Effect of complementary small molecules on the properties of bicomponent hydrogel of riboflavin†

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Three new bicomponent hydrogels of riboflavin (R) with salicylic acid (S), dihydroxybenzoic acid (B) and acetoguanamine (D) in 1 : 1 molar ratio have been reported. FTIR and UV-vis spectra suggest formation of H-bonded complexes in 1 : 1 molar ratio of the components. The network consists of tape, bar and helical tubes for RB11, RS11 and RD11 systems, respectively. Reversible first order phase transition and invariant storage modulus (G′) with angular frequency (ω) characterise the systems as forming thermoreversible hydrogels. The RD11 gel has the highest gel melting temperature and highest critical strain compared to other gels. WAXS study indicates different crystal structures for different gels. NMR spectra reveals higher shielding of protons in RD11 gel suggesting better π-stacking compared to RS11 and RB11 gels. RD11 gel shows two-fold enhancement of photoluminescence (PL) intensity with a substantial red shift of emission peak but RB11 and RS11 gels show PL-quenching. The gels exhibit a small decrease in lifetime and the PL property is very much temperature and pH dependent. So the complementary molecules have a pronounced effect on morphology, structure, stability and optical property of riboflavin gels.

Introduction

Supramolecular chemistry, a chemistry of non-covalent interactions coupled with molecular recognition, is an important tool to produce different semisolid elastic materials suitable for various technological applications.[1–15] Recently, the search for new molecules producing hydrogels led to the discovery of a new class of bicomponent hydrogelators.[10–15] In water, non-covalent self-assemblies of these small molecules produce a fibrillar/tubular/rodlike network superstructure, entrapping a large amount of water for their large solid-liquid interface forming a gel. Hydrogels are promising materials for their potential applications in drug delivery,[16,17] tissue engineering,[18,19] pollutant capture and release,[20] templated nanomaterial synthesis,[21] for designing different microarray kits,[22] and soft lithography.[23] Bicomponent hydrogels are superior over single component analogues due to dynamic reversibility of the assembly; beneficial for the end use of gels.[24] Also tuning of gel properties is possible by varying the composition of the components.[14c,25] The hydrogels are prepared by intelligent choice of complementary molecules dissolving in water at high temperature and producing a gel on cooling. The two complementary molecules produce a significant amount of supramolecular bonding leading to a stable supramolecular complex which breaks at higher temperatures and reproduces at low temperature producing the gel.[14]

Recently, riboflavin (R)–melamine (M),[14] melamine–uric acid (U),[13] melamine–gallic acid (G)[15a] and melamine–quinazolinedione derivative[15b] bicomponent hydrogels have been discovered. All the hydrogels exhibit interesting photoluminescent (PL) properties, stimulating us to search for new complementary small molecules to produce hydrogels. R is an important bioactive molecule (Vitamin B2) and it is involved in various biochemical processes in plants.[26–29] So the new hydrogel systems may be suitable for various *in vitro* and *in vivo* applications,[30] as well as for designing new fluorescence sensors.[31,32] Indeed, we succeeded in finding three new molecules having complementary hydrogen bonding sites to form supramolecular complexes with the isoalloxazine moiety of riboflavin. They are 2,4-diamino-6-methyl-s-triazine (acetoguanamine, D), salicylic acid (S) and 3,5-dihydroxybenzoic acid (B) (ESI, Scheme SS1†) and are chosen for the possibility of forming H-bonds with the >C═O group and imido (>NH) group of R. The disposition of the H-bonding in the different complexes may produce different isomeric supramolecular architectures. The π stacking of different supramolecular complexes generates different secondary structures like fibril, rod, tube, tape *etc.*, producing hydrogels.[14c] Such different hydrogels are expected to have different physical properties suitable for various applications. Here, the properties of three hydrogels of R with B, S and D are compared restricting to the 1 : 1 molar composition.

Results and discussion

Morphology

The optical micrograph of the RD11 gel presented in Fig. 1a [RS11 and RB11 in Fig. S1 (a,b), ESI†] shows a birefringent network morphology of gel fibres. FESEM micrographs of xerogels (Fig. 1b) reveal that RD11 has a twisted tubular morphology with a high aspect ratio. RB11 has a tape-like morphology with small width and long length [Fig. S1 (c)]. These tapes on multi-stacking produce long parallelepiped structure. RS11 also has a similar morphology [Fig. S1 (d)] except for a smaller width and is bar like. In the inset of Fig. 1b the tubular morphology is clarified

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† Electronic supplementary information (ESI) available: optical micrograph of hydrogels and xerogels, DSC thermograms, storage and loss modulus plot, FTIR, UV-VIS, PL and NMR spectra, time resolved PL spectra, lifetime data and structure of molecules used in work. See DOI: 10.1039/c0ob00670j

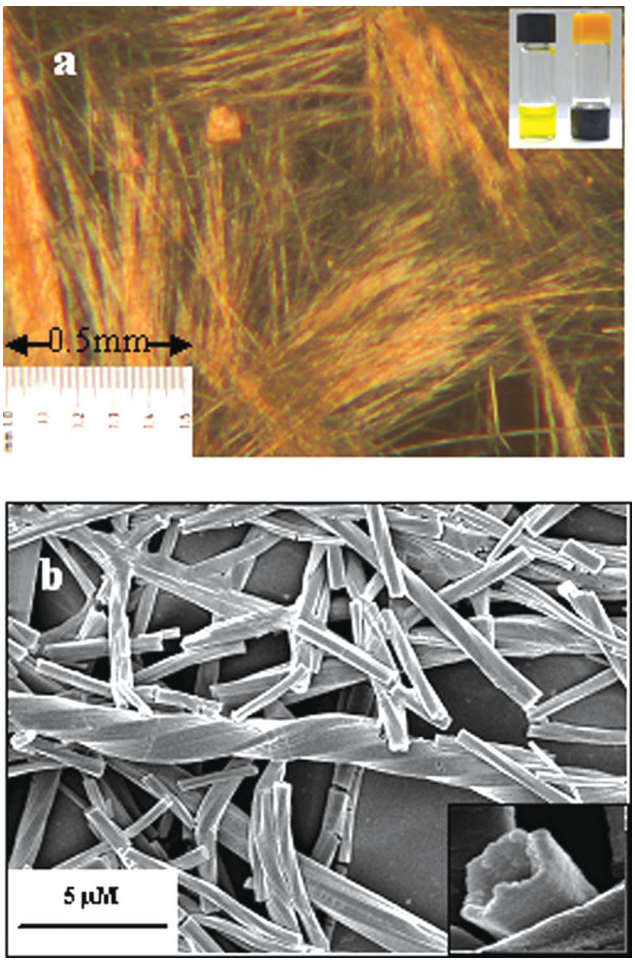
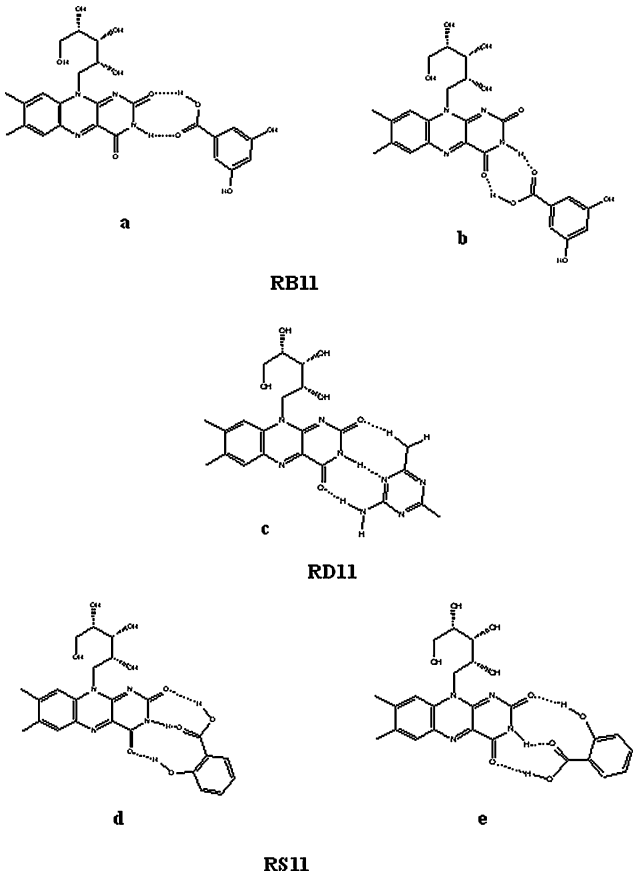


Fig. 1 (a) Polarised optical micrographs of RD11 (0.5% w/v) hydrogel. (b) SEM images of xerogels of RD11 (0.5%) (w/v) [inset of (b): enlarged picture of tubular RD11 hydrogel].



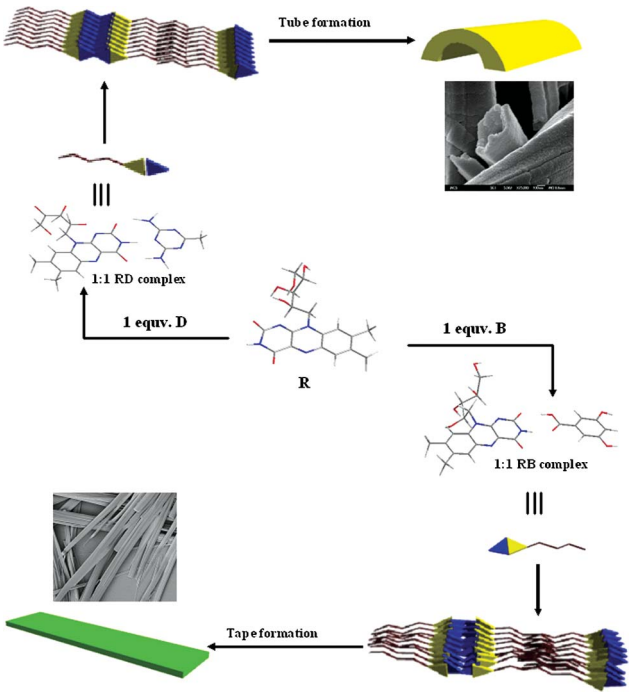
Scheme 1 Possible supramolecular structures of RB11 (a, b); RD11 (c), and RS11 (d, e) complexes (RB11 and RS11 shows isomeric structures).

from the enlarged picture of a broken tube. Thus with the three different complementary molecules, R gels exhibit three different morphology, *viz.* tape, bar and tubular type. It may be noted that RM11 gel also showed a similar tubular morphology and the tubular morphology is produced from a π-stacking process making a sheet-like structure where the inherent chirality of the ribityl chain bends the sheet to form the tube.[14c] One difference between RD11 and RM11 morphology arises from the twisted nature of the tube in the former case and replacement of one planar amino group of melamine by nonplanar methyl group in D is the probable cause.

The formation of different supramolecular complexes between RD, RB and RS systems at 1 : 1 molar compositions is presented in Scheme 1. The formation of two isomeric complexes is possible in both the RB11 (a,b) and the RS11 (d,e) systems due to the difference in H-bonding linkages as shown in Scheme 1. Due to their similarity in structure both the isomers of RB11 and RS11 are capable of producing tape and bar morphology, respectively. The origin of long tape or bar-type morphologies in RB11 and RS11 systems is due to the one-dimensional stacking of sheets[14c] produced from the π-stacking process. Due to the differences in structure of B and S from M or D, the spreading of the RB11/RS11 complexes in both planar directions is not as favourable as in the RD11 system,[14c] for the restricted planarity of RS11/RB11 supramolecular complexes (Scheme 2) hinders the longer interdigitation of ribityl chains yielding tapes and bars.

Thermal analysis

The thermoreversible nature of hydrogels is evidenced from DSC thermograms (Fig. S2, ESI†). During the first heating, RS11 (2.5% w/v) hydrogel shows a broad endotherm at 66.7 °C, whereas an exotherm at 56.6 °C during cooling and an endotherm at 62.8 °C on reheating appear. The higher melting temperature ($T_{g,m}$) in the first heating than in the second heating is for annealing after gel formation. Also there is a hysteresis of about 6 °C between gelation temperature and gel melting temperature. So the DSC results are indicative of reversible first order phase transition which is also true for RB11 and RD11 systems (ESI, Fig. S2†). The presence of a fibrillar network and reversible first order phase transition concludes the formation of thermoreversible hydrogels for the RS11, RD11 and RB11 supramolecular polymers.[33–35] The $T_{g,m}$ *vs.* concentration plot (Fig. 2a) indicates an increase of $T_{g,m}$ with concentration for all three systems (ESI, Fig. S3). Also compared to RS11 and RB11 gels, the $T_{g,m}$ curve of the RD11 system is at a higher temperature indicating better organization of RD complex producing a tubular structure, which has strong crosslinking junctions due to a larger surface area than those of the RS & RB systems. The minimum gelation concentration, gel melting temperature and morphology are summarised in Table 1.



Scheme 2 Schematic illustration of 1 : 1 RD and RB supramolecular complexes and their assembly to tube and sheet formation.

Table 1 Summary of morphology, critical gelation concentration (CGC) and gel melting temperature ($T_{g,m}$) of riboflavin containing gels at 1 : 1 molar ratio of different complimentary of bicomponent hydrogels produced at 30 °C

	Riboflavin (R)			
Samples	Composition	CGC (w/v)	Morphology	$T_{g,m}$ [a]
Melamine (M)	RM11	0.1%	Tube	93 °C
Acetoguanamine (D)	RD11	0.3%	Twisted tube	71 °C
Salicylic acid (S)	RS11	1%	Bar-like	67 °C
3,5-Dihydroxybenzoic acid (B)	RB11	1%	Tape	66 °C

[a] The concentrations are 0.2% for RM11 and 2.5% for RD11, RS11 and RB11 gels.

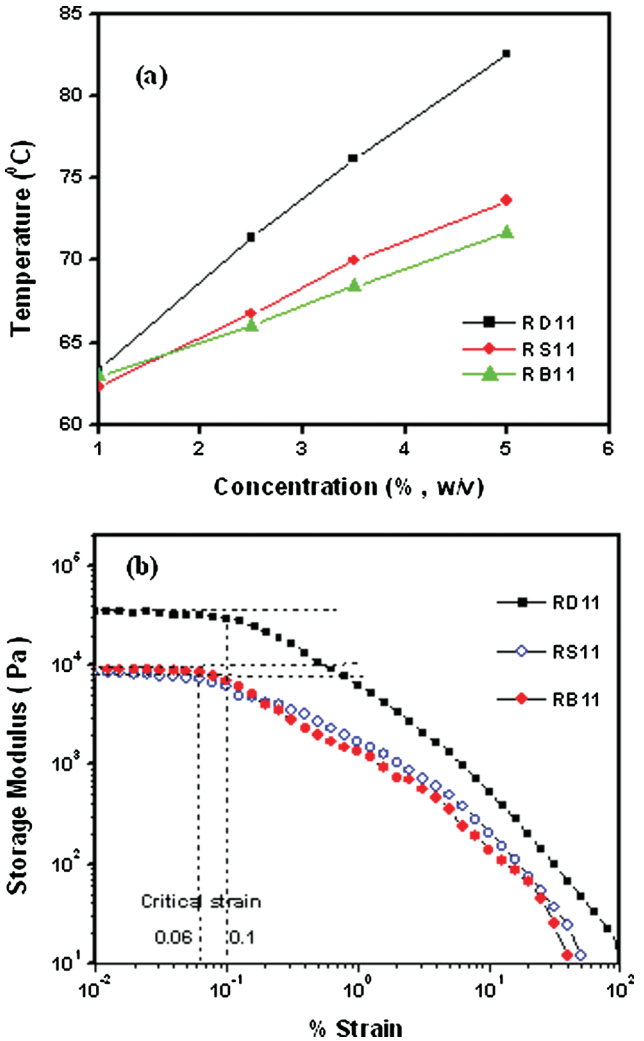


Fig. 2 (a) Gel melting temperature *vs.* concentration plot for RS11, RB11 and RD11 hydrogels. (b) Storage modulus (G′) *vs.* % strain plot of RD11, RB11 and RS11 hydrogels at 30° at a constant frequency of 1 Hz.

Rheology

The moduli *vs.* frequency (ω) plots (ESI, Fig. S4†) are linear in all the systems. The exponent values of storage modulus (G′) *vs.* ω plots are 0.037, 0.055 and 0.041 for the RS11, RB11 and RD11 respectively, characterizing the systems to be in gel form at 30 °C [$G'(\omega) \sim \omega^0$].[36–39] The G′ *vs.* % strain plots is compared for the three gels at 30 °C (Fig. 2b). The critical strain (minimum strain for gel breaking) is higher in the RD11 system (0.1) than in the others. Besides, G′ is much higher in the RD11 system indicating that RD11 gel is stronger than RB11 and RS11 gels.[40] The G′ value does not change on aging for up to 7 days indicating that structure evolution is negligible with aging.

FTIR study

The FTIR spectra of the RS11 complex (ESI, Fig. S5a†) shows a lower energy shift of the >C═O vibration peak of R (6 cm^{-1}) and the carboxyl peak of S shifts from 1660 cm^{-1} to 1644 cm^{-1}. The vibration peaks of phenolic –OH group of S at 3240 cm^{-1} disappears in the RS11 complex indicating H-bonded complex formation between >C═O of R and carboxyl and phenolic –OH groups of S (Scheme 1). In RB11 complex (ESI, Fig. S5b), shifts of the >C═O group of R from 1734 cm^{-1} to 1723 cm^{-1} and of the carboxyl group of B from 1680 cm^{-1} to 1646 cm^{-1} indicate supramolecular complex formation between R and B *via* H-bonding interaction. The phenolic –OH group of B shows a broad FTIR peak at 3310 cm^{-1} due to intermolecular hydrogen bonding of B and the broadness of the peak vanishes indicating prohibition of intermolecular aggregation of B due to complexation with R. FTIR spectra of pure R, D and RD11 complex (ESI, Fig. S5c) indicates a shift of the vibration peak of >C═O group of R from 1734 cm^{-1} to 1713 cm^{-1} in RD11 complex and the vibration peaks of $-NH_2$ group in 3000–3500 cm^{-1} region of D is broadened due to H-bond formation[41] So FTIR spectra clearly indicate that H-bonds are the cause of bicomponent supramolecular complex formation in all the systems.

Table 2 Comparison of ^{1}H NMR data (ppm) of RS, RB and RD sols and gels with that of the pure components

	Peak position (in ppm)					
Sample	Aliphatic			Aromatic		
R	2.36	2.44		7.44	7.79	
RS11 Gel	2.36	2.47		6.92 (2H)	7.47 (1H)	7.81 (1H)
RS11 Sol	2.43	2.53		6.99 (2H)	7.55 (1H)	7.88 (1H)
S	—	—		6.93 (2H)	7.47 (1H)	7.82 (1H)
RB11 Gel	2.33	2.44		6.50 (1H)	6.89 (2H)	7.65 (R)[a]
RB11 Sol	2.41	2.52		6.59 (1H)	6.98 (2H)	7.76 (R)[a]
B	—	—		6.53 (1H)	6.93 (2H)	
RD11 Gel	2.18	2.29	2.12	7.64 (R)[a]		
RD11 Sol	2.39	2.50	2.17	7.83 (R)[a]		
D	—	—	2.03			

[a] (R) = aromatic protons of R.

^{1}H NMR spectra

The ^{1}H NMR spectra of R, B, RB11 sol, RB11 gel (Table 2 and Fig. S6–9†) in D_2O indicates that peaks at 7.79 & 7.74 ppm of pure R correspond to aromatic protons and 2.44 & 2.36 ppm for aliphatic protons. Pure B has peaks at 6.93 and 6.53 ppm for aromatic protons; however no peak corresponding to –COOH and phenolic –OH protons is observed because of rapid exchange of the above protons with D_2O. In RB11 sol the peaks are shifted to down field region (7.76, 6.98 and 6.59 ppm for aromatic protons, and 2.52, 2.41 ppm for aliphatic protons) due to supramolecular complex formation. In the gel state the signals of all these protons move upfield (Table 2). This is true for all three systems. On gelation, π-stacking occurs causing a shielding of aromatic as well as aliphatic protons[15,42] of the supramolecular complexes. The shielding of protons is higher in RD11 gel compared to the RS11 and RB11 systems (*cf.* Table 2) indicating better π stacking in the former.

We also investigated the gelation of riboflavin with benzoic acid but this pair does not produce gel, indicating some contribution of phenolic –OH group in H-bonding and π-stacking processes. The use of a stronger acid than benzoic acid ($pK_a = 4.17$) may facilitate H-bonding with R. So, S ($pK_a = 2.98$) and B ($pK_a = 4.04$) are chosen and both produce gels with R in water. A comparison of the pK_a values of S and B indicates that S is a stronger acid than B so RS11 complex is stronger than RB11 complex. Another requirement is the π–π stacking which is highly favoured if electron withdrawing groups are attached to the benzene ring as the repulsion between the electronic charges of two rings is reduced.[43] The stronger the acid, the greater the withdrawal of electronic charge by the +R effect from the benzene ring by the carboxylate ion attached to it.[44] So π–π stacking should be better in RS gel than that in RB gels causing a higher melting point in RS gels. However the NMR spectral data (Table 2) indicate similar shielding of the aromatic protons in RS and RB systems. This may occur due to H-bond formation involving –OH group at the *ortho* position of S causing a loss of planarity (*ortho* effect).[44] Hence π–π stacking is not as good as expected from the planar structure. So probably the strength of H-bonds yields higher $T_{g,m}$ of RS gel than that of RB gels. RM gels are already reported,[14] so we chose a melamine (M) derivative, acetoguanamine (D), where a methyl group is present in place of amine group of M. The methyl group inductively donates electrons to the benzene ring and this causes a decrease of H-bonding capacity of $–NH_2$ group due to greater electron density on the nitrogen of $–NH_2$ group than that of M. Also the attachment of the methyl group increases the π-electron density in the benzene ring of M with a loss of planarity to some extent. These cause a lesser π-stacking between the two benzene rings of D than those in M. Hence $T_{g,m}$ of RD gels are lower than that of RM gels.

WAXS patterns

The XRD patterns of xerogels of RB11, RS11 and RD11 systems (Fig. S10, ESI†) indicate that RB11 has new peaks at $2\theta = 19.9°$, 23.0°, 26.5°, 27.3° and 28.3° compared to those of the components. Similarly, xerogels of RS11 show new peaks at $2\theta = 10.9°$, 14.3° and at 17.0° and RD11 system also new peaks at $2\theta = 6.7°$, 7.8°, 10.4°, 13.6°, 14.1° and 26.7°. So WAXS study indicates formation of new crystals of supramolecular complexes than that of the components. Also WAXS patterns of the three xerogels are different from each other indicating that the gels are composed of different crystallites. Also Fig. S11 shows that a majority of the new diffraction peaks of the xerogel match well with those of the hydrogels. So it may be surmised that the structures of the hydrogels remain mostly unaffected upon drying.

UV-vis spectra

Fig. 3 shows representative UV-vis spectra of RD sols [0.01% (w/v)] at the indicated compositions (Fig S12a & S13a (ESI†) for RS and RB systems). R has absorption peaks at 373 nm and 445 nm where absorption of B is absent. The 445 nm peak is for π–π* transition and the 373 nm peak is attributed to the mixing of n–π* transition coupled with π–π* transition of riboflavin.[29] The absorption peaks of RB of different compositions appear at the same position but intensity of the peaks decreases considerably with decrease of R. In the inset of the Fig. 3 the intensity *vs.* mol fraction of R plots are presented for RD system (RS and RB systems: ESI Fig. S12b & S13b) and two straight lines are required to represent the data points. They intercept at a common point at

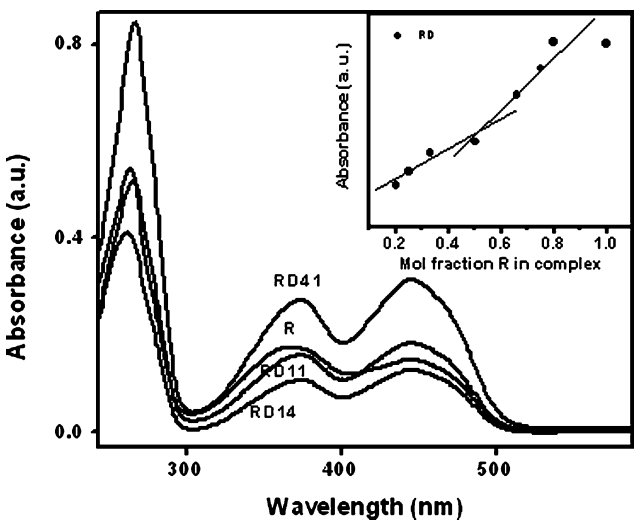


Fig. 3 UV-vis spectra of RD sols, pure R and pure D solutions (at 0.01% w/v concentration); inset: absorbance at 445 nm *vs.* mol fraction plot of R in different RD complexes.

the mol fraction of R of 0.5 indicating the complex composition at 1 : 1 molar ratio, satisfying the schematic models of Scheme 1.

Fluorescence properties

Riboflavin has good PL property[26,29] and usually PL quenching occurs in H-bond forming solvents or in the presence of electrolytes, proteins, metal ions, and organic compounds such as phenols, purines, pyrimidine, and thiols *etc.*[45,46] PL study has been carried out with the RS11 (1%), RD11 0.5% and RB11 1% (w/v) hydrogel (Fig. 4a). The fluorescent image of RD11 (0.5%) hydrogel (inset) produced by excitation with 380 nm radiation, is shown. The system emits bright green light and may be useful for sensing biological processes[32] Two new observations are noted: (a) enhancement (~2 times) of normalized PL intensity than that of R for RD11 system but in RB11 and RS11 system PL-quenching occurs and (b) appreciable red shift of the emission peak from 545 nm to ~580 nm in the three gels. The enhancement in PL intensity in the RD11 system is for hydrophobic core formation[14,15,32,47–50] during π-stacking of the H-bonded complex of R and D. This reduces quenching with water (solvent), for inhibition of further H-bonding by the hydrophobic core. In RB11 and RS11 a difference is that H-bonding occurs with the –OH groups rather than $–NH_2$ groups as in RD/RM systems. This H-bonding between the hydroxyl group of S and B causes formation of a less fluorescent complex[26,29,51] compared to that of the RD/RM systems. The red shift of λ_{max} is for π stacking of the complexes, which stabilize the excited state through resonance. It is largest (36 nm) in the case of the RD system compared to RS (31 nm) and RB (32 nm) systems. This supports our earlier view that the π stacking is better in the RD system than others.

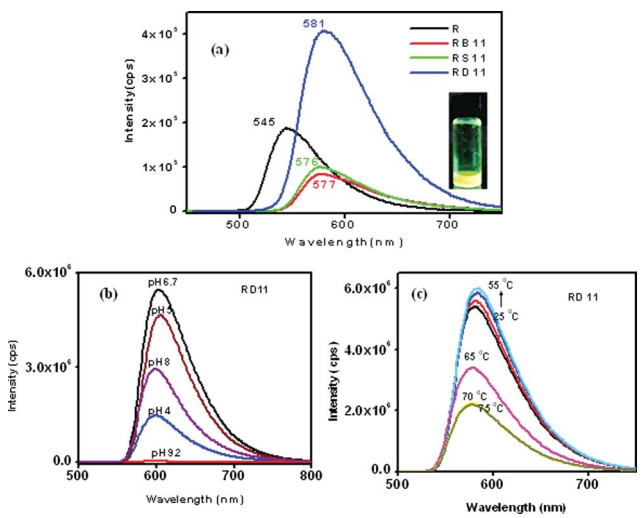


Fig. 4 (a) Normalized fluorescence spectra of RB11 1.0% w/v, RS11 1.0% w/v, RD11 0.5% w/v hydrogels and the same for pure R in water (excited at 373 nm). (b) PL spectra of RD11 at 30 °C for different pH (4, 5, 6.7, 8 and 9.2) and (c) and at pH 6.7 for different temperatures (25–75 °C).

The decay profile of RS11 1% hydrogel for excitation at 375 nm (Fig. S14, ESI†) represents a biexponential curve. The average lifetimes measured from the decay times and relative amplitudes (ESI, Table ST1) are 4.43, 3.87 and 3.12 ns for pure R, RD11 and RS11 gels, respectively. So, a decrease in lifetime of R in gel state (RS11/RD11) compared to that of pure R solution certainly indicates dynamic quenching in the gels and it might occur through the fibrilar/tubular surface of the network. The steady state intensity enhancement and quenching is usually related to the static quenching, *i.e.* formation of fluorescent/nonfluorescent complex in the ground state.[51] The RS and RB systems produce a less fluorescent complex but the RD11 system produces a strongly fluorescent complex due to the difference in H-bonding moieties. The excimer formation is also another cause of PL-quenching. Though there is a red shift in the emission peak of the gels than that of R, the possibility of excimer formation in RS11, RD11 and RB11 is not the case here because both the average lifetime and component lifetime values are lower than that of R in all the gels (ESI, Table ST1). If excimer formation occurs PL lifetime values should increase.[52,53]

The PL property of the RD11 gel is strongly dependent on pH and temperature (Fig. 4 b, c). At neutral pH the PL-intensity is the highest (Fig. 4b, and ESI Fig. 15 a,c for RS11 and RB11 gels) but it decreases both in acidic and basic media. The cause of decrease of intensity is due to the protonation of >C═O group of R at lower pH, disfavoring the H-bonding interactions required for complex formation, thereby inhibiting gel formation. At higher pH the abstraction of acidic protons and hydrogen of imino group of the components disfavors hydrogen bonding and hence gelation. At pH 6.7 the PL intensity first increases with increase of temperature (up to 45–55° C) and then it drastically decreases at higher temperatures (Fig. 4c and ESI Fig. S15 b, d). The gradual increase of PL intensity is explained by thinning of fibrils as the number of decaying paths of excitons decrease. At higher temperature the fibrils start melting and the PL-intensity decreases abruptly. So above the results demonstrate that the system may be used as a pH and temperature responsive fluorescent material. The PL spectra of xerogels (Fig. S16, ESI) correspond well to those in the gel state, further supporting that the gel structure remains unaffected on drying.

Experimental

Gel preparation

Riboflavin (R), 2,4-diamino-6-methyl-1,3,5-triazine (acetoguanamine) (D), salicylic acid (S) and 3,5-dihydroxybenzoic (B) acid are purchased from Aldrich Chemical Co., USA. To prepare different hydrogels of 1 : 1 molar composition, appropriate quantities of R and any of the D, S and B are dissolved in water at 90 °C and cooled to 30 °C. The gel is freeze dried to obtain dry 1 : 1 complex. Then the hydrogels in different concentrations (w/v) are made by taking appropriate amounts of the above mixtures in water. The minimum gelation concentration for RD11, RS11 and RB11 is found to be 0.3%, 1.0% and 1.0% in (w/v), respectively.

Characterization

The morphology of the gel is studied by optical microscope (Leitz, Biomed) with crossed polarizer using a digital camera (Leica D-LUX 3). Small portions of the hydrogels are placed on a glass cover slip, dried in air at 30 °C and finally in vacuum, and observed in a FESEM instrument (JEOL, JSM 6700F) operating at 5 kV after platinum coating.

Differential Scanning Calorimetry (DSC) of the hydrogels (2.5%) in large volume capsules (LVC) fitted with O-rings was performed using a Perkin Elmer Diamond DSC. No weight loss was detected after the run. Rheological experiments are performed with advanced rheometer AR 2000 (TA Instruments, USA) using cone plate geometry in a peltier plate. The plate diameter is 40 mm and an angle of 4° with the plate gap 121 μm. Two types of experiments are performed at 30° C: (i) by frequency sweep and (ii) by strain sweep at constant frequency of 1 Hz. The WAXS experiments of xerogels and of pure components have been performed using a Bruker AXS diffractomer (model D8 Advance) using a Lynx Eye detector. The instrument is operated at a 40 KV voltage and at a 40 mA current. Samples are scanned from $2\theta = 5$ to 30° at the scan rate of 0.5 s per step with a step width of 0.02°

The FTIR spectra of xerogels are recorded using KBr pellets of the samples in an FTIR-8400S instrument (Shimadzu). The UV-vis spectra of the samples are recorded on a Hewlett-Packard UV-vis spectrophotometer (model 8453) using solutions in a cuvette of 1 mm path length. PL studies of hydrogels prepared in a sealed cuvette, have been carried out in a Horiba Jobin Yvon Fluoromax 3 instrument. Each gel sample in a quartz cell of 1 cm path length is excited at 373 nm and emission scans are recorded from 400 to 750 nm using a slit width of 2 nm with a 1 nm wavelength increment having an integration time of 0.5 s. PL lifetimes have been measured using a time-correlated single photon counting fluoremeter (Fluorecule, Horiba Jobin Yvon). The system is excited with 375 nm nanoLED of Horiba Jobin Yvon having λ_{max} at 368 nm with pulse duration <200 picoseconds. All the samples are prepared in double distilled water at 30 °C, deoxygenated by purging with argon gas for half an hour. Average fluorescence lifetimes (τ_f) for exponential iterative fitting are calculated from the decay times (τ_i) and the relative amplitudes (a_i) using the following relation:

$$\langle\tau_f\rangle = a_1\tau_1 + a_2\tau_2 + a_3\tau_3 \quad (1)$$

The goodness of fit has been assured with the help of static parameters χ^2 (1.15) and DW (1.85). ^{1}H NMR spectra of pure R, S, D, B and RS, RD, RB sols and gels in D_2O (at minimum gelation concentrations) are recorded *via* a Bruker DPX 300 instrument at 300 MHz (the concentration of R is kept same). The pH variation of PL measurement is made using three buffer solutions of pH 6.7, 4.0, and 9.2 [made from buffer capsules, (Merck, Mumbai)] and pH 5 & pH 8 solutions are made using a mixture of dil. HCl (0.1 N) and $NaHCO_3$ (0.1 N) solutions in required proportion. The pH values are monitored with the pH-meter.

Conclusions

Three new bicomponent hydrogels containing riboflavin have been discovered through supramolecular organization with S, B and D in 1 : 1 molar ratio. The complex formation between the components occurs due to H-bonding and the composition of the complexes is found to be 1 : 1 molar ratio. Isomerism in RS and RB complexes through H-bonding linkages in the RS11 and RB11 complexes is proposed. These supramolecular complexes self-assemble *via* π-stacking producing the network morphology consisting of tape, bar and helical tubes for RB, RS and RD systems, respectively. Reversible first order phase transition and invariant G′ with angular frequencies is observed for all the hydrogels, suggesting the formation of thermoreversible hydrogels. The RD11 gel has the highest gel melting temperature and the higher shielding of protons suggesting better π-stacking in RD11 system compared to that in the RS11 and RB11 systems. The higher acid strength of S causes higher $T_{g,m}$ in RS11 gels than in RB11 gels. The PL intensity is enhanced in RD system but the RB and RS show PL quenching. The gels exhibit a small decrease in fluorescence lifetime and the differences in PL intensity has been attributed to the less fluorescent complex formation of R with S and B than that with D. The PL property is very much temperature and pH dependent, at pH 7 highest PL intensity is observed in all the gels. So, the morphology, structure, stability and PL property of the bicomponent riboflavin gel depends on its complementary molecule.

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