By introducing multi-self-assembly driving forces, coordination binding sites and signal groups into the same molecule, a well designed functional gelator $G_1$ was synthesized. The gelator $G_1$ could form a stable $\text{Pb}^{2+}$-coordinated supramolecular metallogel ($\text{PbG}$) accompanied with aggregation-induced fluorescence emission (AIE). $\text{PbG}$ shows the reversible selective fluorescent response for $I^-$ under a gel-gel state. The detection limit of $\text{PbG}$ for $I^-$ is $1.0 \times 10^{-7}$ M. The AIE fluorescence of $\text{PbG}$ could be reversibly switched ‘on–off–on’ under gel–gel states via alternatively adding $I^-$ and $\text{Pb}^{2+}$ water solution into $\text{PbG}$. Other anions could not induce similar stimuli-response for $\text{PbG}$. Interestingly, when a writing brush dipped in $I^-$ water solution was used to write on the xerogel film of $\text{PbG}$, the film did not show any color changes. However under UV at 365 nm, a clear dark writing image appeared. This dark writing could be erased by brushing $\text{Pb}^{2+}$ on the film. More interestingly, when the $\text{PbG}$ film containing the invisible $I^-$ writing was exposed to iodine vapor, a clear brown writing appeared on the film. However, when this film was placed under the room atmosphere for one minute, the brown writing gradually disappeared. Therefore, the $\text{PbG}$ film could act as not only a convenient reversible $I^-$ detection test kit, but also an erasable dual-channel security display material.

However, although a significant amount of effort has been devoted to the development of metal ions coordinated supramolecular gels,\textsuperscript{48} it is still a big challenge to design and synthesize supramolecular gels that can optically sense a given chemical stimulus with a specific selectivity. In view of this, as a part of our research interest in supramolecular chemistry,\textsuperscript{44–45} we attempted to control the stimuli-response properties of supramolecular gels through the competitive coordination between supramolecular gelators, metal ions and guest compounds.

Herein, we designed and synthesized a gelator $G_1$ based on multi-assembly driving forces,\textsuperscript{46–49} fluorescent signal groups\textsuperscript{59} and coordination binding sites.\textsuperscript{54,52} The gelator $G_1$ could form a stable supramolecular organogel in various solvents at very low critical gelation concentrations (CGCs). After the addition of $\text{Pb}^{2+}$ to the $G_1$ ethanol organogel (OG), OG could form a stable $\text{Pb}^{2+}$-coordinated supramolecular metallogel $\text{PbG}$ accompanied by the pale blue aggregation-induced fluorescence emission (AIE).\textsuperscript{53–56} The AIE of $\text{PbG}$ could be reversibly controlled by iodide anions with a specific selectivity in gel-gel states. $\text{PbG}$ could act as not only a convenient reversible $I^-$ detection test kit, but also an erasable dual-channel security display material. It is worth mentioning that the security display materials have become of increasing importance.\textsuperscript{57,58}
2. Experimental

As shown in Scheme 1, the compound 3,4,5-tris(hexadecyloxy)benzohydrazide was synthesized according to the literature-reported methods.\(^{59}\) G1 was synthesized as follows: p-nitrobenzaldehyde (1 mmol), 3,4,5-tris(hexadecyloxy)benzohydrazide (1 mmol) and acetic acid (0.1 mL, as a catalyst) were added to ethanol (20 mL). Then, the reaction mixture was stirred under refluxed for 24 hours. After the solvent was removed, the precipitated G1 was yielded and recrystallized with CHCl\(_3\)-EtOH to get the solid G1. Yield: 60%, m.p.: 106–110 °C; ¹H NMR (400 MHz, CDCl\(_3\), Fig. S1†) \(\delta\) 9.30 (s, -NH, 1H), 8.26 (d, \(J = 8.7\) Hz, -ArH, -CH\(_3\), 3H), 7.90 (s, -ArH, 2H), 7.07 (s, ArH, 2H), 4.01 (d, \(J = 3.8\) Hz, -CH\(_2\)_6, 6H), 1.95–1.71 (m, -CH\(_2\)_6, 1H), 1.36 (m, -CH\(_2\)_7, 18H), 0.88 (t, \(J = 6.5\) Hz, -CH\(_3\), 9H). ¹³C NMR (150 MHz, CDCl\(_3\), Fig. S2†) \(\delta\) 152.76, 123.99, 107.96, 77.19, 76.98, 74.77, 73.59, 73.46, 69.44, 69.16, 60.93, 31.91, 30.30, 29.70, 29.64, 29.62, 29.55, 29.40, 29.38, 29.35, 29.30, 29.26, 22.67, 14.38, 14.08; IR (KBr, cm\(^{-1}\)) v: 3455 (NH), 1715 (C=O), 1650 (CH=CH), 1595, 1545 (ArH, 2H), 1380, 1370, 1365, 1350, 1330, 1320, 1310, 1300, 1290, 1280, 1270, 1260, 1250, 1240, 1230, 1220, 1190, 1180, 1170, 1160, 1150, 1140, 1130, 1120, 1110, 1100, 1090, 1080, 1070, 1060, 1050, 1040, 1030, 1020, 1010, 1000, 990, 980, 970, 960, 950, 940, 930, 920, 910, 900, 890, 880, 870, 860, 850, 840, 830, 820, 810, 800, 790, 780, 770, 760, 750, 740, 730, 720, 710, 700, 690, 680, 670, 660, 650, 640, 630, 620, 610, 600, 590, 580, 570, 560, 550, 540, 530, 520, 510, 500, 490, 480, 470, 460, 450, 440, 430, 420, 410, 400, 390, 380, 370, 360, 350, 340, 330, 320, 310, 300, 290, 280, 270, 260, 250, 240, 230, 220, 210, 200, 190, 180, 170, 160, 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0. MS: ESI [M + H]+ m/z (Fig. S3†) found: 990.8284, calcd: 990.8233.

3. Results and discussion

First, we carefully investigated the gelation properties of G1. As shown in Table S1,† the gelator G1 could form a stable supramolecular organogel in various solvents at very low critical gelation concentrations. Among these solvents, the gelator G1 showed the lowest CGC (0.40%, wt/v%, 10 mg mL\(^{-1}\)) and the highest gel–sol transition temperature (78 °C) in ethanol. The G1-based supramolecular organogel OG in ethanol is more stable than the gel in other solutions. Therefore, we investigated the influence of metal ions on the G1 organogel in ethanol.

Interestingly, after the addition of Pb\(^{2+}\) to the G1 ethanol organogel (OG), OG could form a stable Pb\(^{2+}\)-coordinated supramolecular metallogel PbG. As shown in Fig. 1, PbG has no fluorescence emission in hot ethanol solution (\(T > T_{gel}\)). However, when the temperature of this hot ethanol solution dropped below the \(T_{gel}\) of PbG, the emission intensity at 340 nm showed an evident increase and reached a steady state, which indicated that the fluorescence emission of metallogel PbG was aggregation-induced emission (AIE).

The anion response capability of the supramolecular metallogel PbG was primarily investigated by adding various anions in water solutions (AcO\(^-\), HSO\(_4\)\(^-\), H\(_2\)PO\(_4\)\(^-\), F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\), N\(_3\)\(^-\), SCN\(^-\), ClO\(_3\)\(^-\), CN\(^-\), CO\(_3\)\(^{2-}\), S\(^2-\) and SO\(_4\)\(^{2-}\), 1 mol L\(^{-1}\)) to PbG. As shown in Fig. 2, when adding water solutions of various anions to the small amount of metallogel PbG on a spot plate, only I\(^-\) could quench the fluorescence of PbG, while other anions could not. These results indicated that PbG could selectively sense I\(^-\), which was attributed to I\(^-\) competitively binding with Pb\(^{2+}\).

Moreover, the I\(^-\) response properties of PbG were investigated by fluorescence titrations. As shown in Fig. 3, with the addition of I\(^-\) into PbG, the spectra showed evident red shifts, which was attributed to the coordination of I\(^-\) with Pb\(^{2+}\). In PbG, Pb\(^{2+}\) coordinated with the gelator through the acylhydrazone moiety. When I\(^-\) was added into PbG, Pb\(^{2+}\) coordinated with I\(^-\) and the acylhydrazone moiety was released, which induced the fluorescence spectra of the gel to undergo the red shifts. In addition, the emission intensity at 474 nm decreased with increasing the concentration of I\(^-\). The detection limit of the fluorescence spectra changes, which was calculated on the basis of 3\(\Delta I/\Delta S\)\(^8\), was 2.037 \(\times\) 10\(^{-6}\) M (Fig. S4†) for I\(^-\) anion.

Interestingly, after the addition of Pb\(^{2+}\) into the I\(^-\) containing PbG, the fluorescence of PbG recovered, which was attributed to the Pb\(^{2+}\) coordination with G1 again. These properties...
make PbG act as an I⁻ and Pb²⁺ controlled “on–off–on” fluorescent switch. By alternate addition of I⁻ and Pb²⁺, the switching could be performed reversibly at least for three cycles with a small fluorescent efficiency loss (Fig. 4).

In order to facilitate the use of the metallogel PbG, the I⁻ detection film based on PbG was prepared by pouring the heated ethanol solution of PbG onto a clean glass surface and then drying in air. The PbG film was white under natural light and showed a blue fluorescence emission under UV at 365 nm. When a writing brush dipped in I⁻ water solution was used to write on the film, the film did not show any color changes. However, under UV at 365 nm, a clear dark writing image appeared (Fig. 5). This dark writing image could be erased by brushing Pb²⁺ on the film. More interestingly, when the PbG film containing the invisible I⁻ writing was exposed to iodine vapor, a clear brown writing appeared on the film. However, when the film was put under the room atmosphere for one minute, the brown writing disappeared gradually. Therefore, the PbG film could act as not only a convenient reversible I⁻ detection test kit, but also an erasable dual-channel security display material.

In order to investigate the self-assembly and stimuli-response mechanism of PbG, a series of experiments was carried out. First, in the concentration dependent ¹H NMR of G1 (Fig. 6), the –NH– (H₆) and –N=CH– (H₇) resonance signals showed significant downfield shifts as the concentration of G1 rose. These results revealed that in the gelation process, the –NH– (H₆) and –N=CH– (H₇) groups formed hydrogen bonds with the –C=O groups on the adjacent gelators. On the other hand, with a gradual increase in concentration, the ¹H NMR signal of phenyl protons (H₈, H₉, H₁, and H₂) showed an evident upfield shift, indicating that the π–π stacking interactions between the phenyl groups involved in the gelation process. Therefore, the gelator G1 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 mechanism of supramolecular metallogel was also investigated by ¹H NMR titrations, as shown in Fig. 7. With the addition of Pb²⁺, the –NH– (H₆) group on the gelator showed significant downfield shifts, which indicated that the gelator coordinated with Pb²⁺ via the acylhydrazone moiety. In addition, in the IR spectra (Fig. S5†) the stretching vibrations of –C=O and –C=NN of G1 showed obviously shifts from 3455 and 1650 cm⁻¹ to 3583 and 1588 cm⁻¹, respectively. These phenomena indicated that in PbG, Pb²⁺ coordinated with the nitrogen and oxygen atoms on the acylhydrazone group.

This presumed self-assembly and coordination mechanism was also supported by the Tgel of OG and PbG. For instance, as shown in Fig. 8, under the same condition, the Tgel of OG was significantly higher than that of PbG. The large differences of

Fig. 3 Fluorescence spectra of PbG (1%, in ethanol, G1–Pb²⁺ = 1 : 1) with increasing concentration of I⁻ (using 1 mol L⁻¹ TBA in water solution as the I⁻ sources), λex = 340 nm.

Fig. 4 Fluorescent “on–off–on” cycles of PbG, controlled by the alternative addition of I⁻ and Pb²⁺, λex = 340 nm.

Fig. 5 Writing, erasing and coloration of a natural light invisible image on a PbG supramolecular gel film (obtained from 1% ethanol metallogel, PbG, G1–Pb²⁺ = 1 : 1. Writing: write in I⁻ water solution; erasing: brush Pb²⁺ water solution; coloration: expose the PbG film into the iodine vapor ca. 5 s). The photographs were taken at room temperature under room light and exposed to a 365 nm UV light.

Fig. 6 Partial ¹H NMR spectra of G1 in CDCl₃ with different concentrations.
T\textsubscript{gel} between OG and PbG were ascribed to the breakage of intermolecular hydrogen bonds between –N=C–H on one gelator and –C=O on the other one in OG, which was caused by the coordination of Pb\textsuperscript{2+} with the gelator G1. Moreover, the Pb\textsuperscript{2+} coordination process reduced the distance of π–π stacking between the phenyls, which enhanced the aggregation induced emission of PbG.

This proposed mechanism was also supported by the XRD patterns (Fig. S6†). The XRD patterns of OG, PbG and the PbG treated with I\textsuperscript{−} showed the peaks at 2\(\theta\) = 18.62–27.70°, corresponding to the d spacing 3.5 Å, 3.45 Å, and 3.8 Å, respectively. As shown in Scheme 2 and Fig. S6† in OG, the peaks at 21.28° and the d spacing 3.5 Å were attributed to the π–π stacking, which existed in the phenyl groups of OG. While, in PbG, the d spacing changed to 3.45 Å, which was attributed to the Pb\textsuperscript{2+} coordination process reducing the distance of π–π stacking between the phenyls. Meanwhile, the d spacing 3.8 Å was attributed to the interlamellar spacing between the supramolecular chains. In addition, after the formation of PbG, the peaks of OG (at 2\(\theta\) = 21.28, 23.22, 23.90, 25.30°) disappeared and these peaks reappeared after PbG was treated with I\textsuperscript{−}. These phenomena confirmed that Pb\textsuperscript{2+} coordinated with OG and induced a change in the XRD pattern of OG, while the addition of I\textsuperscript{−} into PbG induced the competitive coordination of I\textsuperscript{−} with Pb\textsuperscript{2+} and led to the recovery of XRD peaks. According to \(^1\)H NMR, IR and XRD, the ion response mechanism of OG and PbG could be presumed as in Scheme 2.

To get further insight into the morphological features of the supramolecular organogel OG, metallogel PbG and PbG treated with I\textsuperscript{−}, SEM studies were carried out with their xerogels, respectively. As shown in Fig. S7† the SEM images of OG showed an overlapped rugate layer structure. The metallogel PbG also showed overlapped rugate layer structures and the aggregation structure of layer was compacted. However, after I\textsuperscript{−} was added into the PbG xerogel, the micro states experienced obvious changes. There were a large number of micro cavities formed in the xerogel of PbG. These micro cavities provided the PbG xerogel with the properties for the adsorption of iodine vapor. Therefore, the mechanism of iodine vapor-caused color change could be attributed to the iodine vapor adsorption into these micro cavities.

4. Conclusions

In summary, a novel supramolecular gelator G1 has been designed and synthesized. The gelator G1 could form a stable supramolecular metallogel PbG. Through the competitive coordination of Pb\textsuperscript{2+} and I\textsuperscript{−} with the gelator G1, the aggregation-induced emission of the supramolecular metallogel PbG was controlled as “on−off−on”. More interestingly, after Pb\textsuperscript{2+} competitive coordinated with I\textsuperscript{−}, there were a large number of micro cavities formed in the PbG xerogel, which enabled the PbG xerogel to absorb the iodine vapor and show a brown color. PbG could act as not only a convenient high selective and sensitive I\textsuperscript{−} detection test kit, but also an erasable dual-channel secret documentation medium.

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Notes and references


