

Electronic Supplementary Information

Squaramide-based supramolecular gels for the removal of organic dyes from water matrices

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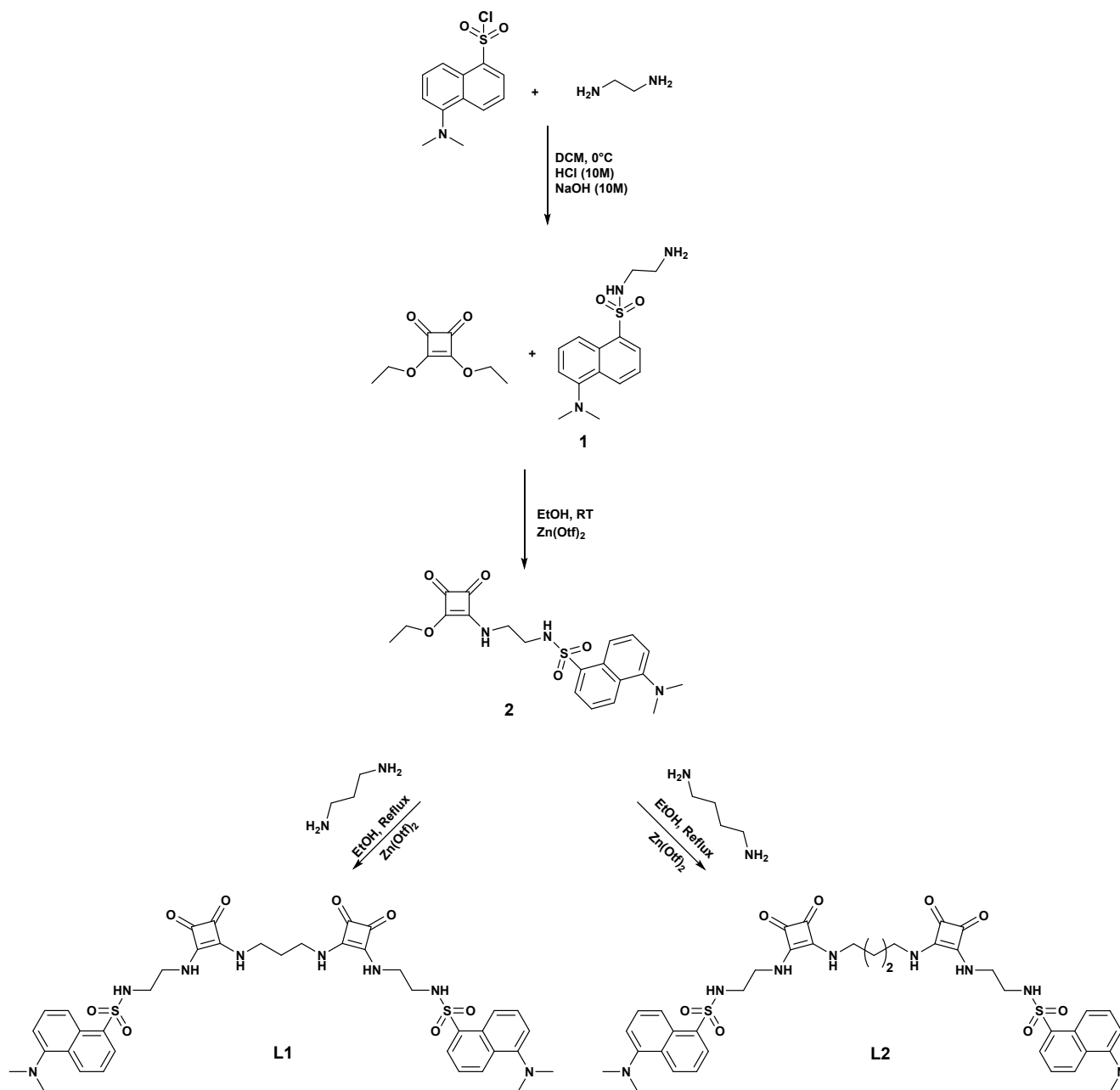
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1. GENERAL PROCEDURES AND METHODS

All reactions were performed in oven-dried glassware under a slight positive pressure of nitrogen. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 600 MHz (Nicholas Terrace, New York, NY, USA). Chemical shifts for ^1H NMR are reported in parts per million (ppm), calibrated to the residual solvent peak set, with coupling constants reported in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, s_b = broad singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet. Chemical shifts for ^{13}C NMR are reported in ppm, relative to the central line of a septet at $\delta = 39.52$ ppm, for $\text{DMSO}-d_6$. Elemental analyses were obtained using a PerkinElmer Series II – 2400 (Waltham, MA, USA). All solvents and starting materials were purchased from commercial sources where available and used as received without any further purification. Rheological experiments were carried out on an Anton Paar Physica MCR 301 rheometer at a constant temperature of 25 °C, TEM images were recorded on an instrument TEM JeolJEM 1400 Plus at an accelerating voltage of 80 kV. UV-Vis spectra were recorded in quartz cuvettes (optical path length 1 cm) on a Cary 60 spectrometer. Fluorescence spectra was recorded in quartz cuvettes (optical path length 1 cm) on a Cary Eclipse spectrometer. Small angle X-ray scattering data was collected at the CoSAXS beamline at the diffraction limited 3 GeV storage ring at the MAX IV Laboratory in Sweden.

2. SYNTHESIS SCHEME



Scheme S1: General synthetic scheme.

2.1. Synthesis of Intermediates

2.1.1. Synthesis of **1**

For the synthesis of **1**, a procedure already reported in the literature has been used,¹ starting from dansyl chloride and ethylenediamine in dichloromethane.

2.1.2. Synthesis 5-(dimethylamino)-N-(2-((2-ethoxy-3,4-dioxocyclobut-1-en-1-yl)amino)ethyl)naphthalene-1-sulfonamide (2)

To a stirred solution of 3,4-diethoxy-3-cyclobutene-1,2-dione (0.68 g, 3.99 mmol, 1.1 eq.) in 10 mL of anhydrous ethanol in presence of catalyst $\text{Zn}(\text{Otf})_2$ (20% squarate, 0.26 g, 0.72 mmol, intermediate 1 that is N-(2-aminoethyl)-5-(dimethylamino) naphthalene-1-sulfonamide (1.06 g, 3.61 mmol, 1 eq.) was added. The reaction was conducted at room temperature and then stirred overnight. The reaction mixture was purified by chromatography column (Hex: EtAcO, 1:2 v/v) collecting the sample as pale-yellow fluorescent solid. Yield: 1.19 g, 2.85 mmol, 79%. ^1H NMR (600 MHz, $\text{DMSO}-d_6$, 298K) δ (ppm): 8.46 (d, J = 8.5 Hz, 1H), 8.25 (d, J = 8.6 Hz, 1H), 8.09 (d, J = 7.5 Hz, 2H), 7.59 (dt, J = 26.2, 8.1 Hz, 2H), 7.24 (d, J = 7.5 Hz, 1H), 4.55 (dq, J = 21.2, 7.1 Hz, 2H), 3.46 (q, J = 6.3 Hz, 1H), 3.27 (q, J = 6.2 Hz, 1H), 2.98 (d, J = 6.2 Hz, 2H), 2.82 (s, 6H), 1.29 (m, 3H). ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$, 298K) δ (ppm): 188.9, 182.3, 181.8, 176.9, 176.3, 172.7, 172.3, 151.3, 135.9, 135.8, 129.5, 129.1, 128.9, 128.2, 128.2, 127.8, 123.5, 119.0, 115.2, 68.6, 45.0, 43.9, 43.4, 42.8, 42.4, 15.5. Elemental analysis: % calc. for $\text{C}_{20}\text{H}_{23}\text{N}_3\text{O}_5\text{S}$ (% found): C, 57.54; H, 5.55; N, 10.07; O, 19.16; S, 7.68. Melting point: 148°C -150°C.

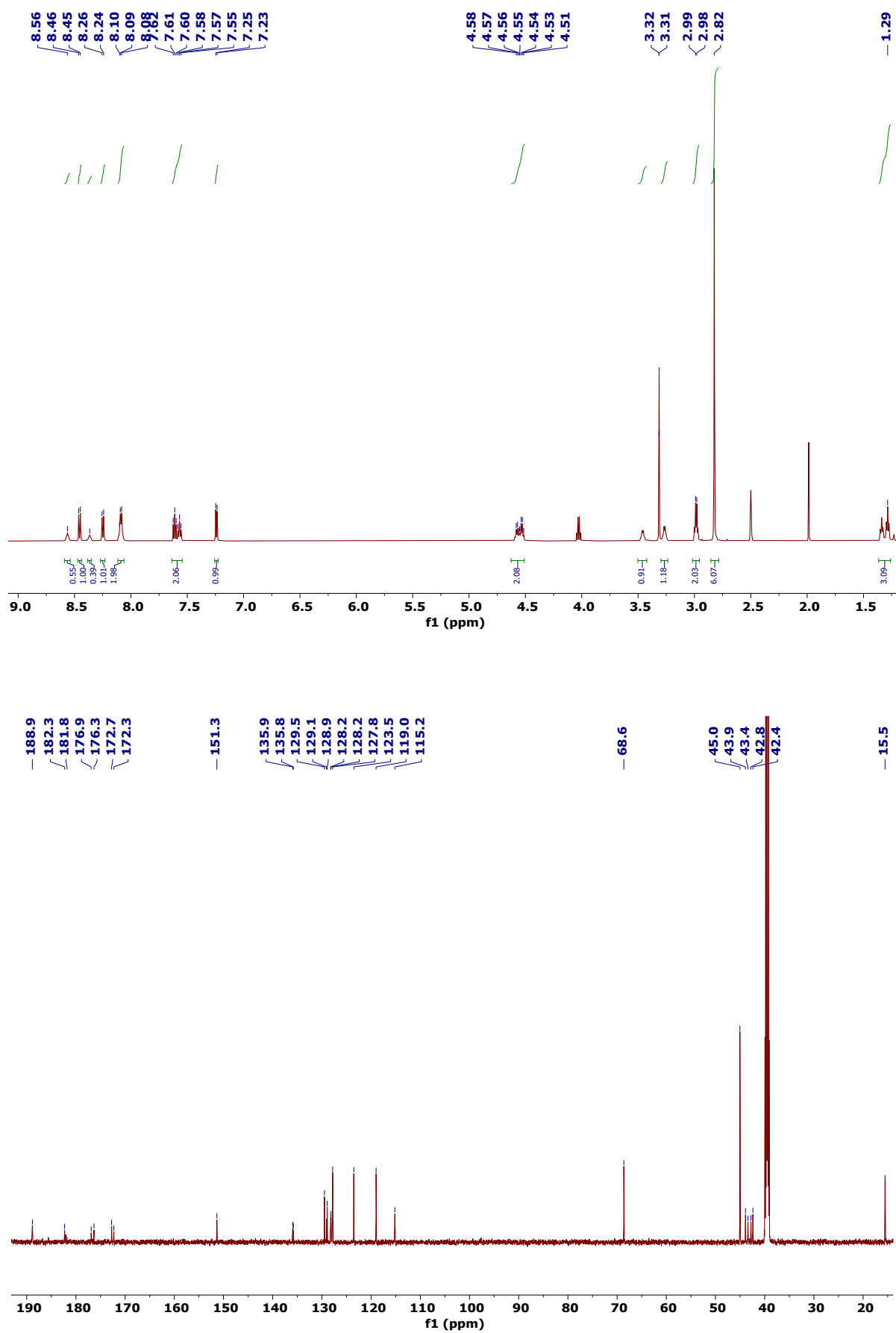


Figure S1: ^1H -NMR and ^{13}C -NMR spectra of **2**.

2.2. Synthesis of Gelators

2.2.1. Synthesis of N,N'-((((propane-1,3-diylbis(azanediyl))bis(3,4-dioxocyclobut-1-ene-2,1-diyl))bis(azanediyl))bis(ethane-2,1-diyl))bis(5-(dimethylamino)naphthalene-1-sulfonamide) (**L1**)

A stirred solution of **2** that is 5-(dimethylamino)-N-(2-((2-ethoxy-3,4-dioxocyclobut-1-en-1-yl) amino) ethyl) naphthalene-1-sulfonamide (0.46 g, 1.11 mmol, 2 eq.) in 12 mL of anhydrous ethanol in presence of catalyst Zn(Otf)₂ (20% squarate, 0.09 g, 0.25 mmol) was heated until completely solubilization. Then 1,3-diaminopropane (0.04 g, 0.54 mmol, 1 eq.) in 3 mL of anhydrous ethanol was added dropwise to the reaction mixture. After half an hour a ppt/gel started to form. The reaction was conducted at 80° C and stirred overnight. The ppt/gel was filtered and washed with ethanol (2x10 mL) and then dried under pressure, collecting a pale-yellow solid (**L1**). Yield: 0.41 g, 0.50 mmol, 93%. ¹H NMR (600 MHz, DMSO-*d*₆, 298K) δ (ppm): 8.45 (d, J = 8.5 Hz, 1H), 8.26 (d, J = 8.6 Hz, 1H), 8.10 (dd, J = 7.3, 1.3 Hz, 2H), 7.64 – 7.54 (m, 2H), 7.39 (s, 2H), 7.24 (d, J = 7.6 Hz, 1H), 3.51 (s, 4H), 2.96 (t, J = 6.1 Hz, 2H), 2.82 (s, 6H), 1.77 (s, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆, 298K) δ (ppm): 182.6, 182.3, 167.8, 151.4, 135.6, 129.5, 129.1, 129.0, 128.3, 127.9, 123.5, 119.0, 115.1, 45.0, 43.5, 43.1, 40.6, 32.3. Elemental analysis: % calc. for: C₃₉H₄₄N₈O₈S₂ (% found): C, 57.34; H, 5.43; N, 13.72; O, 15.67; S, 7.85. Melting point: 213 °C -214 °C.

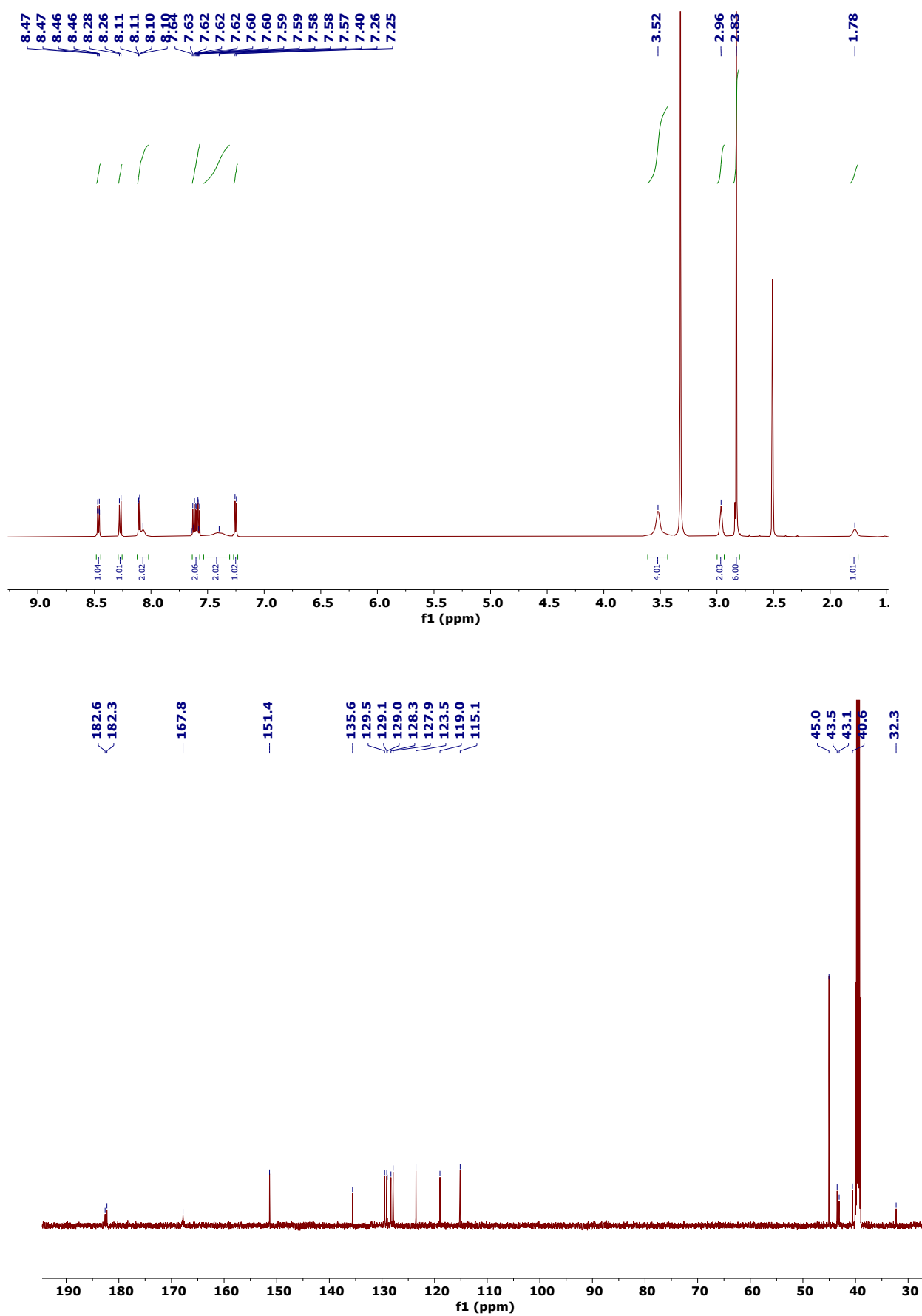
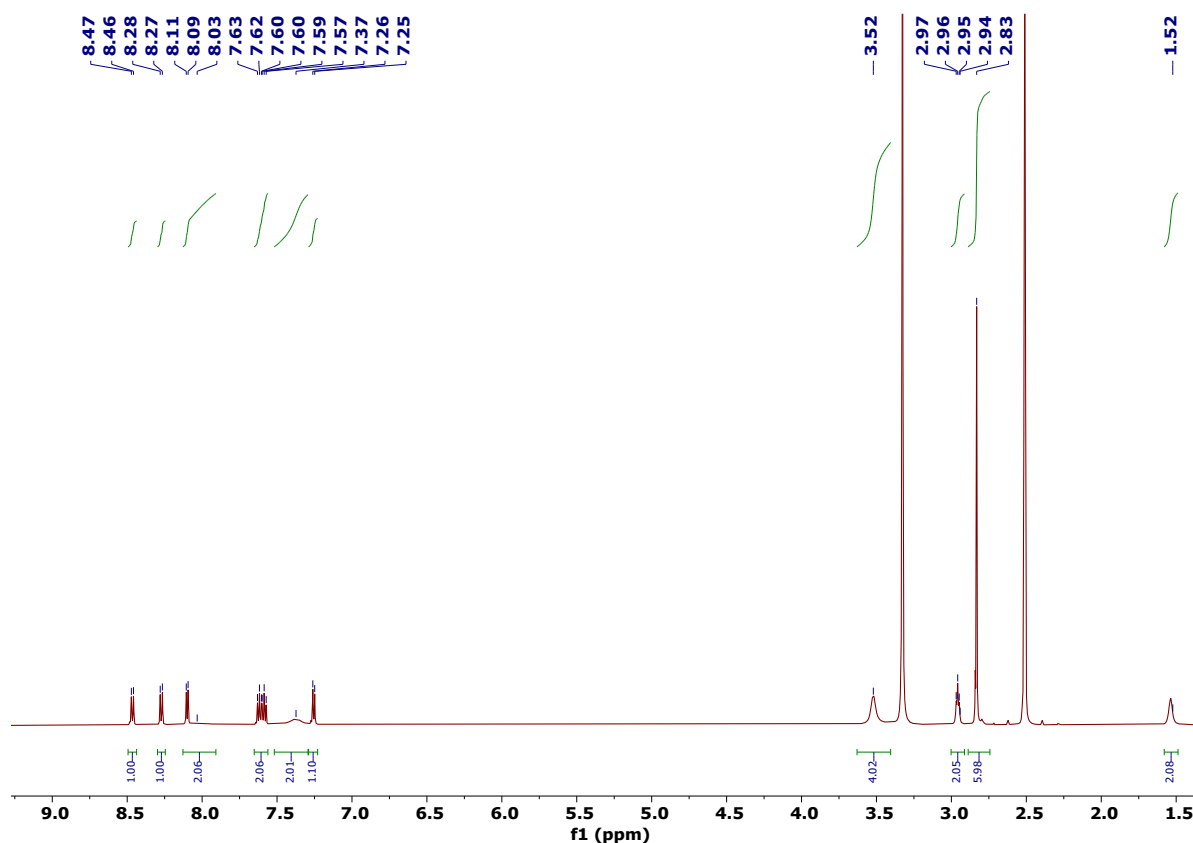


Figure S2: ^1H -NMR and ^{13}C -NMR spectra of L1.

2.2.2. Synthesis of N,N'-((((butane-1,4-diylbis(azanediy))bis(3,4-dioxocyclobut-1-ene-2,1-diyl))bis(azanediy))bis(ethane-2,1-diyl))bis(5-(dimethylamino)naphthalene-1-sulfonamide) (**L2**)

A stirred solution of **2** that is 5-(dimethylamino)-N-(2-((2-ethoxy-3,4-dioxocyclobut-1-en-1-yl) amino) ethyl) naphthalene-1-sulfonamide (0.39 g, 0.93 mmol, 2 eq.) in 12 mL of anhydrous ethanol in presence of catalyst $\text{Zn}(\text{Otf})_2$ (20% squarate, 0.07 g, 0.19 mmol) was heated until completely solubilization. Then 1,4-diaminobutane (0.04 g, 0.45 mmol, 1 eq.) in 3 mL of anhydrous ethanol was added dropwise to the reaction mixture. After half an hour a ppt/gel started to form. The reaction was conducted at 80° C and stirred overnight. The ppt/gel was filtered and washed with ethanol (2x10 mL) and then dried under pressure, collecting a pale-yellow solid (**L2**). Yield: 0.31 g, 0.37 mmol, 82%. ^1H NMR (600 MHz, $\text{DMSO}-d_6$, 298K) δ (ppm): 8.51 (dt, $J = 8.5, 1.1$ Hz, 1H), 8.32 (dt, $J = 8.7, 1.0$ Hz, 1H), 8.15 (dd, $J = 7.3, 1.3$ Hz, 2H), 7.65 (ddd, $J = 18.9, 8.6, 7.4$ Hz, 2H), 7.42 (s, 2H), 7.30 (dd, $J = 7.6, 0.9$ Hz, 1H), 3.69 – 3.45 (m, 4H), 3.00 (q, $J = 6.3$ Hz, 2H), 2.88 (s, 6H), 1.59 (s, 2H). ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$, 298K) δ (ppm): 182.6, 182.2, 168.1, 167.3, 151.4, 135.6, 129.5, 129.1, 129.0, 128.3, 127.9, 123.5, 119.0, 115.1, 45.0, 43.5, 43.1, 42.9, 27.7. Elemental analysis: % calc. for: $\text{C}_{40}\text{H}_{46}\text{N}_8\text{O}_8\text{S}_2$ (% found): C, 57.82; H, 5.58; N, 13.48; O, 15.40; S, 7.72. Melting point: 255 °C -256 °C.



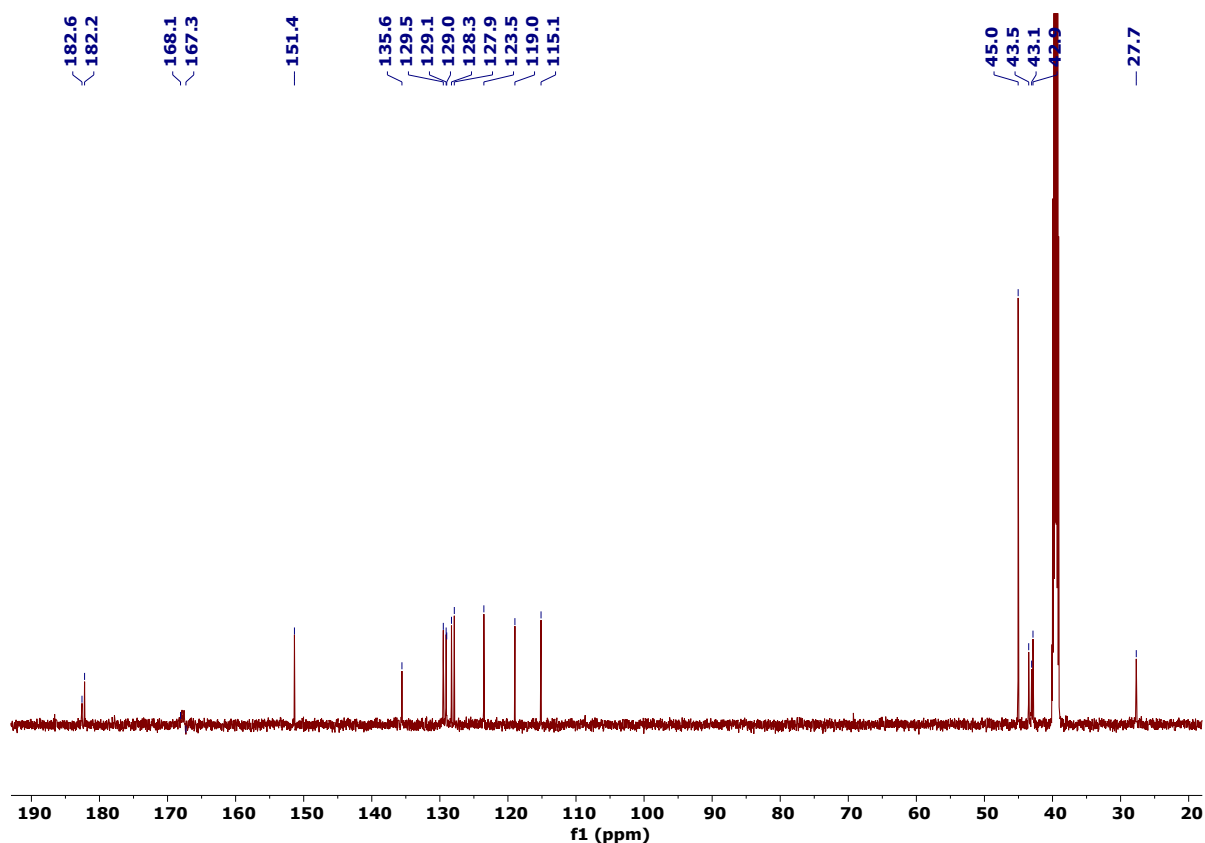


Figure S3: ^1H -NMR and ^{13}C -NMR spectra of L2.

3. GELATION TEST

L1 gelation tests (Temperature trigger)									
	<i>EtOH</i>	<i>THF</i>	<i>MeCN</i>	<i>MeOH</i>	<i>2-propanol</i>				
1% w/v	ppt/gel	insoluble	ppt/gel	insoluble	insoluble				
0.75% w/v	ppt/gel	insoluble	ppt/gel	insoluble	insoluble				
0.67 % w/v	ppt/gel	ppt	ppt/gel	ppt	ppt				
0.5% w/v	ppt	ppt	ppt/gel	ppt	ppt				
0.33% w/v	no gel	no gel	no gel	no gel	no gel				
	<i>DMSO: H₂O</i> 9:1 (v/v)	<i>DMSO: H₂O</i> 4:1 (v/v)	<i>DMSO: H₂O</i> 7:3 (v/v)	<i>DMSO: H₂O</i> 3:2 (v/v)	<i>DMSO: H₂O</i> 1:1 (v/v)	<i>DMSO: H₂O</i> 2:3 (v/v)	<i>DMSO: H₂O</i> 3:7 (v/v)	<i>DMSO: H₂O</i> 1:4 (v/v)	<i>DMSO: H₂O</i> 1:9 (v/v)
2% w/v	no gel	no gel	no gel	weak gel	gel	weak gel	ppt	ppt	ppt
1.5% w/v	no gel	no gel	no gel	weak gel	gel	weak gel	ppt	ppt	ppt
1% w/v	no gel	no gel	no gel	weak gel	gel	gel	ppt	ppt	ppt
0.5% w/v	no gel	no gel	no gel	no gel	no gel	no gel	ppt	ppt	ppt
L1 gelation tests (Solvent trigger)									
	<i>DMSO: H₂O</i> 1:4 (v/v)	<i>DMSO: H₂O</i> 3:7 (v/v)	<i>DMSO: H₂O</i> 3.5:6.5 (v/v)	<i>DMSO: H₂O</i> 2:3 (v/v)	<i>DMSO: H₂O</i> 1:1 (v/v)				
0.5 % w/v	ppt	gel	gel	gel	weak gel				
0.4 % w/v	ppt	ppt/gel	ppt/gel	ppt/gel	ppt				
0.3 % w/v	ppt	ppt	ppt	ppt	ppt				

L2 gelation tests (Temperature trigger)						
	<i>EtOH</i>	<i>THF</i>	<i>MeCN</i>	<i>MeOH</i>	<i>2-propanol</i>	
1% w/v	insoluble	insoluble	insoluble	insoluble	insoluble	
0.5% w/v	insoluble	insoluble	insoluble	insoluble	insoluble	
0.33% w/v	insoluble	insoluble	insoluble	insoluble	insoluble	
	<i>DMSO: H₂O</i> 9:1 (v/v)	<i>DMSO: H₂O</i> 4:1 (v/v)	<i>DMSO: H₂O</i> 7:3 (v/v)	<i>DMSO: H₂O</i> 3:2 (v/v)	<i>DMSO: H₂O</i> 1:1 (v/v)	<i>DMSO: H₂O</i> 2:3 (v/v)
2% w/v	no gel	no gel	weak gel	gel	no gel	no gel
1.5% w/v	no gel	no gel	gel	weak gel	no gel	no gel
1% w/v	no gel	no gel	no gel	no gel	no gel	no gel
0.5% w/v	no gel	no gel	no gel	no gel	no gel	no gel
L2 gelation tests (Solvent trigger)						
	<i>DMSO: H₂O</i> 1:4 (v/v)	<i>DMSO: H₂O</i> 3:7 (v/v)	<i>DMSO: H₂O</i> 2:3 (v/v)	<i>DMSO: H₂O</i> 1:1 (v/v)		
0.5 % w/v	ppt	ppt	ppt	gel		
0.4 % w/v	ppt	ppt	ppt	ppt		
0.3 % w/v	ppt	ppt	ppt	ppt		

Table S1: Gelation Tests of **L1** and **L2** carried out in different organic solvent and DMSO:H₂O mixture by using both temperature and solvent triggers; “ppt”: precipitate and “ppt/gel”: mixture of gel and precipitate.

4. GELS CHARACTERIZATION

<i>Gels</i>	<i>Gelation Method</i>	<i>G' (Pa)</i>	<i>G'' (Pa)</i>	<i>tan δ</i>
L1 , Gel in DMSO:H ₂ O (3:7, v/v), 0.5% w/v	Solvent Trigger	2500 ± 250	190 ± 35	0.076 ± 0.003
L1 , Gel in DMSO:H ₂ O (2:3, v/v), 1% w/v	Temperature Trigger	5300 ± 800	320 ± 70	0.061 ± 0.005
L1 , Gel in DMSO:H ₂ O (1:1, v/v), 1% w/v	Temperature Trigger	41000 ± 5000	3170 ± 970	0.077 ± 0.005
L1 , Gel in DMSO:H ₂ O (1:1, v/v), 2% w/v	Temperature Trigger	6000 ± 750	450 ± 90	0.075 ± 0.007
L2 , Gel in DMSO:H ₂ O (1:1, v/v), 0.5% w/v	Solvent Trigger	2100 ± 360	195 ± 35	0.093 ± 0.008
L2 , Gel in DMSO:H ₂ O (3:2, v/v), 2% w/v	Temperature Trigger	3100 ± 900	225 ± 63	0.073 ± 0.009
L2 , Gel in DMSO:H ₂ O (7:3, v/v), 1.5% w/v	Temperature Trigger	5120 ± 620	480 ± 72	0.094 ± 0.007

Table S2: Summary of *G'*, *G''* and *tan δ* values with associated errors of all gels obtained with gelators **L1** and **L2**.

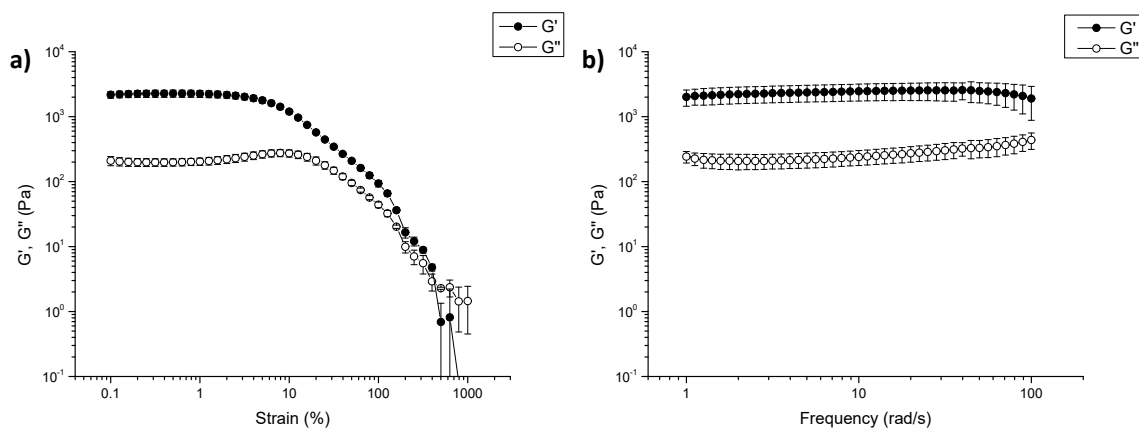


Figure S4: a) Strain sweep rheology of **L1** in DMSO: H₂O (3:7, v/v), 0.5% w/v and (b) Frequency Sweep rheology of **L1** in DMSO: H₂O (3:7), 0.5% w/v. Both experiments were performed in triplicate.

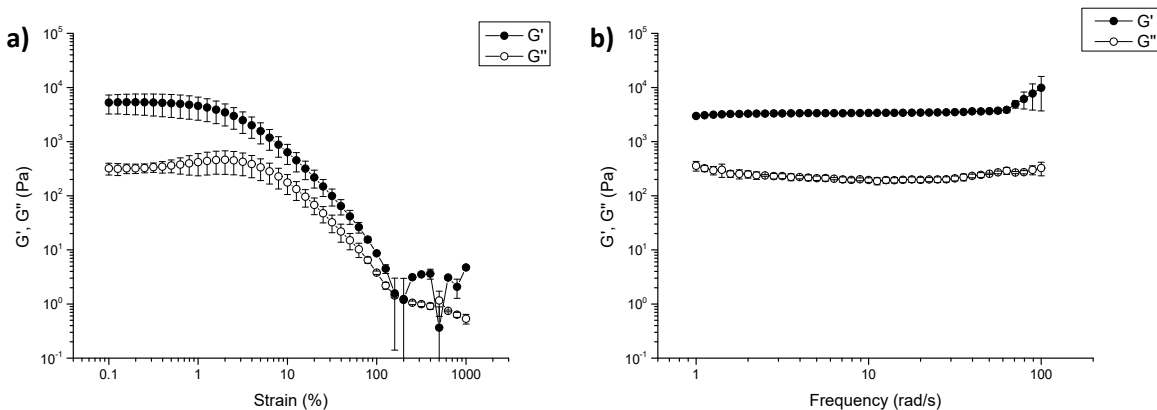


Figure S5: a) Strain sweep rheology of **L1** in DMSO: H₂O (2:3, v/v), 1% w/v and (b) Frequency Sweep rheology of **L1** in DMSO: H₂O (2:3), 1% w/v. Both experiments were performed in triplicate.

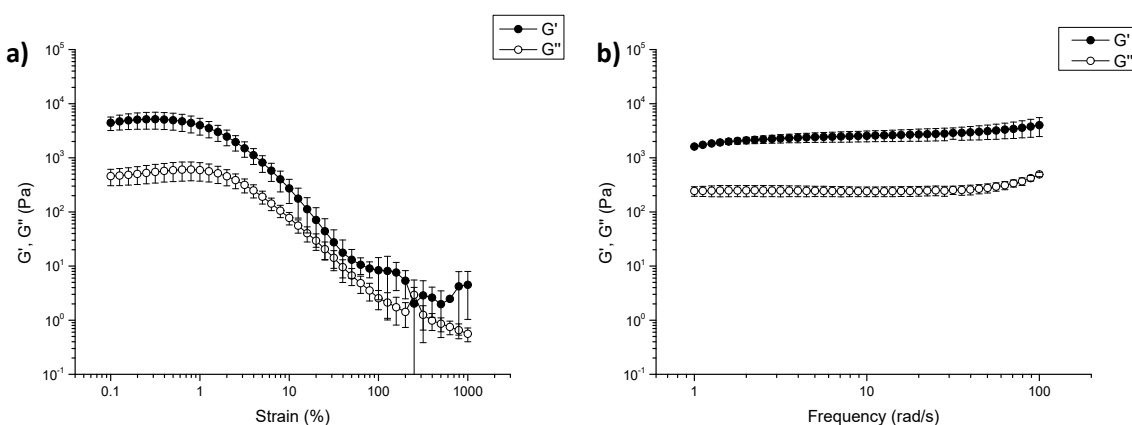


Figure S6: a) Strain sweep rheology of **L1** in DMSO: H₂O (1:1, v/v), 2% w/v and (b) Frequency Sweep rheology of **L1** in DMSO: H₂O (1:1), 2% w/v. Both experiments were performed in triplicate.

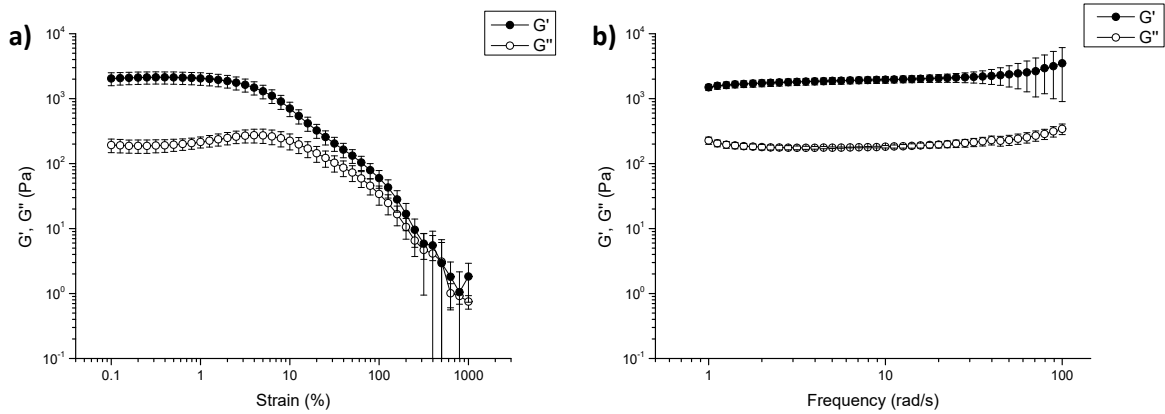


Figure S7: a) Strain sweep rheology of **L2** in DMSO: H₂O (1:1, v/v), 0.5% w/v and (b) Frequency Sweep rheology of **L2** in DMSO: H₂O (1:1), 0.5 % w/v. Both experiments were performed in triplicate.

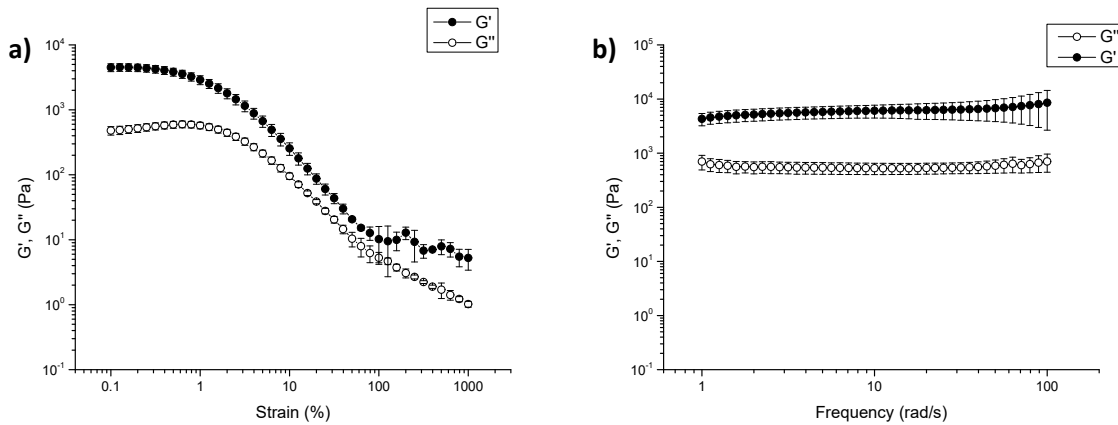


Figure S8: a) Strain sweep rheology of **L2** in DMSO: H₂O (3:2, v/v), 2% w/v and (b) Frequency Sweep rheology of **L2** in DMSO: H₂O (3:2), 2% w/v. Both experiments were performed in triplicate.

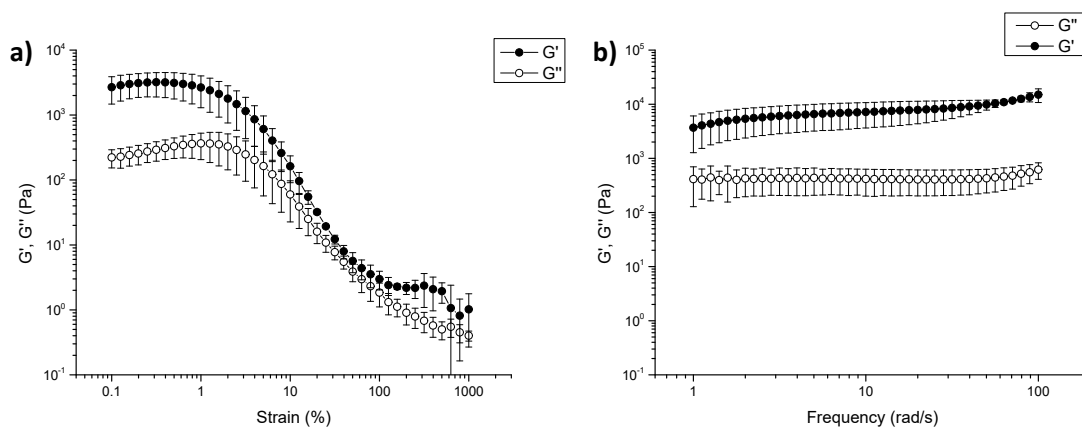


Figure S9: a) Strain sweep rheology of **L2** in DMSO: H₂O (7:3, v/v), 1.5% w/v and (b) Frequency Sweep rheology of **L2** in DMSO: H₂O (7:3), 1.5% w/v. Both experiments were performed in triplicate.

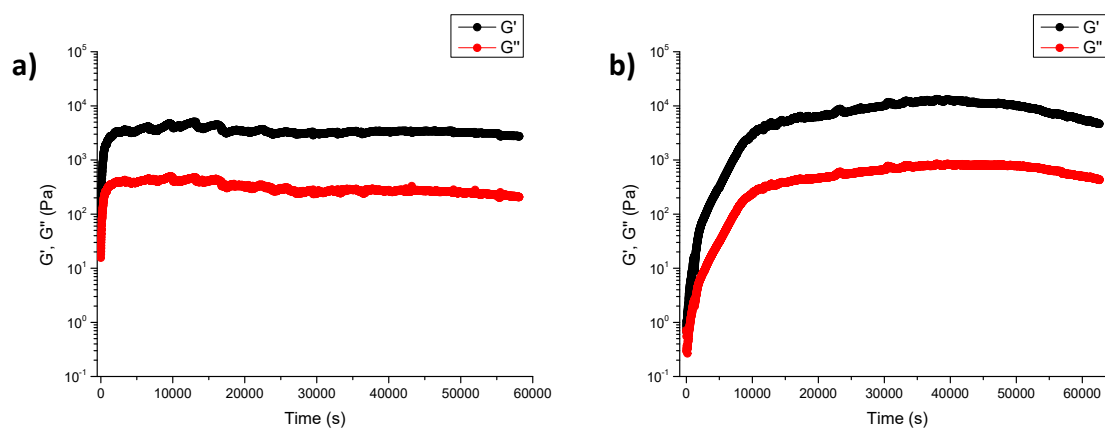


Figure S10: Time sweep rheology of **L2** gels a) in DMSO: H₂O (3:2, v/v), 2% w/v and b) in DMSO: H₂O (3:7, v/v), 1.5% w/v.

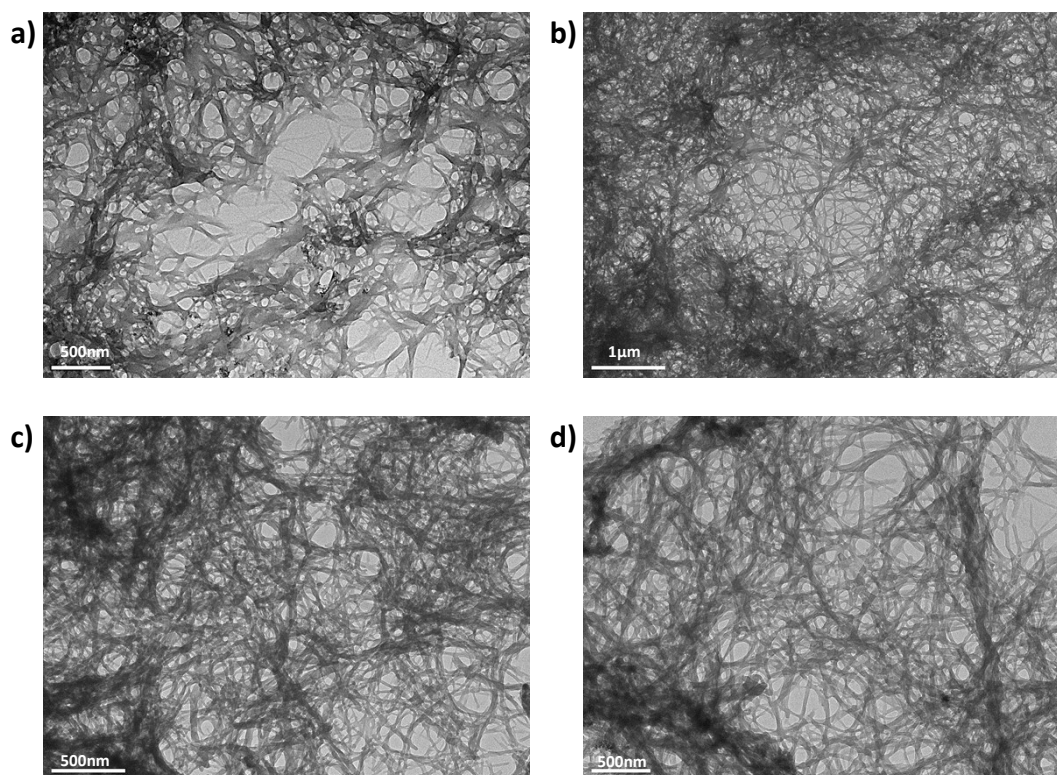


Figure S11: TEM images of **L1** gels in a-b) DMSO: H₂O, (3:7, v/v), 0.5% w/v (scale bar of 500nm and 1μm), c) DMSO: H₂O, (2:3 v/v), 1% w/v (scale bar of 500nm) and d) DMSO: H₂O, (1:1 v/v), 2% w/v (scale bar of 500nm).

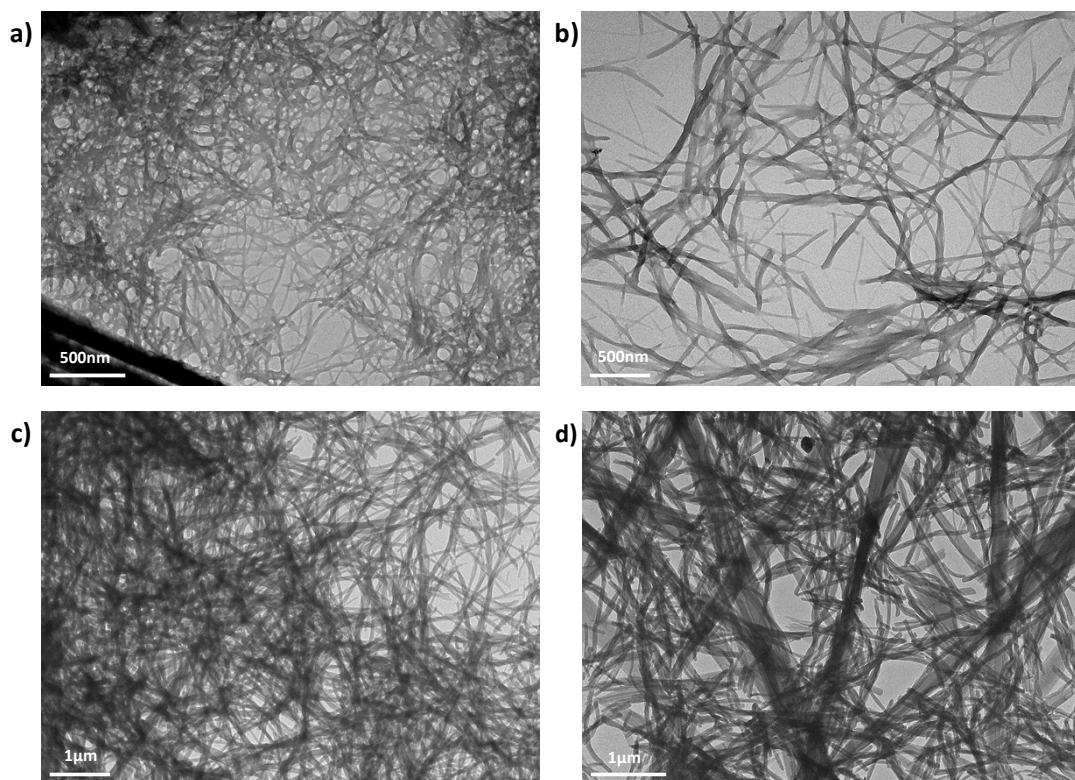


Figure S12: TEM images of **L2** gels in a) DMSO: H₂O, (1:1 v/v), 0.5% w/v (scale bar of 500nm), b) DMSO: H₂O, (3:2 v/v), 2% w/v (scale bar of 500nm) and c-d) DMSO: H₂O, (7:3 v/v), 1.5% w/v (scale bar of 1μm).

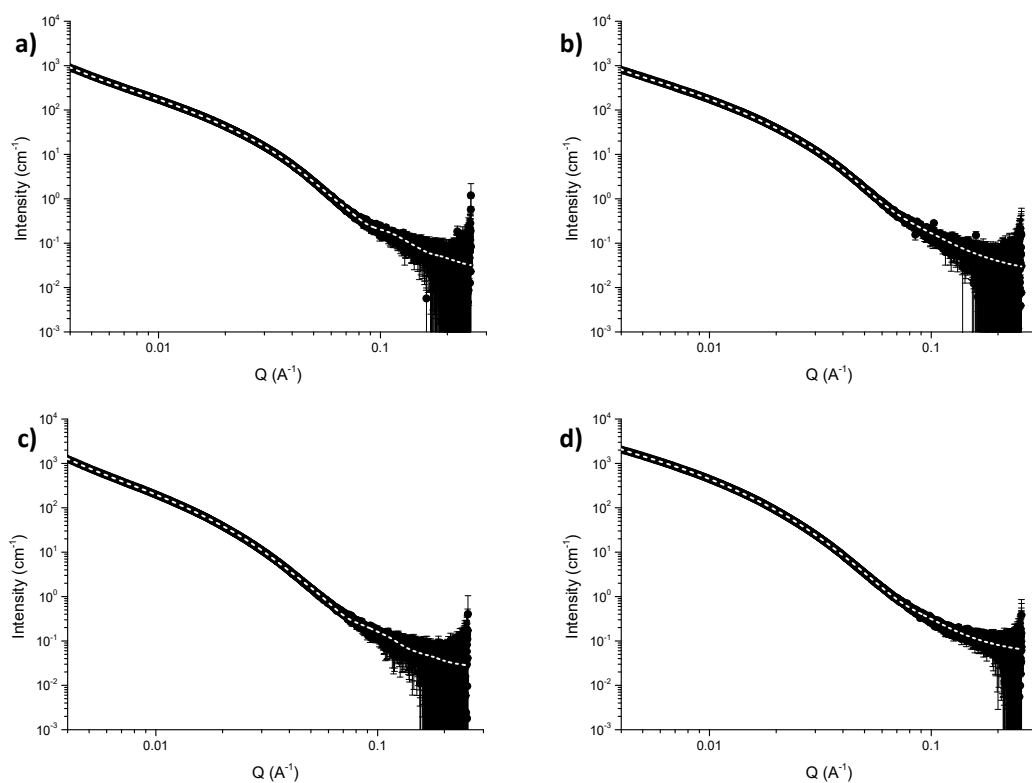


Figure S13: SAXS data with fitting of **L1** a) in DMSO: H₂O (3:7 v/v), 0.5% w/v, b) in DMSO: H₂O (2:3 v/v), 1% w/v, c) in DMSO: H₂O (1:1 v/v), 1% w/v and d) in DMSO: H₂O (1:1 v/v), 2% w/v.

	L1, DMSO:H ₂ O (3:7, v/v), 0.5% w/v		L1, DMSO:H ₂ O (2:3, v/v), 1% w/v		L1, DMSO:H ₂ O (1:1, v/v), 1% w/v		L1, DMSO:H ₂ O (1:1, v/v), 2% w/v	
	Free gel (FCE_PL)		Free gel (FCE_PL)		Free gel (FCE_PL)		Free gel (FCE_PL)	
	Value	Error	Value	Error	Value	Error	Value	Error
Scale	1		1		1		1	
Background (cm ⁻¹)	0.02*		0.02*		0.02*		0.05*	
A_scale	0.0062	1.73×10 ⁻⁵	0.0043	8.49×10 ⁻⁵	0.0043	8.49×10 ⁻⁵	0.0098	7.14×10 ⁻⁵
A_length (Å)	853.3	8.3	1930.8	78.81	1930.8	78.81	2127.3	46.71
A_Kuhn_length (Å)	178.1	3.3	92.75	5.33	92.75	5.33	113.56	3.19
A_radius (Å)	40.7	0.09	42.099	0.28	42.099	0.28	45.09	0.20
Polidispersity	/	/	/	/	/	/	0.2	/
A_axis_ratio (Å)	1.991	0.009	1.98	0.012	1.98	0.012	2.17	0.0063
B_scale	0.00023	5.17×10 ⁻⁶	0.00026	5.65×10 ⁻⁶	0.00026	5.65×10 ⁻⁶	0.00032	4.08×10 ⁻⁶
B_power	2.67	0.003	2.62	0.004	2.62	0.004	2.72	0.002
χ ²	1.1717		1.5456		1.5456		2.2159	

Table S3: SAXS fitting data of **L1** gels obtained from DMSO:H₂O mixtures in different ratios at different concentrations.

5. DYES ADSORPTION STUDIES

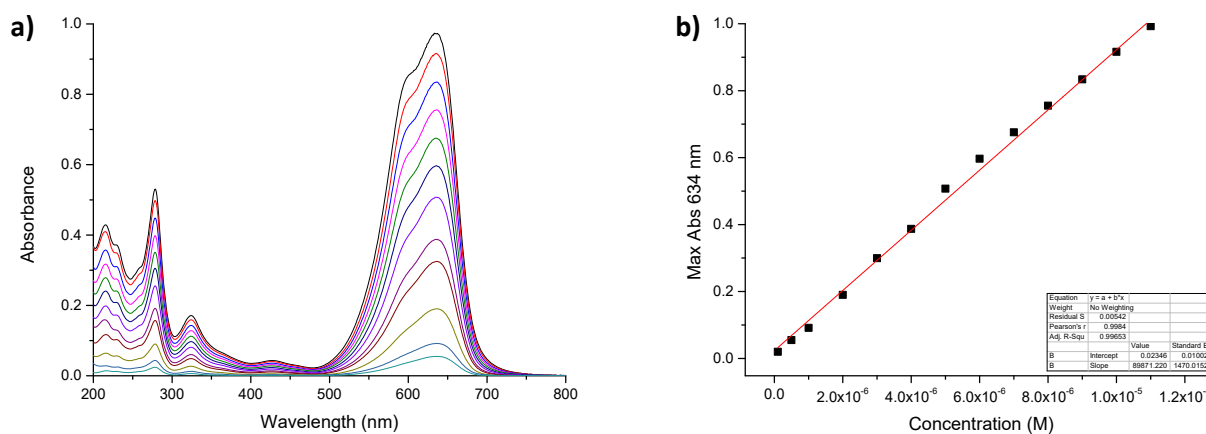


Figure S14: UV-Vis spectra of calibration curve a) of Nile Blue A in H₂O, starting solution concentration 1.2·10⁻⁵ M and b) linear fitting of calibration curve.

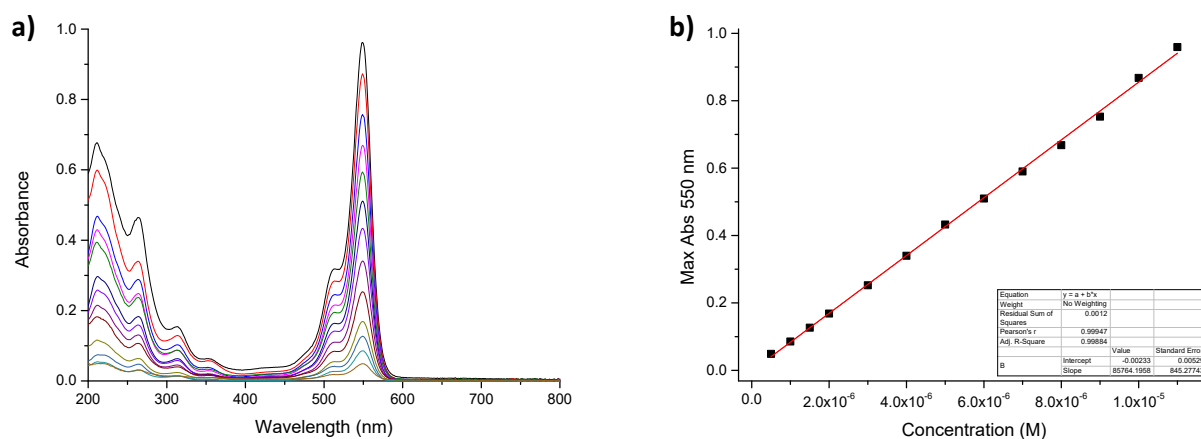


Figure S15: UV-Vis spectra of calibration curve a) of Rose Bengal in H₂O, starting solution concentration $1.1 \cdot 10^{-5}$ M and b) linear fitting of calibration curve.

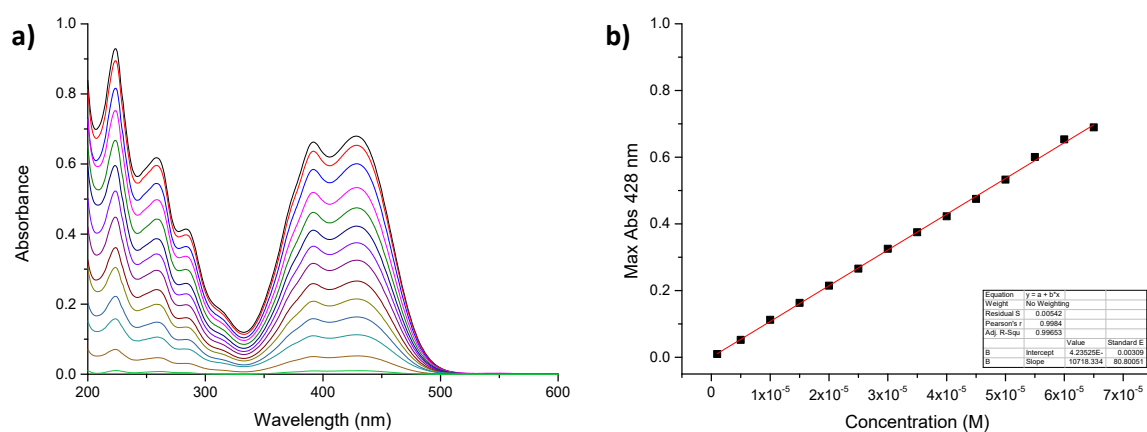


Figure S16: UV-Vis spectra of calibration curve a) of Naphthol Yellow S in H₂O, starting solution concentration $6.5 \cdot 10^{-5}$ M and b) linear fitting of calibration curve.

Gels	RE% Nile Blue A	RE% Rose Bengal	RE% Naphthol Yellow
L1, Gel in DMSO:H ₂ O (3:7, v/v), 0.5% w/v	75.2%	93.3%	44.8%
L1, Gel in DMSO:H ₂ O (2:3, v/v), 1% w/v	57.6%	71.5%	54.8%
L1, Gel in DMSO:H ₂ O (1:1, v/v), 1% w/v	40.6%	66.3%	48.8%
L2, Gel in DMSO:H ₂ O (1:1, v/v), 0.5% w/v	67.5%	73.3%	43.1%

Table S4: Summary of RE% values of all gels studied as potential adsorbent materials (value averaged over three measurements).

5.1. Contact Analysis

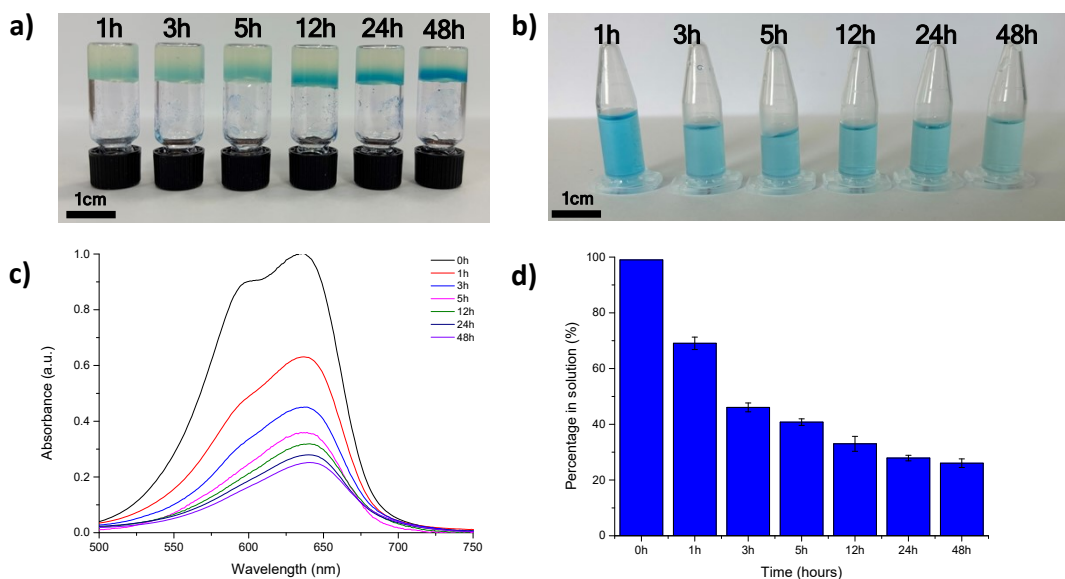


Figure S17: L1, DMSO:H₂O (3:7, v/v), 0.5% w/v in presence of Nile Blue A ($1.2 \cdot 10^{-5}$ M) a) gels adsorption at different hours (scale bar of 1 cm), b) withdraw solution at different hours (scale bar of 1 cm), c) UV-Vis spectra of characteristic peak of dye at 634 nm and c) histogram with percentage of dye in solution.

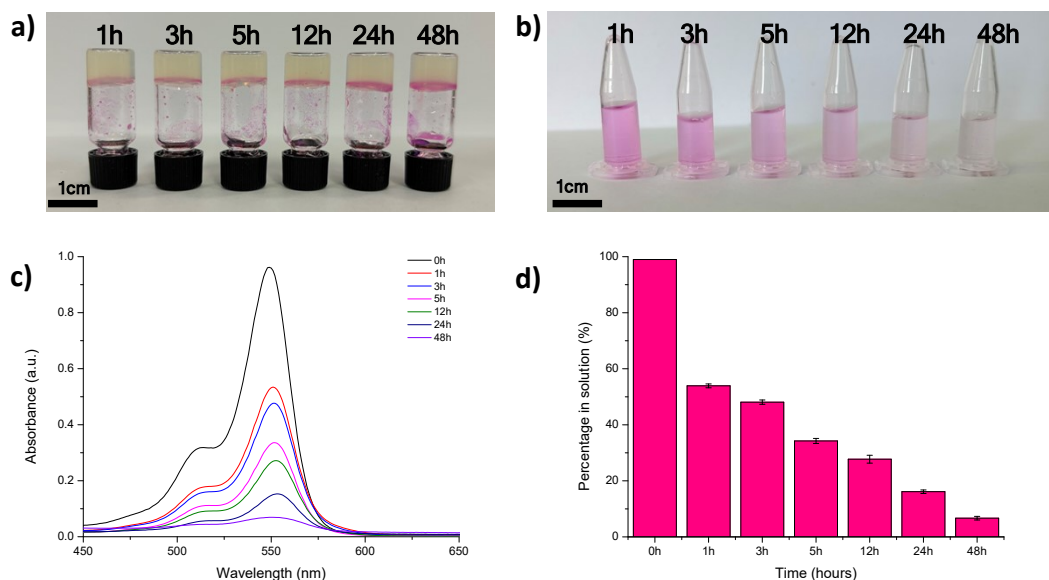


Figure S18: L1, DMSO:H₂O (3:7, v/v), 0.5% w/v in presence of Rose Bengal ($1.1 \cdot 10^{-5}$ M) a) gels adsorption at different hours (scale bar of 1 cm), b) withdraw solution at different hours (scale bar of 1 cm), c) UV-Vis spectra of characteristic peak of dye at 550 nm and c) histogram with percentage of dye in solution.

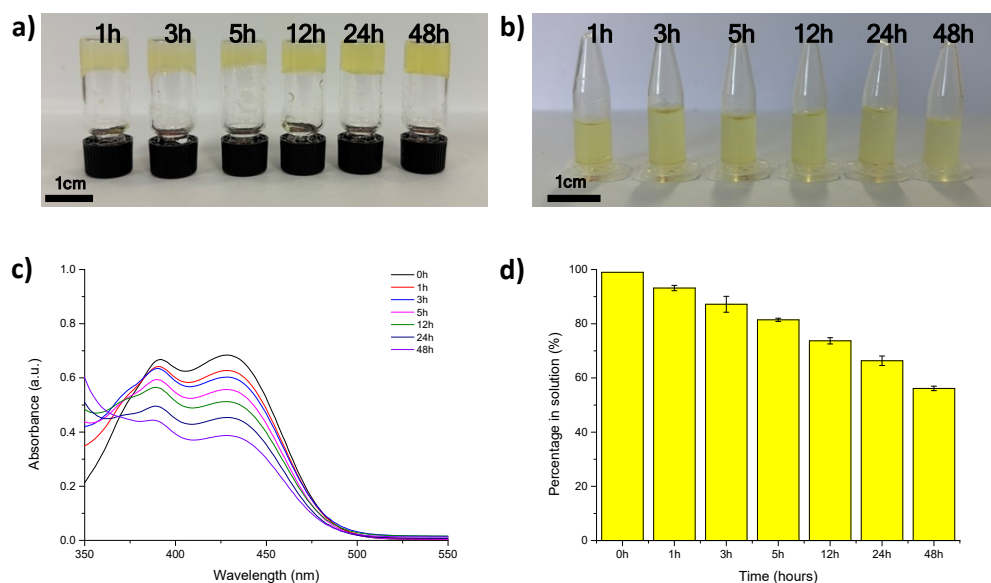


Figure S19: L1, DMSO:H₂O (3:7, v/v), 0.5% w/v in presence of Naphthol Yellow S ($6.5 \cdot 10^{-5}$ M) a) gels adsorption at different hours (scale bar of 1 cm), b) withdraw solution at different hours (scale bar of 1 cm), c) UV-Vis spectra of characteristic peak of dye at 428 nm and c) histogram with percentage of dye in solution.

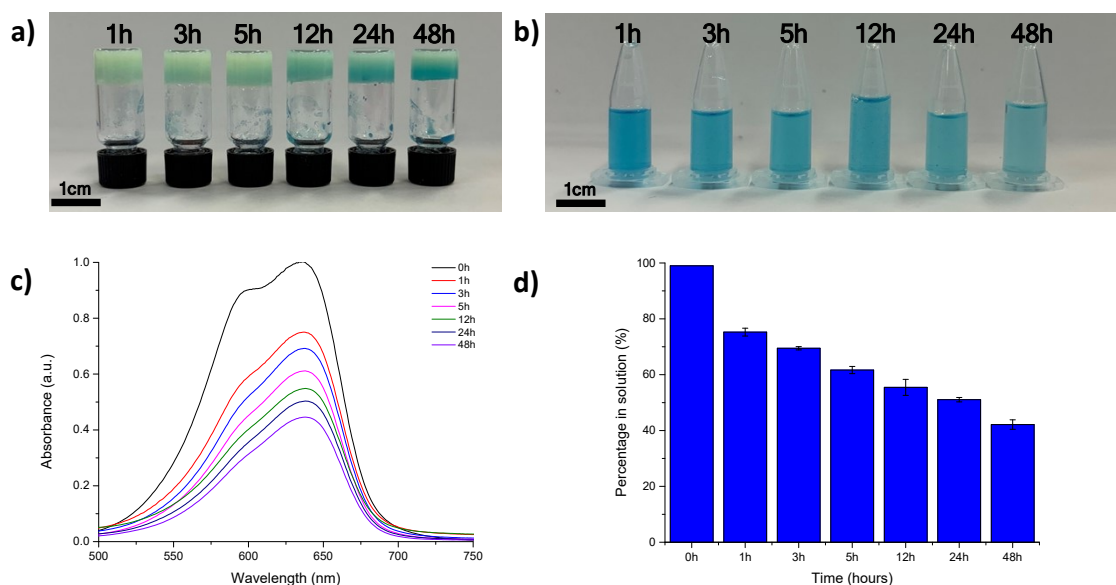


Figure S20: L1, DMSO:H₂O (2:3, v/v), 1% w/v in presence of Nile Blue A ($1.2 \cdot 10^{-5}$ M) a) gels adsorption at different hours (scale bar of 1 cm), b) withdraw solution at different hours (scale bar of 1 cm), c) UV-Vis spectra of characteristic peak of dye at 634 nm and c) histogram with percentage of dye in solution.

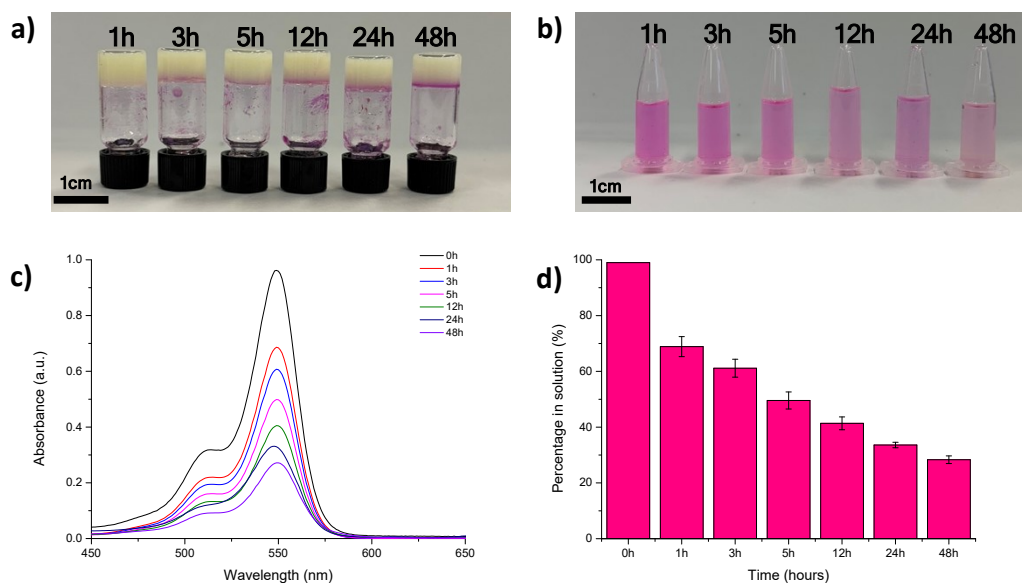


Figure S21: L1, DMSO:H₂O (2:3, v/v), 1% w/v in presence of Rose Bengal ($1.1 \cdot 10^{-5}$ M) a) gels adsorption at different hours (scale bar of 1 cm), b) withdraw solution at different hours (scale bar of 1 cm), c) UV-Vis spectra of characteristic peak of dye at 550 nm and c) histogram with percentage of dye in solution.

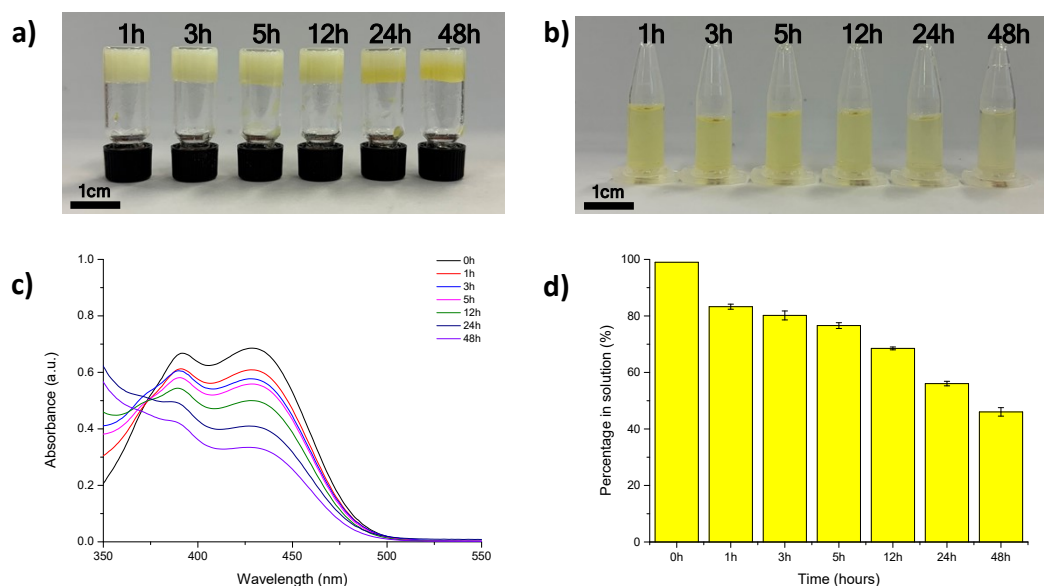


Figure S22: L1, DMSO:H₂O (2:3, v/v), 1% w/v in presence of Naphthol Yellow S ($6.5 \cdot 10^{-5}$ M) a) gels adsorption at different hours (scale bar of 1 cm), b) withdraw solution at different hours (scale bar of 1 cm), c) UV-Vis spectra of characteristic peak of dye at 428 nm and c) histogram with percentage of dye in solution.

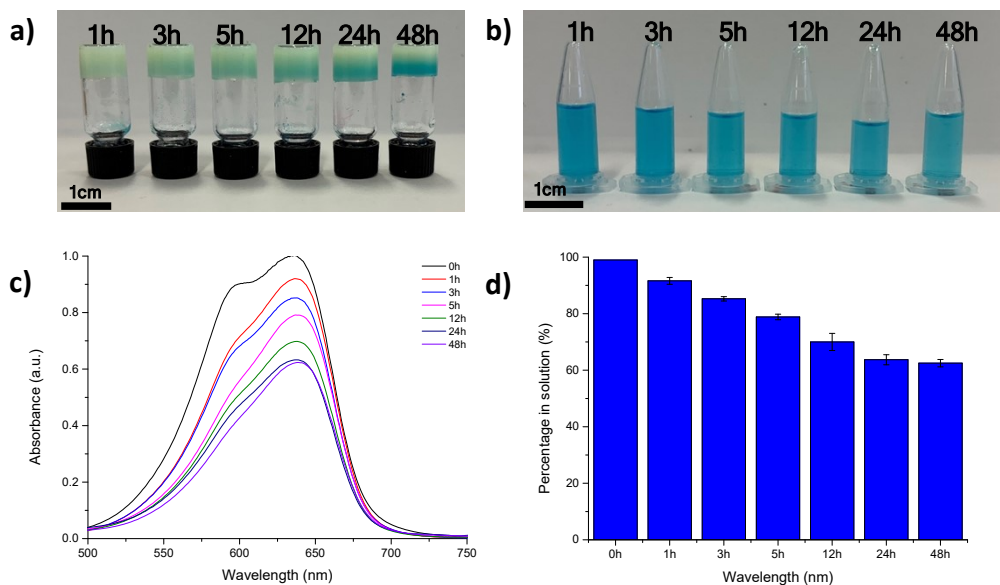


Figure S23: L1, DMSO:H₂O (1:1, v/v), 1% w/v in presence of Nile Blue A ($1.2 \cdot 10^{-5}$ M) a) gels adsorption at different hours (scale bar of 1 cm), b) withdraw solution at different hours (scale bar of 1 cm), c) UV-Vis spectra of characteristic peak of dye at 634 nm and c) histogram with percentage of dye in solution.

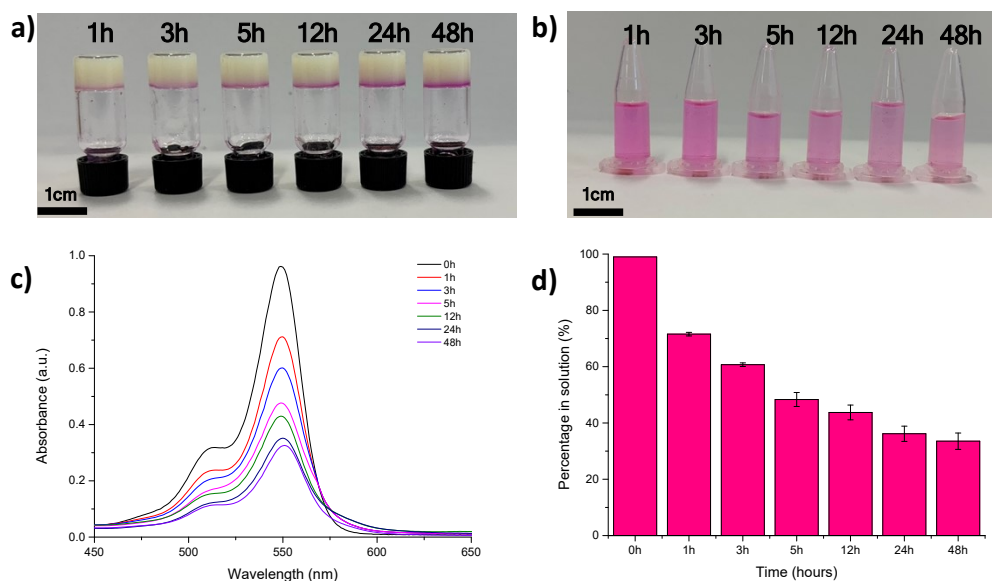


Figure S24: L1, DMSO:H₂O (1:1, v/v), 1% w/v in presence of Rose Bengal ($1.1 \cdot 10^{-5}$ M) a) gels adsorption at different hours (scale bar of 1 cm), b) withdraw solution at different hours (scale bar of 1 cm), c) UV-Vis spectra of characteristic peak of dye at 550 nm and c) histogram with percentage of dye in solution.

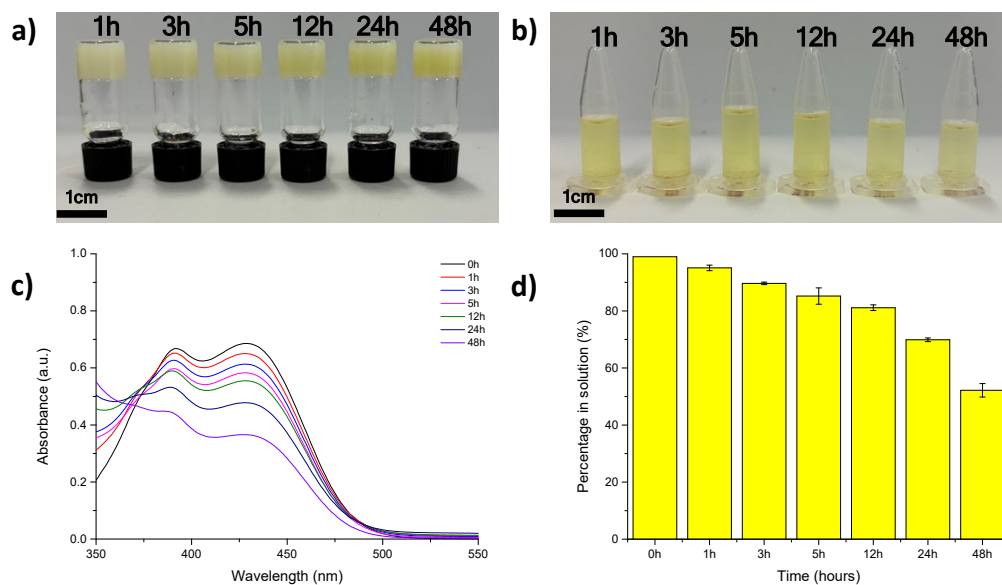


Figure S25: L1, DMSO:H₂O (1:1, v/v), 1% w/v in presence of Naphthol Yellow S ($6.5 \cdot 10^{-5}$ M) a) gels adsorption at different hours (scale bar of 1 cm), b) withdraw solution at different hours (scale bar of 1 cm), c) UV-Vis spectra of characteristic peak of dye at 428 nm and c) histogram with percentage of dye in solution.

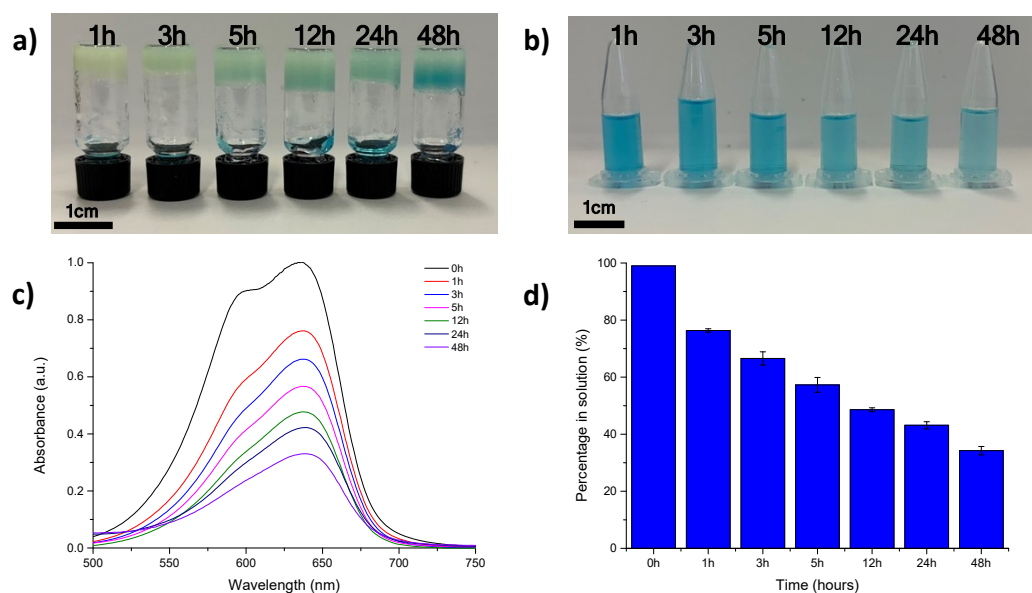


Figure S26: L2, DMSO:H₂O (1:1, v/v), 0.5% w/v in presence of Nile Blue A ($1.2 \cdot 10^{-5}$ M) a) gels adsorption at different hours (scale bar of 1 cm), b) withdraw solution at different hours (scale bar of 1 cm), c) UV-Vis spectra of characteristic peak of dye at 634 nm and c) histogram with percentage of dye in solution.

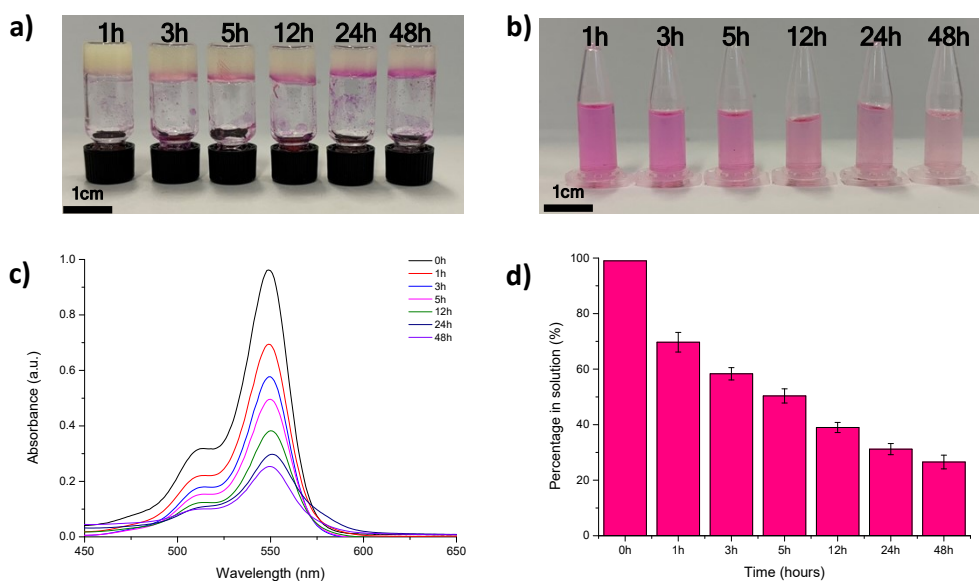


Figure S27: L2, DMSO:H₂O (1:1, v/v), 0.5% w/v in presence of Rose Bengal ($1.1 \cdot 10^{-5}$ M) a) gels adsorption at different hours (scale bar of 1 cm), b) withdraw solution at different hours (scale bar of 1 cm), c) UV-Vis spectra of characteristic peak of dye at 550nm and c) histogram with percentage of dye in solution.

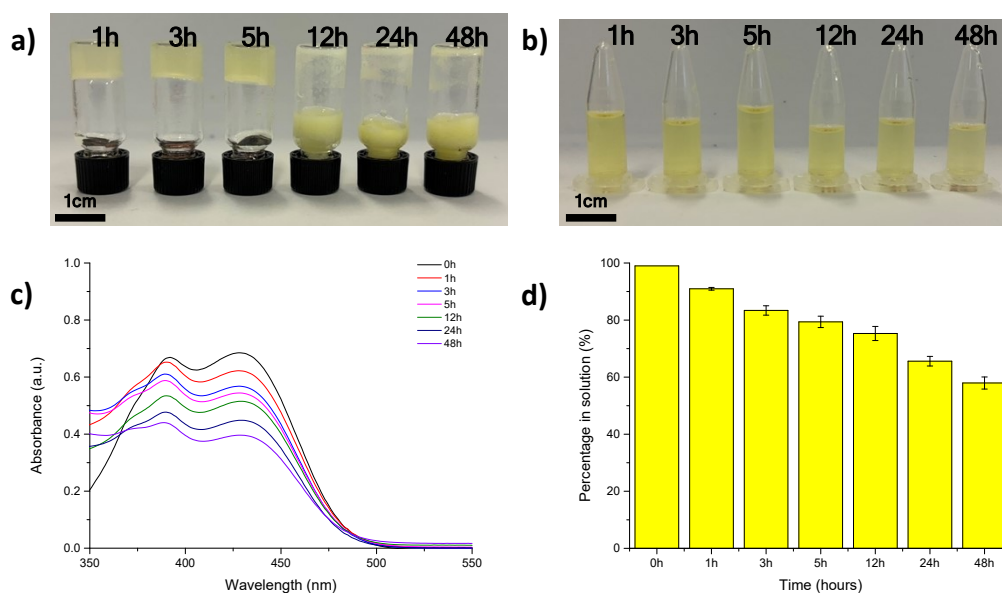


Figure S28: L2, DMSO:H₂O (1:1, v/v), 0.5% w/v in presence of Naphthol Yellow S ($6.5 \cdot 10^{-5}$ M) a) gels adsorption at different hours (scale bar of 1 cm), b) withdraw solution at different hours (scale bar of 1 cm), c) UV-Vis spectra of characteristic peak of dye at 428 nm and c) histogram with percentage of dye in solution.

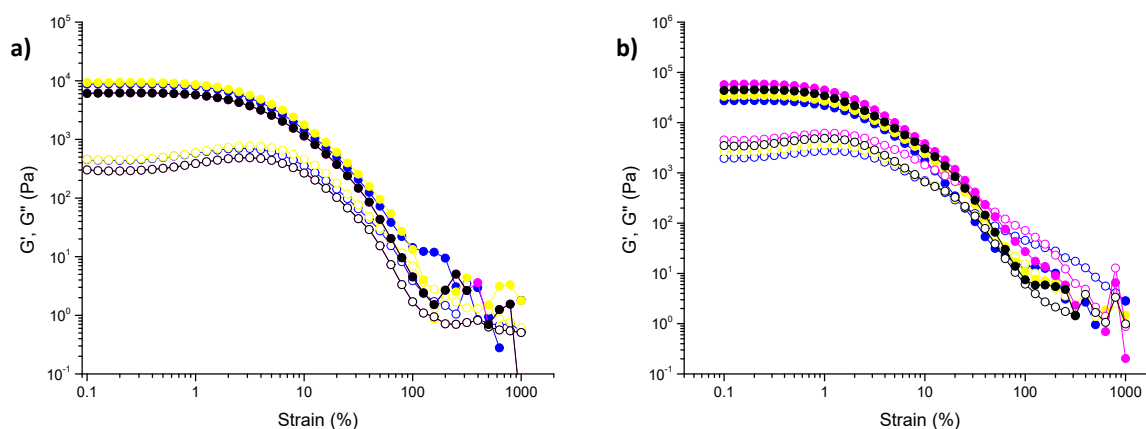


Figure S29: Strain Sweep after dyes adsorption of **L1**, a) in DMSO: H₂O (2:3, v/v), 1% w/v and b) in DMSO: H₂O (1:1, v/v), 1% w/v. Full points indicate G' and empty points indicate G'' , black points are free gels, blue point are gels in presence of Nile Blue A, yellow point are gels in presence of Naphthol Yellow S and pink points are gels in presence of Rose Bengal.

x_{water}	0.7
x_{DMSO}	0.3
$d_{DMSO} (g mL^{-1})$	1.1
$m_{DMSO} (g)$	0.4092
$n_{DMSO} (mol)$	$5.23 \cdot 10^{-3}$
$n_{DMSO\ extr} (mol)$	$7.42 \cdot 10^{-4}$

$$\frac{n_{DMSO,extr}}{n_{DMSO,tot}} \% = \frac{7.42 \cdot 10^{-4}}{5.23 \cdot 10^{-3}} 100 = 14.2\%$$

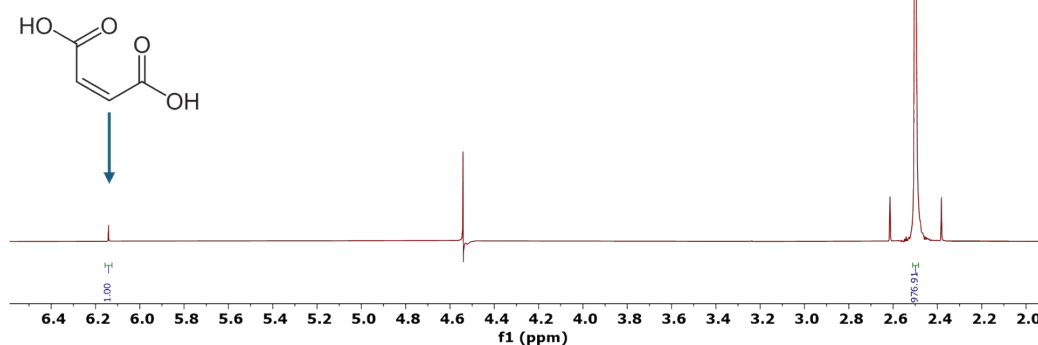


Figure S30: ¹H-NMR Spectrum of D₂O put in contact with gel **L1**, DMSO:H₂O (3:7, v/v), 0.5% w/v after 48h.

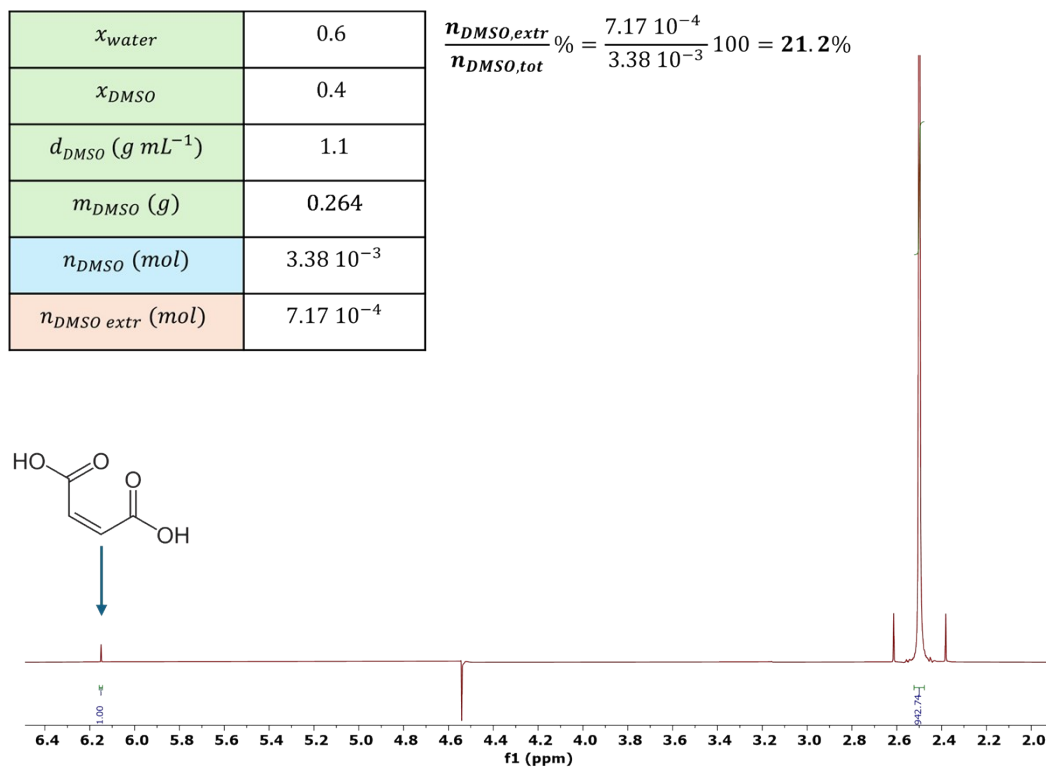


Figure S31: ^1H -NMR Spectrum of D_2O put in contact with gel **L1**, DMSO: H_2O (2:3, v/v), 1% w/v after 48h.

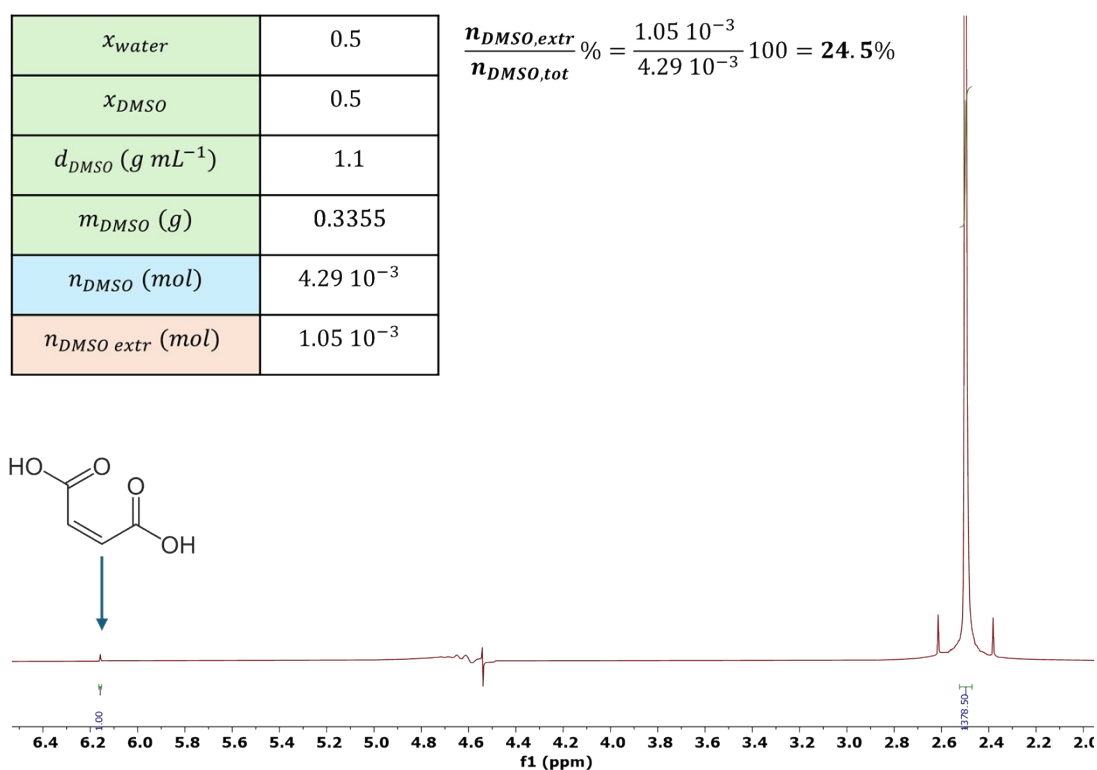


Figure S32: ^1H -NMR Spectrum of D_2O put in contact with gel **L1**, DMSO: H_2O (1:1, v/v), 1% w/v after 48h.

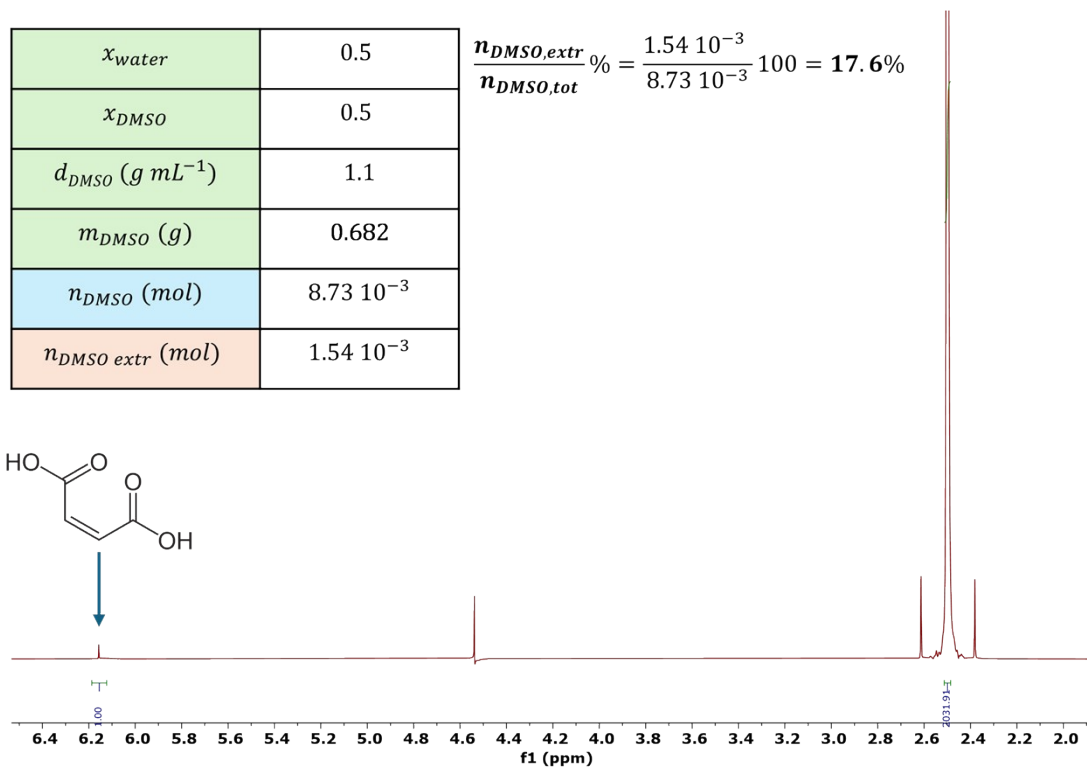


Figure S33: ^1H -NMR Spectrum of D_2O put in contact with gel **L2**, $\text{DMSO}:\text{H}_2\text{O}$ (1:1, v/v), 0.5% w/v after 48h.

5.2. Flow Analysis

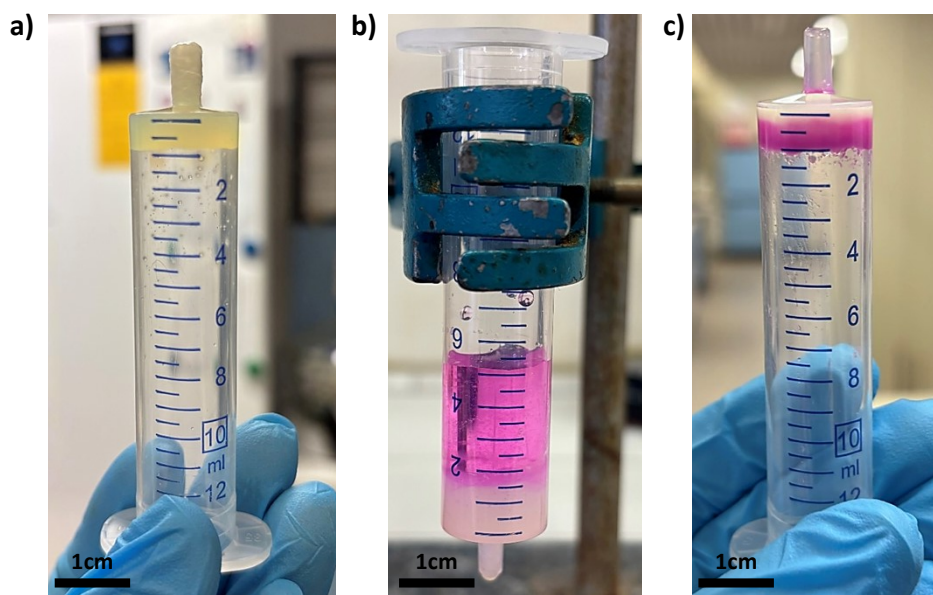


Figure S34: Experiment setup of flow test for **L1** gel in $\text{DMSO}:\text{H}_2\text{O}$ (3:7, v/v), 0.5% w/v, a) inversion tube test of free gel, b) Rose Bengal solution ($1.1 \cdot 10^{-5} \text{ M}$) flowing through the gel, c) inversion tube test of gel after dyes removal (scale bars of 1 cm).

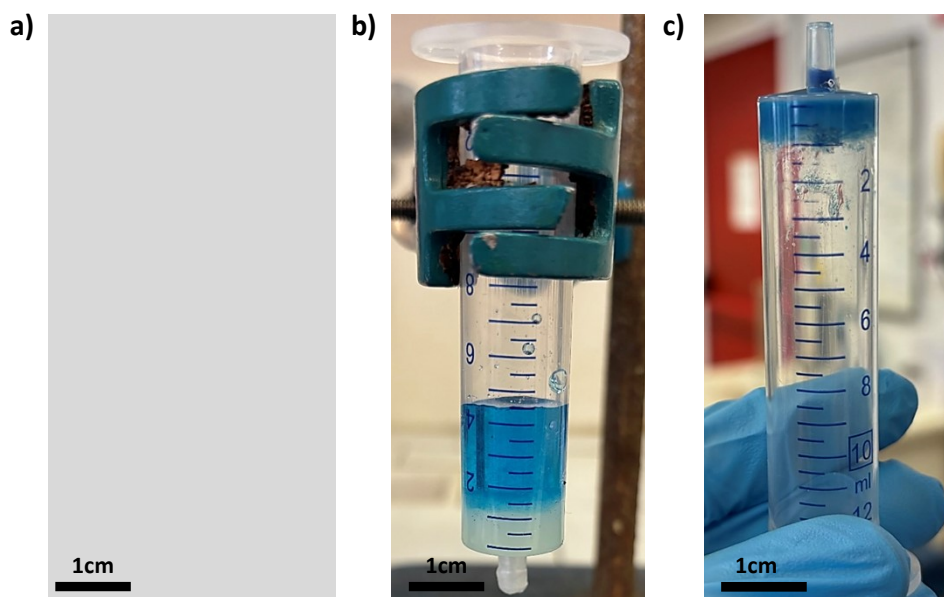


Figure S35: Experiment setup of flow test for **L1** gel in DMSO:H₂O (3:7, v/v), 0.5% w/v, a) inversion tube test of free gel, b) Nile Blue A solution ($1.2 \cdot 10^{-5}$ M) flowing through the gel, c) inversion tube test of gel after dyes removal (scale bars of 1 cm).

	L1, DMSO:H ₂ O (3:7, v/v), 0.5% w/v	L1, DMSO:H ₂ O (2:3, v/v), 1% w/v	L1, DMSO:H ₂ O (1:1, v/v), 1% w/v	L2, DMSO:H ₂ O (1:1, v/v), 0.5% w/v
	RE % Nile Blue A	RE % Nile Blue A	RE % Nile Blue A	RE % Nile Blue A
Cycle 1	88.1%	97.5%	97.5%	86.3%
Cycle 2	75.4%	96.7%	91.9%	75.9%
Cycle 3	71.2%	88.6%	89.3%	69.9%
Cycle 4	/	85.9%	87.6%	/
Cycle 5	/	82.1%	84.3%	/
Cycle 6	/	75.9%	73.9%	/
Cycle 7	/	56.6%	/	/
Cycle 8	/	40.2%	/	/

Table S5: Summary of RE% values of all gels studied by using flow test in presence of Nile Blue A ($1.2 \cdot 10^{-5}$ M).

	L1, DMSO:H ₂ O (3:7, v/v), 0.5% w/v	L1, DMSO:H ₂ O (2:3, v/v), 1% w/v	L1, DMSO:H ₂ O (1:1, v/v), 1% w/v	L2, DMSO:H ₂ O (1:1, v/v), 0.5% w/v
	RE % Rose Bengal	RE % Rose Bengal	RE % Rose Bengal	RE % Rose Bengal
Cycle 1	97.5%	97.6%	98.7%	98.1%
Cycle 2	96.8%	97.1%	97.7%	74.3%
Cycle 3	95.3%	92.7%	97.6%	61.8%
Cycle 4	94.5%	72.9%	97.5%	47.1%
Cycle 5	82.8%	64.8%	96.7%	41.1%
Cycle 6	63.9%	58.9%	85.3%	/
Cycle 7	57.9%	40.6%	73.9%	/
Cycle 8	49.8%	36.5%	66.4%	/
Cycle 9	/	/	52.4%	/
Cycle 10	/	/	40.4%	/

Table S6: Summary of RE% values of all gels studied by using flow test in presence of Rose Bengal ($1.1 \cdot 10^{-5}$ M).

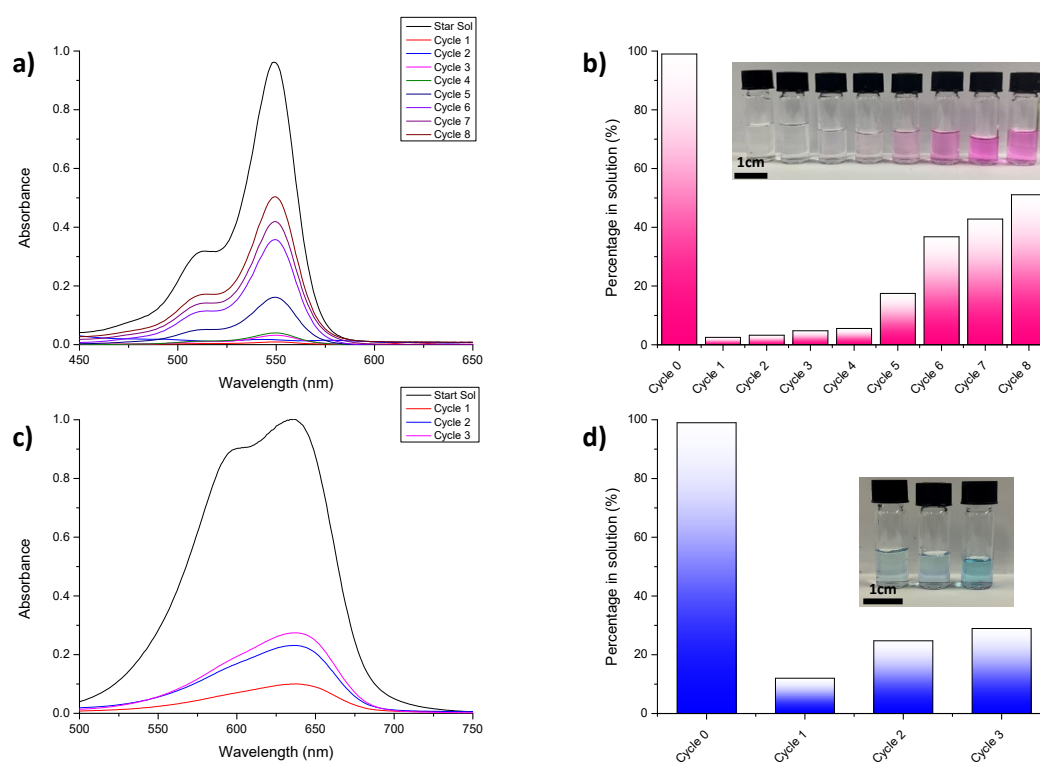


Figure S36: Reuse Analysis of L1, DMSO:H₂O (3:7, v/v), 0.5% w/v in presence of a-b) Rose Bengal ($1.1 \cdot 10^{-5}$ M) and c-d) Nile Blue A ($1.2 \cdot 10^{-5}$ M), UV-Vis Spectra, histogram with percentage of dye in solution and picture of water solution analysed (scale bar of 1 cm).

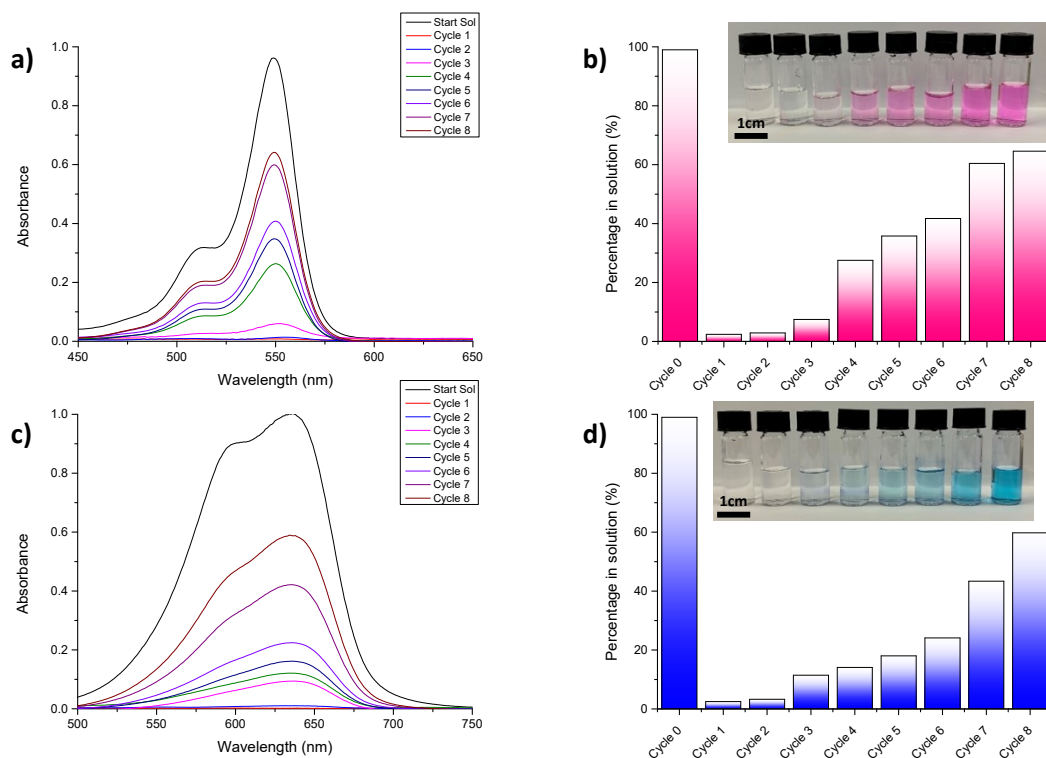


Figure S37: Reuse Analysis of **L1**, DMSO:H₂O (2:3, v/v), 1% w/v in presence of a-b) Rose Bengal (1.1·10⁻⁵ M) and c-d) Nile Blue A (1.2·10⁻⁵ M), UV-Vis Spectra histogram with percentage of dye in solution and picture of water solution analysed (scale bar of 1 cm).

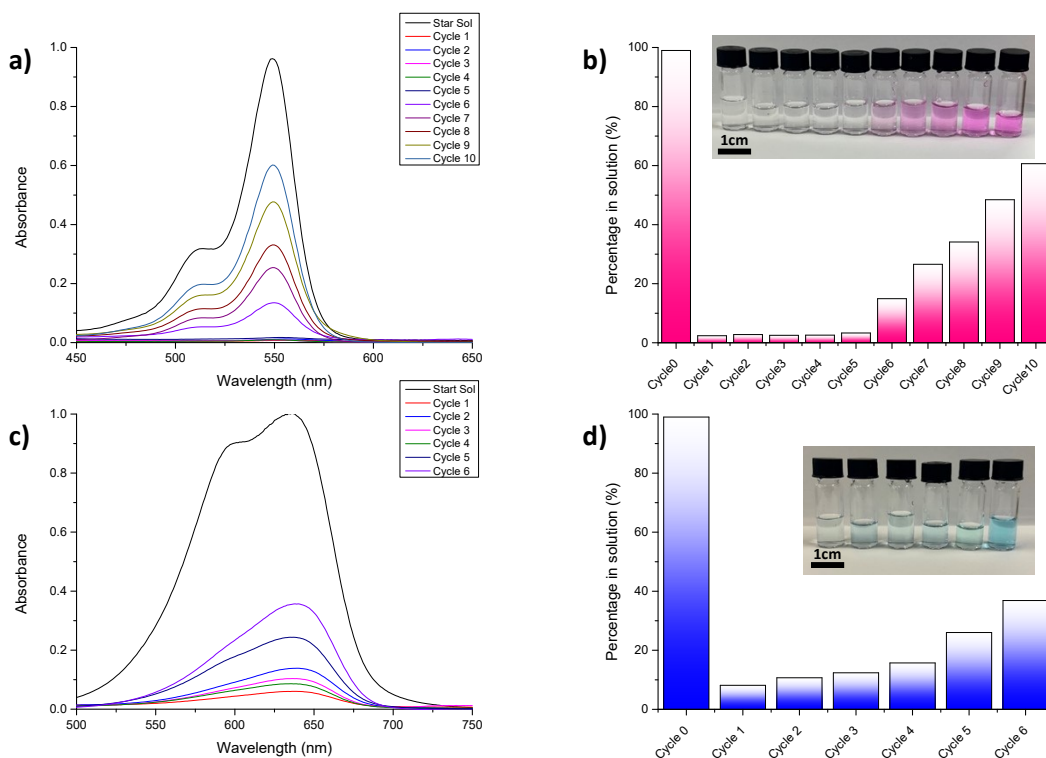


Figure S38: Reuse Analysis of **L1**, DMSO:H₂O (1:1, v/v), 1% w/v in presence of a-b) Rose Bengal (1.1·10⁻⁵ M) and c-d) Nile Blue A (1.2·10⁻⁵ M), UV-Vis Spectra, histogram with percentage of dye in solution and picture of water solution analysed (scale bar of 1 cm).

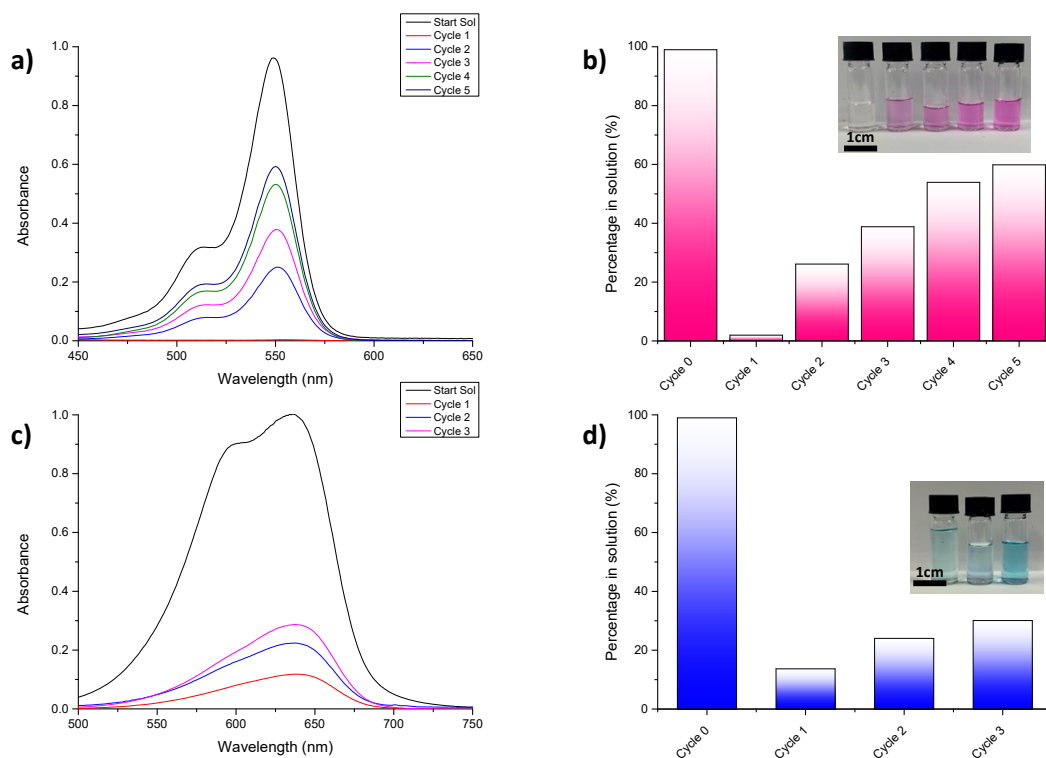


Figure S39: Reuse Analysis of **L2**, DMSO:H₂O (1:1, v/v), 0.5% w/v in presence of a-b) Rose Bengal ($1.1 \cdot 10^{-5}$ M) and c-d) Nile Blue A ($1.2 \cdot 10^{-5}$ M), UV-Vis Spectra, histogram with percentage of dye in solution and picture of water solution analysed (scale bar of 1 cm).

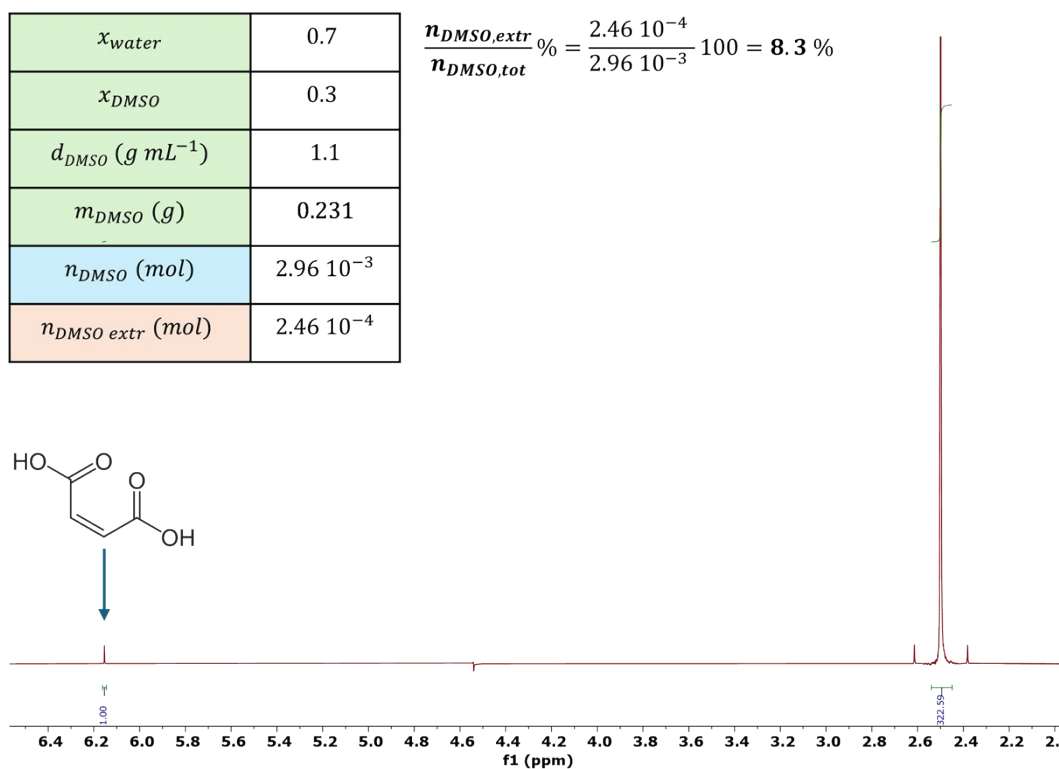


Figure S40: ¹H-NMR Spectrum of D₂O flow with gel **L1**, DMSO:H₂O (3:7, v/v), 0.5% w/v.

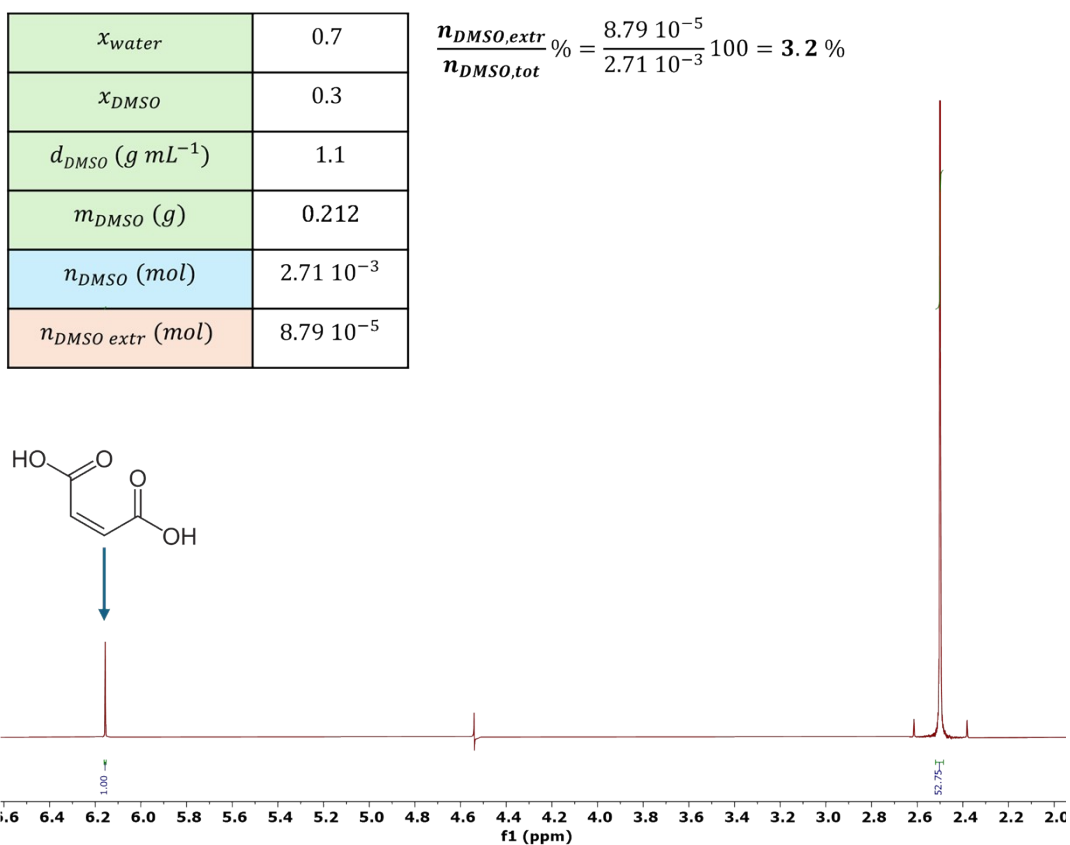


Figure S41: ^1H -NMR Spectrum of D_2O flow with washed gel **L1**, $\text{DMSO}:\text{H}_2\text{O}$ (3:7, v/v), 0.5% w/v.

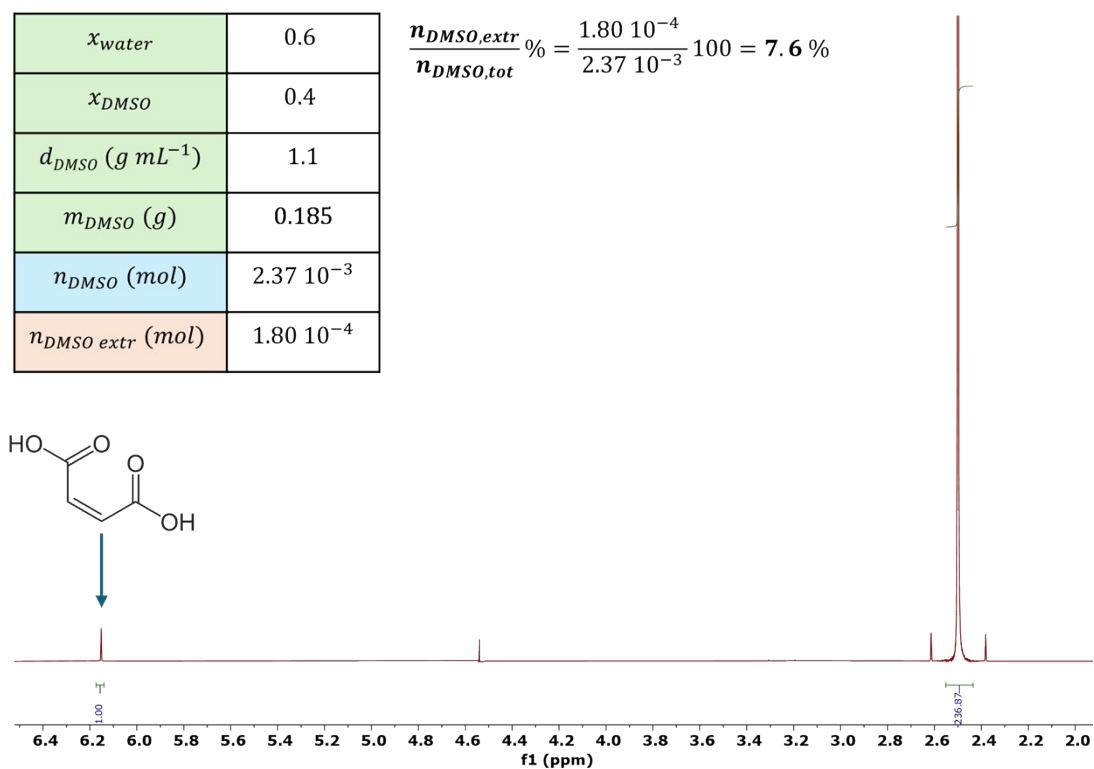


Figure S42: ^1H -NMR Spectrum of D_2O flow with gel **L1**, $\text{DMSO}:\text{H}_2\text{O}$ (2:3, v/v), 1% w/v.

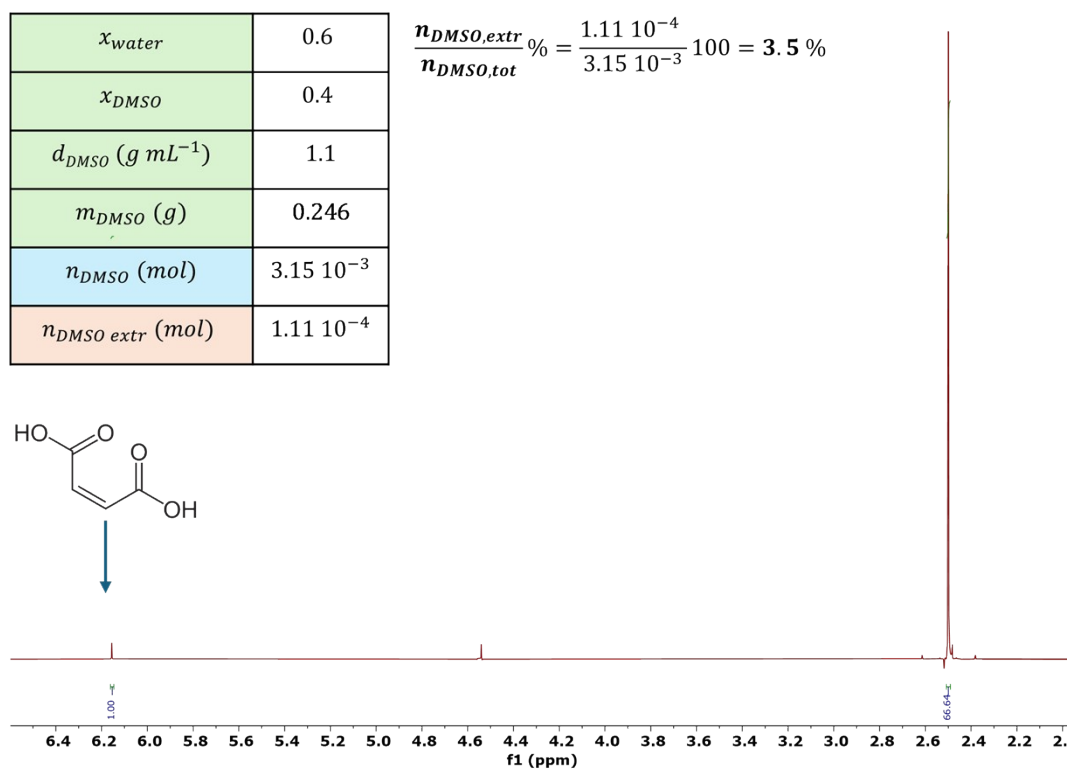


Figure S43: ^1H -NMR Spectrum of D_2O flow with washed gel **L1**, $\text{DMSO}:\text{H}_2\text{O}$ (2:3, v/v), 1% w/v.

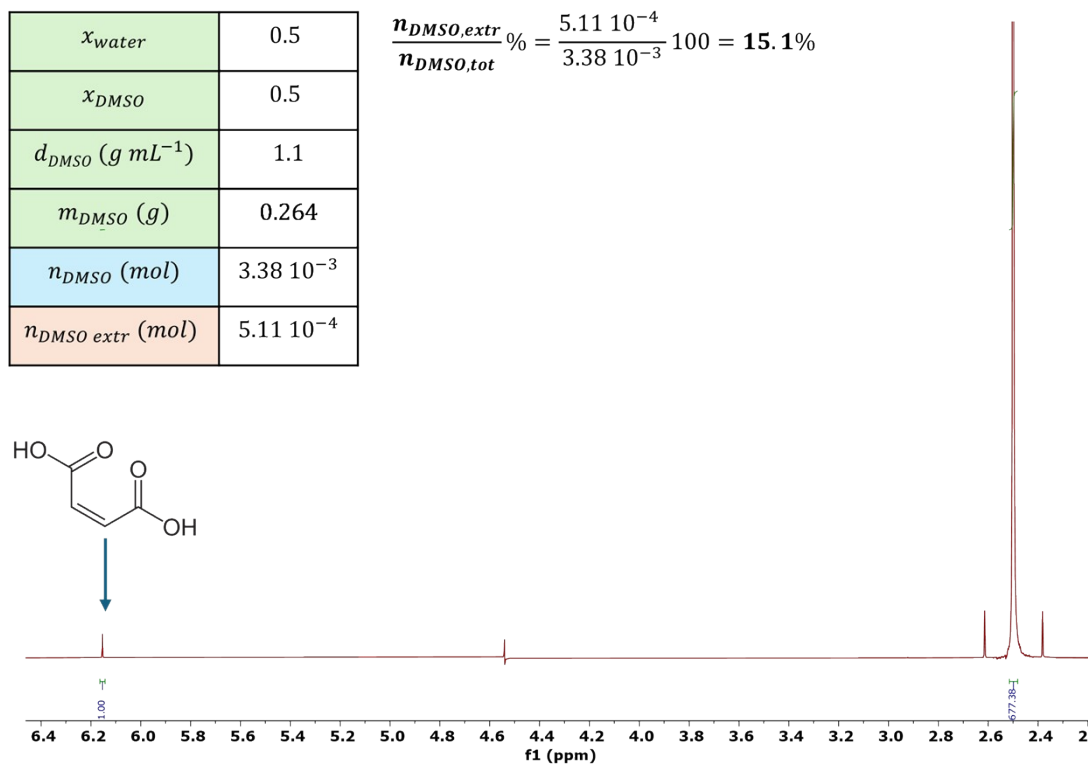


Figure S44: ^1H -NMR Spectrum of D_2O flow with gel **L1**, $\text{DMSO}:\text{H}_2\text{O}$ (1:1, v/v), 1% w/v.

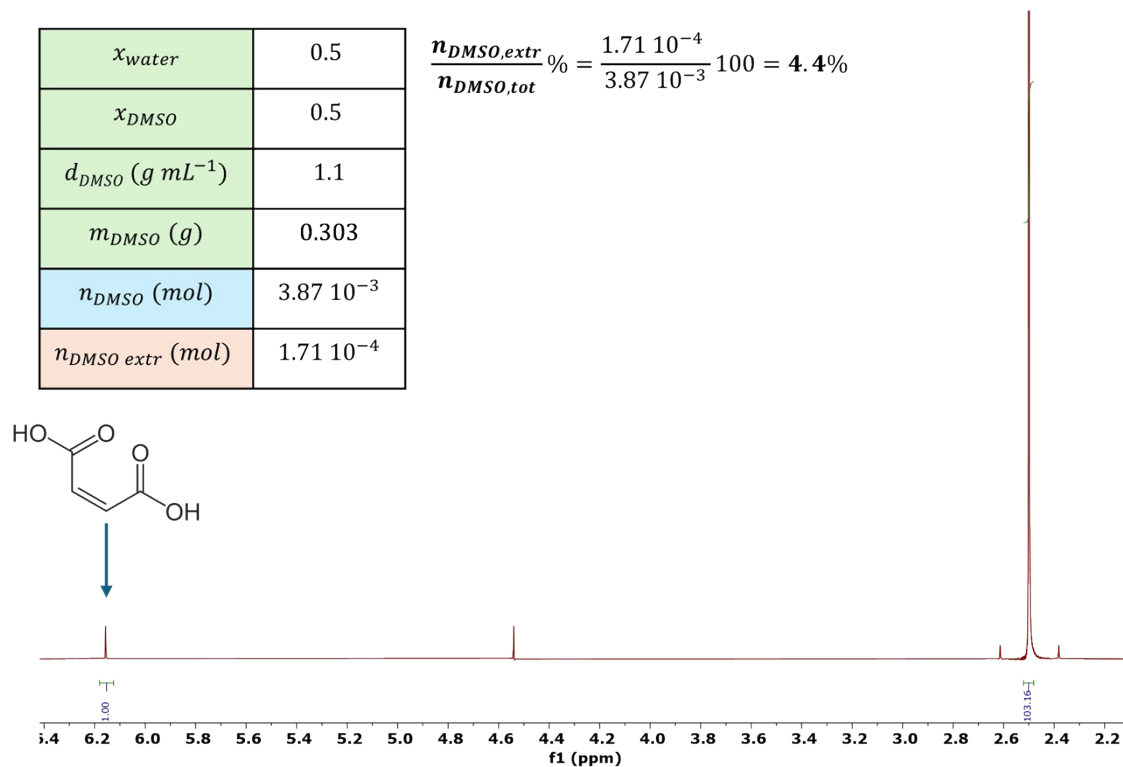


Figure S45: ^1H -NMR Spectrum of D_2O flow with washed gel **L1**, $\text{DMSO}:\text{H}_2\text{O}$ (1:1, v/v), 1% w/v.

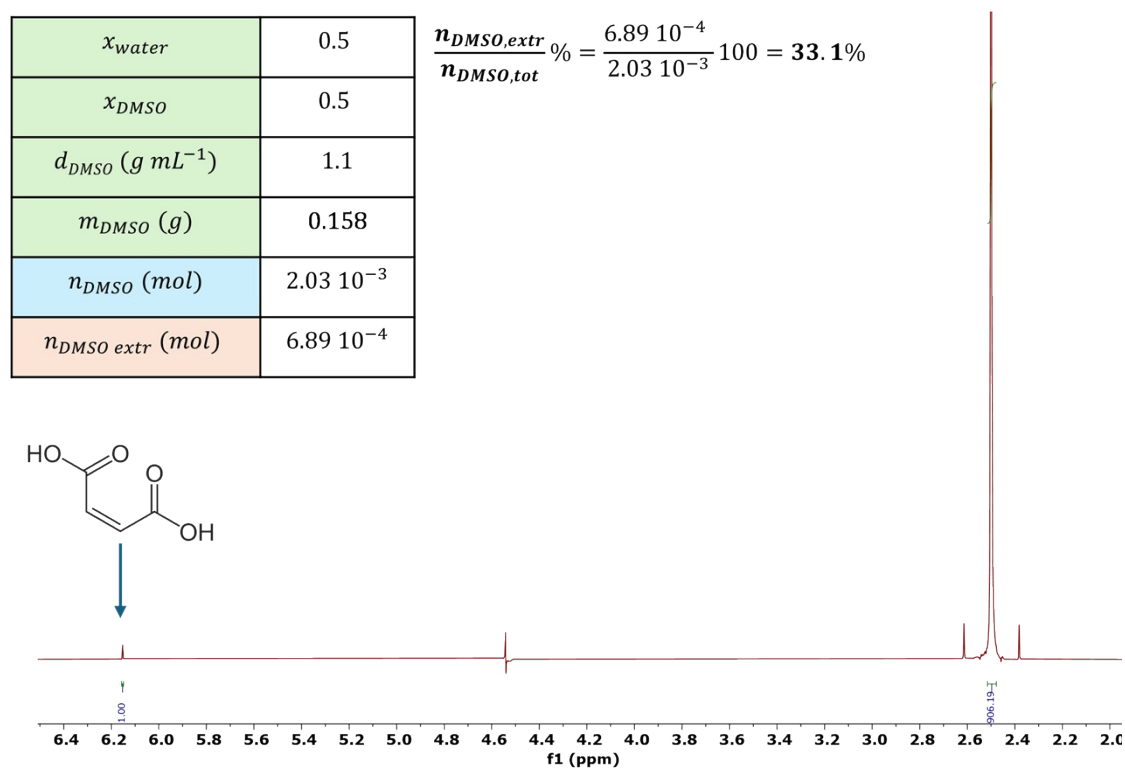


Figure S46: ^1H -NMR Spectrum of D_2O flow with gel **L2**, $\text{DMSO}:\text{H}_2\text{O}$ (1:1, v/v), 0.5% w/v.

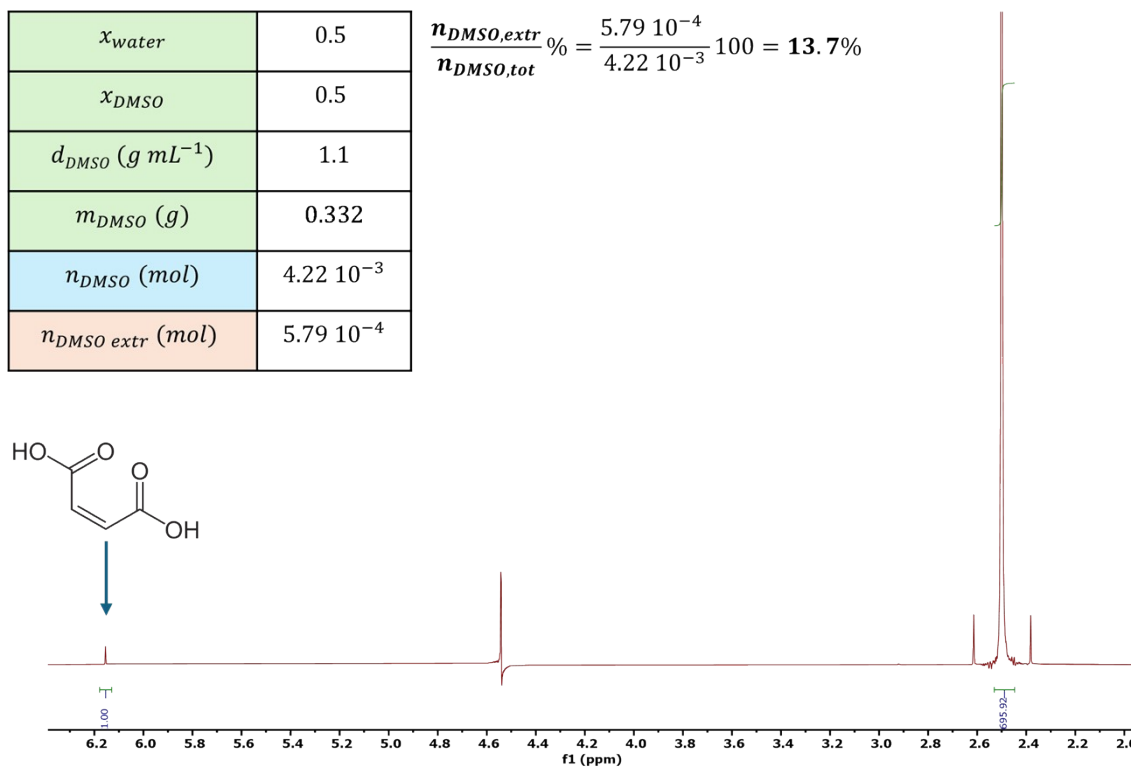


Figure S47: ^1H -NMR Spectrum of D_2O flow with washed gel **L2**, $\text{DMSO:H}_2\text{O}$ (1:1, v/v), 0.5% w/v.

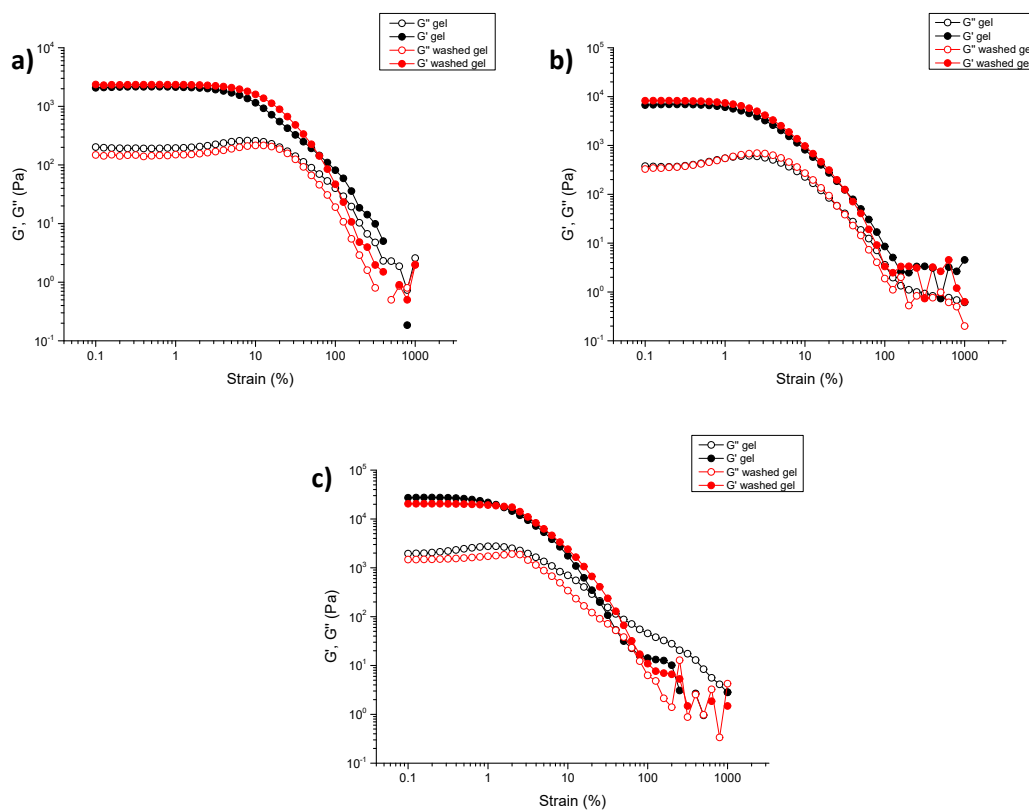


Figure S48: Strain Sweep after washing treatment of **L1** gels a) in $\text{DMSO:H}_2\text{O}$ (3:7, v/v), 0.5% w/v, b) in $\text{DMSO:H}_2\text{O}$ (2:3, v/v), 1% w/v, c) in $\text{DMSO:H}_2\text{O}$ (1:1, v/v), 1% w/v.

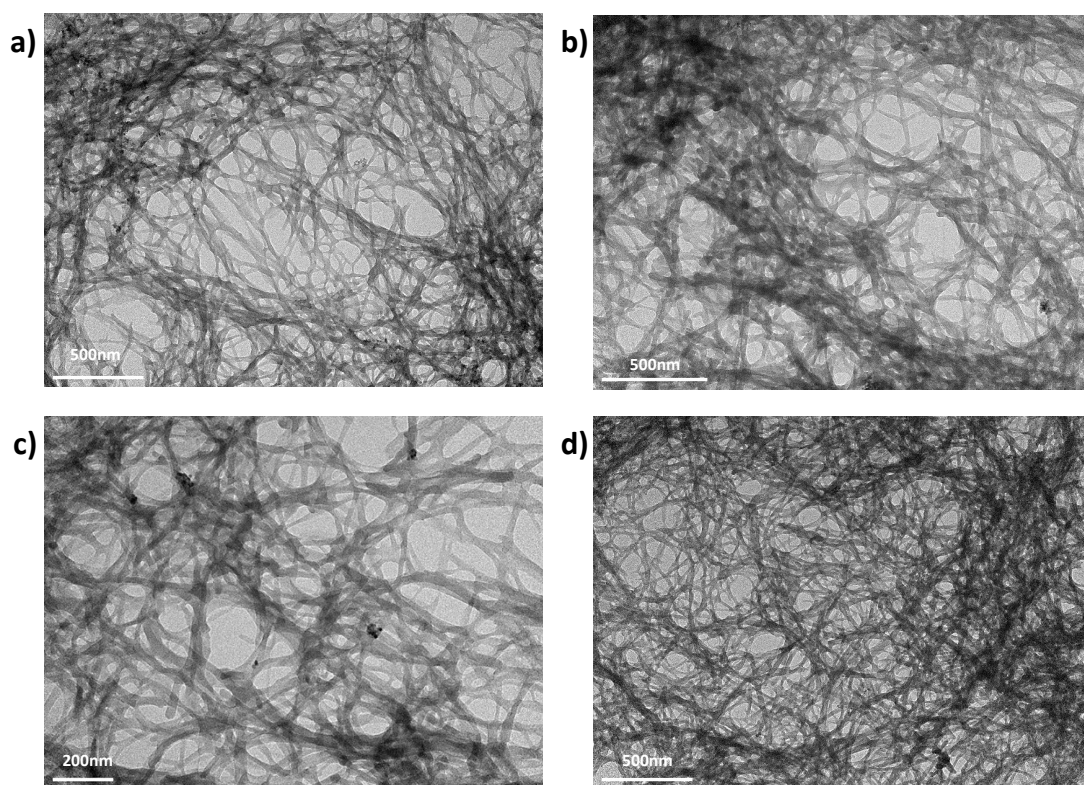


Figure S49: TEM images of **L1** gels after been washed with water in a) DMSO: H₂O, (3:7, v/v), 0.5% w/v (scale bar of 500nm), b) DMSO: H₂O, (2:3, v/v), 1% w/v (scale bar of 500nm) and c-d) DMSO: H₂O, (1:1, v/v), 1% w/v (scale bar of 200nm and 500nm).

	L1, DMSO:H ₂ O (3:7, v/v), 0.5% w/v	L1, DMSO:H ₂ O (2:3, v/v), 1% w/v	L1, DMSO:H ₂ O (1:1, v/v), 1% w/v	L2, DMSO:H ₂ O (1:1, v/v), 0.5% w/v
	RE % Nile Blue A (after washing)	RE % Nile Blue A (after washing)	RE % Nile Blue A (after washing)	RE % Nile Blue A (after washing)
Cycle 1	97.5%	97.8%	97.8%	97.6%
Cycle 2	97.5%	97.2%	97.7%	97.2%
Cycle 3	97.5%	95.5%	96.1%	95.8%
Cycle 4	97.5%	89.2%	93.4%	92.1%
Cycle 5	97.4%	80.3%	88.9%	86.3%
Cycle 6	97.3%	/	/	/
Cycle 7	88.6%	/	/	/
Cycle 8	82.1%	/	/	/
Cycle 9	75.1%	/	/	/
Cycle 10	/	/	/	/

Table S7: Summary of RE% values of all washed gels studied by using flow test in presence of Nile Blue A ($1.2 \cdot 10^{-5} \text{M}$).

	L1, DMSO:H ₂ O (3:7, v/v), 0.5% w/v	L1, DMSO:H ₂ O (2:3, v/v), 1% w/v	L1, DMSO:H ₂ O (1:1, v/v), 1% w/v	L2, DMSO:H ₂ O (1:1, v/v), 0.5% w/v
	RE % Rose Bengal (after washing)	RE % Rose Bengal (after washing)	RE % Rose Bengal (after washing)	RE % Rose Bengal (after washing)
Cycle 1	98.6%	98.1%	98.3%	97.8%
Cycle 2	98.4%	97.6%	98.3%	97.2%
Cycle 3	98.4%	97.5%	98.2%	89.5%
Cycle 4	98.4%	97.4%	98.2%	80.5%
Cycle 5	98.3%	97.3%	98.2%	78.3%
Cycle 6	94.9%	96.1%	97.9%	/
Cycle 7	87.1%	88.4%	95.7%	/
Cycle 8	79.9%	/	90.6%	/
Cycle 9	/	/	85.4%	/
Cycle 10	/	/	/	/

Table S8: Summary of RE% values of all washed gels studied by using flow test in presence of Rose Bengal ($1.1 \cdot 10^{-5} \text{M}$).

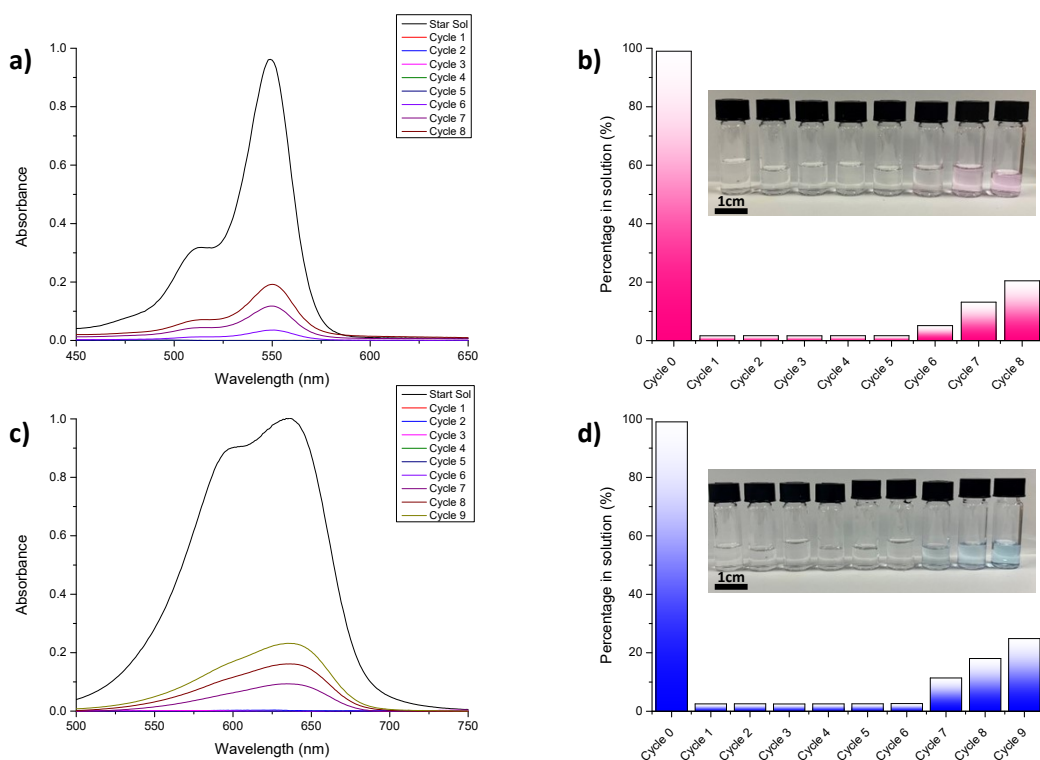


Figure S50: Reuse Analysis of L1 washed gel, DMSO:H₂O (3:7, v/v), 0.5% w/v in presence of a-b) Rose Bengal ($1.1 \cdot 10^{-5} \text{M}$) and c-d) Nile Blue A ($1.2 \cdot 10^{-5} \text{M}$), UV-Vis Spectra, histogram with percentage of dye in solution and picture of water solution analysed (scale bar of 1 cm).

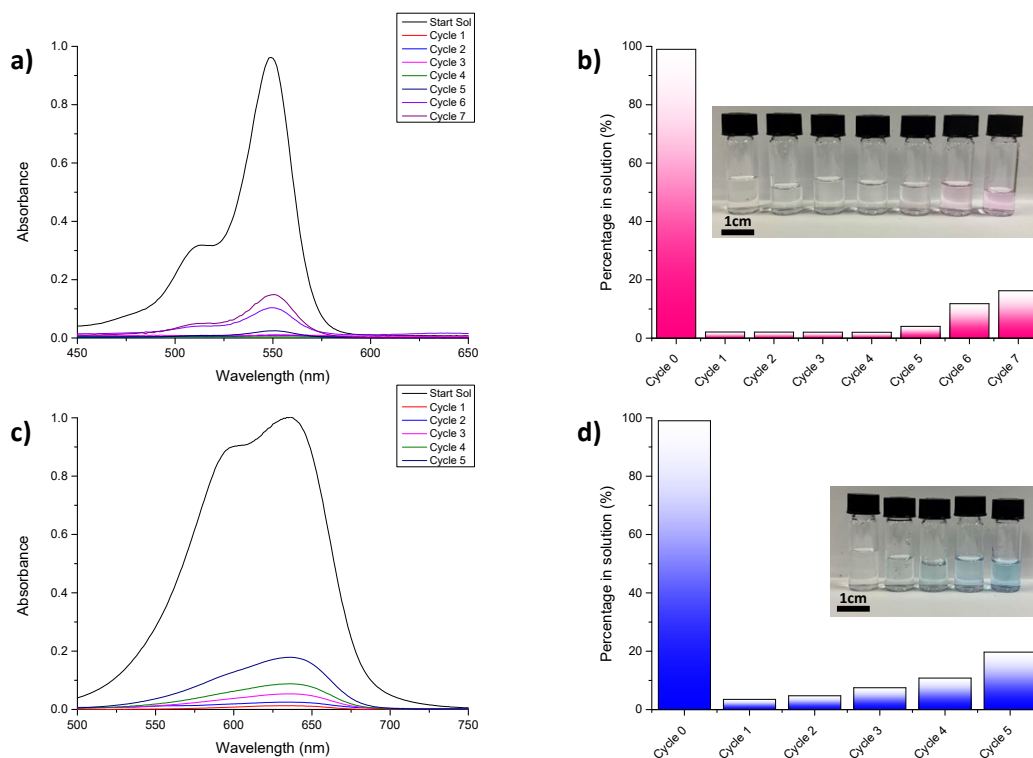


Figure S51: Reuse Analysis of **L1** washed gel, DMSO:H₂O (2:3, v/v), 1% w/v in presence of a-b) Rose Bengal ($1.1 \cdot 10^{-5}$ M) and c-d) Nile Blue A ($1.2 \cdot 10^{-5}$ M), UV-Vis Spectra, histogram with percentage of dye in solution and picture of water solution analysed (scale bar of 1 cm).

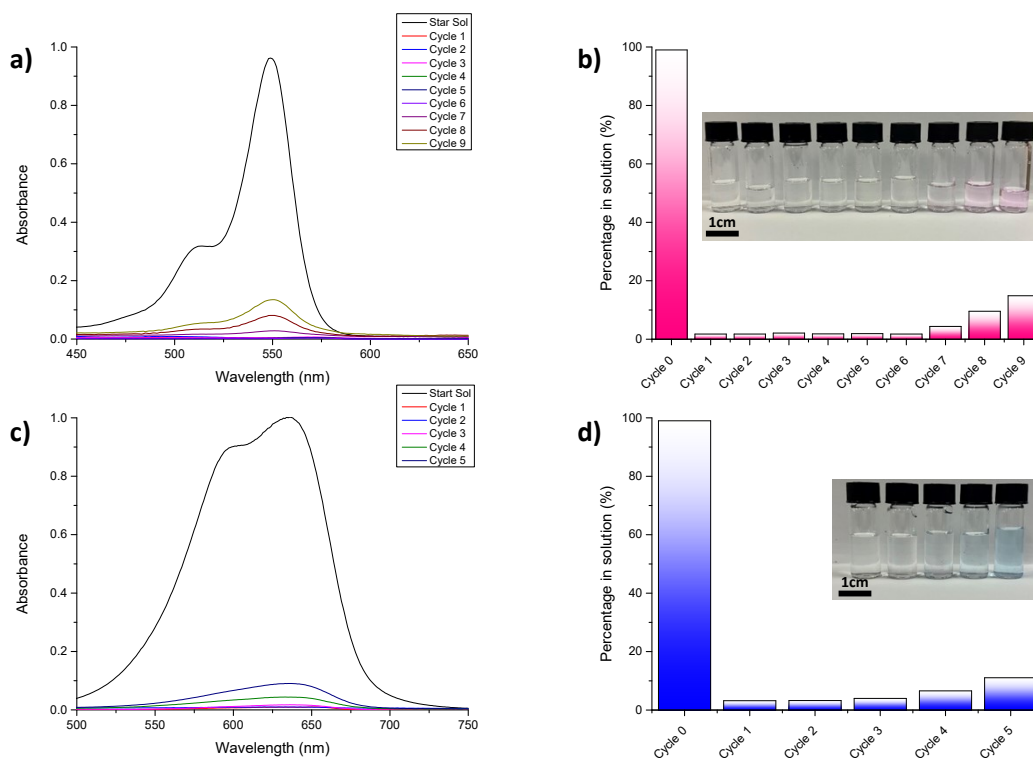


Figure S52: Reuse Analysis of **L1** washed gel, DMSO:H₂O (1:1, v/v), 1% w/v in presence of a-b) Rose Bengal ($1.1 \cdot 10^{-5}$ M) and c-d) Nile Blue A ($1.2 \cdot 10^{-5}$ M), UV-Vis Spectra, histogram with percentage of dye in solution and picture of water solution analysed (scale bar of 1 cm).

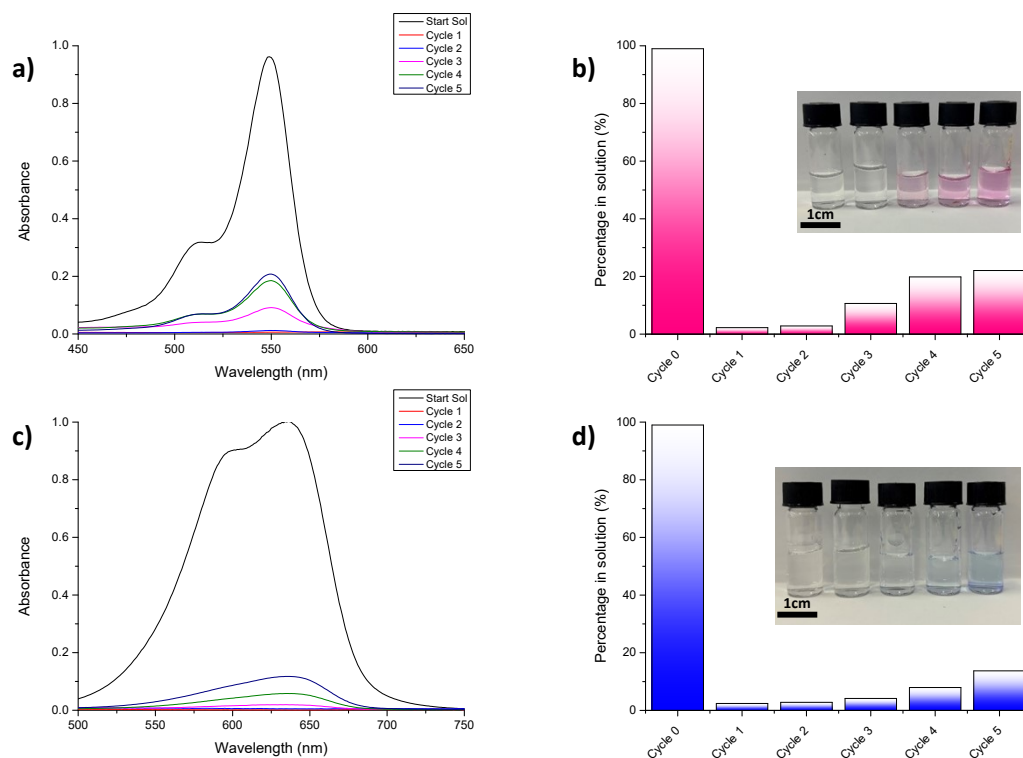


Figure S53: Reuse Analysis of **L2** washed gel, DMSO:H₂O (1:1, v/v), 0.5% w/v in presence of a-b) Rose Bengal ($1.1 \cdot 10^{-5}$ M) and c-d) Nile Blue A ($1.2 \cdot 10^{-5}$ M), UV-Vis Spectra, histogram with percentage of dye in solution and picture of water solution analysed (scale bar of 1 cm).

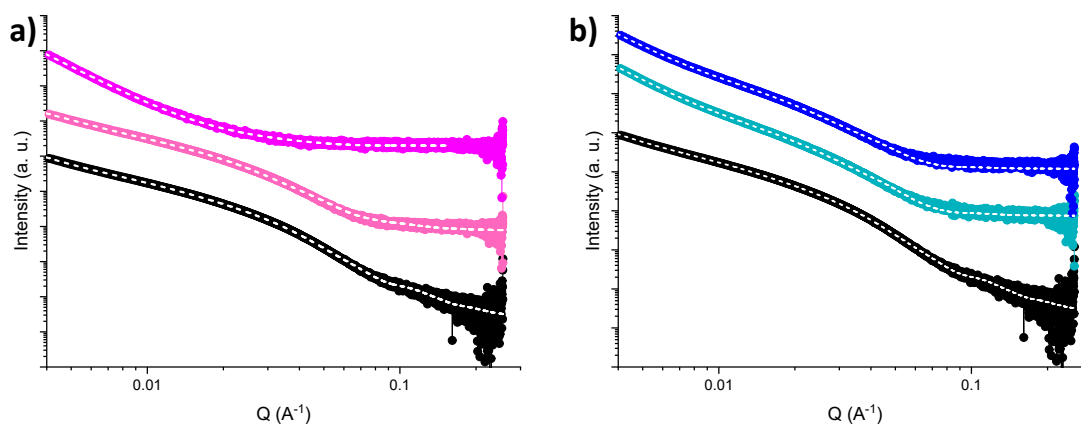


Figure S54: SAXS data with fitting of **L1** in DMSO: H₂O (3:7, v/v), 0.5% w/v after adsorption of a) Rose Bengal ($1.1 \cdot 10^{-5}$ M) in two different depths and b) Nile Blue A ($1.2 \cdot 10^{-5}$ M) at two different depths. Black points indicate the free gel, while light pink and light blue indicate the gel in presence of the respective dyes and pink and blue indicate the measurement at 3 mm and 5 mm of depth, respectively.

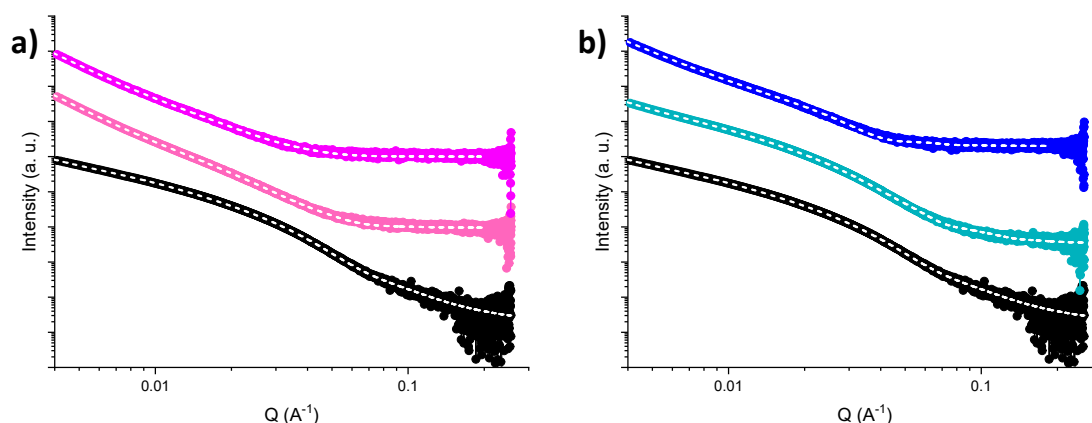


Figure S55: SAXS data with fitting of **L1** in DMSO: H₂O (2:3, v/v), 1% w/v after adsorption of a) Rose Bengal (1.1·10⁻⁵ M) in two different depths and b) Nile Blue A (1.2·10⁻⁵ M) at two different depths. Black points indicate the free gel, while light pink and light blue indicate the gel in presence of the respectively dyes and pink and blue indicate the measurement at 3 mm and 5 mm of depth, respectively.

	<i>L1, DMSO:H₂O (3:7, v/v), 0.5% w/v Gel + Nile Blue A (EC_PL)</i>		<i>L1, DMSO:H₂O (3:7, v/v), 0.5% w/v Gel (5mm) + Nile Blue A (EC_PL)</i>		<i>L1, DMSO:H₂O (3:7, v/v), 0.5% w/v Gel + Rose Bengal (EC_PL)</i>		<i>L1, DMSO:H₂O (3:7, v/v), 0.5% w/v Gel (3mm) + Rose Bengal (C_PL)</i>	
	Value	Error	Value	Error	Value	Error	Value	Error
Scale	1		1		1		1	
Background (cm ⁻¹)	0.16*		0.15*		0.15*		0.2*	
A_scale	0.0022	1.19× 10 ⁻⁵	0.0034	1.31× 10 ⁻⁵	0.0047	2.45× 10 ⁻⁵	0.00014	7.35× 10 ⁻⁶
A_length (Å)	1000*	/	1000*	/	1000*	/	1007.5	406.49
A_Kuhn_length (Å)	/	/	/	/	/	/	/	/
A_radius (Å)	42.08	0.14	41.64	0.09	45.16	0.15	43.45	1.66
A_axis_ratio (Å)	3.11	0.022	2.94	0.014	2.56	0.012	/	/
B_scale	1.74× 10 ⁻⁶	8.02× 10 ⁻⁸	2.24× 10 ⁻⁶	6.26× 10 ⁻⁸	0.00022	5.87× 10 ⁻⁶	1.52× 10 ⁻⁷	6.28× 10 ⁻⁹
B_power	3.48	0.008	3.58	0.005	2.50	0.0045	3.63	0.007
χ ²	1.1229		1.5628		1.8853		1.6622	

Table S9: SAXS fitting data of gel **L1**, DMSO:H₂O (3:7, v/v), 0.5% w/v after Nile Blue A and Rose Bengal adsorption (SAXS data collected at two different depths of capillary).

	<i>L1, DMSO:H₂O (2:3, v/v), 1% w/v Gel + Nile Blue A (FCE_PL)</i>		<i>L1, DMSO:H₂O (2:3, v/v), 1% w/v Gel (5mm) + Nile Blue A (C_PL)</i>		<i>L1, DMSO:H₂O (2:3, v/v), 1% w/v Gel + Rose Bengal (FCE_PL)</i>		<i>L1, DMSO:H₂O (2:3, v/v), 1% w/v Gel (3mm) + Rose Bengal (EC_PL)</i>	
	<i>Value</i>	<i>Error</i>	<i>Value</i>	<i>Error</i>	<i>Value</i>	<i>Error</i>	<i>Value</i>	<i>Error</i>
<i>Scale</i>	1		1		1		1	
<i>Background (cm⁻¹)</i>	0.135*		0.2*		0.19*		0.2*	
<i>A_scale</i>	0.0043	9.0×10 ⁻⁶	0.0004	4.38×10 ⁻⁶	0.0045	4.81×10 ⁻⁶	0.0003	7.17×10 ⁻⁶
<i>A_length (Å)</i>	1513.5	5.83	1236.1	70.03	873.16	28.57	1000*	/
<i>A_Kuhn_length (Å)</i>	121*	/	/	/	150*	/	/	/
<i>A_radius (Å)</i>	46.46	0.087	84.485	0.31	43*	/	44.25	0.97
<i>A_axis_ratio (Å)</i>	2.19	0.0058	/	/	2.64	0.017	3.19	0.13
<i>B_scale</i>	0.00014	2.52×10 ⁻⁶	4.84×10 ⁻⁶	1.67×10 ⁻⁷	1.46×10 ⁻⁶	4.76×10 ⁻⁶	4.74×10 ⁻⁷	2.78×10 ⁻⁸
<i>B_power</i>	2.86	0.003	3.15	0.006	3.7	0.006	3.56	0.01
<i>χ²</i>	1.2611		1.1261		1.0197		1.4016	

Table S10: SAXS fitting data of gel **L1**, DMSO:H₂O (2:3, v/v), 1% w/v after Nile Blue A and Rose Bengal adsorption (SAXS data collected at two different depths of capillary).

	<i>L1, DMSO:H₂O (1:1, v/v), 1% w/v Gel + Nile Blue A (FCE_PL)</i>		<i>L1, DMSO:H₂O (1:1, v/v), 1% w/v Gel (5mm) + Nile Blue A (C_PL)</i>		<i>L1, DMSO:H₂O (1:1, v/v), 1% w/v Gel + Rose Bengal (FCE_PL)</i>		<i>L1, DMSO:H₂O (1:1, v/v), 1% w/v Gel (3mm) + Rose Bengal (FCE_PL)</i>	
	<i>Value</i>	<i>Error</i>	<i>Value</i>	<i>Error</i>	<i>Value</i>	<i>Error</i>	<i>Value</i>	<i>Error</i>
<i>Scale</i>	1		1		1		1	
<i>Background (cm⁻¹)</i>	0.135*		0.25*		0.15*		0.2*	
<i>A_scale</i>	0.01	5.14×10 ⁻⁵	0.0009	6.45×10 ⁻⁶	0.0047	1.06×10 ⁻⁵	0.009	1.06×10 ⁻⁵
<i>A_length (Å)</i>	2398.1	68.38	1226.7	34.9	2331.4	10.79	1846*	/
<i>A_Kuhn_length (Å)</i>	134	4.84	/	/	100*	/	100*	/
<i>A_radius (Å)</i>	45.73	0.23	85.36	0.18	45*	/	48.2	0.067
<i>Polidispersity</i>	0.2	/	0.2	/	0.2	/	0.2	/
<i>A_axis_ratio (Å)</i>	2.29	0.013	/	/	2.21	0.0024	2.16	0.005
<i>B_scale</i>	0.0003	4.01×10 ⁻⁶	1.72×10 ⁻⁵	2.61×10 ⁻⁷	8.39×10 ⁻⁵	1.14×10 ⁻⁶	0.00016	1.67×10 ⁻⁶
<i>B_power</i>	2.71	0.003	3.14	0.003	2.91	0.002	3.03	0.002
<i>χ²</i>	1.4232		1.9156		1.0123		2.2193	

Table S11: SAXS fitting data of gel **L1**, DMSO:H₂O (1:1, v/v), 1% w/v after Nile Blue A and Rose Bengal adsorption (SAXS data collected at two different depths of capillary).

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