



A relay identification fluorescence probe for Fe³⁺ and phosphate anion and its applications



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ABSTRACT

A simple relay identification fluorescence probe for Fe³⁺ and phosphate anion with “on-off-on” switching was designed and synthesized based on the phenylthiazole and biphenylcarbonitrile. Probe 1 displayed highly selective and sensitive recognition to Fe³⁺ in HEPES aqueous buffer (EtOH/H₂O = 2:8, v/v, pH = 7.4) solutions. The optimized structures and HOMO and LUMO of probe 1 and [1-Fe³⁺] complex were obtained by the density functional theory (DFT) calculations with B3LYP as the exchange and correlation functional using a suite of Gaussian 09 programs. The [1-Fe³⁺] complex solution also showed a high selectivity toward PO₄³⁻. The lower limits of detection of probe 1 to Fe³⁺ and [1-Fe³⁺] complex to PO₄³⁻ were estimated to 1.09 × 10⁻⁷ M and 1.86 × 10⁻⁷ M. Besides, the probe 1 also was used to detected the target ions in real water sample and living cells successfully.

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1. Introduction

Among the heavy metals, iron is an essential trace elements for the growth of almost all types of biological cells [1]. It is the active center of many enzymes. It is not only involved in hematopoiesis in vivo, but also involved in the transport of oxygen [2]. However, people cannot blindly excessive intake of iron. When the dose of iron exceeds a certain content, it may cause adverse effects to the organisms. The excessive of storage iron in the body will enhance the lipid peroxidation, resulting in the imbalance between oxidation and anti-oxidation, which will damage DNA and induced mutation [3]. Besides, an increase in the amount of Fe³⁺ in the body is associated with the presence of methemoglobin. When the levels of the Fe³⁺ were too high in environment water system, its migration and enrichment in the environment can also cause serious pollution. Eventually Fe³⁺ will enter the human through the food chain, which will cause potential health hazards. Therefore, it is essential to monitor the content of Fe³⁺ ions in the environment water system or in vivo.

Optical chemosensor have been widely used in many fields such as chemical analysis [4], environmental monitoring [5], life science [6]

and biomedicine [7]. At present, the design, synthesis and application of fluorescence probes has become one of the most active research areas. Fluorescent probes for the detection of metal ions and anions have the advantages of simple method, high sensitivity, good selectivity and fast response. In addition, many fluorescence probes can also be used for tracing the metal ions or anions in living cells and organisms [8,9]. So far, a large variety of fluorescence probes designed based on various identification mechanisms have been reported [10–17]. The vast majority of probes are designed for highly selective recognition of a particular ion and to meet the specific recognition function, A custom synthesis of fluorescence probes and detected ions “one to one” greatly increased the workload of the synthetic research. In order to develop and utilize the function of fluorescence probe molecules deeply, many researchers at home and abroad have turned their attention to multi-functional fluorescence probes.

Relay identification is a new direction for the function enhancement for fluorescence probe molecular [18,19]. The term “relay identification” refers to the selective identification of an ion by probe molecule under certain conditions, then the new other ion recognition was carried out directly under the original test conditions by using the special effects between the in situ formed intermediates (or complexes) and the new ionic species [20]. Obviously, the relay identification type fluorescence probes enable continuous identification of the two ions under the same test conditions. It has the obvious advantages of simple operation,

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and can reduce the workload of the probe synthesis, and is beneficial to energy conservation and emission reduction. At present, the study of the relay identifications of metal ions and anions is the most common. Because the charge of metal ion and anion is complementary, some “fluorescence probe - metal ion” complexes can also be used as fluorescence probes for the indirect identification of anions. At present, the design and synthesis of fluorescence probes of specific metal ions and anions with the function of relay identification has attracted much attention [21,22], and it has become the main direction of the research of relay identification fluorescence probe. Relay identification function fluorescence probes designed based on a continuous and specific reaction of two kinds of ions to probe molecules are still scarce. The design and synthesis of probes with relay identification function and the potential for continuous use is of significance for reducing the amount of synthesis and achieving energy saving and emission reduction.

Here, a novel fluorescence probe based on phenylthiazole and biphenylcarbonitrile as on-off-on fluorescence probe for Fe^{3+} and PO_4^{3-} was designed and synthesized. Because of its large conjugated system, the probe exhibits a strong red fluorescence. It has high selectivity to Fe^{3+} and the corresponding respond signal is displayed by the fluorescence quenching. Meanwhile, the $[\text{1-Fe}^{3+}]$ complex can also be used as fluorescence probes for the identification of the phosphate anion under the original test conditions. A series of optical properties were studied by the fluorescence emission spectra. The structural geometry optimizations of probe 1 and $[\text{1-Fe}^{3+}]$ complexes were carried out by the Gaussian 09 program. Meanwhile, the cell imaging of probe 1 for monitoring of target ions in living cells were studied.

2. Material and Methods

2.1. Materials and Instruments

All organic solvents (ethanol, methanol, dichloromethane, trifluoroacetic acid,) and chemicals (Acetophenone, thiourea, I_2 , 4-Hydroxy-4-biphenylcarbonitrile and hexamethylenetetramine) were of analytical reagent grade and were purchased from Aladdin Chemical Reagent Ltd., chloride salt of all metal ions and anion salts were purchased from Sinopharm Chemical Reagent Ltd., and used without further purification. HEPES buffer solution (pH 7.4) was prepared using 0.05 M HEPES in water and was adjusted with 0.5 M NaOH solution.

^1H NMR and ^{13}C NMR were measured at an AVANCEII 400 MHz spectrometer (Bruker BioSpin). Mass Spectrometry (MS) were

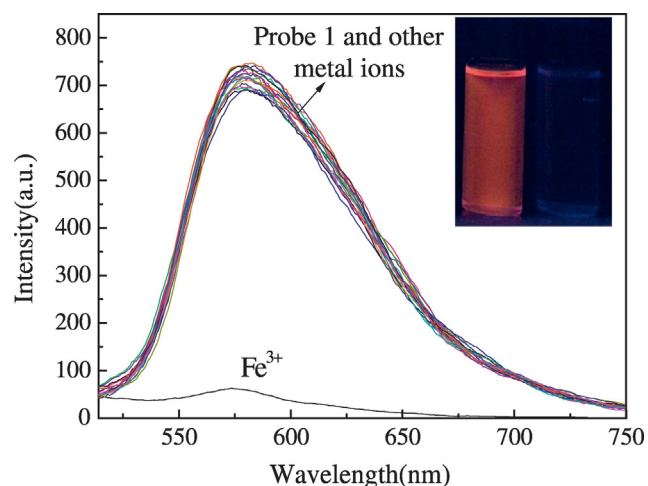
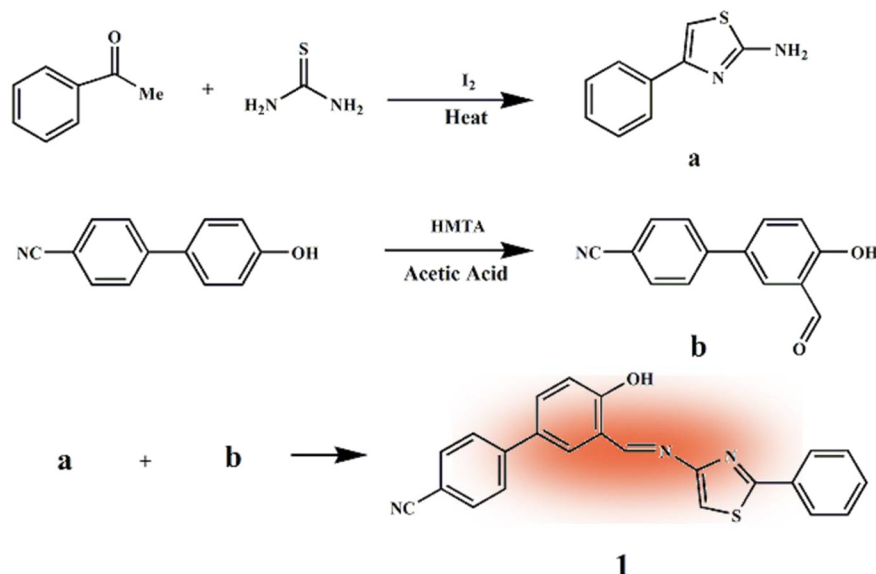


Fig. 1. Fluorescence responses of probe 1 (10 μM) to 10.0 equiv. of different metal ions (Ni^{2+} , Ca^{2+} , Co^{2+} , Zn^{2+} , Cr^{3+} , Fe^{3+} , Al^{3+} , Na^+ , Cd^{2+} , K^+ , Mg^{2+} , Li^+ , Fe^{2+} , Cu^{2+} , Mn^{2+} , Sr^{2+} , Cs^{2+} , Pb^{2+} and Hg^{2+}) in HEPES aqueous buffer (EtOH/ H_2O = 2:8, pH = 7.4) solution, λ_{Exc} = 420 nm.

measured by a Liquid Chromatography-Ion Trap Mass Spectrometry (Thermo LXQ). Fluorescence emission spectra were examined on a Cary Eclipse fluorescence spectrometer (CaryEclipse) with excitation slit at 5.0 nm and emission at 5.0 nm. The cell imaging experiment were carried out by an inverted fluorescence microscope (Leica DMI4000B, Germany). Density functional theory (DFT) calculations with B3LYP were carried out by using the Gaussian 09 package. The 6-311 + G^* and LanL2DZ effective core potential (ECP) basis sets were used in the calculation process.

2.2. Synthesis of Probe 1

The synthetic procedure of probe 1 was depicted in Scheme 1. The 2-amino-4-phenylthiazole and 3-formyl-4-Hydroxy-4-biphenylcarbonitrile were synthesized according to previously reported methods [23,24]. A solution of 2-amino-4-phenylthiazole (0.35 g, 2 mmol) and 3-formyl-4-Hydroxy-4-biphenylcarbonitrile (0.45 g, 2 mmol) in absolute ethanol (30 mL) was refluxed for 3 h at 70 $^\circ\text{C}$. Then the solution system was cooled to room temperature and the solvent was removed by vacuum



Scheme 1. The synthetic route of probe 1.

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