Sensors and Actuators B 174 (2012) 231–236

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Four Rhodamine B-based fluorescent chemosensor for Fe^{3+} in aqueous solution

Meimei Chai[a], Di Zhang[a], Min Wang[a], Huijie Hong[a], Yong Ye[a,b,*], Yufen Zhao[a,b,c]

[a] Phosphorus Chemical Engineering Research Center of Henan Province, Department of Chemistry, Zhengzhou University, Zhengzhou, China
[b] Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing, China
[c] Key Laboratory for Chemical Biology of Fujian Province, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

ARTICLE INFO

Article history:
Received 7 June 2012
Received in revised form 31 July 2012
Accepted 1 August 2012
Available online 10 August 2012

Keywords:
Rhodamine B
Fe^{3+}
Fluorescent probes
On–off

ABSTRACT

A series of Rhodamine B derivative was synthesized and characterized by NMR, HR-MS and IR. The probes exhibited highly selective and sensitive recognition toward Fe^{3+} over other metal ions. The significant changes in the fluorescence color could be used for naked-eye detection. The Job's plot, MS, IR and ^1H NMR indicated the formation of 1:2 complexes between 1 and Fe^{3+}. The reversibility establishes the potential of these probes as chemosensors for Fe^{3+} detection.

1. Introduction

The design and synthesis of compounds for sensing environmentally and biologically relevant ionic species, particularly for heavy metal and transition metal cations, has attracted a great deal of attention [1]. As one of the most essential trace elements in biological systems, Fe^{3+} performs a major role in many biochemical processes [2]. It provides the oxygen-carrying capacity of heme and acts as a cofactor in many enzymatic reactions involved in the mitochondrial respiratory chain [3]. Considerable efforts have been devoted to the development of Fe^{3+}-selective sensors. Unfortunately, there have been relatively few fluorescent chemosensors for Fe^{3+} [4]. It might be due to its paramagnetic nature which leads to their fluorescence quenching [5]. Therefore, the development of new fluorescent Fe^{3+} indicators, especially those that exhibit selective Fe^{3+}-amplified emission, is still a challenge and interest.

Rhodamine B has attracted considerable interest from chemists on account of its excellent photophysical properties [6,7]. The spirolactam ring form of rhodamine derivatives is non-fluorescent and colorless, whereas its ring-opened form gives a strong fluorescence and a pink color. Thereby, the rhodamine fluorophore can be an ideal framework to construct OFF–ON system for the specific metal ion [8–10]. Recently, some rhodamine-based fluorescent probes were reported for the detection of Fe^{3+} metal ions [11]. In this paper, we report four new rhodamine-based turn-on fluorescent sensors (Scheme 1, 1a-b and 2a-b) for Fe^{3+}. Sensor 1b shows very high sensitivity and selectivity toward Fe^{3+} over other metal ions in CH_3CN—H_2O (1:1, v/v) solution. Moreover, the interaction between sensor 1b and Fe^{3+} was reversible, which can be verified by the introduction of AcO^- ion into the system containing 1b and Fe^{3+}.

2. Experimental

2.1. Apparatus reagents and chemicals

Mass spectral determinations were made on a HPLC Q-Tof HR-MS spectrometer (Waters Micromass) by using methanol as mobile phase. NMR spectra were recorded on a Bruker DTX-400 spectrometer. UV–vis performed on a UV-1800PC spectrometer, Shanghai Mapada company. Fluorescence spectra measurements performed on HITACHIF-4500 fluorescence spectrophotometer. The melting points were determined by an X-4 microscopic melting point apparatus with a digital thermometer. Redistilled water was made for Milli-Q Water Machine.

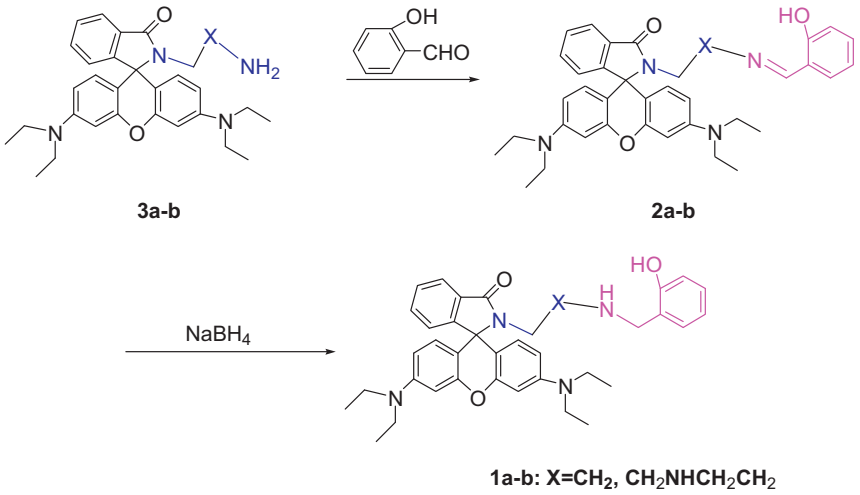
All the chemicals and solvents involved were analytical reagents. The solutions of metal ions were prepared from their chloride salts.

2.2. Synthesis of 2b

As shown in Scheme 1, title compounds can be prepared from the reaction of Rhodamine B derivative (3a or 3b) and 2-hydroxybenzaldehyde. Rhodamine B derivative 3a and 3b were synthesized according to the literature [12–14].

* Corresponding author at: Phosphorus Chemical Engineering Research Center of Henan Province, Department of Chemistry, Zhengzhou University, Zhengzhou, China. Tel.: +86 371 67767050.
E-mail address: yeyong@zzu.edu.cn (Y. Ye).

0925-4005/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2012.08.003



Scheme 1. Synthesis of target compounds.

To the solution of 2-hydroxy-benzaldehyde (0.17 g, 1.4 mmol) in 30 ml of chloroform, anhydrous aluminum chloride (0.34 g, 1.8 mmol) was added at 0 °C, and then the mixture was stirred at room temperature for 6 h. A solution of **3b** (0.74 g, 1.4 mmol) in triethylamine (0.70 g, 5.1 mmol) was slowly dropped and the resulting mixture was stirred at room temperature for 5 h. The mixture was quenched with a 1N sodium hydroxide solution. The layers were separated and the water layer was extracted with CH_2Cl_2 (2× 15 mL). The combined extracts were dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. After recrystallization from MeOH, 2b was obtained in 69.8%. M.p. 88–90 °C. ESI-MS: $[M+H]^+$: 632.3; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 (t, J = 7.0 Hz, 12H), 2.47 (t, J = 6.1 Hz, 2H), 2.77 (t, J = 10.86 Hz, 2H), 3.40–3.23 (m, 10H), 3.61 (t, J = 9.37 Hz, 2H), 6.29 (d, J = 9.8 Hz, 2H), 6.45–6.35 (m, 4H), 6.98–6.75 (m, 2H), 7.07 (dd, J = 5.4, 3.1 Hz, 1H), 7.26 (dd, J = 15.2, 6.5 Hz, 2H), 7.47–7.40 (m, 2H), 7.86 (dd, J = 5.4, 3.0 Hz, 1H), 8.33 (s, 1H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$): δ 12.6, 39.9, 44.3, 47.4, 48.9, 59.0, 65.0, 97.7, 105.5, 108.1, 116.9, 118.4, 122.7, 123.7, 127.9, 128.7, 131.0, 132.1, 132.4, 148.7, 153.3, 153.4, 161.1, 166.2, 168.5 ppm. HR-MS (ESI) $C_{39}H_{46}N_5O_3$ $[M+H]^+$: found 632.3604, cacd. 632.3601.

Similar to 2b, 2a was obtained in 67.8%, ESI-MS: $[M+H]^+$: 589.3, M.p. 92–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (t, J = 7.1 Hz, 12H), 3.54–3.28 (m, 12H,), 6.27 (dd, J = 8.9, 2.6 Hz, 2H), 6.44 (dd, J = 12.7, 5.7 Hz, 4H), 6.83 (td, J = 7.5, 1.1 Hz, 1H), 6.95–6.88 (m, 1H), 7.19–7.08 (m, 2H), 7.31–7.22 (m, 1H), 7.46 (dt, J = 7.4, 3.7 Hz, 2H), 7.94 (dd, J = 5.6, 3.1, 0.6 Hz, 1H), 8.09 (s, 1H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$): δ 12.6, 40.9, 44.3, 57.1, 64.9, 97.7, 105.4, 108.0, 117.6, 118.3, 118.7, 122.8, 123.8, 128.0, 128.8, 131.1, 131.1, 132.0, 133.7, 148.8, 153.3, 153.5, 161.1, 166.0, 168.2 ppm. HR-MS (ESI) $C_{37}H_{41}N_4O_3$ $[M+H]^+$: found 589.3174, cacd. 589.3179.

2.3. Synthesis of compound 1b

To the solution of 2b in MeOH (30 mL), sodium borohydride (0.27 g, 7 mmol) was added in portions at 0 °C. The mixture was stirred at room temperature for 8 h and was quenched with concentrated HCl. Then neutralized with 1N NaOH, and extracted with CH_2Cl_2 (2× 50 mL). The organic solution was dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography (silica gel, 6% MeOH in CH_2Cl_2) afforded the title compound 1b. Yield 74.9%, HR-MS (ESI) $C_{39}H_{48}N_5O_3$ $[M+H]^+$: found 634.3759, cacd. 634.3757; M.p. 90–92 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (t, J = 7.0 Hz, 12H), 2.42 (t, J = 6.2 Hz, 2H), 2.54 (s, 4H), 3.29 (t, J = 6.37 Hz, 2H), 3.36 (q, J = 8.19 Hz, 8H), 3.94 (s, 2H), 6.30 (dd, J = 8.9, 2.3 Hz, 2H), 6.43 (dd, J = 19.9, 5.5 Hz, 4H), 6.80 (m, 2H), 6.96 (d, J = 7.3 Hz, 2H), 7.16 (m, 2H), 7.46 (dd, J = 5.5, 3.1 Hz, 2H), 7.91 (dd, J = 5.5, 3.1 Hz, 1H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ 12.6, 40.1, 44.3, 47.6, 47.7, 52.2, 65.0, 97.7, 105.5, 108.1, 116.2, 118.7, 122.5, 122.7, 128.0, 128.3, 128.5, 128.7, 131.1, 132.4, 148.8, 153.3, 153.5, 158.3, 168.6 ppm.

Similar to 1b, 1a was obtained in 79.8%. HR-MS: $C_{37}H_{43}N_4O_3$ $[M+H]^+$: found 591.3334, cacd. 591.3335; M.p. 96–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (t, J = 7.0 Hz, 12H), 2.50 (t, J = 5.7 Hz, 2H), 3.34 (q, J = 7.0 Hz, 10H), 3.74 (s, 2H), 6.27 (dd, J = 8.9, 2.5 Hz, 2H), 6.39 (s, 2H), 6.42 (dd, J = 23.1, 5.6 Hz, 2H), 6.81–6.67 (m, 2H), 6.87 (d, J = 7.2 Hz, 1H), 7.17–7.07 (m, 2H), 7.48 (dd, J = 5.6, 3.1 Hz, 2H), 7.93 (dd, J = 5.6, 3.0 Hz, 1H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$): δ12.6, 39.4, 44.3, 47.6, 54.6, 65.1, 97.7, 105.3, 108.2, 116.2, 118.7, 122.3, 122.8, 123.8, 128.1, 128.2, 128.4, 128.6, 131.0, 132.5, 148.8, 153.3, 153.4, 158.2, 168.8 ppm.

2.4. Procedures for metal ion sensing

A 1 mM stock solution of compound 1 was prepared by dissolving Rhodamine B derivative in acetonitrile. A standard stock solution of Fe^{3+} (10 mM) was prepared by dissolving an appropriate amount of ferric chloride in water and adjusting the volume to 100 mL in a volumetric flask. This was further diluted to 1 mM. Stock solutions of other metal ions were prepared in water with a similar procedure. All measurements of spectra were carried out in a CH_3CN—H_2O (1:1, v/v) solution. For all measurements of fluorescence spectra, excitation was fixed at 550 nm with excitation slit set at 4.0 nm.

3. Results and discussion

3.1. Synthesis

The synthesis of Rhodamine B derivative was shown in Scheme 1, which can be prepared in high yield. Compound **1** was synthesized in two steps: production of Schiff's bases from **3** and 2-hydroxy-benzaldehyde, followed by reduction by $NaBH_4$ in MeOH. Their structures have been confirmed using ^{1}H NMR, ^{13}C NMR, MS and IR (see Supporting Information). Although **1 and 2** is a derivative of Rhodamine B, it forms a nearly colorless solution in CH_3CN—H_2O (1:1, v/v) solution, indicating that the spirocyclic form exists predominantly. The characteristic peak near 65.0 ppm (9-carbon) in the ^{13}C NMR spectrum of **1 and 2** also supports this consideration.