Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Light Harvesting Bi-component Hydrogel with Riboflavin Acceptor

Partha Bairi, Bappaditya Roy and Arun K. Nandi*

Polymer Science Unit,

Indian Association for the cultivation of Science,

Jadavpur, Kolkata-700 032, INDIA

Preparation of gel:

Melamine (M), 6, 7-dimethoxy-2, 4[1H, 3H]-quinazolinedione (**Q**) and riboflavin (**R**) were purchased from Aldrich, USA and was used as received. The pure **MQ** hydrogel was prepared by dissolving **M** and **Q** in double distilled water in a sealed gel tube followed by addition of few drops of DMSO to increase the solubility of Q. They were heated to make a homogeneous solution which on cooling to 30^0C produced hydrogels. The co-assembled hydrogels were prepared by following the same procedure mentioned above with the addition of desired amount of **R** (mole %).

Microscopy:

Fluorescence micrographs of the pure **MQ** and co-assembled **MQ** gel were taken by a fluorescence microscope (Olympus, BX61) by exciting the gel sample with UV radiation (λ = 300nm) using a FITC filter.

Wide-angle X-ray Diffraction study:

The wide-angle X-ray scattering (WAXS) experiments of the xerogel of MQ and MQ with R were performed using a high resolution X- Ray diffractometer model expert pro PANalytical. Samples were placed on glass slides and were scanned in the range of $2\theta = 4 - 60^0$.

Rheology:

To understand the mechanical property of the MQ gel rheological experiment was performed with an advanced rheometer (AR 2000, TA Instrument,USA) using cone plate geometry on a peltier plate. The diameter of the plate was 40nm and angle 4^0 with plate gap of 121μm and frequency sweep was performed

Spectroscopy:

The UV-vis spectra of the samples were recorded with a Hewlett-Packard UV-vis spectrophotometer (model 8453) using a cuvette of 0.1 cm path length. Fluorescence study of **MQ** and hybrid hydrogel samples prepared in a sealed cuvette were 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 297 nm wavelength and emission scans were recorded from 320 to 700 nm using excitation slit width of 2 nm and emission slit is 5nm with a 1 nm wavelength increment having an integration time of 0.1 s. Fluorescence lifetimes were measured by using a time-correlated single photon counting fluoremeter (Fluorecule, Horiba Jobin Yvon). The system is excited with 295 nm nano LED of Horiba Jobin Yvon having λ_{max} at 368 nm with pulse duration <200 pico second. All the samples are prepared for room temperature measurement (30^0C) in double distilled water. Average fluorescence lifetimes ($<\tau_f>$) for exponential iterative fitting are calculated from the decay times (τ_i) and the relative amplitudes (a_i) using the following relation

$$<\tau_f> = a_1 \tau_1 + a_2 \tau_2 + a_3 \tau_3 \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where a_1, a_2 , a_3 are relative amplitudes and τ_1, τ_2 , τ_3 are lifetime respectively.

The percentage of energy transfer[S1] from **MQ** to **R** was calculated from the equation:

$$E_{eff} = 1- \tau_{DA} / \tau_D \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where τ_{DA} and τ_D are fluorescence lifetime of donor (**Q**) in presence and absence of acceptor (**R**), respectively. The energy transfer rate constant K_{ET} can be calculated[1] from the Stern-Volmer equation.

$$I_0 / I = 1 + K_{ET} \tau_0 [\mathbf{R}] \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where I_0 and I represent the fluorescence intensity of the donor in the absence and presence of acceptor respectively, [**R**] is the molar acceptor concentration and τ_0 is the fluorescence lifetime of the donor in the absence of acceptor.

Determination of rate constant by Avrami equation:

The Avrami equation[13] is usually expressed as

$$1 - V(t) = \exp(-kt^n) \ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where V (*t*) is the fraction transformed, *k* is the rate constant, *t* is the time of transformation, and *n* is a constant whose value depends on the nature of the nucleation and growth process. The fraction transformed can be obtained from the fluorescence data SI fig. X. If the intensity at t = 0 is I_0 and at t = ∞ is I_∞, V (*t*) is equal to $I_\infty - I_t / I_\infty - I_0$. Putting these values into equation 1, we obtain

$$I_\infty - I_t / I_\infty - I_0 = \exp(-kt^n) \ldots\ldots\ldots\ldots\ldots\ldots 2$$

Taking logarithms on both sides, the equation transforms to

$$\ln(- \ln I_\infty - I_t / I_\infty - I_0) = \ln k + n \ln t \ldots\ldots 3$$

Thus, by plotting the left-hand side of eq 2 with ln t, straight lines are expected, and from the slope the Avrami exponent n can be obtained. The rate constant k of the process can be obtained from the intercept of the plot and for **MQ** gel k has been found 8.4×10^{-4} min^{-1}.

Reference:

S1. S. Bhattacharyya, T. Sen, and A. Patra**,** *J. Phys. Chem. C* 2010**, 114**, 11787.

Table S1: Fluorescence life time and percent energy transfer of **MQ** hydrogel with different mole % of **R** at 30^0 C.

Hydrogel	Mole % of **R**	Av. life time (ns)	% of energy transfer
MQ (0.5% (w/v))	0	16.01	0
	0.25	5.25	67.2
	0.50	4.99	68.9
	0.71	3.77	76.6
	1.0	3.61	77.5
	1.25	2.76	82.8

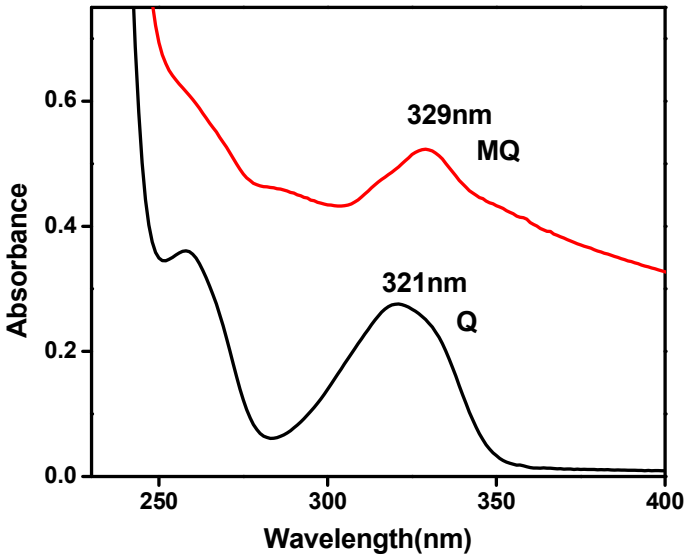

Fig.S1 Uv-vis spectra of pure **Q** and **MQ** hydrogel at 0.01% (v/w)

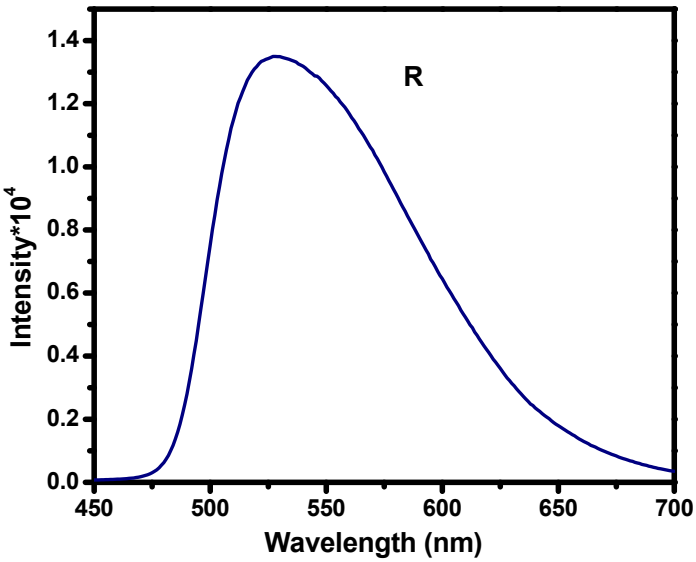

Fig.S2 Fluorescence spectrum of **R** on excitation at 373nm.

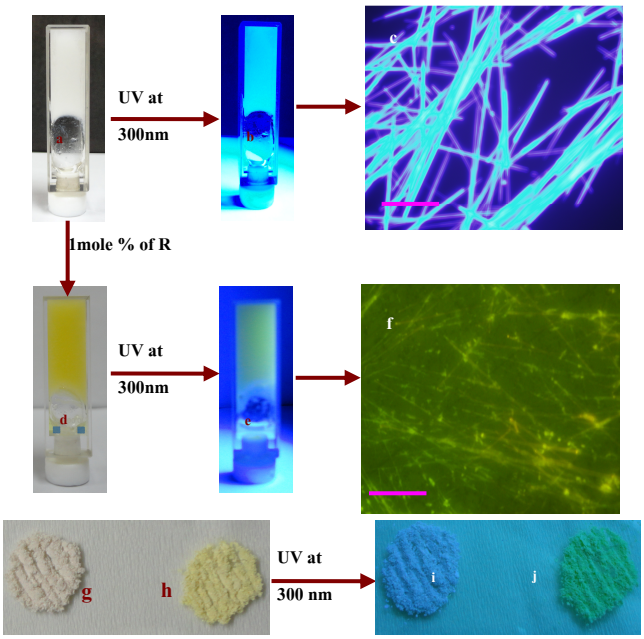

Fig.S3 (**a**) pure **MQ** hydrogel, (**b**) under UV light (λ = 300nm) showing blue fluorescence emission, fig.3**c** Fluorescence micrograph of **MQ** gel and fig. 3(**d**) **MQ** gel with 1 mole % of **R**, fig. 3(**e**) under uv light (λ_{max} = 300nm) showing green fluorescence emission, fig. 3(**f**) Fluorescence micrograph of **MQ** gel with 1 mole % of **R** (scale bar 210 um) fig (**g**) and (**h**) are **MQ** xerogels in absecnce and present of 1 mole % of **R**, fig (**I**) and (**j**) after irridation of uv light (λ_{max} = 300nm).

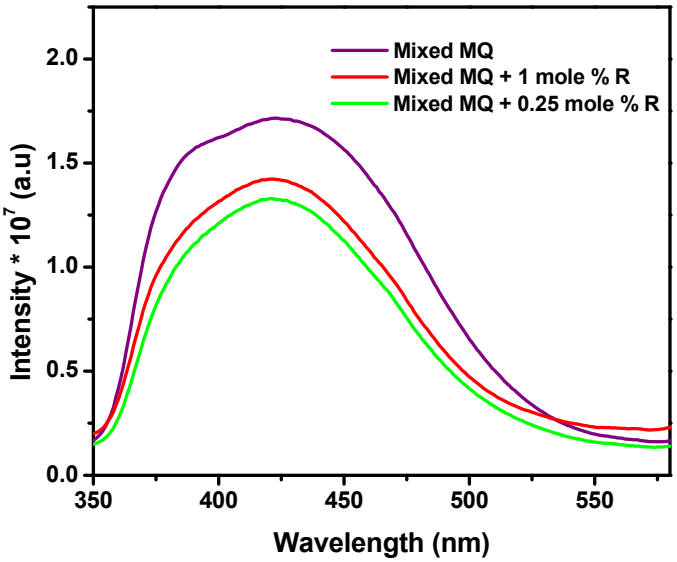

Fig.S4 Solid state fluorescence spectra of intimate mixture of M and Q, mixed MQ with different mole % R dried from DCM solution excited at 297nm.

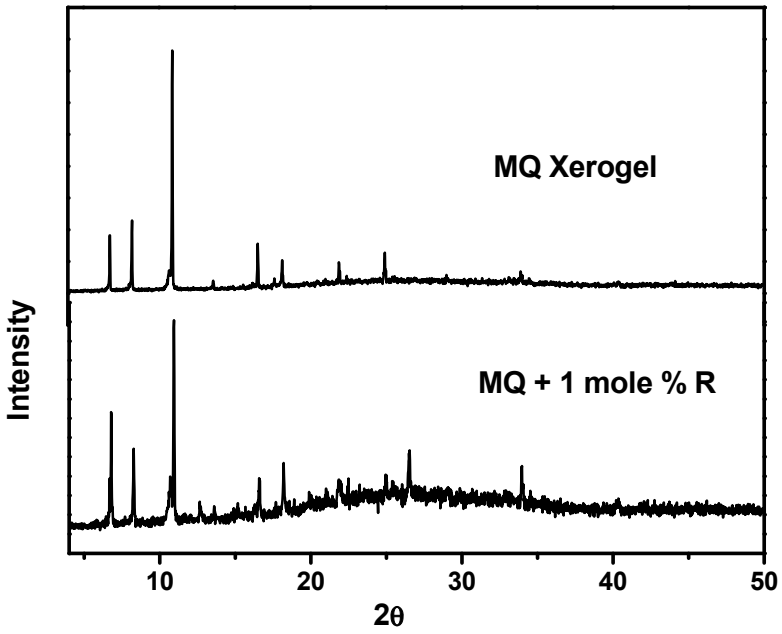

Fig.S5 WAXS patterns of xerogel MQ and MQ with 1 mole % R.

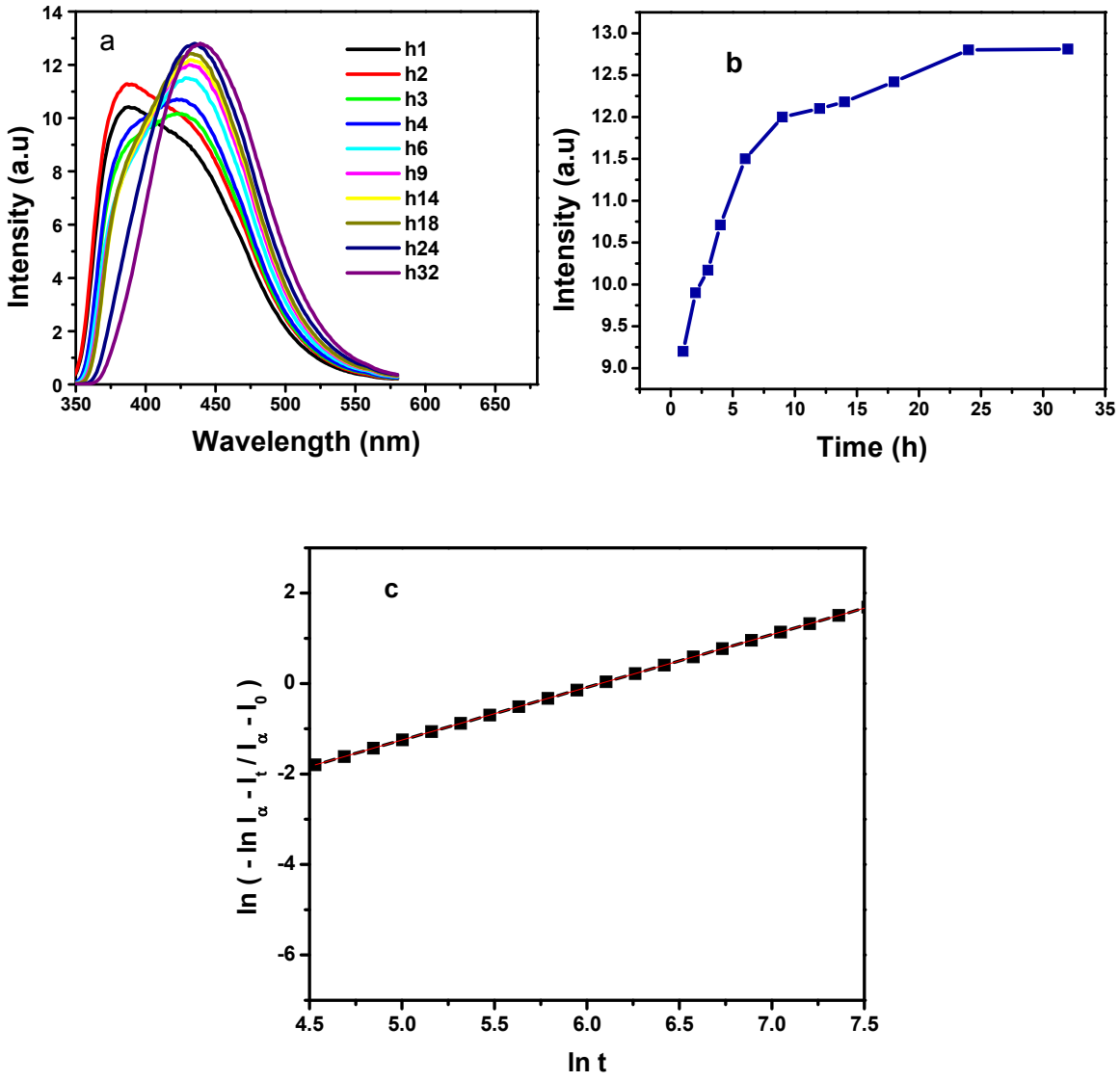

Fig.S6 (a) Time dependent fluorescence spectra of MQ hydrogel at 30 ^{0}C (E_x = 297nm). (b) Plot of fluorescence intensity vs time at 25 ^{0}C (c) Avrami plot of the fluorescence intensity data of Figure b of MQ gel.

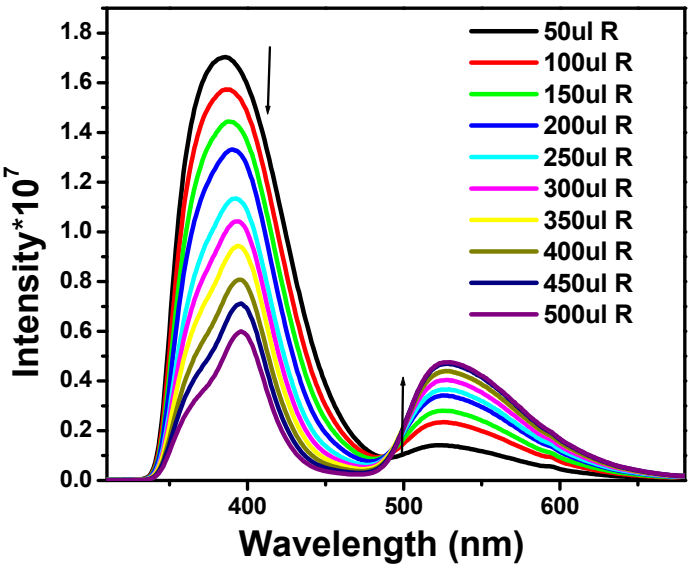

Fig.S7 The fluorescence intensity of donor **MQ** (10^{-3} M) decreases while that of **R** increases at solution phase with addition of acceptor **R** (10^{-3} M).

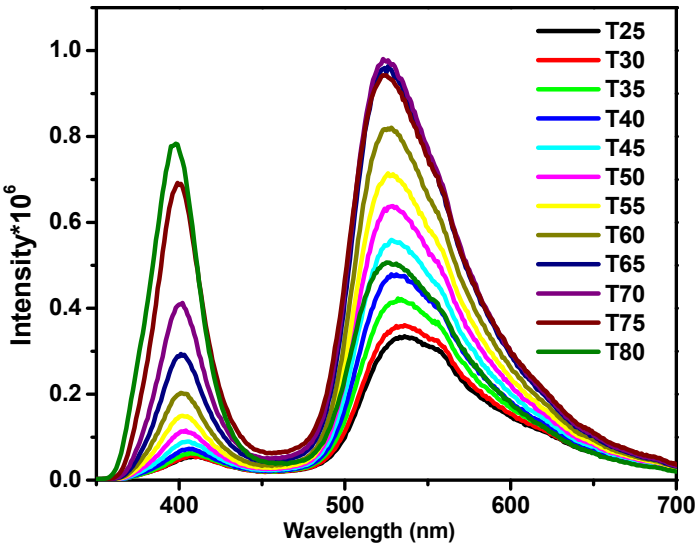

Fig.S8a Temperature dependent fluorescence spectra of **MQ** gel in presence of 1 mole % **R.**

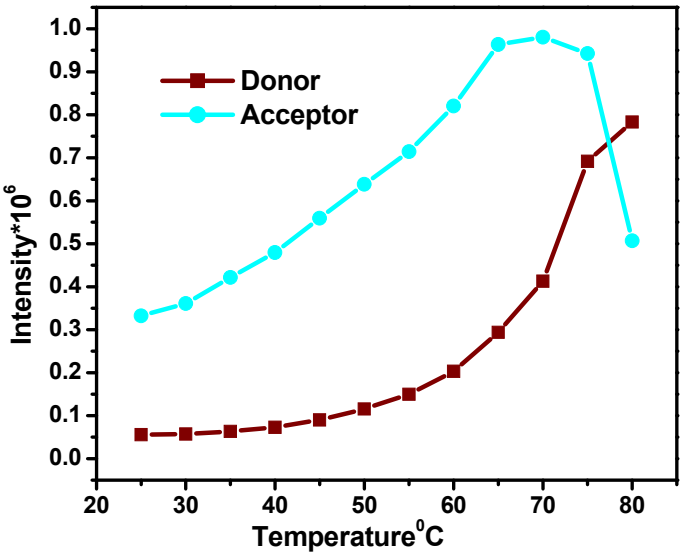

Fig.S8b Variation of fluorescence Intensity of donor and acceptor (1 mole % **R**) with temperature.

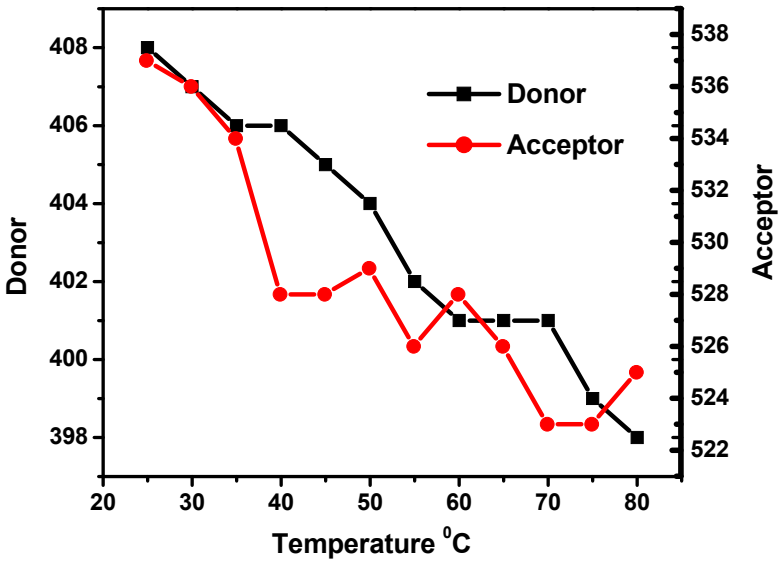

Fig.S8c Variation of fluorescence wavelength maxima of donor and acceptor (1 mole % **R**) with temperature.

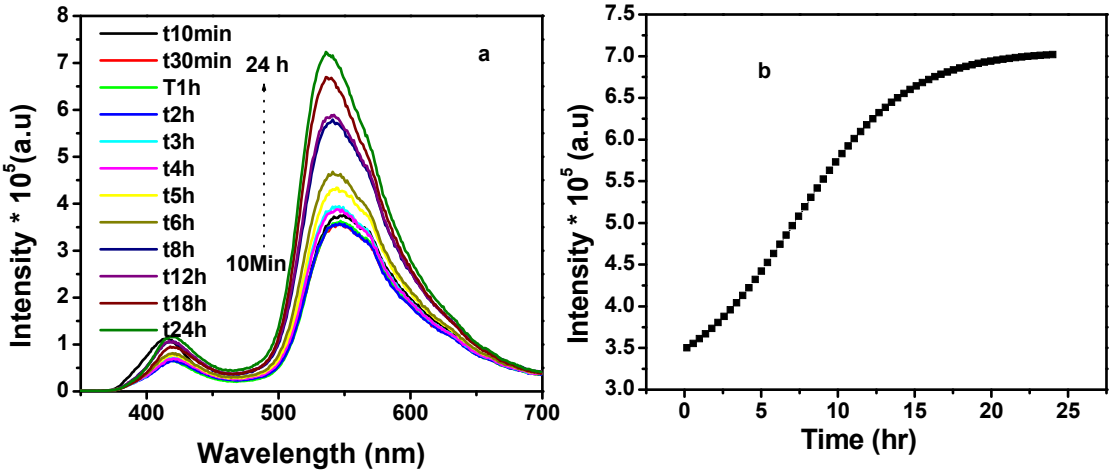

Fig.S9 (a) Time dependent fluorescence spectra of MQ gel with 1 mole % R excited at 297nm.(b) intensity vs time plot (sigmoidal fit).

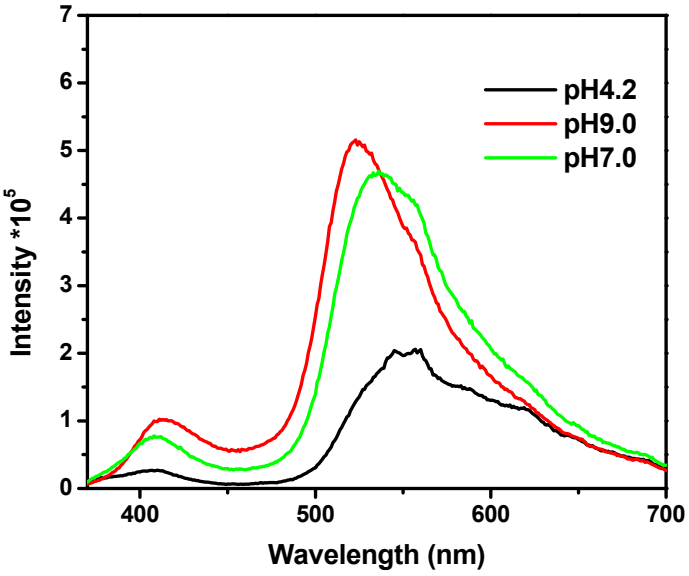

Fig.S10 pH dependent fluorescence spectra of **MQ** gel in presence of 1 mole % **R**.

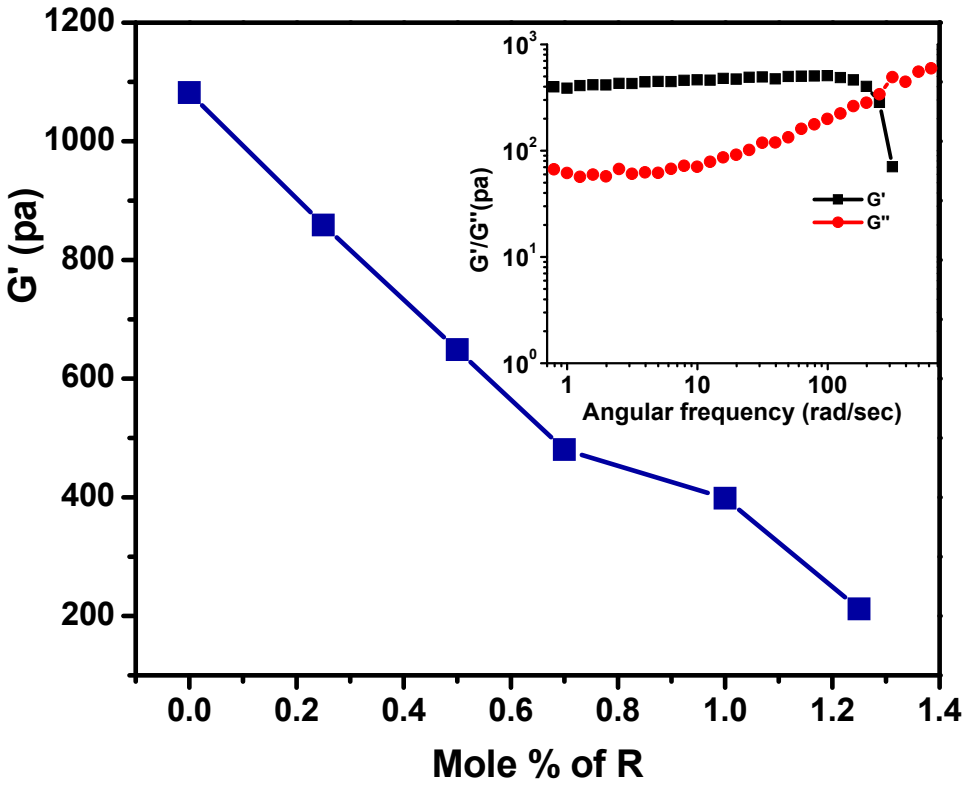

Fig.S11 Storage modulus vs different mole % of R plot. Inset A representative plot of modulus (G', G'') vs. angular frequency plot of MQ gel in presence of 1 mole % of R.