

## Experimental Section

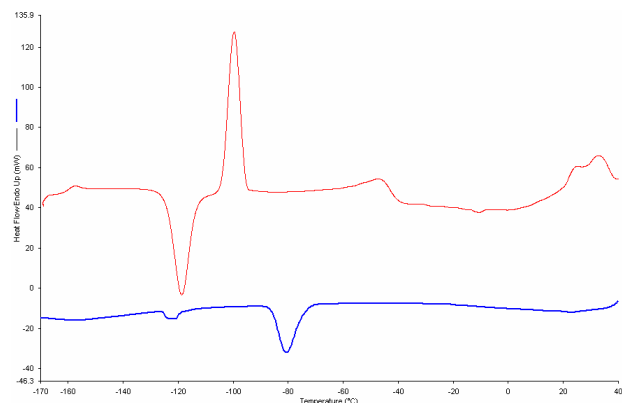
**1-[2-(Bis-{2-[3-((S)-1-phenyl-ethyl)-ureido]-ethyl}-amino)-ethyl]-3-((S)-1-phenyl-ethyl)-urea (1).** A solution of tris(2-aminoethyl)amine (0.7245 g, 5.0 mmol) in dried dichloromethane (80 mL) was added dropwise with stirring to a solution of (S)-(-)- $\alpha$ -methylbenzyl isocyanate (2.1893g, 14.9 mmol) in dried dichloromethane (400 mL) over a period of *ca.* 24 hours during which the reaction mixture was allowed to reflux at 40 °C under an atmosphere of nitrogen. The solid that had subsequently formed was collected and then washed with dichloromethane (*ca.* 15 mL) and diethyl ether (*ca.* 15 mL). The filtrate was worked up via a series of repetitive steps including partial evaporation of the solvent under pressure, collection by suction and washing of the resulting white solid in order to maximise the yield of **1** (2.0g, 70% yield). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, *J* / Hz): 1.27 (3H, d, *J* = 7.2, CH<sub>3</sub>), 2.39 (2H, t, *J* = 6.0, NCH<sub>2</sub>), 2.99 (2H, m, *J* = 6.0, CH<sub>2</sub>), 4.71 (1H, d of q, *J* = 8.0 & 7.2, C(CH<sub>3</sub>)H), 5.88 (1H, t, *J* = 5.4, NH), 6.42 (1H, d, *J* = 8.0, NH), 7.15-7.28 (5H, m, ArH); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  24.1 (H<sub>3</sub>C), 38.3 (H<sub>2</sub>C<sub>e</sub>), 49.3 (H<sub>3</sub>C(H)C), 54.9 (H<sub>2</sub>C<sub>d</sub>), 126.4, 127.1, 128.9 and 146.5 (ArC), 158.1 (O=C);  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3319 (NH), 1624 (C=O); *m/z* (ES<sup>+</sup>-MS): 588 ([M+H]<sup>+</sup>, 10%), 610 ([M+Na]<sup>+</sup>, 100), 1197 ([2M+Na]<sup>+</sup>, 7); Anal. calcd for C<sub>33</sub>H<sub>45</sub>N<sub>7</sub>O<sub>3</sub>: C, 67.44; H, 7.72; N, 16.68. Found: C, 66.89; H, 7.69; N, 16.36%.

**Crystallographic Details.** Crystal data for **1**: C<sub>33</sub>H<sub>45</sub>N<sub>7</sub>O<sub>3</sub>, *M* = 587.76, colourless block, 0.30 × 0.20 × 0.10 mm<sup>3</sup>, orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (No. 19), *a* = 12.5899(16), *b* = 13.1834(17), *c* = 20.085(2) Å, *V* = 3333.7(7) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.171 g/cm<sup>3</sup>, *F*<sub>000</sub> = 1264, Smart 1k, MoK $\alpha$  radiation,  $\lambda$  = 0.71073 Å, *T* = 120(2)K, 2 $\theta_{\text{max}}$  = 46.6°, 17563 reflections collected, 4815 unique (*R*<sub>int</sub> = 0.0402). Final *Goof* = 1.037, *R*1 = 0.0299, *wR*2 = 0.0602, *R* indices based on 4350 reflections with *I* > 2 $\sigma$ (*I*) (refinement on *F*<sup>2</sup>), 416 parameters, 0 restraints. *Lp* and absorption corrections applied,  $\mu$  = 0.077 mm<sup>-1</sup>. Absolute structure parameter = -0.9(9). The structure has been deposited with the CCDC as CCDC 604537.

**Gel Syntheses.** Compound **1** (0.02 g, 0.03 mmol) was dissolved in DMSO or MeOH (1 mL) and sonicated for three minutes to aid the dissolution process. An equivalent volume of water (1 mL) was added to the solution and the mixture allowed to stand for *ca.* 5-10 minutes.

**NMR Titrations.** The NMR titration of **1** was carried out by addition of small aliquots of tetrabutylammonium chloride to an NMR tube containing **1** in DMSO-*d*<sub>6</sub> solution. Five equivalents of guest were added to the starting concentration of **1** (0.03 M) leading to an overall dilution of **1** to 0.02 M. The resulting data was evaluated using three independent resonances and the association constant obtained using the program HypNMR 2000.<sup>1</sup>

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**Figure S1.** Low temperature DSC scan of methanol/water gel formed from **1** (20°C min<sup>-1</sup> top - heat cycle; bottom cool cycle 0.0180g **1** in 1ml MeOH/1ml H<sub>2</sub>O)