Supporting Information

Non-invasive and continuous monitoring of the *sol-gel* phase transition of supramolecular gels by a fast open-ended coaxial microwave sensor

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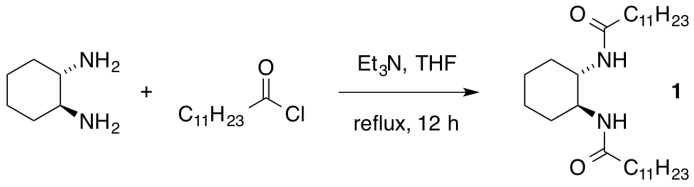
Contents List

1. Preparation of gelators

• **General remarks:** Unless otherwise indicated, ^{1}H and ^{13}C NMR spectra were recorded at 25 ºC on a Bruker Avance 600. Chemical shifts are reported in δ (ppm) relative to the residual solvent signal. Coupling constants (*J*) are given in Hertz (Hz). Mass spectroscopy (ESI) was carried out on a Finnigan MAT TSQ 7000. Melting points (m.p.) were measured with an Opti Melt Automated Melting Point System (Stanford research systems). FT-IR spectra were recorded on a Bio-Rad Excalibur FTS 3000 MX spectrophotometer equipped with a Specac Golden Gate Diamond ATR. UV-vis spectroscopy was performed using a Varian Cary 50 UV spectrophotometer and quartz-glass cuvettes. Column chromatographies were performed on silica gel (70–230 or 100–200 mesh) from Merck. Thin-layer chromatography (TLC) was performed on fluorescent-indicating plates (aluminum sheets precoated with silica gel 60 F_{254}, thickness 0.2 mm, Merck). The products were visualized by exposure to UV light (λ_{max} = 254 nm) and/or staining with phosphomolybdic acid. Unless otherwise stated, all reagents used in the preparation of the library of gelators were of p.a. grade and purchased from commercial suppliers. Solvents were dried according to standard procedures. The following compounds were purchased from commercial suppliers and used as received without further purification: **4** (12-hydroxy stearic acid; TCI), **6** (*N*,*N'*-dibenzoyl-*L*-cystine; Sigma-Aldrich). Compounds **1**,[1] **2**,[2] **3**,[3] **5**,[4] **7**[5] and **8**[6] were synthesized following the procedures reported in the literature. Samples thus obtained exhibited spectroscopic data in agreement to those published. Gelator systems **9**[7] and **10**[8] were also prepared as previously described.

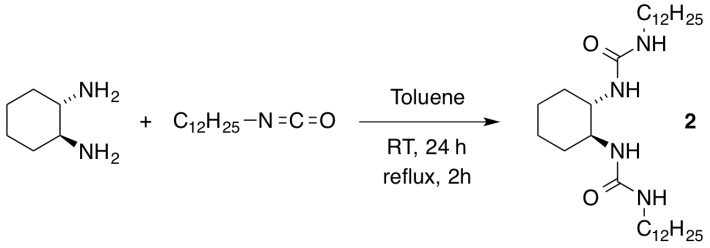
• **Synthesis and characterization of compounds.**

***trans*-(1*S*,2*S*)-1,2-Bis(dodecylamido)cyclohexane (1):**[1]



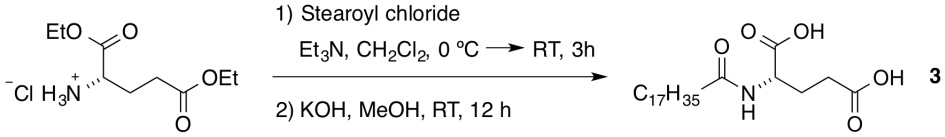
Triethylamine (2.0 mL, 14.69 mmol) was added to a stirred mixture of *trans*-(1*S*,2*S*)-1,2-diaminocyclohexane (0.5 g, 4.37 mmol) and *n*-lauroyl chloride (2.05 mL, 8.84 mmol) in THF (50 mL). The reaction mixture was refluxed for 12 h under argon atmosphere. After this time, the mixture was stirred 30 min at RT, filtered, and the filtrate evaporated to dryness. The obtained residue was carefully washed with HCl (1 M aqueous solution) and diethyl ether (3 × 5 mL), and dried under vacuum. The desired product was obtained as a white solid (69% yield). M.p. 175 ± 1 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.85 (t, *J* = 6.6 Hz, 6H), 1.09-1.26 (m, 36H), 1.52 (m, 4H), 1.73 (m, 2H), 2.01-2.09 (m, 6H), 3.61 (m, 2H), 5.86 (brs, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 14.1, 22.7, 24.7, 25.8, 29.3, 29.4, 29.5, 29.6, 31.9, 32.4, 36.9, 53.6, 173.8. FT-IR (ATR) ν_{max} (cm^{-1}) = 3275, 2919, 1636, 1548 cm^{-1}. MS (ESI): m/z = 479 $[M]^{+}$.[1]

1,1'-((1*S*,2*S*)-Cyclohexane-1,2-diyl)bis(3-dodecylurea) (2):[2]



To a stirred solution of (*S*,*S*)-1,2-cyclohexyldiamine (1.0 g, 8.75 mmol) in toluene (180 mL) was added a solution of dodecylisocyanate (3.96 g, 18,75 mmol) in toluene (50 mL) at RT over a period of 30 min. The reaction mixture was stirred for 24 h RT and refluxed for 2 h. The reaction mixture was cooled down to RT and filtered over glassfilter. The obtained waxy white solid was suspended in CH_2Cl_2 (60 mL), stirred for 12 h and filtered. The procedure was repeated twice and the obtained residue washed thoroughly with cold Et_2O (2 × 50 mL). The desired product was isolated as a white solid upon drying under vacuum (92% yield). M.p. 233 ºC (decomposition). ^{1}H NMR (300 MHz, 50 ºC, $CDCl_3$) δ (ppm) = 0.88 (t, J = 6.6 Hz, 6H), 1.29 (brs, 40H), 1.47 (m, 4H), 1.72 (m, 2H), 2.03 (d, J = 12.1 Hz, 2H), 3.10 (m, 4H), 3.46 (m, 2H), 4.41 (t, J = 5.3 Hz, 2H), 4.95 (d, J = 6.6 Hz, 2H). ^{13}C NMR (75 MHz, 50 ºC, $CDCl_3$) δ (ppm) = 13.8, 22.5, 25.1, 27.1, 29.2, 29.4, 29,5, 30.4, 31.8, 33.5, 40.8, 55.0, 159.3. FT-IR (ATR) ν_{max} (cm^{-1}) = 3359, 1650, 1562 cm^{-1}. MS (ESI): m/z = 538 $[M+1]^+$.[2]

Stearoyl-*L*-glutamic acid (3):[3]



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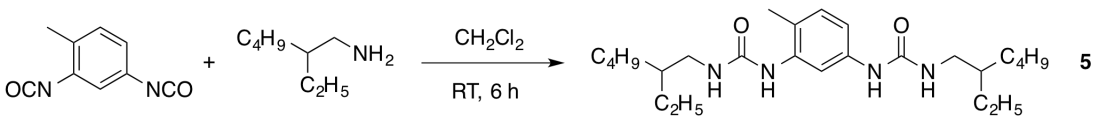
To a stirred solution of *L*-glutamic acid diethyl ester hydrochloride (1.72 g, 7.2 mmol) and triethylamine (3.0 mL, 21.5 mmol) in dry CH_2Cl_2 (150 mL) at 0 °C, was added slowly a solution of stearoyl chloride (2.39 g, 7.9 mmol) in dry CH_2Cl_2 (20 mL) over a period of 1 h. The mixture was allowed to warm to RT and stirred for additional 3 h. After this time, H_2O (50 mL) was added. The organic layer was separated, washed with H_2O (3 × 50 mL), dried over anhydrous Na_2SO_4, filtered, and the solvent evaporated. The obtained residue was dissolved in a 1:1 mixture of CH_3OH/H_2O (150 mL) and KOH (1.21 g, 21.5 mmol) was added. The resulting suspension was stirred for 12 h at RT. After this time, CH_3OH was removed under reduced pressure and the aqueous phase acidified with HCl (2 M aqueous solution) until pH 2. The formed precipitate was filtered off, washed thoroughly with H_2O, dried, and recrystallized from acetone to obtain the desired compound as a white solid (81% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) = 0.85 (t, J = 6.8 Hz, 3H), 1.23 (s, 28H), 1.48-1.41 (m, 2H), 1.81-1.67 (m, 1H), 1.89 (td, J = 13.4, 7.5 Hz, 1H), 2.08 (td, J = 7.1, 1.5 Hz, 2H), 2.24 (t, J = 7.6 Hz, 2H), 4.19-4.14 (m, 1H), 7.95 (d, J = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) = 13.8, 22.0, 25.2, 26.6, 28.5, 28.6, 28.7, 28.9, 28.9, 29.0, 30.3, 31.2, 35.0, 51.1, 172.1, 173.4, 173.7. FT-IR (ATR) ν_{max} (cm^{-1}) = 3309, 2937, 2914, 2848, 1730, 1714, 1701, 1651, 1624, 1543. MS (ESI): *m/z* = 414 $[MH]^+$.[3]

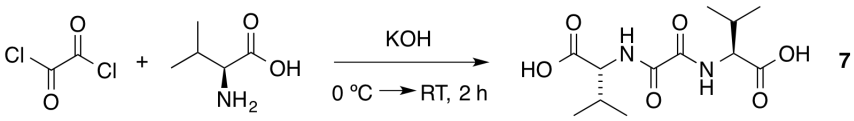
1,1'-(4-Methyl-1,3-phenylene)bis(3-(2-ethylhexyl)urea) (5):[4]



5

To a stirred solution of 2,4-toluene diisocyanate (6.6 g, 38 mmol) in dry CH_2Cl_2 (125 mL), a solution of 2-ethylhexylamine (10 g, 77.6 mmol) in dry CH_2Cl_2 (50 mL) was slowly added under argon atmosphere over a period of 1 h. The reaction mixture was stirred for 6 h at RT and the precipitated was filtered, washed with cold CH_2Cl_2 and dried under vacuum. The desired product was isolated as a white solid after recrystallization from EtOAc (87% yield). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 0.9 (t, 12H), 1.3 (m, 18H), 2.1 (s, 3H), 3.0 (m, 4H), 6.2 (t, 2H), 7.0 (d, 2H), 7.8 (s, 1H), 7.5 (s, 1H), 8.3 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) = 10.6, 14.0, 17.2, 22.5, 23.6, 28.4, 30.5, 39.2, 41.4, 109.4, 111.1, 118.5, 129.9, 138.4, 138.8, 155.3, 155.5.[4]

(2-(((*R*)-1-carboxy-2-methylpropyl)amino)-2-oxoacetyl)-*L*-valine (7):[5]

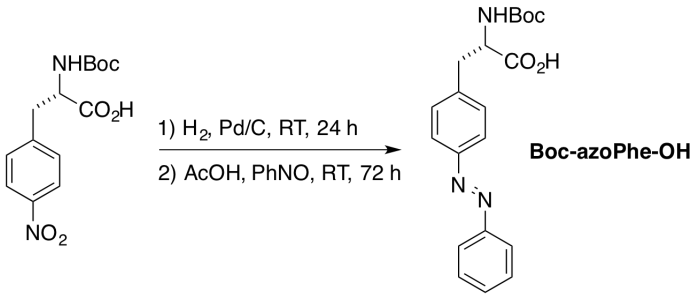


To a stirred cooled solution of *L*-valine (1.17 g, 10 mmol) in KOH (4.0 mL from a 4M solution) were added dropwise and simultaneously a solution of oxalyl chloride (0.65 mL, 7.5 mmol) in CH_2Cl_2 (5 mL) and KOH (3.2 mL from a 4M aqueous solution) over a period of 1 h. The reaction mixture was stirred for 1 h at 0 ºC and for additional 2 h at RT. The organic layer was separated, and the aqueous layer diluted with H_2O (20 mL) and acidified with 10% formic acid until pH 2.5. The formed precipitate was filtered, washed thoroughly with H_2O and dried under vacuum to afford the desired product as a white solid (52% yield). M.p. 124 ± 1 ºC. ^{1}H NMR (300 MHz, CD_3OD) δ (ppm) = 1.07 (d, J = 6.8 Hz, 3H), 1.08 (d, J = 6.8 Hz, 3H), 2.35 (m, 2H), 4.46 (d, J = 5.1 Hz, 2H), 8.55 (d, J = 8.6 Hz, 2H). ^{13}C NMR (75 MHz, CD_3OD) δ (ppm) = 18.4, 19.6, 32.2, 59.5, 161.5, 174.1. FT-IR (ATR) ν_{max} (cm^{-1}) = 3250, 1725, 1660, 1525. MS (ESI): m/z = 288 $[M]^+$.[5]

4-Benzyl 1-methyl ((*S*)-2-((*S*)-2-((*S*)-2-amino-4-(benzyloxy)-4-oxobutanamido)-4-(benzyloxy)-4-oxobutanamido)-3-(4-((*E*)-phenyldiazenyl)phenyl)propanoyl)-*L*-aspartate (8):[6]

General procedure for the cleavage of the N-Boc protecting group and peptide bond formation, which is repeated 3 times during the synthesis: TFA (5 mL) was added to a solution of the *N*-Boc-protected compound (1 g) in CH_2Cl_2 (20 mL) at 0 ºC. The solution was stirred at RT for 2 h and evaporated. The obtained residue was dissolved in CH_2Cl_2 and the solvent evaporated (× 3) to yield the crude trifluoroacetate salt. To a solution of the trifluoroacetate salt (1 equiv) in CH_2Cl_2 (10 mL), *N*-methylmorpholine (1.5 equiv) was added at 0 ºC to deprotect the amino group. Separately, to a solution of *N*-Boc-protected amino acid (1 equiv) in CH_2Cl_2 (10 mL), EDC·HCl (1 equiv) and HOBt (1 equiv) were added at 0 ºC. The mixture was stirred for 1 h and *N*-methylmorpholine (1 equiv) added. The two above solutions were combined and stirred at RT for 24 h. After this time, the solvent was evaporated and the residue redissolved in EtOAc (100 mL). The solution was washed with 5% aqueous $KHSO_4$ (3 × 50 mL), 5% aqueous $NaHCO_3$ (3 × 50 mL) and brine (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, the solvent evaporated and the residue purified by column chromatography if necessary.

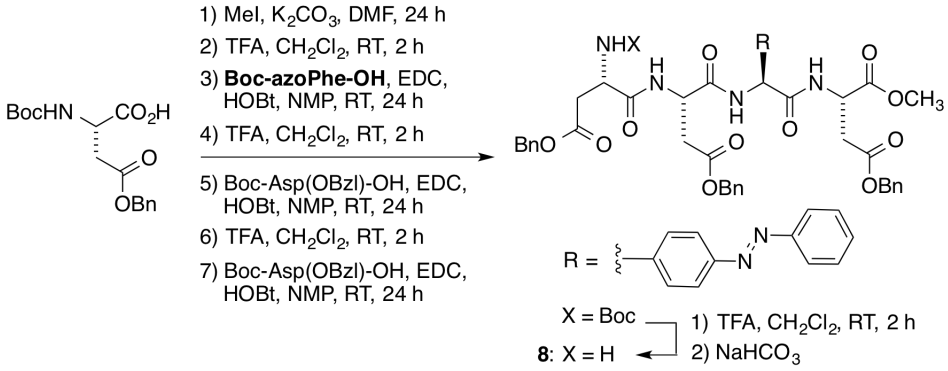
*Synthesis of **Boc-azoPhe-OH**:*



A mixture of *N*-Boc-(*p*-nitro)-*L*-phenylalanine (2 g, 6.45 mmol) and 10% Pd/C (0.3 g) in CH_3OH (20 mL) was stirred at RT under H_2 (1 atm) for 24 h. After this time, the catalyst was filtered off and the solvent evaporated. The residue was dissolved in glacial acetic acid (50 mL) and nitrosobenzene (0.8 g, 7.47 mmol) in glacial acetic acid (20 mL) was added and stirred at

RT. After 72 h the solvent was evaporated, the residue was dissolved in EtOAc (80 mL) and washed with 5% aqueous $KHSO_4$ (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvent evaporated. Purification by column chromatography afforded the desired product **Boc-azoPhe-OH** as a yellow solid (62% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 50 ºC) δ (ppm) = 1.43 (s, 9H), 3.15 (dd, J = 14.0, 6.7 Hz, 1H), 3.29 (dd, J = 14.0, 5.7 Hz, 1H), 4.62 (m, 1H), 4.96 (d, J = 8.3 Hz, 1H), 7.39-7.32 (m, 2H), 7.54-7.41 (m, 3H), 7.95-7.83 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$, 50 ºC) δ (ppm) = 28.5, 38.2, 54.8, 81.0, 123.1, 123.3, 129.2, 130.3, 131.1, 139.4, 152.4, 153.3, 155.7, 173.7.

*Synthesis of **8**:*



K_2CO_3 (6.4 g, 46.3 mmol) was added to a solution of Boc-Asp(OBzl)-OH (5 g, 15.5 mmol) in DMF (50 mL). After 2 h at room temperature, iodomethane (2.9 g, 46.6 mmol) was added and stirring was continued for additional 24 h. The solvent was evaporated to dryness and the residue was partitioned between EtOAc (50 mL) and H_2O (60 mL). The phases were separated and the aqueous layer was further extracted with ethyl acetate (2 × 50 mL). The combined organic extracts were washed successively with H_2O (50 mL), 5% aqueous $Na_2S_2O_3$ (3 × 50 mL), and brine (3 × 50 mL), dried over anhydrous Na_2SO_4, filtered and the solvent evaporated. The obtained crude product (*i.e.*, Boc-Asp(OBzl)-OMe)) was coupled with TFA·H-Asp(OBzl)-OMe as indicated in the above general procedure. Boc-Asp(OBzl)-OH was coupled with TFA·H-azoPhe-Asp(OBzl)-OMe (formed upon treatment of Boc-azoPhe-Asp(OBzl)-OMe with TFA). The TFA salt of the obtained product (*i.e.*, TFA·H-Asp(OBzl)-azoPhe-Asp(OBzl)-OMe) was coupled with Boc-Asp(OBzl)-OH. The residue was quickly filtered through a small pad of Celite® and washed with CH_2Cl_2/CH_3OH (95/5, v/v). Finally, the crude product (*i.e.*, Boc-[Asp(OBzl)]$_2$-azoPhe-Asp(OBzl)-OMe) was deprotected with TFA and the obtained salt was redisolved in CH_2Cl_2 and washed with a saturated solution of $NaHCO_3$ (× 3) and brine. The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and the solvent evaporated to afford the desired product as a yellow solid (37% overall yield). M.p. 108 ± 1 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.23 (d, J = 7.8 Hz, 1H), 7.85-7.71 (m, 4H), 7.48-7.35 (m, 3H), 7.33-7.10 (m, 18H), 6.97 (d, J = 8.1 Hz, 1H); 5.08-4.95 (m, 6H), 4.75 (m, 1H), 4.65-4.54 (m, 2H), 3.66-3.59 (m, 1H), 3.54 (s, 3H), 3.20 (dd, J = 14.0, 5.9 Hz, 1H), 3.05 (dd, J = 14.1, 8.0 Hz, 1H), 2.94-2.67 (m, 6H). MS (ESI): m/z = 899 $[M+1]^+$.[6]

2. Preparation and characterization of gel materials

• General procedure for the preparation of gels made of gelators 1-7:[1-6,9,10]

Typically, a given amount of the gelator and the appropriate solvent (2 mL) were placed into a screw-capped glass vial (4 cm length and 1 cm diameter) and gently heated with a heat gun until an isotropic solution was obtained. Part of this solution was quickly transferred to the vial adapted for the sensor and spontaneously cooled down to RT. Continuous monitoring of the material at microwave frequencies was recorded. Note that no control over the temperature rate was applied during the heating-cooling process. The gel state after each measurement could be observed by the absence of gravitational flow upon turning the vial upside-down at RT. Note that the solvents used for the gelation experiments are p.a. and not completely anhydrous, which implies that some water molecules are always presented in the materials.

• General procedure for the preparation of gels made from gelator system 9:[7]

$Cu(OAc)_2 \cdot H_2O$ (0.28 g, 1.40 mmol) was dissolved in dry DMF (5 mL) at RT affording a deep green stock solution (**Sol-1**, 0.28 M). Oxalic acid dihydrate (0.32 g, 2.54 mmol) was dissolved in dry DMF (5 mL) at RT affording a transparent stock solution (**Sol-2**, 0.5 M). 1 mL of **Sol-1** was added at RT to 1 mL of **Sol-2** forming quickly an inhomogeneous blue gel-like material. The mixture was shaken to form a blue homogeneous colloidal suspension (the use of sonication for 5-10 min is advisable), which evolved to a stable gel over time under undisturbed conditions.

• General procedure for the preparation of gels made from gelator system 10:[8]

Preparation of multicomponent gelator solution: A 0.3 M HCl/CH_3OH stock solution was prepared using HCl 37 wt.% in aqueous solution and dry CH_3OH. (1*R*,2*R*)-1,2-Diaminocyclohexane L-tartrate (254 mg, 0.96 mmol) was weighted in a glass vial and dissolved in 7.5 mL of the above HCl/CH_3OH stock solution.

Preparation of organogels: Typically, the desired solvent was placed into the glass vial and cooled down in a Dewar flask close to the freezing temperature of the solvent. The appropriate volume of the multicomponent gelator solution was added under gentle hand stirring of the vial, and the mixture kept at low temperature for 1 min. After this time, the cooling bath was removed and the vial introduced into sensor. The resulting clear homogeneous solution was let to warm up to room temperature allowing the formation of the gels, while continuous monitoring the dielectric properties of the mixture at microwave frequencies.

• General characterization

The gel phases achieved with the library of gelators have been also separately confirmed by various oscillatory rheological measurements as reported in the corresponding references, where studies for the determination of the critical gelation concentrations (CGC) and thermal stabilities are also included.

Figure S1 shows a selection of typical morphologies of different gel-based materials prepared as described above. Xerogels were prepared from the corresponding wet gels by the freeze-drying method. Specimens were observed with JEOL JSM 6400 scanning electron microscope (SEM, resolution 3.5 nm) equipped with a digital camera and operating at 15 kV (accelerating voltage) or a Carl Zeiss Merlin field emission scanning electron microscope (FESEM, resolution 0.8 nm) equipped with a digital camera and operating at 5 kV (accelerating voltage) and 10 μA (emission current). For AFM imaging (tapping mode), the xerogel specimen was suspended in acetone and a drop of this suspension was placed onto mica substrate and dried on air for 24 h before imaging with

a Ntegra Aura, NT-MDT instrument equipped with an Universal measuring head and 100 mKm scanner, and using NSG01/TiN tips from NT-MDT.

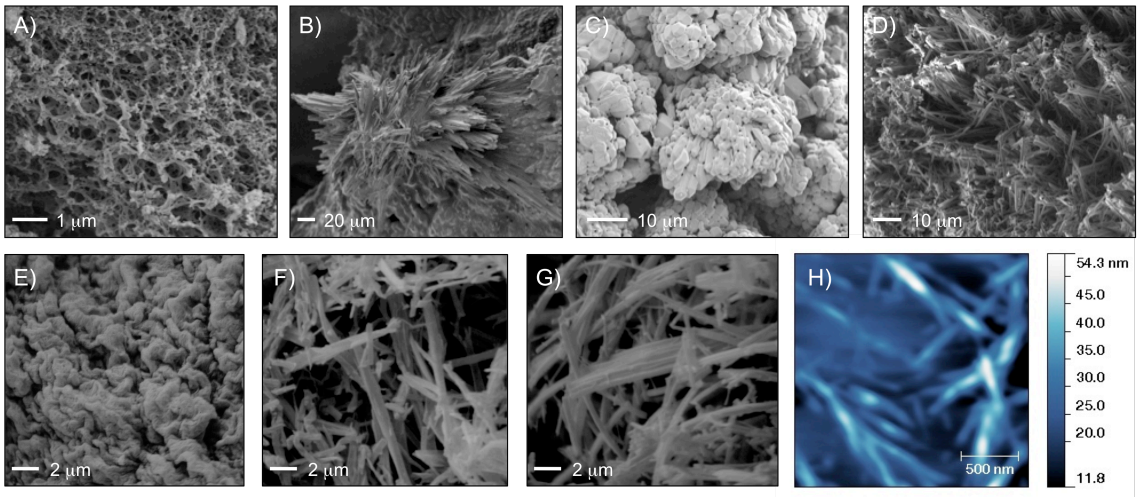


Figure S1. Representative FESEM (A-D) and SEM (E-G) images of xerogels prepared from the corresponding wet gels: A) Gelator **3** in acetonitrile (c = 100 g L^{-1}); B) gelator system **10** in 1,2-dimethoxyethane (100 μL of solution **10** per mL of 1,2-dimethoxyethane); C) gelator system **10** in benzonitrile (150 μL of solution **10** per mL of benzonitrile); D) gelator **6** in DMSO/water (v/v = 0.04/0.96) (c = 2 g L^{-1}); E) gelator **8** in toluene (c = 25 g L^{-1}); F) gelator **1** in acetonitrile (c = 5 g L^{-1}); G) gelator **7** in acetonitrile/chloroform (v/v = 0.1/0.5) (c = 5 g L^{-1}); H) AFM image of the gel made in DMF from gelator system **9** as described above.

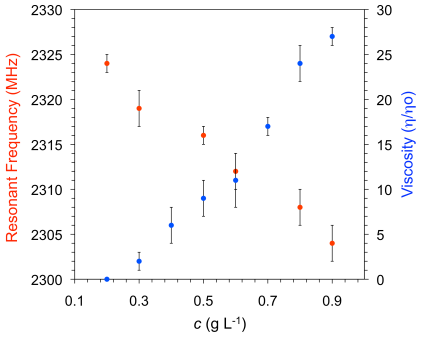
We have previously reported the reversible changes in the UV-vis absorption spectrum of the gels made from gelators of the type **8** due to the photoisomerization process.[6] In this work, the transition from the *trans*-rich gel phase to the *cis*-rich solution phase was induced by UV irradiation at 366 nm for 30 min. The *sol-gel* transition was further achieved by exposure of the cuvette to visible light. The content of the *trans*-isomer upon irradiation has been estimated in ca. 20% of the original concentration in the gel state.

3. Microwave and thermal measurements

For DSC measurements, an appropriate amount of gel was placed into a pre-weighted aluminum pan, which was sealed and weight on a six-decimal plate balance. Heating and cooling scans were measured on a DSC7 or DSC8000 (Perkin Elmer) instrument at a scan rate of 2-3 ºC min^{-1} under nitrogen atmosphere.

The pans were weighted again after each measurement to check for possible leakage. *Gel-sol* transition temperatures are associated to endothermic events, whereas *sol-gel* transition temperatures correspond to exothermic events. Measurements with an inserted thermocouple were also made when the expected exothermic event during the cooling process could not be clearly observed in the DSC thermogram.

A)



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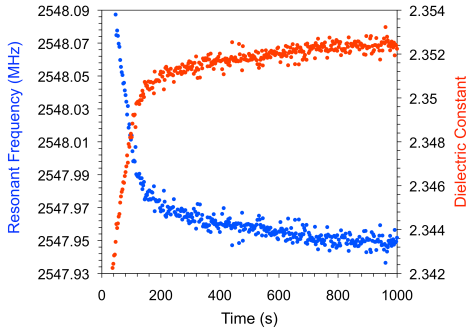
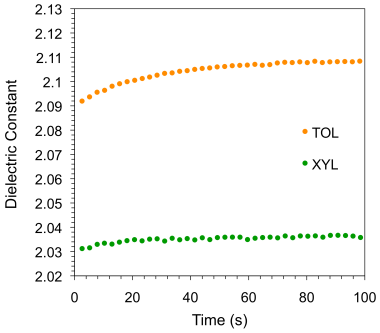
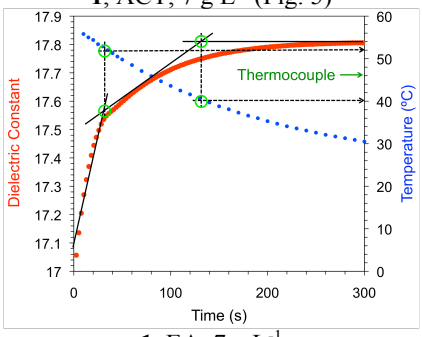


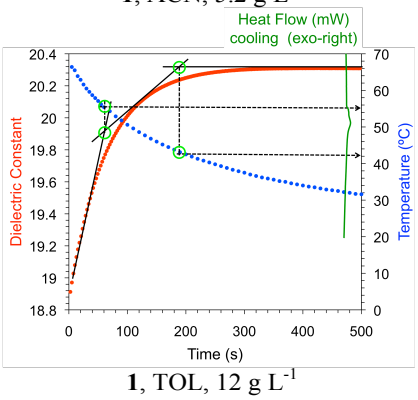
C)



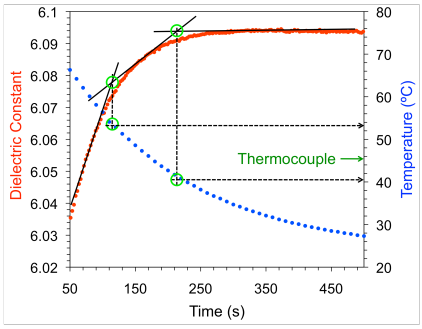
D) **1**, ACT, 7 g L^{-1} (Fig. 5)



E) **1**, ACN, 5.2 g L^{-1}

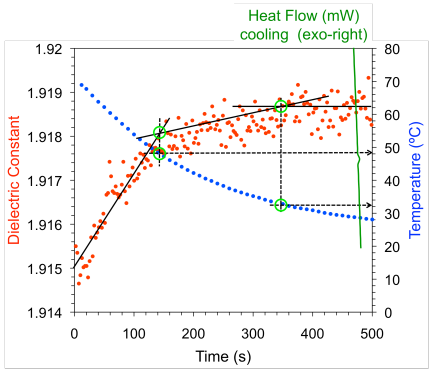


F) **1**, EA, 7 g L^{-1}

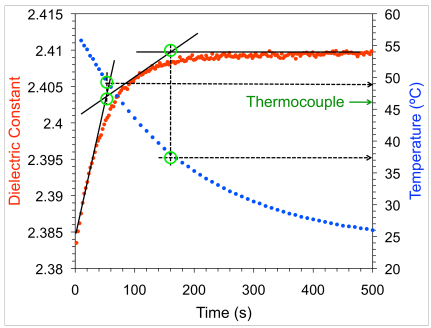


G) **1**, TOL, 12 g L^{-1}

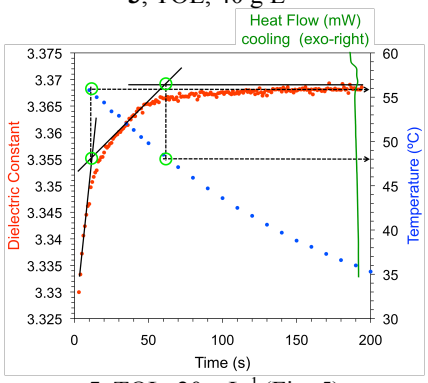
H) **2**, XYL, 5 g L^{-1} (Fig. 5)



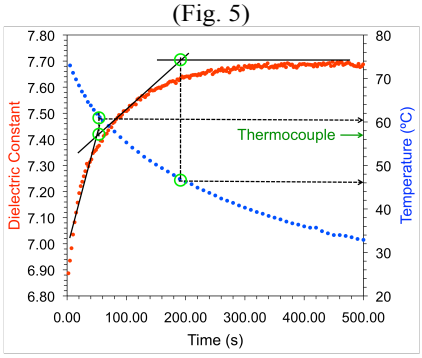
I) **3**, TOL, 40 g L^{-1}



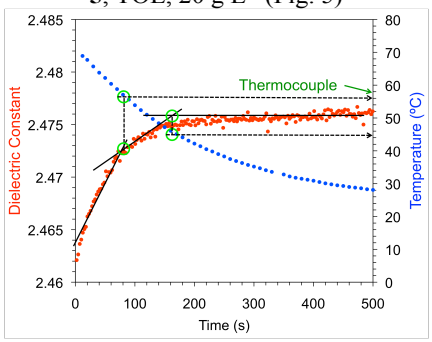
J) **4**, NB, 6 g L^{-1} (Fig. 5)



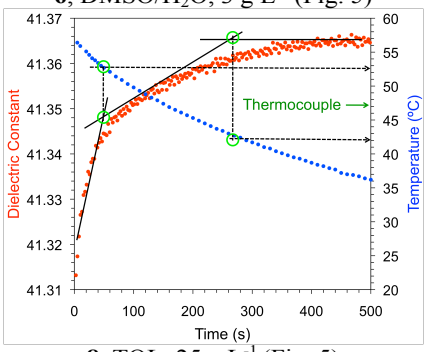
K) **5**, TOL, 20 g L^{-1} (Fig. 5)



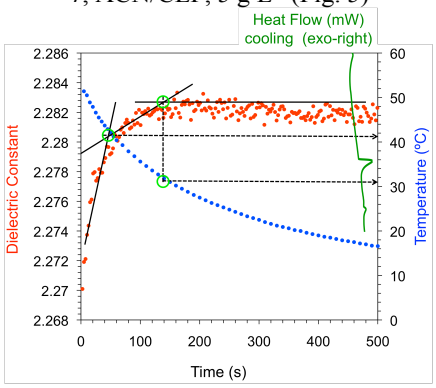
L) **6**, DMSO/H_2O, 3 g L^{-1} (Fig. 5)



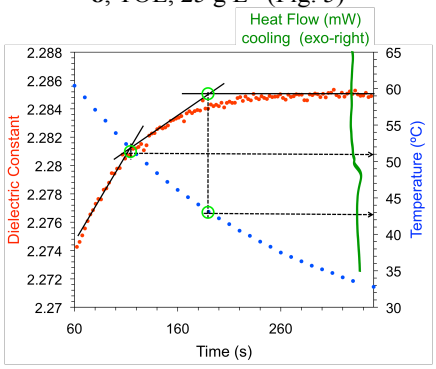
M) **7**, ACN/CLF, 5 g L^{-1} (Fig. 5)



N) **8**, TOL, 25 g L^{-1} (Fig. 5)



O) **9**, DMF, 0.28:0.5 M (section 2; Fig.



P) **10**, BN, 150 µL (section

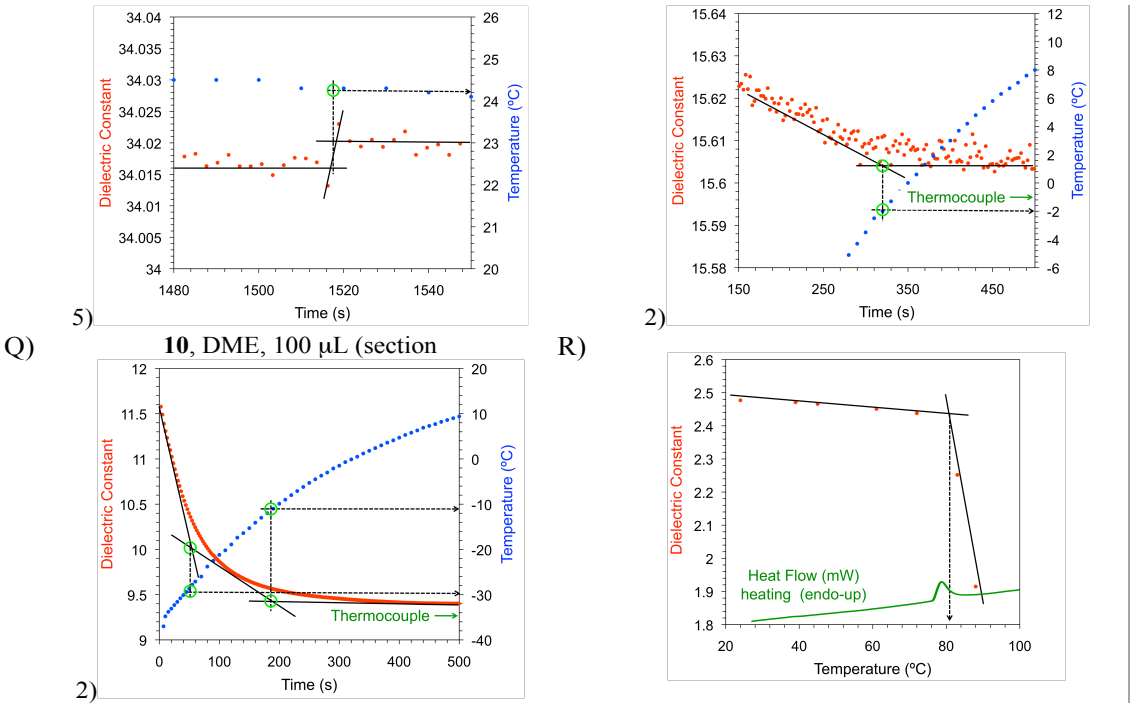


Figure S2. A) Inverse trend profiles of resonant frequency and capillary viscosity data (average of three random experiments) obtained for different solutions of gelator **5** in *p*-xylene at different concentrations below the critical gelation concentration. These earlier results indicated a sensitivity of the sensor to changes in the density of hydrogen bonding interactions associated to the viscosity of the medium. B) Dielectric constant and resonant frequency profiles during the formation of the model gel made of **3** in toluene (c = 25 g L^{-1}). C) Typical changes in the dielectric constant of hot solvents during spontaneous cooling. In each case, the magnitude of the signal differed considerably with that in the presence of the gelator and a plateau value was always reached quicker in the case of pure solvents and without any further alteration over time. D-Q) Dielectric constant and thermal profiles of different *sol-gel* samples. Note: The temporal stability of the gels made with gelator system **10** over time when stored undisturbed at RT in a vertical position was approximately 2 h (ACT), 1 h (DME) and 1 h (BN). The lack of stability was defined when the gel was fragmented or partially liquefied without resistance to inversion of the test tube. R) Preliminary experiment showing the change in the dielectric constant of the gel made from **1** in toluene upon intermittent heating until reaching the melting *gel-sol* transition temperature (T_{GS} ~ 79 ºC). An evident change in the slope of segmental trend lines was observed around the T_{GS}. In this case, the value obtained by the inverse flow method (IFM)[11] was well correlated with the first endothermic transition observed by DSC. However, it should be noted that the T_{GS} values determined by IFM strongly depend, in general, on factors such as cooling rate, aging time, thermal history and degree of hysteresis.

Abbreviations: ACT = acetone; ACN = acetonitrile; BN = benzonitrile; CLF = chloroform; DME = 1,2-dimethoxyethane; DMF = *N*,*N*'-dimethylformamide; DOX = 1,4-dioxane; DMSO = dimethyl sulfoxide; EA = ethyl acetate; NB = nitrobenzene; TOL = toluene; XYL = *p*-xylene.

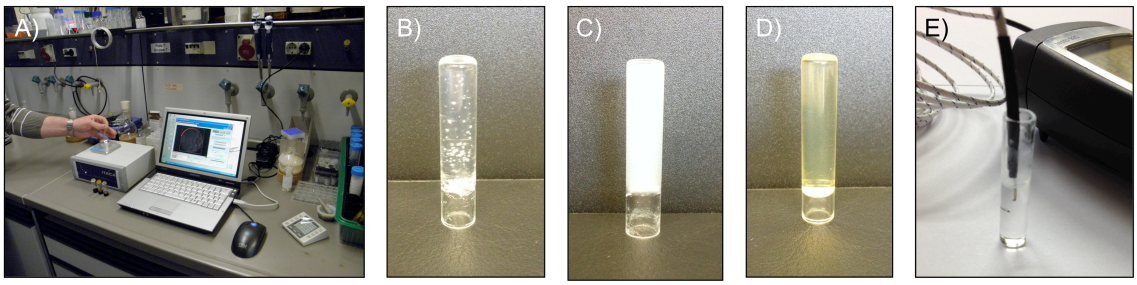


Figure S3. A) Photograph showing the facile setup of the microwave sensor in a small area of the lab bench. B-D) Typical digital photographs of upside-down vials containing gels obtained from gelator (B) **6** in dimethyl sulfoxide/water (v/v = 0.04/0.96) (c = 3 g L^{-1}); (C) **1** in acetonitrile (c = 5 g L^{-1}); and (D) **4** in nitrobenzene (c = 6 g L^{-1}). E) Thermocouple probe inserted into a gel material (Ø 0.1 mm).

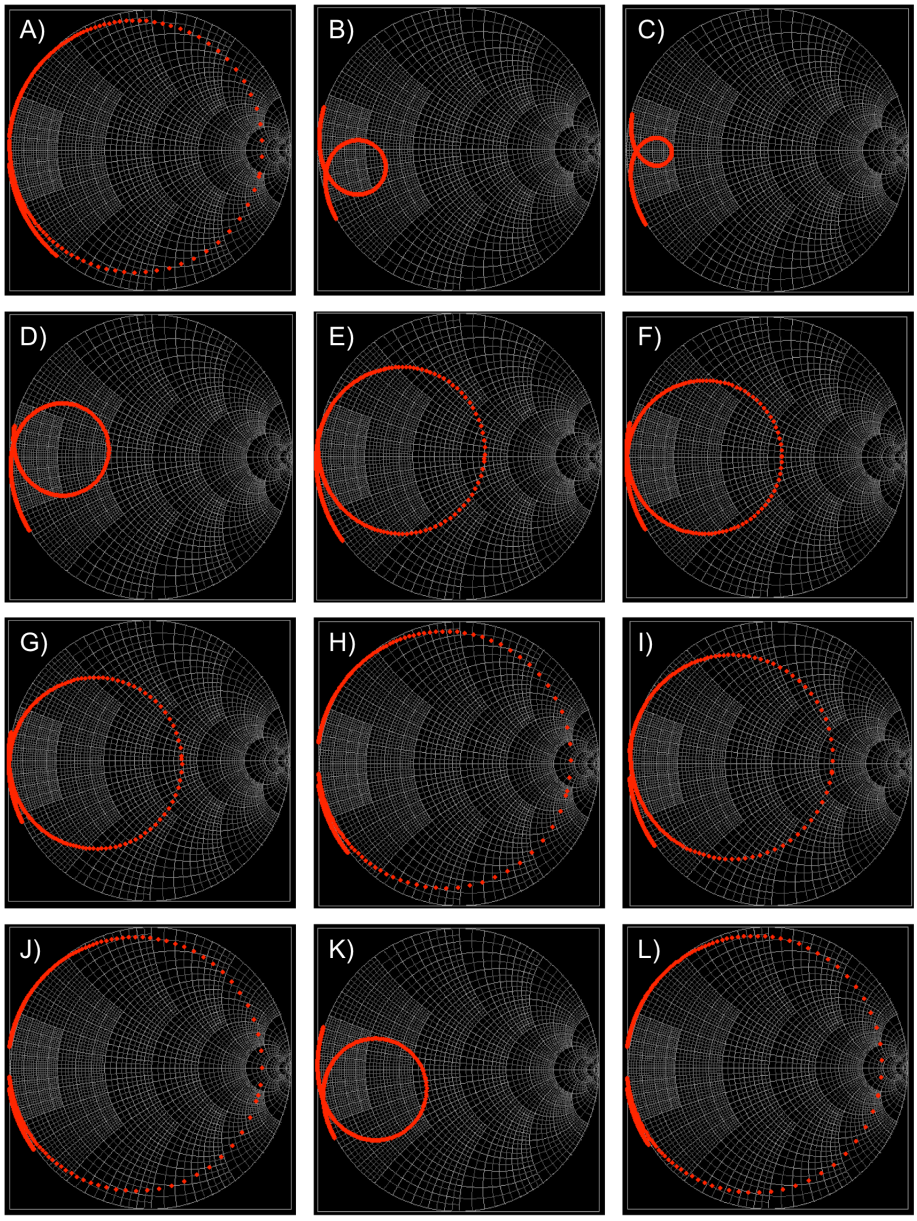


Figure S4. Representative smith charts of microwave measurements of different *sol-gel* samples. A) Gelator **5** in toluene (c = 20 g L^{-1}). B) Gelator **9** in DMF (0.28:0.5 M, v/v = 1/1, refereed to the two stock solutions Sol-1 (0.28 M) and Sol-2 (0.5 M) as described above). C) Gelator **10** in BN (150 μL = volume of the multicomponent gelator stock solution prepared as described above (*i.e.*, 0.3 M in HCl/CH_3OH)).

D) Gelator **10** in DME at the initial solution state (100 μL = volume of the multicomponent gelator stock solution prepared as described above (*i.e.*, 0.3 M in HCl/CH_3OH)). E) Gelator **10** in DME at the final gel state (100 μL = volume of the multicomponent gelator stock solution prepared as described above (*i.e.*, 0.3 M in HCl/CH_3OH)). F) Gelator **1** in ACT (c = 7 g L^{-1}). G) Gelator **1** in ACN (c = 5.2 g L^{-1}). H) Gelator **1** in DOX (c = 9.5 g L^{-1}). I) Gelator **1** in EA (c = 7 g L^{-1}). J) Gelator **1** in TOL (c = 12 g L^{-1}). K) Gelator **6** in DMSO/H_2O (v/v = 0.04/0.96; c = 3 g L^{-1}). L) Gelator **2** in XYL (c = 5 g L^{-1}). Abbreviations: ACT = acetone; ACN = acetonitrile; DME = 1,2-dimethoxyethane; DMF = *N*,*N'*-dimethylformamide; DOX = 1,4-dioxane; DMSO = dimethyl sulfoxide; EA = ethyl acetate; TOL = toluene; XYL = *p*-xylene.

4. Tabular data

Table S1. Measured T_{SG} and actual T_{SG} values obtained for different physical gels.

gelator[a]	solvent system[f]	concentration (g L^{-1})	T_{SG} (measured)[k]	T_{SG} (actual)[l]
1[b]	ACT	7	52	44
1[b]	ACN	5.2	55	51
1[b]	EA	7	53	45
1[b]	TOL	12	48	47
2[b]	XYL	5	49	46
3[b]	TOL	25	48	45
3[b]	TOL	40	56	58
4[b]	NB	6	60	57
5[b]	TOL	20	56	59
6[b]	DMSO/H_2O[g]	3	52	47
7[b]	ACN/CLF[h]	5	41	36
8[b]	TOL	25	51	48
8[c]	TOL	25	23	23
9[d]	DMF	0.28:0.5 M[i]	24	23
10[e]	ACT	250 μL[j]	-31	-33[m]
10[e]	DME	100 μL[j]	-30	-35[m]
10[e]	BN	150 μL[j]	-2	-1[m]

[a] Unless otherwise indicated, formation of the gels was achieved by the heating-cooling process. [b] Gel formation achieved by heating-cooling treatment as described above. [c] Photoinduced *sol-gel* transition as described above (RT was maintained during the entire process). [d] Gel formation achieved at RT as described above. [e] Gel formation achieved below RT as described above. [f] Abbreviations: ACT = acetone; ACN = acetonitrile; BN = benzonitrile; CLF = chloroform; DME = 1,2-dimethoxyethane; DMF = *N*,*N'*-dimethylformamide; DMSO = dimethyl sulfoxide; EA = ethyl acetate; NB = nitrobenzene; TOL = toluene; XYL = *p*-xylene. [g] v/v = 0.04/0.96. [h] v/v = 0.1/0.5. [i] v/v = 1/1, refereed to the two stock solutions Sol-1 (0.28 M) and Sol-2 (0.5 M) as described above. [j] Volume of the multicomponent gelator stock solution prepared as described above (*i.e.*, 0.3 M in HCl/CH_3OH). [k] *Sol-gel* transition temperature obtained by monitoring of the dielectric properties of the mixture during the gel formation. Estimated error ± 2 ºC. [l] Calculated as indicated in Figure S2. [m] Value obtained by means of a digital thermocouple probe (Ø 0.5 mm) inserted into the isotropic solution and visual inspection of the material during the warming up process.

5. References

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11 For the IFM measurements a sealed vial containing the gel was immersed upside-down in a thermostated oil bath. The temperature of the bath was raised at a rate of 2 ºC min^{-1}. T_{GS} was defined herein as the temperature at which the gel was broken. The experimental error of T_{GS} in at least two independent measurements was ± 2 ºC.