Electronic Supplementary Information

Bolaamphiphilic Amino Acid Appended Photo-switching Supramolecular Gel and Tuning of Photo-switching Behaviour

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Table S1. Gelation behaviour of the hydrogelator at different pH's of 50 mM phosphate buffer.

pH at which gel was obtained	MGC (% w/v)
7.46	1.3
8.00	2.04
9.00	2.85

Instrumentation

NMR Experiments

All NMR studies were carried out on a Brüker DPX 500 MHz spectrometer at 300 K.

Mass Spectrometry

Mass spectra were recorded on a Qtof Micro YA263 high-resolution mass spectrometer.

FT-IR Spectrometer

The solid state FT-IR spectra were taken using Shimadzu (Japan) model FT-IR spectrophotometer. A Nicolet FT-IR instrument [magna IR-750 spectrometer (series ii)] was used to obtain the solid state FT-IR spectra. For the solid-state measurements the KBr disk technique was used.

Transmission Electron Microscopy

The morphology of the native hydrogel was investigated by using a transmission electron microscope. The samples were prepared by depositing a drop of the highly diluted gel-phase materials onto a TEM grid (300 mesh Cu grid) that was coated with Formvar and carbon film. Then, the grid was dried under vacuum at 30 ˚C for two days. Images were recorded on a JEOL electron microscope at an accelerating voltage of 200 kV.

Atomic Force Microscopy

The morphology of the highly diluted hydrogel was investigated on an atomic force microscope in tapping mode. AFM studies were conducted by placing a small amount of the wet hydrogel at a very dilute concentration on a mica foil. Then, the material was allowed to first dry in air by slow evaporation and then under vacuum at room temperature for two days. Images were recorded on an Auto probe CP Base Unit di CP-II instrument (Model AP-0100).

UV/Vis spectroscopy

Variable Temp UV-Vis experiments: A hydrogel of 13.46 mM was prepared and it was diluted to 2.69 mM for studying all UV-Vis experiments. 2.69 mM hydrogelator solution was then placed in a quartz cuvette (l = 1 mm) and all spectra were recorded at different temperatures with an interval 5 °C in each case by using an attached peltier system on a perkin-elmer spectrophotometer. 10 min equilibrium time was given after a desired temperature was reached.

Fluorescence study

The fluorescence spectra were obtained using a perkin-elmer spectrofluorimeter and excitation and emission wavelengths of 450 and 700 nm respectively.

X-ray diffraction study

X-ray diffraction study of xerogel material dust was carried out by using an X-ray diffractometer (Bruker D8 Advance) with a parallel beam optics attachment. The instrument was operated at a 35 kV voltage and 30 mA current using Ni-filtered Cu K_α radiation and was calibrated with a standard silicon sample. Samples were scanned from 1º to 30º (2θ) at the step scan mode (step size 0.016°, preset time 2 s) and the diffraction patterns were recorded using a scintillation scan detector.

MALDI-TOF MS

MALDI-TOF MS analysis has been performed by using Applied Biosystems MALDI TOF/TOF Analyzer in dithranol matrix.

TCSPC study

TCSPC measurements have been performed by means of Horiba Jobin Yvon IBH having MCP PMT Hamamatsu R3809 detector instrument and all data were fitted using Data Station v2.3. The fluorescence decay time were fitted using the following well defined equation

$$\mathbf{P(t) = b} \sum_{i=1}^{n} \alpha_i \exp(-t/\tau_i)$$

Where b is the correction of base line, n is the no. of discrete emissive species, α_i and τ_i are the pre-exponential factors and excited state fluorescence life time of the i^{th} component respectively.

I-V measurements

For I-V measurements, the DC currents were measured between two Au sputtered electrodes (diameter 2 mm) on the xerogel pellets under a certain bias voltage using Keithley source meter (model 2410). The

dark I-V characteristics were measured after keeping the samples in dark for several hours. For photocurrent transient measurement, a xenon light source (model no. 66902; Newport Corp. USA) was used for light illumination.

Raman Spectroscopic study

Raman spectroscopy is a powerful tool to establish the nano/micro-structure of carbon-based materials, and thus it can also be used to reveal the framework nano/microstructure of the GO and graphene hydrogels as shown in the Fig. S13. Two fundamental vibrations have been observed, at 1598 cm^{-1}, 1611 cm^{-1} and 1349 cm^{-1}, 1348 cm^{-1}, corresponding to the G band and D band of grapheneoxide and reduced graphene oxide respectively. This as-synthesized PBI-C11-Y shows Raman bands at 1295 cm^{-1}, 1371 cm^{-1} (in plane 'ring breathing'), 1446 cm^{-1} (small peak for ring deformation), 1573 cm^{-1} (in-plane C-C streaching) and 1711 cm^{-1} (small peak for imide bending). These signals are superimposed graphene signals. This is very difficult to identify seperately the corresponding D and G band of graphene within the hybrid xerogel state. However, this problem can be rectify partly by using very dilute concentration of gelator molecules (276 μM gelator) containing GO and RGO solution. Very small shoulder at 1600-1015 cm^{-1} was observed in both GO and RGO containing gelator samples corresponding to the graphene characteristics G band signal.

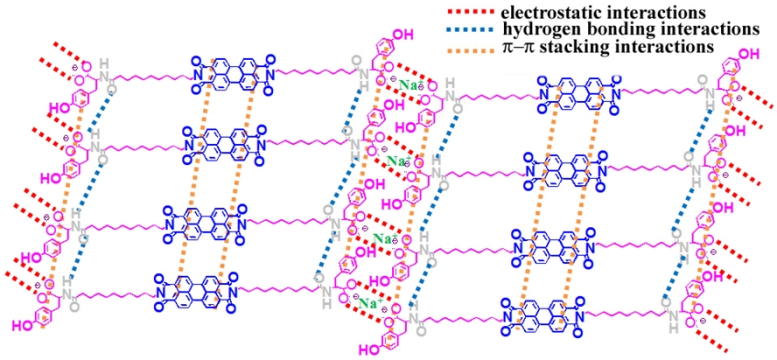
Rheology

Rheological studies were carried out at a constant oscillatory frequency of 1 Hz at room temperature (25 ˚C). Rheological experiments were performed with an AR 2000 advanced rheometer (TA Instruments) using cone plate geometry in a Peltier plate. The plate diameter has 40 mm, with a cone angle of 4 degrees. Rheological experiment have been performed using 4 % w/V native hydrogel and 4 % w/v GO and RGO containing hydrogel keeping the concentration of GO and RGO within the gels are 0.05 % w/v.

Gel formation and thermal study of the native hydrogel

In this study, 2-(11-aminoundecanamido)-L-tyrosine based perylene bisimide derivative is self-asssembled to form gel based soft material within the pH range 7.40 to pH 9.00 at 50 mM phosphate buffer with a nanofibrillar network structure. Gel formation has been occurred at pH 7.46 of 50 mM phosphate buffer with a minimum gelation concentration of 1.3 % w/v. (Table S1). The hydrogelator PBI-C_{11}-Y has been dissolved in 1 mL phosphate buffer of 50 mM at required pH (from 7.40 to 9.00) using sonication followed by heating at about 90 °C in a sealed glass tube. Then the gel tube has been kept at room temperature for 12 hrs to get a gel phase material (Fig. 1). Fig. S14 shows gel melting temperatures (T_{gel}) of this new hydrogel at different concentrations of the gelator molecule at pH 7.46. As pH 7.46 is the physiological pH, we have performed all studies at pH 7.46. This plot (concentration vs. temperature) suggests that the Tgel value increases with an enhancement of the concentration of the gelator till a typical concentration is attained. This concentration is known as ''plateau region'', suggesting the hydrogel network formation is basically completed and saturation point is reached. All xerogels (PBI-

C11-Y, PBI-C11-Y-GO and PBI-C11-Y-RGO) have been prepared by freeze drying the hydrogels by using lifolizer from their respective hydrogels samples.



Scheme S1: A probable molecular packing of the gelator in gel state showing different noncovalent interactions.

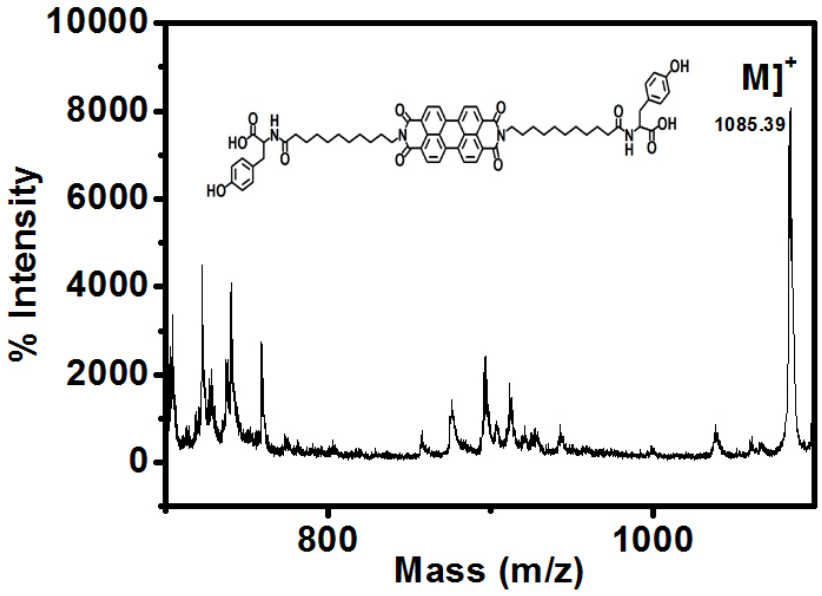


Fig. S1: MALDI-TOF MS spectrum of the **PBI-C_{11}-Y** using the dithranol matrix.

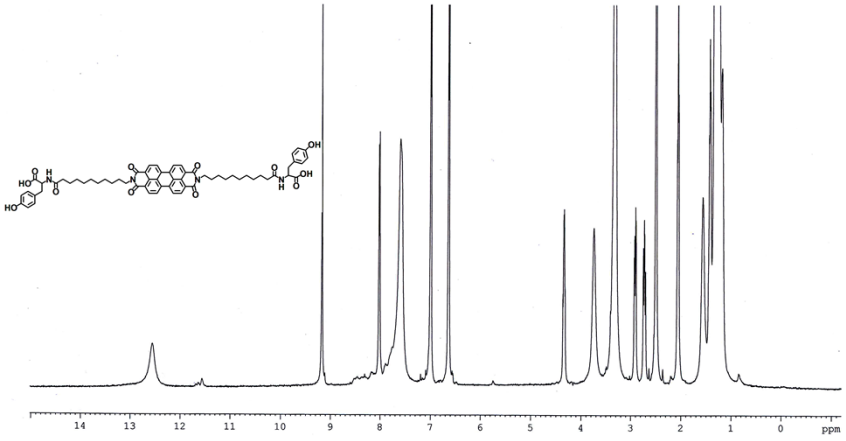


Fig. S2: ^{1}H NMR spectrum of the **PBI-C$_{11}$-Y** in DMSO-d$_6$.

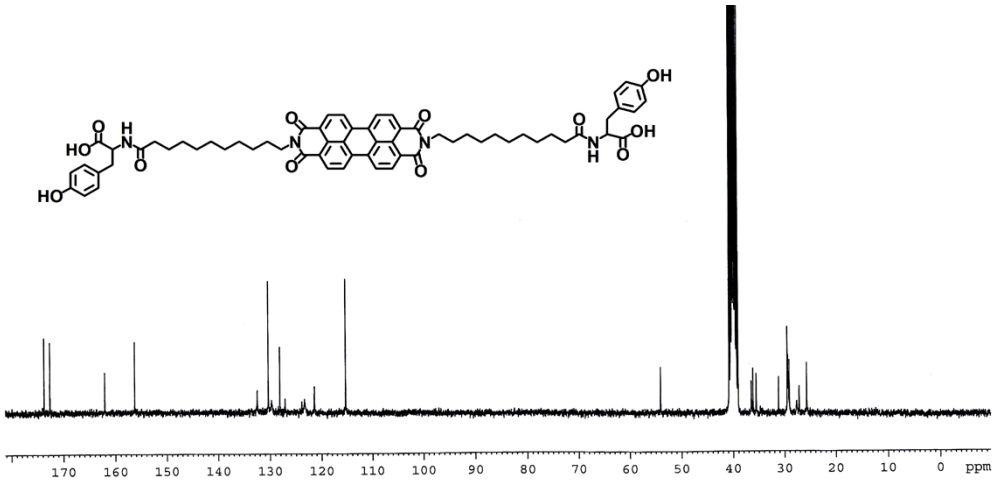


Fig. S3: ^{13}C NMR spectrum of the **PBI-C$_{11}$-Y** in DMSO-d$_6$.

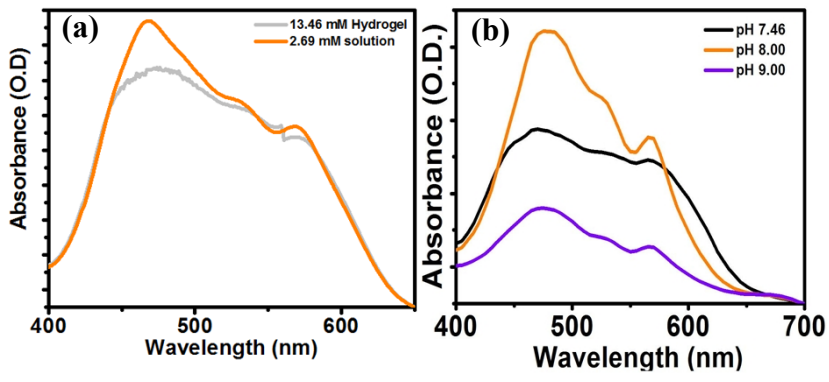


Fig. S4: (a) UV-Vis spectra of the sol and gel. (b) UV-Vis spectra of the native hydrogelator in gel state at different pHs showing a clear red shifting from 470 nm peak (at pH 7.46) to 475 nm (at pH 9.00). The observed hyperchromic shift from pH 7.46 to pH 8.00 can be due to the formation of tyrosinate species (of the phenolate moiety) of the gelator molecule and this prevents the aggregation of gelator molecules due to the charge-charge repulsion.

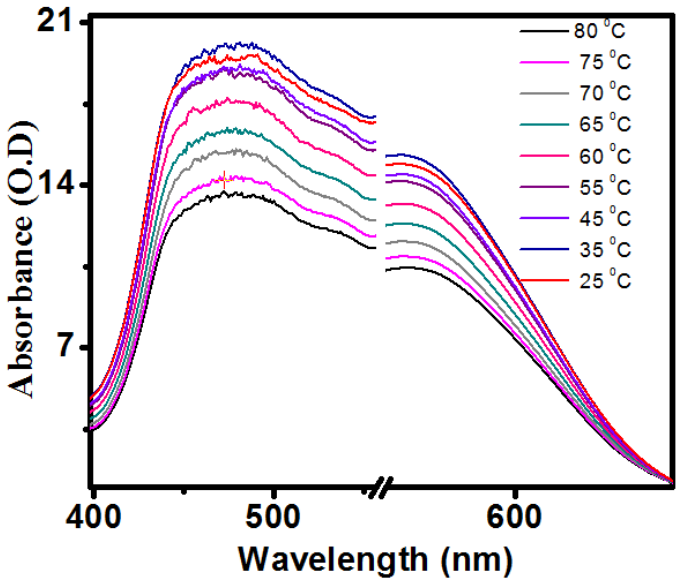


Fig. S5: Temperature dependent UV-Vis absorption study of the 13.46 mM hydrogel.

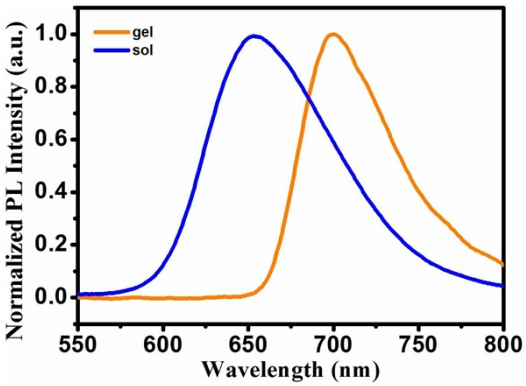


Fig. S6: Fluorescence emission spectrum of the native hydrogelator in sol and in gel state.

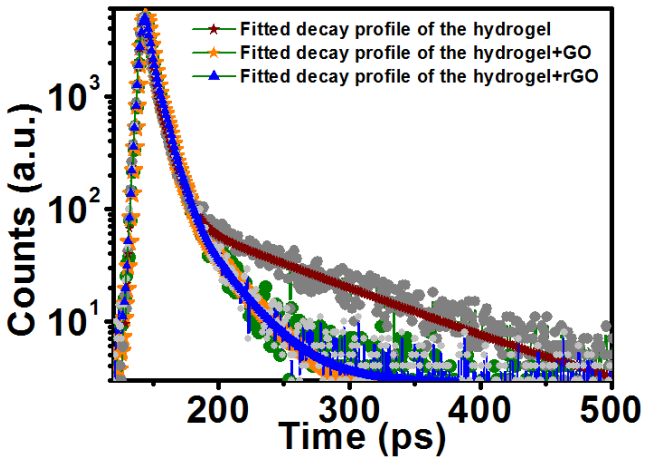


Fig. S7: Time resolved fluorescence life time decay profile of the hydrogels.

Table S2: Time resolved fluorescence study of the hydrogels.

system	$\bar{N}_1$	$\bar{N}_2$	$\bar{N}_3$	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	$\langle\tau\rangle$ (ps)	χ^2
PBI-C_{11}-Y hydrogel	0.068	0.002	0.403	0.246	2.677	0.081	120	1.06
PBI-C_{11}-Y + GO hydrogel	0.34	0.193	0.006	0.046	0.18	0.754	103	1.04
PBI-C_{11}-Y + RGO hydrogel	0.163	0.0063	0.358	0.016	0.797	0.005	101	1.08

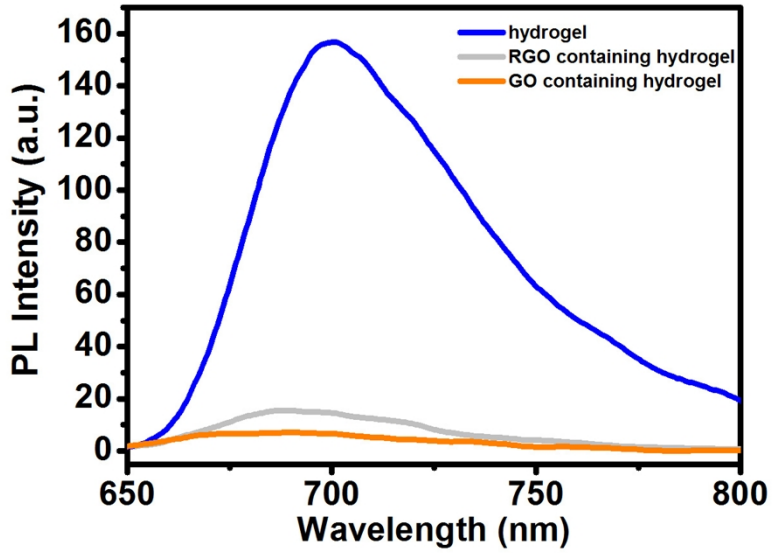


Fig. S8: Fluorescence emission spectrum of the native hydrogel towards the GO and RGO.

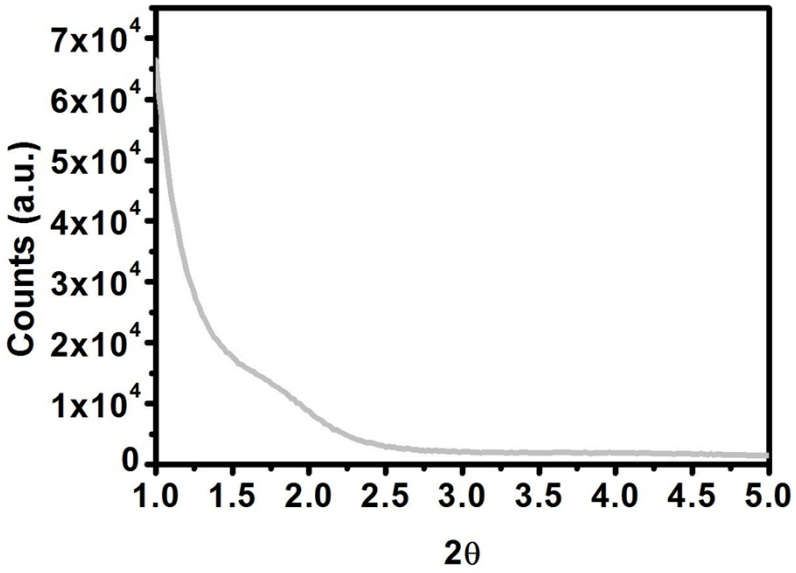


Fig. S9: Small angle X-ray diffraction analysis the **PBI-C_{11}-Y** xerogel.

Table S3. X-ray diffraction peaks pattern in xerogel state.

Peaks assigned	2θ (degree)	d (Å)
a	5.22	17.11
b	7.67	11.66
c	12.22	7.23
d	15.96	5.57
e	19.96	4.47
f	24.43	3.64

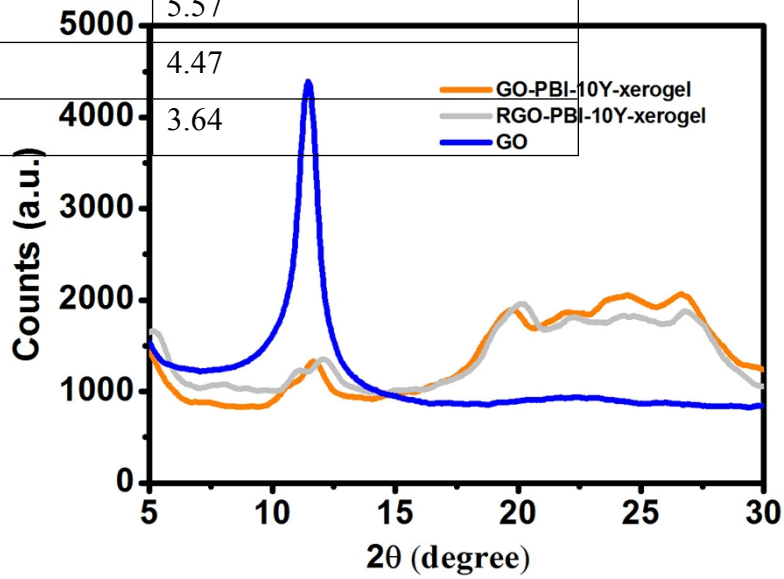


Fig. S10: X-ray diffraction analysis of both GO and RGO containing xerogel as indicated in the Figure.

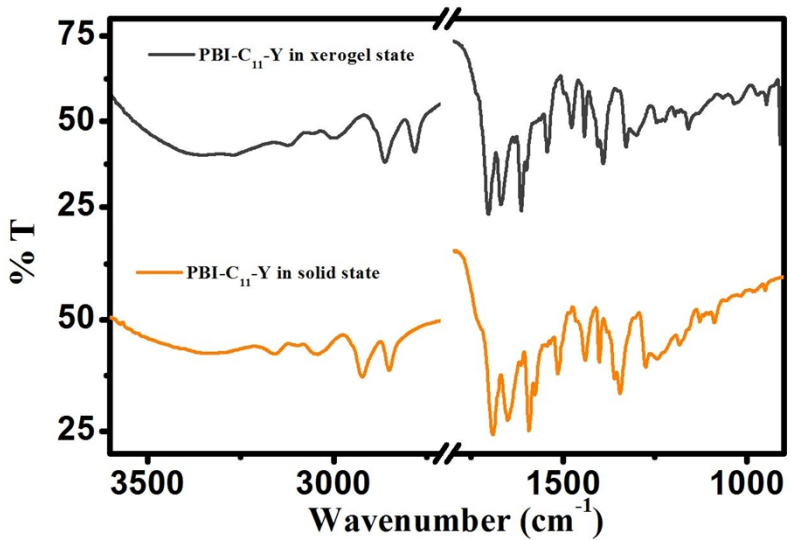


Fig. S11: FT-IR spectroscopic study of the solid **PBI-C_{11}-Y** compound and **PBI-C_{11}-Y** xerogel.

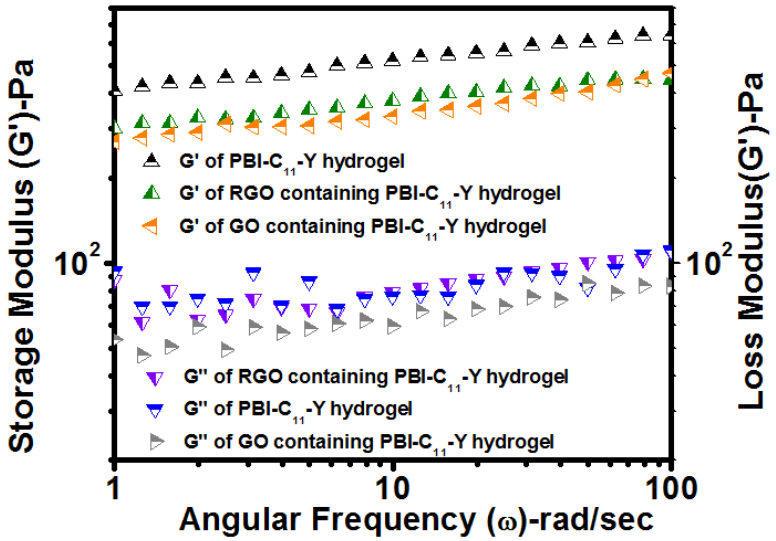


Fig. S12: Plots of the angular frequency (ω) versus the storage modulus (G′) and loss modulus (G″) of different hydrogels.

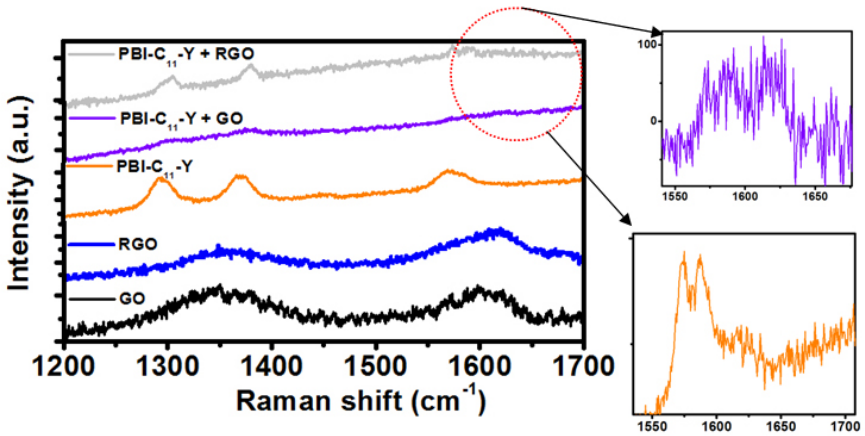


Fig. S13: Raman spectroscopic analyses of GO, RGO, gelator compounds and the hybrid systems.

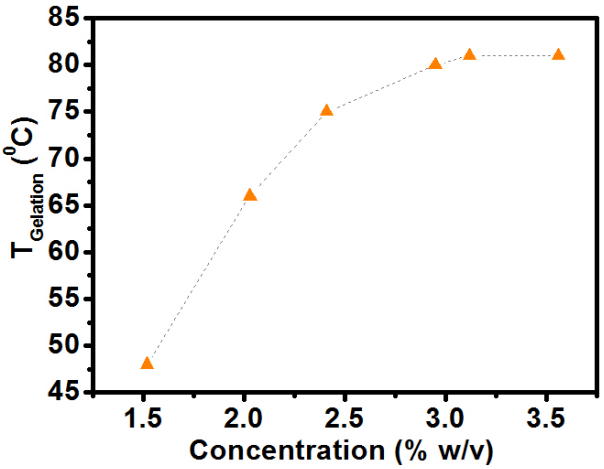


Fig. S14: T_{gel} profile of the native hydrogel.