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A simple turn-on fluorescent chemosensor based on Schiff base-terminated water-soluble polymer for selective detection of Al³⁺ in 100% aqueous solution

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ABSTRACT

A simple water-soluble polymer PEGBHB based on polyethylene glycol bearing a Schiff base derivative moiety was successfully designed and synthesized. PEGBHB showed high selectivity and sensitivity towards Al^{3+} as a turn-on fluorescent chemosensor without influence by other competitive metal ions in 100% aqueous solution. The detection limit of PEGBHB for Al^{3+} was found to be 9.67 × 10⁻⁹ M. A 1 : 1 stoichiometry between PEGBHB and Al^{3+} has been confirmed by Job plot analysis. PEGBHB could detect Al^{3+} over a wide pH range from 4 to 10. The chemosensor was reversible by adding EDTA to the solution of PEGBHB- Al^{3+} complex. An INHIBIT molecular logic gate was constructed with the help of OFF-ON-OFF signal on alternate addition of Al^{3+} and EDTA to the chemosensor. Furthermore, test papers were fabricated facilely using PEGBHB for convenient and visual detection of practical Al^{3+} .

Keywords: Al³⁺ ions; Fluorescent chemosensor; Schiff base; Water-soluble polymer; Test paper

1. Introduction

As the most abundant metallic element in the earth's crust, aluminum (Al) is widely used in

many fields, such as aluminum-based pharmaceuticals, food additives, cooking utensils, water purification instruments and computers [1-4]. However, environmental acidification has greatly increased the amount of free Al³⁺ ions, which are harmful to environment and humans. About 40% of the acidic soils, which are detrimental to growing plants, are caused by Al^{3+} toxicity [5-7]. Al^{3+} has been assigned as prime food pollutants by World Health Organization (WHO), and the average daily human intake range of Al^{3+} has been recommended to be around 3-10 mg [8,9]. Unregulated overloading of Al³⁺ can cause aluminum-related bone disease, reversible microcytic hypochromic anaemia, encephalopathy and neurodegenerative diseases [10-14]. Therefore, the highly sensitive and selective detection of Al³⁺ ions in aqueous media has significant importance for environment protection and human health. Some conventional methods such as inductively coupled plasma atomic emission spectrometry, inductively coupled plasma mass spectrometry, graphite furnace atomic absorption spectrometry and electrochemical methods, are expensive, relatively complex and time consuming in practice [15-18]. Recently, fluorescent chemosensors for metal ions have attracted great interest due to their high sensitivity, low detection limit, low cost, operational simplicity, real-time detection and time saving [19,20]. Unfortunately, the development of fluorescent chemosensors for Al^{3+} ions in aqueous media is still challenging because of the lack of spectroscopic characteristics, poor coordination ability and strong hydration ability of Al³⁺ ions [21,22]. Therefore, it is highly essential to develop effective fluorescent chemosensors for the sensitive and selective detection of Al³⁺.

To date, a large number of Schiff base derivatives have been developed for the detection of various metal ions including Al^{3+} due to their ease of synthesis, low cost and excellent photophysical properties [23-36]. Most of the Schiff base based fluorescent chemosensors are

constructed by small-molecule Schiff base derivatives, which exhibit poor solubility in aqueous solution, and organic cosolvent must be applied in the detection process. To some extent, the use of organic solvent may limit the potential applications of fluorescent chemosensors in environmental and biological fields. Furthermore, it is still a challenge to fabricate fluorescent chemosensor devices using small molecules. Over the past few years, polymer has been proved as promising matrices for the construction of fluorescent chemosensors [37-40]. Compared with small-molecule fluorescent chemosensors, fluorescent chemosensors based on polymer exhibit several distinct advantages including better water solubility, signal amplification and ease of fabrication into devices. Zhang et al. prepared a well-defined alternating copolymer P(VBCDEG-alt-SaAEMI) based on a salicylaldimine Schiff base via alternating RAFT copolymerization for highly sensitive Zn^{2+} detection [41]. Patra et al. synthesized π -conjugated polymers poly(metaphenylene-alt-fluorene) with pendant terpyridyl binding sites through Suzuki coupling polymerization for Cu²⁺ detection [42]. In our previous works, two kind of water-soluble polymer-based chemosensors, P(NIPAM-co-RhBBA) with pendant rhodamine B moieties and PEGRh terminated with rhodamine B derivative, have been reported, which both showed high selectivity to Cu^{2+} in pure aqueous solution [43,44]. Thus, the poor water solubility of small-molecule Schiff base derivatives can also be overcome by covalently incorporating small amounts of Schiff base derivatives into hydrophilic polymers, and the secondary pollution caused by organic cosolvent can be prevented completely in metal ion detection. To the best of our knowledge, the development of fluorescent chemosensors based on water-soluble polymers containing Schiff base derivatives for selective detection of Al³⁺ ions in pure aqueous solution is relatively backward.

In continuation to our interest on water-soluble polymer chemosensors [43-46], we have designed and synthesized a simple Schiff base-terminated water-soluble polymer PEGBHB, which could serve as an efficient and highly selective fluorescent chemosensor for AI^{3+} in 100% aqueous solution. The detection properties of PEGBHB towards AI^{3+} were investigated using UV-Vis absorption spectroscopy and fluorescence emission spectroscopy. PEGBHB exhibited excellent recognition for AI^{3+} with no influence by other metal ions, and could detect AI^{3+} in a wide pH range. An INHIBIT molecular logic gate was constructed based on the reversible sensing property of PEGBHB. Meanwhile, test papers coated with PEGBHB were prepared for the practical detection of AI^{3+} in real water samples.

2. Experimental

2.1. Materials

Polyethylene glycol monomethyl ether (PEG, Mn = 5000) was purchased from Sigma-Aldrich. Benzoyl hydrazine, 2,4-dihydroxybenzaldehyde, 4-(dimethylamino) pyridine (DMAP), N,N'-dicyclohexylcarbodiimide (DCC), nitrate salts of metal ions (Al³⁺, Ba²⁺, Ce³⁺, Cd²⁺, Co²⁺, Cr³⁺, Cu²⁺, Fe³⁺, Hg²⁺, In³⁺, K⁺, Mn²⁺, Na⁺, Ni²⁺, Pb²⁺ and Zn²⁺) and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and used as received. Carboxylated PEG was synthesized according to the published procedure [47], and dried by azeotropic distillation in toluene for 6 h before use. The normal filter papers for the preparation of test papers were purchased from Hangzhou Special Paper Industry Co., Ltd. (Hangzhou, China).

2.2. Instruments

¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were measured on a Varian Mercury 400 spectrometer using DMSO-*d*₆ or CDCl₃ as the solvents and TMS as the internal standard. The ESI-MS spectrum was recorded on a LTQ Orbitrap mass spectrometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescent spectra were obtained on a Hitachi F-7000 fluorescence spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet IR-100 infrared spectrometer using KBr pellets. The pH value was measured with a Mettler-Toledo FE20 pH-meter.

2.3. Synthesis

2.3.1. Synthesis of the compound BHB

Benzoyl hydrazine (1.0 g, 7.3 mmol) and 2,4-dihydroxybenzaldehyde (1.064 g, 7.7 mmol) were dissolved in ethanol (25 mL). After refluxing for 6 h under nitrogen, the solution was allowed to cool and stand overnight at room temperature. The precipitate was filtered and washed three times with 15 mL cold ethanol. After drying under vacuum overnight, the final product BHB was obtained as a light pink solid (1.56 g, yield 83%). ¹H NMR (400MHz, DMSO-*d*₆), δ (ppm): 6.30 (d, 1H, *J* = 2 Hz), 6.32 (dd, 1H, *J* = 8.4 Hz, *J* = 2 Hz), 7.19 (d, 1H, *J* = 8.4 Hz), 7.47-7.54 (m, 3H), 7.89 (d, 2H, *J* = 6.8 Hz), 8.46 (s, 1H), 9.86 (s, 1H), 11.52 (s, 1H), 11.87 (s, 1H); ¹³C NMR (100MHz, DMSO-*d*₆), δ (ppm): 78.91, 79.24, 79.57, 103.15, 107.99, 110.75, 127.92, 128.72, 131.91, 133.39, 149.94, 160.11, 161.14, 162.91; ESI-MS m/z: [M + Na]⁺ calcd. for C₁₄H₁₂N₂O₃: 279.0746; found: 279.0735.

2.3.2. Synthesis of PEGBHB

To the solution of carboxylated PEG (1.0 g, 0.196 mmol) in dry THF (20 mL), BHB (52.8 mg, 0.206 mmol), a catalytic amount of DMAP (10 mg) and DCC (61.9 mg, 0.3 mmol) were added rapidly. The reaction mixture was stirred for 48 h at room temperature. After filtration, the filtrate was concentrated under reduced pressure and precipitated in cold diethyl ether three times. The desired white solid product PEGBHB was obtained by filtration and dried under vacuum for 24 h at room temperature (0.91 g, yield 87%).

2.4. General spectroscopic measurements

The stock solutions of various metal salts (0.015 M) were prepared using deionized water as solvent. PEGBHB was dissolved in deionized water to form the stock solution $(1 \times 10^{-4} \text{ M})$. 3 mL solutions containing required concentration of PEGBHB and metal salts were made by mixing appropriate amount of stock solutions and deionized water, and the spectra of the mixed solutions were recorded 30 s after each preparation at room temperature. The pH value of the solutions was adjusted using HCl for pH 2-6 and NaOH for 8-13.

2.5. Application as test paper

Test papers were prepared by immersing normal filter papers into the methanol solution of PEGBHB (10 mg·mL⁻¹) for 5 min, and then dried in air at room temperature. The solutions of various metal salts (10⁻⁴ M) were prepared using deionized water as solvent. Three solutions of Al^{3+} (10⁻⁴ M) were prepared using deionized water, tap water and river water (Tuhai River) as solvent, respectively. After being dipped in different aqueous solution for 5 s, the test papers were taken out and observed under a 365 nm UV lamp.

3. Results and discussion

3.1. Synthesis of the chemosensor PEGBHB

The synthesis of PEGBHB is shown in Scheme 1. A simple Schiff base derivative BHB was firstly synthesized by a one-step condensation reaction of benzoyl hydrazine with 2,4-dihydroxybenzaldehyde, and the structure was supported by ¹H NMR, ¹³C NMR and ESI-MS spectral data (Fig. S1-S3). As most of Schiff base derivatives, BHB also exhibited poor solubility in water. The post-modification approach has been proven to be a facile strategy for the preparation of functional polymers [48]. In order to prepare water-soluble polymer chemosensor, the hydrophilic polymer PEG was chosen as water-soluble polymer matrix. And then, Schiff base derivative BHB-terminated polymer PEGBHB was obtained by post-modification of carboxylated PEG with BHB. The formation of PEGBHB was verified by ¹H NMR analysis (Fig. S4). Compared to small-molecule Schiff base derivatives, PEGBHB showed excellent solubility in 100% water.



3.2. Absorption studies of PEGBHB

UV-Vis absorption spectrum recorded for PEGBHB in pure aqueous solution showed an absorption maximum at 328 nm, while the intensity of the 328 nm band of PEGBHB decreased with the concomitant appearance of a new band at 367 nm upon the addition of Al³⁺ ions (Fig. S5). Various metal ions (Al³⁺, Ba²⁺, Ce³⁺, Cd²⁺, Co²⁺, Cr³⁺, Cu²⁺, Fe³⁺, Hg²⁺, In³⁺, K⁺, Mn²⁺, Na⁺, Ni²⁺,

Pb²⁺ and Zn²⁺) have been added to aqueous solutions of PEGBHB and the absorption spectra showed new bands for Al³⁺, Cu²⁺, Zn²⁺, Ni²⁺, Co²⁺ and Pb²⁺ (Fig. S6). The mixture of PEGBHB and Al³⁺ gave the highest absorbance centered at 367 nm. And then, the Al³⁺-binding behaviors of PEGBHB in aqueous solution were first studied by UV-Vis absorption titration. Upon the addition of increasing concentrations of Al³⁺ ions, the absorption intensity at 328 nm decreased gradually, and a new strong absorption band appeared at 367 nm with increase of the intensity (Fig. 1a). As shown in Fig. 1b, the changes in absorbance of its two bands both became steady when about 1 equiv. of Al³⁺ ions were added. The result suggested that the stoichiometry between PEGBHB and Al³⁺ was 1 : 1. According to the linear Benesi–Hildebrand expression, the measured absorbance [1/(A – A₀)] at 367 nm varied as a function of 1/[Al³⁺] in a linear relationship, and the association constant of PEGBHB with Al³⁺ was calculated to be 2.14 × 10⁵ M⁻¹ (Fig. S7).



Fig. 1. (a) UV-Vis absorption spectra of PEGBHB (10 μ M) in aqueous solution with variable concentration of Al³⁺ in range of 0-5 equiv.; (b) plot of absorbance intensity of PEGBHB (10 μ M) in aqueous solution at 328 nm and 367 nm depending on the equivalents of Al³⁺.

3.3. Fluorescence studies and binding behavior

The fluorescence selectivity of PEGBHB was examined in the presence of various metal ions in pure aqueous solution (Fig. 2a). An excitation maximum of 345 nm did not show any significant

change in fluorescence emission spectra of free PEGBHB in aqueous solution. Upon the addition of 2 equiv. of Al³⁺ ions, a significant turn-on fluorescence response at 435 nm occurred with the change of the solution from non-fluorescence to strong bright blue fluorescence within 20 s under a 365 nm UV lamp. In contrast, the addition of 2.0 equiv. of other metal ions (Ba²⁺, Ce³⁺, Cd²⁺, Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , In^{3+} , K^+ , Mn^{2+} , Na^+ , Ni^{2+} , Pb^{2+} and Zn^{2+}) caused negligible spectral changes, and led to no obvious fluorescence changes of the solutions under a 365 nm UV lamp (Fig. 2b). The changes in fluorescence of PEGBHB before and after addition of Al^{3+} could be explained by a combination of excited state intramolecular proton transfer (ESIPT), C=N isomerization, and chelation enhanced fluorescence (CHEF) mechanism [49-52] (Scheme 2). In the absence of Al3+, free PEGBHB exhibited no fluorescence emission due to ESIPT and C=N isomerization of imine double bond. After addition of Al³⁺, a stable chelation of PEGBHB with Al3+ prevented ESIPT and C=N isomerization, resulting in the enhancement of fluorescence emission intensity, which could also be ascribed to the CHEF mechanism. The fluorescence change indicates that PEGBHB can act as a "turn-on" fluorescent chemosensor for Al³⁺ in pure aqueous solution.



Fig. 2. (a) Fluorescence emission spectra of PEGBHB (10 μ M) in aqueous solution upon the addition of various metal ions (2 equiv. of each, excited at 345 nm); (b) the emission photographs

 $E_x=345 \text{ nm}$ H_N H_N H_2 H_2 H_1 H_2 H_2 H_2 H_1 H_2 H_2

of PEGBHB (10 µM) in the presence of various metal ions (2 equiv.) under a 365 nm UV lamp.

Scheme 2. Proposed mechanism for the detection of Al³⁺ by PEGBHB.

The Al3+-binding behaviors of PEGBHB in aqueous solution were further evaluated by fluorescence titration experiments. In the absence of Al³⁺ ions, the aqueous solution of free PEGBHB exhibited no obvious fluorescence emission, which could be attributed to the ESIPT mechanism. Upon the addition of an increasing amount of Al³⁺ ions, the fluorescence of the aqueous solution changed from non-fluorescence to bright blue fluorescence gradually under a 365 nm UV lamp (Fig. S8), and the fluorescence band centered at 435 nm increased obviously (Fig. 3). The complexation of Al^{3+} with PEGBHB increased the rigidity of the complex and restricted the ESIPT effect and C=N isomerization of the complex, resulting in the enhancement of the fluorescence intensity. The gradual enhancement of the fluorescence intensity with the increase amount of Al³⁺ ions further confirmed the CHEF mechanism. When the amount of Al³⁺ ions was increased to 1 equiv., the fluorescence intensity was saturated. The fluorescence emission intensity of the aqueous solution did not change obviously on excess addition of Al³⁺. The Job plot analysis also confirmed the 1 : 1 stoichiometry for complexation of Al^{3+} with PEGBHB (Fig. 4). Based on the result of fluorescence titration, the stoichiometry was further supported by the Benesi-Hildebrand equation, and the association constant was determined to be $1.30 \times 10^5 \text{ M}^{-1}$ (Fig. S9). The detection limit of PEGBHB as a fluorescent chemosensor for Al^{3+} ions was found

to be 9.67×10^{-9} M according to the equation $3\sigma/K$, where σ is the standard deviation of 10 replicate measurements of blank PEGBHB solution and K is the slope of the calibration curve (Fig. S10). The detection limits of some previously reported Schiff base-based chemosensors for Al³⁺ ions were compared with this work (Table 1).

The binding mode of PEGBHB with Al³⁺ was further confirmed by ¹H NMR titration experiments and FT-IR titration experiments. As shown in Fig. S11, the proton peak of phenolic hydroxyl group (-OH) at 11.44 ppm disappeared after addition of Al³⁺, meaning the deprotonation of the hydroxyl group and the binding of Al³⁺. Additionally, the proton peak of -CH=N- at 8.45 ppm shifted to 8.36 ppm, which could also be attributed to the binding of Al³⁺. The FT-IR spectrum of PEGBHB showed characteristic peaks of –OH at 3326 cm⁻¹ and -CH=N- at 1627 cm⁻¹ (Fig. S12). Upon the addition of Al³⁺, the peak of –OH disappeared and the peak of -CH=Nshifted to 1602 cm⁻¹. These results suggest that PEGBHB complexes with Al³⁺ as proposed mechanism in Scheme 2.

Fig. 3. Fluorescence emission spectra of PEGBHB (10 μ M) in aqueous solution with variable concentration of Al³⁺ in range of 0-5 equiv. Inset: plot of fluorescence intensity of PEGBHB (10 μ M) in aqueous solution at 435 nm against the equivalents of Al³⁺.

Comparison of PEGBHB with some reported Schiff base-based chemosensors for Al ³⁺ ions.						
Sl. No.	Chemosensor	Testing media	Detection limit (M)	Refs.		
1		Methanol/H ₂ O (1/999, V/V)	1.93 × 10 ⁻⁷	[23]		
2	$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array}\\ \end{array}\\ \end{array}\\ \end{array}\\ \end{array}\\ \end{array}\\ \end{array} $	Methanol	5.25×10^{-7} 2.38×10^{-6}	[24]		
3		Near 100% aqueous solution	4.00×10^{-6}	[52]		
4		Nearly perfect aqueous solution	1.12×10^{-6}	[29]		
5		Methanol/H ₂ O (3/7, V/V)	$5.00 imes 10^{-8}$	[30]		
6		DMF/H2O (9/1, V/V)	6.70 × 10 ⁻⁶	[32]		
7		DMSO/H ₂ O (7/3, V/V)	9.00 × 10 ⁻⁹	[33]		
8	$ \begin{array}{c} \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	DMSO/H ₂ O (1/5, V/V)	$1.05 imes 10^{-8}$	[34]		
9		Ethanol	2.78×10 ⁻⁶	[36]		
10		100% aqueous solution	$9.67 imes 10^{-9}$	This work		

Table 1

Fig. 4. Job plot of PEGBHB and Al^{3+} in aqueous solution. The total concentration of PEGBHB and Al^{3+} is 10 μ M.

3.4. Selectivity of PEGBHB to Al^{3+}

To check the applicability of PEGBHB as a selective fluorescent chemosensor for Al^{3+} , competitive experiments were performed in the presence of 2 equiv. of Al^{3+} ions mixed with 2 equiv. of other competitive metal ions, such as Ba^{2+} , Ce^{3+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , In^{3+} , K^+ , Mn^{2+} , Na^+ , Ni^{2+} , Pb^{2+} and Zn^{2+} . As shown in Fig. 5, no significant variation of the fluorescence intensity at 435 nm was observed by comparison with or without other metal ions, indicating that the presence of other metal ions has no influence on the selectivity of the fluorescent chemosensor to Al^{3+} ions. All these selective results demonstrate that PEGBHB has excellent recognition for Al^{3+} ions, and can satisfy the practical application requirement.

Fig. 5. Competition analysis of PEGBHB (10 μ M) to various metal ions in aqueous solutions. The black bars represent the intensity of PEGBHB mixed with 2 equiv. of other metal ions; the red bars represent the intensity of PEGBHB mixed with 2 equiv. of Al³⁺ and 2 equiv. of other metal ions.

3.5. Effect of pH

The wide applicable range of pH was also an important factor for the property evaluation of the fluorescent chemosensors. The effect of pH on the fluorescence response of PEGBHB to Al³⁺ was evaluated in the pH range from 2 to 13 (Fig. 6). The aqueous solutions of the free PEGBHB showed no obvious changes in the fluorescence intensity at 435 nm over the pH range of 2-13, which meaning that PEGBHB was stable over the wide pH range. Upon the addition of Al³⁺ ions, the fluorescence intensity at 435 nm enhanced, indicating the formation of the PEGBHB-Al³⁺ complex. The fluorescence intensity of the complex maintained stable with pH value from 4 to 10. Under strong acidic conditions, the protonation of PEGBHB occurred and hampered its binding ability with Al³⁺. The fluorescence intensity decreased significantly with the continuous increase of pH value because of the formation of Al(OH)₃ under higher pH conditions. Both strong acidic and strong alkaline conditions could block the complexation of PEGBHB with Al³⁺. However, the

high activity of PEGBHB over such a wide pH range makes it favorable for the analysis of environmental samples over this extended range of pH, and suitable for its application in unbuffered solutions.

Fig. 6. Effect of pH on the fluorescence intensity (at 435 nm) of PEGBHB (10 μ M) in aqueous solutions in the absence and presence of Al³⁺ (2 equiv.).

3.6. Reversibility studies

The reversibility of the fluorescent chemosensor to Al³⁺ was explored by titration of the PEGBHB-Al³⁺ complex with EDTA, which was known as a strong chelating agent for Al³⁺. As shown in Fig.7a, the fluorescence intensity of PEGBHB-Al³⁺ complex in aqueous solution was decreased to that of free PEGBHB after addition of 1 equiv. of EDTA. The quenching of the bright blue fluorescence was also observed by naked eyes under a 365 nm UV lamp (Fig. 7b). The fluorescence quenching could be attributed to the decomplexation of Al³⁺ and the formation of more stable EDTA-Al³⁺ complex, leading to regaining of free PEGBHB. The addition of Al³⁺ to the non-fluorescent aqueous solution of free PEGBHB displayed a bright blue fluorescence, which could act as ON switch. On the other hand, the titration of PEGBHB-Al³⁺ complex with EDTA resulted in the complete quenching of fluorescence, and so serving as OFF switch. The ON/OFF

behavior of the fluorescent chemosensor, supported by the distinguished fluorescence changes from non-fluorescence to bright blue fluorescence and then again to non-fluorescent state, clearly demonstrates the reversible recognition property of PEGBHB to Al³⁺.

Fig. 7. (a) Reversible sensing nature of PEGBHB (10 μ M) with Al³⁺ (1 equiv.) and EDTA (1 equiv.); (b) visual fluorescence changes of PEGBHB (10 μ M) after alternate addition of Al³⁺ and EDTA under a 365 nm UV lamp.

3.7. Construction of logic gate

Recently, great attention has been paid to the development of molecular logic gates based on the transformation of chemically encoded information into fluorescent signals. The above study of fluorescence emission clearly demonstrated that PEGBHB could serve as molecular system which exhibited logic gate properties [53,54]. The OFF-ON-OFF behavior of the chemosensor offered the scope to construct INHIBIT type molecular logic gate [24,34,55-59]. Here, Al³⁺ and EDTA

were used as two chemical inputs whereas the change of fluorescence emission at 435 nm was considered as output signal. Truth table was depicted for the input responses where "1" and "0" represented the presence and absence of the input signals which were Al³⁺ or EDTA respectively. Similarly for the output responses, "1" was defined as fluorescence appearance (ON) and "0" as fluorescence quenching (OFF). The output value was 1 only when individual Al³⁺ was present, and the output values of all other actions were 0. Thus the change of emission at 435 nm with Al³⁺ and EDTA as chemical inputs can be interpreted as a monomolecular circuit exhibiting an INHIBIT molecular logic gate (Fig. 8).

Fig. 8. Truth table and the monomolecular circuit based on Al³⁺and EDTA as chemical inputs and fluorescence emission as output.

3.8. Application as test paper

As a facile and efficient strategy to detect metal ions in real water samples, the test paper method has attracted considerable attention [60-62]. To further evaluate the practical application of the fluorescent chemosensor, test papers coated with PEGBHB were prepared by a simple immersion and drying process. As shown in Fig. 9a, only when the test paper was dipped in the aqueous solution of Al³⁺ ions, the strong bright blue fluorescence was visualized immediately by naked eyes under a 365 nm UV lamp. No obvious changes of the test papers were observed after being immersed into the aqueous solutions of other potentially competitive metal ions. Furthermore, the practicability of the test paper was demonstrated using Al³⁺ samples in deionized water, tap water and river water (Tuhai River). The color of the test papers all changed to bright

blue immediately under a 365 nm UV lamp after being dipped into different solutions of Al³⁺ ions (Fig. 9b). Therefore, test papers coated with PEGBHB are extremely suitable for on-site detection of Al³⁺ ions in real water samples.

Fig. 9. Fluorescent detection of Al^{3+} by test paper under a 365 nm UV lamp: (a) after being immersed into different aqueous solutions (10⁻⁴ M) (from left to right, up: blank, Al^{3+} , Co^{2+} , Cr^{3+} , Cu^{2+} and Fe^{3+} ; down: Hg²⁺, Mn²⁺, Na⁺, Ni²⁺, Pb²⁺ and Zn²⁺); (b) after being dipped into different solutions of Al^{3+} (10⁻⁴ M) (from left to right: deionized water, tap water and river water).

4. Conclusions

In conclusion, we have successfully designed and developed a novel and simple water-soluble polymer based fluorescent chemosensor PEGBHB by incorporating Schiff base derivative moiety into the hydrophilic polymer PEG. PEGBHB showed a remarkable turn-on fluorescence response for the detection of Al³⁺ with high selectivity and sensitivity in pure aqueous solution. PEGBHB maintained excellent fluorescence sensing ability to Al³⁺ over a wide pH range from 4 to 10, and the detection limit for Al³⁺ was calculated to be 9.67×10^{-9} M. In addition, the reversible fluorescence response of PEGBHB to Al³⁺ has been proved by the EDTA-titration experiments, and an INHIBIT molecular logic gate was constructed based on two inputs (Al³⁺ and EDTA) and one output. Furthermore, the test papers coated with PEGBHB have been fabricated facilely, which could act as a practical fluorescent chemosensor for on-site detection of Al³⁺ ions in real

water samples. This work provides a new strategy to develop Schiff base-based water-soluble chemosensors for metal ion detection in 100% aqueous solution.

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Highlights

- A novel and simple Schiff base-terminated water-soluble polymer PEGBHB has been successfully developed.
- PEGBHB exhibited high selectivity and sensitivity toward Al³⁺ as turn-on fluorescent chemosensor in 100% aqueous solution over a wide pH range.
- Test papers coated with PEGBHB have been fabricated facilely for on-site detection of Al³⁺ ions in real water samples.