

Colorimetric detection of Hg^{2+} using a mixture of an anionic azo dye and a cationic polyelectrolyte in aqueous solution

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Abstract

We investigated a colorimetric chemosensor for Hg^{2+} based on a mixture of xylydyl blue I as an anionic organic dye and poly(diallyldimethylammonium chloride) as a cationic polyelectrolyte in an aqueous solution at pH 7.5. The addition of Hg^{2+} to the mixture induced a bathochromic shift in the absorption spectra with a distinct color change from red to green which was readily identifiable by the naked eye, whereas the other metal ions gave rise to insignificant color changes. By contrast, upon adding Hg^{2+} to xylydyl blue I alone, the solution underwent no significant change in color. Moreover, a stoichiometric ratio for the complex between xylydyl blue I and Hg^{2+} in the presence of poly(diallyldimethylammonium chloride) was determined to be 1:1 by the absorption titration curve and Job's plot. Thus, the mixture can be used as a selective naked-eye colorimetric chemosensor for Hg^{2+} over other common metal ions. This study raises the possibility that the combination of an organic dye and an oppositely charged polyelectrolyte is a potential candidate for the easy construction of a new chemosensor system.

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Supporting information may be found in the online version of this article.

Keywords: colorimetric detection; chemosensor; mercury ion; XB-I; polyelectrolyte

INTRODUCTION

The detection of heavy metal ions is of significance for analytical, biomedical and environmental chemistry due to their adverse effects on human health and the global environment.^{1–12} Among heavy metal ions, mercury is considered as one of the most extremely toxic and dangerous metal ions for the environment and human health because of its easy accumulation and difficult biodegradation.^{13–15} Mercury has been widely used in batteries, paints and electronic equipment, leading to an increase of its release to the environment. Its accumulation in the human body through the food chain could lead to serious health problems including brain damage, motion disorders and neurological diseases even at very low concentration owing to its high affinity for thiol groups in enzymes and proteins.^{16,17} Therefore, there is great demand for the development of selective and sensitive analytical techniques for quantifying trace amounts of Hg^{2+} in aqueous samples with remarkable reliability and specificity.

So far, some effective detecting methods have been widely used for the determination of Hg^{2+} concentration including inductively coupled plasma mass spectrometry,¹⁸ cold vapor atomic absorption spectrometry¹⁹ and electrochemical techniques,²⁰ and fluorescence techniques.^{21–23} Although these methods have good sensitivity and low detection limits, most of the methods need costly equipment and disciplined operators. In contrast, as colorimetric methods provide a powerful technology for detecting analytes because of its simplicity, short response time and visual observation without the aid of instruments, considerable effort has been devoted to designing colorimetric chemosensors for detecting Hg^{2+} .^{24,25} In addition, in living organisms and in the

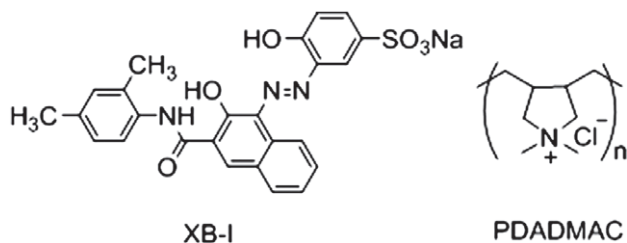
environment, Hg^{2+} is mainly to be found in aqueous systems under physiological pH conditions. Therefore, the development of water-soluble colorimetric sensors is clearly required. However, most of the reported chemosensors have poor water solubility and are synthesized by cumbersome organic synthetic processes with biologically toxic solvents.^{26,27} Therefore commercially available water-soluble organic dyes as colorimetric chemosensors are very attractive.

Xylydyl blue I (XB-I) is an anionic azo dye with naphtholic and phenolic moieties as shown in Scheme 1. It is a widely accepted reagent in clinical and chemical fields for the detection of a magnesium ion with a color change from purple to red in basic pH conditions.^{28,29} Poly(diallyldimethylammonium chloride) (PDADMAC) is a water-soluble cationic polyelectrolyte with quaternary ammonium groups.^{30,31} Anionic dyes can interact with PDADMAC by electrostatic interactions to have the potential to form their self-aggregate and show distinct spectroscopic and sensing properties from those of monomeric dyes.^{32,33} Our previous study reported that a chemosensor through the electrostatic combination of an anionic organic dye, pyrogallol red (PR), and PDADMAC exhibited a colorimetric selective detection for Zn^{2+} distinct from

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Scheme 1. Chemical structures of XB-I and PDADMAC.

PR.³⁴ Thus, the combination of an organic dye and an oppositely charged polyelectrolyte is a useful tool for the facile preparation of a novel chemosensing system. In this study, we describe the development of a colorimetric chemosensor for selective recognition of Hg²⁺ over other metal ions in an aqueous solution by a simple mixture of two commercially available reagents, XB-I and PDADMAC.

EXPERIMENTAL

Materials and instrumentation

XB-I was obtained from Dojindo Laboratories (Mashiki, Kumamoto, Japan). PDADMAC was available from Sigma-Aldrich (St. Louis, MO, USA) and its concentration was defined as that of the repeating unit. All chemicals were available from commercial sources and were used as received. Absorption spectra were monitored on a Jasco V-530 spectrophotometer (Hachioji, Tokyo, Japan) at ambient temperature.

Absorption spectral study

On adding 40 μmol L⁻¹ of each metal ion to 40 μmol L⁻¹ XB-I and 200 μmol L⁻¹ PDADMAC (10 mmol L⁻¹ phosphate buffer, pH 7.5), the absorption spectra were measured to estimate metal ion selectivity. The absorption titration experiment was performed upon adding various amounts of Hg²⁺ to 40 μmol L⁻¹ XB-I and 200 μmol L⁻¹ PDADMAC (10 mmol L⁻¹ phosphate buffer, pH 7.5). The competitive test toward Hg²⁺ was performed by monitoring the absorption spectrum of 40 μmol L⁻¹ XB-I, 200 μmol L⁻¹ PDADMAC, 40 μmol L⁻¹ Hg²⁺ and 40 μmol L⁻¹ of each other metal ion (10 mmol L⁻¹ phosphate buffer, pH 7.5).

Determination of the detection limit

The limit of detection of XB-I for Hg²⁺ was calculated according to the following equation: detection limit = 3σ/k, where σ is the standard deviation of 10 blank measurements and k is the slope of the plot of absorbance at 610 nm against [Hg²⁺].³⁵

Determination of the binding constant (K_a) by the Benesi–Hildebrand equation

The binding constant (K_a) was determined from the Benesi–Hildebrand equation as follows:

$$(A_{\infty} - A_0) / (A_x - A_0) = 1/K_a [Hg^{2+}] + 1$$

where A_∞ and A_x are the absorbances in the presence of Hg²⁺ at saturation and an intermediate concentration, respectively, and A₀ is the absorbance of XB-I in the absence of Hg²⁺. K_a could be calculated from the slope of (A_∞ - A₀)/(A_x - A₀) against 1/[Hg²⁺].³⁶

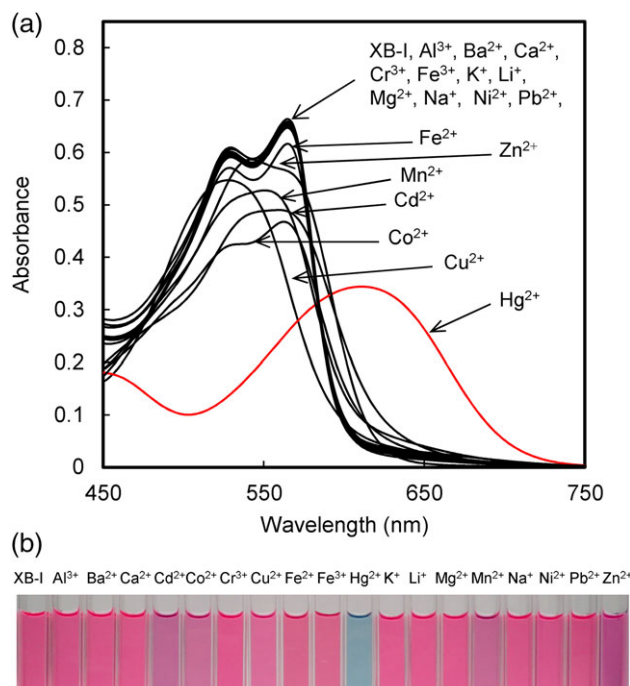


Figure 1. (a) Absorption spectra of XB-I (40 μmol L⁻¹) in the presence of PDADMAC (200 μmol L⁻¹) upon addition of various metal ions (40 μmol L⁻¹) in 10 mmol L⁻¹ phosphate buffer at pH 7.5. (b) The color changes of XB-I (40 μmol L⁻¹) in the presence of PDADMAC (200 μmol L⁻¹) upon addition of various metal ions (10 μmol L⁻¹) in 10 mmol L⁻¹ phosphate buffer at pH 7.5.

RESULTS AND DISCUSSION

The responses of XB-I (40 μmol L⁻¹) to Hg²⁺ in the absence or presence of PDADMAC were examined by monitoring the absorption spectra in aqueous solution at pH 7.5 with 10 mmol L⁻¹ phosphate buffer. The absorption spectrum of XB-I exhibited two intense bands at 528 and 562 nm in the absence of Hg²⁺ and PDADMAC (Fig. S1). Although addition of Hg²⁺ led to slight hypochromicity at 528 and 562 nm with a subtle increase in absorbance around 620 nm, the solution underwent no significant change in color. Meanwhile, in the presence of PDADMAC, the addition of Hg²⁺ resulted in a bathochromic shift to 610 nm with a clearly discernible color change from red to green by the naked eye (Fig. 1). However, insignificant changes in absorption spectra and solution color were induced by adding other metal ions including Al³⁺, Ba²⁺, Ca²⁺, Cd²⁺, Co²⁺, Cr³⁺, Cu²⁺, Fe²⁺, Fe³⁺, Hg²⁺, K⁺, Li⁺, Mg²⁺, Mn²⁺, Na⁺, Ni²⁺, Pb²⁺ and Zn²⁺. Furthermore, in order to ascertain the interaction between XB-I and PDADMAC, the absorption spectra of XB-I in the absence of any metal ion as a function of PDADMAC concentration were monitored (Fig. S2). Gradual addition of PDADMAC to the XB-I solution generated a slightly bathochromic shift to 529 and 565 nm with an isosbestic point at 583 nm, suggesting that XB-I was bound to PDADMAC by electrostatic interaction to assemble into the corresponding aggregate having equilibrium between them. Thus, XB-I aggregate formation could be essential for the selective recognition of Hg²⁺.

To investigate the influence of PDADMAC concentration on the colorimetric sensing capabilities of XB-I for Hg²⁺, the absorption spectra and visual response of XB-I in the presence of Hg²⁺ were measured with different PDADMAC concentrations from 0 to 200 μmol L⁻¹ (Fig. 2). The absorbance at 610 nm gradually increased with PDADMAC concentration and reached a maximum

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