Gelation by supramolecular dimerization of mono(urea)s

Abigail E. Hooper, Stuart R. Kennedy, Christopher D. Jones and Jonathan W. Steed*

Supplementary information

Synthesis of compounds

All starting materials and solvents were bought commercially and used as obtained with no further purification.

Characterisation

CHN elemental microanalysis was performed using an Exeter CE-440 Elemental Analyser. All materials submitted were dried for at least three hours under vacuum in a drying pistol to remove residual solvents.

FT-IR spectra of all solids were taken in the lab on a Perkin-Elmer Spectrum 100 Series spectrometer.

^{1}H, ^{13}C, COSY and DEPT NMR experiments were all run in DMSO-d6 (unless otherwise specified) on a Bruker Avance 400 with TMS as an internal reference.

Liquid chromatography electrospray ionisation mass spectrometry was conducted on 1 mg ml^{-1} methanol solutions using a Waters Ltd. TQD mass spectrometer.

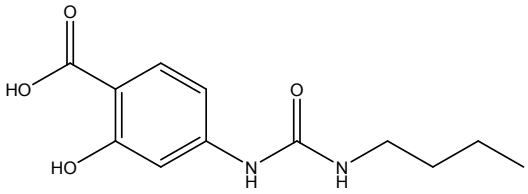
Oscillatory stress sweep experiments were performed between 0.1 – 1000 Pa at a constant frequency of 1 Hz on a TA instruments AR 2000 rheometer equipped with a rough plate geometry. When preparing the sample, 2 ml of hot gelator solution was transferred to a sealed glass cylinder on the lower plate. The gels were allowed 30 minutes to equilibrate before the geometry was lowered onto the sample at a pre-determined gap of 2.5 mm, and the glass cylinder gently removed before running the experiment.

Single crystal data was collected at 120.0(2) K on a Bruker D8Venture diffractometer (PHOTON-100 CMOS detector, IμSmicrosource, focusing mirrors, MoKα, λ = 0.71073Å) and processed using Bruker APEX-II software. The temperature of the samples was maintained by the Cryostream (Oxford Cryosystems) open-flow nitrogen cryostat. The structure was solved by direct method and refined by full-matrix least squares on F2 for all data using Xseed and SHELXTL software. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in the calculated positions.

SEM samples were dried in vacuo for two days, and coated with 2 nm of platinum of chromium using a Cressington 328 Ultra High Resolution EM Coating System. Imaging was

performed using an FEI Helios NanoLab DualBeam microscope in immersion mode with beam settings of 1.5 kV and 86 pA..

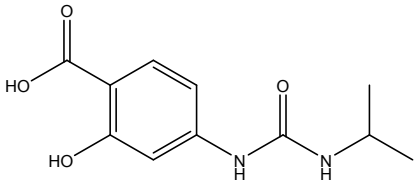
Compound 1a



4-Aminosalycylic acid (4-ASA, 0.50 g, 3.26 mmol) was suspended in a mixture of $CHCl_3$: ethanol (30mL:1.5mL) and heated to 60 °C. Triethyl amine (0.5mL) was added whereupon the suspension dissolved. n-Butyl Isocyanate (0.37mL, 3.26 mmol) was added and the mixture brought to reflux and left stirring at 60°C for 24 hours. The solution was cooled and extracted with water (2x30mL). The aqueous layer was then acidified with 1M HCl which formed a white precipitate. The precipitate was filtered and washed with hexane and diethyl ether. The powder was then dried to yield the target compound as a white powder (0.43g, 1.70 mmol, 52%): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.88 (t, *J* = 7.2 Hz, 3H), 1.23 – 1.45 (m, 4H), 3.07 (m, 2H), 6.32 (s, 1H), 6.79 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.16 (d, *J* = 2.0 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 8.86 (s, 1H), 11.34 (s, 1H), 13.37 (s, 1H).^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 14.1, 20.0, 32.2, 39.1, 104.1, 105.7, 109.3, 131.4, 147.8, 155.1, 162.9, 172.2. m/z (ES$^+$-MS): 253.1 ([M]$^+$, 100%), 254.3 ([M+H]$^+$, 5%), 275.0 ([M+Na]$^+$, 20%), 505.2 ([2M]$^+$, 30%), 527.0 ([2M+Na]$^+$, 25%). Anal. calc'd for $C_{12}H_{16}N_2O_4$: C, 57.13; H, 6.39; N, 11.1. Found: C, 56.26; H, 6.37; N, 10.93%. Samples were found to retain small amounts of chloroform very tenaciously as evidenced by ^{1}H NMR spectroscopy. Recalc. for $C_{12}H_{16}N_2O_4 \cdot 0.04CHCl_3$: C, 56.15; H, 6.28; N, 10.88 %.

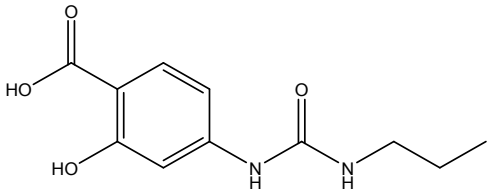
Recrystallization from ethyl acetate yielded single crystals of **1a**. Crystal Data: $C_{24}H_{32}N_4O_8$, *M* = 504.54, 0.18 × 0.11 × 0.06 mm^3, monoclinic, space group $P2_1$ (No. 4), *a* = 5.1412(4), *b* = 26.4969(19), *c* = 9.2776(7) Å, β = 105.207(2)°, *V* = 1219.59(16) Å^3, *Z* = 2, D_c = 1.374 g/cm^3, F_{000} = 536, MoKα radiation, λ = 0.71073 Å, *T* = 0(2)K, $2\theta_{max}$ = 53.3º, 16141 reflections collected, 5107 unique (R_{int} = 0.0477). Final *GooF* = 1.026, *R1* = 0.0431, *wR2* = 0.0961, *R* indices based on 4133 reflections with I >2σ(I) (refinement on F^2), 327 parameters, 1 restraint. Lp and absorption corrections applied, μ = 0.104 mm^{-1}. Absolute structure parameter = 0.5(9).

Compound 1b



4-ASA (0.50 g, 3.26 mmol) was suspended in a mixture of $CHCl_3$: ethanol (30mL:1.5mL) and heated. Triethyl amine (0.5mL) was added whereupon the suspension dissolved. Isopropyl Isocyanate (0.37mL, 3.26 mmol) was added and the mixture brought to reflux and left stirring at 60°C for 24 hours. The solution was cooled and extracted with water (2x30mL). The aqueous layer was then acidified with 1M HCl which formed a white precipitate. The precipitate was filtered and washed with hexane. The powder was then dried to yield the target compound as a white powder(0.43g, 1.81mmol, 56%): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.09 (d, *J* = 6.6 Hz, 6H), 3.73 (pseudo-hept, *J* = 6.6 Hz, 1H), 6.20 (d, *J* = 7.5 Hz, 1H), 6.78 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.14 (d, *J* = 2.1 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 8.72 (s, 1H), 11.34 (s, 1H), 13.43 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO) δ: 23.3(2C, -CH_3), 41.5, 104.0, 105.7, 109.2, 131.4, 147.7, 154.3, 162.9, 172.2. m/z (ES$^+$-MS): 238.8 ([M]$^+$, 100%), 239.2 ([M+H]$^+$, 10%), 261.1 ([M+Na]$^+$, 46%), 476.4 ([2M]$^+$, 25%), 476.9 ([2M+H]$^+$, 3%), 498.9 ([2M+Na]$^+$, 44%), 500.1 ([2M+H+Na]$^+$, 4%). Anal. calc'd for $C_{11}H_{14}N_2O_4$: C, 55.46; H, 5.92; N, 11.76. Found: C, 54.67; H, 5.89; N, 11.49%. Samples were found to retain small amounts of chloroform very tenaciously as evidenced by ^{1}H NMR spectroscopy. Recalc. for $C_{11}H_{14}N_2O_4 \cdot 0.04CHCl_3$: C, 54.45; H, 5.81; N, 11.50 %.

Compound 1c

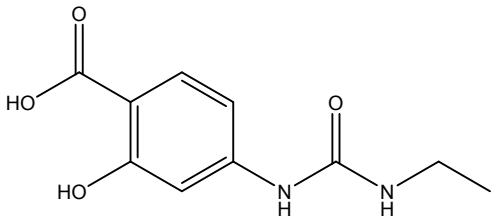


4-ASA (0.50 g, 3.26 mmol) was suspended in a mixture of $CHCl_3$: ethanol (30mL:1.5mL) and heated. Triethyl amine (0.5mL) was added whereupon the suspension dissolved. Propyl isocyanate (0.31mL, 3.26 mmol) was added and the mixture brought to reflux and left stirring at 60°C for 24 hours. The solution was cooled and extracted with water (2x30mL). The aqueous layer was then acidified with 1M HCl which formed a white precipitate. The precipitate was filtered and washed with hexane and diethyl ether. The powder was then dried to yield the target compound as a white powder (0.38 g, 1.59 mmol, 48%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.86 (t, *J* = 7.4 Hz, 3H), 1.43 (tq, *J* = 7.3, 7.1 Hz 2H), 3.04 (td, *J* = 7.1, 5.7 Hz, 2H), 6.31 (t, *J* = 5.6 Hz, 1H), 6.80 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.16 (d, *J* = 2.1 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 8.82 (s, 1H), 11.34 (s, 1H), 13.43 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO) δ

11.8, 23.5, 41.4, 112.8, 117.5, 119.3, 127.0, 132.8, 155.9, 156.2, 172.3. m/z (ES^+-MS): 101.7 ($[Et_3N]^+$, 40%), 102.2 ($[Et_3N+H]^+$, 36%), 239.1 ($[M]^+$, 30%), 261.1 ($[M+Na]^+$, 73%), 477.1 ($[2M]^+$, 14%), 499.1 ($[2M+Na]^+$, 100%). Anal. calc'd for $C_{11}H_{14}N_2O_4$: C, 55.46; H, 5.92; N, 11.76. Found: C, 54.65; H, 5.84; N, 11.50%. Samples were found to retain small amounts of chloroform very tenaciously as evidenced by ^{1}H NMR spectroscopy. Recalc. for $C_{11}H_{14}N_2O_4 \cdot 0.04CHCl_3$: C, 54.45; H, 5.81; N, 11.50 %.

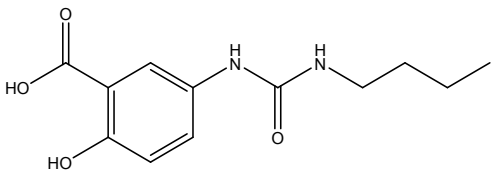
Recrystallization from acetone yielded single crystals of **1c**. Crystal Data: $C_{11}H_{14}N_2O_4$, M = 238.24, triclinic, space group P-1 (No. 2), a = 4.6214(8), b = 8.2787(14), c = 14.248(2) Å, α = 92.962(5), β = 94.351(5), γ = 95.330(5)°, V = 540.23(16) Å^3, Z = 2, D_c = 1.465 g/cm^3, F_{000} = 252, MoKα radiation, λ = 0.71073 Å, T = 0(2)K, $2\theta_{max}$ = 45.3º, 4645 reflections collected, 1418 unique (R_{int} = 0.0543). Final *GooF* = 1.019, *R1* = 0.0473, *wR2* = 0.0978, *R* indices based on 956 reflections with I >2σ(I) (refinement on F^2), 155 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.113 mm^{-1}.

Compound 1d



4-ASA (0.50 g, 3.26 mmol) was suspended in a mixture of $CHCl_3$: ethanol (30mL:1.5mL) and heated. Triethyl amine (0.5mL) was added whereupon the suspension dissolved. Ethyl Isocyanate (0.258mL, 3.26 mmol) was added and the mixture brought to reflux and left stirring at 60°C for 24 hours. The solution was cooled and extracted with water (2x30mL). The aqueous layer was then acidified with 1M HCl which formed a white precipitate. The precipitate was filtered and washed with hexane. The powder was then dried to yield the target compound as a white powder (0.36g, 1.61 mmol, 49%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.04 (t, J = 7.2 Hz, 3H), 3.10 (qd, J = 7.2, 5.4 Hz, 2H), 6.26 (t, J = 5.5 Hz, 1H), 6.80 (dd, J = 8.8, 2.1 Hz, 1H), 7.16 (d, J = 2.0 Hz, 1H), 7.61 (d, J = 8.7 Hz, 1H), 8.82 (s, 1H), 11.34 (s, 1H), 13.43 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 15.8, 34.4, 104.1, 105.8, 109.3, 131.4, 147.8, 155.0, 162.9, 172.2. m/z (ES^+-MS): 101.8 ($[Et_3N]^+$, 32%), 225.5 ($[M]^+$, 100%), 226.2 ($[M+H]^+$, 10%), 246.7 ($[M+Na]^+$, 75%), 247.3 ($[M+H+Na]^+$, 3%), 449.1 ($[2M]^+$, 25%), 470.7 ($[2M+Na]^+$, 73%). Anal. calc'd for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.39; N, 12.46. Found: C, 53.09; H, 5.33; N, 12.36%.

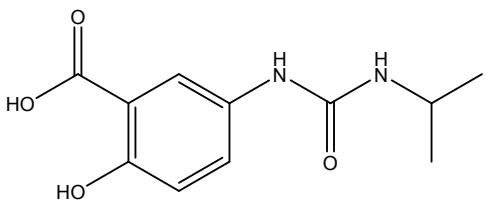
Compound 2a



5-Aminosalycylic acid (5-ASA, 0.50 g, 3.26 mmol) was suspended in a mixture of chloroform: ethanol (30mL:1.5mL) and heated to 60 °C. Triethylamine (1mL) was added whereupon the suspension dissolved. n-Butyl Isocyanate (0.37mL, 3.26 mmol) was added and the mixture brought to reflux and left stirring at 60°C for 24 hours. The solution was cooled and extracted with water (2x30mL). The aqueous layer was then acidified with 1M HCl which formed a white precipitate. The precipitate was filtered and washed with hexane and diethyl ether. The powder was then dried to yield the target compound as a light brown powder (0.69g, 2.74 mmol, 83%): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.88 (t, *J* = 7.3 Hz, 3H), 1.23 – 1.45 (m, 4H), 3.05 (q, *J* = 6.6 Hz, 2H), 6.03 (t, *J* = 5.7 Hz, 1H), 6.83 (d, *J* = 8.9 Hz, 1H), 7.43 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.89 (d, *J* = 2.8 Hz, 1H), 8.32 (s, 1H), 10.84 (s, 1H), 13.84 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 13.7, 19.5, 32.0, 38.8, 112.3, 117.0, 118.8, 126.5, 132.4 (obscured by residual solvent peak), 155.5, 155.7, 171.9. m/z (ES$^+$-MS): 252.8 ([M]$^+$, 90%), 253.4 ([M+H]$^+$, 100%), 505.1 ([2M]$^+$, 50%), 506.0 ([2M+2H]$^+$, 20%). Anal. calc'd for $C_{12}H_{16}N_2O_4$·0.057$CHCl_3$: C, 55.90; H, 6.25; N, 10.81. Found: C, 55.90; H, 6.36; N, 10.87%. Samples were found to retain small amounts of chloroform very tenaciously as evidenced by ^{1}H NMR spectroscopy.

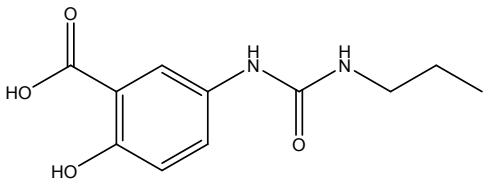
Recrystallization from methanol yielded single crystals of **2a**. Crystal Data: $C_{12}H_{16}N_2O_4$, *M* = 252.27, triclinic, space group *P*-1 (No. 2), *a* = 4.5290(11), *b* = 9.009(3), *c* = 15.234(4) Å, α = 101.869(9), β = 93.598(9), γ = 101.742(9)°, *V* = 592.0(3) Å^3, *Z* = 2, D_c = 1.415 g/cm^3, F_{000} = 268, MoKα radiation, λ = 0.71073 Å, *T* = 0(2)K, 2θ_{max} = 42.0º, 3421 reflections collected, 1125 unique (R_{int} = 0.1033). Final *GooF* = 1.050, *R1* = 0.0689, *wR2* = 0.1555, *R* indices based on 717 reflections with I >2σ(I) (refinement on F^2), 164 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.107 mm^{-1}.

Compound 2b



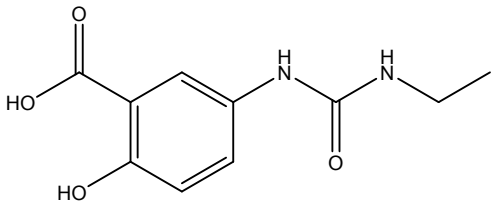
5-Aminosalicylic acid (0.50 g, 3.26 mmol) was suspended in a mixture of $CHCl_3$: EtOH (30mL : 1.5mL) and heated until a solution was obtained. Isopropyl Isocyanate (0.37mL, 3.26 mmol) was added and the reaction was brought to reflux and left stirring at 60°C for 24 hours. The solution was cooled and extracted with water (2x30mL). The aqueous layer was then acidified with 1M HCl which formed a white precipitate. The precipitate was filtered and washed with hexane. The powder was then dried to yield the target compound as a light brown powder (0.58g, 2.44 mmol, 74%): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.07 (d, *J* = 6.2 Hz, 6H), 3.72 (p, *J* = 6.3 Hz, 1H), 5.97 (s, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 2.1 Hz, 1H), 8.33 (s, 1H), 10.83 (s, 1H), 13.87 (s, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO) δ: 23.5, 41.4, 112.7, 117.5, 119.1, 126.8, 132.8, 155.2, 156.1, 172.3. m/z (ES$^+$-MS): 238.7 ([M]$^+$, 100%), 239.1 ([M+H]$^+$, 10%), 260.8 ([M+Na]$^+$, 15%), 261.3 ([M+H+Na]$^+$, 11%), 476.6 ([2M]$^+$, 20%). Anal. calc'd for $C_{11}H_{14}N_2O_4$·0.09$CHCl_3$: C, 53.50; H, 5.70; N, 11.25. Found: C, 53.56; H, 5.76; N, 11.25%. Samples were found to retain small amounts of chloroform very tenaciously as evidenced by ^{1}H NMR spectroscopy.

Compound 2c



5-ASA (0.50 g, 3.26 mmol) was suspended in a mixture of $CHCl_3$: ethanol (30mL:1.5mL) and heated. Triethyl amine (1mL) was added whereupon the suspension dissolved. Propyl isocyanate (0.31mL, 3.26 mmol) was added and the mixture brought to reflux and left stirring at 60°C for 24 hours. The solution was cooled and extracted with water (2x30mL). The aqueous layer was then acidified with 1M HCl which formed a white precipitate. The precipitate was filtered and washed with hexane. The precipitate was then dried to yield the target compound as a light brown powder (0.56g, 2.35 mmol, 72%): ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.85 (t, *J* = 7.4 Hz, 3H), 1.41 (tq, *J* = 7.4, 6.5 Hz, 2H), 3.01 (q, *J* = 6.5 Hz, 2H), 6.02 – 6.10 (m, 1H), 6.83 (d, *J* = 8.9 Hz, 1H), 7.44 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.89 (d, *J* = 2.7 Hz, 1H), 8.33 (s, 1H), 10.85 (s, 1H), 13.85 (s, 1H).^{13}C{^{1}H} NMR (101 MHz, DMSO) δ 11.8, 23.5, 41.4, 112.8, 117.5, 119.3, 127.0, 132.8, 155.9, 156.2, 172.3. m/z (ES$^+$-MS): 101.8 ([Et_3N]$^+$, 65%), 102.1 ([Et_3N+H]$^+$, 5%), 238.7 ([M]$^+$, 90%), 239.6 ([M+H]$^+$, 10%), 261.1 ([M+Na]$^+$, 70%), 476.7 ([2M]$^+$, 100%), 477.6 ([2M+H]$^+$, 6%), 499.4 ([2M+Na]$^+$, 45%). Anal. calc'd for $C_{11}H_{14}N_2O_4$: C, 55.46; H, 5.92; N, 11.76. Found: C, 55.14; H, 5.89; N, 11.64%.

Compound 2d



5-ASA (0.50 g, 3.26 mmol) was suspended in a mixture of $CHCl_3$: ethanol (30mL:1.5mL) and heated. Triethyl amine (1.5mL) was added whereupon the suspension dissolved. Ethyl Isocyanate (0.258mL, 3.26 mmol) was added and the mixture brought to reflux and left stirring at 60°C for 24 hours. The solution was cooled and extracted with water (2x30mL). The aqueous layer was then acidified with 1M HCl which formed a white precipitate. The precipitate was filtered and washed with hexane. The powder was then dried to yield the target compound as a light brown powder (0.49 g, 2.16 mmol, 66%): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.03 (t, *J* = 7.1 Hz, 3H), 3.08 (qd, *J* = 7.1, 5.1 Hz, 2H), 5.97 – 6.05 (m, 1H), 6.83 (d, *J* = 8.9 Hz, 1H), 7.44 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.89 (d, *J* = 2.8 Hz, 1H), 8.33 (s, 1H), 10.84 (s, 1H), 13.83 (s, 1H).^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 16.0, 34.5, 112.8, 117.4, 119.4, 127.0, 132.8, 155.8, 156.2, 172.3. m/z (ES$^+$-MS): 102.1 ([Et_3N+H]$^+$, 59%), 224.5 ([M]$^+$, 94%), 225.7 ([M+H]$^+$, 70%), 448.7 ([2M]$^+$, 100%), 449.5 ([2M+H]$^+$, 42%), 471.0 ([2M+Na]$^+$, 50%). Anal. calc'd for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.39; N, 12.46. Found: C, 53.38; H, 5.38; N, 12.48%.

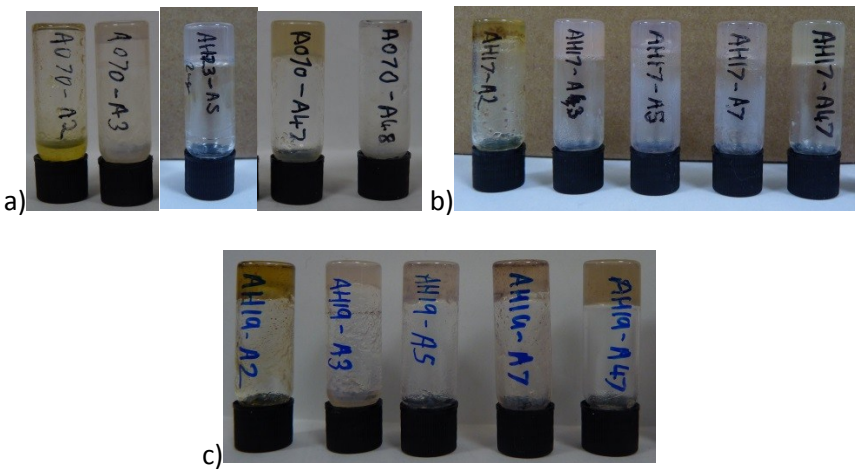


Figure S1 1 % w/v gels and sols of a) **2a** b) **2c** and c) **2d** in various solvents: A2 – 1,2,4-trichlorobenzene, A3 – 1,2-dibromoethane, A5 – 1,2-dichlorobenzene, A7 – 1,3-dichlorobezene, A47 – Nitrobenzene and A48 – Nitromethane.

Figure S2 SEM image of a xerogel of **1a** obtained from nitromethane showing a mixture of fibres and solid crystalline particles.

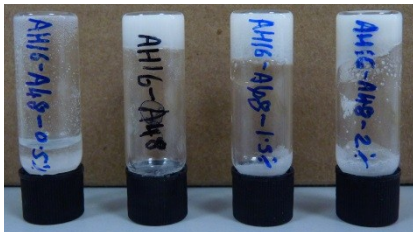


Figure S3 Gels and partial gels of **1a** in nitromethane 0.5, 1, 1.5 and 2 wt. %

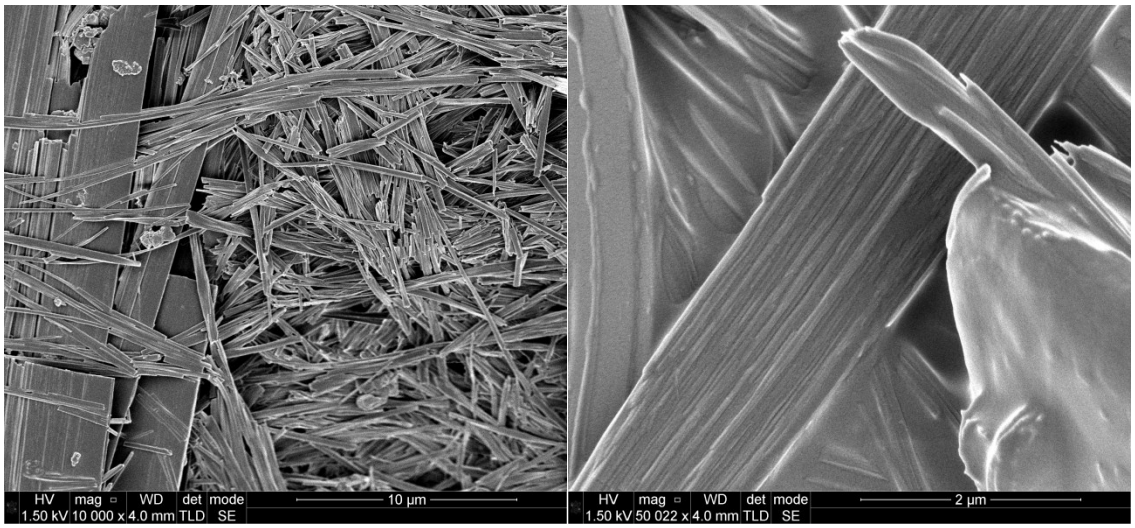
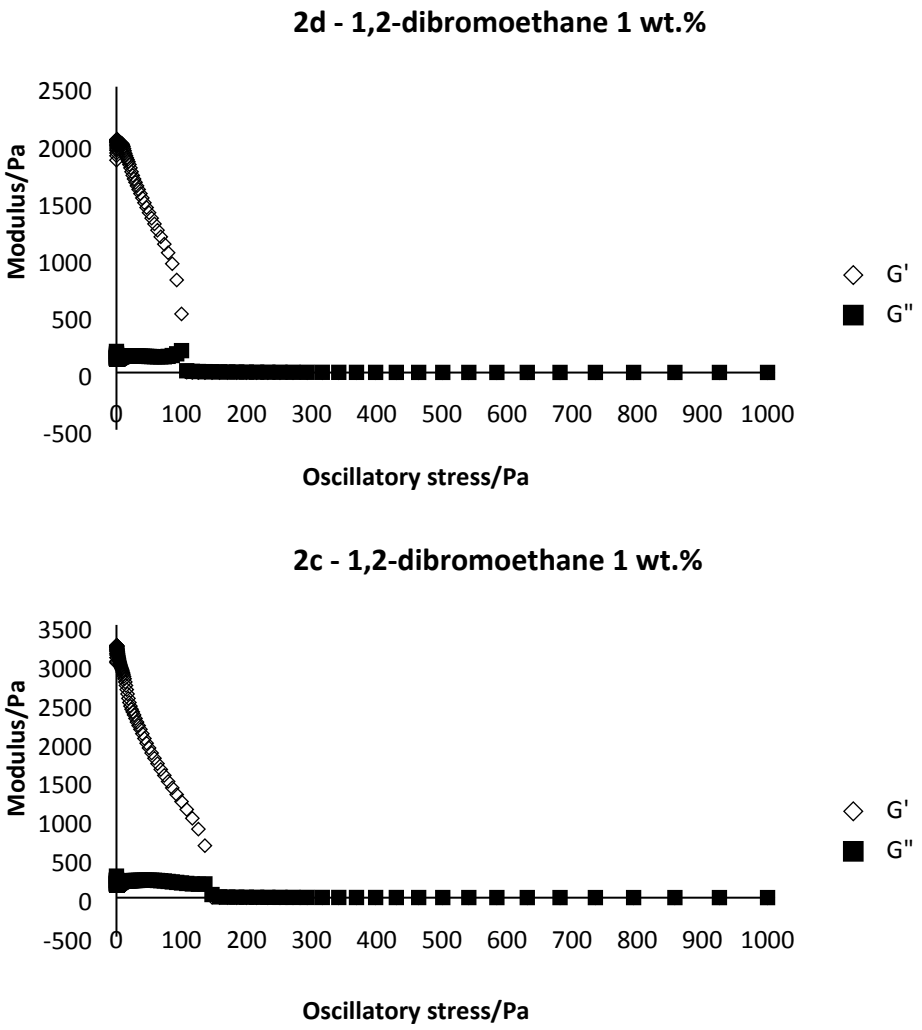


Figure S4 SEM images of gels of **1a** in nitromethane at various magnifications.



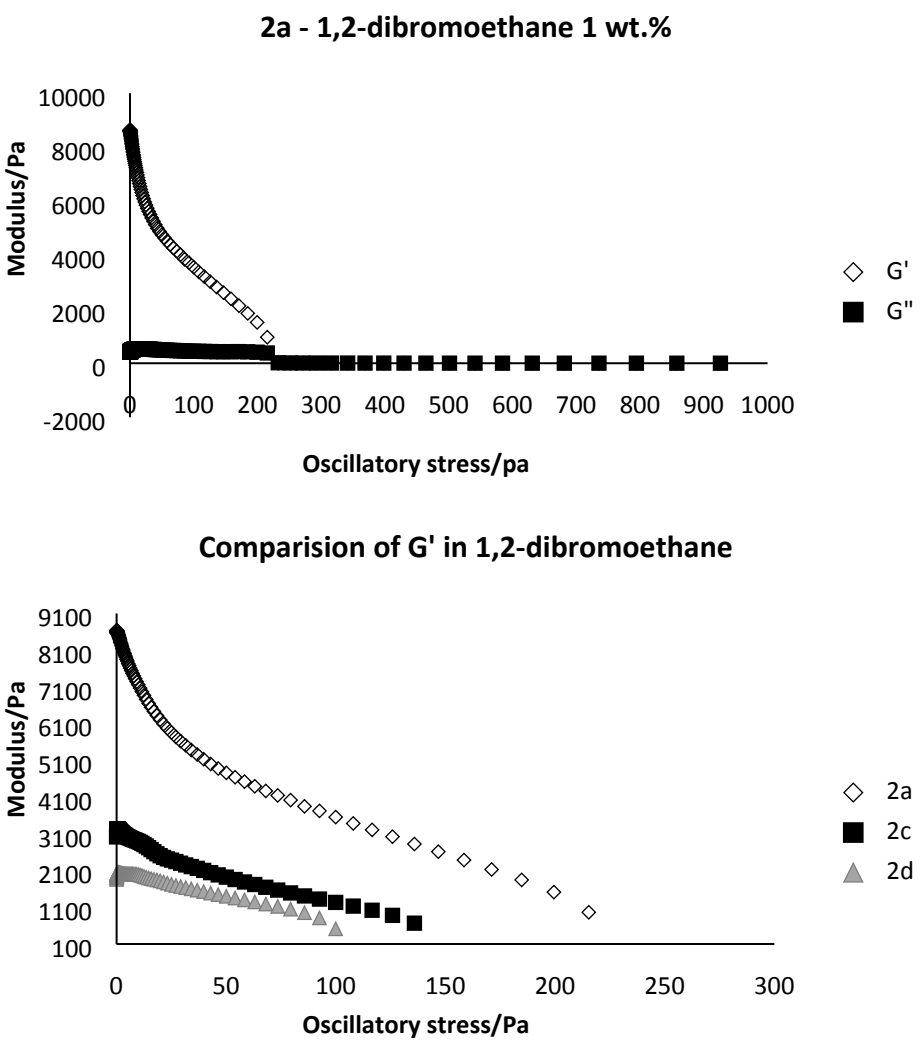


Figure S5 Stress sweep rheology for 1 wt. % gels in 1,2-dibromoethane.

Table S1 Solubility and Gelation Experiments

Red	Insoluble
Orange	Partially soluble
Green	Soluble
G	gel
WG	weak gel
PG	partial gel
Ppt	precipitate
Colap	gel collapsed over time
Xtal	Crystal formed

5-ASA and derivatives

Compound	**Solvents**	**2a**	**2c**	**2d**	**2b**		**5-ASA**
A2	1,2,4-trichlorobenzene	WG	G	PG Colap	WG		
A3	1,2-dibromoethane	PG	G	G	WG		
A4	2-Butanone			Ppt			
A5	1,2-dichlorobenzene	G	G	G			
A7	1,3-dichlorobenzene		G	G Colap			
A9	1,4-dioxane			Ppt			
A10	1-butanol						
A11	1-pentanol						
A12	1-propanol						
A13	2-butanol						

A14	2-Ethyl pyridine			Ppt			
A15	2-Picoline			Ppt			
A16	2-propanol						
A17	3-chloro-1-propanol						
A18	3-Picoline						
A19	4-Ethyl pyridine						
A20	4-Picoline						
A21	Acetic acid						
A22	Acetone						
A23	Acetonitrile			Ppt			
A25	Benzyl alcohol						
A26	Chlorobenzene	G Xtal					
A27	Chloroform						
A28	Cyclohexane						
A29	Cyclohexanone						
A31	Dichloromethane						
A33	Diethyl ether						
A34	Diethylene glycol						
A35	Diisopropyl ether						
A36	Dimethylacetamide						
A37	DMF						
A38	DMSO						
A39	Ethanol						
A40	Ethyl acetate		Xtal	Ppt			
A41	Ethylene glycol						

A42	Ethylene glycol butyl ether						
A43	Hexane						
A44	Mesitylene						
A45	Methanol						
A47	Nitrobenzene	G	G	PG			
A48	Nitromethane	PG	G opaque	G			
A49	o-xylene						
A50	p-xylene						
A51	Pyridine						
A52	THF						
A53	Toluene						
A54	Triethylene glycol						
A55	Water			G			

4-ASA and derivatives

Compound	**Solvents**	**1a**	**1c**	**1d**	**1b**		**4-ASA**
A2	1,2,4-trichlorobenzene			PG Colap			
A3	1,2-dibromoethane						
A4	2-Butanone						
A5	1,2-dichlorobenzene						
A7	1,3-dichlorobenzene						
A9	1,4-dioxane						
A10	1-butanol						
A11	1-pentanol						

A12	1-propanol						
A13	2-butanol						
A14	2-Ethyl pyridine						
A15	2-Picoline						
A16	2-propanol						
A17	3-chloro-1-propanol						
A18	3-Picoline						
A19	4-Ethyl pyridine						
A20	4-Picoline						
A21	Acetic acid						
A22	Acetone						
A23	Acetonitrile						
A25	Benzyl alcohol						
A26	Chlorobenzene						
A27	Chloroform						
A28	Cyclohexane						
A29	Cyclohexanone						
A31	Dichloromethane						
A33	Diethyl ether						
A34	Diethylene glycol						
A35	Diisopropyl ether						
A36	Dimethylacetamide						
A37	DMF						
A38	DMSO						
A39	Ethanol						
A40	Ethyl acetate						

A41	Ethylene glycol						
A42	Ethylene glycol butyl ether						
A43	Hexane						
A44	Mesitylene			G xtal			
A45	Methanol						
A47	Nitrobenzene	G					
A48	Nitromethane	G Xtal					
A49	o-xylene						
A50	p-xylene						
A51	Pyridine						
A52	THF						
A53	Toluene						
A54	Triethylene glycol						
A55	Water			PG			

DFT Calculations

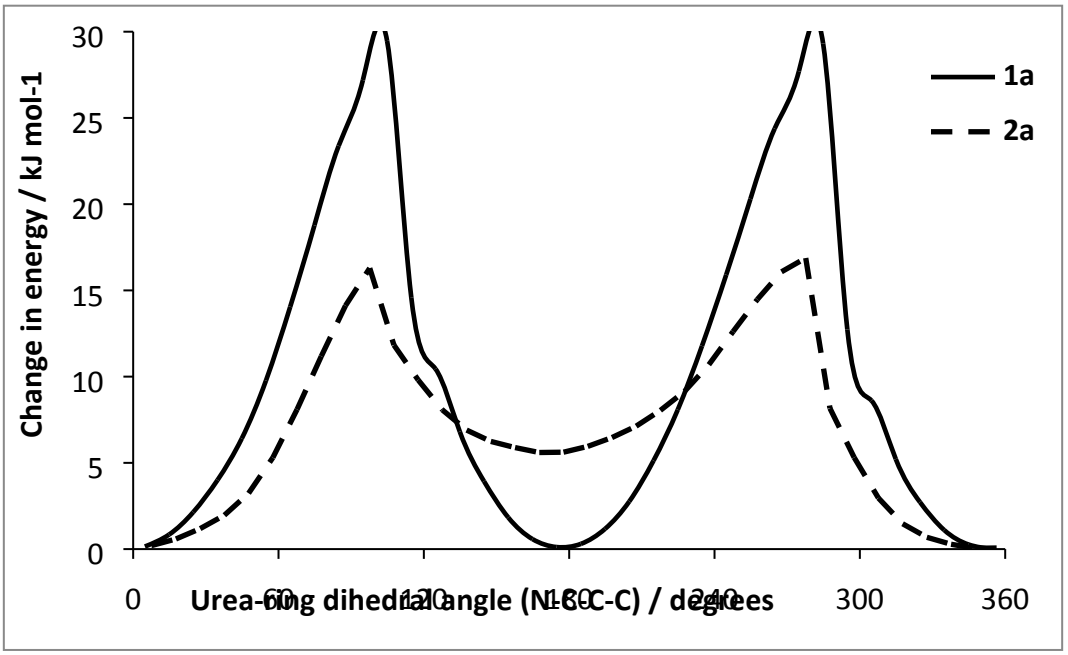


Figure S6 DFT calculated change in energy relative to ground state energy with rotation of urea groups relative to the aryl ring, for 4-ASA derivative **1a** and 5-ASA derivative **2a**.

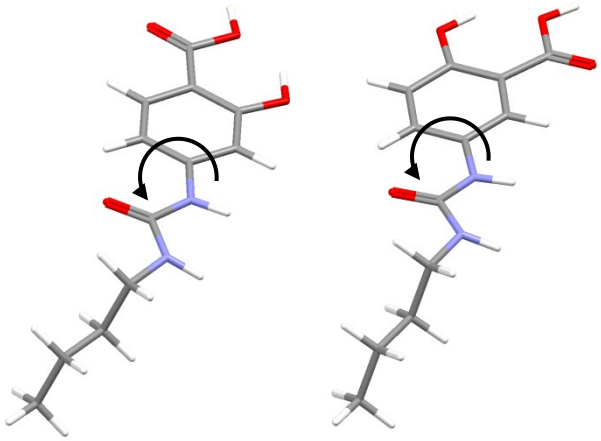


Figure S7 Optimised conformations of **1a** (left) and **2a** (right). The geometries shown exhibit urea-ring dihedral angles of 354.8 and 347.7 degrees respectively. Energy profiles were calculated by rotating urea groups anticlockwise from their starting geometries, as shown.

Conformations for the comparative modelling of **1a** and **2a** were obtained by molecular mechanics in Scigress, followed by an unconstrained optimisation in Gaussian 09, via the B3LYP method with a cc-PVTZ basis set. After the initial optimisation, the torsion angle of the urea group with the ring was constrained at a range of values from 0 to 360 degrees with 10-degree increments, and the molecular geometry optimisation repeated after each step. Whilst the plots should be symmetrical about 180 and 360 degrees in accordance with the mirror symmetry of the compounds, slight asymmetry was observed in practice

due to incomplete equilibration, predominantly in the butyl end groups. Energy profiles were analysed using Gauss view 4.1.2.

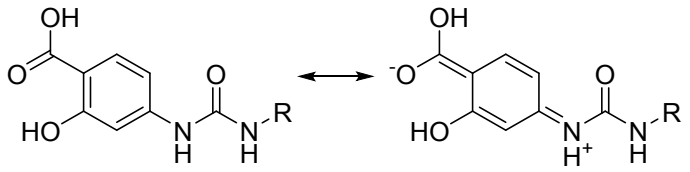


Figure S8 Resonance forms of 4-ASA derivatives showing the tendency towards partial double bond formation at the urea nitrogen atom and hence increased tendency towards a planar geometry that disfavours gelation because of steric hindrance of the urea carbonyl acceptor.