

# A photochromism of spiropyran derivative based reversible colorimetric chemosensor for recognition of common trivalent metal ions (Al, Cr and Fe)

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A designed photochromism of spiropyran derivative, 1'-ethyl-3',3'-dimethyl-6-nitrospiro[4',5'-benzoindeole-2,2'-chromene] (BI-SP) as a chemosensor has been synthesized successfully. The as-prepared BI-SP as colorimetric sensor is sensitive to common trivalent metal ions ( $M^{3+}$ ), such as  $Al^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$ . The dye solution is colorless under visible-light irradiation and remains so even upon addition of the  $Al^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$  metal ions. However, the dye solution originally appears purple-red in the darkness and gradually turned yellow upon addition of the metal ions at room temperature. Moreover, the sensing abilities of the BI-SP toward the metal ions ( $Al^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$ ) were also investigated by UV-Vis absorption spectra and Infrared (IR) spectra. The results indicated that BI-SP could be applied as a sensitive and reversible colorimetric sensor for  $Al^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$ .

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**Keywords:** Spiropyran derivative, Metal ions recognition, Photochromism, Colorimetric chemosensor

## 1. Introduction

Trivalent metal ions ( $M^{3+}$ ) have important biological properties, and directly involved in the cell's function which is one of the key to critical control for  $M^{3+}$  levels [1]. Aluminum plays an important role in environment and biology because of its wide application in human activities [2-4]. The  $Al^{3+}$  toxicity not only hinders the growth of animal and floral, but also damages the human nervous system, causing diseases such as Parkinson's disease, osteomalacia and breast cancer [3, 5]. Cr, a necessary trace element to maintain the body's normal physiological function and tissue structure, it plays a special role in glucose and lipid metabolism in the body [6]. Excessive intake and deficiency of trivalent chromium can lead to a series of disease, such as genetic disease, diabetes, cardiovascular disease, uremia, blindness and even cancer [7-8]. As the most important component of human hemoglobin, iron is a critical element in the blood supply of oxygen and exchange of oxygen, but also the composition of many enzymes and redox enzyme activation agent [9]. However, the amount of iron ion needs to be efficiently controlled on account of that in the body, iron deficiency can lead to iron deficiency anemia, iron storage too much can cause many diseases such as heart disease, cancer, diabetes, bone disease and so on [10].

Therefore, the development of analytical method for the sensitive and selective determination of  $M^{3+}$  in samples analysis is highly noteworthy [11-14].

As an important kind of photochromic compounds, spiropyrans attracted much interest from both the mechanism of photochromism [15,16] and the potential applications of optoelectronic devices and sensors [17-21]. The mechanism of photochromism in spiropyrans (SP) is usually results from the light induced splitting of C-O bond, generating a ring-opened merocyanine (MC) that displays a wide range of absorption in the visible light region and the MC form can be changed back to the ring-closed SP form which is colorless by another irradiation [22]. In present work, a photochromic spiropyran derivative (BI-SP) based colorimetric probe of  $M^{3+}$  ( $Al^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$ ) was designed and synthesized. The reversible colorimetric chemosensor for  $Al^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$  were studied. The performance of metal recognition and its signaling molecule provides a reversible color sensor for  $M^{3+}$  detection under the laboratorial condition.

## 2. Experimental

### 2.1. Reagents and chemicals

The salts of the different cations ( $Cd^{2+}$ ,  $Al^{3+}$ ,  $Na^+$ ,  $Ca^{2+}$ ,

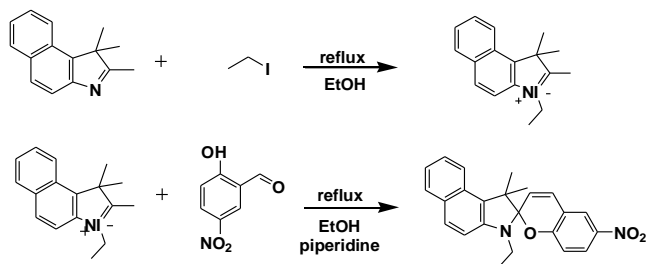
Mg<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, K<sup>+</sup>, Pb<sup>2+</sup>, Cr<sup>3+</sup>, Ba<sup>2+</sup>, Ag<sup>+</sup> and Fe<sup>3+</sup> ions) were obtained from Shanghai Chemical Reagents Company (China) and used without further purification.

## 2.2. Apparatus

Mass Spectrometry (MS) spectra were recorded with LCMS-2020 mass spectrometer with skipping the LC step. Nuclear magnetic resonance hydrogen (<sup>1</sup>H NMR) spectrum was recorded on a Bruker Avance III 300 MHz with tetramethylsilane (TMS) as internal reference and CDCl<sub>3</sub> as solvent. The IR spectra were performed on a PROTÉGÉ 460 spectrometer, using KBr discs. Absorption spectra were measured by UV-759 spectrophotometer.

## 2.3. Synthesis of 1-ethyl-2,3,3-trimethyl-4,5-benzo-3H-indole-1-ium iodide

A mixture of 2,3,3-trimethyl-4,5-benzo-3H-indole (6.28 g, 0.03 mol) and iodoethane (5.46 g, 0.035 mol) were refluxed with a magnetic stirring bar in 30 mL anhydrous ethanol (Scheme 1). After 48 h cool the reaction mass. Removed the solvent by vacuum distillation and washed the dried solid with ethyl acetate to afford target intermediate product (1-ethyl-2,3,3-trimethyl-4,5-benzo-3H-indole-1-ium iodide) in 59% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.16 - 8.04 (m, 3H), 7.82 - 7.66 (m, 3H), 4.89 (q, J = 7.4 Hz, 2H), 3.23 (s, 3H), 1.88 (s, 6H), 1.68 (t, J = 7.5 Hz, 3H). MS (ESI): m/z = 238.10 [M-I], calcd m/z=365.25 for C<sub>17</sub>H<sub>20</sub>IN.



Scheme 1. Synthetic route of BI-SP

## 2.4. Synthesis of BI-SP

1-ethyl-2,3,3-trimethyl-4,5-benzo-3H-indole-1-ium iodide (2.19 g, 0.006 mol) and piperidine (0.51 g, 0.006 mol) were dissolved in 20 mL distilled ethanol and stirred for 1 h. Then 5-nitrosalicylaldehyde (1.00 g, 0.006 mol) was added to the solution and the mixture was refluxed for 5 h (Scheme 1). About half of the solvent was removed by vacuum evaporation. After cooling down to room temperature, the precipitate was obtained by filtration. The solid product was further purified via recrystallization in dichloromethane for twice [23]. Finally, the yellow powder of the product was obtained in 10% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.02 (s, 1H), 8.02 - 7.97 (q, J = 2.7, 5.6

Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.6 Hz, 1H), 6.96 (d, J = 10.3 Hz, 1H), 6.69 (d, J = 9.4 Hz, 1H), 5.93 (d, J = 10.4 Hz, 1H), 3.37 (m, 2H), 1.63 (s, 3H), 1.34 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H). IR (KBr) cm<sup>-1</sup>: 1638 (C=O), 1512 (C=C), 1285 (C-N), 1016 (C-O-C), 848 (C-N, NO<sub>2</sub>). MS (ESI): m/z = 387.10 [M+H]<sup>+</sup>, calcd m/z=386.44 for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>.

## 3. Results and discussion

### 3.1. Photochromic behavior of BI-SP

Fig. 1 shows the photochromic behavior of BI-SP. Under visible-light irradiation, the solutions (40 μM) of BI-SP (ethanol: water = 4:1, V/V) were colorless with an absorption band at 350 nm. Under dark conditions, the solution changed obviously from colorless to purple-red, with a reduced absorption at 350 nm. A new band appeared at 542 nm corresponding to open form of BI-SP (BI-MC). The clear isobestic points disclosed that BI-SP converted to BI-MC when the solution of BI-SP underwent the photo-induced reaction. It's worthy of note that BI-MC could not be completely bleached back to BI-SP with visible-light irradiation, and the reversible conversion did not effected by the oxygen in the air [17].

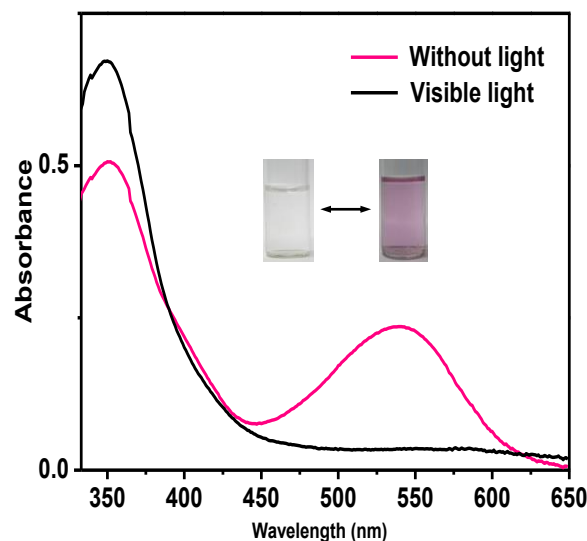


Fig. 1. Absorption changes of BI-SP (40 μM; in ethanol-water, 4:1, V/V)

### 3.2. Metal-induced activation of BI-SP

The UV-vis spectra of BI-SP (40 μM; in ethanol-water = 4:1, V/V) were studied in presence of a variety of cations (Cd<sup>2+</sup>, Al<sup>3+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, K<sup>+</sup>, Pb<sup>2+</sup>, Cr<sup>3+</sup>, Ba<sup>2+</sup>, Ag<sup>+</sup> and Fe<sup>3+</sup> ions) (10 mM) under visible-light irradiation. No significant change was found in color and absorption (Figs. 2A and 2B). However, under

dark conditions, after adding  $\text{Al}^{3+}/\text{Cr}^{3+}/\text{Fe}^{3+}$ , the color of the mixed solutions changed from purple-red to yellow and other solutions still remain purple-red (Fig. 2C). Further researches demonstrate that the absorption at 542 nm decreased and a new band at 445 nm appeared when  $\text{M}^{3+}$  was added (Fig. 2D). As presented in Fig. 3, the absorption intensity at 445 nm was increased and 542 nm was decreased significantly with addition of  $\text{M}^{3+}$ . Furthermore, the binding constant ( $K_a$ ) was estimated

using Benesi-Hildebrand plot, which was achieved by absorbance ( $A_0 - A$ , at 542 nm) changes of consequent titration against  $\text{M}^{3+}$  (Fig. 4). Above phenomenon descriptions were found that in dark, the new band at 445 nm was probably resulted from the complex of  $\text{M}^{3+}$ -BI-MC. Photostability experiments shows that in darkness the complex of  $\text{M}^{3+}$ -BI-MC was stable, and no marked change was found when the yellow solution was kept for several days.

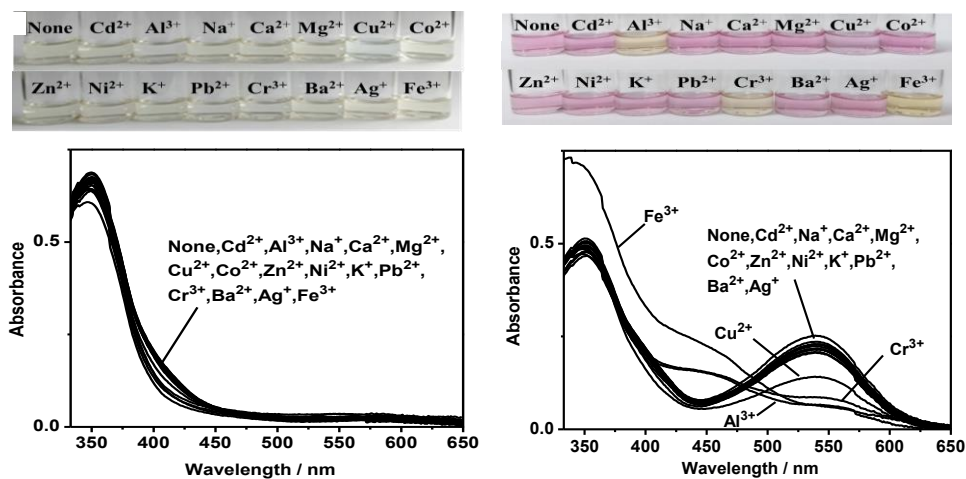


Fig. 2. Absorption change of BI-SP ( $40 \mu\text{M}$ ; in ethanol-water, 4:1, V/V) with addition of different metal ions ( $10 \text{ mM}$ , in water). (A) Photographs of the color with visible-light irradiation; (B) Absorbance with visible-light irradiation; (C) Photographs of the color without light irradiation; (D) Absorbance without light irradiation

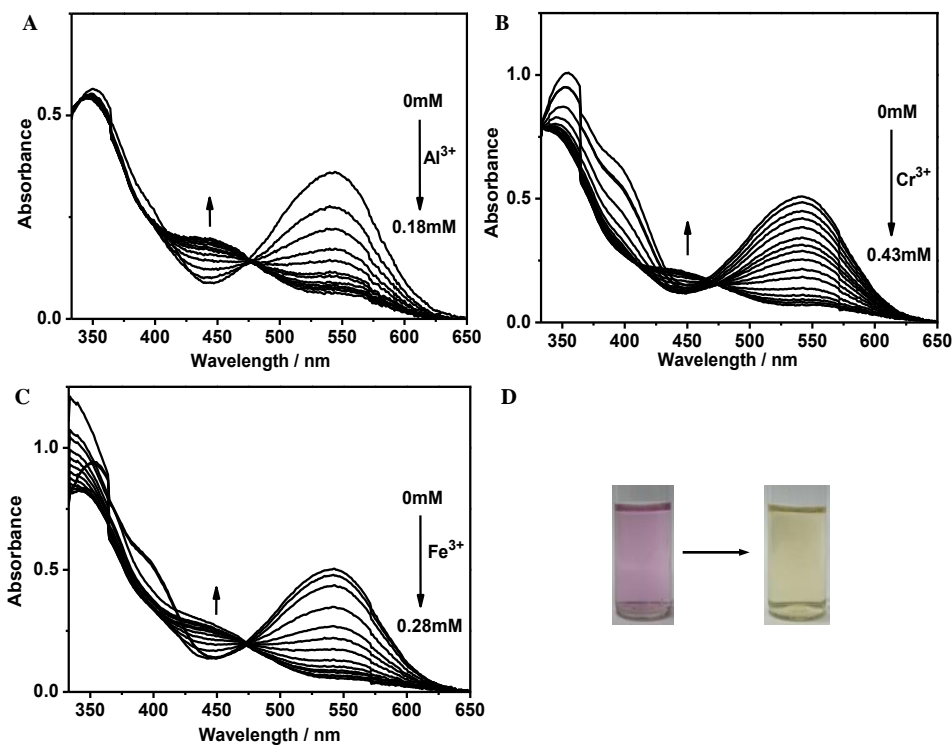


Fig. 3. Absorption spectra of the BI-MC ( $40 \mu\text{M}$ ; in ethanol-water, 4:1, V/V) solution with increasing amounts of  $\text{M}^{3+}$  ( $10 \text{ mM}$ , in water). (A)  $\text{Al}^{3+}$ ; (B)  $\text{Cr}^{3+}$ ; (C)  $\text{Fe}^{3+}$  and (D) Photographs of the color

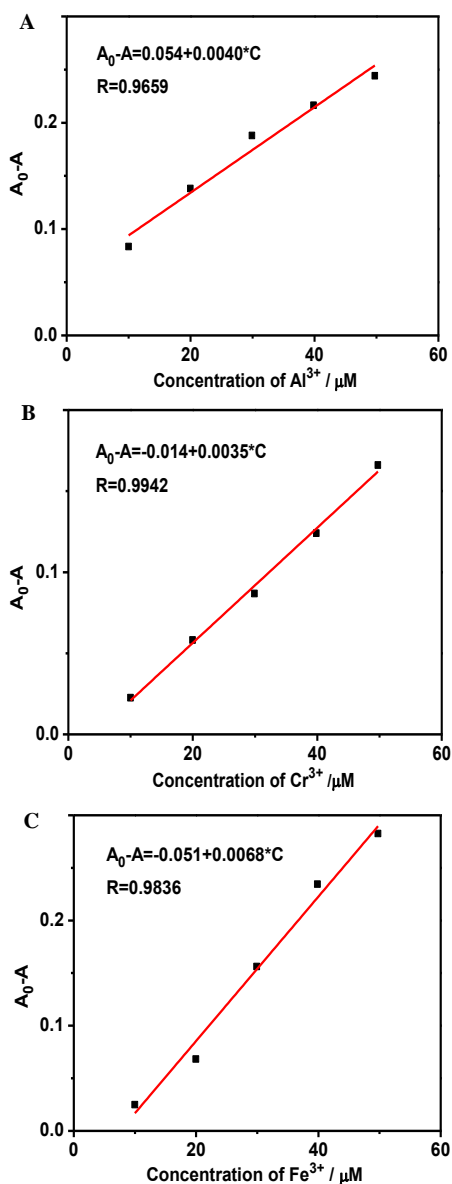


Fig. 4. Concentration responses of the BI-MC ( $\lambda = 542$  nm) and the Benesi-Hildebrand plot. (A)  $\text{Al}^{3+}$ ; (B)  $\text{Cr}^{3+}$ ; (C)  $\text{Fe}^{3+}$

### 3.3. Complexation mechanism of $\text{M}^{3+}$

To further investigate  $\text{M}^{3+}$  ( $\text{Al}^{3+}/\text{Cr}^{3+}/\text{Fe}^{3+}$ ) binding properties of the probe, IR spectra of BI-MC and of the  $\text{M}^{3+}$ -BI-MC complex were recorded (Fig. 5D). Near the characteristic stretching vibration peak of carbonyl ( $\text{C}=\text{O}$ ) at  $1637$   $\text{cm}^{-1}$  appeared a new peak at  $1617$   $\text{cm}^{-1}$  in the presence of  $\text{M}^{3+}$ , meanwhile the weak stretching vibration peak of C-N in tertiary amino at  $1285$   $\text{cm}^{-1}$  disappeared, indicating that the  $\text{C}=\text{O}$  and C-N of the BI-MC units were involved in the recognition of  $\text{M}^{3+}$  [24]. Binding stoichiometry between BI-MC and  $\text{M}^{3+}$  was determined using the method of continuous variations (Job's plot) in dark. The stoichiometry of the  $\text{Al}^{3+}/\text{Cr}^{3+}/\text{Fe}^{3+}$ -BI-MC complex was estimated to be 1:1 (Fig. 5). According to the above discussions, the complexation mechanism of  $\text{M}^{3+}$  with BI-MC is proposed and shown in Scheme 2.

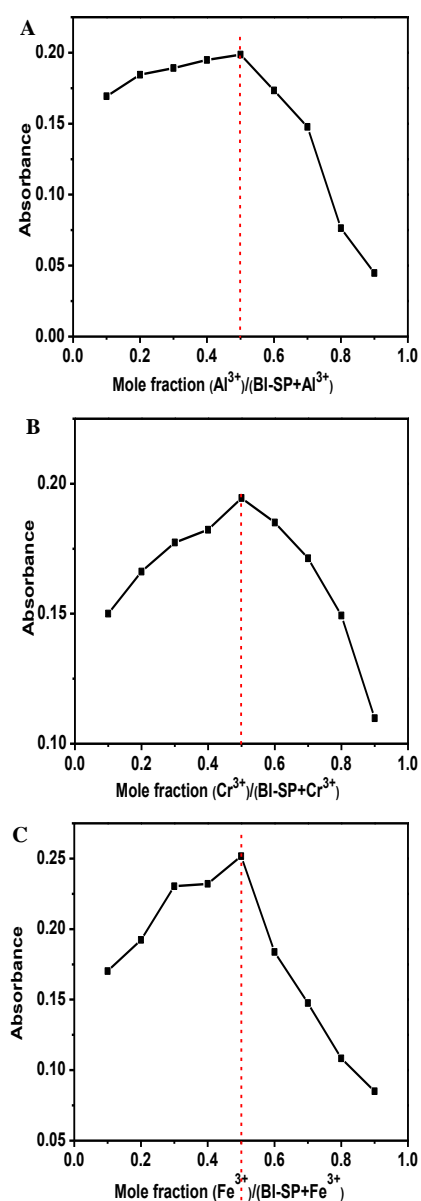
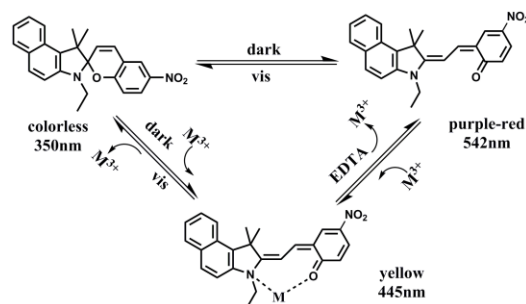


Fig. 5. Job plot for the complexation of BI-MC with  $\text{M}^{3+}$  ions ( $\lambda = 445$  nm) in ethanol-water solution. The total concentration of BI-MC and  $\text{M}^{3+}$  is  $40$   $\mu\text{M}$ . (A)  $\text{Al}^{3+}$ ; (B)  $\text{Cr}^{3+}$ ; (C)  $\text{Fe}^{3+}$ ; (D) Comparison of the IR spectral data for BI-MC and its  $\text{M}^{3+}$  ion complex. Black, BI-MC; Red,  $\text{Al}^{3+}$ -BI-MC; Blue,  $\text{Cr}^{3+}$ -BI-MC; Green,  $\text{Fe}^{3+}$ -BI-MC



Scheme 2. Isomerization of open form and closed form and a possible mechanism of complexation with  $\text{M}^{3+}$

### 3.4. Colorimetric detection of $M^{3+}$

To investigate the utility of BI-MC as an ion-selective chemosensor for  $M^{3+}$  ( $Al^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$ ), the competition experiments were conducted in darkness in the presence of  $Al^{3+}$ / $Cr^{3+}$ / $Fe^{3+}$  mixed with other metal ions, respectively. The specific content was conducting in the presence of 1 equiv.  $Al^{3+}$  with 1 equiv. other metal ions, 1 equiv.  $Cr^{3+}$  with 4 equiv. other metal ions and 1 equiv.  $Fe^{3+}$  with 2 equiv. other metal ions, respectively. The results are shown in Fig. 6. It was found that no obvious absorption change was found in the presence and absence of other metal ions. The consequence revealed that the recognition of  $Al^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$  by BI-MC was not under the influence of other metal ions. The above results indicated that as a colorimetric probe for  $Al^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$ , the BI-MC has a good anti-jamming ability.

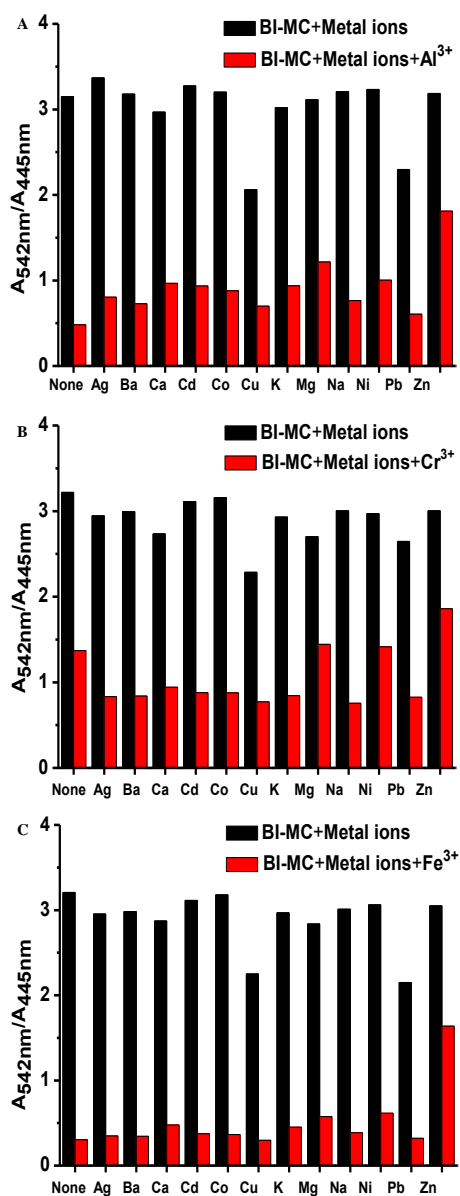


Fig. 6. Absorption spectra of  $M^{3+}$ -BI-MC complex with different metal ions (10 mM, in water). (A)  $Al^{3+}$ -BI-MC; (B)  $Cr^{3+}$ -BI-MC; (C)  $Fe^{3+}$ -BI-MC

### 3.5. Reversibility of BI-SP for sensing $M^{3+}$

The reversibility experiment was conducted for 3 cycles by alternately adding  $M^{3+}$  ( $Al^{3+}$ / $Cr^{3+}$ / $Fe^{3+}$ ) and Ethylene Diamine Tetraacetic Acid (EDTA) [25] in dark. As shown in Fig. 7, according to the strong affinity adsorption of metal ions on EDTA, the color of  $M^{3+}$ -BI-MC complex changed from yellow to purple-red and the absorbance of  $M^{3+}$ -BI-MC turned off by introduction of EDTA. The absorption intensity decreased at 445 nm could be observed with adding EDTA (as shown in inset of Fig. 7). After addition of  $Al^{3+}$ / $Cr^{3+}$ / $Fe^{3+}$ , the purple-red solution turned back and the signals recovered more than 60% for each cycle. The results of the experiment confirmed that BI-SP has a better reproducibility in the sensing process and could be used as a reversible chemosensor in darkness.

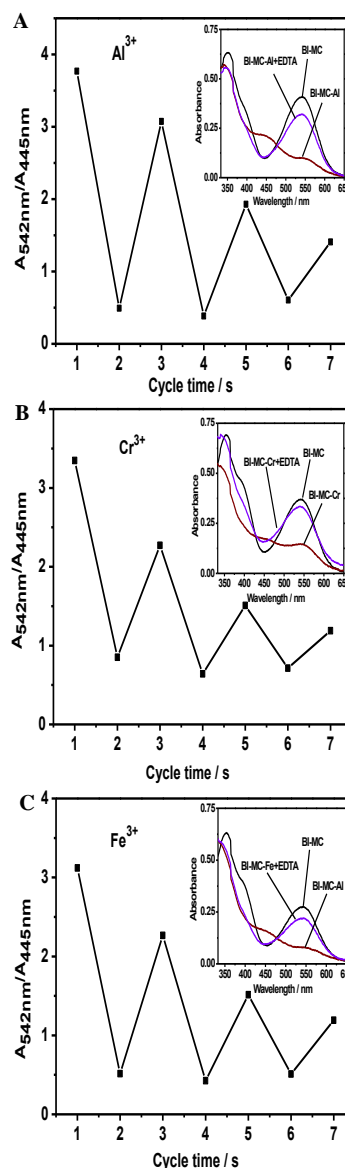


Fig. 7. Absorbance responses of BI-MC by alternated adding  $M^{3+}$  and EDTA. The cyclic time is the number of alternating  $M^{3+}$  and EDTA cycles. Insets: UV-vis absorption of the BI-MC in the presence of  $M^{3+}$  with EDTA. (A)  $Al^{3+}$ ; (B)  $Cr^{3+}$ ; (C)  $Fe^{3+}$

#### 4. Conclusions

In summary, a metal recognition sensor for  $M^{3+}$  ( $Al^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$ ) has been built. The activation of C-O bond in BI-SP and the formation of C=O in BI-MC can be induced in darkness, which led to the conversion of colorless (BI-SP form) to purple-red (BI-MC form), and happened complexation reaction with  $M^{3+}$  ( $Al^{3+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$ ). Accompanied by the conversion of colored (purple-red) form to yellow ( $M^{3+}$ -BI-MC form), it could be used as a “naked eye” indicator for  $M^{3+}$ . The BI-MC spectral responses toward  $M^{3+}$  ( $Al^{3+}/Cr^{3+}/Fe^{3+}$ ) were robust over competitive ions and reversible by introducing EDTA. This property of molecules provides a reversible colorimetric sensor for trivalent metal ion detection.

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