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Organophosphorus chemical warfare agent simulant DMMP promotes structural reinforcement of urea-based chiral supramolecular gels

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SUPPLEMENTARY INFORMATION

Table of contents

1. Materials and apparatus

^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra were collected on a Bruker AV300 spectrometer. Chemical shifts values (δ) are reported in parts per million (ppm) relative to residual dimethyl sulfoxide (δ 2.50 ppm for ^{1}H, δ 39.51 ppm for ^{13}C). All spectra were reprocessed using ACD/Labs software version: 12.1. Coupling constants (*J*) were recorded in Hz. The following abbreviations for the multiplicity of the peaks are s (singlet), d (doublet), t (triplet), m (multiplet), br s (broad signal). Infrared (IR) spectra were recorded on a Thermo Scientific Nicolet 380 FT-IR (Smart Orbit ATR) and reported in wavenumbers (cm^{-1}). Low-resolution mass spectra were recorded on a Micromass Platform II Single Quadrupole mass spectrometer. High-resolution mass spectra were recorded on a VG 70-250-SE normal geometry double focusing mass spectrometer. Melting points were obtained in open capillaries on a Gallenkamp melting point apparatus and are uncorrected. Isocyanates have been purchased from TCI UK Ltd. Amines were purchased from Sigma-Aldrich. All solvents and reagents were used as supplied.

For the synthesis of gelator **1**: **1,1'-(hexane-1,6-diyl)bis(3-((*R*)-1-(naphthalen-1-yl)ethyl)urea)**. A solution of (*R*)-(–)-1-(1-naphthyl)ethyl isocyanate (0.29 mL, 1.67 mmol) and hexane-1,6-diamine (0.10 g, 0.84 mmol) in CH_2Cl_2 was stirred at room temperature in a sealed vial for 24 h. A white precipitate was collected after filtration. Purification by trituration in EtOAc was necessary. Yield: 0.55 g, 1.09 mmol, 87%; mp: 193 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.21 (4H, br s, NH-CH_2-CH_2-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.32 (4H, br s, NH-CH_2-C**H**$_2$-CH_2- CH_2-C**H**$_2$-CH_2-NH), 1.45 (6H, d, *J* = 6.6 Hz, C**H**$_3$), 2.94-3.00 (4H, m, NH-C**H**$_2$-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 5.52–5.57 (2H, m, C**H**), 5.77 (2H, t, *J* = 5.5 Hz, N**H**-CH_2), 6.39 (2H, d, *J* = 8.1 Hz, N**H**-CH), 7.45–7.57 (8H, m, Ar**H**), 7.79–7.82 (2H, m, Ar**H**), 7.91–7.94 (2H, m, Ar**H**), 8.11–8.14 (2H, m, Ar**H**) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 26.3 (CH_2), 28.7 (CH_2), 30.0 (CH_2), 44.5 (CH_3), 121.9 (CH), 123.3 (ArCH), 125.4 (ArCH), 125.5 (ArCH), 125.9 (ArCH), 126.0 (ArCH), 127.0 (ArCH), 128.5 (ArCH), 130.3 (ArC), 133.4 (ArC), 141.3 (ArC), 157.2 (CO) ppm; FT-IR: ν_{max} (neat)= 3332 (urea NH stretching), 1616 (urea CO stretching) cm^{-1}; LRMS (ES$^+$) *m/z* 533 Da [M+Na]$^+$; HRMS (ES$^+$) for $C_{32}H_{38}N_4O_2$ *m/z* act: 533.2878 Da [M+Na]$^+$, cal: 533.2887 Da [M+Na]$^+$.

For the synthesis of gelator **2**: **1,1'-(nonane-1,9-diyl)bis(3-((*R*)-1-(naphthalen-1-yl)ethyl)urea)**. A solution of (*R*)-(–)-1-(1-naphthyl)ethyl isocyanate (0.29 mL, 1.67 mmol) and nonane-1,9-diamine (0.13 g, 0.82 mmol) in CH_2Cl_2 was stirred at room temperature in a sealed vial for 24 h. A white precipitate was collected after filtration. Purification by trituration in EtOAc was necessary. Yield: 0.69 g, 1.05 mmol, 84%; mp: 212 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.21 (10H, br s, NH-CH_2-CH_2-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.33 (4H, br s, NH-CH_2-C**H**$_2$-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 1.45 (6H, d, *J* = 6.6 Hz, C**H**$_3$), 2.94–3.00 (4H, m, NH-C**H**$_2$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 5.52–5.57 (2H, m, C**H**), 5.77 (2H, t, *J* = 5.6 Hz, N**H**-CH_2), 6.39 (2H, d, *J* = 8.1 Hz, N**H**-CH), 7.45–7.57 (8H, m, Ar**H**), 7.79–7.82 (2H, m, Ar**H**), 7.91–7.94 (2H, m, Ar**H**), 8.12–8.14 (2H, m, Ar**H**) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 22.4 (CH_2), 26.1 (CH_2), 30.0 (CH_2), 44.6 (CH_3), 121.9 (CH), 123.3 (ArCH), 125.4 (ArCH), 125.5 (ArCH), 126.0 (ArCH), 127.0 (ArCH), 128.5 (ArCH), 130.3 (ArC), 133.4 (ArC), 141.3 (ArC), 157.2 (CO) ppm. Two missing CH_2 signals and one missing ArCH signal due to peak overlapping; FT-IR: ν_{max} (neat)= 3320 (urea NH stretching), 1620 (urea CO stretching) cm^{-1}; HRMS (ES$^+$) for $C_{35}H_{44}N_4O_2$ *m/z* act: 575.3346 Da [M+Na]$^+$, cal: 575.3356 Da [M+Na]$^+$.

For the synthesis of gelator **3**: **1,1'-(((2-3-((*R*)-1-(naphtylen-2-yl)ethyl)ureido)ethyl)azanediyl)bis(ethane-2,1-diyl))bis(3-((*R*)-1-(naphthalen-1-yl)ethyl)urea)**. A solution of (*R*)-(–)-1-(1-naphthyl)ethyl isocyanate (0.29 mL, 1.67 mmol) and tris(2-aminoethyl)amine (0.08 g, 0.56 mmol) in CH_2Cl_2 was stirred at room temperature in a sealed vial for 24 h. A white precipitate was collected after filtration. Purification by trituration in EtOAc was necessary. Yield: 0.90 g, 1.22 mmol, 80%; m.p.: 203 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.42 (9H, d, *J* = 7.0 Hz, C**H**$_3$), 2.44 (6H, t, *J* = 6.2 Hz, NC**H**$_2$$CH_2$NH), 3.04 (6H, br s, NCH_2C**H**$_2$NH), 5.51–5.58 (3H, m, C**H**), 5.86 (3H, t, *J* = 5.5 Hz, N**H**CH_2), 6.53 (3H, d, *J* = 8.1 Hz, N**H**CH), 7.40–7.55 (12H, m, Ar**H**), 7.76–7.78 (3H, m, Ar**H**), 7.90–7.93 (3H, m, Ar**H**), 8.09–8.12 (3H, m, Ar**H**) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 22.3 (CH_2), 44.6 (CH_3), 54.3 (CH_2), 121.9 (CH), 123.2 (ArCH), 125.4 (ArCH), 125.5 (ArCH), 126.0 (ArCH), 127.0 (ArCH), 128.5 (ArCH), 130.3 (ArC), 133.4 (ArC), 141.2 (ArC), 157.3 (CO) ppm. One missing ArCH signal due to peak overlapping; FT-IR: ν_{max} (neat)= 3317 (urea NH stretching), 1616 (urea CO stretching) cm^{-1}; LRMS (ES$^+$) *m/z* 760 Da [M+Na]$^+$; HRMS (ES$^+$) for $C_{45}H_{51}N_7O_3$ *m/z* act: 760.3933 Da [M+Na]$^+$, cal: 760.3946 Da [M+Na]$^+$.

2. Gel formation and perturbation tests

Gel formation procedure

20, 15, 10, 5 mg of gelators **1**–**3** were measured in 3 mL vials. 1 mL of every solvent listed in tables S1-S3 was added. The samples were heated with a heat gun until a homogeneous and clear solution was formed. The samples, then, were allowed to stand at room temperature in order for gelation to occur. Gel formation was confirmed by an inversion test.

Perturbations tests procedure

Solutions of the appropriate amine in tetralin were prepared. Solutions of both (*R*)-(–)-1-(1-naphthyl)ethyl isocyanate and (±)-1-(1-naphthyl)ethyl isocyanate in tetralin were prepared. Aliquots (0.5 mL) of these solutions at appropriate concentrations have been mixed to produce gels **1**–**6**. Since it did not appear to make any differences if the amine was added before than the isocyanate or vice-versa both orders were tried as a double check of the validity of the results. DMMP was added in various volumes (1.0 μL, 2.5 μL, 5.0 μL, 0.01 mL, 0.025 mL, 0.05 mL, 0.1 mL) in either one of the reagent solutions before the addition of the second one. The samples were allowed to stand and inverted at 30 sec intervals until a gel has formed. Time = 0 was recorded as the time at which the amine and isocyanate solutions were mixed together and all experiments were halted after 10 min. A gel was deemed to have fully formed when, upon inversion, no solution remained. All the experiments were carried out at an ambient temperature of 20-21 °C.

NOTE: “traffic light coding system” has been used to enable a fast evaluation of the results in tables.

- Green → positive result
- Yellow → intermediate result
- Red → negative result

For example, gelation is considered positive result in the gelation behaviour studies since the main aim of these tests is to assess in which solvent gelation can occur; conversely, in perturbation tests gelation represents a negative result as highlights the absence of a delay in gel formation.

Table S1: Gelation behaviour of gelator **1**. Green = Gel; Yellow = Partial gel; Red = No gel.

Solvent	Concentration of gelator **1**			
	20 mg/ 1 mL	15 mg/ 1 mL	10 mg/ 1 mL	5 mg/ 1 mL
tetralin				
toluene				
DMSO				
ethanol				
DCM				
2-octanol				
cyclohexanone				
hexane	Not soluble	Not soluble	Not soluble	Not soluble
ethyl acetate	Not soluble	Not soluble	Not soluble	Not soluble
H_2O	Not soluble	Not soluble	Not soluble	Not soluble
chloroform	Precipitation	Precipitation		
acetone	Not soluble	Not soluble	Not soluble	Not soluble
methanol				Precipitation
1-octanol				

Table S2: Gelation behaviour of gelator **2**. Green = Gel; Yellow = Partial gel; Red = No gel.

Solvent	Concentration of gelator **2**			
	20 mg/ 1 mL	15 mg/ 1 mL	10 mg/ 1 mL	5 mg/ 1 mL
tetralin				
toluene				
DMSO				
ethanol				
DCM				
2-octanol				
cyclohexanone				
hexane	Not soluble	Not soluble	Not soluble	Not soluble
ethyl acetate	Not soluble	Not soluble	Not soluble	Not soluble
H_2O	Not soluble	Not soluble	Not soluble	Not soluble
chloroform				
acetone				
methanol				
1-octanol				

Table S3: Gelation behaviour of gelator **3**. Green = Gel; Yellow = Partial gel; Red = No gel.

Solvent	Concentration of gelator **3**			
	20 mg/ 1 mL	15 mg/ 1 mL	10 mg/ 1 mL	5 mg/ 1 mL
tetralin				
toluene	Not soluble	Not soluble	Not soluble	Not soluble
DMSO				
ethanol	Not soluble	Not soluble	Not soluble	Not soluble
DCM	Not soluble	Not soluble	Not soluble	Not soluble
2-octanol				
cyclohexanone				
hexane	Not soluble	Not soluble	Not soluble	Not soluble
ethyl acetate	Not soluble	Not soluble	Not soluble	Not soluble
H_2O	Not soluble	Not soluble	Not soluble	Not soluble
chloroform	Not soluble	Not soluble	Not soluble	Not soluble
acetone	Not soluble	Not soluble	Not soluble	Not soluble
methanol	Not soluble	Not soluble	Not soluble	Not soluble
1-octanol				

Table S4: Number of equivalents.

	Equivalents guest/gelator for gels **1** and **4** (5 mg/ mL)							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
DMMP (1.1597 g/ mL at 20°C)	0	1	2	5	9	23	47	94

Table S5: Number of equivalents.

	Equivalents guest/gelator for gels **1** and **4** (2.3 mg/ mL)							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
DMMP (1.1597 g/ mL at 20°C)	0	2	5	12	19	47	93	187

Table S6: Number of equivalents.

	Equivalents guest/gelator for gels **2** and **5** (5 mg/ mL)							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
DMMP (1.1597 g/ mL at 20°C)	0	1	3	5	10	26	52	104

Table S7: Number of equivalents.

	Equivalents guest/gelator for gels **2** and **5** (1.7 mg/ mL)							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
DMMP (1.1597 g/ mL at 20°C)	0	3	8	16	31	78	156	312

Table S8: Number of equivalents.

	Equivalents guest/gelator for gels **3** and **6** (5.2 mg/ mL)							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
DMMP (1.1597 g/ mL at 20°C)	0	1	3	7	13	33	67	134

Table S9: Number of equivalents.

	Equivalents guest/gelator for gels **3** and **6** (3.7 mg/ mL)							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
DMMP (1.1597 g/ mL at 20°C)	0	2	5	9	19	47	93	187

Table S10: *In situ* gelation and effects of the presence of DMMP. Green = No Gel; Yellow = Partial gel; Red = Gel.

In situ gel **1** in tetralin (5 mg mL^{-1}) – isocyanate addition to the amine and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5							10 s	
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **1** in tetralin (5 mg mL^{-1}) – amine addition to the isocyanate and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5							10 s	
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **1** in tetralin (2.3 mg mL^{-1}) – isocyanate addition to the amine and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5						22 s		
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **1** in tetralin (2.3 mg mL^{-1}) - amine addition to the isocyanate and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5						18 s		
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

Table S11: *In situ* gelation and effects of the presence of DMMP. Green = No Gel; Yellow = Partial gel; Red = Gel.

In situ gel **4** in tetralin (5 mg mL^{-1}) – isocyanate addition to the amine and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5	10 s	10 s	11 s	7 s	12 s			
1.0								
1.5						85 s		
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **4** in tetralin (5 mg mL^{-1}) – amine addition to the isocynate and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5	10 s	11 s	8 s	10 s	12 s	18 s		
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **4** in tetralin (2.3 mg mL^{-1}) – isocyanate addition to the amine and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5								
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **4** in tetralin (2.3 mg mL^{-1}) - amine addition to the isocyanate and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5								
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

Table S12: *In situ* gelation and effects of the presence of DMMP. Green = No Gel; Yellow = Partial gel; Red = Gel.

In situ gel **2** in tetralin (5 mg mL^{-1}) – isocyanate addition to the amine and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5	0 s				0 s	0 s		
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **2** in tetralin (5 mg mL^{-1}) – amine addition to the isocyante and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5	0 s				0 s	0 s		
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **2** in tetralin (1.7 mg mL^{-1})– isocyanate addition to the amine and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5	5 s							
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **2** in tetralin (1.7 mg mL^{-1}) - amine addition to the isocyanate and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5	5 s							
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

Table S13: *In situ* gelation and effects of the presence of DMMP. Green = No Gel; Yellow = Partial gel; Red = Gel.

In situ gel **5** in tetralin (5 mg mL^{-1}) –isocyanate addition to the amine and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5	15 s	15 s	15 s	9 s	9 s			
1.0						49 s		
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **5** in tetralin (5 mg mL^{-1}) - amine addition to the isocyanate and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5	16 s	15 s	13 s	9 s	20 s			
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **5** in tetralin (1.7 mg mL^{-1})– isocyanate addition to the amine and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5								
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **5** in tetralin (1.7 mg mL^{-1}) - amine addition to the isocyanate and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5								
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

Table S14: *In situ* gelation and effects of the presence of DMMP. Green = No Gel; Yellow = Partial gel; Red = Gel.

In situ gel **3** in tetralin (5.2 mg mL^{-1}) – isocyanate addition to the amine and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5								
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **3** in tetralin (5.2 mg mL^{-1}) – amine addition to the isocyanate and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5								
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **3** in tetralin (3.7 mg mL^{-1}) – isocyanate addition to the amine and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5	22 s	10 s	15 s	10 s	18 s			
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **3** in tetralin (3.7 mg mL^{-1}) - amine addition to the isocyanate and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5	24 s	10 s	11 s	10 s	23 s			
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

Table S15: *In situ* gelation and effects of the presence of DMMP. Green = No Gel; Yellow = Partial gel; Red = Gel.

In situ gel **6** in tetralin (5.2 mg mL^{-1}) – isocyanate addition to the amine and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5	10 s	8 s	17 s	18 s	18 s			
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **6** in tetralin (5.2 mg mL^{-1}) - amine addition to the isocyanate and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5	15 s	11 s	21 s	14 s	24 s			
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **6** in tetralin (3.7 mg mL^{-1}) – isocyanate addition to the amine and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5	13 s	15 s	17 s					
1.0								
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

In situ gel **6** in tetralin (3.7 mg mL^{-1}) - amine addition to the isocyanate and DMMP solution								
Time (min)	DMMP							
	0 mL	1.0 µL	2.5 µL	5 µL	0.01 mL	0.025 mL	0.05 mL	0.1 mL
0.5	15 s	10 s	16 s					
1.0				52 s				
1.5								
2.0								
2.5								
3.0								
3.5								
4.0								
4.5								
5.0								
10.0								

3. Differential Scanning Calorimetry

Measurements were carried out using a Mettler Toledo DSC821[e]. Gels **1**-**6** (5 mg mL^{-1}) were investigated. All gels were prepared in tetralin following the perturbation tests procedure described in Section 2. In the tests with DMMP (2.5 µL, 5.0 µL, 0.01 mL) gels **1**–**3** were prepared at the gelation concentration of 5 mg mL^{-1}.

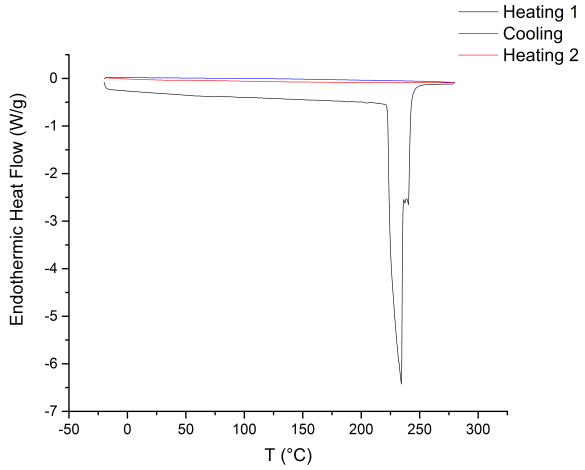

Figure S1: DSC trace of tetralin.

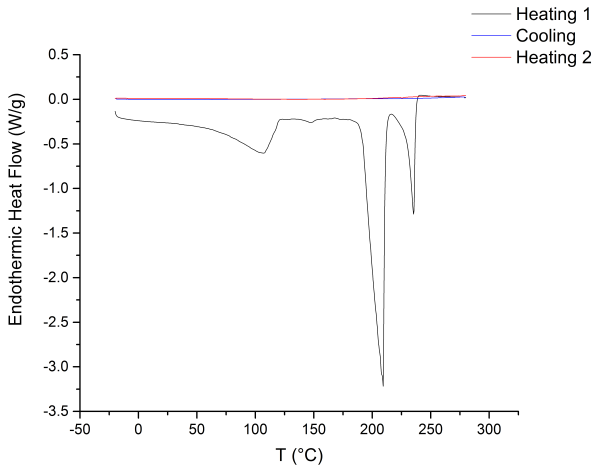

Figure S2: DSC trace of gel **1**.

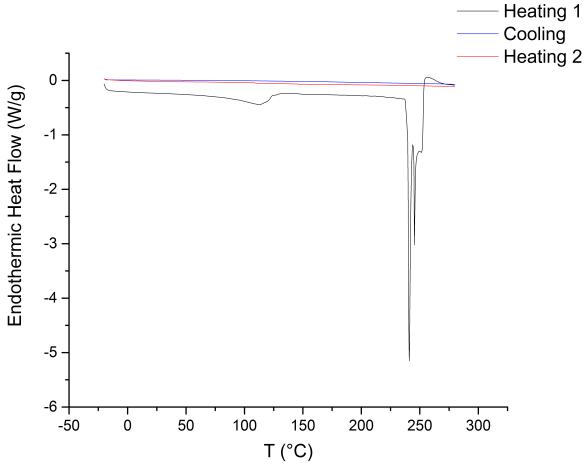

Figure S3: DSC trace of gel **1** with 0.01 mL of DMMP.

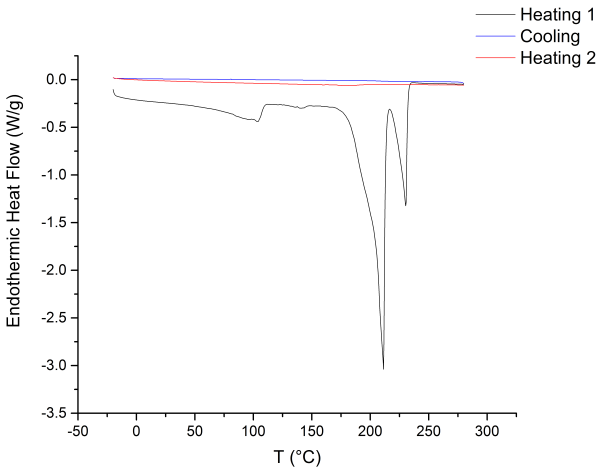

Figure S4: DSC trace of gel **2**.

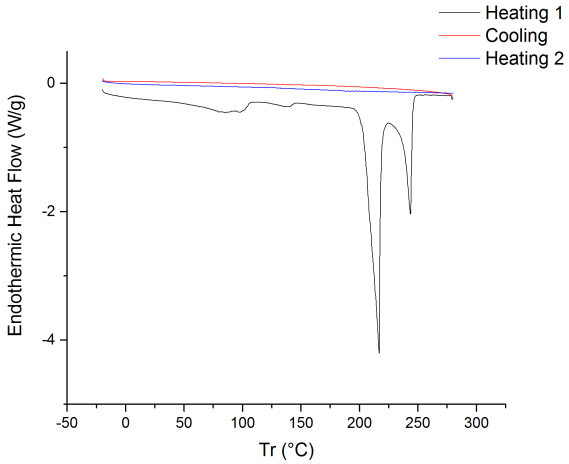

Figure S5: DSC trace of gel **2** with 2.5 µL of DMMP.

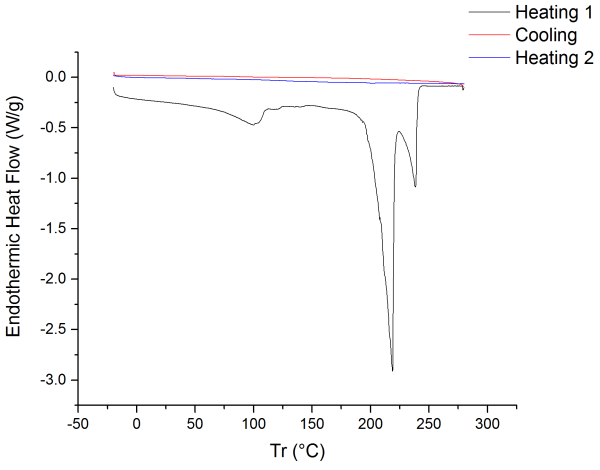

Figure S6: DSC trace of gel **2** with 5.0 µL of DMMP.

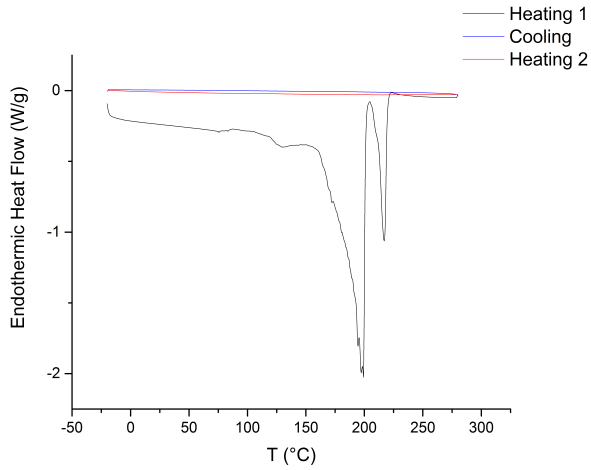

Figure S7: DSC trace of gel **2** with 0.01 mL of DMMP.

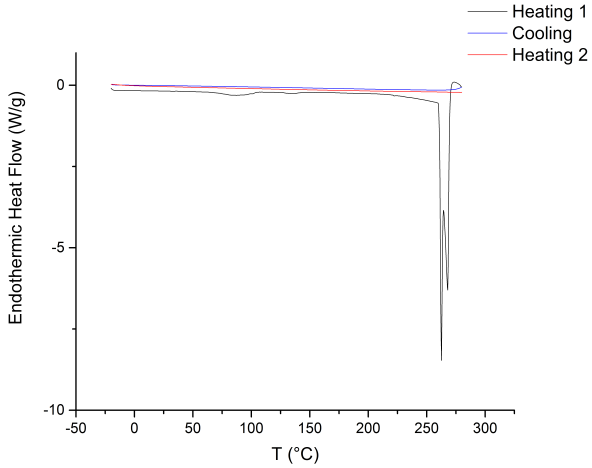

Figure S8: DSC trace of gel **3**.

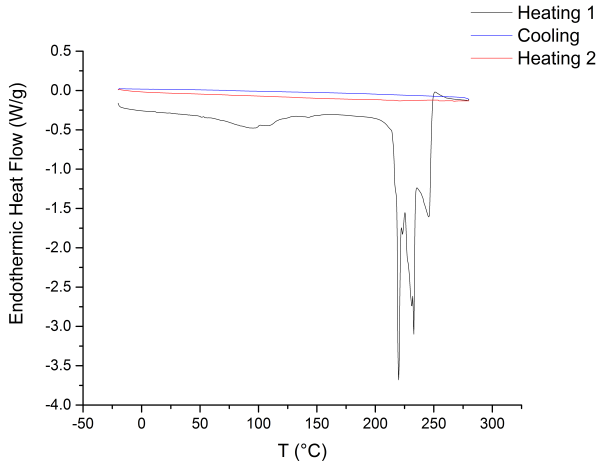

Figure S9: DSC trace of gel **3** with 0.01 mL of DMMP.

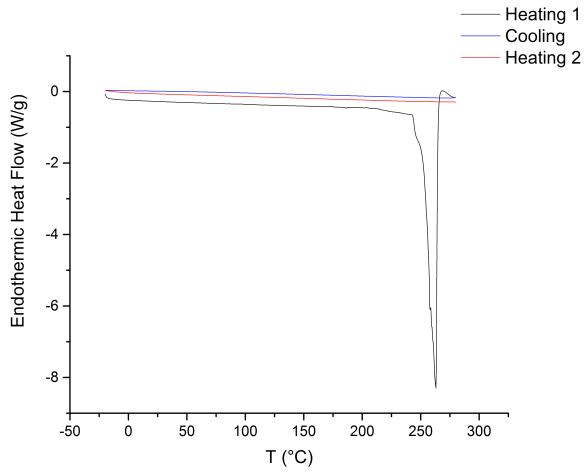

Figure S10: DSC trace of gel **4**.

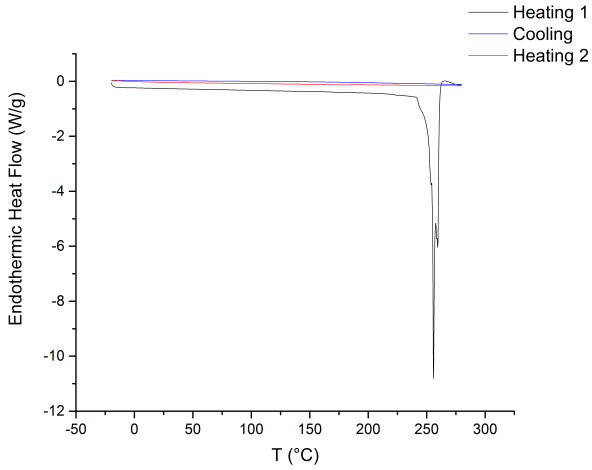

Figure S11: DSC trace of gel **5**.

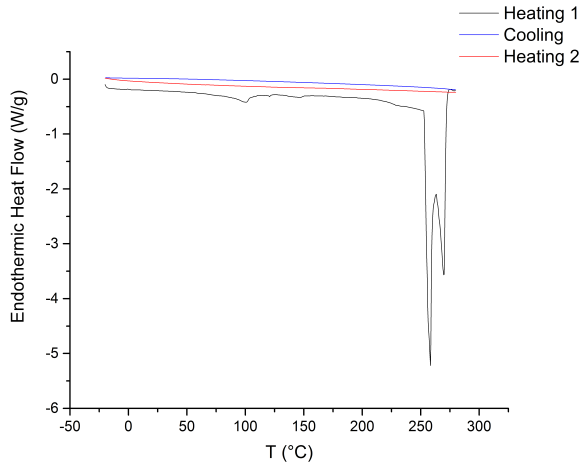

Figure S12: DSC trace of gel **6**.

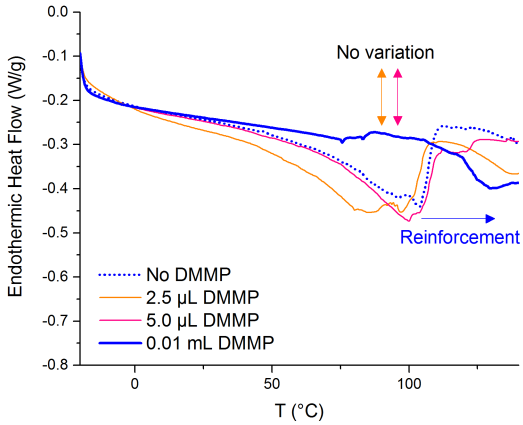

Figure S13: Comparison of the variations of T_{gel} in the presence of low amounts of DMMP for gel **2**, showing a shift only upon addition of 0.01 mL.

4. Thermo Gravimetric Analysis

Measurements were carried out using a Perkin Elmer Pyris 1 Thermogravimetric Analyzer. Each gel sample (around 30 mg) underwent a heating ramp from rt to 230–280°C at a rate of 10°C min^{-1} in aluminium pans. Final temperature was chosen 10° later than the complete weight loss. Gels **1–3** (20 mg mL^{-1}) were investigated. All gels were prepared in tetralin following the perturbation tests procedure described in Section 2.

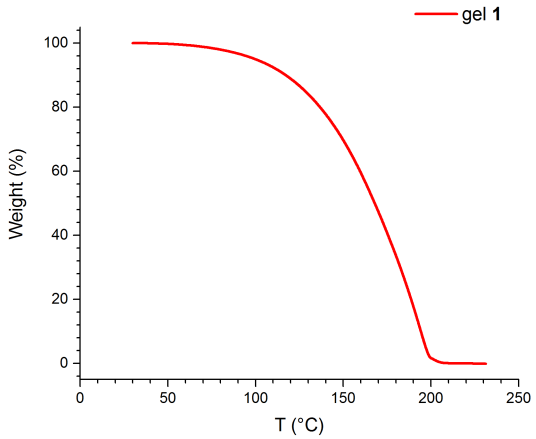

Figure S14: TGA trace of gel **1**.

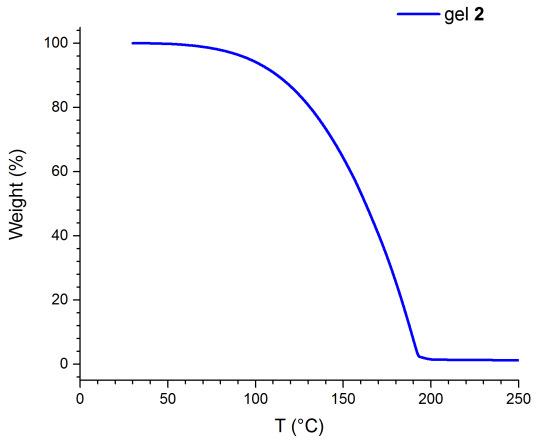

Figure S15: TGA trace of gel **2**.

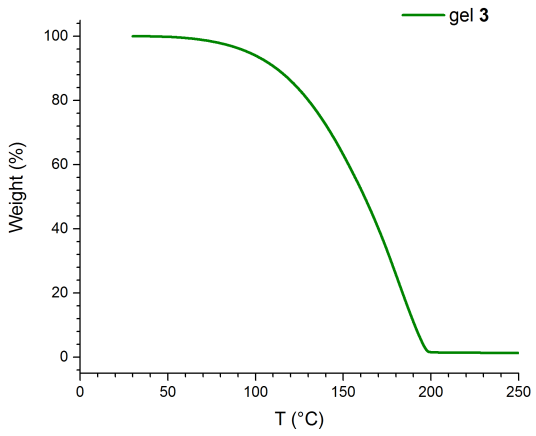

Figure S16: TGA trace of gel **3**.

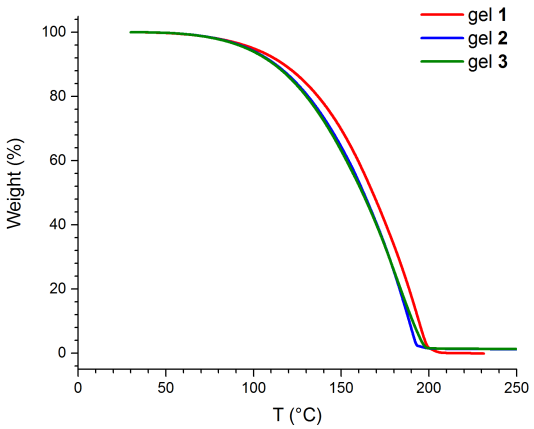

Figure S17: Comparison between the three TGA traces.

5. Rheology of gels

Rheology experiments were performed using an AR2000EX rheometer. Measurements of the gels were made using 40 mm crosshatched stainless steel plates with a gap of 1000 μm. Stress sweep experiments were carried out to study the linear viscoelasticity region (LVER) and dynamic stress yield values of the gels (angular frequency = 6.28 rad s^{-1} = 1 Hz, oscillatory stress = 0.1-10000.0 Pa). In the LVER region a constant oscillatory shear stress of 10.0 Pa was applied to monitor the dependence on angular frequency ranging between 6.28 and 628.0 rad s^{-1} (1-100 Hz). Rheological experiments were carried out at r.t.. Storage and loss moduli were also calculated from sweep measurements. Gels **1–3** (5 mg mL^{-1}) were investigated. In the tests with DMMP (0.01 mL) gels **1–3** were prepared at the same gelation concentration of 5 mg mL^{-1}. All gels were prepared in tetralin following the perturbation tests procedure described in Section 2. Reproducibility was found satisfactory (Fig. S15).

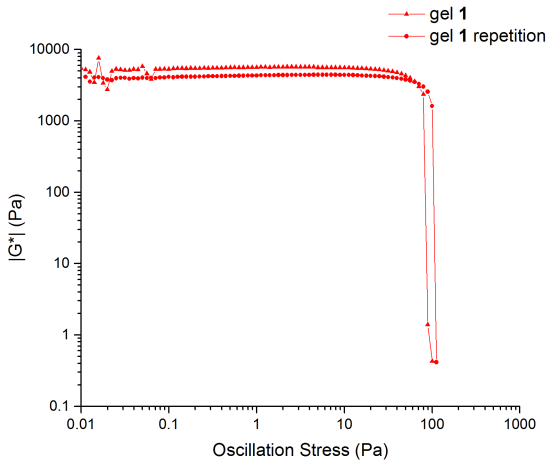

Figure S18: Stress sweeps of gel **1** to test the measurement's reproducibility.

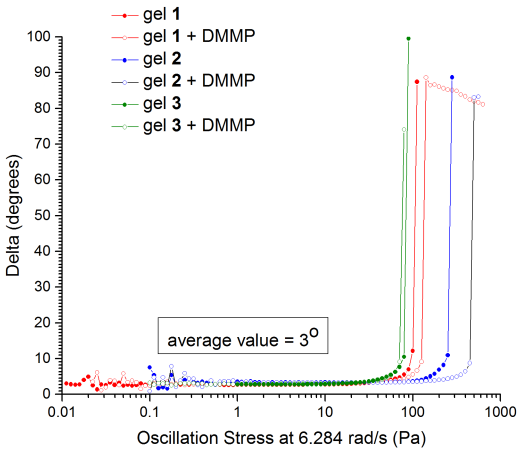

Figure S19: Stress sweep of gels **1–3** with and without DMMP with average phase angle value.

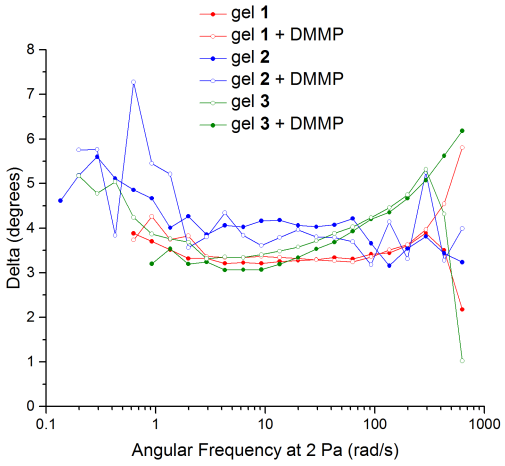

Figure S20: Angular frequency sweeps of gels **1**–**3** with and without DMMP.

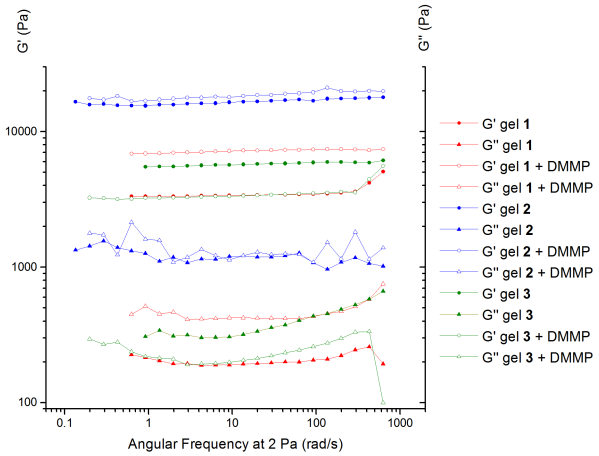

Figure S21: Angular frequency sweeps of gels **1**–**3** with and without DMMP showing the storage moduli (G') and the loss moduli (G'').

6. Molecular electrostatic potential surfaces

Molecular electrostatic potential surfaces were calculated with Spartan'10 using the semi-empirical method AM1. Negative regions are shown in red, positive in blue while green is neutral. The maximum in electrostatic potential always lies over the NH group of the gelator.

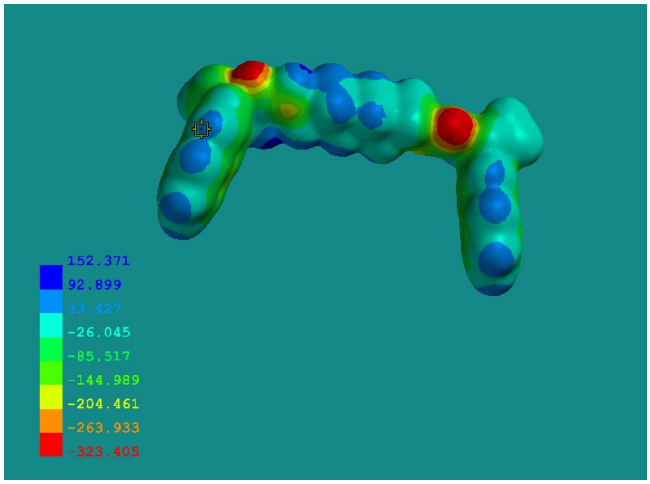

Figure S22: Molecular electrostatic potential surface of gelator **1**.

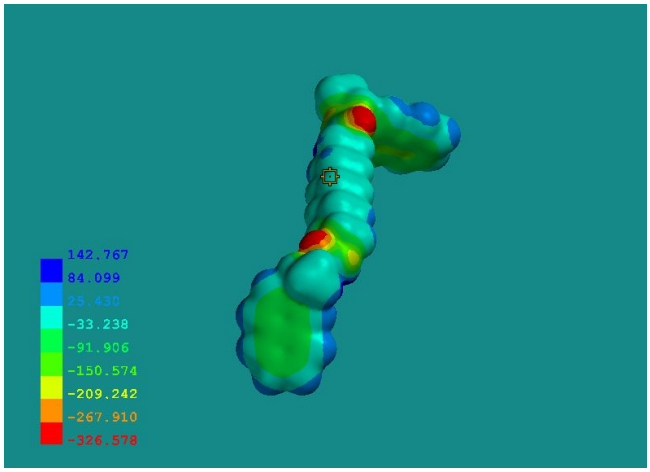

Figure S23: Molecular electrostatic potential surface of gelator **2**.

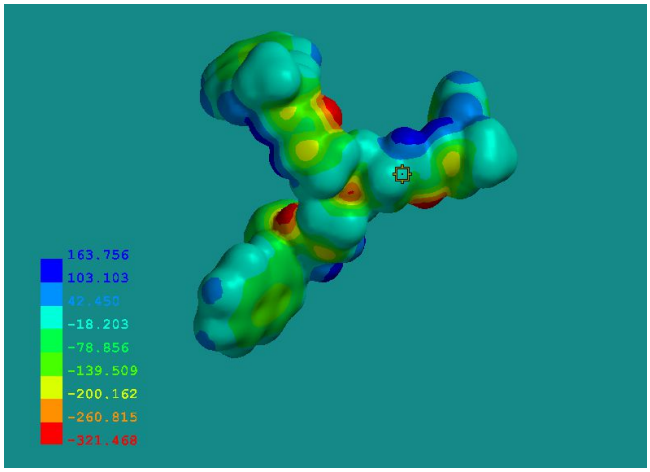

Figure S24: Molecular electrostatic potential surface of gelator **3**.

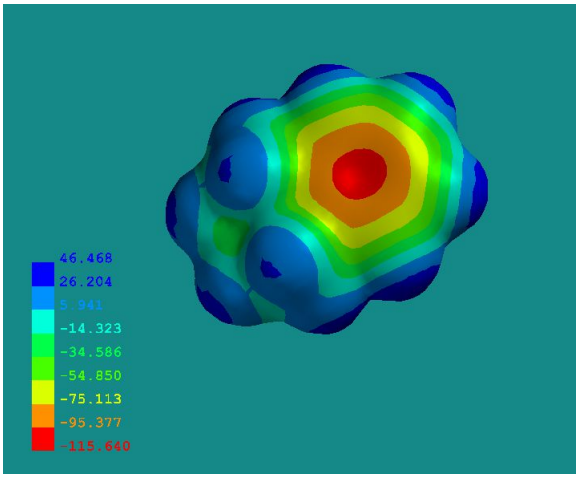

Figure S25: Molecular electrostatic potential surface of tetralin.

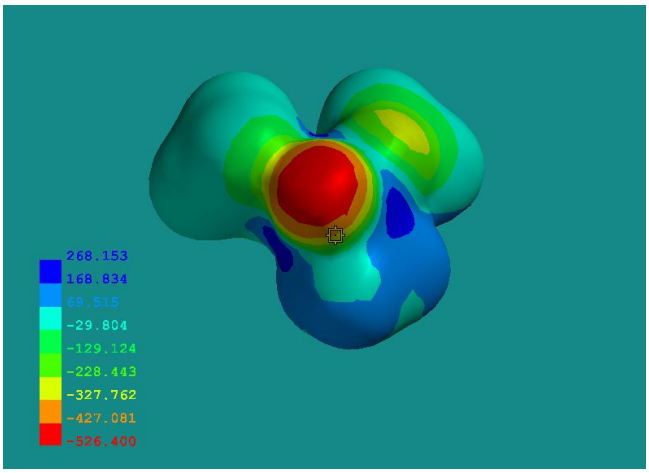

Figure S26: Molecular electrostatic potential surface of DMMP.

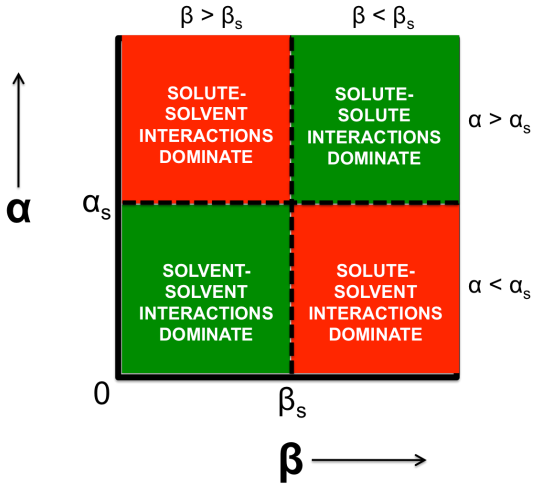

Figure S27: Generalized hydrogen-bond interactions profile, function of the H-bond donor (α) and the H-bond acceptor (β) constants with respect to a solvent (α_s; β_s).

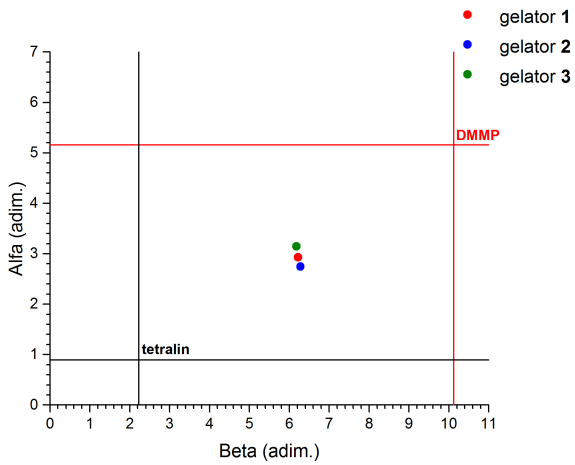

Figure S28: Hydrogen-bond interactions profile for gelators **1**–**3** with respect to tetralin (black) and DMMP (red).

7. ^{31}P-{^{1}H} NMR

^{31}P-{^{1}H} NMR spectra have been recorded on a Bruker Avance III 500 MHz spectrometer using a 10 mm double resonance probe. The NMR sample has been prepared using two concentric tubes. The external 10 mm OD tube was filled with a 4 mM solution of $POPh_3$ used for chemical shift reference. The inner 5 mm OD tube was filled with the sample under investigation. A Waltz 16 3 kHz decoupling has been used in all cases. Below a list of the samples investigated:

1. 0.01 mL DMMP in 0.7 mL toluene-d_8
2. 0.0003 mL DMMP / 15 mg gelator **2** (molar ratio 1/10) in 0.7 mL toluene-d_8 → gel phase
3. 0.003 mL DMMP / 15 mg gelator **2** (molar ratio 1/1) in 0.7 mL toluene-d_8 → gel phase
4. 0.03 mL DMMP / 15 mg gelator **2** (molar ratio 10/1) in 0.7 mL toluene-d_8 → gel phase
5. 0.3 mL DMMP / 15 mg gelator **2** (molar ratio 100/1) in 0.7 mL toluene-d_8 → liquid, gel formation suppressed
6. 0.001 mL DMMP / 5 mg urea (molar ratio 1/10) in 0.7 mL toluene-d_8
7. 0.01 mL DMMP / 5 mg urea (molar ratio 1/1) in 0.7 mL toluene-d_8
8. 0.3 mL DMMP / 1.6 mg urea (molar ratio 100/1) in 0.7 mL toluene-d_8

The samples were prepared following the gel formation procedure outlined in Section 2. DMMP was added together with the gelator and the solvent before heat gun treatment.

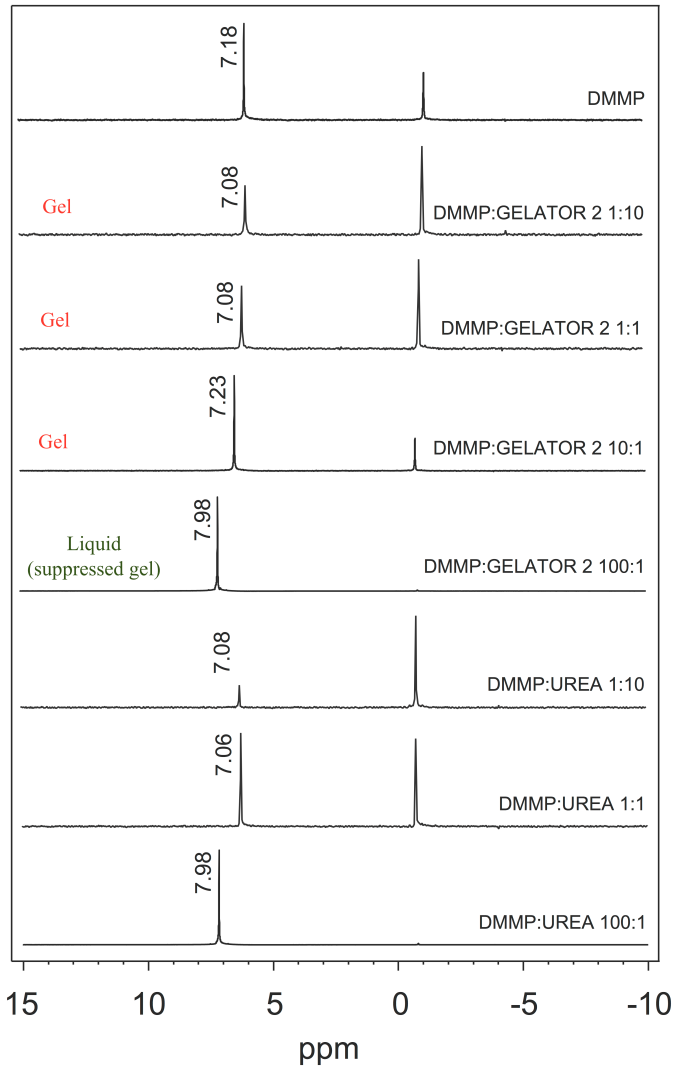

Figure S29: Stacked ^{31}P-{^{1}H} NMR spectra of DMMP in presence of gelator **2** and urea.

8. Environmental SEM

The instrument used was a Philips XL–30. Samples were analysed together using a multiple pin sample holder. No sample coating was necessary. Accelerating voltage was set between 10.0 and 10.2 kV, while GSE (Gaseous Secondary Electrons) were collected in imaging mode to acquire images at different magnification from each sample. Vacuum was considered established after 6 flushes of water vapour. WD (Working Distance) varied between 5.3 and 5.5 mm and the spot size parameter varied between 4.1 and 4.3, while contrast and brightness were adjusted accordingly. No significant stigmatism was observed. Partial pressure of water in the chamber was kept constant at 0.6 Torr.
Environmental SEM images were taken on xerogels obtained from gels **1**–**6** (5 mg mL^{-1}) in tetralin. In the tests with DMMP (0.01 mL) gels **1**–**3** were prepared at the same gelation concentration of 5 mg mL^{-1}. All gels were prepared following the perturbation tests procedure described in Section 2. Being all gels produced in a high boiling point solvent (tetralin, bp = 207 °C) it was not possible to effectively remove it from the network upon simply drying at the vacuum pump. Nonetheless, it is believed that exposure of the pre-dried samples to the vacuum level inside the microscope analysis chamber was enough to strip away all remaining traces of tetralin. For this reason we consider that all pictures taken were of xerogels.

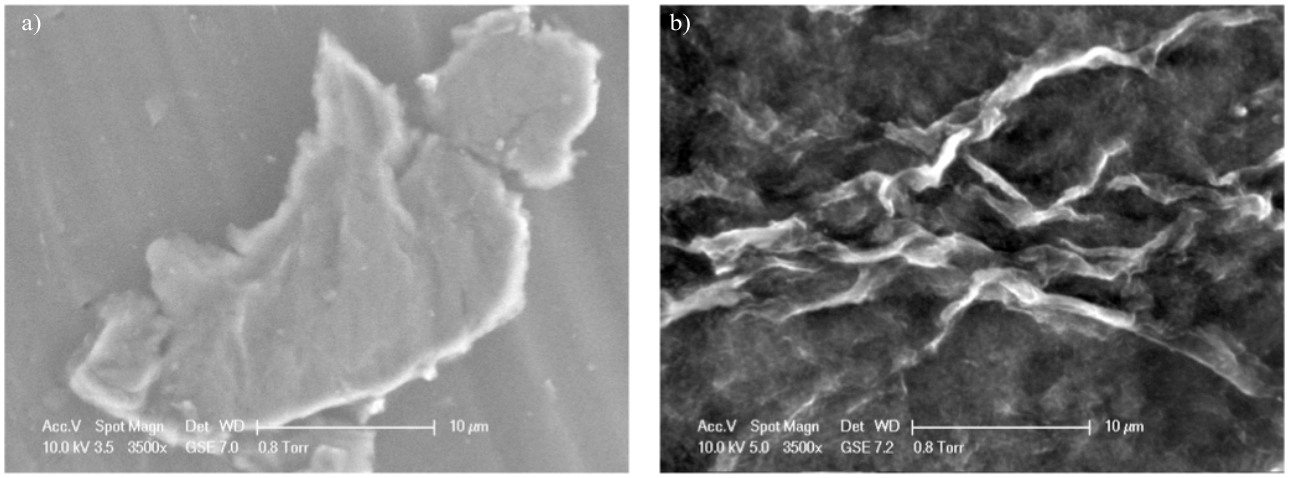

Figure S30: ESEM images at 3500x magnification for: a) xerogel **4**; b) xerogel **1**.

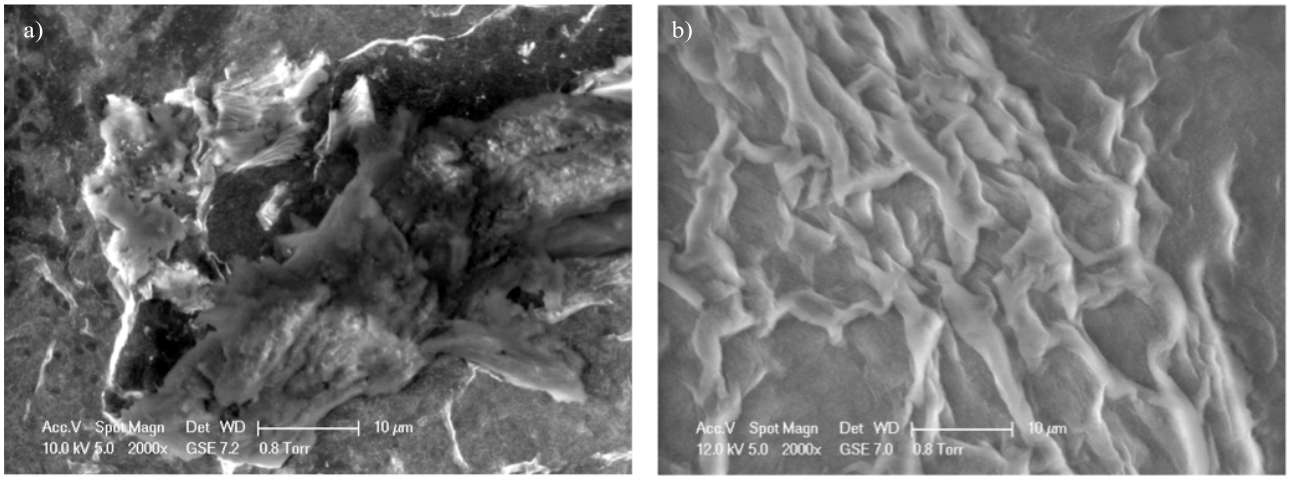

Figure S31: ESEM images at 2000x magnification for: a) xerogel **1**; b) xerogel **1** + DMMP.

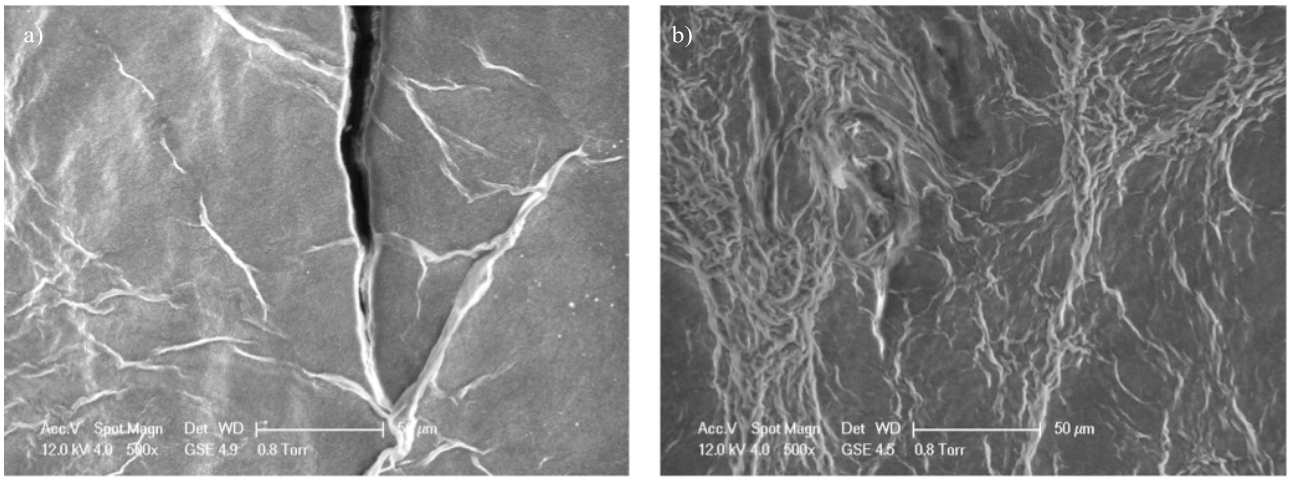

Figure S32: ESEM images at 500x magnification for: a) xerogel **6**; b) xerogel **3**.

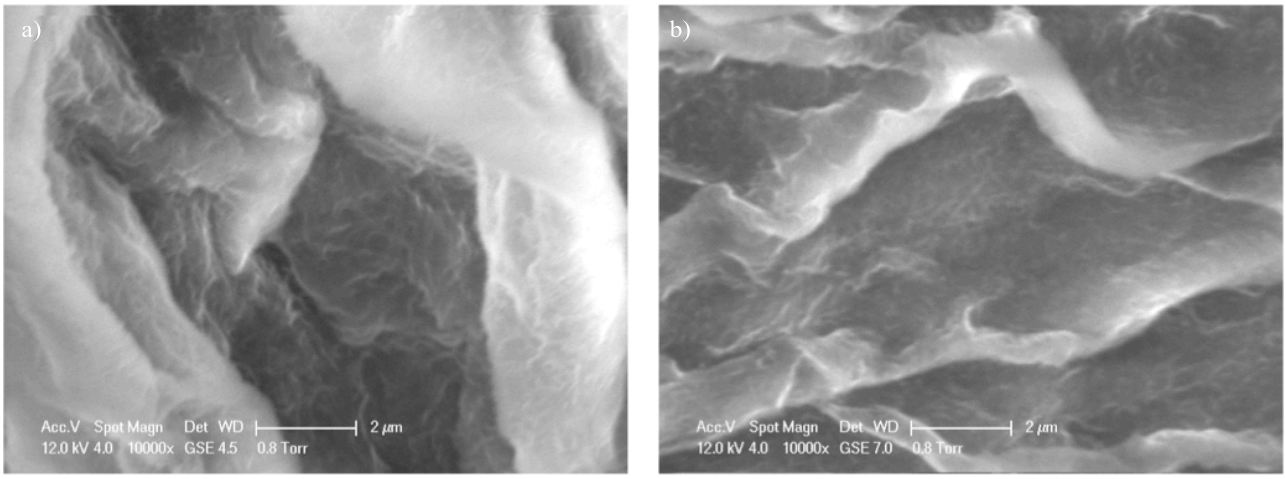

Figure S33: ESEM images at magnification of 10000x for: a) xerogel **3**; b) xerogel **3** + DMMP.