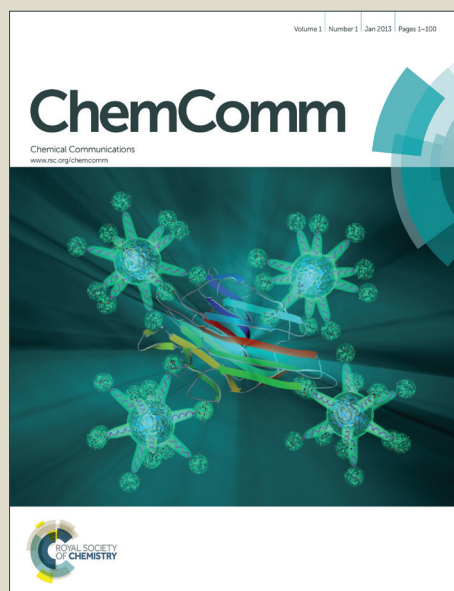


ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

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^{*}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

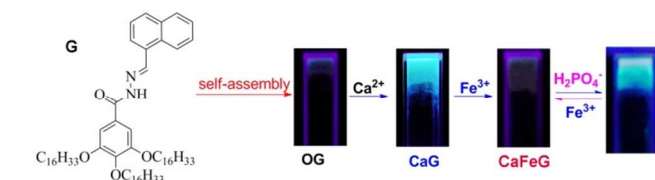
By rationally introduced Ca^{2+} and Fe^{3+} into a supramolecular gel, a bimetal-gel CaFeG was prepared. CaFeG could reversibly fluorescent “turn-on” sense H_2PO_4^- with specific selectivity under gel-gel states through competitive coordination of Ca^{2+} and Fe^{3+} with gelators and H_2PO_4^- . The CaFeG could act as H_2PO_4^- test kit and rewritable security display materials.

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 chemosensors, drug delivery, biomaterials, displays, and so on.¹⁻³ 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.^{1,4,5} Recently, metal ions-coordinated supramolecular gels have become a focus of the 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 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,⁶ 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.



Scheme 1 (a) Molecular structure of **G** and fluorescence photograph of organogel **OG** (1%, in ethanol), metallogels **CaG**, **CaFeG** (1%, in ethanol, for **CaG**, $\text{G} : \text{Ca}^{2+} = 1 : 1$; for **CaFeG**, $\text{G} : \text{Fe}^{3+} : \text{Ca}^{2+} = 1 : 2 : 1$) and **CaFeG** treated with H_2PO_4^- , illuminated at 365 nm.

We investigated the influence of metal ions on the **G** 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 ($T > T_{\text{gel}}$). 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).⁷ 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 VIIB 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+}

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%).

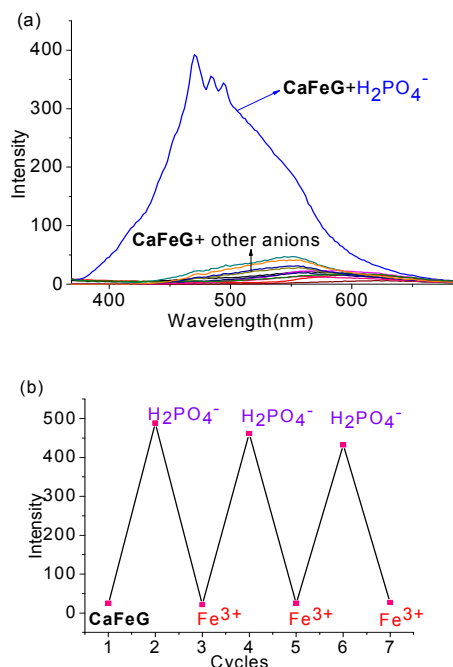


Fig. 1 (a) Fluorescence spectra of **CaFeG** (1%, in ethanol, **CaFeG**, **G** : Fe^{3+} : Ca^{2+} = 1 : 2 : 1) in the presence of various anions (5 equiv. of F^- , Cl^- , Br^- , I^- , AcO^- , HSO_4^- , H_2PO_4^- , N_3^- , SCN^- , ClO_4^- and CN^- , respectively, using their 1.0×10^{-3} M sodium salts 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_2PO_4^- , $\lambda_{\text{exc}} = 350$ 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_2PO_4^- , N_3^- , 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_2PO_4^- to the **CaFeG** at 20 °C, with the diffusion of H_2PO_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_2PO_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_2PO_4^- -contained **CaFeG**, the fluorescence of **CaFeG** could be quenched, which was attributed to the Fe^{3+} coordination with **G** again. These properties make **CaFeG** act as a H_2PO_4^- and Fe^{3+} controlled “OFF-ON-OFF” fluorescent switch. By alternating addition of H_2PO_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_2PO_4^- with specific selectivity (Fig. 1a & 2a). Moreover, the H_2PO_4^- response sensitivity of **CaFeG** is very high. As shown in Fig. S7, with the gradual addition of H_2PO_4^- , the emission intensity at 469 nm increasing along with the increasing in the concentrations of H_2PO_4^- . The detection limit of the fluorescence spectra changes calculated on the basis of $c_L = k s_B / S$ (where s_B is the standard deviation of the blank measures, S is the sensitivity of the method, $k = 3$)⁸ was 1.0×10^{-6} M (1 μM) for H_2PO_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_2PO_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_2PO_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_2PO_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_2PO_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 photocopied, 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

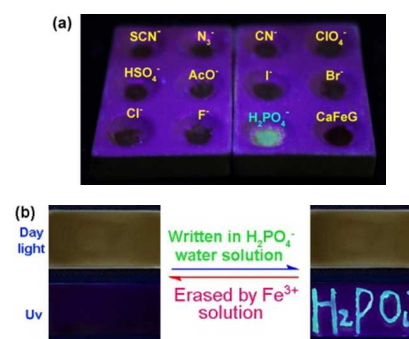


Fig. 2 (a) Photograph of metallogel **CaFeG** (1%, in ethanol, **CaFeG**, **G** : Fe^{3+} : Ca^{2+} = 1 : 2 : 1) selectively detects H_2PO_4^- (5 equiv., using 0.1 mol L^{-1} NaH_2PO_4 water solution as the H_2PO_4^- sources) in water solution on a spot plate, illuminated at 365 nm. (b) Writing and erasing 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). 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 ^1H NMR (Fig. S8a-c) of **G**, the -NH (H_a)

and $-N=CH$ (H_b) 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_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, with the 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 $\pi-\pi$ stacking interactions between the naphthyl groups were involved in the gelation process.¹⁰ Therefore, as illustrated in Scheme S2, the gelator **G** self-assembled to organogel **OG** by the hydrogen bonds, $\pi-\pi$ stacking as well as the van der Waals existing in the long alkyl chains.

The formation of metallogels was also investigated. As shown in Fig. S8d, after addition of 1 equiv. Ca^{2+} to the solution of **G**, the $-NH$ (H_a) and $-N=CH$ (H_b) showed significant downfield shifts, and the phenyl proton H_g and H_h which is neighbouring the acyl ($-C=O$) group shifted upfield. Meanwhile, in the IR spectra (Fig. S10) the stretching vibrations of $-C=O$ and $-C=N-$ of **G** shifted to lower wavenumbers when **G** interacted with 1 equiv of 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 took place on the self-assembly states. Moreover, the XRD patterns (Fig. S12) of the **OG**, **FeG**, **CaFeG** and the **CaFeG** treated with $H_2PO_4^-$ showed periodical diffraction peaks, indicating that they indeed assembled into the ordered structures. the peaks at $2\theta = 22.96-23.76^\circ$ corresponding to the d -spacing 3.73-3.87 Å, which suggested that $\pi-\pi$ 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 $H_2PO_4^-$, 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 $H_2PO_4^-$ detection test kit, but also an erasable secret documentation medium.

This work was supported by the National Natural Science Foundation of China (NSFC) (Nos. 21064006; 21161018; 21262032), the Natural Science Foundation of Gansu Province (1308RJZA221) and the Program for Changjiang Scholars and Innovative Research Team in University of Ministry of Education of China (IRT1177).

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: linqi2004@126.com; weitaibao@126.com

† Electronic Supplementary Information (ESI) available: Experimental details, synthesis of **G**, and other materials. See DOI: 10.1039/b000000x/ ‡ These authors contributed equally.

- M. D. Segarra-Maset, V. J. Nebot, J. F. Miravet and B. Escuder, *Chem. Soc. Rev.*, 2013, **42**, 7086; X. Yan, F. Wang, B. Zheng and F. Huang, *Chem. Soc. Rev.*, 2012, **41**, 6042; J. M. Hu, G. Q. Zhang and S. Y. Liu, *Chem. Soc. Rev.*, 2012, **41**, 5933.
- G. O. Lloyd and J. W. Steed, *Nat. Chem.*, 2009, **1**, 437.
- Z. Qi, P. M. de Molina, W. Jiang, Q. Wang, K. Nowosinski, A. Schulz, M. Gradzielski and C. A. Schalley, *Chem. Sci.*, 2012, **3**, 2073; P. Cordier, F. Tournilhac, C. Soulié-Ziakovic and L. Leibler, *Nature*, 2008, **451**, 977; J. Zhou, X. Du, Y. Gao, J. Shi and B. Xu, *J. Am. Chem. Soc.*, 2014, **136**, 2970; H. Maeda, *Chem. -Eur. J.* 2008, **14**, 11274.
- G. Yu, X. Yan, C. Han and F. Huang, *Chem. Soc. Rev.*, 2013, **42**, 6697; T. Aida, E. W. Meijer and S. I. Stupp, *Science*, 2012, **335**, 813; Z. X. Liu, Y. Feng, Z. C. Yan, Y. M. He, C. Y. Liu and Q. H. Fan, *Chem. Mater.*, 2012, **24**, 3751; S. S. Babu, V. K. Praveen and A. Ajayaghosh, *Chem. Rev.*, 2014, **114**, 1973.
- J. H. van Esch and B. L. Feringa, *Angew. Chem. Int. Ed.*, 2000, **39**, 2263; A. R. Hirst, B. Escuder, J. F. Miravet and D. K. Smith, *Angew. Chem. Int. Ed.*, 2008, **47**, 8002; Y. M. Zhang, Q. Lin, T. B. Wei, X. P. Qin and Y. Li, *Chem. Commun.*, 2009, 6074; Y.-M. Zhang, B.-B. Shi, H. Li, W.-J. Qu, G.-Y. Gao, Q. Lin, H. Yao and T.-B. Wei *Polym. Chem.*, 2014, DOI: 10.1039/C4PY00186A.
- M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke and J. W. Steed, *Chem. Rev.* 2010, **110**, 1960; A. Y.-Y. Tam and V. W.-W. Yam, *Chem. Soc. Rev.*, 2013, **42**, 1540; M. J. Mayoral, C. Rest, V. Stepanenko, J. Schellheimer, R. Q. Albuquerque and G. Fernández, *J. Am. Chem. Soc.*, 2013, **135**, 2148; W. Weng, J. B. Beck, A. M. Jamieson, and S. J. Rowan, *J. Am. Chem. Soc.*, 2006, **128**, 11663; F. Fages, *Angew. Chem., Int. Ed.*, 2006, **45**, 1680; J. Zhang and C.-Y. Su, *Coord. Chem. Rev.*, 2013, **257**, 1373.
- Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361.
- Analytical Methods Committee, *Analyst*, 1987, **112**, 199.
- A. Kishimura, T. Yamashita, K. Yamaguchi and T. Aida, *Nat. mater.*, 2005, **4**, 546; S. Srinivasan, P. A. Babu, S. Mahesh and A. Ajayaghosh, *J. Am. Chem. Soc.*, 2009, **131**, 15122.
- C. Po, Z. Ke, A. Y.-Y. Tam, H.-F. Chow and V. W.-W. Yam, *Chem. -Eur. J.*, 2013, **19**, 15735.