Molecular Crystals and Liquid Crystals

Highly Selective Colorimetric Signaling of Iron Cations Based on Fluoran Dye

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Highly Selective Colorimetric Signaling of Iron Cations Based on Fluoran Dye

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*A highly selective colorimetric chemosensor based on fluoran dye for iron cations, 2′-anilino-3′methyl-6′-dibuthylamino-N-(2′-(2″-hydroxybenzylideneamino)ethyl) iso-indolin-1-one-fluoran (***5***), was designed and synthesized. The chemical structures of all the intermediates and fluoran dye* **5** *were characterized by* ^{1}*H-NMR,* ^{13}*C-NMR, MS and elemental analysis. And its sensing behavior toward metal ions was investigated by UV-visible absorption spectroscopes. The fluoran dye* **5** *chemosensor showed an extreme selectivity for* Fe^{2+} *and* Fe^{3+} *in acetonitrile solution. Whereas other ions including* Mg^{2+}, Pd^{2+}, Ni^{2+}, Hg^{2+}, Cd^{2+}, Ag^{+}, Cu^{2+}, Zn^{2+} *and* Al^{3+} *induced basically no spectral change, which constituted a* Fe^{2+} *highly sensitive and selective colorimetric chemosensor from colorless to black by "naked eyes." Spectral responses at* $\lambda max = 653\,nm$ *reveals that dye* **5** *can function as OR logic gate with* Fe^{2+} *and* Fe^{3+} *as input variables.*

Keywords: chemosensor; colorimetric; fluoran dye; iron cation; selective; sensitive

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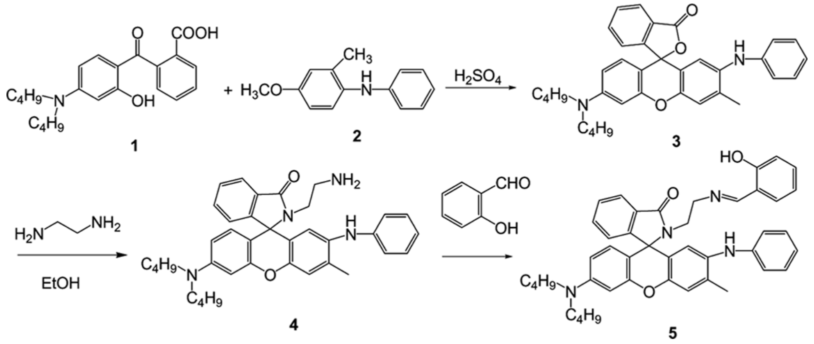
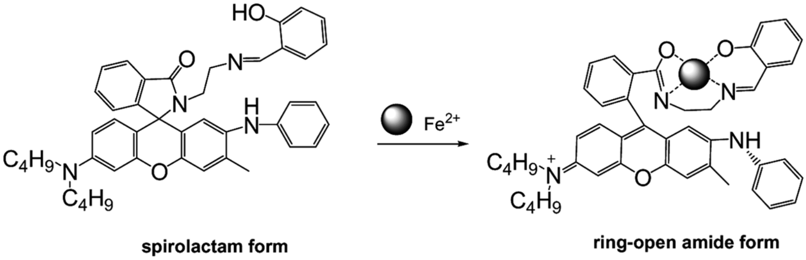
INTRODUCTION

The development of sensitive chromogenic probes has been receiving much attention in recent years because of the potential application in clinical biochemistry and environment. There are already many chromogenic chemosensors developed for selective recognition of different species so far due to their high selectivity, sensitivity and simplicity [1–3]. Iron is one of the most important elements among heavy metals for metabolic processes, being indispensable for plants and animals and therefore it is extensively distributed in environmental and biological materials [4]. If iron concentration exceeds the normal level it may become potential health hazard. Iron deficiency leads to anemia. Therefore, it is important to explore new chromogenic chemosensors for selective detection of Iron. Over the past years, some examples for iron detection, including chromogenic [5] and fluorescent [6–10] chemical sensors, electrochemical devices [11] have been reported. Currently, colorimetric sensors are popular due to their capability to detect analyses by naked eye without resorting to any expensive instruments [12]. Therefore, to develop simple-to-use and naked eye diagnostic tool for selective detection of iron is a hot and interesting topic.

Fluoran dyes have the remarkable feature of giving a wide variety of colors depending on their substituents [13]. In particular, fluoran type dyes are very important in theirs ability to yield singly black color on the addition of an acidic compound. The fluoran dyes are only applied for use in thermosensitive recording paper. No one almost care about the fluoran chromophore as metal recognization chromophore. From the fluoran dyes parents structures can be seen that it is closely resembles the Rhodamine dye. Rhodamine is a dye used extensively as a chemosensor reagent due to its excellent photophysical properties,



SCHEME 1 The synthesis routes of fluoran dye **5**.



SCHEME 2 Proposed binding mode and color change of fluoran dye **5** with Fe^{2+}.

such as long absorption and emission wavelengths elongated to visible region, high absorption coefficient and high fluorescence quantum yield [14]. Various rhodamines fluorescent probes for heavy metal have been developed [15,16]. To be their enlightened, we designed and synthesized a highly selective chemosensor based on fluoran dye **5** for iron ion as shown in Scheme 1.

To the best of our knowledge, there have no report on fluoran dye as colorimetric chemosensor that show the black color for highly sensitive and selective Iron metal cations.

EXPERIMENTAL

Melting points were determined using an Electrothermal IA 900 and are uncorrected. Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. UV-visible absorption spectra were measured on an Agilent 8453 spectrophotometer. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using electron energy of 70 eV and the direct probe EI method. ^{1}H NMR, ^{13}C NMR spectra were recorded using a Varian Inova 400 MHz FT-NMR spectrometer with TMS as internal standard.

Fluoran Dye 3

Fluoran dye 3 was synthesized according to the literature method [17]. Yield: 58%, m.p. 187°C; mass (m/z) 532(M^+); ^{1}H NMR (400 MHz, DMSO-d6): δ (ppm) 7.93 (d, $J = 7.56$, 1H), 7.76 (t, $J = 7.56$, 1H), 7.66 (t, $J = 7.36$, 1H), 7.41 (s, 1H), 7.26 (t, $J = 7.84$, 1H), 7.22 (s, 1H), 6.99 (t, $J = 7.84$, 2H), 6.62 (t, $J = 7.04$, 1H), 6.55 (d, $J = 7.6$, 2H), 6.49 (d, $J = 8.08$, 2H), 6.43 (s, 1H), 6.41 (d, $J = 9.08$, 1H), 3.25 (t, $J = 7.6$, 4H), 2.21 (s, 3H), 2.07 (s, 1H), 1.48 (m, 4H), 1.29 (m, 4H), 0.87 (t, 6H).

^{13}C NMR (400 MHz, DMSO-d6): δ (ppm), 13.78, 17.84, 19.63, 28.86, 30.59, 49.89, 83.55, 96.98, 104.1, 108.5, 114.63, 116.99, 118.32, 118.53, 119.49, 123.92, 124.45, 126.24, 128.59, 128.77, 129.94, 134.92, 135.40, 136.85, 145.25, 146.58, 149.63, 152.43, 152.49, 168.66.

Fluoran Dye 4

Fluoran dye **3** (1.0 g, 1.9 mmol) was dissolved in 100 mL of ethanol, followed by addition of ethylenediamine (2.0 mL, 24.7 mmol). The reaction mixture was refluxed for 12 hours. After cooling to the room temperature, the solvent was evaporated in vacuo. The CH_2Cl_2 and water (200 mL) were added, and the organic layer was separated, washed twice with water and dried over anhydrous sodium sulfate. After filtration of sodium sulfate, the solvent was removed under reduced pressure. Then 1 M HCl (50 ml) was added to the solid in the flask to generate a clear red solution After that, 2 M NaOH was added slowly with stirring until the pH of the solution reached 7–8. The resulting pink solid was filtered and obtained 1.1 g of dye **4**.

Yield: 91%, m.p. 223–225°C; mass (m/z) 574 (M^+); ^{1}H NMR (400 MHz, DMSO-d6): δ (ppm) 7.72 (d, $J = 7.08$, 1H), 7.54 (t, $J = 6.8$, 1H), 7.48 (t, $J = 7.32$, 1H), 7.16 (s, 1H), 7.04 (d, $J = 7.32$, 1H), 6.99(d, $J = 7.84$, 2H), 6.61 (t, $J = 7.32$, 1H), 6.49 (d, $J = 7.84$, 2H), 6.38 (s, 1H), 6.33 (d, $J = 7.56$, 4H), 3.42 (m, 2H), 3.22 (t, $J = 6.8$, 4H), 3.0 (m, 2H), 2.17 (s, 3H), 2.08 (s, 1H), 1.48 (m, 4H), 1.30 (m, 4H), 0.9 (t, 6H).

^{13}C NMR (400 MHz, DMSO-d6): δ (ppm), 13.89, 17.76, 18.59, 19.69, 25.24, 28.95, 32.14, 43.58, 49.88, 63.89, 97.11, 103.91, 108.41, 114.48, 117.35, 118.32, 118.18, 118.60, 119.70, 122.38, 123.57, 128.38, 128.86, 130.14, 132.81, 133.81, 136.58, 145.43, 146.32, 146.86, 152.39, 153.35, 167.10.

Fluoran Dye 5

Fluoran dye **4** (0.2 g, 0.35 mmol) was dissolved in 15 mL absolute ethanol. An excessive 2-hydroxybenzaldehyde (0.171 g, 1.4 mmol) was added then the mixture was refluxed for 6 h. After that, the solution was cooled (concentrated to 10 mL) and allowed to stand at room temperature overnight. The precipitate was filtered and washed 3 times with 10 mL cold ethanol to obtain the crude product. Then, the crude product was purified by column chromatography on silica gel ($CHCl_3$/EtOH: 8/1 (v/v)) to give 0.14 g white powder.

Yield: 59%, m.p. 169–171°C; mass (m/z) 678 (M^+); ^{1}H NMR (400 MHz, DMSO-d6): δ (ppm) 12.93 (s, 1H), 8.02 (s, 1H), 7.72 (d, $J = 7.56$, 1H), 7.55 (t, $J = 7.6$, 1H), 7.50 (t, $J = 7.32$, 1H), 7.32 (s, 1H), 7.18 (d, $J=5.32$, 1H), 7.09 (d, $J=7.32$, 1H), 6.95 (t, $J=7.60$, 2H), 6.81 (t, $J=7.84$, 2H), 6.58 (t, $J=5.32$, 1H), 6.48 (d, $J=8.36$, 2H), 6.36 (s, 1H), 6.29 (d, $J=9.8$, 2H), 3.4 (m, 2H), 3.26 (m, 2H), 3.23 (t, $J=7.6$, 4H), 2.17 (s, 3H), 2.08 (s, 1H), 1.48 (m, 4H), 1.29 (m, 4H), 0.89 (t, 6H).

^{13}C NMR (400 MHz, DMSO-d6): δ (ppm), 13.82, 17.78, 20.49, 28.91, 40.47, 49.86, 56.63, 63.97, 97.16, 97.43, 103.92, 108.44, 114.32, 116.32, 117.20, 118.19, 118.36, 118.48, 118.66, 119.73, 122.51, 123.62, 128.42, 128.57, 128.78, 130.10, 131.56, 132.20, 132.95, 133.97, 136.68, 145.30, 147.0, 148.97, 152.55, 152.96, 160.32, 166.27, 167.12, 173.71.

Anal. Cald. for $C_{44}H_{46}N_4O_3$: C, 77.84; H, 6.83; N, 8.25 Found; C, 77.11; H, 7.14; N, 8.16%.

RESULTS AND DISCUSSION

Fluoran dye **5** was synthesized according to the Scheme 1. At first, the intermediate fluoran dye **3** was synthesized from 2-(4-(dibutylamino)-2-hydroxybenzoyl) benzoic acid **1** and 4-methoxy-2-methyl-N-phenylbenzenamine **2** as starting materials using H_2SO_4 as catalyst. Then, fluoran dye **3** was transferred to fluoran dye **4** via condensation reaction. At last, fluoran dye **5** was prepared from fluoran dye **4** and 2-hydroxybenzaldehyde by Schiff's base condensation.

The recognition between fluoran dye **5** and different metal cations were investigated by UV-vis spectroscopy in the CH_3CN solution. The solution of fluoran dye **5** is at a concentration of 1.0×10^{-5} mol/L. From the absorption spectrum of fluoran dye **5** in the CH_3CN solution, it was not found that an absorption band appeared in visible region, fluoran dye **5** solution is colorless. Variation of absorption spectra of fluoran dye **5** upon addition of different metal cations including Cd^{2+}, Mg^{2+}, Pd^{2+}, Hg^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, H^+, alkali metal and alkaline earth metal cations, are shown in Figures 1 and 2. Figure 1 show the UV-vis spectra of fluoran dye **5** (1.0×10^{-5}mol · L^{-1}) upon addition of ClO_4^- salt of X = Cd^{2+}, Mg^{2+}, Pd^{2+}, Hg^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, H^+ (10 equiv) in CH_3CN solution. The absorption maximum show no obvious change upon the addition of the metal ions Cd^{2+}, Mg^{2+}, Pd^{2+}, Hg^{2+}, Ni^{2+}, and H^+. A small increase at 565 nm was observed in the presence of Cu^{2+}. While upon addition of Fe^{2+}, we also found new absorption bands appeared including the absorption at wavelength peaked at 433 nm and 653 nm. The color changed from colorless to black. The color of 433 nm is complementary to the color of 653 nm. As a result, a black color hue can be obtained by use of only one chromophore. While upon addition of Fe^{3+}, we also found new absorption bands appeared including the absorption at wavelength peaked at 640 nm, which is similar to Fe^{2+} (Fig. 1). Figure 2 show the

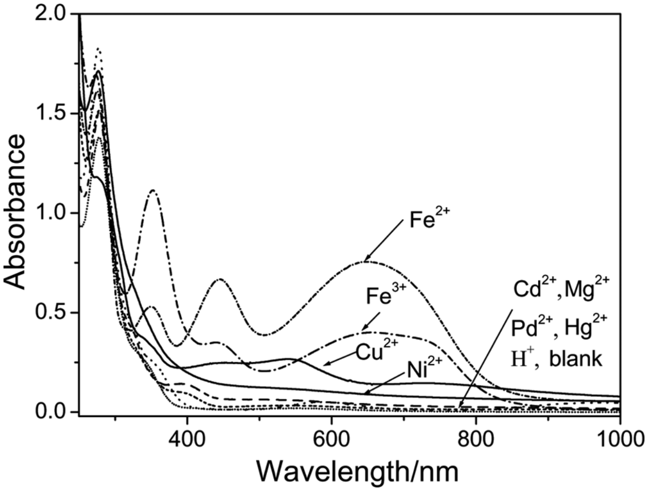


FIGURE 1 The UV-vis spectra of fluoran dye **5** ($1.0 \times 10^{-5}\,\text{mol} \cdot \text{L}^{-1}$) upon addition of ClO_4^- salt of $X = H^+$, Cd^{2+}, Mg^{2+}, Pd^{2+}, Hg^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+} (10 equiv) in CH_3CN solution.

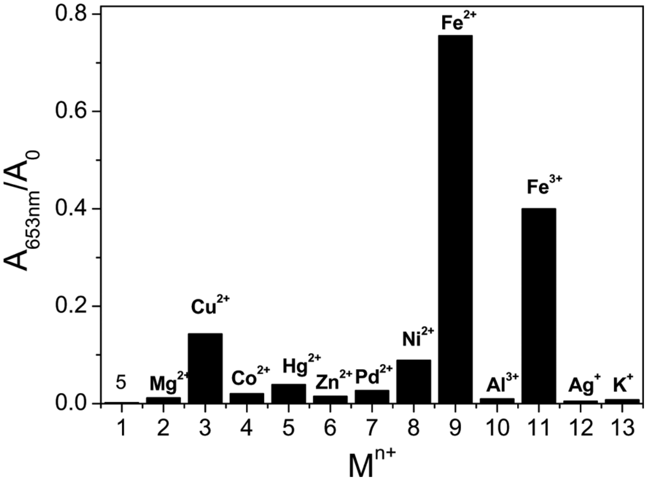


FIGURE 2 The absorbance response of fluoran dye **5** to 1.0 μM of various cations in CH_3CN solution. The bar represent the absorbance intensities at 653 nm ($A_{653\,nm}$) over the absorbance intensity of the blank dye **5** solution. From left to right: 1. no cation (blank: dye 5), 2. Mg^{2+}, 3. Cu^{2+}, 4. Co^{2+}, 5. Hg^{2+}, 6. Zn^{2+}, 7. Pd^{2+}, 8. Ni^{2+}, 9. Fe^{2+}, 10. Al^{3+}, 11. Fe^{3+}, 12. Ag^+, 13. K^+.

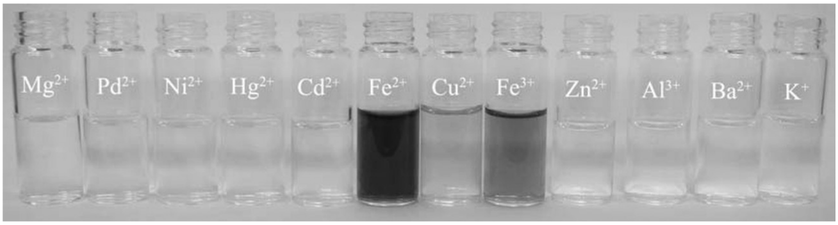


FIGURE 3 The color changes of fluoran dye **5** ($1.0 \times 10^{-5}\,\mathrm{mol \cdot L^{-1}}$) upon addition of ClO_4^- salt of X = Mg^{2+}, Pd^{2+}, Ni^{2+}, Hg^{2+}, Cd^{2+}, Fe^{2+},Cu^{2+}, Fe^{3+}, Zn^{2+}, Al^{3+}, Ba^{2+}, K^+ in CH_3CN solution (10 equiv).

absorbance intensities at 653 nm ($A_{653\,nm}$) over the absorbance intensity of the blank fluoran dye **5** solution. With the addition of Fe^{2+}, the absorbance intensity of fluoran dye **5** at 653 nm was increased. With the addition of the other metal ions, the absorbance intensity of fluoran dye **5** at 653 nm was almost no evidently changed. While upon addition of Fe^{3+}, we also found new absorption bands appeared including the absorption at wavelength peaked at 650 nm, which is similar to Fe^{2+}. Figure 3 show the color change photographs of fluoran dye **5** ($1.0 \times 10^{-5}\,\mathrm{mol \cdot L^{-1}}$) upon addition of ClO_4^- salt of X = Mg^{2+}, Pd^{2+}, Ni^{2+}, Hg^{2+}, Cd^{2+}, Fe^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+}, Al^{3+}, Ba^{2+}, K^+ in CH_3CN solution (10 equiv).

These results indicate that fluoran dye **5** shows sensing ability for Iron cations (Scheme 2). It has high-sensitivity and selectivity toward Fe^{2+} ions. The dependence of absorption spectroscopy of fluoran dye **5** in the solution on the concentration of Fe^{2+} was investigated by the UV titration method. With the addition of Fe^{2+}, the 290 nm was decreased accomplished with the increase of the wavelength at 443 nm and 653 nm. An isosbestic point in the titration curves shows new specie appeared with the addition of Fe^{2+}, which could be assigned to the formation of the Fe^{2+} complex of fluoran dye **5** as shown in Figure 4. Figure 4 set shows the absorbance intensities change at 443 nm ($A_{443\,nm}$) and 653 nm ($A_{653\,nm}$) over the absorbance intensity of the blank fluoran dye **5** solution. With the addition of Fe^{2+}, the absorbance intensity of fluoran dye **5** at 443 nm and 653 nm was all increased. So the color of solution gradually became black from the colorless. Actually, an obvious color change from colorless to black was observed by the naked eyes.

These behaviours may be conveniently described using logic notation [18,19]. The input signals are Fe^{2+} and Fe^{3+}. The presence of Fe^{2+} and Fe^{3+} can be characterized by the typical absorption band

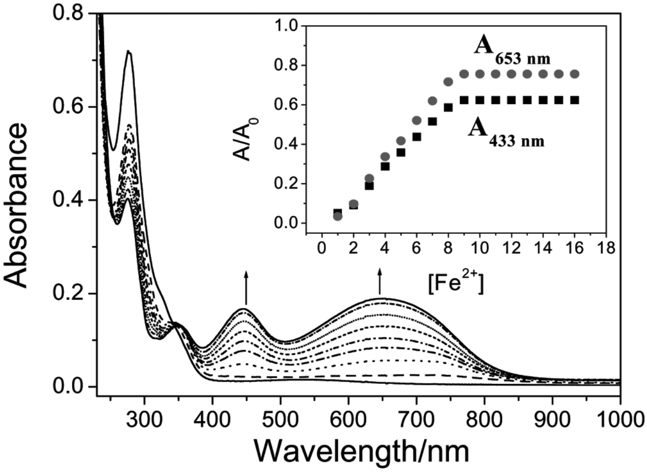


FIGURE 4 The absorbance spectra of fluoran dye **5** in the presence of Fe^{2+} in CH_3CN solution. The Fe^{2+} concentration is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 μM, respectively. Inset: absorbance at 433 nm and 653 nm change with Fe^{2+} concentration change.

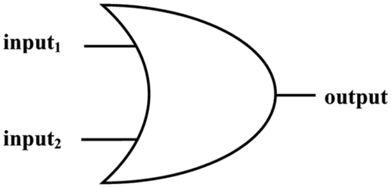
at 653 nm. The absorption band with λmax = 653 nm can be considered as output signals: output = 0 when the absorbance at 653 nm is low (<0.4); output = 1 when the absotbance at 653 nm is high (>0.4).

TABLE 1 (a) Truth Table; (b) Physical Electronic Symbol of 2-Input OR Logic Gate

(a)

Input$_1$ (Fe^{2+})	Input$_2$ (F^{3+})	Output (A_{653})
0	0	0 (low, <0.4)
0	1	1 (high, >0.4)
1	0	1 (high, >0.4)
1	1	1 (high, >0.4)

(b)



Due to the dependence of the absorption intensity of adding Fe^{2+} and Fe^{3+}, it is possible to mimic the function of the truth table of an OR gate (see Table 1).

CONCLUSION

In conclusion, a new chromogenic chemosensor based on fluoran dye derivative was developed. It shows a good selectivity and sensitivity for Fe^{2+} and Fe^{3+}. An obvious color change from colorless to black was observed by the naked eyes, in other words, a colorimetric signal could be easily read by the naked eye without resort to any spectroscopic instrumentation. This is a very simple and effective method for detecting the Iron cations.

These responses follow the truth table of an OR logic gate.

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