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Renewable resource-derived thixotropic self-assembled supramolecular gel: Magnetic stimuli responsive and real-time self-healing behaviour†

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We designed and synthesized a simple fluorescent self-assembled molecular gel from renewable resource and well characterized using various techniques. The self-assembly mechanism was studied in relative to the molecular structure. We also demonstrate that Fe_3O_4 nanoparticle were encapsulated *in situ* into the organogel by a simple process, which generated magnetic gel with remarkable self-healing features. More importantly stimuli responsive self-healing properties of magnetic gel have been characterized by visual inspection, morphological and rheological analysis.

Plants and animals have the unique capability to alter their physiological functions in response to environmental conditions such as temperature, light, pH, electromagnetic fields, mechanical stress, and chemical stimuli. The basic science behind nature's activity has always been an interesting source of knowledge for scientists to develop new technologies for advanced "smart" materials.[1,2] Among these, magnetic responsive gel materials have attracted a great deal of research interest in the field of actuators, image enhancement, separation science and drug delivery, to name a few.[3] Generally polymeric gels possesses covalently cross-linked irreversible structures with certain limitations in the real time field applications, whereas physical gels, are self-assembled structures based on reversible intermolecular interactions, which overcome the limitations of polymeric gel systems.[4] Recently, Weiss presented a brief perspective on the status quo of molecular gels with inputs from scientists across a broad range of interests such as rheology, structural characterization, soft matter, thermodynamics, etc.[4a] Generally self-assembled gels are continuous in structure and own solid-like rheological behaviour due to the entrapment of solvent in a self-assembled 3D solid matrix through surface tension and capillary forces.[5] We report herein the ability of small amphiphilic π-gelators derived from cashew nut shell liquid (CNSL), a renewable resource, and pyrene, to generate a stimuli responsive self-healing magnetic gel. Establishing and optimizing efficient materials from renewable resources has been a focus that substantially addresses the needs of the 21st century.[6] Cardanol, a bio-based non-isoprene unit derived from CNSL, is comprised of a rich mixture of phenolic lipids: 5% of 3-(pentadecyl) phenol (3-PDP), 50% of 3-(8*Z*-pentadecenyl) phenol, 16% of 3-(8Z,11Z-pentadecadienyl) phenol and 29% of 3-(8*Z*,11*Z*,14-pentadecatrienyl) phenol.[7] The uniqueness of cardanol stems from its structural features and easily accessible saturated and unsaturated hydrocarbon chains. Although few stimuli responsive self-healing molecular gels and polymer gels were reported in the literature,[8] the preparation of supramolecular gel through non-covalent interactions with special properties, such as self-healability, stimuli responsive character are becoming an important strategy to develop advanced materials. Recently our research group has explored the self-assembled molecular gels and its application in medicine and biology.[9] In the present study, we demonstrate the design, synthesis and stimuli responsive self-healing behaviour of super gel and magnetic gel derived from renewable resource.

The π-gelators were constructed from renewable resources in two steps. First step involves the nucleophilic substitution reaction of cardanol, **1a** and 3-n-pentadecylphenol, **1b** with methyl bromoacetate resulted in the formation of corresponding methylesters, **2a** and **2b** in good yield. Reaction of compound **2a** and **2b** with hydrazine followed by Schiff base formation with a fluorescent signaling unit, 1-pyrenecarboxaldehyde resulted in the formation of π-gelators, **3a** and **3b** respectively in good yield (Scheme 1). Here we have adapted a simple and economical synthetic pathway that could be used directly for practical applications. The gelation ability of compounds **3a** and **3b** were consistently studied for different solvents by the "stable to inversion" method.[2] Compound **3a** forms supramolecular organogels in a number

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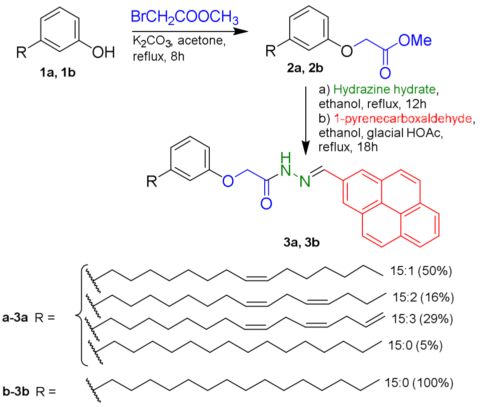
of solvents at very low critical gelation concentrations (CGCs). The gelation ability of π-gelators in various solvents and oils is summarized in Table S1. Among the various solvents studied, gelator **3a** showed excellent organogelation ability with lowest CGC of 0.18 % (wt/v) in heavy paraffin oil. Gels thus formed are thermos reversible in nature, and stable at ambient conditions.



Scheme 1. Synthesis of π-gelators, **3a** and **3b**.

In the case of **3b,** a remarkable change in gelation ability was observed; **3b** formed a weak gel in heavy paraffin oil with CGC of 0.75 wt/v%. From this result, we presume that the existence of a kink in the hydrophobic part of **3a,** which stabilizes on self-assembly, might be the driving force for the formation of a strong gel (SG).[10] We also report a straightforward method to prepare a magnetic gel (MG) by mixing Fe_3O_4 nanoparticles into SG, followed by sonication for 5 min. A detailed procedure for the preparation of MG has been given in the experimental section. FTIR is very useful tool for investigating hydrogen bonding interactions or non-covalent interactions between molecular building blocks and interacting component. More specifically, stretching frequencies of -OH, -NH and -C=O are more distinctive, shift in wave number can be observed as a result of non-covalent interactions.[11] The clustering of Fe_3O_4 on gel was observed mainly due to the interaction between the imine nitrogen (-*N*=CH-) and carbonyl carbon (-NH-*C*=*O*) with Fe_3O_4 nanoparticles, as inferred from FTIR studies (See ESI). A plot of T_{gel} vs gelator concentration (Figure 1a) clearly depicts a steady increase in T_{gel} with respect to the concentration of the gelator. The positive influence of Fe_3O_4 nanoparticles in the gelation of SG could also be directly ascertained from Figure 1a. The fluorescent nature of SG and MG was studied using emission spectral technique. In a self-assembled state, SGs in heavy paraffin oil (1 X 10^{-5}M) show emission peaks at 408, 428, 453 and 483 nm, which upon further titration with heavy paraffin oil, show increased peak intensity near 408 nm with an observed blue shift. This result clearly demonstrates the disassembly of self-assembled SG. Further, the addition of Fe_3O_4 nanoparticles into SG dissolved in heavy paraffin oil (1 X 10^{-5}M) leads to the hypochromic shift in emission peak centred at 428 nm. The introduction of Fe_3O_4 cause little distortion in self-assembly, thus this effect intends that the intensity of the absorption maximum is lowered (Figure 1b).

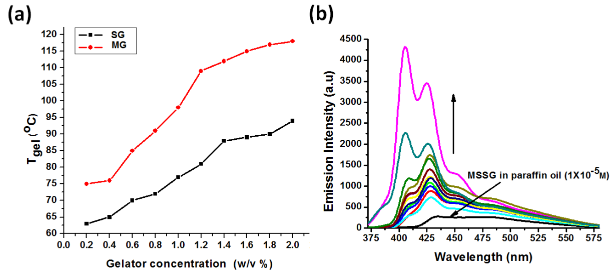


Figure 1. (a) A plot of T_{gel} vs gelator. (b) Fluorescence titration of SG with heavy paraffin oil [λ_{ex} = 350 nm]. In titration experiments, direction of arrow shows the response of emission intensity with piecemeal addition of 100 μL of heavy paraffin oil. 2 mL of initial volume of solution (1 X 10^{-5} M) was taken for titration experiments. Black line pointed by arrow is for MG in paraffin oil (1 X 10^{-5} M solution).

The morphology of Fe_3O_4 nanoparticles, SG and MG, were obtained through high-resolution transmission electron microscopy (HRTEM). HRTEM analysis of Fe_3O_4 clearly depicts the existence of particle sizes of 20-40 nm (Figure 2a). The formation of 3D entangled fibrous network with a diameter ranging from 100-200 nm for SG can be consistently observed by HRTEM analysis. (Figure 2b). In the case of MG, an attachment of Fe_3O_4 nanoparticles on the fibrous network was observed.[12] Li et al. clearly explain the morphology of magnetic nanoparticles doped gel, where non-covalent interaction between gelator and magnetic nanopartclies plays a vital role.[12c] We also beleive that the binding of Fe_3O_4 with SG by means of noncovalent interaction might be the driving force for such morphological changes. After incorporation of appropriate magnetic nanoparticles into the 3D-fiberous network of gel, their response to the external magnetic stimuli gel may alter gel network structure, thereby mechanical property of the system changes and becomes magnetic responsive.

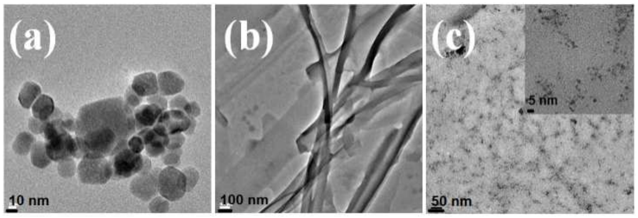


Figure 2. HRTEM image of (a) Fe_3O_4 nanoparticles, (b) SG and (c) MG. For morphological analysis, 100 mL of self-assembled fibers of SG/MG in heavy paraffin oil was dispersed in 1 mL of acetone and drop casted the resultant solution on HRTEM grid.

Small angle X-Ray diffraction (SAXD) was employed to gain the additional insight into the molecular packing of gelator molecule in supramolecular self-assembled state. SAXD of the SG gave a Bragg's reflection at 3.1 nm indicating an ordered arrangement of the molecule in gel state, obtained from the packing of hydrophobic unit due to the van der Waals interaction. The peaks observed at 1.5 nm, 0.81 nm and 0.54 nm articulates the stacking of phenyl moiety, H-bonding and π-

π stacking. The observed d-spacing value is greater than the molecular length of SG, determined by molecular modelling studies using energy minimized calculations, suggest that during the course of self-assembly process, hydrophobic part intercalates to form a supramolecular structure. Typically, crystalline plane diffraction pattern of Fe_3O_4 is observed at 21º, 30º, 35º, 41º, 51º, 63º and 67º respectively.[13] In the case of MG, in addition to the peaks corresponding to SG, moderately intense peak at 30.5º, 35.7º, 43.4º, 57.1º and 62.5º was also observed (Figure 3a). Based on spectroscopic, microscopic and SAXD results, one can easily predict the mechanism for the formation of self-assembled supramolecular structure by utilizing H-bonding, π-π stacking and weak van der Waals interaction. A schematic representation of gelator arrangement in MG is given in Figure 3b.

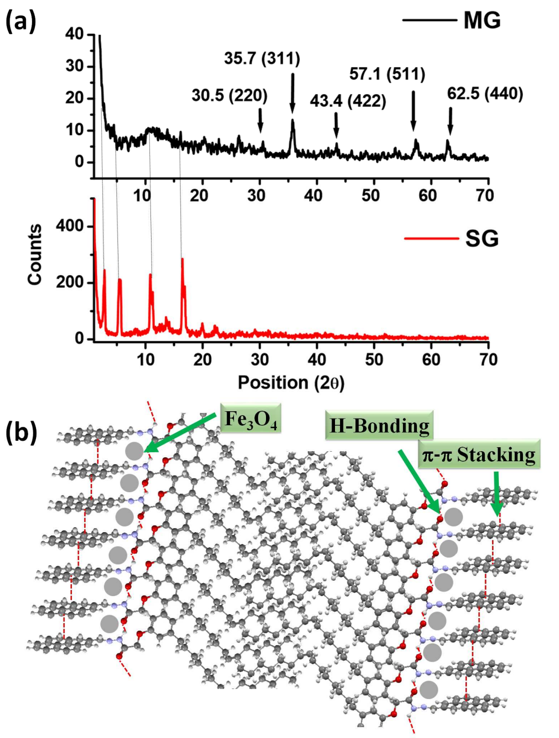


Figure 3. (a) SAXD pattern of SG and MG. (b) Schematic representation of possible molecular packing model for MG.

The elastic behaviour of a gel could be directly keyed by measuring the difference between storage moduli (G′) and loss moduli (G′′).[14] In SG and MG, the value of G′ was found to be much higher than that of G′′ in the entire range of frequency sweep, and this result clearly suggests the formation of strong gel with good tolerance to external forces (Figure 4a). In the strain sweep experiment, G′ and G′′ remain constant up to a certain level. Afterwards, a gradual drop was observed and a crossover occurred between G′ and G′′. This crossover point is considered as the critical strain (γ_c) of the gel (Figure 4b).[15] The γ_c values for SG and MG are 13.61 (G′=G″=312 Pa) and 4.95% (G′=G″=819 Pa) respectively (Figure 4b).

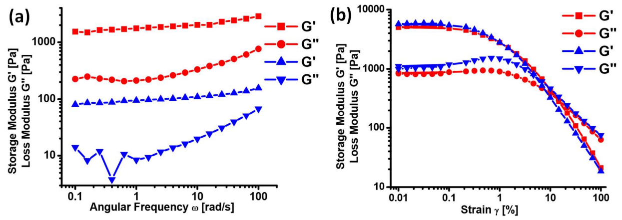


Figure 4. (a) Angular frequency dependence of G′ and G′′ and (b) strain amplitude dependence of G′ and G′′. SG - red line and MG -blue line.

Thermo-responsive behaviour and processability of SG and MG, for various practical applications at different temperatures was studied by continuous temperature ramp up and ramp down experiments (Figure 5a and 5b). These results clearly depict the structural and mechanical integrity of both SG and MG even after continuous ramp up and ramp down in temperature for more than three cycles. After looking at the exceptional mechanical behaviour of these gels, we planned to analyse the thixotropic or self-healing nature of SG and MG by performing the step strain experiment of G′ and G′′ (Figure 5c and 5d). Generally thixotropic materials that change their physical property in response with mechanical action, such systems were well known in natural systems. Functions of protoplasm, red blood cells, nerve regeneration and muscular activities were specific examples.[16] Thixotropic gels are dynamic self-assembled system constitutes a challenging and unique self-healing property. A detailed investigation on the behaviour of these self-assembled system under mechanical stress and resting time is required. Shinkai et al. clearly demonstrate the requirements of thixotropic gelator, which are as follows; (a) it should an efficient super gelator, (2) gel should display the thixotropic property even at a very low concentration, and (c) gels should not lost its property during the cycles of breaking and regeneration process.[17] Thixotropic or self-healing nature of SG and MG was identified using step strain experiment. By applying high magnitude of strain (100%), both G′ and G′′ values were apparently decreased because of the broken network structure.[17] Recovery of G′ and G′′ was observed within 5 seconds by simultaneous decline in strain to 0.5% in the case of SG, and 0.01% in case of MG. This result clearly argues the self-healing nature by reconstruction of network structure and fast recovery of the mechanical property (Figure 5c and 5d). It is interesting to note that even after 5 cycles of breaking and regeneration process, there is no significant loss in mechanical behaviour. Most of the self-healing materials reported in literature were polymer gels and only little is known related to the self-healing of gels.[8] Recently Shi and co-workers reported the spontaneous, macroscopic supramolecular assembly of building blocks into an advanced assembled structures, the assembly process joined the hydrophobic surfaces, thereby minimizing the overall interfacial free energy of the system.[18] In this report we present a low molecular weight gel, SG and MG displaying remarkable self-healing property. In particular, owing to increasing interest of magnetic gels in the fields of controlled drug-delivery, separation science, artificial muscle and smart biomaterials,[19] we have investigated the macroscopic supramolecular assembly of building blocks prepared from SG and MG. In order to differentiate SG from MG, SG has been loaded with rhodamine dye.

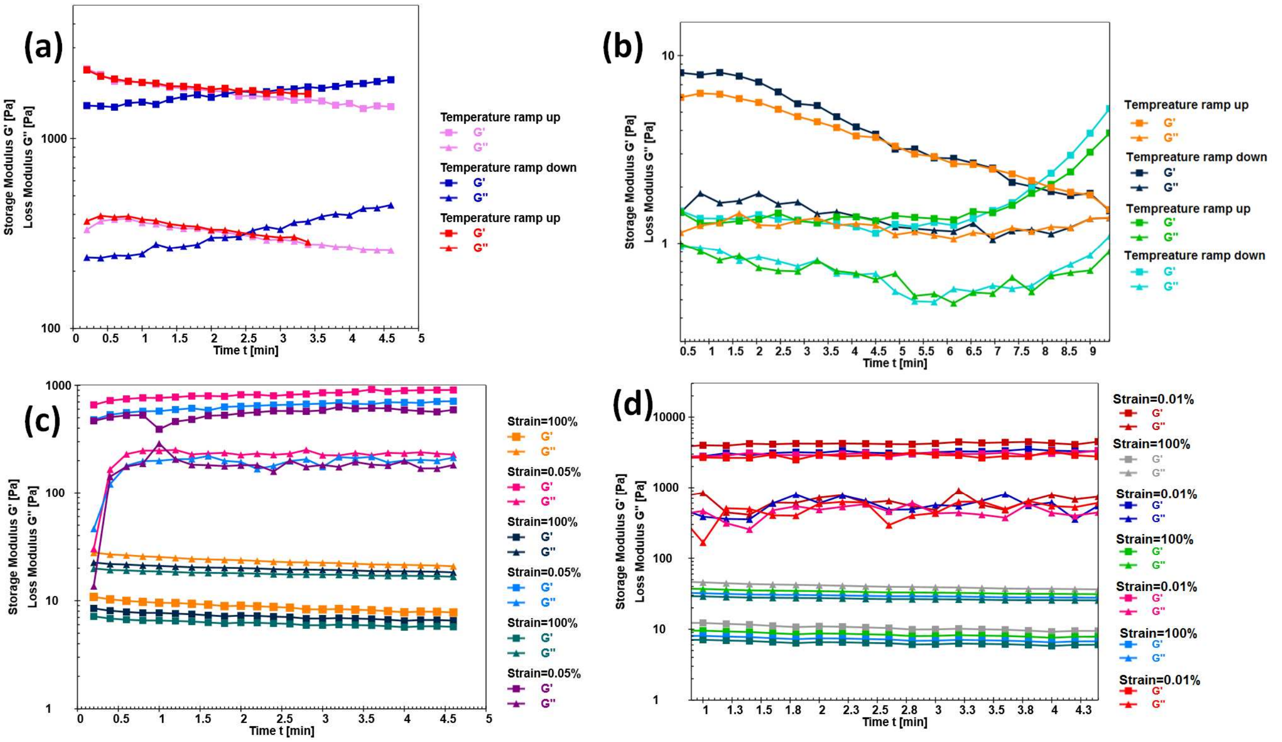


Figure 5. (a and b) Storage (G') and loss modulus (G'') of SG and MG in temperature ramp experiment respectively. Ramp up and ramp down temperature for SG and MG are 25-to-55ºC and 15-to-60 ºC. (c & d) Time course change of G' and G'' of SG and MG in step strain experiment respectively. For SG, 100% strain (4.5 min) and 0.05% strain (4.5 min) were applied alternatively and for MG 100% strain (4.5 min) and 0.01% strain (4.5 min) were applied alternatively. Concentration of SG and MG: 1 wt/v% in heavy paraffin oil.

Self-healing of SG to MG started immediately after connecting the two pieces of gels one over the other, and within 5 min, the two pieces of gels start healing themselves via non-covalent interactions and were strong enough to hold vertically by using tweezer (Figure 6a). By utilizing self-healing process, non-magnetic SG has been connected with magnetic responsive MG, and the entire system attains magnetic stimuli responsive character. Owing to the interesting self-healing behaviour displayed by SG and MG, we were more curious in investigating self-healing behaviour in water medium. In the absence of external magnetic stimuli, hydrophobic SG and MG come close to each other by mere shaking and self-healing occurred, in order to minimizing the overall interfacial free energy. The resultant self-healed gel could be picked by tweezer (Figure 6b, see ESI for supporting video). To understand the mechanism of self-healing process, we designed a gel fusion experiment. Fusion of SG with gel prepared from **3b** (moiety without kink) was not proceeded well because of absence of kink in **3b**, whereas fusion or self-heling of SG with SG or SG with MG worked very well. From this result, we presume that the cooperative effect of hydrophobic interaction and kink present in it were responsible for self-healing mechanism.[18,20]

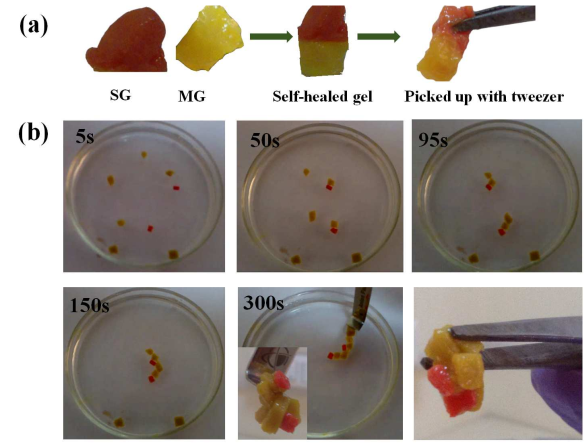


Figure 6. (a) Macroscopic level self-healing of SG and MG and picking up of the resultant by tweezer. (b) Self-healing of SG and MG in water with the evolution of time, 5s-to-300s. After 300s, self-healed gel were scooped by spatula and picked up using tweezer. To show the colour difference between SG and MG, pieces of SG was tagged with red colour using rhodamine dye.

Thus the magnetism cooperates well with the self-healing process and induces the stimuli responsive behaviour. Small pieces of MG in water could be systematically aligned and self-healed under the guidance of external magnetic field (see supporting video). This phenomenon can be potentially used for the development of advanced materials operated from remote place. The bulk conveyance path guided under an external magnetic field strength of 0.556T in both water and air medium is shown in supporting video.

In summary, a fluorescent, self-healing and magnetic stimuli responsive gel was obtained from renewable resources by a simple process utilizing self-assembly phenomenon. Hydrogen bonding and π-π stacking interactions that exist in the SG and MG stabilize the self-assembled structures, which was identified by various techniques. Morphological analysis clearly depicted the formation of a highly entwined fibrous network with attached Fe_3O_4 nanoparticles. Stability and mechanical strength of SG and MG has been identified by rheological measurements. The magnetic properties and self-healing behaviour of this system have been demonstrated, and work well on the macroscopic level. SG and MG were both compatible for practical applications since they retained their inherent mechanical properties, even after processing the gels several times under different magnitudes of strain and temperature. We envision that this self-healing and magnetic stimuli responsive gel might have potential applications in the medical, biological, environmental, and electronics fields. Further detailed investigation of these gel materials are in progress.

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Notes and references

1 Recent reviews on stimuli responsive materials: (a) E.-K. Lim, T. Kim, S. Paik, S. Haam, Y.-M. Huh, K. Y. Lee, *Chem. Rev.* **2015**, 10.1021/cr300213b; (b) L. Cheng, C. Wang, L. Feng, K. Yang, Z. Liu, *Chem. Rev.* **2014**, *114*, 10869–10939; (c) J. Yao, M. Yang, Y. Duan, *Chem. Rev.* **2014**, *114*, 6130–6178; (d) X. Zhang, J. Yin, J. Yoon, *Chem. Rev.* **2014**, *114*, 4918–4959; (e) S. S. Babu, V. K. Praveen, A. Ajayaghosh, *Chem. Rev.* **2014**, *114*, 1973–2129; (f) J. E. Stumpel, D. J. Broer, A. P. H. J. Schenning, *Chem. Commun. (Camb)*. **2014**, *50*, 15839–15848; (g) S. Mura, J. Nicolas, P. Couvreur, *Nat. Mater.* **2013**, 12, 991–1003; (h) O. Kuksenok, D. Deb, P. Dayal, A. C. Balazs, *Annu. Rev. Chem. Biomol. Eng.* **2014**, *5*, 35–54; (i) A. S. Hoffman, *Adv. Drug Deliv. Rev*. **2013**, *65*, 10–16; (j) X. Hou, W. Guo, L. Jiang, *Chem. Soc. Rev.* **2011**, *40*, 2385–2401; (k) Y. Chen, H. Chen, J. Shi, *Adv. Mater.* **2013**, **25**, 3144–3176; (l) C.-H. Lu, B. Willner, I. Willner, *ACS Nano* **2013**, *7*, 8320–8332. (m) N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, *34*, 821–836; (n) M. Suzuki, K. Hanabusa, *Chem. Soc. Rev.* **2009**, *38*, 967–975.

2 For book chapters: (a) R. G. Weiss, P. Terech, *Molecular Gels, Materials with Self-Assembled Fibrillar Networks*, Springer, New York, **2006**; (b) B. Escuder, J. F. Miravet, *Functional molecular gels*, RSC soft Matter Series, **2014** and references cited there in

3 (a) V. N. Rao, M. N. Ganivada, S. Sarkar, H. Dinda, K. Chatterjee, T. Dalui, J. D. Sarma, R. Shunmugam, *Bioconjugate Chem.* **2014**, *25*, 276–285; (b) R. Libanori, F. B. Reusch, R. M. Erb, A. R. Studart, *Langmuir* **2013**, *29*, 14674–14680; (c) S. Bolisetty, J. J. Vallooran, J. Adamcik, R. Mezzenga, *ACS Nano* **2013**, *7*, 6146–6155; (d) W.-H. Chiang, V. T. Ho, H.-H. Chen, W.-C. Huang, Y.-F. Huang, S.-C. Lin, C.-S. Chern, H.-C. Chiu, *Langmuir* **2013**, *29*, 6434–6443.

4 (a) R. G. Weiss, *J. Am. Chem. Soc.* **2014**, *136*, 7519-7530; (b) S. Dong, Y. Luo, X. Yan, B. Zheng, X. Ding, Y. Yu, Z. Ma, Q. Zhao and F. Huang, *Angew. Chem. Int. Ed. Engl.*, 2011, **50**, 1905–9; (c) X. Yan, D. Xu, X. Chi, J. Chen, S. Dong, X. Ding, Y. Yu and F. Huang, *Adv. Mater.*, 2012, **24**, 362–9; (d) M. Zhang, D. Xu, X. Yan, J. Chen, S. Dong, B. Zheng and F. Huang, *Angew. Chem. Int. Ed. Engl.*, 2012, **51**, 7011–5; (e) S. Dong, B. Zheng, D. Xu, X. Yan, M. Zhang and F. Huang, *Adv. Mater.*, 2012, **24**, 3191–5.

5 (a) T. G. Barclay, K. Constantopoulos, J. Matisons, *Chem. Rev.* **2014**, *114*, 10217–10291; (b) S. I. Stupp, L. C. Palmer, *Chem. Mater.* **2014**, *26*, 507–518; (c) D. Ivnitski, M. Amit, B. Rubinov, R. Cohen-Luria, N. Ashkenasy, G. Ashkenasy, *Chem. Commun.* **2014**, *50*, 6733–6736; (d) J. D. Tovar, *Acc. Chem. Res.* **2013**, *46*, 1527–1537; (e) R. Marty, R. Nigon, D. Leite, H. Frauenrath, *J. Am. Chem. Soc.* **2014**, *136*, 3919 – 3927.

6 V. S. Balachandran, S. R. Jadhav, P. K. Vemula, G. John, *Chem. Soc. Rev.* **2013**, *42*, 427-438.

7 (a) K. Lalitha, P. Jenifer, Y. S. Prasad, K. Muthusamy, G. John, S. Nagarajan, S. *RSC Adv.* **2014**, *4*, 48433–48437; (b) L. Faure, S. Nagarajan, H. Hwang, C. L. Montgomery, B.R. Khan, G. John, P. Koulen, E. B. Blancaflor, K. D. Chapman, *J. Biol. Chem.* **2014**, *289*, 9340-9351.

8 (a) W. Miao, D. Yang and M. Liu, *Chemistry*, **2015**, *21*, 7562–70; (b) M. J. Gao, J. L. Wang, Q. Cong, B. Zhang, X. C. He, X. F. Ma and G. Li, *Mater. Sci. Forum*, **2015**, *815*, 675–683; (c) K. Miyamae, M. Nakahata, Y. Takashima and A. Harada, *Angew. Chem. Int. Ed. Engl.*, **2015**, 10.1002/anie.201502957; (d) T. Rossow and S. Seiffert, *Supramolecular Polymer Networks and Gels*, Springer International Publishing, Cham, **2015**, vol. 268;(e) L. Peng, H. Zhang, A. Feng, M. Huo, Z. Wang, J. Hu, W. Gao and J. Yuan, *Polym. Chem.*, **2015**, *6*, 3652–3659; (f) X. Yu, L. Chen, M. Zhang and T. Yi, *Chem. Soc. Rev.*, **2014**, *43*, 5346–71; (g) K. Imato, T. Ohishi, M. Nishihara, A. Takahara and H. Otsuka, *J. Am. Chem. Soc.*, **2014**, *136*, 11839–45; (h) Z. Qi and C. A. Schalley, *Acc. Chem. Res.*, **2014**, *47*, 2222–33; (i) A. Harada, Y. Takashima and M. Nakahata, *Acc. Chem. Res.*, **2014**, *47*, 2128–40; (j) S. Dong, B. Zheng, F. Wang and F. Huang, *Acc. Chem. Res.*, **2014**, *47*, 1982–94; (k) P. Xing, X. Chu, M. Ma, S. Li and A. Hao, *Phys. Chem. Chem. Phys.*, **2014**, *16*, 8346–59; (l) R. Du, J. Wu, L. Chen, H. Huang, X. Zhang and J. Zhang, *Small*, **2014**, *10*, 1387–93; (m)S. Basak, J. Nanda and A. Banerjee, *Chem. Commun. (Camb).*, **2014**, *50*, 2356–9; (n) M. Vatankhah-Varnoosfaderani, S. Hashmi, A. GhavamiNejad and F. J. Stadler, *Polym. Chem.*, **2014**, *5*, 512–523.

9 (a) K. Lalitha, S. Nagarajan, S. *J. Mater. Chem. B* **2015**, *3*, 5690-5701; (b) K. Lalitha, Y. S. Prasad, C. U. Maheswari, V. Sridharan, G. John, S. Nagarajan, S. *J. Mater. Chem. B* 2015**,** **3**, 5560-5568.

10 D. Chandler, *Nature* **2005**, *437*, 640-647.

11 (a) Y. Zhang, B. Yang, X. Zhang, L. Xu, L. Tao, S. Li, Y. Wei, Chem. Commun. **2012**, *48*, 9305–9307; (a) Y. Zhang, L. Tao, S. Li, Y. Wei, Biomacromolecules **2011**, *12*, 2894–2901.

12 (a) E. Taboada, L. N. Feldborg, A. Pérez del Pino, A. Roig, D. B. Amabilino, J. Puigmartí-Luis, *Soft Matter* **2011**, *7*, 2755; (b) I. O. Shklyarevskiy, P. Jonkheijm, P. C. M. Christianen, A. P. H. J. Schenning, A. Del Guerzo, J.-P. Desvergne, E. W. Meijer, J. C. Maan, *Langmuir* **2005**, *21*, 2108–2112; (c) S. Li, V. T. John, G. C. Irvin, S. H. Rachakohda, G. L. McPherson, C. J. O'Connor, *J. App. Phy.* **1999**, *85*, 5965.

13 M. R. Guilherme, R. S. Oliveira, M. R. Mauricio, T.S. P. Cellet, G. M. Pereira, M. H. Kunita, E. C. Muniz, A. F. Rubira, *Soft Matter* **2012**, *8*, 6629–6637.

14 Y. Zhang, B. Yang, X. Zhang, L. Xu, L. Tao, S. Li, Y. Wei, *Chem. Commun. (Camb).* **2012**, *48*, 9305–9307.

15 D. Liu, D. Wang, M. Wang, Y. Zheng, K. Koynov, G. K. Auernhammer, H.-J. Butt, T. Ikeda, *Macromolecules* **2013**, *46*, 4617–4625.

16 (a) U. Proske, D. L. Morgan, J. E. Gregory, *Prog. Neurobiol.* **1993**, *41*, 705 – 721; (b) R.W. Briehl, *Nature* **1980**, *288*, 622 – 624; (c) K. E. Hagbarth, J. Hugglund, M. Nordin, E. U. Wallin, *J. Physiol.* **1985**, *368*, 323 – 342.

17 P. Mukhopadhyay, N. Fujita, A. Takada, T. Kishida, M. Shirakawa, S. Shinkai, *Angew. Chem. Int. Ed.* **2010**, *49*, 6338–6342.

18 M. Cheng, G. Yu, Y. Zhang, M. Song, Y. Zhang, F. Shi, *Small*, **2014**, *10*, 3907-3911.

19 (a) C. He, S. W. Kim and D. S. Lee, *J. Control. Release*, **2008**, *127*, 189–207; (b) A. Fernández-Barbero, I. J. Suárez, B. Sierra-Martín, A. Fernández-Nieves, F. J. de Las Nieves, M. Marquez, J. Rubio-Retama and E. López-Cabarcos, *Adv. Colloid Interface Sci.*, **2009**, *147-148*, 88–108; (c) L. Frkanec and M. Zinić, *Chem. Commun. (Camb).*, **2010**, *46*, 522–37; (d) J. Ramos, A. Imaz, J. Callejas-Fernández, L. Barbosa-Barros, J. Estelrich, M. Quesada-Pérez and J. Forcada, *Soft Matter*, **2011**, *7*, 5067; (f) C. Aimé and T. Coradin, *J. Polym. Sci. Part B Polym. Phys.*, **2012**, *50*, 669–680; (g) J. Estelrich, E. Escribano, J. Queralt and M. A. Busquets, *Int. J. Mol. Sci.*, **2015**, *16*, 8070–8101.

20 Z. Wei, J. H. Yang, J. Zhou, F. Xu, M. Zrinyi, P. H. Dussault, Y. Osada, Y. M. Chen, *Chem. Soc. Rev.* **2014**, *43*, 8114-8131 and references cited therein.