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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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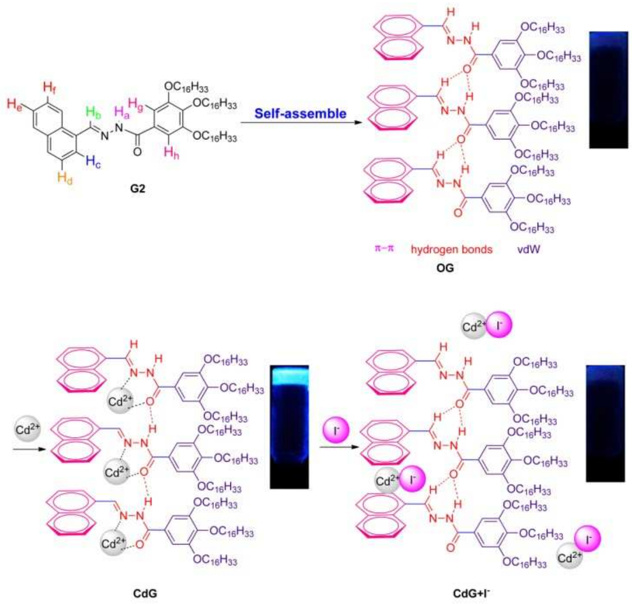
An organogelator (**G2**) based on multi self-assembly driving forces, fluorescent signal groups and coordination binding sites was designed and synthesized. **G2** could form a stable Cd^{2+}-coordinated supramolecular metallogel (**CdG**) companied with strong brilliant blue aggregation-induced fluorescence emission (AIE). By competitive coordination of Cd^{2+} with gelator and I^-, the AIE of **CdG** could be reversibly switched “on-off-on” under gel-gel states via alternative adding I^- and Cd^{2+} into **CdG**. Interestingly, owing to the competitive coordination of Cd^{2+} with I^-, 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. The **CdG** could act as not only a convenient high selective and sensitive I^- detection test kit (detection limit for I^- is 1.0×10^{-7} M) but also rewritable dual-channel security display materials.

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.[1] Among them, stimuli-responsive supramolecular gel (SRSGs)[2] have attracted more and more attentions due to their promising applications, including chemosensors, optoelectronic devices, drug delivery, tissue engineering, biomaterials, surface science, displays, etc.[3,4] The SRSGs are derived from the noncovalent self-assembly of small molecules.[2,4] 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.[2,5] 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.[5] 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.[5,6] 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,[7] more and more interests have been attracted to anion response SRSGs.[2] Although a number of the reported SRSGs could response some anions such as F^-, AcO^- etc.[8] *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,[9] 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 Cd^{2+} to the **G2** ethanol organogel (**OG**), the **OG** could form a stable Cd^{2+}-coordinated supramolecular metallogel (**CdG**) companied with strong brilliant blue aggregation-induced fluorescence emission (AIE).[10] 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 Cd^{2+} 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. These results indicated that the **CdG** could act as a I^- anion and I_2 molecular sensing materials. And more importantly, these interesting observations gave us the idea of rewritable dual-channel security display materials. This strategy can provide an important step towards the security technology for information handling.



Scheme 1 Chemical structure of the **G2** and the presumed self-assembly and reversible stimuli-response mechanism.

Results and discussion

The synthesis procedure of the **G2** is shown in Scheme S1 in supporting information (SI). We introduced naphthyl groups as fluorescent signal groups to provide **G2** with fluorescent response abilities. Moreover, we rationally introduced the multi-self-assembly driving forces such as strong van der Waals (vdW) existing in the long alkyl chains, hydrogen bonds existing in the acylhydrazone groups and π–π stacking existing in naphthyl groups to provide the gelator with better self-assembly abilities. The self-assembly abilities of **G2** were examined in various solvents by means of the "stable to inversion of a test tube" method (Table S1 in SI). **G2** showed excellent self-assembly abilities in various solutions. Among these solvents, the gelator **G2** 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 SI). Therefore, the **G2**-based supramolecular organogel **OG** in ethanol is more stable than the gels in other solutions.

Thus, we investigated the influence of 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) on the **G2** organogel in ethanol (Fig. S2). The addition and diffusion of 1 equiv. of Cd^{2+} to the **OG** (1%) generated the corresponding Cd^{2+}-coordinated supramolecular metallogel **CdG**. Moreover, the dissolution of the gelator **G2** and 1 equiv. of Cd^{2+} in heated ethanol could also form the same metallogel **CdG** (1%). Upon excitation at 365 nm with a hand-held UV lamp, the organogel **OG** emitted very weak fluorescence (Scheme 1 and Fig. S3), while the metallogel **CdG** emitted strong brilliant blue fluorescence emission (Scheme 1). In the corresponding fluorescence spectra (Fig. 1a), the fluorescence intensity of **CdG** at 469 nm is ca. 10 times higher than that of the **OG**. More interestingly, as shown in Fig. 1b, **CdG** has no fluorescence in hot ethanol solution (T > T_{gel}). However, with the temperature of hot ethanol solution dropping below the T_{gel} of **CdG**, the emission intensity at 469 nm showed a sudden increase and reached a steady state, which indicated that the fluorescence of metallogel **CdG** was the aggregation-induced emission (AIE).

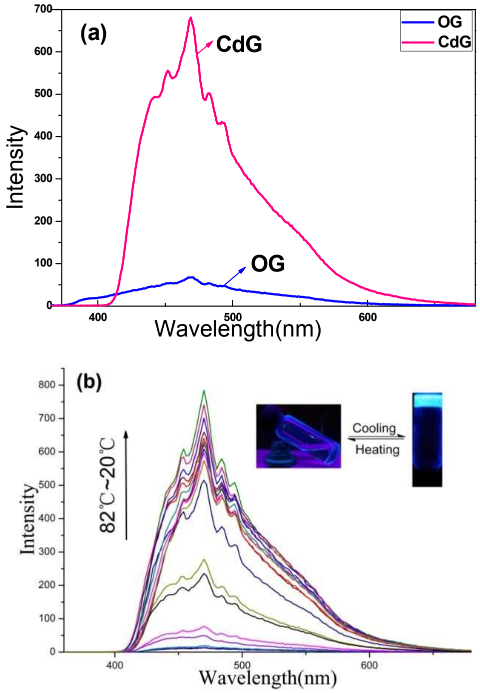


Fig. 1 (a) Fluorescence spectra of organogel **OG** (1%, in ethanol) and metallogels **CdG** (1%, in ethanol, **G2** :Cd^{2+} = 1 : 1). (b) Temperature-dependent fluorescent spectra of the **CdG** (1%, in ethanol, **G2** :Cd^{2+} = 1 : 1) during gelation process (λ_{ex} = 350 nm).

The anion response capability of the supramolecular metallogel **CdG** was primarily investigated by adding various anions (F^-, Cl^-, Br^-, I^-, AcO^-, HSO_4^-, $H_2PO_4^-$, N_3^-, SCN^-, ClO_4^- 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 Cd^{2+}. Interestingly, upon the addition of Cd^{2+} into the I^- containing **CdG**, the fluorescence of **CdG** could recovered, which was attributed to the Cd^{2+} coordination with **G2** again. These properties make **CdG** act as a I^- and Cd^{2+} controlled "on-off-on" fluorescent switch. By alternating addition of I^- and Cd^{2+}, 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 Mg^{2+}, Ca^{2+},

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.

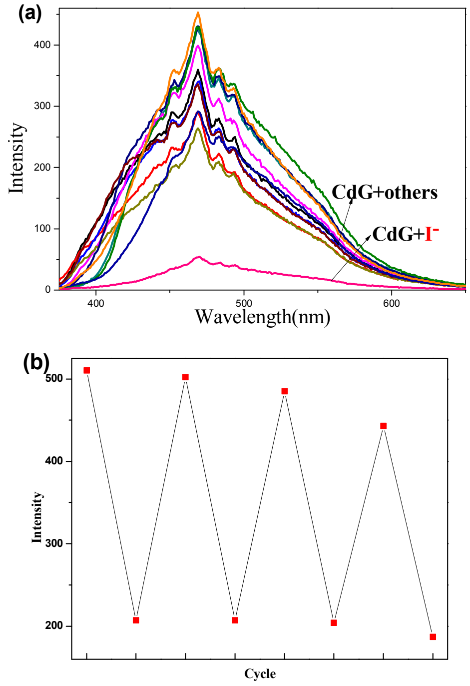


Fig. 2 (a) Fluorescence spectra of **CdG** (1%, in ethanol, **G2** : Cd^{2+} = 1 : 1) in the presence of various anions (5 equiv. of F^-, Cl^-, Br^-, I^-, AcO^-, HSO_4^-, $H_2PO_4^-$, N_3^-, SCN^-, ClO_4^- and CN^-, respectively, using their 0.1 mol L^{-1} sodium or potassium salts water solution as the sources) at room temperature. (b) Fluorescent "on-off-on" cycles of **CdG**, controlled by the alternative addition of I^- and Cd^{2+}, λ_{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 $3s_B/S$ was 1.0×10^{-7} M (0.1 μM) for I^- anion.[14]

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.[11] 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[12] and liquid crystals,[13] security display materials that allow rewriting of invisible printed images are very rare.

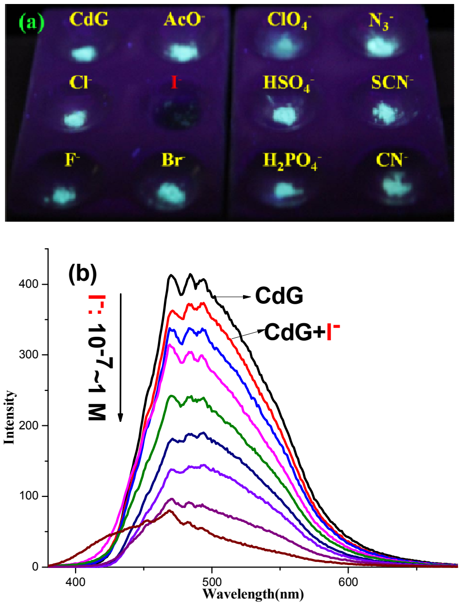


Fig. 3 (a) Photograph of metallogel **CdG** (1%, in ethanol, **G2** : Cd^{2+} = 1 : 1) selectively detects I^- (5 equiv., using 0.1 mol L^{-1} KI water solution as the I^- sources) in water solution on a spot plate, illuminated at 365 nm. (b) Fluorescence spectra of **CdG** (1%, in ethanol, **G2** :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

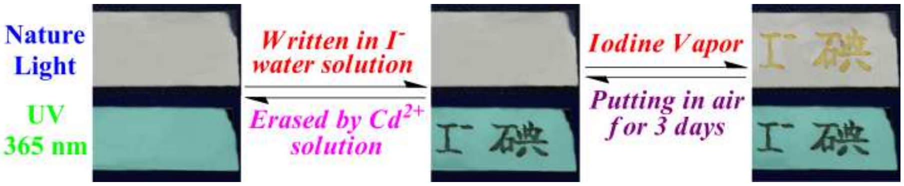


Fig. 4 Writing, erasing and coloration of a nature light invisible image on a **CdG** supramolecular gel film (obtained from 1% ethanol metallogel, **CdG**, **G2** : Cd^{2+} = 1 : 1. Writing: written in I^- water solution; erasing: brushed by Cd^{2+} water solution; coloration: exposing the **CdG** film 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 of 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 ^1H NMR (Fig.5) of **G2**, the -NH (H_a) and –N=CH (H_b) resonance signals showed obvious downfield shifts as the concentration of **G2** rose. Moreover, in the FT-IR (Fig. S5 in SI) the C=O vibration absorption of powder **G2** shifted to low wavenumbers 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. 5a-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 π–π stacking interactions between the naphthyl groups were involved in the gelation process.[15] Therefore, as illustrated in scheme 1, the gelator **G2** self-assembled to supramolecular organogel **OG** by the hydrogen bonds, π–π stacking as well as the vdW existing in the long alkyl chains.

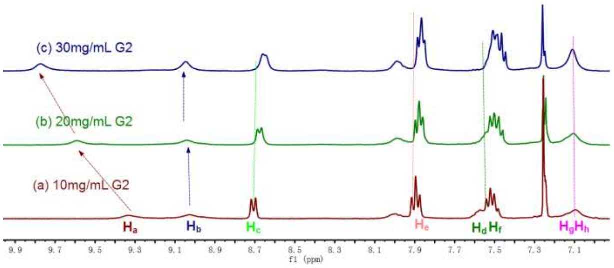


Fig. 5 Partial ^1H NMR spectra of **G2** in $CDCl_3$ with different concentrations.

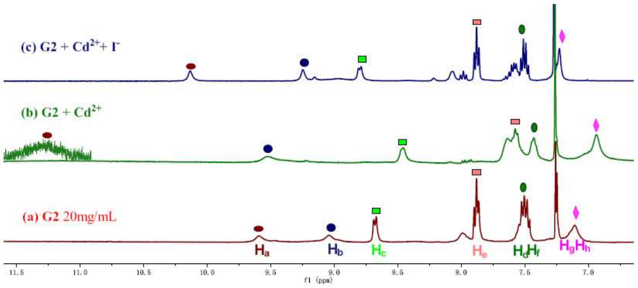


Fig. 6 Partial ^1H NMR spectra of (a) **G2** (20mg/mL), (b) **G2** mixed with 1 equiv. of Cd^{2+} (c) after addition of 2 equiv. of I^- in $CDCl_3$.

The formation of supramolecular metallogels was also investigated. As shown in Fig. 6, after addition of 1 equiv. Cd^{2+} to the solution of **G2**, the -NH (H_a) and -N=CH (H_b) 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 **G2** shifted to lower wavenumbers when **G2** 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 **G2** and Cd^{2+} mixture solution, owing to the competitive coordination of I^- with Cd^{2+}, the ^1H NMR of **G2** almost recovered.

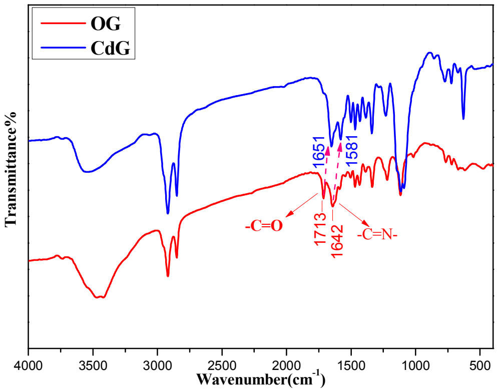


Fig. 7 IR Spectra of xerogel of organogel **OG** (obtained from 1% ethanol organogel) and metallogel **CdG** (obtained from 1% ethanol metallogel, **CdG**, **G2** : Cd^{2+} = 1 : 1)

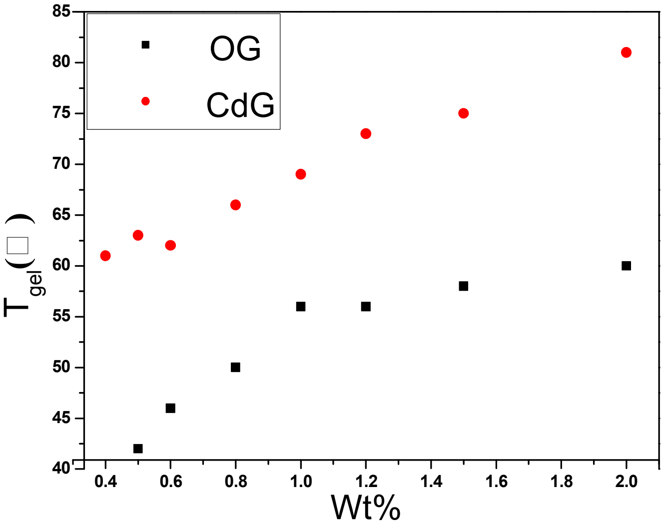


Fig. 8 Plots of T_{gel} against the concentrations of organogel **OG** and metallogels **CdG** (**G2** : Cd^{2+} = 1 : 1) in ethanol.

This presumed self-assembly and competitive coordination mechanism was also supported by the T_{gel} of **OG** and **CdG**. For instance, as shown in Fig. 8, in the same condition, the T_{gel} of **OG** is obvious higher than **CdG**. The large differences of T_{gel} 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 **G2**.

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 **G2** 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**$^{-}$ + Cd^{2+} + 2ClO$_4^{-}$] (m/z calcd: 1305.6469). These results confirmed that the coordination ratio of Cd^{2+} : **G2** is 1:1.

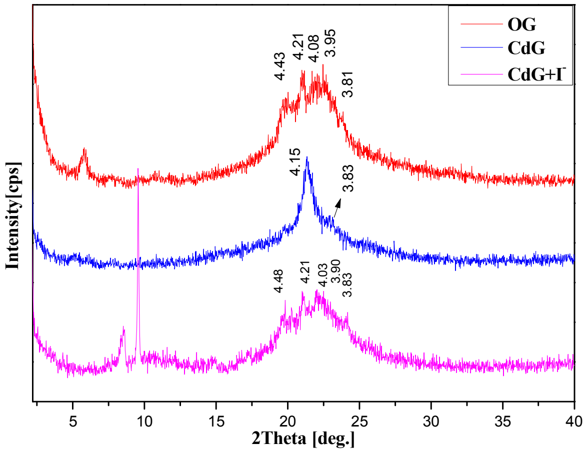


Fig. 9 Powder XRD patterns of xerogel of **OG** (obtained from 1 % ethanol organogel), **CdG** (obtained from 1 % ethanol metallogel, **G2**: Cd^{2+} = 1 : 1) and **CdG** xerogel treated with I$^-$ (5 equiv., using 0.1 mol L^{-1} KI water solution as the I$^-$ sources).

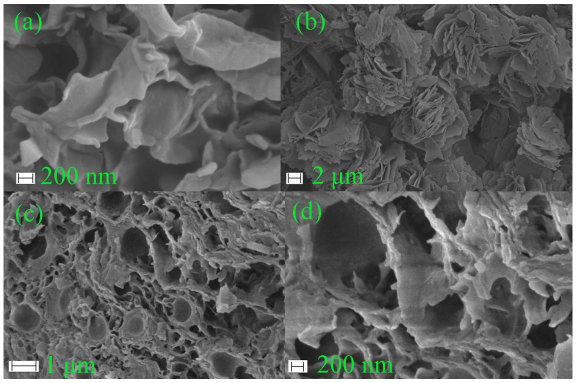


Fig. 10 SEM images of (a) **OG** xerogel (obtained from 1 % ethanol organogel) (b) **CdG** xerogel (obtained from 1 % ethanol metallogel, **G2**: Cd^{2+} = 1 : 1) (c) & (d) **CdG** xerogel treated with I$^-$ in situ.

Moreover, the XRD patterns (Fig. **9**) of the **OG**, **CdG** and the **CdG** treated with I$^-$ showed the peaks at 2θ = 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 caculated 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 2θ 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$^-$. These phenomena confirmed that the Cd^{2+} coordinated with **OG** and induced the XRD of **OG** changed, while the addition of I$^-$ into the **CdG** induced the competitive coordination of I$^-$ with Cd^{2+} and lead to the XRD peaks recovered. Moreover, after the addition of I$^-$ into the **CdG**, a new strong peak appeared at 2θ = 9.56°, which was attributed the coordination of Cd^{2+} with **I**$^-$.

To get further insight into the morphological features of the supramolecular organogel **OG**, metallogels **CdG** and **CdG** treated with I$^-$, SEM studies were carried out with their xerogels respectively. As shown in Fig. 10, the SEM images of **OG** showed an overlapped rugate layer structure. The thickness of each layer was approximately 10-20 nm. The metallogels **CdG** also showed overlapped rugate layer structures. However, after adding I$^-$ into the **CdG** xerogel, the micro states carried out obvious changes. There are lots of micro cavities formed in the xerogel of **CdG**. The diameters of the cavities are ca. 0.1-2 μm. These micro cavities provided the **CdG** xerogel with properties for adsorption iodine vapour. Therefore, the mechanism of iodine vapor-caused color change could be attributed to the iodine vapour adsorption of these micro cavities.

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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Notes and references

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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

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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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 rewritable dual-channel security display materials.