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Colorimetric sensing of metal ions by bis(spiropyran) podands: Towards naked-eye detection of alkaline earth metal ions

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ABSTRACT

In order to develop a selective and sensitive colorimetric sensor for metal ions, a series of oligoether-linked bis(spiropyran) podands were prepared and their ability to colorimetrically sense alkaline earth metal ions was investigated. UV–vis absorption and ^{1}H NMR spectroscopic studies showed that the podands isomerized from the colorless spiropyran form to the colored merocyanine form upon complexation with alkaline earth metal ions, whereas spectral changes were not visible in the presence of alkali metal ions. Podands of spiropyran subunits linked by a spacer of a 3-oxapentan-1,5-dioxy group, *i.e.* **X-BSP-1** (**X** = **MeO**, ***t*Bu**, ***i*Pr**, **H**, **Cl**, **Br**), exhibited high selectivity to Ca^{2+}. Introduction of an electron-donating group to the 5-position of each indoline ring of the podand gave rise to an increase in affinity to alkaline earth metal ions, enhancing the sensitivity. The absorption maximum of the colored metal–**X-BSP-1** complex varied over a range of *ca.* 30 nm, from reddish purple to bluish purple. Clear discrimination of the Ca^{2+} complex from that of Mg^{2+} was possible using the naked eye. These results indicate the potential application of the **X-BSP-1** podands as a colorimetric sensor for Ca^{2+}.

1. Introduction

Chemosensory systems for specific chemicals based on receptor–guest complexation promise a method of non-destructive and convenient analysis of biologically and environmentally important species, and a number of synthetic receptors integrated with chromophores and fluorophores have so far been reported for colorimetric and fluorometric sensing, respectively [1–7]. In this context, colorimetric sensing, with naked-eye detection based on coloration–decoloration or color changes on sensor–analyte (*i.e.*, receptor–guest) complexation, affords convenient analysis without resorting to any spectroscopic instruments. To this purpose, numerous chemosensors have so far been developed, aimed at analyses of metal ions [8–15], inorganic anions [16–19], peptides and amino acid derivatives [20,21], and other organic analytes [22–26].

Among a variety of analytes, alkali and alkaline earth metal ions are frequently singled out for attention due to their significant biological role in homeostasis [27]. In order to develop colorimetric chemosensors for these metal ions, macrocyclic [7,9,10] as well as acyclic [8,13,14] oligoethers have been employed as analyte-binding sites. These binding sites are linked to chromophores that are electronically affected by metal binding and, thus, perturbation upon electronic transition of the chromophores leads to dramatic color changes.

Spiropyran derivatives, which are usually colorless, are well-known photochromic compounds [28,29]. Spiropyrans are also capable of isomerizing in the presence of metal ions even under dark conditions, since the merocyanine form is stabilized by coordination to the metal ions [30–32]. When spiropyrans are linked to selective metal binding sites such as crown ethers, potentially useful colorimetric sensors for various metal ions are formed. Indeed, crowned spiropyrans have been developed as chemosensors for alkali metal ions, in which the metal ion binding in the crown ether moiety induced a large spectral change accompanied by isomerization to the merocyanine form [33]. There have been several recent reports [34,35] of crowned bis(spiropyran)s for chromogenic sensing of a series of metal ions, in which two phenolate moieties of the merocyanines can coordinate to the metal ion bound to the diazacrown ether. These chemosensors were obtained in relatively short synthetic steps, and the stability of the sensor–analyte complexes was very large ($\log K = 8.38$ for Ca^{2+}, determined by ESI-MS spectroscopy). However, in spite of significant efforts to develop crowned spiropyran chromoionophores, no example of a spiropyran-appended oligoether podand has been reported.

In this study, the facile construction of chemosensors for alkaline earth metal ions is provided, in which an oligoether is conjugated with two spiropyrans resulting in a bis(spiropyran) podand (**X-BSP-*n***, shown in Scheme 1). **X-BSP-*n*** has several advantageous characteristics: (1) a large molar absorption coefficiency due to appending two spiropyran chromophores; (2) short-step synthesis

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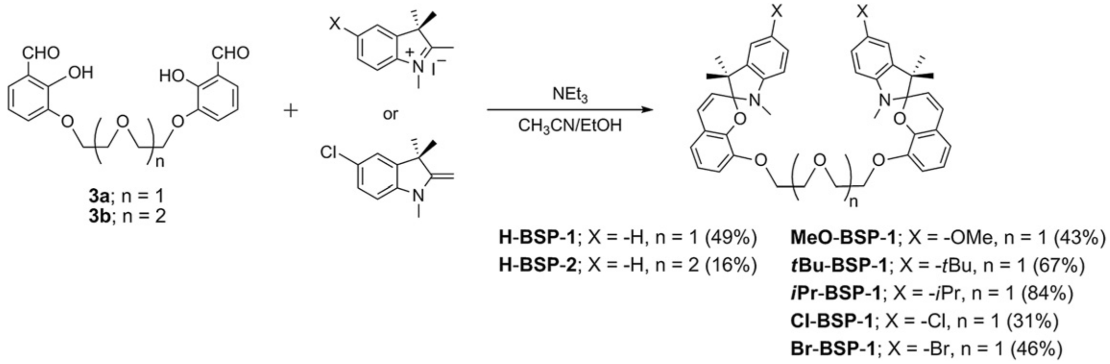
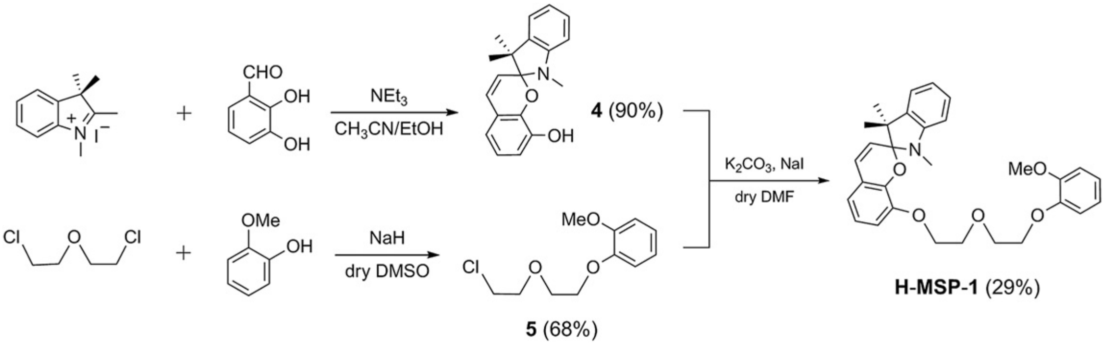


Scheme 1. Synthesis of **X-BSP-*n*** ($n = 1, 2$).



Scheme 2. Synthesis of **H-MSP-1**.

from well-known starting materials, 1,2,3,3-tetramethyl-3*H*-indolium salt, 2,3-dihydroxybenzaldehyde and diethyleneglycol ditosylate; and, (3) effective coordination of two merocyanine phenolates to lead to discrimination of alkaline earth metal ions from alkali metal ions.

2. Results and discussion

2.1. Synthesis of bis(spiropyran) podands

The synthesis of bis(spiropyran) podands **X-BSP-*n*** is shown in Scheme 1. Precursor **3** was obtained from 2,3-dihydroxybenzaldehyde and di- or triethylene glycol ditosylate using the reliable Reinhoudt method [36,37]. **H-BSP-1** and **H-BSP-2** were prepared in 49 and 16% yields, respectively, by the reaction of 1,2,3,3-tetramethylindolium iodide with **3a** and **3b** in a solvent mixture of acetonitrile and ethanol containing a small amount of NEt_3 as a base. **X-BSP-1** (**X** = **MeO**, ***t*Bu**, ***i*Pr**, and **Br**) was also prepared by similar reactions of the corresponding indolium salts with **3a** (yields: 43–84%). For the preparation of **Cl-BSP-1**, the commercially available enamine, 5-chloro-2-methylene-1,3,3-trimethylindoline, was used in place of the indolium salt (yield: 31%). The preparation of the reference compound **H-MSP-1** is shown in Scheme 2. The spirobenzopyran **4** was prepared in 90% yield according to a typical spiropyran synthesis employing 1,2,3,3-tetramethylindolium iodide and 2,3-dihydroxybenzaldehyde as starting materials. Compound **5** was prepared in 68% yield by the reaction of *o*-methoxyphenol with 1,5-dichloro-3-oxapentane in dry DMSO using NaH as a base. The reaction of **4** with **5** in the presence of anhydrous K_2CO_3 and NaI afforded **H-MSP-1** in 29% yield. All prepared compounds were characterized by ^{1}H NMR, mass spectra (FAB MS or MALDI-TOF MS), and elemental analyses prior to further use.

2.2. Complexation behavior of bis(spiropyran) podands with alkaline earth metal ions

Complexation behaviors of the bis(spiropyran) podands with metal ions were investigated by UV–vis absorption spectroscopy. As a typical spectral profile of the podands upon metal ion binding, UV–vis absorption spectral changes of **H-BSP-1** in the presence of varying concentrations of $Ca(ClO_4)_2$ in CH_3CN at 293 K are shown in Fig. 1. Although **H-BSP-1** exhibited no absorption in the visible region in the absence of Ca^{2+}, absorption bands appeared at 397 and 534 nm when Ca^{2+} was present and increased in intensity as the concentration of Ca^{2+} increased. Larger amounts of Ca^{2+} are required to attain maximum absorbance, indicating that the isomerization of the spiropyran moieties to the merocyanine forms was induced by complexation with Ca^{2+}. Similar spectral changes were also observed for **X-BSP-1**, **H-BSP-2**, and **H-MSP-1** upon addition of alkaline earth metal ions such as Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, where the solutions of the podand–M^{2+} mixture were deeply colored. None of the **X-BSP-*n*** ($n = 1, 2$) podand complexes were colored upon addition of any alkali metal ions. Thus, **X-BSP-*n*** can discriminate alkaline earth metal ions from alkali metal ions.

The complexation stoichiometry was determined by either the molar ratio method or Job's analysis. The UV–vis absorbance changes of **H-BSP-1** at the absorption maxima upon addition of $Ca(ClO_4)_2$ and $Sr(ClO_4)_2$ are shown in Fig. 2. The absorbance changes reached a plateau when the concentration of each metal ion reached an equimolar amount to the podand, indicating 1:1 complexation stoichiometry of **H-BSP-1** towards Ca^{2+} and Sr^{2+}. Larger amounts of Mg^{2+} and Ba^{2+} were required to reach a similar spectral saturation point, indicating a lower complexation ability (discussed later). Consequently, the complexation stoichiometry for these metal ions was determined by Job's analysis, as shown in Fig. 3. Each plot shows a peak maximum at [**H-BSP-1**]/([**H-BSP-1**] + [M^{2+}]) = 0.5,