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A novel strategy for the design of smart supramolecular gels: control the 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‡

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By rationally introduced Ca$^{2+}$ and Fe$^{3+}$ into a supramolecular gel, a bimetal-gel CaFeG was prepared. CaFeG could reversibly fluorescent “turn-on” sense H$_2$PO$_4^-$ with specific selectivity under gel-gel states through competitive coordination of Ca$^{2+}$ and Fe$^{3+}$ with guests and H$_2$PO$_4^-$.

Over the past few decades, stimuli-responsive gel, acting as one kind of smart materials, have attracted more and more attentions due to their promising applications, including chemo-sensors, drug delivery, biomaterials, displays, and so on. By taking advantage of the dynamic and reversible nature of noncovalent interactions of the supramolecular gels, the stimuli-responsive supramolecular gels can sense, process, and actuate a response to an external change without assistance. Recently, metal ions-coordinated supramolecular gels have become a focus of the research due to 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. However, although a great deal of effort have been devoted to the development of metal ions-coordinated supramolecular gels, it is still a big challenge to design and synthesize novel smart supramolecular gels that can optically sense a given chemical stimulus with specific selectivity.

Up to now, most of reported metal ions-coordinated supramolecular gels commonly contains only one kind of metal ions, few of them employ two kinds of metal ions to extend their stimuli-response properties. Could the cooperation of the two different kinds of metal ions in the same supramolecular gel system improve the stimuli-response abilities of the metal ions-coordinated supramolecular gel? The reports on such attempts are very rare. In view of these, herein, we provide a novel strategy for the design of stimuli-responsive supramolecular gels. In this way, by rationally introduced 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 design 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%) and the highest gel-sol transition temperature (T$_{gel}$) in ethanol (Fig. S1 and Table S1 in ESI). Therefore, the G-based supramolecular organogel OG in ethanol is more stable than the gels in other solutions.

We investigated the influence of metal ions on the OG organogel in ethanol. The addition and diffusion of 1 equiv. of various metal ions (Mg$^{2+}$, Ca$^{2+}$, Cr$^{3+}$, Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Ag$^{+}$, Cd$^{2+}$, Hg$^{2+}$ and Pb$^{2+}$ using their solid perchlorate salts as the sources) to the OG (1%) generated the corresponding metallogels (Figure S2). The organogel OG emitted very weak fluorescence, while the Ca$^{2+}$ coordinated metallogel CaG emitted strong brilliant blue fluorescence emission (Scheme 1 and Fig. S2). In the corresponding fluorescence spectra (Fig. S3 & S4), the fluorescence intensity of CaG at 469 nm is ca. 10 times higher than that of the OG. More interestingly, as shown in Fig. S5, CaG has no fluorescence in hot ethanol solution (T > T$_{gel}$). However, with the temperature of hot ethanol solution dropping below the T$_{gel}$ of CaG, the emission intensity at 469 nm showed a sudden increase and reached a steady state, which indicated that the fluorescence of metallogel CaG was the aggregation-induced emission (AIE). Meanwhile, the Fe$^{3+}$-coordinated metallogel FeG showed no fluorescence emission (Fig. S2 and S4). 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.

Since the Ca$^{2+}$ belongs to the IIA group and the Fe$^{3+}$ belongs to the VIIIB group, the coordination ability of Fe$^{3+}$ with acylhydrazone is much stronger than Ca$^{2+}$. Therefore, we presumed that when adding Fe$^{3+}$ to the metallogel CaG, the Fe$^{3+}$

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Scheme 1 (a) Molecular structure of G and fluorescence photograph of organogel OG (1%, in ethanol), metallogels CaG, CaFeG (1%, in ethanol, for CaG, G : Ca$^{2+}$ = 1 : 1; for CaFeG, G : Fe$^{3+}$ : Ca$^{2+}$ = 1 : 2 : 1 ) and CaFeG treated with H$_2$PO$_4^-$, illuminated at 365 nm. (b) Molecular structure of FeG.
could competitively coordinate with the gelator G in CaG and release Ca$^{2+}$. This process could quench the AIE of the CaG. Interestingly, the experiment results confirmed the presumption. 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) and the white color of CaG changed to brown which is similar as the color of FeG. In the corresponding UV-vis spectra, a broad absorption at ca. 374 nm appeared (Fig. S6). 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%).

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![Fluorescence spectra of CaFeG](image)

**Fig. 1** (a) Fluorescence spectra of CaFeG (1%, in ethanol, CaFeG, G: Fe$^{3+}$: Ca$^{2+}$ = 1 : 2 : 1) in the presence of various anions (5 equiv. of F, Cl$^-$, Br$^-$, I$^-$, AcO$^-$, HSO$_4^-$, H$_2$PO$_4^-$, N$_2$, SCN$^-$, ClO$_4^-$ 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: Fe$^{3+}$: Ca$^{2+}$ = 1 : 2 : 1), controlled by the alternative addition of Fe$^{3+}$ and H$_2$PO$_4^-$, $\lambda_{em} = 350$ nm.

The anion response capability of the metallogel CaFeG was primarily investigated by adding 5 equiv. of various anions (F, Cl$^-$, Br$^-$, I$^-$, AcO$^-$, HSO$_4^-$, H$_2$PO$_4^-$, N$_2$, SCN$^-$, ClO$_4^-$ and CN$^-$, using their sodium salts water solution as the sources) to the CaFeG. As shown in Scheme 1 and Fig. 1a, upon the addition of H$_2$PO$_4^-$ to the CaFeG at 20 °C, with the diffusion of H$_2$PO$_4^-$, the CaFeG emitted strong brilliant blue fluorescence emission at 469 nm, meanwhile, 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$_2$PO$_4^-$ competitively bound to the Fe$^{3+}$ while the Ca$^{2+}$ coordinated with the gelator G again. Interestingly, upon the addition of Fe$^{3+}$ into the H$_2$PO$_4^-$-containing CaFeG, the fluorescence of CaFeG could quenched, which was attributed to the Fe$^{3+}$ coordination with G again. These properties make CaFeG act as a H$_2$PO$_4^-$ and Fe$^{3+}$ controlled “OFF-ON-OFF” fluorescent switch. By alternating addition of H$_2$PO$_4^-$ and Fe$^{3+}$, the switch could be reversibly performed at least for three cycles with little fluorescent efficiency loss (Fig. 1b). Moreover, other anions couldn’t cause similar fluorescent response, therefore, the CaFeG could detect H$_2$PO$_4^-$ with specific selectivity (Fig. 1a & 2a). Moreover, the H$_2$PO$_4^-$ response sensitivity of CaFeG is very high. As shown in Fig. 1, with the gradual addition of H$_2$PO$_4^-$, the emission intensity at 469 nm increasing along with the increasing in the concentrations of H$_2$PO$_4^-$. The detection limit of the fluorescence spectra changes calculated on the basis of $c_l = k_{th}/S$ (where $k_{th}$ is the standard deviation of the blank measures, S is the sensitivity of the method, $k = 3$) was 1.0×10^{-6} M (1 nM) for H$_2$PO$_4^-$ anion.

It is very interesting that unlike most of the reported stimuli-responsive gels which showed gel-sol phase transition according to the anions’ stimulation, the gel state of CaFeG didn’t show any gel to sol changes in the whole H$_2$PO$_4^-$ response process. This special stability could be attributed to the cooperation of the multi self-assembly forces we rationally introduced to the gelators. Simply stated, 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.

In order to facilitate the use of the CaFeG, the H$_2$PO$_4^-$ response film based on CaFeG were prepared by pouring the heated ethanol solution of CaFeG onto a clean glass surface and drying in the air. The CaFeG film has no fluorescence emission, when writing on the film with a writing brush dipped in H$_2$PO$_4^-$ water solution, a brilliant blue fluorescent writing image appeared (Fig. 2b). This fluorescent image could be erased by brushing Fe$^{3+}$ on the film again. Therefore, the CaFeG film could act as not only a convenient reversible H$_2$PO$_4^-$ detection test kit, but also an erasable dual-channel security display materials. It is worth noting that security display materials are composed of invisible substances that provide printed images that are not able to be copied, and are readable only under special environments. Although thermally rewritable printing media have already been developed, security display materials that allow rewriting of invisible printed images are very rare. 9

![Photograph of metallogel CaFeG](image)

**Fig. 2** (a) Photograph of metallogel CaFeG (1%, in ethanol, CaFeG, G: Fe$^{3+}$: Ca$^{2+}$ = 1 : 2 : 1) selectively detects H$_2$PO$_4^-$ (5 equiv., using 0.1 mol L$^{-1}$ NaH$_2$PO$_4$ water solution as the H$_2$PO$_4^-$ 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: Ca$^{2+}$: Fe$^{3+}$ = 1 : 1 : 2) with different light exposure conditions. The photographs were taken at room temperature under room light and exposure to a 365-nm ultraviolet light.

The self-assembly and stimuli-response mechanism of the supramolecular gels were carefully investigated. In the concentration dependent $^1$H NMR (Fig. S8a-c) of G, the -NH (H$_2$)
and –N=CH (H$_3$) resonance signals showed obvious downfield shifts as the concentration of G rose. Moreover, in the FT-IR (Fig. S9) the C=O vibration absorption of OG shifted to low wavenumber in the corresponding OG xerogel. These results revealed that in the gelation process, the -NH (H$_3$) and -N=CH (H$_3$) groups formed hydrogen bonds with the -C=O groups on adjacent gelators. On the other hand, as shown in Fig. S8a-c, with the gradual increase in concentration, the $^1$H NMR signal of naphthyl groups of these gels.

Therefore, as illustrated in Scheme S2, the gelator G self-assembled to organogel OG by the hydrogen bonds, π–π stacking as well as the van der Waals existing in the long alkyl chains.

The formation of metalloegels was also investigated. As shown in Fig. S8d, after addition of 1 equiv. Ca$^{2+}$ to the solution of G, the -NH (H$_3$) and -N=CH (H$_3$) showed significant downfield shifts, and the phenyl proton H$_a$ and H$_b$ which is neighboring the acyl (-C=O) group shifted upfield. Meanwhile, in the IR spectra (Fig. S10) the stretching vibrations of -C=O and -C=N of acyl (-C=O) group shifted to lower wavenumbers when G interacted with 1 equiv. Ca$^{2+}$. These phenomena indicated that in CaG, the Ca$^{2+}$ coordinated with the nitrogen and oxygen atoms on acylhydrazone group (Scheme S2). In addition, after adding 2 equiv. of Fe$^{3+}$ to the CaG, the stretching vibrations of -C=O and -C=N of G shifted to lower wavenumbers again. Meanwhile, the absorption bands of -C=O merged with the absorption bands of -C=N, which indicated that in the CaFeG, the Fe$^{3+}$ formed more stable coordination bonds with oxygen and nitrogen atom on acylhydrazone group and the Ca$^{2+}$ was replaced by Fe$^{3+}$ (Scheme S2).

This presumed 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, in the same condition, the $T_{gel}$ of OG is obvious 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 ascribed to the breakage of intermolecular hydrogen bonds among –N=C=H on one gelator and the –C=O on the other ones (Scheme S2) in OG, which was caused by the coordination of Ca$^{2+}$ or Cu$^{2+}$ with gelator G.

To get further insight into the morphological features of the organogel OG and metallogels CaG and CaFeG, SEM studies were carried out with their xerogels respectively. As shown in Fig. S11, the SEM images of OG showed an overlapped rugate layer structure. The thickness of each layer was approximately 10-20 nm. The metallogels CaG and CaFeG also showed overlapped rugate layer structures. These phenomena indicated that although the gelator G coordinated with Ca$^{2+}$ or Fe$^{3+}$, significant changes didn’t take place on the self-assembly states. Moreover, the XRD patterns (Fig. S12) of the OG, FeG, CaFeG and the CaFeG treated with H$_3$PO$_4$ showed periodical diffraction peaks, indicating that they indeed assembled into the ordered structures. The peaks at 20 = 22.96-23.76° corresponding to the d-spacing 3.73-3.87 Å, which suggested that π–π stacking existed in the naphthyl groups of these gels.

Conclusions

In summary, we have demonstrated a new strategy for the design of stimuli-responsive supramolecular gels. In this way, the stimuli-response selectivity and signal reporting property of the supramolecular gels are controlled by the competitive coordination of the two different metal ions with gelators and guest. In present work, by the competitive coordination of Ca$^{2+}$/ Fe$^{3+}$ with gelator and H$_3$PO$_4$, the strong aggregation-induced emission of the metallogel CaG was controlled as “OFF-ON-OFF”. The CaFeG could act as not only a convenient high selective and sensitive H$_3$PO$_4$ detection test kit, but also an erasable secret documentation medium.

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Notes and references

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: liumi@126.com: weitaibao@126.com

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‡ These authors contributed equally.


