Electronic Supplementary Material (ESI) for Soft Matter

Anion Tuning of Chiral Bis(urea) Low Molecular Weight Gels

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Supplementary Material

Table S1. Gelation ability and characteristics of compounds **1** (*n* = even) and compound **2**.

Solvents	**Phase**[a]	**Appearance**	**CGC** (%)[b]
$CHCl_3$	G	Transparent to Opaque	0.02
MeCN	G	Opaque	0.05
THF	G	Opaque	0.05
Acetone	G	Opaque	0.05
Ethyl Acetate	G	Transparent to Opaque	0.03
Alcohols, DMSO, DMF	S	n/a	n/a
Tolune, Hexane, Cyclohexane	I	n/a	n/a
Water	P	n/a	n/a
DMSO:H_2O[(c)] / EtOH:H_2O[(d)] / MeOH:H_2O[(e)] /	G/C/S	Opaque	0.04
Tol:co-solvent[(f)]	G/S	Transparent to Opaque	0.06

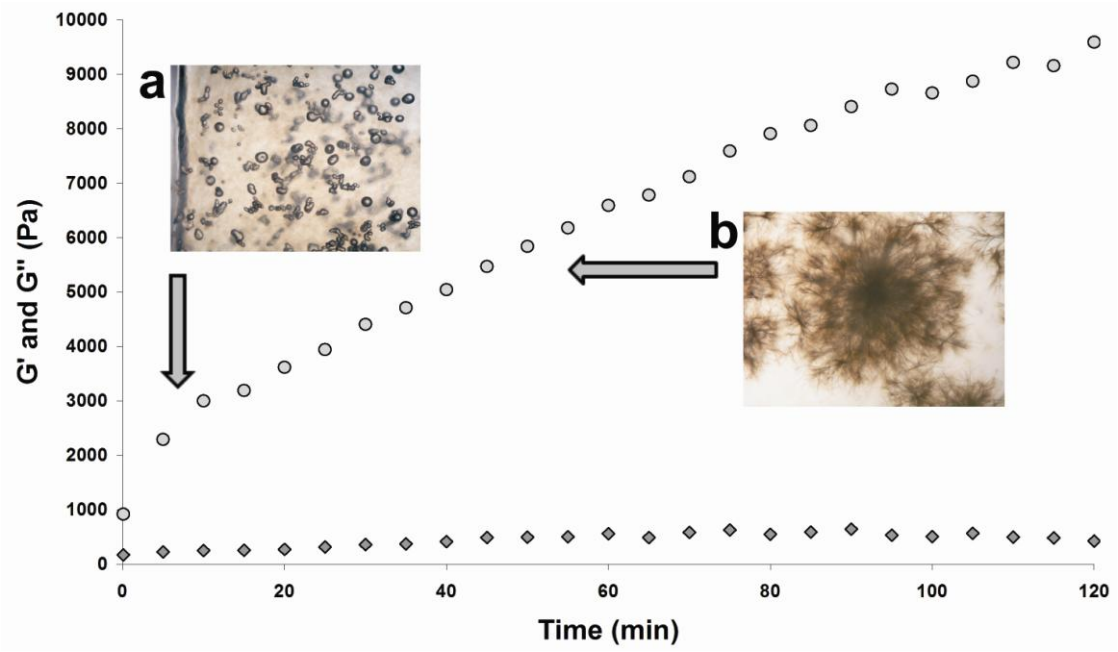

Figure S1. A time sweep of the rheological character of a gel of **1**[2] at 0.3% by weight in MeCN. It shows how even though a gel has formed instantaneously upon cooing the gel continues to 'mature'. The strengthening is highlighted by the increase in the *G′* value (Light grey filled O) while the *G″* value (Grey filled ◇) stays relatively the same. a) Inset showing a micrograph image of air trapped in a clear gel as seen upon brief sonication of a gel solution. b) Inset shows the branching by growing fibres which resulted in spherulitic networks within the gels as they mature.

Figure S2. DMSO:Water gels formed by the addition of water to a solution of **1**[2] 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, 1:9; 2:8; 3:7, are precipitated and/or form weak gels. Note the 8:2; 9:1 and pure DMSO samples are clear solutions.

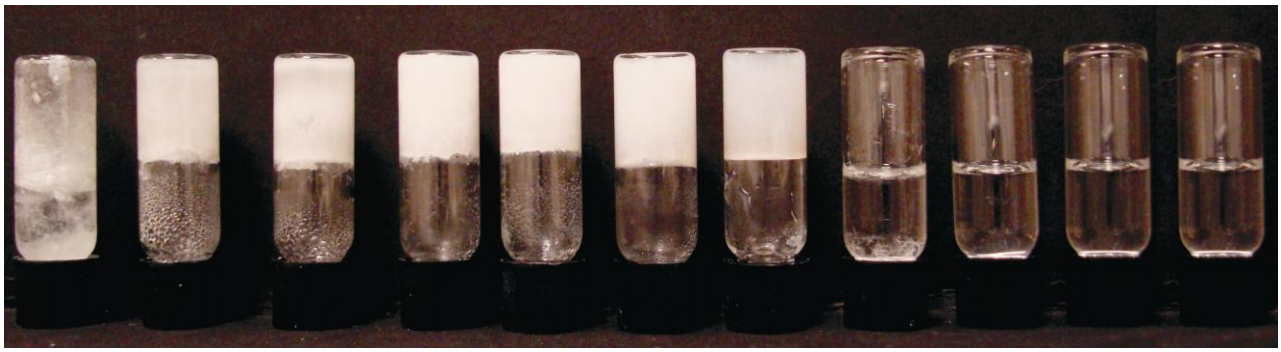

Figure S3. Image of the same samples as in Figure S2 but after heating to dissolution followed by cooling to room temperature. Homogenous gels were obtained for the more aqueous solutions. Only pure water and ratios 7:3; 8:2; 9:1 DMSO:H_2O and pure DMSO did not form gels. Compound **1**[2] is partially 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 compound's crystal structure.

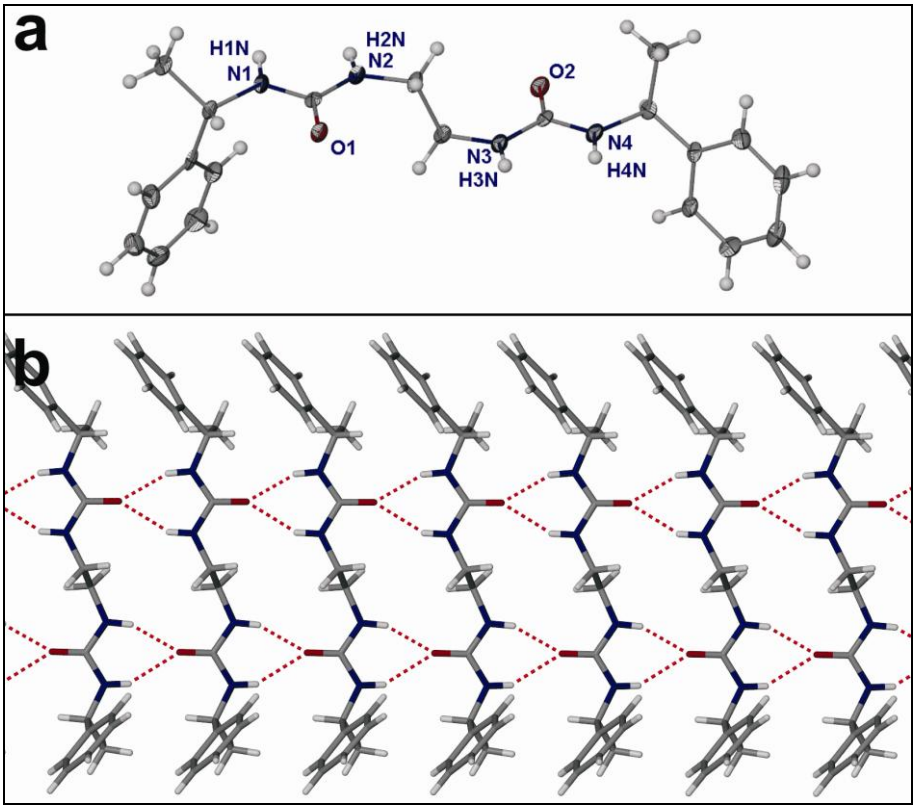

Figure S4. a) Ellipsoid plot of **1**[2]. Atoms shown as 50% ellipsoids and with labels for atoms involved in the hydrogen bonding. **b)** Anti-parrallel urea-urea tapes formed within the structure of **1**[2]. Molecules shown in capped-stick representation. $R_2^1(6)$ hydrogen bonding shown by dashed red lines. Selected hydrogen bond distances: N1–H1N···O1 2.875(6) Å, N2–H2N···O1 2.956(6) Å, N3–H3N···O2 2.871(6) Å and N4–H4N···O2 2.939(6) Å.

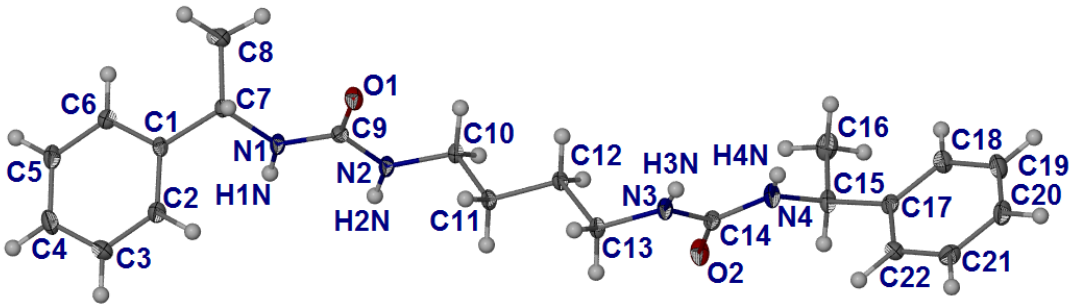

Figure S5. Molecular structure of **1**[4] in form II. Atoms are shown as ellipsoids at 50% probability.

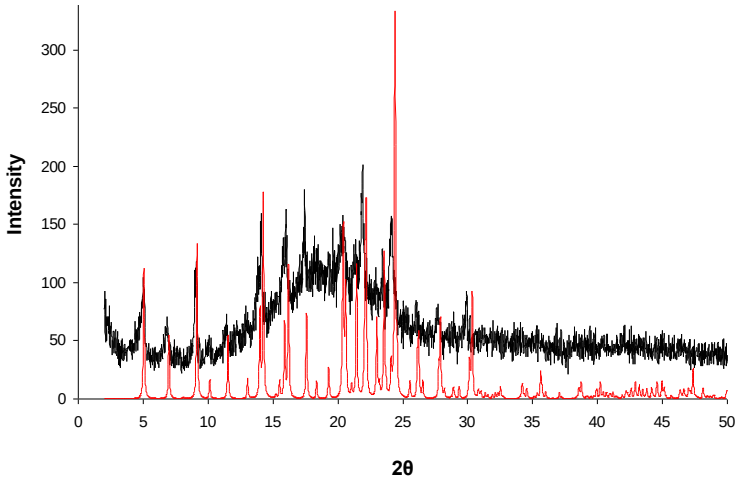

Figure S6. PXRD pattern of the xerogel of compound **1**[4] at room temperature formed from the drying of a $CHCl_3$ gel (Black line) and the simulated PXRD pattern from the single crystal determination of form II (performed at 120K) (Red line). Intensity of the simulated PXRD has been normalised to that of the xerogel.

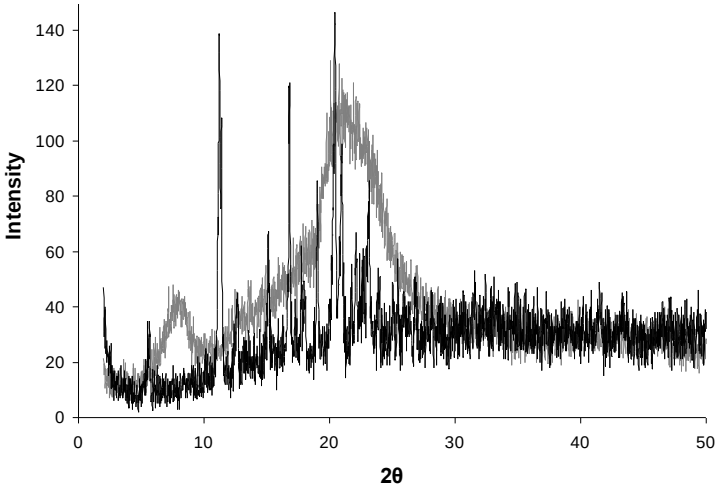

Figure S7. PXRD patterns at room temperature of a powder sample of the as synthesised **1**[6] from the precipitation/gel formation in the synthesis solvent $CHCl_3$ (Black line) and the xerogel of **1**[8] formed from the drying of the $CHCl_3$ gel (Grey line). Intensity of **1**[8] PXRD normalised to that of **1**[6].

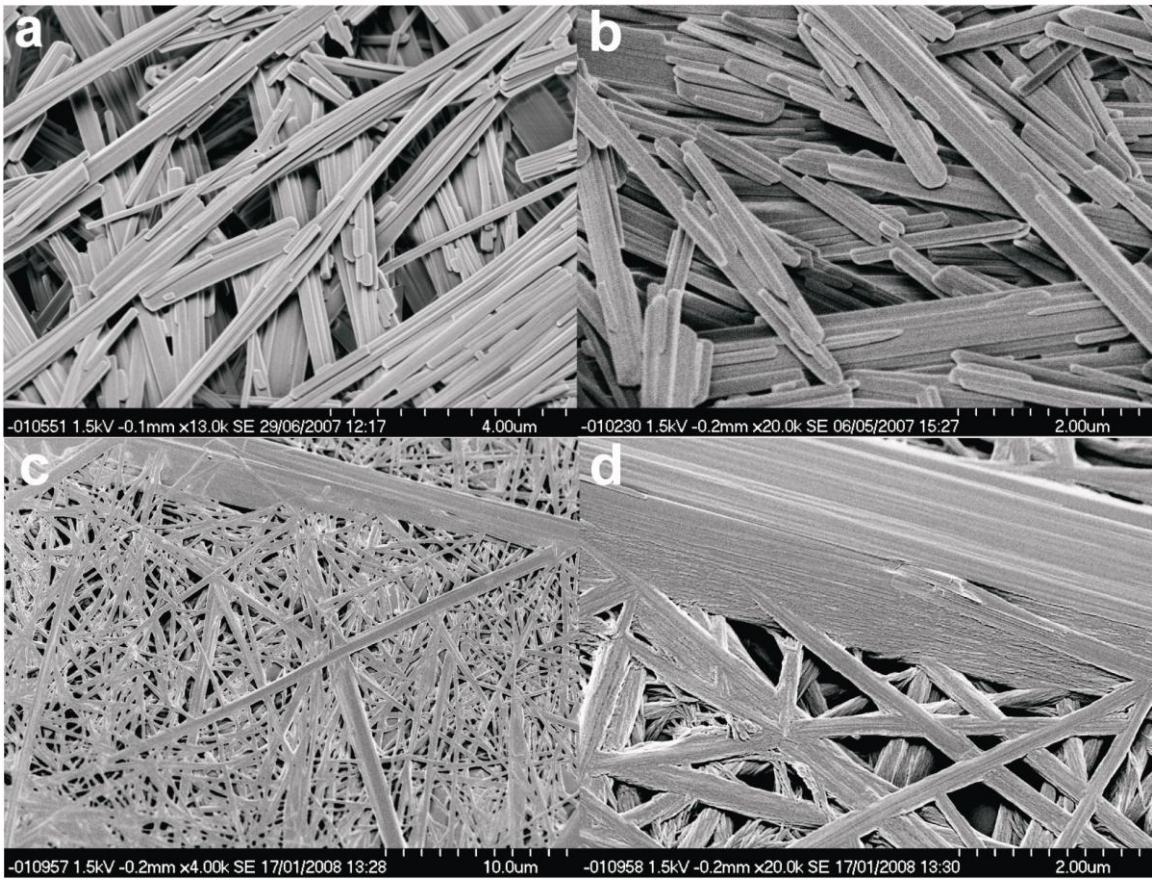

Figure S8. a) Crystalline material seen upon drying a gel sample of **1**[2] in MeCN using SEM. **b)** Crystalline material seen upon drying a gel sample of **1**[2] in $CHCl_3$ using SEM. **c)** SEM image of compound **1**[2] xerogel formed from a gel made in a DMSO:H_2O mixture at 6:4. This image is

better representation of the gel structure than images seen in parts a and b. Note how the gel fibres are rod-shaped and show no indication of the chirallity of the gelator. **d)** Higher resolution image of the fibre connections of the DMSO:H_2O gel. There are large fibres/crystals that are bound to the smaller gel fibres.

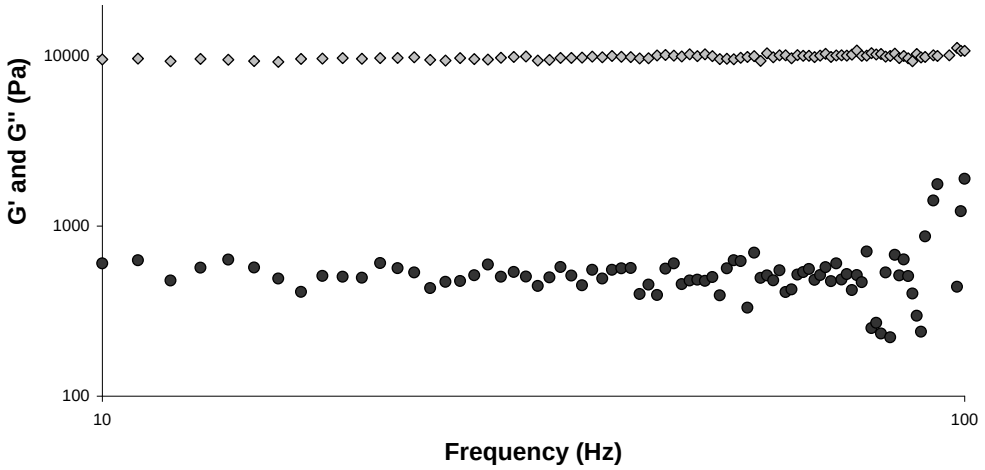

Figure S9. Rheology of **1**[2] showing a frequency sweep performed on a gel of **1**[2] at 0.3% by weight in MeCN. Typically the consistency of the *G′*(Light grey filled ◇) and *G″*(Dark grey filled ○) values over the frequency range indicates the solid-like nature of the gel material. The greater than a magnitude value of *G′* over the *G″* value demonstrates the elastic behaviour of the gel. Both axis values are shown as a logarithmic (log) scale.

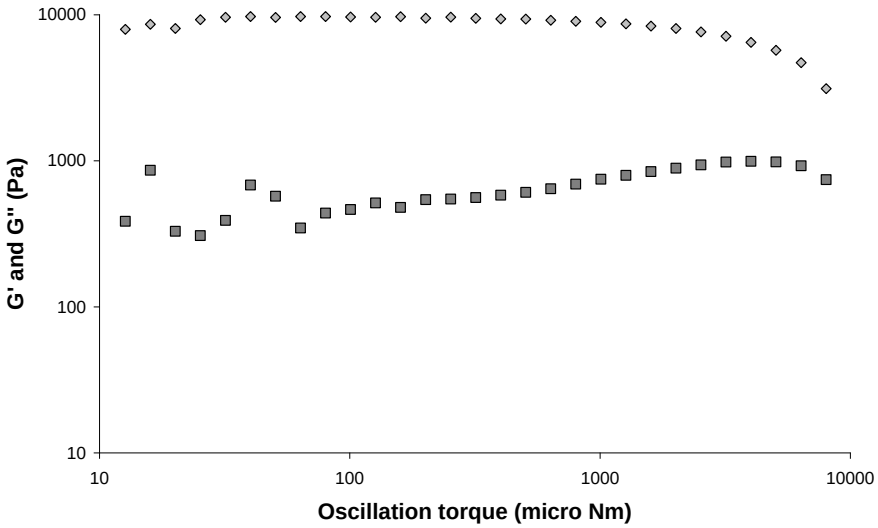

Figure S10. Rheology of $\mathbf{1}^{2}$ showing a stress sweep, as a function of oscillation (osc.) torque, on a gel of $\mathbf{1}^{2}$ at 0.3% by weight MeCN gel. The stress sweep shows the rigidity and strength of the gel which breaks at a relatively high shear strength. *G´*value (Light grey filled ◇) stays constant until the torque begins to become too strong and the struts start to break under the strain. Eventually *G´*for the samples drops to below the *G´´*value (Dark grey filled □) and the sample is said to be flowing. This transition point were the *G´´*value becomes greater the *G´*value gives the "yield stress". Both axis values are shown as a log scale.

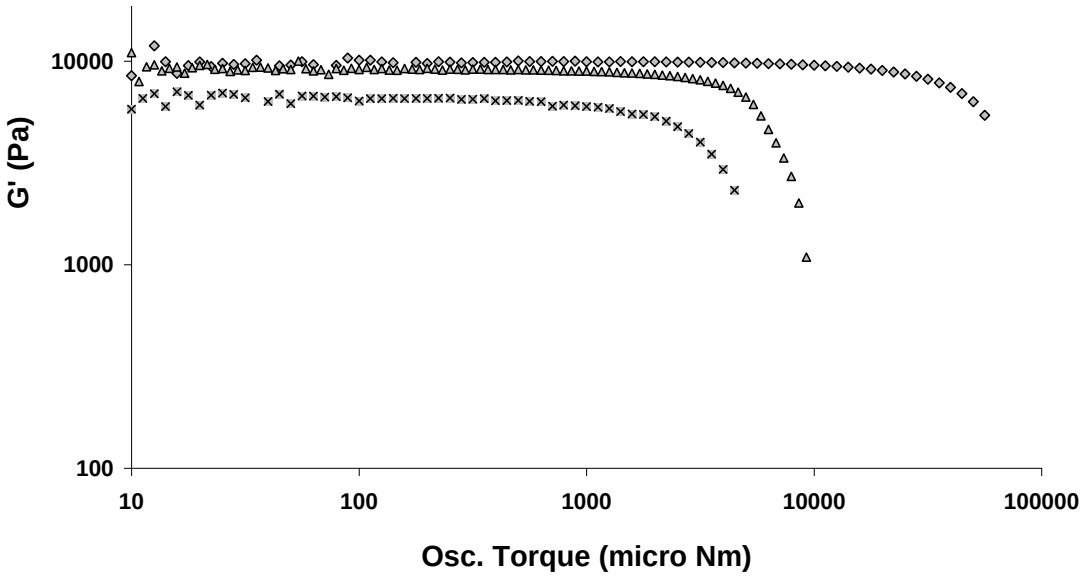

Figure S11. Rheology of $\mathbf{1}^{4}$ (X), $\mathbf{1}^{6}$ (◇) and $\mathbf{1}^{8}$ (△) showing a stress sweep, as a function of oscillation (osc.) torque, on gels at 1.0% by weight $CHCl_3$ gel.

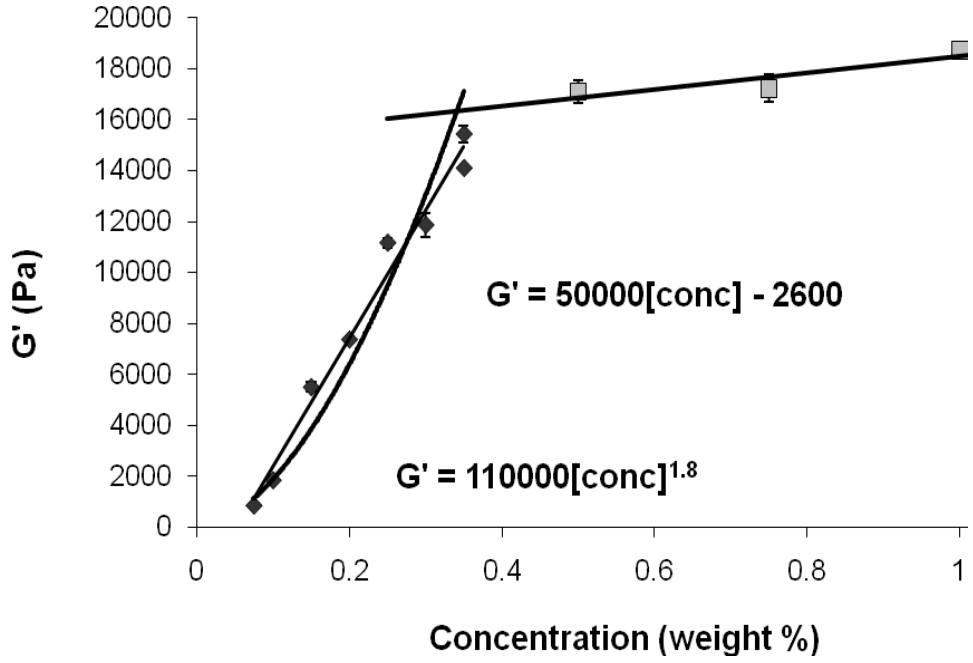

Figure S12. The dependence of *G*′ on gelator concentration for compound **1**^{2} in MeCN. The plateau point, at around 0.45 % by weight, is used as the cut off point for the determination of the $G' \propto [\text{conc}]^{n}$ relationship. Errors bars on all points represent standard deviation for values from the rheometer for a given sample. The actual reproducibility is exemplified by the measurements on samples at 0.35% by weight. Lines are for a power law and a linear best fits.

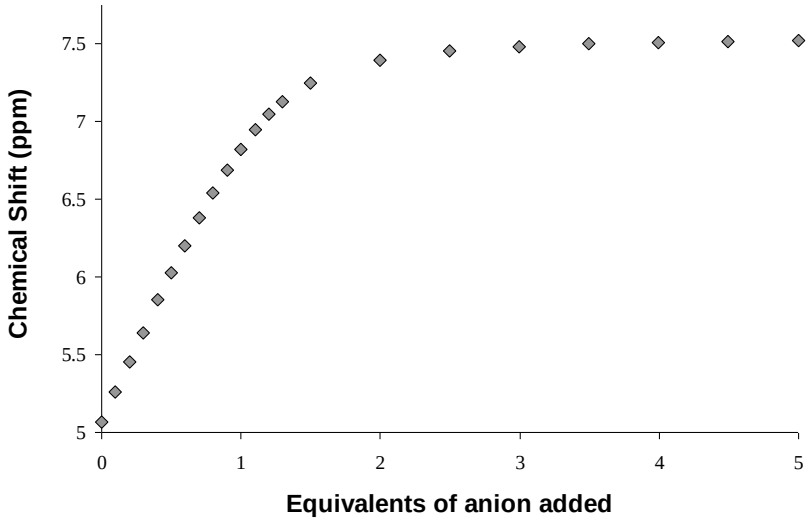

Figure S13. The change in chemical shift of one of the NH protons of compound **1**(*n* = 2) during the titration of TBA^{+} $MeCO_2^{-}$ done in MeCN at 50 ^{o}C from which the binding strengths of **1**(*n* = 2) for the anion is determined.

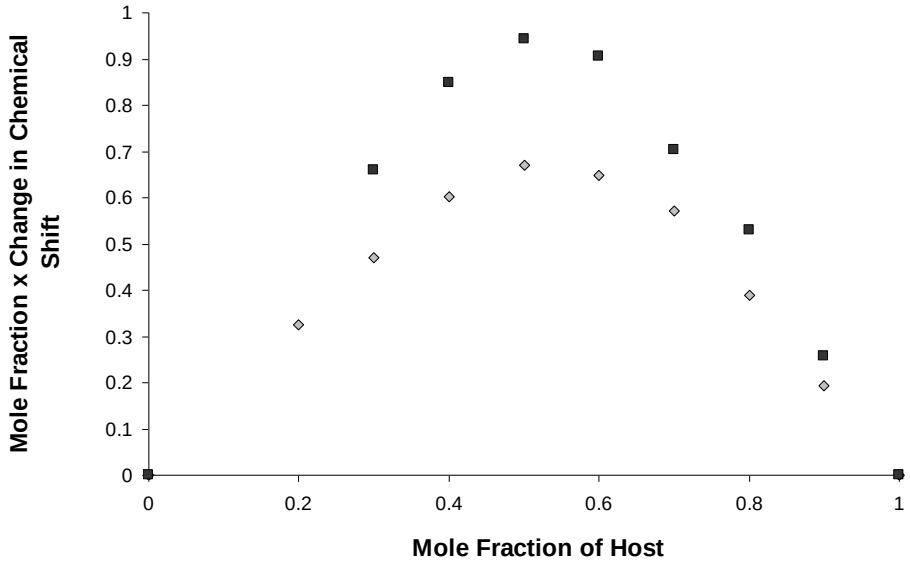

Figure S14. Figure showing the results of a Job Plot analysis for the binding of TBA^+ $MeCO_2^-$ by compound **1**[2] giving a 1:1 binding ratio (0.5 mole fraction of host). The two NMR signals are those assigned to the NH protons of the urea groups.

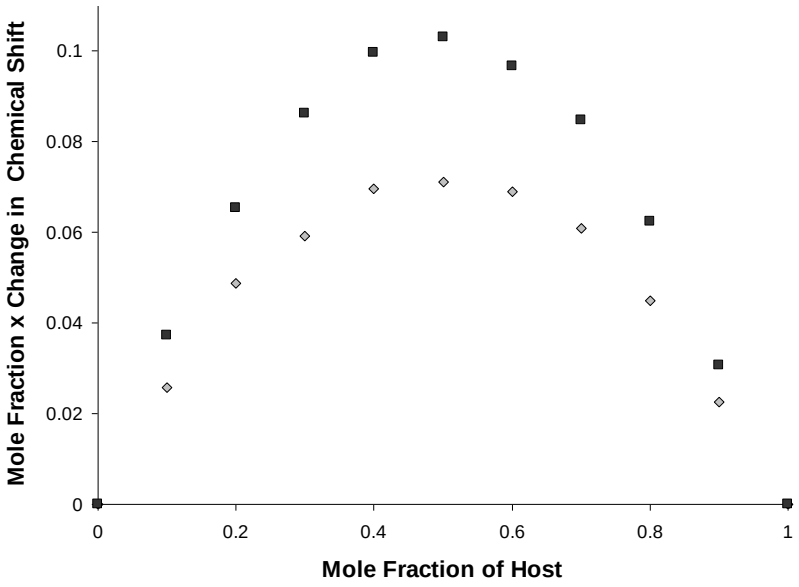

Figure S15. Figure showing the results of a Job Plot analysis for the binding of TBA^+ Cl^- by compound **1**[2] giving a 1:1 binding ratio (0.5 mole fraction of host). The two NMR signals are those assigned to the NH protons of the urea groups.

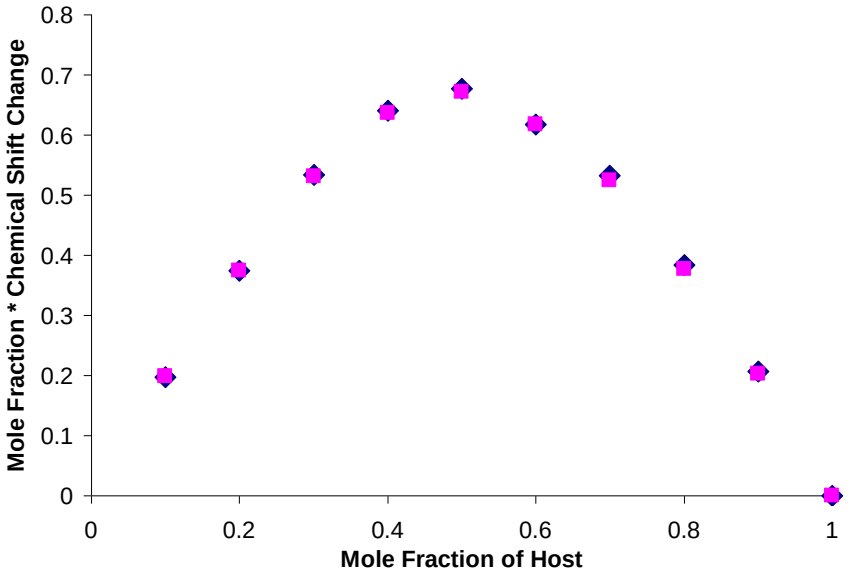

Figure S16. Figure showing the results of a Job Plot analysis for the binding of TBA^+ $MeCO_2^-$ by compound **1**[4] giving a 1:1 binding ratio (0.5 mole fraction of host). The two NMR signals are those assigned to the NH protons of the urea groups.

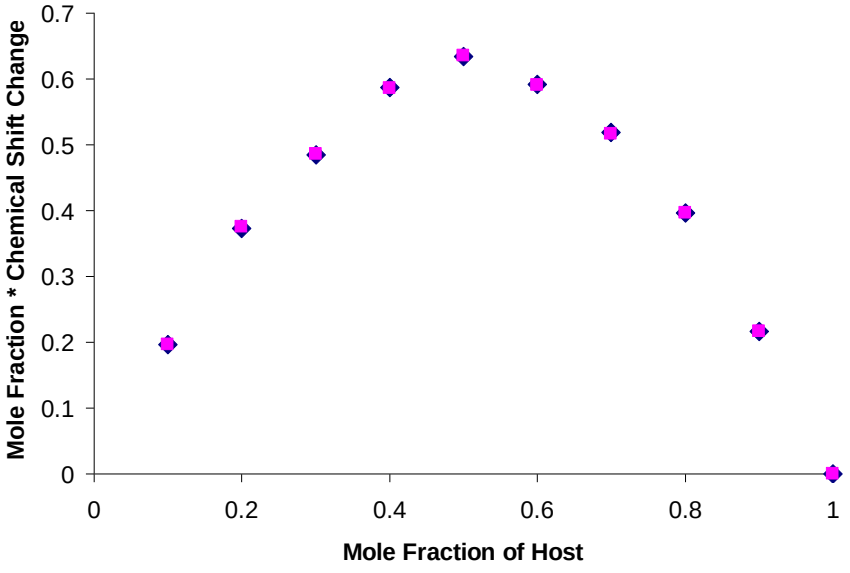

Figure S17. Figure showing the results of a Job Plot analysis for the binding of TBA^+ $MeCO_2^-$ by compound **1**[6] giving a 1:1 binding ratio (0.5 mole fraction of host). The two NMR signals are those assigned to the NH protons of the urea groups.

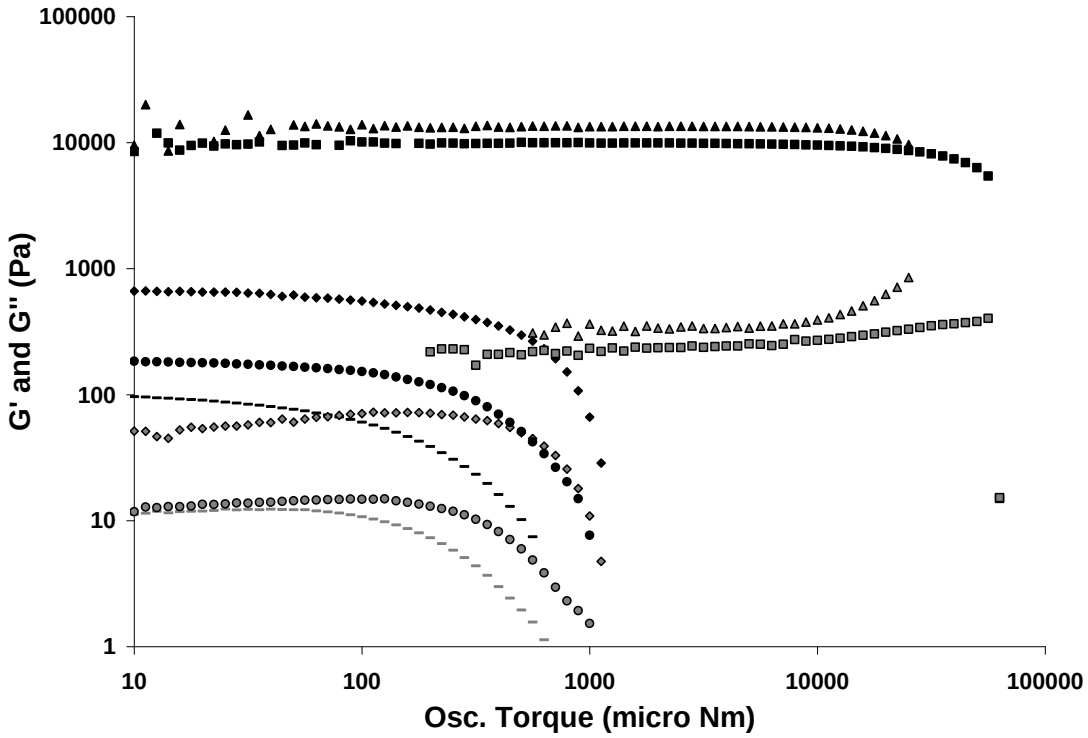

Figure S18. Influence of different anions (0.1 equivalents of anion added as their TBA^+ salts) on the storage modulus (*G′*, *G″* and "yield stress") at a frequency of 1 Hz and a temperature of 20 °C, as a function of osc. torque of the 1% by weight gel of compound **1**[6] in $CHCl_3$. The anions added are BF_4^- (△); Br^- (◇);Cl^- (O) and $MeCO_2^-$ (−). The pure gel is represented as □. *G′* values are show as black filled symbols and *G″* values are shown as grey filled symbols. Both axis values are shown in log scale.

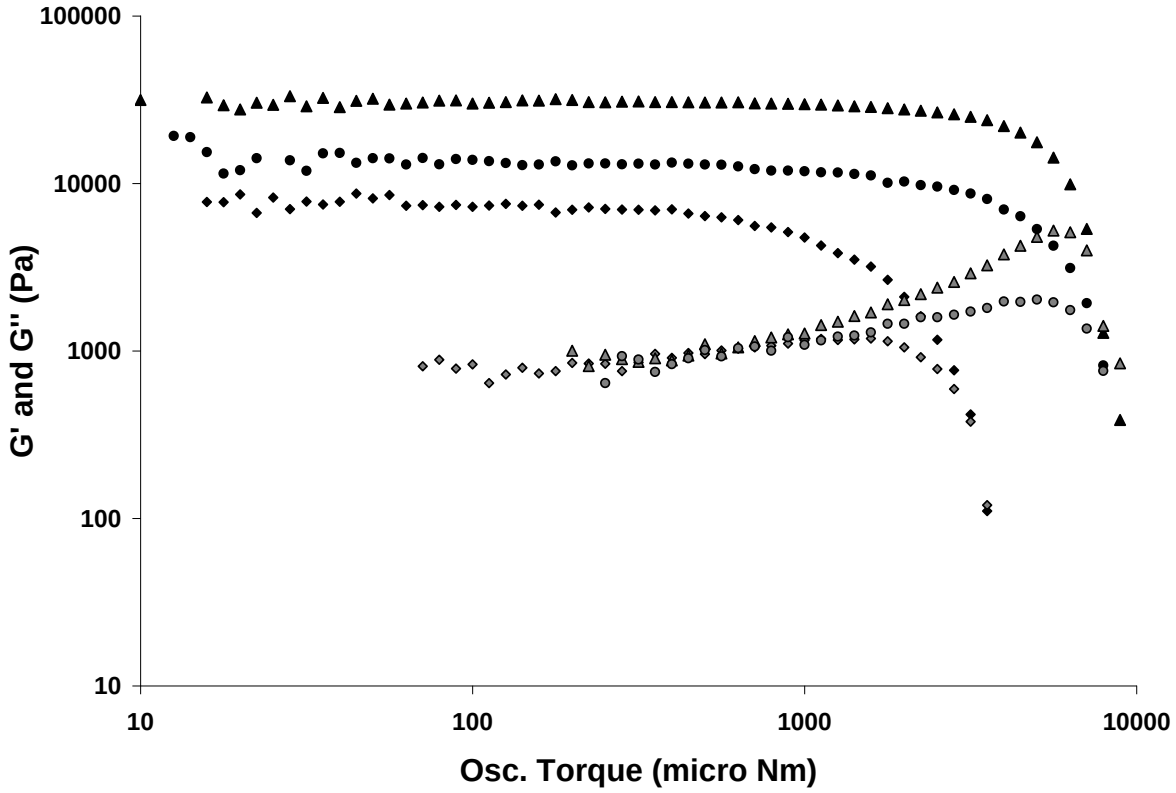

Figure S19. Influence of different anions (0.1 equivalents of anion added as their TBA^+ salts) on the storage modulus (*G′*, *G″* and "yield stress") at a frequency of 1 Hz and a temperature of 20 °C, as a function of osc. torque of the 1% by weight gel of compound **1**[4] in MeCN. The anions added are BF_4^- (○) and $MeCO_2^-$ (◇). The pure gel is represented as △. *G′* values are show as black filled symbols and *G″* values are shown as grey filled symbols. Both axis values are shown in log scale

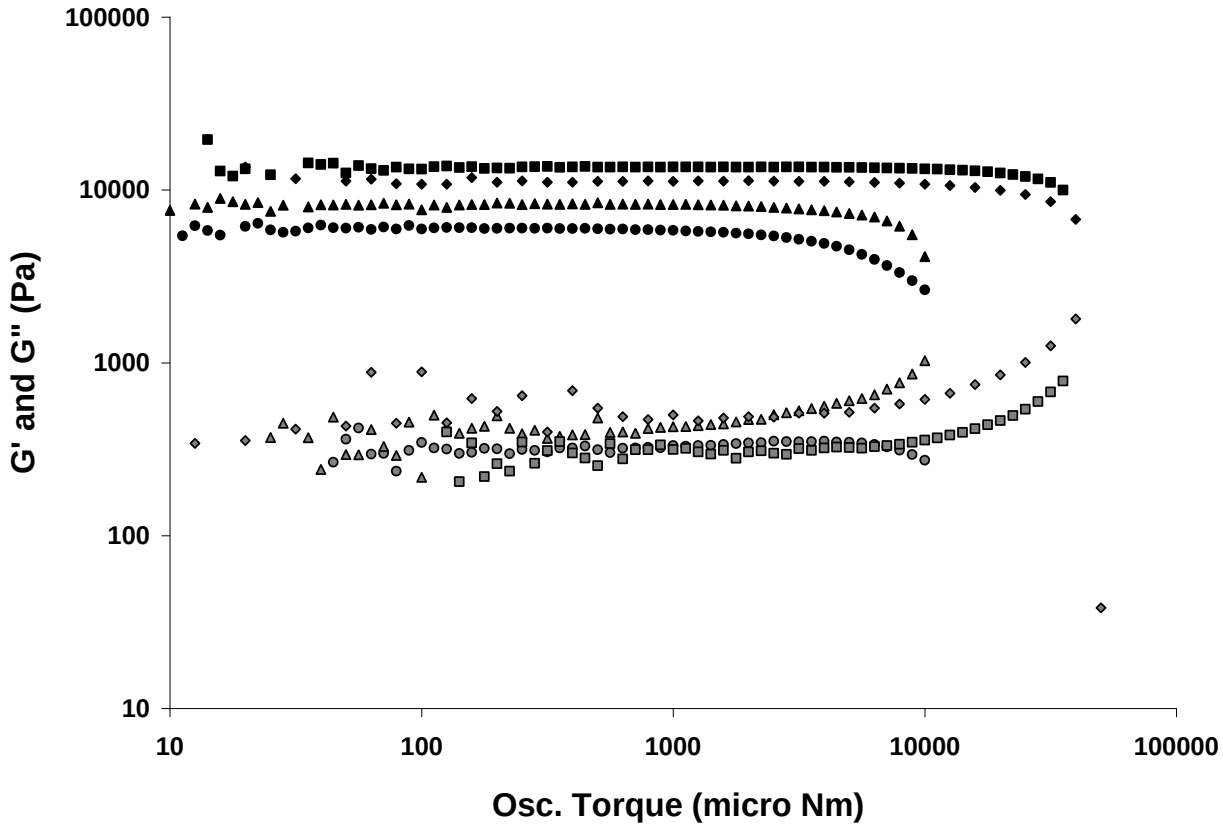

Figure S20. Influence of different anions (0.1 equivalents of anion added as their TBA^+ salts) on the storage modulus (*G′*, *G″* and "yield stress") at a frequency of 1 Hz and a temperature of 20 °C, as a function of osc. torque of the 1% by weight gel of compound **1**[8] in $CHCl_3$. The anions added are BF_4^- (□); Cl^- (△) and $MeCO_2^-$ (○). The pure gel is represented as ◇. *G′* values are show as black filled symbols and *G″* values are shown as grey filled symbols. Both axis values are shown in log scale.

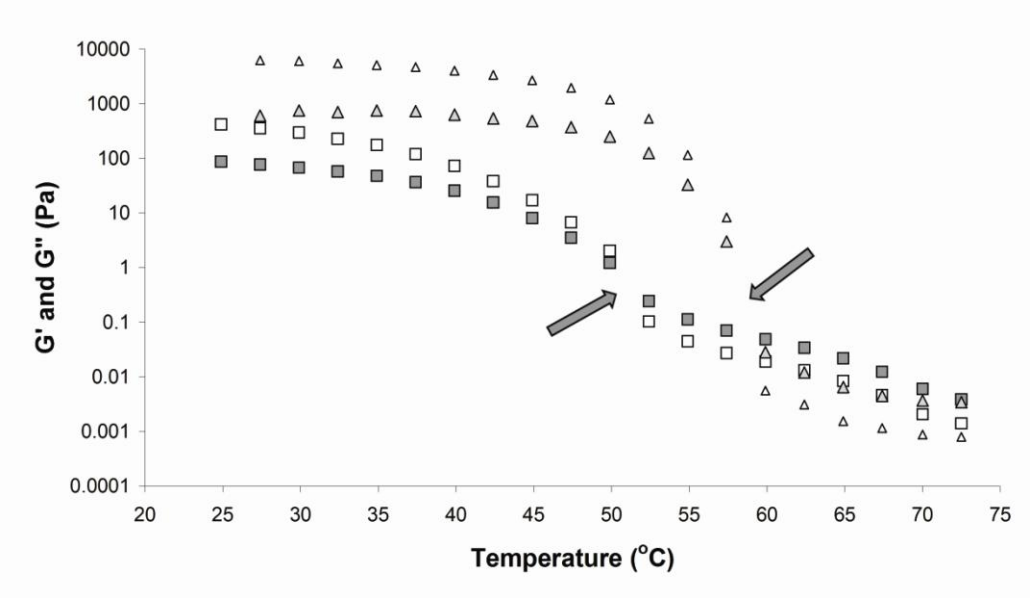

Figure S21. The effect of adding anion in form of TBA^+ Cl^- on *G′*, *G″* and T_{sg} for a gel of **1**(*n* = 2) at 0.3% by weight and in MeCN, as measured by varying the temperature from 70°C to 25°C. The △ symbols (*G′* open; *G″* filled) represent 0.1 equivalents of anion added and the □ symbols (*G′* open; *G″* filled) represent 0.2 equivalents added. Arrows indicate T_{sg} points. *G′* and *G″* axis values are shown in log scale.

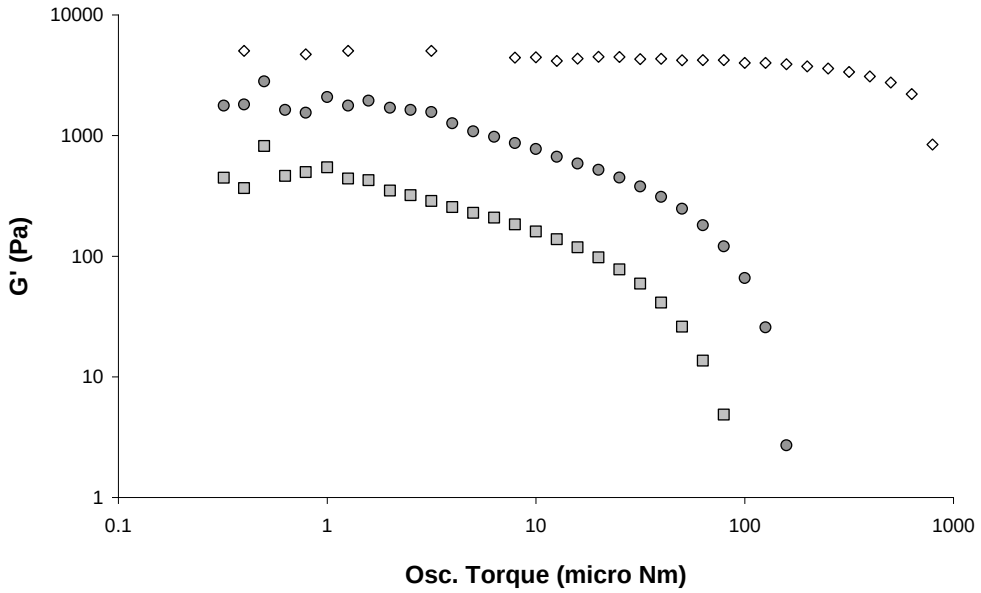

Figure S22. The effect of adding the anion TBA^+ NO_3^- on the storage moduli for a gel of $\mathbf{1}^2$ at 0.3% by weight and in MeCN measured by varying the osc. torque from 10 micro N.m to

1000 micro N.m, at a fixed frequency of 1 Hz. The ◇ symbols represent 0.1 equivalents of anion added; the ○ symbols represent 0.2 equivalents added and the □ symbols represent 0.5 equivalents added. *G′* decreases as more anion is added to the gel. *G′* and *G″* axis are values shown in log scale.

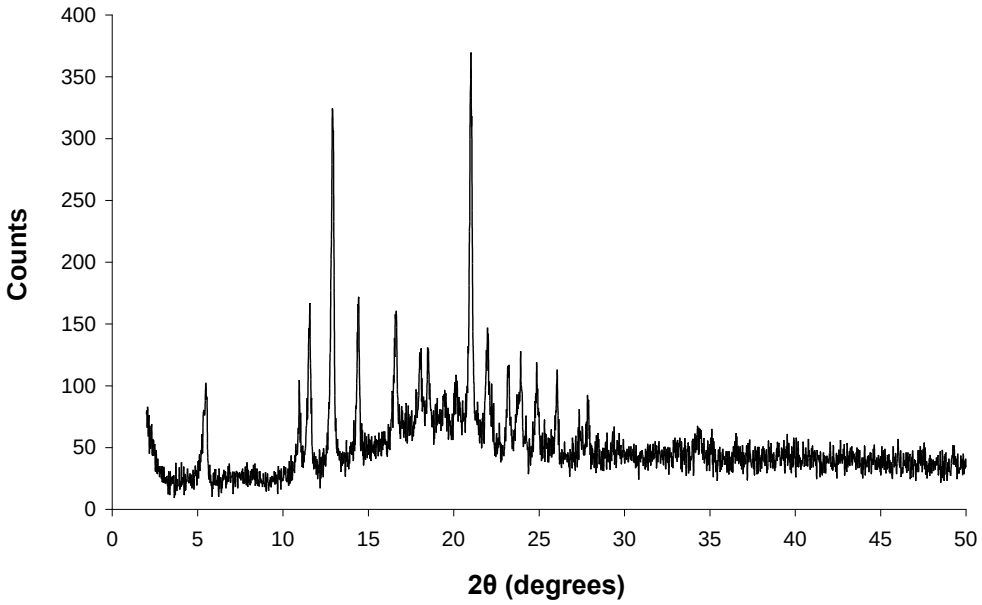

Figure S23. PXRD pattern of **2** from the as-synthesised materials.

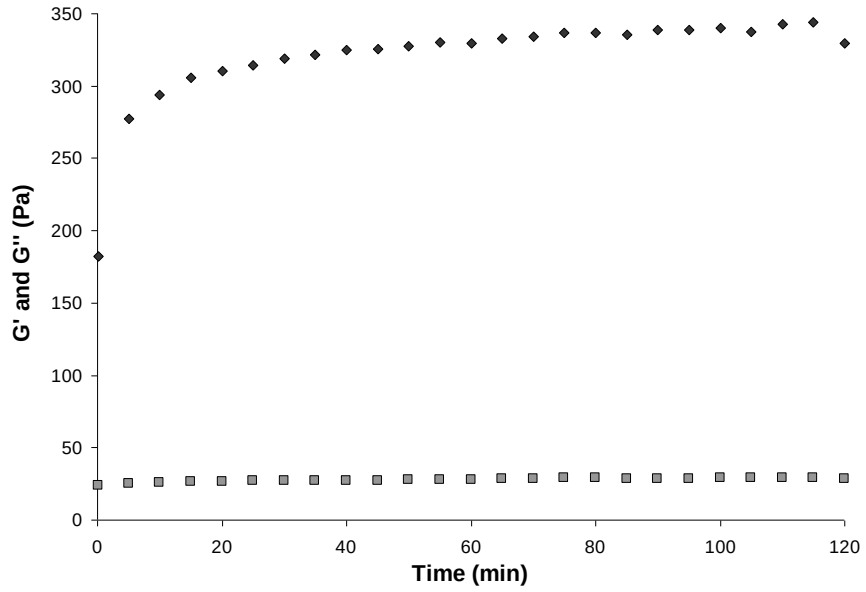

Figure S24. Rheology of **2** showing a time sweep performed on a gel of **2** at 0.1% by weight MeCN gel. Typically the gel's strength increases over time as shown by the increase in *G′* (Dark grey filled ◇) with time while *G″*(Light grey filled □) does not change.

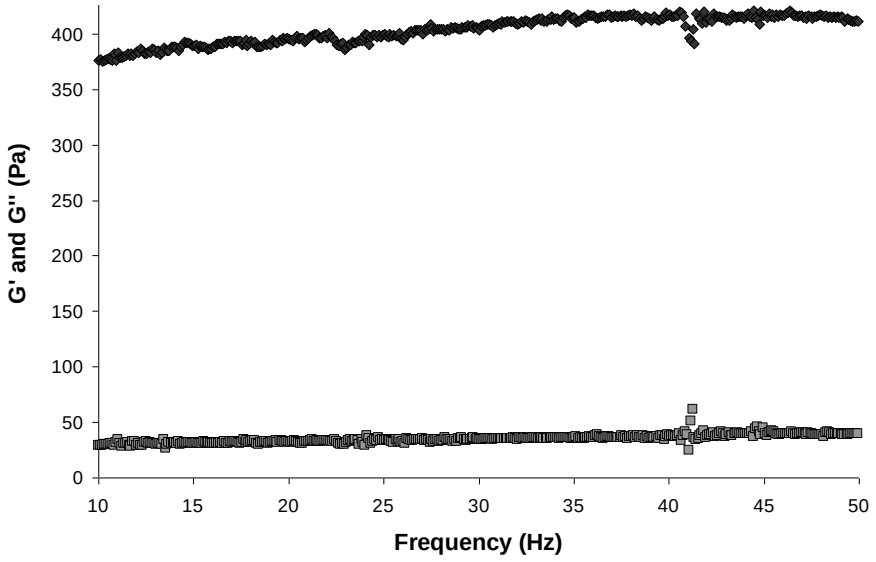

Figure S25. Rheology of **2** showing a frequency sweep performed on a gel of **2** at 0.1% by weight MeCN gel. Typically the consistency of the *G′*(Dark grey filled ◇) and *G″*(Light grey filled □) values over the frequency range indicates the solid-like nature of the gel material. The greater than a magnitude value of *G′* over the *G″* value demonstrates the elastic behaviour of the gel.

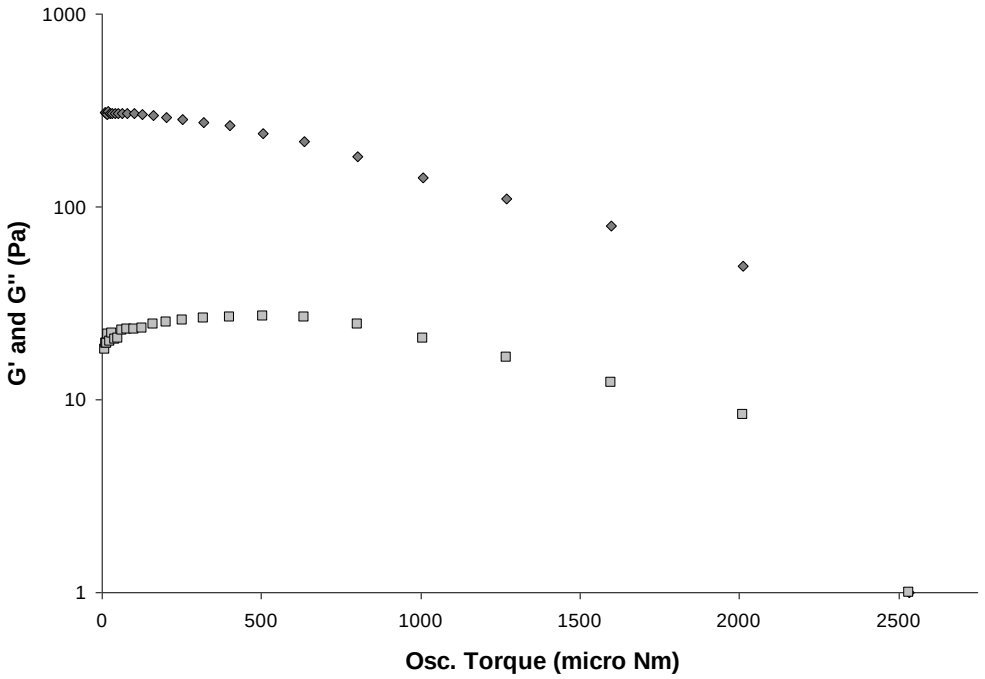

Figure S26. Rheology of **2** showing a stress sweep on a 0.1% by weight MeCN gel. The stress sweep shows the rigidity and strength of the gel which breaks at a relatively high shear strength. *G′* value (Grey filled ◇) stays relatively constant until the torque begins to become too strong and the struts start to break under the strain. Eventually *G′* for the samples drops to below the *G″* value (Light grey filled □) and the sample is said to be flowing. *G′* and *G″* axis values shown in log scale.

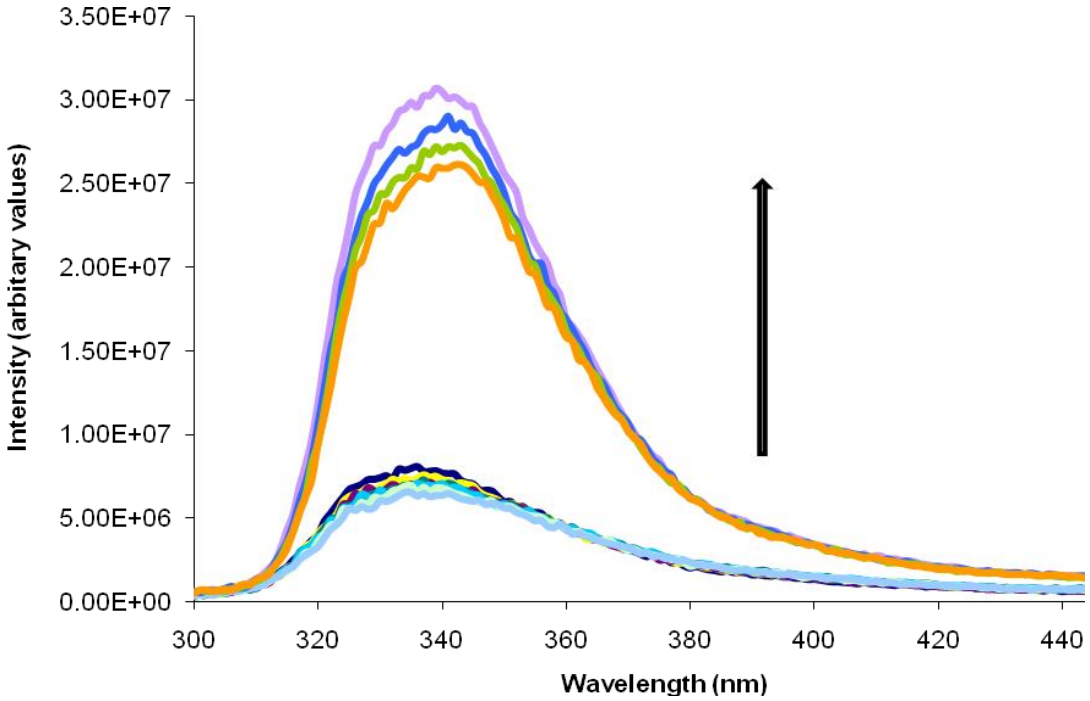

Figure S27. Fluorescence spectra of a gel of **2** at 0.003% by weight in DMSO:H_2O. The spectra do not change by much as the solution cools. When the solution is given a shake, gel formation starts to occur and the band intensity increases.

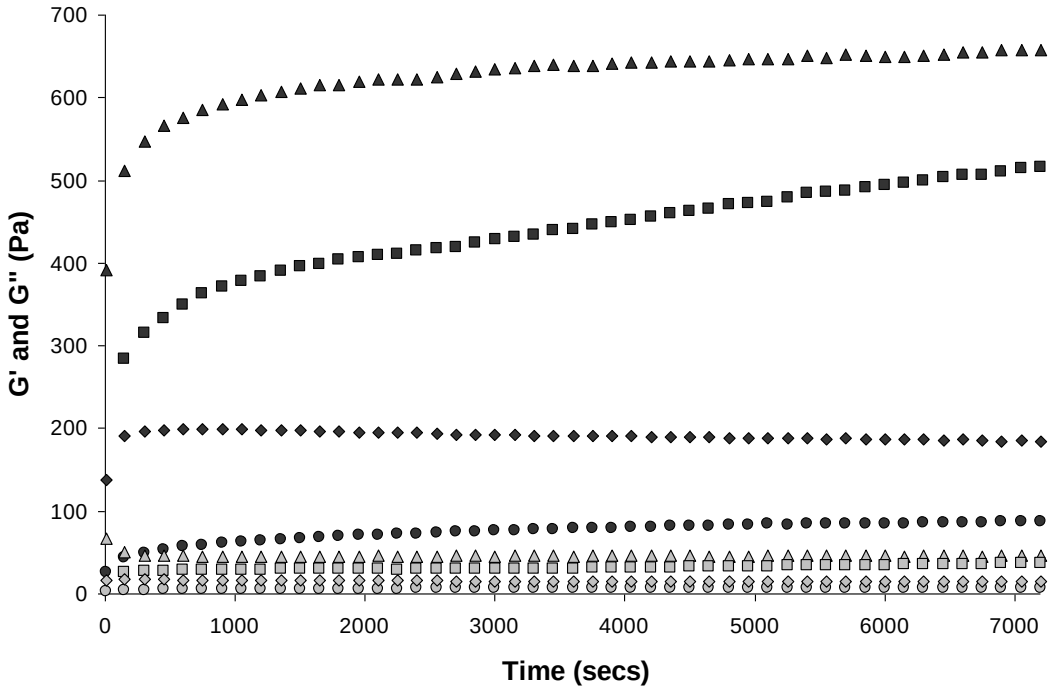

Figure S28. Rheology of gels of **2** upon addition of TBA^+ $MeCO_2^-$. Time sweep measurements are performed on gels of **2** at 0.1% by weight in MeCN with varied amounts of TBA^+ $MeCO_2^-$

added. *G′* represented as dark filled symbols and *G″* as light filled symbols. △ symbols are for the pure gel, □ symbols are for 0.05 equivalents of TBA^+ $MeCO_2^-$ added, ◇ symbols are for 0.2 equivalents of TBA^+ $MeCO_2^-$ added and ○ symbols are for 0. 5 equivalents of TBA^+ $MeCO_2^-$ added.

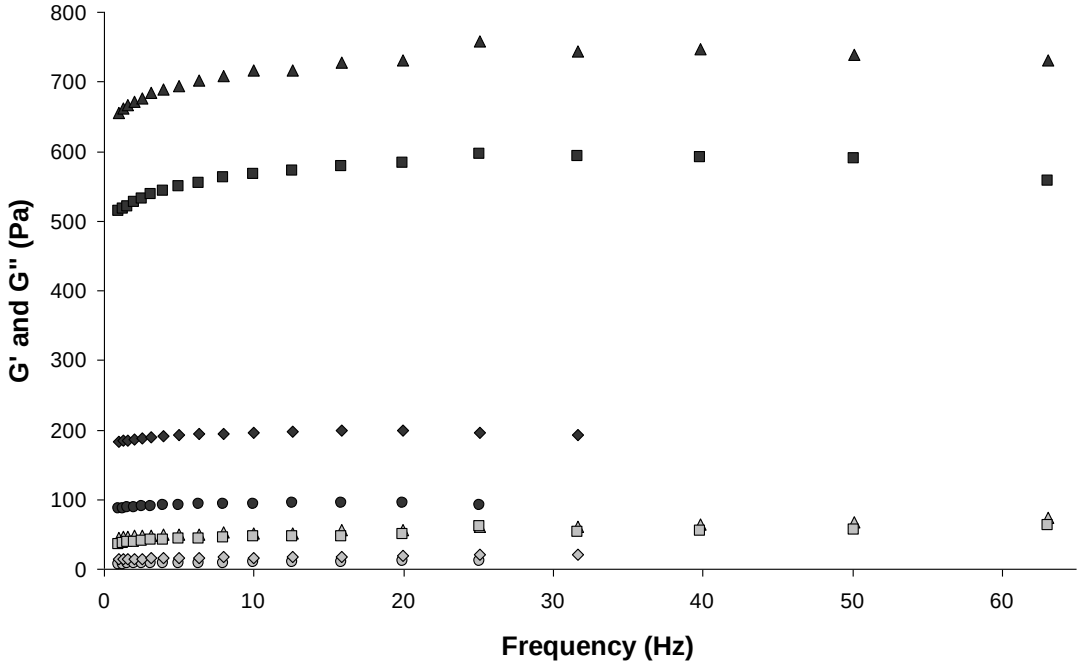

Figure S29. Rheological study of the tuning of gels of **2** using the addition of anion in the form of TBA^+ $MeCO_2^-$. Frequency sweep measurements are performed on gels of **2** at 0.1% by weight in MeCN with varied amounts of TBA^+ $MeCO_2^-$ added. *G′* represented as dark filled symbols and *G″* as light filled symbols. △ symbols are for the pure gel, □ symbols are for 0.05 equivalents of TBA^+ $MeCO_2^-$ added, ◇ symbols are for 0.2 equivalents of TBA^+ $MeCO_2^-$ added and ○ symbols are for 0. 5 equivalents of TBA^+ $MeCO_2^-$ added.

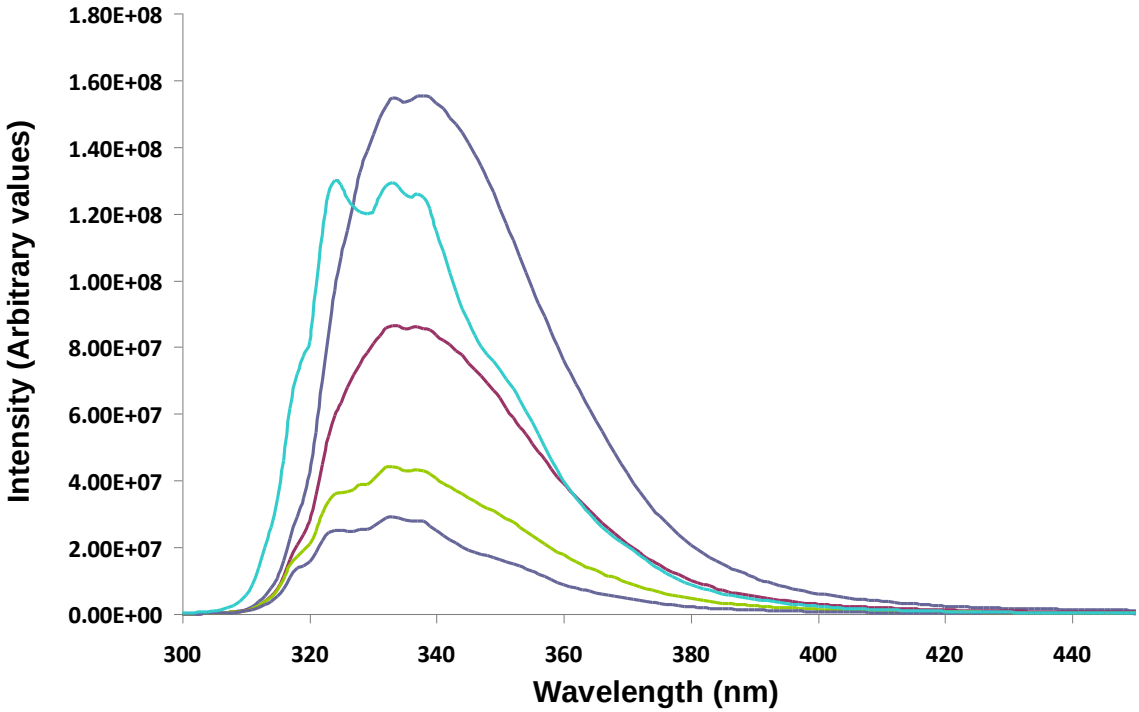

Figure S30. The diminishing intensity in the fluorescence of compound 2 within a gel of MeCN as the added $MeCO_2^-$ breaks the gel down. The light blue spectrum is of the hot solution of the dissolved gel. The dark blue spectrum is of the set cooled gel. The anion is added and the diminishing intensity spectra are the gel over time as the $MeCO_2^-$ dissolves the gel.