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

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Abstract: A new synergistic multicomponent organogelator liquid system (MOGLS) was discovered during the standard protocol of tartaric acid-mediated racemic resolution of (\pm)-*trans*-1,2-diaminocyclohexane. The MOGLS is formed by a 0.126 M methanolic solution of (1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartrate and 1 equiv of concentrated hydrochloric acid. Nonreversible gelation of oxygenated and nitrogenated solvents occurs efficiently at low temperature. Several features make this system unique: (1) it is a multicomponent solution where each of the five components is required for the organogelation property; (2) the multicomponent organogelator liquid system (MOGLS) is formed by simple, small, and commercially available chiral building blocks dissolved in a well-defined solvent system (MeOH/HCl/H₂O); (3) the chiral building blocks are easily amenable for further modifications in structure–property relationship studies; (4) the gelation phenomenon takes place efficiently at low temperature upon warming up the isotropic solution, conversely to the typical gel preparation protocol (gel formation upon cooling down the isotropic solution); (5) the formed organic gels are not thermoreversible in spite of the noncovalent interactions that hold the 3D-fibrillar network together.

Introduction

In a fascinating journey from serendipity to rational design, materials made by means of gelation of organic solvents have received increasing attention over the last 10–15 years,¹ because of their unique supramolecular architectures and potential applications² as functional soft materials in the fabrication of sensors,³ liquid crystallines,⁴ electrophoretic and electrically conductive matrices,⁵ templates for cell growth or the growth of sol–gel structures,⁶ and in many other industrial fields such as cosmetics, oils, and foods.¹ These systems, so-called orga-

nogels, are thermoreversible, viscoelastic materials consisting of an organic liquid and a low molecular-mass compound (usually <5 wt%) self-assembled into gel fibers, often of micrometer scale lengths and nanometer scale diameters.^{7a} Thus, the gel architecture strongly reflects the molecular shape of unit components. The aggregation of such low molecular-mass organic gelators (LMOGs) typically occurs spontaneously upon cooling down their isotropic solutions, being driven by multiple, weak interactions such as dipole–dipole, van der Waals (long alkyl, aromatic groups, etc.), and hydrogen-bonding interactions (amide, urea, hydroxyl, etc.).¹ It is widely accepted that the entanglement of such microheterogeneous fibrillar phases gives complex nanoscale three-dimensional (3D) networks through new “junction zones”, which immobilizes a large volume of organic liquid into the network compartments primarily by surface tension and capillary forces.⁸ Despite the extensive and remarkable achievements of supramolecular chemistry in many

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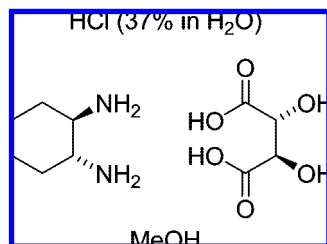


Figure 1. New multicomponent organogelator liquid system (MOGLS), in which the presence and stoichiometry of each component is critical for the gelation of organic fluids. Molar ratio of diaminocyclohexane:tartaric acid:MeOH:HCl:H₂O = 1:1:195:1:3.25.

controlled self-assembly processes,⁹ most of LMOGs have been found by serendipity rather than rational design. Thus, the control of gelation phenomena and the design of new LMOGs are still challenging tasks,¹⁰ in particular when multiple dynamic noncovalent interactions are taken into account.

One of the main attributes of the gelling phenomenon is the one-dimensional kinetic growth of the superstructure that leads to the formation of a fiber.¹⁸ In this regard, the discovery of new organogelators based on organic ammonium salts has become a scientific topic of great interest. This is primarily due to their flexible and versatile hydrogen bond pattern, which allows control of the dimensionality of the network.¹¹ On the other hand, organic ammonium salts have been recognized as structurally simple supramolecular synthons,¹² which could permit the fine-tuning of the noncovalent molecular aggregation mode by the incorporation of selected functional groups. In comparison with the conventional one-component gelators, the two-component ammonium-based systems provide additional interest because multicomponent systems allow a further complexity of the hierarchical self-assembling process to form higher aggregates, which are responsible for the microphase separation in the gel state.^{7b,13}

In this communication, we report on the serendipitous discovery of a new synergistic multicomponent organogelator liquid system, which shows intriguing organogelation properties. The MOGLS is formed by a methanolic solution of (1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartrate and hydrochloric acid (Figure 1).

Several features make this system unique in comparison with other organogelators, specially those based on ammonium carboxylates:¹¹ (1) it is a multicomponent solution where each of the five components is required for the organogelation property; (2) the multicomponent organogelator liquid system (MOGLS) is formed by simple, small, and commercially available chiral building blocks dissolved in a well-defined solvent system (MeOH/HCl/H₂O); (3) the chiral building blocks are easily amenable for further modifications in structure–property relationship studies; (4) the gelation phenomenon takes place efficiently at low temperature upon warming up the isotropic

solution, conversely to the typical gel preparation protocol (gel formation upon cooling down the isotropic solution); (5) the formed organic gels are not thermoreversible in spite of the noncovalent interactions that hold the 3D-fibrillar network together.

Results and Discussion

Discovery of the Multicomponent Organogelator Liquid System (MOGLS). The serendipitous discovery of this MOGLS took place when we were using the standard protocol of tartaric acid-mediated racemic resolution of (±)-*trans*-1,2-diaminocyclohexane¹⁴ for other purposes. During the cleaning of the glassware used during the experimental work, we were fascinated to observe the instantaneous formation of a transparent jellylike 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 (1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartrate, MeOH, and aqueous HCl.

The stunning discovery was followed by a rational design of experiments in order to disclose the nature of the jellylike material and the required components for its formation, as well as their possible synergistic effect. Such comprehensive study (see below) led to a 0.126 M methanolic solution of (1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartrate and 1 equiv of concentrated hydrochloric acid (37% HCl) as the optimum multicomponent organogelator solution, which corresponds to a molar ratio of diaminocyclohexane:tartaric acid:MeOH:HCl:H₂O = 1:1:195:1:3.25. As it will be discussed later, the presence of each component, including the water,¹⁵ was found to be crucial for the gelation event.

We were delighted to observe that the addition of tiny amounts of this solution to a variety of organic solvents instantaneously induced their gelation at room temperature. Nevertheless, a closer inspection of the formed jellylike materials revealed a nonhomogeneous gel phase, which often leaked a small amount of solvent after turning the test tube upside-down. In order to prepare clear homogeneous and stable gels, we found that the organic solvents must be cooled down close to their freezing point prior to addition of an appropriate volume of the MOGLS. Then, the homogeneous mixture was allowed to warm up to promote formation of the gels. Interestingly, both the solvent–MOGLS mixture and the MOGLS solution remain as clear solutions at temperatures as low as −100 °C for any period of time. As far as we are aware, this is the first example where the gelation phenomenon efficiently takes place upon warming up instead of cooling down the isotropic solution of the gelator.¹⁶ The only example that might be considered rather similar is the uncommon gelation of organic fluids at room temperature without the heating/cooling cycle.^{11b} It is worth noting that the formation of higher aggregates upon raising the temperature is also observed in nature. Living organisms have developed an impressive molecular machinery to achieve motion and other biological functions by free energy transductions of any chemical event (protein folding/unfolding or self-assembling

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Table 1. Organogelation Ability of the Optimal MOGLS^a

entry	solvent ^b	mgv ^c (mL)	mgc ^d (%)	T _{mix} (°C)	T _i ^e (°C)	T _d ^f (°C)	T _d ^g (°C)
1	acetone	0.10	0.40	-78	-35	74	74
2	ethyl acetate	0.15	0.50	-78	-38	98	83
3	tetrahydrofuran	0.10	0.50	-78	-44	71	70
4	1,2-dimethoxyethane	0.14	0.60	-78	-40	69	69
5	2-methoxyethyl ether	0.10	0.40	-60	-40	75	76
6	diethyl ether	0.18	0.90	-100	-30	40	45
7	cyclohexanone	0.08	0.30	-20	-6	66	64
8	3-methyl-2-butanone	0.07	0.30	-80	-45	42	52
9	acetonitrile	0.06	0.03	-40	-26	76	78
10	benzonitrile	0.25	0.90	-10	-1	50	49
11	1,4-dioxane	0.08	0.30	15	15	-- ^h	-- ^h
12	dichloromethane	M	--	--	--	--	--
13	chloroform	M	--	--	--	--	--
14	1,2-dichloroethane	M	--	--	--	--	--
15	carbon tetrachloride	I	--	--	--	--	--
16	chlorobenzene	I	--	--	--	--	--
17	1,2-dichlorobenzene	I	--	--	--	--	--
18	dimethylformamide	M	--	--	--	--	--
19	dimethylsulfoxide	M	--	--	--	--	--
20	ethanol	M	--	--	--	--	--
21	<i>n</i> -hexane	P	--	--	--	--	--
22	pyridine	M	--	--	--	--	--
23	isooctane	M	--	--	--	--	--
24	benzene	I	--	--	--	--	--
25	toluene	I	--	--	--	--	--
26	methyl <i>tert</i> -butyl ether	P	--	--	--	--	--

^a Abbreviations: M = miscible, I = immiscible, P = precipitated. ^b 1 mL of solvent was used to prepare the gels using (1*R*,2*R*)-1,2-diaminocyclohexane L-tartrate complex 0.126 M in MeOH and 1 equiv of 37% HCl (solution A_L). Transparent or slightly turbid gels were formed in each case, except for diethyl ether and ethyl acetate for which opaque and translucent gels were attained, respectively. ^c Minimum gelation volume. ^d Minimum gelation concentration referred to HCl-diamine-tartaric salt complex. ^e Gel formation temperature determined by setting a digital thermocouple ($\emptyset = 2$ mm) into the solution. ^f Gel destruction temperature determined by the "dropping ball method" (ramping rate > 2 °C, average of three independent measurements). ^g Maximum endo transition observed by DSC. ^h Partial gel formation. The estimated error for the T_d obtained by the "dropping ball method" and DSC was ± 1 °C and ± 3 °C, respectively.

processes). This chemical phenomenon is referred to as *inverse temperature transition* and has been studied in detail by Urry and co-workers.¹⁶ At this stage, we believe that the origin for this transition might be the same for our system.

In 1998, Huc and co-workers^{15b} reported a series of LMOGs based on gemini surfactants consisting of dimers of nonchiral cetyltrimethylammonium (CTA) ions with chiral L- or D-tartrate as counterions, which self-organize, locating the polar groups at the core of the aggregate and the nonpolar long hydrocarbon chains in contact with the solvent. In contrast to the MOGLS reported herein, (CTA)₂-tartrate were reported to gel in mostly chlorinated solvents and water at concentrations of about 10–30 mM upon the heating/cooling process. These gels are disrupted easily by the addition of small amounts of alcohols, and only the pure enantiomers yield gels.

Gelation Studies and Gel Characterization. The gelation ability of the MOGLS was assayed for 25 organic solvents, and the gelation was visually monitored using the tube inversion technique. Interestingly, the MOGLS was found to be selective for the gelation of oxygenated and nitrogenated organic solvents (Table 1). The gels were stables for months when stored at 12 °C. For halogenated, hydrocarbon, or aromatic solvents, complete miscibility or precipitate formation was observed upon addition of the MOGLS. The minimum gelation volume (mgv) was established in the range 60–250 μ L, which corresponds to a minimum gelation concentration (mgc) range of 0.03–0.9 wt% of gelator based on the tartaric–diamine–HCl complex. For instance, this means that the MOGLS can entrap approximately 20 000 molecules of acetonitrile per gelator (tartaric-diamine-HCl complex) particle. These values position this MOGLS in

the family of the most efficient organogelator systems so far reported, acting as supergelator¹⁷ for several organic solvents.

Preliminary oscillatory rheological measurements¹⁹ were reproducible from batch to batch and confirmed the gel state (storage modulus $G' >$ loss modulus G'') of the samples within the linear viscoelastic regime. The material rigidity as indicated by G' followed no uniform trend with respect to T_d. In general, dynamic frequency sweep (DFS) experiments covering a pulsation (ω) range from 0.1 to 60 rad/s highlighted the viscoelastic nature of the gels. On the other hand, dynamic strain sweep (DSS) experiments in the range 0.01–100% strain showed that these gels fracture at ca. 5–10% strain, confirming their brittle nature. Taking into account the DFS and DSS results, further dynamic time sweep (DTS) experiments at strain and frequency constant (1% and 6 rad/s, respectively) showed that the storage moduli was always 1 order of magnitude greater than the respective loss moduli, indicating that the gels were quite rigid. As could be expected for these types of materials, an increase in the organogelator system concentration usually causes a decrease in the $\tan \delta$ (G''/G') value, which is a measure of the internal resistance of the material, suggesting an increase in the mechanical damping properties.

Thermal Studies. Thermal characterization of gels was first carried out by the "dropping ball method"¹⁸ to determine the temperature at which the gels are destroyed, T_d (Table 1). As

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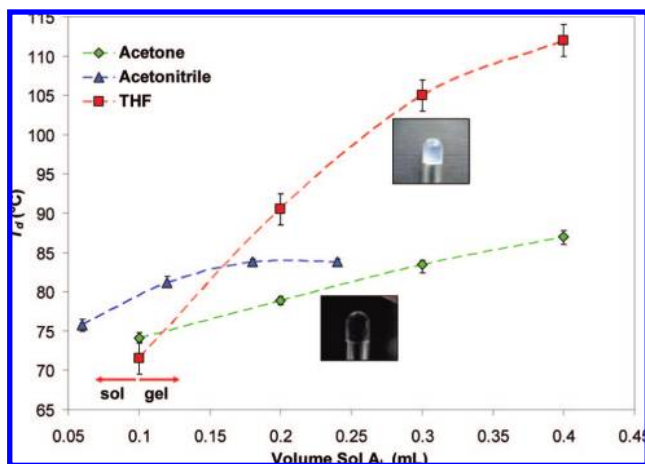


Figure 2. Phase diagram for THF-gel (red line), CH₃CN-gel (blue line), and acetone-gel (green line) from the critical mgv to $4 \times$ mgv. Inset: representative digital photographs of inverted test tubes containing THF and acetone-gels. Inset: digital photographs of the organogels. Collapse of the gels started to become evident at concentrations higher than the maximum values outlined in the graphic (e.g., only 60% of the total volume remained gelled at $6 \times$ mgv).

Table 2. Thermodynamic Parameters of the Gels

entry	solvent	weight of gel (mg)	T_d^a (°C)	T_d^b (°C)	ΔH^c (J/g)
1	ethyl acetate	7.1	98	82.2–83.1	0.61
2	tetrahydrofuran	6.5	71	69.4–70.2	0.73
3	acetonitrile	9.0	76	77.4–78.3	0.82
4	benzonitrile	5.4	50	47.9–48.9	0.54
5	cyclohexanone	12.9	66	62.5–64.4	1.93
6	acetone	10.0	74	73.4–73.6	2.26
7	2-methoxyethyl ether	22.8	75	75.4–75.7	2.20
8	1,2-dimethoxyethane	18.0	69	67.5–69.1	1.47
9	3-methyl-2-butanone	10.0	42	51.6–52.5	0.082
10	diethyl ether	19.0	40	43.1–45.0	5.93

^a Gel destruction temperature determined by the “dropping ball method” (ramping rate < 2 °C). ^b The first value corresponds to the onset of the endothermic peak observed by DSC and the second value to the maximum. ^c Enthalpic change. The estimated error for the T_d obtained by the “dropping ball method” and DSC were ± 1 °C and ± 3 °C, respectively.

might be expected, T_d was found to rise as the concentration of the organogelator system increases (Figure 2).

The gel formation temperature was ascertained between -45 and -1 °C. A particular situation was observed for 1,4-dioxane, since at its freezing point (12 °C) the gelation process is still too fast to enable the complete gelation of the solvent. Despite the noncovalent nature of the supramolecular aggregate, the metastable gel state in these materials was found to be nonreversible. 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. Differential scanning calorimetry (DSC) analyses showed an acceptable correlation, within the experimental error, between the observed maximum endothermic peak with the T_d determined by the “dropping ball method” (Table 1). Thermodynamic data obtained through DSC measurements showed endothermic transitions characterized as relatively narrow peaks ($\Delta T \sim 1$ – 8 °C) with modest enthalpic changes ($\Delta H \sim 0.5$ – 5.9 J/g) (Table 2).¹⁹

FT-IR Studies. FT-IR was used in order to ascertain how the complex aggregated into a supramolecular structure. The difference of the spectra between the gel state and the solid

salt (1*R*,2*R*)-(+)–1,2-diaminocyclohexane L-tartrate was evident from these studies. Thus, a broadband appears at 3250 – 2350 cm^{-1} assignable to the ammonium stretching vibration, and three intense bands at 1560 , 1530 , and 1378 cm^{-1} assignable to the carboxylate carbonyl overlapped with the ammonium deformation bands. A very intense band at *ca.* 1710 – 1749 cm^{-1} assignable to the carbonyl stretching vibration of the carboxylic group was identified for the liquid MOGLS, gel, and xerogel states. Strong hydrogen bond association bands at *ca.* 3600 – 3200 cm^{-1} , overlapping the alkane stretching bands, were consistently found for all gels and xerogels. The intensity of this broadband is dramatically reduced for the xerogel state as it might be expected once the aggregate gelator–solvent²⁰ interactions disappear. The liquid MOGLS showed also a characteristic intense band at *ca.* 3516 cm^{-1} assignable to nonassociated hydroxycarbonyl groups. According to the FT-IR data, the molecular species responsible for the separation-phase phenomenon presents the same ionization state for both the gel and xerogel state but clearly different from that of tartrate ammonium salt.

Microscopy Studies. In order to gain better insight into the molecular organization the gel specimens were analyzed by transmission (TEM) and scanning (SEM) electron microscopy. Images obtained from both TEM and SEM observations were complementary. The xerogels consist of 3D highly entangled fiberlike aggregates through numerous junction zones²¹ (Figures 3a–d). Most of the straight fibers presented relatively uniform diameters of 180 ± 30 nm and lengths on the micron scale. The high aspect ratios of the gel fibers plainly point out that the intergelator interactions are highly anisotropic. However, no remarkable changes in general appearance were observed on the fibers morphology for specimens prepared at different concentrations (Figures 3e–j).

Initial atomic force microscopy (AFM) images showed a densely entangled network in good agreement with TEM and SEM images (Figure 4a). Dimensions of 1.8 μm width and 700 nm height was often found for largest fibers with the fiber unit of about 2.5 nm height \times 25 nm width (Figure 4b). The entanglement of four unit fibers forms bundles (Figure 4c) with dimensions of *ca.* 10 nm height \times 100 nm width.

Synergism of the Components in the Organogelling System. The importance of each component in the MOGLS was studied by means of a systematic set of experiments where each of the putative components responsible for the gelation phenomenon was individually, or in combination, assayed for gelling properties. Thus, different solutions were prepared and their gelling abilities determined for acetone, 1,2-DME, and THF, using the tube inversion method (Table 3). However, all experiments were unsuccessful in producing stable organogels, except when an exact amount of each component was utilized: 0.126 M of (1*R*,2*R*)-(+)–1,2-diaminocyclohexane L-tartrate in MeOH, and 1 equiv of 37% HCl (entry 9). Hence, it is concluded that there is an exquisite stoichiometric balance between all components in the mixture, the amount of water¹⁵ (exactly the amount

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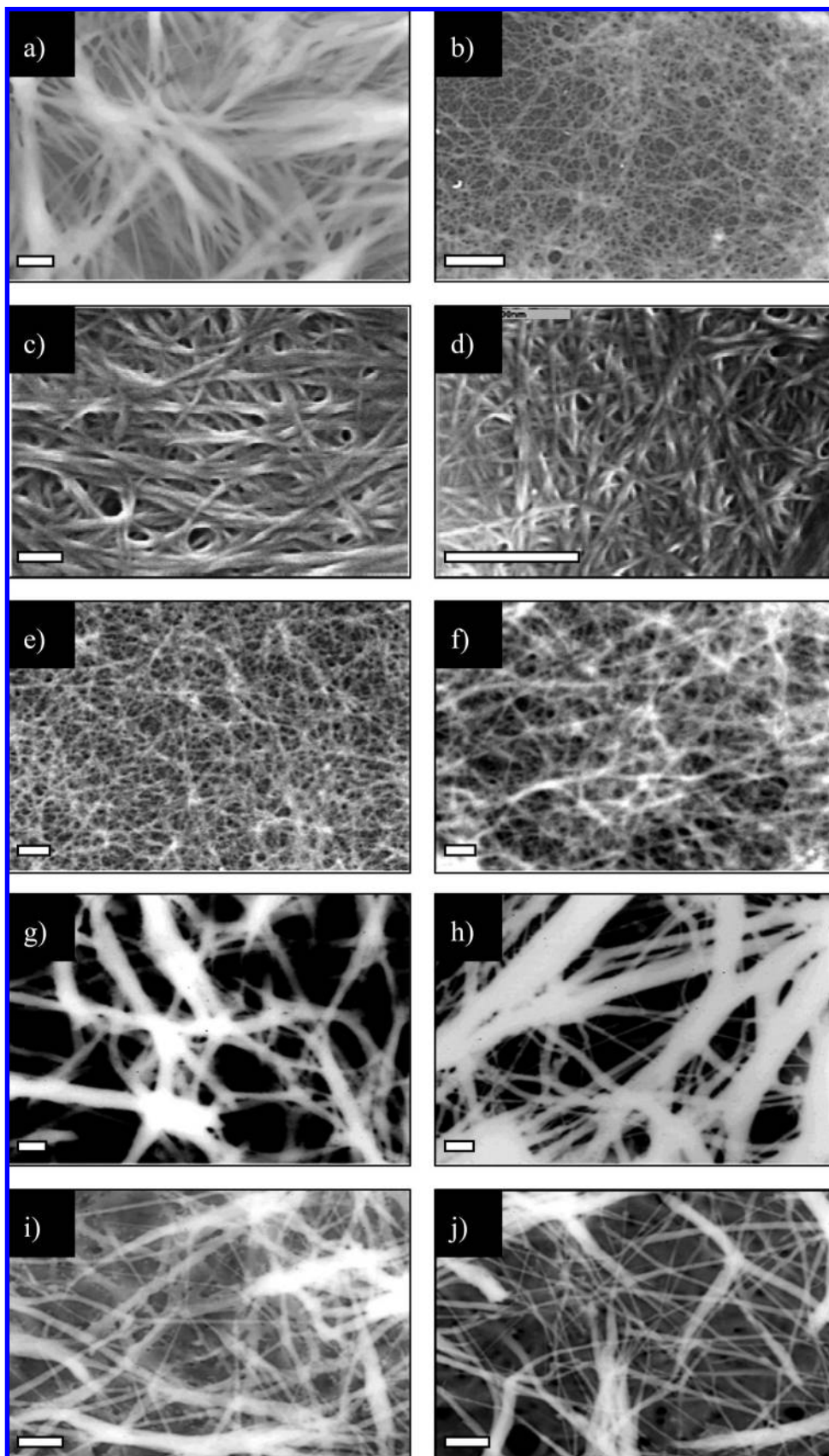


Figure 3. Electron micrograph images of self-assembled fibrils: (a) TEM for CH₃CN-gel, scale bar = 500 nm; (b) TEM for THF-gel, scale bar = 500 nm; (c) SEM for CH₃CN-gel, scale bar = 500 nm; (d) SEM for THF-gel, scale bar = 2 μ m; (e) TEM of the gel made of solution A_L in 1,2-DME, scale bar = 500 nm; (f) TEM of the gel made of solution A_L in acetone-gel, scale bar = 200 nm; (g) TEM of the gel made of solution A_L in CH₃CN-gel prepared at 2 \times mgv, scale bar = 500 nm; (h) TEM of the gel made of solution A_L in CH₃CN-gel prepared at 3 \times mgv, scale bar = 500 nm; (i) TEM of the gel made of solution A_L in THF-gel prepared at 2 \times mgv, scale bar = 500 nm; (j) TEM of the gel made of solution A_L in THF-gel prepared at 3 \times mgv, scale bar = 500 nm.

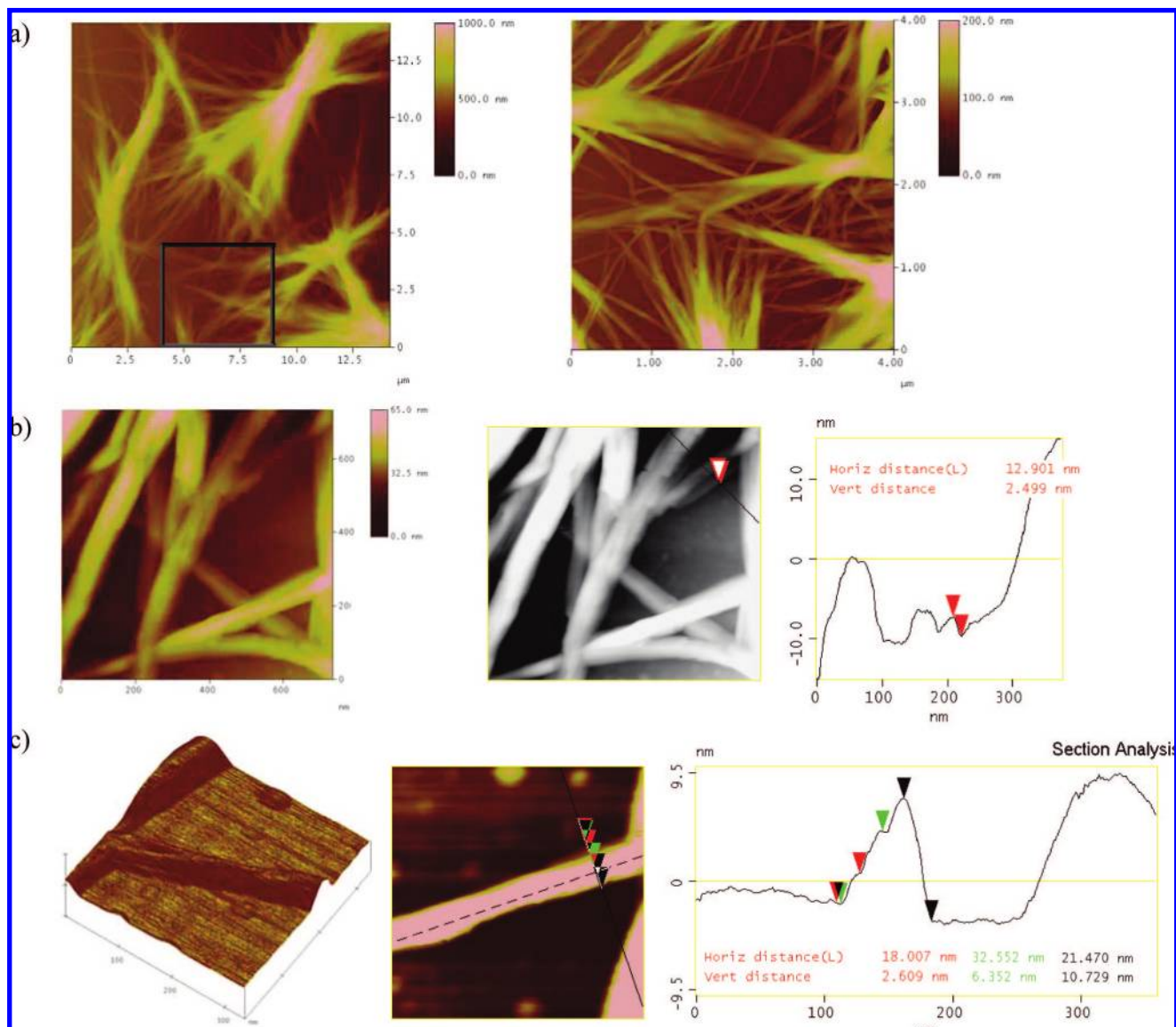


Figure 4. (a) AFM image of self-assembled fibrils in CH₃CN-gel (left) and zoom-in of the black squared area (right); (b) cross-section of the basic fiber unit; (c) four fibers bundle (left) and its cross-section (right).

contained in the hydrochloric solution) being crucial for the stability of gels. Indeed, when the MOGLS was prepared using anhydrous methanolic HCl (entry 10), very weak gels were formed.

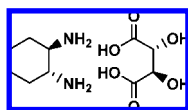
The role of the alcoholic component of the gelator system was also studied. MOGLSs prepared in branched alcohols such as *i*-propanol, *i*-butanol, or isoamyl alcohol did not show any gelation ability. Nevertheless, solutions prepared in ethanol or *n*-butanol were also able to yield gels at the same concentration than those in methanol, albeit much weaker (Table 4). Interestingly, and independent of the gelled solvent, a dramatic drop of the T_d between 12 and 42 °C was observed when either ethanol or *n*-butanol were used as solvent for the organogelator system in comparison with methanol.

Chirality doubtless plays a central role in the functional property of organogels.²² Since our system is formed by chiral

building blocks, we addressed this subject through the study of the thermal stability of the gels formed by using salts with an ee varying in the range 0–100%. Gels of higher thermostability were obtained when the enantiomerically pure MOGLS based on (1*R*,2*R*)-1,2-diaminocyclohexane L-tartrate was used (Table 5, entry 1). Less stable gels were obtained when MOGLSs of lower ee were used (Table 5, entries 2 and 3), and no gel was observed for the racemic MOGLS. Moreover, MOGLS based on (1*R*,2*R*)-1,2-diaminocyclohexane D-tartrate yielded thermally less stable gels than its diastereomeric counterpart when prepared under identical experimental conditions (Table 5, entry 4). All gels were transparent except entries 2–3 for which opaque gels were attained. As expected, enantiomeric MOGLS showed identical gelation properties.

Concerning the role of the mineral acidic component, the use of 48% HBr instead of 37% HCl remarkably decreased the gelation ability of the MOGLS affording much weaker gels (Table 5, entry 5 and 6, respectively). For any other inorganic acid such as 65% HNO₃ or 78% HClO₄, no gel formation was observed.

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Table 3. Gelation Properties of Aqueous MOGLS^a

entry	(mg, mmol)	MeOH (mL)	H ₂ O ^b (mL, equiv)	HCl 37% (equiv)	solution (M) ^c	phase ^c
1	50,0.19	1.5	—	—	I	N
2	50,0.19	1.5	0.2, 58.5	—	I	N
3	50,0.19	1.5	0.2, 58.5	0.64	0.111	N
4	50,0.19	1.5	0.2, 58.5	0.88	0.111	WG
5	50,0.19	4.5	—	—	I	N
6	50,0.19	4.5	—	1.3	0.042	WG
7	50,0.19	1.5	0.011, 3.26	—	I	N
8	50,0.19	1.5	0.011, 3.26	0.9	0.126	WG
9	50,0.19	1.5	—	1.0	0.126	G
10	163,0.63	4.5	0.5 mL HCl/MeOH 1.25 M, 1.0 equiv HCl	—	0.126	WG

^a The gelation properties were found to be the same for acetone, 1,2-DME, and THF. ^b Additional H₂O added to the system. ^c Abbreviations: I = insoluble; N = no gel formation; G = stable gel; WG = weak gel, easily disrupted upon shaking.

Table 4. Influence of the Alcoholic Component of the MOGLS on the Thermal Stability of Organogels in THF, EtOAc, and 1,2-DME

solvent ^b	Sol A _L ^a MeOH, T _d ^c (°C)	Sol A _L ^a EtOH, T _d ^c (°C)	Sol A _L ^a <i>n</i> -BuOH, T _d ^c (°C)
THF	71	42	59
EtOAc	98	56	63
1,2-DME	69	38	44

^a Sol A_L = (1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartrate, 0.126 M in MeOH, EtOH or *n*-BuOH, 1 equiv of 37% HCl. ^b Minimum gelation volumes for THF, EtOAc, and 1,2-DME were 0.10, 0.15, and 0.14 mL, respectively. ^c Gel destruction temperature (±1 °C) determined by the “dropping ball method” (ramping rate <2 °C).

Table 5. Thermostability of THF-Gels Prepared with Different MOGLSs

entry	MOGLS ^a	mgv ^b (mL)	T _d ^c (°C)
1	Sol A _L	0.10	71
2	Sol A _{9:1}	0.12	62
3	Sol A _{8:2}	0.12	44
4	Sol A _D	0.10	68
5	Sol B _L	0.10	54
6	Sol C _L	0.10	66
7	Sol D _L	0.18	57
8	Sol E _L	0.13	62

^a Sol A_L: (1*R*,2*R*)-1,2-diaminocyclohexane L-tartrate 0.126 M in MeOH, 1 equiv of 37% HCl; Sol A_{*x*:*y*}: [(1*R*,2*R*)-1,2-cyclohexyldiamine L-tartrate: (1*S*,2*S*)-1,2-cyclohexyldiamine D-tartrate, at a molar ratio *x*:*y*, respectively] 0.126 M in MeOH, 1 equiv of 37% HCl; Sol A_D: (1*R*,2*R*)-1,2-diaminocyclohexane D-tartrate 0.126 M in MeOH, 1 equiv of 37% HCl; Sol B_L: (1*R*,2*R*)-1,2-diaminocyclohexane L-tartrate 0.126 M in MeOH, 1 equiv of dry HCl; Sol C_L: (1*R*,2*R*)-1,2-diaminocyclohexane L-tartrate 0.126 M in MeOH, 1.77 equiv 48% HBr; Sol D_L: (1*R*,2*R*)-1,2-diaminocyclohexane dibenzoyl-L-tartrate 0.126 M in MeOH, 1 equiv of 37% HCl; Sol E_L: (1*R*,2*R*)-1,2-diaminocyclohexane L-malate 0.126 M in MeOH, 1 equiv of 37% HCl. ^b Minimum gelation volume. ^c Gel destruction temperature (±1 °C) determined by the “dropping ball method” (ramping rate <2 °C). Additional notes: (1) All gels were transparent except entries 2–3 for which opaque gels were attained. (2) As expected, enantiomeric MOGLS showed identical gelation properties.

Structure–property studies revealed the importance of the hydroxyl groups of the tartaric acid and the architecture of the diamine in the formation of the gels. Thus, the use of a dicarboxylic unit lacking one the hydroxyl groups or having both protected (e.g., L-malic acid, dibenzoyl-L-tartaric acid) yielded thermally weaker gels (Table 5, entries 7 and 8, respectively). The above observations are somehow aligned to

those reported earlier for the gemini surfactant-based LMOGs.^{15b} Moreover, no gelation capability was observed whatsoever for the multicomponent solution if the dicarboxylic component lacks the two hydroxyl functional groups (e.g., succinic, maleic, or 1,2-benzenedicarboxylic acid). Also, no evidence of gelation was observed when using either 1,4-diamines, nonconformational diamines, or tertiary diamines (e.g., ethylenediamine, benzene-1,2-diamine, *N,N,N',N'*-tetramethylethane-1,2-diamine).

Summary and Conclusions

The above-described results indicate that a judicious thermodynamic balance flanked by the two main driving forces for the self-assembling event, hydrogen bonding and electrostatic forces, seems to be critical for the gelation property shown by the MOGLS. A comprehensive study on the shelflike aggregation mode of the (1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartrate salt in the crystalline state has already been reported.²³ Nevertheless, the ionization state of the species involved in the phase separation during the gel formation using the MOGLS is rather different to the one in the crystalline state, as indicated by the FT-IR studies. The foregoing results including requirement of the five components (diamine, tartaric acid, MeOH, HCl, and H₂O) for the gelation property points toward the existence of an aggregate with at least one nonionized carboxylic group. In principle, such arrangement would favor the tartrate carboxyls to form chainlike head-to-tail structures.

In summary, we have presented the discovery of the first fluid five-component organogelator system based on chiral ammonium salts. The described synergistic MOGLS, hidden for decades behind the classical resolution of the (±)-*trans*-1,2-diaminocyclohexane with L- or D-tartaric acid, enables the effective, instantaneous, and non-thermoreversible gelation of a variety of organic fluids at low temperature. This gift of casual discovery supports the statement that serendipity frequently provides a major stage of opportunity for scientific discovery.²⁴ We believe that the finding of this peculiar system opens the door for the design of new low-cost and efficient liquid multicomponent organogelators. An evaluation of practical applications, the influence of the chirality on the morphology and mechanical properties of these gels, and X-ray scattering studies to conclusively describe the self-assembled pattern of the MOGLS in the gel state are currently underway and will be reported in future publications.

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Supporting Information Available: Synthetic procedures, complete experimental details, ¹H NMR spectra, ¹³C NMR spectra, FTIR spectra, and DSC thermograms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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