

Supporting Information

Ultrasonication enhanced gelation properties of an amphiphilic formamidine-based gelator molecule

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1. Material characterization

1.1. Compound characterization:

- a) Thin layer chromatography (TLC) analyses were performed using fluorescent-indicating plates (aluminum sheets precoated with silica gel 60 F₂₅₄, thickness 0.2 mm, Merck), and visualization achieved by UV light ($\lambda_{\text{max}} = 254 \text{ nm}$) and staining with phosphomolybdic acid and/or iodine.
- b) Nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on Bruker Avance-300 instrument. Chemical shifts are denoted in δ (ppm) relative to residual solvent peaks. Coupling constants, J , are given in Hertz. The following standard abbreviations are used for characterization of ¹H-NMR signals: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets. Estimated error of reported values: 0.01 ppm (δ , ¹H-NMR), 0.1 ppm (δ , ¹³C-NMR), 0.1 Hz (J , coupling constant).
- c) Melting points (m. p.) were measured with an Opti Melt Automated Melting Point System (Stanford research systems).
- d) Low resolution mass spectroscopy was carried out on a Varian MAT 311A.
- e) Elemental analysis was performed on a Heraeus Mikro-Rapid analyzer.
- f) UV-vis spectroscopy was performed using a Varian Cary 50 UV spectrophotometer and quartz-glass cuvettes of 0.5 cm thickness.

1.2. Characterization of gel-based materials:

- a) Critical gelation concentration (*CGC*) values were estimated by continuously adding aliquots of solvent (0.02-0.1 mL) into vials containing the formamidine compound and performing a typical heating-cooling or ultrasonication enhanced protocol for gel-formation until no gelation was observed. The starting point for *CGC* determinations was 200 mg/mL.
- b) Thermal *gel-to-sol* transition temperature (T_{gel}) values were determined using a custom made set-up (the sealed vial was placed in a mold of an alumina block which was heated up using an electric heating plate equipped with a temperature control couple at 1 °C/ 5 min, values obtained have been crosschecked with data from literature known compounds). The hereby obtained values have been verified by the inverse flow method¹ (the sealed vial containing the gel-material was hung horizontally into an oil bath, which was heated up at 1 °C/ 5 min) and DSC measurements. Herein, the temperature at which the gel started to break was defined as T_{gel} . Each measurement was made at least by duplicate and the average value reported. T_{gel} values were found almost unaltered within a difference of 1-2 °C after several heating-cooling cycles. Also verification on the independence of the position inside the apparatus has been carried out.



Fig. S1 Custom made set-up for T_{gel} -determinations. A) Front view showing the composition between electric heating plate, alumina block and digital thermo-couple. B) Top view of the set-up during experimentation containing vials (4 cm length x 1 cm diameter) with gel-materials. It is important to mention that the alumina block was constructed especially for one type of vials which fit smoothly inside the molds to ensure a good transmission of the heat-flow.

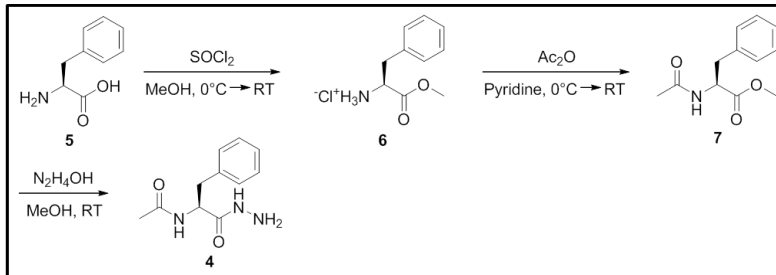
- c) Fourier transform infrared (FT-IR) spectra were recorded at room temperature using an Excalibur FTS 3000 FT-IR spectrometer (Biorad) equipped with a single reflection ATR (attenuated total reflection) accessory (Golden Gate, Diamond).
- d) Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo Differential Scanning Calorimeter using a DSC 30 measuring cell. The DSC thermograms were obtained under dynamic argon atmosphere (gas flow rate = 25 mL min⁻¹) at a heating rate of 5 °C min⁻¹. Samples were placed in closed aluminum pans (Mettler Toledo). An empty sample holder was used as reference and the runs were performed by heating the samples from 25 to 100 °C. The values were reported as the average of two independent measurements.
- e) Field Emission Scanning Electron Microscopy (FESEM) images of xerogels were obtained with a Zeiss Merlin, Field Emission Scanning Electron Microscope operated at an accelerating voltage of 10 kV. Scanning Electron Microscope (SEM) was performed using a JEOL JSM 6400 scanning electron microscope equipped with a digital camera and operating at 15 kV. For visualization, samples were prepared by the freeze-drying (FD) method: An Eppendorf tube containing the corresponding gel-material (100–200 µL) was frozen in liquid nitrogen or dry ice/acetone and the solvent immediately evaporated under reduced pressure (0.6 mmHg) for 2 days at RT. A fibrous solid was obtained, which was placed on top of a tin plate and shielded by Pt (40 mA during 30-60 s (film thickness = 5-10 nm).
- f) Oscillatory rheology was performed with an AR 2000 Advanced rheometer (TA Instruments) equipped with a Julabo C cooling system. A 1000 µm gap setting and a torque setting of 40,000 dynes/cm² at 25 °C were used for the measurements in a plain-plate (20 mm, stainless steel). The data were found to be highly reproducible for independent batches. The following experiments were

carried out for each sample, using 2 mL total gel volume: a) Dynamic strain sweep (DSS): variation of G' and G'' with strain (from 0.01 to 100%); b) dynamic frequency sweep (DFS): variation of G' and G'' with frequency (from 0.1 to 10 Hz at 0.1% strain); c) dynamic time sweep (DTS): variation of G' and G'' with time keeping the strain and frequency values constant and within the linear viscoelastic regime (strain = 0.1% strain; frequency = 1 Hz). Mechanical inertial effects of the measuring head was accounted by the software package to accurately evaluate the thixotropic nature of the materials through loop tests. For this, fixed rest time after sample loading and pre-shearing to equilibrium at different shear rates were routinely made in order to minimize prehistory effects. Loop-tests involved the following steps: (1) Application of a low stress phase for 10 min at 0.1% oscillatory strain and 1Hz frequency as defined by DTS experiments (gel state, $G' > G''$), (2) increase of the shear strain rate until 100% strain and 1 Hz frequency for 5 min to ensure gel-to-sol transition ($G' < G''$) and minimize inertial effects, and (3) relaxation for 30 min at the same conditions as for step (1) (recovered gel state, $G' > G''$). Steps (2) and (3) were repeated once to show the reversible thixotropic nature of the gel-materials.

2. Synthesis and characterization of compounds

2.1. General synthetic approach towards the precursor molecule 4

Compounds **4**, **6** and **7** have been synthesized according to literature known procedures and exhibited identical spectroscopic properties.



(S)-Methyl-2-amino-3-phenylpropanoate hydrochloride (**6**)

(L)-Phenylalanine (5.00 g, 42.0 mmol) was added carefully in portions to a cooled solution of thionyl chloride (15.30 mL, 210.0 mmol) in MeOH (50 mL) at 0°C. After stirring for 1h, the solution was allowed to warm to RT and stirred for additional 24h. The solvent was removed under reduced pressure and the resulting residue was co-evaporated with MeOH (5 x 20 mL) to give compound **6** (9.05 g, 42.0 mmol, 100%) as white solid in quantitative yield without need of purification. ¹H-NMR (300 MHz, MeOD): δ (ppm) = 7.42 – 7.32 (m, 3H), 7.29 – 7.24 (m, 2H), 4.33 (dd, J = 7.3, 6.2 Hz, 1H), 3.81 (s, 3H), 3.29 – 3.13 (m, 2H).

(S)-Methyl-2-acetamido-3-phenylpropanoate (**7**)

Compound **6** (5.00 g, 23.0 mmol) was added in one portion to a cooled solution of acetic anhydride (11.0 mL, 120.0 mmol) in pyridine (9.5 mL) at 0°C. After stirring for 0.5h, the solution was allowed to warm to RT and stirred for additional 12h. After addition of ice-water (50 mL), the aqueous mixture was extracted with CH₂Cl₂ (4 x 25 mL) and the combined organic layers were washed with sat. NH₄Cl (3 x 25 mL),

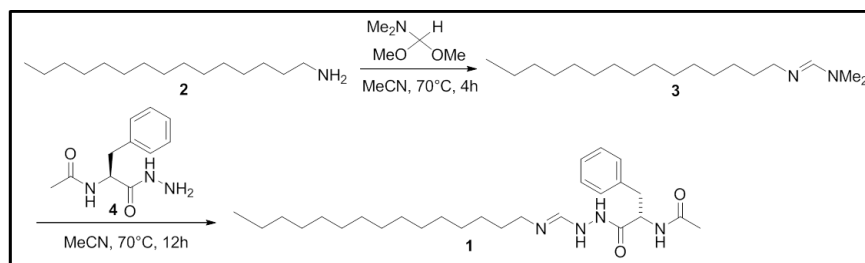
0.1M HCl (3 x 25 mL) and water (3 x 25 mL). The organic layer was dried over Na₂SO₄, filtered and the solvent removed under reduced pressure to give compound **7** (4.14 g, 18.4 mmol, 80%) as white solid in good yield. ¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 7.31 – 7.20 (m, 3H), 7.11 – 7.05 (m, 2H), 5.98 (s, 1H), 4.88 (dt, *J* = 7.9, 5.8 Hz, 1H), 3.71 (s, 3H), 3.18 – 3.03 (m, 2H), 1.97 (s, 3H).

(S)-*N*-(1-hydrazinyl-1-oxo-3-phenylpropan-2-yl)acetamide (**4**)

To a stirred solution of compound **7** (4.14 g, 18.4 mmol) in MeOH (125 mL) was added carefully hydrazine*H₂O (2.0 mL, 40.1 mmol) and the mixture was stirred at RT for 2d. The solvent was removed under reduced pressure to give compound **4** (4.35 g, 18.4 mmol, 100%) as white solid in quantitative yield. ¹H-NMR (300 MHz, MeOD): δ (ppm) = 7.31 – 7.16 (m, 5H), 4.55 (dd, *J* = 8.5, 6.6 Hz, 1H), 3.08 (dd, *J* = 13.7, 6.5 Hz, 1H), 2.87 (dd, *J* = 13.7, 8.6 Hz, 1H), 1.89 (s, 3H).

2.2. General synthetic approach towards gelator molecule **1**

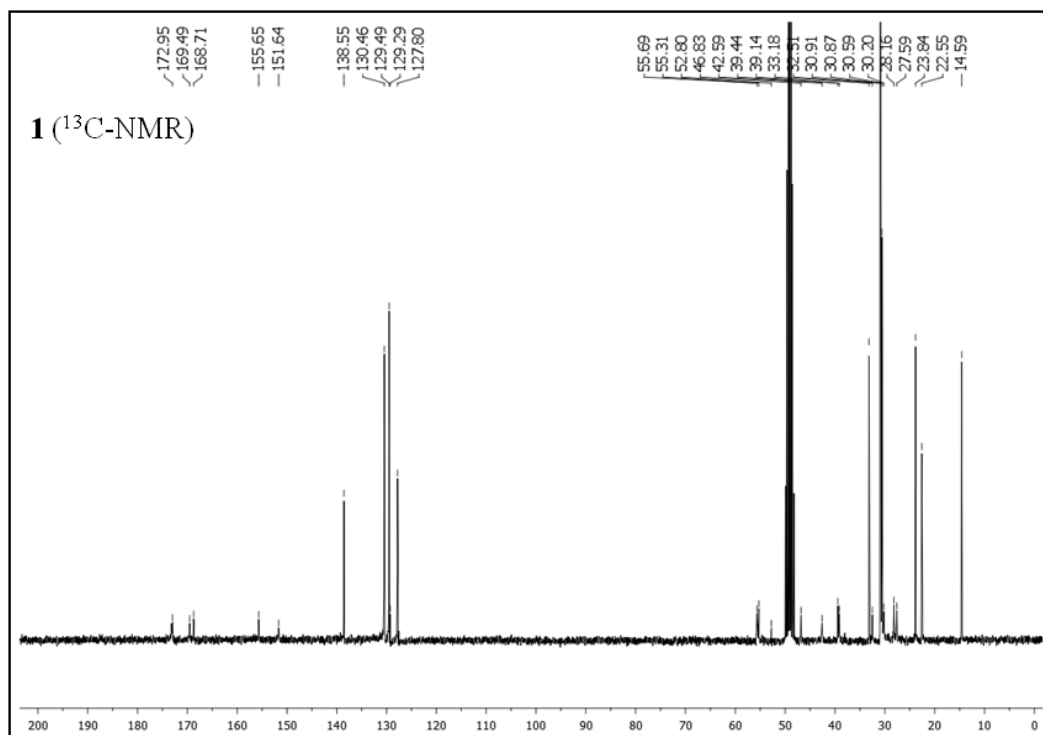
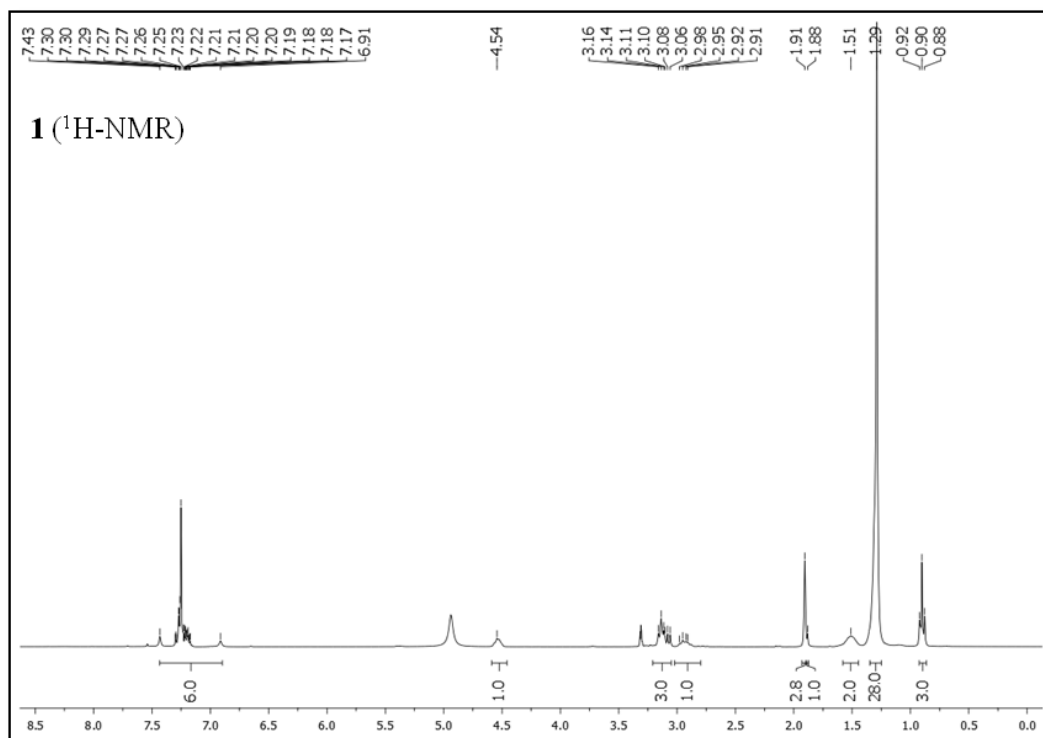
It is important to mention in this context that the applied synthetic route may not be selective towards the formation of a specific isomer, which could potentially be formed, and would need further and rather complicate experimentation. As we obtained a clear and rather simple proton NMR-spectra, we assumed the formation of a single isomer, which should have a trans-orientation around the double-bond due to a huge sterical demand of the substituents.

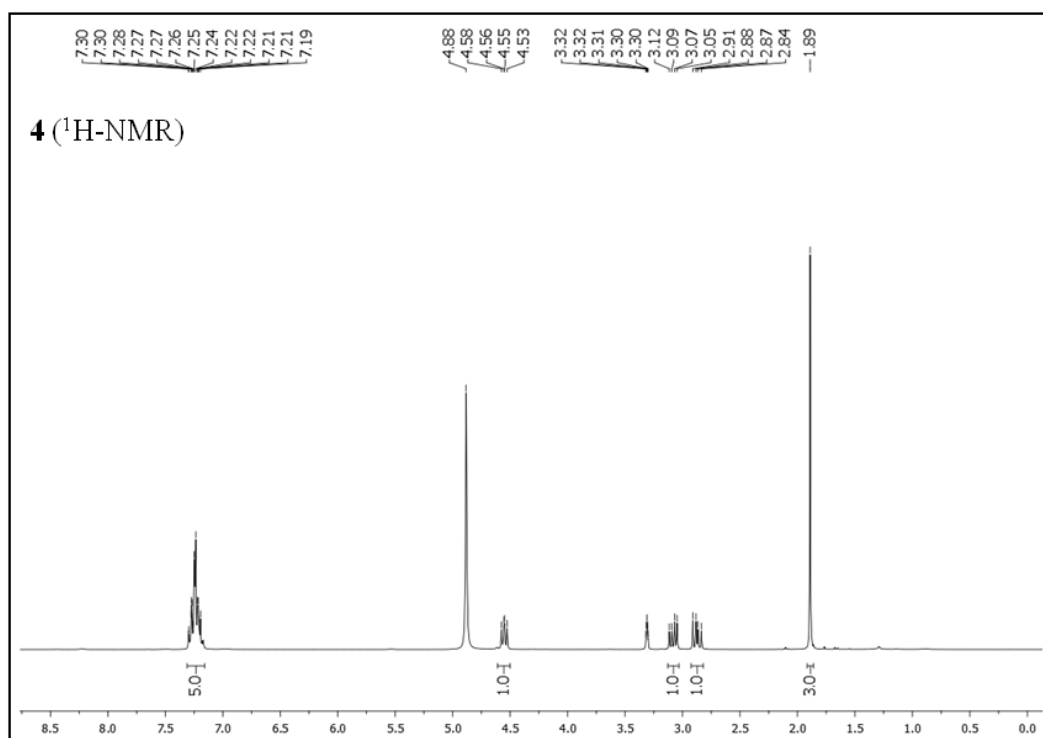
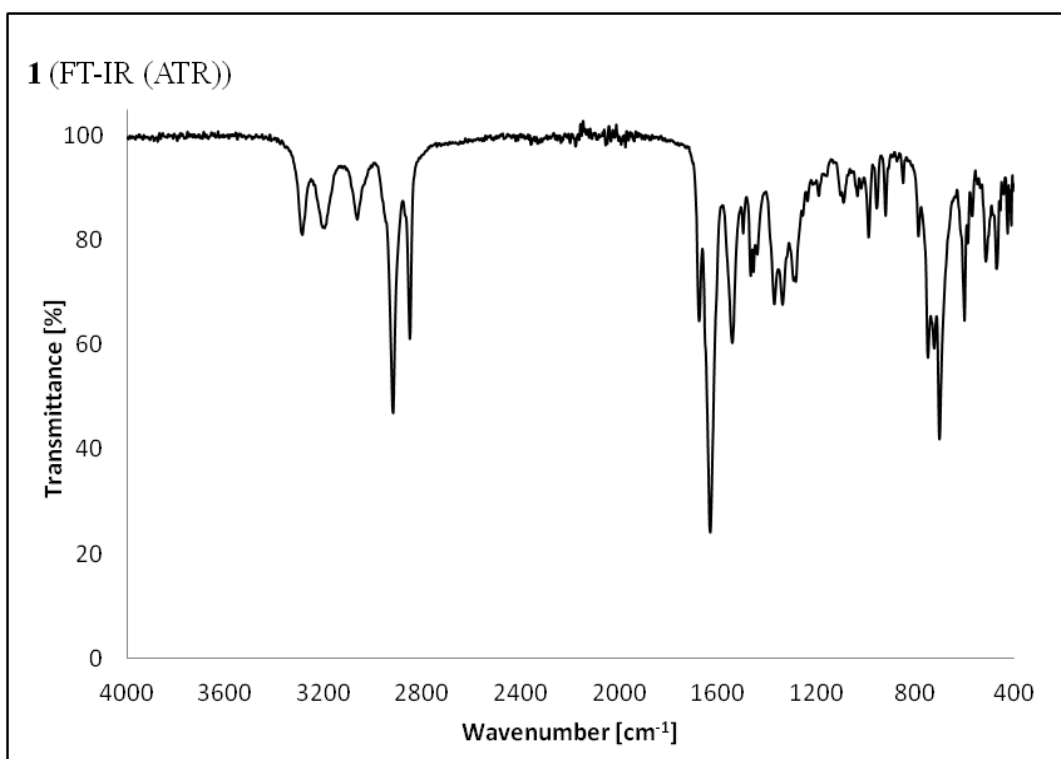


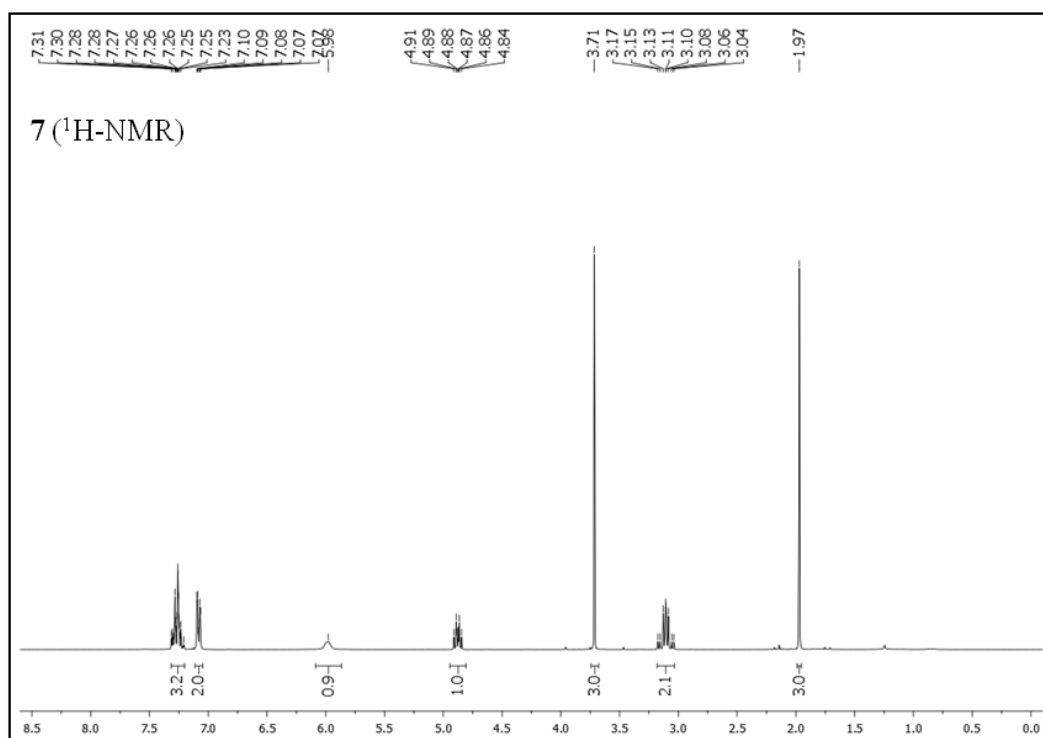
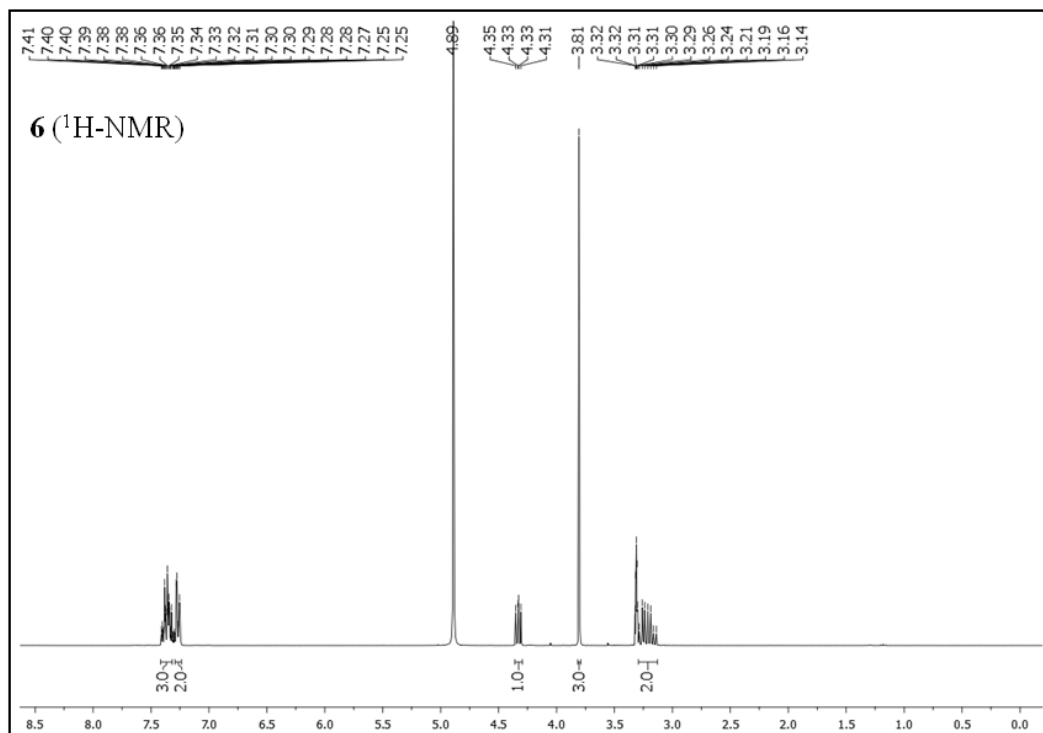
(S)-*N*-(1-oxo-1-(2-((hexadecylimino)methyl)hydrazinyl)-3-phenylpropan-2-yl)acetamide (**1**)

A solution of hexadecylamine (0.50 g, 2.1 mmol) and 1,1-dimethoxy-*N,N*-dimethylmethanamine (0.30 mL, 0.27 g, 2.3 mmol) was stirred in dry MeCN (50 mL) under nitrogen-atmosphere for 4h at 70°C until TLC-analysis showed full consumption of the amine starting material. The solvent was removed under reduced pressure using a rotary evaporator and trace amounts of the acetal were removed by co-evaporation with toluene (3 x 15 mL). The resulting residue (non-isolated compound **3**) was redissolved in a minimum amount of dry MeCN (30 mL) under a nitrogen-atmosphere at 70°C when compound **4** (0.46 g, 2.1 mmol) was added in one portion. After stirring for 12 h at 70°C the reaction solution was allowed to cool down to RT resulting in the formation of a precipitate, which was filtered off, washed with MeCN (3 x 10 mL) and recrystallized from acetone to yield the desired product as a white solid in moderate yield (0.61 g, 1.3 mmol, 62%). ¹H-NMR (300 MHz, MeOD): δ (ppm) = 7.44 – 6.90 (m, 6H), 4.54 (s, 1H), 3.21 – 3.05 (m, 3H), 3.02 – 2.80 (m, 1H), 1.91 (s, 3H), 1.88 (s, 1H), 1.51 (s, 2H), 1.29 (s, 28H), 0.90 (t, *J* = 6.7 Hz, 3H); ¹³C-NMR (75 MHz, MeOD): δ (ppm) = 172.95, 169.49, 168.71, 155.65, 151.64, 138.55, 130.46, 129.49, 129.29, 127.80, 55.69, 55.31, 52.80, 46.83, 42.59, 39.44, 39.14, 33.18, 32.51, 30.91, 30.87, 30.59, 30.20, 28.16, 27.59, 23.84, 22.55, 14.59; m.p. = 133±1°C; FT-IR (ATR): ν_{max} (cm⁻¹) = 3287, 3203, 3064, 2919, 2850, 1676, 1627, 1541; MS (ESI): *m/z* = 473.2 [MH]⁺, 945.9 2[MH]⁺; Elemental analysis calculated for C₂₈H₄₈N₄O₂: C, 71.14; H, 10.23; N, 11.85; found: C, 70.88; H, 9.97; N, 11.60.

2.3. Spectroscopic characterization of synthesized compounds







3. Additional data on gelation properties of compound 1

3.1. Tabular data on comparing a classical heating-cooling protocol towards ultrasound enhanced gelation (extension of Tab. 1 of main paper)

Tab. S1 Comparison of gelation properties derived from heating-cooling and ultrasonication enhanced protocol for gelation. ^{a)}

Entry	Solvent	Heating-cooling protocol				Ultrasound-enhanced protocol ^{b)}				Ultrasound-enhanced protocol			
		CGC [mg/mL]	Gel-Time [min]	T_{gel} [°C]	OA	Conc. [mg/mL]	Gel-Time [min]	T_{gel} [°C]	OA	CGC [mg/mL]	Gel-Time [min]	T_{gel} [°C]	OA
1	MeOH	>200	-	-	PG	-	-	-	-	170 (15)	2.5 (0.5)	33 (1)	OG
2	EtOH	>200	-	-	PG	-	-	-	-	95 (10)	3.5 (0.5)	32 (2)	OG
3	<i>i</i> -PrOH	>200	-	-	PG	-	-	-	-	62 (6)	13 (1)	30 (2)	OG
4	2-BuOH	>200	-	-	PG	-	-	-	-	71 (8)	19 (2)	31 (1)	OG
5	1-HexOH	>200	-	-	PG	-	-	-	-	95 (10)	36 (3)	33 (1)	OG
6	Glycerine	0.1-200	-	-	I	-	-	-	-	0.1-200	-	-	I
7	DMSO	54 (5)	25 (5)	36 (2)	OG	54	4.5 (0.5)	38 (1)	OG	18 (2)	48 (7)	32 (1)	OG
8	DMF	>200	-	-	CS	-	-	-	-	>200	-	-	CS
9	MeCN	110 (10)	12 (2)	42 (1)	OG	110	0.8 (0.1)	50 (1)	OG	9 (1)	0.8 (0.1)	40 (1)	OG
10	THF	>200	-	-	CS	-	-	-	-	>200	-	-	CS
11	Et ₂ O	27 (4)	7 (1)	41 (1)	OG	27	1.3 (0.1)	43 (1)	OG	12 (1)	0.8 (0.1)	36 (2)	OG
12	EtOAc	67 (7)	10.5 (0.5)	49 (1)	OG	67	0.8 (0.1)	54 (2)	OG	10 (1)	1.3 (0.1)	46 (1)	OG
13	CH ₂ Cl ₂	>200	-	-	CS	-	-	-	-	>200	-	-	CS
14	CHCl ₃	>200	-	-	CS	-	-	-	-	>200	-	-	CS
15	DCE	>200	-	-	CS	-	-	-	-	>200	-	-	CS
16	PheCN	175 (15)	145 (15)	47 (1)	TLG	175	11 (0.5)	51 (1)	TLG	47 (4)	12.5 (1.5)	36 (2)	TPG
17	PheCl	167 (13)	180 (30)	36 (1)	TLG	167	9.5 (0.5)	44 (1)	TLG	42 (4)	10.5 (1)	37 (2)	TPG
18	Benzene	120 (10)	210 (15)	38 (2)	TPG	120	4 (0.5)	48 (2)	TPG	20 (2)	5.5 (0.5)	38 (1)	TPG
19	Toluene	72 (6)	780 (60)	40 (1)	TPG	72	2.5 (0.2)	52 (2)	TPG	17 (2)	2.5 (0.5)	40 (1)	TPG
20	Xylene	50 (4)	65 (5)	47 (2)	TPG	50	1.5 (0.2)	51 (1)	TPG	13 (1)	1.8 (0.2)	38 (1)	TPG
21	DOX	87 (8)	160 (20)	37 (2)	OG	87	5 (0.5)	42 (1)	OG	28 (3)	3.5 (0.5)	33 (2)	OG
22	Acetone	87 (8)	135 (15)	45 (1)	OG	87	0.8 (0.1)	55 (2)	OG	14 (2)	1.8 (0.2)	39 (1)	OG
23	<i>n</i> -Hexane	20 (2)	10 (0.5)	40 (1)	OG	20	1.3 (0.1)	41 (2)	OG	8 (1)	0.8 (0.1)	37 (1)	OG
24	IL-1	25 (3)	30 (5)	72 (1)	OG	25	8.5 (0.5)	74 (2)	OG	14 (2)	20 (5)	68 (2)	OG
25	IL-2	48 (4)	7 (1)	78 (2)	OG	48	3.5 (0.5)	82 (2)	OG	29 (3)	17 (3)	71 (1)	OG
26	O-oil	14 (2)	45 (5)	62 (1)	TLG	14	5.5 (0.5)	72 (1)	TLG	8 (1)	13 (1)	60 (1)	TLG
27	R-oil	13 (2)	75 (10)	63 (1)	TLG	13	45 (5)	67 (1)	TLG	5 (1)	125 (15)	58 (2)	TLG
28	S-oil	42 (4)	90 (15)	61 (2)	OG	42	13 (1)	71 (2)	OG	23 (3)	17 (3)	65 (1)	OG
29	Gasoline	85 (8)	125 (15)	39 (1)	TLG	85	16.5 (1.5)	43 (1)	TLG	63 (6)	6 (0.5)	33 (2)	TLG
30	Diesel	82 (8)	80 (10)	44 (2)	TLG	82	7.5 (0.5)	53 (1)	TLG	25 (3)	25 (5)	35 (1)	TLG

a) Values in brackets indicate errors from at least 2 randomized experiments. ^{d)} Values determined at the corresponding CGC of the heating-cooling protocol. Abbreviations: OA = optical appearance; CS = clear solution; I = insolubility of the compound in the corresponding solvent; P = precipitation of the compound from an isotropic solution after cooling; PG = partial gel; OG = opaque gel; TLG = translucent gel; TPG = transparent gel; DCE = 1,2-dichloroethane; DOX = 1,4-dioxane; 1-HexOH = 1-hexanol; IL-1 = 1-butyl-3-methylimidazolium hexafluoro phosphate; IL-2 = 1,3-dibutylimidazolium hexafluoro phosphate; PheCl = chlorobenzene; PheCN = benzonitrile; O-oil = olive oil; R-oil = rapeseed oil; S-oil = silicon oil.

3.2. Tabular data for crosschecking the accuracy of the costume made apparatus to determine T_{gel} -values

Tab. S2 Evaluation of the accuracy of T_{gel} -values determined using the costume made set-up as described in Fig. S1. ^{a)}

Entry	Compound	Solvent	Conc. [mg/mL]	T_{gel} [°C]		
				IFM ¹	DBM ^{2 d)}	CM
1	1 ^{b)}	DMSO	18	34 (1)	- ^{e)}	32 (1)
2	1 ^{b)}	MeCN	9	39 (2)	37 (1)	40 (1)
3	1 ^{b)}	EtOAc	10	47 (2)	43 (1)	46 (1)
4	1 ^{b)}	Toluene	17	39 (2)	40 (1)	40 (1)
5	1 ^{b)}	IL-1	14	66 (1)	63 (2)	68 (2)
6	1 ^{b)}	n-Hexane	8	35 (2)	35 (1)	37 (1)
7	1 ^{b)}	O-Oil	8	58 (1)	54 (2)	60 (1)
8	1 ^{b)}	MeOH	170	36 (1)	- ^{e)}	33 (1)
9	1 ^{b)}	Diesel	25	37 (1)	31 (1)	35 (1)
10	1 ^{b)}	Et ₂ O	12	36 (1)	35 (1)	36 (2)
11	A4 ^{c)}	<i>i</i> -PrOH	19	54 (1)	56 (1)	51 (1)
12	A4 ^{c)}	Toluene	20	40 (2)	36 (2)	40 (1)
13	A4 ^{c)}	EtOH	70	51 (1)	51 (1)	53 (2)

^{a)} Abbreviations: IFM = Inverse flow method; DBM = dropping ball method; CM = costume made set-up; IL-1 = 1-butyl-3-methylimidazolium hexafluoro phosphate; O-oil = Olive oil. Values in brackets indicate errors from at least two randomized experiments. ^{b)} All values for compound **1** derive from gels prepared by the ultrasound enhanced protocol. ^{c)} For comparative purposes literature-known compound **A4**³ in *i*-PrOH (19 mg/mL, T_{gel} = 52 °C determined by IFM and verified by correlation to the first transition in modulated DSC (56±1 °C)), toluene (20 mg/mL, T_{gel} = 37 °C determined by IFM) and EtOH (70 mg/mL, T_{gel} = 52 °C determined by IFM) was also investigated. ^{d)} Balls used for the determinations: 0.1±0.02 mm diameter, 0.105±0.010 g weight. ^{e)} Values could not be determined as the gels were too soft to keep the ball used on top of the gels.

3.3. Additional data on rheological characterization of compound 1

Tab. S3 Tabular data on rheological properties of gels derived from **1** in MeCN (9 mg/mL) and toluene (17 mg/mL) prepared by US treatment.

Entry	Solvent	Conc. [mg/mL]	G' [Pa]	G'' [Pa]	$\tan \delta$	strain at break
1	MeCN	9	575328±464.0	95360±2228.4	0.17±0.004	4±0.4
2	Toluene	17	7946±514.0	1120±117.8	0.14±0.006	4±0.6

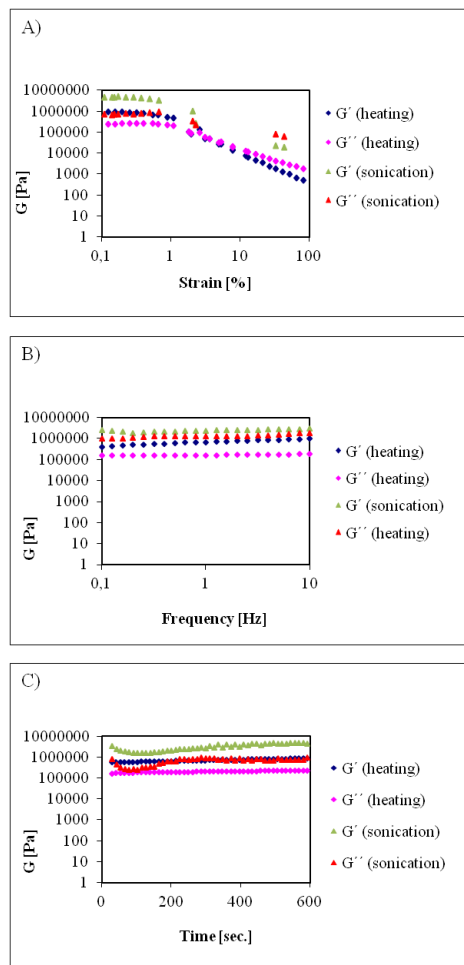


Fig. S2 Comparing the 2 methods for gel preparation by oscillatory rheological measurements at the corresponding CGC (110 mg/mL) of the heating-cooling protocol in MeCN as model system: A) DSS, B) DFS and C) DTS experiments.

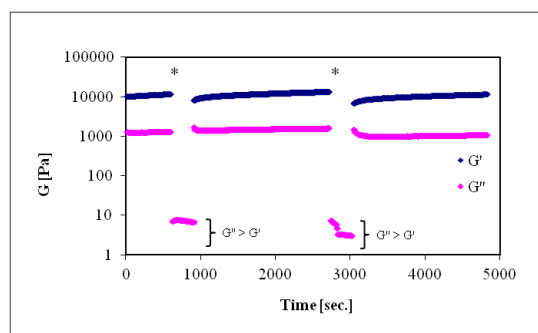


Fig. S3 Typical thixotropy loop test of the model gel made from **1** in toluene (17 mg/mL). The strain for each step during shear was first increased from 0.1% (linear viscoelastic regime –gel state–) to 100% (rupture of the gel –solution state–) and subsequently returned to the original value (recovery of the gel state). Asterisks indicate the increase of the shear strain at the time scale.

3.4. Additional data on the responsive nature of compound 1

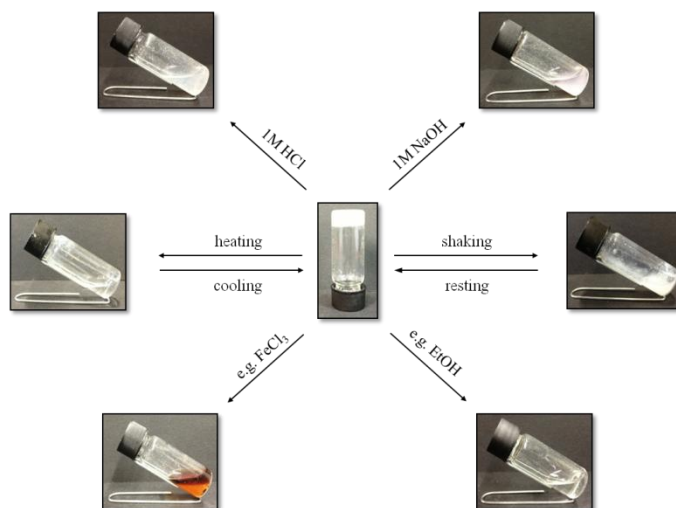


Fig. S4 Diagram showing the preparation of multi stimuli-responsive organogels from **1** in MeCN (9 mg/mL) prepared by the ultrasound enhanced protocol.

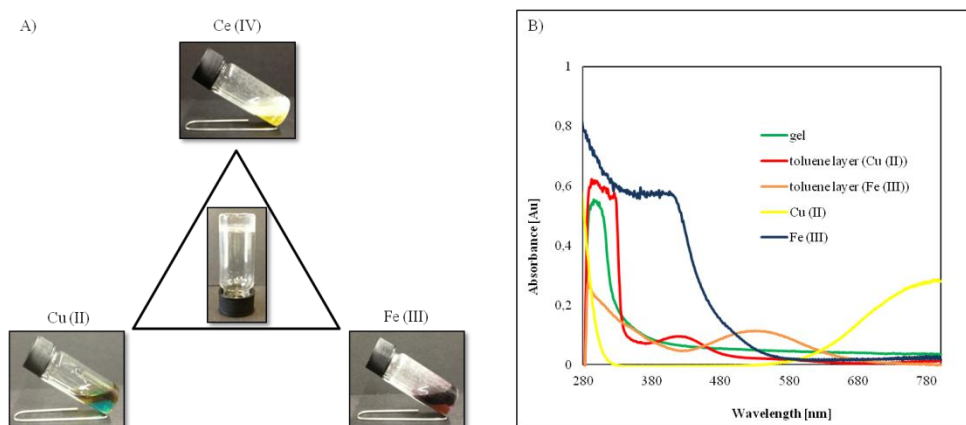


Fig. S5 Responsive nature of gels derived from toluene (17 mg/mL) against aqueous solutions of metals. A) Digital photographs demonstrating the change of coloration of the toluene layer in comparison to metal-solution accompanied by a *gel-to-sol* phase transition. B) Corresponding UV-spectra of aqueous metal-solution (0.1M), the gel derived from toluene (17 mg/mL) and the toluene layers (diluted by a factor of 1:10) after phase separation.

3.5. Additional SEM-images

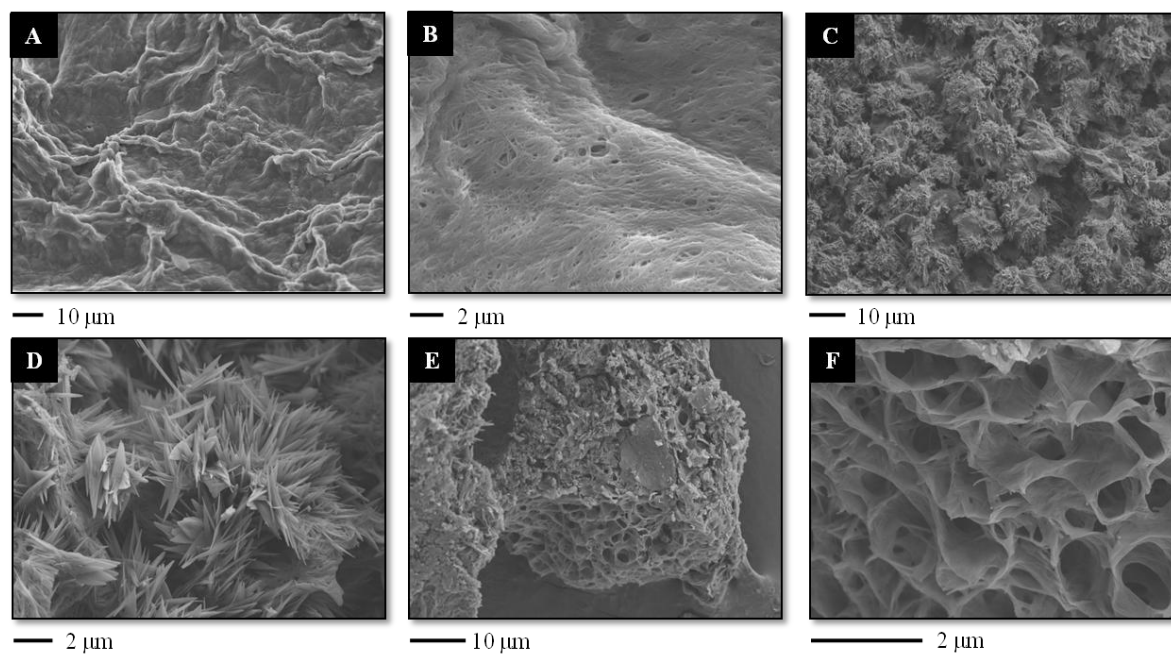


Fig. S6 SEM (A, B) and FESEM (C-F) images of cryogels prepared by the freeze-drying method from corresponding organogels prepared by US-treatment. A, B: EtOAc (10 mg/mL); C, D: DMSO (18 mg/mL); E, F: Et₂O (12 mg/mL).

3.6. Additional FTIR

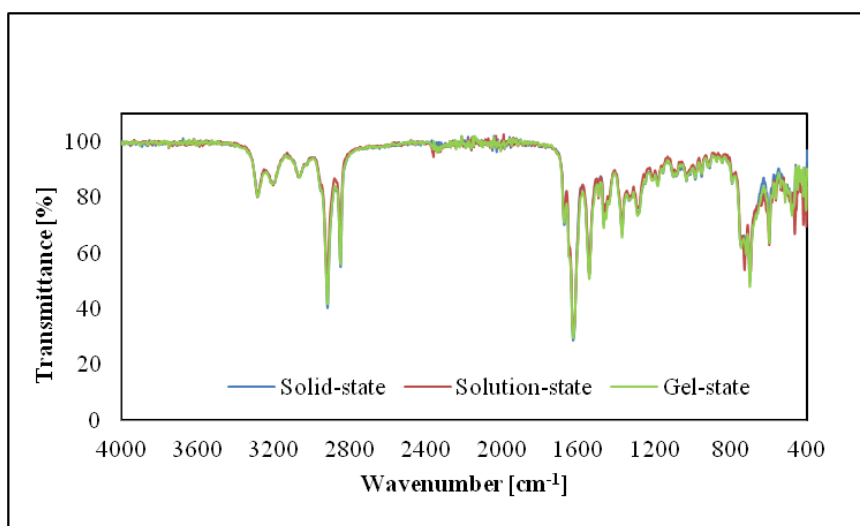


Fig. S7 Comparative FT-IR spectra derived from MeCN (9 mg/mL) prepared by ultrasound treatment showing solid state, gel-state and solution state (e.g. NH stretching bands are shifted to lower energies from 3287 cm^{-1} in the solid state to 3286 and 3285 cm^{-1} in the solution and gel state respectively).

4. Acid-mediated hydrolysis of compound **1**⁴

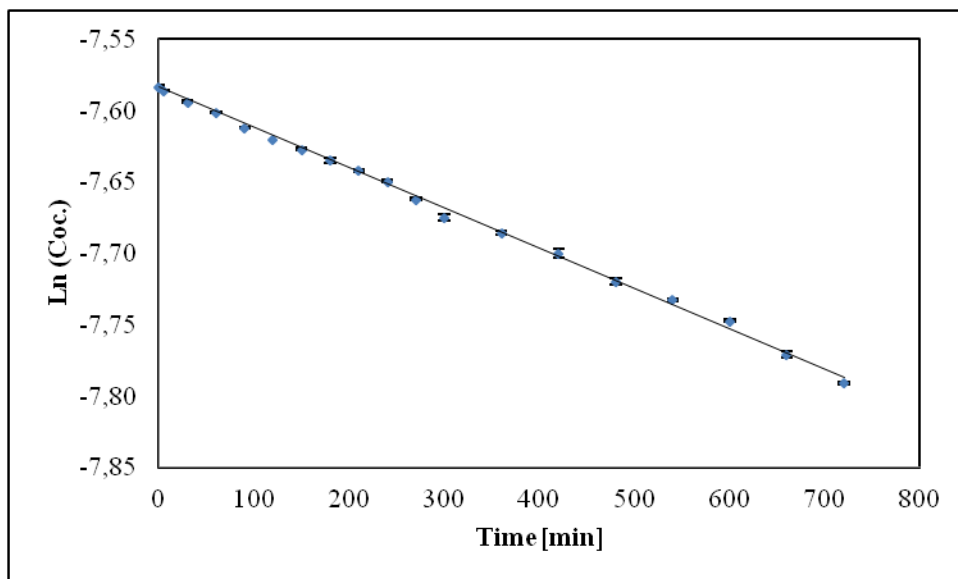


Fig. S8 Hydrolysis kinetics of compound **1** (starting conc. = 5.29×10^{-4} M) in 80% MeOH/citrate buffer (pH = 4.7) monitored every 30 min at 20 ± 1 °C. First order rate constant k_{obs} has been determined to be $2.83 \pm 0.012 \times 10^{-4} \text{ min}^{-1}$ with a half live of 41 ± 0.2 h. This finding suggests an acid-mediated hydrolysis of compound **1** which is dramatically slowed down in the gel-state. Base-mediated hydrolysis still needs to be established.

5. References

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6. Potential gelation mechanisms

Network of interactions proposed to promote gelation. An example of organogel-formation in toluene (17 mg/mL) is illustrated by digital photographs. TEM-imaging in MeCN (9 mg/mL) and toluene (17 mg/mL) illustrates the fibrillar nature of the materials.

