Supporting Information

Competition between gelation and crystallisation of a peculiar multicomponent liquid system based on ammonium salts

Iti Kapoor,^{‡a} Eva-Maria Schön,^{‡a} Jürgen Bachl,^a Dennis Kühbeck,^a Subhadeep Saha,^b Rahul Banerjee,^b Carlos Cativiela,^c Stefano Roelens,^d José Juan Marrero-Tellado^{*e} and David Díaz Díaz^{*a,c}

^a Institut für Organische Chemie, Universität Regensburg, Universitätsstr. 31, 93040 Regensburg, Germany
 ^b Physical/Materials Chemistry Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411008, India
 ^c Departamento de Química Orgánica, ISQCH, Universidad de Zaragoza-CSIC, Pedro Cerbuna 12, 50009 Zaragoza, Spain
 ^d Istituto di Metodologie Chimiche (IMC), Consiglio Nazionale delle Ricerche (CNR), Dipartimento di Chimica, Università di Firenze, Via della Lastruccia 13, I-50019 Sesto Fiorentino, Firenze, Italy
 ^e Instituto Universitario de Bio-Orgánica "Antonio González", Universidad de La Laguna, Astrofísico Francisco Sánchez 2, 38206 La Laguna, Tenerife, Spain

E-mail: David.Diaz@chemie.uni-regensburg.de; Fax: + 49 941 9434121; Tel.: + 49 941 9434373

‡ These authors contributed equally to this work.

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1. Discovery origin on the racemic resolution of trans-1,2-diaminocyclohexane

The discovery of this synergistic multicomponent organogelator liquid system (MGS) (2, Figure S1) took place during the realization of the standard protocol of tartaric acid-mediated racemic resolution of (\pm) -*trans*-1,2-diaminocyclohexane.¹ During the cleaning of the glassware used during the experimental work, we observed the instantaneous formation of a transparent jelly-like material upon addition of acetone to wash out any remained substance. The unexpected phenomenon took place, based on the experimental protocol, only in the beaker containing (1R,2R)-1,2-diaminocyclohexane L-tartrate (1), MeOH, and aqueous HCl.² In the original publication regarding the racemic resolution,¹ the above composition was co-existing as an intermediate solution during the synthesis of (1R,2R)-1,2-diaminocyclohexane L-tartrate salt (1) (10 g, 37.8 mmol) was dissolved in a minimum amount of 10% HCl in methanol. To this solution was added ether dropwise until a white precipitate appeared. The precipitate was filtered and dried under vacuum (6.9, 96% yield)".





2. Solubility of (1R,2R)-1,2-diaminocyclohexane L-tartrate

No solubility data were found in the literature for (1R,2R)-1,2-diaminocyclohexane L-tartrate (1). In our hands, the commercial salt was found to be insoluble either at RT, after heat treatment (heat gun) or after sonication (Figure S2) in the entire series of tested solvents: methanol, ethanol, isopropanol, *n*-butanol, *n*-hexanol, glycerol, acetone, acetonitrile, dioxane, tetrahydrofuran, diethyl ether, methylene chloride, chloroform, xylol and *n*-hexane. In glycerol, the white colour of the starting material turned into brown upon heating with the heat gun probably due to a decomposition process, although no further investigations were carried out. The preliminary solubility tests were carried out under the following conditions: Concentration ca. 0.04–0.08 M; time of heat gun treatment ca. 1 min; time of sonication treatment ca. 15 min. Note that in a previous publication from Gilheany and co-workers³ a <u>suspension</u> of this salt was prepared using 52 mmol of 1 in 50 mL of MeOH (concentration = 1.04 M).



Fig. S2 Solubility tests of **1** using < 2 equiv of HCl respected to the salt. A: 1.0 equiv (left) and 1.7 equiv (right) of HCl after 30 min sonication (the mixtures were undisturbed for sometime to allow the insoluble material to settle down; B: same mixtures placed over the logo of the University of Regensburg; C: same mixtures after hand-shaking the vials.

3. General synthesis of ammonium tartrate salts

No significant difference in the results were found when tartrate salts were either purchased from commercial suppliers or synthesized following the general protocols reported in the literature and providing same spectroscopic data:

(1R,2R)-1,2-diaminocyclohexane L-tartrate (1):^{4,5} (±)-*trans*-1,2-diaminocyclohexane (1.0 mmol) was added dropwise to a solution of L-tartaric acid (1.0 mmol) in H₂O (0.03 M) at 90 °C. If necessary, the temperature can be increased gradually until 120 °C in order to keep the mixture solubilised. The isotropic solution was allowed to spontaneously cool down to RT and then kept at 4 °C overnight. The recrystallization process was repeated twice. The formed crystals were filtered out, washed with ice-water and MeOH and dried under vaccum to afford **1** as a white crystalline solid. Elemental analysis for C₁₀H₂₀N₂O₆ (%): calcd: C: 45.45, H: 7.63, N: 10.60; found: C: 45.49, H: 7.65, N: 10.58.

(1R,2R)-1,2-diaminocyclohexane D-tartrate:⁶ A mixture of (1R,2R)-(-)-1,2-diaminocyclohexane⁷ (1 mmol) and D-tartaric acid (1 mmol) suspended in dry benzene (0.1 M) was refluxed overnight. After this time, the homogeneous solution was allowed to cool down to RT. The obtained crystals were filtered out, washed with MeOH and dried under vaccum to afford (1R,2R)-1,2-diaminocyclohexane D-tartrate as a white crystalline solid. Elemental analysis for C₁₀H₂₀N₂O₆ (%): calcd: C: 45.45, H: 7.63, N: 10.60; found: C: 45.46, H: 7.67, N: 10.63.

4. Solvents: Relative permittivity, Kamlet-Taft parameters, freezing and boiling points

Table S1 outline the most important solvent properties used during the experiments and analysis of the results. Note that only in the cases of diethyl ether, the T_d of the gel was clearly higher (52 °C higher) than the boiling point (bp) of the solvent (35 °C). For all the other cases, T_d was always lower than the corresponding bp.

| entry | solvent | $\epsilon_r^{\ b}$ | α^{c} | β^d | π^{*^e} | fp ^f (°C) | bp ^g (°C) |
|-------|------------------------|--------------------|--------------|-----------|-------------|----------------------|----------------------|
| 1 | water | 80.0 | 1.17 | 0.47 | 1.09 | 0 | 100 |
| 2 | dimethyl sulfoxide | 46.7 | 0.00 | 0.76 | 1.00 | 19 | 189 |
| 3 | glycerol | 43.0 | 1.21 | 0.51 | 0.62 | 18 | 290 |
| 4 | dimethylformamide | 38.0 | 0.00 | 0.69 | 0.88 | -61 | 153 |
| 5 | dimethylacetamide | 37.8 | 0.00 | 0.76 | 0.88 | -20 | 164-166 |
| 6 | ethylene glycol | 37.0 | 0.90 | 0.52 | 0.92 | -13 | 197 |
| 7 | nitromethane | 37.3 | 0.22 | 0.06 | 0.85 | -29 | 100-103 |
| 8 | acetonitrile | 36.6 | 0.19 | 0.40 | 0.75 | -45 | 82 |
| 9 | N-methyl-2-pyrrolidone | 32.2 | 0.00 | 0.77 | 0.92 | -24 | 202-204 |
| 10 | nitrobenzene | 26.3 | 0.00 | 0.30 | 1.01 | 6 | 211 |
| 11 | benzonitrile | 25.9 | 0.00 | 0.37 | 0.90 | -13 | 188-191 |
| 12 | 2-nitropropane | 25.5 | NF | NF | NF | -93 | 120 |
| 13 | ethanol | 24.5 | 0.86 | 0.75 | 0.54 | -114 | 78 |
| 14 | 1-nitropropane | 23.2 | 0.00 | 0.25 | 0.75 | -108 | 131 |
| 15 | acetone | 21.0 | 0.08 | 0.43 | 0.71 | -95 / -93 | 56-57 |
| 16 | nitroethane | 19.7 | 0.00 | 0.25 | 0.80 | -90 | 112-116 |
| 17 | cyclohexane | 18.5 | 0.00 | 0.00 | 0.00 | 7 | 81 |
| 18 | cyclohexanone | 16.1 | 0.00 | 0.53 | 0.76 | -16 | 156 |

Table S1 Selection of solvent properties and parameters.^a

| 19 | pyridine | 12.4 | 0.00 | 0.64 | 0.87 | -42 | 115 |
|----|--|------|------|------|-------|------|--------------|
| 20 | 1-butyl-3-methylimidazolium hexafluorophosphate | 11.4 | 0.63 | 0.21 | 1.03 | -8 | > 340 (dec.) |
| 21 | 3-methylbutan2-one | 10.4 | NF | NF | NF | -92 | 93-95 |
| 22 | 1,2-dichloroethane | 10.4 | 0.00 | 0.10 | 0.81 | -35 | 84 |
| 23 | methylene chloride | 9.1 | 0.13 | 0.10 | 0.82 | -97 | 40 |
| 24 | 1,2-dimethoxyethane | 7.3 | 0.00 | 0.41 | 0.53 | -58 | 85 |
| 25 | 2-methoxyethyl ether | 7.2 | 0.00 | 0.40 | 0.64 | -64 | 162 |
| 26 | ethyl acetate | 6.1 | 0.00 | 0.45 | 0.55 | -84 | 77 |
| 27 | tetrahydrofuran | 5.7 | 0.00 | 0.55 | 0.58 | -108 | 66 |
| 28 | chloroform | 4.8 | 0.20 | 0.10 | 0.58 | -64 | 61 |
| 29 | diethyl ether | 4.3 | 0.00 | 0.47 | 0.27 | -116 | 35 |
| 30 | dibutyl ether | 3.1 | 0.00 | 0.46 | 0.27 | -93 | 142 |
| 31 | 1,2-dichlorobenzene | 2.8 | 0.00 | 0.03 | 0.80 | -17 | 181 |
| 32 | methyl <i>tert</i> -butyl ether | 2.6 | NF | NF | NF | -109 | 55 |
| 33 | carbon disulfide | 2.6 | 0.00 | 0.07 | 0.61 | -111 | 46 |
| 34 | tetrachloroethylene | 2.5 | 0.00 | 0.05 | 0.28 | -19 | 121 |
| 35 | toluene | 2.4 | 0.00 | 0.11 | 0.54 | -93 | 111 |
| 36 | benzene | 2.3 | 0.00 | 0.10 | 0.59 | 6 | 80 |
| 37 | 1,4-dioxane | 2.2 | 0.00 | 0.37 | 0.55 | 12 | 101 |
| 38 | carbon tetrachloride | 2.2 | 0.00 | 0.10 | 0.28 | -23 | 77 |
| 39 | <i>n</i> -octane | 2.0 | 0.00 | 0.00 | 0.01 | -57 | 126 |
| 40 | <i>n</i> -hexane | 1.9 | 0.00 | 0.00 | -0.04 | -95 | 69 |

^{*a*} Abbreviations: NF = not found; dec. = decomposes. ^{*b*} Relative permitivity (dielectric constant)⁸ measured in the range 20–25 °C. The values were rounded off to one decimal place and those highlighted in red color correspond to solvents that were not gelled with the MGS. ^{*c*} Kamlet-Taft parameter⁹ defining the hydrogen bond donor ability. ^{*d*} Kamlet-Taft parameter defining the hydrogen bond aceptor ability. ^{*e*} Kamlet-Taft parameter defining the polarisability of the solvent. ^{*f*} Freezing point (values rounded off wihout decimals are presented). These values were considered to define approximately the cooling bath temperarature in each case. ^{*g*} Boiling point (values rounded off wihout decimals are presented). Note: From the series of nitroalkanes, only nitromethane provided a gel stable to the inversion of the test tube (the appearance of crystals inside the bulk gel was observed after 1 h). Nitroethane also presented tendency to gel but much weaker than nitromethane, whereas the rest provided miscible mixtures. No optimization of the gv were further attempted in those cases where no increase of viscosity was observed after addition of 100 µL of MGS.

5. Two-variables screening matrix

In order to determine the optimal molar composition of the gelator solution we first carried out a twovariables screening defined by the tartrate salt concentration and number of equivalents of HCl. This study provided a 2D-rectangular matrix of 132 elements. The results demonstrated the necessity of at least 2 equivalents of HCl (respect to the tartrate salt) to dissolve **1**. However, sonication treatment was necessary to complete solubilisation except when 2.4 equiv of HCl were used. The use of non-isotropic systems (e.g. after filtration of insoluble material) in the gel preparation was proven to provide results rather difficult to reproduce from batch to batch. The different spontaneous solutions achieved within the 2D-matrix were evaluated in terms of their gelation ability for a few of the solvents listed in Table 1 (main text) (e.g. DOX, ACT, ACN, THF). The obtained preliminary gel-like materials were compared based on their temporal stability and showed an optimal salt concentration between 0.1-0.15 M and 2.4 equiv of HCl. It is worth to mention that during our investigation some combinations other than those shown in Table S2 were also investigated and the results are discussed along this manuscript. For example the use of > 2.4 equiv of HCl

provided also gels but with much lower temporal stability. In the other hand, the use of MGS prepared with 2–2.3 equiv of HCl resulted also effective as a gelator system. However, more number gels could be obtained using the MGS made with 2.4 equiv of HCl.

| [M]↓/ HCl⇒ | 1.0 | 1.3 | 1.5 | 1.7 | 1.8 | 1.9 | 2.0 | 2.1 | 2.2 | 2.3 | 2.4 |
|------------|--------|--------|--------|--------|--------|--------|------|------|------|------|------|
| 0.06 | I (30) | I (30) | I (30) | I (30) | I (10) | I (10) | S(2) | S(2) | S(1) | S(1) | S(0) |
| 0.07 | I (30) | I (30) | I (30) | I (30) | I (10) | I (10) | S(2) | S(2) | S(1) | S(1) | S(0) |
| 0.08 | I (30) | I (30) | I (30) | I (30) | I (10) | I (10) | S(2) | S(2) | S(1) | S(1) | S(0) |
| 0.09 | I (30) | I (30) | I (30) | I (30) | I (10) | I (10) | S(2) | S(2) | S(1) | S(1) | S(0) |
| 0.1 | I (30) | I (30) | I (30) | I (30) | I (10) | I (10) | S(2) | S(2) | S(1) | S(1) | S(0) |
| 0.13 | I (30) | I (30) | I (30) | I (30) | I (10) | I (10) | S(2) | S(2) | S(1) | S(1) | S(0) |
| 0.2 | I (30) | I (30) | I (30) | I (30) | I (10) | I (10) | S(2) | S(2) | S(1) | S(1) | S(0) |
| 0.25 | I (30) | I (30) | I (30) | I (30) | I (10) | I (10) | S(2) | S(2) | S(1) | S(1) | S(0) |
| 0.3 | I (30) | I (30) | I (30) | I (30) | I (10) | I (10) | Crys | Crys | Crys | Crys | Crys |
| 0.4 | I (30) | I (30) | I (30) | I (30) | I (10) | I (10) | Crys | Crys | Crys | Crys | Crys |
| 0.5 | I (30) | I (30) | I (30) | I (30) | I (10) | I (10) | Crys | Crys | Crys | Crys | Crys |
| 1.0 | I (30) | I (30) | I (30) | I (30) | I (10) | I (10) | Crys | Crys | Crys | Crys | Crys |

Table S2 2D-Matrix showing the concentration of the salt 1 in MeOH [M] and the amount of HCl (equivalents respect to the salt) necessary to prepare a transparent and stable MGS solution.^a

^{*a*}Abbreviations: I(t) = visible insoluble material after t min of sonication. The sonication time was extended to several hours for [M] ca. 0.13 M without any significant improvement in terms of salt solubility; S(t) = completely soluble after t min of sonication; Crys = crystallization over time. The crystals were visible within hours for the higher concentration.

It is important to remark that the evaluation of the gels formed with the above different solutions was not exhaustively carried out for all the solvents. Therefore, it could be also possible to find a more appropriate molar composition for individual cases.

6. Experimental considerations



Fig. S3 Additional digital photographs of the MGS-based materials prepared in different solvents and at different gelling solution volume. A: solvent = DME, gelling solution volume = $150 \,\mu$ L (in this case the optimal volume was established in 100 μ L to avoid the collapse of the gel); B: solvent = DEE, gelling solution volume = $200 \,\mu$ L (left) and $250 \,\mu$ L (right); C–E: solvent = MEM, gelling solution volume $150 \,\mu$ L (C), $200 \,\mu$ L (D); $250 \,\mu$ L (E).

a) The gelation volumes (gv) were determined by varying the added MGS volume within the range of 100– 300 μ L per mL of tested solvent (with variations of 50 μ L between experiments). The reported volume values were choosen based on both the minimum amount of non gelled solvent and the higher temporal

stability of the formed gels (Figure S3). Although it was attended to adjust the gv values to the minimun gelation volume, it should be indicated that a more comprehensive study with smaller volume intervals would be necessary to unequivocally define the volumes as the minimun ones required for gel formation. The volume of MGS that afforded reproducible gel samples was established in the range 100–250 μ L, which corresponds to a concentration range of 0.3–0.9 wt.% referred to the tartrate salt.¹⁰

b) Recommendations for the good scientific practice with the described systems:

(1) Use glass volumetric materials to prepare the stock solutions (e.g. HCl/MeOH; MGS). Plastic syringes and/or metallic needles should be avoided when working with aqueous HCl because they difficult the accurate measurement of the volumes. However, they could be used used if the measurements are fast. Note that we could not detect any influence of the type of syringe/needle used on the salt solubility (e.g. by any uncontrolled reaction of HCl with the metal needles). Automatic syringes could be used for the preparation of stock solutions after proper calibration.

(2) It was found that adding the MGS in such a way that the drops slip at the wall of the galss vial reduce the effect of the container diameter. This was specially observed for solvents like ETAC and ACT.

(3) It is important to let the solvent into the cooling bath for at least 5 minutes before adding the MGS to ensure that the mixing will take place at the desired low temperature. The use of wet solvents to prepare the cooling bath usually adquire a white opaque look, which made imposible to visually monitor the status of the mixture inside the test tube.

(4) An effective mixing of the solvent-MGS mixture is mandatory to obtain the most homogeneous and stable gels. The formation of partial cloudy areas inside transparent gels usually indicates a poor mixing (e.g. gels made in DOX). We found that a small magnetic stirring bar could be used to improve the mixing (ca. 1000–2500 rpm) if necessary. In that case, the stirring bar should be removed before the cooling bath. A good mixing helps to control excessive nucleation and fast crystal growth rate, which represents a key for enhancing the half-life of a transient gel.

(5) All solvents should be purchased anhydrous or dried following the corresponding standard procedure.¹¹ This helps for the standarization of the experimental protocols and preparation of MGS with higher stability over time. Thus, MGS solutions sealed in vials and stored in dark for at least 7 days provided consistent results. The use of older MGS may cause a detriment in the gel properties as a result of microcrystallization of the dichloride salt **4**.

(6) During the evaluation of the temporal stability the test tube should be kept in vertical position (not upside-down) and undisturbed. If the test tube is kept upside-down the gravitational force causes the gel to fall down within hours and fragment into small pieces with the consecuent leak of liquid phase. Moreover, tubes of same dimensions should be used in order to draw the most reliable comparisons between samples.

(7) The temporal stability of the transient gels could be moderately extended by decreasing the rate of the warming-up step after addition of the MGS, which slows down the formation of **4**. This could be done by keeping the materials for example in the refrigerator at 4 °C (except for DOX) or by holding the test tube inside the cooling bath until it reaches room temperature) either keeping them at 4 °C.

(8) In general, all transient gels leak solvent over time. The careful removal of this solvent is necessary to maintain the integrity of the bulk gel for the longest period of time.

(9) A thermocouple could be introduced into the solution at low temperature in order to determine approximately the temperature at which the gelation process starts after removing the cooling bath. However, these values should be interpretated considering that the gelation kinetics may be altered at least at the interface metal-solution, which may cause important variations compared to other positions in the gel.

7. Gel made in 3-methylbutan-2-one

A remarkable change in color was observed in the case of the gels made in 3-methylbutan-2-one (MBN) (Figure S4). These gels were initially colorless and slighly turbid, which started to turn into dark yellowishgreenish gels within 1–3 hours. Nevertheless, the gels were still stable to the inversion of the test tube for some time after changing the color. Preliminary studies showed that the visual change was due to the presence of aqueous HCl as it was demonstrated by preparing solutions with different compositions. Indeed, just a colorless solution of MBN in MeOH adquires quickly a yellowish tone after addition of a catalytic amount of HCl (37 wt.% in aqueous solution). Acid-catalysed formation of a highly colored compound (e.g. self-aldol condensation product, conjugated polymer) seems to be responsible for this observation.



Fig. S4 A: Gel made in MBN as explained in Table 1 (main text); B: same gel after 3–4 hours; C: solution of MBN in MeOH in the presence of a catalytic amount of aqueous HCl (37 wt.%).



8. FT-IR spectra

Fig. S5 A: MeOH/HCl solution used to prepare the MGS; B: (1R,2R)-1,2-diaminocyclohexane L-tartrate; C: MGS solution; D: xerogel from the gel made in DOX.

9. NMR spectra

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Fig. S6 Selected NMR spectra. A: ¹H NMR (300 MHz, D₂O) of L-tartaric acid (**3**) obtained from the liquid phase after DOX-gel destruction (70 min after gel formation); B: ¹³C NMR (75 MHz, D₂O) of **3** obtained from the liquid phase after DOX-gel destruction (70 min after gel formation); C: ¹H NMR (300 MHz, D₂O) of (1*R*,2*R*)-1,2-diaminocyclohexane dichloride (**4**) obtained as crystals from MGS; D: ¹³C NMR (75 MHz, D₂O) of **4** obtained as crystals from MGS; E: ¹H NMR (300 MHz, D₂O) of **4** obtained as precipitate after DOX-gel destruction (70 min after gel formation); F: ¹³C NMR (75 MHz, D₂O) of (1*R*,2*R*)-1,2-diaminocyclohexane L-tartare (**1**); H: ¹³C NMR (75 MHz, D₂O) of (1*R*,2*R*)-1,2-diaminocyclohexane L-tartrate (**1**); H: ¹³C NMR (75 MHz, D₂O) of (1*R*,2*R*)-1,2-diaminocyclohexane dichloride (**4**) obtained as crystals from MGS; J: ¹³C NMR (750 MHz, D₂O) of (1*R*,2*R*)-1,2-diaminocyclohexane dichloride (**4**) obtained as crystals from MGS; J: ¹³C NMR (750 MHz, DMSO-*d*₆) of (1*R*,2*R*)-1,2-diaminocyclohexane dichloride (**4**) obtained as crystals from MGS; J: ¹³C NMR (750 MHz, DMSO-*d*₆) of (1*R*,2*R*)-1,2-diaminocyclohexane dichloride (**4**) obtained as crystals from MGS; J: ¹³C NMR (750 MHz, DMSO-*d*₆) of (1*R*,2*R*)-1,2-diaminocyclohexane dichloride (**4**) obtained as crystals from MGS; J: ¹³C NMR (750 MHz, DMSO-*d*₆) of (1*R*,2*R*)-1,2-diaminocyclohexane dichloride (**4**) obtained as crystals from MGS. The signals of the solvents were calibrated as following: D₂O = 4.79 ppm (¹H NMR); DMSO-*d*₆ = 2.50 ppm (¹H NMR); DMSO-*d*₆ = 39.5 ppm (¹³C NMR); H₂O residual peak in DMSO-*d*₆ = 3.34 ppm (¹H NMR).

• (1*R*,2*R*)-1,2-Diaminocyclohexane L-tartrate (1): 1.31–1.46 (m, 2H, C*H*₂CH₂CHN), 1.50–1.54 (m, 2H, C*H*₂CH₂CHN), 1.80–1.83 (m, 2H, C*H*₂CHN), 2.12–2.17 (m, 2H, C*H*₂CHN), 3.33–3.37 (m, 2H, CHN), 4.32 (s, 2H, OC*H*), 4.79 (br s, 6H, NH₃ –overlapped with solvent peak–); ¹³C NMR (75 MHz, D₂O) δ /ppm = 22.8, 29.4, 52.3, 73.9, 178.5.

• L-Tartaric acid (3): ¹H NMR (300 MHz, D₂O) δ /ppm = 4.61 (s, 2H, OC*H*); ¹³C NMR (75 MHz, D₂O) δ /ppm = 71.8, 174.4.

• (1*R*,2*R*)-1,2-Diaminocyclohexane dichloride (4): ¹H NMR (300 MHz, DMSO-*d*₆) δ /ppm = 1.15–1.21 (m, 2H, C*H*₂CH₂CHN), 1.42–1.45 (m, 2H, C*H*₂CH₂CHN), 1.67–1.70 (m, 2H, C*H*₂CHN), 2.03–2.07 (m, 2H, C*H*₂CHN), 3.17–3.21 (m, 2H, CHN), 8.61 (br s, 6H, NH₃); ¹³C NMR (75 MHz, DMSO-*d*₆) δ /ppm = 22.7, 28.8, 51.3; ¹H NMR (300 MHz, D₂O) δ /ppm = 1.33–1.40 (m, 2H, C*H*₂CH₂CHN), 1.49–1.56 (m, 2H, C*H*₂CH₂CHN), 1.81–1.84 (m, 2H, C*H*₂CHN), 2.15–2.19 (m, 2H, C*H*₂CHN), 3.38–3.43 (m, 2H, CHN), 4.79 (br s, 6H, NH₃ overlapped with solvent peak–); ¹³C NMR (75 MHz, D₂O) δ /ppm = 22.8, 29.3, 52.2.

10. DSC measurements

In contrast to most supramolecular gels, in which the gel-to-sol transition temperature clearly increases with the concentration of the gelator, the T_d in our materials was only slightly enhanced with the amount of MGS used in the experiments. Nevertheless, some insights into the dynamic of the network in function of the gelator concentration can be obtained by DSC analysis of the first endothermic transition.

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Fig. S7 A: DSC thermograms of the gels made in DOX using different volumes of MGS. The volumes are refereed to 0.5 mL of DOX; B: DSC thermograms showing the first endothermic transition of the gels made in MEE and BN as indicated in Table 1 (main text). Notes: (1) The endothermic transitions are usually below the bp of the solvents. Both empty and solvent-filled pans were used as reference samples. (2) We found usually a weight error of ca. ± 2 mg due to the fast evaporation of the solvent. Thus, any calculation of enthalpy values based on the current DSC thermograms of these non-thermoreversible materials should be considered carefully.

As indicated in the main text, the gel made in 1,4-dioxane showed the first endothermic transition at ca. 81, 84 and 88 °C using 40, 50 and 75 μ L of MGS respectively. However, the use of higher amounts of MGS, i.e. 100 μ L, destabilized the gel phase decreasing the T_d value until ca. 83 °C (Figure S7A). This was somehow related to the weaker nature of the gel network for the latter gel, which colapsed earlier than the former under identical store conditions.

11. Dropping-ball limitations and alternative Kugelrohr-based measurements

As mentioned in the main text, the use of the dropping-ball technique to determine the temperature of destruction of such delicate transient gels resulted in erratic values (no reproducible values from independent evewitnesses). Among the inconveniences, the major dificulties were found in: 1) preventing the ball from sinking when placed on the gel surface, making the judgment of the gel status too subjective, and 2) preventing abrupt evaporation of inner pools of solvent. Hence, a method that could provide information without manipulating the transient gel seemed appropriate in this scenario. Figure S8 shows an alternative method (similar to the known "inversed-tube" method in its principle) to the dropping-ball based on a Kugelrohr distillation apparatus. The vial containing the gel sample is hold inside the chamber together with a standard thermometer close to the area where the bulk gel is located. Heating is initiated after the chamber is turned upside-down (vertical position). In spite that this method provided is still dependent on human judgement to determine the exact moment in which a change takes place in the gel-material, the agreement of the obtained T_d values with those indicated by DSC was extraordinary (Figure S9). These results validated both methods to provide a reliable fingerprint for the thermal destruction of the gel network. Nevertheless, in order to obtain reliable thermodynamic data (e.g. enthalpic contributions), DSC measurements should be optimized for each material. In this sense, the use of sample holders where one can achieve much higher sample volume to container volume ratio and/or the *in situ* preparation of the gels prior measurment could be more appropriate for investigating these kind of transient gels.

Supporting Information



Fig. S8 Use of a Kugelrohr as an alternative visual method to determine the T_d of the gels. A: Photograph of the set-up before starting the measurement. The vial with the gel material and the thermometer inside the chamber are indicated with red arrows; B-C: Vertical position of the Kugelrohr chamber during heating (both the vial and thermomethers are now turned upside-down).



Fig. S9 Comparison between T_d of selected gels determined using the Kugelrohr method and DSC. The results represent the average of multiple randomized experiments.

12. Rheological measurements

Rheological characterization was only performed for two model systems (i.e. gels made in THF and DOX). However, based on the experimental evidences shown in this manuscript, a similar flow behavior can be also expected for other solvents. A significant rise in the tan δ value of the materials was evident as progressing the deterioration of the gel phase over time (Figure S10). The limited resistance of the gel network to shear stress can be quickly observed by manipulating the bulk gels with a spatula, which causes either a quick colapse of the transient gels or the rupture of the gels into small gel pieces together with the release of a considerable amount of liquid phase. In both cases, the systems undergo an evolution towards a clear liquid (3) – solid (4) phase separation.

Supporting Information



Fig. S10 A: DFS experiments of the gels made in THF at different ageing times, showing a remarkable variation of the moduli only in less than 1 h between experiments. The observed frequency dependance was traslated into an increment of ca. 2-fold in the original tan δ value (0.172) of the material; B: DFS experiments of the gels made in 1,4-dioxane at different ageing times. In this case, the consequent increment of tan δ was ca. 3-fold respect to the original value (0.192). The indicated time values are referred to the time after gel formation.

13. XRD structures

The crystal structure of (1R,2R)-1,2-diaminocyclohexane L-tartrate (1) and its diastereomer (1R,2R)-1,2diaminocyclohexane D-tartrate were previously reported (Figure S11).⁶ Salt 1 presented a highly interconnected bidirectional hydrogen-bonding network defined by a tweezer-shaped constitutional unit (consisting of 10-membered hydrogen-bonded rings) involving ammonium nitrogen donors and oxygen acceptors (in one direction with hydroxyl groups and in another with carboxylate groups). The side views showed a hollow-brick structure of the bilayered core. In contrast, the diastereomer (1R,2R)-1,2diaminocyclohexane D-tartrate showed opened gaps in the crystal lattice as a result of an imperfect matching of partners. As explained in the original publication,⁶ these gaps were found to be filled with the two water molecules hydrogen-bonded to one hydroxyl group and one carboxylate oxygen. Despite the disruption of the hydrogen-bonding interactions, the layered structure of the core, the stacking of the cyclohexane residues and the canal-like framework are still retained, albeit with a lower level of organization. The optimal molecular recognition that occurs between the matched pairs of partners in the case of 1 compared to its diastereoisomer was also observed during the formation of the transient gels as explained in the main text (e.g. the use of 1 provided stable gels in THF for about 4–5 days, whereas the use of its diastereoisomer

provided transient gels that were destroyed after 8 hours). Thus, (1R,2R)-1,2-diaminocyclohexane D-tartrate also aforded the formation of gel-like materials but with much lower temporal stability than its diastereoisomer **1**. Crystal structures of tartrate salts have been proven useful allowing to discuss reasonable supramolecular synthons of gelator and non-gelator salts.¹² Hence, we believe that both experimental evidences and literature precedents support the proposed mechanism for the formation of transient gels made from MGS.



Fig. S11 A: Top view of **1** down the *a* axis and showing a tweezer-shaped hydrogen-bonding between amino and hydroxy groups; B: two of the previous network overlapped; C: side view of **1** down the *b* axis showing the bilayered cored; D: side view of **1** down the *c* axis showing the hydrogen-bonded network; E: top view of diastereomer (1R,2R)-1,2-diaminocyclohexane D-tartrate down the *b* axis showing two molecules of water bound to tartrate hydroxy and carboxylate groups; F: side view of diastereomer (1R,2R)-1,2-diaminocyclohexane D-tartrate down the *a* axis showing the hydrogen-bonded network. Note: These figures were made from the available CIF files and with permission from the authors.⁶

Compound **4** isolated after gel destruction consisted in intergrown crystals that made it not suitable for PXRD measurement. However, the product was unequivocally characterized by NMR and elemental analysis. The structure of **4** spontaneously crystallized from the MGS was confirmed by XRD (Figure S12).



Fig. S12 A: A: Crystal isolated from a MGS prepared using a 9:1 MeOH:HCl solution. The inset image shows 2 dimensions of the isolated single crystal; B: ortep diagram of the crystal structure [(1R,2R)-1,2-diaminocyclohexane (4)].¹³

14. Gaussian fit parameters

Correlations studies between gelation ability and solvent-parameters were made based on a Gaussian distribution defined by equation (1)

$$\mathcal{F}(x) = A \times e^{\frac{-(x - SD)^2}{2c^2}}$$
(1)

where *A* and *c* are real constants (> 0), SD is the standard deviation and $e \approx 2.718281828$ (Euler's number). The fitting values upon minimisation of the sum of square errors of experimental with expected data were:

- Fitting values for the Kamlet-Taff β parameter: Mean value = 0.4; standard deviation = 0.13; A parameter = 33.1; number of calculated data points = 100
- Fitting values for the Kamlet-Taff π * parameter: Mean value = 0.6; standard deviation = 0.15; A parameter = 38; number of calculated data points = 100

15. Effects of MGS composition and additional digital pictures

a) The structure and stoichiometry of each component of the MGS presents a tremendous effect on the crystal growth rate, and therefore on the temporal stability of the transient gels (Figures S13–S15).



Fig. S13 Digital photographs of the gel made in ethyl acetate showing the formation of small crystals over time and subsequent destruction of the bulk gel.

Supporting Information



Fig. S14 Photographs of different materials discussed in this manuscript. A: gel made in DOX with the optimal MGS as described in Table 1 (main text) after 3 days; B: gel made in DOX using a MGS prepared without the tartaric acid counterpart after 20 h; C = THF-gel obtained as A but in the presence of 1 extra equivalent of water; D: DOX-gel prepared with 80 μ L of anhydrous MGS (prepared from commercial 1.25 M MeOH/HCl solution) after 1 h; F: THF-gel prepared using a MGS based on the tartrate salt with 80% ee; E = Aspect of the mixture made of THF and the MGS based on the racemic tartrate salt; G: Partial gel obtained in THF using MGS based on L-malic (**ac-5**); H: material obtained in THF upon addition of the MGS based on succinic acid (**ac-2**); I: Gel-like material obtained in THF using MGS based on L-diethyl tartrate (**ac-1**) (a first crack can be clearly observed in one lateral of the gel, which is quickly propagated through the gel causing its collapse); J: THF-gel prepared using 150 μ L of anhydrous MGS is after 30 min; L: A different batch of experiment D under the same conditions. Note that the arrows in this figure do not mean interconversions.

In this sense, the amount of water added with the use of aqueous HCl resulted also crucial. However, gels in the absence of water or in the presence of 1 extra equivalent of water could be also formed, albeit they were destroyed faster than those prepared with the optimized MGS system. For example, the addition of 1 extra equivalent of water usually induces crystallization within 30–60 minutes.

b) Moreover, we also studied the effect of the salt structure by replacing in the original MGS either the Ltartaric acid by different dicarboxylic acids derivatives (Table S3, ac1-ac6) or the (1*R*,2*R*)-1,2diaminocyclohexane by alternative diamines (Table S3, am1-am10). Non-stable gels could be obtained with the potential gelator solutions prepared with diamines am1-am3. In the other hand, the multicomponent mixtures in MeOH using diamines am4-am9 (ca. 0.13 M) were always turbid even in the presence of higher amounts of HCl (> 2.4 equiv). Therefore, no further optimization studies were made with these diamines. However, the gelator system showed a higher tolerance towards the structure of the diacid counterpart. Thus, transient gels could be obtained using MGS based on diethyl L-tartrate (ac1), succinic acid (ac2), adipic acid (ac3), dibenzoyl L-tartrate (ac4) and L-(-)-malic acid (ac5). The use of pthalic acid (ac-6) afforded only a partial loose gel-like material.

| | HO HO HO | HO HO OH | | HO HO HO | | | H₂N ↔ NH₂ |
|---|---------------------|-----------------------------------|-----------------------|----------------------|---------|----------------------------------|------------------------------------|
| ac1 | ac2 | ac3 | ac4 | ac5 | ac6 | am1 | am2 |
| | | | | | | | |
| G; stable: 2-3 h ^{b} | G; stable: 3–4 h | G; stable: 2–3 h | G; stable: 10–15 h | G; stable: 8–12 h | PG | Р | P ^c |
| no gel: 650 μL | no gel: 10 μL | no gel: 150 μL | no gel: 80 μL | no gel: 150 μL | - | - | - |
| | NHTs '''NHTs | Ph Ph NH ₂ Ph | $\binom{NH_2}{NH_2}$ | | | H ₂ N NH ₂ | NH ₂ NH ₂ |
| am3 | am4 | am5 | am6 | am7 | am8 | am9 | am10 |
| \mathbf{P}^{c} | I (MLS) | I (MLS) | I (MLS) | I (MLS) | I (MLS) | I (MLS) | Р |

Table S3 Effect of salt structure on the gelation ability.^a

^{*a*} For comparative purposes, 1 mL of THF was used in each experiment under standard conditions: $mgv = 150 \mu L$; $T_{mix} = -78$ °C. Abbreviations: G = gel with different degrees of translucence; PG = partial loose gel; P = precipitates (either compact or spongy material); I (MLS) = insoluble in the stock solution MeOH/HCl, yielding a milky-like suspension that was not used for gelation tests. Temporal stability and amount of non-gelled liquid are presented in each case where gel formation was successful. Temporal stability values refer to the systems after removing the nongelled liquid. In general, no further studies were performed if the viscosity of the solvent was not altered (> 0.3 cP) upon addition of the potential gelator system. ^{*b*} Formation of the first crystals was observed after 1h inside the gels made with **ac1–ac3**, and after 20 h in those made with **ac4–ac5**. ^{*c*} In these cases, the precipitate (ca. 20–40% of the original volume) was formed by a mixture of gel-like material and amorphous crystals.

Despite the gel formation using ac1-ac5, the temporal stability of these gels was at best half of that made with the MGS based on (1R,2R)-1,2-diaminocyclohexane and L-tartaric acid under the same conditions. Although the same general trend could be observed when the corresponding salt (i.e. (1R,2R)-1,2diaminocyclohexane•ac4) was synthesized prior the preparation of the MGS, the improvement on the temporal stability was rather limited). In general, the amount of non-gelled liquid was also much higher with the acids ac1-ac5 than with L-tartaric acid. These results indicate that the latter is at least a better partner to stabilize the supramolecular transient network. Among the different acids, the gels with higher stability (ca. 1 day) were obtained with ac4 and ac5, which pointed out the importance of both carboxylic acids groups (somewhat higher than the hydroxyl groups) and a chiral moiety for the formation of relatively self-standing gel networks. In addition, it is worth to mention that these transient gels based on compounds ac1-ac5 could be also formed in different solvents. As shown in Figure S15, their first endothermic transition located at ca. 81-86 °C was also characterized by DSC.



Fig. S15 DSC thermograms of gels based on alternative diacids derivatives in 1,4-dioxane (gv = 75 μ L; T_{mix} = 13 °C).

In addition, a series of experiments demonstrated that each component presented in the optimal MGS was necessary for the formation of relatively stable gels. Thus, the use of a solution prepared in the absence of L -tartaric acid (i.e. (1R,2R)-1,2-diaminocyclohexane + MeOH (ca. 0.13 M in diamine) + HCl 37 wt.% in aqueous solution) resulted in the formation of either very weak partial gel-like materials or precipitates in less than 1 h (Figure S16). In the other hand, the replacement of MeOH by other alcohols like EtOH, *i*-PrOH or *n*-BuOH did not allow to dissolve the tartrate salt not even in the presence of 2.4 equiv of HCl.



Fig. S16 Digital photographs of the materials obtained in different solvents using the MGS gelator (symbol +) or the equivalent system prepared in the absence of L-tartaric acid (symbol –).

Despite the gel formation achieved using **ac1–ac5**, the temporal stability of these gels was in general much lower than that using L-tartaric acid in the gelator composition. The same trend is expected if the corresponding ammonium salts are synthesized prior the preparation of the MGS. The salts can be prepared following the same procedure used for the synthesis of **1** but using the appropriate tartaric acid-derivative. For instance, (1R,2R)-1,2-diaminocyclohexane 1,2-dibenzoyl-L-tartrate was easly obtained from (1R,2R)-1,2-diaminocyclohexane and 1,2-dibenzoyl-L-tartaric acid. Elemental analysis for C₂₄H₂₈N₂O₈ (%): calcd: C: 61.01, H: 5.97, N: 5.93; found: C: 61.28, H: 5.89, N: 5.73.

c) In general, the opacity of the gels was found to be a function of the solvent, amount of the gelator solution, temperature and stirring efficiency. Some degree of turbidity could be also observed at early stages of the gelation process (e.g. THF, 1,4-dioxane), although it may progress towards a transparent gel after some time indicating the growth of aggregates up to the wavelength range of visible light (Figure S17-D).

d) Attempts to increase the half-life of the gels by adding polymers¹⁴ to either the MGS or the solvent have been so far unsuccessful. However, other strategies are currently under investigation.



Fig. S17 A: Photograph of the methanolic solution of 1,2-diaminobenzene (**am-10**) (ca. 0.13 M) in the presence of 2.4 equivalents of HCl (37 wt.% in aqueous solution); B: Typical precipitate obtained 30 min after adding the previous solution (100, 200 or 300 μ L) to 1 mL of THF at -78 °C; C: Photograph of the a gel prepared in ETAC using a 0.38 M MGS and 2.4 equivalents of HCl added from a 9:1 MeOH:HCl stock solution. The gel collapsed within hours giving a mixture of small remaining gel pieces (G), solution (S) and crystals (C); D: Test tube during the preparation of the DOX-gel. The photograph was taken a 5 minutes after removing the cooling bath. The observed turbidity corresponds indeed to the evolution of the gel phenomenon, which ends up in a transparent gel after ca. 30 minutes.



Fig. S18 Fotograph of the test tube after destruction (using a spatula and hand-shaking) of the gel made in DOX (inset). The white precipitate (compound 4) is completely deposited at the bottom of the test tube after few hours. The liquid was decanted and the solid, filtered, washed with MeOH and dried under vacuum for further analysis.

e) Effect of the enantiomeric purity of 1,2-diaminocyclohexane tartrate salt on the gel formation (Figure S19).



Fig. S19 Digital photographs of the materials obtained in THF using MGS (150 μ L; $T_{mix} = -78$ °C) of different ee ranging from 0 to 100%.

16. Electron microscopy: Selection of additional pictures



Fig. S20 SEM images of xerogels prepared from the gels made in different solvents: A: gel made in DME, scale bar = $10 \mu m$; B: different region of the gel made in DME, scale bar = $10 \mu m$; C: gel made in THF, scale bar = $1 \mu m$; D: gel made in BN scale bar = $20 \mu m$; E: gel made in BN, scale bar = $10 \mu m$; F: gel made in ACN, scale bar = $1 \mu m$; G: gel made in MIPK, scale bar = $20 \mu m$; H: gel made in MIPK, scale bar = $1 \mu m$; I: different region of the gel made in MIPK, scale bar = $10 \mu m$; H: gel made in MIPK, scale bar = $10 \mu m$; H: gel made in MIPK, scale bar = $10 \mu m$; E: different region of the gel made in MIPK, scale bar = $10 \mu m$; H: gel made in MIPK, scale bar = $10 \mu m$; E: different region of the gel made in MIPK, scale bar = $10 \mu m$; E: different region of the gel made in MIPK, scale bar = $10 \mu m$; E: different region of the gel made in MIPK, scale bar = $10 \mu m$.

17. AFM imaging



Fig. S21 2D-AFM image and height histograms of the xerogel prepared from the gel in BN (*top*); B: 2D-AFM image and height histogram of the xerogel prepared from the gel in ETAC (*bottom*).

18. References

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