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Co-assembled White-Light-Emitting Hydrogel of Melamine

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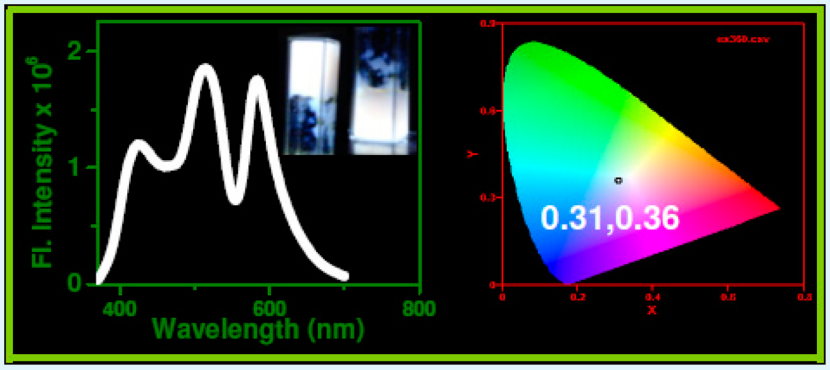
Supporting Information



ABSTRACT: A coassembled light-harvesting hydrogel of melamine (M), 6,7-dimethoxy-2,4[1H, 3H]-quinazolinedione (Q) with riboflavin (R), is used to produce a white-light-emitting hydrogel (W-gel) by mixing with the dye rhodamine B (RhB) in a requisite proportion. Addition of R to the Q solution causes both static and dynamic quenching to the emission of Q as evident from the Stern−Volmer plot and the emission of R shows a gradual increase in intensity. On addition of RhB to an aqueous solution of R, fluorescence resonance energy transfer (FRET) occurs, showing an emission peak at 581 nm. In a solution of constant molar ratio of Q and R, addition of RhB causes a quenching of emission of R with no effect on the emission of Q, indicating that the energy transfer takes place only between R and RhB. In the MQR coassembled hydrogel containing RhB, the gel melting temperature is lower than those of MQ and MQR gel, but the storage modulus remains almost unaffected. The oscillatory stress experiment indicates a gradual decrease of critical stress values for breaking of MQ, MQR, and W-gels attributed to the coassembly. In contrast to the solution of Q and R, energy transfer occurs on addition of RhB to the MQ gel. By varying the RhB and R concentration in the 1:1 MQ gel white light emission is observed for the W-gel composition having molar ratio of M:Q:R:RhB = 100:100:0.5:0.02 with the Commission Internationale de L'eclairage (CIE) coordinates of 0.31 and 0.36 for the excitation at 360 nm. However, in the sol state, the CIE coordinates of the hybrid differ significantly from those of the white light.

KEYWORDS: *riboflavin, supramolecular gel, rheology, quenching, energy transfer, white light emission*

INTRODUCTION

Fluorescence resonance energy transfer (FRET) from donor to acceptor molecules is an important step for making light-harvesting materials.[1,2] A variety of light-harvesting materials has been reported based on polymer,[3] nanomaterial,[4] small organic molecules,[5] metal−organic framework,[6] low molecular weight gelator,[7−10] etc. Light-harvesting materials are interesting and promising because of their potential uses in different fields, e.g., solar cell devices, artificial photosynthesis, light-emitting diodes, photonics, sensors, etc.[7−10] In this context, supramolecular principle plays an important role because it provides an organized molecular architecture that helps in the efficient excitation energy transfer from donor to acceptor molecules. Basic design principles for the energy transfer in photochromic gels are that the emission spectrum of the donor should overlap strongly with the absorption spectrum of the acceptor, and the separation between the donor and acceptor should be small enough for the energy transfer to occur.[11] Excitation energy transfer in the supramolecular gel[12−15] scaffolds has played a significant role and Ajayaghosh and his co-workers have reported several light harvesting organogels with the π- conjugated oligo(*p*-phenylenevinylene)[16−22] (OPV) molecule which acts as an efficient light harvesting antennae. With the help of partial fluorescence resonance energy transfer in a multicomponent donor−acceptor assembly one can tune the emission property and generate white-light-emitting materials.[23−27] The white-light-emitting materials are attractive for the application in flexible full-color light-emitting diodes (LEDs) and in backlights for liquid crystalline displays.[28−30] Many researchers have developed white-light-emitting materials using fluorescence energy transfer from donor to acceptor molecules in either the solution or solid state and few reports are available on the supramolecular organogel,[31,32] whereas in the hydrogel system, it is very rare until recent reports by Bhattacharyya et al.[33−35]

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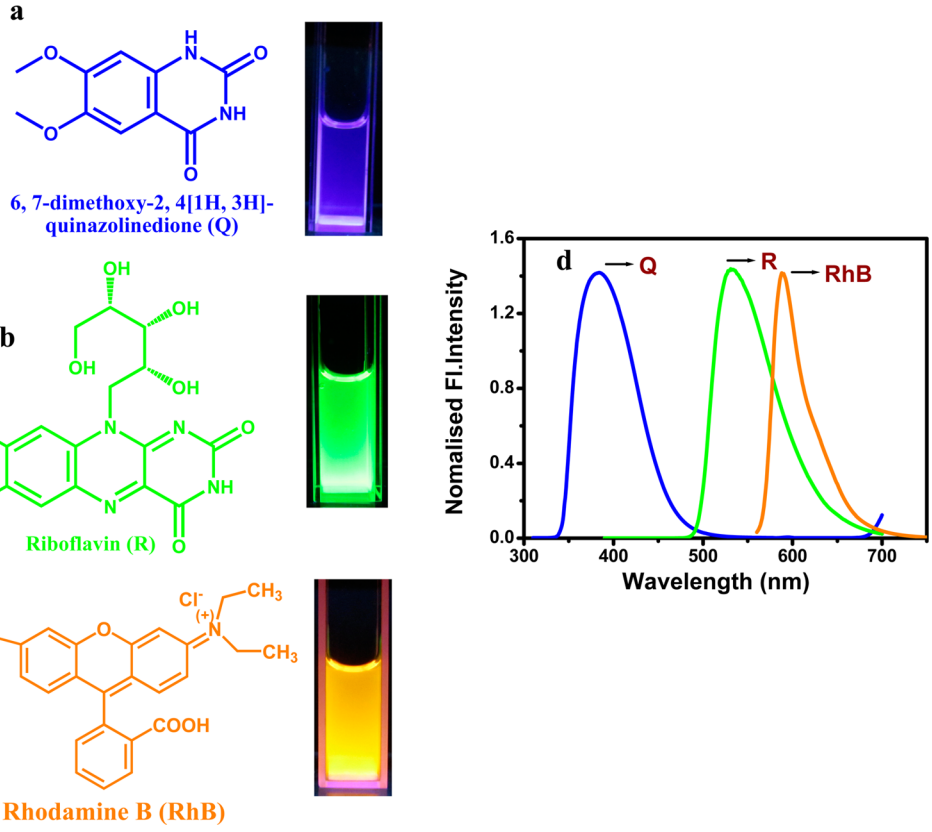
Scheme 1. (a–c) Chemical Structure of Q, R, and RhB, the Photograph of the Respective Solutions under UV Light Irradiation (365 nm); (d) Normalized Fluorescence Spectra of Q, R, and RhB in Their Aqueous Solution



Melamine (M) is a good supramolecular synthon that can bind with different complementary molecules through hydrogen bonding and the resultant supramolecular complex can self-assemble to produce both hydro and organo gels. The most important complementary molecules are riboflavin (R), lumichrome, 6,7-dimethoxy-2, 4[1H, 3H]-quinazolinedione (Q), uric acid, aromatic hydroxy acids, etc.[36−39] This bicomponent self-assembly can import new optical properties suitable for sensing, energy harvesting, etc. which can be tuned by changing the composition of the components. There are other bi component systems[40−42] consisting of stearic acid, eicosanoic acid and bile acids, which when mixed with di- or oligomeric amines in specific molar ratios produce stable hydrogels whose formation depends on the hydrophobicity of the fatty acid, and also on the type of amine used. In presence of proteinous amino acid (arginine, tryptophan, histidine) or nucleoside (adenosine, guanosine, cytidine), graphene oxide (GO) form two-component supramolecular stable hydrogels showing nanofiber and nanosheet morphology.[43] Bicomponent gels formed from pseudo enantiomeric ethynylhelicene oligomers in toluene show different properties depending on difference in numbers of helicenes in the individual components.[44]

We have recently reported a light harvesting hydrogel[45] working in a wide range of temperature and pH of a two-component supramolecular complex of M and Q acting as a donor and R as an acceptor. This light-harvesting hydrogel shows an unusal gradual quenching of fluorescence intensity of acceptor (R) and also a large red shift of its emission peak ($\Delta\lambda$ = 51 nm) with increasing it is concentration through coassembly process. The MQ hydrogel[38] exhibits blue fluorescence and the coassembled MQ gel with R shows green fluorescence through FRET process for excitation at 297 nm. Motivation of the present work on the white light-emitting hydrogel is stemmed from the report on bischolesterol-OPV-based[20] white-light-emitting organogel, engineered from the partial excitation energy transfer between the components yielding Commission Internationale de L'eclairage (CIE) coordinates x = 0.31 and y = 0.35. To make a white-light-emitting MQR hydrogel, we have to search a fluorescent dye that has the ability to accept excitation energy from either of the donors Q or R. Also, the emission spectra of the dye could cover the red light region as Q and R emits blue and green light, respectively. Therefore, a probability of efficient energy transfer exists if a spectral overlap between the absorption spectra of the dye and fluorescence spectra of either Q or R is possible. Hence in the coassembled gel of MQR with the dye partial fluorescence energy transfer may occur to the dye. For this partial energy transfer from the components of the coassembled gel to the dye, we chose a water-soluble dye, rhodamiine B (RhB), which has characteristic absorbance maxima at 554 nm and emission maxima 588 nm with a quantum yield of 0.32 in water[46]

EXPERIMENTAL SECTION

Materials. 6,7-Dimethoxy-2, 4[1H, 3H]-quinazolinedione (Q), melamine (M), riboflavin (R), and rhodamine B are purchased from Aldrich Chemical.Co., USA and are used as received.

Preparation of Gel. A mixture of Q and M in a molar ratio of 1:1 and water are taken in a glass tube and few drops of DMSO are added to solubilize Q; the water: DMSO mixture has the composition 100: 3.3 (by volume).. The final MQ concentration has been taken to be 0.5% (w/v). The mixture is sealed in a glass tube sonicated and heated

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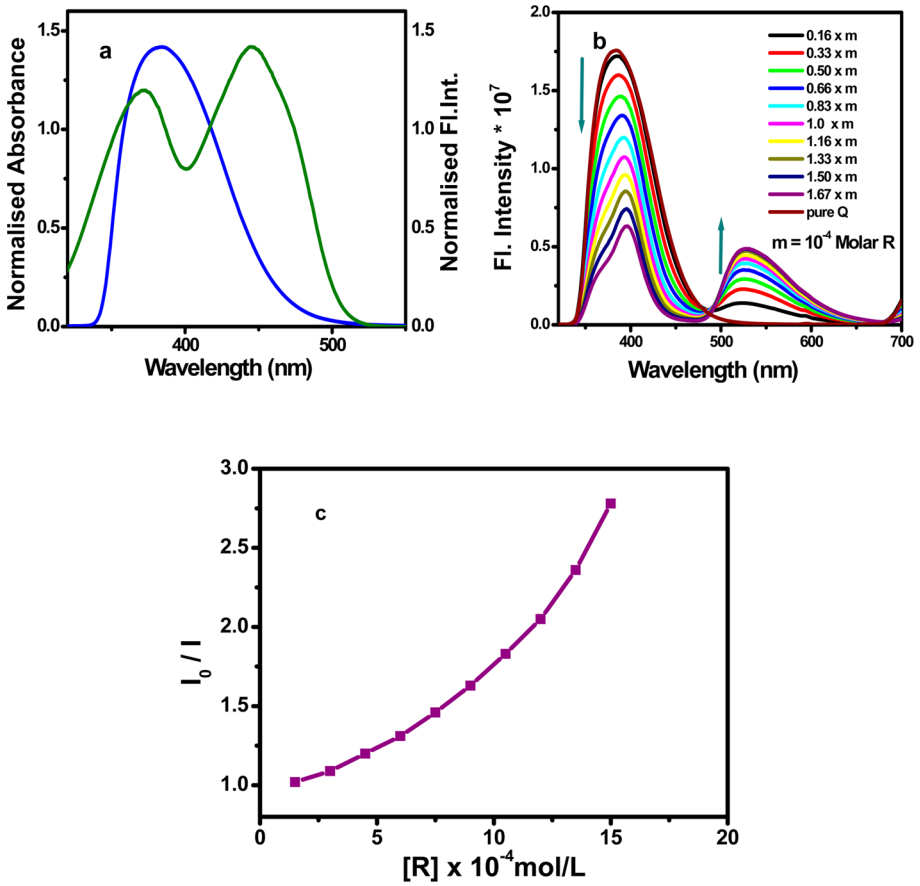

Figure 1. (a) Fluorescence spectra of Q (blue) and absorption spectra of R (olive) in aqueous solution showing spectral overlap, (b) Fluorescence spectra of Q solution (3.3×10^{-4} mol/L) on gradual addition of 1×10^{-4} mol/L R solution for excitation at 297 nm and (c) intensity ratio (I_0/ I) vs R concentration for emission peak of Q.

to 120 °C to make a homogeneous solution that on cooling to 30 °C produces hydrogels. The coassembled MQR gel and the white-light-emitting hydrogel (W-gel) are prepared by following the same procedure with the addition of desired amount of R to MQ system and rhodamine B to the MQR system. The minimum gelation concentration (MGC) of W-gel is found to be 0.17% (w/v) by test tube tilting method at 30 °C.

Measurement of Gel–Sol Transition Temperature (T_{gel}). The gel–sol transition temperature is determined using the "falling ball method".[47] For the measurement, a gelator solution is filled into a screw cap vial (inner diameter: 11.8 mm, filling height: 16 mm), sealed and is kept at room temperature for 24 h. A steel ball (diameter, 2.1 mm; weight, 45 mg) is put on the top of the gel, and the vial is heated slowly in a temperature controlled water bath (heating rate: 1 °C min^{-1}). T_{gel} is defined as the temperature at which the steel ball reached the bottom of the vial. An average of four such measurements is taken as T_{gel}. The temperature is measured in a reference vial filled with 1 mL of pure water.

Rheology. To understand the mechanical property of the MQ, coassembled MQR gel and W-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.

Spectroscopy. Fluorescence study of MQ, coassembled MQR and W-gel samples prepared in a sealed cuvette are carried out in a Horiba Jobin Yvon Fluoromax 3 instrument. Each gel sample in a quartz cell of 1 cm path length has been excited at 297 nm and the emission scans are recorded from 310 to 700 nm using excitation slit width of 2 nm and emission slit of width 5 nm with an increment of 1 nm wavelength having an integration time of 0.1 s.

Microscopy. The morphology of W-gel is investigated using a field emission scanning electron microscopy (FESEM) and fluorescence microscopy. Small portion of the gel is taken on a glass coverslip and is dried in air at 30 °C and finally in vacuum. It is observed through the FESEM instrument (JEOL, JSM 6700F) operating at 5 kV after platinum coating. Fluorescence micrograph of the W-gel is taken in a fluorescence microscope (Olympus, BX61) by exciting the gel sample with an unfocused UV radiation (330–385 nm).

RESULTS AND DISCUSSION

In scheme-1 the structure of the fluorescent molecules used here and their emission spectra are presented to understand the blue, green and orange light emission by Q, R, and RhB, respectively.

Energy Transfer in the Solution State. Figure 1a shows an overlap of the absorption spectrum of R with the emission spectrum of Q in the aqueous solution. R exhibits absorption peaks at 373 nm corresponding to the $\pi-\pi^*$ transition coupled with the $n-\pi^*$ transition and at 444 nm for the $\pi-\pi^*$ transition of flavin moiety, respectively.[48] On excitation by a radiation of 297 nm Q emits at 384 nm (scheme-1) in the aqueous solution and its quantum yield is 0.53 measured using RhB as a standard.[45] R on excitation with a radiation of 373 nm emits at 532 nm in aqueous solution having its quantum yield 0.27 .[45]

An efficient fluorescence energy transfer from donor to acceptor needs to fulfill some criteria including, spectral overlap, distance between chromophore (1–10 nm) etc.[49] A good spectral overlap of the absorption spectra of R and fluorescence spectra of Q is observed (Figure 1a) in the

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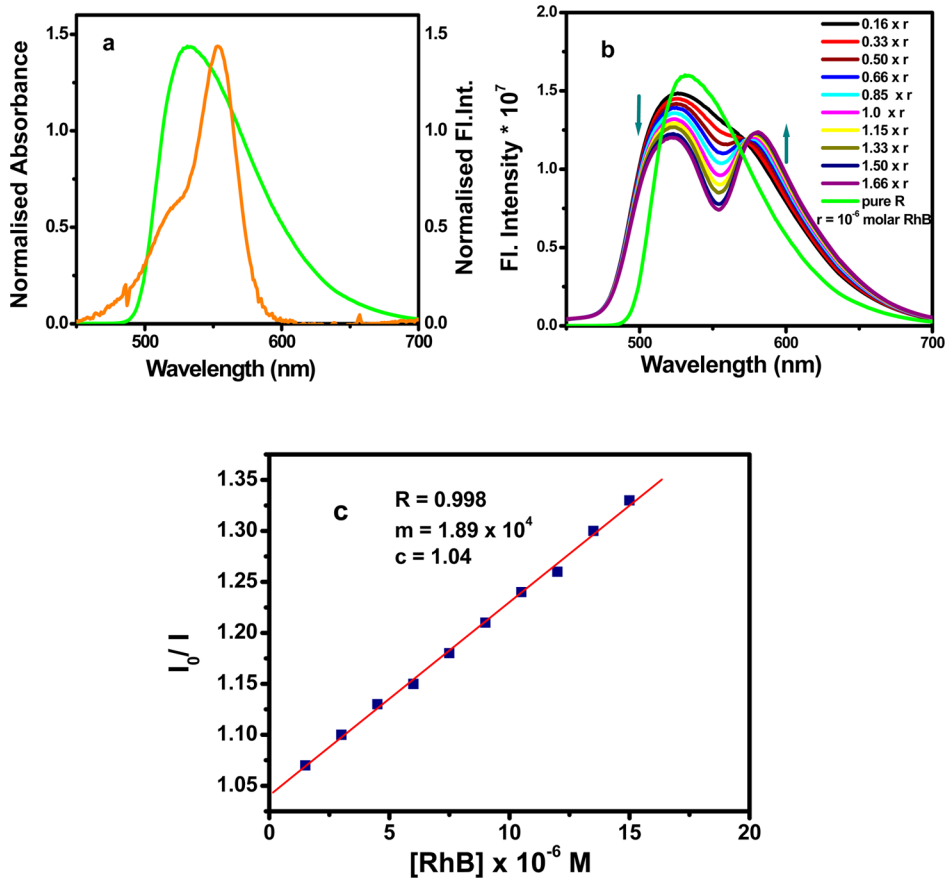

Figure 2. (a) Spectral overlap of fluorescence spectra of R (green) and absorption spectra of RhB (orange) in solution, (b) Fluorescence spectra of R (3×10^{-4} mol/L) with the addition of RhB excited at 373 nm and (c) Intensity ratio (I_0/I) of R vs concentration of RhB (red line is the least-squares fitting of the data).

solution state. From the Figure 1b it is clear that on gradual addition of R (1.67×10^{-4} mol/L) to the aqueous solution of Q (3.3×10^{-4} mol/L) there is a gradual decrease of fluorescence intensity of Q indicating fluorescence energy transfer from Q (donor) to R (acceptor). It is to be noted here that the intensity of emission peak of R increases by 2.5 times with a gradual shift of the peak position from 523 to 529 nm for the addition of 1.67×10^{-4} mol/L R solution.

So, to know whether the quenching takes place only for energy transfer from donor to acceptor Stern − Volmer plot[49] (Figure 1c) is applied and it exhibits a curvilinear increase of I_0/I with an increase in R concentration where I_0 and I are the fluorescence intensity of donor in the absence and presence of a quencher. It can be explained from Stern−Volmer equations as follows

$$I_0/I = 1 + k_a[q] \quad (1)$$

$$I_0/I = 1 + \tau_0 k_q[q] \quad (2)$$

$$I_0/I = (1 + k_a[q])(1 + \tau_0 k_q[q]) \quad (3)$$

Where k_a is the association constant of the ground state complex, k_q is the bimolecular quenching rate constant, τ_0 is the lifetime of donor in the absence of acceptor, and [q] is the quencher concentration, respectively. In the case of static quenching, eq 1, and for dynamic quenching, eq 2, is obeyed and in both cases the plot of I_0/I vs [q] should be a straight line nature. If in the system both the dynamic and static quenching occurs simultaneously the eq 3 is followed. In the plot of Figure 1c, the I_0/I vs [q] plot is bending upward, suggesting that it obeys eq 3, indicating the presence of both static and dynamic quenching. The static quenching occurs generally for the complex formation at the ground sate and the dynamic quenching occurs due to the energy transfer at the excited state.[49] To understand the ground-state complex formation, we present UV−vis spectra for the same sets of solution in Figure S1 in the Supporting Information and it is noticed that all the characteristics absorption peaks of Q (258 and 321 nm) are gradually red-shifted with the gradual addition of R. In the case of Q, the red shift is ≈ 6 nm from the addition of 1.67×10^{-4} mol/L R solution in 3.3×10^{-4} mol/L Q solution. This red shift indicates that there is an interaction between the two chromophores Q and R at the ground state. So, static quenching takes place for the formation of a complex between Q and R at the ground state. Also dynamic quenching occurs here due to the energy transfer from the excited state of Q to R as we get a curvilinear I_0/I vs [R] plot bending upward. So we can argue that both the static and dynamic quenching occurs simultaneously in the mixture of Q and R during the whole energy transfer process.

A good spectral overlap is also observed between the absorption spectrum of rhodamine B and the fluorescence spectrum of R in water (Figure 2a) so energy transfer from R to RhB is expected. On the gradual addition of RhB the fluorescence intensity of R at 531 nm decreases and that of RhB emitting at 575 nm increases. Further, the emission peak

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of R exhibits a gradual blue shift of 10 nm for the addition of 1.67×10^{-6} mol/L RhB solution (Figure 2b). In the Stern–Volmer plot of I_0/I vs [RhB] a straight line (Figure 2c) is observed so the dynamic quenching occurs probably for the energy transfer from R to RhB at the excited state. The emission wavelength of RhB is gradually red-shifted with increasing amount of RhB and this may be to the aggregation of RhB.[45] We have measured the lifetime of R and (R+RhB) solutions containing the same concentration of R (3×10^{-4} mol/L) and 1×10^{-6} mol/L RhB solution (see Figure S2 in the Supporting Information). The average lifetime of the R+RhB mixture has decreased from 5.05 ns of pure R to 3.81 ns indicating dynamic quenching and suggesting the excited state energy transfer from R to RhB.

To check whether the energy transfer is possible between Q and RhB, we compaed the absorption spectrum of RhB and fluorescence spectra of Q in Figure S3a in the Supporting Information, and they do not show any significant overlap. The overlapping of bands and the close distance the donor and acceptor are important criteria for an efficient energy transfer from Q to RhB. In the fluorescence titration spectra of Q (3.33×10^{-4} mol/L) with the gradual addition of RhB at an excitation of 297 nm, there is no decrease in the fluorescence intensity of Q (see Figure S3b in the Supporting Information), though a small increase in fluorescence intensity of RhB occurs. During the FRET, a dynamic fluorescence quenching occurs at the excited state of donor but here fluorescence intensity of Q (donor) remains unchanged so no energy transfer from Q to RhB occurs. Therefore, in the mixture of Q, R, and RhB on excitation by the radiation of 297 nm we expect only the energy transfer in the sequence: Q to R to RhB. The fluorescence spectra of a mixture of a constant composition of Q (3.33×10^{-4} mol/L) and R (6.6×10^{-5} mol/L) with the gradual addition of RhB when excited at 297 nm (Figure 3) shows a

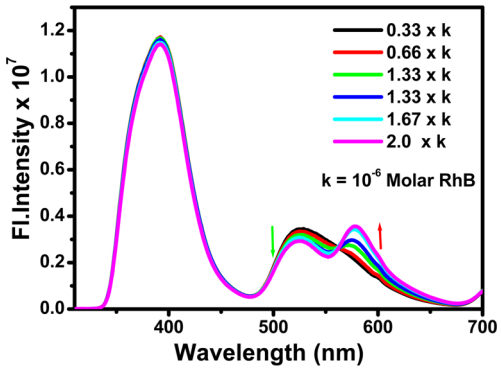
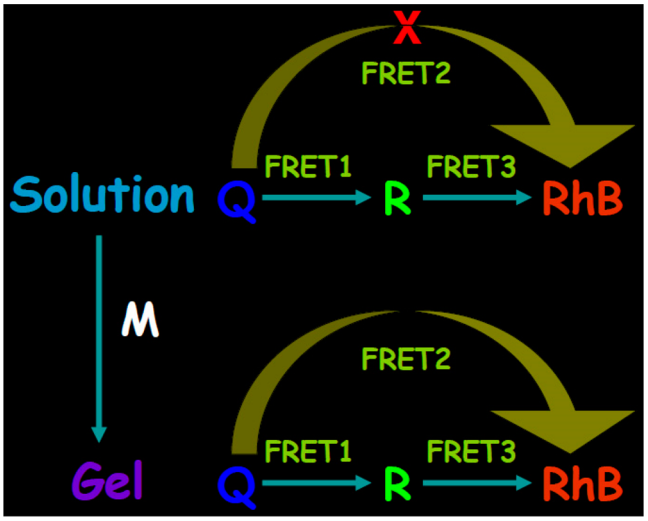


Figure 3. Fluorescence spectra of a mixture of Q and R at a constant composition of (3.33×10^{-4} mol/L Q and 6.6×10^{-5} mol/L R with the gradual addition of RhB and excited at 297 nm with the addition of RhB excited at 297 nm.

decrease of fluorescence intensity of R, whereas the fluorescence intensity of RhB increases gradually but the fluorescence intensity of Q remains unchanged. In the solution state, at a constant composition of Q and R of the mixture (1:0.2 mol ratio) for the addition of RhB energy transfer does not occur from Q to RhB, the energy transfer occurs only from R to RhB (Figure 3). This is the reason why fluorescence intensity of Q remains unchanged but that of R decreases causing an increase of fluorescence intensity of RhB (Scheme 2). So, from this result it may be inferred that in a mixture of these three chromophores energy transfer occurs in the sequence of Q to R to RhB, respectively.

Scheme 2. Schematic Presentation of the Fluorescence Resonance Energy Transfer (FRET) Processes in a Mixture of Q, R, and RhB in Solution and in the Gel State with M



Energy Transfer in the Gel State. Both Q and R produce two-component supramolecular hydrogels with M at different stoichiometric ratio and the gels exhibit excellent photophysical properties.[36,38] The MQ gel emits bright blue fluorescence where as RM gel emits a green fluorescence. The formation time of MQ gel is higher than that of RM gel as the rate constant of formation of RM is higher than that of MQ gel.[45] MQR coassembled gel acts as a light harvesting supramolecular hydrogel and has almost 83% energy transfer efficiency from Q to R with the addition of only 1.25 mol % donor R.[45] R coassembles with MQ hydrogel (1:1 molar ratio) in an autocatalytic process, i.e., a R molecule first coassembles with MQ by hydrogen bonding very slowly and as soon as it is complete, it catalyzes the other R molecules to coassemble with MQ in a rapid rate. As a result of the coassembly very fast energy transfer occurs from MQ to R ($K_{ET} = 1.7 \times 10^{12}$ s^{-1}) consequently decreasing the fluorescence intensity of acceptor R.

We have prepared W-gel using a mixture of M, Q, R, and RhB with a molar ratio of 100:100:0.5:0.02, and adding water and DMSO (water:DMSO 100:3.3, by vol.) to solublize Q. The mixture is then heated to 120 °C, followed by cooling at room temperature to produce light orange color hydrogel (Figure 4a inset). The SEM image (see Figure S4a in the Supporting Information) of the W-gel shows smooth fibrillar network morphology signifying that R and RhB are not separately deposited on the gel fibers. In other words, the W-gel fibers are also coassembled fibers like those of the MQR gel.[45] The fluorescence micrographs of MQ and MQR gels exhibit a change of color of the respective fibers from blue to green when viewed under fluorescence microscope.[45] In the W-gel (MQR +RhB), the fluorescence image (see Figure S4b in the Supporting Information) shows all the fibrils are emitting bluish white light. This bluish tinge may arise from the use of unfocused UV light of the range 330–385 nm for excitation.[50,51] In the "falling ball method" the melting point of the W-gel appears at 71 °C which is lower than those of MQ

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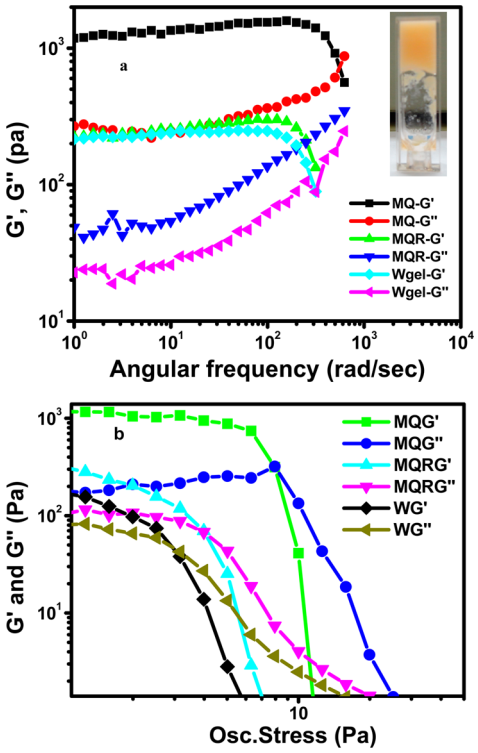

Figure 4. (a) Storage (G') and Loss (G'') modulus vs angular frequency plot of MQ gel, MQR coassembled gel and W-gel (Inset photograph of W-gel). (b) Storage (G') and Loss (G'') modulus vs oscillator stress plot at a constant frequency of 1 Hz of the three different hydrogels at a concentration of 0.5% (w/v).

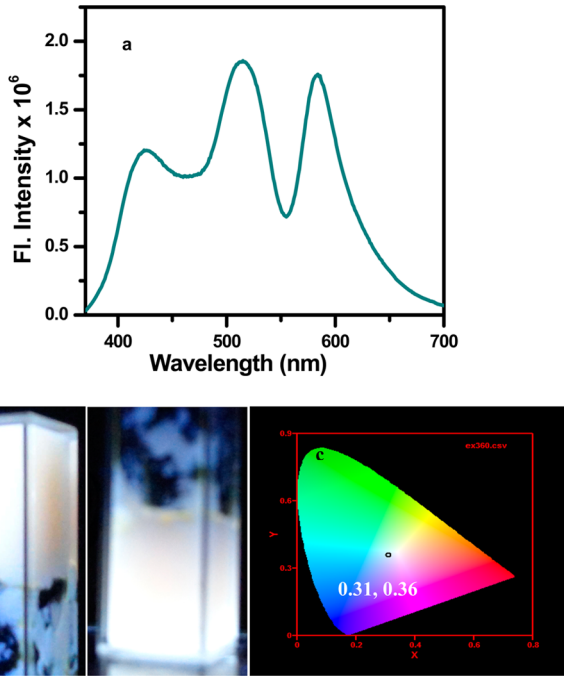

Figure 5. (a) Fluorescence spectra of W- gel having molar ratio Q:M:R:RhB 100:100:0.5:0.02 for excitation at 360 nm, (b) photograph of W-gel under UV light at 365 nm, and (c) CIE coordinate for W-gel (0.31, 0.36).

gel (77 °C) and MQR gel (71.7 °C). This lowering of gel melting temperature may be the attributed to the coassembly of MQ with R and RhB and the lower depression of gel melting point in the later case is due to the comparatively lower concentration of RhB added than that of R.

The gel formation and the gel strength of the W-gels are characterized by the rheological experiments (Figure 4a). The frequency independent storage modulus (G') with a significantly higher value of G' than that of loss modulus (G'') supports their gel nature.[52] From Figure 4a, it is clear that pure MQ gel has higher G' value than that of the MQR gel and W-gel due to the coassembly. Also it is evident that the later two gels are almost equal in strength (G' values are almost equal) because of the addition of very small amount of RhB to the coassembled gel. In the oscillatory stress experiment at a concentration of 0.5% (w/v), the critical stress values for MQ, MQR and W-gels are 7.9, 4.0, and 3.2 Pa, respectively (Figure 4b). These results indicate a gradual decrease of gel stability under oscillatory stress presumably due to the coassembly formation of R and RhB with the MQ gel.

To make a white-light-emitting hydrogel system we varied both R as well as RhB in the MQ gel and we obtained W-gel with 0.5 mol % of R and 0.02 mol % of RhB with respect to Q or M. The gel emits bright white light when excited at 360 nm and is found to be stable for about four weeks with the property of white light emission. In Figure S5 in the Supporting Information, the fluorescent spectra of MQ and MQR coassembled gel for 0.5 mol % R are compared. Here, 69% energy transfer from Q to R occurs causing a significant decrease of fluorescence intensity of Q.[45] From Figure 5a, it is clear that because of the partial energy transfer from MQ to R & RhB and R to RhB the emission spectra is broad in nature (400 to 700 nm) containing three emission peaks characterizing the three primary colors blue, green and red yielding a white light emission. The presence of the three emission peaks corresponding to Q, R, and RhB at 426, 515, and 584 nm, respectively, indicates the energy transfer is partial for both Q and R and a combination of the three partial emissions in requisite proportion produces white light. We have also tested the energy transfer between MQ gel and RhB in the gel state as in the gel state a decrease in intermolecular distance occurs. Here the fluorescence maxima (434 nm) of Q in the gel state shows a red shift of 50 nm (emission maxima of Q in solution state ~384 nm) making it closer to the absorption maxima of RhB (554 nm) (see Figure S6 in the Supporting Information) On the addition of different amounts of RhB in the MQ gel, the emission maxima of Q shows a gradual decrease of fluorescence intensity and the emission intensity of RhB gradually increases showing a red shift. This suggests that energy transfer between MQ gel and RhB is occurring and the energy transfer from MQ is 24% with the addition of 1×10^{-5} mol/L of RhB. The absence of energy transfer in the solution state but its presence in the gel state suggest that the closer proximity between the donor (Q) and acceptor (RhB) molecules in the gel state is the cause of an appreciable energy transfer between the two. Hence the energy transfer process may be summarized that in the gel state energy transfer occur between Q to R, Q to RhB, and R to RhB, but in the solution state, FRET occurs only between Q to R and R to RhB (Scheme-2). So, a combination of energy transfer process in suitable proportion in the gel state emits the white light.

In Figure5c, the Commission Internationale de L'eclairage (CIE) coordinate diagram for the white light emission of the coassembled W-gel is presented. The (CIE) coordinates of the system for excitation at 360 nm is calculated to be 0.31 and 0.36

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which values are very close to the pure white light coordinates (0.33, 0.33).[53] The fluorescence spectra of the white-light-emitting W-gel with different excitation wavelength is shown in Figure 6. With the different excitation wavelength we get the

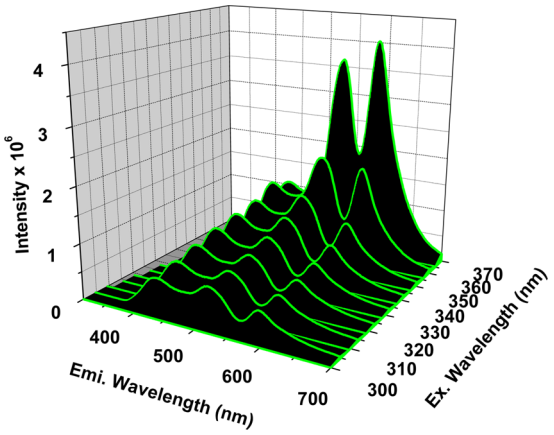

Figure 6. Fluorescence spectra of W-gel for irradiation with light of different wavelengths.

different intensity of the W-gel and its corresponding CIE coordinates are presented in Table S1a in the Supporting Information. It is apparent from the table that the excitation at 360 nm exhibits best matches of the CIE coordinates to that of white light.[53] Although excitation by light of 370 nm causes higher intensity of emission peaks of R and RhB, but the emission intensity of Q are significantly lower and the spectrum yields CIE coordinates that differ to a large extent from that of white light. This sharp increase of emission of R and RhB is due to the fact that 370 nm is very close to the absorbance peak of R (373 nm). This result therefore suggests that all the partial energy transfer between the component chromophores would not emit white light and a suitable tuning of the above emissions is required to produce the white light. We note that the excitation by the radiation of 300−350 nm also yields CIE coordinates that are not too far from that of the white light. Hence it may be concluded that on excitation in the broad range of 300−360 nm white light can be generated from the above W-gel. The composition of the W-gel is also varied for different mole % of R and RhB dye and their CIE coordinates are presented in Table S1b−d in the Supporting Information. It is apparent from the results that the 0.5 mol % R and 0.02 mol % RhB with respect to Q is the best composition to get white-light-emitting hydrogel. However, for the MQ gel with 0.5 mol % R and 0.015 mol % of RhB also produce CIE coordinates close to that of white gel. In the sol state produced at very low concentration (10 times dilute than that of W-gel) it does not exhibit any white light emission (CIE coordinates 0.20, 0.20), see Figure S7 in the Supporting Information. To understand the reason, the intensity ratios I_R/I_Q and I_R/I_{RhB} of W-gel and W-sol are compared (see Table S2 in the Supporting Information). It is apparent from the table that there is a significant mismatch in the two system for both the ratios indicating that the fluorescence energy transfer is not as good in the sol state as in the gel state. Probably in the coassembled gel the distances between the chromophores meet the requisite level necessary for optimum partial energy transfer for all the chromophor molecules. The difference in thermal movement of the chromophores in the sol state is the probable reason for the absence of optimum energy transfer required to emit the white light.

CONCLUSION

A coassembled hydrogel of M, Q, and R is used to produce white-light-emitting hydrogel (W-gel) by mixing with the RhB dye in requisite proportion. In the solution, Q emits blue light that overlaps with the absorption spectrum of R emitting green light at 531 nm. On gradual addition of R to the Q solution, both static and dynamic quenching for the emission of Q occurs as evident from the Stern−Volmer plot. FRET also occurs for the gradual addition of RhB to an aqueous solution of R, showing an emission peak at 581 nm (orange light). In a solution of constant molar composition of Q and R (1:0.02), the gradual addition of RhB causes a gradual quenching of R with no effect on the emission of Q, indicating that the energy transfer is occurring between R and RhB only. In the MQR coassembled hydrogel containing RhB the gel melting temperature is lower than those of MQ and MQR gel suggesting coassembly. The storage modulus (G′) of MQR gel is lower than that of MQ gel due to the coassembly but on addition of small amount of RhB to MQR it remains almost unchanged. By varying the RhB and R concentration in the 1:1 MQ gel white light emission is observed for the W-gel composition having molar ratio of M:Q:R:RhB = 100:100:0.5:0.02 with the CIE coordinates of 0.31 and 0.36 on excitation at 360 nm the values being very close to those of white light. But in the sol state, the CIE coordinates differ significantly from that of white light.

ASSOCIATED CONTENT

Supporting Information

CIE coordinates, Intensity ratio, UV−vis spectra, Fluorescence spectra, Fluorescence decay curves, FESEM, Fluorescence image etc. This is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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