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Luminescence properties of a thermal-responsive organogel to various metal cations

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ABSTRACT

A new gelator (L) containing Schiff base, benzoimidazol and naphthayl moieties was synthesized and its self-assembly was investigated in various solvents. Gelation test revealed that it could form a thermal-responsive gel in ethylene glycol (GL) or the mixture solution of ethylene glycol and DMF. Different fluorescence behaviors were observed upon adding different metal ions. The addition of Mg^{2+} maintained the gelating ability of L, meanwhile the Mg^{2+}-ion-mediated organogel in ethylene glycol can enhance the fluorescence of GL. The addition of Al^{3+} can destroy GL and lead to a state transition from gel to clear solution; the solution can give a brilliant blue emission excited at 365 nm UV. Interestingly, the luminescence of GL increased sharply at first but decreased finally. The fluorescence of GL was quenched when other metal cations were added.

1. Introduction

In recent years, considerable attention has been focused on gels, especially those self-assembled supramolecular gels, which are constructed by low-molecular-mass organic gelators (LMOGs), on account of their practical applications such as pollution control [1], drug delivery [2], tissue engineering [3], sensors [4], and so on. Gels are often prepared by heating a suspension of the gelator in the solvent until dissolution; subsequent slow cooling induces thermoreversible viscoelastic liquidlike or solidlike material, which is stable to the tube inversion experiment [5]. Gels can establish distinct supramolecular structures from gelator molecules in solvents through spontaneous as well as controlled self assembly processes [6]. The self-assembly of LMOGs to 3D networks structure entrapping/immobilizing solvent molecules is commonly driven by weak non-covalent interactions including hydrogen bonding, π–π stacking, van der Waals interactions, and electrostatic interactions etc. [7]. The weak nature of the non-covalent interactions usually makes supramolecular gels sensitive to external stimulus [8]. Some stimulus can induce the entrapped solvent molecules to be released, resulting in shrinking or even a gel-to-sol transition of supramolecular gels. For example, Edwards and co-workers reported the first example about gel-to-solution disassembly through Ag^{+}-alkene weak interaction as driving forces [9]. Deng and co-workers displayed gels based on cyclodextrin amine derivatives which can quickly exhibit response to Co^{3+}, Ni^{2+}, Cu^{2+} and Ag^{+}. Meanwhile, the process was reversed in the presence of Ag^{+} after precipitation when adding the solution of KI [10]. In addition, Liu et al. have recently reported amphiphilic Schiff base organogels which possessed different behaviors with various metal ions. The gel was maintained in the presence of Cu^{2+} and Mg^{2+}, whereas destroyed when Zn^{2+} and Ni^{2+} were added [11]. Above all, various efforts have been devoted to developing facile, straightforward and low-cost visual recognition based on nanostructured gel matrices, which has been counted as one of the future trends and challenging tasks in the field of supramolecular chemistry [12].

As we have known, Schiff base is a category of compounds containing C=N groups, which has efficient coordination ability for many metal ions, especially those with ortho-hydroxy substituents in the aromatic ring [13]. Recently, several Schiff base derivatives have been reported which possess better gelation abilities and related properties [14], but there are still many areas that can be explored further. In this paper, we synthesized a case of gelator L containing Schiff base and benzimidazol moieties, discussed its self-assembly behaviors in various solvents and the response performances between the organogel formed by L and various metal ions.

A new gelator of 2-(2-hexyl-1 H-benzoimidazol-1-yl)-N′-(2-hydroxy-naphthayllidene) acetohydrazide (L) was synthesized as Scheme 1. The structure of gelator L was characterized by NMR, MS, and elemental analysis. According to two set of signals (integral area ratio ≈ 1:1) appearing in the ^{1}H NMR spectra, we consider that the molecule has two kinds of conformers (Scheme 1), one of which is a cis-C(O)-N molecule and the other is a trans-C(O)-N) molecule. Heating the ethylene glycol (2.0 mL) suspension of gelator L until forming a transparent solution, subsequently cooling the resulting solution to

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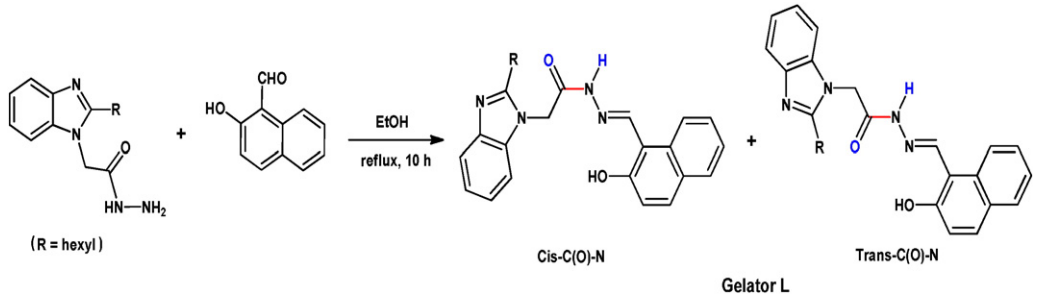

Scheme 1. Synthesis of gelator L.

ambient temperature for a period of time, a yellow organogel GL could be obtained. Gels were also prepared in other various solvents (Table S1, 1.2 *w/v%* for DMF/H_2O, 2.0 *w/v%* for DMF/ethylene glycol and 0.8 *w/v%* for H_2O/ethylene glycol, respectively), but the minimum gelation concentration (MGC) in ethylene glycol (0.6 *w/v%* for ethylene glycol) is the lowest. In addition, the gel–sol transition temperatures (Tsg) of the gels were 98 °C (0.6 *w/v%* in ethylene glycol) and 69 °C (2.0 *w/v%* in the mixed solvent of DMF/ethylene glycol), respectively, which were determined by the tube inversion method. The relationship about concentrations and Tsg indicated that gelator L possessed a better gelation capacity in ethylene glycol (Fig. S1). Furthermore, the organogel GL is thermally reversible because it can turn back to a liquid-like material after heating (Fig. S2). By the way, we also found that a metallogel can be formed upon addition of 0.5 equivalent $Mg(ClO_4)_2$ to L in ethylene glycol (MGC is 0.8 *w/v%*). Scanning electron microscope (SEM) images (Fig. 1) exhibited the extended and entangled three-dimensional fibrous structure of the xerogel GL obtained from ethylene glycol. Meanwhile, similar entangled nanofibers morphology of Mg^{2+}-ion-mediated organogel was also observed.

To investigate the main driving forces of GL in self-assembly process, temperature-dependent ^{1}H NMR studies of the gelator L in DMSO-d_6 were recorded. As shown in Fig. 2(A), it appears two sets ^{1}H NMR resonance signals due to the gelator L possessing two rotamers (Scheme 1) [15]. The ^{1}H NMR spectrum of gelator L gives well-resolved resonance signals at 23.2 °C. With the temperature increasing, chemical shift variations of some signals are clearly observed. For example, the resonance signals of -NH and -OH at 12.29 ppm and 11.79 ppm shifted upfield to 12.02 ppm and 11.60 ppm at 83.2 °C, respectively. Meanwhile, these two signals were widened gradually. These changes of chemical shifts indicated that hydrogen-bonding played an important role in the gel formation. It is to note that the signals of two rotamers also fuse to one set due to the fast transformation between them at 103.2 °C. In addition, GL shows weak fluorescence in hot ethylene glycol (T > Tgel) as shown in Fig. 2(B), while strong fluorescence appears at 473 nm in gel state with the temperature decreasing (T < Tgel). The fluorescence enhancement may be attributed to the phenomenon of the aggregation-induced emission (AIE) [16], which limited the transformation between the two rotamers.

In order to explore the response behaviors of GL with metal ions, we studied their fluorescence performances between GL and various metal cations (Cr^{3+}, Fe^{3+}, Ag^{+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Na^{+}, Ca^{2+}, Pb^{2+}, Zn^{2+}, K^{+}, Al^{3+}, Mn^{2+}, Mg^{2+}, Fe^{2+}, Cd^{2+}) in DMF solution. First, upon adding the DMF solutions (50 μL, 10^{-2} mol·L^{-1}) of above-mentioned metal ions to a small quantity of organogel GL on a spot plate and exciting at 365 nm under a hand-held UV lamp, those metal ions could cause distinct fluorescence changes as shown in Fig. S3a. Except Al^{3+}, Mg^{2+} and Zn^{2+}, other cations quenched the fluorescence of GL which was basically in accordance with experiments in solutions (Fig. S4). Interestingly, the concentration of sensing Al^{3+} in this condition was as low as 1×10^{-3} mmol·mL^{-1} (Fig. S3b). Moreover, in order to investigate their influences on morphology structure of GL, we added their ethylene glycol solutions (0.5 mL, 1.0 eq.) to fore-prepared gels and violently shook. It was observed that the gel containing Al^{3+} could change to a transparent solution immediately. However, the morphologies of other metal ion gels (except non-fluorescent Cu^{2+}, Fe^{3+} and Fe^{2+} solution) remained unchanged (Fig. S5). In addition, the fluorescence intensity of metallogel constructed by Mg^{2+} and L increased about 3 times by comparison to the GL (Fig. S6A). These luminescent changes could be reasonably explained. The GL showed weaker fluorescence due to the transfer of lone pair electrons of oxygen or nitrogen atoms to excited luminophores of benzimidazole and naphthaldehyde Schiff-base via a PET mechanism [17]. When adding Al^{3+} and Mg^{2+}, the carbonyl O, acylhydrazone N and hydroxyl O on naphthalene ring can coordinate to the Al^{3+}, Mg^{2+} cations, which led to the interruption of PET processes and the luminescence of benzimidazole and naphthaldehyde Schiff-base was recovered. The fluorescent selectivity of GL towards Al^{3+}, Mg^{2+} may be attributed to smaller ionic radii (0.5 Å and 0.65 Å for Al^{3+}, Mg^{2+}, respectively) that allowed a suitable coordination

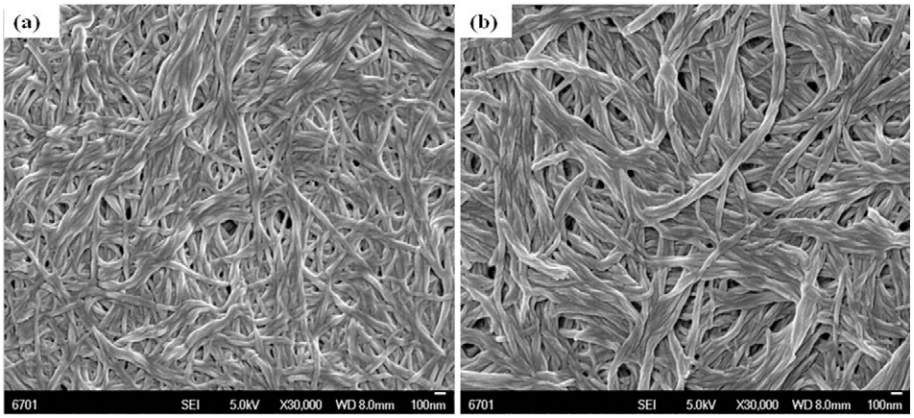

Fig. 1. SEM images of xerogel of GL (0.6 w/v% in ethylene glycol) (a) and (b) a metallogel constructed by Mg^{2+} and L (0.8 *w/v%* in ethylene glycol).