**Introduction**

Stimuli-responsive supramolecular gels (SRSGs) are an important class of smart materials. It is of practical importance to develop an SRSG which can both detect and remove toxic metal ions. We have designed and synthesized an aggregation induced emission (AIE)-active oligourethane (OU) gelator which self-assembles into a supramolecular gel (OUG), through hydrogen-bonding, π–π stacking and van der Waals interactions. By taking advantage of the weak and dynamic nature of these non-covalent bonds, OUG shows stimuli-response to multiple factors. Importantly, OUG has the capacity for real-time detection and high selectivity for Fe$^{3+}$, HSO$_4^-$ and F$^-$. The lowest detection limits are in the range of $5.89 \times 10^{-9}$ to $8.17 \times 10^{-8}$ M, indicating high sensitivity. More importantly, OUG is shown to adsorb and separate Fe$^{3+}$ from aqueous solution, with an absorbing rate of up 97.5%. A simple writing board was fabricated, which could be written repeatedly and reused. OUG acts as a reversible and recyclable “on–off–on” fluorescence sensor via competitive cation–π and cation–anion interactions. OUG has great potential as an environmentally sustainable probe for ions.

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and easily recognized fluorescent output, offer a more significant practical method.\textsuperscript{6,32}

Herein, we report an AIE-active supramolecular oligourethane gel (OUG) and demonstrate its usage as a specific Fe\textsuperscript{3+} sensor in an aqueous environment. The material is based on the following design criteria: (i) inserting benzophenone into an oligourethane (OU) backbone provides C=O units with prominent hydrogen-bonding sites for self-assembly, and formation of oxygen clusters, which could enhance fluorescent emission.\textsuperscript{33} (ii) Inserting linear 1,6-diisocyanatohexane offers hydrogen-bonding sites for self-assembly, and for the oligourethane skeleton,\textsuperscript{34–41} we introduced solvents with rich hydrogen bond acceptors/donors (C=O/N–H) among the oligourethane skeleton,\textsuperscript{42} relying on multiple hydrogen bonds.

\section*{Results and discussion}

\subsection*{Synthesis and characterization}

The OU was synthesized through a facile procedure as shown in Scheme S1 (ESI\textsuperscript{†}), by the reaction of 4,4\'-dihydroxybenzophenone, hexamethylene disiocyanate and DABCO in anhydrous tetrahydrofuran and end-capping with polyethylene glycol monomethyl ether to give a viscous solution. The product was purified by a counter precipitation method. \textsuperscript{1}HN MNa.rand\textsuperscript{13}C TIR h a r a c t e r i z a t i o n data are given in Fig. 1a and in the ESI, confirming the structure of OU. The M\textsubscript{n} value of 1814 g mol\textsuperscript{−1}, calculated from the \textsuperscript{1}H NMR data, established that OU should be classified as an oligomer.\textsuperscript{42} The FTIR spectra (Fig. S1, ESI\textsuperscript{†}) showed absorbance bands at 3323 cm\textsuperscript{−1} and 1706 cm\textsuperscript{−1}, assigned to stretching vibrations of N–H and C=O, indicating the formation of amide bonds. Absorbance bands at 2936 cm\textsuperscript{−1} and 2860 cm\textsuperscript{−1} correspond to \textnu(–CH\textsubscript{2}–) and at 1163 cm\textsuperscript{−1} correspond to \textnu(C=O–C) stretching vibrations. The UV-Vis absorption spectrum of OU in the solid-state (Fig. S2, ESI\textsuperscript{†}) showed a major peak at 277 nm from a π−π* transition of the aromatic rings.\textsuperscript{43}

\subsection*{Self-assembly gelation}

OU spontaneously self-assembles in certain solvents (notably dimethyl formamide and dimethylsulfoxide) transforming into a supramolecular gel (Table S1, ESI\textsuperscript{†}). The lowest critical gelation concentration (CGC) of OU is 4\% (w/v, 10 mg mL\textsuperscript{−1}) = 1\%), and the corresponding gel–sol transition temperature (T\textsubscript{gel}) is 85–87 °C. In order to gain an insight into the self-assembly mechanism, \textsuperscript{1}H NMR, FTIR, XRD and urea addition experiments were conducted. \textsuperscript{1}H NMR spectra were recorded for different concentrations of OU in DMSO-\textit{d}\textsubscript{6} (Fig. 1b). The H\textsubscript{a} and H\textsubscript{b} proton signals are shifted ca. 0.04 and 0.03 ppm upfield compared to pure OUG upon adding 25 mM Fe\textsuperscript{3+}. Meanwhile, the signals of protons H\textsubscript{e} (the NH groups) shifted slightly downfield ca. 0.01 ppm.\textsuperscript{44} These results confirmed the H-bonding interactions between amide groups and van der Waals interactions between alkyl chains. Comparing the FTIR data before and after gelation (Fig. S1, ESI\textsuperscript{†}), the N–H stretching absorbance bands of OUG are broader and move to significantly higher wavenumbers (3323 to 3361 cm\textsuperscript{−1}) in the solid state compared to the gel state: these data suggest hydrogen bonds play a critical role in the gelation process.\textsuperscript{45,46}

It is well known that adding urea, which has a high propensity to form hydrogen bonds, can disrupt existing hydrogen bonds in a supramolecular structure.\textsuperscript{47,48} Accordingly, adding urea (10 equiv.) into OUG and heating the gel, led to the formation of a sol. It was observed that after adding urea, the sol did not revert back to gel, even when the OUG-urea mixture was cooled at 15 °C for several days, indicating that the gelation is driven by hydrogen bonds among OU molecular chains (Fig. 2a). Besides, the X-ray diffraction (XRD) peaks of OUG

![Fig. 1](image1.png)

\textbf{Fig. 1} (a) \textsuperscript{1}H NMR spectrum of OU in DMSO-\textit{d}\textsubscript{6} (* indicates peaks from the solvent and water); H-atom labeling is shown on the structure of OU. (b) The partial \textsuperscript{1}H NMR spectra of OU in DMSO-\textit{d}\textsubscript{6} at different concentrations: (i) 0.925 mM, (ii) 3.7 mM, and (iii) 25.0 mM.

![Fig. 2](image2.png)

\textbf{Fig. 2} (a) Structure of OU and its self-assembly gelation process. (b) Schematic diagram for the ion sensing processes of OUG.
2θ = 20.54°, 23.22°, corresponding to d-spacings of 4.32 Å and 3.83 Å, respectively, also indicated the presence of π–π stacking interactions (Fig. S11b, ESI†), further promoting the self-assembly behavior. OUG showed weak fluorescence in the solid state, however, after transforming to the gel state, the emission intensity of OUG at 439 nm increased 6 times (Fig. S3, ESI†), indicating that OU is an AIE-active gelator.49

Stimuli-responsive behaviors
OUG exhibits a high selectivity to Fe³⁺ over other metal ions. By monitoring the change of fluorescence, we investigated the recognition characteristics of OUG towards metal ions. Using nitrate salts as the cation sources, an aqueous metal ion solution of Na⁺, Ca²⁺, Co²⁺, Cu²⁺, Mn²⁺, Ni²⁺, Cr³⁺, La³⁺, Fe³⁺, Sr²⁺, Ce³⁺, Ag⁺, Al³⁺, Mg²⁺, Cd²⁺, Pb²⁺ or Fe²⁺ (c = 0.2 M) was added to the OUG to generate the corresponding metal-gels.50-53

As shown in Fig. 3a and c, initially, the OUG had a strong blue fluorescence emission. When different metal ions were added, only Fe³⁺ quenched the fluorescence of OUG. Thus, the OUG could effectively and selectively detect Fe³⁺. To further evaluate the sensitivity of OUG for Fe³⁺, the fluorescence behavior of OUG was monitored by continuous titrations with Fe³⁺. As shown in Fig. S5a (ESI†), with the increasing addition of Fe³⁺ (0–1.1 equiv.), the emission intensity of the corresponding metal-gels (OUFeG) at 439 nm gradually decreased. The limit of detection (LOD) of OUG towards Fe³⁺ was calculated to be 5.89 × 10⁻⁹ M based on the 3σ/S method (Fig. S4 and S5a, ESI†), confirming the high selectivity of OUG as a sensor for Fe³⁺ compared with other reported sensor systems (Table S2, ESI†). The high selectivity of OUG to Fe³⁺ is attributed to two reasons: firstly, unpaired electrons in Fe³⁺ cause a paramagnetic effect, promoting energy dissipation of excited states through non-radiative pathways.55 Secondly, the high ionic strength of Fe³⁺ could easily induce the transfer of π-electrons from the urethane backbone to Fe³⁺ through cation–π interactions.56 both of these effects will cause the fluorescence quenching of OUG.

The response of OUFeG towards anions was further investigated, using tetrabutylammonium salts as the anion sources, adding aqueous solutions of anions including HSO₄⁻, ClO₄⁻, I⁻, CN⁻, PF₆⁻, F⁻, Cl⁻, Br⁻, NO₃⁻, AcO⁻ (c = 0.2 M) to OUFeG.57-60 As shown in Fig. 3b and c, when HSO₄⁻ and F⁻ were added the emission at 439 nm recovered immediately, whereas the other anions did not lead to a comparable fluorescence recovery of OUFeG. These phenomena confirmed the excellent selectivity of OUFeG towards HSO₄⁻ and F⁻. This selectivity is explained by the strong coordinating capacity of HSO₄⁻ and F⁻ with Fe³⁺, in contrast to (metal-free) OUG. These two anions could competitively bind to Fe³⁺ in OUFeG and induce the re-emission of OUG. Titration experiments evaluated the sensing efficiency of OUFeG to HSO₄⁻ and F⁻. Limit of detection (LOD) values were calculated according to the 3σ/S method to be 8.17 × 10⁻⁸ M for F⁻ and 1.16 × 10⁻⁸ M for HSO₄⁻ (Fig. S5b and Fig. S7–S9, ESI†). Notably the LOD values of OUFeG are lower than many other reported F⁻ and HSO₄⁻ fluorescence sensors (Table S2, ESI†). The gel OUG selectively senses Fe³⁺, and the metal-gel OUFeG selectively responds to F⁻ and HSO₄⁻. This property makes gel OUG and metal-gel OUFeG act as an efficient “on–off–on” fluorescence sensor controlled by Fe³⁺, HSO₄⁻ or F⁻ with excellent reversibility. A simple regeneration treatment verified the recyclability of OUG. An anion solution (F⁻ or HSO₄⁻, 2 × 10⁻⁴ mol L⁻¹, 10 mL) was added into metal-gel OUFeG, stirring the mixture for 5 min, centrifuging and recycling OUG for again detecting ions. As shown in Fig. S10 (ESI†), after five consecutive cycles, the intensity of the OUG signal is essentially unchanged, indicating the excellent recyclability and reversibility of the OUG for the detection of Fe³⁺ and HSO₄⁻ or F⁻.

Mechanism of cation–anion sensor
When adding aqueous solution of Fe³⁺ into OUG, Fe³⁺ can diffuse in the solution. Due to the high ionic strength of Fe³⁺, the π-electrons in the urethane groups of OUG are easily induced to form cation–π interactions quenching the fluorescence. The recognition mechanisms of OUG to Fe³⁺ were investigated via a combination of H NMR, FTIR, XRD and SEM analysis. In the H NMR titration experiments, with the increasing amount of Fe³⁺ added into OU, protons H2, H3 and H4 all displayed clear upfield shifts (Fig. 4a), indicating that the OUG combined with Fe³⁺ via cation–π interactions between the urethane groups and Fe³⁺.56,61 As Fig. 4b shows, by adding F⁻ or HSO₄⁻ (3.7 mM) into a sample of OU (with 2 equiv. Fe³⁺), all the protons recovered the chemical shifts as in the original OU: H2 (from 7.85 to 7.93 ppm and 7.09 to 7.19 ppm), H3 (from 3.94 to 4.03 ppm) and H4 (from 3.01 to 3.09 ppm and 2.87 to
2.95 ppm), which indicated the cation–anion interactions between Fe$^{3+}$ and F$^-$ or HSO$_4^-$ could release the π-electrons of urethane groups, thus recovering the fluorescence of OUG.

In the FTIR experiments (Fig. S11a, ESI†), when Fe$^{3+}$ was added into OUG to form OUFeG, the stretching absorbance bands of N–H, C=O and C–O–C shifted from 3361 cm$^{-1}$, 1708 cm$^{-1}$ and 1161 cm$^{-1}$ to 3480 cm$^{-1}$, 1673 cm$^{-1}$ and 1158 cm$^{-1}$ respectively, which further confirmed that Fe$^{3+}$ interacts with π-electrons of the urethane groups, thus influencing H-bonds between the amide groups. After the addition of F$^-$ or HSO$_4^-$ into the OUFeG, the C=O, N–H and C–O–C all reverted to their initial positions (Fig. S11a, ESI†). These observations suggested that F$^-$ and HSO$_4^-$ competitively bound to Fe$^{3+}$ rather than to OUG. Moreover, the XRD peaks of OUG moved with adding Fe$^{3+}$ into OUFeG, and recovered when F$^-$ or HSO$_4^-$ was added into OUFeG (Fig. S11b, ESI†).

To get further insight into the mechanism of cation–anion sensing, as shown in Fig. 5, the SEM studies were carried out. Fig. 5a demonstrates that gel OUG shows a lamellar stacking structure with a smooth surface. This structure was converted into a honeycomb structure in the metal-gel OUFeG (Fig. 5b), while in gel OUFeG + HSO$_4^-$ and OUFeG + F$^-$, the image again showed a smooth lamellar stacking structure (Fig. 5c and d). Such morphological change is attributed to the cation–π interactions between OUG and Fe$^{3+}$, breaking hydrogen bonding between the OUG chains and modifying the supramolecular structure. After adding F$^-$ or HSO$_4^-$ into OUFeG, π-electrons of OUG were released, hydrogen bonds are rebuilt and the morphology is recovered. These experimental results indicated that the fluorescence of OUG can be reversibly switched by Fe$^{3+}$ (off) and then by F$^-$ or HSO$_4^-$ (on), through repeated competition between cation–π and cation–anion interactions (Fig. 2b).

**Application in the rapid removal of Fe$^{3+}$**

The development of new sorbents for the sensing and extraction of metal ions from environmental and biological samples is of current importance. The performance of OUG to effectively remove Fe$^{3+}$ from aqueous solution was analyzed by atomic absorption spectrometry (Table S3, ESI†). Specifically, OUG (0.2 g) was added to a dilute aqueous solution of Fe$^{3+}$ (1 × 10$^{-3}$ mol L$^{-1}$ in 10 mL water) and the mixture was stirred for 10 min. The precipitate was separated by centrifuging at 5000 rpm for 5 min and the supernatant was retained, the residual concentration of Fe$^{3+}$ was about 2.5 × 10$^{-7}$ mol L$^{-1}$. Experimental results demonstrated that 97.5% of Fe$^{3+}$ could be efficiently removed by OUG even from extremely dilute solutions, which indicated the excellent adsorption capacity of OUG towards Fe$^{3+}$. As shown in Fig. S6 (ESI†), adsorption tests of OUG toward Fe$^{3+}$ in the pH range from 4 to 10 showed that the adsorption of OUG toward Fe$^{3+}$ showed excellent stability at different pH conditions (in the range of 92.1–97.5%). OUG can selectively detect with high-efficiency and rapidly remove toxic Fe$^{3+}$, offering potential practical applications in combating heavy metal ion pollution and in environmental remediation.

**Application as a writing display material**

Based on the above-mentioned “on–off–on” properties, the OUG has a great potential as a rewritable fluorescent display material. As a proof-of-concept a rewritable board was constructed (Fig. 6). The detailed steps are described as follows: (i) OUG sol (10%) was poured onto a clean quartz plate surface and dried under ambient conditions to give a film emitting strong blue fluorescence under ultraviolet radiation (365 nm), (ii) Writing the symbol “Fe” on the film with a brush dipped in
aqueous Fe$^{3+}$ solution (0.3 M), a dark “Fe” image was clearly displayed due to the fluorescence quenching effect of Fe$^{3+}$ on OUG. (iii) The whole OUG film was transformed into a non-fluorescent display board by brushing with Fe$^{3+}$ solution. (iv) Two new letters “S” and “F” could be written again with the same brushing method using HSO$_4^-$ and F$^-$ solutions (0.3 M), respectively. Visually, the letters emitted blue fluorescence under a UV lamp. Combining these practically very simple processes with the excellent recyclability of OUG (discussed above; Fig. S10, ESI) means that OUG has promising applications as a fluorescent writing display material.

**Conclusion**

In conclusion, a novel supramolecular AIE gel, OUG, was designed and synthesized by a straightforward “one-pot” procedure. The dynamic and reversible noncovalent interactions endow OUG with distinct advantages of a reversible and highly sensitive response to Fe$^{3+}$, HSO$_4^-$, and F$^-$, acting as an “on-off-on” fluorescent sensor for these cationic and anionic species. Importantly, OUG can absorb up to 97.5% Fe$^{3+}$ from a water environment. This rapid, simple, low cost and highly sensitive material has great potential for practical applications in intelligent sensing, handling heavy metal ion pollution and environmental remediation.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**