Electronic Supplementary Material (ESI) for Chemical Communications.

Light Induced E-Z Isomerization in a Multi-responsive Organogel : Elucidation from ^{1}H NMR Spectroscopy

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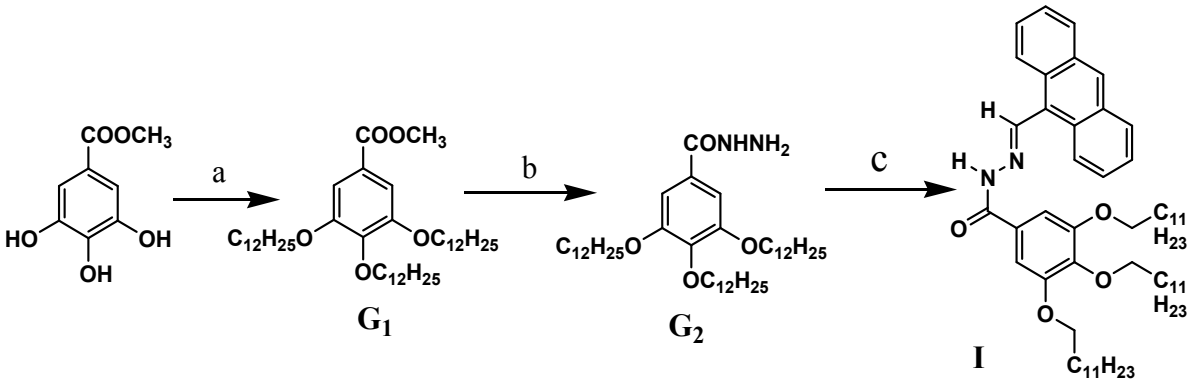
Experimental section:

Materials: Methyl 3,4,5-trihydroxybenzoate was purchased from Sigma Aldrich Chemical Co. 1-Bromo dodecane was purchased from Spectrochem Pvt Ltd (Mumbai, India). Hydrazine hydrate and potassium carbonate (K_2CO_3) were purchased from Merck, India. *N, N*-Dimethylformamide (DMF) was purchased from Ranbaxy Pvt Ltd, (Delhi, India). All other solvents used in the gelation study were purchased from local commercial sources. The solvent DMF was purified by distillation, and water was purified by double distillation before use.

Synthesis of (E) -N'-(anthracene-10-ylmethylene)-3,4,5-tris(dodecyloxy)benzohydrazide (I)

The (E) -N'-(anthracene-10-ylmethylene)-3,4,5-tris(dodecyloxy)benzohydrazide (I) was synthesized according to the following scheme and the details of each step is given below:

Reaction scheme:



Reagents and conditions:

a) $C_{12}H_{25}Br$, K_2CO_3, DMF, 75 ^{O}C, 48h, yield = 91.39%, b) NH_2NH_2. H_2O, THF, CH_3OH,

70 ^{O}C, 12h, yield = 83%; c) 9-anthracene carboxaldehyde, CH_3OH, $CHCl_3$, r.t, 2h, yield = 94%

Synthesis of Methyl 3,4,5-tris(dodecyloxy)benzoate (G1): Methyl 3,4,5-trihydroxy benzoate (1000 mg, 5.43 mmol), anhydrous K_2CO_3 (3300 mg, 23.87 mmol), n-dodecyl bromide (4362 mg, 17.5 mmol) and 20 mL dry DMF were taken together in a round bottom flask and stirred at 75 °C for 48 h under N_2 atmosphere. The reaction mixture was cooled to room temperature and poured into 100 ml ice-cold water and was extracted with diethyl ether (3 x 25 mL). The organic layer was washed with brine (2 x 25 mL) and was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to get the crude product as light brown color solid. It was purified by column chromatography using basic alumina as stationary phase and petroleum ether as eluent to obtain pure product as colorless solid (3420 mg, 91.39%); **1H NMR (500 MHz, CDCl3): δ (ppm):** 7.27 (s, 2H), 4.00 - 4.04 (m, 6H), 3.89 (s, 3H), 1.79 - 1.84 (m, 4H), 1.73 - 1.76 (m, 2H), 1.45 - 1.50 (m, 6H), 1.27 - 1.35 (m, 48H), 0.89 (t, *J* = 6.5 Hz, 9H) (Fig. SA).

Synthesis of 3,4,5-tris(dodecyloxy)benzohydrazide (G_2):

Compound **G_1** (1000 mg, 1.45 mmole) and hydrazine monohydrate (3.6 mL, 72.54 mmole) were dissolved in MeOH (10 mL) and THF (3 mL). The reaction mixture was stirred at 70°C for 12 hours. After the heating was stopped, the reaction mixture was allowed to cool to room temperature, and the volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed with H_2O. The organic layer was then dried over anhydrous Na_2SO_4, and the solvent was evaporated to get crude product, which was purified by column chromatography using silica gel as the stationary phase and 5% MeOH in CH_2Cl_2 as the eluent to get the pure product as a white solid. (830 mg, 83 %); **^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm):** 6.92 (s, 2H),

3.96 - 3.99 (m, 6H), 1.71 - 1.81 (m, 6H), 1.42-1.45 (m, 6H), 1.26 – 1.29 (m, 48H), 0.88 (t, J=6.4 Hz, 9H) (Fig. SB); **IR (KBr) ν** = 3422, 3245, 2921, 2850, 1627, 1582, 1500, 1468, 1426, 1389, 1344, 1239, 1119, 844 and 720 cm^{-1}.

Synthesis of (E) -N'-(anthracene-10-ylmethylene)-3,4,5-tris(dodecyloxy)benzohydrazide (I):

A solution of 9-anthracene carboxaldehyde (119.6 mg, 0.58 mmole) in methanol was added drop wise to a $CHCl_3$ solution of compound **G_2** (400 mg, 0.58 mmole). The mixture was stirred for 2 hour and the resulting product was dried under vacuum and then washed with ethanol to get pure product as a yellow powder (478.7 mg, 94 %); **^{1}H NMR (400 MHz , $CDCl_3$): δ (ppm):** 9.71 (s, CH=N, 1H), 9.61 (s, NHCO, 1H), 8.59 (broad, AnH, 2H), 8.47 (s, AnH, 1H), 8.0 (d, J= 8.4 Hz, AnH, 2H), 7.44 - 7.52 (m, AnH, 4H), 7.18 (broad, ArH, 2H), 4.0 - 4.03 (m, $ArCH_2O$, 6H), 1.73 - 1.78 (m, 6H), 1.45 - 1.47 (m, 6H), 1.26 (m, 48H), 0.88 (t, J=6.4 Hz, 9H) (Fig. SC); **^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm):** 153.07, 144.54, 141.28, 131.41, 130.17, 129.38, 128.69, 127.89, 126.18, 124.82, 123.31, 105.51, 73.54, 68.86, 32.08, 30.35, 29.86, 29.82, 29.65, 29.52, 29.27, 26.16, 26.12, 22.84, 14.26 (Fig. SD); **IR (KBr) ν** = 3433, 3184, 3057, 2920, 2850, 1644, 1582, 1543, 1501, 1467, 1426, 1368, 1334, 1227, 1118, 1074, 1015, 840, 783 and 728 cm^{-1}; **MS (MALDI-TOF):** ***m/z*** Calcd for $C_{58}H_{88}N_2O_4$: 876.67, found: 877.655 $[M+H]^+$, 899.640 $[M+Na]^+$ (Fig. SE).

Preparation of organogel:

Compound **I** (10 mg) was taken in a glass tube and 1 ml methyl cyclohexane was added to it. The mixture is sealed in a glass tube sonicated and heated to 70 ^{O}C to make a homogeneous solution that on cooling to 30 ^{O}C produces fluorescent, transparent, thixotropic gel. The compound **I** yields gel in many organic solvents (Table S1) but thixotropic behavior is mainly found in methyl cyclohexane. The minimum gelation concentration (MGC) of **I** gel is found to be 0.05% (w/v) in methyl cyclohexane by test tube tilting method at 30 °C.

Thermal study.

Thermal study of the **I** gel (3%, w/v) is investigated by differential scanning calorimetry (Perkin Elmer, Diamond DSC) using large volume capsules (LVC) fitted with O-rings under nitrogen atmosphere. The instrument is calibrated with indium before each set of experiment. The sample is taken at the LVC pan and is hermetically sealed with rubber O-ring. It is equilibrated at 0 ^{O}C for 10 min. and heated at the heating rate of 10 ^{O}C /min. to 70 ^{O}C. It is then cooled at the cooling rate 5 ^{O}C/min. to 0 ^{O}C. The melting point is determined from the computer attached to the instrument.

Rheology. To understand the mechanical property of the **I** gel we have performed rheological experiment with an advanced rheometer (AR 2000, TA Instrument, USA) using cone plate geometry on a peltier plate. The diameter of the plate is 40 mm and cone angle 4° with plate gap of 121 μm.

Diffraction Study.

The wide-angle X-ray scattering (WAXS) experiment of xerogels and powder of compound **I** were performed using a Bruker AXS diffractometer (model D8 Advance) using a Lynx Eye detector. The instrument was operated at 40 kV voltage and at 40 mA current. Samples were

placed on the glass slides and were scanned in the range of 2θ = 4-50° at the scan rate of 0.5 s/step with a step width of 0.02°.

Microscopy.

The morphology of the gels was investigated by transmission electron microscopy (TEM; JEOL, model 2010EX). A small portion of the **I** gel in methyl cyclohexane was diluted and was drop-casted on carbon-coated copper grid (300 mesh) and the sample was dried in open air at 30 °C. Finally, the sample was kept in a vacuum for one day at 30 °C before the experiment. SEM images of the sample was observed through a FESEM instrument (JEOL, JSM 6700F) operating at 5 kV after platinum coating. A small portion of the gel **I** (in methyl cyclohaxane) was placed on a glass coverslip and dried in air at 30 °C for one day and finally in a vacuum. The AFM study was conducted in the non contact mode at a resonance frequency of the tip end of ~250 KHz by casting a film of the gel on a fresh silicon wafer. The morphology of the dried films were studied using an atomic force microscope (Veeco, model AP 0100).

Spectroscopy: ^{1}H and ^{13}C NMR data of synthesized compounds were collected on a Bruker spectrometer (^{1}H: 400 MHz and 500 MHz; ^{13}C: 300 MHz). The xerogels before and after irradiation with UV- light were dissolved in the $CDCl_3$ to get the NMR spectra. The FTIR spectra of **I** powder and the xerogel were recorded using the KBr pellets of the samples in an FTIR-8400S instrument (Shimadzu). The UV-vis spectra of the samples were recorded on a Hewlett-Packard UV-vis spectrophotometer (model 8453) using a cuvette of 1 mm and 1cm path length. In fluorescence studies of the **I** gel samples were prepared in a sealed cuvette, and carried out in a Horiba Jobin Yvon Fluoromax 3 instrument. Each gel sample in a quartz cell of 1 cm

path length was excited at 370 nm and the emission scans were recorded from 390 to 700 nm using slit width of 5 nm with an increment of 1 nm wavelength having an integration time of 0.1 s.

Avrami Treatment.

The Avrami equation is expressed as

$$\ln(-\ln(I_\infty - I_t)/(I_\infty - I_0)) = \ln k + n \ln t$$

k is the rate constant, t is the time of transformation, and n is a constant. I_0 is the intensity at t = 0 and I_∞ is the intensity at $t = \infty$. Thus, by plotting the left-hand side of the above equation with ln t, straight lines are expected, and the rate constant k of the process can be obtained from the intercept of the plot.

MALDI-TOF. Mass spectra of **I** solution in dichloro methane was recorded using MALDI TOF Ultraflextreme (Bruker Daltonics) instrument using Dithranol as matrix.

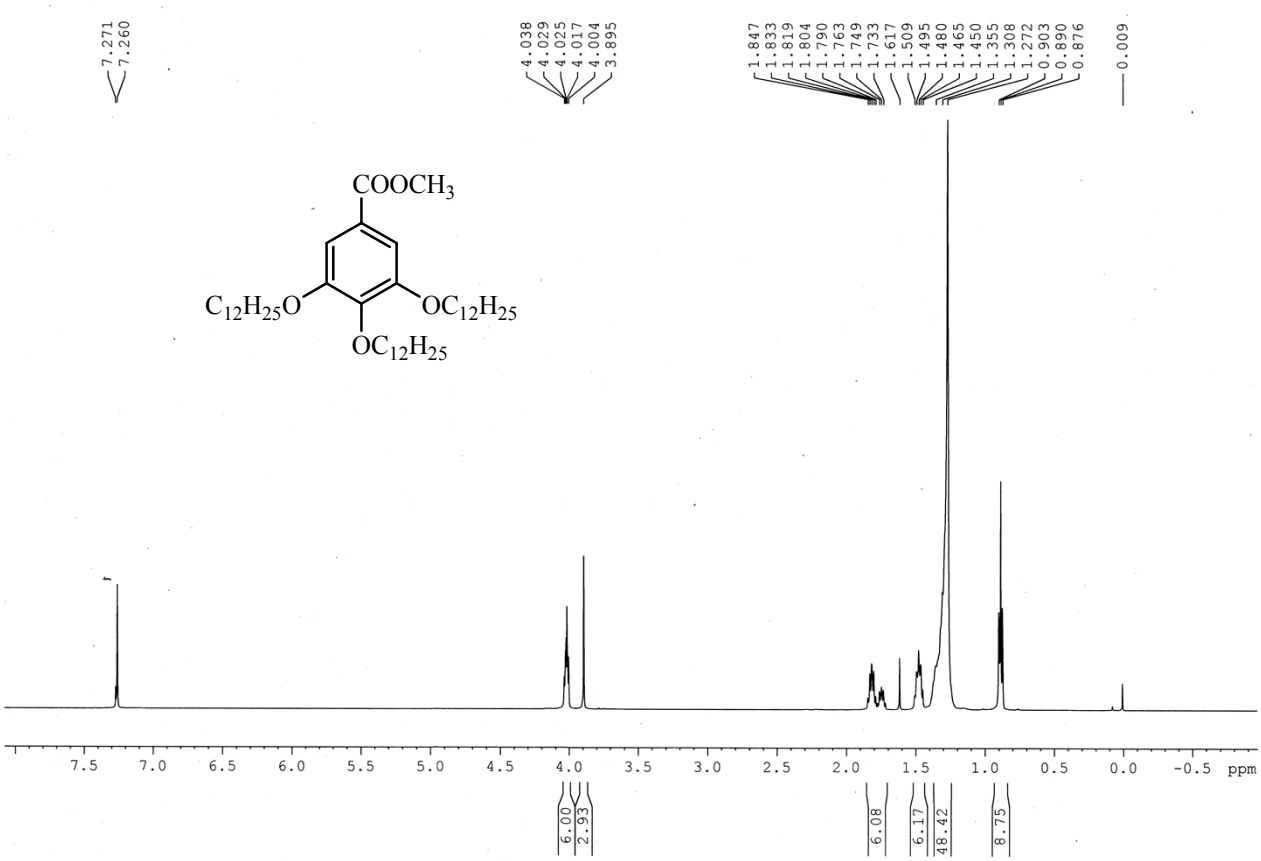


Fig. SA ^{1}H NMR (500MHz) spectrum of compound $\mathbf{G_1}$ in $CDCl_3$.

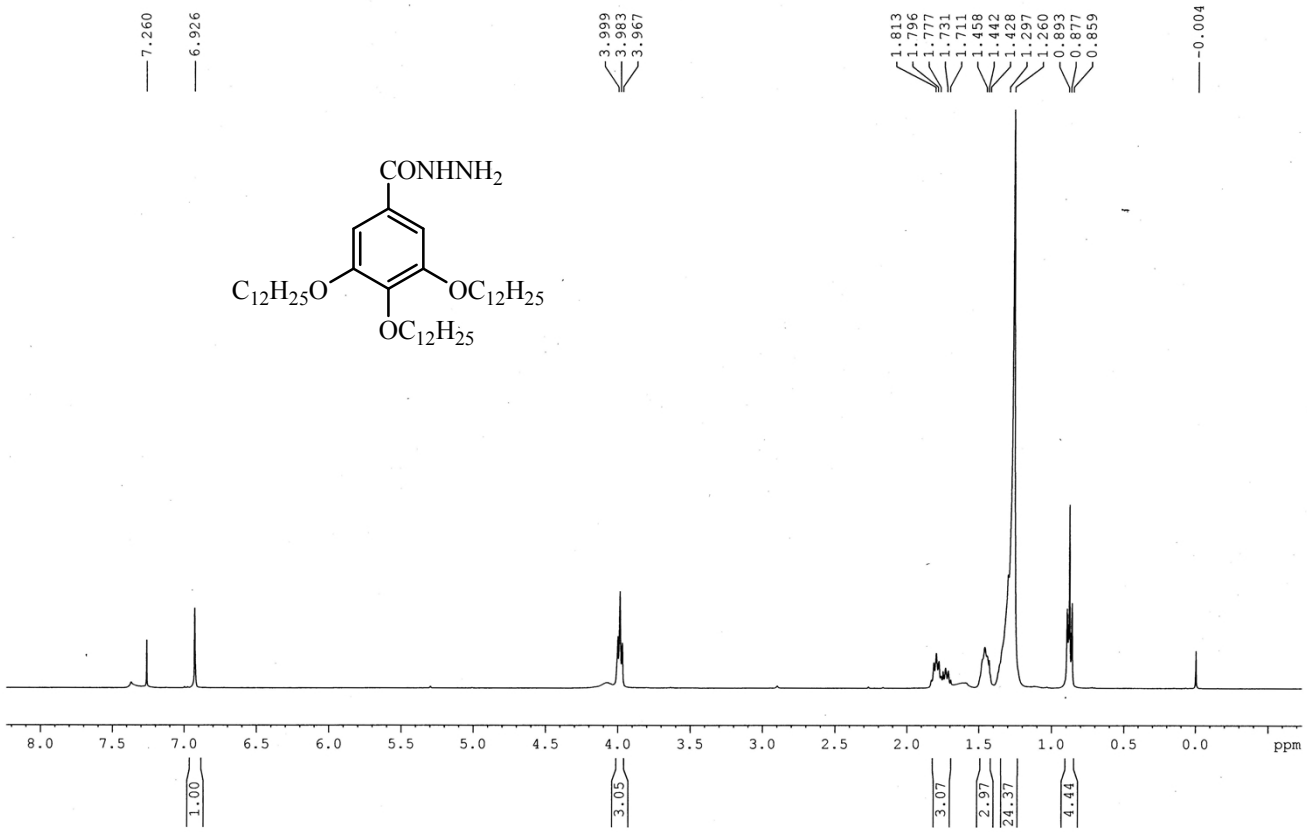


Fig. SB ^{1}H NMR (400MHz) spectrum of compound $\mathbf{G_2}$ in $CDCl_3$.

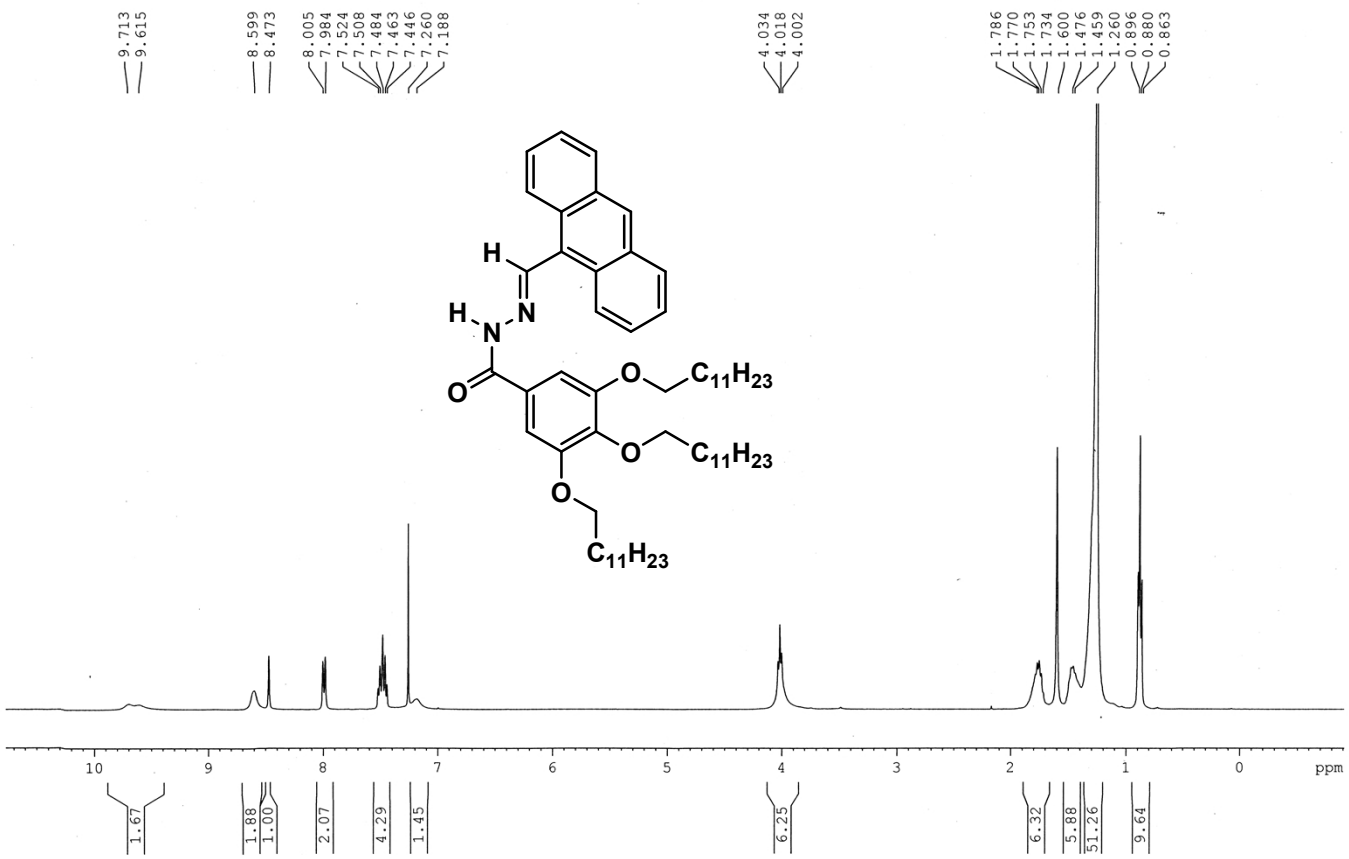


Fig. SC ^{1}H NMR (400MHz) spectrum of compound **I** in $CDCl_3$.

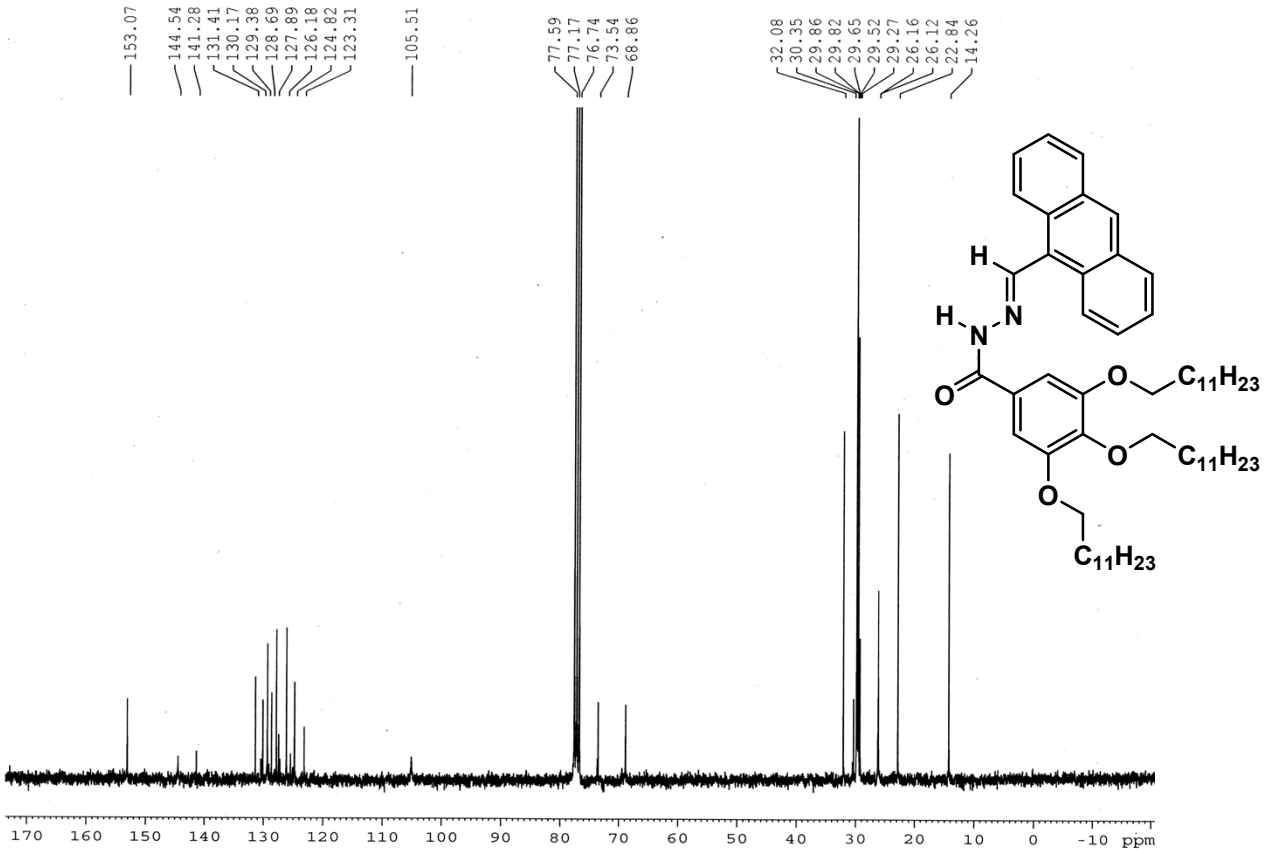


Fig. SD ^{13}C NMR (300MHz) spectrum of compound **I** in $CDCl_3$.

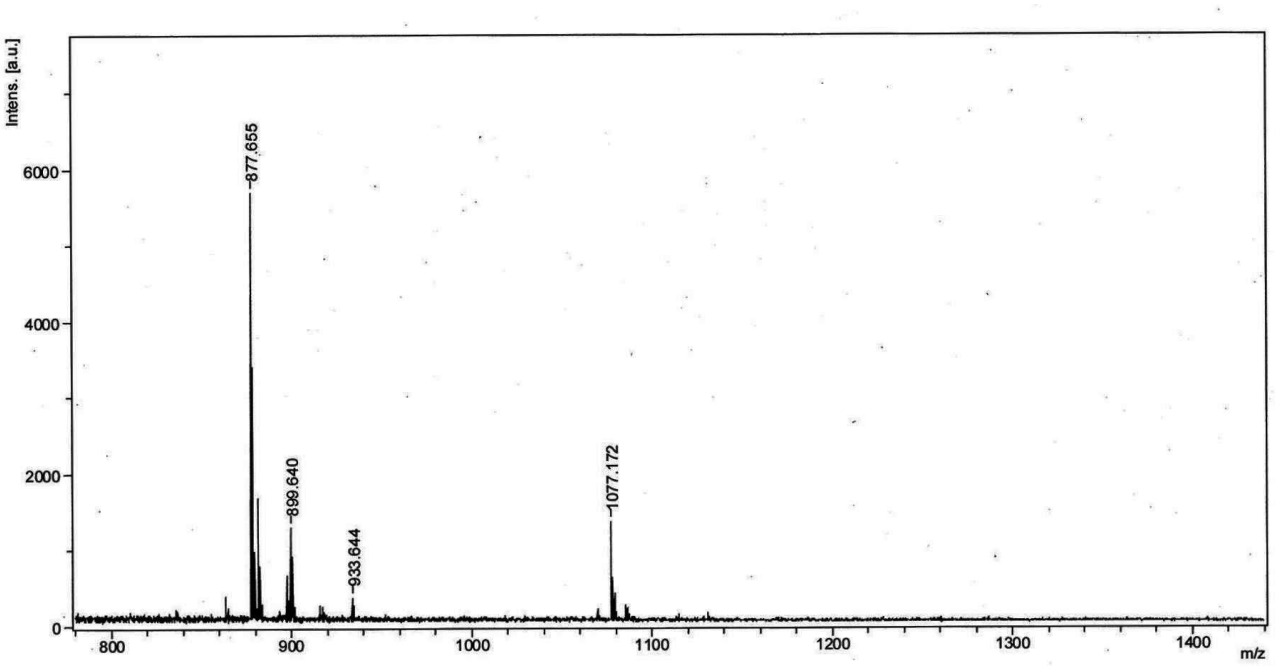


Fig. SE The MALDI-TOF of compound **I**

Table S1: Gelation test of compound I in different solvents, G = gelation, **NG** = no gelation, **SA** = self-assembly, **CGC** = critical gelation concentration, **r.t** = room temperature (30 ^{O}C).

S.N	**Name of the solvents**	**Gelation test (CGC, % w/v))**	**Solubility of I**	**Observation**
1.	Methyl cyclohexane	G (0.05)	Soluble on heating	Transparent gel at r.t
2.	Petrolium ether	G (0.06)	soluble on heating	Transparent gel at r.t
3.	Cyclohexane	G (0.05)	Soluble on heating	Transparent gel at r.t
4.	Methanol	NG	Insoluble on heating	-
5.	Ethanol	NG	Insoluble on heating	-
6.	Propanol	SA (1)	Partial soluble on heating	-
7.	t-butanol	SA (1)	Partial soluble on heating	-
8.	Acetone	NG	Insoluble on heating	-
9.	Dimethylsulphoxide	G (0.1)	Soluble on heating	Opaque gel at r.t
10.	Dimethylformamide	G (0.1)	Soluble on heating	Opaque gel at r.t
11.	Water	NG	Insoluble on heating	-
12.	Tetrahydrofurane	G (1.5)	Soluble at r.t	Opaque gel at 0 ^{O}C
13.	Acetonitrile	NG	Insoluble on heating	-
14.	Chloroform	G (3)	Soluble at r.t	Opaque gel at 0 ^{O}C
15.	Dicloromethane	G (1)	Soluble at r.t	Opaque gel at 5 ^{O}C
16.	Benzene	G (1.5)	Soluble on heating	Opaque gel at r.t
17.	Toluene	G (1)	Soluble on heating	Opaque gel at r.t

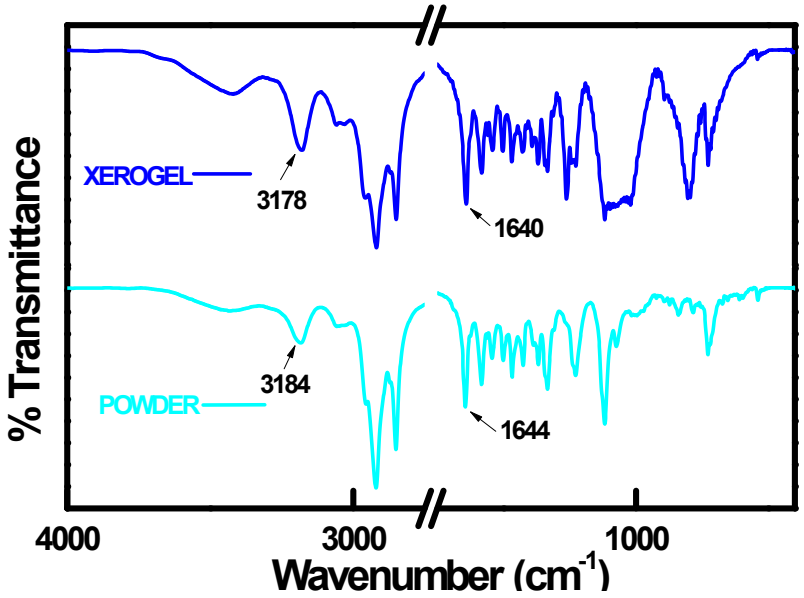


Fig. S1 FTIR spectra of **I** powder and its xerogel.

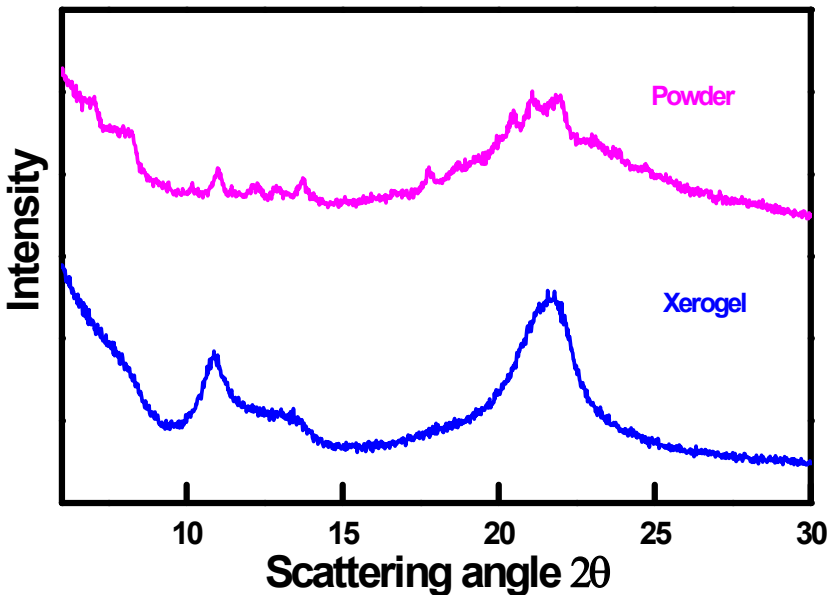


Fig. S2 WAXS patterns of **I** powder and its xerogel.

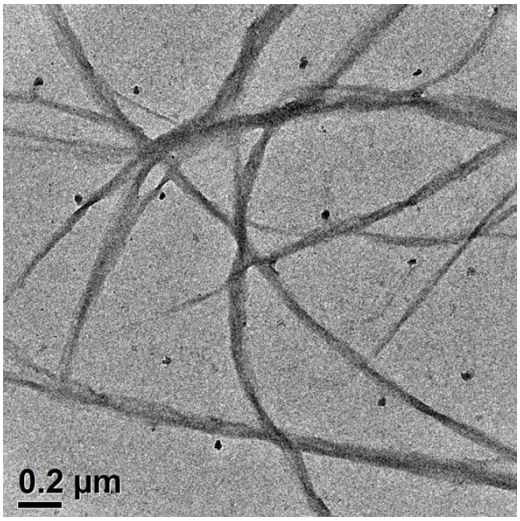


Fig. S3 TEM images of **I** xerogel at 0.3% (w/v).

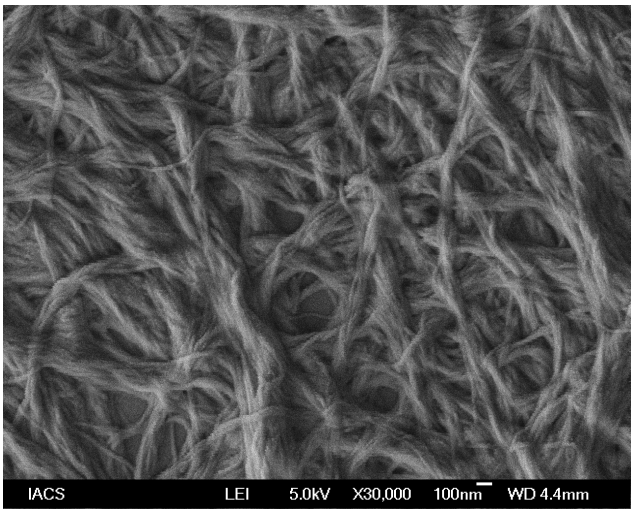


Fig. S4 FESEM images of **I** xerogel at 0.3% (w/v).

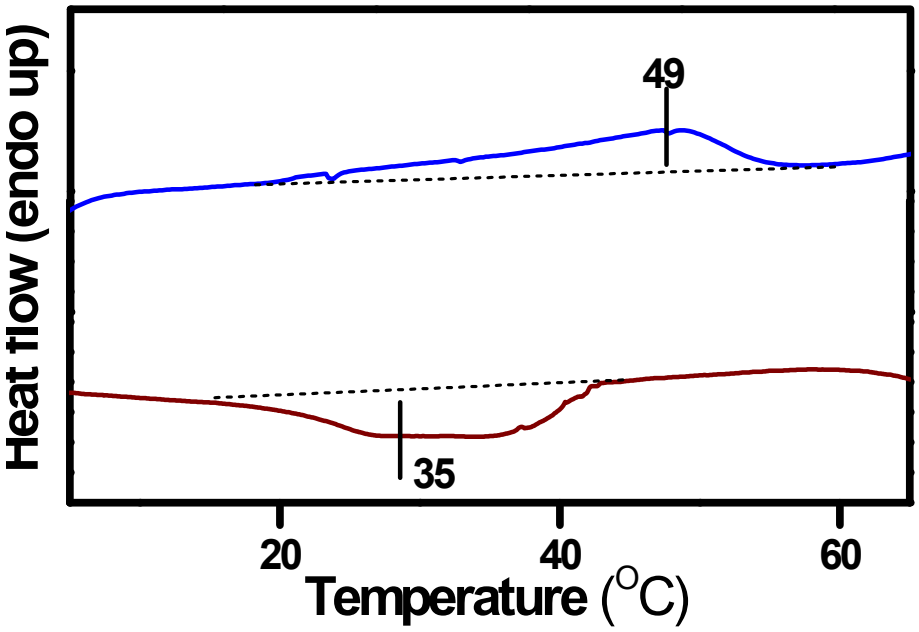


Fig. S5 DSC heating and cooling thermograms of **I** gel at a concentration of 3 % w/v.

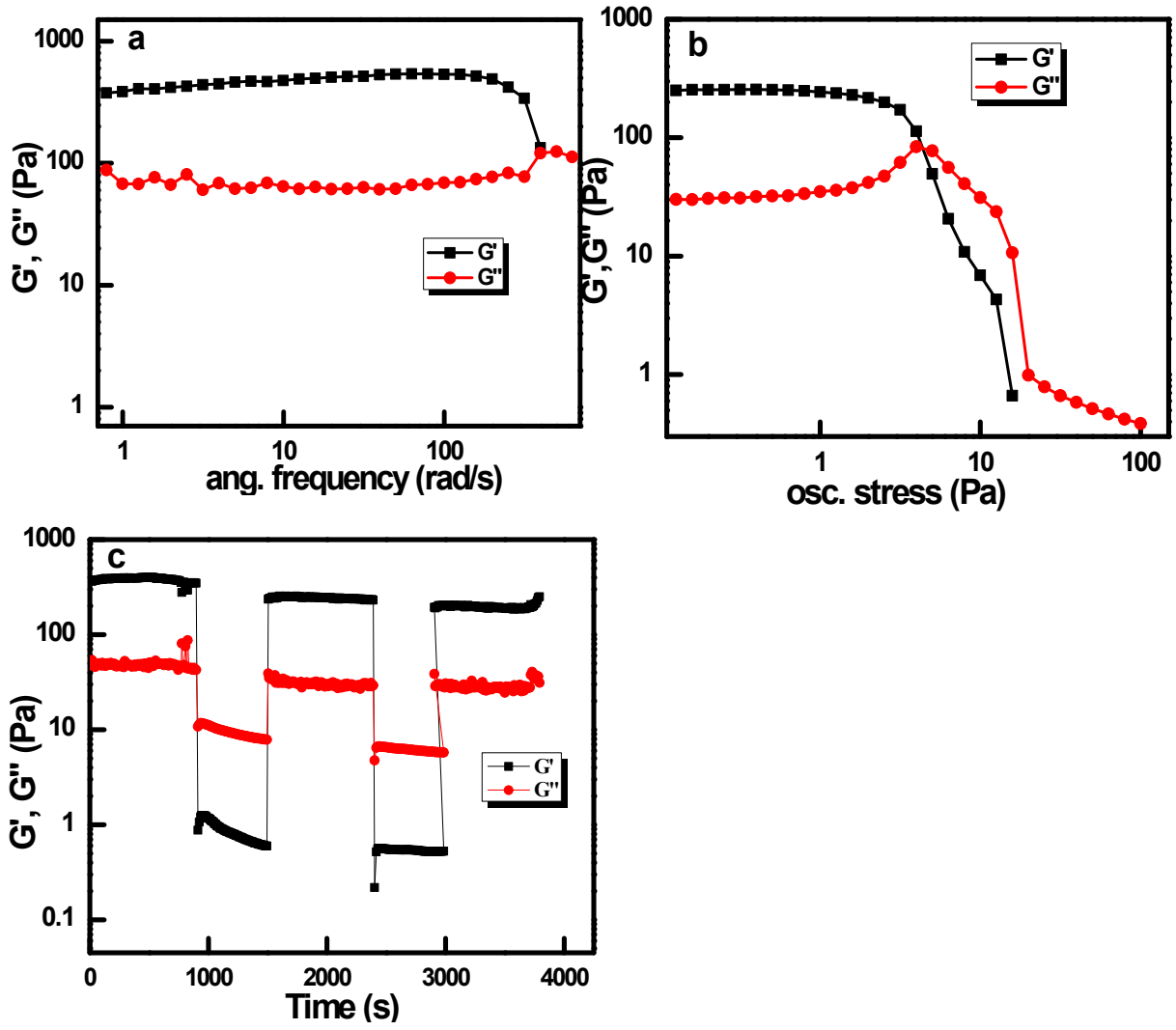


Fig. S6 Rheological properties of the **I** gel at 1.0 % (w/v) at 25 ^{0}C.(a) Frequency sweep data showing variation of G' and G" with frequency, (b) Stress sweep measurement at a constant frequency 1 Hz, (c) Continuous step strain measurement at alternate 100% and 0.1% strain with time scale.

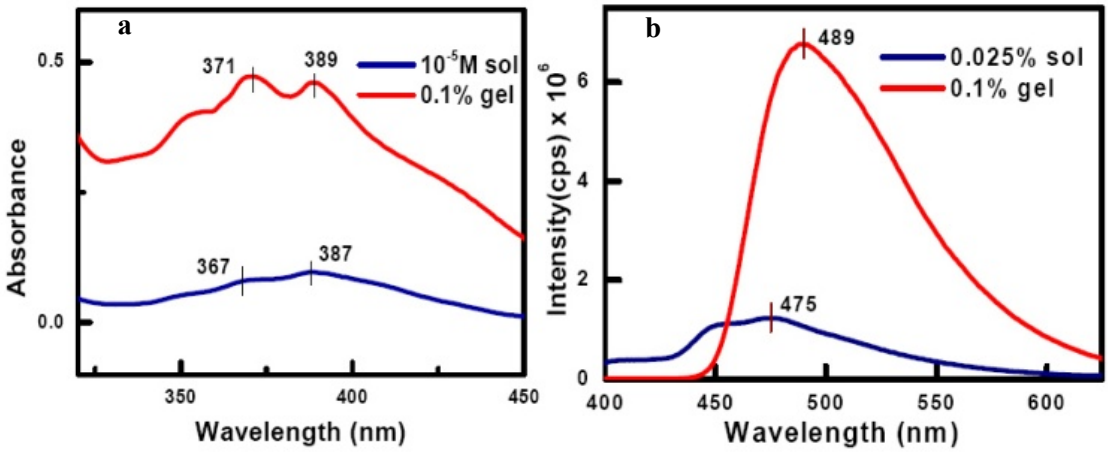


Fig. S7 (a) UV-vis spectra of **I** solution (10^{-5} M) and gel (0.1 % w/v) in methyl cyclohexane. (b) Fluorescence spectra of **I** sol (0.025% w/v) and gel (0.1% w/v) for excitation at 370 nm.

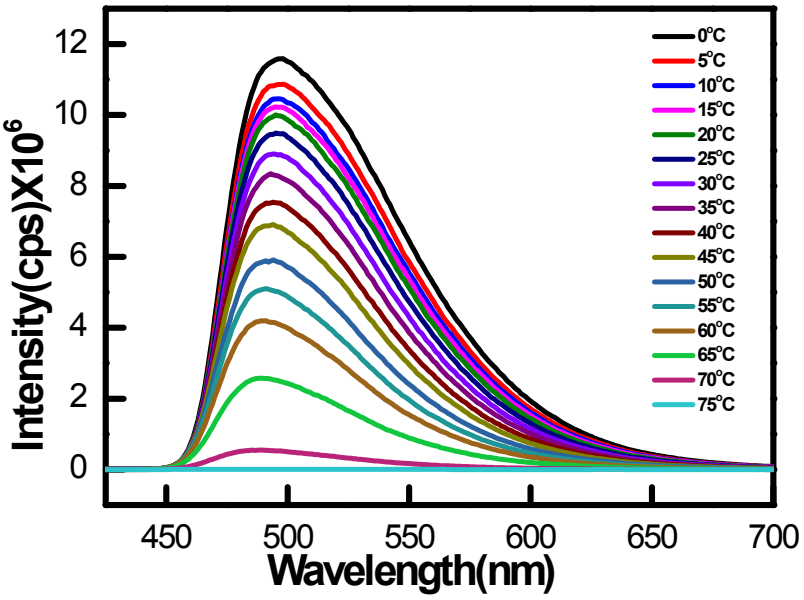


Fig. S8 Temperature dependent fluorescence spectra of **I** gel 0.2% w/v for excitation at 370 nm.

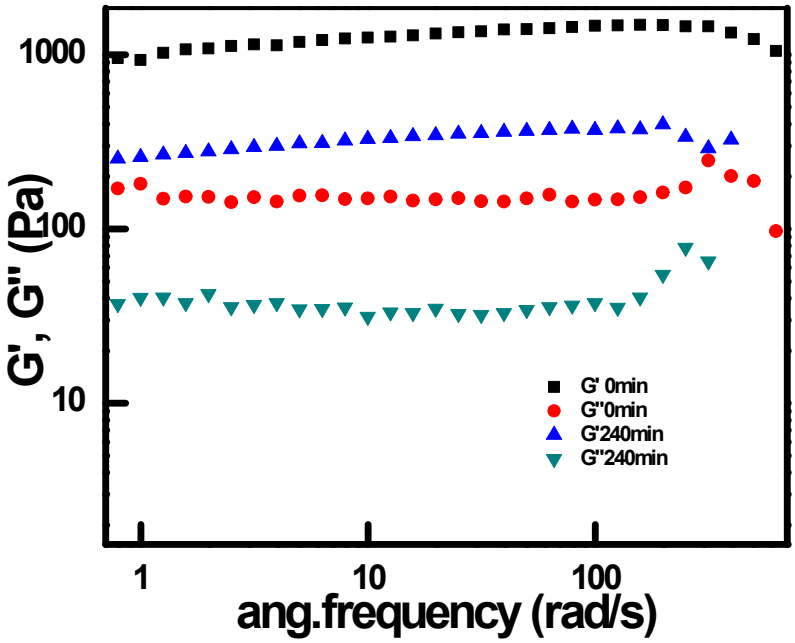


Fig. S9 Frequency sweep experiments on the **I** gel 1% (w/v) at different time intervals after photoirradiation at 365 nm.

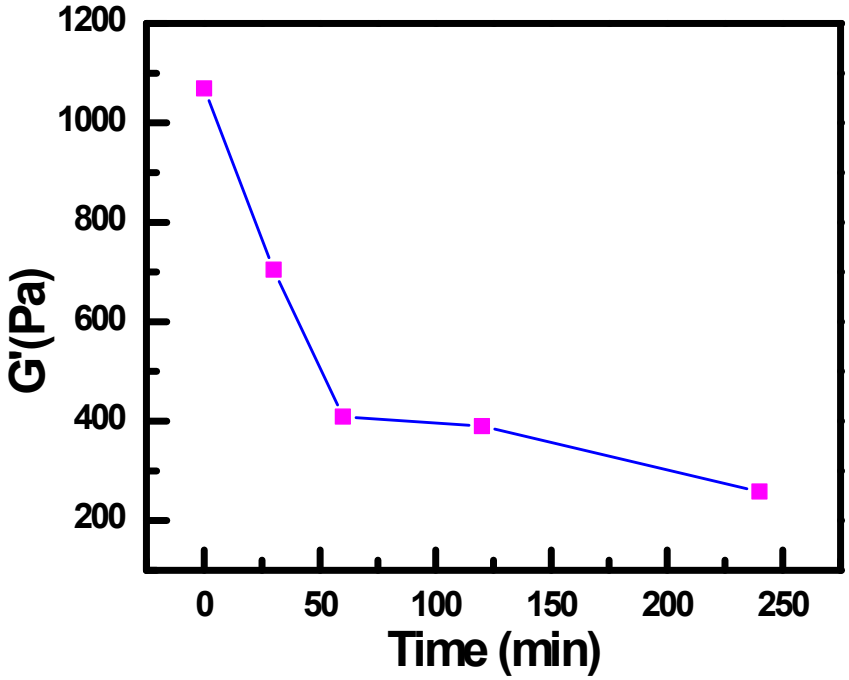


Fig. S10 Variation of G' of **I** gel 1% (w/v) at different time of UV-irradiation at 365 nm wavelength.

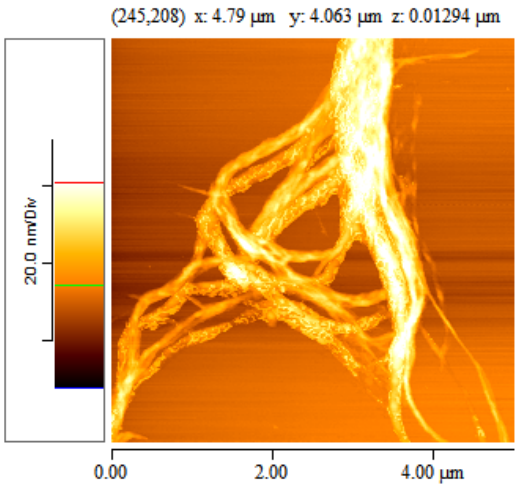


Fig. S11 AFM image of **I** after photoirradiation.

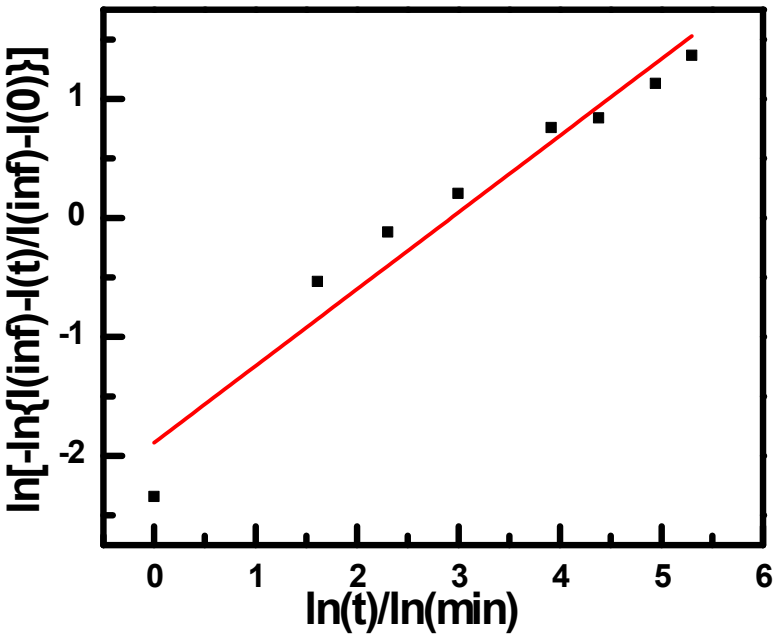


Fig. S12 Avrami plot of **I** gel 0.6 % (w/v) at different time intervals upon photo-irradiation at 365 nm.

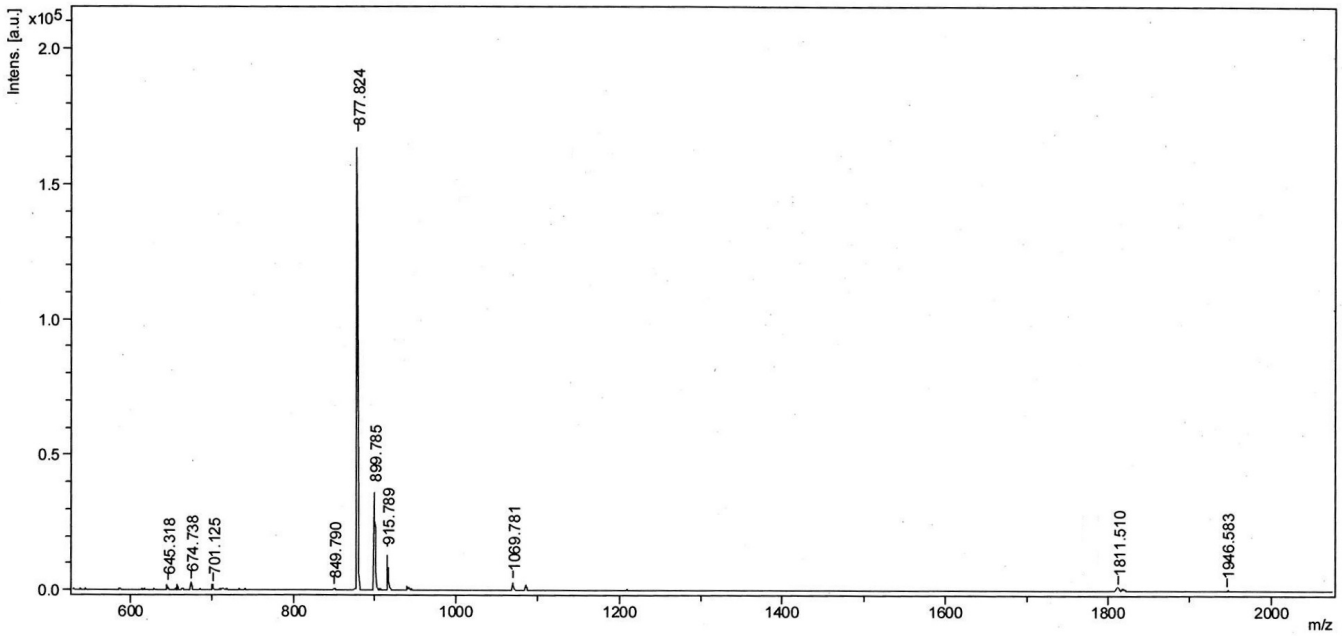


Fig. S13 MALDI-TOF of compound **I** after UV-irradiation at 365 nm wavelength for 24 hours.