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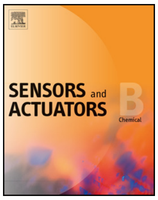

Study on a highly selective fluorescent chemosensor for Fe^{3+} based on 1,3,4-oxadiazole and phosphonic acid

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ABSTRACT

A high selectivity and novel phosphonic acid-functionalized fluorescent sensor 2,5-bis[2-phosphonic acid methyl)phenyl]-1,3,4-oxadiazole (**2**) for Fe^{3+} ions has been designed and synthesized. It can display on–off type fluorescence change with high selectivity and sensitivity toward Fe^{3+} in DMF–H_2O solution. The recognition mechanism of the sensor toward Fe^{3+} was evaluated by FTIR through the disappearance of the characteristic sorption peak of P═O, P—OH and the form of new broad band (P—OFe stretching bands) in FTIR spectra. It was verified that the Fe^{3+} ion caused the quenching of sensor **2** fluorescence emission, due to the Fe^{3+} ion binding to sensor **2** via the O-atoms of the phosphonic group. A linear relationship that flowed with the Perrin model of static quenching was observed between the relative fluorescence intensity ($\ln F_0/F$) of sensor **2**. The detection limit of the sensor **2** toward Fe^{3+} was 1×10^{-8} M, while other ions including Hg^{2+}, Ni^{+}, Pb^{2+}, Ca^{2+}, Mg^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Na^{+}, K^{+}, Mn^{2+}, Ag^{+}, Cr^{3+} and Fe^{2+} had no influence on the probing behavior. Stern–Volmer analysis showed the binding stoichiometry to be 1:1 (host–guest) and a binding constant of $1.6 \times 10^4\ M^{-1}$, calculated using the Benesi–Hilderbrand equation.

1. Introduction

The development of selective chemosensors used for detecting the presence of metal ions has received considerable attention since these ions show important functions or produce toxic effects in environmental chemistry and biology [1]. During the last decades, the fluorescence chemosensors, which combine a recognition functional moiety with optical transduction, have received much attention as an efficient analytical technique for the detection of a particular species [2], such as Rhodamine B derivatives as fluorescent sensor to detect Cu^{2+} [3], Pb^{2+} [4], Fe^{3+} [5], Hg^{2+} [6,7] and Cr^{3+} [8], calixarene fluoroionophores to detect Hg^{+} [9], cryptand derivatives [10] to detect $Ni^{2+}$and Cu^{2+}, ring-structured moieties such as crown ethers to detect Pb^{2+} [11], Hg^{2+} [12], cyclodextrins to detect Pb^{2+} [13]. For the above fluorescent chemosensors, there are two important parts to be considered, an ionophore and a fluorophore. While the ionophore part containing nitrogen, sulfur or oxygen can selectively trap the metals ions, such as carboxylate groups [14,15], sulfonate groups [16,17], phosphonate groups [18–20], carbohydrate groups [21,22] and ammonium groups [23–25]. The other part fluorophore with very useful optical and optoelectronic properties is attached to the vicinity of the binding site for signal detection and transduction. So we could introduce an ionophore group to the pendant chains of fluorescent derivatives to trap the ion. Moreover, the fluorescence of the fluorescent derivatives could be quenched by trace of charged molecules (quenchers) via charge transfer or energy transfer.

Iron ion plays an important role in the physiology of human beings, such as cellular metabolism, energy generation, oxygen transport, gene expression, neurotransmission and regulation of metalloenzymes [26]. It is also found as the essential element in myoglobin, hemoglobin, cytochromes [27,28]. These functions are dependent on the iron homeostasis in human body, thus both iron deficiency and iron overload are harmful to human health. For example, Fe^{3+} deficiency leads to anemia and excess iron in the body causes liver and kidney damage (hemochromatosis). Moreover, excessive of iron ion is also harmful to the environment [29–32]. According to the U.S. Environmental Protection Agency (EPA), the maximum acceptable level of iron in drinking water is ~5.357 μM. So detection of trace amounts of Fe^{3+} is of great importance for most organisms. Callan designed an aminobisulfonate as fluorescent chemosensor for Fe^{3+} [16] through metal coordination. Qin et al. [33], Stork et al. [34] developed a variety of polyfluorenes (PFs) for Fe^{3+} detection.

Up to now, oxadiazole dyes have been extensively studied due to their applications as key intermediates in organic synthesis [35], biological activity studies [36,37] and theoretical chemistry [38,39].

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It is remarkable that 1,3,4-oxadiazole derivatives are most used as fluorescent materials in organic light emitting diodes (OLED) [40]. However, to the best of our knowledge, the small organic molecules of 1,3,4-oxadiazole derivatives to detect Fe^{3+} are rarely reported until now.

In our work, we designed and synthesized a novel phosphonic acid-functionalized 1,3,4-oxadiazole derivatives 2,5-bis[2-phosphonic acid methyl)phenyl]-1,3,4-oxadiazole (**2**) (Scheme 1). We investigated the fluorescence response of sensor **2** and its parent sensor **1** and examined the selectivity of sensor **2** and sensor **1** to metal ions. Sensor **1** against common metal ions and propose sensor **2** as a fluorescent chemosensor for Fe^{3+}, operable over a wide pH range. Interestingly, the sensor **2** displayed a high sensitive fluorescence response toward Fe^{3+} over competitive cations in DMF–H_2O solution, it showed a fluorescent “on–off” switch toward Fe^{3+}, thus sensor **2** could be employed as a fluorescent chemosensor for Fe^{3+}. Further, a novel fluorescence method has been developed based on the selective quenching effect of sensor **2** by Fe^{3+} in DMF–H_2O solution.

2. Experimental

2.1. Materials and characterizations

^{1}H and ^{13}C NMR spectra were obtained on a Varian Unity Inova Spectrometer (500 MHz). The FTIR spectra were obtained on a Nicolet 6700 Fourier transform infrared spectrometer. The absorbance spectra were recorded on Varian Cary 500 Spectrophotometer. Excitation and emission spectra were recorded on Varian Cary Eclipse Fluorescence Spectrophotometer. The pH values of solutions were measured using a pH meter model Sartorious PB-10. Common reagent grade chemicals are commercially available and were used without further purification. Deionized water was used throughout all experiments. Solutions of Cu^{2+}, Fe^{2+}, Mn^{2+}, Na$^+$, K$^+$, Ca^{2+} were prepared from their chloride salts, solutions of Zn^{2+}, Cd^{2+}, Fe^{3+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Ag$^+$, Mg^{2+}, Cr^{3+}and Hg^{2+} were prepared from their nitrate salts. The column chromatography was conducted over silica gel (200–300 mesh).

2.2. 2,5-Bis[2-phosphonic acid methyl)phenyl]-1,3,4-oxadiazole (*2*)

Bromotrimethylsilane (8.5 mL, 80 mmol) was added dropwise to a solution of 2,5-bis[2-diethoxylphosphorylmethyl)phenyl]-1,3,4-oxadiazole (see Supporting materials) (2.69 g, 5 mmol) in 50 mL dry CH_2Cl_2 under nitrogen. After the addition, the resulting solution was stirred for 12 h at room temperature. The solvent was removed under vacuum and methanol (50 mL) was added. The resulting solution was stirred for 12 h. Methanol was removed under vacuum, then the crude product was washed with water three times and filtrated to afford white solid of sensor **2**, 1.84 g, yield, 86.4%, ^{1}H NMR ($CDCl_3$, 500 MHz) (Fig. S1): δ 1.56 (s, 4*H*), 2.96 (s, 4*H*), 7.42–7.45 (t, 2*H*), 7.50–7.53 (t, 2*H*), 7.58–7.60 (d, *J* = 4.0 Hz, 2*H*), 8.06–8.07 (d, *J* = 2.0 Hz, 2*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 30.98, 32.07, 123.31, 127.39, 129.41, 131.32, 132.18, 163.96.

2.3. Fluorescence titration procedure

Measurements of UV–vis absorption spectra were carried out on Varian Cary 500 spectrometer, with a scan rate of 500 nm per min. Fluorescence spectra were recorded on a Perkin-Elmer LS 50B luminescence spectrometer with Xenon discharge lamp excitation. A 10 × 10 mm quartz cuvette was used for solution spectra, and emission was collected at 90° relative to the excitation beam. The solutions of sensor **2** and sensor **1** were diluted to a concentration of 10 μM in DMF–H_2O with 50 mM Tris–HCl (pH = 7.4; Tris) tris(hydroxymethyl)aminomethane) buffer solution. Solutions of cationic perchloride or nitric salts with the concentration of typically 5×10^{-4} M were prepared by successive dilution in water. Fluorescence quenching experiment was carried out by sequentially adding small aliquots of cationic salts stock solutions to the sensor **2** or sensor **1** solutions by using calibrated microliter pipet. The solutions were vibrated prior to obtaining fluorescence spectra. The pH-dependent experiment was carried out by adding HCl or NaOH to sensor **2** or sensor **1** (10 μM), then the solutions were vibrated prior to obtaining fluorescence spectra.

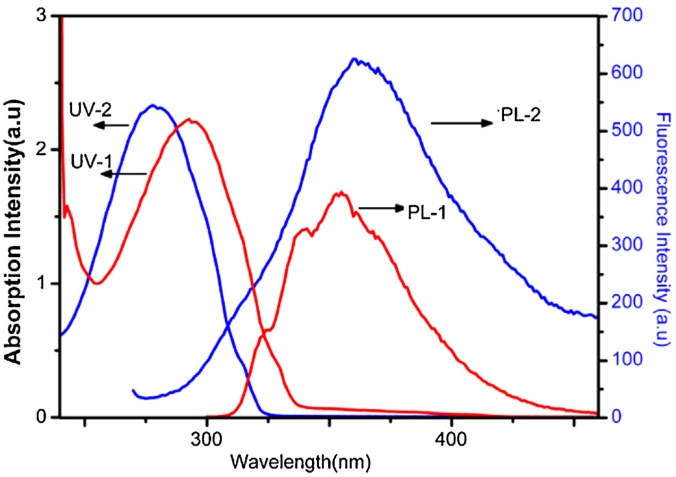

Fig. 1. Absorption and fluorescence spectra of sensor **2** and sensor **1** in DMF/H_2O solution (1:1, v/v, 10 μM, pH = 7.4).

3. Results and discussion

3.1. Photophysical properties (absorption and emission spectra)

The absorption and photoluminescence (PL) spectra of sensor **2** and its parent sensor **1** in DMF–H_2O solution (1:1, v/v, 10 μM, pH = 7.4) are shown in Fig. 1. The maximum absorption peak of sensor **2** was at 277 nm, which was attributed to the absorbance of oxadiazole. Hypsochromic shift was observed compared with the absorption spectra of its parent **1** (291 nm), which might be due to the changing of the ethoxylphosphorylmethyl. The sensor **2** had intensive PL emission, and the maximum emission peak was at 362 nm in DMF–H_2O solution (1:1, v/v, pH = 7.4). The quantum yield (Φ_F) of sensor **2** was 0.23, determined at room temperature using quinine sulfate ($\Phi_F = 0.55$ in 0.05 mol/L H_2SO_4) as standard [41]. The Φ_F showed that sensor **2** was a candidate as fluorescence material.

3.2. UV–vis absorption spectra of **2** and **1** with metal ions

The recognition behavior of sensor **2** toward various metal ions was investigated. Solutions of sensor **2** (10 μM) and sensor **2**-metal salt (10 μM) were prepared. UV–vis absorption spectra were then obtained. Sensor **2** and sensor **2-**metal ion complexes presented a strong absorption transition in the 277 nm (Fig. 2a), which can be attributed to the S_0–S_1 transition of the 1,3,4-oxadiazole component. Additionally, no remarkable changes in maximum absorption intensities or wavelengths were observed with other sensor **2**-metal cation ions (Hg^{2+}, Ni$^+$, Pb^{2+}, Ca^{2+}, Mg^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Na$^+$, K$^+$, Mn^{2+}, Ag$^+$, Cr^{3+}, Fe^{2+}). As Fig. 2b clearly showed, when adding 10 μM of Fe^{3+}, the change in the absorption intensity fell off very quickly and decreased the absorption intensity