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An efficient and ultrasensitive rhodamine B-based reversible colorimetric chemosensor for naked-eye recognition of molybdenum and citrate ions in aqueous solution: Sensing behavior and logic operation



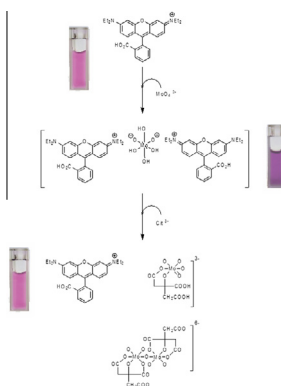
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HIGHLIGHTS

- The described rhodamine B (Rh_B) chemosensor is commercially available.
- It is the first colorimetric chemosensor for Mo⁶⁺ and Cit³⁻ in aqueous media.
- The response of the chemosensor toward Mo⁶⁺ and citrate is fast.
- An IMPLICATION logic operation can be achieved using Mo⁶⁺ and Cit³⁻ as the inputs.
- Rhodamine B (Rh_B) chemosensor is a promising candidate for further applications in molecular logic devices.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper we manifest a novel rhodamine B (Rh_B) based colorimetric chemosensor for molybdenum and citrate ions (Cit³⁻) in an absolutely aqueous media. It has been identified as highly sensitive probe for Mo⁶⁺ which responds at 4.0 nmol L⁻¹ concentration levels. Rh_B while combined with Mo⁶⁺ in aqueous solution displays a color changing from pink to purple which could be quickly dissociated by the addition of citrate in this system so that reversible color changes from purple to pink can be achieved. The comparison of this method with some other methods for citrate indicates that this is the only method which can detect citrate in aqueous solution by color changes. This chemosensor can be applied for quantification of citrate with a linear range covering from 1.67 × 10⁻⁷ to 1.22 × 10⁻⁵ M and a detection limit of 2.0 × 10⁻⁸ M. Moreover, the response of the chemosensor toward Mo⁶⁺ and citrate is fast. In addition, based on above sensing mechanism, an IMPLICATION logic operation can be achieved using Mo⁶⁺ ion and Cit³⁻ as the inputs, making Rh_B a promising candidate for further applications in molecular logic devices and also indicates that Rh_B is suitable for the detection of Mo⁶⁺ and Cit³⁻ ions in real samples.

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Introduction

Molecular logic gates are one of research focuses of chemistry for further miniaturization in information technology since the first AND logic gate was mimicked with optical signals by de Silva et al. [1]. Various chemical systems have been developed to get different functions such as AND, OR, NOT and their integrated operations [2]. Among them, those exhibiting more than one output channel with single molecules are currently of particular interest because they are the basis for construction of molecular logic circuits capable of executing some special arithmetic operations [3]. In addition, many useful integrated logic gates such as INHIBIT, half subtractor, half adder, full adder, and full subtractor with various single molecules have been exploited [4]. However, with respect to the IF-THEN and the NOT operations, IMPLICATION gates has rarely been reported [5].

Development of new synthetic receptors for the detection of physiologically important cations and anions is of considerable importance [6]. High sensitivity and easy operational use have encouraged the recent interest in UV-Vis and fluorescence spectroscopy-based analytical techniques. Numerous chromogenic and fluorescent receptors which are selective for a particular analyte have been reported in the literature [7]. However, few receptors have been designed based on the concept of 'single sensor for multiple analytes', that is, analysis of more than one analyte by one receptor using a single detection method, or alternatively, an array of detection methods [8].

Molybdenum can exist in five oxidation states (II–VI) but its predominant form occurring in soil and natural waters is the molybdate anion, MoO_4^{2-} [9]. This transition element is found naturally in soil and is used in the manufacture of special steels and in the production of tungsten and pigments [10]. Molybdenum is an essential trace element for both plants and animals, including humans, first of all because it plays an important role in enzymatic redox reactions. Nevertheless, it is harmful at higher contents, so monitoring the molybdenum content in environmental samples is desirable and highly recommended [9,10].

Trace concentrations of Mo can be determined using UV-Visible spectrophotometry [11,12], flame atomic absorption spectrometry (FAAS) [13], graphite furnace atomic absorption spectrometry (GFAAS) [14], inductively coupled plasma optical emission spectrometry (ICP-OES) [15], inductively coupled plasma mass spectrometry (ICP-MS) [16], and voltammetry [17]. FAAS is commonly used due to its simplicity and relatively low cost. The direct determination of Mo in environmental samples is difficult due to its low concentration, the occurrence of matrix interferences and formation of refractory compounds [18]. However, all these effects can be minimized by adopting steps of separation and preconcentration prior to analytical measurements by FAAS. The most widely used method for separation and preconcentration of trace amounts of metal ions is liquid-liquid extraction (LLE) [11]. However, LLE is time-consuming and requires large volumes of expensive and toxic organic solvents.

Colorimetric sensors for organic materials, cations, anions and gases have recently drawn much research attention due to their fast detection character and the feasibility of naked-eye detection for analytes [19]. For a typical colorimetric sensing procedure, a colorimetric sensor usually recognizes the analyte by forming a large conjugation plane with the analyte, showing a red shift of electronic transition and corresponding color-switching [19–36], which enables naked-eye detection. In addition, the combination of various analytes and their adding sequence can lead to various responses of colorimetric sensors, which further widens their applications [20]. For example, the published work by Raymo et al. has suggested that such dyes can mimic logic operation, which sparks their utilization

in molecular logic devices [21]. A more complicated logic operation has been recently reported by Li and coworkers with acid and base as the inputs, and asymmetric porphyrin as the indicator [22]. Wang and coworkers have reported a similar logic keypad, with a rhodamine derivative as the colorimetric indicator, and ions of Hg^{2+} , Cu^{2+} and S^{2-} as the inputs [20].

Citrate is an organic tricarboxylate that plays an important role in the Krebs cycle to provide the vast majority of energy used by aerobic cells in human beings. It has been used as a molecular marker for the diagnosis of urological diseases, since its concentration in urine can be linked to some pathological states such as nephrolithiasis (kidney stones) or glycogen storage disease. Accordingly, the development of methods to detect citrate in biological samples is of considerable significance and has become the important subject of current chemical research. There have been some successful achievements in the development of fluorescent chemosensors for citrate based on the fluorophores [23–25]. However, most of the chemosensors are prone to suffer the influence of the background fluorescence because they have a shorter emission wavelength (below 500 nm) [23–25]. Therefore, the chemosensors for citrate based on color changes with excellent performance are still urgently needed. At present, considerable attention has been paid to the development of rhodamine-based chemosensors through naked-eye observation and/or fluorescence method in recent years because of their particular structural properties [26]. The rhodamine with spirolactam structure is colorless and nonfluorescent, whereas ring-opening of the spirolactam induced by the analyte gives rise to pink color and a strong fluorescence emission. Actually, it is an ideal mode to construct chemosensors. Moreover, rhodamine has a longer emission wavelength (about 580 nm), which is often preferred to serve as reporting groups for analyte to avoid the influence of the background fluorescence (below 500 nm) [26–28]. Up to date, many rhodamine-based chemosensors have been designed for metal cations including Cu^{2+} [29], Hg^{2+} [30], Zn^{2+} [31], Fe^{3+} [32], Pb^{2+} [28], and Cr^{3+} [33] and conventional anions such as CN^- [34], $\text{P}_2\text{O}_7^{4-}$ [35] and CH_3COO^- [27]. However, to the best of our knowledge, no such chemosensor for molybdenum and citrate was reported.

The previous receptors have been reported above were organic based synthetic compounds. These are rather difficult to synthesize or require expensive instruments for detections. Taking this dilemma into consideration recently, we have undertaken an extensive research program to explore bromo pyrogallol red (BPR) as an easily available dye demonstrated a high chromogenic receptor for cations and anions [36–38]. Our group has reported a novel development of a simple probe, dithizone and dithizone-cobalt as colorimetric chemosensors for detection and determination of cyanide ion [39,40]. Recently we have reported Rh_B based fluorescent and chromogenic chemosensor, with characteristics of an ON-OFF-ON fluorescence switch. Like other molecular keypad lock, the chemosensor reported here could mimic the function of a security keypad lock on sequential addition of phosphotungstic acid and CN^- ions [41]. In this paper, we devote our effort to a colorimetric sensor of Rh_B (Scheme 1) for molybdenum and citrate detection. It is found that Rh_B can recognize molybdenum by forming an ion-pair, resulting in a color change from pink to purple. In detail, the absorbance of Rh_B was reduced upon addition of Mo^{6+} and the absorbance was increased after addition of citrate anions through a demetalization process, and this colorimetric switch could be repeated. $(\text{Rh}_B)_2 \cdot \text{MoO}_4^{2-}$ complex was acted as a potential indirect chemosensor for citrate recognition via Mo^{6+} displacement approach and correspondingly color-switching of Rh_B . In addition, based on above sensing mechanism, an IMPLICATION logic operation can be achieved using Mo^{6+} ion and Cit^{3-} as inputs, making Rh_B a promising candidate for further applications in molecular logic devices.

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