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Tunable fluorescent probes for selective detection of copper(II) and sulphide with completely different modes

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ABSTRACT

Diacylhydrazine-based fluorescent probes are designed for selective detection of copper(II) and sulphide with two modes. The probes can not only be decomposed into rhodamine B by Cu^{2+}, but can also be tuned to construct Cu ensembles for selective detection of sulphide.

1. Introduction

Copper is an essential trace element and the third most abundant transition metal (after Fe^{2+} and Zn^{2+}) in the human body [1]. Cu is usually present at low levels in biological system, although it plays vital roles in different physiological and pathological processes. However, an elevated Cu level in the liver and kidney is associated with Wilson's disease [2], amyotrophic lateral sclerosis and Menkes syndrome [3]. Therefore, the development of efficient technologies for Cu^{2+} detection is urgently needed. Fluorescent probes offer promising applications [4,5] owing to their high selectivity [6], low detection limits [7], real-time detection [8] and potential biological applications [9]. However, fluorescent 'turn-on' detection of Cu^{2+} is particularly difficult because of the paramagnetic nature of Cu^{2+} [10]. Fun and co-workers reported a diacylhydrazine-based fluorescent 'turn-on' probe that shows single selective sensing of Cu^{2+} over other cations [11]. Furthermore, Cu^{2+} can not only selectively recognize guests but also acts as hydrolytic promoter for the decomposition of diacylhydrazine and release of rhodamine B, resulting in a considerably larger fluorescence enhancement (as high as over 1000-fold) than probes based on Cu^{2+} complexation [12–15]. Although decomposition-based probes demonstrate excellent detection, they are single functional. By contrast, complexation-based probes may be used as multifunctional chemosensing ensemble for other analytes, such as NO [16], HNO [17], cyanides [18], pyrophosphates [19], histidine [20,21], thiols [22], and sulphides [23–25].

Cu^{2+}-based fluorescent chemosensing ensemble has demonstrated outstanding characteristics in sulphide detection owing to the high affinity between Cu^{2+} and sulphide (K_{sp} of CuS = 1.27×10^{-36}). Sulphide anion (S^{2-}), being a toxic and traditional pollutant, can be widely found in industrial processes and biological systems. An elevated sulphide level can lead to irritation in mucous membranes, unconsciousness and respiratory paralysis [26,27]. Fast and accurate detection of S^{2-} in different samples has thus become very important. Therefore, we aimed to design a tunable fluorescent probe that can not only realize the fluorescent 'turn-on' detection of Cu^{2+} through decomposition-based method but can also be tuned to construct a chemosensing ensemble with Cu^{2+} for difunctional detection of S^{2-}. However, tuning a balanced

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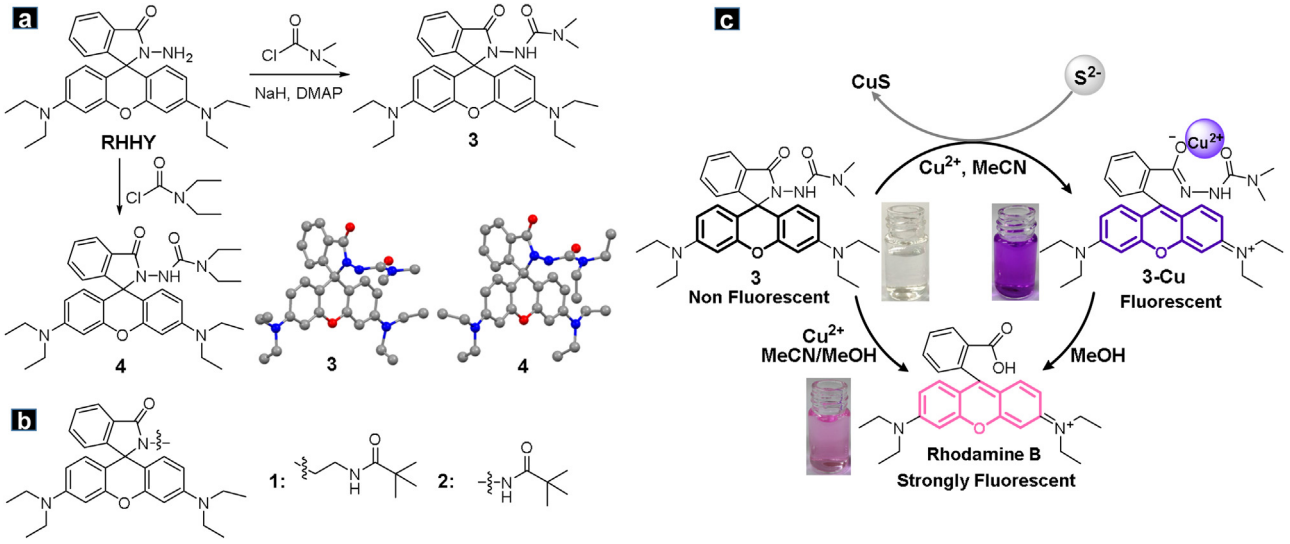

Fig. 1. (a) Synthesis and crystal structure of probes **3** and **4** (grey atom, C; red atom, O; blue atom, N). (b) Structure of control molecules **1** and **2**. (c) Detection process of probe **3** for Cu^{2+} and S^{2-}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

decomposition and coordination between the probe and Cu^{2+} is difficult.

2. Experimental section

2.1. General information and materials

All chemicals were purchased from commercial suppliers and used without further purification. All the solvents were of analytic grade. Deionized distilled water was used throughout. All the metal cations and anions were used as their nitrate and sodium salts, respectively. Solvents were dried according to standard procedures. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using Spectrochem GF254 silica gel coated plates. ^1H and ^{13}C NMR spectra were measured on a JEOL-ECX 500 NMR spectrometer at room temperature using TMS as an internal standard. Mass spectra were recorded on an Agilent LC/MSD Trap VL and Thermo Scientific Q Exactive mass spectrometers. Elemental analysis was recorded on an Elementar Vario-III CHN analyzer. Fluorescence spectra measurements were performed on a Fluoromax-4 spectrofluorimeter (Horiba Trading CO., LTD). UV–vis spectra were performed on a TU-1900 spectrophotometer (Beijing Pgeneral Instrument Co., China). The crystal data were collected by Bruker Smart Apex II CCD diffractometer. The following abbreviations are used to describe spin multiplicities in ^1H NMR spectra: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet.

2.2. Synthesis of probes *1*, *2*, *3* and *4*

2.2.1. Synthesis of probe *1*

2-(2-aminoethyl)-3′,6′-bis(diethylamino)spiro[isoindoline-1,9′-xanthen]-3-one (0.96 g, 2.0 mmol, synthesized according to the procedure reported by Qiao et al. [28] and Bao et al. [29] in 90.1% yield.) was dissolved in a mixture of 20 mL dry CH_2Cl_2 and 0.67 mL triethylamine in ice bath. Then pivaloyl chloride (1.26 mL, 10 mmol) in 5 mL dry CH_2Cl_2 was added dropwise with vigorous stirring. After the addition, the ice bath was kept for about 2 h, and then the mixture was stirred at room temperature for another 4 h. Finally, the mixture was washed by water, dried with anhydrous sodium sulfate, filtered, and followed by the removal of the solvent under vacuum. The product was purified by column chromatography on silica gel and eluted with petrol ether-ethyl acetate (5:1 to 1: 1) to afford 0.57 g of **1** in 50.2% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.94–7.88 (m, 1H), 7.44 (dd, J = 5.6, 3.1 Hz, 2H), 7.36 (s, 1H), 7.09–7.04 (m, 1H), 6.41 (d, J = 8.8 Hz, 2H), 6.37 (d, J = 2.5 Hz, 2H), 6.25 (dd, J = 8.9, 2.6 Hz, 2H), 3.36–3.29 (m, 10H), 2.98–2.93 (m, 2H). 1.20–1.13 (m, 21H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.7, 170.1, 154.1, 153.3, 149.0, 132.8, 130.5, 128.4, 128.2, 124.0, 122.9, 108.3, 104.8, 97.9, 65.7, 44.4, 41.0, 40.1, 38.6, 27.7, 12.7. Anal. Calcd for $C_{35}H_{44}N_4O_3$: C, 73.91; H, 7.80; N, 9.85. Found: C, 73.89; H, 7.82; N, 9.82. ESI^+-MS, m/z = 569.6, $[M+H]^+$, calc. for $C_{35}H_{44}N_4O_3$ = 568.34.

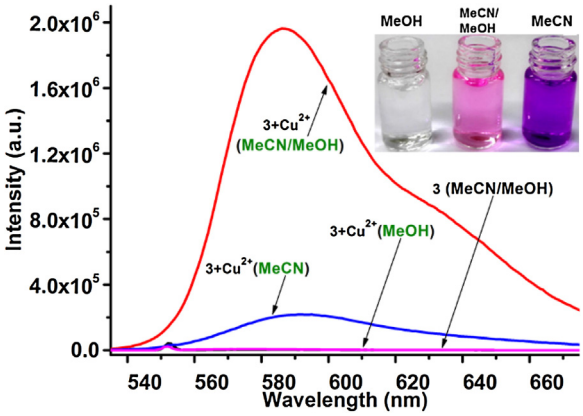

Fig. 2. Fluorescence spectra of **3** (10 μM) in the presence of Cu^{2+} (10 μM) in different solvents. Inset shows the visible colour of **3-Cu** in different solvents. (λ_{ex} = 553 nm, slit = 2).

2.2.2. Synthesis of probe *2*

Rhodamine B hydrazide (**RHHY**) was synthesized according to the procedure reported by Liu et al. [30] in 87.5% yield. The synthesis of compound **2** was carried out by the same method of probe **1**, and the only difference is that **RHHY** was used to replace 2-(2-aminoethyl)-3′,6′-bis(diethylamino)spiro[isoindoline-1,9′-xanthen]-3-one. Finally, a white solid was obtained 0.51 g in 47.2% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.99–7.94 (m, 1H), 7.56–7.47 (m, 2H), 7.18 (d, J = 6.8 Hz, 1H), 6.78 (s, 1H), 6.58 (d, J = 8.9 Hz, 2H), 6.35 (d, J = 2.5 Hz, 2H), 6.30 (dd, J = 8.9, 2.5 Hz, 2H), 3.33 (qd, J = 14.9, 7.4 Hz, 8H), 1.15 (t, J = 7.0 Hz, 12H), 1.02 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.5, 164.8, 154.1, 150.6, 149.0, 133.1, 130.3, 129.7, 128.5, 124.3, 123.6, 108.1, 104.6, 97.5, 66.3, 44.5, 38.4, 27.3, 12.7.