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Rhodamine 6G hydrazone bearing thiophene unit: A highly sensitive and selective off–on fluorescent chemosensor for Al^{3+}

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ABSTRACT

A rhodamine derivative (**R1**) has been synthesized by a hydrazone formation of rhodamine 6G hydrazide with 3-methylthiophene-2-carbaldehyde, which exhibits high selectivity and sensitivity as an "off–on" fluorescent sensor toward Al^{3+} in water containing media. The binding process was confirmed by UV–vis absorption, fluorescence measurements, mass spectroscopy and DFT calculation. The probe functions by Al^{3+} induced hydrolytic cleavage of the imine-bond to produce an intense rhodamine-based emission. To test the practical use of the probe, the determination of Al^{3+} in real water samples was also evaluated.

1. Introduction

Aluminum is the most abundant (8.3% by weight) metallic element and the third most prevalent of all elements (after oxygen and silicon), and it plays an important role in many fields, including food packaging, drinking water supplies, cookware, manufacturing industry, antacids and so on [1–3]. However, aluminum is a non-essential element for living systems, for it is a competitive inhibitor of several essential elements like Mg^{2+}, Ca^{2+} and Fe^{3+}. Excess aluminum can damage the human nervous system and induce several health hazards such as anemia, encephalopathy, dementia, gastrointestinal diseases, cardiotoxicity, Parkinson's disease, and most frequently Alzheimer's disease [4]. The World Health Organization (WHO) limits Al^{3+} concentration in drinking water to 200 μg/L (7.41 μM) [5]. Furthermore, nearly 40% of acidic soils worldwide are thought to be polluted due to the effects of aluminum toxicity, which is the critical factor that hampers crop performance in acidic soils [6]. Therefore, the determination of Al^{3+} in environmental and biological samples is of great importance for human health.

Particularly, fluorescence sensors appear to be attractive on account of their highly sensitive and selective, easy to fabricate, and non-destructive properties, especially the noninvasive *in vivo* imaging potential [7–9]. Generally, Al^{3+} prefers hard donor sites like O and N in its coordination sphere because of its strong acidity [10]. On the other hand, the strong hydration of Al^{3+} in aqueous media led to its weak coordination ability [11], so it is a challenge to design a selective and sensitive fluorescence probe for Al^{3+} in aqueous media.

Recently, several successful attempts have resulted in the development of selective chemiluminescence probes towards Al^{3+} ion with rhodamine backbone, because of its excellent photo physical properties such as high extinction coefficients, excellent quantum yields and relatively long emission wavelengths in the visible region [2–4,6,10–17]. Herein, as a continuation of our research on fluorescent sensors [18], we report here the rhodamine 6G hydrazone **R1** (Scheme 1) of 3-methylthiophene-2-carbaldehyde and its potential properties as an "off-on" fluorescent Al^{3+} sensor. The binding process was also confirmed by DFT calculation. The probe functions by Al^{3+} induced hydrolytic cleavage of the imine-bond to produce an intense rhodamine-based emission, which is different from the coordination mechanism of the reported Al^{3+} sensor with both rhodamine and thiophene moiety [17].

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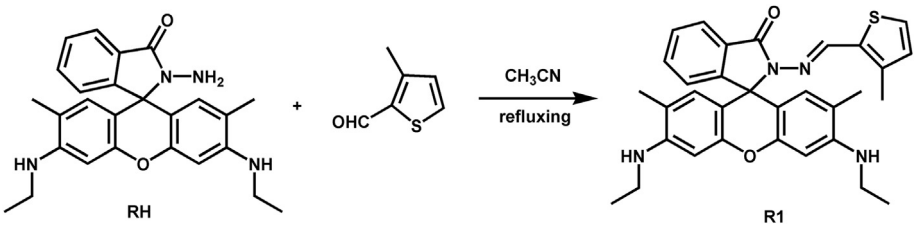

Scheme 1. Synthesis route of the sensor **R1**.

2. Experimental section

2.1. Materials and instrumentation

Solvents and starting materials for syntheses were purchased commercially and used as received. Elemental analyses were carried out on an Elemental Vario EL analyzer. ^{1}H NMR spectra of the sensor is recorded on a Bruker AV400 NMR spectrometer in DMSO-d_6 solution. The UV spectra were recorded on a Purkinje General TU-1800 spectrophotometer. Fluorescence spectra were determined on a Varian CARY Eclipse spectrophotometer, in the measurements of emission and excitation spectra the pass width is 5 nm. ESI-MS spectra were obtained on a Bruker Daltonics Esquire 6000 mass spectrometer. The X-ray diffraction measurement was performed on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) by using ϕ-ω scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program [19]. The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-97 program [20]. All non-hydrogen atoms were refined anisotropically. All H atoms were positioned geometrically and refined using a riding model.

2.2. Synthesis of *R1*

A quantity of rhodamine 6G hydrazide (**RH**, 428 mg, 1 mmol) [18] was added to a CH_3CN solution (20 ml) containing 3-methylthiophene-2-carbaldehyde (126 mg, 1 mmol). The mixture was refluxed for 3 h, and then cooled to room temperature. The separated solid was filtered, washed with CH_3CN and finally dried under vacuum. Yield 69%. Anal. Calc. for $C_{39}H_{43}N_5O_4$: C, 76.61; H, 6.01; N, 10.44. Found: C, 76.52; H, 6.18; N, 10.50%. ^{1}H NMR (400 MHz, DMSO-d_6),δ(ppm): 8.32 (s, 1H, CH=N), 7.83–7.85 (m, 1H, Aryl-H), 7.49–7.53 (m, 2H, Aryl-H), 7.39–7.40 (d, 1H, Aryl-H), 6.94–6.96 (t, 1H, Aryl-H), 6.76–6.78 (d, 1H, Aryl-H), 6.25 (s, 2H, Aryl-H), 6.08 (s, 2H, Aryl-H), 5.08–5.11 (t, 2H, 2NH), 3.03–3.10 (m, 4H, $2CH_2$), 1.96 (s, 3H, CH_3), 1.78 (s, 3H, $2CH_3$), 1.11–1.14 (t, 3H, $2CH_3$). ESI-MS: m/z = 537.2444 for $[M+1]^+$. Crystals of **R1** suitable for X-ray diffraction analysis were obtained by recrystallization from CH_3CN solution. Crystal data for $C_{32}H_{32}N_4O_2S$: crystal size: 0.15 × 0.12 × 0.10 mm, triclinic, space group P-1. a = 10.024(2) Å, b = 11.487(3) Å, c = 12.961(3) Å, α = 84.748(5), β = 68.343(4)°, γ = 88.943(5), V = 1381.1(5) Å^3, Z = 2, T = 296(2) K, θ = 1.70–24.99°, 7156 reflections measured, 4852 unique (R_{int} = 0.0450). Final residual for 354 parameters and 4852 reflections with $I > 2\sigma(I)$: R_1 = 0.0770, wR_2 = 0.1727 and GOF = 0.995 (Fig. 1). CCDC: 1456543.

2.3. General UV–vis and fluorescence spectra measurements

The spectral analyses were accomplished in CH_3CN/H_2O (9/1, v/v) solution at room temperature. The concentration of the sensor

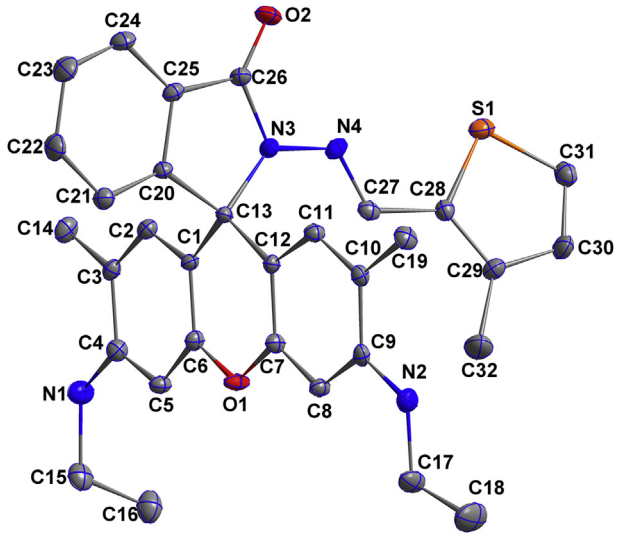

Fig. 1. The crystal structure of **R1**.

R1 for UV–vis and fluorescence measurement was 5 μM. Solutions of metal ions were prepared with nitrate or chloride salts in CH_3CN or water. UV–vis and fluorescence spectrophotometric titration were conducted directly in 2 mL cuvette by successive addition of corresponding chemical reagent using a microliter syringe. Upon addition of every aliquot, the solution was well mixed then the spectrum was measured.

3. Results and discussions

3.1. Selectivity of *R1* to Al^{3+} and other metal cations

The selectivity to various metal cations of probe **R1** was investigated. As shown in Fig. 2, free sensor **R1** exhibits almost none absorption at 450–650 nm in CH_3CN/H_2O (9/1, v/v) solution, indicating that **R1** exists in a spirocycle-closed form, which is in agreement with the observation previously reported [2]. Upon the addition of Al^{3+} to CH_3CN/H_2O (9/1, v/v) solution of **R1** (5 μM), the mixture solution exhibits a significant absorbance at 530 nm in UV–vis spectra (Fig. 2) and a fluorescence emission at 555 nm (Fig. 3, λ_{ex} = 350 nm), which results from the Al^{3+}-induced ring opening of the spirolactam form. Noticeably, in the case of other metal cations, such as Ag^+, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, K^+, Mg^{2+}, Na^+, Ni^{2+}, Pb^{2+} and Zn^{2+} ions, the fluorescence emission at 555 nm could not be observed. Also, upon the addition of Al^{3+}, the CH_3CN/H_2O (9/1, v/v) solution of **R1** (5 μM) shows a yellow fluorescence under 365 nm UV lamp (Fig. 3, inset). As expected, **R1** is a highly selective "off–on" fluorescent chemosensor for Al^{3+}. However, several metal ions, including Co^{2+}, Cu^{2+}, Hg^{2+} and Ni^{2+} could also induce obvious absorption peak of **R1** solution in the visible region.