Hierarchical tuning of 1-D macro morphology by changing the composition of a binary hydrogel and its influence on the photoluminescence property†

Abhijit Saha, Swarup Manna and Arun K. Nandi*

Received (in Cambridge, UK) 31st March 2008, Accepted 6th May 2008
First published as an Advance Article on the web 18th June 2008
DOI: 10.1039/b805344h

1-D morphological tuning in the riboflavine(R)–melamine(M) hydrogel system (from helical fiber to rod-like to tubular morphology) with an interesting photoluminescence property by changing the composition of the RM components.

Designing the order and orientation of molecular self assembly through supramolecular interaction is a fascinating area of research to fabricate nano- and macro-structured materials like fibers, tapes, rods, helices, ribbons and hollow tubes.[1,2] These materials have new electronic, optical, thermal and stimuli-responsive properties, promoting them for applications in optoelectronic devices, catalysis, drug delivery, sensors, light harvesting medium *etc*.[3,4] The synthesis of different supramolecular structures is continuously growing because they produce gels in organic/aqueous media and these yield different properties; characteristics of the molecular structure of the components. Use of binary gel systems[5] is more advantageous over one component gels to tailor the properties by functional modification of the components,[5c] changing one of the components[2c] or using different isomers[2a] and by changing the molar ratio of the components.[3b] So to explore the properties of small molecular gels for practical use, different superstructures are to be tailored. Among the small molecular gels, hydrogels have drawn great attention because of their use in tissue engineering, pollutant capture and in drug delivery.[5,6] Recently a bicomponent hydrogel of riboflavin (R) (an important member of flavin family) and melamine (M) was reported. R and M produce a supramolecular complex in the molar ratio of 3 : 1 by hydrogen bonding and the complex is organized into a fibrillar network structure, producing the gel. The complex has an oriented structure where the riboflavin molecules are in different planes to those of melamine.[7a,b] So addition of an insufficient amount of riboflavin may change the orientation character of the complex significantly and a different morphology may be generated.

Here, for the first time, we are reporting the hierarchical tuning of one-dimensional (1-D) morphology in a hydrogel system, from helical bunched fibers to rods and hollow tubes, by changing the composition. So far, little attention has been paid on making linear macrostructures, especially the microtubes from small organic molecules as most of the microtubes have been synthesized from lipids, amphiphiles, bola-amphiphiles, copolymers, polyelectrolytes and organogelators *etc*.[1,2c–e] So this R–M system is important as synthesis is not required to prepare complex organic molecules nor are any amphiphiles, surfactants or other charged species used. Besides, R is a well-known vitamin and also behaves as a photoreceptor in the phototropism of plants,[8,9] pertaining its use in biological system. Also, the RM hydrogels have a good photoluminescence (PL) property and it would be interesting to observe if there is any effect of the morphology on the PL property.

RM hydrogels are made by taking R and M in different proportions and making a 0.2% w/v solution in water at 120 °C. The system was cooled to room temperature; producing gels. A field emission scanning electron microscopy (FESEM) of freeze dried samples are presented in Fig. 1 (and suppl. Fig. 1, see ESI†) and it is evident that as the R content in the complex decreases there is a change in the morphology. Both RM41 and RM31 gels have helical fibers, RM21 exhibits rod like morphology and RM11, RM12 and RM13 systems exhibit tubular morphology. It is an interesting and important observation where the transformation of 1-D morphology from fiber to rod to tube occurs simply by changing the composition of the complex.

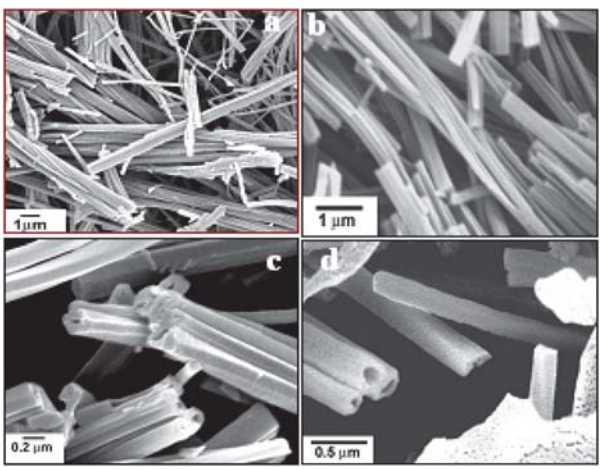

Fig. 1 FESEM images of xerogels of 0.2% w/v hydrogels of (a) RM31 (helical fiber), (b) RM21 (rod), (c) RM11 (tube) and (d) RM13 (tube).

Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, India. E-mail: psuakn@mahendra.iacs.res.in; Fax: (+91) 33 2473 2805
† Electronic supplementary information (ESI) available: Experimental details, FESEM & AFM images, normalized PL spectra of hydrogels, UV-vis spectra of hydrogels and xerogels. See DOI: 10.1039/b805344h

Scheme 1 Molecular structure of riboflavin and melamine and their proposed mode of 1 : 1 and 3 : 1 self-assembly to form tubes and helical bunched fibers.

In Scheme 1 a probable mechanism of helical fibril and hollow tube formation is presented. The RM31 complex (energy minimized) is nonplanar in structure and one R molecule in upper plane and another R molecule at lower plane generate a small twist which grows during the π stacking process, producing helical fibrils (suppl. Fig. 2, see ESI†). In the RM21 complex, as the R concentration decreases compared to that in RM31, one hydrogen-bonding site of the melamine remains free and so no orienting effect of the RM complex occurs, resulting in rod like structure. With a further decrease in the amount of R the complex structure became single sided (Scheme 1) and the chiral ribityl chain (shown as a tail) has directional character suitable for H-bonding through the –OH groups. The R and M supramolecular complex may alternate in position, during π stacking, spreading the complex in both ways through interdigitation and making a sheet like structure and due to the inherent chirality of the ribityl chain, the sheet then bends to produce tubes. The π stacking occurs both longitudinally and laterally, the former gives the long dimension of the tube and the later yields the thickness of the tubes. As the diameter increases, the interdigitation of the ribityl chains becomes poorer giving a limit to the thickness (60–70 nm). The length of the tube is probably controlled from an enthalpy–entropy balance of the self-organization process. In RM12 and RM13 systems, tubes are produced in same fashion and there is some excess melamine, which is evident from the irregular species in the micrographs (Fig. 1d & suppl. Fig. 1e and f, see ESI†).

Pure riboflavin has a good photoluminescence property.[8a,9b] It shows quenching in hydrogen bond forming solvents and also in the presence of electrolytes, proteins, purines, pyrimidines, thiols *etc*.[9a–c] In the RM gels, the hydrogen bonding sites of isoalloxazine moieties are used by melamine, thereby reducing the H-bonding ability with water, resulting in a sharp increase in the PL intensity.[7] In Fig. 2 the PL intensity is compared for the different RM compositions normalized to same R content. It is evident that PL intensity is much lower in the xerogels than that of pure R and it increases with increasing melamine content in the complex. It is an interesting new

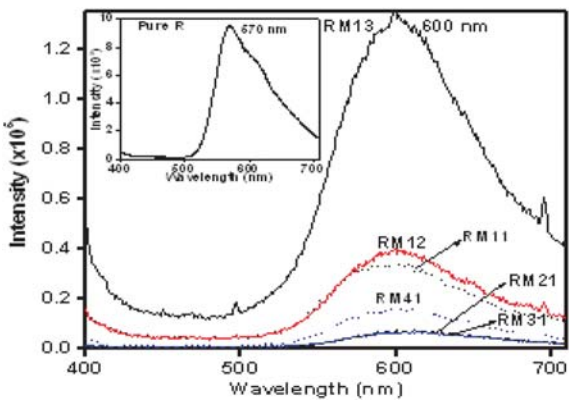

Fig. 2 PL spectra of different RM xerogels produced from 0.20% (w/v) hydrogels (excited at 365 nm) normalized to the same R content (inset: fluorescence spectrum of pure R).

observation and a sharp fall of normalized intensity is due to H-bonding with melamine molecules that increase the nonradiative decay paths of the π* electrons of riboflavin in the complex. PL intensity enhancement in the lower R content samples may be explained from the nature of supramolecular complex and its morphology. Probably it may be due to the static quenching that depends on the stability of the RM complex which is greater for RM41 and RM31 complexes than for the RM11 complex due to increased number of H-bonds in the former. Also, the hollow space in the tubes reduces the nonradiative decay paths compared to those of compact fibrils. One important observation is that the emission peak in the RM complexes has red shifted by ~30 nm. This large red shift is due to the formation of an organized structure by the π stacking process and this structure reduces the π–π* energy band through resonance stabilization of the π* electrons between the ordered isoalloxazine rings in the self-assembly.

In the RM hydrogels, the PL intensities (normalized to the same riboflavin concentration) show similar behaviour (suppl. Fig. 3, see ESI†) as for solid spectra, *i.e*., RM41, RM31 and

Table 1 Comparison of the fluorescence property in RM gels and their xerogels, normalized to same riboflavin content

	Hydrogels		Xerogels		
Composition	λ_{max}/nm	Intensity ($\times 10^5$)	Morphology	λ_{max}/nm	Intensity ($\times 10^5$)
Pure R	540	0.4	—	570	9.57
RM41	565	2.5	HF[a]	601	0.15
RM31	571	2.1	HF[a]	612	0.067
RM21	570	2.0	Rod	610	0.064
RM11	569	3.6	Tube	600	0.34
RM12	568	3.8	Tube	601	0.40
RM13	559	9.5	Tube	600	1.30

[a] HF = Helical fiber.

RM21 gels have almost the same PL intensity but this increases when tubes are produced (Table 1). RM13 exhibits the highest increase ($\sim$5 times that of RM31). The pure R solution at the same concentration has $\sim$20 times lesser PL intensity than that of the RM13 gel. The increase of the PL intensity in R–M gels compared to that of pure R (in solution) is due to the blocking of the hydrophilic part of isoalloxazine ring by melamine, inhibiting quenching by polar water molecules.[9] Here λ_{max} also exhibits a red shift (20–30 nm) as in xerogels (Table 1). So morphology has strong effect on the PL property in both hydrogels and xerogels.

The higher λ_{max} values in the xerogels compared to the hydrogels can be explained as from the greater stabilization of the exitons through the solid aggregate than that in the solution state. A substantial decrease in PL intensity of the xerogels compared to those of hydrogels may be due to the increased nonradiative decay paths in the solid state.

In Fig. 3 the π–π* transition peak of the UV-vis spectra is compared for different R contents in both xerogel and hydrogel. As the R content is decreased there is a red shift of the π–π* peak in both cases. The red shift in xerogels and hydrogels is due to the molecular stacking of the RM complexes with the π* electrons becoming more stabilized through the stacked isoalloxazine rings. It is interesting that for lower R content samples where tubes are formed the red shift is larger, probably due to the planar structure of RM aggregates causing fruitful overlapping compared to the twisted aggregates of helical fibrils. Also, the red shift in the hydrogels are lower than those of xerogels, indicating that molecular stacking is more effective in xerogels than that in hydrogels.

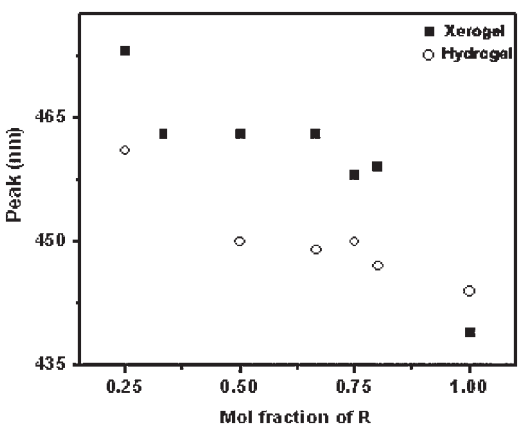

Fig. 3 UV-Vis spectral plot of the π–π* transition peak *vs.* the mol fraction of riboflavin for different RM gels of 0.09% (w/v) concentration.

Thus, changing the compositions of the RM complex in the bicomponent gel can tune the macro morphology from helical fiber to rod to hollow tube, which exhibits a higher PL intensity than that of helical fibers. This is indeed a unique bottom-up approach for the hierarchical tuning of the 1-D macro morphology of a binary hydrogel and for controlling its photoluminescence property.

We gratefully acknowledge CSIR and DST, New Delhi (Grant No. SR/SI/PC-32/2004) for financial support.

Notes and references

1 (*a*) G. C. L. Wong, J. X. Tang, A. Lin, Y. Li, P. A. Janmey and C. R. Safinya, *Science*, 2000, **288**, 2035; (*b*) P. Terech and R. G. Weiss, *Chem. Rev*., 1997, **97**, 3133; (*c*) R. V. Ulijn and A. M. Smith, *Chem. Soc. Rev*., 2008, **37**, 664; (*d*) D. Yan, Y. Zhou and J. Hou, *Science*, 2004, **303**, 65; (*e*) A. Ajayaghosh and V. K. Praveen, *Acc. Chem. Res*., 2007, **40**, 644; (*f*) T. Shimizu, M. Masuda and H. Minamikawa, *Chem. Rev*., 2005, **105**, 1401; (*g*) A. Ajayaghosh, S. J. George and A. P. H. J. Schenning, *Top. Curr. Chem*., 2005, **258**, 83.

2 (*a*) P. Mukhopadhyay, Y. Iwashita, M. Shirakawa, S.-i. Kawano, N. Fujita and S. Shinkai, *Angew. Chem., Int. Ed*., 2006, **45**, 1592; (*b*) S. Yagai, T. Nakajima, K. Kishikawa, S. Kohmoto, T. Karatsu and A. Kitamura, *J. Am. Chem. Soc*., 2005, **127**, 11134; (*c*) H. Y. Lee, S. R. Nam and J.-I. Hong, *J. Am. Chem. Soc*., 2007, **129**, 1040; (*d*) C. Zhan, P. Gao and M. Liu, *Chem. Commun*., 2005, 462; (*e*) J.-P. Douliez, C. Gaillard, L. Navailles and F. Nallet, *Langmuir*, 2006, **22**, 2942; (*f*) A. P. H. J. Schenning and E. W. Meijer, *Chem. Commun*., 2005, 3245; (*g*) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev*., 2005, **105**, 1491.

3 (*a*) S. Yagai, Y. Monma, N. Kawauchi, T. Karatsu and A. Kitamura, *Org. Lett*., 2007, **9**, 1137; (*b*) D. K. Smith, *Chem. Commun*., 2006, 34; (*c*) Y. Ono, K. Nakashima, M. Sano, Y. Kanekiyo, K. Inoue, J. Hojo and S. Shinkai, *Chem. Commun*., 1998, 1477; (*d*) A. Ajayaghosh, C. Vijayakumar, R. Varghese and S. J. George, *Angew. Chem., Int. Ed*., 2006, **45**, 456; (*e*) N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev*., 2005, **34**, 821; (*f*) A. Ajayaghosh, V. K. Praveen and C. Vijayakumar, *Chem. Soc. Rev*., 2008, **37**, 109.

4 *Molecular Gels: Materials with Self assembled Fibrillar Network*, ed. R. G. Weiss and P. Terech, Spinger, Dordrecht, 2006.

5 (*a*) L. A. Estroff and A. D. Hamilton, *Chem. Rev*., 2004, **104**, 1201; (*b*) A. R. Hirst and D. K. Smith, *Chem.–Eur. J*., 2005, **11**, 5496; (*c*) S. Yagai, M. Higashi, T. Karatsu and A. Kitamura, *Chem. Mater*., 2004, **16**, 3582.

6 (*a*) Z. Yang, H. Gu, Y. Zhang, L. Wang and B. Xu, *Chem. Commun*., 2004, 208; (*b*) Y. Zhang, H. Gu, Z. Yang and B. Xu, *J. Am. Chem. Soc*., 2003, **125**, 13680; (*c*) M. de Loos, B. L. Feringa and J. H. van Esch, *Eur. J. Org. Chem*., 2005, 3615; (*d*) H. Kobayashi, A. Friggeri, K. Koumota, M. Amaike, S. Shinkai and D. N. Reinhoudt, *Org. Lett*., 2002, **4**, 1423; (*e*) S. Kiyonaka, K. Sugiyasu, S. Shinkai and I. Hamachi, *J. Am. Chem. Soc*., 2002, **124**, 10954; (*f*) M. Suzuki, M. Yumoto, M. Kimura, H. Shirai and K. Hanabusa, *Chem.–Eur. J*., 2003, **9**, 348.

7 (*a*) S. Manna, A. Saha and A. K. Nandi, *Chem. Commun*., 2006, 4285; (*b*) A. Saha, S. Manna and A. K. Nandi, *Langmuir*, 2007, **23**, 13126.

8 (*a*) G. R. Penzer and G. K. Radda, *Q. Rev. Chem. Soc*., 1967, **21**, 43; (*b*) V. Massey, *Biochem. Soc. Trans*., 2000, **28**, 283; (*c*) K. V. Thimann and G. M. Curry, in *Comparative Biochemistry*, ed. M. Florkin and H. S. Mason, Academic Press, New York, 1960, vol. 1, p. 281.

9 (*a*) P. F. Heelis, *Chem. Soc. Rev*., 1982, **11**, 15; (*b*) G. Weber, *Biochem. J*., 1950, **47**, 114; (*c*) W. J. Rutter, *Acta Chem. Scand*., 1958, **12**, 438.

