Dyes and Pigments 127 (2016) 94–99

Contents lists available at ScienceDirect

Dyes and Pigments

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

A novel facilely prepared rhodamine-based Hg^{2+} fluorescent probe with three thiourea receptors

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ARTICLE INFO

Article history:
Received 19 October 2015
Received in revised form
25 December 2015
Accepted 26 December 2015
Available online 2 January 2016

Keywords:
Rhodamine
Thiourea
Fluorescent probe
Hg^{2+}
Comprehensive performance
Sensing mechanism

ABSTRACT

A novel rhodamine-based turn-on fluorescent probe with three thiourea receptors was designed, synthesized and fully characterized. In acetonitrile/4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid buffer (9/1, v/v, pH = 7.21), the probe showed high selectivity and sensitivity to Hg^{2+} with a 20-fold fluorescence enhancement at 583 nm. The increase in fluorescence intensity was linearly proportional to the concentration of Hg^{2+} in the range of 25–200 μM with a detection limit of 3.04×10^{-7} M. The probe could work in a nearly neutral pH span of 6.41–8.33 and exhibited excellent interference immunity. Real sample assay showed the probe had good practicability. The results from Job's plot, reversibility experiment, mass and infrared spectra analysis suggested a 1:3 probe/Hg^{2+} complex with an association constant of 9.88×10^{11} M^{-3} and a new interaction way between the probe and Hg^{2+}.

1. Introduction

Mercury, one of the common toxic elements in the environment, contaminates the atmosphere, soil and water ubiquitously. When absorbed in human body, mercury will cause damage to the brain, central nervous system, endocrine system and so on, leading to motional and cognitive disorders [1,2]. Thus, it is crucial to detect the presence of mercury. Due to high sensitivity, simplicity, non-destructive, as well as onsite and instantaneous response, fluorescent probe has been particularly attractive in the detection of noble, heavy or transition metal ions [3–7].

Rhodamine derivatives are regarded as a popular framework for fluorescent probe because of their long absorption and emission wavelengths, large extinction coefficients, high fluorescence quantum yields, and typical analyte-mediated spectroscopic changes resulting from lactonization–delactonization [3,8–10]. Despite the reported existing studies on rhodamine-based fluorescent probes for Hg^{2+} [1,2,11–16], there are still much room for improvement in order to attain probes with simple preparation method, good selectivity, high sensitivity, fast response speed, aqueous working media and ecological working pH range [17].

Herein, we designed a rhodamine-based Hg^{2+} fluorescent probe as advancement in this field. The probe is easily prepared, highly selective and sensitive, and quickly responsive to Hg^{2+} at room temperature in CH_3CN/HEPES buffer (9/1, v/v, pH = 7.21). A rare 1:3 probe/Hg^{2+} complex [18] formed and a new sensing mechanism was explored.

2. Experimental

2.1. Reagents and chemicals

The reagents and chemicals comprise rhodamine B (RB) (AR, The Third Reagent Factory, Shanghai), triethylenetetramine (TETA) (CR, Sinopharm Chemical Reagent Co., Ltd.), phenyl isothiocyanate (PITC) (≥98%, Aladdin Industries, Inc.), ethanol (EtOH), acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2) (AR, Jiangsu Powerful Features Chemical Co., Ltd.,), NaCl, KCl, $MgCl_2$, $CaCl_2$, $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, $Pb(NO_3)_2$, $Ni(NO_3)_2 \cdot 6H_2O$, $MnSO_4 \cdot H_2O$, $CoCl_2 \cdot 6H_2O$, $CdCl_2 \cdot 2.5H_2O$ and $HgCl_2$ (Sinopharm Chemical Reagent Co., Ltd.). HEPES buffer (0.02 mol/L, pH = 7.21) was prepared in deionized water (H_2O). The solvents used in synthesis were of analytical grade, other solvents were

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http://dx.doi.org/10.1016/j.dyepig.2015.12.023
0143-7208/

spectroscopic grade. All reagents were commercially available and were put into use without further purification.

2.2. Apparatus

MALDI-TOF mass spectrum was recorded on an ultrafleXtreme Mass spectrometer (Bruker, America) using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyl] malononitrile (DCTB) as matrix. LC-mass was recorded on a Brukermicro TOF-QIII LC/MS (Bruker Daltonics Co., Germany). ^{1}H NMR and ^{13}C NMR spectra were carried out on an UNITY INOVA400 and an UNITY INOVA 300 high-resolution superconducting NMR spectrometer (Varian, America) in $CDCl_3$ respectively. Infrared (IR) spectra were recorded on a MagNa-IR550 Fourier transform infrared spectrometer (Nicolet, America) using KBr pellet. Elemental analysis (EA) was done on an EA1110 CHNO-S elemental analyzer (Carlo-Elmer, Italy). Fluorescence spectra measurements were obtained by a Fluoromax-4 spectrofluorometer (HORIBA Jobin Yvon, France). Absorption spectra were obtained by a U-3900 spectrophotometer (Perkin–Elmer, America). pH value was tested on a METTLER TOLEDO FE20 pH meter (Mettler Toledo Co., Ltd. Shanghai, China). Melting point was determined on an X-6 Microscopic melting point tester (Beijing Taike Instrument Co., Ltd., China). The spectra and pH values were measured at 25 °C.

2.3. Synthesis of the probe

RTTU was synthesized from the reaction of rhodamine B (RB), triethylenetetramine (TETA) and phenyl isothiocyanate (PITC), as illustrated in Scheme 1. The structure of RTTU was fully characterized by ^{1}H NMR, ^{13}C NMR, MALDI-TOF-MS, IR, and elemental analysis.

The intermediate RTTA was synthesized following the Refs. [11,19,20]. RB (0.1 g, 0.209 mmol) was dissolved in EtOH (10 mL) and then TETA (1 mL, 5.2 mmol) was added dropwise. The solution was heated to reflux for 24 h until it turned from red to colorless. The solvent was removed under reduced pressure. Water was added to the residue and the mixture was extracted with CH_2Cl_2. The organic phase was separated and washed three times with water, followed by the evaporation of the solvent. The resultant mixture was then dried in vacuo to afford RTTA as a yellow solid (0.103 g, 86.6%). Next, to a stirring solution of RTTA (0.1 g, 0.163 mmol) in CH_3CN (10 mL), PITC (200 μL, 1.67 mmol) was added dropwise and the resulted mixture was reacted for 5 h under room temperature until white solid was precipitated. After standing for 12 h, the solid was filtrated, washed three times with CH_3CN to get RTTU as a white solid. Yield: 0.089 g (52.0%), m.p. 181.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (Fig. S1, Supporting information (ESI)), δ/ppm: 1.16 (*t*, 12H, J = 6.4 Hz), 3.33 (*q*, 8H, J = 6.8 Hz), 3.43 (*t*, 2H, J = 4.4 Hz), 3.51 (*s*, 3H), 3.87 (*t*, 8H, J = 3.6 Hz), 4.05 (*t*, 2H, J = 4.4 Hz), 6.31 (*d*, 2H, J = 6.8 Hz), 6.41–6.43 (*m*, 4H), 7.13 (*d*, 6H, J = 7.2 Hz), 7.20–7.24 (*m*, 6H), 7.30–7.39 (*m*, 3H), 7.48 (*q*, 3H, J = 6.8 Hz), 7.87 (*d*, 1H, J = 7.2 Hz), 9.50 (*s*, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) (Fig. S2, ESI), δ/ppm: 12.65, 29.47, 38.20, 44.43, 49.52, 65.70, 97.94, 104.15, 108.40, 122.84, 124.09, 125.65, 126.08, 126.45, 127.53, 128.22, 128.53, 130.07, 133.10, 135.86, 139.68, 149.08, 153.40, 181.41, 181.80. MALDI-TOF-MS (Fig. S3, ESI): $[M + H]^+$ = 976.420, $[M + Na]^+$ = 998.415. FTIR (cm^{-1}) (Fig. S4, ESI): ν(NH) 3206.49; ν(CH_3, CH_2) 2969.26, 2923.94, 2854.50; ν(C=O) 1665.44; ν(ArH) 3037.73, 1615.30, 1515.01, 1494.76. Elemental analysis: Calculated for $C_{55}H_{61}N_9O_2S_3$ (%): C, 67.66; N, 12.91; H, 6.30. Found (%): C, 67.34; N, 12.81; H, 6.24.

2.4. Testing and calculating methods

2.4.1. Sample preparation

RTTU was dissolved in CH_3CN to form a 0.1 mM stock solution. Metal salts were dissolved in H_2O to get 10 mM stock solutions. When the sensing behavior of RTTU towards metal ions was studied, 5 mL of the RTTU stock solution was mixed with one of the metal salt stock solutions (250 μL) in a 10 mL volumetric flask and diluted with HEPES buffer solution (0.02 mol/L, pH = 7.21) and CH_3CN to volume. The concentration of RTTU was 50 μM. The solvent was CH_3CN/HEPES buffer (9/1, v/v, pH = 7.21). The pH was adjusted by 0.02 mol/L HEPES buffer with different pH values.

2.4.2. Fluorescent quantum yield [21]

The fluorescent quantum yield was estimated from the absorption and fluorescence spectra of RTTU according to Eq. (1), where the subscript s and r stand for the sample and the reference (rhodamine B, $\phi_r = 0.97$ in ethanol), respectively. ϕ is the quantum yield, A represents the absorbance at the excitation wavelength, S refers to the integrated emission band areas and n_D is the solvent refractive index. The absorbance of the solutions was kept under 0.05 in order to make the testing results reliable.

$$\phi_s = \phi_r \frac{S_s}{S_r} \frac{A_r}{A_s} \frac{n_{Ds}^2}{n_{Dr}^2} \quad (1)$$

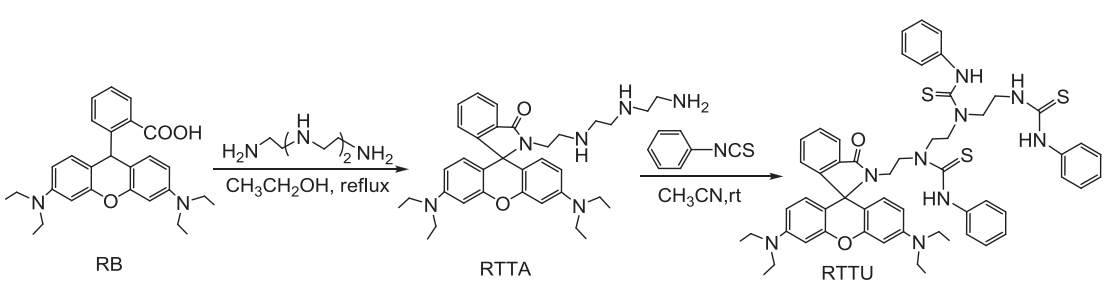
2.4.3. Detection limit [21]

The detection limit (δ) was calculated based on Eq. (2), where S is the standard deviation of blank measurement and K is the slope of the fit line in fluorescence titration. The emission fluorescence intensity of RTTU in CH_3CN/HEPES buffer (9/1, v/v, pH = 7.21) without any metal ions was measured 5 times.

$$\delta = 3S/K \quad (2)$$

2.4.4. Association constant [18]

The association constant for RTTU/Hg^{2+} was obtained from nonlinear curve fitting of the fluorescence titration data with



Scheme 1. Synthetic route of RTTU.