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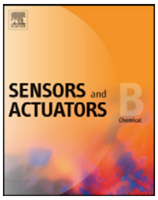

Short communication

Facile synthesis and characterization of rhodamine-based colorimetric and “off–on” fluorescent chemosensor for Fe^{3+}

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ABSTRACT

A fluorescent chemosensor for Fe^{3+}, rhodamine-aminobenzothiazole conjugate has been synthesized and characterized by ^{1}H NMR, ^{13}C NMR and X-ray crystallography. The sensor demonstrates strong Fe^{3+}-selective orange fluorescence and a pink color switch. Furthermore, the recognizing behavior has been investigated both experimentally and computationally.

1. Introduction

Iron is considered to be one of the most important trace element in the body and an essential element in most biological systems [1]. It plays a crucial role in the areas of biological, environmental, and chemical regions [2–4]. There is an increasing evidence that either its deficiency or overload can induce various disorders. Recent research results reveal that Fe^{3+} is involved in the mechanisms of many neurodegenerative diseases, such as Alzheimer’s and Parkinson’s disease [5,6]. Therefore, great importance is attached to developing selective chemosensors for Fe^{3+} [7].

As a convenient and efficient method, the fluorescence detection has found its wide application in biological and environmental science. Many excellent fluorescent indicators for transition metal ions have been reported, such as Cu^{2+}, Pb^{2+}, Zn^{2+}, Hg^{2+}, and so on [8–13]. However, the fluorescence sensors for Fe^{3+} ion are extremely scarce. Limiting factors for design of such a sensor molecule are the paramagnetic nature of Fe^{3+}, which can cause fluorescence quenching [14–17].

In light of excellent spectroscopic properties, large molar extinction coefficient and high fluorescence quantum yield, rhodamine-based dyes have currently become a popular topic of molecular probes [18]. Recently, based on the principle of metal coordination inducing spiro-ring opening of a sensing molecule, rhodamine B spirolactam as a molecular scaffold was employed to design novel chemosensors for selective recognition of many metal ions and small molecules [19–23]. Dong et al. [24] synthesized a new rhodamine B schiff-base fluorescent sensor which showed potential application ability for the determination of trace Fe^{3+} in neutral medium.

Herein we report a new fluorescent probe **1** based on rhodamine B for Fe^{3+}. The structure of compound **1** was confirmed by X-ray crystallography in addition to NMR data. This probe exhibits “turn-on” type fluorogenic and chromogenic behavior toward Fe^{3+} in methanol solution with high sensitivity and selectivity compared with other metal ions examined (Scheme 1).

2. Reagents and general methods

2.1. Apparatus

Fluorescence spectra measurements were performed on a HITACHI F-4500 fluorescence spectrophotometer equipped with a xenon discharge lamp, 1 cm quartz cell. The excitation and emission wavelength bandpasses were both set at 5.0 nm. Absorbance spectra measurements were measured on a Shimadzu UV-1700 spectrophotometer. Mass spectra were obtained on Model

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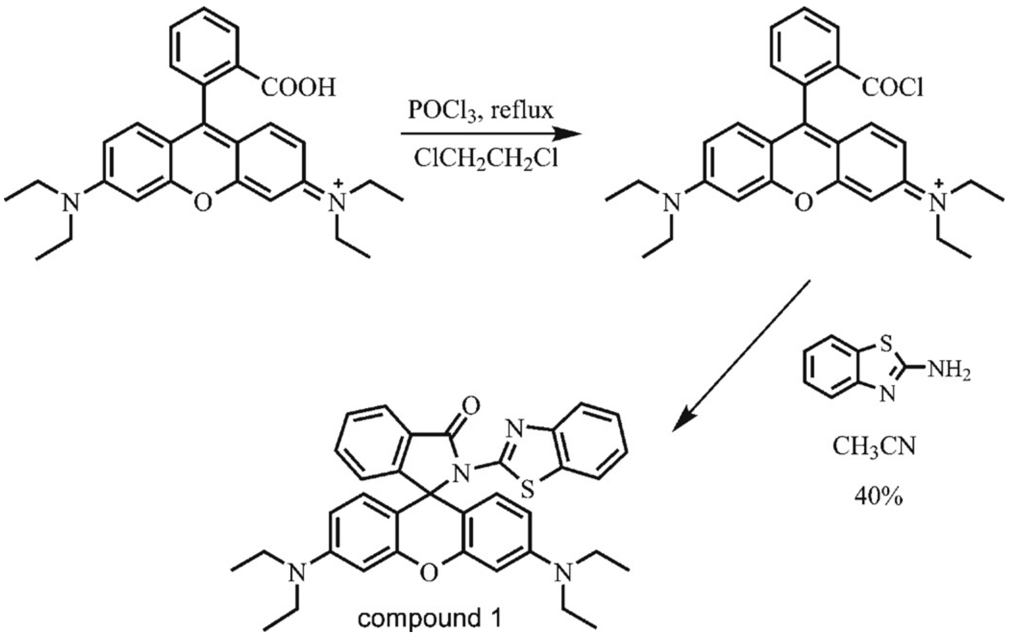

Scheme 1. Synthetic pathway of **1**.

AXIMA-CFR™ plus MALDI-TOF Mass Spectroscopy. IR spectra were taken in KBr disks on a Bruker Tensor 27 spectrometer. NMR spectra were recorded on a Varian INOVA-400 MHz spectrometer (at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) with tetramethylsilane (TMS) as internal standard. X-ray data were collected on Bruker Smart APEX II CCD diffractometer.

2.2. Reagents

Rhodamine B was obtained from Beijing Chemical Works. $FeCl_3$ was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. Methanol was obtained from Tianjin Fuchen Chemical Reagent Plant and used with further purification. The solutions of metal ions were performed from their nitrate or chloride salts. Silica gel (200–300 mesh, Qingdao Haiyang Chemical Reagent Plant) was used for column chromatography. Analytical thin layer chromatography was performed by Merck 60 GF254 silica gel (precoated sheets, 0.25 mm thick). All the reagents were of analytical-reagent grade. Double distilled water was used throughout the experiment.

Rhodamine B based sensor **1** stock solution (6.25 mmol L^{-1}): in a 25 mL volumetric flask, 89.80 mg of **1** was dissolved in acetone and then diluted to the mark with acetone. 8.00 mL of the solution was then transferred to a 100 mL volumetric flask, diluted to the mark with methanol.

Fe^{3+} stock solution (5.00 mmol L^{-1}) in a 25 mL volumetric flask, 20.27 mg anhydrous $FeCl_3$ was dissolved in methanol, and then diluted to the mark with methanol.

The hydrochloride salts of Ca^{2+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+} and the nitrate salt of Ag^+ ions were used to evaluate the metal ion binding properties of compound. The metal ions were prepared as 5.00 mmol L^{-1} in methanol solution.

2.3. Synthesis and crystal growth

2.3.1. Synthesis of compound 1

To a stirred solution of rhodamine hydrochloride (4.78 g, 0.01 mol) in 1, 2-dichloroethane (10 mL), 5 mL phosphorus oxychloride was added. The solution was refluxed for 6 h and concentrated by evaporation. The obtained crude acid chloride was dissolved in acetonitrile (10 mL), and a solution of 2-aminobenzothiazole (1.50 g, 0.01 mol), triethylamine (5 mL) in acetonitrile (20 mL) was added dropwise within 30 min. After refluxing for 4 h, the solvent was removed under reduced pressure to give a violent-oil. Water was then added to the mixture and the aqueous was extracted with dichloromethane (15 mL × 3). The organic layer was washed with water, dried over anhydrous $MgSO_4$ and filtered. Purification by column chromatography on silica gel (CH_2Cl_2) gave 2.4 g of white solid in a yield of 42%. The proposed molecular structure and its purity were confirmed by various spectroscopic analyses. m.p.: 173–174 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.128 (12H, t, J = 7.0 Hz), 3.288 (8H, q, J = 7.0 Hz), 6.13 (2H, dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz), 6.39 (2H, d, J = 8.4 Hz), 6.45 (2H, d, J = 2.4 Hz), 7.15 (1H, td, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.22–7.29 (2H, m, benzothiazole), 7.533–7.584 (3H, m, benzothiazole + xanthene), 7.711 (1H, d, J = 4), 8.068 (1H, d, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 12.618, 44.255, 76.713, 77.027, 77.346, 97.445, 106.383, 107.135, 120.727, 122.016, 123.140, 123.482, 124.884, 125.203, 127.990, 128.659, 129.133, 132.243, 134.437, 148.868, 149.596, 153.567, 153.890, 154.359, 166.940. MALDI-TOF-MS: 575.54 $[M + H]^+$.

2.3.2. Crystal growth and conditions

The single-crystal of compound **1** was obtained from acetonitrile solution by slow evaporation at room temperature after 5 days, and then mounted it on the goniometer of single-crystal diffractometer. The crystal data has been collected by using Cu $K\alpha$ radiation (λ = 0.71073) in the θ range of 2.66–25° with φ/ω scan technique at room temperature. The intensities were corrected for Lorentz and polarization effects as well as for empirical absorption based on multiscan techniques. The structure was solved using the direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97.

2.4. General procedure

2.4.1. Procedure for fluorimetric method

To a 25 mL volumetric tube, 1.00 mL of 500 μM **1**, different concentration of Fe^{3+} was added and the reaction mixture was diluted to 25 mL with methanol. Then, 3.0 mL each solution was transferred to a 1 cm cuvette and the fluorescence intensity of the above