Supporting Information

A DAC tartrate-based gelator system featuring markedly improved gelation properties: enhancing lifetime and functionality of gel networks

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1. Two-variables screening for the optimization of MGS-II

Table S1 2D-Matrix showing the concentration of DAC tartrate **1** in DMSO [M] and the amount of HCl (equivalents with respect to **1**) necessary to prepare a transparent and stable MGS-II solution.[a]

[M]⇓/HCl⇒	1.9	2.0	2.1	2.2	2.3	2.4	2.5
0.08	I (30)	I (60)	S (5)	S (2)	S (10 s)	S (0)	S (0)
0.10	I (30)	I (60)	S (5)	S (2)	S (10 s)	S (0)	S (0)
0.128	I (30)	S (60)	S (5)	S (2)	S (10 s)	S (0)	S (0)
0.20	I (60)	S (30)	S (5)	S (2)	S (10 s)	S (0)	S (0)
0.20	I (60)	S (5)	S (5)	S (2)	S (10 s)	S (0)	S (0)

[a] Abbreviations: I (t) = insoluble after t min of sonication; S (t) = clear solution after t min of sonication; s = seconds.

2. Screening of experimental conditions for the formation of gels with MGS-II

Table S2 Optimization of experimental conditions for the preparation of stable gels in acetone as model solvent using MGS-II (0.128 M of **1** in DMSO and 2.4 equivalents of HCl).

Procedure[a]	Remarks	Result
A	200 μL of acetone; 30-70 μL of MGS-II	Gelation
B	200 μL of acetone; 30-70 μL of MGS-II	No gelation
C	200 μL of acetone; 30-50 μL of MGS-II	No gelation
D	200 μL of acetone; 150-200 μL of MGS-II	No gelation
E	200 μL of acetone; 30-70 μL of MGS-II	No gelation (crystals formed within 5 min)
F	200 μL of acetone; 50-100 μL of MGS-II	No gelation
G	200 μL of acetone; 50 μL of MGS-II	No gelation

[a] A: Addition of MGS-II to solvent at room temperature. B: Addition of solvent to MGS-II at room temperature. C: Addition of MGS-II to solvent at room temperature while gently shaking. D: Addition of solvent to higher concentration of MGS-II at room temperature. E: Solvent pre-cooled in a cooling batch (0 ºC). F: Addition of warmed MGS-II to solvent or addition of warmed solvent to MGS-II. G: Ultrasonication of the mixture [MGS-II + solvent] for several minutes at room temperature.

3. Additional pictures of gels prepared with MGS-II in different solvents

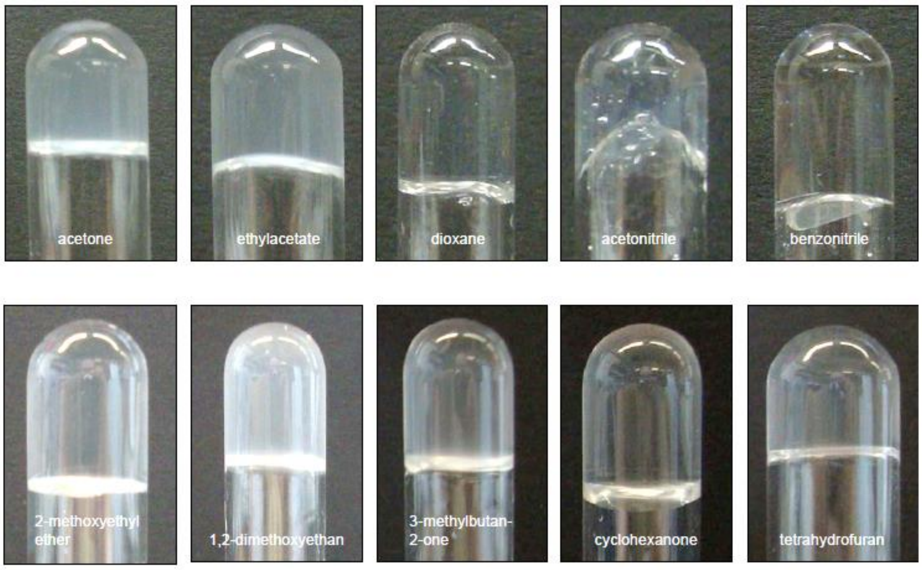


Fig. S1 Organogels prepared with MGS-II in different solvents as depicted in Table 1.

4. Effect of additional water on the stability of the gels

Table S3 Effect of overstanding solvent in the temporal stability of the gels prepared with MGS-II as indicated in Table 1.[a]

Entry	Tested solvent	Overstanding solvent	Temporal stability	Remarks
1	DME	DME	2 d - 3 d	
3	DME	water	< 10 min	dissolved
4	NM	NM	2 d	
6	NM	water	30 min	3 phases (gel + 2 solvents)
7	MEE	MEE	1 d	
9	MEE	water	< 10 min	dissolved
10	ETAC	ETAC	1 d	
12	ETAC	water	-	immediately dissolved
13	ACT	ACT	-	precipitation and solution
15	ACT	water	-	immediately dissolved
16	MBN	MBN	> 20 h	
18	MBN	water	<10 min	quickly dissolved
19	THF	THF	> 1 d	
21	THF	water	<10 min	quickly dissolved
22	DCM	DCM		
24	DCM	water		
25	CHN	CHN		
27	CHN	water	< 10 min	3 phases (gel + 2 solvents)
28	BN	BN		
30	BN	water	< 10 min	3 phases (gel + 2 solvents)
31	ACN	ACN		
33	ACN	water	-	immediately dissolved
34	DOX	DOX		
36	DOX	water	< 10 min	3 phases (gel + 2 solvents)

[a] Abbreviations: ACT = acetone; ACN = acetonitrile; BN = benzonitrile; CHN = cyclohexanone; DCM = dichloromethane; DME = 1,2-dimethoxyethane; DOX = 1,4-dioxane; ETAC = ethyl acetate; MBN = 3-methylbutan-2-one; MEE = 2-methoxyethyl ether; NM = nitromethane; THF = tetrahydrofuran; d = days; min = minutes.

Table S4 Effect of additional water incorporated into MGS-II.[a]

Entry	Tested solvent	Additional water [µl]	Aspect of the phase	Temporal stability	Remarks
1	DME	5	TG	few hours	-
2	DME	10	S	-	-
3	ACT	5	PG	< 30 min	-
4	ETAC	5	S	-	-
5	CHN	5	PG	-	small piece of gel
6	NM	5	TG	> 14 h	-
7	NM	10	TG		
8	NM	20	S	-	-
9	MEE	5	TG	> 14 h	-
10	MEE	10	TG	> 8 h	
11	MEE	20	S	-	-
12	BN	5	S	-	-
13	DOX	5	TG	very weak	destroyed with vial upside-down
14	DOX	10	S	-	-
15	ACN	5	TG	< 30 min	-
16	ACN	10	TG	1 h	-
17	ACN	20	S	-	-
18	THF	5	PG	-	-
19	MBN	5	S	-	-
20	DCM	5			

[a] Abbreviations: ACT = acetone; ACN = acetonitrile; BN = benzonitrile; CHN = cyclohexanone; DCM = dichloromethane; DME = 1,2-dimethoxyethane; DOX = 1,4-dioxane; ETAC = ethyl acetate; MBN = 3-methylbutan-2-one; MEE = 2-methoxyethyl ether; NM = nitromethane; THF = tetrahydrofuran; min = minutes; S = solution; PG = partial gel; TG = transparent or slightly translucent gel.

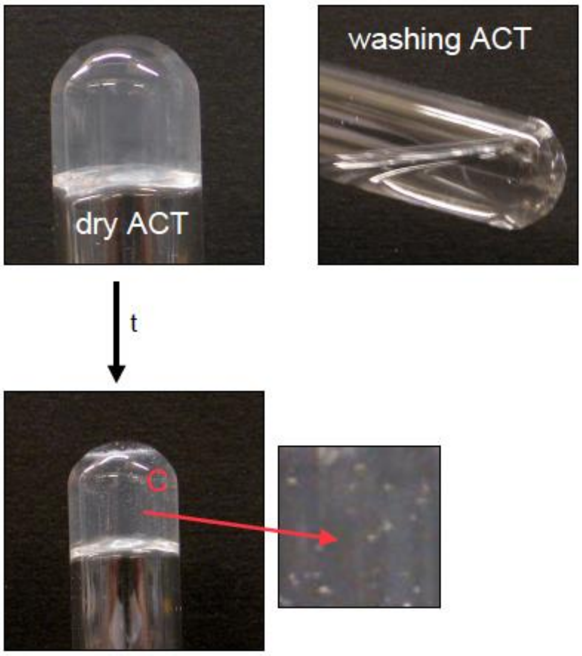


Fig. S2 Comparison of MGS-II derived gels prepared using dry acetone and washing acetone. No gelation was achieved in the latter case. Abbreviations: ACT = acetone; t = time (aging); C = crystals.

5. Differential scanning calorimetry

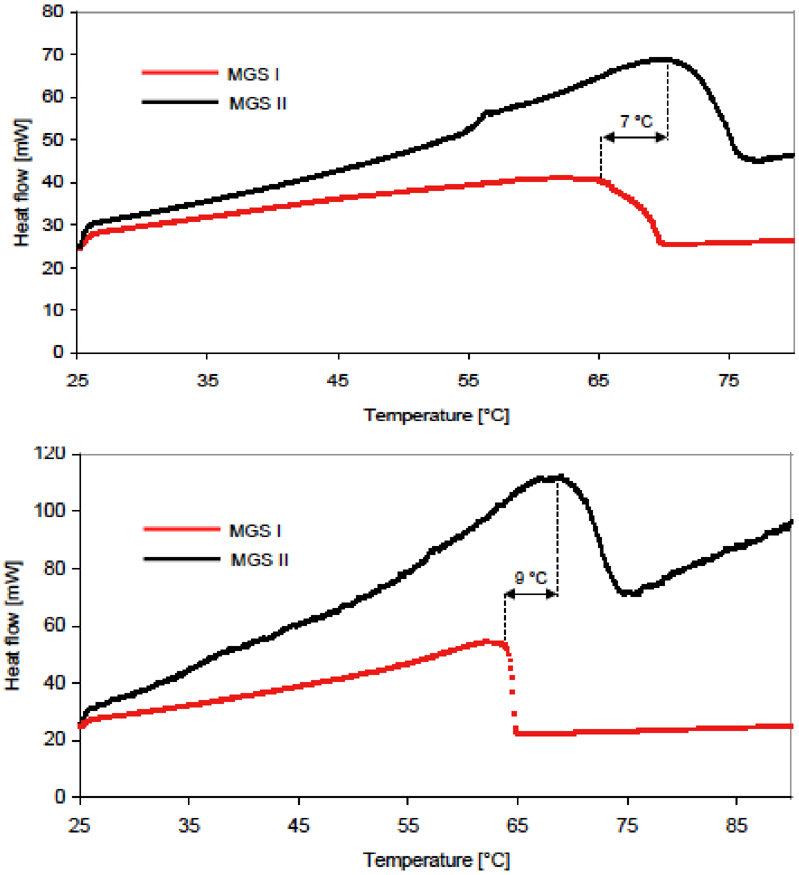


Fig. S3 DSC thermograms showing the comparison of T_d between MGS-I and MGS-II gels from dimethoxyethane (*top*) and acetonitrile (*bottom*).

6. Structure-property relationships of MGS-II

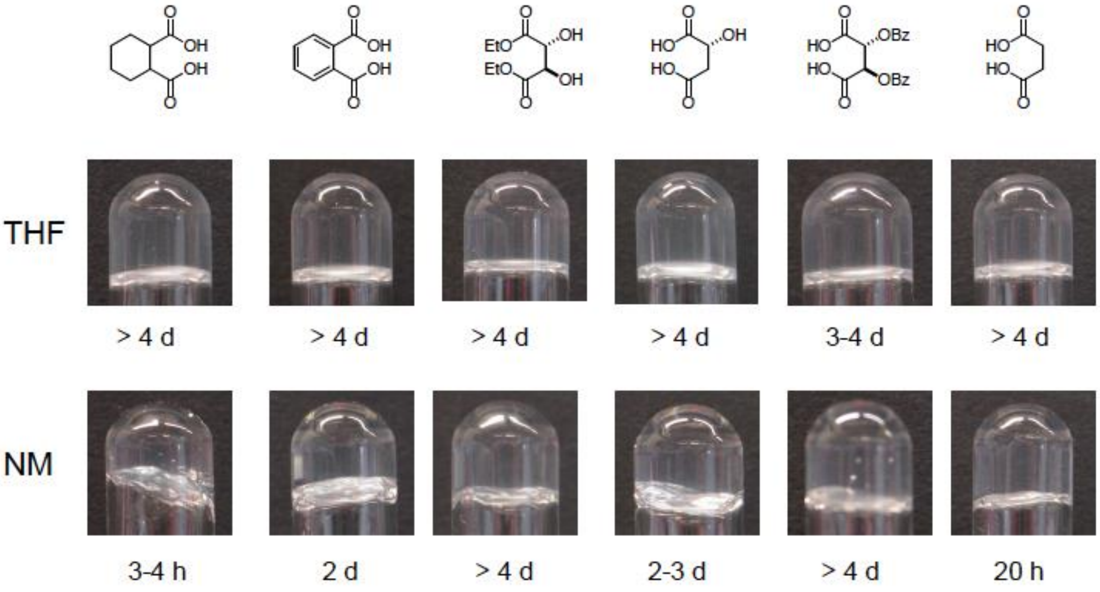


Fig. S4 Tolerance of MGS-II toward the exchange of tartaric acid by other dicarboxylic derivatives. The temporal stability is indicated for each gel. Abbreviations: THF = tetrahydrofuran; NM = nitromethane; d = days; h = hours.

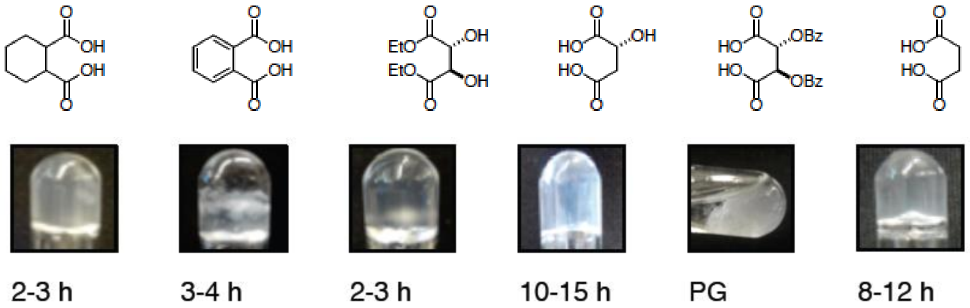


Fig. S5 Aspect and temporal stability of the materials obtained in THF using MGS-I where the tartaric acid was exchanged by other dicarboxylic derivatives. Abbreviations: PG = partial gel; h = hours.

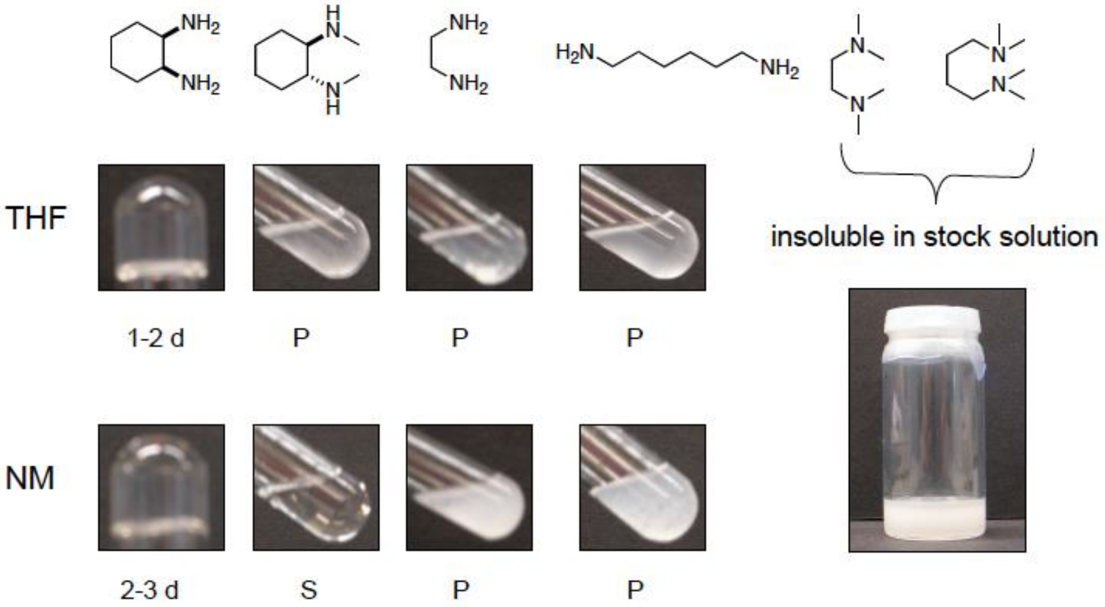


Fig. S6 Tolerance of MGS-II toward the exchange of DAC by other diamines. Abbreviations: THF = tetrahydrofuran; NM = nitromethane; P = precipitates; S = clear solution; d = days.

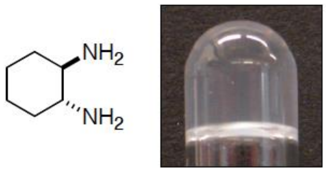


Fig. S7 Transient gel made in THF using MGS-II prepared with (1*R*,2*R*)-1,2-diaminocyclohexane without tartaric acid counterpart. Collapse of the gel took place within 24 h.

7. Additional pictures of *gel*-to-*crystal* transitions

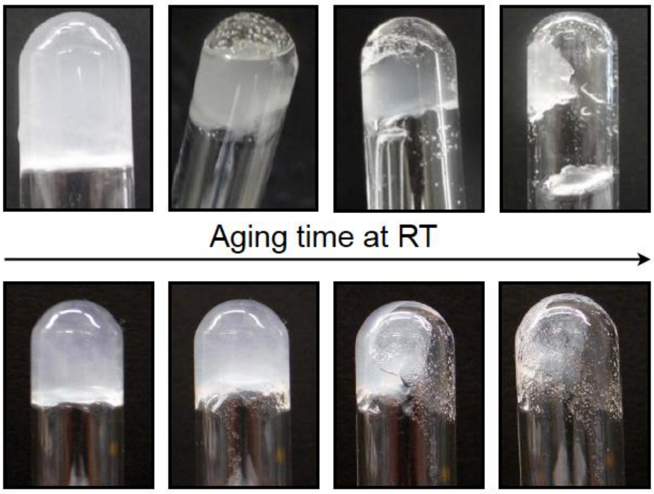
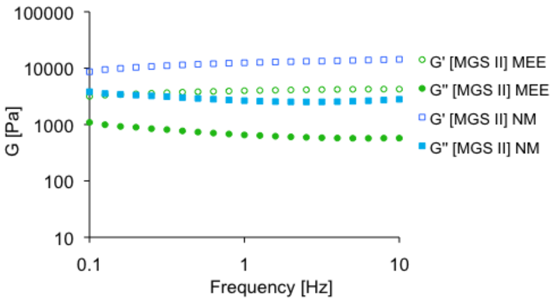


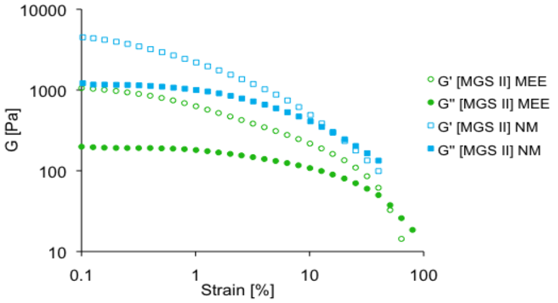
Fig. S8 Digital photographs of a gel made from MGS-I in ethyl acetate (*top*) and from MGS-II in methylene chloride (*bottom*) over time. The gels were prepared as indicated in Table 1.

8. Rheological experiments

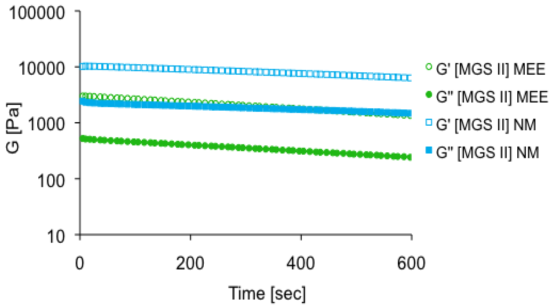
A) DFS (gelator: MGS-II; solvent: MEE; NM)



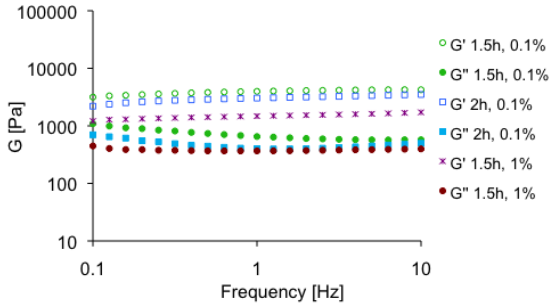
B) DSS (gelator: MGS-II; solvent: MEE; NM)



C) DTS (gelator: MGS-II; solvent: MEE; NM). Decrease of moduli: MEE = 55%, NM = 38%

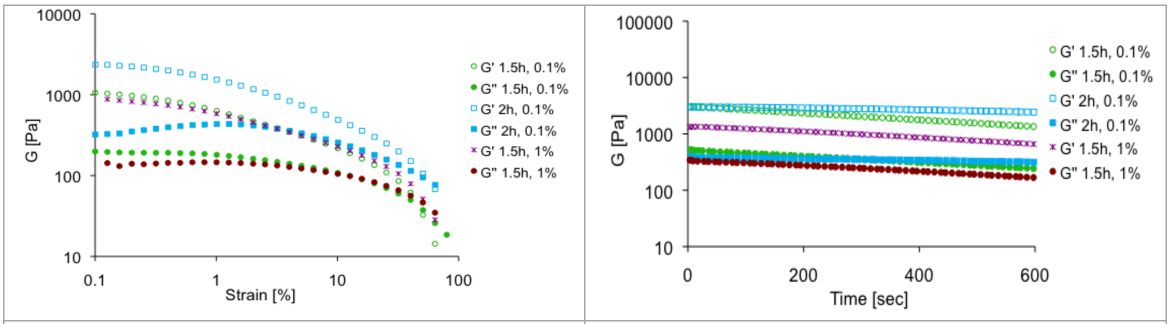


D) DFS (gelator: MGS-II; solvent: MEE; time after precipitation: 1.5-2 h; strain: 0.1-1%)



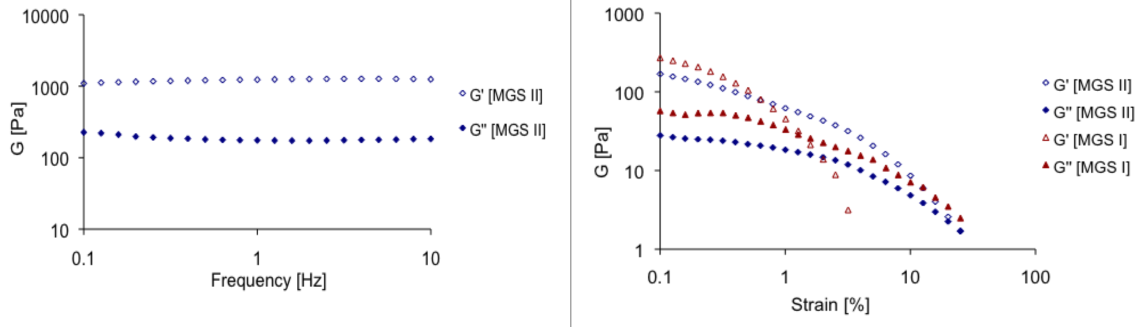
E) DSS (gelator: MGS-II; solvent: MEE; time after precipitation: 1.5-2 h; strain: 0.1-1%)

F) DTS (gelator: MGS-II; solvent: MEE; time after precipitation: 1.5-2 h; strain: 0.1-1%)



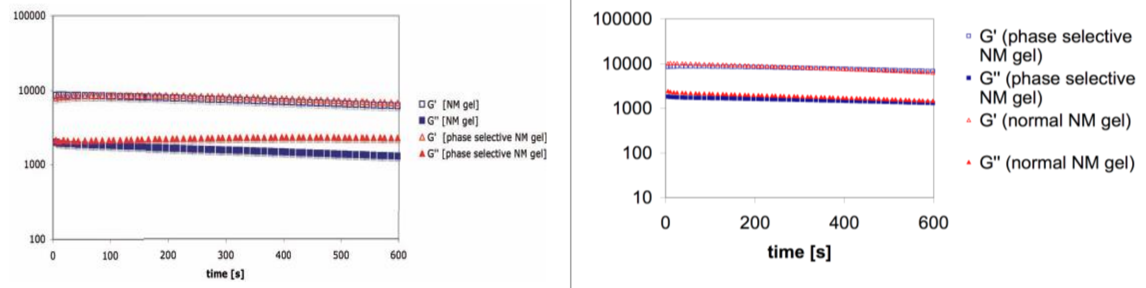
G) DFS (gelator: MGS-II; solvent: THF)

H) DSS (gelator: MGS-I *vs* MGS-II; solvent: THF)



I) DTS (phase selective gelation; solvent: NM)

J) DTS (phase selective gelation; solvent: NM)



K) DSS (phase selective gelation; solvent: NM)

L) DTS (hybrid; solvent: ACT -5 vials-)

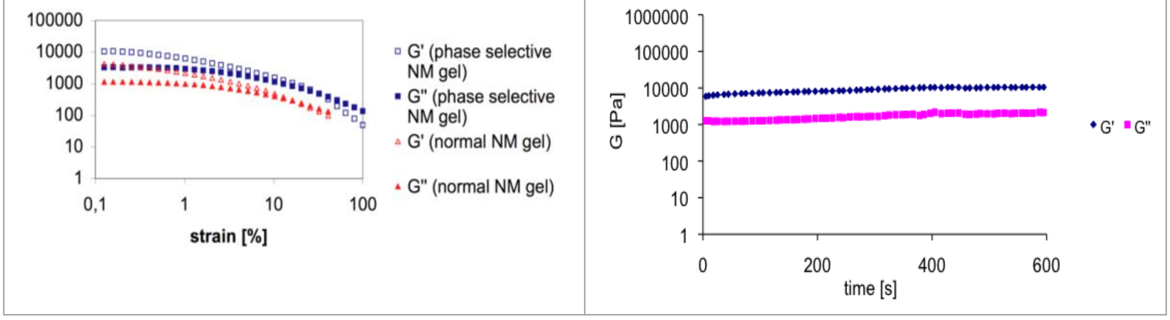


Fig. S9 Rheological experiments of gels prepared with MGS gelators under different conditions ad described in the main manuscript. Abbreviations: ACT = acetone; MEE = 2-methoxyethyl ether; NM = nitromethane; THF = tetrahydrofuran. Average of two measurements are reported. Unless otherwise indicated, frequency and strain in DTS experiments were adjusted to 1Hz and 0.1% strain, respectively.

9. Characterization of 2 and 3

The experimental data were identical to those reported for the MGS-I system (see reference 11 in the main text).

- (1*R*,2*R*)-1,2-Diaminocyclohexane dichloride (**2**) isolated from either (a) MGS solution or (b) after collapse of the organogels as described in the main manuscript: ^{1}H NMR (300 MHz, D_2O) δ/ppm = 1.33−1.40 (m, 2H, CH_2CH_2CHN), 1.49−1.56 (m, 2H, CH_2CH_2CHN), 1.81−1.84 (m, 2H, CH_2CHN), 2.15−2.19 (m, 2H, CH_2CHN), 3.38−3.43 (m, 2H, CHN), 4.79 (br s, 6H, NH_3);

^{13}C NMR (75 MHz, D_2O) δ/ppm = 22.8, 29.3, 52.2.

- L-Tartaric acid (**3**) that remains in solution during precipitation of **2**: ^{1}H NMR (300 MHz, D_2O) δ/ppm = 4.61 (s, 2H, OC*H*); ^{13}C NMR (75 MHz, D_2O) δ/ppm = 71.8, 174.4.

- Ortep diagram of the crystal structure of isolated (1*R*,2*R*)-1,2-diaminocyclohexane (**2**) (see, A. S. Abu-Surrah, T. A. K. Al-Allaf, M. Klinga and M. Ahlgren, *Polyhedron*, 2003, **22**, 1529):