\nu = 3280, 2933, 1639, 1548 \text{ cm}^{-1}$ . MS(EI) for  $\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_2$ :  $m/z$  226 [ $\text{M}^+$ ], HRMS calcd: 226.168, found: 226.168.

#### **(+)-(R,R)-Butyl-3-[2-(3-butylamido)cyclohexyl]amide (a4)**

Compound **a4** was synthesised as for **a2** starting from (0.5 g, 4.3 mmol) (*1R,2R*)-(-)-1,2-diaminocyclohexane, (1.04 g, 8.6 mmol) valeryl chloride, and (1 g, 10 mmol) triethylamine. Compound **a4** was obtained as a white solid (0.80 g, 2.9 mmol, 66.3 %). mp. 236 - 238 °C. <sup>1</sup>H-NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.89$  (t,  $J=6.6$  Hz, 6H), 1.10-1.30 (m, 8H), 1.54 (m, 4H), 1.71 (m, 2H), 2.00 (d,  $J=9.5$  Hz, 2H), 2.14 (dt,  $J=7.6$  Hz, 4H), 3.63 (m, 2H), 5.84 (bs, 2H) ppm. <sup>13</sup>C-NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.73$  (p), 22.35 (s), 24.70 (s), 27.85 (s), 32.33 (s), 36.57 (s), 53.56 (t), 173.83 (q) ppm. FTIR (KBr):  $\nu = 3282, 2933, 1637, 1547 \text{ cm}^{-1}$ . MS(EI) for  $\text{C}_{16}\text{H}_{30}\text{N}_2\text{O}_2$ :  $m/z$  282 [ $\text{M}^+$ ], HRMS calcd: 282.231, found: 282.231. Anal. Calcd. for  $\text{C}_{16}\text{H}_{30}\text{N}_2\text{O}_2$ : C, 68.04%; H, 10.71%; N, 9.92%; found (%): C, 68.20 %; H, 10.87%; N, 9.63%.

#### **(+)-(R,R)-Butyl-3-[2-(3-butylureido)cyclohexyl]urea (u4)<sup>2</sup>**

The synthesis of the bisurea gelator compounds used in this research was performed as described previously for compound **u12**. Compound **u4** was synthesised by adding slowly (1.70 g, 17.2 mmol)

butylisocyanate dissolved in 5 ml toluene to a solution of (0.99 g, 8.6 mmol) (*1R,2R*)-(-)-1,2-diaminocyclohexane in 20 mL of freshly distilled toluene. Immediately upon adding, the solution became viscous. After adding the isocyanate, the solution was heated at reflux temperature for 4 h. The solution was cooled down and the gel-like mixture was filtered over a glass filter (P3) to give a waxy solid. This was collected and stirred for 16 h in 100 mL of CH<sub>2</sub>Cl<sub>2</sub>. The solution was filtered afterwards over a glass filter (P3) and the precipitate was stirred in 100 mL of diethyl ether for 16 h. Subsequently, it was filtered over a glass filter (P3) and the white precipitated left, was dried *in vacuo* for 1 h at 60 °C. Compound **u4** was obtained as a white solid (1.90 g, 6.1 mmol, 93.3 %). mp. 185 - 187 °C (dec). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ= 0.89 (t, J=7.4 Hz, 6H), 1.24-1.35 (mp, 8H), 1.36-1.53 (mp, 4H), 1.80 (d, J=8.8 Hz, 2H), 2.02 (d, J=12.4 Hz, 2H), 3.15 (mp, 4H), 3.44 (mp, 2H), 4.38 (bs, 2H), 4.95 (bs, 2H) ppm. <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>, TFA): δ= 13.23 (p), 19.60 (s), 24.20 (s), 30.73 (s), 32.16 (s), 41.49 (s), 55.54 (t), 159.32 (q) ppm. FTIR (KBr): ν = 3330, 2933, 1633, 1599 cm<sup>-1</sup>. MS(EI) for C<sub>16</sub>H<sub>32</sub>N<sub>4</sub>O: m/z 312 [M<sup>+</sup>], HRMS calcd: 312.253, found: 312.253.

#### **(+)-(R,R)Hexyl-3-[2-(3-hexylureido)cyclohexyl]urea (u6)**

Compound **u6** was synthesised as for **u4** starting from (0.35 g, 3.0 mmol) (*1R,2R*)-(-)-1,2-diaminocyclohexane and (0.77 g, 6.1 mmol) hexylisocyanate. Compound **u6** was obtained as a white solid (0.27 g, 0.7 mmol, 24.8 %). mp. 224 - 226 °C (dec). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ= 0.88 (t, J=7.4 Hz, 6H), 1.20-1.30 (m, 16H), 1.49 (d, J=7.2 Hz, 4H), 1.78 (s, 2H), 2.10 (d, J=10.3 Hz, 2H), 3.13 (m, 4H), 3.49 (m, 2H), 4.72 (m, 2H), 5.26 (m, 2H) ppm. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, TFA): δ= 13.67 (s), 22.35 (s), 24.17 (s), 26.12 (s), 28.70 (s), 31.15 (s), 32.12 (s), 41.86 (s), 55.58 (t), 159.29 (q) ppm. FTIR (KBr): ν = 3330, 2926, 1633, 1586 cm<sup>-1</sup>. MS(EI) for C<sub>20</sub>H<sub>40</sub>N<sub>4</sub>O<sub>2</sub>: m/z 368 [M<sup>+</sup>], HRMS calcd: 368.315, found: 368.316. Anal. Calcd. for C<sub>20</sub>H<sub>40</sub>N<sub>4</sub>O<sub>2</sub>: C, 65.16%; H, 10.95%; N, 15.21%; found (%): C, 65.25%; H, 10.98%; N, 15.17%.

**(+)-(R,R)-Octyl-3-[2-(3-Octylureido)cyclohexyl]urea (u8)**

Compound **u8** was synthesised as for **u4** starting from (0.28 g, 2.4 mmol) (*1R,2R*)-(-)-1,2-diaminocyclohexane and (1.50 g, 4.9 mmol) octylisocyanate. Compound **u4** was obtained as a white solid (0.88 g, 2.1 mmol, 86.1 %). mp. 178 - 184 °C (dec). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ= 0.88 (t, J=6.6 Hz, 6H), 1.20-1.30 (m, 24H), 1.51 (m, 2H), 1.64 (m, 2H), 1.77 (m, 2H), 2.10 (d, J=10.3 Hz, 2H), 3.15 (m, 4H), 3.50 (m, 2H), 4.37 (m, 2H), 4.95 (m, 2H) ppm. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ= 13.75 (p), 22.58 (s), 24.14 (s), 26.53 (s), 28.73 (s), 29.04 (s), 29.08 (s), 31.74 (s), 32.14 (s), 42.08 (s), 55.76 (t), 159.28 (q) ppm. FTIR (KBr): ν = 3331, 2926, 1633, 1586 cm<sup>-1</sup>. MS(EI) for C<sub>24</sub>H<sub>48</sub>N<sub>4</sub>O<sub>2</sub>: m/z 424 [M<sup>+</sup>], HRMS calcd: 424.378, found: 424.379. Anal. Calcd. for C<sub>24</sub>H<sub>48</sub>N<sub>4</sub>O<sub>2</sub>: C, 67.86%; H, 11.40%; N, 13.20%; found (%): C, 67.65%; H, 11.42%; N, 13.18%.

**(+)-(R,R)-Decyl-3-[2-(3-decylureido)cyclohexyl]urea (u10)**

Compound **u10** was synthesised as for **u4** starting from (1.10 g, 9.6 mmol) (*1R,2R*)-(-)-1,2-diaminocyclohexane and (3.90 g, 20.8 mmol) decylisocyanate. Compound **u10** was obtained as a white solid (2.00 g, 4.2 mmol, 43.4 %). mp. 170 - 178 °C (dec). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ= 0.86 (t, J=6.6 Hz, 6H), 1.20-1.40 (m, 32H), 1.43 (m, 4H), 1.70 (m, 2H), 2.00 (d, J=10.6 Hz, 2H), 3.07 Hz (m, 4H), 3.42 (m, 2H), 4.53 (s, 2H), 5.08 (s, 2H) ppm. <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>): δ= 13.94 (p), 22.67 (s), 24.16 (s), 26.51 (s), 28.76 (s), 29.07 (s), 29.28 (s), 29.41 (s), 29.49 (s), 31.89 (s), 32.14 (s), 41.95 (s), 55.65 (t), 159.26 (q) ppm. FTIR (KBr): ν = 3331, 2924, 1633, 1591 cm<sup>-1</sup>. MS(EI) for C<sub>28</sub>H<sub>56</sub>N<sub>4</sub>O<sub>2</sub>: m/z 480 [M<sup>+</sup>], HRMS calcd: 480.440, found: 480.441. Anal. Calcd. for C<sub>28</sub>H<sub>56</sub>N<sub>4</sub>O<sub>2</sub>: C, 69.90%; H, 11.75%; N, 11.66%; found (%): C, 69.62%; H, 11.69%; N, 11.51%.

**(+)-(R,R)-Dodecyl-3-[2-(3-dodecylureido)cyclohexyl]urea (u12)<sup>2</sup>**

Compound **u12** was synthesised as for **u4** starting from (0.80 g, 7.0 mmol) (*1R,2R*)-(-)-1,2-diaminocyclohexane and (3.17 g, 15.0 mmol) decylisocyanate. Compound **u12** was obtained as a white solid (3.00 g, 5.6 mmol, 80.0 %). mp. 180 - 188 °C (dec). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 62 °C): δ= 0.89



(t, J=6.6 Hz, 6H), 1.20-1.40 (m, 40H), 1.47 (m, 4H), 1.72 (m, 2H), 2.05 (d, J=10.6 Hz, 2H), 3.12 Hz (m, 4H), 3.44 (m, 2H), 5.00 (bs, 4H) ppm.  $^{13}\text{C}$ -NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$ = 14.00 (p), 22.67 (s), 25.08 (s), 27.04 (s), 29.36 (s), 29.45 (s), 29.65 (s), 30.34 (s), 31.94 (s), 33.29 (s), 40.85 (s), 55.17 (t), 159.15 (q) ppm. FTIR (KBr):  $\nu$  = 3330, 2922, 1634, 1587  $\text{cm}^{-1}$ . MS(EI) for  $\text{C}_{32}\text{H}_{64}\text{N}_4\text{O}_2$ : m/z 537 [ $\text{M}^+$ ], HRMS calcd: 536.503, found: 536.502.

**(+)-(R,R)-Hexadecyl-3-[2-(3-hexadecylureido)cyclohexyl]urea (u16)**

Compound **u16** was synthesised as for **u3** starting from (0.30 g, 2.6 mmol) (*IR,2R*)-(-)-1,2-diaminocyclohexane and (1.49 g, 5.6 mmol) hexadecylisocyanate. Compound **u16** was obtained as a white solid (1.45 g, 2.2 mmol, 86.1 %). mp. 164 - 166 °C (dec).  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ , 62 °C):  $\delta$ = 0.88 (t, J=6.6 Hz, 6H), 1.20-1.40 (m, 56 H), 1.45 (m, 4H), 1.71 (m, 2H), 2.08 (d, J=10.6, 2H), 3.13 (m, 4H), 3.47 (m, 2H), 5.00 (bs, 4 H) ppm.  $^{13}\text{C}$ -NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$ = 14.02 (p), 22.71 (s), 24.16 (s), 26.52 (s), 28.78 (s), 29.08 (s), 29.42 (s), 29.56 (s), 29.73 (s), 31.98 (s), 32.14 (s), 41.92 (s), 55.61 (t), 159.25 (q) ppm. FTIR (KBr):  $\nu$  = 3329, 2919, 1633, 1589  $\text{cm}^{-1}$ . MS(EI) for  $\text{C}_{40}\text{H}_{80}\text{N}_4\text{O}_2$ : m/z 649 [ $\text{M}^+$ ], HRMS calcd: 648.628, found: 648.628. Anal. Calcd. for  $\text{C}_{40}\text{H}_{80}\text{N}_4\text{O}_2$ : C, 74.00%; H, 12.43%; N, 8.64%; found (%): C, 74.02%; H, 12.60%; N, 8.57%.

**(+)-(R,R)-Octadecyl-3-[2-(3-octadecylureido)cyclohexyl]urea (u18)<sup>2</sup>**

Compound **u18** was synthesised as for of **u4** starting from (0.34 g, 3.0 mmol) (*IR,2R*)-(-)-1,2-diaminocyclohexane and (1.96 g, 6.6 mmol) octadecylisocyanate. Compound **u18** was obtained as a white solid (1.54 g, 2.2 mmol, 73.0 %). mp. 170 - 178 °C (dec).  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ , 62 °C):  $\delta$ = 0.87 (t, J=6.6 Hz, 6H), 1.20-1.40 (m, 64H), 1.46 (m, 4H), 1.69 (m, 2H), 2.02 (d, J=12.1 Hz, 2H), 3.08 (m, 4H), 3.43 (m, 2H), 4.30 (m, 2H), 4.86 (m, 2H) ppm.  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$ = 13.95 (p), 22.75 (s), 24.17 (s), 26.57 (s), 28.80 (s), 29.14 (s), 29.48 (s), 29.63 (s), 29.71 (s), 29.81 (s), 32.04 (s), 32.15 (s), 42.06 (s), 55.75 (t), 159.33 (q) ppm. FTIR (KBr):  $\nu$  = 3329, 2918, 1634, 1589  $\text{cm}^{-1}$ . MS(EI) for  $\text{C}_{44}\text{H}_{88}\text{N}_4\text{O}_2$ : m/z 705 [ $\text{M}^+$ ], HRMS calcd: 704.691, found: 704.688.

## 2) Single crystal X-ray analysis of a3.

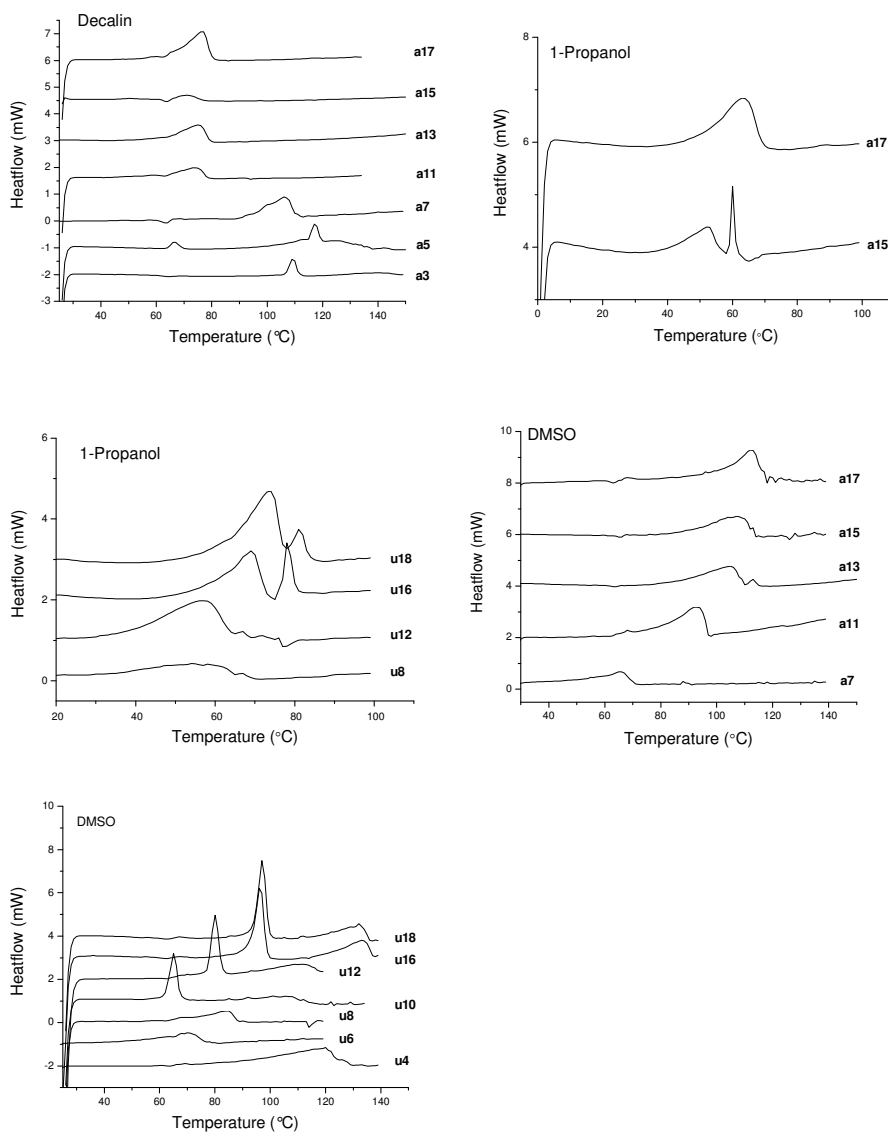
A crystal fragment, cut to size to fit in the homogeneous part of the X-ray beam, with dimensions of 0.41 x 0.29 x 0.04 mm was mounted on top of a glass fiber and aligned on a *Bruker*<sup>3</sup> *SMART APEX* CCD diffractometer (Platform with full three-circle goniometer). The diffractometer was equipped with a 4K CCD detector set 60.0 mm from the crystal. The crystal was cooled to 100 ( $\pm$  1) K using the *Bruker KRYOFLEX* low-temperature device. Intensity measurements were performed using graphite monochromated Mo-K $\bar{\alpha}$  radiation from a sealed ceramic diffraction tube (*SIEMENS*). Generator settings were 50 KV, 40 mA. *SMART* was used for preliminary determination of the unit cell constants and data collection control. The intensities of reflections of a hemisphere were collected by a combination of 3 sets of exposures (frames). Each set had a different  $\phi$  angle for the crystal and each exposure covered a range of 0.3° in  $\omega$ . A total of 1800 frames were collected with an exposure time of 45.0 seconds per frame. The overall data collection time was 28.0 h. Data integration and global cell refinement was performed with the program *SAINT*. The final unit cell was obtained from the xyz centroids of 3025 reflections after integration. Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption: a multi-scan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*),<sup>4</sup> and reduced to  $F_o^2$ . The program suite *SHELXTL* was used for space group determination (*XPREP*).<sup>3</sup> The intensity data were corrected for decay and absorption: a multi-scan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*)<sup>4</sup> and reduced to  $F_o^2$ . The unit cell<sup>5</sup> was identified as monoclinic. Reduced cell calculations did not indicate any higher metric lattice symmetry.<sup>6</sup> Space group  $P2_1$  was determined from considerations of the unit cell parameters, statistical analyses of intensity distributions; the *E*-statistics<sup>7</sup> were indicative of a non-centrosymmetric space group. Examination of the final atomic coordinates of the structure did not yield extra crystallographic or metric symmetry elements.<sup>8,9</sup> The structure was solved by direct methods using the program *SIR-97*.<sup>10</sup> The positional and anisotropic displacement

parameters for the non-hydrogen atoms were refined. A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, which coordinates and isotropic displacement parameters were refined. Final refinement on  $F^2$  carried out by full-matrix least-squares techniques converged at  $wR(F^2) = 0.1033$  for 1574 reflections and  $R(F) = 0.0425$  for 1324 reflections with  $F_o \geq 4.0 \sigma(F_o)$  and 267 parameters and 1 restraints. The final difference Fourier map was essentially featureless: no significant peaks ( $0.21(\pm 5) e \text{ \AA}^{-3}$ ) having chemical meaning above the general background were observed. Because this light-atom structure does not reveal sufficient anomalous dispersion, the absolute configuration of the structure could not be confirmed, as known by the synthesis route; therefore the Friedel pairs were merged (prior to the refinement). The absolute exhibited configuration should be the one as stated in this article (C6 and C10 both have *R*-configuration). The positional and anisotropic displacement parameters for the non-hydrogen atoms and isotropic displacement parameters for hydrogen atoms were refined on  $F^2$  with full-matrix least-squares procedures minimizing the function  $Q = \sum_h [w(|(F_o^2) - k(F_c^2)|)^2]$ , where  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ,  $P = [\max(F_o^2, 0) + 2F_c^2] / 3$ ,  $F_o$  and  $F_c$  are the observed and calculated structure factor amplitudes, respectively; ultimately the suggested  $a$  ( $= 0.0686$ ) and  $b$  ( $= 0.0$ ) were used in the final refinement. Neutral atom scattering factors and anomalous dispersion corrections were taken from *International Tables for Crystallography*.<sup>11</sup> All refinement calculations and graphics were performed on a HP XW6200 (Intel XEON 3.2 Ghz) / Debian-Linux computer at the University of Groningen with the program packages *SHELXL*<sup>12</sup> (least-square refinements), a locally modified version of the program *PLUTO*<sup>13</sup> (preparation of illustrations) and *PLATON*<sup>14</sup> package (checking the final results for missed symmetry with the *MISSYM* option, solvent accessible voids with the *SOLV* option, calculation of geometric data and the *ORTEP*<sup>14</sup> illustrations). Each asymmetric unit contains one formula unit (molecule) with no atom setting at special position. The monoclinic unit cell contains two discrete units of the title compound. The chiral centers of C6 and C10 showed both the *R*-configuration.

<sup>14</sup> A search of the distances yielded intermolecular and intramolecular contacts shorter than the sum of the van der Waals radii<sup>15</sup> for the atoms: the moieties are linked<sup>15,16,17</sup> by hydrogen bonds forming an

infinite one-dimensional network along the [0 1 0] base vector. No missed symmetry (*MISSYM*) or solvent-accessible voids were detected by procedures implemented in *PLATON*.<sup>16</sup>

### 3) DSC-traces of the gels in decalin, 1-propanol and DMSO and the lists of the corresponding enthalpy of the gel –sol transition



The procedure for DSC sample preparation is described in the experimental section. The concentration of the gelators in the selected solvents is 20-40 mg/mL. It should be noted that gels were prepared in the sample pans to ensure accuracy in concentration as transferring between vials typically expels solvent from the gels mechanically. Gel formation and homogeneity was confirmed by visual inspection of the content of sample pans subsequent to each measurement.

**Table 1.** Melting enthalpies,  $\Delta H_m$  in  $\text{kJ mol}^{-1}$ , of bisurea and bisamide gelators in different solvents ( $\pm 2$   $\text{kJ mol}^{-1}$ ).

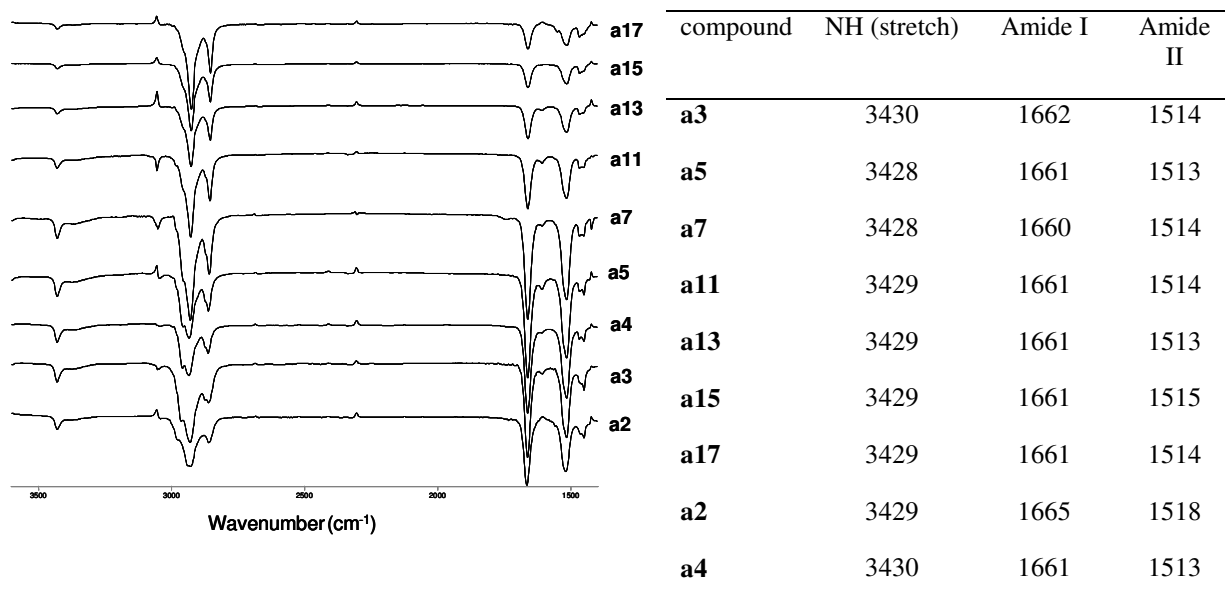
Compound	$\Delta H_m$ in Decalin	$\Delta H_m$ in 1-Propanol	$\Delta H_m$ in DMSO
<b>a3</b>	15.1	- <sup>b</sup>	- <sup>b</sup>
<b>a5</b>	18.0	- <sup>b</sup>	- <sup>b</sup>
<b>a7</b>	26.4	- <sup>b</sup>	34.3
<b>a11</b>	38.3	- <sup>b</sup>	59.5
<b>a13</b>	49.0	52.1	75.2
<b>a15</b>	70.3	69.8	93.0
<b>a17</b>	74.5	84.5	102.8
<b>a2</b>	15.6	- <sup>b</sup>	- <sup>b</sup>
<b>a4</b>	19.0	- <sup>b</sup>	- <sup>b</sup>
<b>u4</b>	- <sup>a</sup>	- <sup>b</sup>	19.4
<b>u6</b>	- <sup>a</sup>	- <sup>b</sup>	30.5
<b>u8</b>	- <sup>a</sup>	- <sup>b</sup>	43.7
<b>u10</b>	- <sup>a</sup>	37.1	59.4
<b>u12</b>	- <sup>a</sup>	51.2	75.2
<b>u16</b>	- <sup>a</sup>	87.0	102.6
<b>u18</b>	- <sup>a</sup>	101.7	115.9

[a] Melting enthalpy could not be determined as the gelator decomposed before the gel has melted completely. [b] Melting enthalpy could not be determined as the compound does not form a gel in his solvent.

#### 4) FTIR spectra of the gels and solids and lists of selected absorption bands

##### Bisamides

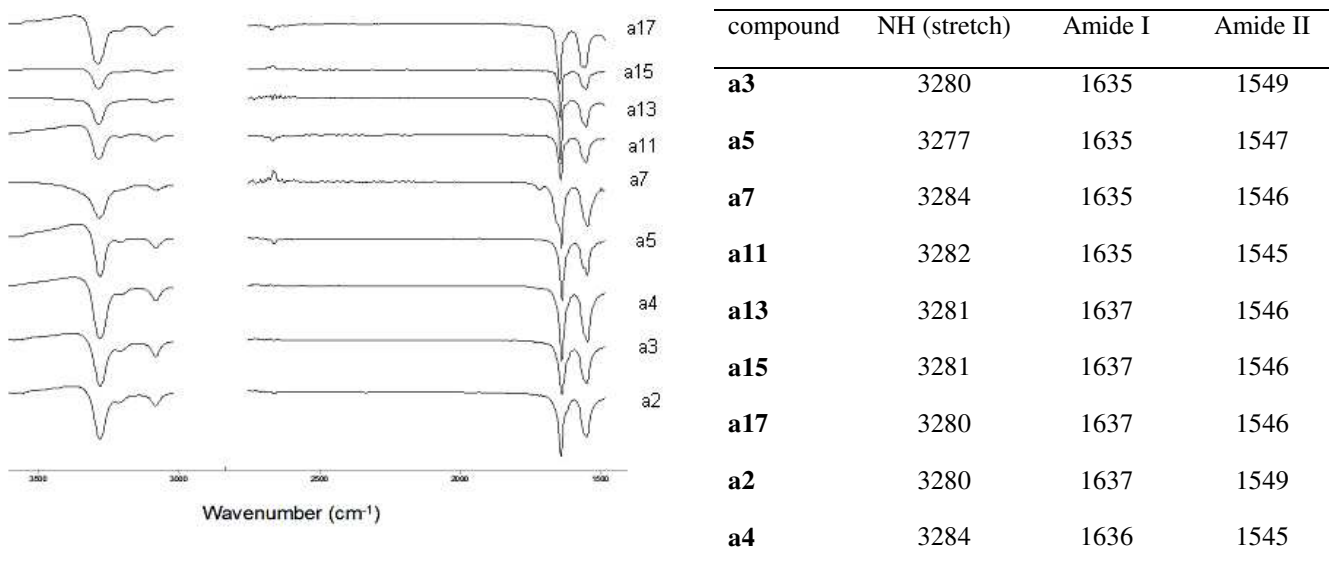
**Table 2.** Selected FTIR bands ( $\nu$ ,  $\text{cm}^{-1}$ ) of bisamide gelators ( $1 \text{ mg mL}^{-1}$ ) dissolved in  $\text{CH}_2\text{Cl}_2$  ( $\pm 2 \text{ cm}^{-1}$ ).<sup>a</sup>



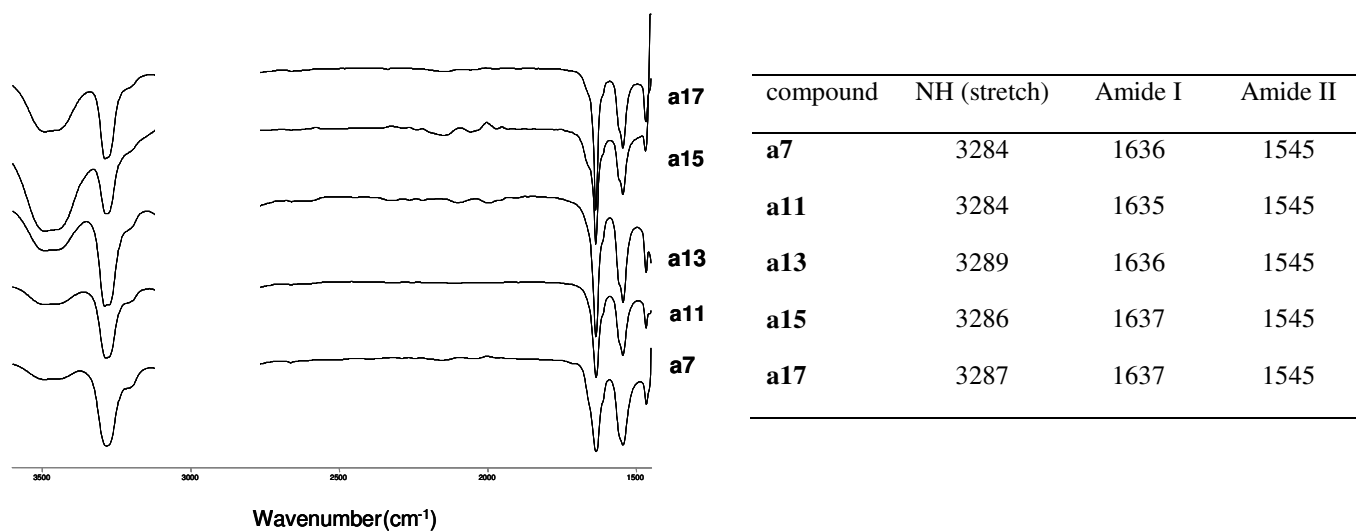
[a]

Recorded in  $\text{CaF}_2$ -cell with 0.1 mm spacing.

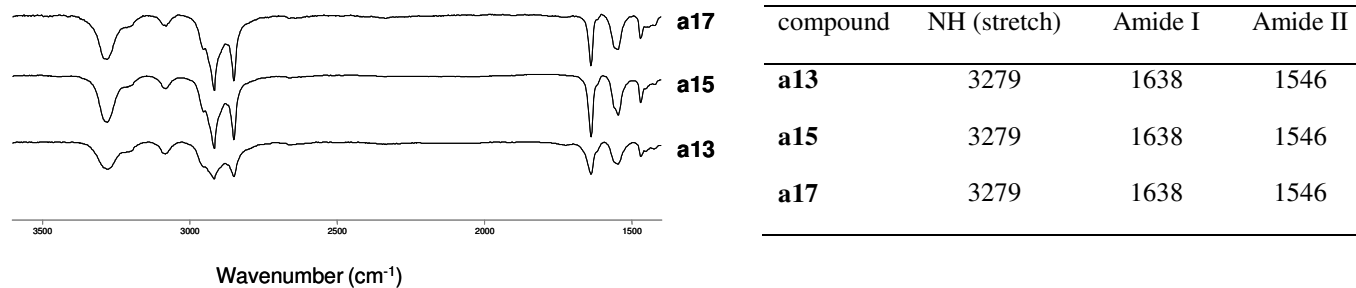
**Table 3.** Selected FTIR bands ( $\nu$ ,  $\text{cm}^{-1}$ ) of bisamide gelators ( $5 \text{ mg mL}^{-1}$ ) as gel in decalin ( $\pm 2 \text{ cm}^{-1}$ ).<sup>a</sup>



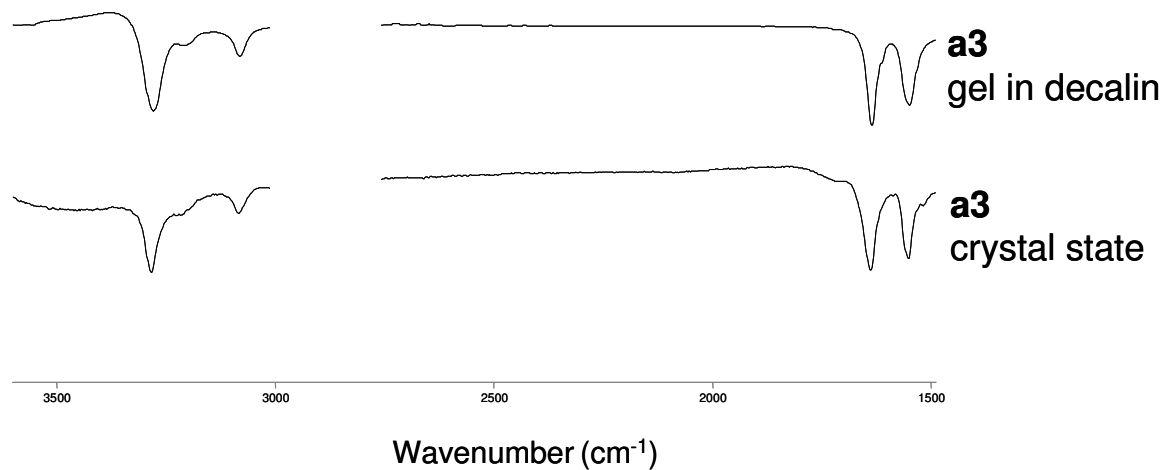
[a] Recorded in a  $\text{CaF}_2$ -cell with 0.1mm spacing.

**Table 4.** Selected FTIR bands ( $\nu$ ,  $\text{cm}^{-1}$ ) of bisamide gelators ( $5 \text{ mg mL}^{-1}$ ) as gel in DMSO ( $\pm 2 \text{ cm}^{-1}$ ).<sup>a</sup>

[a] Recorded in a  $\text{CaF}_2$ -cell with 0.1 mm spacing.

**Table 5.** Selected FTIR bands ( $\nu$ ,  $\text{cm}^{-1}$ ) of bisamides aerogels from 1-propanol ( $\pm 2 \text{ cm}^{-1}$ ).<sup>a</sup>

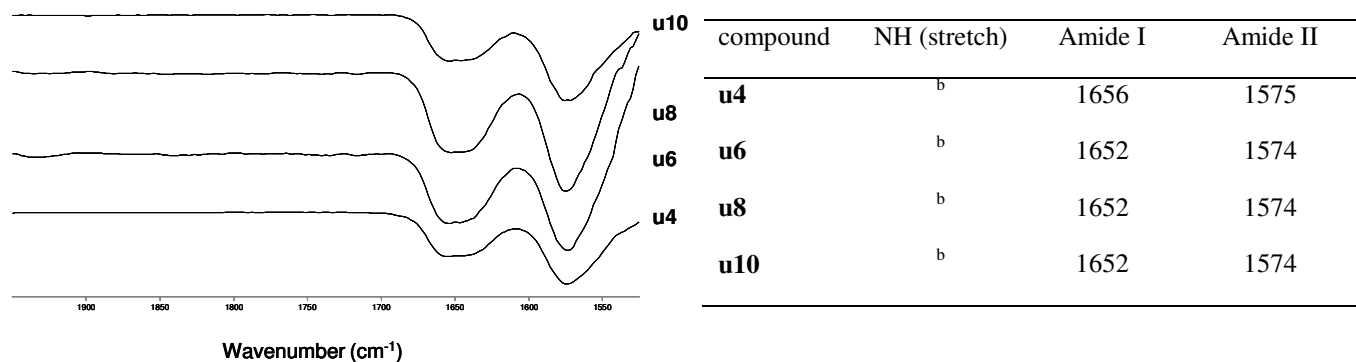
[a] Recorded as an intimate mixture with KBr.





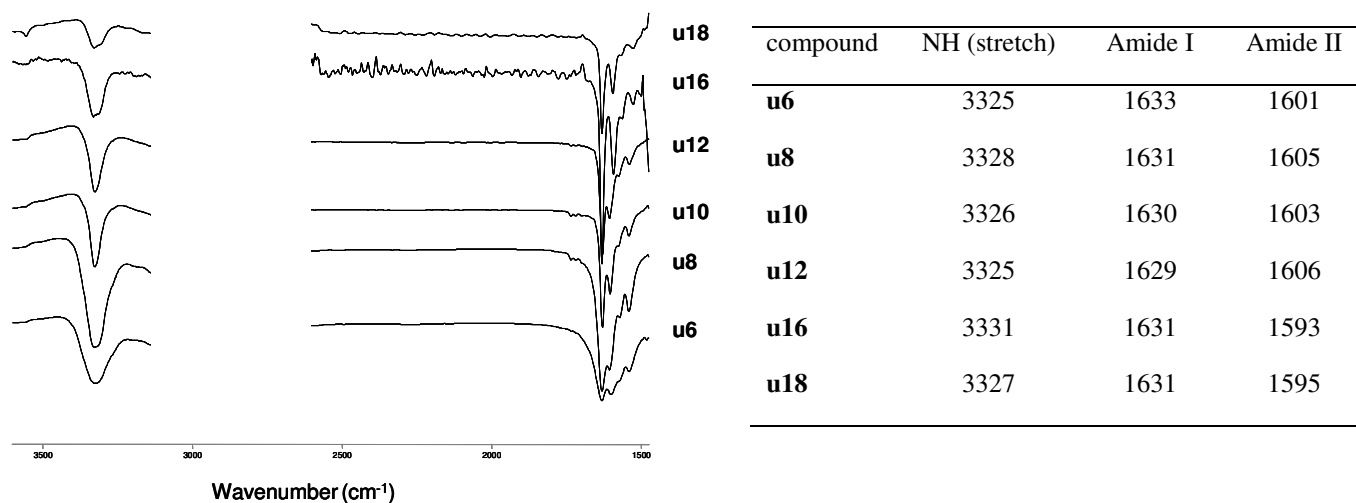
## Bisurea gelators

**Table 6.** Selected FTIR bands ( $\nu$ ,  $\text{cm}^{-1}$ ) of bisurea gelators ( $1 \text{ mg mL}^{-1}$ ) in methanol ( $\pm 2 \text{ cm}^{-1}$ ).<sup>a</sup>



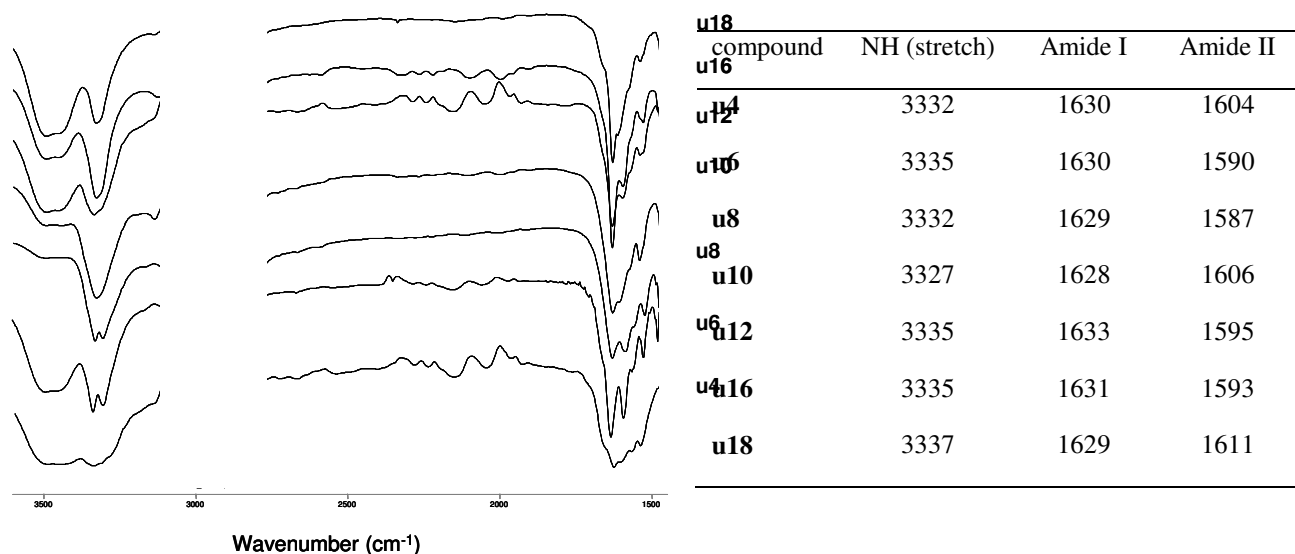
[a] Recorded in a  $\text{CaF}_2$ -cell with 0.1 mm spacing. [b] Region blocked due to solvent absorption.

**Table 7.** Selected FTIR bands ( $\nu$ ,  $\text{cm}^{-1}$ ) of bisurea gelators ( $10 \text{ mg mL}^{-1}$ ) as gel in decalin ( $\pm 2 \text{ cm}^{-1}$ ).<sup>a</sup>



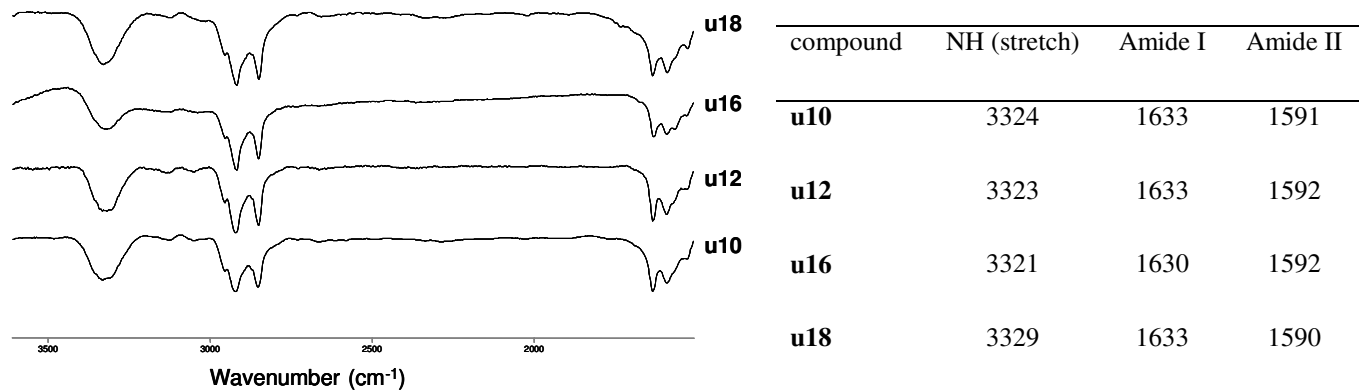
[a] Recorded in a  $\text{CaF}_2$ -cell with 0.1mm spacing.

**Table 8.** Selected FTIR bands ( $\nu$ ,  $\text{cm}^{-1}$ ) of bisurea gelators ( $10 \text{ mg mL}^{-1}$ ) as gel in DMSO ( $\pm 2 \text{ cm}^{-1}$ ).<sup>a</sup>

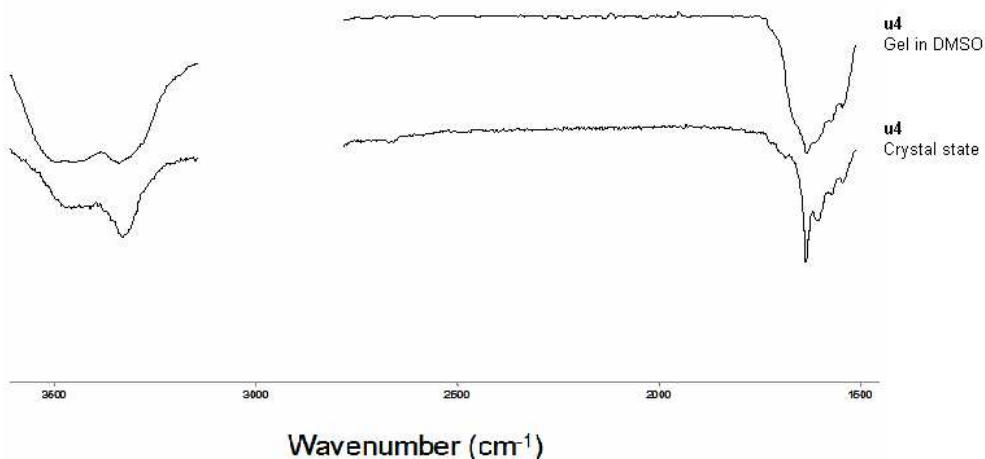


[a] Recorded in a  $\text{CaF}_2$ -cell with 0.1 mm spacing.

**Table 9.** Selected FTIR bands ( $\nu$ ,  $\text{cm}^{-1}$ ) of bisurea aerogels from 1-propanol ( $\pm 2 \text{ cm}^{-1}$ ).<sup>a</sup>



[a] Recorded as an intimate mixture with KBr.



## 5) Results from the linear fitting of DSC traces

Table 10. Linear fitting of DSC traces.

		Decalin	DMSO	1-propanol
<b>a2 – a17</b>	stability increase per CH <sub>2</sub>	2.2 (±1) kJ mol <sup>-1</sup>	3.6 (±1) kJ mol <sup>-1</sup>	4.1 (±1) kJ mol <sup>-1</sup>
	intercept x-axis	1.5	1.7	6.3
	intercept y-axis	-7.4	-16.1	-52.6
<b>u4 – u18</b>	stability increase per CH <sub>2</sub>	n.d.	3.5 (±1) kJ mol <sup>-1</sup>	4.2 (±1) kJ mol <sup>-1</sup>
	intercept x-axis	n.d.	2.2	5.4
	intercept y-axis	n.d.	-12.7	-46.3

n.d. = not determined

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