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A photoswitchable Zn (II) selective spiropyran-based sensor

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ABSTRACT

A spiropyran-based fluorescent and photoregenerable receptor, that is, selective towards zinc(II) ions over a series of biologically and environmentally relevant cations has been designed and synthesized. The complex formation gives rise to colour changes that are visible to the naked eye and reversible upon visible light irradiation. ^{1}H NMR studies confirm that the closed form is converted to the open *trans*-merocyanine complex upon addition of zinc ions.

1. Introduction

The importance of zinc for maintaining the structural integrity of proteins, and for regulating gene expression are well known.[1] Although at low levels zinc is an essential mineral used by plants and animals, at higher levels, zinc pollution is suspected of causing cardiovascular, reproductive, immune and respiratory problems.[2] The detrimental effects of zinc contamination on plants and fish may be even greater due to their increased sensitivity to low aqueous Zn(II) concentrations.[3] Ever increasing concerns for ecological issues such as the potential toxicity of zinc pollutants drive the need for more effective detection methods and selective and versatile sensors. Noteworthy examples of such compounds have been reported by Lippard and Gunnlaugsson in literature.[4]

Spiropyrans are photochromic compounds that can isomerize in response to UV/vis irradiation as a result of a reversible heterolytic cleavage of the spiro C–O bond followed by *cis*–*trans* isomerization which generates a metastable merocyanine.[5] The presence of a negatively charged phenolic oxygen in the zwitterionic open form produces a moiety that can act as a chelating site for a variety of metal ions.[6] By functionalizing a photochromic compound with a suitable metal-binding site, it is therefore possible to affect light-induced release of the metal ion and thus a regenerable sensing system.[7] The ability of spirochromenes to chelate cations has been known since the 1960s,[8] and spiropyran-based chemosensory systems for alkali and alkaline earth,[9] lanthanides,[10] transition[11] and *non*-transition[12] metals have been reported. Since many existing zinc sensors suffer from irreversibility and high background fluorescence, there is a need for new systems that offer better performance and increased versatility.[13] In this article we report the design, the synthesis and the activity evaluation of a highly selective and photoregenerable spiropyran derivative for the detection of Zn(II) ions that can be switched off using light in order to overcome the problem of a one-time use sensor.

2. Results and discussion

2.1. Design

To achieve the required selectivity towards a specific metal-ion, it is necessary to complement the optical properties of the spiropyran backbone with appropriate functional groups that, collectively, provide a binding site that matches the specific coordination requirements of the targetted ion. Our design brings together elements that can facilitate metal-ion binding and promote photoinduced control of the metal ligation. First, a methoxy group in the 8′ position on the benzopyran moiety has been a common motif in several spirochromenes aimed at metal coordination and this functional group can cooperate with the phenolate anion of the open merocyanine in the chelation of the ion.[14] Second, the indolic nitrogen offers another functionalizable site on the molecule and several examples of *N*-modified spirochromenes for metal chelation applications are known.[15] Considering the interference with other metal ions that often affects zinc sensors,[16] the presence of a functional group with relatively low conformational flexibility

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would be desirable. A methyl pyridinyl group is often present on the chelating moiety of several zinc-selective sensing agents[17] and such a moiety is readily attached to the spirochromene indolic nitrogen by using an appropriate precursor. Thus, in the merocyanine form of the molecule, a phenolate anion and the oxygen atom of the vicinal methoxy group would be in close proximity of the pyridine lone pair thereby producing a potential tris-chelating site appropriate for effective and selective metal binding. Third, it is known that the presence of a strongly electron-withdrawing group in the 6′ position stabilizes the open form whereas an electron-donating group produces a more stable photostationary closed form. Consequently, we decided to also attach a nitro group to the spiropyran in order to obtain a zinc receptor with ionochromic behaviour where the cation release may be photo-controllable. The target molecule, **SP** (Fig. 1) contains three different functional groups positioned in such a way that selective binding may be attained while promoting photo-induced switchability of the resulting metal complex.

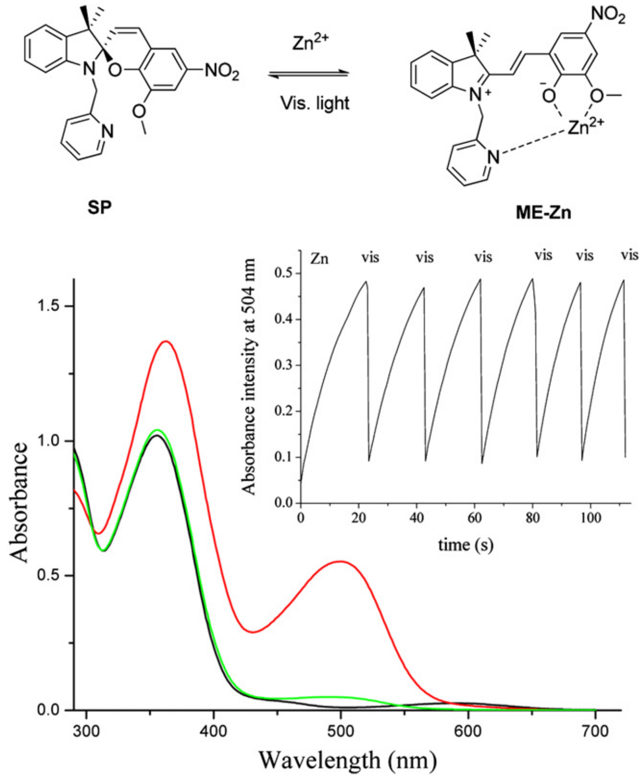
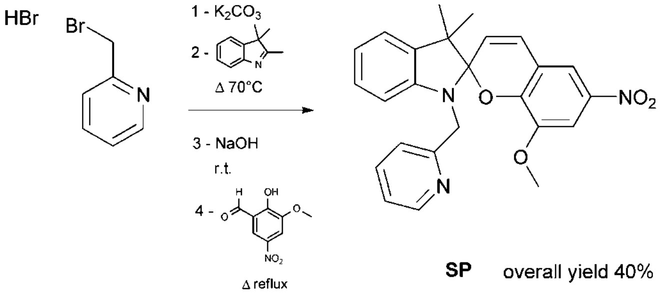


Figure 1. Reversible interconversion between the closed spiropyran **SP** and a hypothetical merocyanine-zinc complex **ME**–**Zn**. Absorption spectra of **SP** (1.0×10^{-4} M, CH_3CN, 293 K) (black line) before, (red line) after the addition of 1 equiv of $Zn(ClO_4)_2$ and (green line) after the subsequent irradiation with visible light for 1 min; (Inset) sequential cycles of conversion between **SP** and **ME**–**Zn** controlled by visible light.

2.2. Synthesis

Compound **SP** was synthesized starting from the alkylation of 2,3,3-trimethyl-3*H*-indole with 2-bromomethyl pyridine freshly prepared from its hydrobromide salt. This step afforded an indolium salt as an intermediate, which was used without any further purification in the following synthetic step. Basification with a strong base afforded a more reactive olefin that was readily condensed with 3-methoxy-5-nitrosalicylaldehyde to obtain the target molecule (Scheme 1). Finally the product was purified via flash chromatography and its partial ^1H NMR spectrum is shown in Figure 8a.



Scheme 1. Synthesis of **SP**.

2.3. Binding studies

In order to establish whether the combination of the three functional groups were, in fact, capable of offering selective metal-ion recognition, systematic binding studies were performed on **SP** with twelve different metal ions, using a spiropyran derivative, which contains a hydrogen atom instead of the methoxy group in position 8′ (Fig. 2(B)) as a reference system.[18]

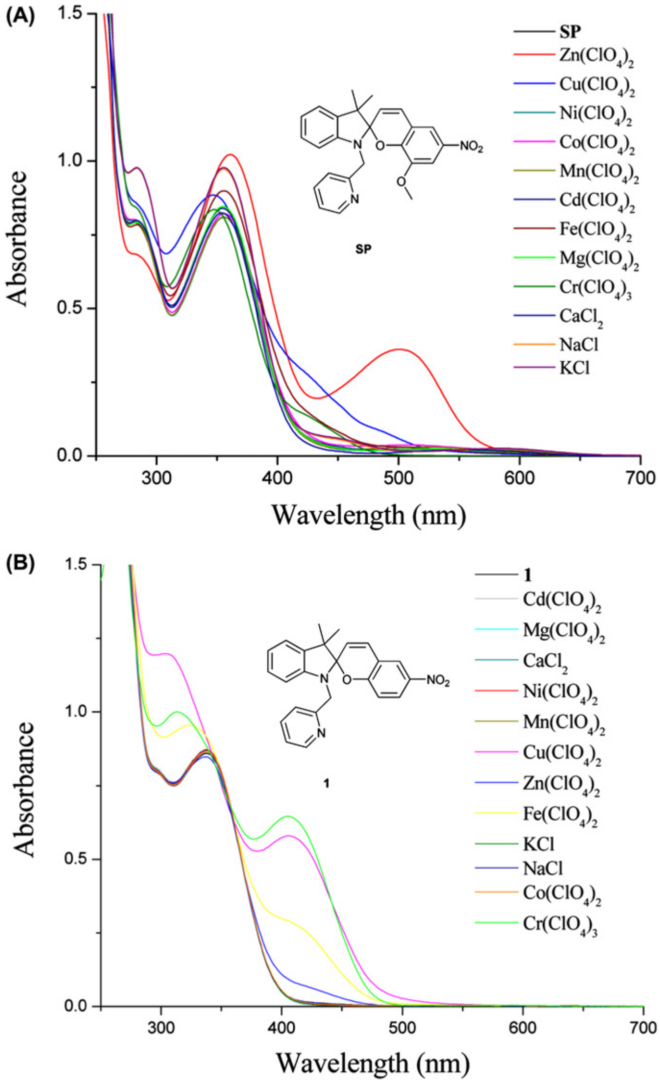


Figure 2. Absorption spectra of spiropyran **SP** (1.0×10^{-4} M, CH_3CN, 293 K) (A) and spiropyran **1** (1.0×10^{-4} M, CH_3CN, 293 K) (B) after 20 min from the addition of 1 equiv of different metal perchlorates and chlorides.

Biologically and environmentally relevant metal ions, such as Zn(II), Cu(II), Ni(II), Co(II), Mn(II), Cd(II), Fe(II), Mg(II), Cr(III), Ca(II), Na and K were tested. The absorption spectra of **SP** were taken before and after the addition of 1 equiv of each metal salt.

The absorption spectrum of a colourless solution of **SP** does not show bands in the visible region of the spectrum (black curve in Fig. 1).

Upon addition of Zn(II) the colourless spiropyran switches to the orange merocyanine metal complex **ME**–**Zn**. The appearance of an absorption band at 504 nm accompanies this process (red curve in Fig. 1). This band disappears when the solution is irradiated with visible light, as **ME**–**Zn** switches back to **SP** (green curve in Fig. 1). Several cycles of irradiation were carried out confirming the reproducibility of the process as shown in the inset of Figure 1. No absorption changes were observed after the addition of other metal cations, such as Ni(II), Co(II), Mn(II), Cd(II), Mg(II), Ca(II), Na, K and only a shoulder appeared around 400–460 nm after the addition of Cu(II), Fe(II) and Cr(III) (Fig. 2(A)). Particularly impressive is the selectivity to Zn(II) over Cd(II) since these cations may compete in the coordination and produce undesirable interference.[19] The same metal solutions were tested on the reference molecule **1**, which differs from **SP** for the presence of a hydrogen instead of the methoxy group in position 8′. As shown in Figure 2(B), **1** responded to the presence of iron (II), chromium (III) and copper (II) with intense bands in the range of 400–450 nm while the presence of zinc produced a negligible response. Additionally all the absorption bands in the presence of these metals are located in the same range making discrimination between the different cations impossible. Thus the choice of a methoxy group as an additional chelating site in **SP** is confirmed. The absorbance intensities at 504 nm of a solution of **SP** before and after the addition of the metal cations tested are reported in Figure 3. The ion selectivity can be quantified in terms of the relative responses based on the absorbance intensities. The ratio of the intensity of absorbance of Zn(II):Cu(II):Co(II):Cd(II):Cr(III) is 100:12:10:6:1.

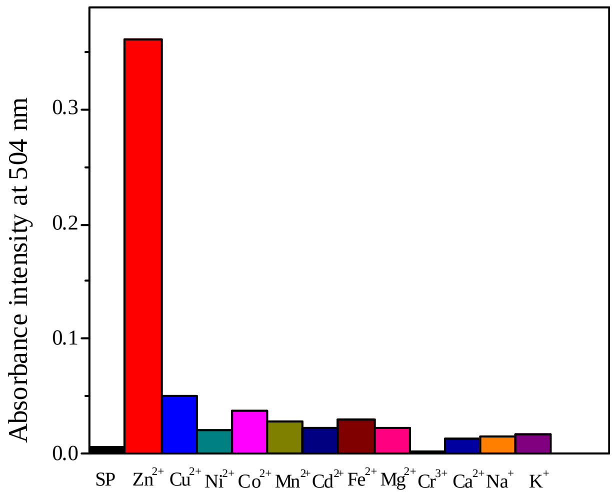


Figure 3. Absorption intensity at 504 nm of solutions of spiropyran **SP** (1.0×10^{-4} M, CH_3CN, 293 K) before and after the addition of 1 equiv of $Zn(ClO_4)_2$, $Cu(ClO_4)_2$, $Ni(ClO_4)_2$, $Co(ClO_4)_2$, $Mn(ClO_4)_2$, $Cd(ClO_4)_2$, $Fe(ClO_4)_2$, $Mg(ClO_4)_2$, $Cr(ClO_4)_3$, $CaCl_2$, NaCl and KCl.

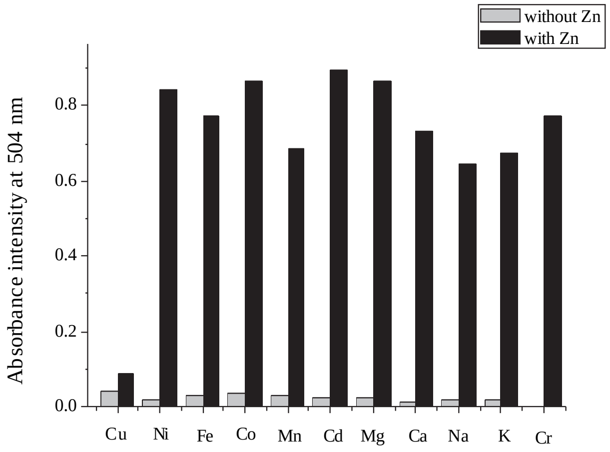


Figure 4. Absorbance intensity responses of **SP** (1×10^{-4} M in acetonitrile) to various metal ion. Grey bars represent the absorption of **SP** at 504 nm in the presence of 1 equiv of a selected metal ion. Black bars represent the absorption of **SP** at 504 nm in the presence of a binary mixture of Zn(II) and a competitive metal ion (1 equiv each).

To further probe the selectivity of **SP** we also examined the response of our sensor when presented with two different metal ions simultaneously. Eleven such experiments were carried out, and the results are displayed in Figure 4. The observed absorption intensities of the binary mixtures at 504 nm, indicative of the presence of a **SP**–**Zn** complex, range between 0.6 and 0.8 a.u. while no absorption is observed at the same wavelength in the absence of zinc. In ten of the eleven competitive experiments, **SP** displays a strong preference for Zn(II) ions, and the only anomalous result was obtained when the **SP** was presented with a solution containing a mixture of Zn(II) and Cu(II). It is not clear, at this point, what the reason is for the solution behaviour of **SP** in the latter case, but we are currently carrying out an in-depth study (involving both solution- and solid-state based techniques) in order to elucidate the exact nature of the binding (stoichiometry, binding strength, possible kinetic factors), which may shed more light on this result. Overall, however, it is clear that the **SP** sensor presented herein, is very effective at distinguishing between Zn(II) and a large number of other, potentially competing metal ions.

The emission spectra of **SP** were taken before and after the addition of 1 equiv of Zn(II), Cu(II), Cr(III) and Fe(II). Only the complex **ME**–**Zn** shows an intense band at 624 nm (Fig. 5), while no emission was observed in all other cases.

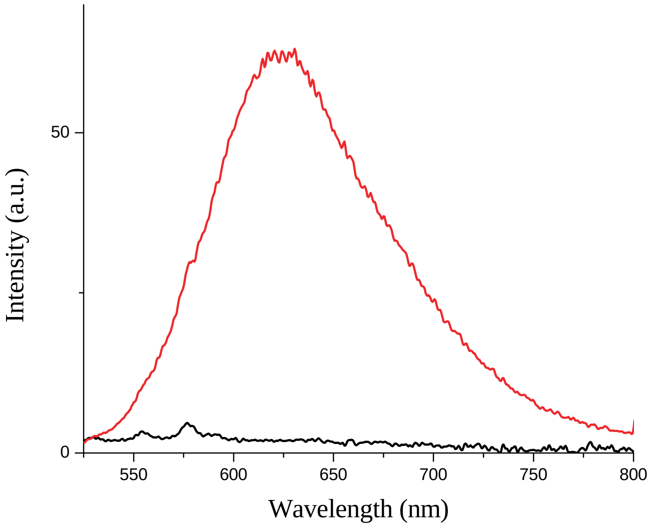


Figure 5. Emission spectra of a solution of (1.0×10^{-5} M, CH_3CN, 293 K, λ_{exc}=492 nm) before (black) and after the addition of 1 equiv of $Zn(ClO_4)_2$ (red).

The dependence of the absorbance on the concentration of metal salt was examined to investigate the composition of the complex **ME**–**Zn**. The absorbance at 504 nm reached a plateau when an equivalent amount of Zn(II) was added to a solution of **SP** (Fig. 6). This suggested a stoichiometry for the zinc–spiropyran complex of 1:1. In order to confirm this result, the composition of the complex

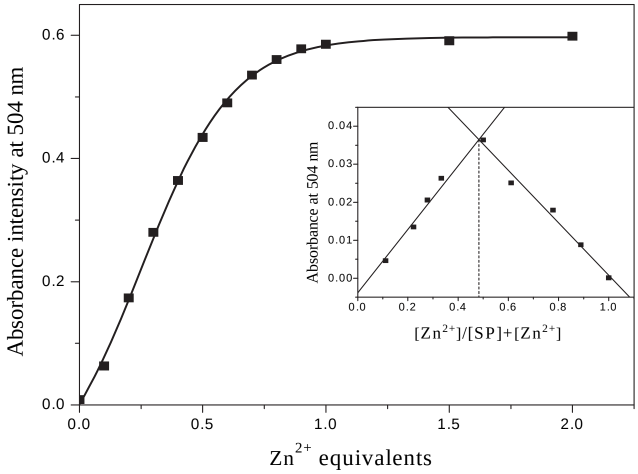


Figure 6. Absorption intensities at 504 nm of a solution of spiropyran **SP** (1.0×10^{-4} M, CH_3CN, 293 K) after increasing the concentration of $Zn(ClO_4)_2$; (Inset) Job's analysis of **ME**–**Zn** complex ($[SP]+[Zn^{2+}]=3.0\times10^{-5}$ M, CH_3CN, 293 K).

was determined spectrophotometrically by means of the isomolar solutions technique (Job's method of continuous variations), which was successfully applied in the analysis of other spirochromene metal complexes.[20] The plot of the absorbance values measured at the absorption maximum of the complex **ME**–**Zn** versus the zinc molar ratio of isomolar solutions is featured in the inset of Figure 6. As shown, the apex is located at a zinc molar ratio of 0.5, which corresponds to a spiropyran–metal stoichiometry of 1:1.

The binding constant K value for the **ME**–**Zn** complex was determined from the absorbance intensities recorded at different zinc concentrations (Fig. 7) following the modified Benesi–Hildebrand equation $1/\Delta A=1\Delta A_{max}+(1/k[C])(1/\Delta A_{max})$.[21]

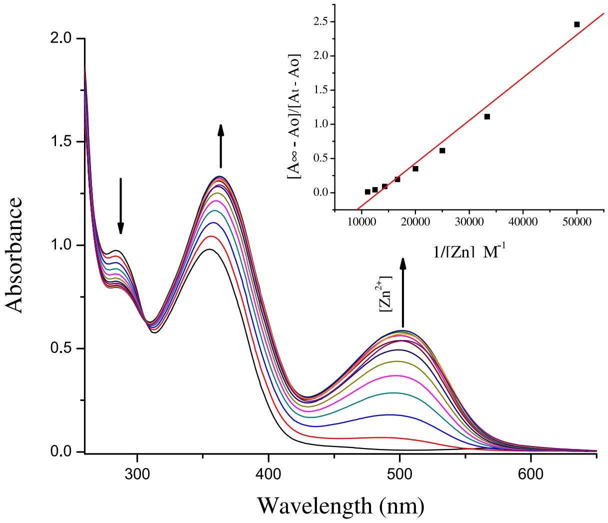


Figure 7. (a) The absorption spectra of a solution of **SP** (1.0×10^{-4} M, CH_3CN, 293 K) after 20 min from the addition of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.5, 2 equiv of ($Zn(ClO_4)_2$); (Inset) Plot of $(A_\infty-A_x)/(A_x-A_0)$ against $1/[C]$, binding constant $k=1.6\times10^4$ M^{-1}.

Here $\Delta A=A_x-A_0$ and $\Delta A_{max}=A_\infty-A_0$ where A_0, A_x and A_∞ are the intensities of the **SP**–**Zn** complex at 504 nm considered in the

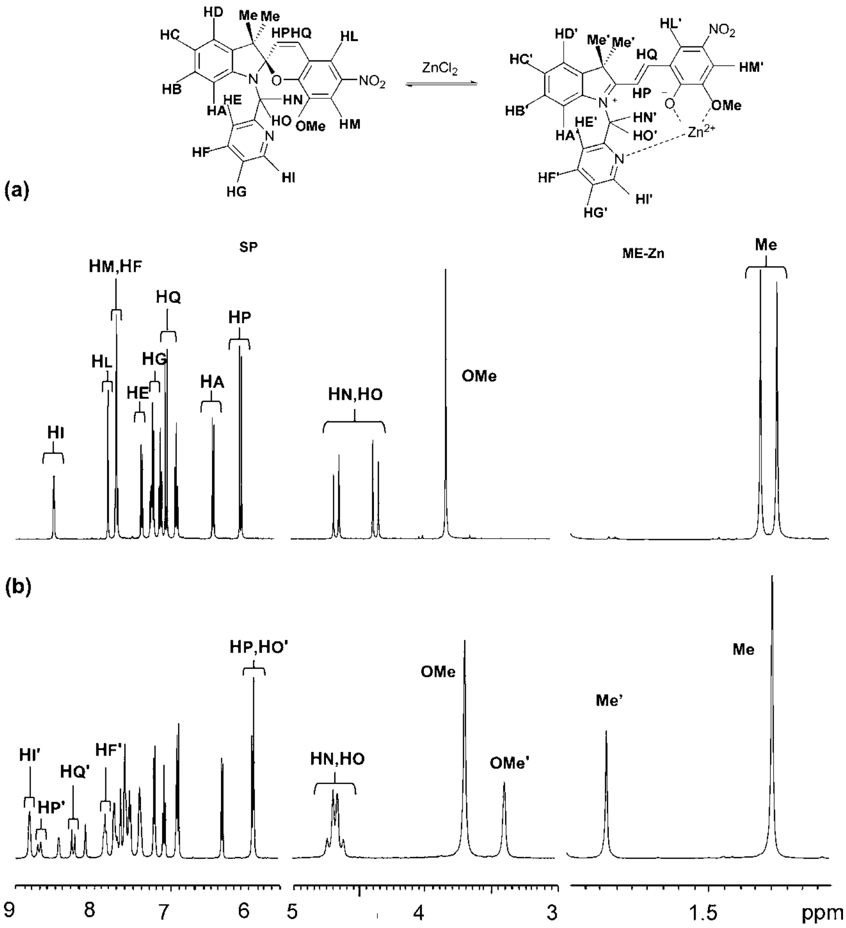


Figure 8. Partial ^1H NMR (400 MHz, 298 K) spectra of **SP** (2×10^{-2} in CD_3CN) (a) before and (b) after the addition of 1 equiv of $ZnCl_2$.

absence of zinc, at a certain concentration of zinc and at a concentration of complete interaction, respectively; k is the binding constant and $[C]$ is the concentration of zinc.

The k value of 1.6×10^4 M^{-1} was extrapolated from the slope of the plot $(A_\infty-A_x)/(A_x-A_0)$ against $1/[C]$ shown in the inset of Figure 7.

^1H NMR studies of the complexation of Zn(II) by **SP** suggested that all three components of the phenoxy–methoxy–pyridine triad participated in metal binding (Fig. 8).

The ^1H NMR spectrum of spiropyran **SP** (Fig. 8a) changed dramatically after the addition of 0.5 equiv of zinc (Fig. 8b). The characteristic signals for the pyridyl protons HF and HI shifted significantly downfield, from 7.67 ppm and 8.48 ppm to 7.91 ppm (HF′) and 8.87 ppm (HI′), respectively due to the opening of the molecule and the formation of the complex. Additionally, the appearance of a new series of peaks in the range of 7.5–7.8 ppm was attributed to the aromatic protons of the **ME**–**Zn** complex (see Table 1a and b). The singlet of the methoxy group in position 8′ at 3.80 ppm (OMe) shifted to 3.68 ppm and a new singlet appeared for the methoxy group of the complex form at 3.54 ppm (OMe′). This new signal is quite broad suggesting coordination with the metal. The typical singlets attributed to the *gem*-methyl groups (Me) in the closed form were located at 1.26 and 1.32 ppm. In the metal complex they are magnetically equivalent due to the *quasi* planar structure of the merocyanine and they appear as a singlet at 1.84 ppm (Me′). The doublet for one of the olefinic protons of *trans*-**ME**–**Zn** can be identified at 8.29 ppm (HQ′). Its large coupling constant (J=16 Hz) confirms the trans configuration of the associated double bond. The ratio between **SP** and the **ME**–**Zn** complex is ca. 73:27 after the addition of 0.5 equiv of $ZnCl_2$ and ca. 60:40 after the addition 1 equiv of $ZnCl_2$ (see Supplementary data).

Table 1
(a) ^1H NMR spectroscopy data (400 MHz, 298 K, CD_3CN) for **SP** and (b) **SP** in mixture with **ME**–**Zn** (1 equiv of Zn)

SP				
Protons	δ (ppm)	No. of protons	Multiplicity	J (Hz)
(a)				
HA	6.40	1	d	7.8
HB	7.09	1	td	7.6 and 1.2
HC	6.88	1	t	7.3
HD	7.21	1	d	7.6
HE	7.33	1	d	8
HF	7.67	1	dd	5.04 and 1.8
HG	7.19	1	m	
HI	8.48	1	d	4.8
HL	7.77	1	d	2.56
HM	7.68	1	d	2.6
HN, HO	4.34 and 4.64	2	d	16.96 and 17
HP	6.03	1	d	10.36
HQ	7.01	1	d	10.36
OMe	3.8	3	s	
CH_3	1.26 and 1.32	6	s	
ME–**Zn**				
(b)				
HA′	7.8–7.5	1	m	
HB′	7.8–7.5	1	m	
HC′	7.8–7.5	1	m	
HD′	7.8–7.5	1	m	
HE′	7.5–7.7	1	m	
HF′	7.91	1	t	7.6
HG′	7.46	1	t	6.08
HI′	8.87	1	d	4.76
HL′	8.16	1	s	
HM′	7.48	1	s	
HN′, HO′	5.88	2 s		
HP′	8.62	1	d	15.4
HQ′	8.29	1	d	16
OMe′	3.54	3	s	
CH_3′	1.84	3	s	

Although the Job's analysis suggests that there is a 1:1 metal ion/spiropyran stoichiometry in solution, it is not possible at this stage to determine if the complex is mono or polynuclear. It is possible that the phenolate/methoxy site acts as a chelate for one metal ion, whereas the pyridine moiety binds to a neighbouring metal ion. Nevertheless, the nature and the orientation of the three binding sites have created a ligand that offers an effective complement to the requirements of Zn(II) ions.

3. Conclusions

In summary, we have developed a highly selective spiropyran-based ion receptor for the naked-eye detection of Zn(II), which is fully reversible upon visible irradiation. The stoichiometry of the zinc complex has been investigated via isomolar solution technique (Job's method) and it has been found to be 1:1. Additionally, fluorescence in the presence of Zn(II) makes such kind of systems promising for the realization of probing devices. Finally, ^1H NMR analysis of the metal complex has shown that all three potential coordinating sites on the spiropyran (methoxy, phenolate and pyridine) are involved in the metal binding of Zn(II). This receptor offers promising versatility as it is robust with respect to a wide range of other metal ions and we are now investigating ways to ensure water solubility.

4. Experimental

4.1. General methods

All chemicals were purchased from Acros Organics or Aldrich and were used as received. Proton Nuclear Magnetic Resonance spectra were recorded in CD_3CN on a Bruker DPX 400 spectrometer. All the solvents were standardised with respect to TMS. Chemical shifts are reported in parts per million and coupling constants in Hertz. Carbon NMR spectra were recorded on the same instrument with total proton decoupling. All melting points were determined with a Stuart SMP3. Flash chromatography was carried out using silica gel, particle size 0.04–0.063 mm. TLC analysis was performed on precoated 60 F_{254} slides, and visualised by either UV irradiation or K_2MnO_4 staining. Infrared spectra were obtained on a Perkin–Elmer Paragon 1000 Fourier Transform spectrometer. Emission measurements were carried out with a Perkin–Elmer LS 55 Fluorimeter. UV/vis absorption measurements were carried out with a Perkin–Elmer Lambda 35 UV/vis Spectrometer.

4.2. Synthesis

*4.2.1. 8-Methoxy-3′,3′-dimethyl-6-nitro-1′-(pyridin-2-ylmethyl)-spiro[chromene-2,2′-indoline] (**SP**).* 2-(Bromomethyl)pyridine hydrobromide (3.9 mmol, 1.00 g) was dissolved in water (4 ml) and cooled in an ice-bath. A solution of 1 M K_2CO_3 was added dropwise to the solution under vigorous stirring until the solution pH was adjusted to 7. The mixture was stirred for 1 h at room temperature and was then extracted with ethyl acetate (20 ml) and dried over Na_2SO_4. After evaporation of the solvent, the red solid obtained (0.46 g) was reacted with 2,3,3-trimethylindolinine (2.1 mmol, 0.43 g) in CH_3CN (15 ml) at 70 °C for 24 h. The solution was cooled to room temperature, the solvent was evaporated under reduced pressure and the viscous residue obtained was stirred in 20 ml of NaOH aq 0.1 M for 2 h at rt. The mixture was then extracted with ethyl acetate (20×2 ml) dried over Na_2SO_4 and the solvent was removed under reduced pressure.

The brown oil obtained (1 equiv) was reacted with 3-methoxy-5-nitrosalicylaldehyde (1 equiv, 1.73 mmol) in 20 ml of ethanol at reflux for 15 h. The solvent was distilled under reduced pressure and the product was purified via flash chromatography using a mixture of hexane/ethyl acetate 8:2 as eluent. The reaction afforded 400 mg of a green powder with an overall yield of 40%. ^{1}H NMR (400 MHz, CD_3CN): δ=1.27 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 4. 34 (d, 1H, J=17.0 Hz, CH_2, Py), 4. 64 (d, 1H, J=17.0 Hz, CH_2, Py), 6.04 (d, 1H, J=10.4 Hz, ethylene), 6.40 (d, 1H, J=7.8 Hz, arom.), 6.87 (t, 1H, J=7.3 Hz, arom.), 7.01 (d, 1H, J=10.4 Hz, ethylene), 7.09 (t, 1H, $J1$=7.6 Hz, arom.), 7.19 (t, 1H, J=6.8 Hz, Py), 7.21 (d, 1H, J=7.6 Hz, arom.), 7.33 (d, 1H, J=8.0 Hz, Py), 7.66 (t, 1H, $J1$=8.0 Hz, Py), 7.75 (d, 1H, J=2.4 Hz, arom.), 7.77 (d, 1H, J=2.4 Hz, arom.), 8.48 (d, 1H, J=4.8 Hz, CHN, Py). ^{13}C NMR (100 MHz, CD_3CN): δ=18.9, 25.6, 49.0, 52.5, 55.9, 106.6, 107.3, 107.4, 115.3, 118.7, 119.8, 121.2, 121.3, 121.9, 122.1, 127.7, 128.7, 136.1, 136.6, 140.6, 146.8, 147.1, 148.7, 149.2, 158.6. HRMS-ES (m/z): Found: 430.1774 ($(M+H)^+$, $C_{25}H_{23}N_3O_4$ requires: 430.1767). ν (cm^{-1}): 1592, 1515, 1477, 1331, 1272, 1088, 910. Mp: 124 °C.

*4.2.2. 3′,3′-Dimethyl-6-nitro-1′-(pyridin-2-ylmethyl)spiro [chromene-2,2′-indoline] (**1**).* Compound **1** was synthesized according to a literature procedure.[13] ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.34 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 4. 46 (d, 1H, J=17.0 Hz, CH_2, Py), 4. 68 (d, 1H, J=17.0 Hz, CH_2, Py), 5.98 (d, 1H, J=10.3 Hz, ethylene), 6.37 (d, 1H, J=7.7 Hz, arom.), 6.81 (d, 1H, J=9.0 Hz, arom.), 6.91 (d, 1H, J=10.3 Hz, ethylene), 6.94 (t, 1H, J=7.6 Hz, arom.), 7.13 (t, 1H, J=7.7 Hz, Py), 7.18 (d, 1H, J=7.2 Hz, arom.), 7.26 (m, 1H, arom.), 7.42 (d, 1H, J=7.6 Hz, Py), 7.59 (t, 1H, J=7.1 Hz, Py), 8.01 (d, 1H, J=2.7 Hz, arom.), 8.06 (dd, 1H, J=8.9 Hz, arom.), 8.59 (d, 1H, J=4.6 Hz, CHN, Py). ^{13}C NMR (100 MHz, $CDCl_3$): δ=20.0, 26.2, 49.0, 52.7, 106.4, 107.7, 115.6, 118.4, 120.4, 121.1, 121.5, 121.9, 122.5, 122.8, 126.0, 127.8, 128.9, 136.0, 138.1, 141.1, 146.5, 148.2, 158.1, 159.2. HRMS-ES (m/z): Found: 400.1675 ($(M+H)^+$, $C_{24}H_{21}N_3O_3$ requires: 400.1661).

4.3. UV/vis absorption and emission studies

In the UV/vis absorption studies, standard solutions of spiropyrans with concentration of 1×10^{-4} M in acetonitrile and standard solutions of metal perchlorates and chlorides in water with concentration of 1×10^{-2} M were used. Quartz cuvettes of 1 cm path length were used. In the experiment of sequential cycles of conversion between **SP** and **ME**–**Zn** controlled by visible light the solutions were irradiated by means of a Schott KL 1500 LCD visible lamp.

In the emission studies a standard solution of **SP** (1.0×10^{-5} M) in spectroscopic grade acetonitrile was prepared and equilibrated overnight at 293 K in the dark. The spiropyran solution (3 ml) was placed into a 1 cm path length cuvette and the emission spectrum was recorded; 1 equiv (3 µl) of standard solution of metal perchlorates (1.0×10^{-2} M) was added and the resulting solution was equilibrated in the dark for 20 min and the emission spectrum was taken.

4.4. ^{1}H NMR studies

Standard solutions of zinc chloride (2 M) were prepared in D_2O. An aliquot of this solution (10 µl) was added to 800 µl of spiropyran solution 2×10^{-2} M. The samples were stored in the dark for 24 h and the spectra were collected.

Acknowledgements

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Supplementary data

^{1}H NMR and ^{13}C NMR spectra of **SP** and **1**, emission titration of **SP**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.07.035. These data include MOL files and InChIKeys of the most important compounds described in this article.

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