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Smart Materials

Double Metal Ions Competitively Control the Guest-Sensing Process: A Facile Approach to Stimuli-Responsive Supramolecular Gels

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Abstract: A facile approach to the design of stimuli-responsive supramolecular gels (SRSGs) termed double-metal-ion competitive coordination control is reported. By this means, the fluorescence signals and guest-selective responsiveness of the SRSGs are controlled by the competitive coordination of two different metal ions with the gelators and the target guest. To demonstrate this approach, a gelator **G2** based on multiple self-assembly driving forces was synthesized. **G2** could form Ca^{2+}-coordinated metallogel **CaG** with strong aggregation-induced emission (AIE). Doping of **CaG** with Cu^{2+} results in AIE quenching of **CaG** and formation of Ca^{2+}- and Cu^{2+}-based metallogel **CaCuG. CaCuG** could fluorescently detect CN^- with specific selectivity through the competitive coordination of CN^- with the Cu^{2+} and the coordination of Ca^{2+} with **G2** again. This approach may open up routes to novel stimuli-responsive supramolecular materials.

Introduction

Stimuli-responsive supramolecular gels (SRSGs),[1] as a class of smart and advanced materials, have attracted more and more attention due to their promising applications, including chemosensors, optoelectronic devices, drug delivery, tissue engineering, biomaterials, surface science, and displays.[2] SRSGs are derived from the noncovalent self-assembly of small molecules.[1,3] On account of the dynamic and reversible nature of noncovalent interactions, the SRSGs can sense, process, and actuate a response to an external change without assistance.[1,4] Though SRSGs formed by organic molecules have been widely reported, SRSGs based on metallogels have only been a subject of study in the last few years.[4] Interestingly, the tunable coordination binding strength, as well as the fascinating redox, optical, electronic, and magnetic properties of the metal ions, would benefit the application of metallogel-based SRSGs in materials science.[4a,b,5]

Although considerable efforts have been dedicated to metallogel-based SRSGs, most metallogel-based SRSGs contain only one kind of metal ions,[4,5] and only in a few of them are two kinds of metal ions employed to extend the stimuli-response properties. On the other hand, it is still a major challenge to design and synthesize novel SRSGs that can optically sense a given chemical stimulus with specific selectivity. Could the cooperation of two different kinds of metal ions in the same gel system improve the signal reporting and selective response abilities of the metallogel-based SRSGs? Reports on such attempts are very rare.

In addition, due to the fundamental role of anions in chemical, biological, and environmental processes,[6] more and more interest has focused on anion sensors based on SRSGs.[1] Although a number of the reported organogels could sense anions such as F^- and AcO^-[7] through their competitive binding with self-assembly sites of the organogels (e.g., hydrogen bonds), there is still great demand for SRSGs that can specifically detect certain anions. For example, despite the fact that CN^- is well known as a hazardous chemical in biology and the environment, and is extremely toxic to mammals,[8] to the best of our knowledge there is no report on CN^--responsive supramolecular gels.

Herein, we provide a novel approach to SRSGs design termed double-metal-ion competitive coordination control. To demonstrate this method, organogelator **G2** based on multiple self-assembly driving forces, fluorescent signal groups, and coordination binding sites was designed and synthesized (Scheme 1). **G2** could form stable supramolecular organogels in various solvents at very low critical gelation concentrations (CGCs). On addition of calcium perchlorate as Ca^{2+} source to the **G2** organogel (**OG**) in ethanol, a stable Ca^{2+}-coordinated metallogel (**CaG**)was formed, accompanied by strong brilliant blue aggregation-induced emission (AIE) of fluorescence.[9] In

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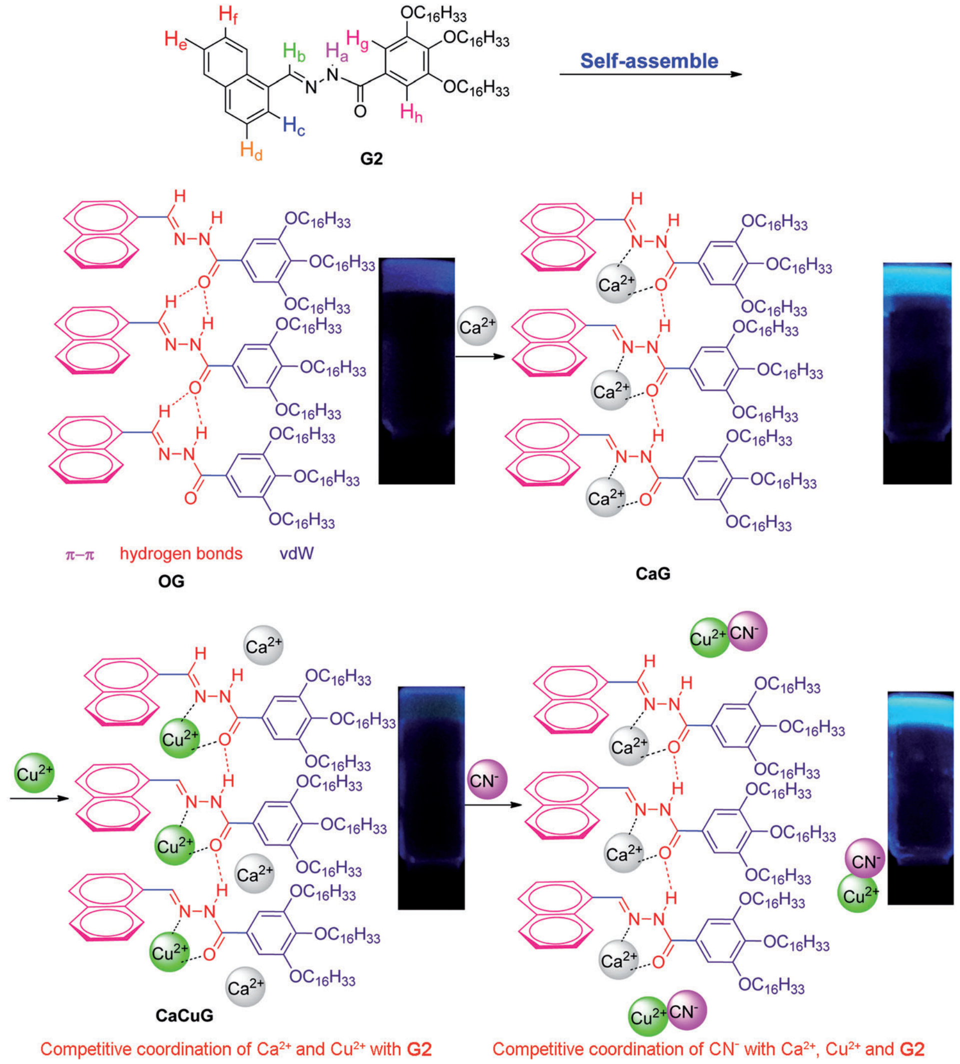
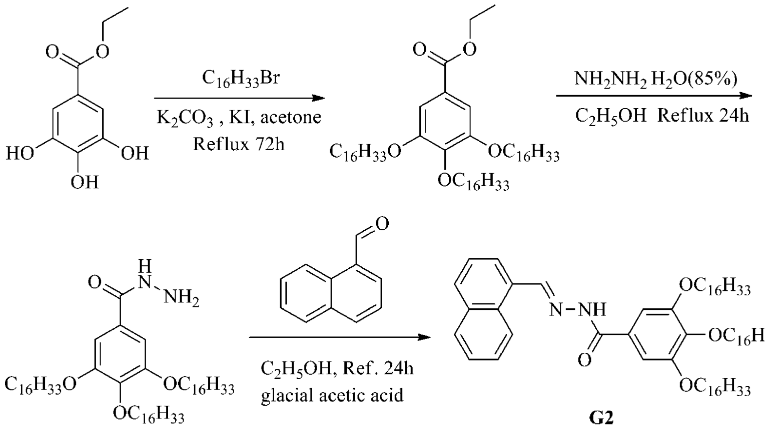


Scheme 1. Chemical structure of the **G2** and the assumed self-assembly and stimuli-responsive mechanism.

addition, continuous addition of copper perchlorate as Cu^{2+} source to **CaG** could form a stable Ca^{2+}/Cu^{2+}-based metallogel (**CaCuG**). The addition of Cu^{2+} resulted in fluorescence quenching of the **CaG**, which was attributed to competitive binding of Cu^{2+} with the organogelator **G2** and the replacement of Ca^{2+}. More interestingly, when CN^- was added to the **CaCuG** gel, its fluorescence completely recovered, which was attributed to competitive binding of CN^- with the Cu^{2+}, while Ca^{2+} in the gel coordinated with **G2** again. During the whole CN^--response process, the gel did not undergo a gel-to-sol transition. Thus **CaCuG** could fluorescently detect CN^- in the gel–gel state with specific selectivity.



Scheme 2. Synthetic route to organogelator **G2**.

Results and Discussion

The synthesis of **G2** is shown in Scheme 2. We rationally introduced multiple self-assembly driving forces, namely, strong van der Waals (vdW) interactions of the long alkyl chains, hydrogen bonds of the acylhydrazone groups, and π–π stacking of naphthyl groups, to provide the gelator with better gelation ability. The gelation ability of **G2** was examined in various solvents by means of stability to inversion of a test tube (Supporting Information Table S1). **G2** showed excellent gelation ability in dimethyl sulfoxide, ethanol, propyl alcohol, *n*-butyl alcohol, and isoamyl alcohol. Among these solvents, **G2** showed the lowest CGC (0.4 % w/v, 10 mg mL^{-1} = 1 %) and the highest gel–sol transition temperature T_{gel} in ethanol (Figure 1 and Supporting Information Table S1). Therefore, the **G2** organogel in ethanol is more stable than the gels in other solvents. Moreover, in ethanol, the sol–gel transition is very rapid. The whole transition process took no more than 1 min after heating of the ethanol solution was stopped. In addition, with increasing concentration of the **G2** in ethanol, T_{gel} reached a limit of 81 °C. This gel was found to be stable in closed tubes for at least three months at room temperature.

Because organogel **OG** is more stable in ethanol than in other solvents, we investigated the influence of metal ions on

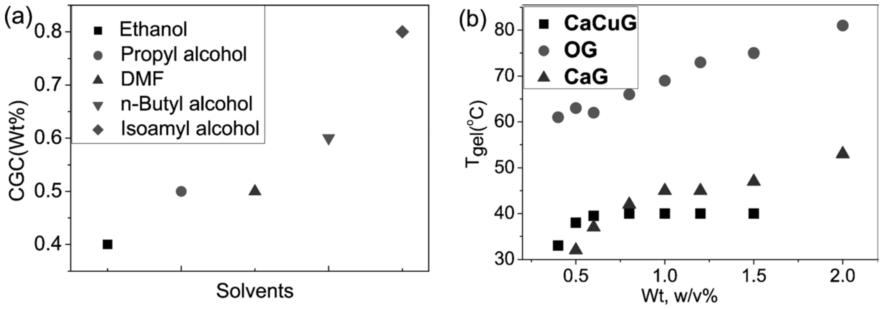


Figure 1. a) CGCs of **G2** in different solvents. b) Plots of T_{gel} against the concentrations of organogel **OG** and metallogels **CaG** and **CaCuG** in ethanol (for **CaG**, **G2**:Ca^{2+} = 1:1; for **CaCuG**, **G2**:Cu^{2+} :Ca^{2+} = 1:2:1).

OG in ethanol. The addition and diffusion of one equivalent 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+}) to **OG** (1 %) generated the corresponding metallogels (Supporting Information Figure S1). Moreover, dissolution of gelator **G2** and one equivalent of various cations in heated ethanol could also form the same metallogels (1 %). On excitation at 365 nm with a hand-held UV lamp, organogel **OG** emitted very weak fluorescence, whereas metallogel **CaG** emitted strong brilliant blue fluorescence (Scheme 1 and Supporting Information Figure S1). In the corresponding fluorescence spectra (Figure 2 a and Supporting Information Figure S2), the fluorescence intensity of **CaG** at 469 nm is about ten times higher than that of **OG**. More interestingly, as shown in Figure 2 b, **CaG** shows no fluorescence in hot ethanolic solution ($T > T_{gel}$). However, when the temperature of a hot ethanol solution dropped below 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 due to AIE. Meanwhile, the Cu^{2+}-coordinated metallogel **CuG** showed very weak fluorescence emission, which was similar to that of **OG** (Scheme 1 and Supporting Information Figure S1). These results illustrated that the formation of metallogel **CaG** could enhance the fluorescence emission of **OG** by AIE, whereas the formation of metallogel **CuG** could not enhance the fluorescence emission of **OG**.

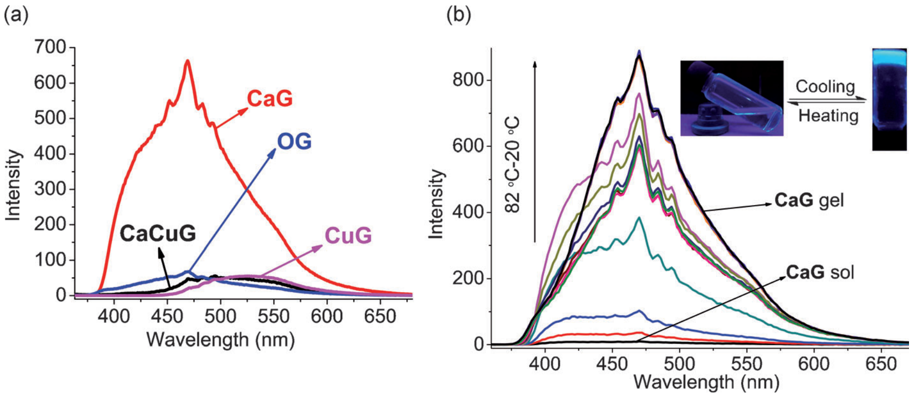


Figure 2. a) Fluorescence spectra of organogel **OG** (1 % in ethanol) and metallogels **CaG**, **CuG**, and **CaCuG** (1 % in ethanol; for **CaG**, **G2**:Ca^{2+} = 1:1; for **CuG**, **G2**:Cu^{2+} = 1:1; for **CaCuG**, **G2**:Cu^{2+}:Ca^{2+} = 1:2:1). b) Temperature-dependent fluorescence spectra of **CaG** (1 % in ethanol) during the gelation process (λ_{ex} = 350 nm).

Since Ca^{2+} belongs to Group 2 and Cu^{2+} to Group 11, the coordination ability of Cu^{2+} with acylhydrazone is much stronger than that of Ca^{2+}. Therefore, we presumed that, on adding Cu^{2+} to the metallogel **CaG**, Cu^{2+} could competitively coordinate with gelator **G2** in **CaG** and release Ca^{2+}. This process could quench the AIE of **CaG**. The experimental results confirmed this hypothesis. The addition and diffusion of two equivalents of Cu^{2+} into **CaG** (1 %) could form Cu^{2+}/Ca^{2+}-based metallogel **CaCuG** (Scheme 1). On diffusion of Cu^{2+}, the fluorescence emission of **CaG** was quenched (Figure 2 a). In addition, dissolution of **G2**, one equivalent of Ca^{2+}, and two equivalents of Cu^{2+} in hot ethanol also generated the same **CaCuG** (1 %). **CaCuG** showed very weak fluorescence emission, similar to that of **CuG** (Figure 2 a).

The anion-response capability of metallogel **CaCuG** was primarily investigated by adding five equivalents of various anions (F^-, Cl^-, Br^-, I^-, AcO^-, HSO_4^-, $H_2PO_4^-$, N_3^-, SCN^-, ClO_4^-, and CN^- as 0.1 mol L^{-1} aqueous solutions of their sodium salts) to the **CaCuG**. As expected, **CaCuG** showed excellent fluorescence changes with CN^- as stimulus (Figure 3 a). On addition of CN^- to **CaCuG** at 20 °C, **CaCuG** emitted strong brilliant blue fluorescence at 470 nm. This fluorescence is similar to that of **CaG**. These results confirmed that CN^- competitively bound to Cu^{2+}, while the Ca^{2+} coordinated with gelator **G2** again. Moreover, other anions did not cause similar fluorescent responses; therefore, **CaCuG** could detect CN^- with specific selectivity. Interestingly, unlike most of the reported SRSGs, which showed gel–sol phase transition on stimulation with anions, the gel state of **CaCuG** did not show any gel-to-sol changes during the whole CN^--response process. This special stability could be attributed to the cooperation of the multiple self-assembly forces that we rationally introduced into the gelator. Simply stated, because there are three kinds of self-assembly driving forces in gelator **G2**, even if the hydrogen bonds were destroyed by metal ions, the two remaining forces could maintain the gel state of the organogel.

CaCuG could act as a smart material for the detection of CN^- in aqueous solutions. For instance, as shown in Figure 4 a,

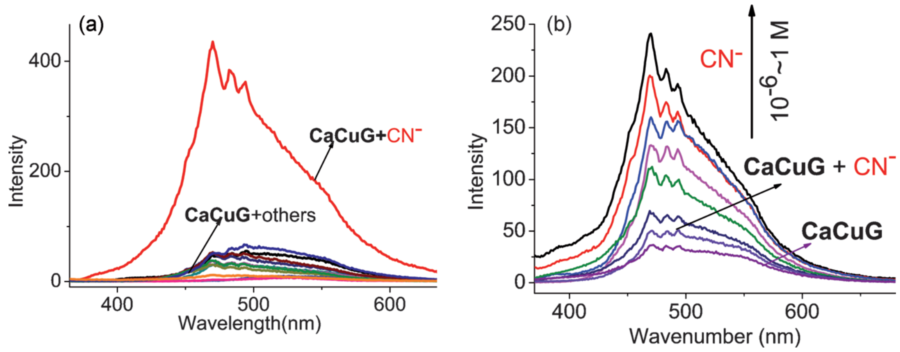


Figure 3. a) Fluorescence spectra of **CaCuG** (1 % in ethanol, **G2**:Cu^{2+}:Ca^{2+} = 1:1:1) in the presence of various anions (5 equiv of F^-, Cl^-, Br^-, I^-, AcO^-, HSO_4^-, $H_2PO_4^-$, N_3^-, SCN^-, ClO_4^-, and CN^- as 0.1 mol L^{-1} aqueous solutions of their sodium salts) at room temperature. b) Fluorescence spectra of **CaCuG** (1 % in ethanol, **G2**:Cu^{2+}:Ca^{2+} = 1:2:1) with increasing concentration of CN^- (0.1 mol L^{-1} aqueous solution of NaCN as CN^- source).

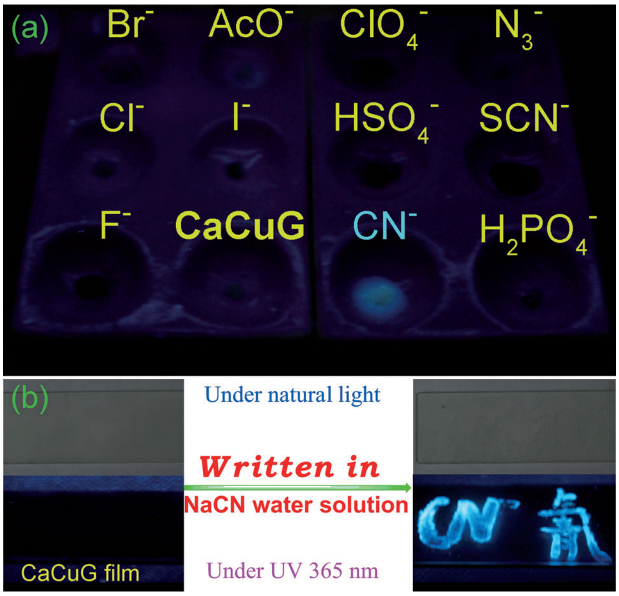


Figure 4. a) Photograph of metallogel **CaCuG** (1 % in ethanol, **G2**:Cu^{2+}:Ca^{2+} = 1:2:1) selectively detecting CN^- (5 equiv, 0.1 mol L^{-1} aqueous NaCN solution as CN^- source) in aqueous solution on a spot plate, illuminated at 365 nm. b) Photograph of a **CaCuG**-based film (obtained from 1 % metallogel **CaCuG** in ethanol, **G2**:Cu^{2+}:Ca^{2+} = 1:2:1) fluorescently detecting CN^- in aqueous solution (0.1 mol L^{-1} NaCN), illuminated at 365 nm.

on adding aqueous solutions of various anions to small amounts of metallogel **CaCuG** on a spot plate, only CN^- could induce an instant fluorescence emission of **CaCuG**. To facilitate the use of **CaCuG**, a CN^--detecting film based on **CaCuG** was prepared by pouring a hot ethanolic solution of **CaCuG** onto a clean glass surface and drying in air. The **CaCuG** film showed no fluorescence emission, but on writing on the film with a brush dipped in an aqueous solution of CN^-, a brilliant blue fluorescent image appeared (Figure 4 b). Moreover, as shown in Figure 3 b, on gradual addition of CN^-, the emission intensity at 470 nm increased with increasing concentration of CN^-. The detection limit of the fluorescence spectral changes calculated on the basis of $3s_B/S$, in which s_B is the standard deviation of the blank measures and S the sensitivity of the method, was 1.0×10^{-6} M (1 μM) for the CN^- anion.[10]

To investigate the self-assembly of organogel **OG**, a series of experiments on metallogels **CaG** and **CaCuG** as well as the CN^--response mechanism of **CaCuG** was carried out. Firstly, in the concentration-dependent ^1H NMR spectrum (Figure 5 a–c) of **G2**, the NH (H_a) and N=CH (H_b) signals showed obvious downfield shifts with increasing concentration of **G2**. Moreover, in the FTIR spectrum (Supporting Information Figure S3) the C=O vibrational band of **G2** powder shifted to lower 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 Figure 5 a–c, with gradual increase in concentration, the ^1H NMR signals of naphthyl protons (H_c, H_d, H_e, and H_f) showed obvious upfield shifts, which indicate that π–π stacking interactions between naphthyl groups were involved in the gelation process.[11] Therefore, as illustrated in Scheme 1, the gelator **G2** self-assembled to organogel **OG** by hydrogen bonding, π–π stacking, and vdW interactions of the long alkyl chains.

The formation of metallogels was also investigated. As shown in Figure 5 d, after addition of one equivalent of Ca^{2+} to a solution of **G2**, the NH (H_a) and N=CH (H_b) signals showed significant downfield shifts, and the signals of phenyl protons H_g and H_h, which are adjacent to the acyl (–C=O) group shifted upfield. In the IR spectra (Supporting Information Figure S4) the C=O and C=N stretching bands of **G2** shifted to lower

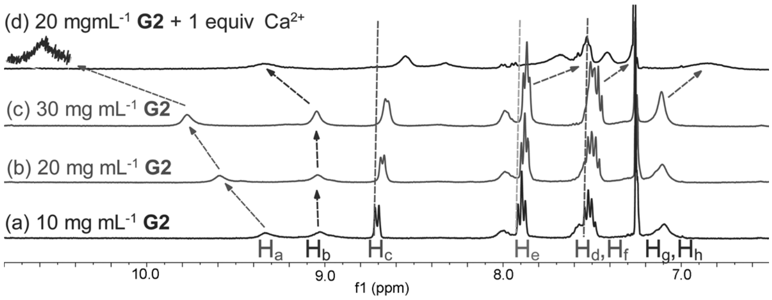


Figure 5. a)–c) Partial ^1H NMR spectra of **G2** in $CDCl_3$ at different concentrations. d) Partial ^1H NMR spectrum of **G2** mixed with 1 equiv of Ca^{2+} in $CDCl_3$.

wavenumbers when **G2** interacted with one equivalent of Ca^{2+}. These phenomena indicated that in **CaG** Ca^{2+} coordinated with the nitrogen and oxygen atoms of the acylhydrazone group (Scheme 1). In addition, after adding one equivalent of Cu^{2+} to **CaG**, the C=N stretching bands of **G2** shifted to lower wavenumbers again, which indicated that in **CaCuG** the Cu^{2+} ions formed more stable coordination bonds with nitrogen atoms of the acylhydrazone groups and Ca^{2+} was replaced by Cu^{2+} (Scheme 1).

This hypothetical self-assembly and competitive coordination mechanism was also supported by the T_{gel} values of **OG**, **CaG**, and **CaCuG**. For instance, as shown in Figure 1 a, under the same conditions, the T_{gel} value of **OG** is obviously higher than those of **CaG** and **CaCuG**, which are similar to each other. The large differences in T_{gel} between **OG** and **CaG** or **CaCuG** are ascribed to the breakage of intermolecular hydrogen bonds between N=CH groups and C=O groups of neighboring gelator molecules in **OG** (Scheme 1) by coordination of Ca^{2+} or Cu^{2+} with gelator **G2**.

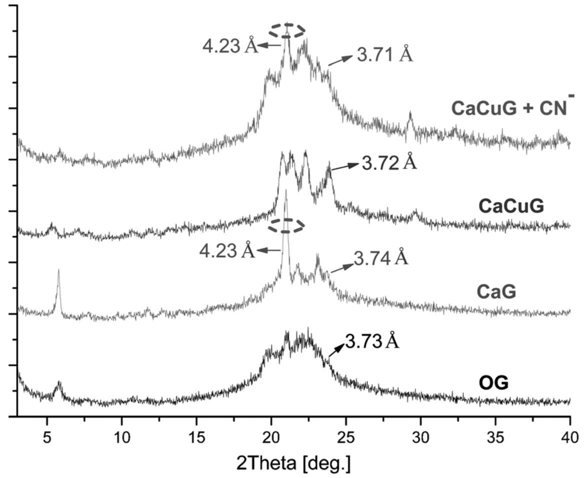


Figure 6. Powder XRD patterns of xerogels of **OG** (obtained from 1 % **OG** in ethanol), **CaG**, **CaCuG** (obtained from 1 % ethanolic solutions of metallogels; for **CaG**, **G2**:Ca^{2+} = 1:1; for **CaCuG**, **G2**:Cu^{2+}:Ca^{2+} = 1:2:1), and **CaCuG** xerogel treated with CN^- (5 equiv, 0.1 mol L^{-1} aqueous NaCN solution as CN^- source).

Moreover, the XRD patterns (Figure 6) of **OG**, **CaG**, **CaCuG**, and **CaCuG** treated with CN^- showed peaks at $2\theta = 23.76$–23.90° corresponding to *d* spacings of 3.71–3.74 Å, which suggested that π–π stacking existed between the naphthyl groups of these gels. In addition, compared with **OG**, **CaG** showed a new strong peak at $2\theta = 20.98^\circ$, which was attributed the coordination of Ca^{2+} with gelator **G2**. However, this peak disappeared when **CaG** changed to **CaCuG**. Interestingly, after adding an aqueous solution of CN^- to **CaCuG**, the strong peak at $2\theta = 20.98^\circ$ appeared again, which confirmed that the CN^- competitively bound to Cu^{2+}, while Ca^{2+} coordinated with the gelator **G2** again.

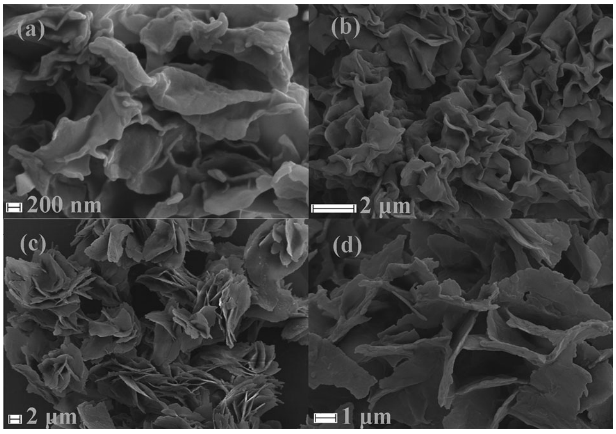


Figure 7. SEM images of xerogels of a) **OG** (obtained from 1 % ethanolic solution of organogel), b) **CaG** (obtained from 1 % ethanolic solution of metallogel **CaG**, **G2**:Ca^{2+} = 1:1), c) **CaCuG** (obtained from 1 % ethanolic solution of metallogel **CaCuG**, **G2**:Cu^{2+}:Ca^{2+} = 1:2:1), and d) **CaCuG** xerogel treated with CN^- in situ.

To get further insight into the morphological features of organogel **OG** and metallogels **CaG** and **CaCuG**, SEM studies were carried out on their xerogels (Figure 7). The SEM image of **OG** showed an overlapping rugate layer structure. The thickness of each layer was approximately 10–20 nm. The metallogels **CaG** and **CaCuG** also showed overlapping rugate layer structures. This indicated that although the gelator **G2** coordinated with Ca^{2+} or Cu^{2+}, no significant changes took place in the self-assembly states.

Conclusion

We have demonstrated a new strategy for the design of stimuli-responsive supramolecular gels termed double-metal-ion competitive coordination control. The stimulus–response selectivity and signal-reporting property of a supramolecular gel are controlled by competitive coordination of the two different metal ions. This is an effective way to achieve selective response of a supramolecular gel to a certain chemical stimulus. There are two key features of this approach. Firstly, the rational introduction of two different metal ions with different coordination abilities into the same metallogel is crucial. In present work, by competitive coordination of Ca^{2+} and Cu^{2+} with gelator **G2**, the strong AIE of metallogel **CaG** was controlled in on–off mode. In addition, through competitive coordination of CN^- with the Cu^{2+} in the metallogel **CaCuG**, Ca^{2+} coordinated with gelator again and the AIE of the metallogel recovered. Secondly, the introduction of multiple self-assembly driving forces provided the gelator with stronger gelation abilities, which ensured that the gelator self-assembled to organogel and double-metal-based supramolecular gels. This concept of double-metal-ion competitive coordination control may open doors to novel metallogel-based smart materials.

Experimental Section

Materials and instruments

All anions were used as the sodium salts, and all cations as the perchlorate salts, which were purchased from Alfa Aesar and used as received. Fresh double-distilled water was used throughout the experiments. NMR spectra were recorded on Varian Mercury 400 and Varian Inova 600 instruments. Mass spectra were recorded on a Bruker Esquire 6000 MS instrument. XRD analysis was performed in transmission mode on a Rigaku RINT2000 diffractometer equipped with graphite-monochromated $Cu_{K\alpha}$ radiation ($\lambda =$ 1.54073 Å). The morphologies and sizes of the xerogels were characterized by field-emission SEM (JSM-6701F) at an accelerating voltage of 8 kV. The IR spectra were recorded on a Digilab FTS-3000 FTIR spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. Elemental analyses were performed with a Thermo Scientific Flash 2000 organic elemental analyzer.

Synthesis of gelator G2

3,4,5-Tris(hexadecyloxy)benzohydrazide was synthesized according to literatures methods.[12] **G2** was synthesized as follows: 1-naphthaldehyde (1 mmol), 3,4,5-tris(hexadecyloxy)benzohydrazide (1 mmol), and acetic acid (0.1 mL, as catalyst) were added to ethanol (20 mL). Then the reaction mixture was stirred under reflux conditions for 24 h, after which removing the solvent yielded a precipitate, which was recrystallized from $CHCl_3/C_2H_5OH$ to give solid **G2**. Yield: 75 %, m.p. 89–91 °C ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 9.77$ (s, 1 H, NH), 9.04 (s, 1 H, $N{=}CH$), 8.85 (d, $J = 6.4$ Hz, 1 H, ArH), 7.99 (s, 1 H, ArH), 7.87 (t, $J = 7.8$ Hz, 2 H, -ArH), 7.51–7.45 (m, 3 H, ArH), 7.11 (s, 2 H, ArH), 3.98 (t, $J = 6.4$ Hz, 6 H, OCH_2), 1.77 (t, $J = 6.9$ Hz, 6 H, OCH_2CH_2), 1.43–1.25 (m, 72 H, CH_2), 0.88 ppm (t, $J = 6.2$ Hz, 9 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 166.94, 152.77, 142.25, 141.33, 133.77, 131.10, 130.70, 129.05, 128.81, 127.73, 127.36, 127.00, 126.18, 125.26, 124.60, 107.81, 105.91, 105.12, 73.55, 73.45, 69.38, 69.10, 68.92, 31.93, 30.34, 29.72, 29.38, 26.08, 22.69, 14.13 ppm; IR (KBr): $\tilde{\nu} = 3450$ (NH), 1717 ($C{=}O$), 1649 cm^{-1} ($C{=}N$); ESI-MS calcd for $C_{66}H_{111}N_2O_4$: 995.8544 [**G2**+H]$^+$; found: 995.8096.

Acknowledgements

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Keywords: aggregation · fluorescence · gels · self-assembly · smart materials

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