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A Novel Supramolecular Metallogel-Based High-Resolution Anions Sensor Array

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A novel anions sensor array based on supramolecular metallogels has been developed. It could accurately identify CN^-, SCN^-, S^{2-} and I^- in water. Interestingly, this sensor array based on a novel design approach to anions-response gels

10 termed "competitive coordination control AIE mode", which needs only one synthesized gelator G1.

Due to the fundamental role of anions in chemical, biological and environmental processes,[1] the developing of anion sensors has attracted more and more interests. One of the most intriguing

15 problems in the sensor field is multianalyte sensing.[2] The increased popularity of sensor array is largely due to their capability to recognize a number of analytes with high classification accuracy.[3] In general, sensor array may be based on multiple target selective sensors, each one of which is with high

20 affinity for one specific target. Therefore, the traditional sensor array often employs lots of selective sensors which need large amounts of work to design and synthesis.[2b] In order to circumvent the difficulties associated with preparation of various selective sensors, could we develop a sensor array which is based on only

25 single synthesized chemosensor? It's a really interesting task.

Recently, due to the dynamic and reversible nature of supramolecular noncovalent interactions, the stimuli-responsive supramolecular gels have attracted more and more attentions.[4] Because their can sense, process, and actuate a response to an

30 external stimulus without assistance. Among of them, metal-ion-coordinated supramolecular gels (metallogels) have become a focus of the research because of the tuneable coordination binding strength, as well as the fascinating redox, optical, electronic, or magnetic properties of the metal ions would benefit

35 the application of these smart materials.[5] Therefore, the metallogels have the very nice prospects to act as chemosensors. However, although a great deal of effort have been devoted to the development of metallogels, it is still a big challenge to design and synthesize novel smart supramolecular gels that can optically

40 sense a given chemical stimulus with specific selectivity.

In our previous work, we developed a novel anion responsive supramolecular bi-metallogel. By rationally introducing two different metal ions into the supramolecular gel, the anions response properties of the gel could selectively controlled by the

45 competition between two different metal ions and target anions.[6] However, these bi-metallogels need to be rationally introduced two different metal ions into the supramolecular gel, which make it more difficult for the design and preparation of the bi-

metallogel. Could we control the metallogels' anions response

50 properties by rationally introducing only one kind of metal ion in each metallogel?

Fig.1 The gelator **G1** and the mechanism of "competitive coordination control AIE mode"

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In order to achieve the selective multi-target fluorescent response for certain anions, we provide a novel design approach to supramolecular gel-based chemosensor termed "competitive coordination control AIE mode". In this approach, as shown in

60 Figure 1, the AIE properties and anions' binding abilities of the supramolecular gel could be adjusted by different metal ions. Because different metal ions possess different coordination abilities, when different metal ions coordinated with the gelator of the **OG**, the AIE of the **OG** can carry out different changes.

65 Moreover, some anions could competitively coordinate with the metal ions in such metal ions coordinated-gels and restored the AIE of the **OG**. By this means, the metallogels could fluorescently response corresponding anions.

In view of these, we designed and synthesized a gelator **G1**

70 (Figure 1) based on multi self-assembly driving forces, fluorescent signal groups and coordination binding sites (Scheme S1). **G1** could form a stable supramolecular organogel **OG** companied with strong brilliant blue aggregation-induced fluorescence emission (AIE).[7] Interestingly, the AIE of the **OG**

75 could be tuned by different metal ions and form different metallogels (**MGs**). These **MGs** could selectively sense different anions by the competitive coordination of the metal ions and target anions. Based on these supramolecular metallogels, we successfully developed a five-member sensor array. This

80 metallogel-based sensor array could accurately identify CN^-, SCN^-, S^{2-} and I^- in water with high selectivity and sensitivity. This sensor array has the merit of easy preparation. Because it needs only one synthesized organogelator. To the best of our knowledge, there is no report on the metallogel-based anions

85 sensor array. Moreover, these metallogels could act as erasable

security display materials.

The synthesis procedure of the gelator **G1** is shown in Scheme S1. **G1** showed excellent gelation abilities in DMF (Figure S1 and Table S1) and could form stable **G1** organogel (**OG**) in DMF.

5 More interestingly, as shown in Figure 2, **OG** has no fluorescence in hot DMF solution (T > T_{gel}). However, with the temperature of hot DMF solution dropping below the T_{gel} of **OG**, the emission intensity at 500 nm showed a sudden increase and reached a steady state, which indicated that the fluorescence of **OG** was the

10 aggregation-induced fluorescence emission (AIE).
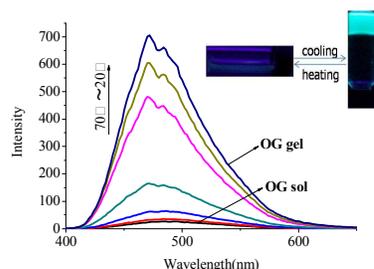
Fig.2 Temperature-dependent fluorescent spectra of the OG (in DMF, 0.8%) during gelation process (λex = 380 nm).
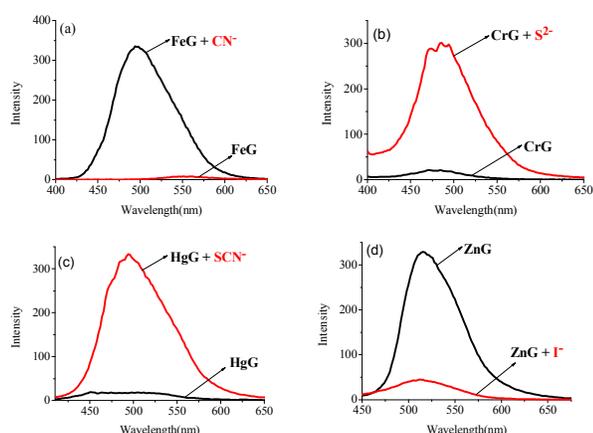
15 **Fig.3** Fluorescence spectra of **MGs** (0.8%, in DMF) in the presence of various anions. (a) **FeG** and **FeG** treated with CN^-; (b) **CrG** and **CrG** treated with S^{2-}; (c) **HgG** and **HgG** treated with SCN^-; (d) **ZnG** and **ZnG** treated with I^-.

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Firstly, we carefully investigated the influence of metal ions on the **OG** in DMF. The addition and diffusion 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 perchloric salts as the sources) to the **OG**

25 generated the corresponding metallogels, respectively (Figure S2). Moreover, the dissolution of the gelator **G1** and such cations in heated DMF could also form the same metallogels. Interestingly, upon excitation at 365 nm with a hand-held UV lamp, the organogel **OG** emitted very strong blue AIE. However,

30 upon the addition and diffusion of 0.5 equiv of metal ions such as Cu^{2+}, Hg^{2+}, Fe^{3+} or Cr^{3+} to the **OG**, respectively, the AIE of **OG** have been quenched and formed corresponding no fluorescence metallogels **MGs** (such as **CuG**, **HgG**, **FeG** or **CrG**, respectively) (Figure S2). In the corresponding fluorescence

35 spectra (Figure S3), the fluorescence intensity of **OG** at 470 nm is

ca. 10 times higher than that of these **MGs**. On the contrary, the Zn^{2+}-based metallogel **ZnG** emitted strong yellow fluorescence (Figure S2). In the corresponding fluorescence spectra (Figure S3), the fluorescence emission of **ZnG** showed an obvious red

40 shift (ca. 40 nm).
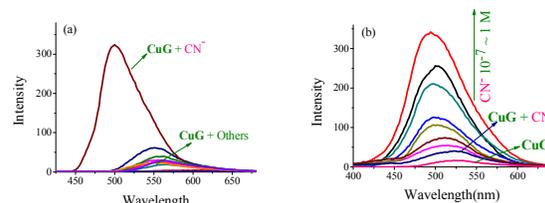
Fig.4 (a) Fluorescence spectra of **CuG** (0.8%, in DMF) in the presence of various anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, N_3^-, SCN^-, ClO_4^-, S^{2-} and CN^-) at room temperature. (b) Fluorescence spectra of **CuG** (0.8%, in DMF)

45 with increasing concentration of CN^- (using 0.1 mol L^{-1} NaCN water solution as the CN^- sources), λ$_{ex}$ = 380 nm.
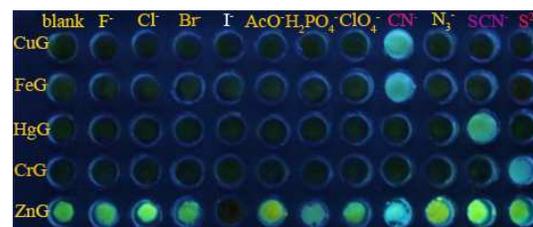
Fig5 Fluorescence responses of the metallogels-based sensor array to the presence of 1 equiv. of various anions (using 0.1 mol L^{-1} anions sodium or

50 potassium salts water solution as anion source).

Secondly, we carefully investigated the anions response capability of the metallogels by adding various anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, N_3^-, SCN^-, S^{2-}, ClO_4^- and CN^-) to the **MG**s

55 respectively. As we expected, the metallogels showed excellent fluorescence changes according to the stimuli of corresponding anions. As shown in Figure 3a and Figure 4a, the metallogels **FeG** and **CuG** could selectively fluorescent "turn-on" sense CN^-. In addition, the metallogels **HgG** (Figure 3c) and **CrG** (Figure 3b)

60 could selectively fluorescent "turn-on" sense SCN^- and S^{2-}, respectively. Moreover, the **ZnG** (Figure 3d) could fluorescent "turn-off" sense I^-. As a soft base, the iodide ions have the strong affinity for Zn^{2+}. When adding excess amount of iodide ions into **ZnG**, the iodide ions competitively bound to the Zn^{2+} and the

65 **G1**-Zn^{2+} complex disassembled. Meanwhile, the excess amounts of iodide ions induce a fluorescence decrease maybe due to heavy atom effect. According to these interesting results, as shown in Figure 5, we successfully developed a metallogel-based five-member sensor array, which could accurately identify CN^-, SCN^-,

70 S^{2-} and I^- in water with high selectivity and sensitivity. The sensor array shows high selectivity for the target anions. As shown in Figure 4a, the CN^- sensing process of **CuG** could not be interfered by other anions. In order to investigate the sensors' selectivity under multi-analytes conditions, we added the water

75 solution of mixed anions (the mixture of F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, N_3^-, SCN^-, S^{2-}, ClO_4^- and CN^-) in to the **MG**s (**FeG**, **CuG**, **HgG**, **CrG**, and **ZnG**) respectively, these metallogels could show similar fluorescent response (Figure S4) as their treated with certain single target anion. Therefore, the metallogels

80 **FeG**, **CuG**, **HgG**, **CrG**, and **ZnG** could selectively sensing CN^-, SCN^-, S^{2-} and I^- in water under multi-analytes conditions.

Moreover, as shown in Figure 4b and Figure S5a-5d, the sensor array also shows high sensitivities for the target anions. The detection limits of the fluorescence spectra changes calculated on the basis of cL = ks_B/S (where s_B is the standard deviation of the blank measures, S is the sensitivity of the method,[8] k = 3) were 1.0×10^{-7} M for CN^{-} (by **CuG**), 1.0×10^{-5} for CN^{-} (by **FeG**), 1.0×10^{-6} for SCN[-] (by **HgG**), 1.0×10^{-6} for S[2-] (by **CrG**) and 1.0×10^{-6} M for I[-] (by **ZnG**), respectively (Figure 4b and Figure S5a-5b).
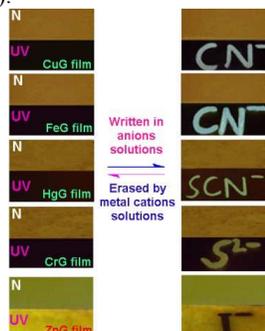
Fig.6 Writing and erasing of a nature light invisible image on **MGs** supramolecular gel films. Writing: written in corresponding anions' water solution; erasing: brushed by corresponding metal ions' water solution. The photographs were taken at room temperature under room light and exposure to a 365-nm ultraviolet light.

In order to facilitate the use of these metallogels, the anions response films based on these metallogels were prepared by pouring the heated ethanol solution of these **MGs** onto a clean glass surface and drying in the air respectively. The metallogels films of **CuG**, **FeG**, **HgG** or **CrG** have no fluorescence emission. When writing on the films with writing brush dipped in anions water solution (CN^{-} for **CuG** and **FeG**, SCN[-] for **HgG**, S[2-] for **CrG**, respectively), brilliant fluorescent writing images appeared (Figure 6). These fluorescent images could be erased by brushing corresponding metal ions such as Cu^{2+}, Fe^{3+}, Hg^{2+} and Cr^{3+} on these films again. Meanwhile, the **ZnG** film is gray under nature light and show strong yellow 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 a clear dark writing image appeared under the UV 365 nm (Figure 6). This dark writing image could be erased by brushing Zn^{2+} on the film again. Figure 7 shows the repeated switching behaviour with altering adding amounts of CN^{-} and Cu^{2+}, which evidently proved the excellent reusability and stability of **CuG** toward CN^{-} within at least three successive cycles. Therefore, these **MGs** films could act as not only convenient reversible anions (CN^{-}, SCN[-], S[2-], I[-]) detection test kits, but also erasable security display materials. It is worth noting that security display materials are composed of invisible substances providing 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]

Moreover, we carried out a series of time-dependency fluorescence tests for the metallogels to target anions (Figure S6).

These experiments results show direct demonstration for the response time of metallogels to target anions. The metallogels show very quick response for target anions. For example, the metallogel ZnG could fluorescently response I[-] in 0.1 min and **CuG** could fluorescently response CN^{-} in 0.5 min. Therefore, the sensor array could quickly detect target anions.
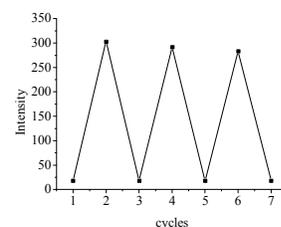
Fig.7 Fluorescent "on-off-on" cycles of **CuG**, controlled by the alternative addition of CN^{-} and Cu^{2+}, λ_{ex} = 380 nm.

Because these metallogels showed such nice anions selective response properties, a series of experiments were carried out to investigate the formation of the organogel **OG**, metallogels **MGs** as well as the anions response mechanism of **MGs**. Firstly, in the concentration dependent ^{1}H NMR (Figure 8a-c) of **G1**, the -NH (H_a, 9.98 ppm) and –N=CH (H_b, 8.46 ppm) resonance signals showed obvious downfield shifts (shifted to 10.75 ppm and 8.57 ppm respectively) as the concentration of **G1** rose. Moreover, in the FT-IR (Figure S7) the C=O vibration absorption of powder **G1** shifted to low wavenumbers (from 1657 to 1651 cm^{-1}) 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 8a-c, with the gradual increase in concentration, the ^{1}H NMR signal of quinoline ring protons (H_c, H_d, H_e, H_f, H_g and H_h) showed obvious upfield shifts (the average shift is ca. 0.11 ppm), indicating that the π–π stacking interactions between the quinoline ring groups were involved in the gelation process.[10] The π–π stacking interactions of **G1** induced the strong AIE of **OG**.[7] Thus, as illustrated in Scheme S2, the gelator **G1** self-assembled to organogel **OG** by the hydrogen bonds, π–π stacking as well as the vdW existing in the long alkyl chains.
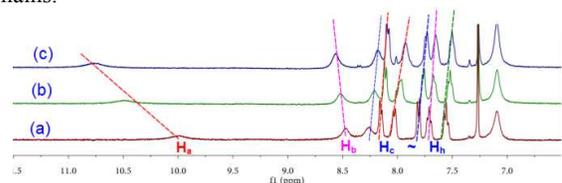
Fig.8 Partial ^{1}H NMR spectra of **G1** in CDCl₃ with different concentrations: (a) 10 mg/mL; (b) 20 mg/mL; (c) 30 mg/mL .

Furthermore, the results of powder-XRD studies also supported the presumed mechanism. The XRD patterns (Figure S8) of the **OG**, **CuG** and the **CuG** treated with CN^{-} showed the peaks at 2θ = 26.53-26.64° corresponding to the d-spacing 3.35-3.36 Å, which suggested that π–π stacking existed in the quinoline groups of these gels. In addition, when adding the Cu^{2+} to the **OG** and forming the **CuG**, the **CuG** showed a new strong peak at 2θ = 22.12° corresponding to the d-spacing 3.84 Å, which was attributed to the coordination of Cu^{2+} with gelator **G1** (form

the **G1**-Cu^{2+} complex). After adding CN^- water solution to the **CuG**, these strong peak disappeared, which perfectly confirmed that the CN^- competitively bound to the Cu^{2+} and the **G1**-Cu^{2+} complex been disassembled.

SEM images were performed to obtain further insight into the self-assembly of **OG** and **CuG**. As shown in Figure S9, the SEM images of **OG** showed an overlapped rugate layer structure. The metallogel **CuG** also showed overlapped rugate layer structures. These phenomena indicated that although the gelator **G1** coordinated with Cu^{2+}, significant changes didn't took place on the self-assembly states. Meanwhile, after treating the **CuG** with CN^- water solution, the micro-structure of **CuG** also kept the overlapped rugate layer structure. These phenomena indicated that the multi self-assembly motifs we rationally introduced to the gelators **G1** provided very strong self-assembly forces for these supramolecular gels.

Conclusions

In summary, a novel supramolecular metallogel-based anions sensor array has been developed. It is worth mentioning that this five-member sensor array only needs a single synthesized organogelator **G1**. The gelator **G1** shows very strong AIE under organogel states. The AIE and anions response properties of the **G1** could be tuned by different metal ions. The sensor array realized the anions selective response properties by the competitive coordination of gelator, different metal ions and anions. This sensor array could sense CN^-, SCN^-, S^{2-} and I^- with high selectivity and sensitivity. Moreover, the **G1**-based metallogels (**MGs)** films could act as not only convenient reversible anions (CN^-, SCN^-, S^{2-}, I^-) detection test kits, but also erasable security display materials. The concept of "competitive coordination control AIE mode" provides a facile way for novel metallogel-based stimuli-responsive fluorescent materials such as sensor array and other supramolecular functional materials

Notes and references

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Graphic Abstract

A Novel Supramolecular Metallogel-Based High-Resolution Anions Sensor Array

Qi Lin,*[a] Tao-Tao Lu,[a‡] Xin Zhu,[a‡] Bin Sun,[a] Qing-Ping Yang,[a] Tai-Bao Wei,[a] You-Ming Zhang[*a,b]

A novel anions sensor array based on supramolecular metallogels has been developed. The sensor array could accurately identify CN⁻, SCN⁻, S²⁻ and I⁻ in water. Interestingly, the metallogel-based sensor array needs only one synthesized gelator **G1.**