Nanomolar colorimetric quantitative detection of Fe^{3+} and PPi with high selectivity

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Zhanxian Li [a,b], Haixia Li [b], Caixia Shi [b], Mingming Yu [b], Liuhe Wei [b], Zhonghai Ni [a,*]

[a] School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, Jiangsu Province, China
[b] College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, China

ABSTRACT

A novel rhodamine and 8-hydroxyquinoline-based derivative was synthesized, which is shown to act as a colorimetric chemosensor for Fe^{3+} in aqueous solution with high selectivity over various environmentally and biologically relevant metal ions and anions with a distinct color change from colorless to pink in very fast response time (<1 min). Fe^{3+} can be detected quantitatively in the concentration range from 6.7 to 16 μM and the detection limit (LOD) on UV–vis response of the sensor can be as low as 15 nM. The 'in situ' prepared Fe^{3+} complex (**1·Fe**) showed high selectivity toward PPi against many common anions, and sensitivity (the LOD can be as low as 71 nM). In addition, both the chemosensor and the 'in situ' prepared Fe^{3+} complex are reusable for the detection of Fe^{3+} and PPi respectively.

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1. Introduction

In recent years, great achievement has been achieved in the development of artificial optical chemosensors toward environmentally and biologically important analytes such as metal ions and anions. As an essential element in the human body, Fe^{3+} plays an important role in many biological processes such as oxygen metabolism to DNA. In addition, the trivalent form of iron provides the oxygen-carrying capacity of heme, acts as a cofactor in many enzymatic reactions, and is indispensable for most organisms. As a result, both its deficiency and excess result in various pathological disorders [1,2]. On the other hand, pyrophosphate $P_2O_7^{4-}$ (PPi) is the product of ATP hydrolysis under cellular conditions and involved in DNA replication catalyzed by DNA polymerase [3–5]. Therefore, it is significant to develop optical chemosensors toward Fe^{3+} and PPi.

In general, fluorescent sensors depend on emission intensity or position power and detector sensitivity [6–8], to contrast, color changes based on absorption properties of the ground state are more suitable for direct observation with the naked eye [9], and considerable efforts have been devoted to designing colorimetric chemosensors toward Fe^{3+} [10–13] and PPi [14–16] in solution during the past few decades, but the reported colorimetric sensors toward Fe^{3+} and PPi are very rare, and as a result, it is still challenging to prepare colorimetric sensors for Fe^{3+} and PPi.

Rhodamine derivatives are extensively employed in fluorescent and colorimetric chemosensors in solution because of their high absorption coefficient, high fluorescence quantum yield and long-wavelength absorption and emission [17–22]. On the other hand, as prototypical fluorophores, 8-hydroxyquinoline (8-HQ)-based derivatives have been widely used in fluorescence detection and imaging of metal ions, because metal binding to 8-HQ can block the excited-state intramolecular proton transfer channel and restore the fluorescence [23–29]. The chemical sensors, in which rhodamine and 8-HQ moieties simultaneously existed, are very rare [30–32].

In this paper, based on rhodamine and 8-HQ, selective colorimetric chemosensor **1** (Scheme 1) was synthesized. Compound **1** can quantitatively detect Fe^{3+} with great color change in aqueous solution. The detection limit on UV–vis response of the sensor can be as low as 15 nM. The 'in situ' prepared Fe^{3+} complex (**1·Fe**) showed high selectivity and sensitivity toward PPi.

2. Experimental

2.1. Methods and materials

Acryloyl chloride (analytical grade) and Rhodamine (95%) were purchased from Sigma Aldrich Inc., USA. SeO_2 (99%) was obtained from the Aladdin Reagent Co., Ltd., China. 1,4-Dioxane (analytical grade) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd., China, hydrazine hydrate (analytical grade) from Tianjin Jiangtian Chemical Technology Co., Ltd., China, methanol and ethanol (gas chromatography grade) from Tianjin Siyou Fine Chemicals Co., Ltd., China. Other reagents
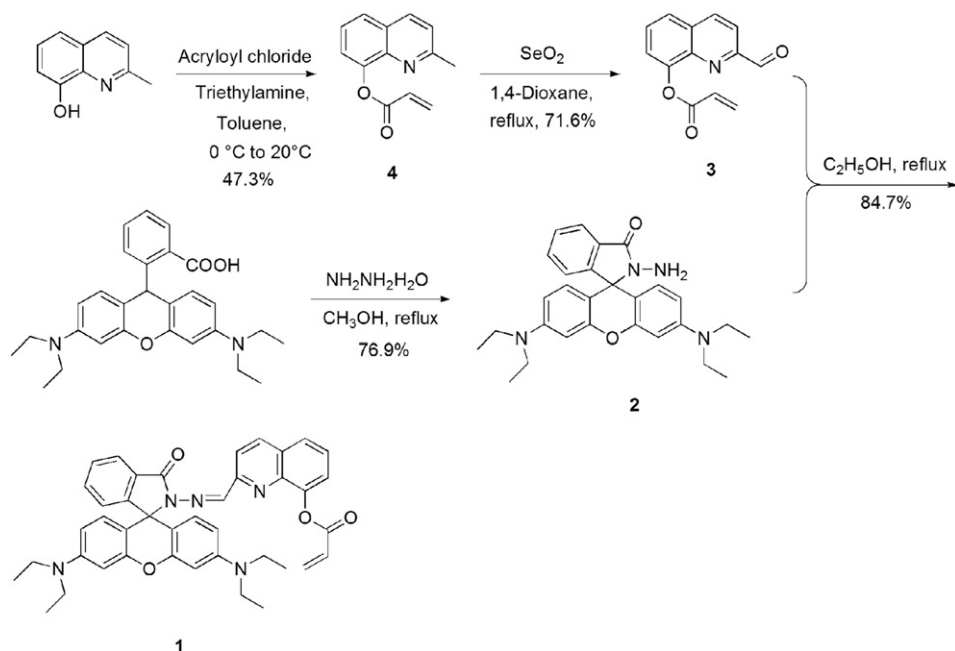
Scheme 1. Synthesis route of chemosensor **1**.

were of analytical grade and provided by Tianjin FengChuan chemical reagent Technology Co., Ltd., China. All chemicals and solvents were used without further purification. Compounds **4**, **3**, **2** and **1** were synthesized by following Scheme 1 and modified reported methods [33,34].

2.2. Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 NMR spectrometer. Chemical shifts are reported in parts per million 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.

2.3. Synthesis of compound 4

A mixture of 8-hydroxy-2-methylquinoline (2.4032 g, 15 mmol) and triethylamine (1.5 mL) was dissolved in 20 mL toluene and the mixture was stirred at 0 °C. After stirring for 30 min, 4 mL acryloyl chloride was slowly added dropwise and the reaction mixture was stirred for 12 h at 20 °C. The mixture was filtered and evaporated to generate the crude residue. The final product **4** was obtained by column chromatography (mesh chromatography silica, 1:4 ethyl acetate/light petroleum) in a yield of 47.3%. Characterization of compound **4**: ^{1}H NMR: δ_H (400 MHz, DMSO-d_6, Me$_4$Si): 8.31 (d, 1H), 7.86 (d, 1H), 7.55 (m, 2H), 7.47 (d, 1H), 6.59 (d, 2H), 6.20 (t, 1H), and 3.36 (s, 3H). ^{13}C NMR: δ_C (100 MHz, DMSO-d_6): 164.71, 159.47, 146.76, 140.37, 136.69, 133.92, 128.23, 127.90, 126.32, 125.85, 123.30, 121.95, 25.72.

2.4. Synthesis of compound 3

A mixture of SeO$_2$ (0.3240 g, 2.9 mmol), compound **4** (0.4638 g, 2.2 mmol), and 10 mL 1,4-dioxane was refluxed under stirring for 4 h in argon atmosphere. The mixture was filtered and evaporated to generate the crude product. The final product **3** was obtained by column chromatography (mesh chromatography silica, 1:15 ethyl acetate/light petroleum) in a yield of 71.6%. Characterization of compound **3**: ^{1}H NMR: δ_H (400 MHz, DMSO-d_6, Me$_4$Si): 9.98 (s, 1H), 8.70 (d, 1H), 8.07 (d, 1H), 7.84 (m, 1H), 7.78 (d, 1H), 6.64 (d, 2H), and 6.27 (t, 1H). ^{13}C NMR: δ_C (100 MHz, DMSO-d_6): 193.75, 164.68, 152.43, 147.76, 140.62, 138.84, 134.62, 131.27, 129.86, 127.87, 126.86, 123.42, 118.31.

2.5. Synthesis of compound 2

Compound **2** was synthesized from rhodamine B *via* a procedure we have reported [33]. Rhodamine B (1.0039 g, 2.76 mmol) and 80% hydrazine hydrate (4 mL) were dissolved in 30 mL methanol. The mixture was refluxed under stirring for 6 h in argon atmosphere. After distillation in vacuum, the residue was recrystallized with methanol to give the final product **2** in a yield of 76.9%.

2.6. Synthesis of compound 1

The mixture of compound **3** (0.1215 g, 0.27 mmol), compound **2** (0.0630 g, 0.30 mmol), and 3.8 mL ethanol was refluxed under stirring for 12 h in argon atmosphere. The crude residue was obtained after distillation in vacuum. The final product **1** was obtained by column chromatography (mesh chromatography silica, 1:1 dichloromethane/light petroleum) in a yield of 84.7%. Characterization of probe **1**: HRMS (EI) calcd. for C$_{41}$H$_{40}$N$_5$O$_4$ [M + H], 666.3080; found, 666.3098. ^{1}H NMR: δ_H (400 MHz, CDCl$_3$, Me$_4$Si): 8.69 (s, 1H), 8.12 (m, 2H), 8.05 (m, 3H), 7.53 (m, 3H), 7.40 (m, 1H), 7.27 (m, 1H), 7.15 (m, 2H), 6.57 (m, 2H), 6.52 (d, 2H), 6.26 (q, 2H), 3.34 (t, 8H), and 1.18 (q, 12H). ^{13}C NMR: δ_C (100 MHz, CDCl$_3$): 165.35, 153.13, 152.62, 152.16, 152.10, 149.07, 146.01, 137.52, 135.83, 133.83, 128.59, 128.40, 128.38, 128.06, 127.86, 123.97, 123.63, 118.81, 117.70, 110.02, 108.07, 105.61, 98.04, 66.13, 44.33, 29.06, 22.62, 12.62.

3. Results and discussion

3.1. Synthesis of sensor 1

In this work, the sensor **1** was synthesized *via* four-step synthetic procedure starting from 2-methy-8-hydroxyquinoline. The reaction of compound 8-hydroxy-2-methylquinoline with acryloyl chloride in toluene gave the product **4** in a 47.3% yield. Compound **4** reacted with SeO$_2$ in 1,4-dioxane and gave compound **3** in a 71.6% yield. The sensor