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Competitive Coordination Control the AIE and Micro States of Supramolecular Gel: an Efficient Approach for Reversible Dual-Channel Stimuli-Response Materials

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An organogelator (G2) based on multi self-assembly driving forces, fluorescent signal groups and coordination binding sites was designed and synthesized. G2 could form a stable Cd2+-coordinated supramolecular metallogel (CdG) companied with strong brilliant blue aggregation-induced fluorescence emission (AIE). By competitive coordination of Cd2+ with gelator and I-, the AIE of CdG could be reversibly switched “on-off-on” under gel-gel states via alternative adding I- and Cd2+ into CdG.

Introduction

Over the past four decades, supramolecular chemistry has matured from a conceptually marvelous scientific curiosity to a technologically relevant science encompassing the broad area of advanced materials. Among them, stimuli-responsive supramolecular gel (SRSGs) have attracted more and more attentions due to their promising applications, including chemosensors, optoelectronic devices, drug delivery, tissue engineering, biomaterials, surface science, displays, etc. The SRSGs are derived from the noncovalent self-assembly of small molecules. By taking advantage of the dynamic and reversible nature of noncovalent interactions, the SRSGs can sense, process, and actuate a response to an external change without assistance. Although the SRSGs formed by organic molecules have been widely reported, the metal cations-coordinated SRSGs have only been a subject of study in the last few years. Interestingly, 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 SRSGs in materials science. Up to now, considerable efforts have been dedicated to metal cations-coordinated SRSGs, however, it is still a big challenge to design and synthesize novel SRSGs that can optically sense a given chemical stimulus with specific selectivity.

In addition, because anions play a fundamental role in chemical, biological and environmental processes, more and more interests have been attracted to anion response SRSGs. Although a number of the reported SRSGs could response some anions such as F-, AcO- etc. via the competitive binding of these anions with SRSGs’ self-assemble sites (e.g. hydrogen bonding), there are still a lot of demands for SRSGs that could specifically detect certain anions. For example, despite the fact that I- is well-known as an important chemical in biology, chemistry and the environment, to the best of our knowledge, there is no report on the I- responsive supramolecular gels.

Herein we report a novel strategy for the design of SRSGs. In this way, the stimuli-response properties such as response selectivity and optical signal output could be controlled by the competitive coordination between supramolecular gelators, metal ions and guest anions in a supramolecular gel. To demonstrate this strategy, an organogelator (G2) based on multi self-assembly driving forces, fluorescent signal groups and coordination binding sites was designed and synthesized (Scheme 1). G2 could form stable supramolecular organogel in various solvents at very low critical gelation concentrations (CGCs). Upon the addition of Cd2+ to the G2 ethanol organogel (OG), the OG could form a stable Cd2+-coordinated supramolecular metallogel (CdG) companied with strong brilliant blue aggregation-induced fluorescence emission (AIE). The AIE of CdG could be reversibly quenched by iodide anions with specific selectivity in gel-gel states. The iodide anions response process was contributed to the competitive binding of I- with the Cd2+ in the supramolecular metallogel. Interestingly, in the reversible I- response process, although the macro phase of the CdG didn’t show any changes, however, the micro structure of the CdG xerogel carried out dramatic changes and formed lots of micro cavities. These micro cavities could absorb iodine vapour and induced the color of CdG xerogel changed from white to brown.
channel security display materials. This strategy can provide an important step towards the security technology for information handling.

Figure 1: (a) Fluorescence spectra of organogel OG (1%, in ethanol) and metallogel CdG (1%, in ethanol, G2 : Cd²⁺ = 1 : 1). (b) Temperature-dependent fluorescent spectra of the CdG (1%, in ethanol, G2 : Cd²⁺ = 1 : 1) during gelation process (λex = 350 nm).

The anion response capability of the supramolecular metallogel CdG was primarily investigated by adding various anions (F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, HSO₄⁻, H₂PO₄⁻, N₃⁻, SCN⁻, ClO₄⁻ and CN⁻, using their 0.1 mol L⁻¹ sodium salts water solution as the sources) to the CdG. As shown in Fig. 2a, upon the addition of various anions into the CdG at 20 °C, respectively, with the diffusion of the anions, only I⁻ could induce the strong brilliant blue fluorescence emission at 469 nm of CdG quenched. These results were attributed to I⁻ competitively bound to the Cd²⁺.

Interestingly, upon the addition of Cd²⁺ into the I⁻ containing CdG, the fluorescence of CdG could recovered, which was attributed to the Cd²⁺ coordination with G2 again. These properties make CdG act as a I⁻ and Cd²⁺ controlled “on-off-on” fluorescent switch. By alternating addition of I⁻ and Cd²⁺, the switch could be reversibly performed at least for four cycles with little fluorescent efficiency loss (Fig. 2b). Moreover, other anions couldn’t cause similar fluorescent response, therefore, the CdG could detect I⁻ with specific selectivity. It is very interesting that unlike most of the reported SRSGs which showed gel-sol phase transition according to the anions’ stimulation, the gel state of CdG didn’t show any gel to sol changes in the whole I⁻ response process. This special stability could be attributed to the cooperation of the multi self-assembly forces we rationally introduced to the gelators.

Meanwhile, as shown in Fig. S2, the addition of Mg²⁺, Ca²⁺,


Zn\(^{2+}\) and Cd\(^{2+}\) could obviously enhance the fluorescence emission of OG. We also carefully investigated the anions response properties of the Mg\(^{2+}\), Ca\(^{2+}\), Zn\(^{2+}\) and Cd\(^{2+}\) based metallogels (MgG, CaG, ZnG, CdG), respectively. Only CdG shown obvious I\(^{-}\) specific selectivity. Therefore, we employed the CdG as I\(-\)response gel.

![Fluorescence spectra of CdG in the presence of various anions](image)

**Fig. 2** (a) Fluorescence spectra of CdG (1\%, in ethanol, G2 : Cd\(^{2+}\) = 1 : 1) in the presence of various anions (5 equiv. of F\(^{-}\), Cl\(^{-}\), Br\(^{-}\), I\(^{-}\), AcO\(^{-}\), HSO\(_4\)\(^{-}\), H\(_2\)PO\(_4\)\(^{-}\), N\(_2\)CN\(^{-}\), SCN\(^{-}\), ClO\(_4\)\(^{-}\) and CN\(^{-}\), respectively, using their 0.1 mol L\(^{-1}\) sodium or potassium salts water solution as the sources) at room temperature. (b) Fluorescent “on-off-on” cycles of CdG, controlled by the alternative addition of I\(^{-}\) and Cd\(^{2+}\), \(\lambda_{ex} = 350\) nm.

CdG could act as a smart material for the reversible detection of I\(^{-}\) in water solutions. For instance, as shown in Fig. 3a, when adding water solutions of various anions to the small amounts of metallogel CdG on a spot plate respectively, only I\(^{-}\) could induce an instant fluorescence quenching of CdG. Moreover, the I\(^{-}\) response sensitivity of CdG is very high. As shown in Fig. 3b, with the gradual addition of I\(^{-}\), the emission intensity at 469 nm decreasing along with the increasing in the concentrations of I\(^{-}\). The detection limit of the fluorescence spectra changes calculated on the basis of 3S\(_{0.05}\)/S was 1.0 \(\times\) 10\(^{-7}\) M (0.1 \(\mu\)M) for I\(^{-}\) anion.

In order to facilitate the use of the CdG, the I\(^{-}\) detection film based on CdG were prepared by pouring the heated ethanol solution of CdG onto a clean glass surface and drying in the air. The CdG film is white under nature light and show strong brilliant blue fluorescence emission under UV 365 nm. When writing on the film with a writing brush dipped with I\(^{-}\) water solution, the film didn’t show any color changes, while under the UV 365 nm, a clear dark writing image appeared (Fig. 4). This dark writing image could be erased by brushing Cd\(^{2+}\) on the film again. More interestingly, when exposing the CdG film containing the invisible I\(^{-}\) image into the iodine vapour, a clear brown image appeared on the film (Fig. 4). However, when putting the film under the room atmosphere for three days, the brown image could gradually disappear. Therefore, the CdG film could act as not only a convenient reversible I\(^{-}\) detection test kit, but also an erasable dual-channel security display materials. It’s worth mentioning that security display materials have become of increasing importance. They 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 using visible dyes and liquid crystals, security display materials that allow rewriting of invisible printed images are very rare.

![Photograph of metallogel CdG in water solution and on a spot plate, illuminated at 365 nm](image)

**Fig. 3** (a) Photograph of metallogel CdG (1\%, in ethanol, G2 : Cd\(^{2+}\) = 1 : 1) selectively detects I\(^{-}\) (5 equiv., using 0.1 mol L\(^{-1}\) KI water solution as the I\(^{-}\) sources) in water solution on a spot plate, illuminated at 365 nm. (b) Fluorescence spectra of CdG (1\%, in ethanol, G2 : Cd\(^{2+}\) = 1 : 1) with increasing concentration of I\(^{-}\) (using 0.1 mol L\(^{-1}\) KI water solution as the I\(^{-}\) sources), \(\lambda_{ex} = 350\) nm.

![Writing and coloration of a nature light invisible image](image)

**Fig. 4** Writing, erasing and coloration of a nature light invisible image on a CdG supramolecular gel film (obtained from 1\% ethanol metallogel, CdG, G2 : Cd\(^{2+}\) = 1 : 1. Writing: written in I\(^{-}\) water solution; erasing: brushed by Cd\(^{2+}\) water solution; coloration: exposing the CdG film into the iodine vapour ca. 5 sec.) The photographs were taken at room temperature under room light and exposure to a 365-nm ultraviolet light.
Moreover, to facilitate and expand the application of the materials, the CdG-based paper was prepared by immersing filter papers into hot CdG sol. As shown in Fig. S4, the CdG-based paper could be used as not only an efficient I’ detection test kit but also a dual-channel secret documentation medium. Unlike the CdG-based film, on the CdG-based paper, the brown image induced by iodine vapour couldn’t disappeared by putting the paper under the room atmosphere for three days. This result could be attributed to the iodine adsorption ability on paper is stronger than that on film.

In order to investigate the self-assembly and stimuli-response mechanism of CdG, a series of experiments have been carried out. Firstly, in the concentration dependent $^1$H NMR (Fig.5) of CdG, the -NH ($H_1$) and -N=CH ($H_2$) resonance signals showed obvious downfield shifts as the concentration of CdG rose. Moreover, in the FT-IR (Fig. S5 in SI) the C=O vibration absorption of powder CdG shifted to low wavenumbers in the corresponding OG xerogel. These results revealed that in the gelation process, the -NH ($H_1$) and -N=CH ($H_2$) groups formed hydrogen bonds with the -C=O groups on adjacent gelators. On the other hand, as shown in Fig. 5a-c, with the gradual increase in concentration, the $^1$H NMR signal of naphthyl protons ($H_3$, $H_5$, $H_6$ and $H_8$) showed obvious upfield shift, indicating that the π-π stacking interactions between the naphthyl groups were involved in the gelation process. Therefore, as illustrated in scheme 1, the gelator CdG self-assembled to supramolecular organogel OG by the hydrogen bonds, π-π stacking as well as the vdW existing in the long alkyl chains.

The formation of supramolecular metallogels was also investigated. As shown in Fig. 6, after addition of 1 equiv. Cd$^{2+}$ to the solution of CdG, the -NH ($H_1$) and -N=CH ($H_2$) showed significant downfield shifts (Fig. 6b), and all of the phenyl protons shifted upfield. Meanwhile, in the IR spectra (Fig. 7) the stretching vibrations of -C=O and -C=N- of CdG shifted to lower wavenumbers when CdG interacted with 1 equiv of Cd$^{2+}$. These phenomena indicated that in CdG, the Cd$^{2+}$ coordinated with the nitrogen and oxygen atoms on acylhydrazone group (Scheme 1). Interestingly, as shown in Fig. 6c, after the addition of I into the CdG and Cd$^{2+}$ mixture solution, owing to the competitive coordination of I with Cd$^{2+}$, the $^1$H NMR of CdG almost recovered.

This presumed self-assembly and competitive coordination mechanism was also supported by the $T_{pol}$ of OG and CdG. For instance, as shown in Fig. 8, in the same condition, the $T_{pol}$ of OG is obvious higher than CdG. The large differences of $T_{pol}$ between the OG and CdG 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 1) in OG, which was caused by the coordination of Cd$^{2+}$ with gelator CdG.

In order to gain an insight into the stoichiometry of the Cd$^{2+}$-gelator complex, the Job’s method and Mass spectra were used. In the Job’s plots (Fig. S6), when the molar fraction of gelator CdG was 0.5, the absorbance value approached a maximum, which...
demonstrated the formation of a 1:1 complex between the gelator G2 and Cd^{2+}. Meanwhile, in the ESI-MS of sensor 1, the [G2+H]^+ peak at 995.8096 (m/z calcd: 995.8544) was observed; however, after addition of excess Cd^{2+} perchlorate salts to the solution of G2, a new peak appeared at 1305.6794, which coincides well with that for the species [G2^2+ + Cd^{2+} + 2ClO_4^-] (m/z calcd: 1305.6469). These results confirmed that the coordination ratio of Cd^{2+} : G2 is 1:1.

![Fig. 9 Powder XRD patterns of xerogel of OG (obtained from 1 % ethanol organogel), CdG (obtained from 1 % ethanol metallogel, G2: Cd^{2+} = 1 : 1) and CdG xerogel treated with I^- (5 equiv., using 0.1 mol L^-1 KI water solution as the I^- sources).](image)

Moreover, the XRD patterns (Fig. 9) of the OG, CdG and the CdG treated with I^- showed the peaks at 20 = 22.46-23.68° corresponding to the d-spacing 3.95, 3.88 3.90 Å, respectively, which suggested that π-π stacking existed in the naphthyl groups of these gels. Moreover, the Cd^{2+}-coordination process decreased the distance of π-π stacking between the naphthyl, which induced the enhance of the aggregation induced emission of CdG. These results coincides well with the DFT calculated results (as shown in Fig. S7, the distance of π-π stacking between the naphthyl are 3.90 Å for OG, and 3.81 Å for CdG, respectively). In addition, after the formation of the CdG, the peaks of OG (at 20 20.02, 21.04, 21.72, 22.46 corresponding to the d-spacing 4.43, 4.21, 4.08, 3.95 Å, respectively) disappeared and these peaks recovered again after treated the CdG via I^-.

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Notes and references

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Conclusions

In summary, we have demonstrated a new strategy for the design of stimuli-response supramolecular gel based on competitive coordination control the AIE and micro states of supramolecular gel. In this way, the fluorescent emission and micro structure of supramolecular metallogel are controlled by the competitive coordination of the gelators, metal ions and guest anions. It’s an effective way for a supramolecular gel to achieve selective response for a certain chemical stimuli. In present work, by the competitive coordination of Cd^{2+} and I^- with gelator G2, the strong aggregation-induced emission of supramolecular metallogel CdG was controlled as “on-off-on”. More interestingly, after the Cd^{2+} competitive coordination with I^-, there are lots of micro cavities formed in the CdG xerogel, which enable the CdG xerogel absorption the iodine vapour and show brown color. The CdG could act as not only a convenient high selective and sensitive I^- detection test kid, but also an erasable dual-channel secret documentation medium. This concept of “competitive coordination control the AIE and micro states of metallogel” may open a window for novel stimuli-response supramolecular gel-based smart materials.

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† Electronic Supplementary Information (ESI) available: Experimental details, synthesis of G2, and other materials. See DOI: 10.1039/b000000x/

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Graphical Abstract

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The optical properties and micro structure of Cd$^{2+}$-coordinated supramolecular metallogel (CdG) were controlled by competitive coordination of Cd$^{2+}$ with gelator and I?. The CdG could act as high selective and sensitive I? sensing material and re writable dual-channel security display materials.