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# Water-soluble fluorescent chemosensor based on Schiff base derivative terminated PEG for highly efficient detection of Al<sup>3+</sup> in pure aqueous media

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## Introduction

Aluminum is the most abundant metal element in the Earth's crust, and its products are widely used in industry and our daily life. Due to the influence of human activity and acid rain, the concentration of  $AI^{3+}$  is increasing year by year in the biosphere and ecosphere. According to the WHO report, the average human intake of aluminum was recommend to be approximately 3–10 mg per day and the permissible limit of  $AI^{3+}$  in drinking water was 7.4  $\mu$ M [1].  $AI^{3+}$  has been proved to be an inessential metal ion for human body, and the excessive intake of  $AI^{3+}$  can cause a series of diseases including Alzheimer's disease, amyotrophic lateral sclerosis, anemia, osteoporosis and Parkinson's disease [2–7]. Furthermore, high concentration of  $AI^{3+}$  can also restrain plant growth and affect aquatic organisms [8–11]. Thus, it is quite significant to develop an efficient method for highly selective detection of  $AI^{3+}$ .

Though many analytical methods have been applied for quantitative or qualitative detection of metal ions, most of them require expensive and sophisticated instrumentation, complicated sample preparation and time-consuming procedure [12–19]. In the past decade, fluorescent chemosensors for metal ion detection exhibited outstanding advantages including low cost, operational

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# ABSTRACT

Schiff base derivative terminated PEG (PEGESB) was synthesized and applied as fluorescent chemosensor in pure aqueous media. PEGESB exhibited excellent selectivity and anti-interference ability for  $Al^{3+}$  with naked eye fluorescence color change from colorless to bright cyan. The detection limit of PEGESB for  $Al^{3+}$ was determined to be as low as  $2.93 \times 10^{-9}$  M. PEGESB was stable and could effectively detect  $Al^{3+}$  over a wide pH range from 5 to 10. PEGESB was proved to be a reversible fluorescent chemosensor upon alternate addition of  $Al^{3+}$  and EDTA to PEGESB aqueous solution. The fluorescence response of PEGESB solution to  $Al^{3+}$  and EDTA was applied to build an INHIBIT logic gate. In addition, test papers coated with PEGESB were facilely prepared for on-site sensing of  $Al^{3+}$  in real water samples.

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simplicity, real-time detection, non-destructive nature and high sensitivity [20–25]. Recently, O/N-rich Schiff base derivatives could provide effective scaffold to coordinate with Al<sup>3+</sup> through hostguest interaction, and a series of fluorescent chemosensors based on small molecular Schiff base derivatives have been designed for selective detection of  $Al^{3+}$  [26–33]. However, owing to the poor water-solubility, most of small molecular Schiff base-based fluorescent chemosensors could only show good selectivity to Al<sup>3+</sup> in the mixed solutions of organic solvent and water or even in pure organic solutions, which limited their practical application. Therefore, it is crucial to design novel Schiff base-based fluorescent chemosensors for Al<sup>3+</sup> in pure aqueous media. Water-soluble polymers integrated with a small amount of metal ion recognition units could be facilely synthesized by copolymerization or post-modification strategy, and various water-soluble polymer-based fluorescent chemosensors have been developed for metal ion detection in pure aqueous media [34–37]. However, to the best of our knowledge, there were quite few reports about polymer-based fluorescent chemosensors functionalized with Schiff base derivatives for Al<sup>3+</sup> detection in pure aqueous media.

In this work, we developed a simple and novel water-soluble polymer-based fluorescent chemosensor PEGESB for selective detection of Al<sup>3+</sup>, which was easily synthesized by the post-modification of PEG using salicylaldehyde-based Schiff base derivative. PEGESB exhibited high selectivity and sensitivity for Al<sup>3+</sup> with turn-on fluorescence response in pure aqueous media. PEGESB





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Scheme 1. Synthetic route of PEGESB.



Fig. 1. UV-vis absorption spectra of PEGESB aqueous solutions (10  $\mu M)$  in the absence and presence of 2 equiv. of different metal ions.

was further successfully used to prepare test papers for on-site sensing of  $Al^{3+}$  in real water environment.

### **Results and discussion**

The synthesis route of the chemosensor PEGESB was shown in Scheme 1. Firstly, a salicylaldehyde-based Schiff base derivative HESB was designed and synthesized through the condensation of

4-(diethylamino)salicylaldehyde with 4-hydroxybenzhydrazide, and the structure of HESB was determined by <sup>1</sup>H NMR, <sup>13</sup>C NMR and ESI-MS spectra (Fig. S1–S3). HESB could not be dissolved in pure aqueous medium, which was the same as most of small molecular Schiff base derivatives. To solve the poor water solubility of HESB, water-soluble polymer PEG was used as water-soluble carrier. The esterification of HESB with carboxylated PEG was conducted to synthesize Schiff base derivative functionalized polymer PEGESB, which was confirmed by <sup>1</sup>H NMR spectrum analysis (Fig. S4). As expected, PEGESB exhibited excellent solubility in pure aqueous media.

To investigate the selectivity of PEGESB to metal ions, the UVvis absorption spectra of PEGESB in pure aqueous media were measured in the presence of 2 equiv. of different metal ions including  $Al^{3+}$ ,  $Ba^{2+}$ ,  $Ca^{2+}$ ,  $Ce^{3+}$ ,  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Cr^{3+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Hg^{2+}$ ,  $K^+$ ,  $Mn^{2+}$ ,  $Na^+$ ,  $Ni^{2+}$ ,  $Pb^{2+}$  and  $Zn^{2+}$  (Fig. 1). The aqueous solution of free PEGESB displayed the absorption band centered at 358 nm. Upon the addition of  $Al^{3+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ , a new absorption band at 394 nm was observed, and the mixture of PEGESB and  $Al^{3+}$  showed the highest absorption enhancement (Fig. S5).

After that, the fluorescence spectra of PEGESB solutions were tested upon the addition of 2 equiv. of different metal ions (Fig. 2a). The aqueous solution of free PEGESB exhibited no distinguishable fluorescence emission. Upon the addition of metal ions to the PEGESB solutions, only  $Al^{3+}$  induced apparent fluorescence emission centered at 459 nm, and other metal ions had almost no influence on fluorescence emission. In accordance with the measurements of fluorescence spectra, the color of PEGESB solution changed from black to bright cyan fluorescence after the addition of  $Al^{3+}$  under the irradiation of a 365 nm lamp, while other



**Fig. 2.** (a) Fluorescence emission spectra of PEGESB aqueous solutions ( $10 \mu$ M) in the absence and presence of 2 equiv. of different metal ions ( $\lambda_{ex}$  = 394 nm). (b) Photograph of PEGESB aqueous solutions ( $10 \mu$ M) in the presence of 2.0 equiv. of different metal ions under the irradiation of a 365 nm UV lamp.



**Fig. 3.** (a) Fluorescence emission spectra of PEGESB aqueous solution (10 μM) upon gradual addition of Al<sup>3+</sup> (0–10 equiv.). (b) Calibration curve of the fluorescence intensity at 459 nm of PEGESB binding with Al<sup>3+</sup>.



Scheme 2. The proposed sensing mechanism of PEGESB for Al<sup>3+</sup>.



Fig. 4. Fluorescence intensity response at 459 nm of PEGESB aqueous solutions (10  $\mu$ M) upon the addition of other competing metal ions in the absence and presence of Al<sup>3+</sup>.



Fig. 5. Effect of pH on the fluorescence intensity at 459 nm of PEGESB aqueous solutions (10  $\mu$ M) in the absence and presence of Al<sup>3+</sup> (2 equiv.).

metal ions caused no naked eye fluorescence (Fig. 2b). Therefore, PEGESB could be used as an effective fluorescence chemosensor for  $Al^{3+}$  in pure aqueous media.

The binding behavior of PEGESB with Al<sup>3+</sup> was investigated by fluorescence titration experiments. The fluorescence emission intensity at 459 nm was enhanced gradually with Al<sup>3+</sup> concentration increasing from 0 to 2 equiv., and after that, there was negligible change even with high concentration of Al<sup>3+</sup> (Fig. 3a). After complexation of Al<sup>3+</sup>, photo-induced electron transfer (PET) and C=N isomerization of Schiff base group of PEGESB might be inhibited, which could cause the chelation-enhanced fluorescence (CHEF) and lead to the fluorescence enhancement of the mixed solution [23]. The 1:1 stoichiometric binding between PEGESB and Al<sup>3+</sup> was confirmed by the Job's plot analysis (Fig. S6). And so, the sensing mechanism of PEGESB for Al<sup>3+</sup> was proposed and shown in Scheme 2. The binding constant of the PEGESB-Al<sup>3+</sup> complex was found to be  $1.01 \times 10^5 \text{ M}^{-1}$  based on the titration data according to the Benesi-Hildebrand equation (Fig. S7) [38,39]. The detection limit of PEGESB for Al<sup>3+</sup> was estimated to be 2.93  $\times$  10<sup>-9</sup> M by using the equation  $3\sigma/k$  (Fig. 3b), which was far below the WHO's permitted limit of Al<sup>3+</sup>in drinking water. The performance of PEGESB was more comparable to that of some reported fluorescent chemosensors for Al<sup>3+</sup> in recent vears (Table S1).

To investigate the anti-interference ability of PEGESB for detecting  $Al^{3+}$ , competition experiments were carried out. The aqueous solutions of PEGESB (10  $\mu$ M) were titrated with 2 equiv. of  $Al^{3+}$ firstly, and then 2 equiv. of other competing metal ions were added separately. It was observed that the fluorescence intensities of PEGESB-Al<sup>3+</sup> solutions at 459 nm displayed little or almost no significant changes in the presence of competing metal ions (Fig. 4). These results indicated that competing metal ions had little effect on Al<sup>3+</sup> detection by PEGESB, and PEGESB could be used to selectively sense Al<sup>3+</sup> in pure aqueous media.

The wide-range pH stability is imperative for fluorescent chemosensors in practical applications. And so, the effect of pH on the fluorescence intensity of PEGESB solutions in the absence and presence of Al<sup>3+</sup> was studied in the pH range from 2 to 13 (Fig. 5). The fluorescence intensities of free PEGESB solutions at 459 nm were not changed significantly in the investigated pH range. Upon the addition of Al<sup>3+</sup>, the fluorescence intensities of the aqueous solutions were still quite weak at low pH (below pH 4), which might be caused by the protonation of the Schiff base



**Fig. 6.** (a) Reversible switching cycles of fluorescence intensity of PEGESB aqueous solution (10  $\mu$ M) upon alternate addition of Al<sup>3+</sup> (1 equiv.) and EDTA (1 equiv.). (b) Photographs of PEGFB aqueous solution (10  $\mu$ M) upon alternate addition of Al<sup>3+</sup> and EDTA under a 365 nm UV lamp.

group of PEGESB inhibiting the complexation of PEGESB with  $Al^{3+}$ in strongly acidic conditions. The fluorescence intensities of PEGESB-Al<sup>3+</sup> solutions increased sharply and maintained strong in the pH range of 5–10. Under strongly basic conditions (pH > 11), stable Al(OH)<sub>3</sub> or Al(OH)<sub>4</sub> were more easily formed, and the binding of Al<sup>3+</sup> with PEGESB was hampered, which induced the fluorescence quenching. The strong fluorescence intensity of PEGESB-Al<sup>3+</sup> solutions in the pH range from 5 to 10 indicated that



Fig. 7. (a) Fluorescence intensity of PEGESB solutions at 459 nm in the presence of four input combinations. (b) Truth table for the INHIBIT logic gate. (c) Monomolecular circuit for the INHIBIT logic gate.



**Fig. 8.** Photographs of test papers under a 365 nm UV lamp: (a) after adding a drop of different metal ion solutions  $(10^{-4} \text{ M})$  (from left to right, up: blank, Ba<sup>2+</sup>, Ce<sup>3+</sup>, Cd<sup>2+</sup>, Al<sup>3+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>; down: Fe<sup>3+</sup>, Hg<sup>2+</sup>, K<sup>+</sup>, Mn<sup>2+</sup>, Na<sup>+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>); (b) after adding a drop of different Al<sup>3+</sup> solutions  $(10^{-4} \text{ M})$  (from left to right: deionized water, tap water and Tuhai River water).

PEGESB could act as an efficient turn-on fluorescent chemosensor for Al<sup>3+</sup> detection in practical applications over this wide pH range, and could be used in unbuffered solutions.

Reversible sensing property is an important feature of an efficient chemosensor. So we performed the fluorescence titration studies of PEGESB solution upon alternate addition of Al<sup>3+</sup> and EDTA. As shown in Fig. S8, the solution of PEGESB-Al<sup>3+</sup> exhibited extremely strong fluorescence intensity at 459 nm. Upon the addition of 1 equiv. of EDTA to the solution, the fluorescence of the aqueous solution was efficiently quenched due to the complexation of Al<sup>3+</sup> with EDTA, and the fluorescence intensity was recovered to the original level of free PEGESB solution. After adding 1 equiv. of Al<sup>3+</sup> to the aqueous solution again, the strong fluorescence emission was observed once more. Under the irradiation of a 365 nm UV lamp, the on-off-on fluorescence responses were observed upon alternate addition of Al<sup>3+</sup> and EDTA to the aqueous solution, and the reversible cycle of the fluorescence response could be repeated for more than four times (Fig. 6). It revealed that PEGESB could be applied to reversibly sense Al<sup>3+</sup> in pure aqueous media.

Recently, reversible fluorescent chemosensors have been widely used to mimic the function of molecular logic gates [40– 42]. An INHIBIT logic gate could be fabricated based on the reversible fluorescence switching response of PEGESB to Al<sup>3+</sup> and EDTA. Al<sup>3+</sup> and EDTA were set as two chemical inputs, and the presence and absence of the chemical inputs were assigned as the Boolean values "1" and "0", respectively. The fluorescence signal at 459 nm was used as the output, and strong fluorescence intensity was considered as "1" (ON state) and weak intensity was as "0" (OFF state). In the conditions of the absence of two inputs (0, 0), only EDTA (0, 1) and the presence of two inputs (1, 1), the output signals were all 0, and the states of the system were OFF because the fluorescence intensities were all weak. When  $Al^{3+}(1, 0)$  was input alone, the fluorescence intensity was strong, and the output signal was 1 displaying the ON state of the system. Thus, the INHI-BIT logic gate was successfully constructed by all these combinations. The truth table and the monomolecular circuit for the INHIBIT logic gate were shown in Fig. 7.

The practical applicability of PEGESB was evaluated by the test paper method, and test papers coated with PEGESB were facilely prepared. As shown in Fig. 8a, only the test paper added a drop of Al<sup>3+</sup> solution exhibited the naked eye bright cyan fluorescence under a 365 nm UV lamp, and no obvious fluorescence responses of the test papers were observed after adding a drop of other metal ion solutions. Furthermore, the practicability of test papers for detecting Al<sup>3+</sup> were evaluated in different water media. It was exciting that the test papers all showed bright cyan fluorescence responses immediately after adding a drop of three different Al<sup>3+</sup> solutions (Fig. 8b). Therefore, test papers coated with PEGESB could be conveniently applied for the on-site sensing of Al<sup>3+</sup> in real water environment.

### Conclusions

In summary, we have successfully designed and synthesized a Schiff base derivative terminated PEG-based fluorescent chemosensor PEGESB for selective detection of Al<sup>3+</sup> in pure aqueous media. Only in the presence of Al<sup>3+</sup>, the aqueous solution of PEGESB exhibited an obvious turn-on fluorescence response at 459 nm, along with naked eye bright cyan fluorescence under a 365 nm UV lamp. PEGESB showed excellent anti-interference ability for Al<sup>3+</sup> detection and low detection limit of  $2.93 \times 10^{-9}$  M. PEGESB could be used to efficiently sense Al<sup>3+</sup> over a wide pH range of 5–10. The reversible fluorescence response of PEGESB upon alternate addition of Al<sup>3+</sup> and EDTA induced the successful construction of an INHIBIT logic gate. Furthermore, test papers coated with PEGESB were conveniently applied to visually detect Al<sup>3+</sup> in real water samples.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2020.152335.

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