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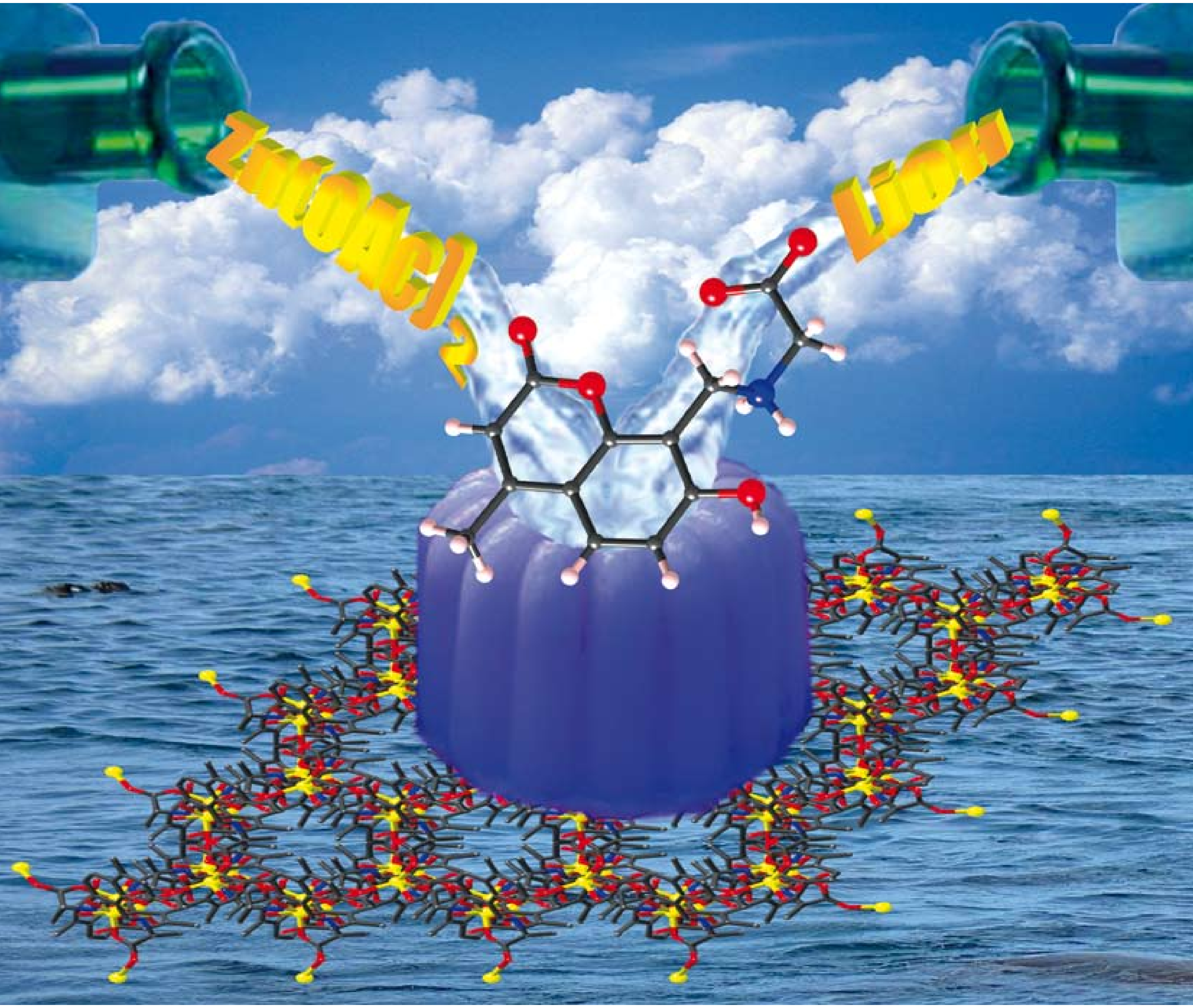

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Fluorescence enhancement of coordination polymeric gel

FEATURE ARTICLE
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Phosphate esters as "tunable" reagents in organic synthesis

Fluorescence enhancement of coordination polymeric gel†‡

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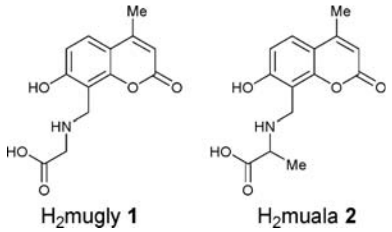
Instant hydrogelation of coumarin-derivatized glycine has been demonstrated in the absence of long-chain hydrophobic groups upon formation of a zinc(II) coordination polymer, which exhibits fluorescence enhancement upon gelation.

Gel formation by small molecules has attracted intense research interest in recent years.[1] Though gel formation by organic molecules has been reported widely in the literature, coordination polymeric gels have only been a recent interest.[2] Metallogels or coordination polymeric gels can be formed by (i) the interaction of metal ions with a gel matrix[3] or (ii) metal–ligand interactions containing small molecules[4] or long-chain molecules.[5,6] Metallogels have found applications in a wide range of fields, *e.g.* stimuli responsive materials,[5,6c] catalysis[4a] and as templates for assembling nanoclusters.[4b]

To date, there is relatively little information in the literature regarding the photoluminescence properties of coordination polymeric gels, including switching of the emission colour,[7] field emission and light emitting properties.[8] In view of the high photoluminescence quantum efficiencies of coumarin derivatives as fluorescence dyes,[9] it is expected that such compounds may exhibit interesting spectroscopic and luminescence properties during the sol–gel transition. Herein we report the formation of a coordination polymeric gel of *N*-(7-hydroxyl-4-methyl-8-coumarinyl)-glycine, H_2mugly (**1**), with Zn^{2+} in the absence of long-chain hydrophobic groups. Remarkably, the fluorescence property is dramatically enhanced upon the formation of a coordination polymeric gel relative to **1** in aqueous solution. Though there are few reports on the enhancement of photoluminescence intensity upon gelation, most of those known are of organic gels,[10a] two component gels[10b,c] or emissive materials immobilized in a gel network.[10d] Fluorescence enhancement upon the formation of a coordination polymeric hydrogel is observed here for the first time.



Scheme 1 Structures of coumarin-derivatized amino acids.

When a basic aqueous solution of **1** (Scheme 1) is reacted with $Zn(OAc)_2 \cdot 2H_2O$, a hydrogel of $[Zn(mugly)(H_2O)] \cdot nH_2O$ (**3**) is formed instantly, confirmed by the inverted test tube method (Fig. 1(a)). No gelation was observed when the same reaction was repeated with other organic solvents (including MeOH and EtOH) or other metal ions (including Co^{2+} and Ni^{2+}). The as-prepared hydrogel, **3**, is pH responsive and converts to a colourless clear solution upon adjustment of the pH to 2, but retains its structure at pH 8. At acidic pH values, the ligand should be protonated, thus disturbing the complexation and gel structure. On adjusting the pH to 8, the formation of a complex allows the recovery of the gel structure. On the contrary, when aqueous solutions of H_2muala (**2**) and $Zn(OAc)_2 \cdot 2H_2O$ are mixed, a viscous liquid is formed that flows under gravity when inverted at room temperature, but yields single crystals of $[Zn(muala)(H_2O)] \cdot 0.5H_2O$ (**4**).

In the absence of a suitable single crystal of **3** to undertake X-ray crystallography, the structural characterization of **4**‡ helps us understand the packing and intermolecular interactions that are responsible for the formation of hydrogel **3** (Fig. S1†). The muala anion is coordinated to the Zn^{2+} center in a tridentate mode, along with a water ligand and carboxylate oxygen from a neighboring unit, thus forming a 1D coordination polymer. These

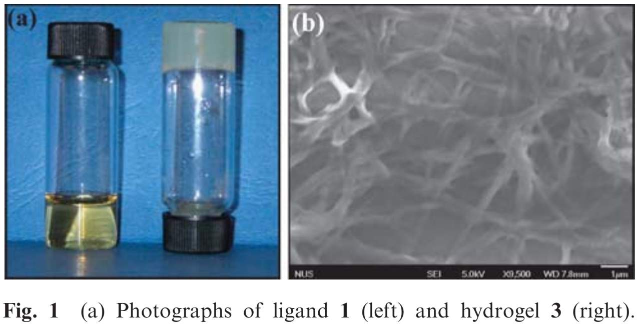


Fig. 1 (a) Photographs of ligand **1** (left) and hydrogel **3** (right). (b) SEM image of freeze dried **3**.

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† Electronic supplementary information (ESI) available: Experimental procedures, crystal structure of **4**, photophysical and rheological data. See DOI: 10.1039/b807478j

‡ Crystal data for **4**: $C_{14}H_{16}NO_{6.5}Zn$, M = 367.65, trigonal, $P3_221$, a = 9.0773(5), c = 31.015(3) Å, V = 2213.2(3) $Å^3$, Z = 6, ρ_{calc} = 1.667 g cm^{-3}, T = 223 K, μ = 1.698 mm^{-1}, 3802 independent reflections, final R indices for 3407 reflections [$I > 2\sigma(I)$], $R1$ = 0.0425, w$R2$ = 0.0895, R_{int} = 0.0528, GoF = 1.094, Flack parameter = 0.005(15). CCDC 661250. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b807478j

1D zigzag coordination polymers are arranged in a criss-crossed fashion, such that the disk-like coumarin rings segregate to form hydrophobic pockets, assisted by various hydrogen bonds generated by the H_2O and N–H donor groups and O atoms as hydrogen bond acceptors. Such packing can easily be expanded to form a hydrogel by accommodating the water molecules firmly in the interstitial hydrophilic pockets, together with hydrogen bond donors and acceptors.

Fig. 1(b) shows the SEM image of freeze dried **3**, which clearly displays a typical fibrillar network structure. The fibers are several micrometers long, with diameters in the range 200–500 nm. From the crystal structure of **4**, it appears that the 1D coordination polymers aggregate to form fibrous nanostructures, which then further organize into a 3D network through non-covalent interactions to entrap water molecules.[1b] Since Ni^{2+} and Co^{2+} ions fail to coordinate to **1** to form 1D polymeric aggregates, no gel formation was observed in these cases.

The electronic absorption and emission of **1** and **3** were studied extensively. Upon addition of Zn^{2+} ions to an aqueous solution of **1** in the presence of 2 equiv. of LiOH ($[\mathbf{1}] = 9.12 \times 10^{-5}$ M), the π–π* absorption band[9] exhibits a blue shift in absorption energy, with a well-defined isosbestic point at 352 nm (Fig. S2†). No spectral change was observed in the control experiment, using NaOAc in place of $Zn(OAc)_2{\cdot}2H_2O$, confirming that the changes could not be due to a change in ionic strength. The log K_s value obtained for Zn^{2+} ions is 5.13 ± 0.12.[11] The 1 : 1 complexation model for Zn^{2+} ion-binding was supported by the good agreement of the experimental data with a theoretical fit (Fig. S2† inset) and a Job's plot (Fig. S3†).

Upon addition of one equiv. of Zn^{2+} ions to a basic solution of **1**, hydrogel **3** was formed instantly. Similar to the ion binding study of Zn^{2+} in aqueous solution, a π–π* absorption band at 350 nm typical of the Zn^{2+}-coordinated species was observed (Fig. 2(a)). Upon addition of concentrated HCl, the π–π* absorption band exhibited a large blue shift in energy (Fig. 2(b)), and the hydrogel **3** was disrupted into its sol state. Since hydrogel **3** is sensitive to pH changes, the binding properties of Zn^{2+} ions have been investigated in buffer solutions at various pH values. At pH 8, the π–π* absorption band at 350 nm is observed, which is similar to that observed for the Zn^{2+}-bound species in water. Upon decreasing the pH, it exhibits a significant blue shift in energy (Fig. S4†). This suggests that an acidic medium causes protonation of the ligand, resulting in the blocking of the coordination site, and hence the gel structure.

Variable temperature UV-vis absorption studies of hydrogel **3** show that it is almost insensitive to changes in temperature below 55 °C. At $T > 55$ °C, it exhibits a slight red shift in energy. Further increasing the temperature results in a drastic drop in absorbance, and **3** turns milky-coloured (Fig. S5†). This suggests that **3** becomes unstable and forms a precipitate at higher temperatures. UV-vis absorption studies have been performed to investigate the effect of other metal ions on gel formation. No gel formation nor apparent spectral changes with Co^{2+} and Ni^{2+} were observed (Fig. S6†). This indicates that only Zn^{2+} ions coordinate to **1** and form a hydrogel.

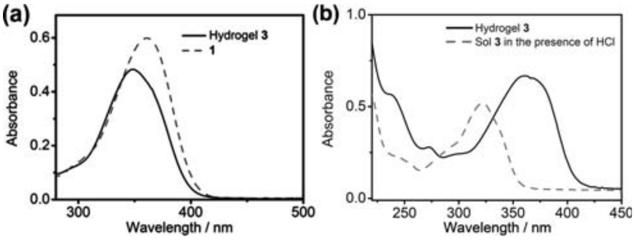

Fig. 2 (a) UV-vis absorption spectra of **1** in H_2O and hydrogel **3** ([**1**] and [**3**] = 25 mM). (b) UV-vis absorption spectra of hydrogel **3** and its corresponding sol state in an acidic medium ([**3**] = 25 mM).

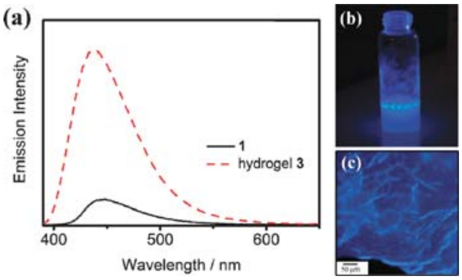

Fig. 3 (a) Emission spectra of **1** in H_2O and hydrogel **3** ([**1**] and [**3**] = 25 mM) upon excitation at λ = 340 nm, where the absorbance of all the samples are the same. (b) Photograph of **3** under UV light. (c) Fluorescence micrograph of freeze dried **3**.

The fluorescence spectral traces of an aqueous solution of **1** and **3** are shown in Fig. 3(a).[12] Hydrogel **3** exhibits a strong blue emission, with a maxima at 440 nm and a pronounced enhancement in fluorescence compared to **1** in solution. A drastic decrease in fluorescence is observed when the pH of **3** is adjusted to low pH. We believe that the dissociation of the complex leads to the disruption of the coordination polymeric gel structure, causing fluorescence quenching. The strong fluorescence property of **3** can be visualized using the naked eye under UV light (Fig. 3(b)). As shown in Fig. 3(c), a fluorescence micrograph of freeze dried **3** displays a fibrous structure, with a strong blue emission.

Controlled experiments were conducted to investigate whether the fluorescence enhancement is due to hydrogel formation or complexation with Zn^{2+}. The fluorescence properties were investigated upon adding Zn^{2+} ions to a basic aqueous solution of **1** ($[\mathbf{1}] = 9.12 \times 10^{-5}$ M). Upon excitation at the isosbestic point at λ = 352 nm, only a small change in fluorescence intensity is observed. The blue shift in emission energy can be rationalized by Zn^{2+} coordination, as observed in the corresponding UV-vis absorption studies. This suggests that complexation with Zn^{2+} ions in solution did not result in fluorescence enhancement (Fig. S7†). In addition, no such enhancement was observed in the controlled experiments with Co^{2+} and Ni^{2+} in place of Zn^{2+} (Fig. S8†), confirming that the fluorescence enhancement is due to the formation of hydrogel **3**. This observation can be rationalized by the rigidification of the media upon gelation, which slows down the non-radiative decay processes that lead to luminescence enhancement. It is worth noting that such fluorescence enhancement in **3** is retained after adjustment of the pH, *i.e.* **3** shows the same luminescent intensity when the pH 2 solution is adjusted back to pH 8, reforming the gel. Hence, hydrogel **3** shows a reversible fluorescence integrity following pH adjustment (Fig. S9†).

To understand the mechanical properties of the 3D structure of hydrogel **3**, dynamic oscillation and steady shear measurements were carried out. The linear viscoelastic region

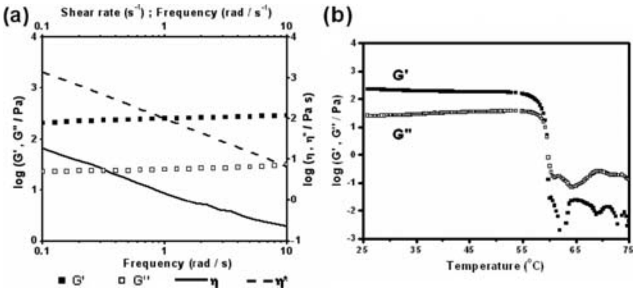

Fig. 4 (a) Primary axis: Dynamic frequency sweep measurements of G' and G'' for hydrogel **3** at a strain of 0.5%. Secondary axis: Steady shear and complex viscosity measurements. (b) Dynamic temperature ramp G' and G'' for hydrogel **3** at a heating rate of 1 °C min^{-1}, strain of 0.5% and frequency of 1 rad s^{-1}.

(LVR) of hydrogel **3** extends to $\approx 2\%$ strain, where both the in-phase storage modulus (G') and the out-of-phase loss modulus (G'') remain constant (Fig. S10†). Subsequent measurements on hydrogel **3** were performed at 0.5% strain, which lies comfortably within the LVR. It was ascertained that within 60 min of an isothermal (25 °C) time sweep carried out at 1 rad s^{-1}, the elastic (G') and viscous (G'') components of the network reach a pseudo-equilibrium plateau. As shown in Fig. 4(a), frequency sweeps display "weak gel" behaviour, with G' and G'' exhibiting a slight frequency dependence, the loss tangent ($\tan \delta = G''/G'$) approaching a value of ≈ 0.1 throughout the experimental frequency range, and the double logarithmic plot of η^* (dynamic viscosity) *vs.* ω (angular frequency) having a gradient close to -1 [note: $\eta^* = (G'^2 + G''^2)^{\frac{1}{2}}/\omega$].[13] The nature of the macromolecular assembly was further probed using the correlation known as the Cox–Merz rule.[14] In complete contrast to macromolecules that interact solely *via* topological entanglements, the formation of hydrogel **3** violates the Cox–Merz rule. Thus, the dynamic viscosity from small deformation oscillatory measurements is substantially higher (about two orders of magnitude) than steady shear viscosity (η) at equivalent rates of deformation. This provides an argument for a tenuous network that remains intact under low amplitude oscillation but is disrupted by continuous shear.

Fig. 4(b) depicts the heating profile of hydrogel **3**, which shows a progressive decrease in G' values, accompanied by an increase in corresponding G'' values. A sharp melting process then ensues, which results in sample "liquefaction" between 55–59 °C, thus indicating a thermally labile assembly. This observation is consistent with the variable temperature UV-vis studies. Subsequent cooling and an isothermal run at 25 °C fail to recover the rigidity of the material prior to heating, with the viscous component being predominant (Fig. S11†). Similarly, shear rate ramps follow a time-dependent shear thinning pattern (partly given in Fig. 4(a)), with hysteresis loops showing pronounced thixotropic behaviour, which precludes recovery and the obtaining of the return curve within the normal course of experimentation.

In summary, we have demonstrated that the formation of a coordination polymeric gel can be facilitated without long-chain hydrophobic groups. A coumarin-derivatized glycine ligand is shown to be able to produce a hydrogel efficiently by simple mixing with Zn^{2+}. The remarkable fluorescence enhancement upon formation of the coordination polymeric gel may find applications in light-emitting diodes and other optoelectronic devices. A complementary armoury of dynamic oscillation and steady shear experiments have indicated the formation of a weak and thermally labile network, whose tenuous supramolecular structure is irreversibly disrupted by mechanical (shear) and thermal (heating) treatments.

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Notes and references

1 (*a*) *Molecular Gels: Materials With Self-Assembled Fibrillar Networks*, ed. R. G. Weiss and P. Terech, Springer, Dordrecht, 2006; (*b*) T. Ishi-i and S. Shinkai, *Top. Curr. Chem.*, 2005, **258**, 119; (*c*) N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev.*, 2005, **34**, 821; (*d*) A. R. Hirst and D. K. Smith, *Chem.–Eur. J.*, 2005, **11**, 5496; (*e*) L. A. Estroff and A. D. Hamilton, *Chem. Rev.*, 2004, **104**, 1201.

2 F. Fages, *Angew. Chem., Int. Ed.*, 2006, **45**, 1680 and references therein.

3 (*a*) K. Hanabusa, Y. Maesaka, M. Suzuki, M. Kimura and H. Shirai, *Chem. Lett.*, 2000, **29**, 1168; (*b*) M. Dukh, D. Šaman, J. Kroulík, I. Černý, V. Pouzar, V. Král and P. Drašar, *Tetrahedron*, 2003, **59**, 4069.

4 (*a*) B. Xing, M.-F. Choi and B. Xu, *Chem.–Eur. J.*, 2002, **8**, 5028; (*b*) Q. Wei and S. L. James, *Chem. Commun.*, 2005, 1555; (*c*) L. Applegarth, N. Clark, A. C. Richardson, A. D. M. Parker, I. Radosavljevic-Evans, A. E. Goeta, J. A. K. Howard and J. W. Steed, *Chem. Commun.*, 2005, 5423; (*d*) P. C. Andrews, P. C. Junk, M. Massi and M. Silberstein, *Chem. Commun.*, 2006, 3317; (*e*) B. S. Luisi, K. D. Rowland and B. Moulton, *Chem. Commun.*, 2007, 2802.

5 (*a*) W. Weng, J. B. Beck, A. M. Jamieson and S. J. Rowan, *J. Am. Chem. Soc.*, 2006, **128**, 11663; (*b*) Y. Zhao, J. B. Beck, S. J. Rowan and A. M. Jamieson, *Macromolecules*, 2004, **37**, 3529.

6 (*a*) K. Kuroiwa, T. Shibata, A. Takada, N. Nemoto and N. Kimizuka, *J. Am. Chem. Soc.*, 2004, **126**, 2016; (*b*) S.-i. Kawano, N. Fujita and S. Shinkai, *J. Am. Chem. Soc.*, 2004, **126**, 8592; (*c*) H.-J. Kim, J.-H. Lee and M. Lee, *Angew. Chem., Int. Ed.*, 2005, **44**, 5810; (*d*) S. Ray, A. K. Das and A. Banerjee, *Chem. Mater.*, 2007, **19**, 1633.

7 (*a*) A. Kishimura, T. Yamashita and T. Aida, *J. Am. Chem. Soc.*, 2005, **127**, 179; (*b*) F. Camerel, R. Ziessel, B. Donnio, C. Bourgogne, D. Guillon, M. Schmutz, C. Iacovita and J.-P. Bucher, *Angew. Chem., Int. Ed.*, 2007, **46**, 2659; (*c*) A. Y.-Y. Tam, K. M.-C. Wong, G. Wang and V. W.-W. Yam, *Chem. Commun.*, 2007, 2028.

8 (*a*) M. Shirakawa, N. Fujita, T. Tani, K. Kaneko and S. Shinkai, *Chem. Commun.*, 2005, 4149; (*b*) M. Shirakawa, N. Fujita, T. Tani, K. Kaneko, M. Ojima, A. Fujii, M. Ozaki and S. Shinkai, *Chem.–Eur. J.*, 2007, **13**, 4155.

9 K. H. Drexhage, in *Dye Lasers*, ed. F. P. Schäfer, Springer-Verlag, New York, 1990.

10 (*a*) F. Camerel, L. Bonardi, M. Schmutz and R. Ziessel, *J. Am. Chem. Soc.*, 2006, **128**, 4548; (*b*) C. Bao, R. Lu, M. Jin, P. Xue, C. Tan, G. Liu and Y. Zhao, *Org. Biomol. Chem.*, 2005, **3**, 2508; (*c*) S. Manna, A. Saha and A. K. Nandi, *Chem. Commun.*, 2006, 4285; (*d*) G. D. Paoli, Z. Džolic, F. Rizzo, L. D. Cola, F. Vögtle, W. M. Müller, G. Richardt and M. Žinic, *Adv. Funct. Mater.*, 2007, **17**, 821.

11 J. Bourson, J. Pouget and B. Valeur, *J. Phys. Chem.*, 1993, **97**, 4552.

12 In order to minimize the inner filter effect, a 4-mm cuvette with a front-face geometry was used.

13 S. Kasapis, I. M. Al-Marhoobi, M. Deszczynski, J. R. Mitchell and R. Abeysekera, *Biomacromolecules*, 2003, **4**, 1142.

14 A. Y. Malkin and A. I. Isayev, *Rheology: Concepts, Methods and Applications*, ChemTec Publishing, Toronto, 2006.