



A fluorescent color/intensity changed chemosensor for Fe³⁺ by photo-induced electron transfer (PET) inhibition of fluoranthene derivative

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ABSTRACT

A fluorescent color/intensity changed fluoranthene derivative chemosensor for Fe³⁺ has been prepared and confirmed by ¹H-NMR, ¹³C-NMR, HRMS, and crystal data, which displays a high selectivity and antidisturbance for Fe³⁺ 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 Fe³⁺-selective dual-emission behavior. Further study demonstrates the detection limit on fluorescence response of the sensor to Fe³⁺ is down to 10⁻⁷ M range. The fluorescence signals of chemosensor can be restored with *o*-phenanthroline, showing the binding of chemosensor and Fe³⁺ 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, Cu²⁺ [5–12], Zn²⁺ [13–22], Pb²⁺ [23–25], and Hg²⁺ [26–30] have been reported. Surprisingly, the reported Fe³⁺-selective fluorescent sensors are relatively rare [31–41] despite the widespread applications of Fe³⁺. Fe³⁺ is a biologically essential element and provides the oxygen-carrying capacity of heme and acts as a cofactor in many enzymatic reactions [42]. Fe³⁺ 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 Fe³⁺-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 Fe³⁺-chemosensors, especially those that exhibit selective Fe³⁺-amplified emission.

Therefore, we are motivated to design and synthesize a novel molecular system which can sense Fe³⁺ 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 Zn²⁺, Cu²⁺, and Fe³⁺ [46,47]. As for compound **1**, Zn²⁺ made the rotation of C–C among the aromatic rings inhibited while Cu²⁺ 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 Fe³⁺ 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-diphenylfluoranthren-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.

^1H and ^{13}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_2SO_4 ($\Phi_{\text{fr}} = 0.546$) selected as the reference.

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

Triethylamine (2.5 mL), *p*-iodoaniline (1.0237 g, 467.4 mmol), CuI (0.0901 g, 0.473 mmol), Pd(PPh₃)₂Cl₂ (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 4-dimethylsilanylethynyl-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 temperature. 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: ^1H -NMR: δ_{H} (400 MHz; CDCl₃; Me₄Si) 7.30 (m, 2H), 6.61 (m, 2H), 3.83 (s, 2H), and 2.98 (s, 1H). ^{13}C -NMR: δ_{C} (100 MHz, CDCl₃): 147.04, 133.48, 114.60, 111.32, 84.42, and 74.92.

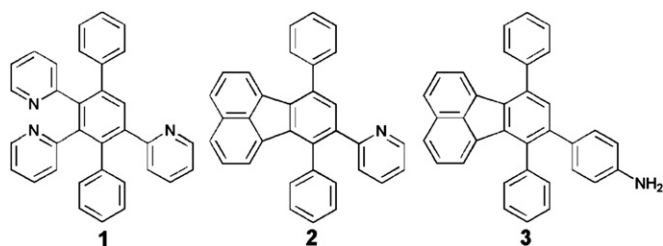


Fig. 1. Molecular structures of compounds **1**, **2**, and **3**.

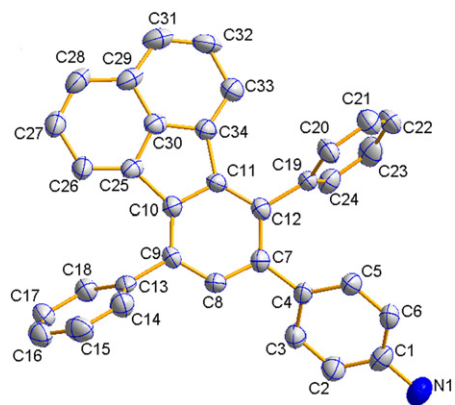
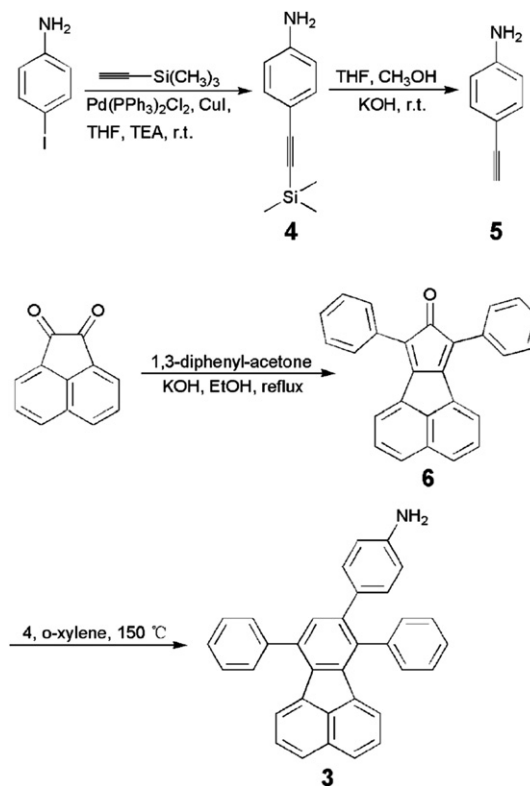


Fig. 2. X-ray crystal structure of **3**. Hydrogen atoms are omitted for clarity.

2.4. Synthesis of 7,9-diphenyl-8H-cyclopenta[1]acenaphthylen-8-one (**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**: ^1H -NMR: δ_{H} (400 MHz; CDCl₃; Me₄Si) 8.08 (m, 2H), 7.87 (m, 6H), 7.61 (m, 2H), 7.55 (m, 4H), and 7.43 (m, 2H). ^{13}C -NMR: δ_{C} (100 MHz, CDCl₃): 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**.

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