



Selective sensing of silver ion using berberine, a naturally occurring plant alkaloid



Abdullah Affrose, Sheik Dawood Shahida Parveen, Basuvaraj Suresh Kumar, Kasi Pitchumani*

School of Chemistry, Madurai Kamaraj University, Madurai 625021, India

ARTICLE INFO

Article history:

Received 2 June 2014

Received in revised form 24 August 2014

Accepted 11 September 2014

Available online 22 September 2014

Keywords:

Berberine

Plant alkaloid

Silver ion sensor

TD-DFT calculations

ICT mechanism

ABSTRACT

Berberine (**Bn**), an important traditional medicinal herb with anticancer, antitumour and antidiabetic activities, is effectively utilized as a sensing probe for silver ion with good sensitivity and selectivity, using absorbance and fluorescence studies. The effect of presence of other metal ions with **Bn** is also investigated and **Bn** is found to be selective towards Ag^+ ion over other metal ions such as Cu^{2+} , Zn^{2+} , Sn^{2+} , Ni^{2+} , Ba^{2+} , Bi^{2+} , Pb^{2+} , Co^{3+} , In^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Li^+ , Hg^{2+} and Ca^{2+} with a detection limit of $0.1 \times 10^{-4} \text{ mol L}^{-1}$. The colour changes from yellow to orange when Ag^+ ion is added and other metal ions failed to show any visible colour change. The effective quenching of **Bn** upon binding with Ag^+ ion is attributed to suppression of intramolecular charge transfer (ICT).

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Herbal medicines play an important role in clinical therapy and are widely accepted as a potential high quality pool for drug screening, owing to their unmatched chemical diversity and minimum side effects. Berberine (**Bn**) is an important herbal medicine for cancer therapy, possessing anticancer activity both *in vitro* and *in vivo* [1–4]. **Bn** is an alkaloid found in roots and barks of *Berberis* species [5–10] and due to its fluorescence behaviour, acts as a probe in biological and analytical studies [11–14]. Fluorescent sensing of metal ions is a widely useful tool in biology, chemistry and environmental analysis. Molecular imaging with such sensors is emerging as a powerful method to interrogate metal ion chemistry in cells and organisms [15–18]. Selective sensors help in collection of information on localization and bioavailability, which is difficult or impossible to obtain using conventional analytical techniques. Recently the fluorophore–spacer–receptor architecture has emerged as one of the most popular designs for fluorescent metal ion sensing. The signals are transduced between the fluorophore and receptor, commonly by any of the following routes;

photoinduced electron transfer (PET), intramolecular charge transfer (ICT), metal–ligand charge transfer (MLCT), twisted intramolecular charge transfer (TICT) and fluorescence resonance energy transfer [19–26].

Environmental pollution especially water pollution caused by heavy-metal ions is among the most important challenges, due to their toxicity and ability to bioaccumulate in organisms [27–30], and consequently are particularly dangerous to the entire ecosystem. This heavy-metal ion contamination also causes irreversible and permanent damage to the human body leading to various diseases. Thus, the detection of heavy-metal ions has become a hot topic in scientific research and numerous approaches have been made for the detection of heavy metal ions [31–34].

Silver ion has widespread usage, applications and broad prospects especially in the imaging, photographic and electronic industries. Upon release into the environment silver ions can bind readily to various metabolites and enzymes [35–47]. As silver(I) ions are extremely toxic to aquatic animals, much attention has been paid recently, to the negative impact of silver ion on the environment, thus necessitating the monitoring of these ions in the environment. The aim of the present study is to suggest a simple system for silver(I) ion detection using naturally occurring molecules and this can also throw light on the bioaccumulation of silver in organisms. Herein we have developed a rapid and

* Corresponding author. Tel.: +91 452 2456614; fax: +91 452 2459181.

E-mail addresses: pit12399@yahoo.com, profpitlab@yahoo.co.in (K. Pitchumani).

selective sensor for detection of Ag^+ ion using a naturally occurring plant alkaloid, berberine (**Bn**) as a sensing probe.

2. Materials and Methods

UV-Vis., absorbance spectra were recorded using a JASCO V-550 double beam spectrophotometer, at a wavelength range 190–500 nm. Fluorescence spectra were recorded using a Fluoromax-4 spectrofluorometer (HORIBA JOBIN YVON) in 1 cm × 1 cm quartz cell at a wavelength range 450–750 nm. Electrospray ionization mass spectrometry (ESI-MS) analysis was performed in the positive ion mode on a liquid chromatography–ion trap mass spectrometer (LCQ Fleet, Thermo Fisher Instruments Limited, US). NMR spectra were recorded on a Bruker 300 MHz spectrometer, with CDCl_3 solvent and TMS as an internal standard.

2.1. Isolation of berberine from *Mahonia leschenaultii*

Berberine is isolated from the stems of *Mahonia leschenaultii* (supporting information) by following the literature procedure [48,49], and the isolated **Bn** is characterized by ^1H NMR spectral peaks [^1H NMR (300 MHz, CDCl_3) δ 10.11 (s, 1H), 8.64 (s, 1H), 7.98 (d, $J=3.3$ Hz, 2H), 6.89 (s, 1H), 6.13 (s, 2H), 5.15–5.06 (m, 2H), 4.25 (s, 3H), 4.12 (s, 3H), 3.32–3.24 (m, 3H)] and mass spectrometry m/z 336.38(M+H) (Figs. S1–S2 in supporting information).

2.2. Preparation of stock solutions and UV titration

All the measurements are carried out in double distilled water which is free from ions. The stock solution of berberine (1×10^{-3} M) is prepared by dissolving 0.037 g of berberine in 100 mL ethanol:water (v/v, 1:1) mixture. Solutions (1×10^{-3} M) of ZnCl_2 , SnCl_2 , NiCl_2 , AgNO_3 , BaCl_2 , BiCl_2 , PbCl_2 , CoCl_3 , InCl_3 , MnCl_2 , FeCl_2 , FeCl_3 , LiCl , HgCl_2 and CaCl_2 are prepared by dissolving them in water. For UV titration, berberine (1 mL of stock), cations (0.1–1.0 mL of stock) are taken in 10 mL SMF and analyzed.

3. Results and discussion

The UV-Vis., absorption spectrum of **Bn** (1×10^{-4} M) exhibits three maxima at 270, 350 and 425 nm in ethanol–water mixture. 270 and 350 nm bands correspond to π – π^* transition of isoquinoline moiety and the band at 425 nm corresponds to n – π^* transition (figure S3 in supporting information). The metal binding ability of **Bn** is evaluated by colorimetric titrations in the presence of various metal ions such as Cu^{2+} , Zn^{2+} , Sn^{2+} , Ni^{2+} , Ag^+ , Ba^{2+} , Bi^{2+} , Pb^{2+} , Co^{3+} , In^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Li^+ , Hg^{2+} and Ca^{2+} in ethanol–water (1:1, v/v) mixture. As can be seen from Fig. 1, except Ag^+ ion, other cations display only less significant change in absorbance spectra with a small bathochromic shift and a very weak absorbance enhancement. Upon varying the concentration of Ag^+ ion from 1×10^{-5} to 1×10^{-4} M, the band at 215 nm is significantly red-shifted to 242 nm. In addition, a new band appears at 310 nm, which is attributed to the complex formation between **Bn** and silver ion. This is also evident from the observation of isobestic points at 333 and 368 nm, which indicate a simple one-step transformation from the free **Bn** and the **Bn**– $\text{Ag}(\text{I})$ complex (Fig. 2).

In order to study the selectivity of **Bn** towards different metal ions, fluorometric titrations are also performed. The fluorescence of **Bn** exhibits a strong emission band at 544 nm when excited at 450 nm. Emission spectra of **Bn** upon addition of various metal ions are given in Fig. 3. It is clear from the figure that, only Ag^+ ion induces significant fluorescence quenching over other metal ions such as Cu^{2+} , Zn^{2+} , Sn^{2+} , Ni^{2+} , Ba^{2+} , Bi^{2+} , Pb^{2+} , Co^{3+} , In^{3+} , Mn^{2+} ,

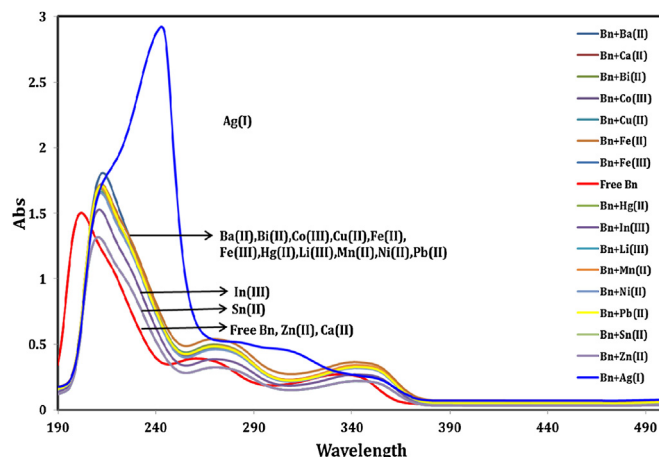


Fig. 1. UV-Vis., spectra of **Bn** (1.0×10^{-4} mol L^{-1}) in the presence of Ag^+ and various metal ions, Cu^{2+} , Zn^{2+} , Sn^{2+} , Ni^{2+} , Ba^{2+} , Bi^{2+} , Pb^{2+} , Co^{3+} , In^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Li^+ , Hg^{2+} and Ca^{2+} (1.0×10^{-4} mol L^{-1}).

Fe^{2+} , Fe^{3+} , Li^+ , Hg^{2+} and Ca^{2+} (1.0×10^{-4} mol L^{-1}). Fluorescence quenching upon addition of Ag^+ ion is attributed to the formation of a **Bn**– Ag^+ complex. Fig. 4 shows the sensitivity of **Bn** towards Ag^+ ion, measured by varying Ag^+ concentration from 1×10^{-5} to 1×10^{-4} mol L^{-1} .

Fig. 5 reports the quenching ratio I/I_0 at 544 nm, where I_0 is the fluorescence of **Bn** and I is the fluorescence in the presence of metal ions taken in a 1:1 molar ratio. Most metal ions has the ratio close to 1, the notable exception being Ag^+ with a ratio <0.2 . It is evident from the figure that fluorescence quenching is much higher for Ag^+ ion, while it is negligible in the case of other metal

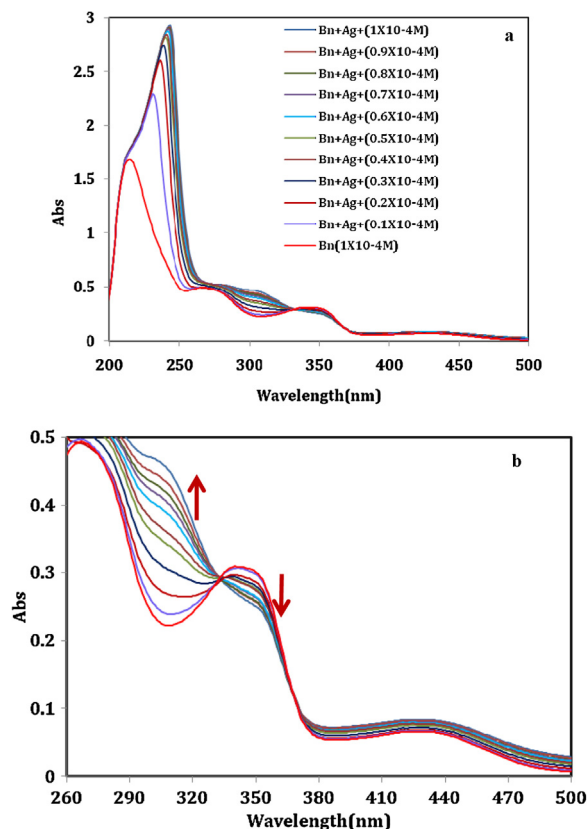


Fig. 2. (a) UV-Vis. spectra of **Bn** (1.0×10^{-4} mol L^{-1}) upon addition of Ag^+ ion (0.1 – 1.0×10^{-4} mol L^{-1}) in ethanol–water (1:1, v/v) mixture and (b) expanded UV-Vis., absorption spectra.

Download English Version:

<https://daneshyari.com/en/article/744356>

Download Persian Version:

<https://daneshyari.com/article/744356>

[Daneshyari.com](https://daneshyari.com)