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An ICT colorimetric chemosensor and a non-ICT fluorescent chemosensor for the detection copper ion

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ABSTRACT

Two new salicylaldehydes derivatives, 5-fluoro-2-hydroxybenzaldehyde and 9-formyl-8-hydroxyjulolidine, were reacted with rhodamine hydrazine. The products were characterized by electrospray ionization mass spectrometry, nuclear magnetic resonance spectroscopy and X-ray single crystal diffraction. The optical properties of the compounds were investigated in a methanol–4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid solution. 5-Fluoro-2-hydroxybenzaldehyde rhodamine hydrazone (compound **1**) was selective toward Cu^{2+} as shown by a colorless to yellow color change. This was characterized by UV–vis spectroscopy and can be used for the visual detection of Cu^{2+}. The selectivity of 9-formyl-8-hydroxyjulolidine rhodamine hydrazone (compound **2**) toward Cu^{2+} was determined by changes in UV–vis and emission spectra. The results show that compound **2** as a fluorescence probe is more sensitive than compound **1** as a UV–vis probe. Furthermore, compound **2** can be used for bioimaging.

1. Introduction

The development of sensitive chromogenic chemosensors has received much attention recently because of their potential application in clinical biochemistry and in environmental fields [1,2]. Pollution by transition metals is dangerous to human health and to the environment [3–6]. Copper is a heavy metal and an essential transition metal found in the human body. It plays a vital role in various biological processes such as bone formation, cellular respiration, and connective tissue development and serves as a significant catalytic co-factor for several metalloenzymes [6–10]. However, an excessive amount of copper in the human body is extremely toxic [11–13]. Thus, it is necessary to design and develop a specific copper ion sensor for the selective and rapid detection of copper.

Currently, rhodamine B is extensively used as a chemosensor because of its high absorption coefficient, high fluorescence quantum yield and its excitation within visible wavelengths [14–23]. Several successful attempts have resulted in the development of selective chemiluminescence, colorimetric and fluorescence sensors for copper ion based on rhodamine B hydrazine using 2-dihydroxy-1,1-binaphthyl-3-carboxaldehyde [24], 8-hydroxyquinoline-2-carboxaldehyde [25], 2-hydroxy-4-methoxybenzaldehyde [26], (R)-2,20-dihydroxy-1,10-binaphthyl-3-carbaldehyde, 2-hydroxy-1-naphthaldehyde and 2-methoxybenzaldehyde [27], salicylaldehyde [23,28,29], glyoxal [30,31], cinnamaldehyde [32], pyridine-2-aldehyde [33], 5-chlorosalicylaldehyde [34], furfural, [35] and 2,4-dihydroxyaldehyde [36].

In this work, two new salicylaldehydes derivatives, 5-fluoro-2-hydroxybenzaldehyde and 9-formyl-8-hydroxyjulolidine were reacted with rhodamine hydrazine. 5-Fluoro-2-hydroxybenzaldehyde rhodamine hydrazone (compound **1**) can be used as a colorimetric chemosensor because of intramolecular charge transfer (ICT). However, 9-formyl-8-hydroxyjulolidine rhodamine hydrazone was used as a fluorescent chemosensor for copper ions because it does not undergo intramolecular charge transfer (ICT). The fluorescent chemosensor was also used for bioimaging.

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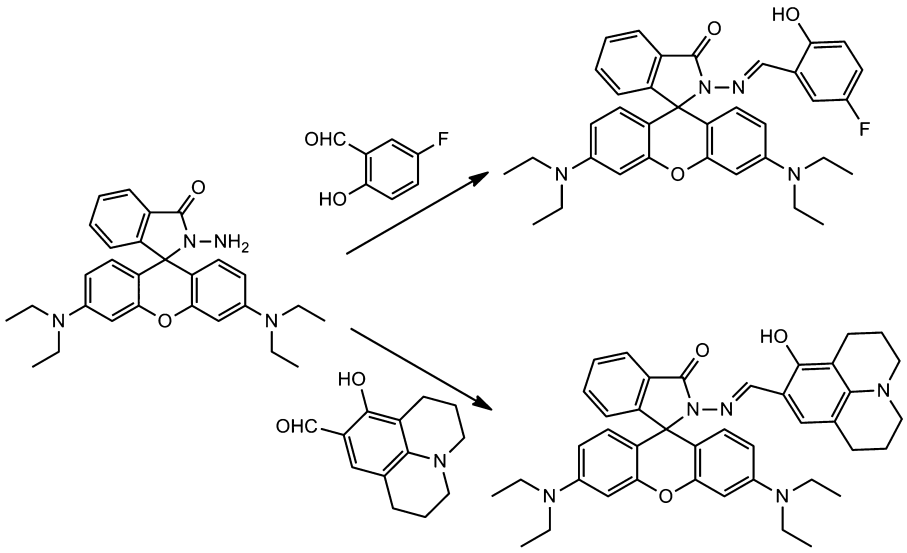

Scheme 1. Compound syntheses.

2. Materials and methods

2.1. Materials

4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) was purchased from Sigma–Aldrich (St. Louis, MO). Compounds **1** and **2** were synthesized using a modification of a literature method [37]. Sodium hydroxide solution (0.1 mol/L) was added to aqueous HEPES (10 mmol/L) to adjust the pH to 7.0. Anionic salts were purchased from Shanghai Experiment Reagent Co., Ltd. (Shanghai, China). All other chemicals used were of analytical grade.

2.2. Instruments

A pH meter (Mettler Toledo, Switzerland) was used to determine the pH. Ultraviolet–visible (UV–vis) spectra were recorded on a Cary 50 Bio UV–vis spectrophotometer. Fluorescence spectra were measured on Cary Eclipse fluorescence spectrophotometer. A PO-120 quartz cuvette (10 mm) was purchased from Shanhai Huamei Experiment Instrument Plants, China. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AVANCE-300 MHz and 75 MHz NMR spectrometer, respectively (Bruker, Billerica, MA). ESI was measured with an LTQ-MS (Thermo) instrument. The ability of compound **2** reacting to Cu^{2+} in the living cells was also evaluated by laser confocal fluorescence imaging using a Leica TCS SP5 laser scanning microscope. The yellow single crystal of compound **1** 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 within 2.42–25.00°, using a Bruker SMART APEX CCD automatic diffractometer. Data were collected at 173 K using Mo Kα radiation (λ = 0.710713 Å) and the ω-scan technique, and corrected for the Lorentz and polarization effects (SADABS) [38]. The structures were solved by direct methods (SHELX97) [38], and subsequent difference Fourier maps were inspected and then refined in F^2 using a full-matrix least-squares procedure and anisotropic displacement parameters.

2.3. Preparation and characterization of compounds

The syntheses of the compounds are summarized in Scheme 1. The compounds were synthesized by a one-step reaction between rhodamine hydrazine and either 5-fluoro-2-hydroxybenzaldehyde or 9-formyl-8-hydroxyjulolidine in ethanol containing acetic acid. 0.22 g (1.5 mmol) 5-fluoro-2-hydroxybenzaldehyde (for **1**) or 0.34 g (1.5 mmol) 9-formyl-8-hydroxyjulolidine (for **2**) were added to 0.46 g (1 mmol) of rhodamine hydrazine dissolved in 20 ml ethanol and the reaction solution was refluxed in an oil bath for 2 h. A light pink solid and a yellow solid appeared, respectively, which were filtered from each solution. Each crude product was recrystallized in CH_3OH to give 5-fluoro-2-hydroxybenzaldehyde rhodamine hydrazone (**1**) or 9-formyl-8-hydroxyjulolidine rhodamine hydrazone (**2**) as a light pink and yellow powder in 62% and 45% yields, respectively. A H_2O/CH_3CH_2OH solution containing the product was allowed to evaporate slowly at room temperature for several days and the light pink crystals (**1**) that subsequently formed were suitable for X-ray crystallography. However, after several attempts no suitable single crystals were obtained for **2**.

1: ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ 10.66 (s, 1H, OH), 9.12 (s, Ar-H, 1H), 8.99 (d, Ar-H, 1H, J = 6.5), 7.54 (t, Ar-H, 2H, J = 11.3), 7.19 (d, Ar-H, 1H, J = 26.9), 6.82 (m, Ar-H, 3H, J = 39.4), 6.49 (d, Ar-H, 4H, J = 8.2), 6.27 (d, Ar-H, 2H, J = 8.7), 3.34 (q, CH_2, 8H, J = 21.0), 1.18 (t, CH_3, 12H, J = 26.7); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.7, 157.5, 155.0, 154.3, 153.9, 151.3, 149.5, 134.0, 130.1, 129.0, 128.5, 124.6, 123.7, 119.1, 118.3, 116.9, 108.5, 105.5, 98.3, 66.8, 44.7, 13.0; ESI-MS m/z 579.25 $[1+H]^+$; elemental analysis (calcd. %) for $C_{35}H_{35}FN_4O_3$: C, 72.64; H, 6.10; N, 9.68; found: C, 72.58; H, 6.14, N, 9.70; crystal data for $C_{35}H_{35}FN_4O_3$: crystal size: 0.26 × 0.25 × 0.20, monoclinic, space group $P2_{(1)}/c$ (No. 14). a = 9.024(2) Å, b = 27.889(8) Å, c = 11.935(3) Å, β = 102.550°, V = 2931.9(14) Å^3, Z = 4, T = 173 K, θ_{max} = 25.00°, 16,501 reflections measured, 5042 unique (R_{int} = 0.0526). Final residual for 413 parameters and 5142 reflections with $I > 2\sigma(I)$: R_1 = 0.0685, wR_2 = 0.1477 and GOF = 1.208 (Figs. 1 and S1).

2: ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ 10.98 (s, 1H), 8.77 (s, Ar-H, 1H), 7.93 (s, Ar-H, 1H), 7.45 (s, Ar-H, 2H), 7.11 (s, Ar-H, 1H), 6.48 (q, Ar-H, 5H, J = 28.6), 6.24 (d, Ar-H, 2H, J = 8.5), 3.32 (d, CH_2, 8H, J = 6.8), 3.12 (d, CH_2, 4H, J = 4.7), 2.61 (s, CH_2, 4H), 1.87 (s, CH_2, 4H), 1.16 (t, CH_3, 12H, J = 13.4); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.6, 156.6, 155.6, 154.3, 152.3, 149.9, 133.8, 131.1, 130.2, 129.1, 124.8, 124.1, 113.4, 109.1, 108.0, 106.8, 99.0, 67.0, 51.1, 50.7, 45.4, 28.1, 23.2, 22.3, 21.5, 13.7; ESI-MS m/z 656.33 $[2+H]^+$ (Fig. S2); elemental analysis (calcd. %) for $C_{41}H_{45}N_5O_3$: C, 75.09; H, 6.92; N, 10.68; found: C, 75.02; H, 6.88, N, 10.60.

2.4. General UV–vis and fluorescence spectra measurements

Stock solutions of compounds were prepared in methanol. UV–vis and fluorescence spectra were obtained in methanol:water