Supplementary Material

Gelation is Crucially Dependent on Functional Group Orientation and may be Tuned by Anion Binding

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Synthesis

1-((S)-1-Phenyl-ethyl)-3-{4-[3-((S)-1-phenyl-ethyl)-ureido]-alkyl}-ureas (1) In a typical synthesis a solution of (S)-(-)-α-methylbenzyl isocyanate (0.90 g, 6.1 mmol) in dry $CHCl_3$ (100 mL) was added dropwise to a stirred solution of the appropriate α-ω-diaminoalkane (3.0 mmol) under reflux. After complete addition the reaction was allowed to reflux under an inert N_2 atmosphere for up to 24h. The resulting precipitate formed was collected by filtration and washed with $CHCl_3$ (3 × 10 mL). The resulting white powders were obtained in good yields (75-82%).

***n* = 2:**
^{1}H NMR (400 MHz, DMSO-d_6, *J*/Hz): 1.30 (6H, d, *J* = 7.1, -CH_3), 2.99 (4H, m, -CH_2-) 4.73 (2H, d of q, -C(CH_3)**H**-) 5.86 (2H, broad m, -NH-C**H$_2$**) 6.42 (2H, d, *J* = 8.1, -CH-N**H**-) 7.29 (10H, m, ArH)
m/z (ES$^+$-MS): 355.3 ([M+H]$^+$, 44%), 377.2 ([M+Na]$^+$, 100%)
Anal. calcd. for $C_{20}H_{26}N_4O_2$: C 66.94% H 7.32% N 15.57% Found C 67.78% H 7.38% N 15.81%

***n* = 3:**
^{1}H NMR (400 MHz, DMSO-d_6, *J*/Hz): 1.35 (6H, d, *J* = 7.0, -CH_3), 1.45 (2H, sept, *J* = 6.6, -CH_2-), 3.00 (4H, m, NH-C**H$_2$**), 4.77 (2H, d of q, *J* = 8.2 & 7.0, C(CH_3)**H**), 5.86 (2H, t, *J* = 5.8, N**H**-CH_2), 6.39 (2H, d, *J* = 8.2, N**H**-CH), 7.25 – 7.36 (10H, m, ArH)
ν_{max}(cm^{-1}): 3316 (NH), 1622 (C=O)
m/z (ES$^+$-MS): 369 ([M+H]$^+$, 34%), 391 ([M+Na]$^+$, 100%), 737 ([2M+H]$^+$, 16%) 759 ([2M+Na]$^+$, 47%)
Anal. calcd. for $C_{21}H_{28}N_4O_2$: C 68.45%, H 7.66%, N 15.20% Found: C 68.33% H 7.69% N 15.13%

***n* = 4:**
^{1}H NMR (400 MHz, DMSO-d_6, *J*/Hz): 1.28 – 1.32 (4H, m, -C**H$_2$**-), 1.29 (6H, d, *J* = 7.0, CH_2), 2.94 (4H, m, NH-C**H$_2$**-), 4.72 (2H, d of q, *J* = 8.2 & 7.1, C(CH_3)**H**), 5.77 (2H, t, *J* = 5.6, N**H**-CH_2), 6.24 (2H, d, *J* = 8.2, N**H**-CH), 7.18 – 7.32 (10H, m, ArH)

ν_{max}(cm^{-1}): 3312 (NH), 1621 (C=O)
m/z (ES$^+$-MS): 383 ([M+H]$^+$, 6%), 405 ([M+Na]$^+$, 100%), 787 ([2M+H]$^+$, 75%)
Anal. calcd. for $C_{22}H_{30}N_4O_2$: C 69.08%, H 7.91%, N 14.65% Found: C 68.83% H 7.92% N 14.55%

***n* = 5:**
^{1}H NMR (400 MHz, DMSO-d_6, *J*/Hz): 1.19 (2H, m, -CH_2-), 1.29 (6H, d, *J* = 7.0, CH_3), 1.30 – 1.36 (4H, m, -CH_2-), 2.94 (4H, m, NH-C**H$_2$-**), 4.72 (2H, d of q , *J* = 8.1 & 7.0, C(CH_3)**H**), 5.75 (2H, t, *J* = 5.6, N**H**-CH_2), 6.23 (2H, d, *J* = 8.1, N**H**-CH), 7.17 – 7.32 (10H, m, ArH)
ν_{max}(cm^{-1}): 3302 (NH), 1618 (C=O)
m/z (ES$^+$-MS): 397 ([M+H]$^+$, 44%), 419 ([M+Na]$^+$, 94%), 793 ([2M+H]$^+$, 25%) 815 ([2M+Na]$^+$, 100%)
Anal. calcd. for $C_{23}H_{32}N_4O_2$: C 69.67%, H 8.13%, N 14.13% Found: C 69.33% H 8.10% N 14.14%

***n* = 6:**
^{1}H NMR (400 MHz, DMSO-d_6, *J*/Hz): 1.18 – 1.20 (4H, m, -CH_2-), 1.29 (6H, d, *J* = 7.0, CH_3), 1.30 – 1.36 (4H, m, -CH_2-), 2.94 (4H, m, NH-C**H$_2$-**), 4.72 (2H, d of q , *J* = 8.1 & 7.0, C(CH_3)**H**), 5.75 (2H, t, *J* = 5.6, N**H**-CH_2), 6.23 (2H, d, *J* = 8.1, N**H**-CH), 7.18 – 7.32 (10H, m, ArH)
ν_{max}(cm^{-1}): 3314 (NH), 1621 (C=O)
m/z (ES$^+$-MS): 411 ([M+H]$^+$, 60%), 433 ([M+Na]$^+$, 98%), 821 ([2M+H]$^+$, 32%) 843 ([2M+Na]$^+$, 100%)
Anal. calcd. for $C_{24}H_{34}N_4O_2$: C 70.21%, H 8.35%, N 13.65% Found: C 70.04% H 8.34% N 13.47%

***n* = 7:**
^{1}H NMR (400 MHz, DMSO-d_6, *J*/Hz): 1.20-1.24 (6H, m, -CH_2-), 1.29 (6H, d, *J* = 7.0, CH_3), 1.30 – 1.36 (4H, m, -CH_2-), 2.94 (4H, m, NH-C**H$_2$-**), 4.71 (2H, d of q , *J* = 8.1 & 7.0, C(CH_3)**H**), 5.74 (2H, t, *J* = 5.6, N**H**-CH_2), 6.23 (2H, d, *J* = 8.1, N**H**-CH), 7.18 – 7.32 (10H, m, ArH)
ν_{max}(cm^{-1}): 3306 (NH), 1621 (C=O)
m/z (ES$^+$-MS): 425 ([M+H]$^+$, 45%), 447 ([M+Na]$^+$, 100%), 871 ([2M+Na]$^+$, 18%)
Anal. calcd. for $C_{25}H_{36}N_4O_2$: C 70.72%, H 8.55%, N 13.20% Found: C 70.48% H 8.55% N 13.19%

***n* = 8:**
^{1}H NMR (400 MHz, DMSO-d_6, *J*/Hz): 1.26-1.30 (8H, m, -CH_2-), 1.35 (6H, d, *J* = 7.0, CH_3), 1.36 – 1.41 (4H, m, -CH_2-), 3.01 (4H, m, NH-C**H$_2$-**), 4.78 (2H, d of q , *J* = 8.1 & 7.0, C(CH_3)**H**), 5.80 (2H, t, *J* = 5.4, N**H**-CH_2), 6.29 (2H, d, *J* = 8.1, N**H**-CH), 7.24 – 7.39 (10H, m, ArH)
ν_{max}(cm^{-1}): 3310 (NH), 1622 (C=O)
m/z (ES$^+$-MS): 439 ([M+H]$^+$, 72%), 461 ([M+Na]$^+$, 100%), 479 ([2M+H]$^+$, 36%) 899 ([2M+Na]$^+$, 92%)

Anal. calcd. for $C_{26}H_{38}N_4O_2$: C 71.20%, H 8.73%, N 12.77% Found: C 71.03% H 8.73% N 12.54%

Results

SEM and Gel Images

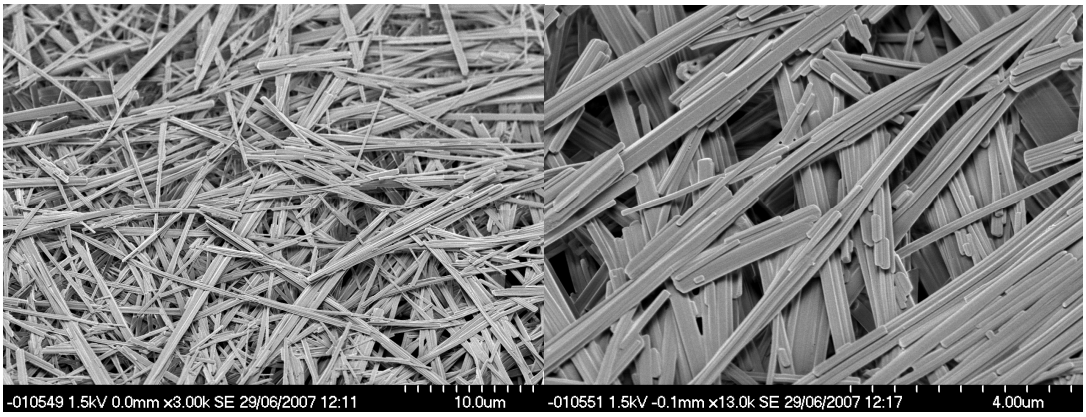

Figure S1. SEM images of compound **1** $n = 2$ xerogel formed from an acetonitrile gel. Note how the gel fibres are rod-shaped and show no indication of the chirallity of the gelator.

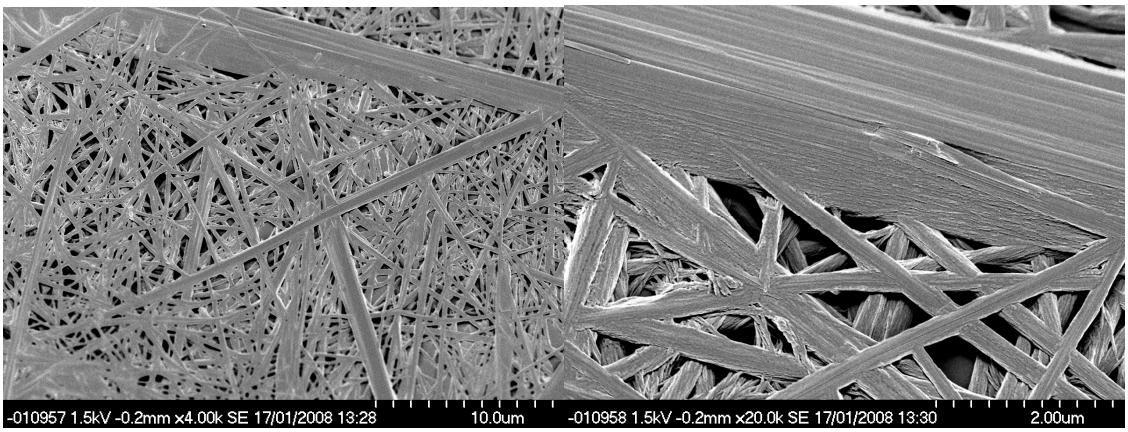

Figure S2. SEM images of compound **1** *n* = 2 xerogel formed from a gel made in a DMSO:WATER mixture at 6:4. Note how the gel fibres are rod-shaped and show no indication of the chirallity of the gelator. There are large fibres/crystals that are bound to the smaller gel fibres (right-hand image).

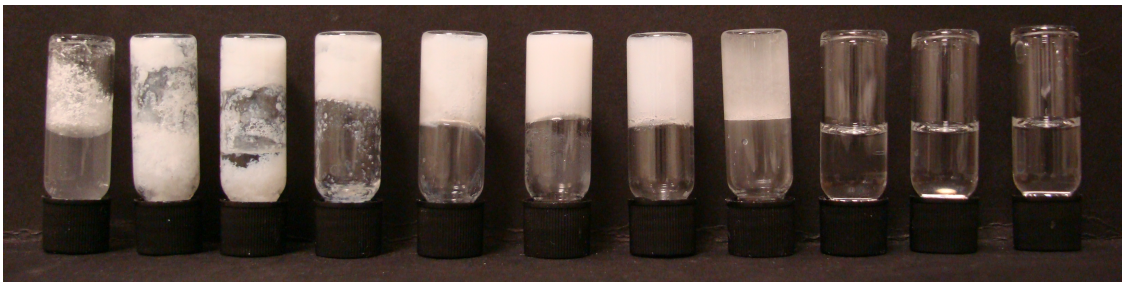

Figure S3. Image of the DMSO:Water gels formed by compound **1** *n*= 2 by addition of water to a solution of the compound in DMSO. From left to right the solvents are: pure water, ratios 1:9; 2:8; 3:7; 4:6; 5:5; 6:4; 7:3; 8:2; 9:1; pure DMSO. Note that the more aqueous samples are precipitated and form weak gels.

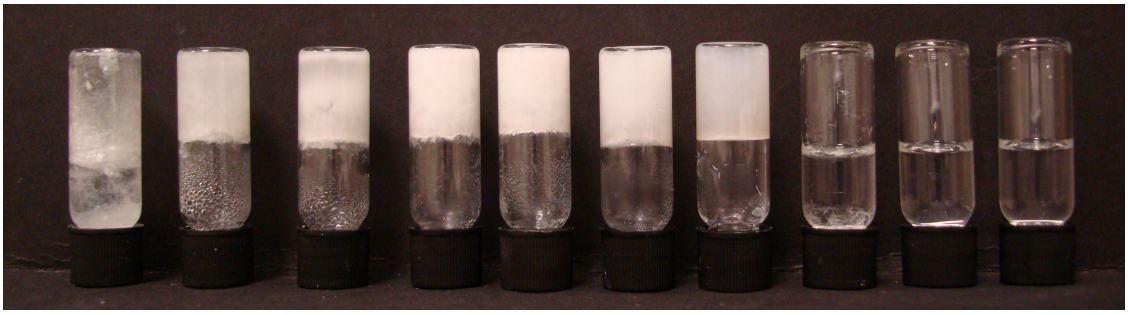

Figure S4. Image of the same vials as in Figure S2 but after heating and dissolution and cooling to room temperature of the compound (pure DMSO vial not shown). Stronger gels were obtained for the more aqueous solutions. Only pure water and ratios 8:2; 9:1 DMSO:Water and pure DMSO did not form gels (pure DMSO vial not shown). Compound **1** *n* = 2 is partially soluble in water but does not form a gel. Note that the vial containing the 7:3 solution contains small crystals which were used for the determination of the compounds crystalline structure which matches that of the dried xerogel and that this same solution is a gel in the above figure showing the fine line between crystallisation and gel formation (arrested crystallisation).

Powder X-ray Diffraction Experiments

PXRD patterns of powder samples and xerogels for *n* = 2, 4 and 5.

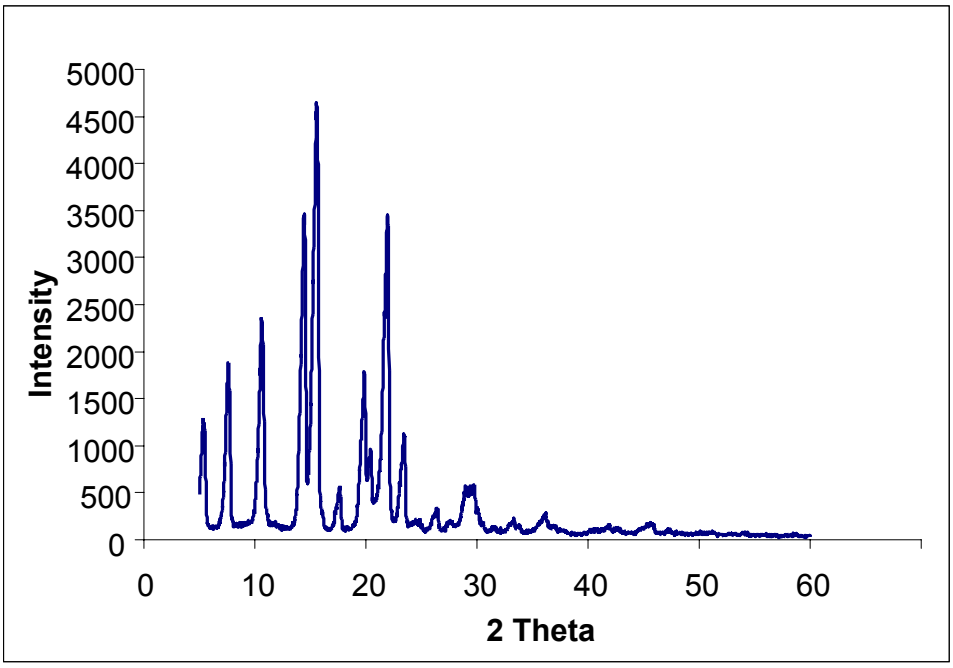

Figure S5. PXRD of the xerogel of compound **1** *n* = 2 formed from the drying of the $CHCl_3$ gel.

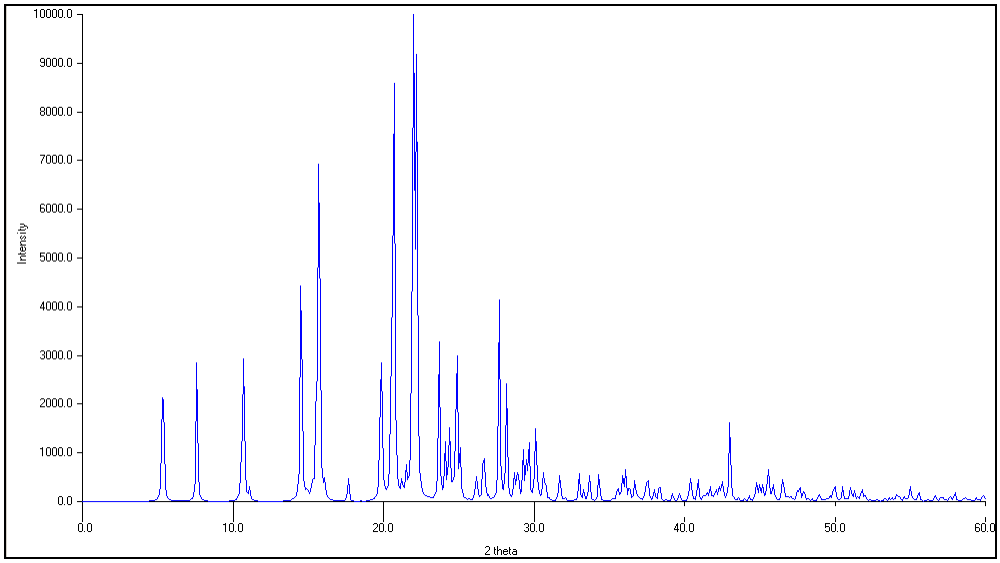

Figure S6. Simulated PXRD of the single crystal data of compound **1** $n = 2$.

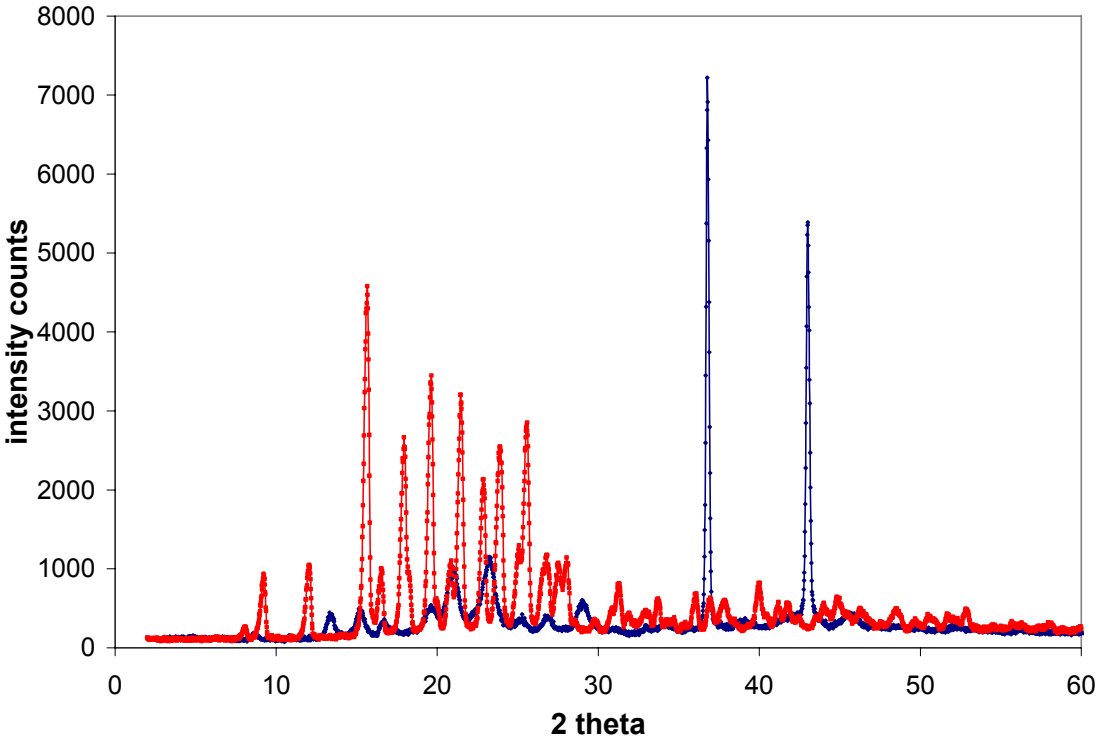

Figure S7. PXRD of the xerogel of compound **1** $n = 4$ formed from the drying of the $CHCl_3$ gel (blue line) and of the as-prepared compound. The sharp peaks at 2 θ = 36.8° and 43.0° in the blue data are artifacts from the sample mount.

Rheology

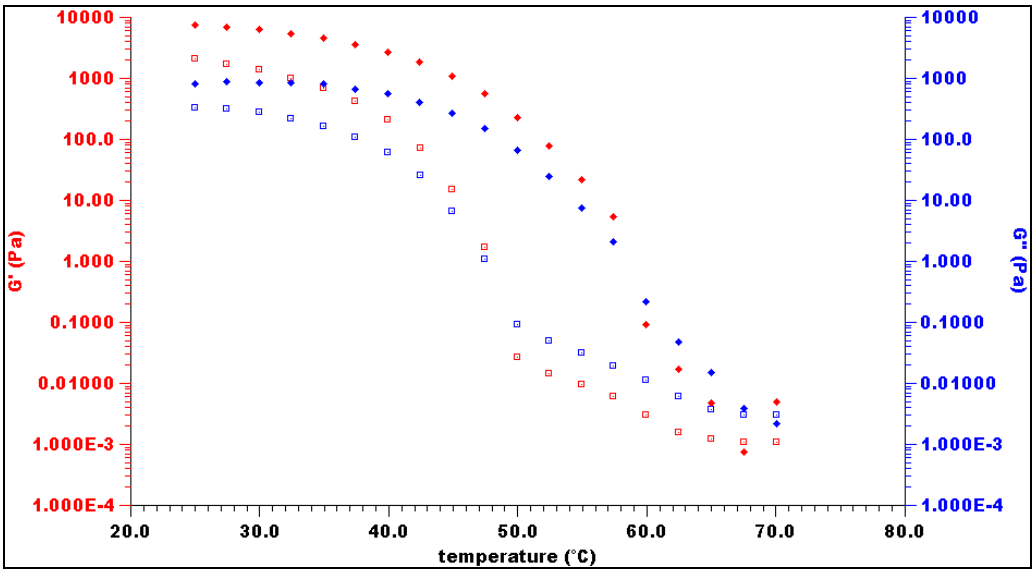

Figure S8. The effect of adding the anion TBA Cl^- on G′, G″ and T_{sg} for a gel made from n = 2 and acetonitrile, as measured by varying the temperature from 70°C to 25°C. The filled-diamond symbols represent 0.1 equivalents of anion added and the open-square symbols represent 0.2 equivalents added. Increasing the amount of anion results in G′, G″ and T_{sg} for the gel all being lowered. The sol to gel transition temperature is defined by the G′, G″ crossover. Hence, T_{sg} = 58.5 ± 1.5 °C for 0.1 equivalents addition of anion and T_{sg} = 48.5 ± 1.5 °C for 0.2 equivalents.

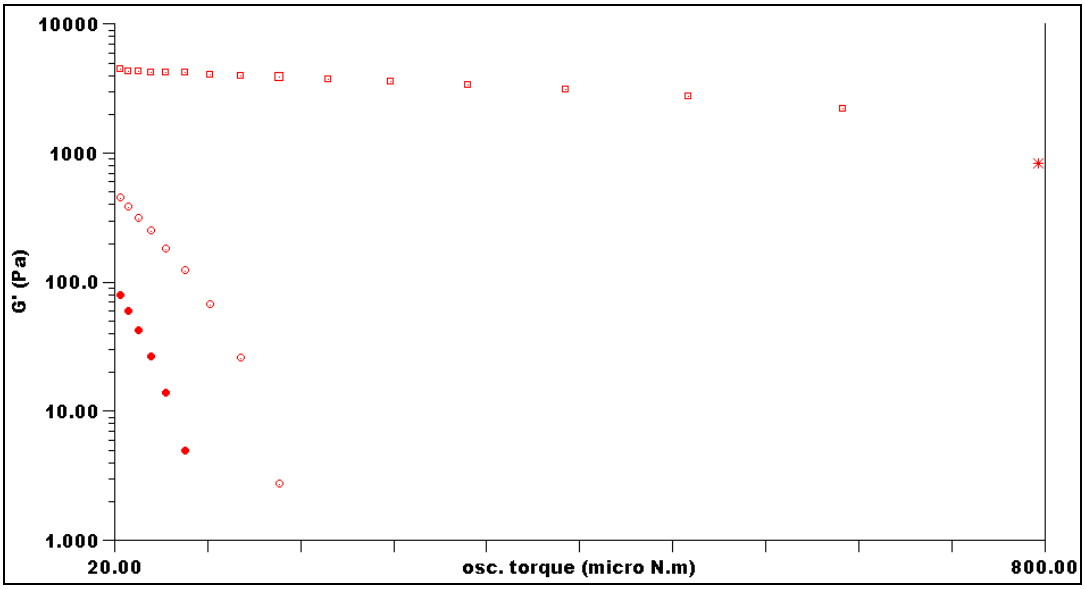

Figure S9. The effect of adding the anion TBA NO_3^- on the storage modulus for a gel made from n = 2 and acetonitrile measured by varying the oscillation (osc.) torque from 10 micro N.m to 1000 micro N.m, at a fixed frequency of 1 Hz. The square symbols represent 0.1 equivalents of anion added; the empty circle symbols represent 0.2 equivalents added and the filled circle symbols represent 0.5 equivalents added. G′ decreases as more anion is added to the gel. The value of the osc. torque that results in a minimal, but measurable, value for G′ also decreases as the anion concentration is increased, from ~794 micro N.m at 0.1 equivalents to 158 micro N.m at 0.2 equivalents to ~79 micro N.m at 0.5 equivalents.

NMR Titrations and Job Plots

^{1}H NMR titration experiments were carried out at 50 ^{o}C in acetonitrile using a Varian Inova 500 operating at 500 MHz (University of Durham). All chemical shifts are reported in ppm relative to solvent chemical shifts as an internal reference. A solution of the host species of known concentration, typically 0.002 M, was made up in an NMR tube using the appropriate deuterated solvent (0.5 ml). Solutions of the anions, as tetrabutylammonium salts, were made up (2 ml) with a concentration five times greater than that of the host. The guest solution was typically added in 10 µl aliquots, representing 0.1 equivalents of the guest with respect to the host. Larger aliquots were used in some cases where none to little inflection of the trace was evident. Spectra were recorded after each addition and the trace was followed simultaneously. Results were analysed using the curve-fitting program HypNMR,[1,2] simultaneously fitting as many peaks as could be accurately followed throughout the experiment.

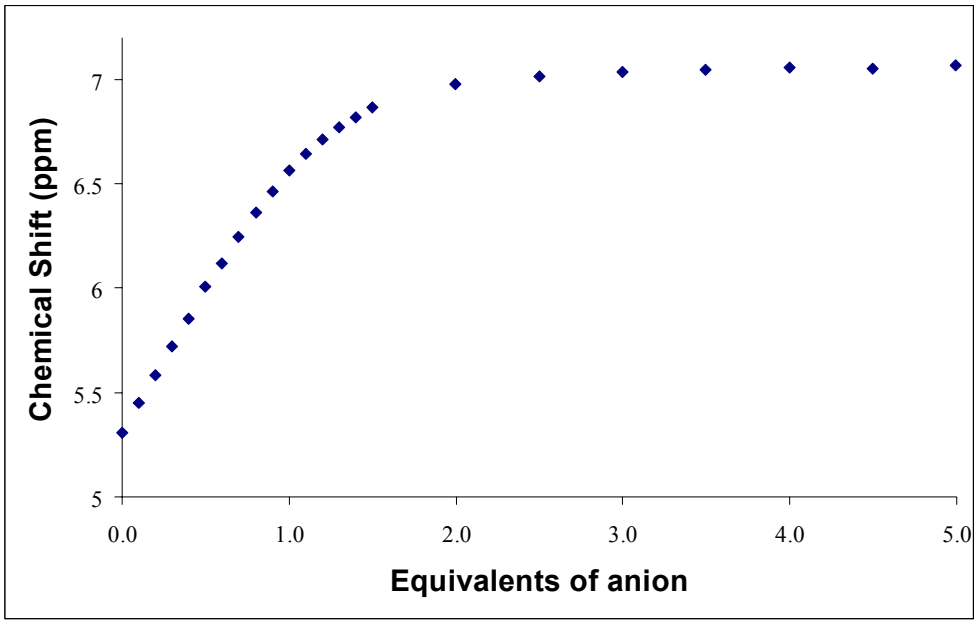

Figure S10. The change in chemical shift of one of the NH protons of compound **1** $n = 2$ during the titration of TBA $MeCO2^-$ done in acetonitrile at 50 ^{o}C.

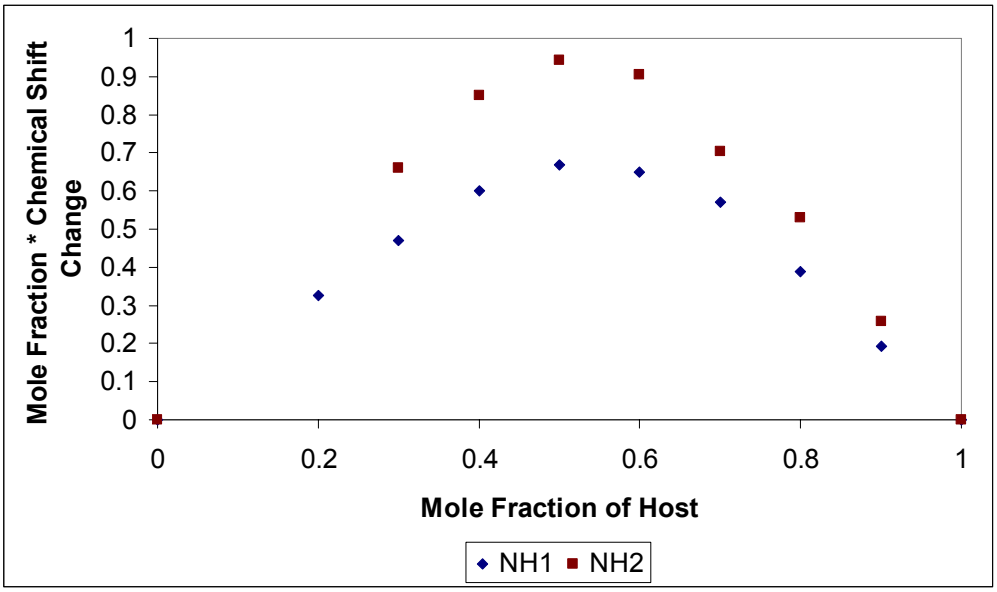

Figure S11. Figure showing the results of a Job Plot analysis for the binding of TBA $MeCO2^{-}$ by compound **1** $n = 2$ giving a 1:1 binding ratio.

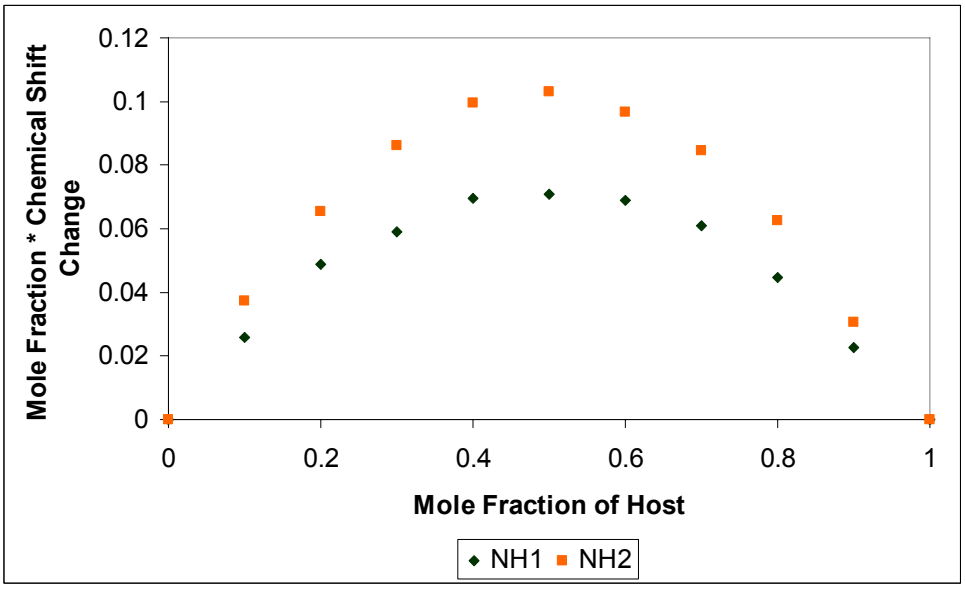

Figure S12. Figure showing the results of a Job Plot analysis for the binding of TBA Cl^{-} by compound **1** $n = 2$ giving a 1:1 binding ratio.

Crystal Data

Crystal data for *n* = *2* : $C_{20}H_{26}N_4O_2$, *M* = 354.45, colourless needle, 0.40 × 0.11 × 0.10 mm^3, monoclinic, space group $P2_1$ (No. 4), *a* = 12.1914(14), *b* = 4.6342(6), *c* = 17.341(2) Å, β = 107.849(5)°, *V* = 932.57(19) Å^3, *Z* = 2, D_c = 1.262 g/cm^3, F_{000} = 380, 6K, MoKα radiation, λ = 0.71073 Å, *T* = 120(2)K, $2\theta_{max}$ = 56.5º, 7921 reflections collected, 4407 unique (R_{int} = 0.2294). Final *GooF* = 0.896, *R1* = 0.0972, *wR2* = 0.2219, *R* indices based on 2170 reflections with I >2sigma(I) (refinement on F^2), 235 parameters, 1 restraint. Lp and absorption corrections applied, μ = 0.084 mm^{-1}. Absolute structure parameter = 4(3) [3]

Crystal data for *n* = *4* : $C_{22}H_{30}N_4O_2$, *M* = 382.50, colourless needle, 0.35 × 0.21 × 0.16 mm^3, monoclinic, space group *C*2 (No. 5), *a* = 35.285(15), *b* = 4.651(2), *c* = 12.784(5) Å, β = 97.518(7)°, *V* = 2079.7(15) Å^3, *Z* = 4, D_c = 1.222 g/cm^3, F_{000} = 824, MoKα radiation, λ = 0.71073 Å, *T* = 120(2)K, $2\theta_{max}$ = 56.4º, 12725 reflections collected, 5076 unique (R_{int} = 0.0619). Final *GooF* = 1.152, *R1* = 0.0761, *wR2* = 0.1907, *R* indices based on 4339 reflections with I >2sigma(I) (refinement on F^2), 253 parameters, 1 restraint. Lp and absorption corrections applied, μ = 0.080 mm^{-1}. Absolute structure parameter = 2(2) [3]

Crystal data for *n* = *5* : $C_{23}H_{32}N_4O_2$, *M* = 396.53, colourless needle, 0.49 × 0.24 × 0.10 mm^3, monoclinic, space group $P2_1$ (No. 4), *a* = 12.317(2), *b* = 4.6108(8), *c* = 19.488(3) Å, β = 107.519(4)°, *V* = 1055.4(3) Å^3, *Z* = 2, D_c = 1.248 g/cm^3, F_{000} = 428, MoKα radiation, λ = 0.71073 Å, *T* = 120(2)K, $2\theta_{max}$ = 55.1º, 7923 reflections collected, 4625 unique (R_{int} = 0.0499). Final *GooF* = 1.018, *R1* = 0.0624, *wR2* = 0.1354, *R* indices based on 3061 reflections with I >2sigma(I) (refinement on F^2), 262 parameters, 1 restraint. Lp and absorption corrections applied, μ = 0.081 mm^{-1}. Absolute structure parameter = -2(2)[3]

References

1) Frassineti, C.; Ghelli, S.; Gans, P.; Sabatini, A.; Moruzzi, M. S.; Vacca, A. Nuclear-Magnetic-Resonance as a Tool for Determining Protonation Constants of Natural Polyprotic Bases in Solution. *Anal. Biochem.* **231**, 374-382 (1995).

2) Gans, P, HypNMR 2006, University of Leeds: Leeds, (2006).

3) H. D. Flack, *Acta Crystallographica Section A*, 1983, **39**, 876.