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# An acylhydrazone-based AIE organogel for the selective sensing of submicromolar level Al<sup>3+</sup> and Al(III)-based metallogel formation to detect oxalic acid<sup>†</sup>

Bin Wang, 🔟 ‡\*ab Juan Li, ‡a Shipeng Shuia and Jie Xua

A tripodal acylhydrazone derivative (**L**) was designed, synthesized, and fully characterized. Through the investigation, it had a typical bluish-green aggregation-induced emission (AIE) effect. Notably, the gelator was reported to accurately detect  $AI^{3+}$  via emitting brilliant green light and decay by oxalic acid, and the detection limit of the sensor for  $AI^{3+}$  was  $8.702 \times 10^{-7}$  M. Interestingly, the fluorescence intensity of gelator **L** would change depending on the water fraction in DMF or DMSO solution. Furthermore, **L** could detect Fe<sup>3+</sup>, Fe<sup>2+</sup>, and Ag<sup>+</sup> through a change in colour or gel phase. Accompanied by colour and fluorescence changes, we hope to provide a useful and effective strategy for preparing novel sensing soft materials.

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## Introduction

In recent years, photoluminescence materials have attracted considerable research interest due to their use in fluorescent sensors, security inks, and lighting devices.<sup>1</sup> Among them, the design and synthesis of supramolecular gel is of primary interest in fluorescent materials due to non-covalent bonding interactions, which are extremely sensitive to external stimuli, including pH, temperature, light, magnetism, ions and redox agents.<sup>2</sup> However, few studies on solid-state fluorescent materials have been reported owing to the aggregation-caused quenching (ACQ) effect.<sup>3</sup> Fortunately, scientists have discovered luminophores with aggregation-induced emission (AIE), which are non-emissive in dilute solution but can be induced to emit intensely in the aggregated state.<sup>4</sup> Furthermore, complexation with metal ions or mixing with different solvents could change the self-aggregation modes and affect the optical properties of molecular materials. For example, Ma et al. synthesized a new gel based on fluorine-containing acylhydrazone, which could show brilliant blue light upon mixing with Al<sup>3+</sup> and erased by F<sup>-</sup> ions.<sup>2a</sup> Fan et al. reported a supramolecular polymer DTB with strong white AIE; it showed excellent coordination with rare earth metal ions and emitted various

fluorescent colours.<sup>5</sup> Ding *et al.* reported a supramolecular gel BTTPA, which exhibited different colour emission depending on the water volume fraction.<sup>6</sup> However, although considerable efforts have been devoted to the development of fluorescent supramolecular gels, it is still rare to design and synthesize novel smart supramolecular gels that can be fluorescence-tunable depending on the water fraction and optically sense Al<sup>3+</sup> without interference (Scheme 1).

Herein, we attempt to obtain a novel molecule that can selfassemble into an organogel with bluish-green AIE. Our strategy for designing such a gel has been as follows. Firstly, tridentate coordinated units are efficient building blocks that could fix the orientation of ligands coordinated to a metal center.<sup>7</sup> Secondly, compound **L** contained multiple acceptors and donors of hydrogen bonds, which might benefit the gelation process. At last, certain molecules based on Schiff base derivatives could



Scheme 1~ The selectivity of L to  $\text{Al}^{3+}$  and the effect of H\_2O on the fluorescence of L in water–DMF solution.



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<sup>&</sup>lt;sup>a</sup> College of Chemistry and Chemical Engineering, China West Normal University, Nanchong, 637000, People's Republic of China

<sup>&</sup>lt;sup>b</sup> Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province of China, China West Normal University, Nanchong, 637000, People's Republic of China. E-mail: wangbin@cwnu.edu.cn, lijuan\_6303@126.com

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<sup>‡</sup> The authors contributed equally to this work.

restrict the intermolecular rotations and vibrations to hinder excimer formation according to the literature.<sup>8</sup> So, we developed gelator **L** that exhibited a strong green emission upon complexation with  $Al^{3+}$ , and it would return to the original fluorescence when oxalic acid was added to the **L**-**Al**<sup>3+</sup> system. This compound could respond to Fe<sup>3+</sup>, Fe<sup>2+</sup>, and Ag<sup>+</sup> not only in solution but also in gel state through change in colour or gel phase. Interestingly, the fluorescence intensity of gelator **L** would change depending on the water volume fraction in DMF or DMSO solution. Therefore, gelator **L** could act as a fluorescence-tunable photoluminescence material and specific cation sensor.

#### Results and discussion

As shown in Scheme S1 (ESI<sup>†</sup>), the gelator L was synthesized by the reaction between 2-hydroxy-1-naphthaldehyde and 1,3,5-tricarbohydrazine benzene in an ethanol solution. The detailed characterization data are shown in the supporting information (Fig. S1–S3, ESI<sup>†</sup>). Gelation abilities of compound L were tested in twenty organic solvents (Table S1, ESI<sup>†</sup>). However, the gel formation was observed only in pure DMF. The critical gel concentration (CGC) of the L-gel was reported to be 10 mg ml<sup>-1</sup>. The compound L was indeed a weak emitter when it was dissolved in DMF. Interestingly, L-gel can emit faint blue-green light under 365 nm ultraviolet light that can be observed by the naked eye, and the emission maximum was at 450 nm (Fig. 1). This phenomenon indicated that compound L exhibited typical AIE characteristics.

Interestingly, the fluorescence intensity of gelator **L** was dependent on the water volume fraction in the DMF/water mixtures (Fig. 2). The photoluminescence (PL) spectra were almost unchanged for water fraction  $f_w$  up to 30%. However, at a 40% water fraction, the PL intensity started to dramatically increase and reached a maximum, which was 384-fold higher than that in pure DMF solution, thus showing a significant AIE effect. Afterwards, the higher the water fraction, the weaker the emission intensity. Similar results were obtained in the water-DMSO system. There was no photoluminescence (PL) signal in the dilute DMSO solution (Fig. S5, ESI†). The fluorescence intensity was unchanged at  $f_w < 20\%$  and reached its maximum value at 40% water fraction. The fluorescence maximum was ~450 nm in water-DMF and water-DMSO solutions.



Fig. 1 (A) Luminescence spectra of L-sol in DMF and L-gel excited at 365 nm with the emission maximum at 450 nm; (B) the photoluminescence of the L-sol (left) and L-gel (right) in pure DMF under UV light at 365 nm.



**Fig. 2** (A) UV spectra of **L** in DMF/water mixtures; (B) fluorescence spectra of **L** in DMF-water mixtures; (C) plot of the relative PL intensity (*I/I*<sub>0</sub>) of **L** *versus* the composition of the DMF/water mixture. *I*<sub>0</sub> = emission intensity in pure DMF solution. Concentration:  $1 \times 10^{-5}$  M; excitation wavelength: 450 nm; (D) images of the different water fraction in DMF/water system under 365 nm UV illumination.

To investigate the possible self-assembly mechanism of **L-gel**, a concentration dependent <sup>1</sup>H NMR experiment was carried out in DMSO- $d_6$ . In the spectra (Fig. S12, ESI<sup>†</sup>), the signals of protons –OH(H1), –NH(H2), and –N=CH(H3) showed downfield shifts as the concentration of **L** increased, which indicated that hydrogen bonds were formed in the gelation process. Furthermore, the naphthyl protons (H4–H9) showed slight upfield shifts, indicating that there were  $\pi$ – $\pi$  interactions between the adjacent naphthyl groups.<sup>9</sup>

To evaluate how water affected the emission behaviour of the compound L, UV absorption spectra were used. As shown in Fig. 2A, when the water content was <30% in the water-DMF solution, only the absorbance value gradually decreased with the increase of water content. However, when the water fraction was >40%, a level-off tail was found after the 420 nm region, indicating the formation of nano-aggregates.<sup>10</sup> Combined with the PL spectrum (Fig. 2C) at  $f_{\rm w}$  > 40%, the reason for the decrease in fluorescence was that the effective concentration reduced in solution. A similar behaviour was observed in DMSO/water mixture (Fig. S5, ESI<sup>†</sup>). More importantly, the water response experiments of L in the gel state were investigated. With the addition of different ratios of water to L, the L-gel displayed gel-to-sol transition in DMF/H<sub>2</sub>O mixtures. However, in DMSO/water mixed system, the gel formed and emitted a strong green fluorescence only at the ratio of DMSO/  $H_2O(90:10, v/v)$  but no sol-gel changes at other ratios. Moreover, the morphology displayed a soft, fine-fiber structure (Fig. S11, ESI<sup>†</sup>). The main reason for this phenomenon is that water affects hydrogen bonding and  $\pi$ - $\pi$  interactions, which would change the packing arrangement of the gelator.<sup>11</sup> As the water content increases, the solubility of L decreases as the polarity of the solution decreases, which makes the gelation difficult.<sup>12</sup>

To investigate the influence of metal ions, we introduced 1.0 equivalent of metal ions (using their nitrate as the source) into the pure DMF solvent  $(1 \times 10^{-5} \text{ M})$ . There were acylhydrazone and hydroxyl groups in the molecule L, which could provide a possible opportunity for sensing metal ions. However, only in the presence of Al<sup>3+</sup>, solution L displayed an obvious green

Fig. 3 (A) Photographs of the colour and luminescence changes in the DMF solution L under the addition of different metal ions. The concentration of solution L was  $10^{-5}$  M; excitation wavelength: 365 nm; (B) fluorescence spectra of L-sol and L-Al<sup>3+</sup> in pure DMF, the molar ratio : Al<sup>3+</sup>/L is 1:1 (excited at 450 nm).

fluorescence, whereas other ions (including Cd<sup>2+</sup>, Co<sup>2+</sup>, Bi<sup>3+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, etc.) could not induce any significant emission (Fig. S6, ESI<sup>+</sup>). In Fig. 3, the solution L emitted strong green fluorescence with an addition of 1.0 equivalent of Al<sup>3+</sup> and the emission maximum shifted from 450 to 492 nm with an evident red shift. The results could be explained by the chelation-enhanced fluorescence (CHEF) effect,<sup>13</sup> which reduced the PET effect and restricted the molecular rotation.<sup>14</sup> It is important to note that the fluorescence intensity of L enhanced as the concentration of Al<sup>3+</sup> increased, accompanied by a new peak at 462 nm (Fig. S6, ESI<sup>†</sup>). Furthermore, as shown in Fig. S7 (ESI<sup>†</sup>), the limit of lowest detection (LOD) calculated using the  $3\delta/S^{15}$  method is  $8.702 \times 10^{-7}$  M. Moreover, there was no interference with the fluorescence when other metal ions were added into the L-Al<sup>3+</sup> solution (Fig. S8, ESI<sup>+</sup>). Colour of the solution L transformed from yellow-green to ginger upon the addition of Fe<sup>3+</sup> or Fe<sup>2+</sup>, respectively. After the addition of 1.0 equivalent of Ag<sup>+</sup>, the colour of solution L changed to gray (Fig. 3). UV-vis absorption spectra were performed. Upon the addition of 1.0 equivalent of Al<sup>3+</sup>, two peaks had a significant blue shift, and the absorption value increased in the range of 400-500 nm. When other metal ions were added, the UV-vis absorption peak did not shift (Fig. S8, ESI<sup>†</sup>).

Then, we introduced the above-mentioned metal ions (including Al<sup>3+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Bi<sup>3+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Ca<sup>2+</sup>,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ) (1 equivalent) into the L-gel to investigate the photoluminescence-tunable properties. We found that only the Al@gel exhibited brilliant green fluorescence but no significant fluorescence response toward other competitive cations (Fig. 4). Compared to the L-gel, the emission maximum of the Al@gel was at 498 nm, accompanied by a peak at 527 nm, which was found to be red-shifted. This behaviour may be attributed to the smaller ionic radius of Al<sup>3+</sup> that allowed it to strongly coordinate with the L ligand.<sup>16</sup> The L-gel showed faint luminescence, probably owing to the transfer of lone pair electrons of O or N atoms to the excited luminophores of benzene and Schiff-base derivatives via a photo-induced electron transfer (PET) mechanism.<sup>17</sup> When Al<sup>3+</sup> was added, the carbonyl O and amide N atoms of the gelator coordinated to the Al<sup>3+</sup> made the energies of the  $n-\pi^*$  transition higher than the corresponding  $\pi$ - $\pi$ \* transition.<sup>18</sup> Thus the PET process was interrupted (Fig. S13, ESI<sup>†</sup>). Moreover, upon the addition of 1.0 equivalent of Fe<sup>3+</sup> or Fe<sup>2+</sup>, the L-gel changed into a solution along with a colour change from light green to dark brown, which indicated





Fig. 4 (A) Luminescence spectra of L-gel and Al@gel excited at 450 nm; (B) the photoluminescence of the L-gel (left) and Al@gel (right) in pure DMF under UV at 365 nm.

that they had a destructive effect on the **L-gel**. (Fig. S9, ESI<sup>†</sup>). Interestingly, when 1.0 equivalent of Ag<sup>+</sup> was added, **Ag@gel** was stable, and the colour changed to grayish-white. After a week, there was a layer of brown material attached to the wall of the small glass vial.

FT-IR and XRD (X-ray diffraction) studies were carried out to investigate the possible self-assembly driving forces in the **L-gel** and metallogel. The IR spectra of the L xerogel showed bands at 1664 and 1573 cm<sup>-1</sup> corresponding to V(C=O) and V(C=N), respectively. With the addition of 1.0 equivalent of Al<sup>3+</sup>, the C=N group of the **Al@gel** disappeared, and the C=O vibration peak was attributed to the coordination of Al<sup>3+</sup> with the acylhydrazone and hydroxyl groups of the gelator L. However, the V(C=O) and V(C=N) bands shifted to lower wavenumbers at 1641 and 1575 cm<sup>-1</sup> in the **Ag@gel** (Fig. S10, ESI†). The XRD of L xerogel showed peaks around  $2\theta = 23.80^{\circ}$  corresponding to the *d*-spacing of 3.70 Å, which suggested the  $\pi$ - $\pi$  stacking in the naphthyl groups of L.<sup>19</sup> The results of XRD analyses confirmed that the xerogels (**Ag@gel** and **Al@gel**) were amorphous (Fig. S10, ESI†).

Subsequently, we investigated the morphologies L-gel and metallogels using field-emission scanning electron microscopy (SEM) and atomic force microscopy (AFM). The gelator L has a tightly connected sheet structure. However, there was a straight fine fiber structure formed after the coordination of L with Al<sup>3+</sup>. After Ag@gel was formed, the image showed a ribbon fiber structure (Fig. S11, ESI<sup>+</sup>). The morphology of the metallogels appeared to be looser compared to that of L-gel. Furthermore, AFM was used to measure the morphology and size of the above gels. Fig. 5A showed that the thickness of the L-gel was about 5-13 nm. However, upon the addition of Al<sup>3+</sup>, the height was about 25–34 nm (Fig. 5B), which possibly showed the coordination effect of compound L with  $Al^{3+}$ . After the addition of  $Ag^+$  to the L (Fig. 5C), the height increased to 40 nm, in accordance with the SEM results. Moreover, the diameter of the L-gel was about 1 µm, which was significantly larger than that of Al@gel and Ag@gel.

Furthermore, the influence of other organic acids (formic acid, acetic acid, phthalate, malonate) and some common materials that tend to complex with  $Al^{3+}$  (EDTA, citric acid, oxalic acid,  $F^-$ ) on the L-Al<sup>3+</sup> system was investigated (Fig. S15, ESI†). It is interesting to find that the L-Al<sup>3+</sup> system could selectively recognize oxalic acid. The fluorescence of the sample



Fig. 5 AFM images of (A) L-gel, (B) Al@gel, and (C) Ag@gel: scan size: 4.8  $\mu$ m  $\times$  4.8  $\mu$ m (left); 5  $\mu$ m  $\times$  5  $\mu$ m (middle); 5  $\mu$ m  $\times$ 5  $\mu$ m (right).



Fig. 6 (A) The recognition process of oxalic acid with L-Al<sup>3+</sup> system in the gel state and in solution; (B) the titration process of oxalic acid with the **L-Al<sup>3+</sup>** system. Concentration:  $1 \times 10^{-5}$  M.

solution and gel (both in DMF) state was studied. As shown in Fig. 6, the solution of L showed almost no fluorescence exposure to a 365 nm ultraviolet light while emitting strong green fluorescence upon adding  $Al^{3+}$  (1.5  $\times$  10<sup>-7</sup> N). Interestingly, the fluorescence disappeared by introducing oxalic acid to the L-Al<sup>3+</sup> solution. However, Al@gel showed excellent green emission. Upon the addition of oxalic acid, the fluorescence was restored to bluish-green similar to the L-gel. More interestingly, in the photoluminescence spectrum, after the addition of oxalic acid to the L-Al<sup>3+</sup> solution, the fluorescence was not immediately decreased but increased. As the titration progressed, the fluorescence began to diminish and peaks appeared again at 450 nm (Fig. 6B).

The possible detection mechanism of Al@gel and L-Al<sup>3+</sup> for oxalic acid was explored by <sup>1</sup>H NMR titration. As shown in Fig. S16 (ESI<sup>†</sup>), with the appropriate addition of  $Al^{3+}$  in DMSO- $d_6$ solution of L, the disappearance of H1 suggested that Al<sup>3+</sup> attacked the -OH group of L and the deprotonation process occurred.<sup>19</sup> Furthermore, the <sup>1</sup>H NMR spectroscopy (Fig. S16, ESI<sup>†</sup>) of complex (L-Al<sup>3+</sup>) showed that the signal of  $H_2O$  in DMSO-d<sub>6</sub> solution gradually widened and shifted downfield with an increase in the concentration of  $Al^{3+}$ . These results revealed that the  $H_2O$  in the system coordinates with  $Al^{3+}$ . Moreover, with increasing concentration of oxalic acid in the L-Al<sup>3+</sup> solution, the signal of  $H_2O$  in DMSO- $d_6$  solution shifted continuously downfield and became wider, which indicated that there were more H<sub>2</sub>O molecules complexed with Al<sup>3+</sup> and oxalic acid in this system.<sup>20</sup>

# Conclusions

In conclusion, we present a new supramolecular gelator based on acylhydrazone derivatives. The compound L has shown

attractive gelation ability in DMF solution and typical bluishgreen aggregation-induced emission (AIE) effect. The L could sense Fe<sup>3+</sup>, Fe<sup>2+</sup>, and Ag<sup>+</sup> ions with high selectivity through the colour or gel-sol change via the naked eye. Specifically, the gelator L was found to detect sensitively and selectively Al<sup>3+</sup> with brilliant green light whether in solution or gel state and even exhibited fluorescence-tunable properties depending on the water fraction. More importantly, the L-Al<sup>3+</sup> system can be recognized by the fluorescence decay. This process leads to a definite colour change, as well as a marked and highly efficient fluorescence quenching, which can therefore be employed for specific sensing of Al<sup>3+</sup> and oxalic acid in wider environment applications.

# Conflicts of interest

There is no conflict to declare.

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