Dyes and Pigments 86 (2010) 50–55

Contents lists available at ScienceDirect

Dyes and Pigments

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

A rhodamine-based dual chemosensor for the visual detection of copper and the ratiometric fluorescent detection of vanadium

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ARTICLE INFO

Article history:
Received 16 October 2009
Received in revised form
24 November 2009
Accepted 25 November 2009
Available online 24 December 2009

Keywords:
Rhodamine derivative
Cu^{2+}
VO^{2+}
UV–visible
Naked-eye
Fluorescent

ABSTRACT

The optical properties of a novel, rhodamine-based derivative, synthesized by reacting rhodamine hydrazide and 5-chlorosalicylaldehyde in ethanol, were investigated in methanol:HEPES solution. The novel sensor displayed selectivity for Cu^{2+}, as evidenced by a colourless to dark red colour change, which was characterized using UV–visible spectroscopy and which also allowed visual detection of Cu^{2+}. In contrast, selectivity towards VO^{2+} was determined from changes in the emission spectra in the nanomolar range. This represents the first reported rhodamine-based sensor capable of detecting both Cu^{2+} and VO^{2+} using two different modes.

1. Introduction

Rhodamine derivatives are excellent fluorophores and chromophores and have attracted considerable interest due to their very good photophysical properties [1–3], such as long absorption and emission wavelength, high fluorescence quantum yield (Φ), large extinction coefficient (ε), and high light stability. Rhodamine derivatives with a spirolactam-ring moiety, which is non-fluorescent and colourless, can be converted to the open-ring form in the presence of a proton or metal ion and display characteristically strong fluorescence emission and red colour [4]. Rhodamine-based spirolactams are considered to offer promise as molecular scaffolds and often are employed in OFF–ON fluorescent or colourimetric chemosensors [4,5]. Recently, several rhodamine-modified chemosensors have been developed for heavy- and transition-metal ions such as Cu^{2+} [6–19], Hg^{2+} [20–36], Fe^{3+} [36–40], Cr^{3+} [40–43], Cd^{2+} [44], Pb^{2+} [45] and Ag^{+} [46] because of the wide use of these metal ions and their subsequent impact on the environment and human health [47,48]. Copper is the third most abundant essential trace element in the human body after iron and zinc, and is important in many fundamental physiological processes in organisms. Copper has been shown to be a biochemically essential metal, such as, copper–zinc superoxide dismutase and its role in the enzymatic defense against oxygen toxicity. The detection of Cu^{2+} has important implications in the areas of environmental and biological analysis [6–19]. Vanadium is an essential trace element due to its significant roles in the environment, industry and physiological systems [49]. Laboratory and epidemiological evidence suggests that vanadium may also play a beneficial role in the prevention of heart-disease, despite its toxicity at ml^{-1} levels [50]. Vanadium remains a relatively unknown trace element, as it is still being targeted for use in various clinical applications worldwide. The development of an analysis method for vanadium is also same important [51].

Herein, we reported a novel dual chemosensor for detecting Cu^{2+} by UV–visible spectroscopy and VO^{2+} using fluorescence spectra. This chemosensor employs a rhodamine-based derivative (CSR), which was prepared by the reaction of excessive 5-chlorosalicylaldehyde (CS) and rhodamine hydrazide.

2. Experimental section

2.1. General

4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES; caution: stable; combustible; incompatible with strong oxidizing

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doi:10.1016/j.dyepig.2009.11.007

agents; protect from moisture) was purchased from Sigma–Aldrich. CSR was synthesized according to literature. HEPES solutions were adjusted to pH 7.0 by adding NaOH (0.1 M) to aqueous HEPES (10 mM). Cation salts were purchased from Shanghai city of China. All the common chemicals were of analytical grade.

A Beckman Φ50 pH meter was used to determined pH. UV–vis spectra were recorded on an HP8453 spectrophotometer. A PO-120 quartz cuvette (10 mm) was purchased from Shanghai city of China. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-300 MHz NMR spectrometer. Fluorescence spectra were measured on Cary Eclipse fluorescence spectrophotometer. Electrospray ionization (ESI) mass spectra were measured with an LC–MS 2010A (Shimadzu) instrument. A yellow single crystal of CSR was mounted on a glass fiber for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from reflections with 3.7–25.0° for CSR using a Bruker SMART APEX CCD automatic diffractometer. Data were collected at 223 K using Mo Kα radiation (λ = 0.710713 Å) and the ω-scan technique and corrected for Lorentz and polarization effect (SADABS) [52]. The structures were solved by direct methods (SHELX97) [53], and subsequent difference Fourier map and then refined in *F*2 using a full-matrix least-squares procedure and anisotropic displacement parameters.

2.2. Preparation of CSR

CSR was prepared in more high yield by reacting rhodamine hydrazide with excessive 5-chlorosalicylaldehyde (Fig. 1). Rhodamine hydrazide (0.46 g, 1 mmol; caution: toxic; contact with water or acids liberates toxic gas; can become highly flammable in use; danger of cumulative effects) was dissolved in 20 mL of absolute ethanol. An excessive of 5-chlorosalicylaldehyde (CS, 4 mmol) was added and the mixture was refluxed for 8 h. The ensuing solution was cooled, concentrated to 10 mL, and allowed to stand at 0 °C overnight in the refrigeratory. The precipitate was filtered and washed three times with 20 mL of cold ethanol. After drying under reduced pressure, the reaction afforded 0.43 g (76%) as a white solid. CSR compound. ^{1}H NMR ($CDCl_3$), δ (ppm): 1.15 (t, J = 6.78 Hz, 12H, CH_3), 3.34 (q, J = 6.78 Hz, 8H, CH_2), 6.27 (dd, J = 8.29 Hz, 2H), 6.49(m, 4H), 6.81 (d, J = 8.76 Hz, 2H,), 7.06 (s, 1H), 7.10–7.13 (d, J = 8.75 Hz, 1H), 7.18–7.20 (d, J = 6.48 Hz, 1H), 7.56 (m, 2H), 8.0 (d, J = 6.27 Hz, 1H), 9.00 (bs, 1H), 10.96 (bs, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 12.4, 44.2, 66.2, 97.8, 104.8, 108.0, 118.2, 119.1, 123.2, 124.0, 127.9, 128.5, 129.3, 130.1, 130.6, 133.2, 149.0, 150.1, 150.7, 153.2, 156.9, 164.2. ESI–MS: *m/z* 595.3 (55%, $[CSR + H]^+$), 617.3 (23%, $CSR + Na]^+$); [CSR] calculated 594.2. Crystal data for $C_{35}H_{35}ClN_4O_3$: crystal size: 0.5 × 0.5 × 0.4 mm, monoclinic, space group *P*ca21 (No. 29). a = 21.467(6) Å, b = 11.827(3) Å, c = 12.344(3) Å, V = 3134.04 (3) Å^3, Z = 4, T = 223 K, θ_{max} = 25.0°, 5104 reflections measured, 4447 unique (R_{int} = 0.0747). Final residual for 388 parameters and 5104 reflections with $I > 2\sigma(I)$: R_1 = 0.1231, wR_2 = 0.2485 and GOF = 1.27. The crystal structure is shown in Fig. 2.

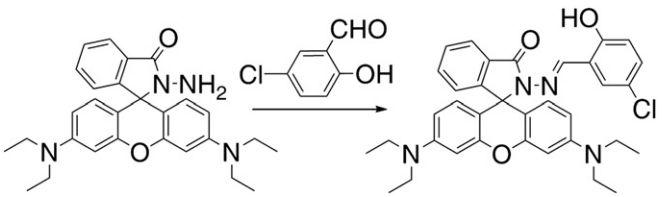

Fig. 1. Synthesis of CSR chemosensor.

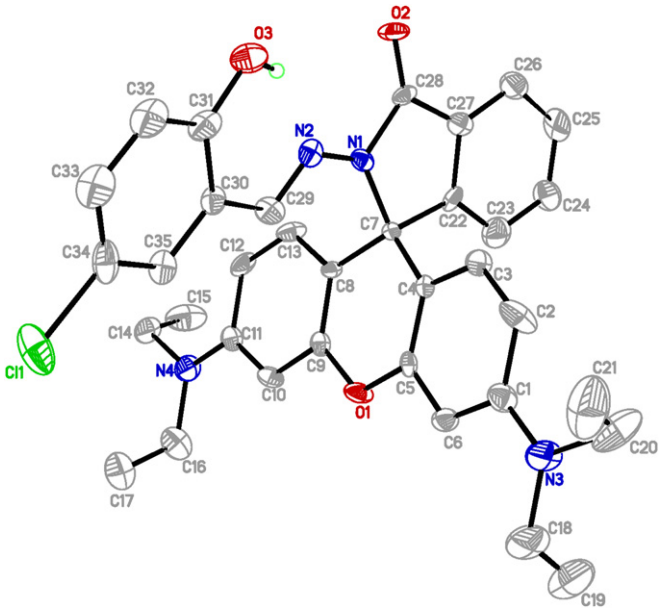

Fig. 2. Crystal structure of CSR, all hydrogen atoms were omitted for clarity.

2.3. Description of the structure of CSR

An intramolecular O3—H3…N2 hydrogen bond is observed in the molecular structure with the O3…N2 distance of 2.620(7) Å and the O3—H3…N2 angle of 146°, which is closed the six-membered pseudo-ring N2–C29–C30–C31–O3–H3. The dihedral angle between the spirolactam-ring system and xanthene ring plane is 88.53(2)°. Weak intermolecular C6—H6a…O3 hydrogen bonds also stabilize the crystal structure, forming one-dimensional infinite molecular chains along the *c* axis with the C6…O3 distance of 3.401 (9) Å and the C6—H6a…O3 angle of 159°.

2.4. General UV–vis and fluorescence spectra measurements

Since the chemosensor was not fully soluble in 100% aqueous media, methanol was used as a solubilizing medium. CSR stock solutions were prepared in methanol. The UV–vis and fluorescence spectra were obtained in mixed methanol/HEPES aqueous buffer (1:1, v/v, 10 mM, pH 7.0) solutions. Aqueous metal ion solutions were also prepared. Fluorescence measurements were carried out with a slit width of 10 nm.

2.5. Detection range

The UV–vis spectrum was characterized by a main band centred at 557 nm. The low detection threshold for Cu^{2+} was in the order of 10^{-6}–10^{-5} M and at this level the colour change was very obvious. The fluorescence emission was measured for each sample by exciting at 530 nm and spectra were measured from 540 to 700 nm. The sensitivity range for VO^{2+} was 10^{-7}–10^{-6} M.

3. Results and discussion

As a rhodamine derivative with a spirolactam group, CSR is non-fluorescent and colourless. Ring opening of the corresponding spirolactam gives rise to strong fluorescence emission and a pink colour. In a similar way, CSR as a ligand on a spirolactam-ring can induce colour change and a fluorescence change upon the addition of metal ions. The chemosensing behavior of CSR was investigated using UV–vis and fluorescence measurements.