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A selective fluorescent chemosensor with 1, 2, 4-triazole as subunit for Cu (II) and its application in imaging Cu (II) in living cells

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ABSTRACT

A chemosensor based on rhodamine B with 1, 2, 4-triazole as subunit was synthesized and characterized. It exhibits high selectivity and sensitivity for Cu^{2+} in ethanol/water (6:4, v:v) of pH 7.0 HEPES buffer solution and undergoes ring opening mechanism, and a 2:1 metal–ligand complex is formed. The chemosensor displays a linear response to Cu^{2+} in the range between 1.0×10^{-7} M and 1.0×10^{-6} M with a detection limit of 4.5×10^{-8} M. Its capability of biological application was also evaluated and the results show that this chemosensor could be successfully employed as a Cu^{2+}-selective chemosensor in the fluorescence imaging of living cells.

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1. Introduction

Detecting the presence of transition metal ions has received considerable attention, mostly because these metal ions play important roles in living systems and have an extremely ecotoxicological impact on the environment and human. Among the various transition metal ions, Cu^{2+} plays a critical role as a catalytic cofactor for a variety of metalloenzymes, including superoxide dismutase, cytochrome *c* oxidase and tyrosinase [1]. However, under overloading conditions, Cu^{2+} exhibits toxicity in that it causes neurodegenerative diseases, probably by its involvement in the production of reactive oxygen species [2]. Chemosensors based on ion-induced changes in fluorescence appear to be particularly attractive due to their simplicity, high sensitivity, high selectivity, and instantaneous response [3]. Therefore, numerous excellent studies focus on the design of fluorescent chemosensors and the analysis of Cu^{2+}. Most of the reported Cu^{2+} fluorescent chemosensors, however, generally undergo fluorescence quenching upon the binding of Cu^{2+} [4–10], which is not as sensitive as a fluorescence enhancement response. Therefore, the development of highly sensitive and selective "off–on" chemosensor for Cu^{2+} is necessary. Based on our previous research [11–13], it is necessary to choose an efficient fluorophore and consider the geometry of coordination sites for a certain cation. Herein, we describe a new and simple fluorescent Cu^{2+} chemosensor **L** based on the equilibrium between the spirolactam (non-fluorescence) and the ring-opened amide (fluorescence) of rhodamine derivatives. In chemosensor **L**, we chose the rhodamine derivative as the fluorophore due to its excellent photophysical properties, such as long wavelength absorption and emission, high fluorescence quantum yield, large extinction coefficient, and high stability against light [14]. In addition, to take advantage of the 1, 2, 4-triazole subunit containing lone electron pairs on N, the semirigid ligand could effectively chelate Cu^{2+} according to the ionic radius and limit the geometric structure of the complex. With this intention, a Cu^{2+}-specific fluorescent and colorimetric chemosensor **L** derived from rhodamine B with 1, 2, 4-triazole as subunit was designed and synthesized (Scheme 1).

2. Experimental

2.1. Reagents and instruments

All reagents and solvents are of analytical grade and used without further purification. The metal ions and anions salts employed are NaCl, $MgCl_2 \cdot 6H_2O$, $CdCl_2$, $HgCl_2$, $CaCl_2 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $AgNO_3$, $CoCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, $PbCl_2$, NaClO, $NaNO_3$, Na_2CO_3, NaCl, NaAc, $NaClO_4$, KBr and Na_2HPO_4, respectively.

Fluorescence emission spectra were conducted on a HORIBA Fluoromax-4 spectrofluometer. UV–vis spectra were obtained on a Beckman DU-800 spectrophotometer (USA). Nuclear magnetic

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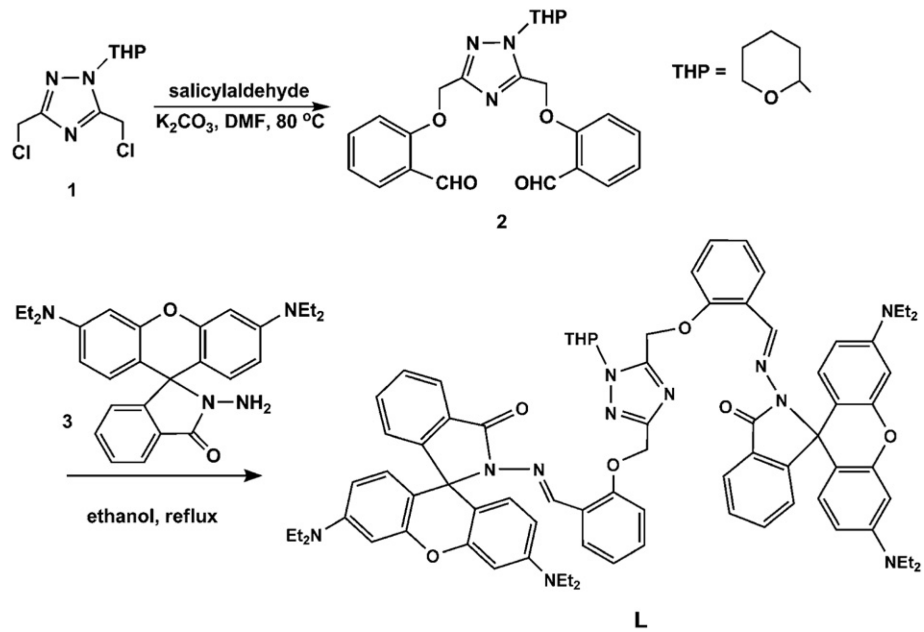

Scheme 1. Synthesis route of **L**.

resonance (NMR) spectra were measured with a Brucker WM-300 instrument and chemical shift were given in ppm from tetramethylsilane (TMS). Mass (MS) spectra were recorded on a Thermo TSQ Quantum Access Agillent 1100. Fluorescence imaging was performed by confocal fluorescence microscopy on an Olympus FluoView Fv1000 laser scanning microscope (USA). Melting points were taken on a WRS-1B digital melting-point apparatus.

2.2. Synthetic procedure

2.2.1. Synthesis of compound 2

Compound **1** was synthesized as described before [15]. Under N_2 gas, salicylaldehyde (2.4 mmol) and Na_2CO_3 (4.0 mmol) were combined in DMF (40 mL) and stirred. Compound **1** (1.0 mmol) in DMF (10 mL) was added dropwise. The reaction mixture was stirred at 80 °C for 24 h, and then was poured into 500 mL cooled water, and the precipitate so produced was filtered off and recrystallized with ethanol to give **2** as white solid. Yields: 85.2%. M.p.: 116.1–117.2 °C. MS (ES+) m/z: 338.2 (M-THP+H^+). ^1H NMR (δ ppm, $CDCl_3$): 10.52 (s, 1H), 10.44 (s, 1H), 7.86 (t, 1H, J = 4.40 Hz), 7.74 (t, 1H, J = 4.40 Hz), 7.58 (d, 1H, J = 12.00 Hz), 7.54 (d, 1H, J = 12.00 Hz), 7.20 (s, 2H), 7.18 (s, 2H), 7.12 (t, 1H, J = 16.00 Hz), 7.06 (t, 1H, J = 16.00 Hz), 5.66 (d, 1H, J = 8.00 Hz) 5.43 (s, 2H), 5.27 (s, 2H), 4.00 (d, 1H, J = 12.00 Hz), 3.63 (d, 1H, J = 18.60 Hz), 2.32 (m, 1H, J = 16.00 Hz), 2.09 (m, 1H, J = 17.20 Hz), 1.99 (m, 1H, J = 10.00 Hz), 1.71 (m, 2H, J = 12.80 Hz), 1.62 (m, 2H, J = 18.40 Hz). ^{13}C NMR (δ ppm, $CDCl_3$): 189.78, 189.05, 160.84, 159.60, 158.25, 151.61, 135.97, 135.70, 129.30, 128.18, 125.44, 125.29, 122.06, 121.40, 113.37, 113.05, 85.02, 61.52,29.61, 24.59, 21.79, 67.67, 63.99.

2.2.2. Synthesis of compound L

Compound **3** was synthesized according to reported method [16]. Compound **2** (1.0 mmol) and compound **3** (2.2 mmol) were mixed in 30 mL ethanol and refluxed for 4 h. After cooling to room temperature, the precipitate so obtained was washed with water and ethanol, and then dried in vacuum. The **L** was obtained by recrystallization with ethanol as pale yellow solid. Yields: 75.3%. M.p.: 186.2–187.8 °C. MS (ES+) m/z: 1320.96 (M+Na^+). ^1H NMR (δ ppm, $CDCl_3$): ^1H NMR: 9.37 (s, 1H), 9.30 (s, 1H), 7.96 (s, 1H), 7.95 (s, 1H), 7.9 (d, 1H, J = 7.5 Hz), 7.76 (d, 1H, J = 6.55 Hz), 7.51 (d, 1H, J = 6.05 Hz), 7.48 (d, 1H, J = 1.60 Hz), 7.47 (s, 1H), 7.46 (d, 1H, J = 1.75 Hz), 7.44 (d, 1H, J = 7.25 Hz), 7.17 (d, 2H, J = 4.26 Hz), 7.13 (m, 2H, J = 6.69 Hz), 6.98 (s, 1H), 6.96 (s, 1H), 6.90 (t, 2H, J = 9.36 Hz), 6.87 (m, 1H, J = 3.35 Hz), 6.84 (m, 1H, J = 7.50 Hz), 6.52 (s, 1H), 6.50 (d, 2H, J = 1.85 Hz), 6.49 (d, 1H, J = 2.90 Hz), 6.44 (d, 1H, J = 2.35 Hz), 6.42 (m, 3H, J = 6.63 Hz), 6.24 (d, 2H, J = 8.16 Hz), 6.22 (d, 1H, J = 2.20 Hz), 5.55 (d, 1H, J = 10.86 Hz), 5.19 (s, 2H, J = 2.80 Hz), 5.03 (s, 2H, J = 2.65 Hz), 3.82 (d, 1H, J = 6.39 Hz), 3.54 (t, 1H, J = 11.37 Hz), 3.30 (m, 8H, J = 10.35 Hz), 2.21 (m, 1H, J = 12.33 Hz), 2.17 (d, 1H, J = 10.32 Hz), 1.95 (t, 1H, J = 7.90 Hz), 1.86 (d, 1H, J = 6.18 Hz), 1.62 (d, 1H, J = 12.00 Hz), 1.56 (m, 1H, J = 14.10 Hz), 1.12 (t, 12H, J = 14.85 Hz). ^{13}C NMR (δ ppm, $CDCl_3$): 164.56, 164.48, 158.87, 157.62, 156.34, 153.51, 153.47, 153.38, 152.01, 151.62, 151.33, 148.83, 148.78, 144.97, 144.15, 133.17, 132.99, 131.04, 130.63, 130.09, 130.05, 128.29, 128.11, 128.04, 126.62, 126.32, 125.20, 124.82, 124.04, 123.92, 123.23, 121.99, 121.44, 114.36, 113.44, 107.90, 107.84, 107.81, 106.51, 106.47, 98.01, 97.92, 84.51, 67.40, 66.32, 66.19, 64.92, 62.10, 58.46, 53.43, 44.31, 29.71, 29.48, 24.75, 21.77, 18.45, 12.56, 12.62.

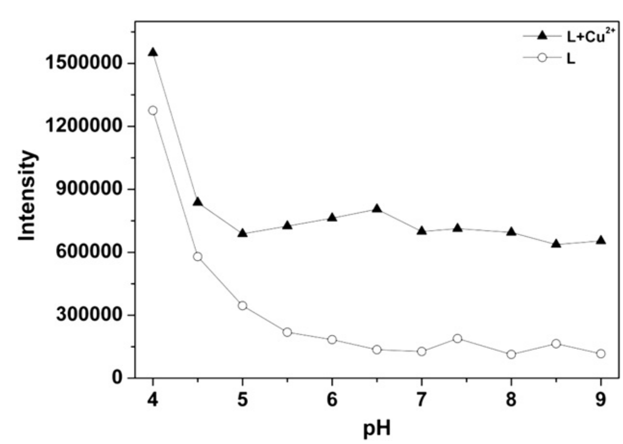

Fig. 1. Influences of pH on the fluorescence spectra of **L** (1.0 μM) (○) and **L** (1.0 μM) plus Cu^{2+} (50 μM) (▲) in ethanol–water solution (6:4, v:v). The pH was modulated by adding 1 M HCl or 1 M NaOH in HEPES buffers.

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