Supporting Information: Instantaneous Low Temperature Gelation by a Multicomponent Organogelator Liquid System Based on Ammonium Salts

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Instantaneous Low Temperature Gelation by a Multicomponent Organogelator Liquid System Based on Ammonium Salts

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1. Experimental section.

A) General remarks

^1H and ^{13}C NMR spectra were obtained on a Bruker Advance 300 instrument. FT-IR spectra were obtained on a Bruker IFS 66 instrument with ATR accessories or on a Bruker IFS 28/55 instrument at room temperature. Gel samples were deposited on NaCl disks and/or ATR module, and the IR spectra recorded at 8 cm^{-1} resolution with 40 scans. Appropriate corrections were made for the solvent. For the xerogel samples a patch of gel was deposited on a NaCl disk and frozen-vacuum dried. Xerogel samples were observed with a Jeol JEM 1010 transmission electron microscope (TEM) operating at a voltage of 90 kV. TEM images were obtained by depositing a patch of the gel onto copper grids (300 mesh) coated with both formvar and silicon monoxide. The specimens were frozen in liquid nitrogen and dried under vacuum at low pressure ($>10^{-5}$ Torr) for 4h. The relatively large size of the gel pieces made negative staining unnecessary for visualization. Differential Scanning Calorimetry (DSC) data were obtained in a Pyris Diamond DSC (Perkin Elmer) instrument at a ramping rate of $10\text{ }^\circ\text{C min}^{-1}$. SEM images were taken from gel samples coated with Au at a working distance of 50 mm under 30 mA electric current for 75 seconds obtaining a film thickness of *ca.* 8–10 nm (19.3 g/cc gold deposition). The coated grids were observed with a Jeol JSM 6300 scanning electron microscope operating at an accelerating voltage of 15 kV. AFM measurements were performed using Tapping Mode (Nanoscope IIIa, Digital Instruments) at 1 Hz scanning rate with a Si_3N_4 (Veeco NanoprobeTM tip RTESP7) tip at drive frequency 200–400 kHz. Drive amplitude ranged from 60 to 100 mV. MeOH was distilled from Na/MeOH mixture and the rest of solvents distilled from CaH_2 and storage under nitrogen atmosphere. Preliminary dynamic and steady flow measurements included DTS, DFS, and DSS experiments, which were reproducible in random replicates. The loss (G'') and elastic (G') moduli were measured in the linear viscoelastic regime. The ammonium tartaric salts were used either as supplied from commercial source (Sigma-Aldrich) or prepared using the standard protocol for the racemic resolution of the 1,2-*trans*-diaminocyclohexane.¹⁴ Melting points of (1*R*,2*R*)-1,2-diaminocyclohexane-*L*-tartrate and (1*S*,2*S*)-1,2-diaminocyclohexane-*D*-tartrate prepared by the classical racemic resolution were 285–288 $^\circ\text{C}$ (m.p._{commercial salt} = 273 $^\circ\text{C}$) and 282–284 $^\circ\text{C}$ (m.p._{commercial salt} = 279 $^\circ\text{C}$) respectively.

B) Preparation of ammonium tartrate salts

(1*R*,2*R*)-1,2-Diaminocyclohexane-*L*-tartrate. In a typical procedure ($\pm$)-*trans*-1,2-diaminocyclohexane was added dropwise to an aqueous solution of *L*-tartaric acid preheated at 90 $^\circ\text{C}$. Crystals of (1*R*,2*R*)-1,2-diaminocyclohexane-*L*-tartrate were formed upon cooling down the clear solution to room temperature, and stood overnight in a refrigerator. The crystals were filtered out, washed with ice-water and MeOH, and dried under vacuum. This salt is also commercially available.

(1*R*,2*R*)-1,2-Diaminocyclohexane-*D*-tartrate. (1*R*,2*R*)-1,2-Diaminocyclohexane-*L*-tartrate (500 mg, 1.9 mmol) was dissolved in the minimum amount of $\text{MeOH:HCl}_{\text{conc}}$ 9:1 (1.8 mL). To this solution Et_2O was added until a white precipitate formed, the solid was filtered and washed with ethyl ether ($\times 3$) after drying under high vacuum (1*R*,2*R*)-1,2-cyclohexane-1,2-diaminium dichloride was obtained as a white solid (348 mg, 98%), m.p.: 363–365 $^\circ\text{C}$, $[\alpha]_{\text{D}}^{20} = -15.6$ ($c = 2.5$, H_2O) (lit.¹ $[\alpha]_{\text{D}}^{20} = -15.8$ ($c = 2.53$, H_2O)). (1*R*,2*R*)-Cyclohexane-1,2-diaminium dichloride (300 mg, 1.6 mmol) was dissolved in NaOH saturated solution (5 mL) and the aqueous phase was extracted with Et_2O ($3 \times 10\text{ mL}$). The organic layers were dried over anhydrous MgSO_4 and the solvent removed by rotvap to yield (1*R*,2*R*)-1,2-diaminocyclohexane (167.8 mg, 92 %) as a viscous colorless oil. The product was next used without further purification. To a partially dissolved (1*R*,2*R*)-1,2-diaminocyclohexane (111 mg, 0.97 mmol) in THF (10 mL), *D*-tartaric acid (146 mg, 0.97 mmol) was added and the suspension refluxed under vigorous stirring for 36 h. After removing the organic solvent by rotvap (1*R*,2*R*)-1,2-diaminocyclohexane-*D*-tartrate was obtained (248 mg, 97 %). Mp: 285–288 $^\circ\text{C}$. $[\alpha]_{\text{D}}^{20} = -15$ ($c = 0.5$, H_2O). FT-IR (cm^{-1}): 3200–2400, 1577, 1526, 1377. ^1H NMR (300 MHz, D_2O , δ ppm): 1.19 (m, $w_{1/2} = 24\text{ Hz}$, 2H), 1.33 (m, $w_{1/2} = 36\text{ Hz}$, 2H), 1.63 (m, $w_{1/2} = 24\text{ Hz}$, 2H), 1.96 (m, $w_{1/2} = 18\text{ Hz}$, 2H), 3.18 (m, $w_{1/2} = 18\text{ Hz}$, 2H), 4.15 (s, 2H), 4.66 (s, 5H). ^{13}C NMR (75.4 MHz, D_2O , δ ppm): 22.48 (t), 29.03 (t), 51.82 (d), 73.55 (d), 178.21 (s). Elemental analysis for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{O}_6$ (%): calcd: C: 45.45, H: 7.63, N: 10.60. Found: C: 45.59, H: 7.66, N: 10.28

(1*R*,2*R*)-1,2-Diaminocyclohexane-1,2-dibenzoyl-*L*-tartrate. To a solution of 1,2-dibenzoyl-*L*-tartaric acid (1.21 g, 3.38 mmol) in water (100 mL) at 90 $^\circ\text{C}$, ($\pm$)-*trans*-1,2-diaminocyclohexane (0.36 mL, 3.38 mmol) was added dropwise. The temperature was increased (bath temperature 150 $^\circ\text{C}$) in order to dissolve a white precipitate formed during the process and be able to complete the addition. The clear solution was gradually cooled to room temperature and stood overnight in a refrigerator affording white crystals that

were filtered out, washed with ice water and MeOH and dried under vacuum giving (1*R*,2*R*)-diaminocyclohexane-1,2-dibenzoyl-*L*-tartrate (500 mg, 33%). Mp: 180–182 °C. $[\alpha]_D^{20} = -83.7$ ($c = 4$, H₂O). FT-IR cm⁻¹: 3000–2500, 2646, 1719.4, 1597, 1549, 1379, 1262, 1070. ¹H NMR (300 MHz, D₂O, δ ppm): 1.21 (m, $w_{1/2} = 20$ Hz, 2H), 1.36 (m, $w_{1/2} = 32$ Hz, 2H), 1.60 (m, $w_{1/2} = 16$ Hz, 2H), 3.23 (m, $w_{1/2} = 16$ Hz, 2H), 5.61 (s, 2H), 7.36 (m, $w_{1/2} = 16$ Hz, 2H), 7.54 (m, $w_{1/2} = 16$ Hz, 1H), 7.92 (m, $w_{1/2} = 8$ Hz, 2H). ¹³C NMR (75.4 MHz, D₂O, δ ppm): 22.39 (t), 28.90 (t), 51.81 (d), 73.89 (d), 128.45 (d), 129.47 (d), 133.90 (d), 167.29 (s), 171.50 (s). Elemental analysis for C₂₄H₂₈N₂O₈ (%): calcd: C: 61.01, H: 5.97, N: 5.93. Found: C: 61.01, H: 5.58, N: 5.20.

C) Preparation of multicomponent organogelator solutions

Solution A_L: To a suspension of salt (1*R*,2*R*)-diaminocyclohexane-*L*-tartrate (1 g, 3.78 mmol) in MeOH (30 mL) HCl 37 % wt (300 μ L, 1 equiv) was added at room temperature affording a solution 0.126 M in the salt. This solution was found to be stable for months. Molar ratio of diaminocyclohexane:tartaric acid:MeOH:HCl:H₂O = 1:1:195:1:3.25.

Solution A_D: This solution was prepared as for solution A_L but using the diastomeric salt (1*R*,2*R*)-1,2-diaminocyclohexane-*L*-tartrate. Molar ratio of diaminocyclohexane:tartaric acid:MeOH:HCl:H₂O = 1:1:195:1:3.25.

Solution B_L: To a suspension of the salt (1*R*,2*R*)-1,2-diaminocyclohexane-*L*-tartrate, (163 mg, 0.63 mmol) in MeOH (4.5 mL) a HCl/MeOH 1.25 M solution (0.5 mL, 1 equiv) was added at room temperature affording an anhydrous solution 0.126 M in the salt. This solution was found to be stable for months. Molar ratio of diaminocyclohexane:tartaric acid:MeOH:HCl = 1:1:195:1

Solution C_L: To a suspension of the salt (1*R*,2*R*)-1,2-diaminocyclohexane-*L*-tartrate, (50 mg, 0.19 mmol) in MeOH (1.5 mL) HBr 48 % wt (38 μ L, 1.75 equiv) was added at room temperature affording a solution 0.126 M in the salt. This solution was found to be stable for months. Molar ratio of diaminocyclohexane:tartaric acid:MeOH:HBr:H₂O = 1:1:195:1.75:8.6.

Solution D_L: To a suspension of the freshly prepared salt (1*R*,2*R*)-1,2-diaminocyclohexane-1,2-dibenzoyl-*L*-tartrate (50 mg, 0.12 mmol) in MeOH (1 mL) HCl 37 % wt (9.5 μ L, 1 equiv) was added at room temperature affording a solution 0.126 M in the salt. This solution must be used within a week period. Molar ratio of diaminocyclohexane:tartaric acid:MeOH:HCl:H₂O = 1:1:195:1:3.25.

Solution E_L: To a suspension of (1*R*,2*R*)-1,2-diaminocyclohexane (50 mg, 0.54 mmol) and *L*-malic acid (59 mg, 0.44 mmol) in MeOH (3.5 mL) HCl 37 % wt (35 μ L, 1 equiv) was added at room temperature affording a solution 0.126 M in the salt. This solution was found to be stable for months. Molar ratio of diaminocyclohexane:tartaric acid:MeOH:HCl:H₂O = 1:1:195:1:3.3.

D) Gelation experiments

The appropriate organic solvent (1 mL) was placed in a glass screw-capped vial (10 cm length $\times$ 1 cm diameter) and cooled down in a liquid nitrogen-acetone bath close to the freezing temperature of the solvent. Then, the appropriate volume of the MOGLS was added under hand-stirring of the vial. The mixture was kept at low temperature for 1 min, after which time the cooling bath was removed and the clear homogeneous solution let to warm up to room temperature. The gel formation was visually monitored by turning the vial upside-down. The material was considered a gel if gravitational flow was not observed. Thermal characterization was first carried out by the “dropping ball method”²⁰ to determine the temperature at which the gels are destroyed, T_d .

A) Determination of gel destruction temperature T_d . The gel destruction temperatures T_d were determined by the “dropping ball method”²⁰: a glass ball (275 mg) was placed on top of the gel and the tube was sealed. The sample was placed in a stirred thermo-stated oil bath. Then the bath was heated at a rate temperature of *ca.* 2 °C/min. The T_d was recorded when the ball began to fall down. Once the gel is destroyed an insoluble white precipitate formed. As expected, the T_d values for the gels prepared using the enantiomeric salts were the same.

B) Gel destruction and products characterization. To a 10 mL of acetone cooled to –80 °C the multicomponent organogelator solution A_L 0.126 M (1 mL) was added. The mixture was hand-shake and after removed from the cooled bath the solution was allowed to warm to room temperature (30 minutes). The formed gel was destroyed by heating, and a white precipitate formed. The solid was dried overnight under high vacuum followed by Kugelrohr drying for 48 h at 70–80 °C and it was identified as (1*R*,2*R*)-1,2-cyclohexane-1,2-diaminium dichloride (12.2 mg, 0.5 equiv). Mp: 364–366 °C. $[\alpha]_D^{20} = -15.6$ ($c = 2.5$, H₂O) (value obtained from three independent measurements, STDV = 0.43) (lit.¹³ $[\alpha]_D^{20} = -15.8$ (c

= 2.53, H₂O). FT-IR cm⁻¹: 2500–3200 (s, broad band, “ammonium band”), 1598 (s), 1531 (s), 1500 (s). ¹H NMR (300 MHz, D₂O, δ ppm): 1.28 (2H, m, w_{1/2} = 29.3 Hz), 1.44 (2H, m, w_{1/2} = 36.6 Hz), 1.74 (2H, m, w_{1/2} = 26.3 Hz), 2.08 (2H, m, w_{1/2} = 32.2 Hz), 3.30 (2H, m, w_{1/2} = 18.9 Hz), 4.67 ppm (16H, m, ammonium and water hydrogen, w_{1/2} = 18 Hz). ¹³C NMR (75.4 MHz, D₂O, δ ppm): 22.44 (t), 28.94 (t), 51.86 (d). Elemental analysis: for C₆H₁₆Cl₂N₂, Calcd (%): C: 38.93, H: 7.62, N: 15.13. Found (%): C: 38.53, H: 7.62, N: 15.67. For comparative purposes the dichloride salt was also prepared by exchanging the tartrate anions by chlorides. Thus, the freshly prepared (1*R*,2*R*)-1,2-diaminocyclohexane-*L*-tartrate was dissolved in the minimum amount of a solution HCl:MeOH (ratio 1:9) and filtered to remove any insoluble impurity. To this solution Et₂O was added dropwise until a white precipitate of the desired dichloride appeared, which was then separated out by filtration and dried under vacuum.

The solvent from the liquid phase was removed by rotavap and the residue freeze-dried under high vacuum affording a white-yellow solid (28.2 mg), which corresponds to 0.5 equivalent of (1*R*,2*R*)-1,2-diaminocyclohexane *L*-tartrate and 0.5 equiv of *L*-tartaric acid. ¹H NMR (300 MHz, D₂O, δ ppm): 1.20 (m, w_{1/2} = 29.8 Hz, 2H), 1.36 (m, w_{1/2} = 37.2 Hz, 2H), 1.66 (m, w_{1/2} = 22.3 Hz, 2H), 1.99 (m, w_{1/2} = 29.8 Hz, 2H), 3.22 (m, w_{1/2} = 29.8 Hz, 2H), 4.35 (s, 3H). ¹³C NMR (75.4 MHz, D₂O, δ ppm): 22.44 (t), 28.97 (t), 51.78 (d), 72.53 (d), 176.15 (s). Elemental analysis: for liquid phase composed of 1 equivalent of tartaric acid and half one of (1*R*,2*R*)-cyclohexane-1,2-diamine: C₁₄H₂₆N₂O₁₂ Calcd (%): C: 40.58, H: 6.32, N: 6.76. Found (%): C: 40.53, H: 5.76, N: 6.79.

2. Spectra for ammonium tartrate salts.

2.1. (1*R*,2*R*)-1,2-Diaminocyclohexane-*L*-tartrate.

Figure S1. FT-IR of (1*R*,2*R*)-1,2-diaminocyclohexane-*L*-tartrate.

Figure S2. ¹H NMR for (1*R*,2*R*)-1,2-Diaminocyclohexane-*L*-tartrate.

Figure S3. ^{13}C NMR of (1*R*,2*R*)-1,2-diaminocyclohexane-*L*-tartrate.

2.2. (1*R*,2*R*)-1,2-Diaminocyclohexane-*D*-tartrate.

Figure S4. FT-IR of (1*R*,2*R*)-1,2-diaminocyclohexane-*D*-tartrate.

Figure S5. ^1H NMR of (1*R*,2*R*)-1,2-diaminocyclohexane-*D*-tartrate.

Figure S6. ^{13}C NMR of (1*R*,2*R*)-1,2-diaminocyclohexane-*D*-tartrate.

2.3. (1*R*,2*R*)-1,2-Diaminocyclohexane-1,2-dibenzoyl-*L*-tartrate.

Figure S7. FT-IR of (1*R*,2*R*)-1,2-diaminocyclohexane-1,2-dibenzoyl-*L*-tartrate.

Figure S8. ¹H NMR of (1*R*,2*R*)-1,2-diaminocyclohexane-1,2-dibenzoyl-*L*-tartrate.

Figure S9. ^{13}C NMR of (1*R*,2*R*)-1,2-diaminocyclohexane-1,2-dibenzoyl-*L*-tartrate.

3. Spectra for Multicomponent OrganoGelator Liquid System (MOGLS).

MOGLS = 0.126M methanolic solution of (1*R*,2*R*)-1,2-diaminocyclohexane *L*-tartrate + 1 equiv of concentrated hydrochloric acid (37% HCl).

Figure S10. FT-IR of Multicomponent OrganoGelator Liquid System (MOGLS).

Figure S11. ^1H NMR of Multicomponent Organogelator Liquid System (MOGLS).

Figure S12. ^{13}C NMR of Multicomponent Organogelator Liquid System (MOGLS).

4. Spectra for products after gel destruction.

Figure S13. ^1H NMR of (1*R*,2*R*)-1,2-cyclohexane-1,2-diaminium dichloride. Once the destruction of the gels is induced either upon heating or by mechanical stress (1*R*,2*R*)-1,2-diaminocyclohexane dihydrochloride is formed as a white precipitate, which is fully insoluble in the solvent medium and unable to get back into the solution.

Figure S14. ^1H NMR of the sobrenadant liquid after gel destruction: (1*R*,2*R*)-1,2-diaminocyclohexane-*L*-tartrate and *L*-tartaric acid.

Figure S15. ^{13}C NMR of the sobrenadant liquid after gel destruction: (1*R*,2*R*)-1,2-diaminocyclohexane-*L*-tartarate and *L*-tartaric acid.

5. FT-IR for gels and xerogels.

5.1. Gels.

Figure S16. FT-IR spectrum of acetone-gel.

Figure S17. FT-IR spectrum of THF-gel.

Figure S18. FT-IR spectrum of 1,2-DME-gel.

5.2. Xerogels.

Figure S19. FT-IR spectrum of acetone-xerogel.

Figure S20. FT-IR spectrum of THF-xerogel.

Figure S21. FT-IR spectrum of 1,2-DME-xerogel.

6. Representative differential scanning (DSC).

Figure S22. Representative DSC spectra of (a) benzonitrile-gel, (b) acetone-gel, and (c) cyclohexanone-gel made using solution **A_L**.

7. Representative digital pictures of the organogels.

Figure S23. (a-d) Digital pictures of the organogels made using solution **A_L** at low temperature: (a) AcOEt (1mL); (b) acetone (1mL); (c) THF (1mL); (d) THF (250 mL); (e) acetone-gel prepared at room temperature. The picture shows a non-homogeneous gel phase due to the formation of liquid pockets, which often make to leak a small amount of solvent after turning the test tube upside-down .

8. Representative rheological plots.

Although the method of placement of the samples between the rheometer plates made difficult the reproducibility of the absolute values of G' and G'' between runs on the same sample, the values of $\tan \delta$ (G''/G'), were reproducible, as they should be if the same type of gel network is formed in each run.

Figure S24. Representative rheological plots for the gel prepared in AcOEt using solution **A_L**. AcOEt-gel prepared at different mvg.

- (1) (a) Fukuta, Y.; Mita, T.; Fukuda, N.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2006**, *128*, 6312–6313. (b) Kawai, M.; Iwase, T.; Butsugan, Y.; Nagai, U. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 304–308.

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