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# A fluorescent color/intensity changed chemosensor for Fe<sup>3+</sup> by photo-induced electron transfer (PET) inhibition of fluoranthene derivative

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# ABSTRACT

A fluorescent color/intensity changed fluoranthene derivative chemosensor for Fe<sup>3+</sup> has been prepared and confirmed by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, HRMS, and crystal data, which displays a high selectivity and antidisturbance for Fe<sup>3+</sup> among environmentally and biologically relevant metal ions. Fluorescence studies show that fluorescent emission peak blue shifts about 100 nm with fluorescent intensity enhancing 75-fold, indicating a Fe<sup>3+</sup>-selective dual-emission behavior. Further study demonstrates the detection limit on fluorescence response of the sensor to Fe<sup>3+</sup> is down to  $10^{-7}$  M range. The fluorescence signals of chemosensor can be restored with *o*-phenanthroline, showing the binding of chemosensor and Fe<sup>3+</sup> is really chemically reversible.

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# 1. Introduction

The design of fluorescent chemosensors for various metal ions is an important area because of their fundamental role in medical, environmental and biological applications [1-4]. Up to now, a number of fluorescent sensors for transition metal ions, such as, Cu<sup>2+</sup> [5–12], Zn<sup>2+</sup> [13–22], Pb<sup>2+</sup> [23–25], and Hg<sup>2+</sup> [26–30] have been reported. Surprisingly, the reported Fe<sup>3+</sup>-selective fluorescent sensors are relatively rare [31–41] despite the widespread applications of Fe<sup>3+</sup>. Fe<sup>3+</sup> is a biologically essential element and provides the oxygen-carrying capacity of heme and acts as a cofactor in many enzymatic reactions [42]. Fe<sup>3+</sup> plays an important role in many biological processes at the cellular level ranging from oxygen metabolism to DNA and RNA synthesis [43]. Iron is indispensable for most organisms, and both its deficiency and excess result in various pathological disorders [44]. In addition, there are very rare examples those that exhibit selective Fe<sup>3+</sup>-amplified emission [31–36] though it is generally believed that chemosensors with fluorescence enhancement are much more efficient when interacting with analytes. Therefore, there is an urgent need to develop fluorescent  $Fe^{3+}$ -chemosensors, especially those that exhibit selective  $Fe^{3+}$ -amplified emission.

Therefore, we are motivated to design and synthesize a novel molecular system which can sense Fe<sup>3+</sup> against environmental and biological samples. Because polyphenyl derivatives are easy to synthesize and their structures are relatively simple, they may be ideal molecular chemosensors [45]. It is a pity that there are very rare examples about such compounds applied in the detection of metal ions except our previous work about two polyphenyl derivatives (compounds 1 and 2 in Fig. 1) in the detection of  $Zn^{2+}$ ,  $Cu^{2+}$ , and  $Fe^{3+}$  [46,47]. As for compound **1**,  $Zn^{2+}$  made the rotation of C–C among the aromatic rings inhibited while  $Cu^{2+}$  made electron and/or energy transfer happen, which resulted in the emission intensity of 1 changing differently [46]. As for compound **2**, the paramagnetic property and unfilled d shell of  $Fe^{3+}$  led to the possibility of electron and/or energy transfer with organic fluorophores opening a non-radiative deactivation channel, resulting in the emission intensity of 2 decreasing. If the electrophilic group pyridyl ring was replaced with electron-donating group aniline, that is, what influence on the emission spectra of 4-



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(7,10-diphenylfluoranthen-8-yl)benzenamine (**3**) (compound **3** in Fig. 1 and 2) will be when different metal ions were added into the solution of compound **3**? This question was answered in this manuscript.

#### 2. Experiment

#### 2.1. Materials and methods

All chemicals were purchased from commercial suppliers and used without further purification. All reactions were performed under an argon atmosphere with the solvents purified with standard methods.

<sup>1</sup>H and <sup>13</sup>C-NMR spectra were recorded on a Bruker 400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane (TMS) as the internal standard. Mass spectra were obtained on high resolution mass spectrometer (IonSpec4.7 Tesla FTMS-MALDI/DHB).

All spectral characterizations were carried out in HPLC-grade solvents at 20 °C within a 10 mm quartz cell. UV–vis absorption spectra were measured with a TU-1901 double-beam UV–vis Spectrophotometer, and fluorescence spectra were determined on a Hitachi F-4500 spectrometer. The fluorescence quantum yield was measured at 20 °C with quinine bisulfate in 1 M H<sub>2</sub>SO<sub>4</sub> ( $\Phi_{\rm fr} = 0.546$ ) selected as the reference.

#### 2.2. Synthesis of 4-dimethylsilanylethynyl-phenylamine (4)

Triethylamine (2.5 mL), *p*-iodoaniline (1.0237 g, 467.4 mmol), Cul (0.0901 g, 0.473 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.1651 g, 0.235 mmol), and ethynyl-trimethyl-silane (0.8 mL, 562 mmol) were added in THF under argon atmosphere and the above mixture was refluxed for 5 h. The crude product was obtained by reduced pressure distillation and the final product (654.9 mg) was gained by column chromatography over silica gel column using dichloromethane/ light petroleum (2:1) as eluent. The yield was 74.5%. Compound 4dimethylsilanylethynyl-phenylamine was directly used in the formation of 4-ethynyl-phenylamine without characterization.

#### 2.3. Synthesis of 4-ethynyl-phenylamine (5)

4-dimethylsilanylethynyl-phenylamine (0.9078 g, 479.5 mmol) and methanol solution of KOH (0.4374 g/8.2 mL) were added in 30 mL THF and the mixture was stirred for 5 h at room temperate. The crude product was obtained from the concentration in vacuum and extraction with ethyl acetate. The final product (280.5 mg) was obtained by column chromatography over silica gel column using dichloromethane/light petroleum (2:1) as eluent. The yield was 50%. Characterization of compound 4-ethynyl-phenylamine: <sup>1</sup>H-NMR:  $\delta_{\rm H}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.30 (m, 2H), 6.61 (m, 2H), 3.83 (s, 2H), and 2.98 (s, 1H). <sup>13</sup>C-NMR:  $\delta_{\rm C}$  (100 MHz, CDCl<sub>3</sub>): 147.04, 133.48, 114.60, 111.32, 84.42, and 74.92.



Fig. 1. Molecular structures of compounds 1, 2, and 3.



Fig. 2. X-ray crystal structure of 3. Hydrogen atoms are omitted for clarity.

#### 2.4. Synthesis of 7,9-diphenyl-8H-cyclopenta[l]acenaphthylen-8one (6)

Acenaphthenedione (546.5 mg, 3 mmol) were added into the ethanol (5 mL) solution of 1,3-diphenylacetone (630.8 mg, 3 mmol) under heating and stirring. Under refluxing and stirring, the ethanol solution (2 mL) of KOH (94.1 mg) was dropwised in the above mixture. After reacting 5 min, the product was obtained after the above solution was cooled for 12 h and was filtrated. The yield: 1.038 g, 90%. Characterization of compound **6**: <sup>1</sup>H-NMR:  $\delta_{\rm H}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.08 (m, 2H), 7.87 (m, 6H), 7.61 (m, 2H), 7.55 (m, 4H), and 7.43 (m, 2H). <sup>13</sup>C-NMR:  $\delta_{\rm C}$  (100 MHz, CDCl<sub>3</sub>): 154.21, 132.14, 131.54, 131.44, 129.07, 128.58, 128.42, 128.29, 127.75 121.66, and 120.93.



Scheme 1. Synthetic route of compound 3.



Fig. 3. Changes in absorption spectra of 3 (8.3  $\times$  10<sup>-6</sup> M) in ethanol upon addition of Fe<sup>3+</sup>. The final ratio of Fe<sup>3+</sup> to 3 is 1.6 equiv.



**Fig. 4.** Changes in fluorescence emission spectra of **3** ( $8.3 \times 10^{-6}$  M) in ethanol upon addition of Fe<sup>3+</sup> with excitation at 360 nm. The final ratio of Fe<sup>3+</sup> to **3** is 1.6 equiv. Inset: fluorescence emission spectra of **3** in ethanol ( $\lambda_{ex} = 360$  nm).

# 2.5. Synthesis of 4-(7,10-diphenylfluoranthen-8-yl) benzenamine (**3**)

A stirred mixture of 4-ethynylaniline (1.0506 g, 6 mmol) and 7,9-diphenyl-8H-cyclopenta[l]acenaphthylen-8-one (2.6708 g, 7.5 mmol) in degassed *o*-xylene (25 mL) was refluxed for 15 h. The solvent was removed under vacuum. The solid was purified by

column chromatography (200–300 mesh), using a CH<sub>2</sub>Cl<sub>2</sub>–hexane (1:1) mixture as eluent (2.1805 g, 65%). Characterization of compound **3**: HRMS (EI) calcd. for C<sub>34</sub>H<sub>23</sub>N [M], 445.1830; found, 445.1824. <sup>1</sup>H-NMR:  $\delta_{\rm H}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.73 (m, 4H), 7.54 (m, 3H), 7.41 (m, 6H), 7.31 (m, 4H), 7.03 (m, 2H), 6.67 (m, 1H), 6.52 (m, 2H), and 3.60 (s, 2H). <sup>13</sup>C-NMR:  $\delta_{\rm C}$  (100 MHz, CDCl<sub>3</sub>): 144.54, 140.93, 138.23, 135.11, 133.11, 130.36, 129.14, 127.15, 126.52, 123.26, 122.70, and 114.50.

#### 3. Results and discussion

Using Diels–Alder reaction, a fluorescent chemosensor 4-(7,10diphenylfluoranthen-8-yl)benzenamine (**3**), as a dual-emission Fe<sup>3+</sup> sensor, was synthesized according to Scheme 1 and modified methods [48–54]. Upon addition of FeCl<sub>3</sub> into the ethanol solution of **3**, it exhibits a great increase of emission intensity ( $I/I_0 = 8$ ) against environmental and biological samples. Moreover, the fluorescence signals can be restored by the addition of orthophenanthroline solution into the mixture solution of **3** and FeCl<sub>3</sub>. Further experiments demonstrate that Fe(NO<sub>3</sub>)<sub>3</sub> have the similar influence as FeCl<sub>3</sub> while Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> has no influence on the emission spectra of **3**.

The absorption spectra of compound **3** ( $8.3 \times 10^{-6}$  M) in ethanol reveals four bands at 206, 235, 300, and 376 nm (molar extinction coefficient  $\varepsilon_{206} = 8.37 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>,  $\varepsilon_{235} = 7.92 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>,  $\varepsilon_{300} = 3.59 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>, and  $\varepsilon_{376} = 1.26 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>). These bands may be assigned to electron transition from  $\pi$  to  $\pi^*$ . The addition of 1.6 equiv of FeCl<sub>3</sub> (Fe<sup>3+</sup>, 1.3  $\times 10^{-5}$  M), led to the great increase of the original absorbance ( $\varepsilon_{206} = 1.48 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup>,  $\varepsilon_{235} = 1.60 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup>,  $\varepsilon_{300} = 7.54 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>, and  $\varepsilon_{376} = 5.96 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>) (Fig. 3). Such absorption change may be ascribed to the newly formed complex and the absorption of Fe<sup>3+</sup> in the UV–vis region [47].

Compound **3** exhibits relatively weak fluorescence emission at 550 nm in ethanol upon excitation at 360 nm (Fig. 4) ( $\Phi_{\rm fr} = 0.055$ ) [55]. Upon titration of Fe<sup>3+</sup> ( $1.3 \times 10^{-5}$  M), the fluorescence of **3** was significantly enhanced ( $\Phi_{\rm fr} = 0.133$ ,  $I/I_0 = 75.4$ ) with fluorescence emission wavelength change from 557 nm to 450 nm (Fig. 3), indicating an efficient Fe<sup>3+</sup>-selective dual-emission behavior. The increased emission intensity is probably due to the complex of Fe<sup>3+</sup> and **3**, in which, the coordination of Fe<sup>3+</sup> and **3** inhibits the photo-induced electron transfer (PET) from electron-donating group aniline to electron-receptor 7,10-diphenyl-fluoranthenyl group (Fig. 5) [54]. Fig. 6 demonstrates the relationship between the concentration of Fe<sup>3+</sup> and the emission intensity at special wavelength. The detection limit on fluorescence response of the sensor to Fe<sup>3+</sup> is  $2.49 \times 10^{-7}$  M. A Job's plot indicated that **3** chelated Fe<sup>3+</sup> with 2:1 stoichiometry (Fig. 7).

The experiments of the counterion effect on the selective properties of  ${\rm Fe}^{3+}$  (Fig. 8) were also measured. Addition of ferric



Fig. 5. Proposed process of 3 in sensing of Fe<sup>3+</sup>.



**Fig. 6.** Emission intensity of compound **3** ( $8.3 \times 10^{-6}$  M in ethanol) at 450 nm (black dot) as a function of addition of Fe<sup>3+</sup> with excitation at 360 nm.



**Fig. 7.** Job plot for determining the stoichiometry of **3** and Fe<sup>3+</sup> ion in ethanol. The variation of the emission intensity at 450 nm were measured as a function of molar ratio  $X_{\rm M}$  ([**3**]/([Fe<sup>3+</sup>] + [**3**])).



Fig. 8. Fluorescence emission spectra of 3 (8.3  $\times$  10<sup>-6</sup> M) in ethanol upon addition of different ferric salts (1.3  $\times$  10<sup>-5</sup> M) with excitation at 360 nm.



**Fig. 9.** Fluorescent responses of **3** ( $8.3 \times 10^{-6}$  M in ethanol) upon addition of different metal salts (0.4 equiv.) ( $\lambda_{ex} = 360$  nm). *I* and *I*<sub>0</sub> represent the emission intensity at 450 nm. The metal salts represent NaCl, MgCl<sub>2</sub>, KCl, CaCl<sub>2</sub>, CrCl<sub>3</sub>, MnCl<sub>2</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, CuCl<sub>2</sub>, ZnCl<sub>2</sub>, CdCl<sub>2</sub>, and HgCl<sub>2</sub>. Inset: solution color change upon addition of Fe<sup>3+</sup> [56].

sulfate made the fluorescence of compound **3** change very little, and ferric nitrate had similar influence as that of ferric chloride.

The specificity of the chemosensor **3** toward Fe<sup>3+</sup> was determined next, as shown in Figs. 9 and 10. Upon addition of the same amount of the various metal ions  $(3.3 \times 10^{-6} \text{ M})$ , respectively, only Fe<sup>3+</sup> enhanced the emission of **3** ( $I/I_0 = 8.4$ ). However, under identical conditions, nearly no fluorescence intensity changes were observed in emission spectra with Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Hg<sup>2+</sup>. That is, sensor **3** can readily distinguish Fe<sup>3+</sup> from environmentally and biologically relevant metal ions by fluorescent spectra.

The competition experiments were also conducted for **3** (Fig. 11). When 0.4 equiv of  $Fe^{3+}$  was added into the solution of **3** in the presence of 10 equiv of other ions, similar fluorescence spectra change was displayed to that with  $Fe^{3+}$  ion only. Because the amount of Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup> is much more than  $Fe^{3+}$  biologically, it is necessary to measure the disturbance when the amount of these metal ions is much higher than that of  $Fe^{3+}$ . The measurement experiments show that no fluorescence change was



**Fig. 10.** Fluorescence spectra changes of **1** (8.3  $\times$  10<sup>-6</sup> M) upon addition of different metal ions (FeCl<sub>3</sub>, NaCl, MgCl<sub>2</sub>, KCl, CaCl<sub>2</sub>, CrCl<sub>3</sub>, MnCl<sub>2</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, CuCl<sub>2</sub>, ZnCl<sub>2</sub>, CdCl<sub>2</sub>, and HgCl<sub>2</sub>, 1.3  $\times$  10<sup>-5</sup> M) in ethanol.



**Fig. 11.** Fluorescence change that occurs upon addition of Fe<sup>3+</sup> (3.3 × 10<sup>-6</sup> M) to the solution containing **3** (8.3 × 10<sup>-6</sup> M) and the background cations (the ratio of background cation to Fe<sup>3+</sup> is 10) ( $\lambda_{ex} = 360$  nm). *I* and *I*<sub>0</sub> represent the emission intensity at 450 nm. The metal salts represent NaCl, MgCl<sub>2</sub>, KCl, CaCl<sub>2</sub>, CrCl<sub>3</sub>, MnCl<sub>2</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, CuCl<sub>2</sub>, ZnCl<sub>2</sub>, CdCl<sub>2</sub>, and HgCl<sub>2</sub>.



**Fig. 12.** Changes in fluorescence emission spectra of **3** (8.3  $\times$  10<sup>-6</sup> M) and Fe<sup>3+</sup> (1.3  $\times$  10<sup>-5</sup> M) in ethanol upon addition of *o*-phenanthroline in ethanol. The excitation wavelength was 360 nm.

found even when the amount of these alkali and alkaline earth metal ions was at a high concentration of 6 mM.

To examine the binding reversibility of chemosensor **3** to the Fe<sup>3+</sup>, ethanol solution of orthophenanthroline were added to the mixture solution of **3** (8.3 × 10<sup>-6</sup> M) and Fe<sup>3+</sup> (1.3 × 10<sup>-5</sup> M) in ethanol. As expected, fluorescence signals the same as those of **3** are completely restored as shown in Fig. 12, demonstrating that the binding of **3** and Fe<sup>3+</sup> is really chemically reversible.

# 4. Conclusions

In summary, a Fe<sup>3+</sup>-selective dual-emission fluorescent chemosensor polyphenyl derivative **3** was synthesized, which displays a high selectivity and antidisturbance for Fe<sup>3+</sup> among environmentally and biologically relevant metal ions. The mechanism of fluorescence change may be explained as below: the coordination of Fe<sup>3+</sup> and **3** inhibits PET from aniline to 7,10-diphenyl-fluoranthenyl group, resulting in the fluorescence enhancement of **3**.

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# Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 835066. Crystallographic data is available.

# Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2011.11.007.

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