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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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A B S T R A C T

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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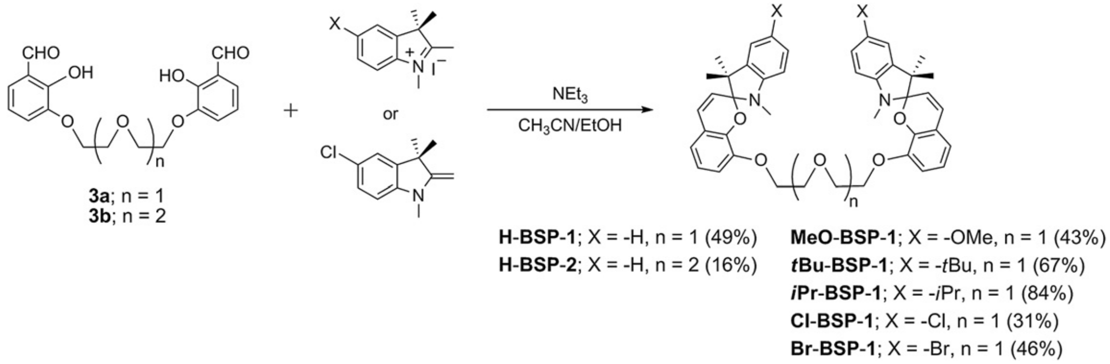
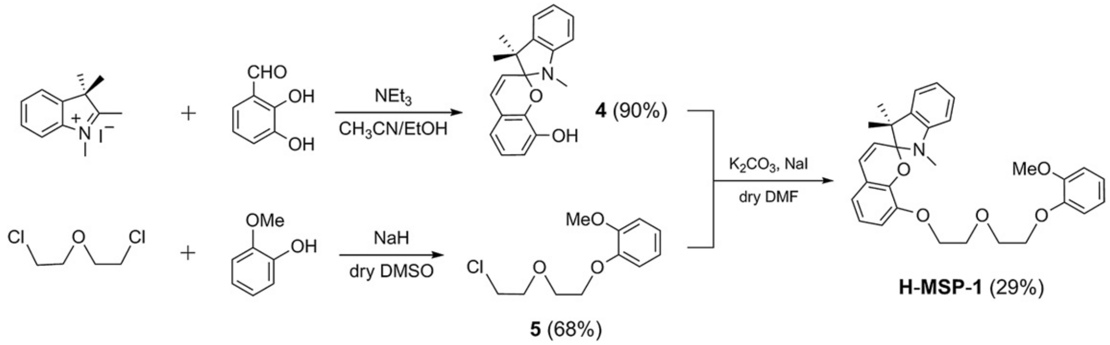


Scheme 1. Synthesis of **X-BSP-*n*** ($n = 1, 2$).



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,

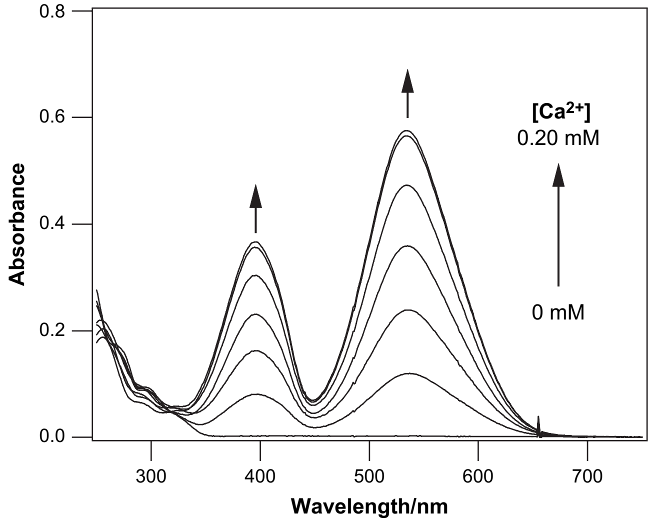


Fig. 1. UV–vis absorption spectral changes of **H-BSP-1** (0.10 mM) in the presence of varying concentrations of $Ca(ClO_4)_2$ (0, 0.020, 0.040, 0.060, 0.080, 0.10, and 0.20 mM) in CH_3CN at 293 K. A quartz cell with 1 mm path length was used.

indicating 1:1 stoichiometry of complexation. For **X-BSP-1**, **H-BSP-2**, and **H-MSP-1**, the stoichiometry of complexation with alkaline earth metal ions was determined as 1:1 in similar ways.

Contribution of the spiropyran moieties to complexation with alkaline earth metal ions was elucidated by ^1H NMR spectroscopy.

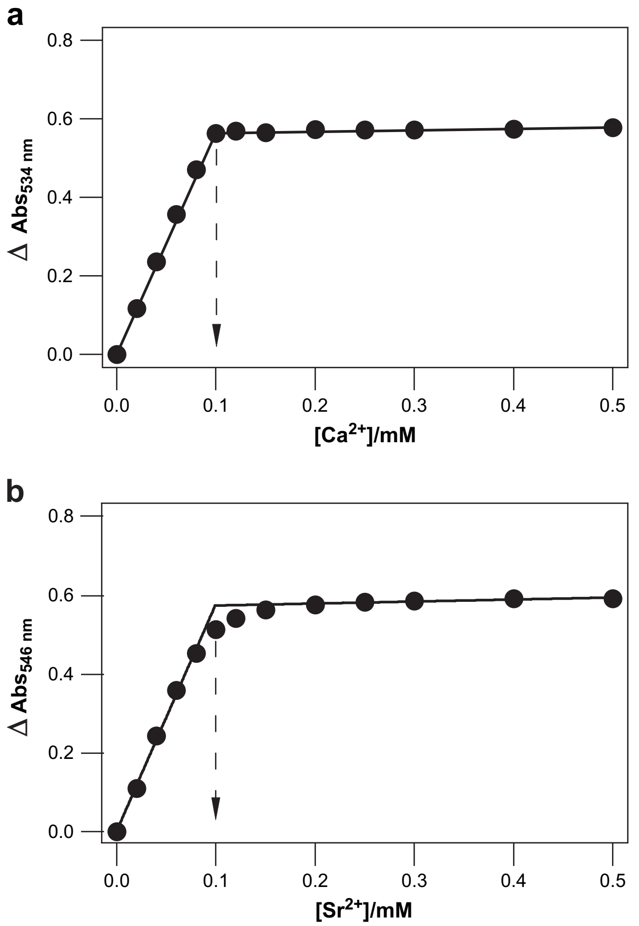


Fig. 2. Absorbance changes of **H-BSP-1** (0.10 mM) upon addition of increasing amounts of alkaline earth metal ions: (a) $Ca(ClO_4)_2$ and (b) $Sr(ClO_4)_2$ in CH_3CN at 293 K. A quartz cell with 1 mm path length was used.

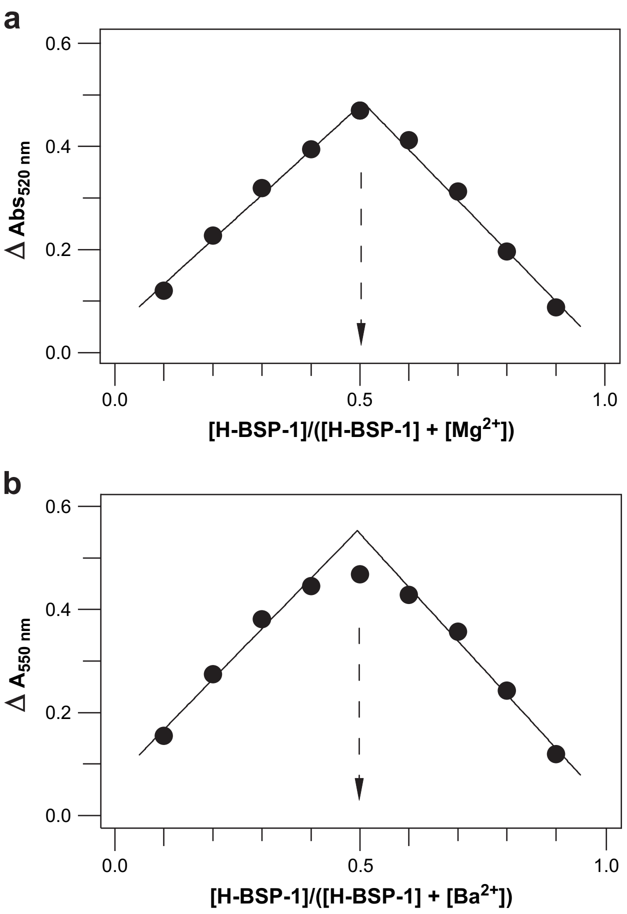


Fig. 3. Job's plots for complexation of **H-BSP-1** with (a) $Mg(ClO_4)_2$ and (b) $Ba(ClO_4)_2$ in CH_3CN at 293 K. The total concentration of the podand and the metal ion was adjusted to 0.30 mM. A quartz cell with 1 mm path length was used.

As an example of the change in the podand's ^1H NMR spectra upon complexation with alkaline earth metal ions, Fig. 4 shows the expanded region of the ^1H NMR spectra of **H-BSP-2** in the absence and presence of Ca^{2+} in CD_3CN at 293 K. As shown in Fig. 4a, **H-BSP-2** exhibits the typical ^1H signals of spiropyrans: two singlets at 1.10 and 1.23 ppm, assigned to the magnetically nonequivalent methyl protons H^a and H^b, and a singlet at 2.67 ppm, assigned to the *N*-methyl protons H^c. The oligoether's protons H^d–H^f were also observed in the usual region. Upon addition of a small amount of Ca^{2+}, a new set of ^1H signals assigned to the podand–Ca^{2+} complex appeared in addition to the original spectrum, indicating the complexation–dissociation rate was slower than the NMR time scale. When an equimolar amount of Ca^{2+} was added, the original signals completely disappeared as shown in Fig. 4b. No further spectral changes were observed despite additional amounts of Ca^{2+}, indicating 1:1 complexation of the podand with Ca^{2+}. The $H^{a'}$–$H^{f'}$ signals clearly showed both spiropyran moieties fully isomerized to the merocyanine forms [38]. That is, the singlet signal at 1.59 ppm was assignable to $H^{a'}$ and $H^{b'}$, having become magnetically equivalent due to the planar structure of the fully π-conjugated merocyanine form. The singlet at 3.58 ppm, assignable to $H^{c'}$, is also a characteristic spectral feature of the merocyanine form; the downfield shift compared to H^c was caused by quaternarization of the nitrogen atom in the indoline ring. The signals of the oligoether moiety were also shifted downfield, magnetically affected by the complexed Ca^{2+}. This complexation-induced spectral change shows that both spiropyran moieties participate in formation of the complex, with the metal ion surrounded *via*

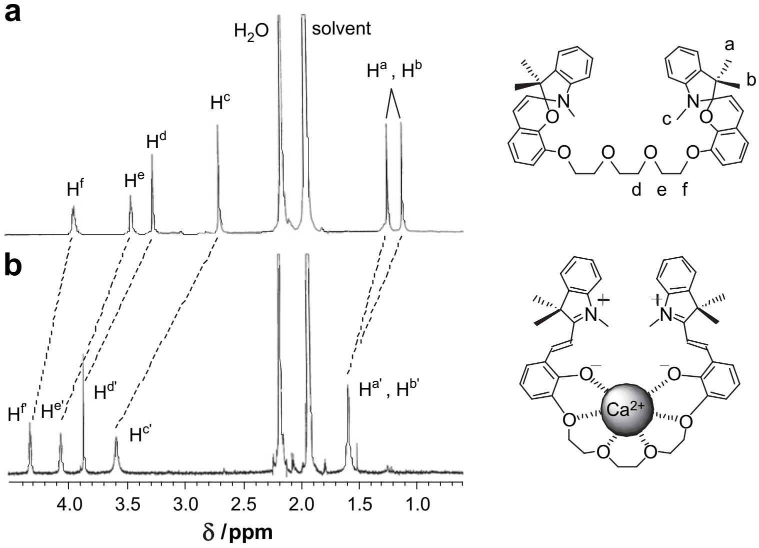


Fig. 4. Expanded ^{1}H NMR spectra of **H-BSP-2** (1.0 mM) in CD_3CN at 293 K (a) in the absence and (b) in the presence of $Ca(ClO_4)_2$ (1.0 mM).

coordination by the oligoether chain as well as the phenolate oxygens of the merocyanines.

2.3. Complexation ability of bis(spiropyran) podands to alkaline earth metal ions

Binding constants (K) for complexation of bis(spiropyran) podands with alkaline earth metal cations were determined by computer-assisted curve-fitting analysis of the UV–vis spectral changes in the presence of increasing amounts of the metal ions (see Section 4.4.1). The quite large complexation ability in several **X-BSP-1**–M^{2+} and **H-BSP-2**–M^{2+} systems (**X** = **MeO**, ***t*Bu** and ***i*Pr**; $M^{2+} = Ca^{2+}$, Sr^{2+} and Ba^{2+}) prevented us from determining the Ks by UV–vis titration. So, the Ks for the **H-BSP-1**–Ca^{2+}, **X-BSP-1**–M^{2+} (**X** = ***t*Bu** and ***i*Pr**; $M^{2+} = Sr^{2+}$ and Ba^{2+}) and **H-BSP-2**–Ca^{2+} systems were determined by the binding competition analysis using ^{1}H NMR spectroscopy, where either **H-BSP-1** or **Br-BSP-1** was employed as a reference podand (also see Section 4.4.2) [39,40]. For the other systems, the podand–M^{2+} complexes were so stable ($K > 10^7$ M^{-1}) that the K could not be determined with high accuracy. The obtained data are summarized in Table 1. The introduction of electron-withdrawing groups (**X** = **Cl**, **Br**) reduced the binding ability to each alkaline earth metal ion, compared to that of **H-BSP-1**. On the other hand, electron-donating substituents (**X** = **MeO**, ***t*Bu**, ***i*Pr**) tended to enhance the binding ability of the bis(spiropyran) podand. The substituent effects on the photochromic properties of indolino-merocyanine compounds, where the substituent at the 5-position of the indoline moiety significantly affects thermodynamic stability of the colored merocyanines, have previously been reported [41]. Roxburgh et al. [35,42] reported in their studies of metal ion chelation of crowned spirobenzopyran derivatives that introduction of an electron-withdrawing group at the indoline's 5-position destabilizes the twitterionic merocyanine form. In the present study, this destabilization effect can be observed in the inhibition of metal ion binding of the bis(spiropyran) podands. Therefore, the sensitivity of **X-BSP-1** towards alkaline earth metal ions is enhanced by the introduction of an electron-donating substituent to the indoline's 5-position.

Table 1
Binding constants (K) for complexation of **X-BSP-*n*** and **H-MSP-1** with alkaline earth metal ions in acetonitrile at 293 K

Podand	K/M^{-1}			
	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
MeO-BSP-1	335 000[a]	–[c]	–[c]	–[c]
***t*Bu-BSP-1**	143 000[a]	–[c]	8 620 000[b]	1 140 000[b]
***i*Pr-BSP-1**	147 000[a]	–[c]	6 420 000[a]	905 000[b]
H-BSP-1	41 000[a]	4 210 000[b]	543 000[a]	43 100[a]
Cl-BSP-1	32 100[a]	245 000[a]	6520[a]	1040[a]
Br-BSP-1	19 800[a]	211 000[a]	3520[a]	881[a]
H-BSP-2	55 400[a]	1 860 000[b]	–[c]	–[c]
H-MSP-1	8530[a]	308 000[a]	27 100[a]	9780[a]

[a] Determined by the UV–vis titration method. The standard deviations are less than 10% except for **X-BSP-1**–Mg^{2+} and **H-BSP-2**–Mg^{2+} systems (7–28%).
[b] Determined by the ^{1}H NMR binding competitive analysis.
[c] Not determined due to too large stability of the podand–M^{2+} complex.

Judging from the values of K for alkaline earth metal ions, the complex with Ca^{2+} was the most stable in the present **X-BSP-1** system. **H-MSP-1** exhibited lower affinity to each metal ion than **H-BSP-1**: K(**H-BSP-1**)/K(**H-MSP-1**) ranged from 4.4 to 20. This indicates that the two merocyanine moieties cooperatively participate in the metal ion binding. The structural difference in the oligoether gave rise to the difference in selectivity to the metal ions. In **H-BSP-2**, the values of K for Mg^{2+} and Ca^{2+} are 55 400 and 1 860 000 M^{-1}, respectively, whereas those of Sr^{2+} and Ba^{2+} are too large to determine ($>10^7$ M^{-1}). Owing to the extension of one oxyethylene unit in the oligoether chain, it is likely that **H-BSP-2** prefers to bind to the ions with larger ionic radii than Ca^{2+}. Indeed, **H-BSP-2** yielded a smaller K for Ca^{2+} than **H-BSP-1**, although the increase in the number of coordination sites to metal ions was expected to increase the stability of the podand–M^{2+} complex. From the comparison between **H-BSP-1** and **H-BSP-2**, the oligoether moiety consisting of two oxyethylene units is more suitable for binding of Ca^{2+} than that consisting of three.

Nakamura et al. [34] reported crowned bis(spirobenzopyran)s where two spiropyran moieties are attached to diaza-12-crown-4 and diaza-18-crown-6. These can form stable complexes with Ca^{2+} with log K of 7.80 and 8.38 (in methanol), respectively. Such large stability owes to the macrocyclic effect of the crown ether moiety as well as ionic interaction between the phenolates of the spiropyran moieties and the bound metal ion. In the presented bis(spiropyran) podand system, the absence of the macrocyclic effect of the polyether ionophore leads to a reduction in stability of the metal ion complex, compared to the crowned bis(spiropyran) system. It is,

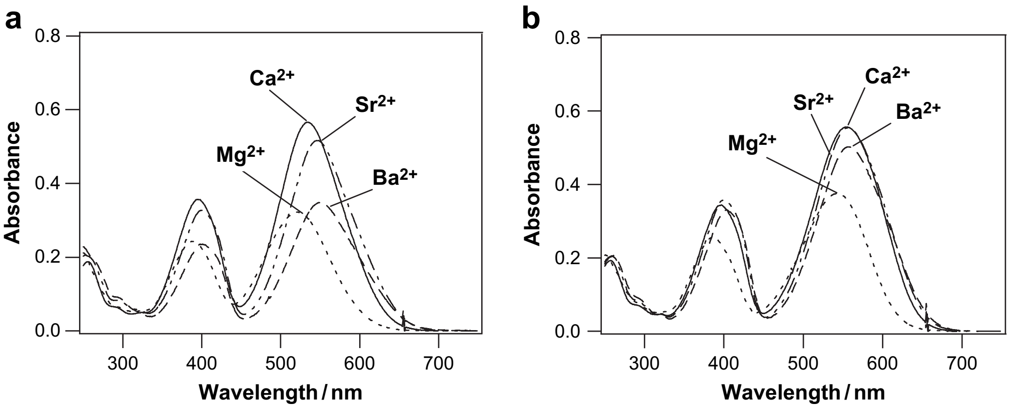


Fig. 5. UV–vis spectra of (a) **H-BSP-1** (0.10 mM) and (b) **H-BSP-2** (0.10 mM) in the presence of Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in CH_3CN at 293 K. The concentration of each metal ion is 0.10 mM. A quartz cell with 1 mm path length was used.

however, interesting that selectivity to a specific metal ion as well as relatively large stability of the metal ion complex is obtained despite of the highly flexible podand moiety.

2.4. Colorimetric sensing of alkaline earth metal ions by bis(spiropyran) podands

As discussed above, selectivity and sensitivity of the bis(spiropyran) podands towards alkaline earth metal ions are tuned by the length of the oligoether moiety and the substituent introduced to the indoline moieties, respectively. In colorimetric sensory systems, a wide range of color variation provides better discrimination of multiple analytes. Fig. 5 shows the UV–vis absorption spectra of **H-BSP-1** and **H-BSP-2** in the presence of equimolar amounts of alkaline earth metal ions. UV–vis absorption spectral data for all podands employed in this study in the presence of excess amounts of the metal ions are listed in Table 2. Photographs of **H-BSP-1** and **H-BSP-2** solutions in the presence of a series of alkali and alkaline earth metal ions are shown in Fig. 6.

In the **H-BSP-1** system, the most intense coloration was observed for Ca^{2+}; Mg^{2+} and Ba^{2+} solutions were less colored due to the lower stability of these complexes (Fig. 5a). The absorption maxima (λ_{max}) of the complexes range from 520 to 550 nm, and the solutions are colored from reddish violet (Mg^{2+}) to bluish purple (Ba^{2+}), as shown in Fig. 6a. Note that no coloration occurred in the presence of any alkali metal ions. Thus, naked-eye discrimination between alkali and alkaline earth metal ions is possible in the **H-BSP-1** system. The clear discrimination of color between Mg^{2+} (reddish violet) and Ca^{2+} (purple) is noteworthy, since these are the alkaline earth metal ions essential for living systems. On the other hand, the range of λ_{max} in the **H-BSP-2** system is narrower (from 542 to 557 nm) than that for **H-BSP-1**, and the λ_{max} of the complexes with Ca^{2+}, Sr^{2+}, and Ba^{2+} is so similar that it is difficult to discriminate these by naked eyes (Fig. 6b). Overall, the colored podands in the present study exhibited molar absorption coefficients ε at λ_{max} (51 000–65 100 $M^{-1}\,cm^{-1}$) about twice as large as those of **H-MSP-1**, except for **Cl-BSP-1**–Ba^{2+} (44 300 $M^{-1}\,cm^{-1}$) and **Br-BSP-1**–Ba^{2+} (36 100 $M^{-1}\,cm^{-1}$) due to low binding ability.

Table 2
UV–vis absorption spectral data (absorption maxima λ_{max} and molar absorption coefficients ε) of the complexes of **X-BSP-*n*** and **H-MSP-1** with alkaline earth metal ions in CH_3CN at 293 K

Podand	λ_{max}/nm (ε/$M^{-1}\,cm^{-1}$)[a]			
	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
MeO-BSP-1	520 (54 700)	534 (59 900)	546 (61 500)	550 (61 600)
***t*Bu-BSP-1**	519 (55 000)	533 (62 500)	546 (65 100)	546 (65 100)
***i*Pr-BSP-1**	519 (53 300)	533 (59 300)	545 (61 900)	552 (62 000)
H-BSP-1	520 (51 000)	534 (57 800)	546 (59 700)	550 (57 000)
Cl-BSP-1	530 (55 600)	542 (62 800)	553 (56 400)	557 (44 300)
Br-BSP-1	533 (54 900)	543 (62 800)	553 (57 200)	558 (36 100)
H-BSP-2	542 (55 800)	555 (56 300)	556 (56 100)	557 (53 800)
H-MSP-1	538 (22 100)	545 (27 300)	553 (27 200)	564 (30 000)

[a] The values of ε were obtained in the presence of excess amounts of the metal ions.

For the **MeO-**, ***t*Bu-**, ***i*Pr-BSP-1** systems of a single metal ion, λ_{max} was mostly observed within 1 nm of the **H-BSP-1** complex, showing that the introduction of the electron-donating substituents to the indoline moieties hardly affected the λ_{max} of the complexes. In the **Cl-** and **Br-BSP-1** systems, slight bathochromic shifts of λ_{max} by *ca.* 10 nm were observed although the color ranges across the series of metal ions were similar to those observed in the podands with the electron-donating groups. Considering that the introduction of the electron-donating groups to the 5-positions of the indoline moieties leads to the most remarkable enhancement of the affinity

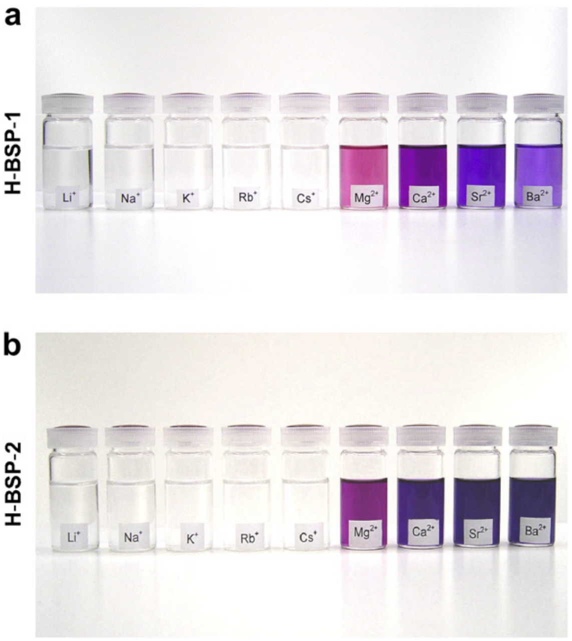


Fig. 6. Coloration of (a) **H-BSP-1** and (b) **H-BSP-2** in the presence of Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} in CH_3CN. The concentration of all species was 0.025 mM.

towards alkaline earth metal ions, **MeO-BSP-1** is the optimized chromogenic podand suitable for colorimetric Ca^{2+} sensing.

3. Conclusions

In the present study, the bis(spiropyran) podands **X-BSP-1** (**X** = **MeO**, ***t*Bu**, ***i*Pr**, **H**, **Cl**, and **Br**) and **H-BSP-2** were readily prepared from well-known starting materials. These podands formed complexes with a series of alkaline earth metal ions in acetonitrile solution with 1:1 stoichiometry, accompanied by coloration due to the isomerization of the spiropyran moieties to the merocyanine structures. No coloration was exhibited upon addition of alkali metal ions. The ^1H NMR measurements of the podands in the presence of alkaline earth metal ions showed that both of the spiropyran moieties isomerized to the merocyanine forms, indicating that the metal ion was bound to the oligoether chain as well as the phenolates of the two merocyanine moieties. **X-BSP-1** exhibited high selectivity to Ca^{2+}, whereas **H-BSP-2** preferred to bind alkaline earth metal ions with larger ionic radii, such as Sr^{2+} and Ba^{2+}. Thus, **X-BSP-1** is potentially applicable to colorimetric Ca^{2+} sensing. The absorption maxima of the **X-BSP-1** upon complexation with a series of alkaline earth metal ions ranged over *ca.* 30 nm. In particular, Mg^{2+} (reddish violet) and Ca^{2+} (purple), which are biologically important ions, can be discriminated by the naked eye. As the electron-donating ability of the substituent **X** increased, the stability of the complex increased. Therefore, **MeO-BSP-1** is the most optimized Ca^{2+} colorimetric sensor developed in the present study.

4. Experimental

4.1. General

^1H NMR spectra were taken on a Jeol JNM GX-270 (270 MHz), a Jeol JNM LA-400 (400 MHz), or a Jeol JNM A-500 (500 MHz) spectrometer, where TMS (0.00 ppm) and CD_2HCN (1.93 ppm) were used as internal standards for $CDCl_3$ and CD_3CN, respectively. UV–vis absorption spectra were measured on a Shimadzu Multispec-1500 spectrometer. In ^1H NMR and UV–vis spectroscopic studies, the prepared samples were left overnight under darkness before the measurements. Fast atom bombardment mass spectra (FAB MS) were taken on a Finnigan MAT TSQ-70 spectrometer using 3-nitrobenzylalcohol as a matrix. Matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF MS) were taken on a Shimazu Kratos Compact MALDI 2 spectrometer using sinapinic acid as a matrix. Elemental analyses were measured on a Yanako CHN CORDER MT-3 analyzer.

4.2. Materials and solvents

1,2,3,3-Tetramethylindolium iodide was obtained by methylation of commercially available 2,3,3-trimethylindolenine (Tokyo Chemical Industry Co., Ltd.) with iodomethane. 5-Methoxy-, 5-(1,1-dimethylethyl)-, 5-(1-methylethyl)-, and 5-bromo-1,2,3,3-tetramethylindolium iodides were prepared by the usual indolenine synthesis starting from the corresponding arylhydrazines and 3-methyl-2-butanone followed by *N*-methylation with iodomethane [43]. 5-Chloro-2-methylene-1,3,3-trimethylindoline was purchased from Tokyo Chemical Industry Co., Ltd., and used without further purification. The precursors **3a** [36] and **3b** [37] were prepared according to the reported procedures, where the starting materials, 2,3-dihydroxybenzaldehyde and di- and triethylene glycol bis(*p*-toluenesulfonate)s, were commercially available. DMSO was dried over calcium hydride and distilled under reduced pressure just prior to use. Column chromatography was performed with silica gel (Wako Gel C-300) or C18 end-capped reverse-phase silica gel (Nakalai 75 C_{18}-OPN). For spectroscopic measurements, spectroscopic-grade CH_3CN was purchased from Nakalai Tesque Inc. The alkaline earth metal perchlorates were dried prior to use over P_2O_5 for at least 7 days.

4.3. Synthesis

4.3.1. 8′,8″-(3-Oxapentylene-1,5-dioxy)bis(spiro[2H-1-benzopyran-2,2′-(1′,3′,3′-trimethylindoline)]) (***H-BSP-1***)

1,2,3,3-Tetramethylindolium iodide (0.964 g, 3.20 mmol) and **3a** (0.520 g, 1.50 mmol) were dissolved in a mixture of CH_3CN (12 mL) and ethanol (4.5 mL). To the mixture was added NEt_3 (0.5 mL), and the resultant mixture was heated at reflux for 1 h. After cooling, the precipitate was removed by filtration, and the filtrate was evaporated to dryness. Purification of the residue by reverse-phase column chromatography (CH_3CN/water, 20:1, v/v, as eluent) afforded **H-BSP-1** (0.486 g, 0.740 mmol, 49% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (s, 6H), 1.29 (s, 6H), 2.69 (s, 6H), 3.23–3.32 (m, 4H), 3.64–3.75 (m, 4H), 5.68 (d, $J = 10.3$ Hz, 2H), 6.42 (d, $J = 7.8$ Hz, 2H), 6.68–6.78 (m, 8H), 6.84 (d, $J = 10.3$ Hz, 2H), 6.97 (d, $J = 7.3$ Hz, 2H), 7.03 (t, $J = 7.8$ Hz, 2H); FAB MS (positive mode) *m*/*z* 657 ($[M + H]^+$). Anal. Calcd for $C_{42}H_{44}N_2O_5$: C, 76.80; H, 6.75; N, 4.27. Found: C, 76.52; H, 6.74; N, 4.32.

4.3.2. 8′,8″-(3-Oxapentylene-1,5-dioxy)bis(spiro[2H-1-benzopyran-2,2′-(5′-methoxy-1′,3′,3′-trimethylindoline)]) (***MeO-BSP-1***)

A mixture of 5-methoxy-1,2,3,3-tetramethylindolium iodide (0.378 g, 1.14 mmol) and NEt_3 (0.2 mL) in a mixture of CH_3CN (4 mL) and ethanol (1.5 mL) was stirred at rt for 10 min. To the mixture was added **3a** (0.173 g, 0.500 mmol) and the resultant mixture was heated at reflux for 2 h. After cooling, the solvent was removed on a rotary evaporator. Purification of the residue by reverse-phase column chromatography (CH_3CN/water, 20:1, v/v, as eluent) afforded **MeO-BSP-1** (0.155 g, 0.216 mmol, 43% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (s, 6H), 1.27 (s, 6H), 2.63 (s, 6H), 3.29–3.32 (m, 4H), 3.65 (s, 6H), 3.65–3.79 (m, 4H), 5.68 (d, $J = 10.0$ Hz, 2H), 6.54–6.64 (m, 4H), 6.70–6.78 (m, 6H), 6.83 (d, $J = 10.0$ Hz, 2H); FAB MS (positive mode) *m*/*z* 717 ($[M + H]^+$). Anal. Calcd for $C_{44}H_{48}N_2O_7$: C, 73.72; H, 6.74; N, 3.91. Found: C, 73.38; H, 6.97; N, 4.03.

4.3.3. 8′,8″-(3-Oxapentylene-1,5-dioxy)bis(spiro[2H-1-benzopyran-2,2′-(5′-(1,1-dimethylethyl)-1′,3′,3′-trimethylindoline)]) (***tBu-BSP-1***)

A solution of 5-(1,1-dimethylethyl)-1,2,3,3-tetramethylindolium iodide (0.393 g, 1.10 mmol) and NEt_3 (0.2 mL) in a mixture of CH_3CN (4 mL) and ethanol (1.5 mL) was stirred at rt for 10 min. To the mixture was added **3a** (0.173 g, 0.500 mmol) and the resultant mixture was heated at reflux for 6 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was dissolved in a small amount of a mixture of ethyl acetate and hexane. The precipitate was removed by filtration and the filtrate was evaporated to dryness. The residue was purified by reverse-phase column chromatography (CH_3CN as eluent) to afford ***t*Bu-BSP-1** (0.256 g, 0.333 mmol, 67% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (s, 6H), 1.26 (s, 18H), 1.29 (s, 6H), 2.66 (s, 6H), 3.16–3.33 (m, 4H), 3.63–3.78 (m, 4H), 5.67 (d, $J = 10.3$ Hz, 2H), 6.33 (dd, $J = 7.8$, 5.4 Hz, 2H), 6.71–6.77 (m, 6H), 6.81 (d, $J = 10.3$ Hz, 2H), 7.03 (d, $J = 2.0$ Hz, 2H), 7.05–7.13 (m, 2H); MALDI-TOF MS (positive) *m*/*z* 769 ($[M + H]^+$). Anal. Calcd for $C_{50}H_{60}N_2O_5 \cdot H_2O$: C, 76.30; H, 7.94; N 3.56. Found: C, 76.39; H, 7.82; N 3.65.

4.3.4. 8′,8″-(3-Oxapentylene-1,5-dioxy)bis(spiro[2H-1-benzopyran-2,2′-(1′,3′,3′-trimethyl-5′-(1-methylethyl)indoline)]) (***iPr-BSP-1***)

A mixture of 1,2,3,3-tetramethyl-5-(1-methylethyl)indolium iodide (0.378 g, 1.10 mmol) and NEt_3 (0.2 mL) in a mixture of CH_3CN

(4 mL) and ethanol (1.5 mL) was stirred at rt for 10 min. To the mixture was added **3a** (0.173 g, 0.500 mmol) and heated at reflux for 6 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was dissolved in a small amount of a mixture of ethyl acetate and hexane. The precipitate was removed by filtration and the filtrate was evaporated to dryness. The residue was purified by reverse-phase column chromatography (CH_3CN as eluent) to afford ***i*Pr-BSP-1** (0.310 g, 0.418 mmol, 84% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (s, 6H), 1.19 (d, $J = 7.3$ Hz, 12H), 1.28 (s, 6H), 2.66 (s, 6H), 2.80 (m, $J = 7.3$ Hz, 2H), 3.19–3.35 (m, 4H), 3.64–3.76 (m, 4H), 5.67 (d, $J = 10.3$ Hz, 2H), 6.33 (dd, $J = 8.1$, 4.2 Hz, 2H), 6.71–6.77 (m, 6H), 6.82 (d, $J = 10.3$ Hz, 2H), 6.86–6.91 (m, 4H); MALDI-TOF MS (positive mode) *m*/*z* 740 (M^+). Anal. Calcd for $C_{48}H_{56}N_2O_5$: C, 77.81; H, 7.62; N 3.78. Found: C, 77.41; H, 7.71; N 3.93.

4.3.5. 8′,8″-(3-Oxapentylene-1,5-dioxy)bis(spiro[2H-1-benzopyran-2,2′-(5′-chloro-1′,3′,3′-trimethylindoline)]) (***Cl-BSP-1***)

To a solution of 5-chloro-2-methylene-1,3,3-trimethylindoline (1.14 g, 5.49 mmol) in a solvent mixture of CH_3CN (20 mL) and ethanol (7.5 mL) was added **3a** (0.865 g, 2.50 mmol), and the mixture was heated at reflux for 2.5 h. After cooling, the solvent was removed on a rotary evaporator. Purification of the residue by reverse-phase column chromatography (CH_3CN/water, 20:1, v/v, as eluent) afforded **Cl-BSP-1** (0.238 g, 0.328 mmol, 13% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 1.15 (s, 6H), 1.26 (s, 6H), 2.66 (s, 6H), 3.28–3.41 (m, 4H), 3.68–3.78 (m, 4H), 5.65 (d, $J = 10.3$ Hz, 2H), 6.31 (dd, $J = 8.3$, 2.0 Hz, 2H), 6.70–6.81 (m, 6H), 6.84 (d, $J = 10.3$ Hz, 2H), 6.92 (d, $J = 2.0$ Hz, 2H), 6.98 (dd, $J = 8.3$, 2.0 Hz, 2H); FAB MS (positive mode) *m*/*z* 725 ($[M+H]^+$). Anal. Calcd for $C_{42}H_{42}Cl_2N_2O_5 \cdot H_2O$: C, 67.83; H, 5.96; N, 3.77. Found: C, 68.15; H, 5.76; N, 3.89.

4.3.6. 8′,8″-(3-Oxapentylene-1,5-dioxy)bis(spiro[2H-1-benzopyran-2,2′-(5′-bromo-1′,3′,3′-trimethyl)indoline]) (***Br-BSP-1***)

A mixture of 5-bromo-1,2,3,3-tetramethylindolium iodide (0.418 g, 1.10 mmol) and NEt_3 (0.2 mL) in a mixture of CH_3CN (4 mL) and ethanol (1.5 mL) was stirred at rt for 10 min. To the mixture was added **3a** (0.173 g, 0.500 mmol) and the resultant mixture was heated at reflux for 2.5 h. After cooling, the solvent was removed on a rotary evaporator. Purification of the residue by reverse-phase column chromatography (CH_3CN/water, 20:1, v/v, as eluent) afforded **Br-BSP-1** (0.188 g, 0.231 mmol, 46% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 1.15 (s, 6H), 1.26 (s, 6H), 2.66 (s, 6H), 3.28–3.38 (m, 4H), 3.70–3.78 (m, 4H), 5.65 (d, $J = 10.0$ Hz, 2H), 6.28 (dd, $J = 8.3$, 2.0 Hz, 2H), 6.71 (dd, $J = 7.4$, 1.5 Hz, 2H), 6.76 (t, $J = 7.4$ Hz, 2H), 6.81 (dd, $J = 7.4$, 1.5 Hz, 2H), 6.85 (d, $J = 10.0$ Hz, 2H), 7.06 (d, $J = 2.0$ Hz, 2H), 7.12 (dd, $J = 8.3$, 2.0 Hz, 2H); FAB MS (positive mode) *m*/*z* 813 ($[M+H]^+$). Anal. Calcd for $C_{42}H_{42}Br_2N_2O_5 \cdot H_2O$: C, 61.93; H, 5.20; N, 3.44. Found: C, 62.03; H, 5.29; N, 3.62.

4.3.7. 8′,8″-(3,5-Dioxaoctylene-1,8-dioxy)bis(spiro[2H-1-benzopyran-2,2′-(1′,3′,3′-trimethylindoline)]) (***H-BSP-2***)

To a mixture of 1,2,3,3-tetramethylindolium iodide (0.964 g, 3.20 mmol) and **3b** (0.586 g, 1.50 mmol) in a solvent mixture of CH_3CN (12 mL) and ethanol (4.5 mL) was added NEt_3 (0.324 g, 3.20 mmol), and the resultant mixture was heated at reflux for 1 h. After cooling, the precipitate was removed by filtration and the filtrate was evaporated to dryness. Purification of the residue by reverse-phase column chromatography (CH_3CN/water, 20:1, v/v, as eluent) afforded **H-BSP-2** (0.167 g, 0.238 mmol, 16% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 6H), 1.31 (s, 6H), 2.70 (s, 6H), 3.27 (s, 4H), 3.45 (dd, $J = 9.0$, 4.4 Hz, 4H), 3.92 (t, $J = 4.4$ Hz, 4H), 5.69 (d, $J = 10.3$ Hz, 2H), 6.46 (d, $J = 7.8$ Hz, 2H), 6.72–6.82 (m, 8H), 6.85 (d, $J = 10.3$ Hz, 2H), 7.10 (d, $J = 7.8$ Hz, 2H), 7.10 (t, $J = 7.8$ Hz, 2H); FAB MS (positive mode) *m*/*z* 701 ($[M+H]^+$). Anal. Calcd for $C_{44}H_{48}N_2O_6 \cdot 0.5H_2O$: C, 74.45; H, 6.96; N, 3.95. Found: C, 74.64; H, 6.97; N, 4.07.

4.3.8. Spiro[2H-1-bensopyran-2,2′-(8′-hydroxy-1′,3′,3′-trimethylindoline)] (***4***)

To a mixture of 1,2,3,3-tetramethylindolium iodide (2.18 g, 7.24 mmol) and NEt_3 (2.00 g, 19.8 mmol) in a solvent mixture of CH_3CN (58 mL) and ethanol (22 mL) was added at a portion 2,3-dihydroxybenzaldehyde (1.00 g, 7.24 mmol), and the mixture was heated at reflux for 5.5 h. After cooling, the mixture was evaporated to dryness. Purification of the residue by recrystallization from $CHCl_3$/hexane afforded **4** (1.91 g, 6.52 mmol, 90% yield); ^1H NMR (270 MHz, $CDCl_3$) δ 1.18 (s, 3H), 1.30 (s, 3H), 2.75 (s, 3H), 5.25 (s, 1H), 5.69 (d, $J = 10.3$ Hz, 1H), 6.53 (d, $J = 7.6$ Hz, 1H), 6.64 (dd, $J = 6.8$, 1.6 Hz, 1H), 6.71–6.88 (m, 4H), 7.07 (d, $J = 6.8$ Hz, 1H), 7.18 (t, $J = 7.6$ Hz, 1H); FAB MS (positive mode) *m*/*z* 293 (M^+). Anal. Calcd for $C_{19}H_{19}NO_2 \cdot 0.2H_2O$: C, 76.85; H, 6.59; N, 4.72. Found: C, 77.06; H, 6.60; N, 4.87.

4.3.9. 1-Chloro-5-(2-methoxyphenyloxy)-3-oxapentane (***5***)

To a suspension of NaH (60% oil dispersion, 1.38 g, 34.5 mmol) in dry DMSO (30 mL) was added a solution of *o*-methoxyphenol (3.66 g, 29.5 mmol) in dry DMSO (20 mL) over 1 h with vigorous stirring under N_2. The mixture was stirred at rt for 1 h, and 1,5-dichloro-3-oxapentane (8.19 g, 57.3 mmol) was added at a portion. The resultant mixture was stirred at 60 °C for 6 h. After cooling, the reaction mixture was poured into water (800 mL), and then, acidified to pH 3 with 2 M HCl. The aqueous mixture was extracted three times with $CHCl_3$. The organic layers were combined, washed well with 1 M HCl, and then dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by silica gel column chromatography (ethyl acetate/hexane, 1:1, v/v, as eluent) to give **5** as a colorless liquid (4.63 g, 20.1 mmol, 68% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 3.65 (t, $J = 5.9$ Hz, 2H), 3.82–3.86 (m, 5H), 3.91 (t, $J = 5.0$ Hz, 2H), 4.19 (t, $J = 5.0$ Hz, 2H), 6.86–6.98 (m, 4H); FAB MS (positive mode) *m*/*z* 231 ($[M+H]^+$). Anal. Calcd for $C_{11}H_{15}ClO_3$: C, 57.27; H, 6.55. Found: C, 56.80; H, 6.73.

4.3.10. 8′-[5-(2-Methoxyphenyloxy)-3-oxapentan-1-oxy]spiro[2H-1-bensopyran-2,2′-(1′,3′,3′-tri-methylindoline)] (***H-MSP-1***)

To a suspension of anhydrous K_2CO_3 (0.587 g, 4.25 mmol) in dry DMSO (10 mL) were added **5** (0.399 g, 1.73 mmol) and NaI (0.128 g, 0.865 mmol), and the resultant mixture was stirred under N_2 at 70 °C for 30 min. Then, **4** (0.507 g, 1.73 mmol) was added, and the mixture was stirred overnight at the same temperature. After cooling, CH_2Cl_2 (50 mL) was added. The mixture was washed with water and saturated brine, and then dried over $MgSO_4$. After removal of the solvent on a rotary evaporator, purification of the residue by reverse-phase column chromatography (CH_3CN as eluent) afforded **H-MSP-1** (0.245 g, 0.503 mmol, 29% yield); ^1H NMR (270 MHz, $CDCl_3$) δ 1.17 (s, 3H), 1.31 (s, 3H), 2.70 (s, 3H), 3.56–3.67 (m, 4H), 3.81 (s, 3H), 3.90–3.97 (m, 4H), 5.70 (d, $J = 10.3$ Hz, 1H), 6.46 (d, $J = 7.6$ Hz, 1H), 6.71–6.94 (m, 5H), 7.03 (d, $J = 10.3$ Hz, 1H), 7.09 (dt, $J = 7.6$, 1.4 Hz, 1H); FAB MS (positive mode) *m*/*z* 488 ($[M+H]^+$). Anal. Calcd for $C_{30}H_{33}NO_5 \cdot 2/3H_2O$: C, 72.14; H, 6.93; N, 2.80. Found: C, 72.10; H, 6.78; N, 2.69.

4.4. Determination of binding constants

4.4.1. UV–vis titration method

The binding constants *K* for complexation of **X-BSP-*n*** and **H-MSP-1** with alkaline earth metal ions (M^{2+}) were basically determined from the plots of the absorbance changes (ΔAbs) at λ_{max} of the merocyanine form against varying concentrations of an alkaline earth metal ion. Supposing 1:1 complexation equilibrium as shown in Eq. (1), binding constant *K* is written as Eq. (2).

$$\mathbf{BSP} + \mathrm{M}^{2+} \overset{K}{\rightleftharpoons} \mathbf{BSP}{-}\mathrm{M}^{2+} \tag{1}$$

$$K = \left[\mathbf{BSP}{-}\mathrm{M}^{2+}\right] / [\mathbf{BSP}]\left[\mathrm{M}^{2+}\right] \tag{2}$$

where [**BSP**], $[\mathrm{M}^{2+}]$, and [**BSP**–M^{2+}] represent the concentrations of the bis(spiropyran) podand, the alkaline earth metal ion, and the 1:1 complex of both species, respectively. Since neither **BSP** nor M^{2+} shows any electronic absorption in the visible region, the absorbance (Abs) at 519–564 nm is expressed as Eq. (3)

$$\mathrm{Abs} = \varepsilon_{\mathrm{complex}}\left[\mathbf{BSP}{-}\mathrm{M}^{2+}\right] \tag{3}$$

where $\varepsilon_{\mathrm{complex}}$ is the molar absorption coefficient of the **BSP**–M^{2+} complex. Total concentrations of **BSP** and M^{2+} are written as Eqs. (4) and (5), respectively,

$$[\mathbf{BSP}]_{\mathrm{total}} = [\mathbf{BSP}] + \left[\mathbf{BSP}{-}\mathrm{M}^{2+}\right] \tag{4}$$

$$\left[\mathrm{M}^{2+}\right]_{\mathrm{total}} = \left[\mathrm{M}^{2+}\right] + \left[\mathbf{BSP}{-}\mathrm{M}^{2+}\right] \tag{5}$$

Substituting Eqs. (4) and (5) for Eq. (2) to eliminate [**BSP**] and $[\mathrm{M}^{2+}]$, [**BSP**–M^{2+}] is given as Eq. (6)

$$\left[\mathbf{BSP}{-}\mathrm{M}^{2+}\right] = \left(b + \left(b^2 - 4K^2[\mathbf{BSP}]_{\mathrm{total}}\left[\mathrm{M}^{2+}\right]_{\mathrm{total}}\right)^{1/2}\right)/2K \tag{6}$$

where $b = 1 + K([\mathbf{BSP}]_{\mathrm{total}} + [\mathrm{M}^{2+}]_{\mathrm{total}})$. Finally, substituting Eq. (6) for Eq. (3), the absorbance of the complex is represented by Eq. (7)

$$\mathrm{Abs} = \varepsilon_{\mathrm{complex}}\left(b + \left(b^2 - 4K^2[\mathbf{BSP}]_{\mathrm{total}}\left[\mathrm{M}^{2+}\right]_{\mathrm{total}}\right)^{1/2}\right)/2K \tag{7}$$

In the present case, Abs is equal to ΔAbs in the visible region. Thus, the K is estimated as a parameter from the computer-assisted least-square curve-fitting analysis for the experimental data using Eq. (7).

4.4.2. ^{1}H NMR binding competition method

The quite large complexation ability in **H-BSP-2**–M^{2+} and **X-BSP-1**–M^{2+} systems (**X** = **MeO**, ***t*Bu**, ***i*Pr**, and **H**, $\mathrm{M}^{2+} = \mathrm{Ca}^{2+}$, Sr^{2+}, and Ba^{2+}, except for **H-BSP-1**–Sr^{2+} and **H-BSP-1**–Ba^{2+}) prevented us from determining K by the UV–vis titration method. So, the values of K for these systems were evaluated by the ^{1}H NMR binding competition analysis. In a ternary system consisting of $\mathbf{BSP_1}$, $\mathbf{BSP_2}$ and M^{2+} ($\mathbf{BSP_1}$ and $\mathbf{BSP_2}$ are different bis(spiropyran) podands each other), the relationship of K_1 and K_2 is defined as described in Eq. (8)

$$K_2/K_1 = \left(\left[\mathbf{BSP}_2{-}\mathrm{M}^{2+}\right]/\left[\mathbf{BSP}_1{-}\mathrm{M}^{2+}\right]\right)\left([\mathbf{BSP}_1]/[\mathbf{BSP}_2]\right) \tag{8}$$

where K_1 and K_2 represent the binding constants of $\mathbf{BSP_1}$ and $\mathbf{BSP_2}$ towards M^{2+}, respectively. As the complexation–dissociation in the podand–M^{2+} system is slower than the NMR time scale, [$\mathbf{BSP_1}$], [$\mathbf{BSP_1}$–M^{2+}], [$\mathbf{BSP_2}$], and [$\mathbf{BSP_2}$–M^{2+}] can be determined from the comparison of the ^{1}H NMR peak integration of these species, and thus, K_2 is estimated using known K_1 according to Eq. (8). In the present study, the analysis was carried out for a mixture of a sample podand (1.0 mM), a reference podand (**H-** or **Br-BSP-1**, 1.0 mM) and a metal ion (1.0 mM) in $\mathrm{CD_3CN}$.

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