Electronic Supplementary Material (ESI) for Soft Matter.

ELECTRONIC SUPPLEMENTARY INFORMATION

Differentiating aliphatic and aromatic alcohols by Triazine-based Supramolecular Organogelators: End Group Specific Selective Gelation with Chain Length of Alcohols

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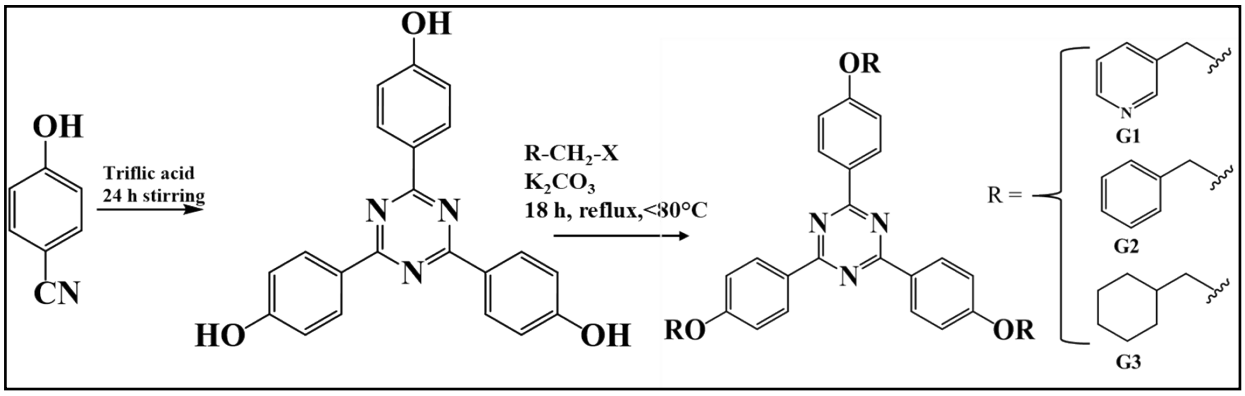
Contents

1. Experimental Section



Scheme S1. Experimental protocol of gelators **G1**, **G2** and **G3**

The gelators were prepared in two steps, starting from 4-cyanophenol, according to the reported literature. First 2,4,6-triazinetriphenol was prepared[1] and then it was subjected to a S_N2 reaction[2] to produce the final product.

Synthesis of 2,4,6-triazinetriphenol:

Trifluoromethanesulfonic acid (12.18 mmol) was slowly added to a stirred solution of 4-cyanophenol (4.2 mmol) in DCM at 0°*C* under a N_2 atmosphere. Then it was allowed to come to room temperature. After stirring for next 24 h, solvent was evaporated and ice-cold water was poured into it to obtain white precipitate. Then it was neutralized by adding ammonia solution. The precipitate was filtered, washed with water and dried to obtain the product as white powder (Yield- 96%). [1]

Synthesis of Gelator G1

A mixture of 2,4,6-Triazinetriphenol (10 mmol) and K_2CO_3 (60 mmol) was taken in a two neck RB in presence of dry DMF solvent and heated for at least half an hour at 80 °C. After this 3-chloromethyl pyridine (50 mmol) was added into this reaction mixture and the entire solution was refluxed at 80 °C for 12 hrs. The reaction was thereafter quenched by adding water and leading to the formation of a white precipitate. The precipitate was filtered and washed thoroughly with water and then dried under vacuum. (Yield- 68%).

Synthesis of Gelator G2

A mixture of 2,4,6-triazinetriphenol (10 mmol) and K_2CO_3 (60 mmol) was taken in a two neck RB in presence of dry DMF solvent and heated for at least half an hour at 80 °C. After this

benzyl chloride (50 mmol) was added into this reaction mixture and the entire solution was refluxed at 80 °C for 12 hrs. The reaction was thereafter quenched by adding water and leading to the formation of a white precipitate. The precipitate was filtered and washed thoroughly with water and then dried under vacuum. (Yield-98%)

Synthesis of Gelator G3

A mixture of 2,4,6-triazinetriphenol (10 mmol) and K_2CO_3 (60 mmol) was taken in a two neck RB in presence of dry DMF solvent and heated for at least half an hour at 80 °C. After this (bromomethyl)cyclohexane (50 mmol) was added into this reaction mixture and the entire solution was refluxed at 80 °C for 12 hrs. The reaction was thereafter quenched by adding water and leading to the formation of a white precipitate. The precipitate was filtered and washed thoroughly with water and then dried under vacuum. (Yield-89%)

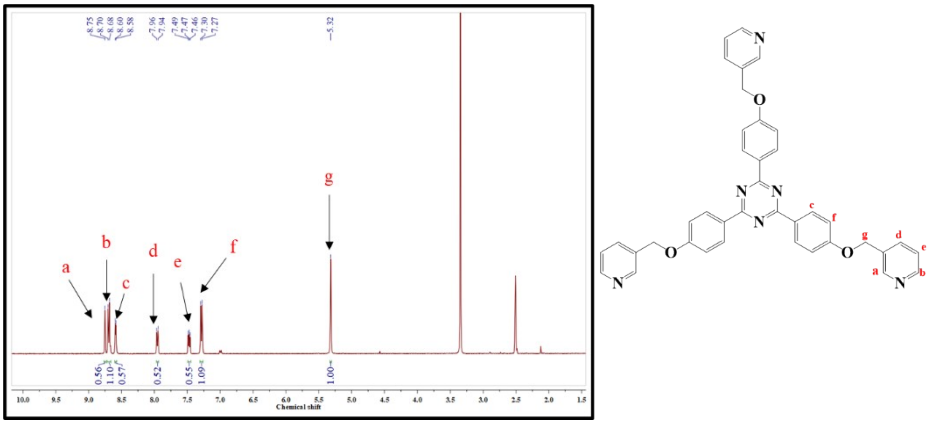


Fig. S1 ^{1}H NMR of gelator G1

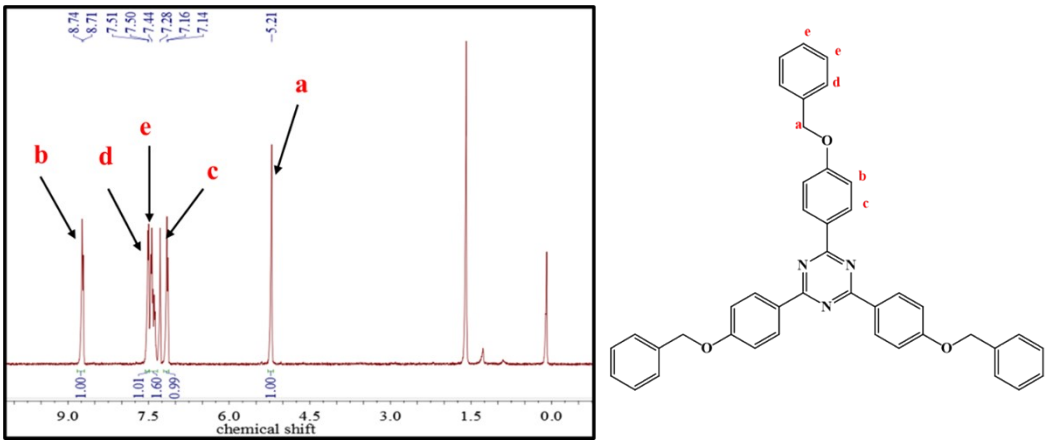


Fig. S2 ^{1}H NMR of gelator G2

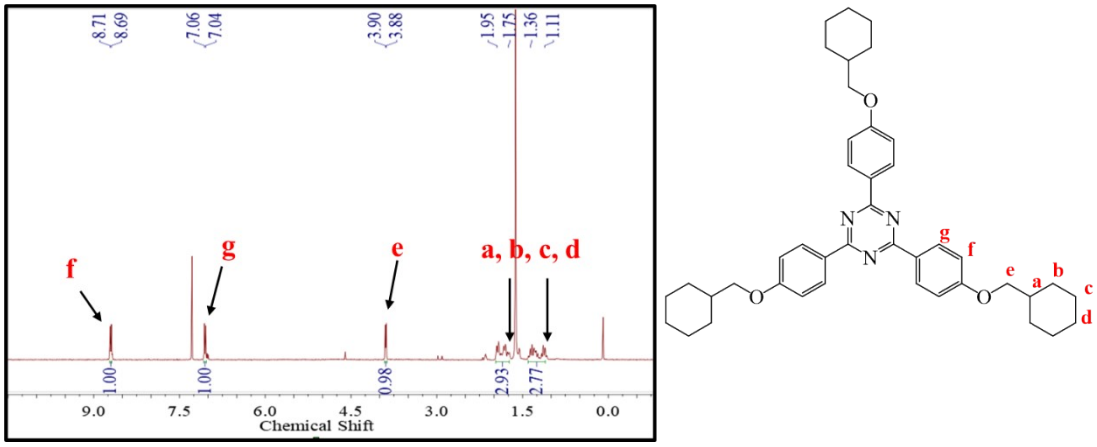


Fig. S3 ^{1}H NMR of gelator G3

Table S1. Behaviour of **G1**, **G2** and **G3** over a series of solvents and MGC and T_{gel} values where gel formation occurs

Class of Solvent	**Solvent System**	**G1(MGC)/ T_{gel} (°C)**	**G2(MGC)/ T_{gel} (°C)**	**G3(MGC)/ T_{gel} (°C)**
Non-polar	Hexane	I	I	I
	Cyclohexane	I	S	I
	DCM	PS	S	S
	$CHCl_3$	PS	S	S
Polar Aprotic	ACN	PS	I	I
	Acetone	PS	I	I
	DMF	S	S	S
	DMSO	S	S	S
	DMA	S	S	PS
Polar Protic	H_2O	I	I	I
Aliphatic alcohol	Methanol	PS	I	I
	Ethanol	G(6)/50	I	I
	Propanol	G(6)/72	I	I
	Isopropanol	G(6)/65	I	PS
	Allylic alcohol	S	I	PS
	Butanol	G(7)/80	I	G(6)/75
	2-butanol	G(7)/69	I	PS
	t-butanol	G(8)/54	I	PS
	1-pentanol	S	PS	G(6)/87
	1-hexanol	S	S	G(8)/102
	1-heptanol	PS	G(8)/110	G(8)/130
	1-octanol	PS	G(10)/116	P
	1-decanol	PS	G(10)/128	P
	3-butene-2-ol	PS	PS	P
	Cyclohexanol	G(15)/72	G(8)/96	G(6)/78

Aliphatic polyalcohol	Ethylene glycol	G(6)/105	PS	I
	1,4-butandiol	G(5)/100	PS	I
	Glycerol	PS	PS	I
Aromatic alcohols	Phenol	S	S	S
	Benzyl alcohol	S	P	S

N.B. I- insoluble, P-Precipitate, PS-partially soluble, S- Clear solution, G-Gel

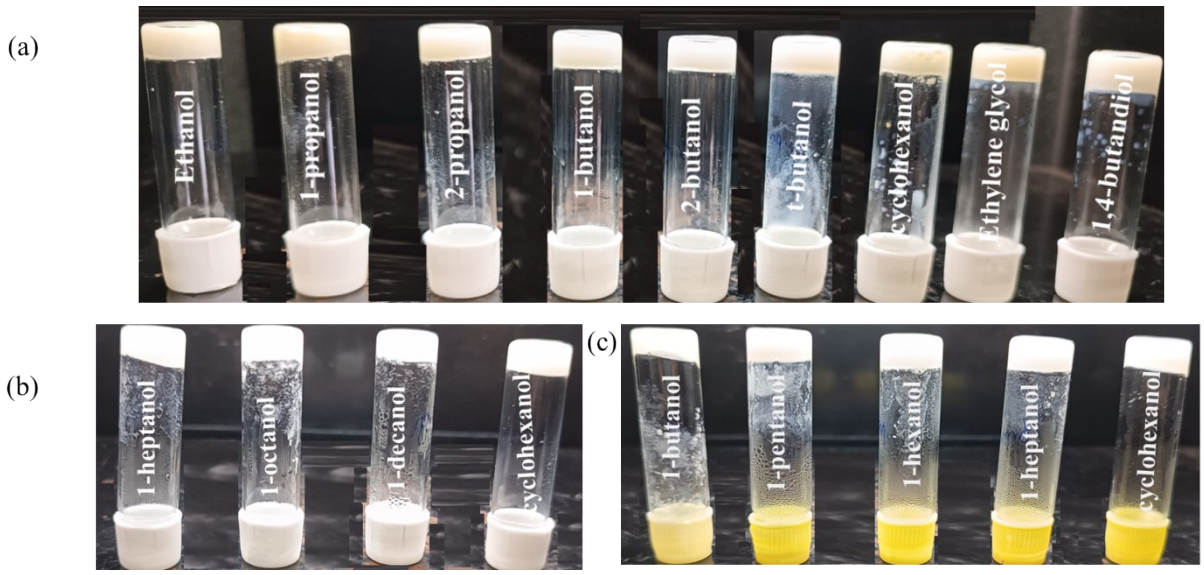


Fig. S4. Inverted vial picture of gels from different alcoholic solution for (a) **G1** (b) **G2** (c) **G3**

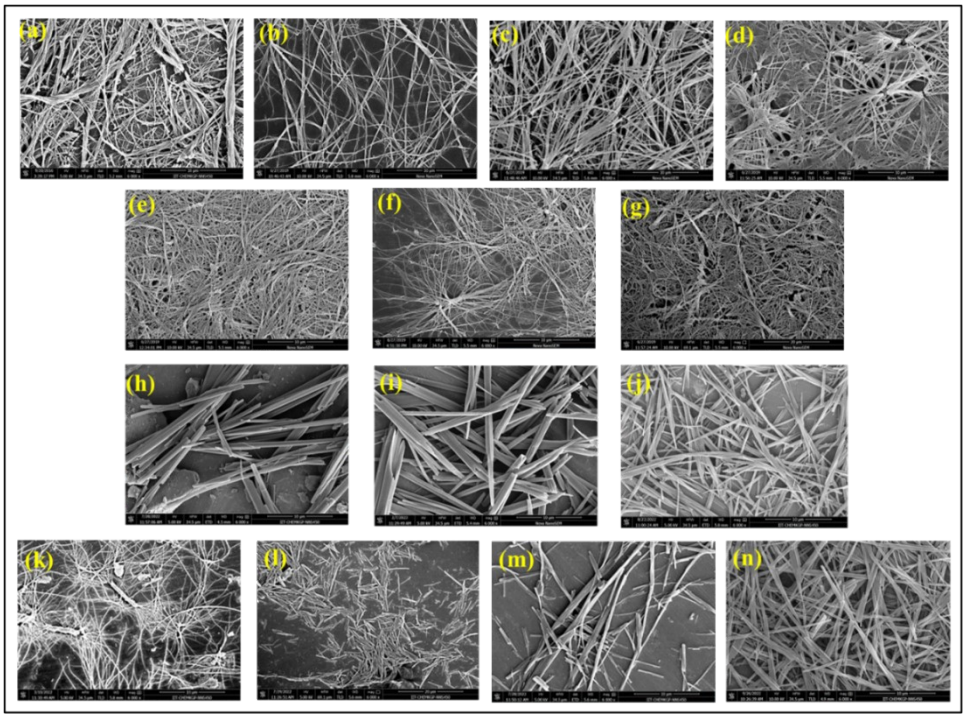


Fig. S5 FESEM images of (a) G1_ethanol (b) G1_ethylene glycol (c) G1_1,4-butandiol (d) G1_cyclohexanol (e) G1_1-butanol (f) G1_2-butanol (g) G1_t-butanol (h) G2_cyclohexanol (i) G2_1-decanol (j) G2_1-heptanol (k) G2_1-octanol (l) G3_1-butanol (m) G3_1-hexanol (n) G3_cyclohexanol

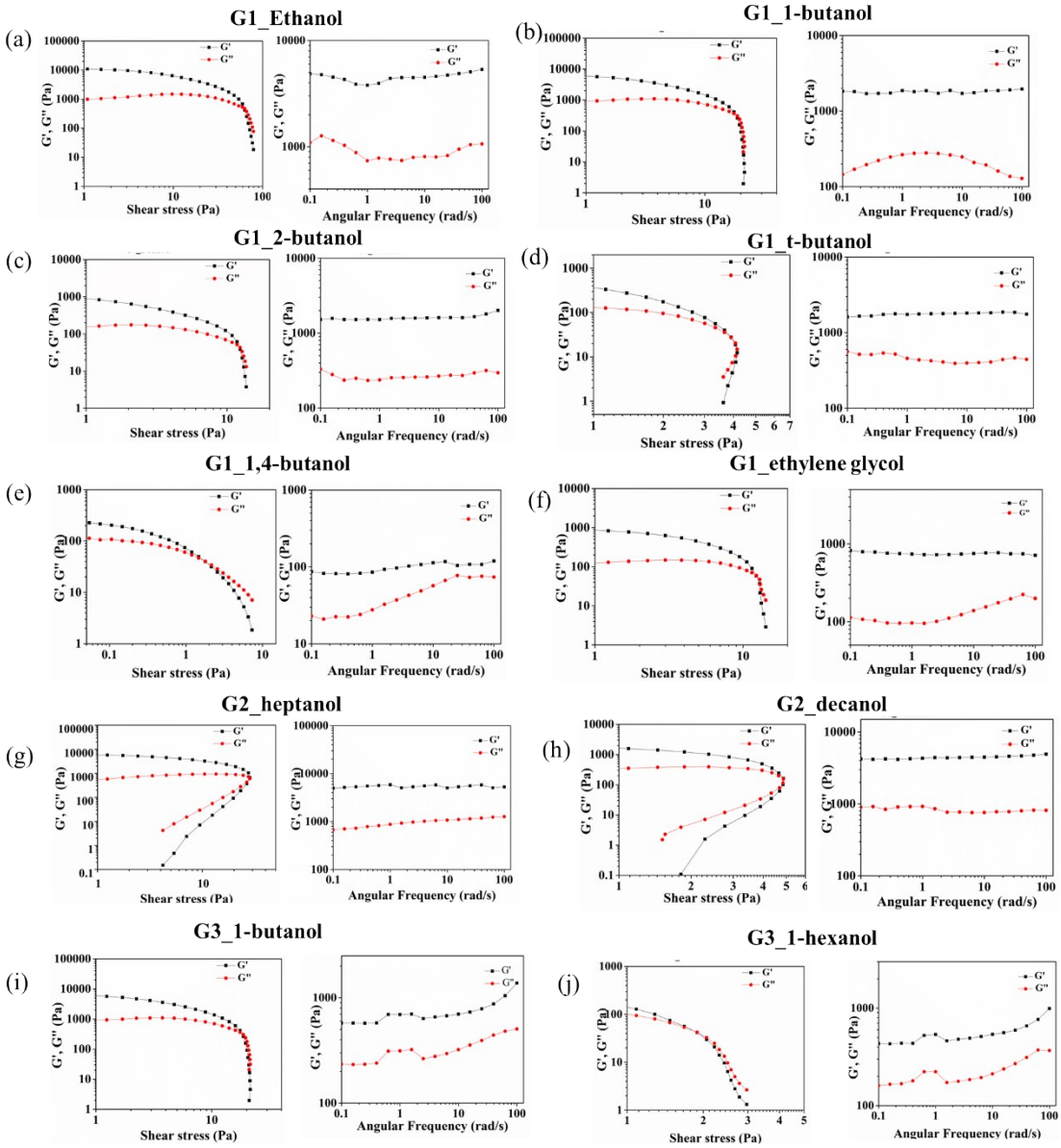


Fig. S6 Rheological parameters of (a) G1_ethanol (b) G1_1-butanol (c) G1_2-butanol (d) G1_ t-butanol (e) G1_1,4-butanol (f) G1_ethylene glycol (g) G2_1-heptanol (h) G2_1-decanol (i) G3_1-butanol (j) G3_1-hexanol

Table S2. Rheological data of various gels obtained from different moieties

	G1		**G2**		**G3**	
	Yield Stress (Pa)	G′–G″ (Pa)	Yield Stress (Pa)	G′–G″ (Pa)	Yield Stress (Pa)	G′-G″ (Pa)
Ethanol	63.55	3427.96	-	-	-	-
1-butanol	21.38	1606.59	-	-	2.84	415.72
2-butanol	12.25	1338.98	-	-	-	-
t-butanol	3.93	1299.97	-	-	-	-

1-hexanol	-	-	-	-	1.39	583.39
1-heptanol	-	-	27.86	4896.61	-	-
1-decanol	-	-	4.89	3592.41	-	-
Ethylene glycol	12.65	577.06	-	-	-	-
1,4-butandiol	1.82	39.69	-	-	-	-
cyclohexanol	14.55	1625.96	133.25	8584.12	11.18	959.94

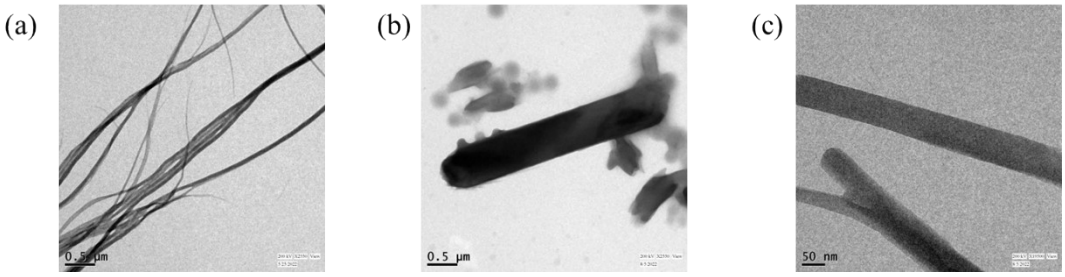


Fig. S7 . TEM images of (a) G1_cyclohexanol (b) G2_cyclohexanol (c) G3_cyclohexanol

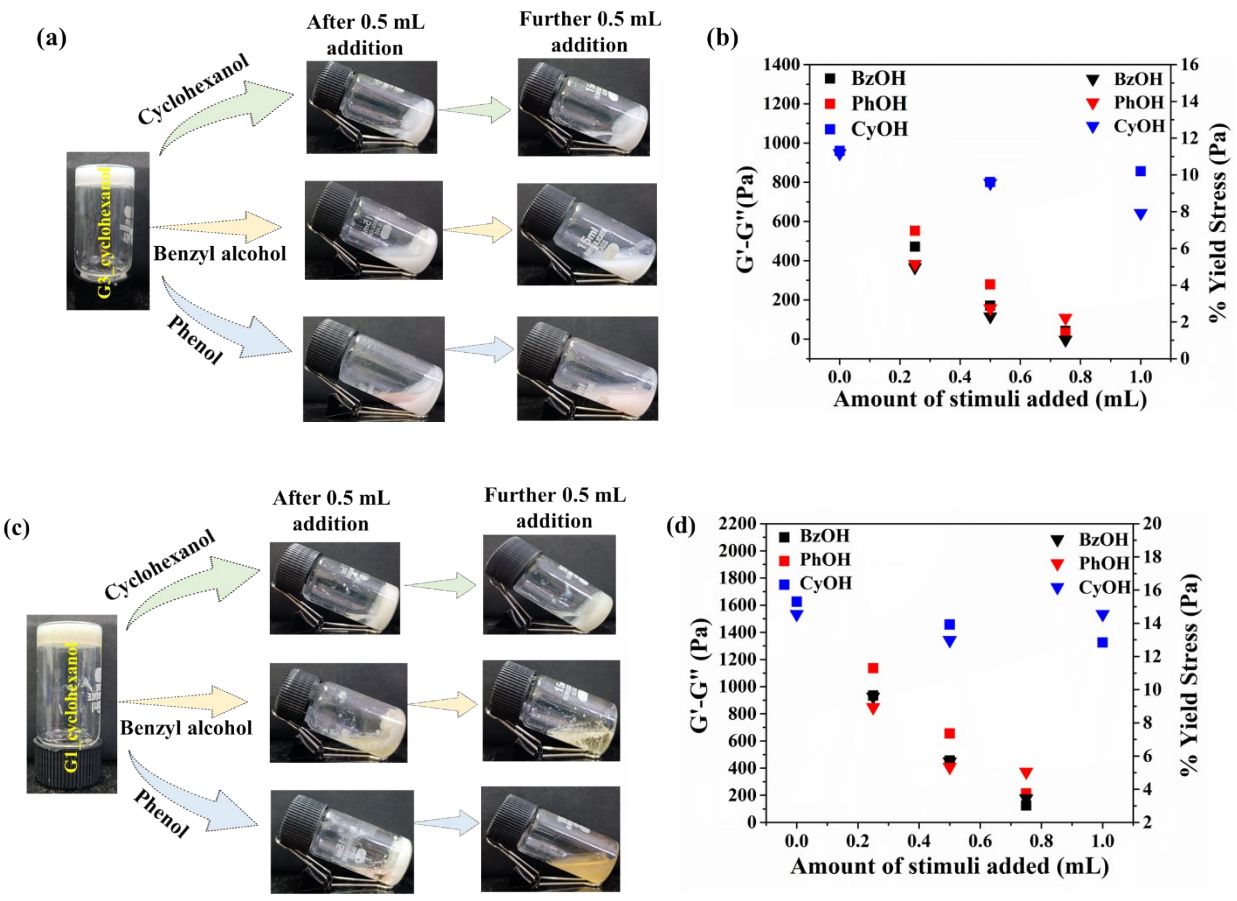


Fig. S8 (a), (c) Stimuli-responsive behaviour of **G1_cyclohexanol** and **G3_cyclohexanol** in presence of various stimuli like cyclohexanol, benzyl alcohol and phenol (b), (d) Stepwise rheological parameter correlation diagram of **G1_cyclohexanol** and **G3_cyclohexanol** gel

Table S3. Rheological data at different stages of degelation studies on gel_cyclohexanol using various chemical stimuli

	Amount of solvent added	**G1_cyclohexanol**		**G2_cyclohexanol**		**G3_cyclohexanol**	
		G′– G″	**Yield stress**	**G′– G″**	**Yield stress**	**G′– G″**	**Yield stress**
Benzyl alcohol	0 mL	1625.9	14.55	8584.12	133.25	959.94	11.18
	0.25 mL	934.89	9.58	2083.52	72.61	471.46	4.97
	0.5 mL	456.34	5.67	1607.07	33.92	170.29	2.30
	0.75 mL	124.8	3.45	498.43	12.40	42.04	1.03
Phenol	0 mL	1625.96	14.55	8584.12	133.25	959.94	11.18
	0.25 mL	1136.78	8.94	3376.16	90.34	552.9	5.15
	0.5 mL	654.98	5.34	3147.22	61.56	278.79	2.74
	0.75 mL	213.9	5.05	1301.96	59.68	31.98	2.22

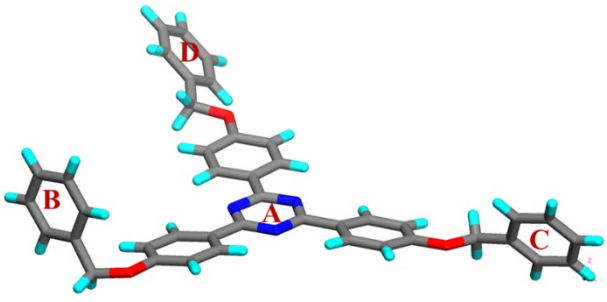
Cyclohexanol	0 mL	1625.96	14.55	8584.12	133.25	959.94	11.18
	0.5 mL	1456.78	12.98	7659.24	111.12	801.25	9.56
	1 mL	1324.87	14.55	7821.46	125.06	856.12	7.92

Table S4. Crystallographic parameters for gelator G2

CCDC 2323438	
Formula	$C_{42}\ H_{33}\ N_3\ O_3$
Crystal System	Monoclinic
MW	627.71
Temperature (K)	296(2)
a (Å)	23.719(3)
b (Å)	5.8937(7)
c (Å)	26.041(3)
α (°)	90
β (°)	117.009(3)
γ (°)	90
Cell Volume (Å^3)	3243.31
Space Group	$P2_1/n$
d (g/cm^3)	1.285
Z	4
R-factor	5.6

Table S5. Angle between the planes

Planes	Interplaner Angles
AB	87º
AC	79º
AD	44º



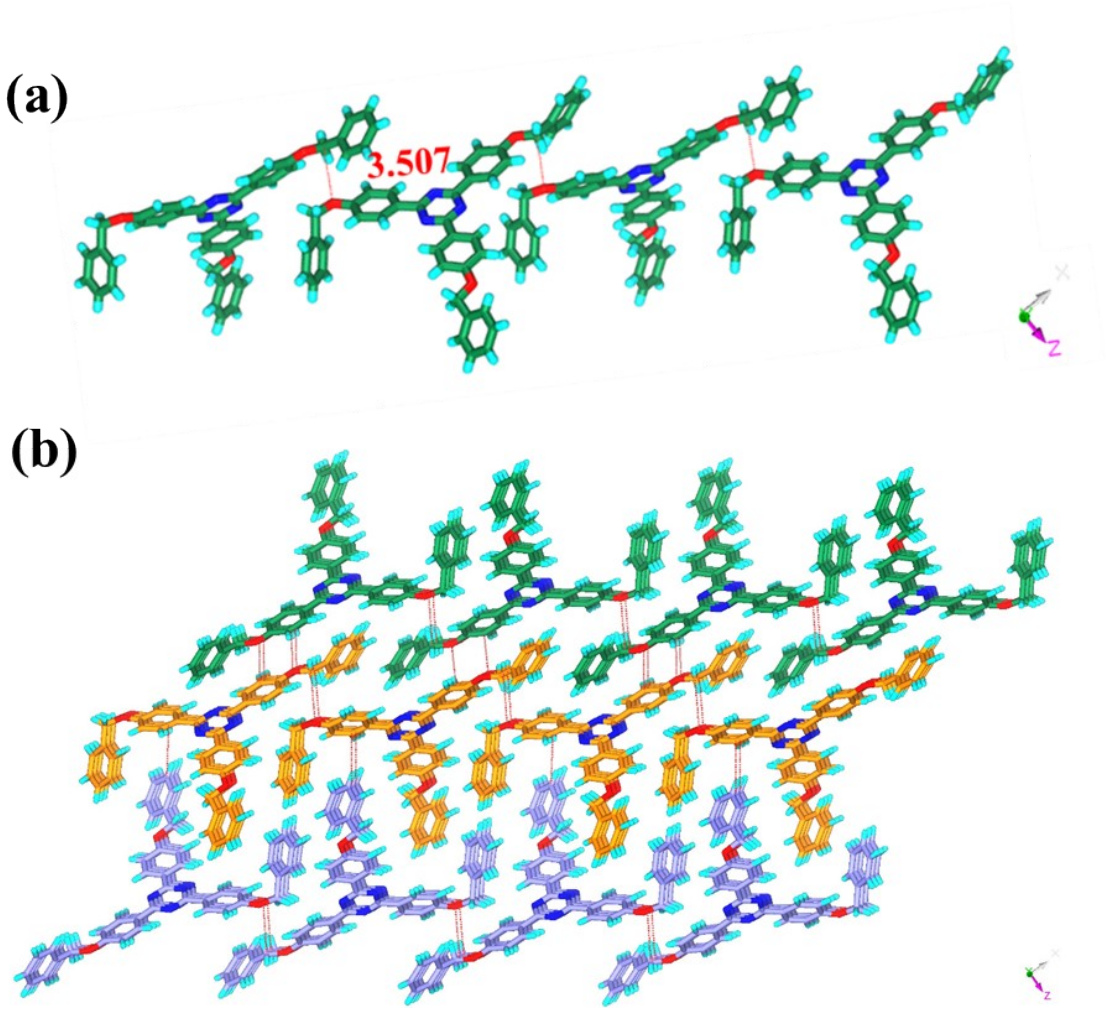


Fig. S9. (a) 1D chain along x-axis propagating *via* H-bonding interactions (b) Overall 3D view of **G2**

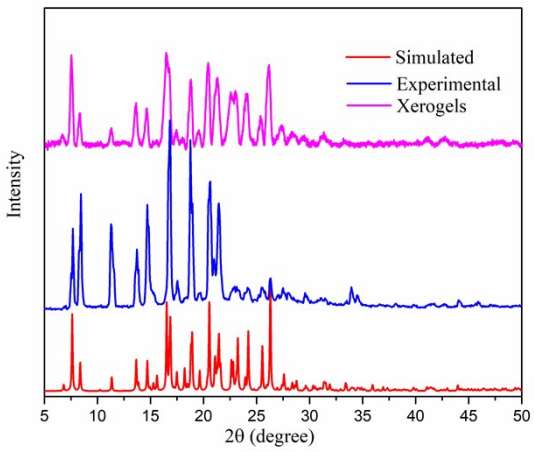


Fig. S10. PXRD of crystal of **G2** and xerogels from **G2_cyclohexanol**

REFERENCES

1. Samanta, J.; Natarajan, R. *Org. Lett.* **2016**, *18*, 14, 3394–3397.
2. Kotha, S.; Solanke, B. U.; Gupta, N.K. *J.Mol.Struct.* **2021**, *1244*,130907.