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A fluorescence ratiometric chemosensor for Fe³⁺ based on TBET and its application in living cells



Cuicui Wang^a, Di Zhang^a, Xiaoyan Huang^b, Peigang Ding^a, Zhenji Wang^b,
Yufen Zhao^{a,c}, Yong Ye^{a,c,*}

^a Phosphorus Chemical Engineering Research Center of Henan Province, The College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450052, China

^b School of Pharmaceutical Science, Zhengzhou University, Zhengzhou, China

^c Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China

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ABSTRACT

Based on a through bond energy transfer (TBET) between rhodamine and naphthalimide fluorophores, a fluorescent ratiometric chemosensor **L** was designed and prepared for highly selective detection of Fe³⁺ in aqueous solution and in living EC109 cells. These significant changes in the fluorescence color could be used for naked-eye detection. The reversibility established the potential of the probe as chemosensor for Fe³⁺ detection.

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1. Introduction

Recently, the design and development of chemosensors for sensing and recognition of environmentally and biologically important heavy and transition metal ions have attracted considerable attention of current researchers [1–4]. Among transition metal ions, iron is the most abundant essential trace element for both plants and animals. It plays an important role in enzyme catalysis, cellular metabolism, and as an oxygen carrier in hemoglobin and a cofactor in many enzymatic reactions involved in the mitochondrial respiratory chain [5–7]. Besides the beneficial effects, less iron in the body has been reported to be linked to diabetes, anemia, liver and kidney damages, and heart diseases [8]. Much effort has been focused on the development of fluorescent Fe³⁺ indicators, especially those that exhibit selective Fe³⁺-amplified emission [9–12].

Most reported Fe³⁺ fluorescent probes were based on fluorescence intensity. Although turn-on probes were more sensitive due

to the lack of background signal, a major limitation was that variations in the sample environment (pH, polarity, temperature, and so forth) might influence the fluorescence intensity measurements. Besides an internal charge transfer (ICT) mechanism using a single fluorophore to obtain ratiometric changes, the exploration of multifluorophores with energy donor–acceptor architectures can achieve large pseudo-Stokes shifts, meanwhile affording simultaneous recorded ratio signals of two emission intensities at different wavelengths, which can provide a built-in correction for the environmental effects. Forster Resonance Energy Transfer (FRET) is generally the most adopted methodology for addressing this issue. The efficiency of FRET is primarily controlled by the spectral overlap between the emission spectrum of the energy donor and the absorption spectrum of the energy acceptor. In contrast to the FRET system, the TBET system is not limited by such a kind of spectral overlap and exhibits high energy transfer efficiencies, fast energy transfer rates and large pseudo-Stokes shift [13]. Therefore, TBET system has attracted attention, and been applied in many fields, such as optical materials [14], photosynthetic models [15], biotechnology [16–18] and chemosensors. However, to the best of our knowledge, a few fluorescent probes for Hg²⁺ and Cu²⁺ are reported on TBET [19], but no probe for Fe³⁺ based rhodamine–naphthalimide conjugate on TBET is

* Corresponding author at: Phosphorus Chemical Engineering Research Center of Henan Province, The College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450052, China. Tel.: +86 371 677 67050.

E-mail address: yeyong03@tsinghua.org.cn (Y. Ye).

reported at present. Thus, it is important to develop ratiometric fluorescent probes for Fe^{3+} with favorable chemical and spectroscopic properties suitable for the imaging of Fe^{3+} in living cells.

As the fluorescence of the naphthalimide moiety was often quenched probably due to the efficient photoinduced electron transfer (PET) from the amide of rhodamine to the naphthalimide fluorophore, these probes could not exhibit any ratiometric fluorescence for metal ion detection [19h]. To solve this problem, herein, we reported a ratiometric fluorescent chemosensor **L** for Fe^{3+} based on TBET, in which (4-morpholine)-1,8-naphthalimide (energy donor) and rhodamine (energy acceptor) were linked by a rigid and conjugated spacer *p*-phenylenediamine. Fortunately, this connection efficiently prevented the fluorescence quenching of naphthalimide. In the absence of Fe^{3+} , the excited energy of the naphthalimide donor could not be transferred to the rhodamine acceptor, as the rhodamine acceptor was in the closed form. Thus, only the emission of the dye naphthalimide was observed. A Fe^{3+} -induced process could change the emission maximum of the system from 535 nm (the characteristic peak of naphthalimide) to 586 nm (the characteristic peak of rhodamine). This wavelength shift allowed highly selective ratiometric detection of Fe^{3+} both in methanol/water solution and in living cells.

2. Experimental

2.1. Apparatus reagents and chemicals

ESI mass spectra were acquired in positive ion mode using a HPLC Q-ToF HR-MS spectrometer (Waters Micromass), which used methanol as mobile phase. NMR spectra were measured on a Bruker DTX-400 spectrometer using CDCl_3 as solvent and tetramethylsilane (SiMe_4) as internal standards. Fluorescence spectra measurements were recorded with a Hitachi F-4500 spectrofluorometer. A Techcomp UV-8500 spectrophotometer (Shanghai, China) was used for absorption measurements. The melting points were determined by an X-4 microscopic melting point apparatus with a digital thermometer.

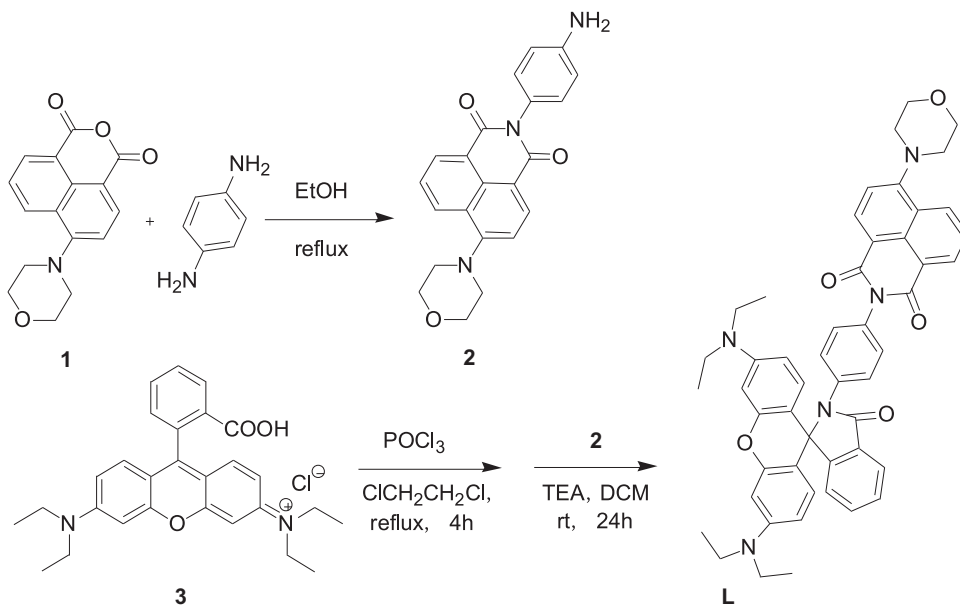
All the materials for synthesis were purchased from commercial suppliers. Solvents for chemical synthesis were purified

according to standard procedures. The solutions of metal ions were prepared from their chloride salts except for AgNO_3 . The metal ions were prepared as 10.00 mM in water solution. Double distilled water was used throughout the experiment.

2.2. Synthesis of **L**

Compound **2** was synthesized according to the literature [20]. Compound **L** was synthesized using a method similar to that recently reported [21]. The concrete method is described as follows.

A stirred solution of rhodamine B (0.07 g, 0.15 mmol) in 1,2-dichloroethane (10 mL) and phosphorus oxychloride (0.3 mL) was added dropwise over 5 min at room temperature. The solution was refluxed for 4 h. The solvent was cooled and evaporated at reduced pressure to give rhodamine B acid chloride, which was impure and used in the next step directly. The crude acid chloride was dissolved in dry dichloromethane (10 mL) and added dropwise over 1 h to a solution of compound **2** (0.06 g, 0.16 mmol) and TEA (10 mL) in dichloromethane (15 mL) in an ice-bath. Then the resultant solution was allowed to warm to room temperature under nitrogen atmosphere over 24 h. The dichloromethane solution was removed under reduced pressure and the residue left was dissolved in dichloromethane, extracted with water, and dried over anhydrous Na_2SO_4 . The organic layer was evaporated and the crude product was purified by column chromatography on silica gel using $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (20:1, v/v) as eluent to give **L** as yellow solid (64 mg, 53%). ^1H NMR (CDCl_3 , 400 MHz, ppm): 1.18 (t, 12H, $J=7.0$ Hz), 3.29 (t, 4H, $J=4.4$ Hz), 3.34 (q, 8H), 4.04 (t, 4H, $J=4.3$ Hz), 6.30 (q, 2H, $J=3.7$ Hz), 6.36 (d, 2H, $J=2.4$ Hz), 6.70 (d, 2H, $J=8.8$ Hz), 7.11 (q, 3H, $J=4.9$ Hz), 7.25 (d, 1H, $J=8.0$ Hz), 7.39 (d, 2H, $J=8.8$ Hz), 7.49 (m, 2H), 7.72 (q, 1H), 8.02 (q, 1H), 8.46 (d, 1H, $J=7.8$ Hz), 8.52 (d, 1H, $J=8.1$ Hz), 8.57 (d, 1H, $J=6.8$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): 12.65, 44.30, 53.43, 66.96, 98.03, 106.34, 108.26, 115.03, 117.19, 123.37, 123.46, 123.72, 125.84, 125.90, 126.22, 127.99, 128.50, 128.68, 129.71, 130.19, 130.30, 131.49, 132.50, 132.83, 133.07, 137.28, 148.82, 152.76, 154.11, 155.82, 163.92, 164.39, 168.26; HRMS calcd. for $\text{C}_{50}\text{H}_{47}\text{N}_5\text{O}_5$ [$\text{M}+\text{H}$] $^+$: 798.3650, found 798.3654; MP: 186–188 °C.



Scheme 1. Synthetic route of TBET-based ratiometric fluorescent Fe^{3+} chemosensor.

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