Wet-spinning multi-component low-molecular-weight gelators to print synergistic soft materials

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SUPPORTING INFORMATION

S1   Experimental methods

S2   Preparation and characterisation of DBS-COOH gel filaments

S3   Preparation and characterisation of DBS-COOH/DBS-CONHNH$_2$ hybrid gel filaments

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S1 Experimental methods

S1.1 General materials and methods.

All compounds used in synthesis and analysis were purchased from standard commercial suppliers and used as received. The synthesis of DBS-CONHNH$_2$ and DBS-COOH was performed in good yields applying previously reported methods.[1] The preparation of DBS-CONHNH$_2$ filaments by wet spinning was performed using an A-99 Razel Syringe Pump. ^{1}H NMR spectra were recorded using a Jeol 400 spectrometer (^{1}H 400 MHz). Samples were prepared in DMSO-d$_6$ or D$_2$O and chemical shifts (δ) are reported in parts per million (ppm). IR spectra of xerogels were recorded on a PerkinElmer Spectrum Two FT-IR spectrometer. SEM images were taken using a JEOL JSM-7600F field emission SEM. TEM images were obtained on a FEI Tecnai 12 G^2 fitted with a CCD camera. Gel nanotube diameters were measured using *Digimizer* software. T_{gel} values were obtained using a high precision thermoregulated oil bath and were recorded in triplicate.

S1.2 Determination of gel filament diameter

The photos showing visible gel filaments were opened in the ImageJ.exe software and several filament diameters measured at random. An average gel filament diameter was calculated for each of the different condition combinations which gave a visible gel filament. This measurement was scaled to actual size using the known vial diameter; 20 mm for the smaller vial and 22 mm for the larger.

S1.3 Determination of T_{gel}

Gel filaments were prepared in two sets of duplicates by wet spinning as described previously in Section 6.3 using a 23G blunt tip needle and a flow rate of 3.4 μL/min. One set of duplicates was left in the water (6 mL) and from the other set the water was removed carefully by pipette and left to air dry overnight. Both sets of duplicate samples were then placed in an oil bath set to 30 °C and ramped up to 100 °C at a rate of 1 °C/min. The samples were closely observed every minute and any degradation recorded. The value of T$_{gel}$ is said to be the temperature at which visible degradation begins.

S1.4 Transmission and Scanning Electron Microscopy (TEM and SEM)

Gel filaments (4.5 % wt/vol) were prepared by wet spinning for TEM and SEM imaging as described previously using a 23 G blunt tip needle and a flow rate of 3.4 μL/min. TEM samples were produced by placing a small amount of each sample onto a copper grid. The excess sample was removed by filter paper before leaving to set for 5 minutes. A negative stain (1% uranyl acetate) was then added, and the samples left to rest for 30 minutes before the images were taken. SEM samples were produced by placing a small amount of each sample onto a copper grid and critical-point freeze-dried. The freeze-dried samples were mounted onto stubs and imaged.

S1.5 IR spectroscopic characterisation

DBS-COOH gel filaments (1.5, 3.0 and 4.5 % wt/vol) and DBS-COOH/DBS-CONHNH$_2$ gel filaments (1.5, 3.0, 4.5 and 6.0 % wt/vol) were prepared by wet spinning for IR Spectroscopy as described previously with 200 μL of the solution, using a 23 G blunt tip needle and a flow rate of 3.4 μL/min was extruded. The water was then mostly removed from the water bath carefully by pipette and the remaining gel filament dried fully under high vacuum to yield a white powder. A small amount of this powder was placed in the infrared spectrophotometer and the spectra recorded in the range 450-4000 cm $^{-1}$.

S1.6   Quantification by ^{1}H NMR experiments

S1.6.a   Quantifying amount of gelator in the filament. ^{1}H NMR was used to quantify the exact amount of the gelator found in the gel filaments made from the wet spinning. Preparation of these gel filaments was done by preparing samples in DMSO as described previously; and 100 µL of the solution injected into a water bath (6 mL) from a 23 G blunt tip needle at a flow rate of 3.4 µL/min. A large proportion of the water was then removed from the filament carefully by pipette and then the sample was completely dried under high vacuum to yield a solid. This was ground before dissolving in DMSO-d^6 (0.7 mL), and acetonitrile (1.4 µL) was added as an internal standard. The sample was sonicated for 30 minutes until completely dissolved. The ^{1}H NMR Spectrum was recorded and the concentration of the gelator in the filaments calculated by comparison of the integrals of the relevant peaks, DBS-COOH (δ = 7.93 ppm) and DBS-CONHNH$_2$ (δ = 7.54 ppm), to that of the acetonitrile (δ = 2.03 ppm).

S1.6.b   Quantifying residual DMSO. ^{1}H NMR was used to quantify any residual DMSO-d^6. Preparation of these gel filaments was done by preparing samples in DMSO as described previously and 100 µL of the solution injected into a vial filled with D$_2$O (6 mL) from a 23 G blunt tip needle at a flow rate of 3.4 µL/min. The D$_2$O was then removed from the filament carefully by pipette. This gel filament was transferred to an NMR tube before D$_2$O (0.7 mL), and an internal standard of acetonitrile (1.4 µL) was added. The ^{1}H NMR spectrum was recorded, and the amount of residual DMSO quantified by comparison of the integral of the DMSO (δ = 2.56/2.63 ppm) peak to that of acetonitrile (δ = 1.90/1.93 ppm).

S1.6.c   Quantifying self-assembled gelator in the filament. ^{1}H NMR was used to quantify the amount of gelator self-assembled in the gel filament produced from the wet spinning. Preparation of these gel filaments was achieved as described previously and 100 µL of the DMSO solution injected into a vial filled with D$_2$O (6 mL) from a 23 G blunt tip needle at a flow rate of 3.4 µL/min. The excess D$_2$O was then removed from the filament carefully by pipette. This gel filament was transferred to an NMR tube before D$_2$O (0.7 mL), and an internal standard of acetonitrile (1.4 µL) was added. The ^{1}H NMR Spectrum was recorded, and the amount of disassembled gelator quantified by comparison of the integrals of relevant peaks, DBS-COOH (δ = 7.79 ppm) and DBS-CONHNH$_2$ (δ = 7.64 ppm), to that of acetonitrile (δ = 1.93 ppm). Multiple ^{1}H NMR spectra were recorded over 4 days to investigate how the amount of gelator self-assembled in the gel filament may change over time.

S1.7   Base-induced disassembly

^{1}H NMR was used to quantify the amount of gelator self-assembled in the DBS-COOH/DBS-CONHNH$_2$ multicomponent and DBS-CONHNH$_2$ gel filaments before and after addition of deuterated sodium hydroxide (NaOD). Preparation of the gel filaments (4.5% wt/vol) was done by preparing a sample in DMSO as previously described and 100 µL of the solution injected into a vial filled with D$_2$O (6 mL) from a 23 G blunt tip needle at a flow rate of 3.4 µL/min. The excess D$_2$O was then removed from the filament carefully by pipette. This gel filament was transferred to an NMR tube before D$_2$O (0.7 mL), and an internal standard of acetonitrile (1.4 µL) was added. The initial ^{1}H NMR Spectrum was recorded, before 0.5 M NaOD (60 µL) was added into the NMR tube. Further ^{1}H NMR Spectra were recorded: immediately and after 2 hours with NaOD. The amount of disassembled gelator quantified by comparison of the integrals of relevant peaks, DBS-COOH (δ = 7.75 ppm) and DBS-CONHNH$_2$ (δ = 7.59 ppm), to that of acetonitrile (δ = 1.91 ppm).

S1.8   Change in pH

Gel filaments were prepared by wet spinning in water baths (6 mL) as described previously using a 23 G blunt tip needle and a flow rate of 3.4 µL/min. The pH of the water bath was measured using a pH meter and recorded over time at intervals to investigate the leaching of the DBS-COOH out of the gel filament.

S1.9 Incorporation of AuNPs into gel filaments

Gel filaments were prepared in triplicates by wet spinning into water baths (6 mL) as described previously using a 23 G blunt tip needle and a flow rate of 3.4 µL/min. A large proportion of the water was then removed from the filaments carefully by pipette. The filaments were then washed with water and immersed in $AuCl_3$ solution (1 mL) and the colour change observed.

S1.10 Quantifying Au(III) uptake into gel filaments by UV-Vis spectroscopy

UV-Vis Spectroscopy was used to quantify the uptake of Au (III) into the gel filaments. Preparation of these filaments (1.5, 3.0 and 4.5% wt/vol) was done by preparing samples in DMSO as described previously using a 20 mM $AuCl_3$ solution (20 µmoles of Au (III)). After 24 hours an aliquot (50 µL) was removed, diluted to 2 mL, and transferred to a cuvette. The UV absorbance was measured at 305-310 nm to give the µmoles of Au (III) that was not incorporated into the gel filaments. This value was then used to calculate the µmoles of Au (III) incorporated into the gel filaments by subtracting from the initial µmoles of Au (III) added. The experiment was repeated in triplicates for each sample.

S1.11 TEM characterisation of AuNP-loaded gels

DBS-COOH and DBS-COOH/DBS-CONHNH$_2$ gel filaments (4.5 % wt/vol) were prepared by wet spinning for TEM imaging as described previously using a 20 mM $AuCl_3$ solution. The solution was removed carefully by pipette and the remaining gel filament washed and immersed in 1 mL water. The TEM samples were produced by placing a small amount of each sample onto a copper grid. The excess sample was removed by filter paper before leaving to set for 5 minutes.

S2 Preparation and characterisation of DBS-COOH gel filaments

DBS-COOH (1.5, 3.0 and 4.5% wt/vol) was dissolved in DMSO. The solution was transferred into a 1.0 mL volume syringe and injected through a blunt tip needle (30G, 23G, 20G, 18G or 15G) into a water bath (40 mL) using a syringe pump at a known flow rate (3.4, 6.8, 10.0, 20.0, 27.0 µL/min). Multiple attempts were made at wet-spinning under each set of conditions, and the reported outcome reflects the most common outcome of the extrusion.
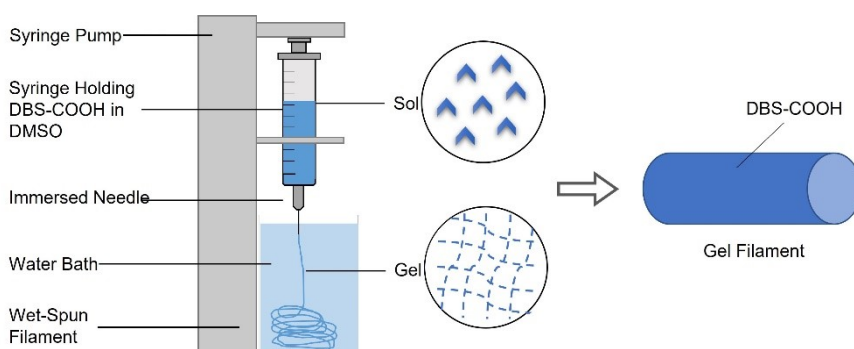

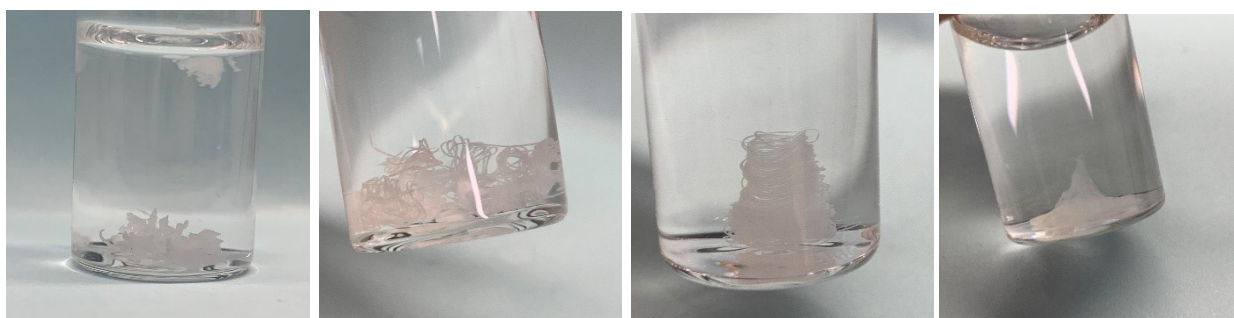Figure S1. Schematic representation of the fabrication of DBS-COOH gel filaments by wet spinning.

Figure S2. Photographic images of some of the possible outcomes of DBS-COOH wet spinning: needle clog, in which the needle blocks repeatedly with solid-like gel and further extrusion is prevented (left), clog and filament where a filament is formed, but then after a period of time the needle clogs (middle left), gel filament (middle right) and uncontrolled gelation, in which the extruded material forms a gel, but without any of the spatial resolution of individual filaments (right).
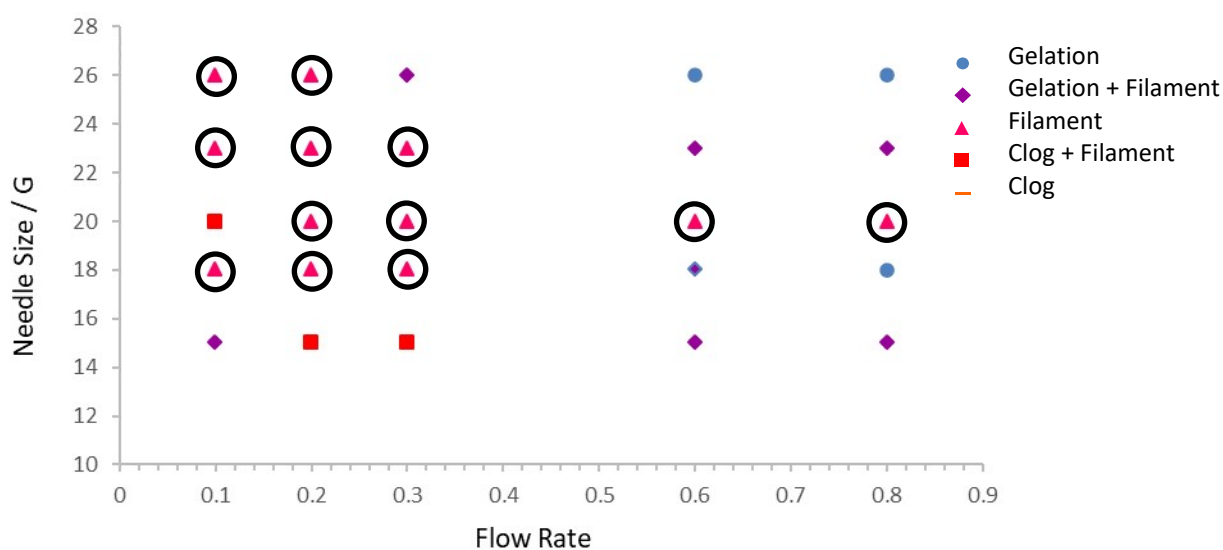

Figure S3. Outcomes of screening for optimal conditions for wet-spinning 15 mg ml^{-1} of DBS-COOH in DMSO. Black circles highlight optimal conditions for filaments.
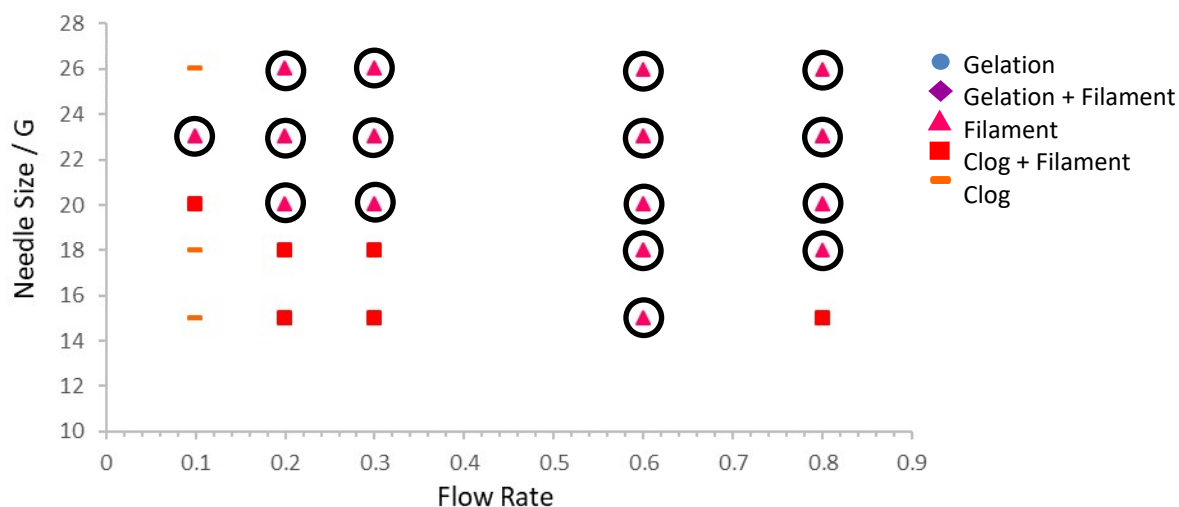
Figure S4. Outcomes of screening for optimal conditions for wet-spinning 30 mg ml^{-1} of DBS-COOH from DMSO into H$_2$O. Black circles highlight optimal conditions for filaments.
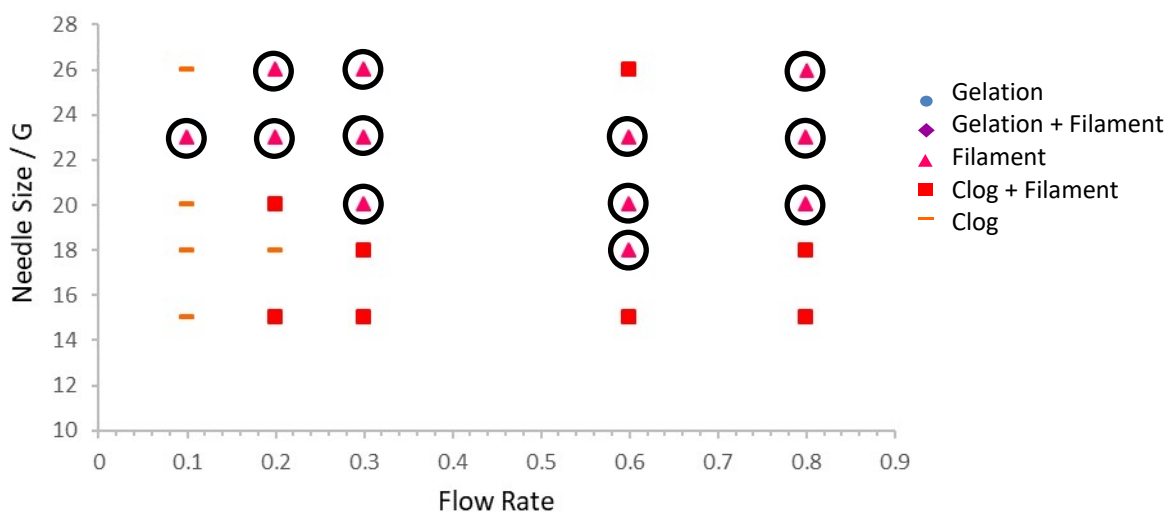
Figure S5. Outcomes of screening for optimal conditions for wet-spinning 45 mg ml^{-1} of DBS-COOH from DMSO into H$_2$O. Black circles highlight optimal conditions for filaments.

Table S1. Single Component DBS-COOH Gel Filament Diameters

Concentration of DBS-COOH / mg ml^{-1}	Flow Rate / μL/min	Needle Gauge / Inner Diameter				
		26 G	23 G	20 G	18 G	15 G
		Gel Filament Average Diameter / μm				
15	3.4	100	98	100	-	-
	6.7	115	110	112	-	-
30	3.4	130	119	103	112	112
	6.7	149	138	130	115	112
45	3.4	185	126	174	-	-
	6.7	211	161	184	-	232

Table S2. T_{gel} values of gel filaments

Gelator	Loading / % wt/vol	T_{gel} / °C
DBS-COOH	1.5	88
	3.0	89
	4.5	98
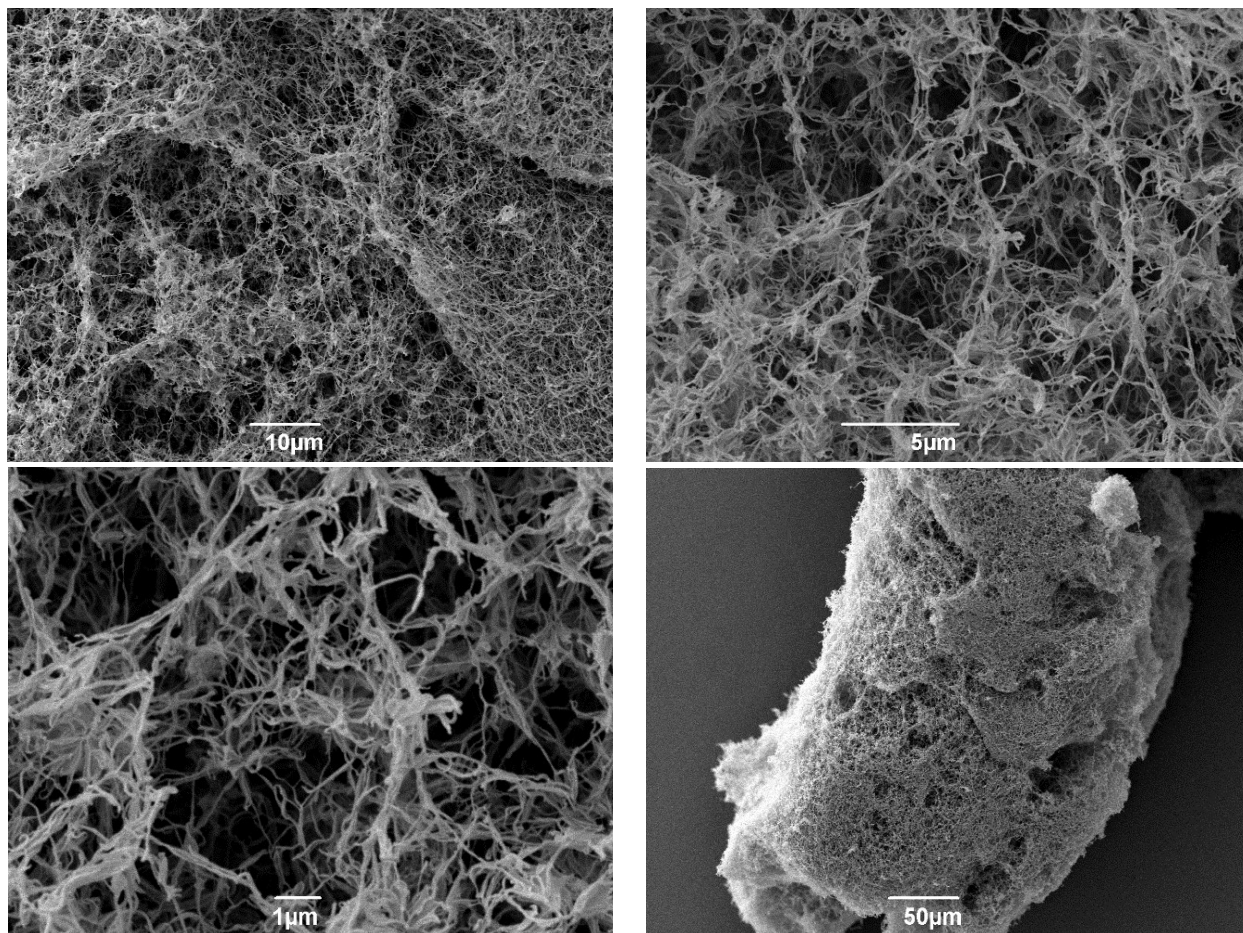
Figure S6. SEM images of nanoscale structures that underpin the gel filaments formed by wet-spinning DBS-COOH (4.5% wt/vol). Top left scale bar = 10 μm, Top right scale bar = 5 μm, Bottom left scale bar = 1 μm, Bottom right scale bar = 50 μm.
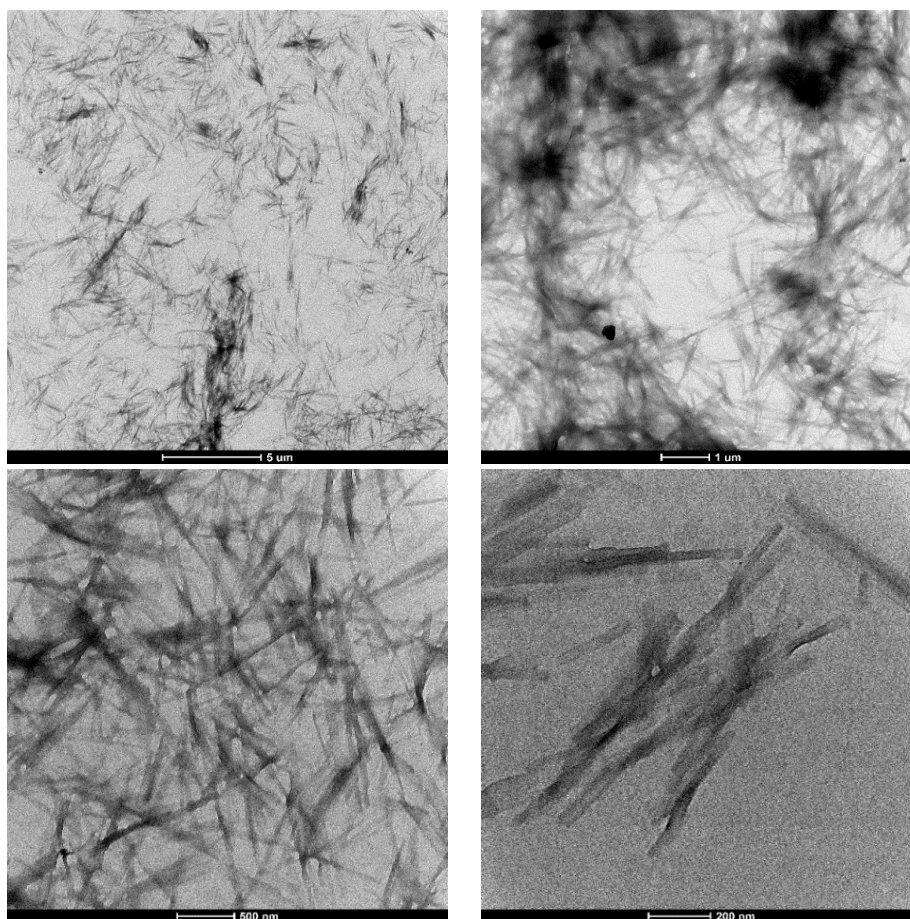
Figure S7. TEM images of nanoscale structures that underpin the gel filaments formed by wet-spinning DBS-COOH (4.5% wt/vol). Top left scale bar = 5 μm, Top right scale bar = 1 μm, Bottom left scale bar = 500 nm, Bottom right scale bar = 200 nm.
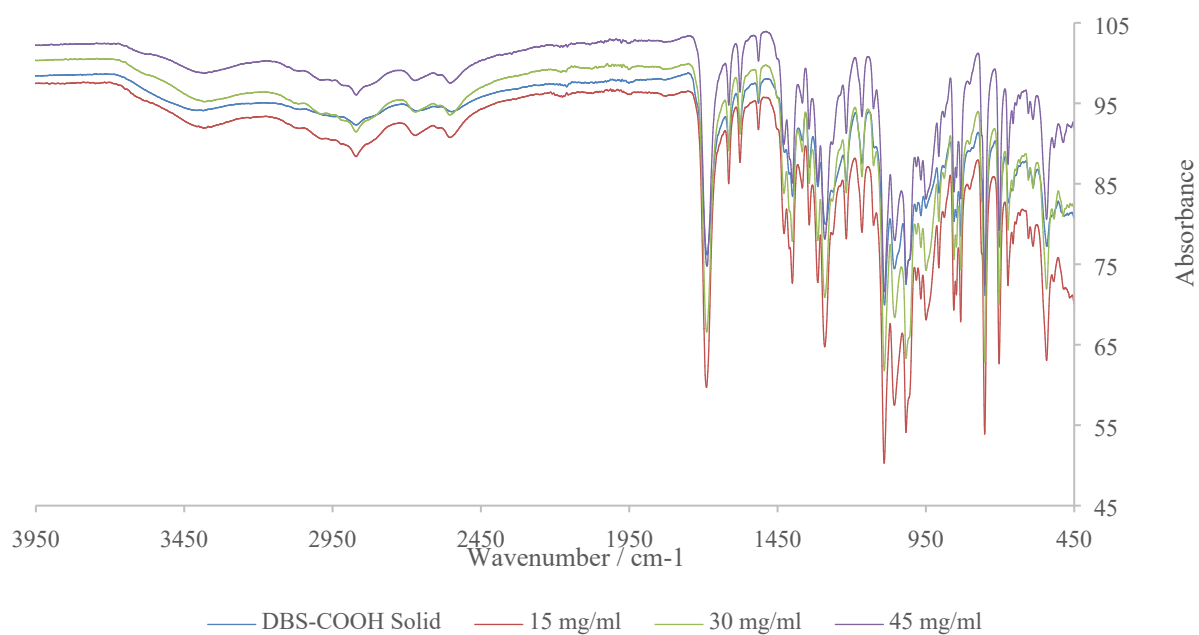
Figure S8. IR Spectra of DBS-COOH solid (blue) and DBS-COOH gel filaments: 1.5% wt/vol (red), 3.0% wt/vol (green) and 4.5% wt/vol (purple). All show very similar IR bands, indicating that the assembled structure of DBS-COOH is similar in both solid and gel filament forms

Table S3 Change in percentage of non-assembled gelator present in DBS-COOH single component system over time

Concentration / % wt/vol	% Non-Assembled Gelator / %				
	2 Hours in D_2O	1 Day in D_2O	2 Days in D_2O	3 Days in D_2O	4 Days in D_2O
1.50	11.21	13.00	12.80	25.00	44.94
3.00	0.10	0.20	0.50	0.60	2.80
4.50	0.87	4.47	4.80	0.67	1.40
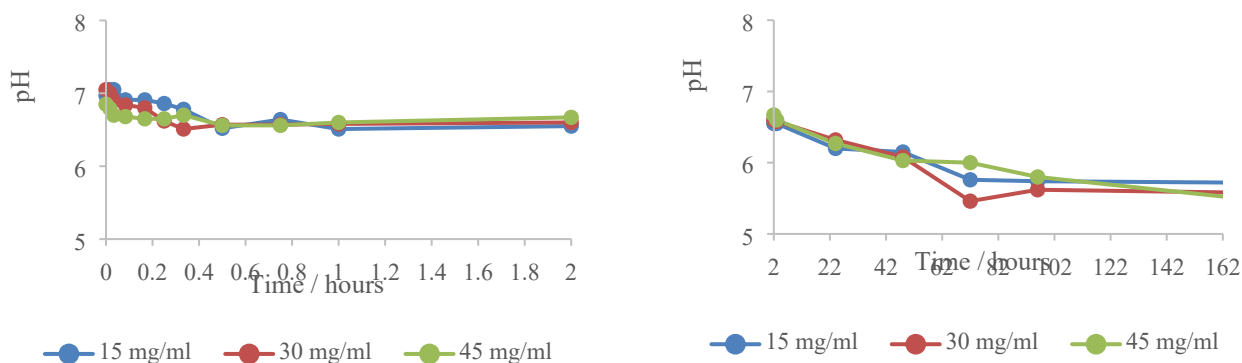
Figure S9. Change in the pH of the aqueous solution in which the DBS-COOH gel filaments (1.5, 3.0 and 4.5% wt/vol) were wet spun. Time = 0 is the initial point of self-assembly. (Left) Shorter periods of time, 0-2 h. (Right) Longer periods of time, 2-168 h.

S3   Preparation and characterisation of DBS-COOH/DBS-CONHNH$_2$ hybrid gel filaments
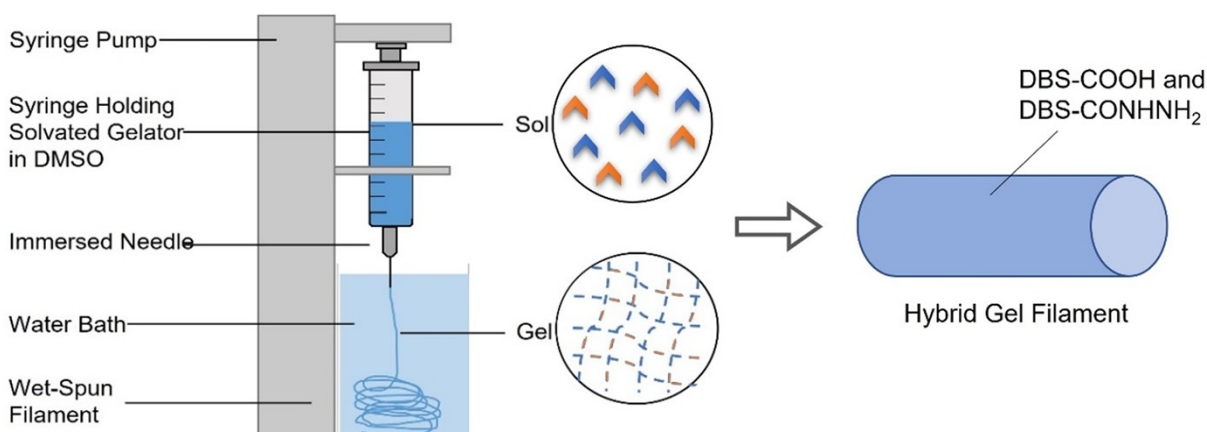
Figure S10. Schematic representation of the fabrication of DBS-COOH/DBS-CONHNH$_2$ hybrid gel filaments by wet spinning indicating random co-assembly mode.
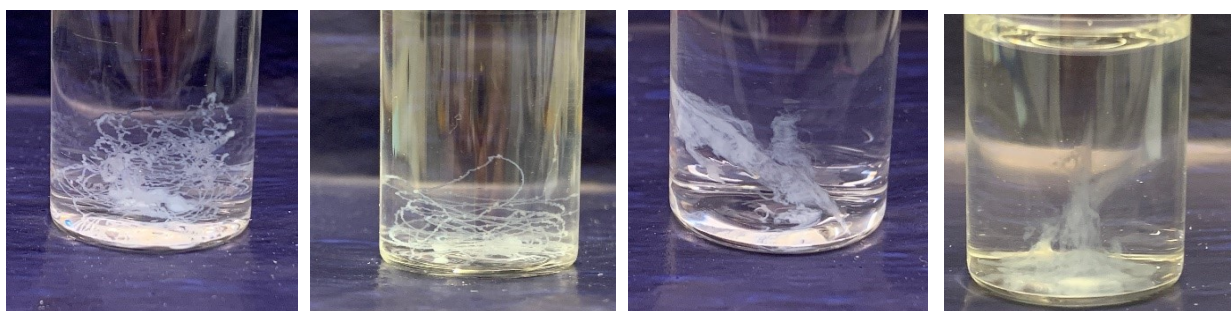
Figure S11. Photographic images of some of the possible outcomes of DBS-COOH/DBS-CONHNH$_2$ wet spinning: clog and filament (left), gel filament (middle left), gelation and filament (middle right) and gelation (right).
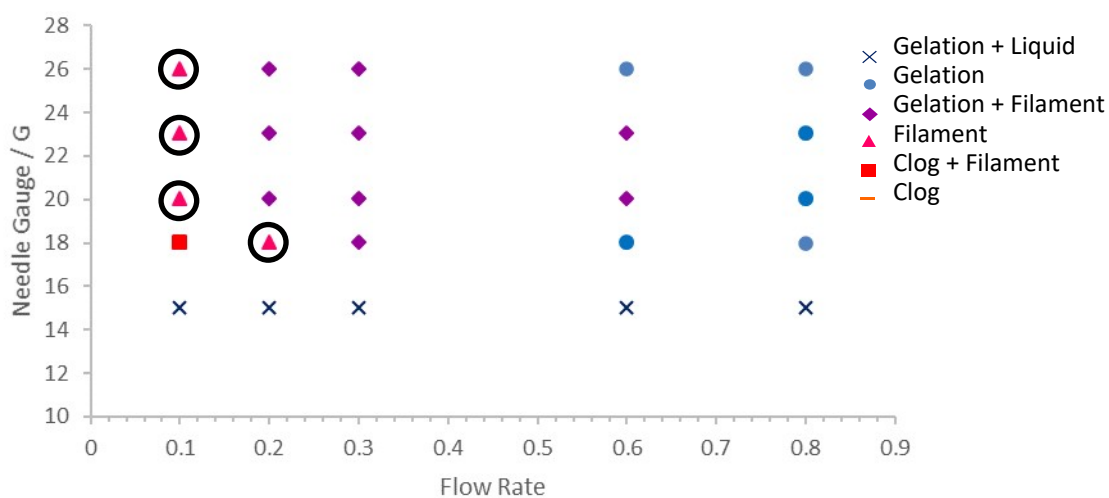
Figure S12. Outcomes of screening for optimal conditions for wet-spinning of 15 mg ml^{-1} of DBS-COOH/DBS-CONHNH$_2$ from DMSO into H$_2$O. Black circles highlight optimal conditions for filaments.
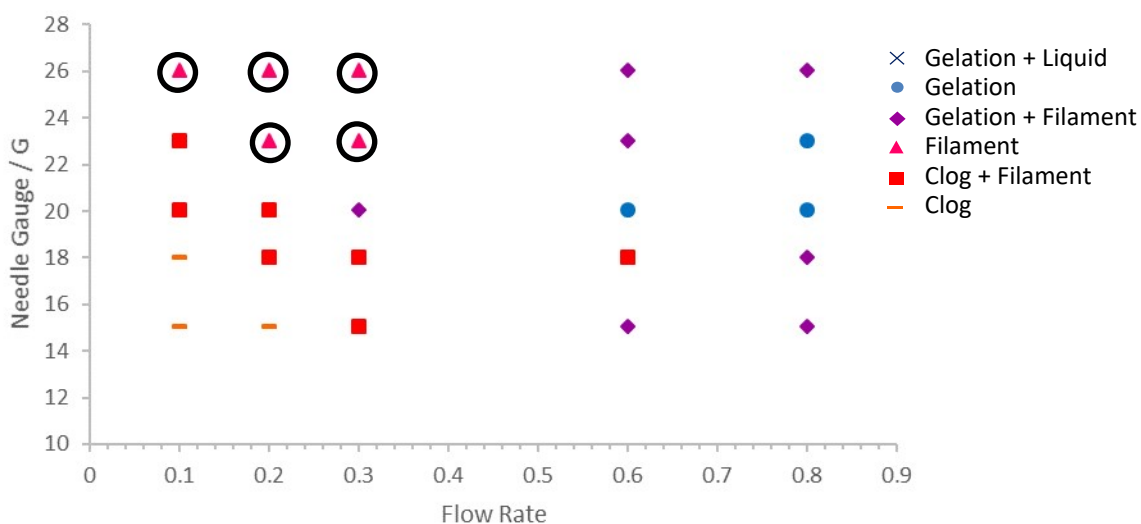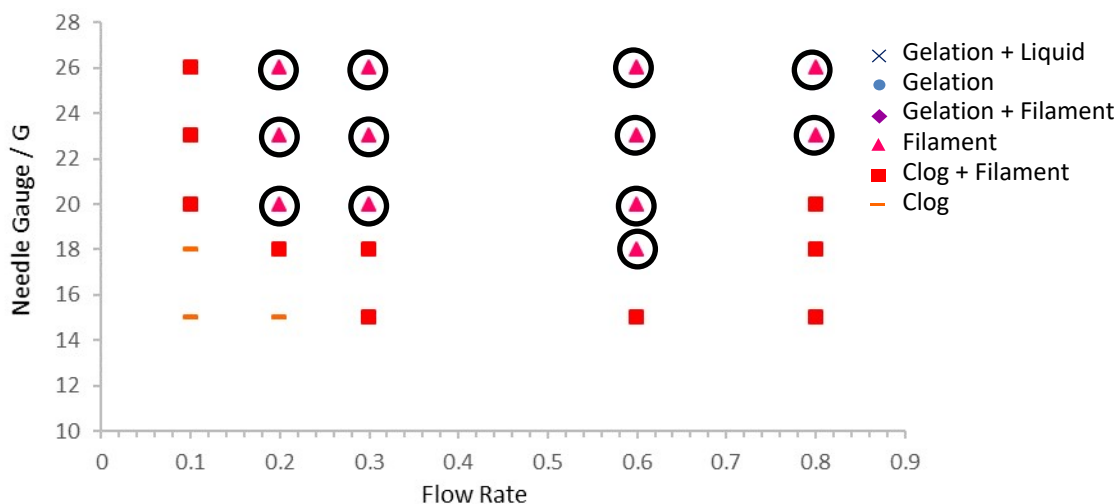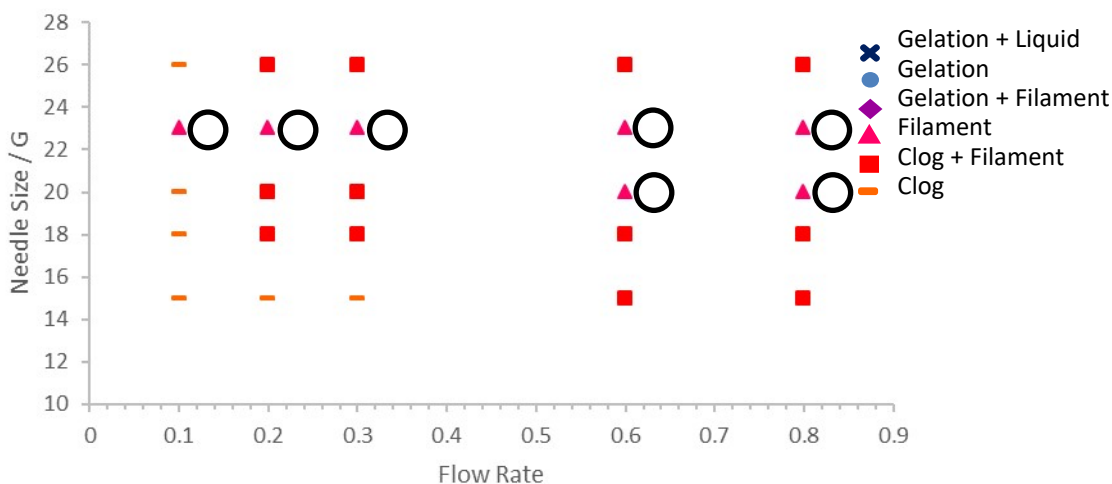

Figure S13. Outcomes of screening for optimal conditions for wet-spinning of 30 mg ml^{-1} of DBS-COOH/DBS-CONHNH$_2$ from DMSO into H$_2$O. Black circles highlight optimal conditions for filaments.

Figure S14. Outcomes of screening for optimal conditions for wet-spinning of 45 mg ml^{-1} of DBS-COOH/DBS-CONHNH$_2$ from DMSO into H$_2$O. Black circles highlight optimal conditions for filaments.

Figur e S15. Outcomes of screening for optimal conditions for wet-spinning of 60 mg ml^{-1} of DBS-COOH/DBS-CONHNH$_2$ from DMSO into H$_2$O. Black circles highlight optimal conditions for filaments.

Table S4. Multicomponent DBS-COOH/DBS-CONHNH$_2$ Gel Filament Diameters

Concentration of DBS-COOH / mg ml^{-1}	Flow Rate / µL/min	Needle Gauge / Inner Diameter				
		26 G	23 G	20 G	18 G	15 G
		Gel Filament Average Diameter / µm				
30	3.4	172	194	-	-	-
	6.7	203	142	-	-	-
	10.0	-	129	-	-	-
45	3.4	-	176	-	-	-
	6.7	220	171	-	-	-
	10.0	165	175	-	-	-
60	3.4	-	191	-	-	-
	6.7	-	225	183	-	-
	10.0	-	207	191	-	-

Table S5. T_{gel} values of gel filaments

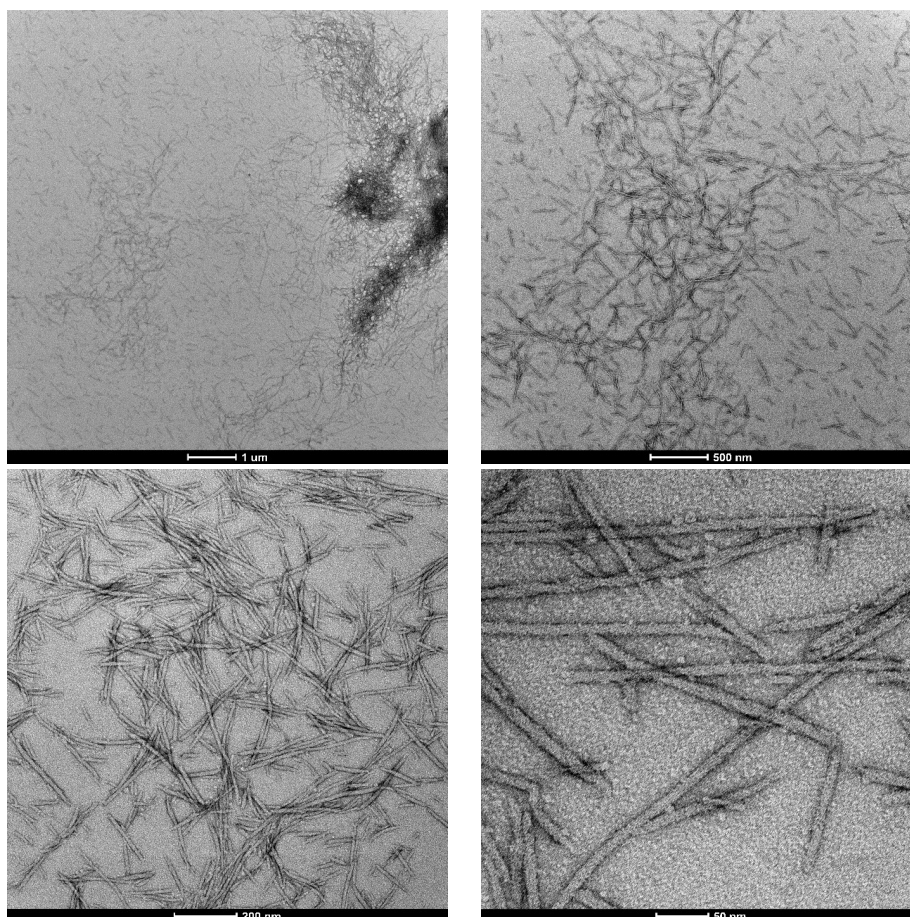| Gelator	Concentration / % wt/vol	T_{gel} / °C
DBS-COOH/DBS-CONHNH$_2$ (Multicomponent Gel)	1.5	87
	3.0	89
	4.5	94
	6.0	96
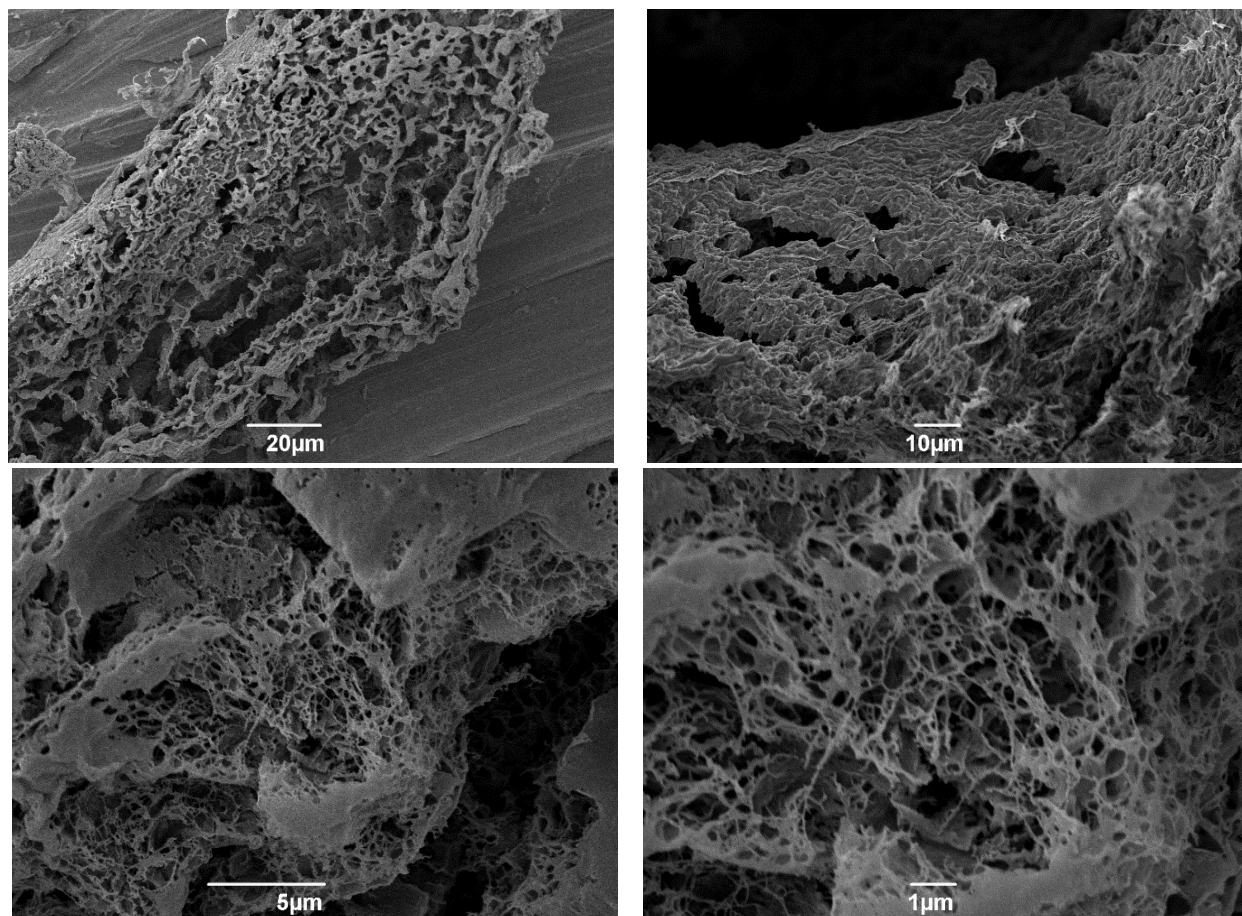
Figure S16. SEM images of DBS-COOH/DBS-CONHNH$_2$ multicomponent gel filament (4.5% wt/vol; 23 G blunt tip needle, 3.4 µL/min flow rate). Scale bars: 20 µm (top left), 10 µm (top right), 5 µm (bottom left) and 1 µm (bottom right).

Figure S17. TEM images of DBS-COOH/DBS-CONHNH$_2$ multicomponent gel filament (4.5% wt/vol; 23 G blunt tip needle, 3.4 µL/min flow rate). Scale bars: 1 µm (top left), 500 nm (top right), 200 nm (bottom left) and 50 nm (bottom right).

Figure S18. IR Spectra of DBS-COOH solid (blue), DBS-CONHNH$_2$ solid (green) and DBS-COOH/DBS-CONHNH$_2$ multicomponent gel filaments: 1.5% wt/vol (red), 3.0% wt/vol (grey), 4.5% wt/vol (yellow) and 6.0% wt/vol (purple).
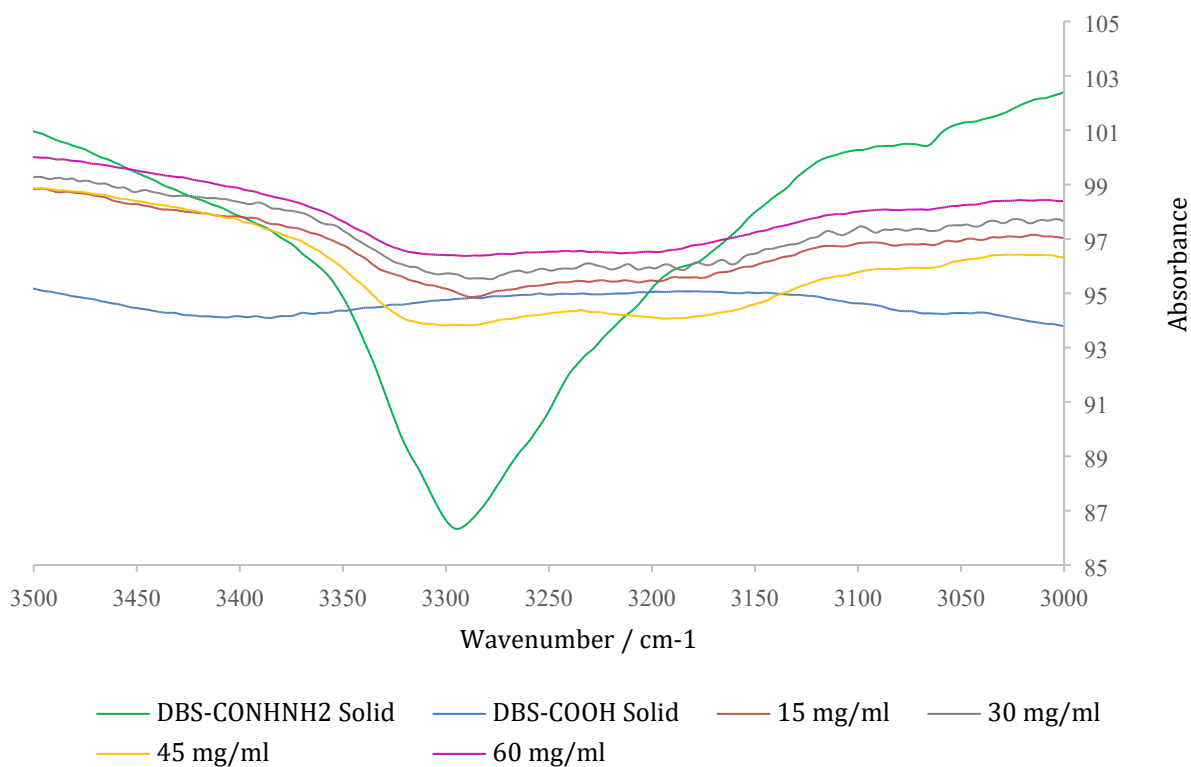
Figure S19. IR Spectra of N-H/O-H stretch region of: DBS-COOH solid (blue), DBS-CONHNH$_2$ solid (green) and DBS-COOH/DBS-CONHNH$_2$ multicomponent gel filaments: 1.5% wt/vol (red), 3.0% wt/vol (grey), 4.5% wt/vol (yellow) and 6.0% wt/vol (purple).
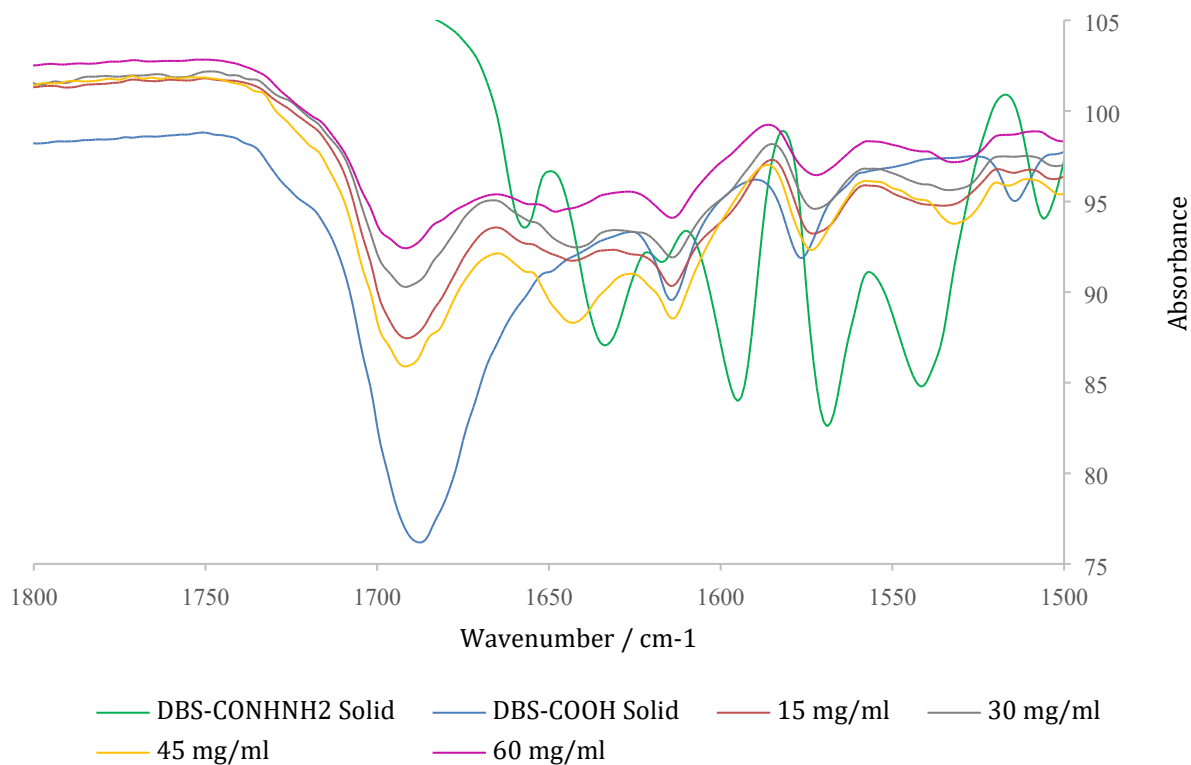
Figure S20. IR Spectra of C=O stretch region of: DBS-COOH solid (blue), DBS-CONHNH$_2$ solid (green) and DBS-COOH/DBS-CONHNH$_2$ multicomponent gel filaments: 1.5% wt/vol (red), 3.0% wt/vol (grey), 4.5% wt/vol (yellow) and 6.0% wt/vol (purple).

Table S6. Percentage of non-assembled gelator present in DBS-COOH/DBS-CONHNH$_2$ multicomponent system at different times on standing in D$_2$O

Gelator	Loading / % wt/vol	Non-Assembled Gelator / %				
		2 Hours in D$_2$O	1 Day in D$_2$O	2 Days in D$_2$O	3 Days in D$_2$O	4 Days in D$_2$O
DBS-COOH	1.50	5.60	9.60	2.40	4.40	6.00
	3.00	3.40	4.00	4.40	4.80	5.20
	4.50	0.53	4.27	8.00	9.60	7.87
	6.00	1.80	1.90	3.30	1.10	3.00
DBS-CONHNH$_2$	1.50	2.13	12.76	3.83	9.36	6.80
	3.00	2.98	5.11	4.68	5.32	5.73
	4.50	0.71	6.38	10.07	9.64	7.51
	6.00	1.06	4.15	3.94	1.70	3.50

Table S7. Percentage of non-assembled gelator present in DBS-COOH/DBS-CONHNH$_2$ multicomponent system at different times on addition of NaOD

Gelator	% Non-Assembled Gelator / %			
	Before NaOD Addition	5 mins with NaOD	2 hours with NaOD	> 12 hours with NaOD
DBS-COOH	0	> 99.5	> 99.5	> 99.5
DBS-CONHNH$_2$	0	52.3	60.4	66.2

Table S8. Percentage of non-assembled gelator present in DBS-CONHNH$_2$-only system at different times on addition of NaOD

Gelator	% Non-Assembled Gelator / %			
	Before NaOD Addition	5 mins with NaOD	2 hours with NaOD	> 12 hours with NaOD
DBS-CONHNH$_2$	0	12.7	14.1	16.6
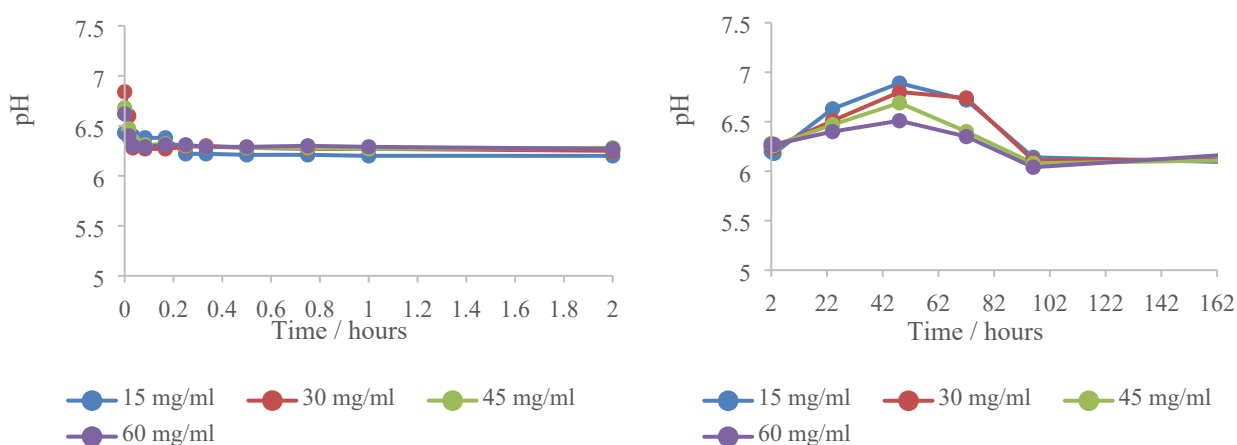
Figure S21. Change in the pH of the solution in which the DBS-COOH/DBS-CONHNH$_2$ multicomponent gel filaments (1.5, 3.0, 4.5 and 6.0% wt/vol) were self-assembled. Time = 0 is the initial point of self-assembly. (Left) Shorter periods of time, 0-2 h. (Right) Longer periods of time, 2-168 h. Lines between points are only intended to act as a guide to the eye.

S4   Preparation and characterisation of gel loaded with Au nanoparticles (NPs)

Table S9. Au (III) uptake calculated from UV-Vis spectroscopy of gel filaments

Gelator	Concentration / % wt/vol	Au (III) incorporated / μmol	Au (III) incorporated / μmol mL^{-1}	% Au (III) incorporated / %
DBS-COOH	1.5	5.03	100.6	25.15
	3.0	5.24	104.8	26.20
	4.5	5.03	100.6	25.15
DBS-COOH/DBS-CONHNH$_2$ (Multicomponent Gel)	1.5	5.73	114.6	28.65
	3.0	7.01	140.2	35.05
	4.5	8.20	164.0	41.00
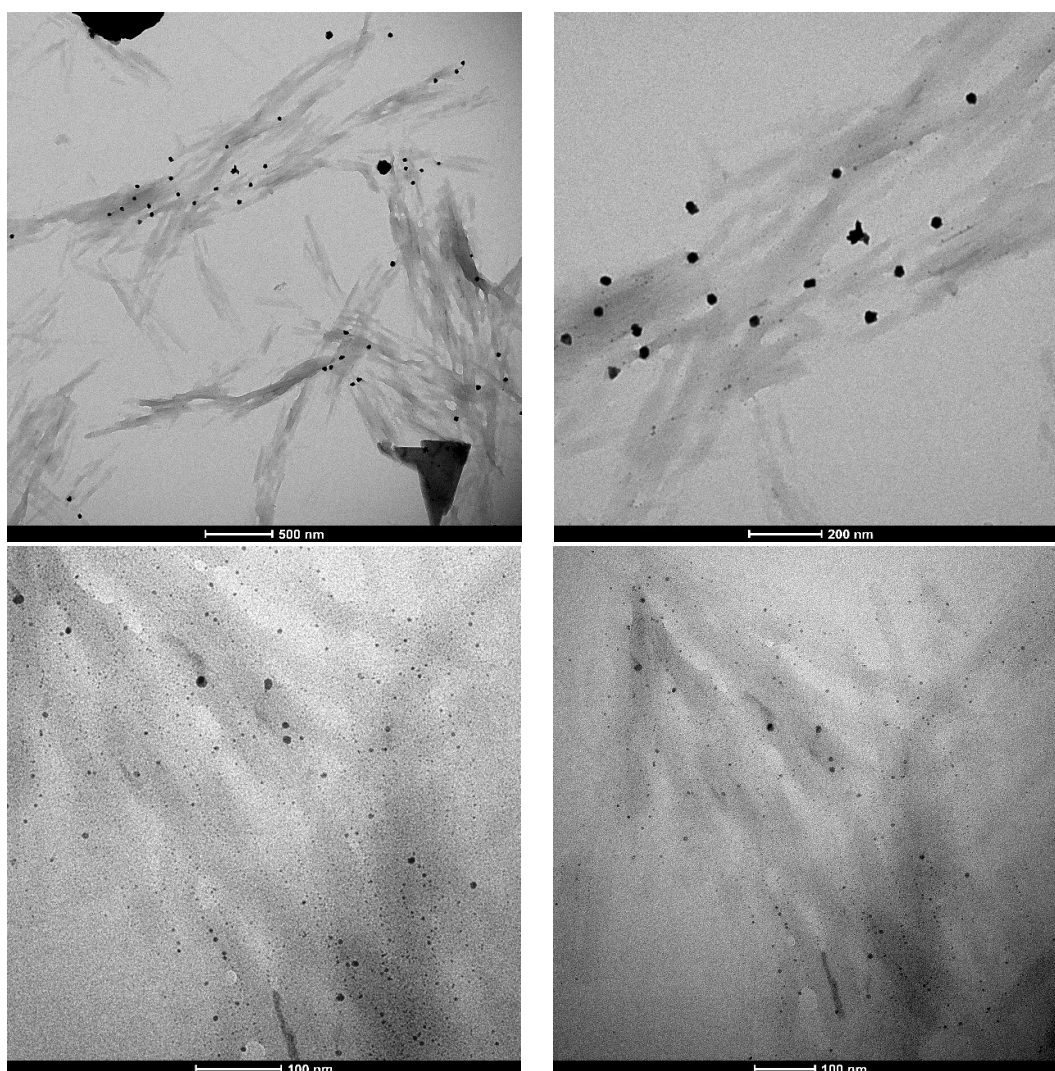
Figure S22. TEM images of DBS-COOH gel filament (4.5% wt/vol; 23 G blunt tip needle, 3.4 μL/min flow rate) loaded with Au (III). Scale bars: 500 nm (top left), 200 nm (top right), 100 nm (bottom left) and 100 nm (bottom right).
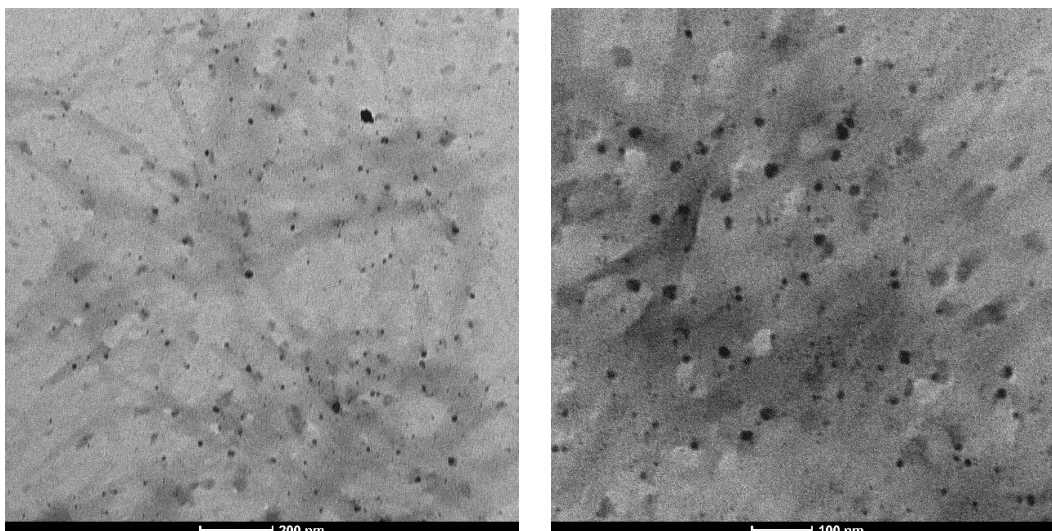
Figure S23. TEM images of DBS-COOH/DBS-CONHNH$_2$ multicomponent gel filament (4.5% wt/vol; 23 G blunt tip needle, 3.4 μL/min flow rate) loaded with Au (III). 200 nm (left) and 100 nm (right).

S5 NMR Spectra

DBS-COOH – 1.5% wt/vol
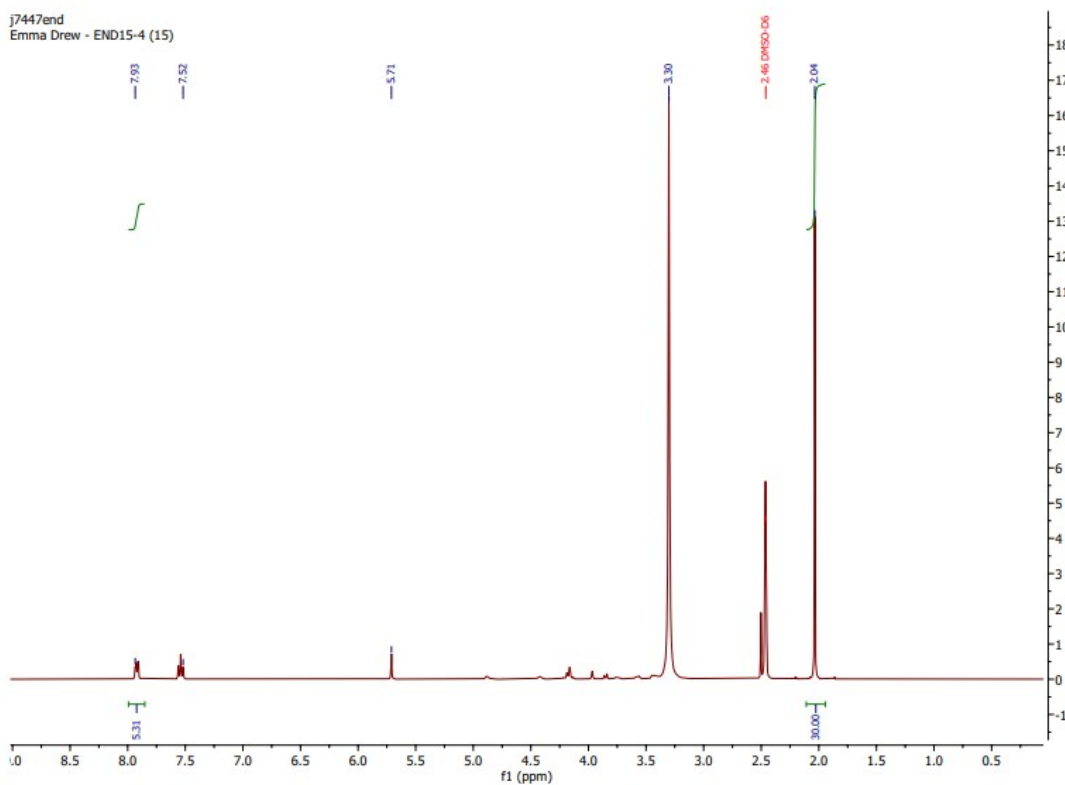
Figure S24. ^{1}H NMR spectrum to quantify the amount of gelator present - DBS-COOH (δ = 7.52) gel filament in DMSO-d^6 (300 MHz) with acetonitrile as internal standard (δ = 2.03 ppm)
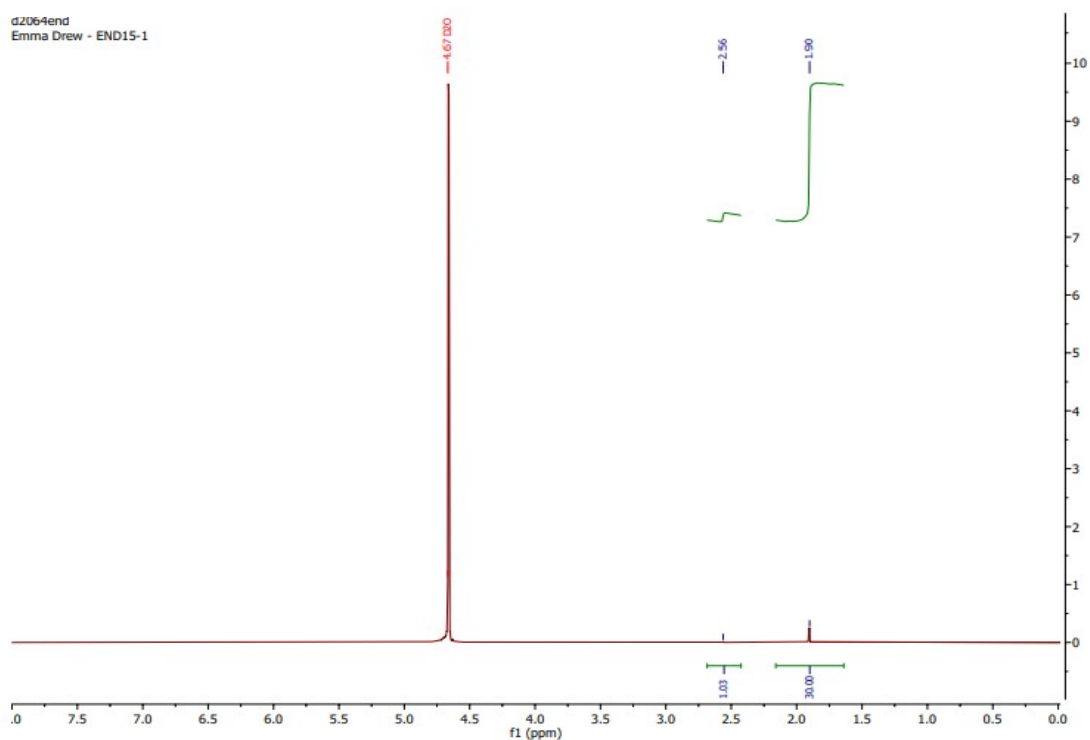
DBS-COOH – 3.0% wt/vol
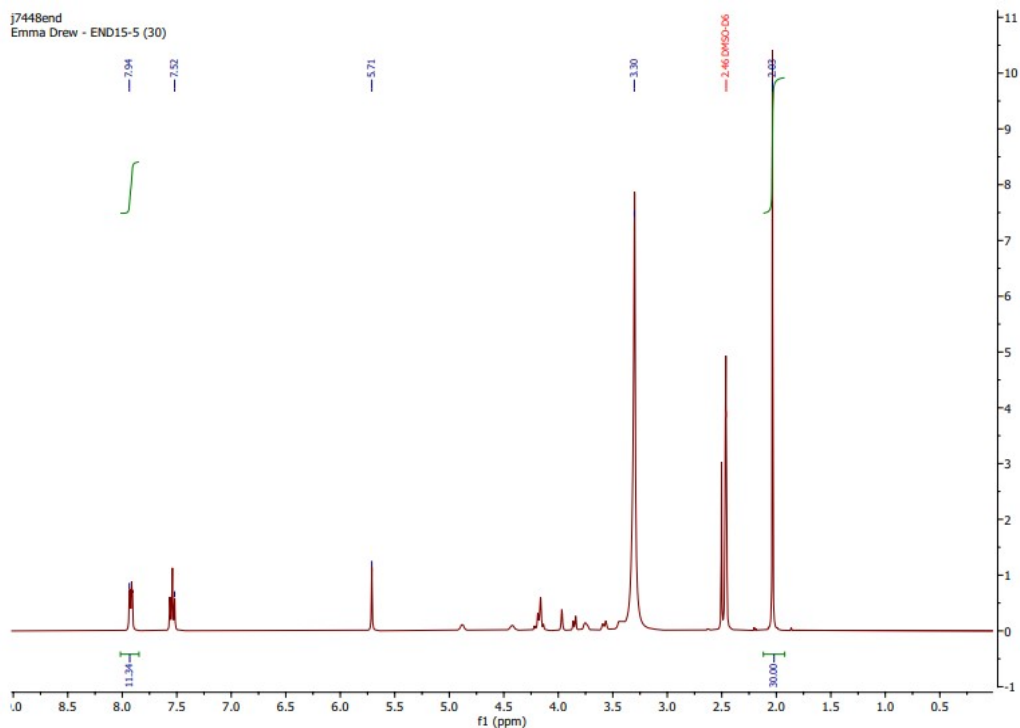
Figure S25. ¹H NMR spectrum to quantify the amount of gelator present - DBS-COOH (δ = 7.52) gel filament in DMSO-d⁶ (300 MHz) with acetonitrile as internal standard (δ = 2.03 ppm)
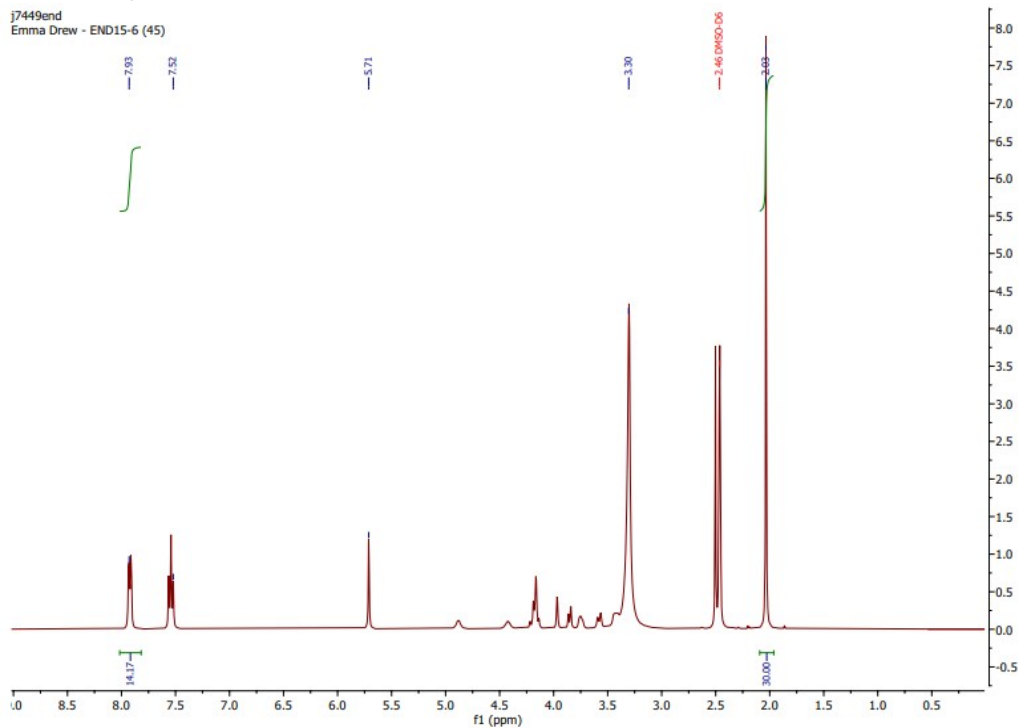
DBS-COOH – 4.5% wt/vol
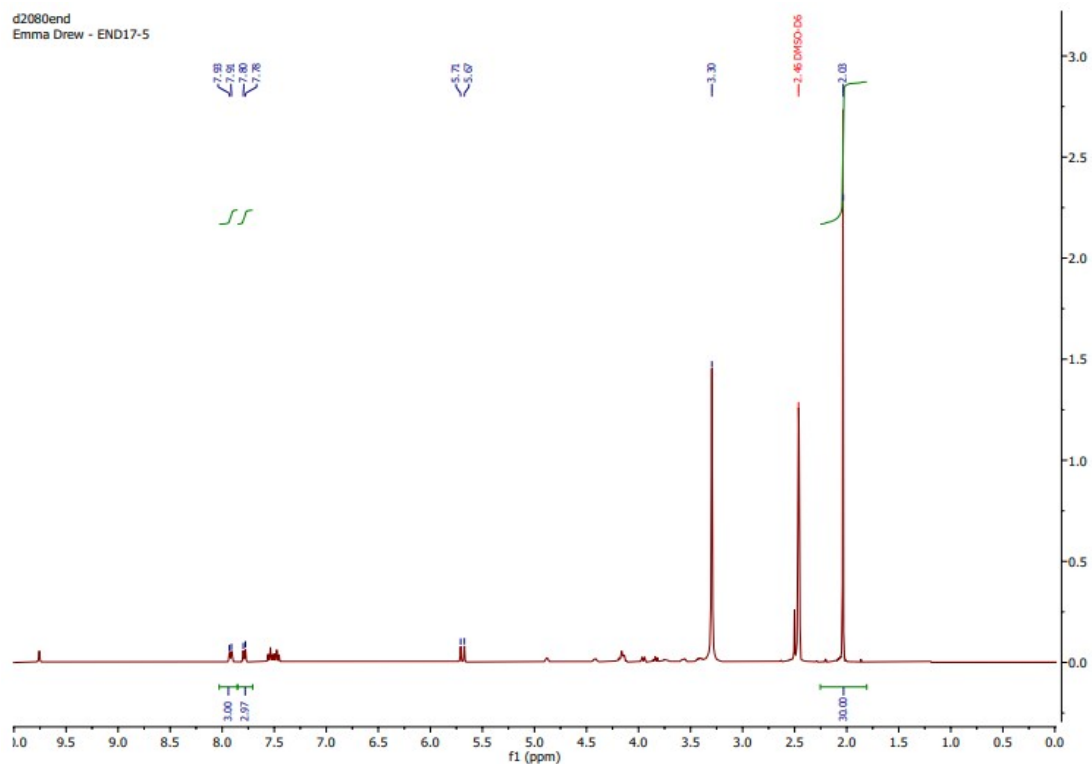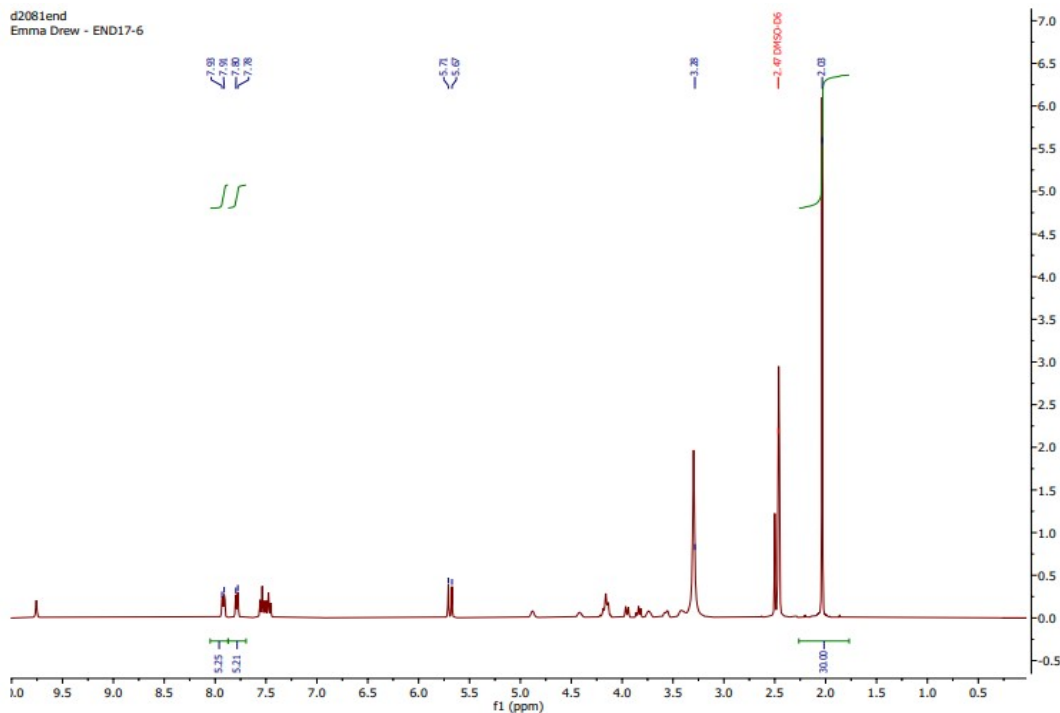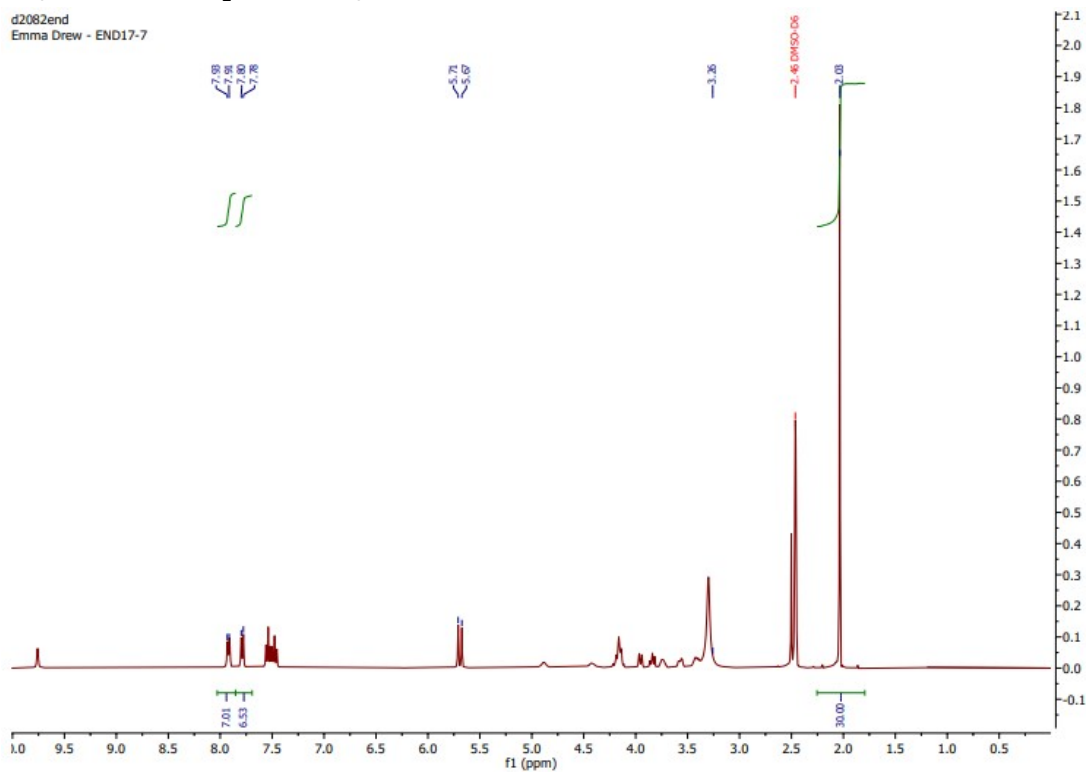

Figure S26. ¹H NMR spectrum to quantify the amount of gelator present - DBS-COOH (δ = 7.52) gel filament in DMSO-d⁶ (300 MHz) with acetonitrile as internal standard (δ = 2.03 ppm)

DBS-COOH – 1.5% wt/vol

Figure S27. ^{1}H NMR spectra to quantify the amount of residual DMSO in a DBS-COOH gel filament in D$_2$O (300 MHz) - DMSO (δ = 2.56) with acetonitrile (δ = 2.03 ppm).

DBS-COOH – 3.0% wt/vol
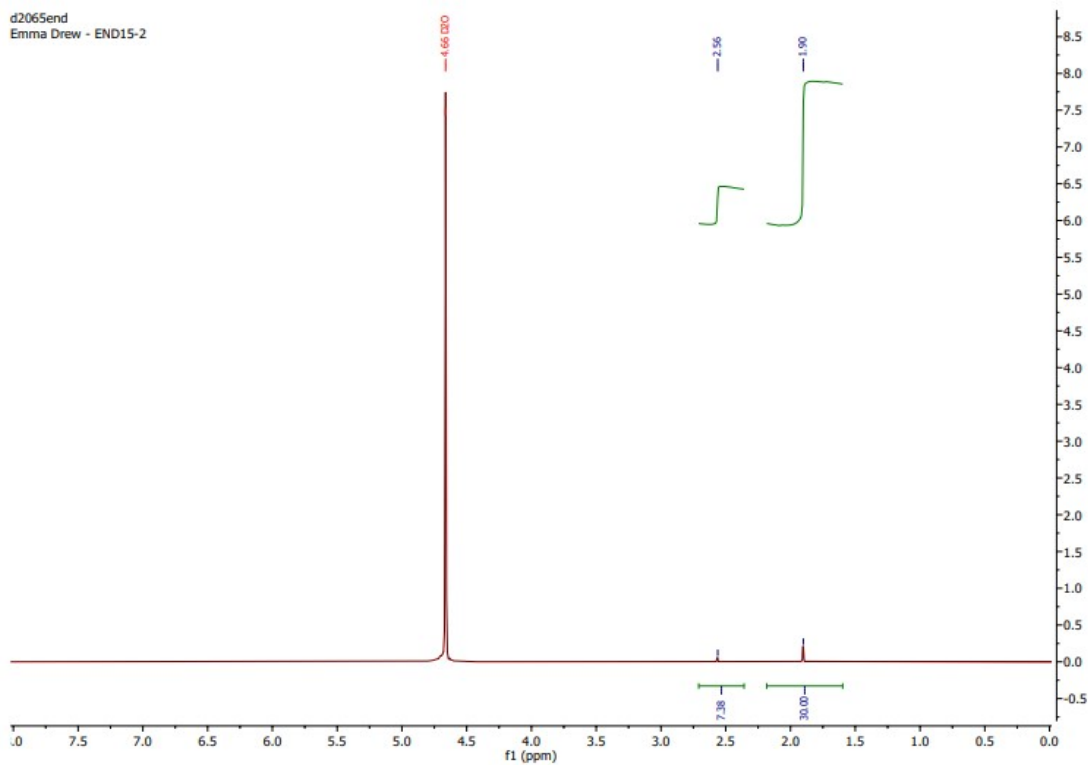
Figure S28. ^{1}H NMR spectra to quantify the amount of residual DMSO in a DBS-COOH gel filament in D$_2$O (300 MHz) - DMSO (δ = 2.56) with acetonitrile (δ = 2.03 ppm).
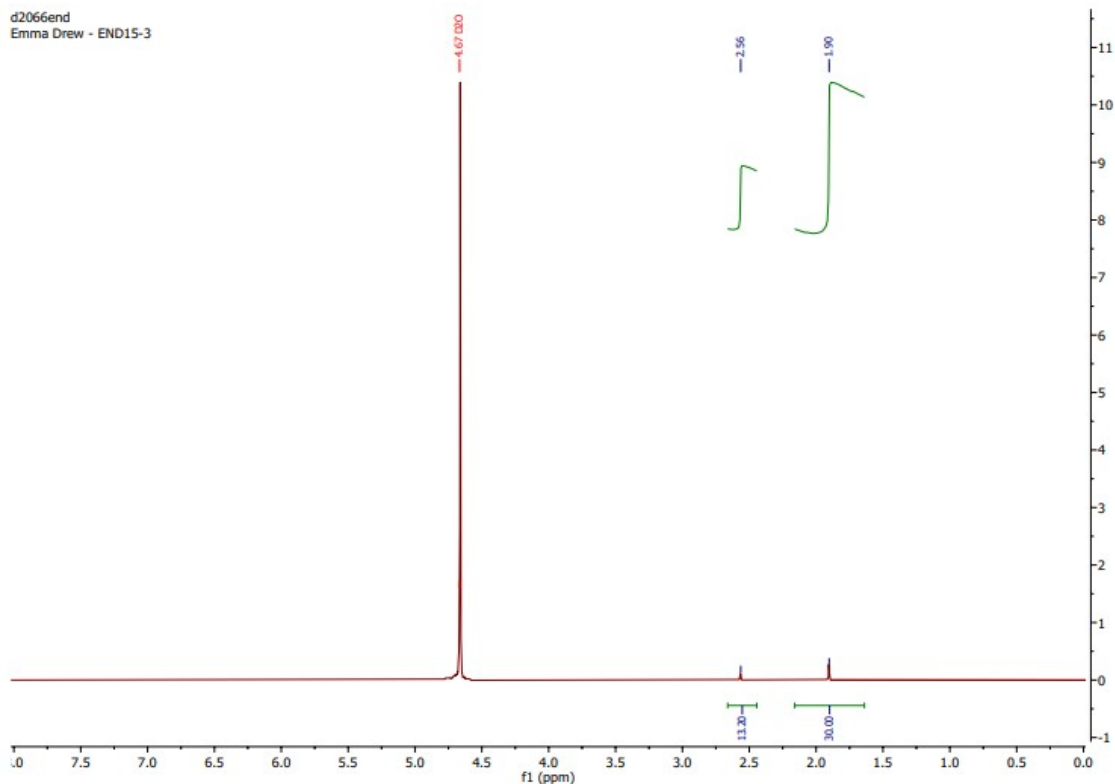
DBS-COOH – 4.5% wt/vol

Figure S29. ^{1}H NMR spectra to quantify the amount of residual DMSO in a DBS-COOH gel filament in D$_2$O (300 MHz) - DMSO (δ = 2.56) with acetonitrile (δ = 2.03 ppm).
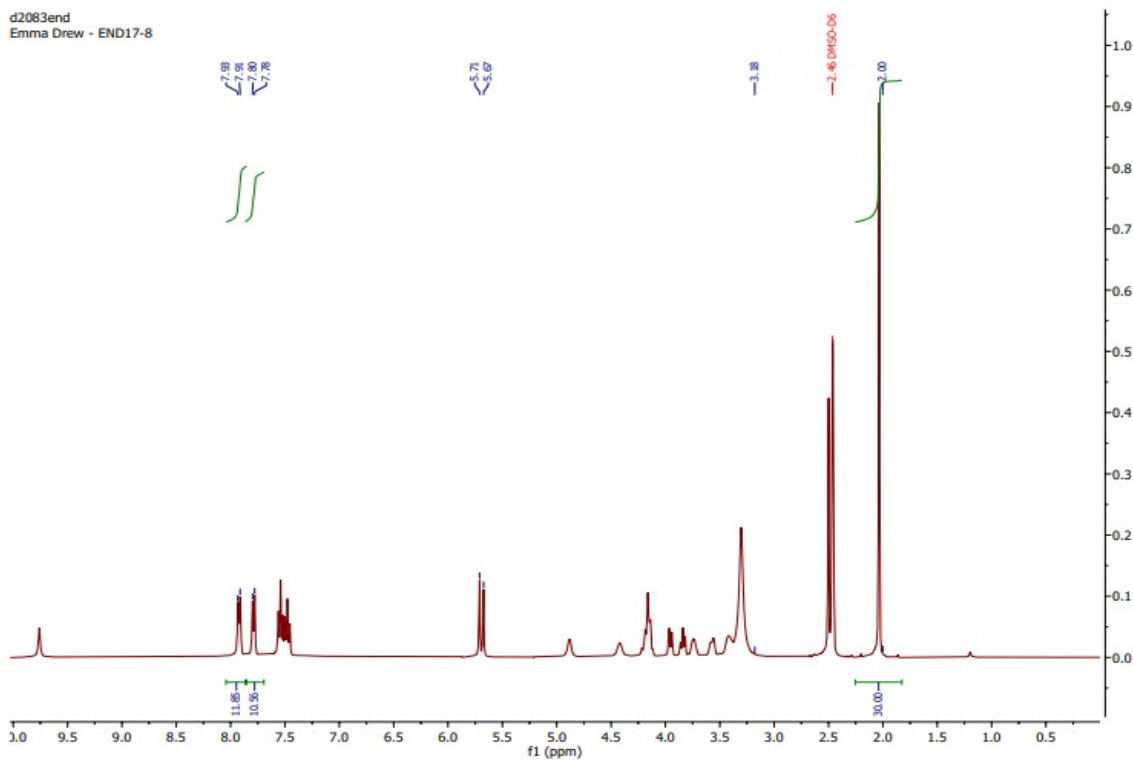
DBS-COOH/DBS-CONHNH$_2$ – 1.5% wt/vol

Figure S30. ^{1}H NMR spectra to quantify the amount of gelator present - DBS-COOH/DBS-CONHNH$_2$ (δ = 7.52) gel filament in DMSO-d^6 (300 MHz) with acetonitrile (δ = 2.03 ppm)
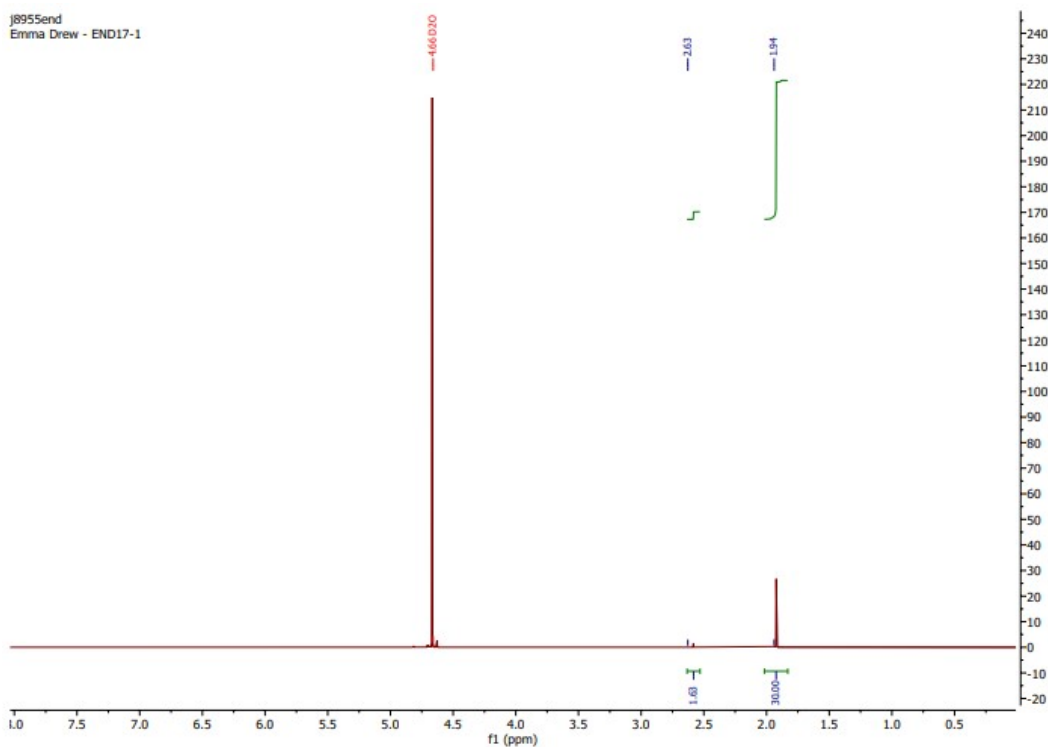
DBS-COOH/DBS-CONHNH₂ – 3.0% wt/vol

Figure S31. ¹H NMR spectra to quantify the amount of gelator present - DBS-COOH/DBS-CONHNH₂ (δ = 7.52) gel filament in DMSO-d⁶ (300 MHz) with acetonitrile (δ = 2.03 ppm)

DBS-COOH/DBS-CONHNH₂ – 4.5% wt/vol

Figure S32. ¹H NMR spectra to quantify the amount of gelator present - DBS-COOH/DBS-CONHNH₂ (δ = 7.52) gel filament in DMSO-d⁶ (300 MHz) with acetonitrile (δ = 2.03 ppm)

DBS-COOH/DBS-CONHNH₂ – 6.0% wt/vol

Figure S33. ^{1}H NMR spectra to quantify the amount of gelator present - DBS-COOH/DBS-CONHNH₂ (δ = 7.52) gel filament in DMSO-d^6 (300 MHz) with acetonitrile (δ = 2.03 ppm).
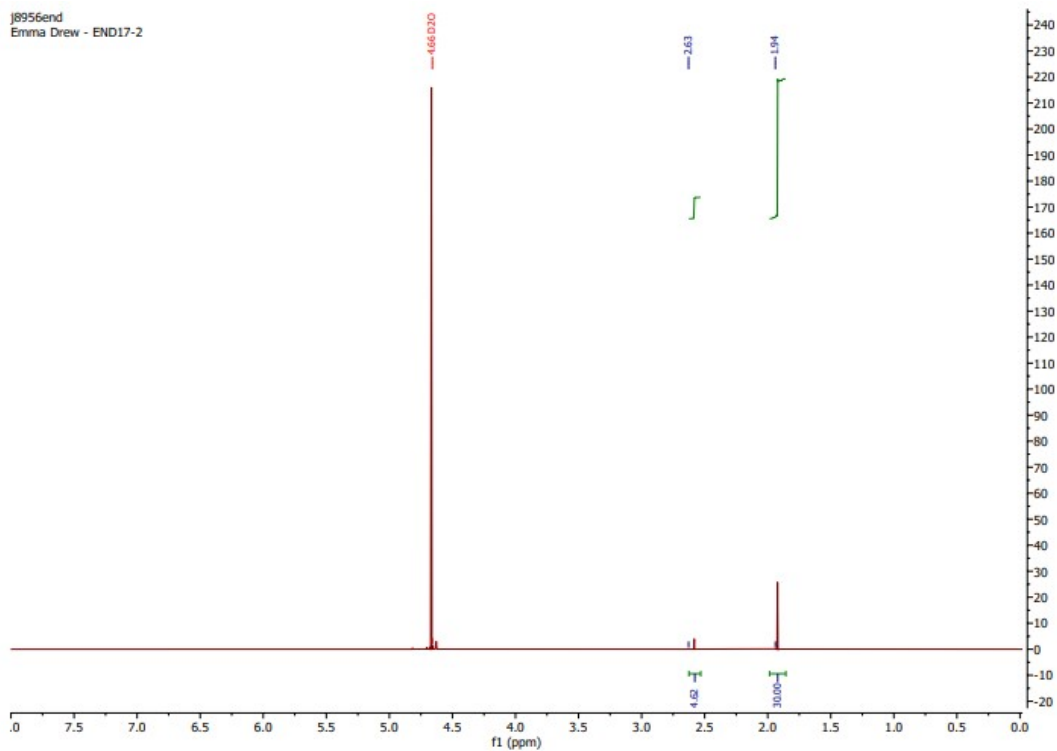
DBS-COOH/DBS-CONHNH₂ – 1.5% wt/vol

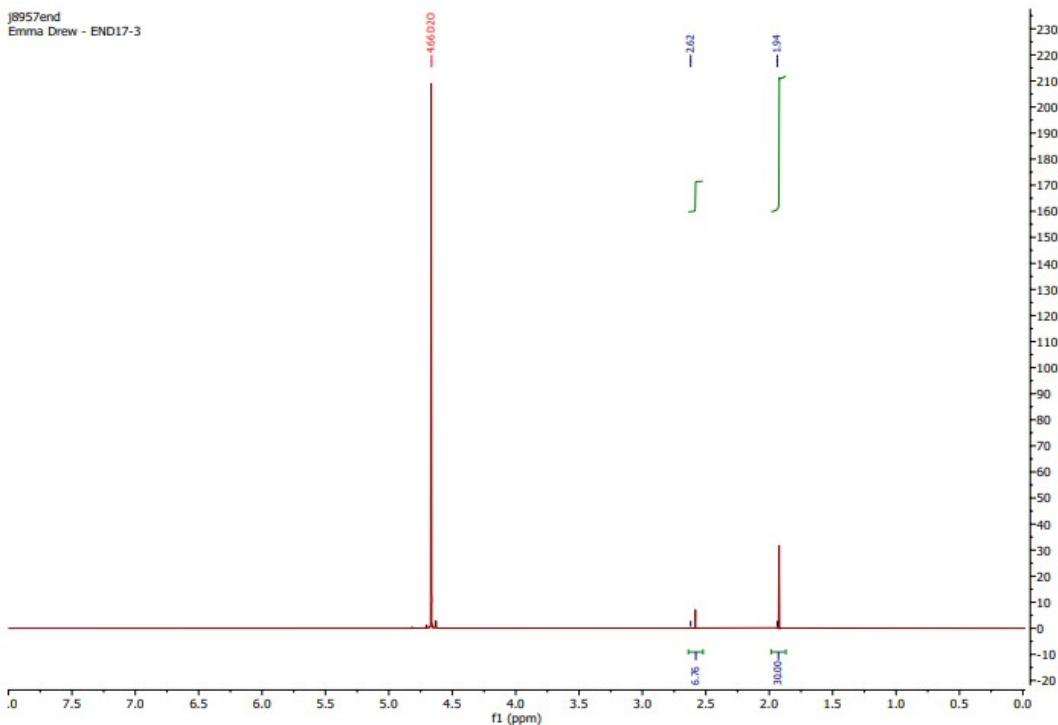
Figure S34. ^{1}H NMR spectra to quantify the amount of residual DMSO – DBS-COOH/DBS-CONHNH₂ gel filament in D₂O (300 MHz) - DMSO (δ = 2.63) with acetonitrile (δ = 1.94 ppm).

DBS-COOH/DBS-CONHNH$_2$ – 3.0% wt/vol
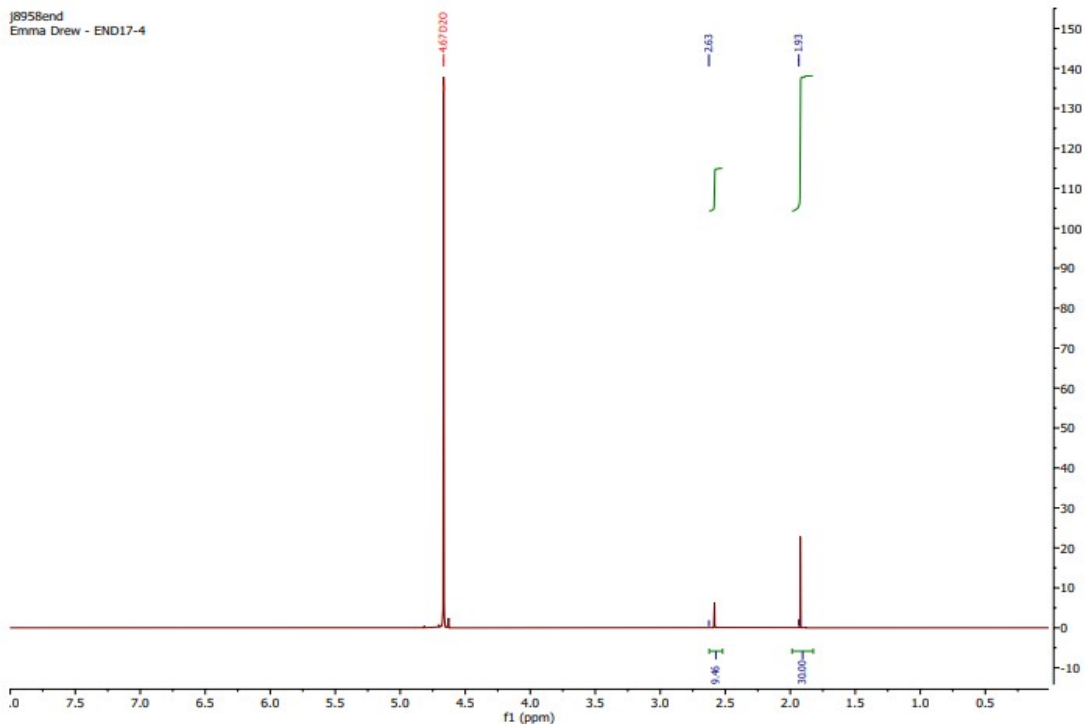

Figure S35. ^{1}H NMR spectra to quantify the amount of residual DMSO – DBS-COOH/DBS-CONHNH$_2$ gel filament in D$_2$O (300 MHz) - DMSO (δ = 2.63) with acetonitrile (δ = 1.94 ppm).

DBS-COOH/DBS-CONHNH$_2$ – 4.5% wt/vol

Figure S36. ^{1}H NMR spectra to quantify the amount of residual DMSO – DBS-COOH/DBS-CONHNH$_2$ gel filament in D$_2$O (300 MHz) - DMSO (δ = 2.63) with acetonitrile (δ = 1.94 ppm).

DBS-COOH/DBS-CONHNH₂ – 6.0% wt/vol

Figure S37. ¹H NMR spectra to quantify the amount of residual DMSO – DBS-COOH/DBS-CONHNH₂ gel filament in D_2O (300 MHz) - DMSO (δ = 2.63) with acetonitrile (δ = 1.94 ppm).

5.1 Example Spectra of Responsive Dynamic Experiments
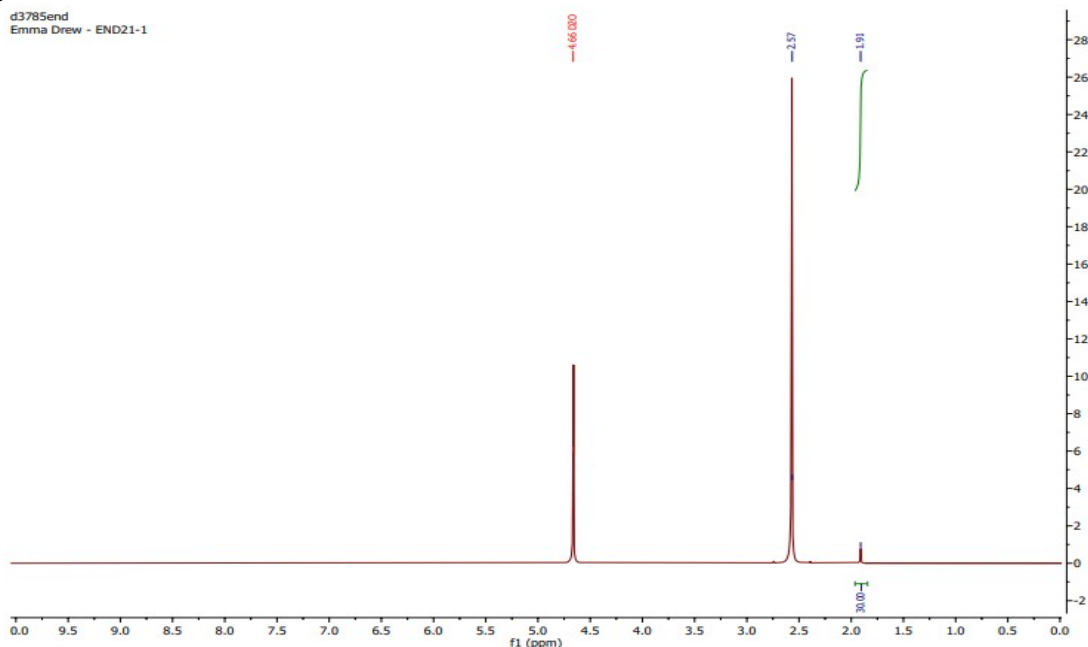
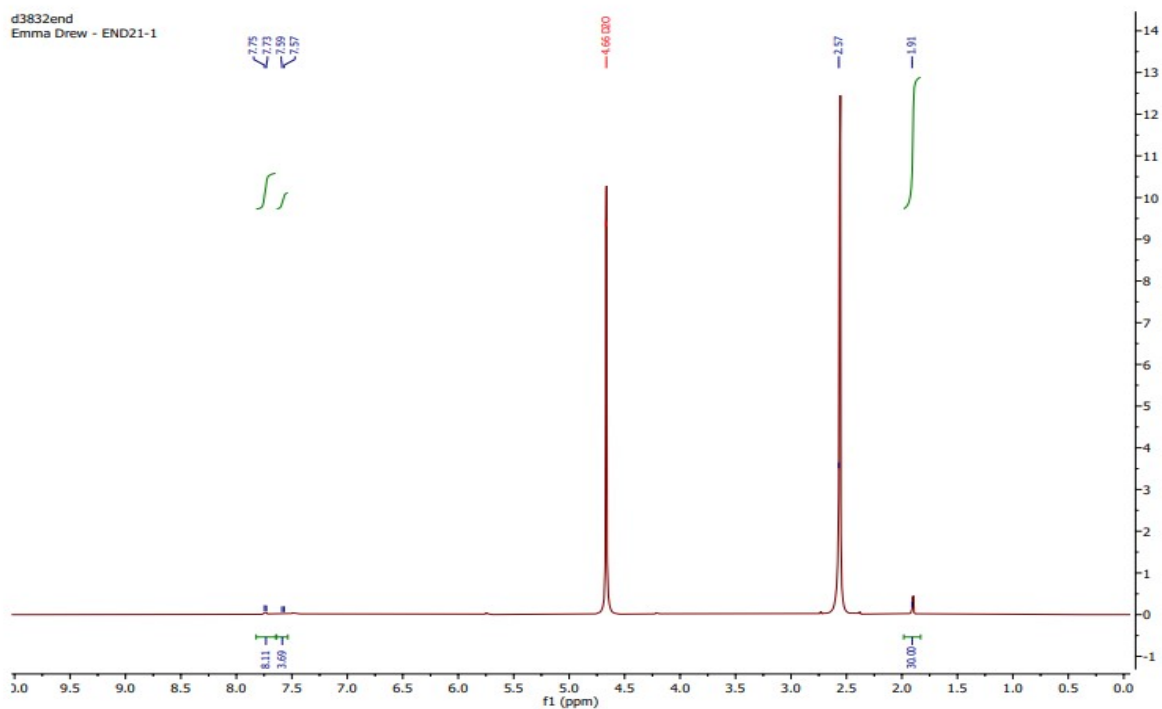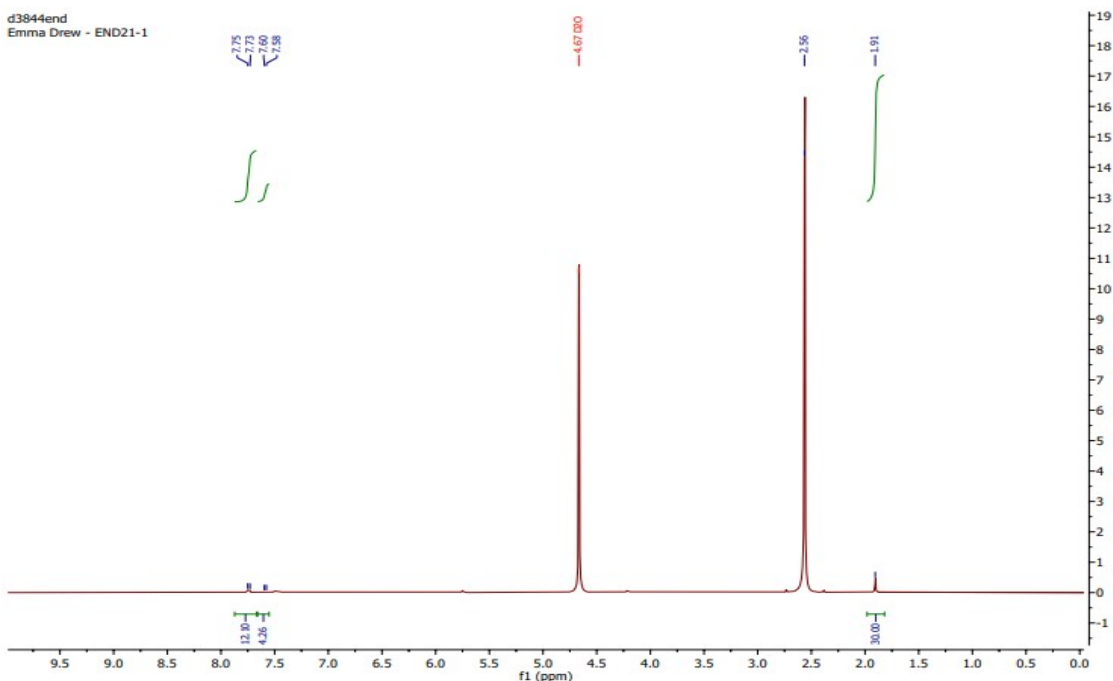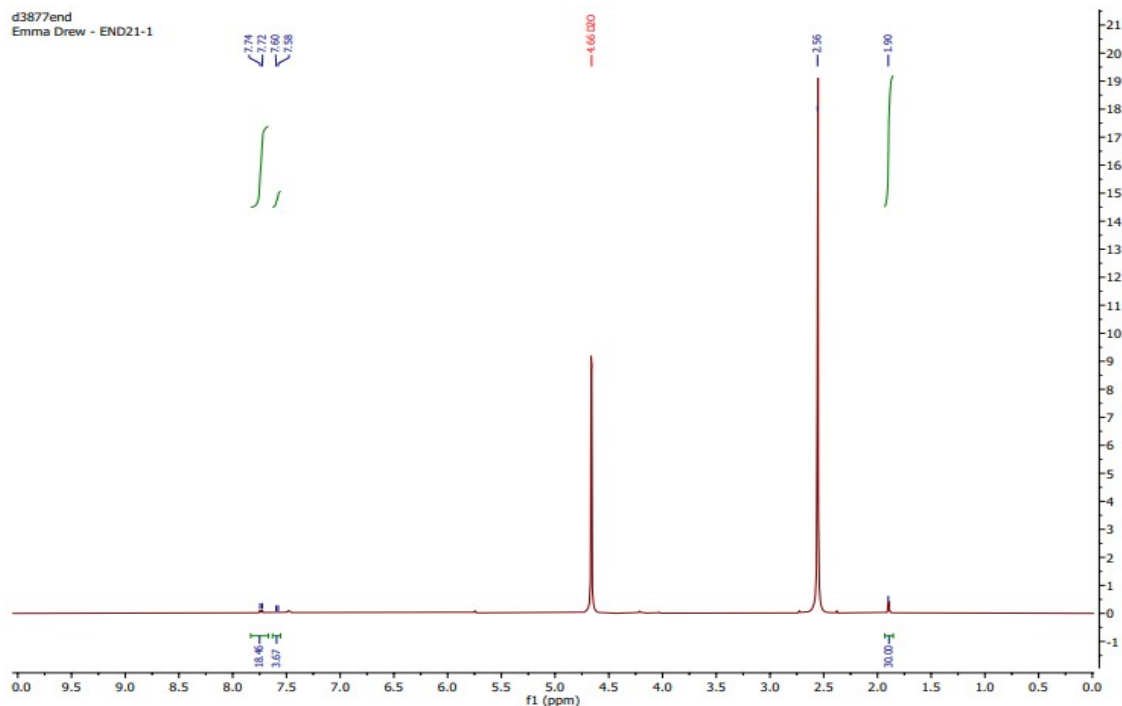**Testing Before addition of NaOD**

Figure S38. ¹H NMR spectra to quantify selective disassembly of DBS-COOH and DBS-CONHNH₂ in basic conditions - DBS-COOH (δ = 7.74 ppm) and DBS-CONHNH₂ (δ = 7.59 ppm) gel filament in D_2O (300 MHz) with acetonitrile (δ = 1.91 ppm).

5 minutes after addition of NaOD

Figure S39. ^{1}H NMR spectra to quantify selective disassembly of DBS-COOH and DBS-CONHNH$_2$ in basic conditions - DBS-COOH (δ = 7.74 ppm) and DBS-CONHNH$_2$ (δ = 7.59 ppm) gel filament in D$_2$O (300 MHz) with acetonitrile (δ = 1.91 ppm).

2 hours after addition of NaOD

Figure S40. ^{1}H NMR spectra to quantify selective disassembly of DBS-COOH and DBS-CONHNH$_2$ in basic conditions - DBS-COOH (δ = 7.74 ppm) and DBS-CONHNH$_2$ (δ = 7.59 ppm) gel filament in D$_2$O (300 MHz) with acetonitrile (δ = 1.91 ppm).

>12 hours after addition of NaOD

Figure S41. ^{1}H NMR spectra to quantify selective disassembly of DBS-COOH and DBS-CONHNH$_2$ in basic conditions - DBS-COOH (δ = 7.74 ppm) and DBS-CONHNH$_2$ (δ = 7.59 ppm) gel filament in D$_2$O (300 MHz) with acetonitrile (δ = 1.91 ppm).
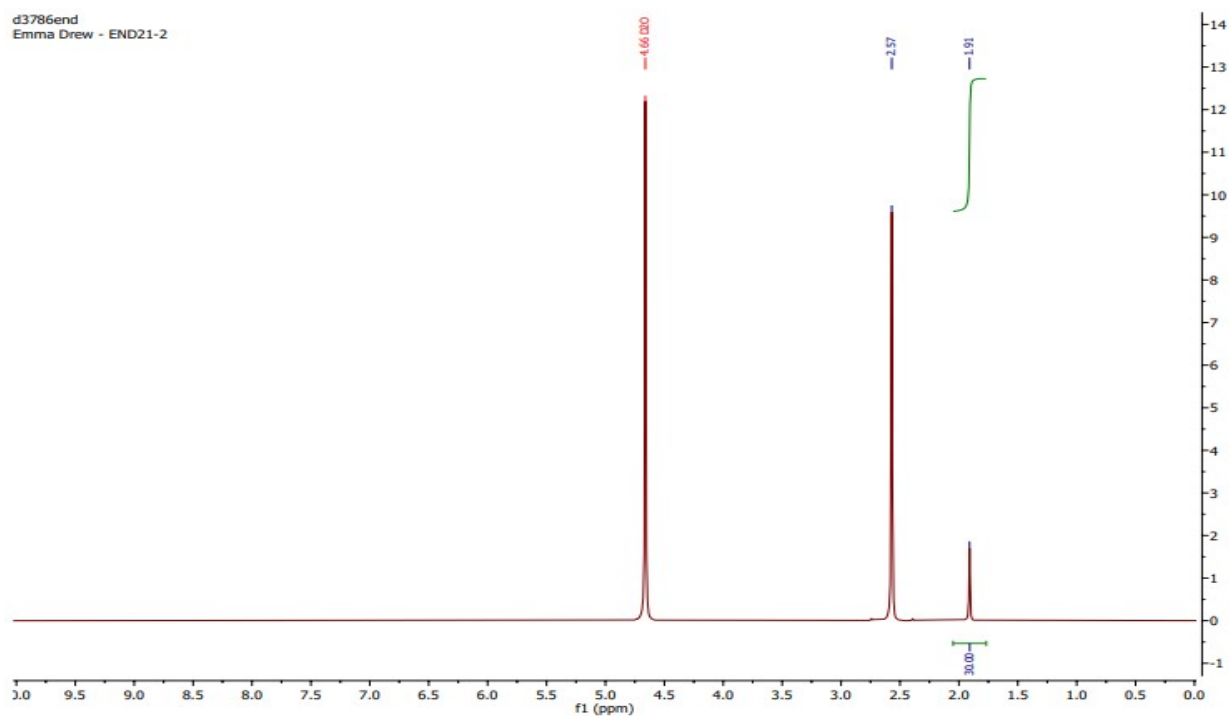
Before addition of NaOD

Figure S42. ^{1}H NMR spectra to quantify selective disassembly of DBS-CONHNH$_2$ in basic conditions - DBS-CONHNH$_2$ (δ = 7.59 ppm) gel filament in D$_2$O (300 MHz) with acetonitrile (δ = 1.91 ppm).
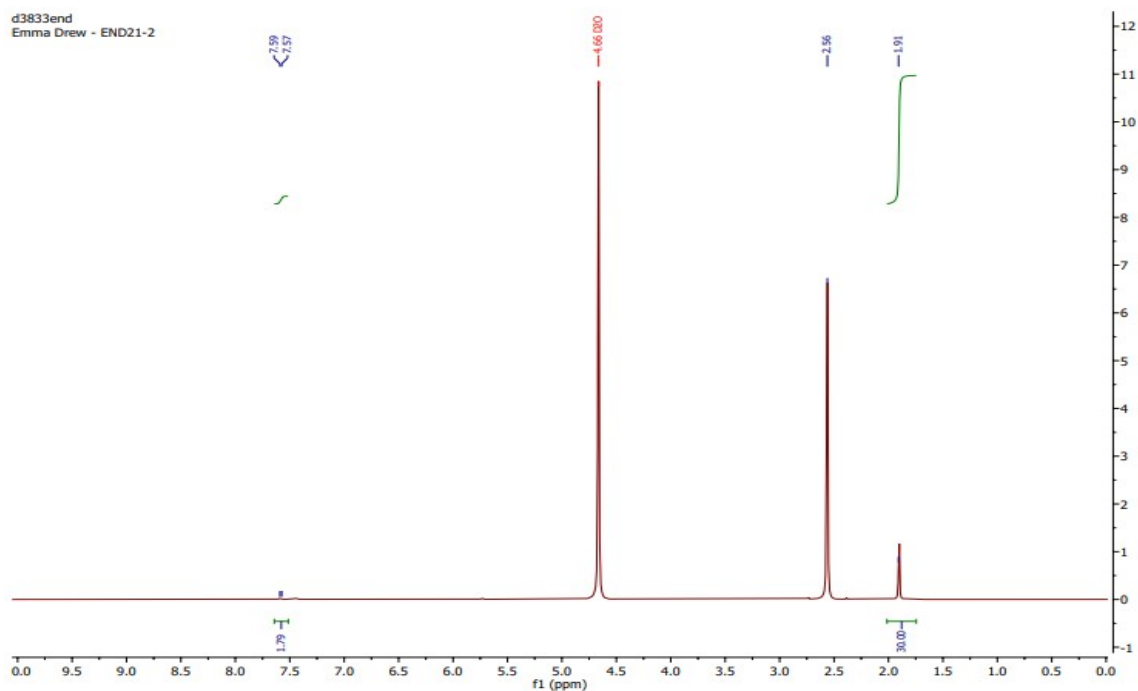
5 minutes after addition of NaOD

Figure S43. ^{1}H NMR spectra to quantify selective disassembly of /DBS-CONHNH$_2$ in basic conditions - DBS-CONHNH$_2$ (δ = 7.59 ppm) gel filament in D$_2$O (300 MHz) with acetonitrile (δ = 1.91 ppm).

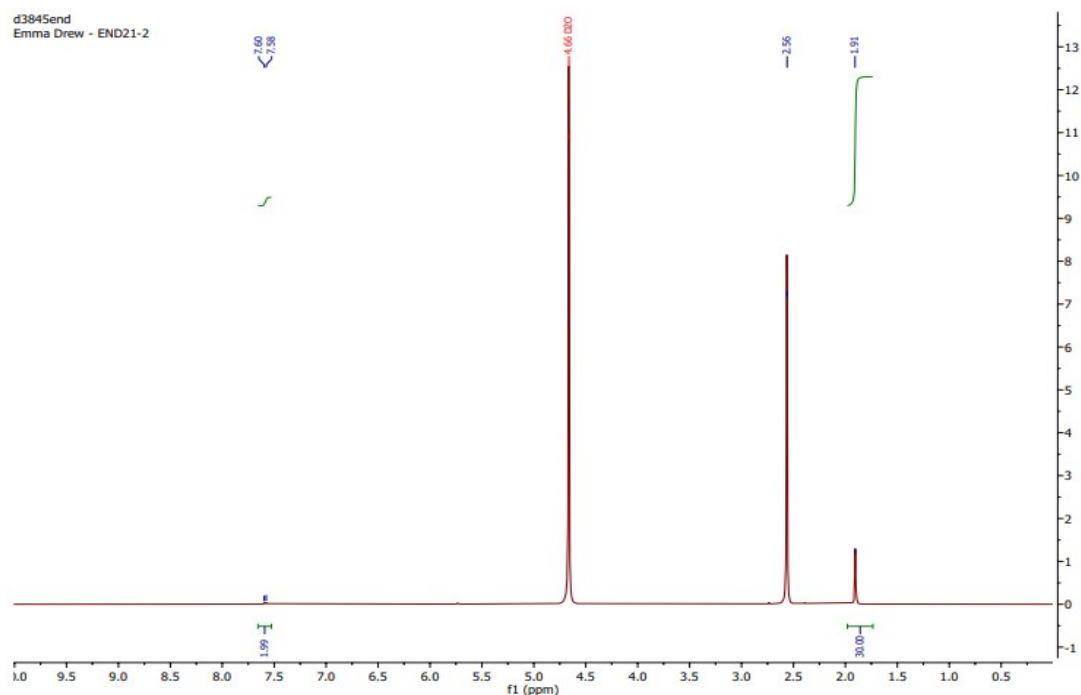**2 hours after addition of NaOD**

Figure S44. ^{1}H NMR spectra to quantify selective disassembly of DBS-CONHNH$_2$ in basic conditions - DBS-CONHNH$_2$ (δ = 7.59 ppm) gel filament in D$_2$O (300 MHz) with acetonitrile (δ = 1.91 ppm).
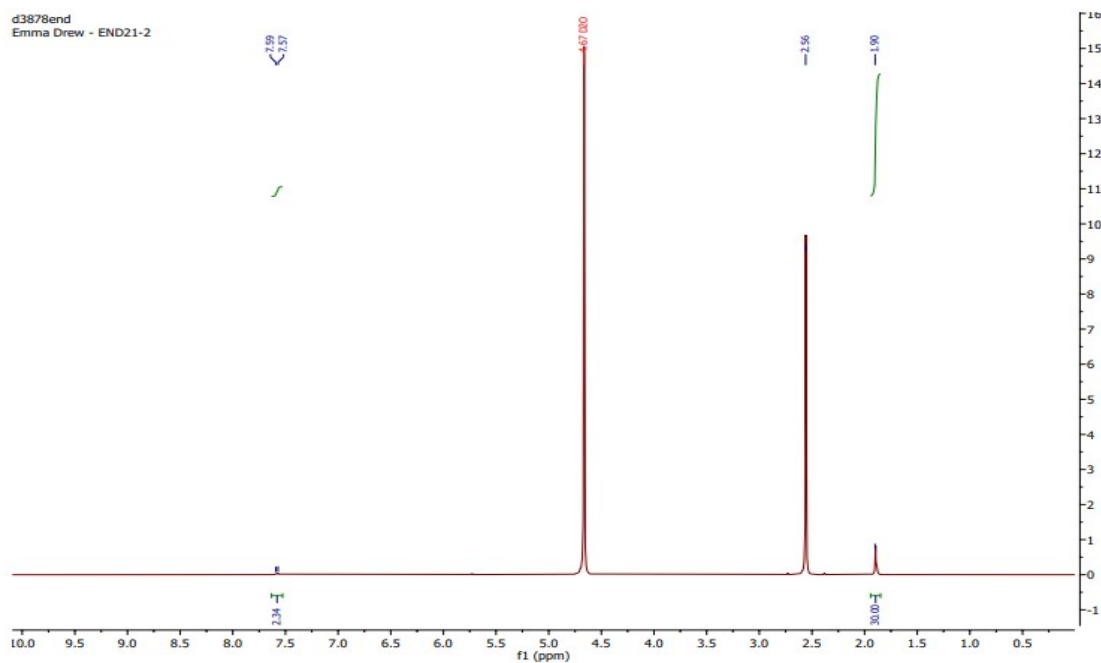
>12 hours after addition of NaOD

Figure S45. ^1H NMR spectra to quantify selective disassembly of DBS-CONHNH$_2$ in basic conditions - DBS-CONHNH$_2$ (δ = 7.59 ppm) gel filament in D$_2$O (300 MHz) with acetonitrile (δ = 1.91 ppm).

S6   References

[1] (*a*) B. O. Okesola and D. K. Smith*, Chem. Commun.*, 2013, **49**, 11164-11166. (*b*) D. J. Cornwell, B. O. Okesola and D. K. Smith, *Soft Matter*, 2013, **9**, 8730-8736. (*c*) P. R. A. Chivers, J. A. Kelly, M. J. S. Hill and D. K. Smith, *React. Chem. Eng.*, 2020, **5**, 1112-1117.