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A novel strategy for the design of smart supramolecular gels: controlling stimuli-response properties through competitive coordination of two different metal ions[†]

Qi Lin,* Bin Sun,‡ Qing-Ping Yang,‡ Yong-Peng Fu, Xin Zhu, You-Ming Zhang and Tai-Bao Wei*

By rationally introducing Ca²⁺ and Fe³⁺ into a supramolecular gel, a bimetal–gel CaFeG was prepared. CaFeG could reversibly "turn-on" its fluorescence upon sensing $H_2PO_4^-$ with specific selectivity under gel–gel states through the competitive coordination of Ca²⁺ and Fe³⁺ with gelators and $H_2PO_4^-$. Thus, CaFeG could act as a $H_2PO_4^-$ test kit and could be utilised in rewritable security display materials.

Over the past few decades, stimuli-responsive gels, a kind of smart materials, have attracted increasing attention because of their promising applications, including chemosensors, drug delivery, biomaterials, displays, *etc.*^{1–3} By taking advantage of the dynamic and reversible nature of noncovalent interactions, the stimuli-responsive supramolecular gels can sense, process, and actuate a response to an external change without assistance.^{1,4,5} Recently, metal ions-coordinated supramolecular gels have become a focus for research because the tunable coordination binding strength, as well as the fascinating redox, optical, electronic, or magnetic properties of the metal ions would benefit the application of these smart materials.⁶ However, although a significant amount of effort has been devoted to the development of metal ions-coordinated supramolecular gels that can optically sense a given chemical stimulus with specific selectivity is still a big challenge.

Up to now, most of the reported metal ion-coordinated supramolecular gels contain only one kind of metal ion,⁶ and a few of them employ two kinds of metal ions to extend their stimuliresponse properties. An important question is whether the cooperation of two different kinds of metal ions in the same supramolecular gel system can improve stimuli-response abilities. The reports on such attempts are very rare. Herein, we provide a novel strategy for the design of stimuli-responsive supramolecular gels. In this manner, by rationally introducing two different metal ions into a supramolecular gel, the stimuli-response properties of the gel could be accurately controlled by the competitive coordination of these metal ions with gelators and guest.

To demonstrate this strategy, we designed and synthesized a gelator **G** based on multi self-assembly driving forces, fluorescent signal groups and coordination binding sites (Scheme 1). **G** could form stable supramolecular organogel in various solvents at very low critical gelation concentrations (CGCs) (Table S1 in ESI†). Among these solvents, the gelator **G** showed the lowest CGC (0.4%, w/v%, 10 mg mL⁻¹ = 1%) and the highest gel–sol transition temperature (T_{gel}) in ethanol (Fig. S1 and Table S1 in ESI†). Therefore, **G**-based supramolecular organogel **OG** in ethanol is more stable than the gels in other solutions.

We investigated the influence of metal ions on **G** organogel in ethanol. The addition and diffusion of 1 equiv. of various metal ions (Mg²⁺, Ca²⁺, Cr³⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Ag⁺, Cd²⁺, Hg²⁺ and Pb²⁺, using their solid perchlorate salts as sources) to the **OG** (1%) generated the corresponding metallogels (Fig. S2, ESI[†]). The organogel **OG** emitted very weak fluorescence, while the Ca²⁺ coordinated metallogel **CaG** exhibited strong brilliant blue fluorescence emission (Scheme 1 and Fig. S2, ESI[†]). In the corresponding fluorescence spectra (Fig. S3 and S4, ESI[†]), the fluorescence intensity of **CaG** at 469 nm is approx. 10 times higher than that of **OG**. More interestingly, as shown in Fig. S5 (ESI[†]), **CaG** has no fluorescence in hot ethanol solution ($T > T_{gel}$). However, with the temperature of hot ethanol solution decreasing below the T_{gel} of **CaG**, the emission



Scheme 1 Molecular structure of **G** and fluorescence photograph of organogel **OG** (1%, in ethanol), metallogels **CaG**, **CaFeG** (1%, in ethanol, for **CaG**, **G**: Ca²⁺ = 1:1; for **CaFeG**, **G**: Fe³⁺: Ca²⁺ = 1:2:1) and **CaFeG** treated with H₂PO₄⁻ and illuminated at 365 nm.

Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu, 730070, P. R. China. E-mail: linqi2004@126.com, weitaibao@126.com

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 ‡ These authors contributed equally.

intensity at 469 nm showed a sudden increase and reached a steady state, which indicated that the fluorescence of metallogel **CaG** was aggregation-induced emission (AIE).⁷ Meanwhile, the Fe³⁺-coordinated metallogel **FeG** did not show fluorescence emission (Fig. S2 and S4, ESI†). These results illustrated that the formation of metallogel **CaG** could enhance the fluorescence emission of **OG** by AIE, while the formation of metallogel **FeG** could quench the weak fluorescence emission of **OG**.

Because Ca^{2+} belongs to the IIA group and Fe^{3+} belongs to the VIIIB group, the coordination ability of Fe^{3+} with acylhydrazone is significantly stronger than Ca^{2+} . Therefore, we presumed that by adding Fe^{3+} to the metallogel **CaG**, Fe^{3+} could competitively coordinate with the gelator **G** in **CaG** and release Ca^{2+} . This process could quench the AIE of the **CaG**. Interestingly, the experimental results confirmed this assumption. The addition and diffusion of 2 equiv. Fe^{3+} into the **CaG** (1%) could form Fe^{3+} and Ca^{2+} -based metallogel **CaFeG** (Scheme 1). With the diffusion of Fe^{3+} , the fluorescence emission of the **CaG** quenched (Scheme 1 & Fig. S4, ESI†) and the white color of **CaG** changed to brown, which is similar to the color of **FeG**. In the corresponding UV-vis spectra, a broad absorption at *ca*. 374 nm appeared (Fig. S6, ESI†). In addition, the dissolution of the gelator **G** with 1 equiv. of Ca^{2+} and 2 equiv. of Fe^{3+} cations in hot ethanol also generated the same **CaFeG** (1%).

The anion response capability of the metallogel CaFeG was primarily investigated by adding 5 equiv. of various anions (F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, HSO₄⁻, H₂PO₄⁻, N₃⁻, SCN⁻, ClO₄⁻ and CN⁻ using their sodium salts water solution as the sources) to CaFeG. As shown in Scheme 1 and Fig. 1a, upon the addition of $H_2PO_4^-$ to CaFeG at 20 °C and with the diffusion of $H_2PO_4^-$, the CaFeG emitted strong brilliant blue fluorescence emission at 469 nm, while the UV-vis absorption at ca. 374 nm decreased. This fluorescence emission is similar to that of the CaG. These results confirmed that the $H_2PO_4^-$ competitively bound to the Fe³⁺, while the Ca²⁺ again coordinated with the gelator G. Interestingly, upon the addition of Fe³⁺ into the H₂PO₄⁻-containing CaFeG, the fluorescence of CaFeG could be quenched, which was also attributed to Fe³⁺ coordination with G. These properties enable CaFeG to act as a H₂PO₄⁻ and Fe³⁺ controlled "OFF-ON-OFF" fluorescent switch. By alternating the addition of $H_2PO_4^-$ and Fe^{3+} , the switch could be reversibly performed at least for three cycles with slight loss in fluorescent efficiency (Fig. 1b). Because other anions could not cause similar fluorescent response, it was clear that the CaFeG could detect H₂PO₄⁻ with specific selectivity (Fig. 1a and 2a). Moreover, the H₂PO₄⁻ response sensitivity of CaFeG was very high. As shown in Fig. S7 (ESI^{\dagger}), with the gradual addition of H₂PO₄⁻, the emission intensity at 469 nm increased along with increasing concentrations of H₂PO₄⁻. The detection limit of the changes in fluorescence spectra calculated on the basis of $c_{\rm L} = k s_{\rm B} / S$ (where $s_{\rm B}$ is the standard deviation of the blank measures, S is the sensitivity of the method, k = 3⁸ was 1.0 × 10⁻⁶ M (1 µM) for H₂PO₄⁻ anion.

It is very interesting that unlike most of the reported stimuliresponsive gels that showed gel-sol phase transition according to the stimulation of anions, the gel state of **CaFeG** did not show any gel to sol changes in the entire $H_2PO_4^-$ response process. This special stability could be attributed to the cooperation of multi self-assembly forces we rationally introduced to the gelators.



Fig. 1 (a) Fluorescence spectra of **CaFeG** (1%, in ethanol, **CaFeG**, **G** : Fe³⁺ : Ca²⁺ = 1:2:1) in the presence of various anions (5 equiv. of F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, HSO₄⁻, H₂PO₄⁻, N₃⁻, SCN⁻, ClO₄⁻ and CN⁻, respectively, using their 1.0 × 10⁻³ M sodium salts water solution as the sources) at room temperature. (b) Fluorescent "OFF-ON-OFF" cycles of **CaFeG** (1%, in ethanol, **G** : Fe³⁺ : Ca²⁺ = 1:2:1), controlled by the alternative addition of Fe³⁺ and H₂PO₄⁻, λ_{ex} = 350 nm.



Fig. 2 (a) Photograph of metallogel **CaFeG** (1%, in ethanol, **CaFeG**, **G**: Fe³⁺: Ca²⁺ = 1:2:1) selectively detects H₂PO₄⁻ (5 equiv., using 0.1 mol L⁻¹ NaH₂PO₄ water solution as the H₂PO₄⁻ sources) in water solution on a spot plate, illuminated at 365 nm. (b) Writing and erasing of a natural light invisible image on a **CaFeG** supramolecular bimetal–gel film obtained from 1% ethanol metallogel, **CaFeG**, **G**: Ca²⁺: Fe³⁺ = 1:1:2. The photographs were taken at room temperature under normal light and exposed to 365 nm ultraviolet light.

Simply, because there are three kinds of noncovalent motifs in the gelator **G**, even if the hydrogen bonds were destroyed by metal ions, the other noncovalent interactions could maintain the gel states of the organogels.

To facilitate the use of the CaFeG, the $H_2PO_4^-$ response film based on CaFeG was prepared by pouring hot ethanol solution of CaFeG onto a clean glass surface and then drying in the air. The CaFeG film has no fluorescence emission but when writing on the film with a writing brush dipped in $H_2PO_4^-$ water solution, a brilliant blue fluorescent image of the writing appeared (Fig. 2b). This fluorescent image could be erased by brushing Fe^{3+} on the film. Therefore, the **CaFeG** film could not only act as a convenient reversible H_2PO_4^- detection test kit, but also act as an erasable dual-channel security display material. It is worth noting that security display materials are composed of invisible substances that provide printed images that cannot be photocopied and are readable only under special environments. Although thermally rewritable printing media have already been developed, security display materials that allow the rewriting of invisible printed images are very rare.⁹

The self-assembly and stimuli-response mechanism of the supramolecular gels were carefully investigated. In concentration dependent ¹H NMR (Fig. S8a-c, ESI^{\dagger}) of G, the -NH (H_a) and -N=CH (H_b) resonance signals showed obvious downfield shifts as the concentration of G increased. Moreover, in FT-IR (Fig. S9, ESI⁺), the C=O vibration absorption of OG shifted to a low wavenumber in the corresponding OG xerogel. These results revealed that during gelation, the $-NH(H_a)$ and $-N=CH(H_b)$ groups formed hydrogen bonds with the -C=O groups on adjacent gelators. On the other hand, as shown in Fig. S8a-c (ESI⁺), with a gradual increase in concentration, the ¹H NMR signal of naphthyl protons (H_c, H_d, H_e and H_f) showed obvious upfield shift, indicating that the π - π stacking interactions between the naphthyl groups were involved in gelation.¹⁰ Therefore, as illustrated in Scheme S2 (ESI[†]), the gelator G self-assembled to organogel OG by hydrogen bonds, π - π stacking, as well as the van der Waals force existing in the long alkyl chains.

The formation of metallogels was also investigated. As shown in Fig. S8d (ESI⁺), after the addition of 1 equiv. Ca²⁺ to the solution of **G**, the -NH (H_a) and -N=CH (H_b) showed significant downfield shifts, and the phenyl proton $H_{\rm s}$ and $H_{\rm h}$, which are neighbouring the acyl (-C=O) group, shifted upfield. Meanwhile, in the IR spectra (Fig. S10, ESI⁺), the stretching vibrations of -C=O and -C=N- of G shifted to lower wavenumbers when G interacted with 1 equiv. of Ca²⁺. These results indicated that in CaG, Ca2+ coordinated with nitrogen and oxygen atoms on acylhydrazone group (Scheme S2, ESI⁺). In addition, after adding 2 equiv. of Fe³⁺ to the CaG, the stretching vibrations of -C=O and -C=N- of G again shifted to lower wavenumbers. Meanwhile, the absorption bands of -C=O merged with the absorption bands of -C=N-, which indicated that in the CaFeG, Fe³⁺ formed more stable coordination bonds with oxygen and nitrogen atom on acylhydrazone group and Ca²⁺ was replaced by Fe^{3+} (Scheme S2, ESI[†]).

This self-assembly and competitive coordination mechanism was also supported by the T_{gel} of **OG**, **CaG** and **CaFeG**. For instance, as shown in Fig. S1b (ESI†), in the same condition, the T_{gel} of **OG** is clearly higher than **CaG** and **CaFeG**, while the T_{gel} of **CaG** and **CaFeG** are close to each other. The large differences of T_{gel} between the **OG** and **CaG** or **CaFeG** were attributed to the breaking of intermolecular hydrogen bonds among -N=C-H on one gelator and -C=O on the other gelators (Scheme S2, ESI†) in **OG**, which was caused by the coordination of Ca²⁺ or Cu²⁺ with gelator **G**.

To get further insights into the morphological features of the organogel **OG** and metallogels **CaG** and **CaFeG**, SEM studies were carried out with their respective xerogels. As shown in Fig. S11 (ESI[†]), the SEM images of **OG** showed an overlapped rugatelayered structure. The thickness of each layer was approximately 10–20 nm. The metallogels **CaG** and **CaFeG** also showed overlapped rugate-layered structures. These results indicated that although gelator **G** coordinated with Ca²⁺ or Fe³⁺, significant changes did not occur in the self-assembly states. Moreover, the XRD patterns (Fig. S12, ESI[†]) of the **OG**, **FeG**, **CaFeG** and the **CaFeG** treated with H₂PO₄⁻ showed periodical diffraction peaks, indicating that they assembled into the ordered structures. The peaks at $2\theta =$ 22.96–23.76° corresponded to *d*-spacing 3.73–3.87 Å, which suggested that π – π stacking existed in the naphthyl groups of these gels.

In summary, we have demonstrated a new strategy for the designing of stimuli-responsive supramolecular gels. In this manner, the stimuli-response selectivity and signal reporting property of the supramolecular gels are controlled by the competitive coordination of two different metal ions with gelators and guest. In the present work, by the competitive coordination of Ca^{2+} , Fe^{3+} with gelator and $H_2PO_4^-$, the strong aggregation-induced emission of the metallogel **CaG** was controlled as "OFF–ON–OFF". The **CaFeG** could not only act as a convenient highly selective and sensitive $H_2PO_4^-$ detection test kit, but could also act as an erasable secret documentation medium.

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