Supporting Information

Cyclohexamer [-(*D*-Phe-azaPhe-Ala)$_2$-]: good candidate to formulate supramolecular organogels.

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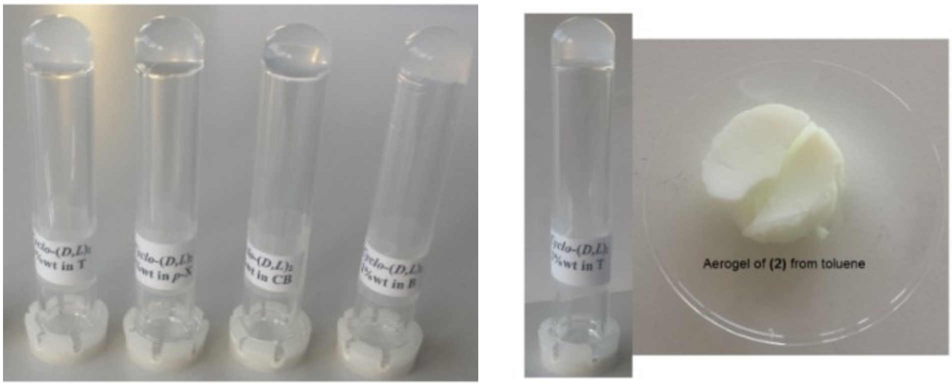

(a) **(b)**

Figure S1. (a) Gelation tests in different solvents (T = toluene, *p*-X = *p*-xylene, CB = chlorobenzene and B = benzene), and (b) aerogel of **(2)** from toluene obtained under supercritical CO_2 condition.

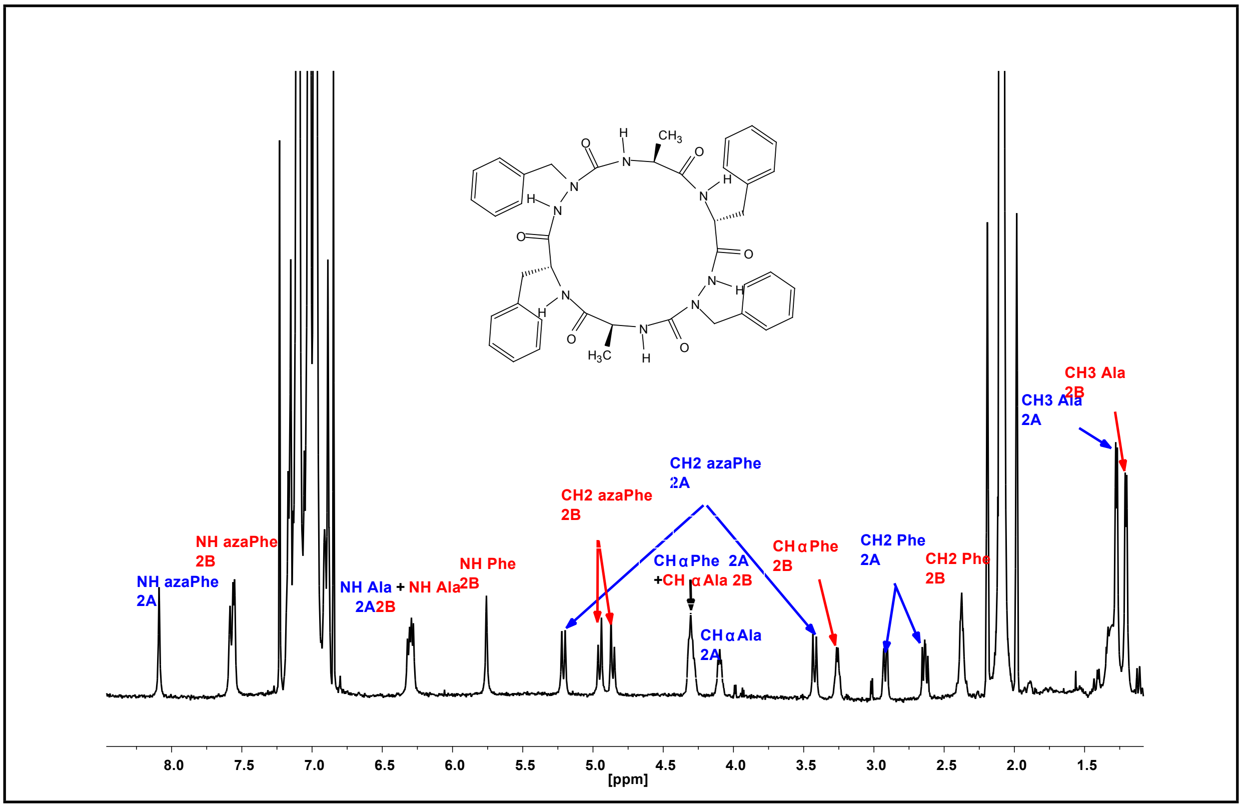

Figure S2. ^{1}H NMR (600 MHz) of compound **(2)** in toluene-d_8; (1.0 mM at 293 K).

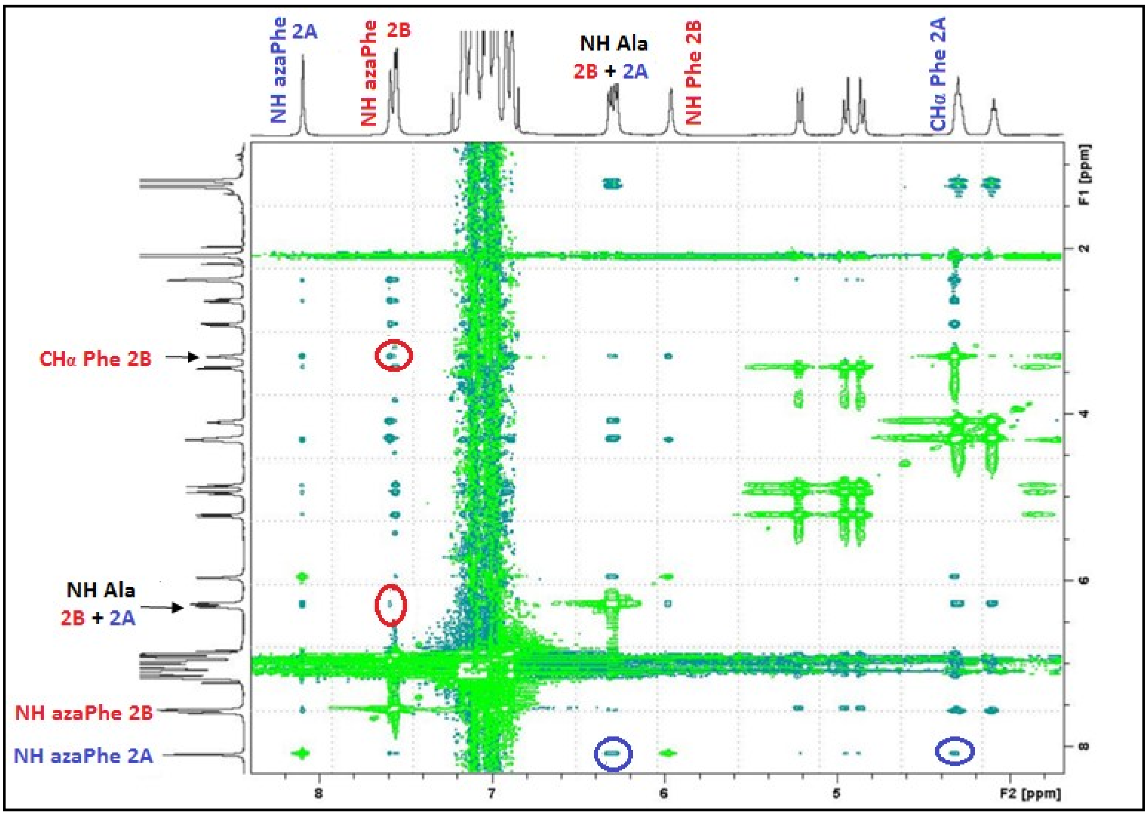

Figure S3. 2D ROESY spectrum of hetero cyclohexamer **(2)** in toluene-d_8; (1.0 mM at 293 K) illustrating the ROE correlations of conformers **2A** and **2B**.

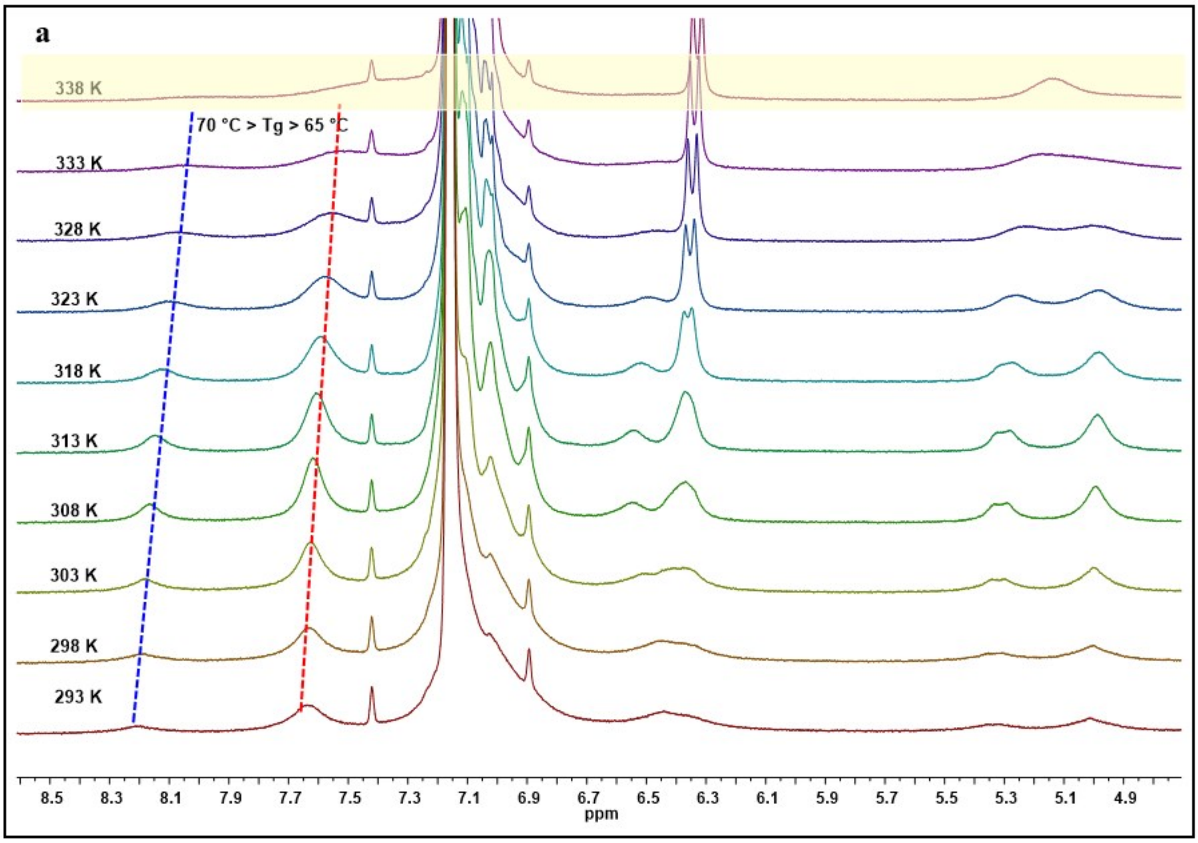

Figure S4a. Temperature-dependent ^{1}H NMR (300 MHz) of compound **(2)** in gel state (0.5 wt%) in benzene-d_6.

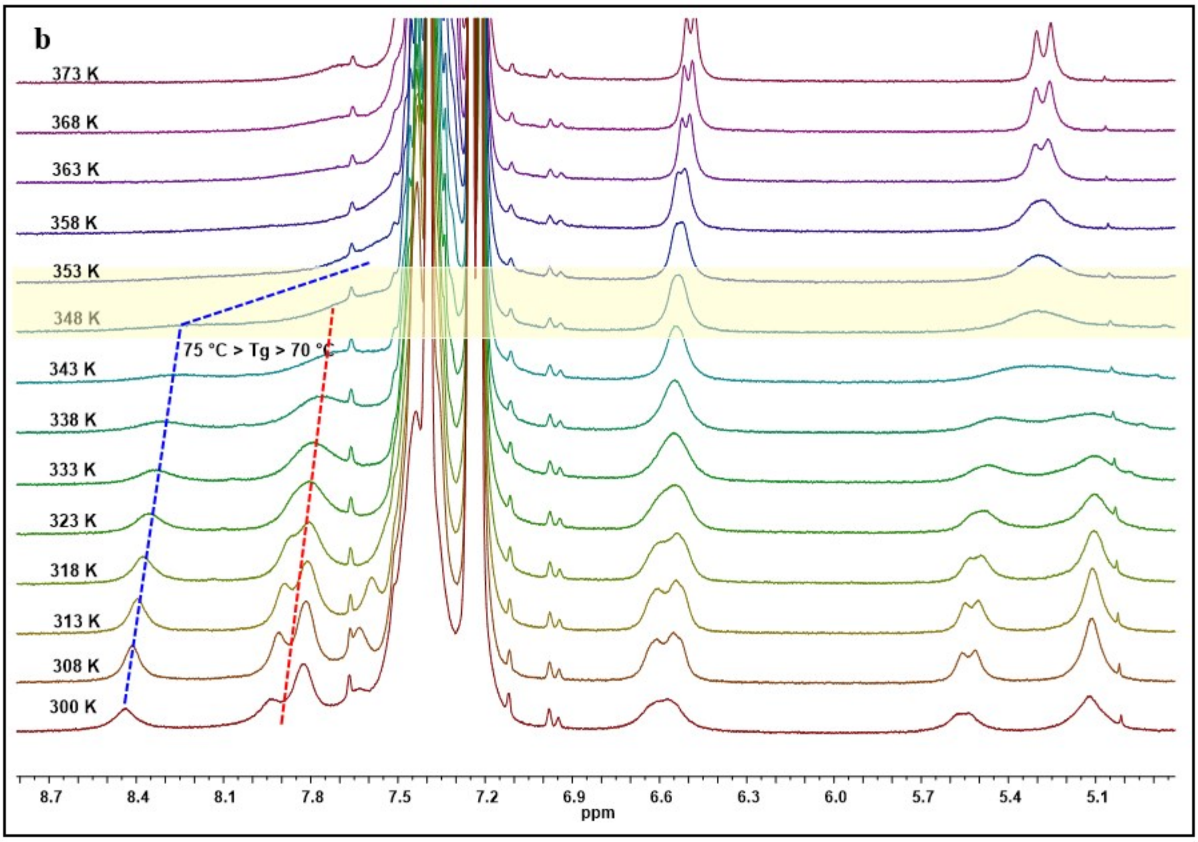

Figure S4b. Temperature-dependent [1]H NMR (300 MHz) of compound **(2)** in gel state (0.5 wt%) in chlorobenzene-d_5.

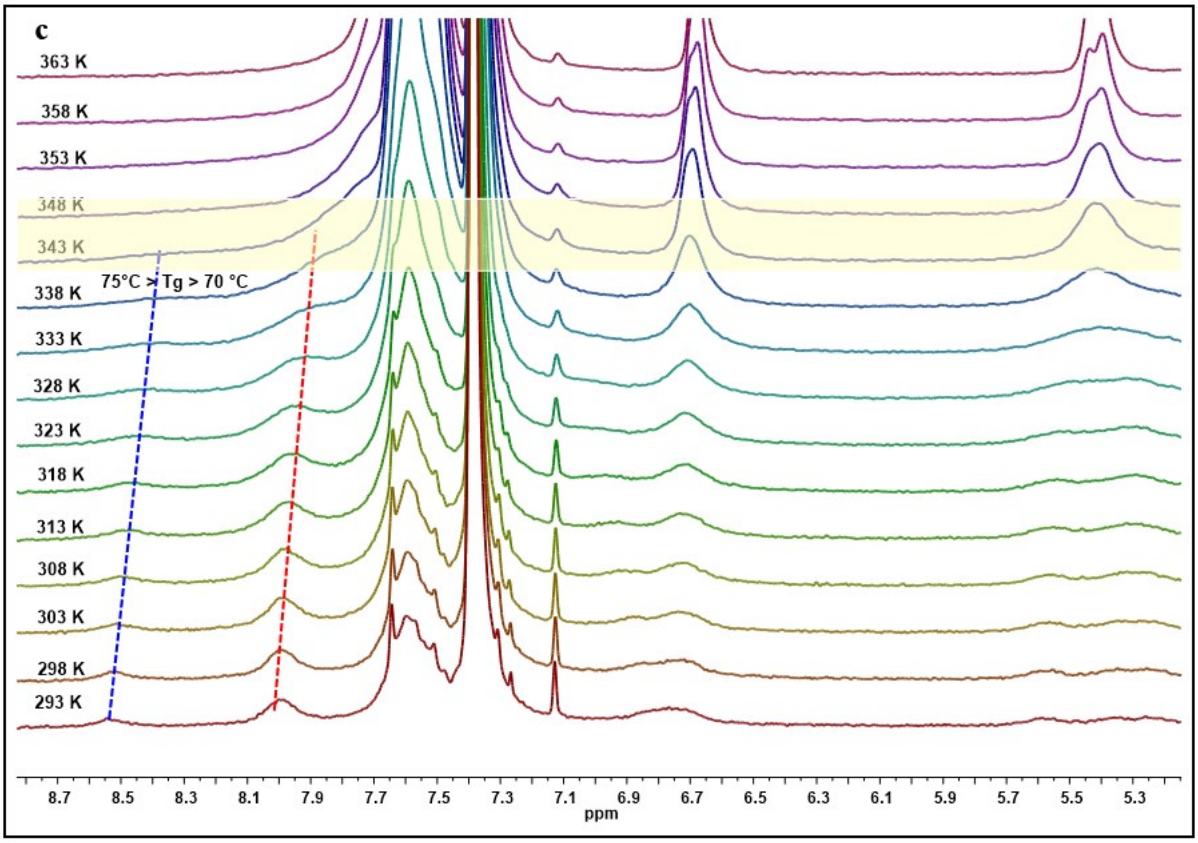

Figure S4c. Temperature-dependent [1]H NMR (300 MHz) of compound **(2)** in gel state (0.5 wt%) in *p*-xylene-d_{10}.

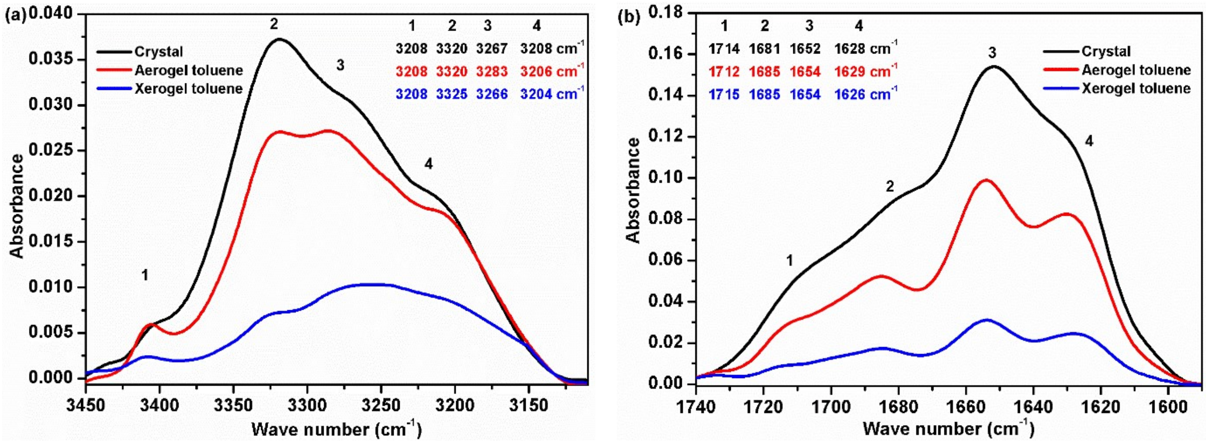

Figure S5. Comparison of the ATR-FTIR spectra in the crystal (black), aerogel (red), and xerogel (blue) states for **(2)**; a) NH stretching region, and b) CO stretching region.

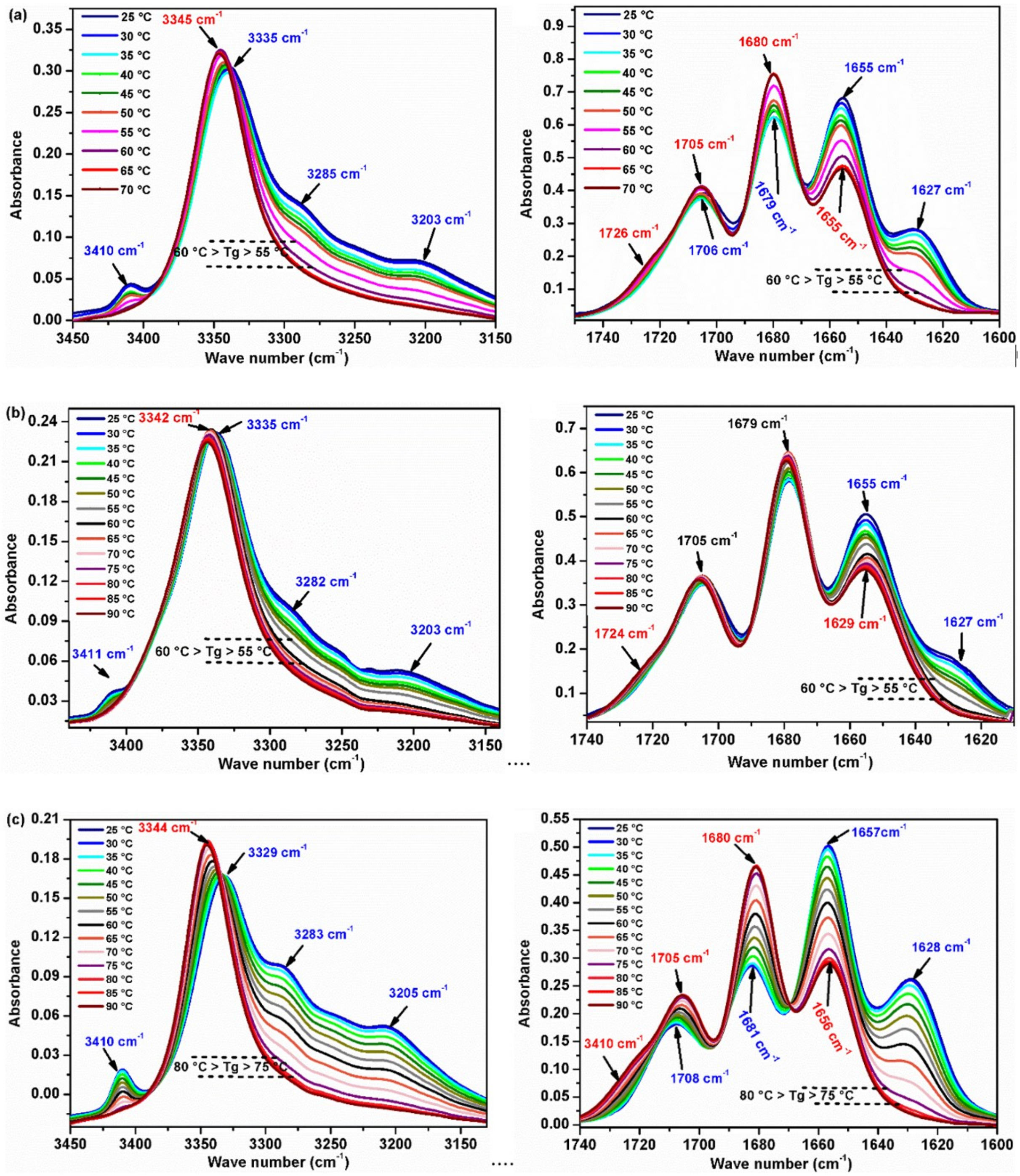

Figure S6. Temperature-dependent FTIR spectra of organogels from **(2)** at c = 0.5 wt %; NH stretching region (left) and CO stretching region (right): (a) benzene (T = 25 to 70 °C), (b) chlorobenzene (T = 25 to 90 °C), and (c) *p*-xylene (T = 25 to 90 °C).

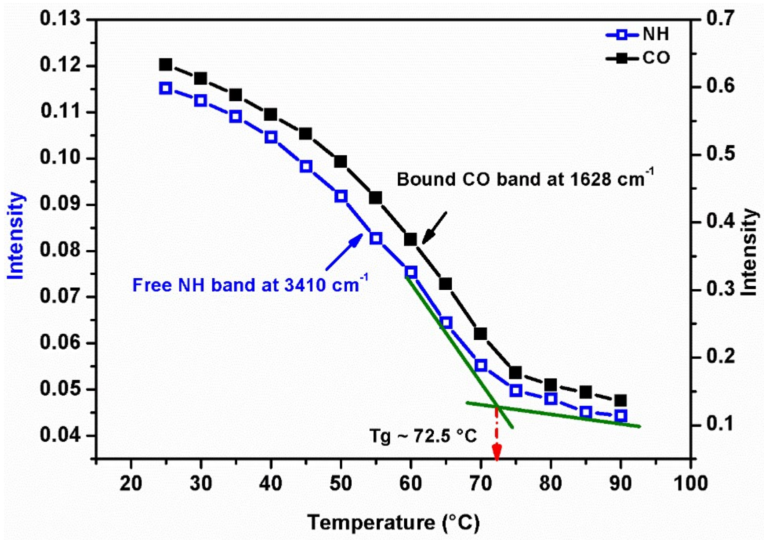

Figure S7. Sol-to-gel transition temperature (Tg) by FTIR at the inflection point of the two curves of the free NH (3410 cm^{-1}) and bound CO (1628 cm^{-1}) groups for toluene-d_8 gel form **(2)** at 0.5 wt %.

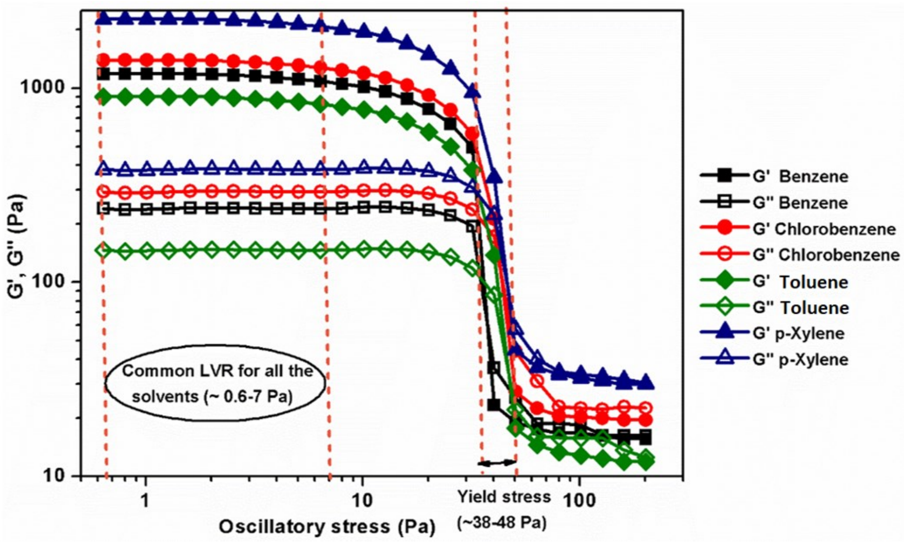

Figure S8. Oscillatory stress sweep experiments (OSS) for organogels of **(2)** (c =0.5 wt%, ω = 0.63 rad. s^{-1}, T = 25 °C).

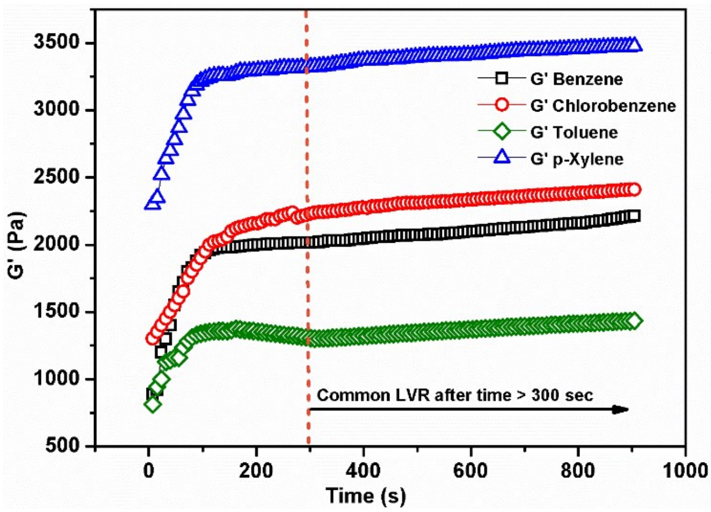

Figure S9. The rheogram shows the oscillatory time sweep experiments (OTS) for the organogels from **(2)**; (c = 0.5 wt%, ω = 0.628 rad s^{-1}, σ = 1.5 Pa, T = 25 °C).

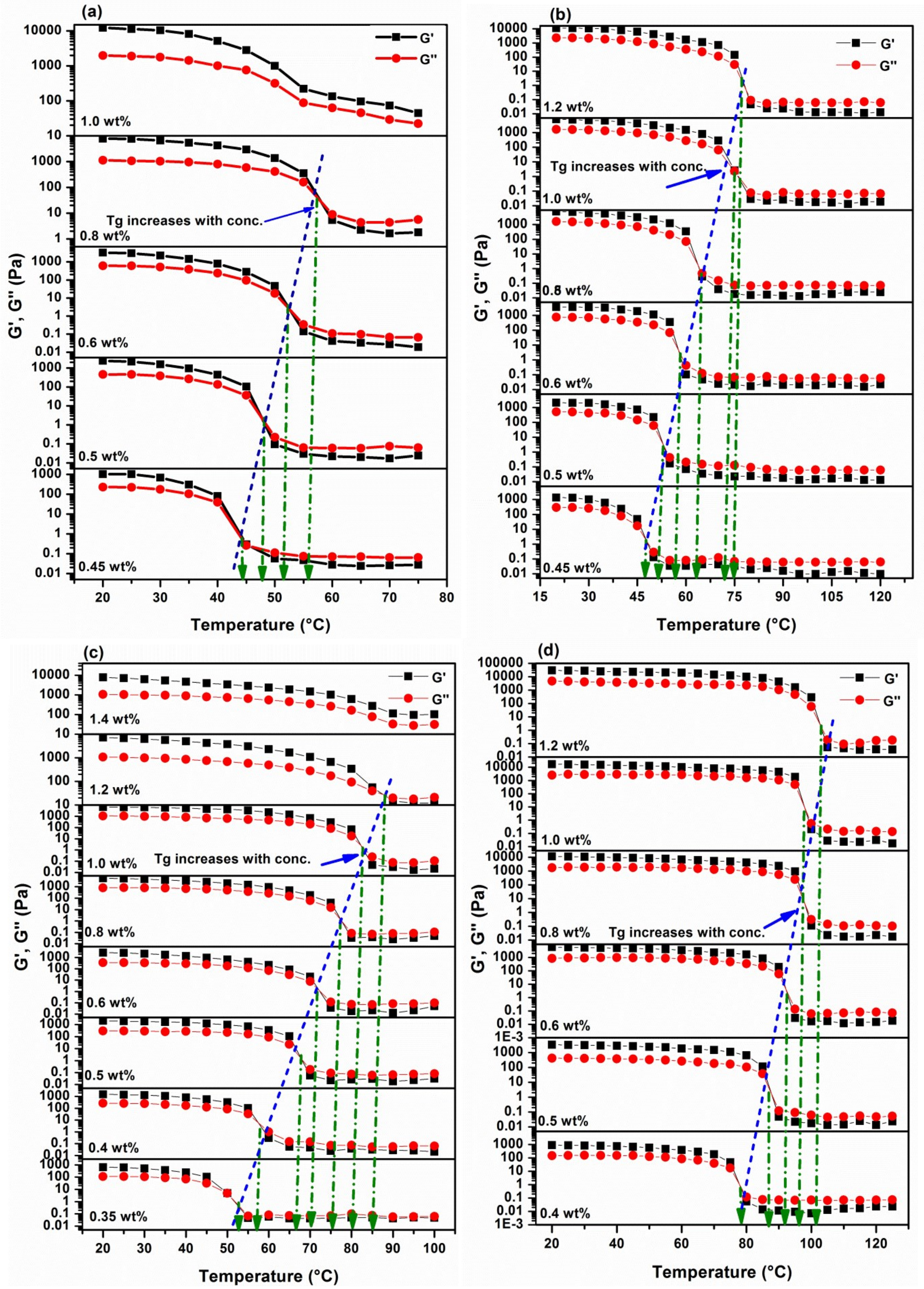

Figure S10. The rheograms for the oscillatory temperature sweep experiments, plot of the elastic (G') and viscous (G'') moduli as a function of temperature (T) for a range of concentrations in the different gelled solvents: a) benzene, b) chlorobenzene, c) toluene, and d) *p*-xylene; (ω = 0.628 rad s^{-1}, σ = 1.5 Pa).

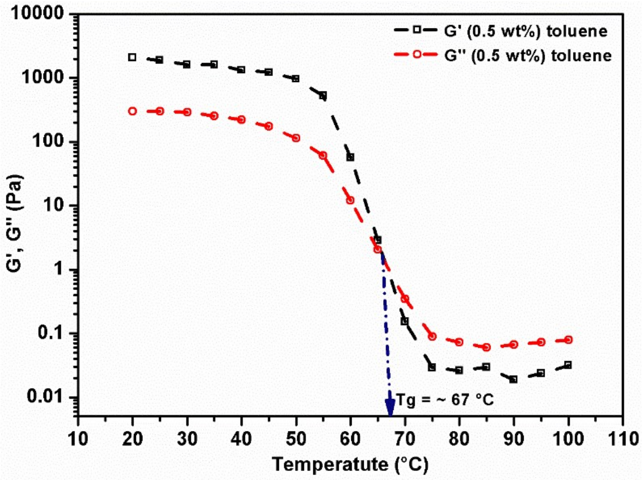

Figure S11. Oscillatory temperature sweep experiment shows the transition temperature of gel **(2)** from toluene (Tg = ~ 67 °C); (c = 0.5 wt%, σ = 1.5 Pa, ω = 0.628 rad s^{-1}).

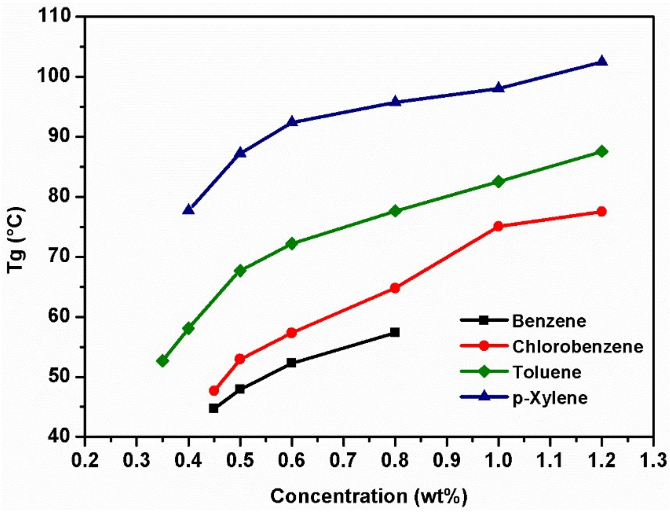

Figure S12. Variation of Tg (°C) as a function of concentration (wt%) for the organogels of **(2)** from different gelled solvents.

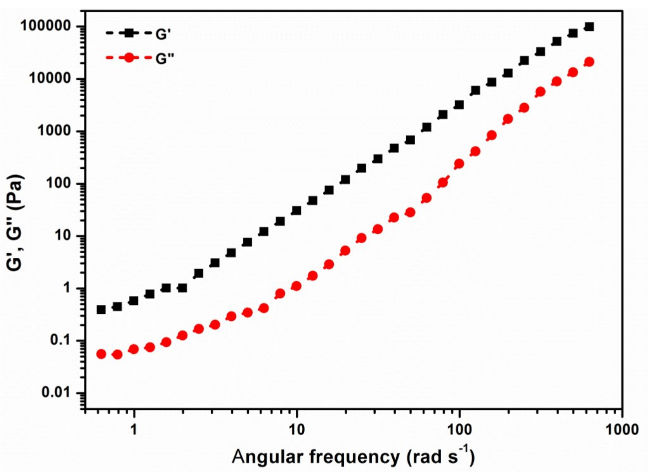

Figure S13. The rheogram of the oscillatory frequency sweep experiments (OFS); G' and G" as a function of angular frequency at the Tg of toluene gel from **(2)**; (c = 0.5 wt %, T = 65 °C, σ = 1.5 Pa).

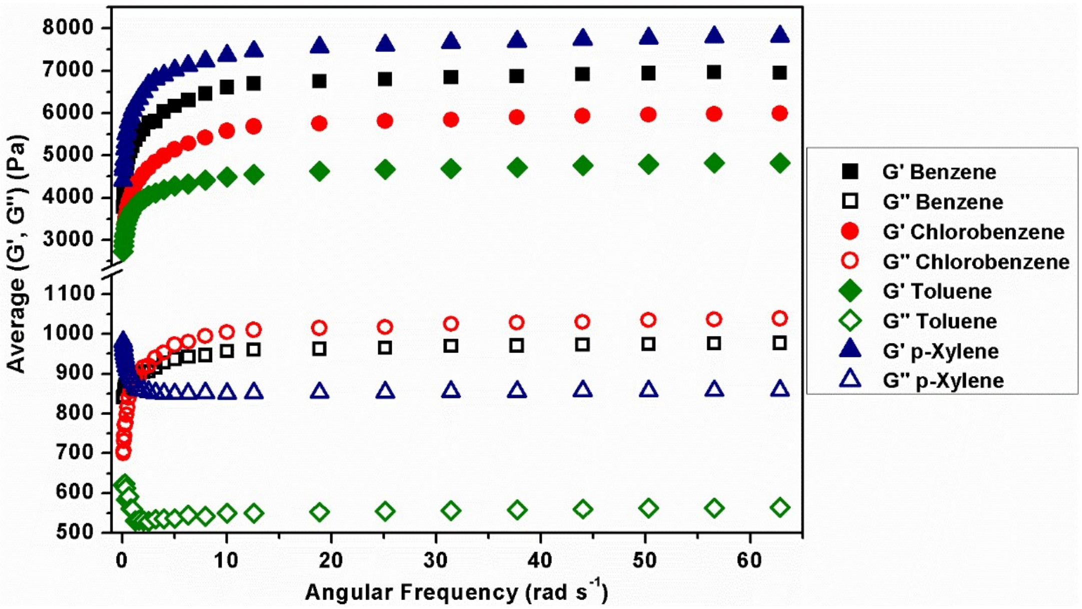

Figure S14. The rheogram shows the oscillatory frequency sweep experiments (OFS), plot of the average values of G' and G" for a range of concentrations in the different gelled solvents as a function of angular frequency (ω); (c = 0.4 - 1.0 wt %, T = 25 °C, σ = 1.5 Pa).

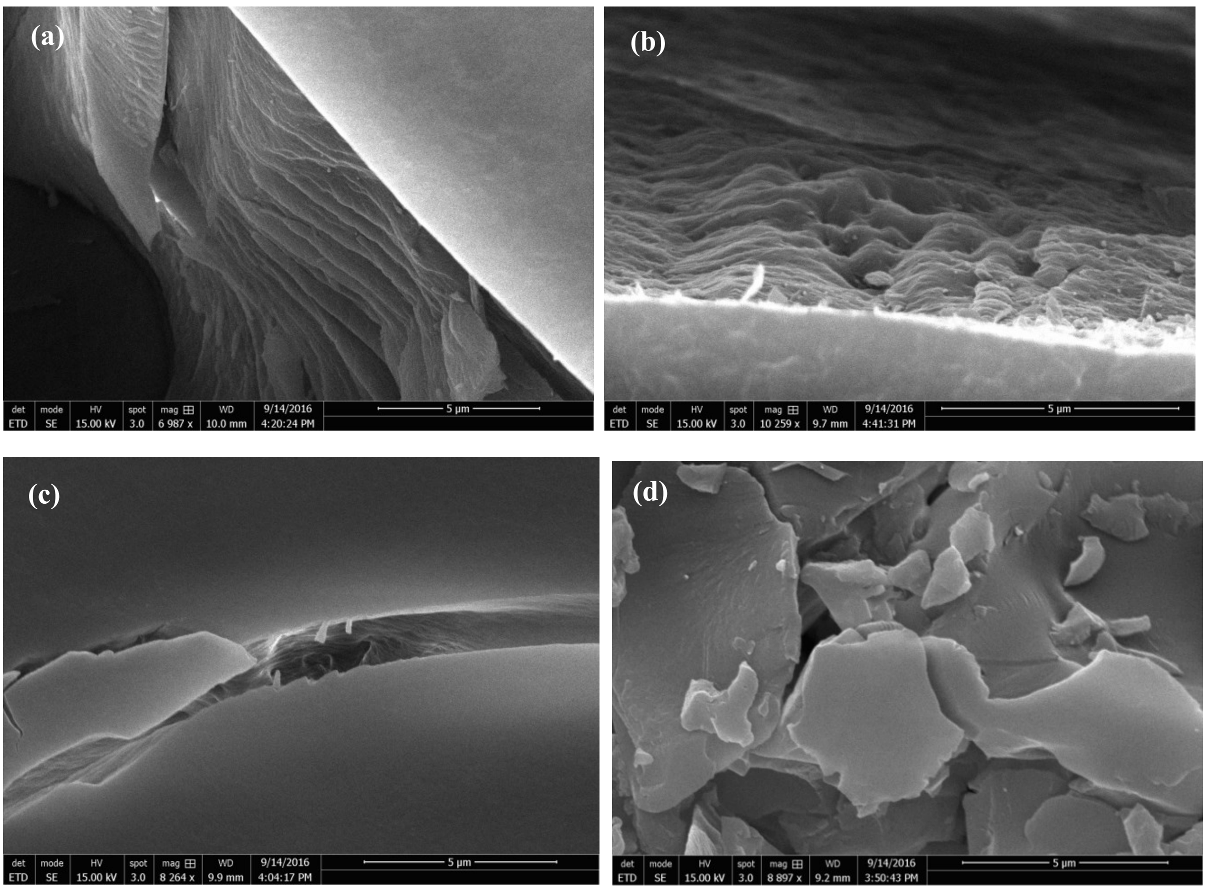

Figure S15. SEM images of xerogels obtained from air-drying of organogels of **(2)** from: (a) toluene, (b) benzene, (c) chlorobenzene, and (d) *p*-xylene**.**

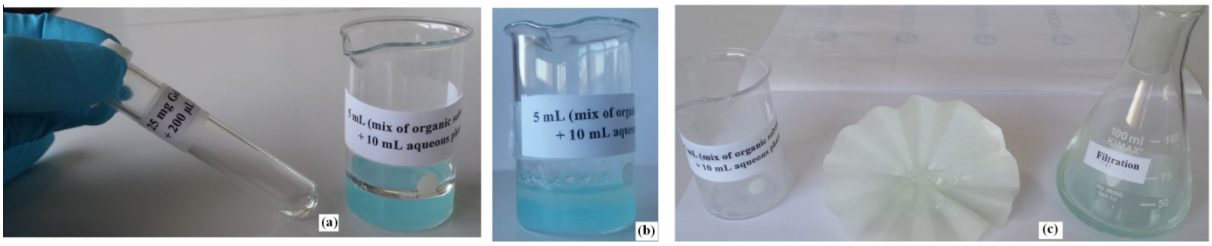

Figure S16. PSG by gelator **(2)**: (a) addition of the concentrated ethanolic solution of **(2)** (c = 12.5 % w/v) to organic/aqueous mixture, (b) gelation of the organic phase, and (c) separation of the organogel by filtration.

Table S1. % of recovered organic solvent from (water/organic) mixture by PSG method

Organic solvent	% Organic solvent recovered
Toluene	96
Benzene	94
***p*-Xylene**	82
Chlorobenzene	77
Mixture	84