Controlled Tuning of the Properties in Optoelectronic Self-Sorted Gels

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SUPPORTING INFORMATION

1. Materials

The gelators **1** and **2** were prepared as previously reported.[1, 2] All other chemicals were purchased from Sigma Aldrich and were used as received unless otherwise stated. Deuterium oxide (D_2O) was used throughout as the solvent. A stock solution of sodium deutroxide (NaOD) at a concentration of 0.1 M was prepared in D_2O from the commercially available 40 wt% solution.

2. Preparation of solutions of 1, 2, and (1+2).

For each single component solution, the gelator was added to D_2O and NaOD (0.1 M, one molar equivalent for **1** and two molar equivalents for **2**), the solution was stirred overnight to ensure all gelator had dissolved to provide solutions at a final concentration of each gelator of 5 mg/mL. For the multicomponent solution, single component solutions were prepared as above at a concentration of 10 mg/mL. The two single component solutions were then mixed in a ratio of 1:1 to provide a solution in which the concentration of **1** and **2** were 5 mg/mL (so total gelator concentration of 10 mg/mL). The pH of all solutions were measured and adjusted to 10.5 before used and were stored at room temperature.

3. Preparation of gels of 1, 2, and (1+2).

For each single component gel, 2 mL of gelator solution was added to 10 mg of GdL (5 mg/mL) in a 7 mL Sterlin vial. The vial was gently swirled to ensure all the GdL had dissolved then placed into a water bath at a controlled temperature of 25 or 30 °C for 16 hours. For the multicomponent gel, 1 mL of each gelator solution were added together. This was added to 20 mg of GdL (10 mg/mL) in a 7 mL Sterilin vial. The vial was gently swirled to ensure all the GdL had dissolved and placed into the water bath for 16 hours. Photographs of the gels are shown in Fig. S1.
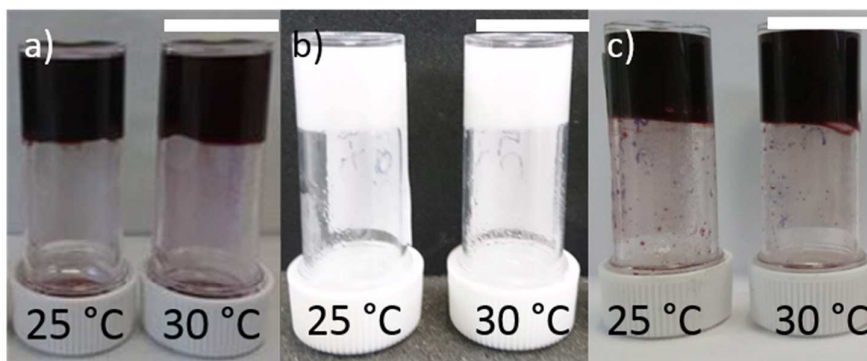
Figure S1. Picture of inverted Sterilin vial showing gel containing (a) **1**; (b) **2**; (c) **1**+**2**. The scale bar represents 1.7 cm in each case.

4. Methods

4.1. SANS data

For the SANS experiments, two sets of solutions were prepared for **1**, **2**, and (**1+2**). The first was prepared in D_2O using NaOD as described above, and the second was prepared in H_2O using NaOH, again as described above. The solutions were then mixed to prepare solutions with different ratios of H_2O to D_2O, whilst maintaining a set concentration of the chosen gelator(s). These samples were then gelled using GdL in a thermostatted oven to ensure that the temperature was constant. Solutions of H_2O and D_2O were mixed to provide the appropriate backgrounds.

For the fitting in 45% D_2O (i.e. the fitting of **1** either alone or in the mixture), the data were found to fit best to a combination of the cylinder model with a power law to take into account the scattering at low Q. The fit was found to be insensitive to the length, which was always large, which indicates that the total length does not lie within the Q-range that was probed in this experiment. Hence, the model was allowed to fit initially, with the length then fixed to the value obtained from the initial fit and the fit optimised (for this, the length was always greater than 1000 nm). Repeating this method produced different absolute values of the length (which were always > 10^3 nm, see Table S1 below), with the other parameters unaffected after optimisation. Additionally, the background was fixed at high Q according to the plateau intensity found in the scattering curves.

For the fitting in 60% D_2O (i.e. the fitting of **2** either alone or in the mixture), the data were best fitted to a flexible cylinder model. For **2** alone at 25 ºC, the data at low Q showed higher intensity than expected using this model. Adding a power law to take this in account did not improve the quality of the fit. The upturn at low Q could not be rendered by fitting using either model. A possible reason for this upturn might be some aggregation of the structures. Hence, the fits were constrained over a narrower Q range ($0.0031 – 0.24$ Å^{-1}). The results obtained are reasonable and confirm the chosen approach. A similarly reduced Q range was used for the data in the mixture at 30 ºC.
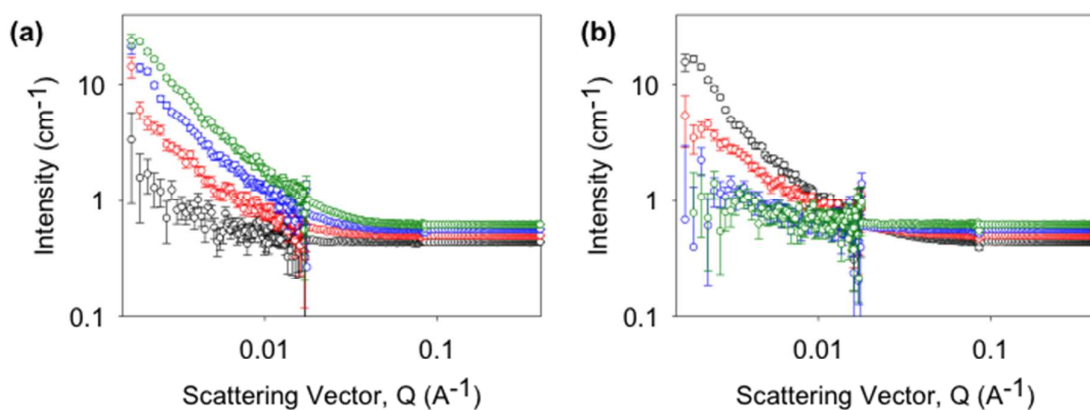
Figure S2. Contrast matching screen for (a) **1** and (b) **2**. Data were collected at (black) 60% D_2O; (red) 55% D_2O; (blue) 50% D_2O; (green) 45% D_2O.
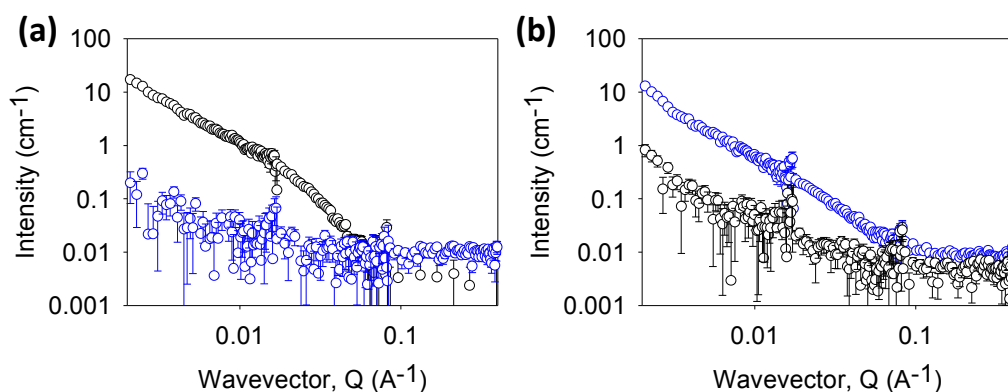

Figure S3. (a) Comparison of the scattering of **1** (black) and **2** (blue) at 45% D_2O. (b) Comparison of the scattering of **1** (black) and **2** (blue) at 60% D_2O. The contrast match for **2** at 45% D_2O is better than could be achieved for **1** at 60% but was the most effective found by scanning a range of H_2O to D_2O ratios. Whilst there is likely a contribution from **1** in the fits to the data from **2** at 60% D_2O, the contribution is small and does not seem to affect the quality of the fit over the Q range used.

|	**1** alone (45% D_2O, 25 ºC)	**1** in (**1**+**2**) (45% D_2O, 25 ºC)	**1** alone (45% D_2O, 30 ºC)	**1** in (**1**+**2**) (45% D_2O, 30 ºC)
Background (1/cm)	0.002*	0.002*	0.003*	0.004*
Power Law	2.20 ± 0.02	2.34 ± 0.02	2.29 ± 0.03	2.12 ± 0.01
Power Law Scale	$1.74 \times 10^{-5} \pm 2.4 \times 10^{-6}$	$1.00 \times 10^{-5} \pm 9.23 \times 10^{-8}$	$1.10 \times 10^{-5} \pm 1.91 \times 10^{-6}$	$3.60 \times 10^{-5} \pm 2.86 \times 10^{-6}$
Length (nm)	> 1000	> 1000	> 1000	> 1000
Radius (nm)	7.2 ± 0.1	6.1 ± 0.1	6.6 ± 0.1	7.0 ± 0.1
Scale	$2.20 \times 10^{-3} \pm 7.37 \times 10^{-5}$	$2.09 \times 10^{-3} \pm 4.1 \times 10^{-5}$	$2.29 \times 10^{-3} \pm 9.26 \times 10^{-6}$	$1.66 \times 10^{-3} \pm 6.99 \times 10^{-5}$
χ^2	2.11	1.88	2.22	1.38

Table S1. Parameters from fits to the scattering data in 45% D_2O. A * indicates that the parameter was fixed during the fitting process.

	2 alone (60% D_2O, 25 ºC)	**2** in (**1**+**2**) (60% D_2O, 25 ºC)	**2** alone (60% D_2O, 30 ºC)	**2** in (**1**+**2**) (60% D_2O, 30 ºC)
Background (1/cm)	0.009	0.007	0.003	0.002
Kuhn Length (nm)	6.0 ± 0.3	11.8 ± 0.4	6.3 ± 0.5	22.5 ± 0.7
Length (nm)	> 1000	> 1000	> 1000	> 1000
Radius (nm)	3.2 ± 0.2	6.1 ± 0.4	3.2 ± 0.4	6.1 ± 0.5
Scale	$2.07 \times 10^{-3} \pm 4.48 \times 10^{-4}$	$1.96 \times 10^{-3} \pm 4.86 \times 10^{-5}$	$1.98 \times 10^{-3} \pm 5.7 \times 10^{-4}$	$1.47 \times 10^{-3} \pm 6.63 \times 10^{-5}$
χ^2	1.21	2.53	2.01	4.21

Table S2. Parameters from fits to the scattering data in 60% D_2O.
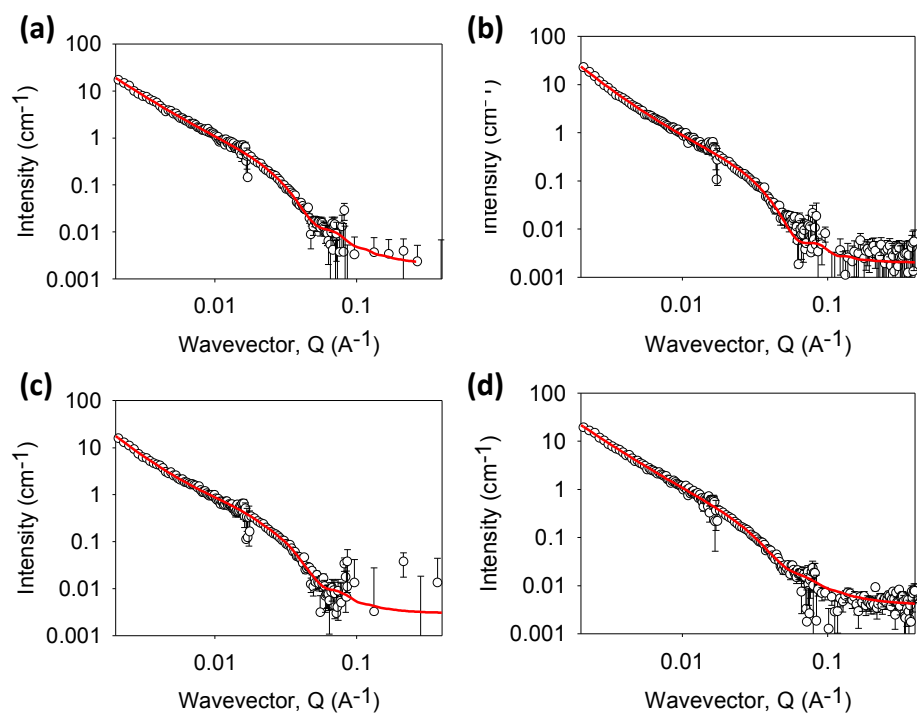
Figure S4. Scattering data and fits for (a) **1** alone (45% D_2O, 25 ºC); (b) **1** in (**1+2**) (45% D_2O, 25 ºC); (c) **1** alone (45% D_2O, 30 ºC); (d) **1** in (**1+2**) (45% D_2O, 30 ºC).
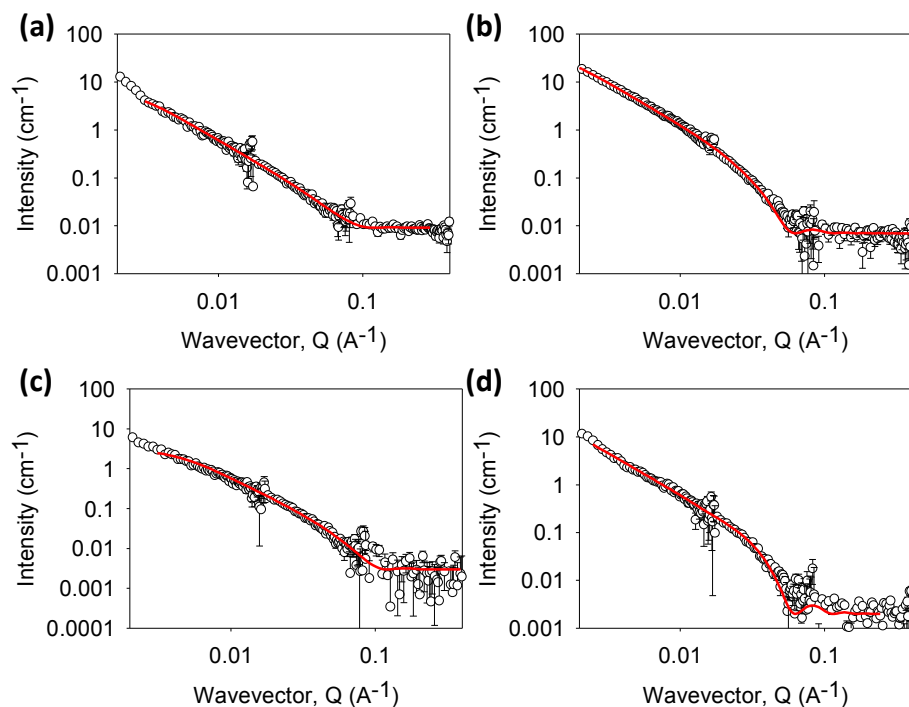
Figure S5. Scattering data and fits for (a) **2** alone (60% D_2O, 25 ℃); (b) **2** in (**1**+**2**) (60% D_2O, 25 ℃); (c) **2** alone (60% D_2O, 30 ℃); (d) **2** in (**1**+**2**) (60% D_2O, 30 ℃). As noted in the text, Fig. S12a and S12d show an upturn at low Q. The reason for this may be aggregation. If this is the reason, this would be at such a low percentage that it still allows fitting the data with a form factor model (no structure factor, and aggregation only visible at very low Q values) and hence the fit at the reduced Q range gives a good fit.

4.2. Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H NMR spectra were recorded using a Bruker Avance III 500 MHz spectrometer with the temperature internally controlled. Samples were run in D_2O/NaOD with ethanol (2 µL/mL) added as an internal standard. For the kinetic measurements, ethanol was added to 2 mL of the solution. 1 mL of this solution was used to record a standard measurement prior to the addition of GdL (i.e. a time zero measurement). After the standard measurement was obtained, GdL (5 mg for **1** or **2**, 10 for **1**+**2**) was added to the remaining 1 mL of the solution which was added to the NMR tube and inserted into the spectrometer. Due to the experimental limitations, there was a time delay of around 5 minutes from addition of GdL to the first sample acquisition. Spectra were recorded every 5 minutes until the gelator's proton peaks were no longer detectable. This took between 10-30 hours depending on the sample. Example spectra recorded over time are shown in Fig. S6-S8. The referenced proton environment was used to determine the percentage assembly over time shown in Fig. 3

(main text); when assembled, each gelator is NMR invisible and hence the percentage that can be detected is the percentage un-assembled).
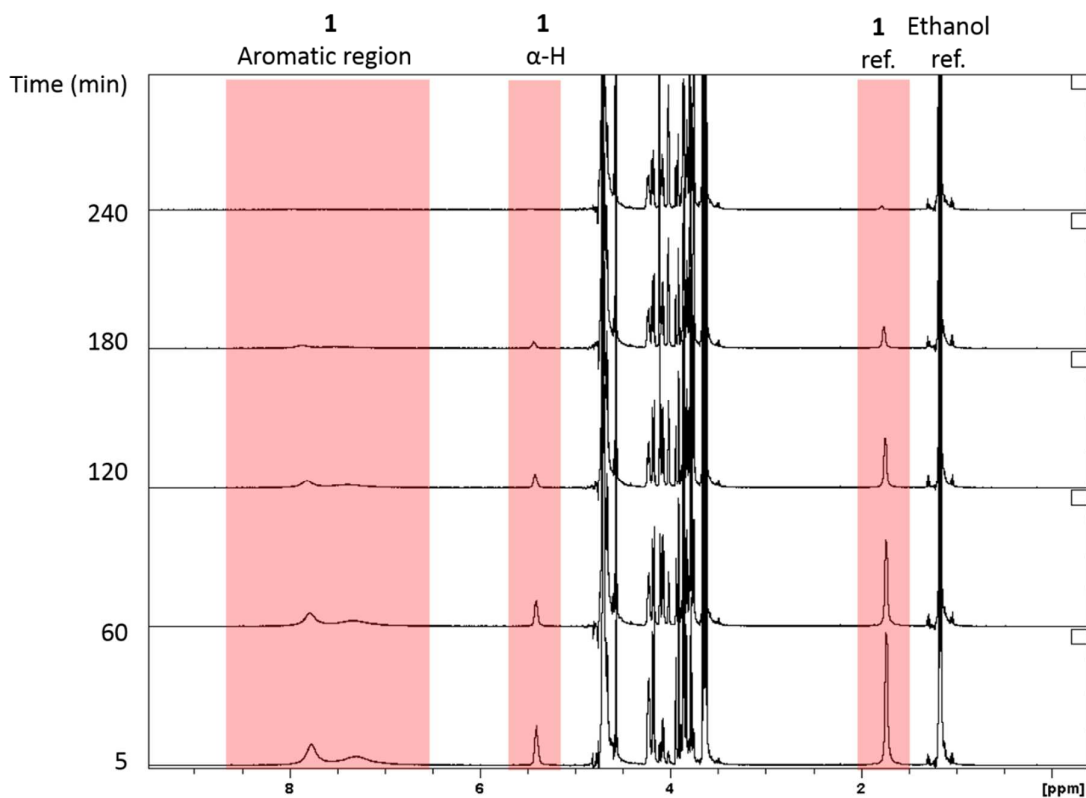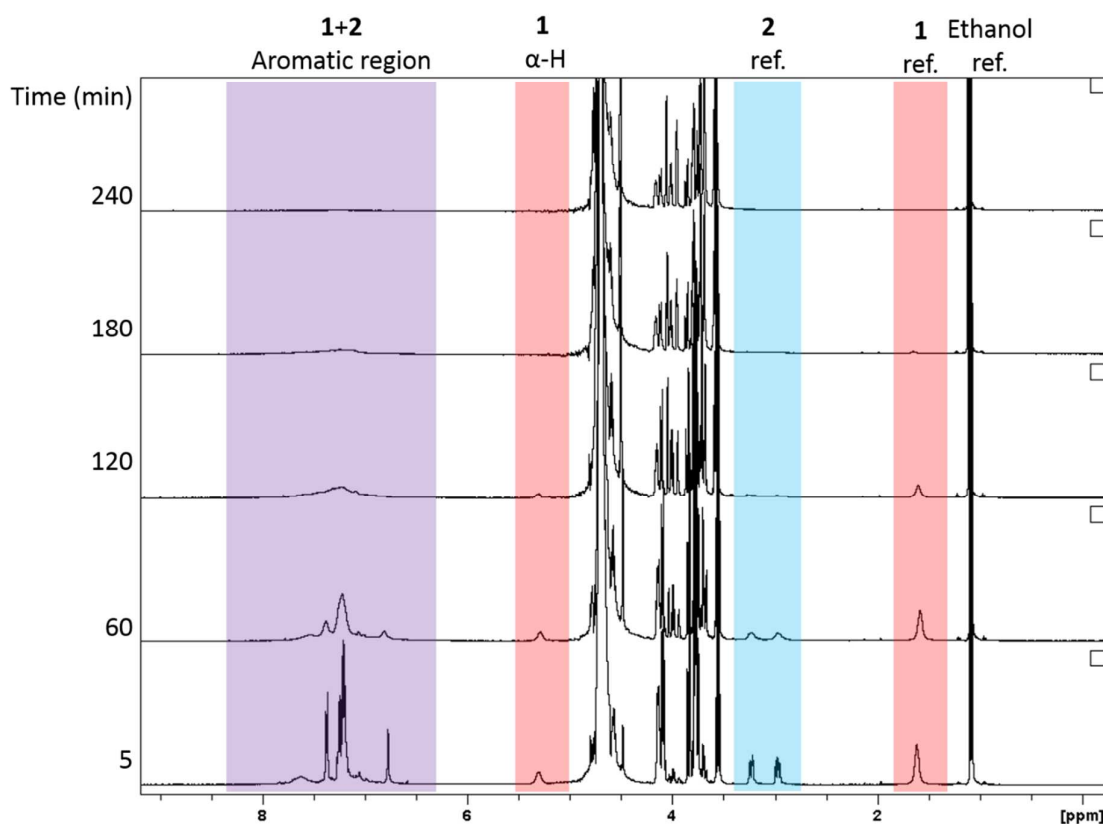

Figure S6. ^{1}H NMR spectra recorded over time after addition of GdL to a solution of **1** in D$_2$O/NaOD. The time at which the data were collected is shown on the left, with the peaks corresponding to **1** being shown in pink. The peaks between around 3.5 and 4.3 ppm are from GdL and its hydrolysis products. The peak at 4.5 ppm is from the solvent. The methyl groups from the ethanol standard against which the peaks of **1** are integrated are at just over 1 ppm. The proton environment labelled **1** ref. was used to determine the percentage assembly over time.
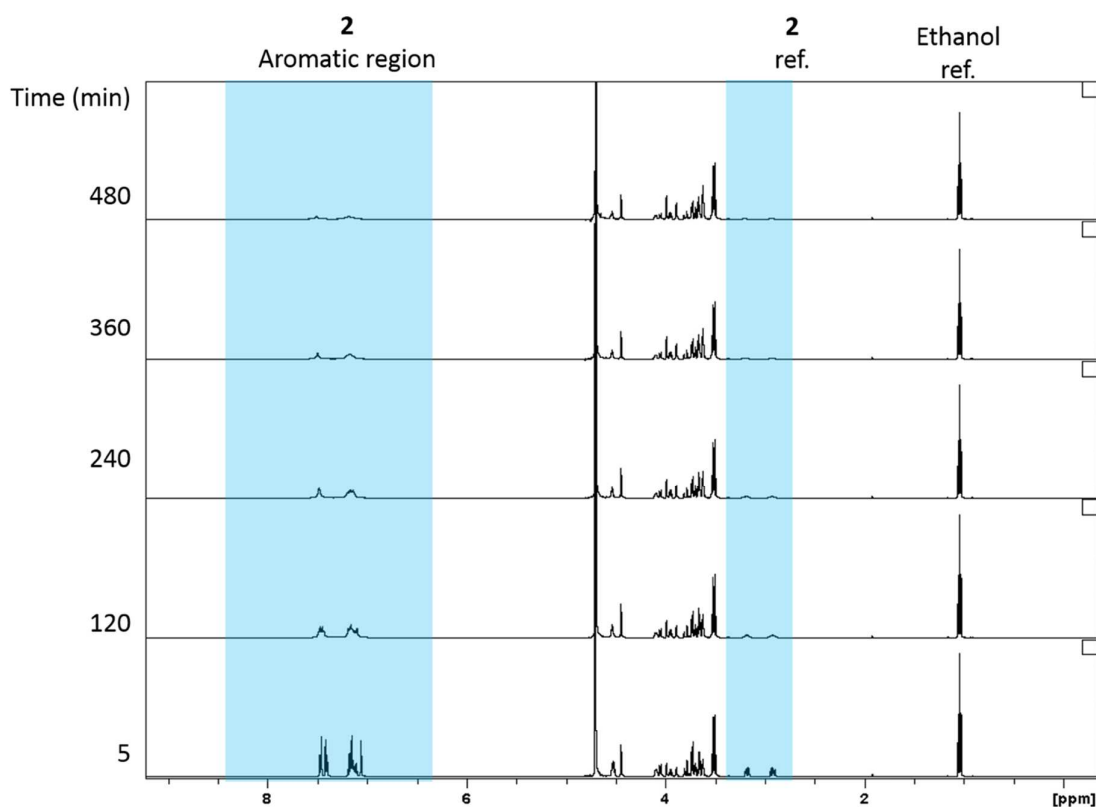
Figure S7. ^{1}H NMR spectra recorded over time after addition of GdL to a solution of **2** in D$_2$O/NaOD. The time at which the data were collected is shown on the left, with the peaks corresponding to **2** being shown in blue. The peaks between around 3.5 and 4.3 ppm are from GdL and its hydrolysis products. The peak at 4.5 ppm is from the solvent. The methyl groups from the ethanol standard against which the peaks of **2** are integrated are at just over 1 ppm. The proton environment labelled **2** ref. was used to determine the percentage assembly over time.

Figure S8. ^{1}H NMR spectra recorded over time after addition of GdL to a solution of both **1** and **2** in D$_2$O/NaOD. The time at which the data were collected is shown on the left, with the peaks corresponding to **1** being shown in pink, the peaks from **2** in blue and where peaks from both **1** and **2** in purple. The peaks between around 3.5 and 4.3 ppm are from GdL and its hydrolysis products. The peak at 4.5 ppm is from the solvent. The methyl groups from the ethanol standard against which the peaks of **1** and **2** are integrated are at just over 1 ppm. The proton environments labelled **1** ref and **2** ref. were used to determine the percentage assembly over time.

4.3. Rheological measurements

Rheological measurements were carried out using an Anton Paar Physical MCR301 rheometer. A vane (ST10-4V-8.8/97.5) and cup geometry was used to measure the frequency and strain sweeps. Parallel plates (50 mm diameter, sandblasted) were used to measure time sweeps. For measuring the frequency and strain sweeps, 2 mL of gelator solution was added to GdL in a Sterilin vial as described in Section 2. This was immersed in a water bath at a controlled temperature for 16 hours whilst gelling at a controlled constant temperature (either 25 or 30 °C). After complete gelation, the samples were transferred to the rheometer and the rheological measurements were then recorded at 25 °C. For the time sweeps, 2 mL of the gelator solution was added to GdL as described above. The solution was then transferred onto the temperature-controlled plate and the plate lowered on top of the solution with a gap distance of 0.8 mm and trimmed. The plate was then flooded with mineral oil to prevent the gel from drying whilst gelling.
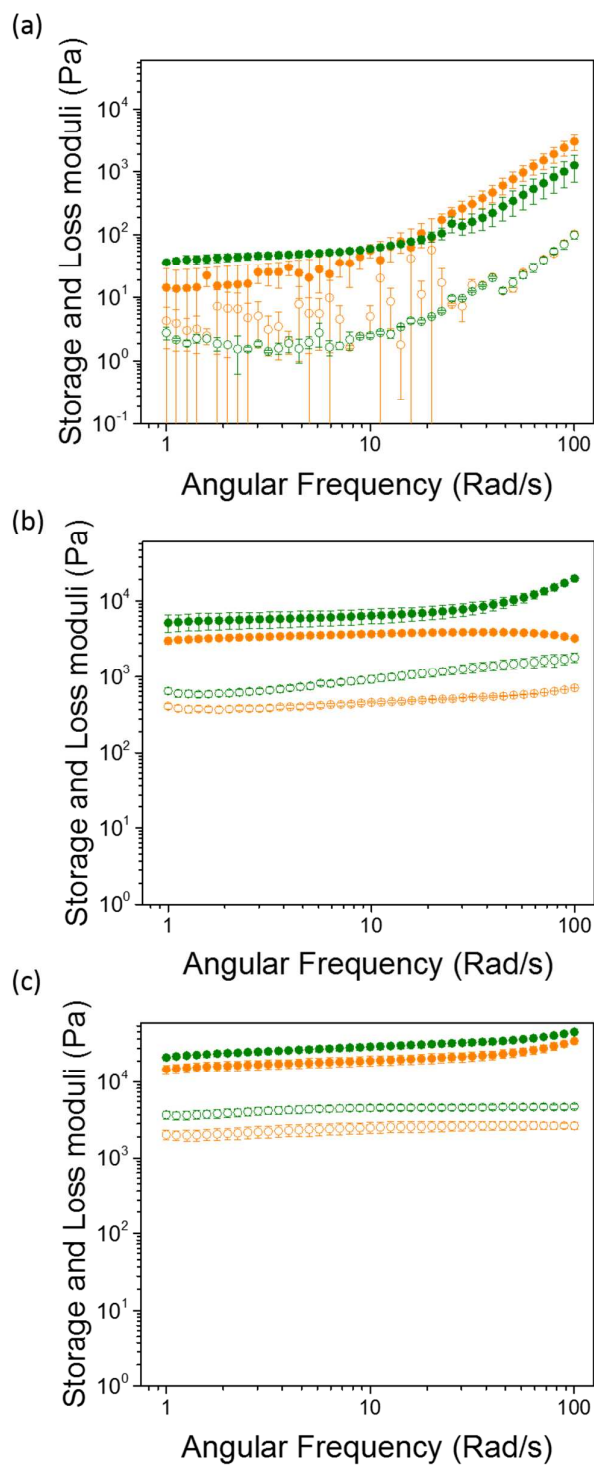
Strain sweep: Strain sweeps were measured from 0.01% to 100% with a constant frequency of 10 rad/s. Measurements were performed in duplicate and errors were calculated from the standard deviation.

Frequency sweep: Frequency scans were performed from 1 rad/s to 100 rad/s under a constant strain of 0.5%. Measurements were performed in duplicate and errors were calculated from the standard deviation.
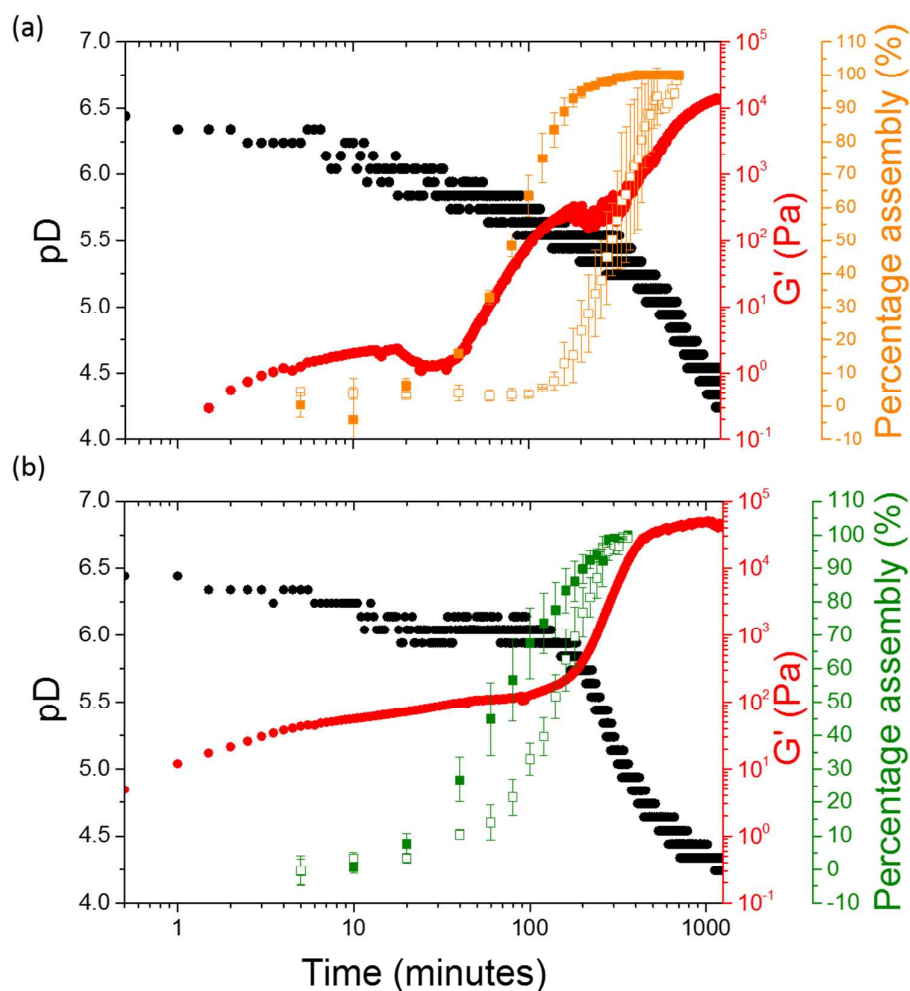
Time sweep: Time sweeps were measured with an angular frequency of 10 rad/s with a strain of 0.5%. Measurements were performed in duplicate and errors were calculated from the standard deviation.

(a)

(b)

(c)
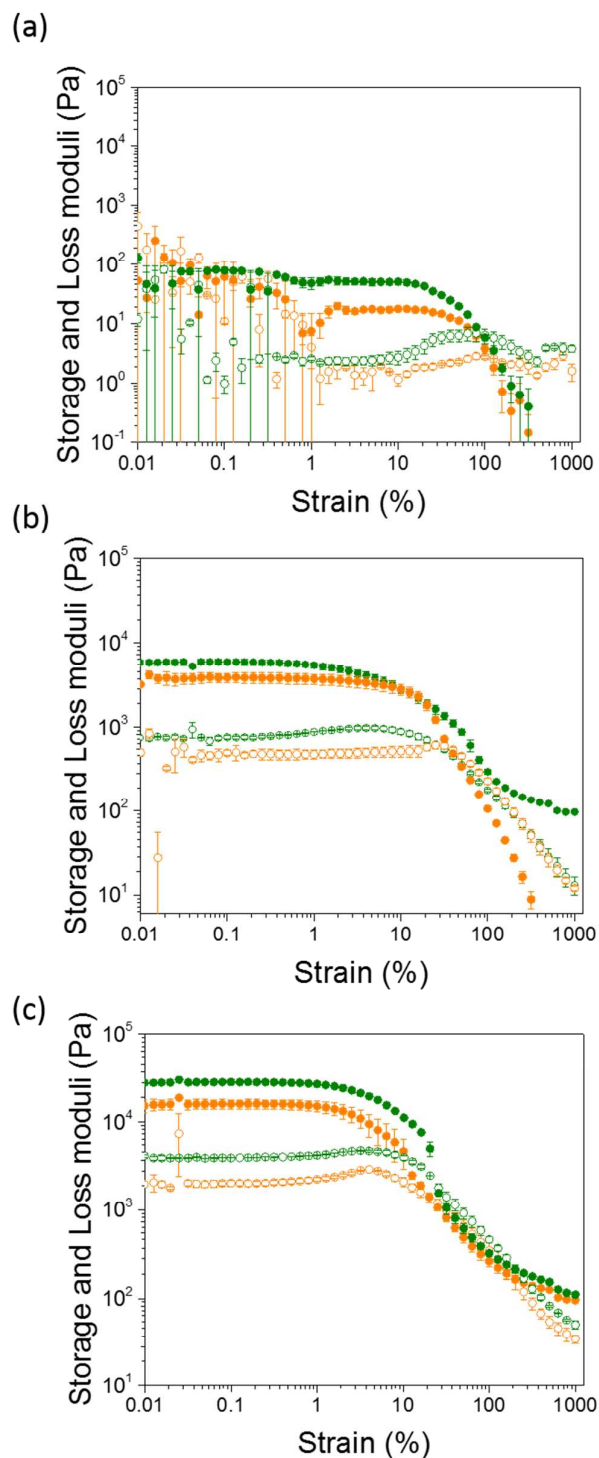
Figure S9. Strain sweep data for (a) **1**; (b) **2**; and (c) **1**+**2**. In all cases, the data in orange were collected from samples prepared at 25 °C and the green data were from samples prepared at 30 °C. In all cases, the storage modulus (G′) is represented by the closed symbols and the loss modulus (G″) is represented by open symbols. Measurements were performed in duplicate and errors were calculated from the standard deviation.

Figure S10. Frequency sweep data for (a) **1**; (b) **2**; and (c) **1+2**. In all cases, the data in orange were collected from samples prepared at 25 °C and the green data were from samples prepared at 30 °C. In all cases, the storage modulus (G′) is represented by the closed symbols and the loss modulus (G″) is represented by open symbols. Measurements were performed in duplicate and errors were calculated from the standard deviation.

Figure S11. Monitoring the gelation of **1** and **2** over time at (a) 25 °C and (b) 30 °C. The change in intensity of peaks from ^{1}H NMR spectroscopy during gelation of the referenced peak of CH_3 at 1.7 ppm from **1** (whole squares) and the referenced peak of CH_2 at 3.0 ppm from gelator **2** (hollow squares) are compared to the change in pH during gelation of **1** and **2** (Black). The change in G′ over time for gel-**1**,**2** (red data) is also shown. Rheological time sweeps were performed at a strain of 0.5%, 10 rad/s and at 25 °C. NMR measurements were performed in duplicate and errors were calculated from the standard deviation.

4.4. pH measurements

pH measurements were recorded using a Hanna PC turtle FC500 pH probe with a given error of ±0.1. For monitoring the pH of gelation over time, 2 mL of gelator solution was added to GdL in a Sterilin vial and this was immersed in a water bath at a controlled temperature. The probe tip was then inserted into the gel with parafilm used to seal the top of the vial/tip. The pH measurements were recorded every 30 seconds for between 16-36 hours until gelation was complete and pH had stabilised.

4.5. pK_a measurements

pK_a measurements were recorded using a Hanna PC turtle FC500 pH probe with a given error of ± 0.1. For pK_a measurements, 2 mL of gelator solution was added to a Sterilin vial which was immersed in a water bath at a controlled temperature and the probe tip was immersed in the solution. 2.5 µL aliquots of DCl (0.05 M) were added to the solution with the pH recorded after the reading had stabilised. The solution was gently swirled between additions of acid to avoid any gel forming. The plateaus in the data represent the apparent pK_a values. The data are shown below in Fig. S12.
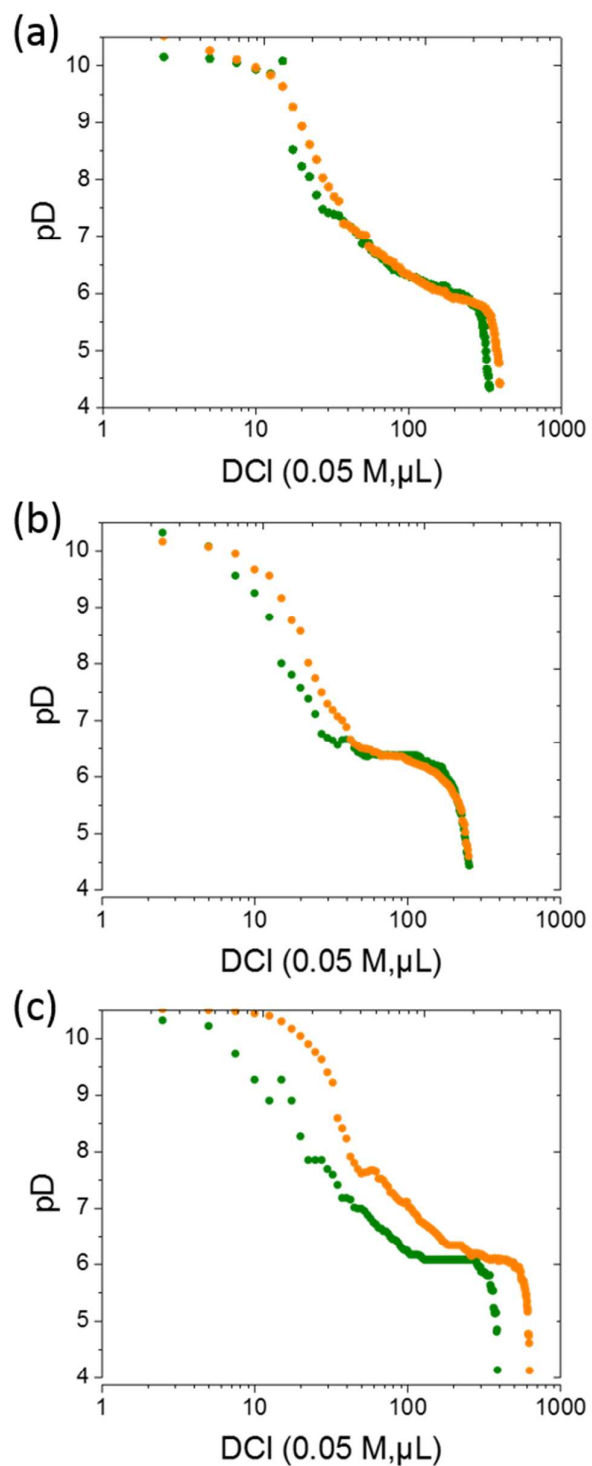
Figure S12. Determination of the pK_a for the single and multicomponent systems by measuring the pH change after additions of DCl (0.1 M) to a solution of (a) **1**; (b) **2**; (c) **1+2**. In all cases, the data in orange were collected at 25 °C and the green data was collected at 30 °C. The data are presented on a log time scale.

4.6. Electron Paramagnetic Resonance (EPR)

To prepare samples for EPR, 1 mL of a gelator solution was added to GdL as described in Sections 2 and 3. Using a needle and syringe, the solution was transferred to a soda glass capillary tube until it reached a 1.5 cm mark. The top was sealed with adhesive tack to prevent sample evaporation, and the sample was allowed to gel at a certain temperature. The sample was irradiated with an LED light source powered by a 70 mA TTi QL564P power supply. All EPR data were recorded at X-band frequency (9.67 GHz) on a Bruker ELEXSYS E500 spectrometer equipped with an ER 4102ST-O optical transmission resonator. Spectra represent 5 scan averages collected over a 5 mT sweep width centered at 344.4 mT, with modulation frequency = 100 kHz, modulation amplitude = 0.2 mT, receiver gain = 60 dB, time constant = 40.96 s, conversion time = 10.24 s, and microwave power = 0.63 mW. Spin counts of solution samples were quantified by double integration of the first derivative spectrum and calibrated to a 0.5 mg mL^{-1} aqueous solution of TEMPO recorded under identical conditions.

4.7. References

1. E. R. Draper, J. J. Walsh, T. O. McDonald, M. A. Zwijnenburg, P. J. Cameron, A. J. Cowan and D. J. Adams, *J. Mater. Chem. C*, 2014, **2**, 5570-5575.

2. E. R. Draper, E. G. B. Eden, T. O. McDonald and D. J. Adams, *Nat. Chem.*, 2015, **7**, 848-852.