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A novel turn-on colorimetric and fluorescent sensor for Fe^{3+} and Al^{3+} with solvent-dependent binding properties and its sequential response to carbonate

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ABSTRACT

A novel bis-rhodamine derivative BRU was designed and synthesized in a simple way. In aqueous media, BRU could efficiently recognize Fe^{3+} and Al^{3+} among other metal ions with different color appearances through a turn-on colorimetric response. In the presence of Fe^{3+} or Al^{3+}, BRU solution also displayed enhanced fluorescent emission. According to the detection limit, BRU had high recognition sensitivity towards Fe^{3+} and Al^{3+} based on either colorimetric absorbance or fluorescent emission. Interestingly, BRU bound to Fe^{3+} or Al^{3+} with a simple 1:1 mode in CH_3OH and a 1:2 mode in CH_3OH/H_2O, displaying solvent-dependent binding property. In addition, the *in situ* generated BRU-Fe^{3+} and BRU-Al^{3+} complex exhibited fluorescence turn-off and color disappearance towards carbonate among other anions. These provide a potential application in sequential detection of Fe^{3+}, Al^{3+} and carbonate with naked-eyes.

1. Introduction

The studies of chemical sensors for metal ions [1] and anions [2] have received considerable attention because of their significant influences on human life. Fe^{3+}, as an indispensable ion in most organisms, plays important roles in a wide range of biological processes at the cellular level including oxygen-carrying, enzymatic reaction, DNA and RNA synthesis [3]. Its deficiency or overload will cause various disorders and diseases such as anemia and hemochromatosis [4]. On the other hand, the poisoning risk of Al^{3+}, a nonessential ion to human body, increases due to the wide use of aluminum products in our daily life. Al^{3+} can stay for a long time in tissues, eventually accumulate in bones and competitively inhibit other essential ions [5]. Al^{3+} is also a causative factor for Alzheimer's and Parkinson's diseases [6]. In addition, Al^{3+} toxicity in acid soils hinders plant growth [7]. Therefore, great efforts have been devoted to develop sensors for the detection of Fe^{3+} [8–15] and Al^{3+} [16–22]. However, most of reported sensors didn't simultaneously exhibit a selective recognition to Fe^{3+} and Al^{3+} with naked-eyes. Considering the application convenience, it is still necessary to develop colorimetric sensors for the recognition of Fe^{3+} and Al^{3+} in aqueous media.

Among anions, carbonate is a physiologically important ion in human body [23]. Furthermore, carbonate has important roles in agricultural planting, soil science [24], hydrology [25], and geology [26]. Hence, many analysis methods have been developed for carbonate including continuous-flow method [24], electrochemistry [27], acoustic method [28] and fourier transform infrared spectroscopy [29]. However, these methods were cumbersome, time-consuming and naked-eye-invisible. Although many sensors have been reported for the recognition of various anions including phosphates, acetates, sulfides, etc. [8,9,30–35], only very few sensors have been reported for carbonate [36]. This possibly results from the difficulty to design a synthetic receptor for carbonate in aqueous media due to its relative strong alkaline and large hydration free energy [37].

Recently, rhodamine-cation complex solution has been documented for the recognition of various species including anions and amino acids [8,9,38–42]. This complexation is usually an equilibrium process, which can shift along with the change in its surroundings and avoid the disadvantage of too strong or too weak binding between the receptor and donor in the detection. In addition, rhodamine can display naked-eye-visible color changes in its turn-on/off states [43]. Therefore, rhodamine is an attractive precursor to conduct colorimetric sensors.

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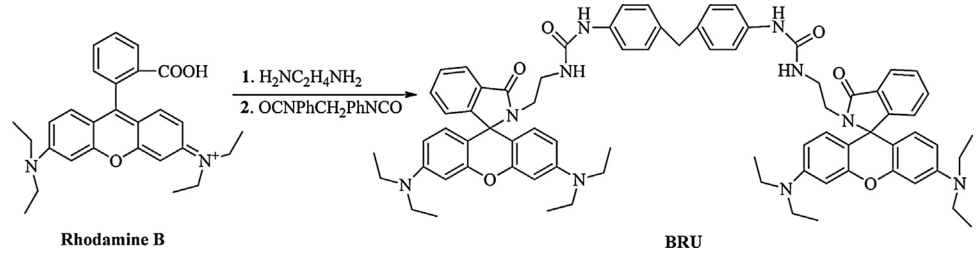

Scheme 1. Synthetic route of BRU.

Herein, we designed and synthesized a new bis-rhodamine urea sensor BRU (Scheme 1), which displayed colorimetric discrimination to Fe^{3+} and Al^{3+} simultaneously via a turn-on response with high selectivity and sensitivity. The *in situ* formed BRU-Fe^{3+} and BRU-Al^{3+} complex solutions exhibited a sensitive response to carbonate via a turn-off response. To the best of our knowledge, this sequential response has not been documented.

2. Experimental

2.1. Materials and measurements

High resolution mass spectra (HRMS) were recorded using a Micromass Q-TOF 2 mass spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 400 spectrometer using TMS as an internal standard. All fluorescence experiments were carried out on a Perkin Elmer LS55 fluorescence spectrometer at the excitation wavelength of 500 nm with the slit set of 5 nm. Absorption spectra were recorded with a HP8543 UV–vis spectrophotometer. *N*-(rhodamine B)lactamethylenediamine was synthesized according to the reported procedures [38]. 4,4′-Methylenebis-(phenylisothiocyanate) and all other reagents (analytical grade) and solvents (spectroscopic grade) were purchased from Sigma–Aldrich and used as received. The pH values in the measurements were the initial values of buffer solution. Distilled water was used throughout the experiment.

2.2. Synthesis of BRU

N-(rhodamine B)lactamethylenediamine (0.242 g, 0.5 mmol) and 4,4′-methylenebis-(phenylisothiocyanate) (0.0626 g, 0.25 mmol) were refluxed for 5 h in anhydrous acetonitrile (5 mL) under N_2. The solvent was removed under reduced pressure and the crude solid was purified by the column chromatography (DCM/EtOH = 8:2) to give 0.25 g of BRU (82%). Its structure was confirmed by the HRMS, ^1H NMR and ^{13}C NMR analyses (Fig. S1, S2). ^1H NMR ($CDCl_3$) δ 7.87 (t, *J* = 4.0, 2H, Ar-H), 7.45 (t, *J* = 4.0, 4H, Ar-H), 7.25 (d, 5H, Ar-H), 7.08 (m, 2H, Ar-H), 7.04 (d, *J* = 8.0, 3H, Ar-H), 6.59 (br s, 2H, N-H), 6.40 (m, 8H, Ar-H), 6.25 (d, *J* = 8.0, 4H, Ar-H), 5.48 (br s, 2H, N-H), 3.84 (s, 2H, CH_2-ph), 3.32 (q, *J* = 8.0, *J* = 4.0, 20H, CH_2), 3.06 (d, *J* = 4.0, 4H, CH_2-N), 1.15 (t, *J* = 8.0, 24H, CH_3); ^{13}C NMR ($CDCl_3$) δ 169.57, 155.40, 153.77, 153.31, 148.93, 137.14, 135.83, 132.77, 130.59, 129.28, 128.51, 128.20, 123.93, 122.77, 120.17, 108.26, 104.89, 97.82, 65.57, 44.40, 40.66, 40.53, 12.64; HRMS (TOF ES^+) m/z = 610.3276 $(M + 2H^+)/2$, Calcd. for $(C_{75}H_{82}N_{10}O_6)/2 = 610.3288$; $\varepsilon = 1.95 \times 10^4$ L mol^{-1} cm^{-1} ($\lambda = 314$ nm, in CH_3OH).

2.3. General procedure

The 1.0×10^{-2} mol L^{-1} stock solutions of metal ions were prepared in methanol using their chlorides (Fe^{3+}, Cr^{3+}, Ni^{2+}, Fe^{2+}, Mn^{2+}, Cu^{2+}, Hg^{2+}, Na^+, K^+) or nitrates (Al^{3+}, Ce^{3+}, Pb^{2+}, Mg^{2+}, Zn^{2+}, Ag^+). The 1.0×10^{-2} mol L^{-1} stock solutions of anions were prepared in deionized water using their sodium salts ($CO_3{}^{2-}$, $HCO_3{}^-$, $HPO_4{}^{2-}$, $H_2PO_4{}^-$, CH_3COO^-, $SO_4{}^{2-}$, $NO_3{}^-$, Cl^-), potassium salt (Br^-, K^-) and NH_4F, respectively. The 1.0×10^{-3} mol L^{-1} stock solution of BRU was prepared in methanol.

The solution containing proper amounts of BRU and metal ions was kept overnight before measurement. BRU-Fe^{3+} and BRU-Al^{3+} solutions for carbonate were prepared by addition of 10 equiv. of Fe^{3+} and Al^{3+} to BRU solution in CH_3OH/H_2O (9:1, v/v, pH 7.0, 10 mM Tris), respectively. To a quartz cell containing the complex solution, proper amount of anion solution was directly added with a micropipette. The fluorescence spectrum was then measured instantly.

3. Results and discussion

3.1. UV–visible responses to cations

The colorimetric property of BRU was first investigated upon the addition of various metal ions in CH_3OH/H_2O. As shown in Fig. 1, BRU solution is colorless. The examined metal ions such as Cu^{2+}, Hg^{2+}, Zn^{2+}, Mg^{2+}, Ag^+, Ce^{3+}, Fe^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Na^+ and K^+ had no effects on the color of BRU solution. Cr^{3+} induced only a little bit pink color to BRU solution. In contrast, Fe^{3+} resulted in BRU solution becoming rose-red, while Al^{3+} induced BRU solution to a red-violet color.

A UV-visible titration was subsequently conducted using a BRU solution in CH_3OH/H_2O with Fe^{3+} and Al^{3+}, respectively. BRU solution only showed an absorption peak at ca. 320 nm. Upon the addition of Fe^{3+}, a new peak at 556 nm appeared (Fig. 2A). Its absorbance increased with the increase of Fe^{3+} concentration. Similarly, the absorbance at 320 nm showed the same change trend. In the case of Al^{3+}, its addition also induced the appearance of a new peak at 556 nm. Moreover, there was also an isobestic point at 335 nm in BRU spectra upon the Al^{3+} addition. And the absorbance at 556 nm gradually increased with the increase of Al^{3+} concentration, while the absorbance at 320 nm decreased concomitantly (Fig. 2B).

As shown in the insets of Fig. 2, the absorbance at 556 nm first increased quickly and then the increase slowed down. In diluted concentration ranges, the absorbance of BRU solution had good linear relationships to the concentration of Fe^{3+} (Fig. 3A) and Al^{3+} (Fig. 3B) with correlation coefficients of 0.9966 and 0.9977, respectively. According to these linear relationships, the detection limits of BRU were 4.30 and 3.90 μmol L^{-1} (3δ/slope) for Fe^{3+} and Al^{3+}, respectively. These results indicated that BRU had sensitive absorption responses to Fe^{3+} and Al^{3+} in aqueous media.

The binding mode between BRU and the cations was studied using their Job's plots analysis, which was based on the absorbance of BRU solution at 556 nm. In aqueous media, the absorbance of BRU solution reached the maximum values when BRU concentration ratios were ca. 0.3 (Fig. 4A), which indicated the formation of a 1:2 binding between BRU and the cation. It is reasonable because BRU has two spirolactam substructures with the same cation-binding activity. In CH_3OH, their Job's plots indicated the