

## Metallo- and ionochromic study of spiropyran as a multiresponsive sensor in liquid and solid state

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**Abstract:** Manipulation of the photo, iono and metallochromic properties for chelating activity was performed on the chosen spiropyran. Benzospiryran was synthesised using one-step reaction of substitute dihydroxyl benzaldehyde and Fisher base derivative. This responsive spiro [2H-1-benzopyran-2, 2'-(8'-hydroxy-1', 3', 3'-trimethylindoline)] was able to undergo conversion in solution from colourless to coloured form when reacted with metal and adjustment of pH. In metallochromic activity, all divalent metal ions exhibited a strong absorption peak range from 400 to 460 nm due to the new formation of complex merocyanine-metal (MC-M). These remarkable metallochromic effects were able to detect up to  $1 \times 10^{-1}$  M (detection limit) of each metal ion. For ionochromic activity, acidic environment was preferred for isomerisation to occur. Lastly, spiropyran was also immobilised within the poly(methyl) methacrylate (PMMA) polymer to investigate its functionality in other forms.

**Keywords:** Spiropyran, responsive, metal, liquid, solid.

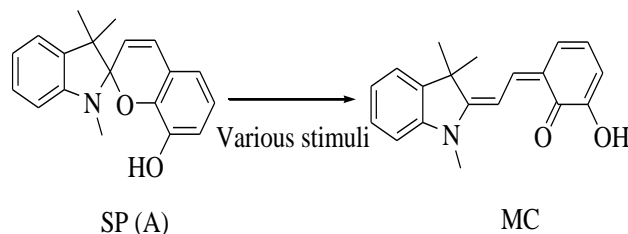
### INTRODUCTION

The emergence of the photochromic compounds back in 18<sup>th</sup> century had encouraged large amount of research towards their development in numerous fields. This eventually becomes one of the promising fields that contribute to great outcomes. One of the well-known classes of organic photochromic compound is spiropyran group. The reversible ability to vary their chemical structure upon exposure to light at appropriate wavelength, and to regain to the original isomer has increased current interest in applying this responsive compound in materials or systems<sup>1</sup>.

The responsive spiropyran has been implemented in various applications including the reversible optical storage<sup>2</sup>, polymer viscosity control<sup>3</sup>, photomechanical transduction and actuation<sup>4</sup>, bioactivity switching of proteins<sup>16</sup>, tissue engineering and drug delivery<sup>5</sup>. Thus, the development of functional polymer that possesses photochromic units has become a cutting-edge technology especially in material sciences.

Despite the great potential of spiropyrans, the repeated cycling and prolonged irradiation have caused the spiropyrans to lose their ability to change colour. This process is usually referred to as photodegradation<sup>6</sup>. Due to the limitation, many simple and efficient multiaddressable switching systems based on metal ion<sup>7</sup> and pH activation have been explored as alternative to the conventional approach. The main interests are to explore the range of optical phenomena, to improve the hindrance during photochromism, and to retard the decolouration process.

Recently, our group has reported the synthesis and activation of novel spiro [2H-1-benzopyran-2, 2'-(8'-hydroxy-1', 3', 3'-trimethylindoline)], abbreviated as **SP-1**<sup>8</sup>. The hydroxyl has been introduced as a group substituent at the 8-position of **SP-1** (Scheme 1). Extending the previous research, this study investigated the ionochromic (pH effect) and metallochromic (metal ion effect) behaviour of **SP-1** in organic solvent. Results showed that the different pH and metal ion binding made a large contribution to the bond cleavage of the **SP-1** ring, accompanied by changes in the absorption spectra<sup>9</sup>. Furthermore, **SP-1** was easily photoisomerised into merocyanine in polymeric system, poly(methyl) methacrylate (PMMA). This solid support is significantly useful in developing cheap and viable colorimetric system for metal detection.



**Scheme 1: Photochromism of SP-1**

## METHODOLOGY

All the chemicals were purchased from Sigma Aldrich, and used without further purification. NMR spectra were recorded on a Bruker Avance MHz instrument (<sup>1</sup>H NMR MHz) in deuterated chloroform, and tetramethylsilane was used as an internal reference. UV-Visible absorption spectra were recorded using UV 2400 PC Series spectroscopy. Photoirradiation was carried out by using UV lamp (245 nm) as the excitation light source. Elemental analyses were determined in a Perkin Elmer 2400 series analyser.

### 2.1 Synthesis of benzospiropyran (SP)

The **SP-1** derivative was synthesised and modified from the reported procedure.

### 2.2 Ionochromic study

A standard solution of **SP-1** (0.1 mM) in ethanol was prepared. The UV/Vis spectra of the solution were recorded upon addition of 2.4  $\mu$ L aliquots of 0.1M HCl or NaOH solution. The effect of the addition of acid, or base on the absorption properties of **SP-1** was studied.

### 2.3 Metallochromic study

Standard solutions of different metals ( $Zn^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Sn^{2+}$ ,  $Al^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ , and  $Cd^{2+}$ ) perchloride were prepared in 5 different concentrations in the range of  $1 \times 10^{-5}$  M to  $1 \times 10^{-2}$  M in ethanol. 1 equivalent (3 mL) of standard solution of metal perchloride was added to the ligand solution (0.1 mM). The absorbance spectra of the resulting solution were measured.

### 2.4 Photochromic study

Irradiation of **SP-1** (10 mM) in the UV region was carried out using a high pressure mercury lamp at 245 nm for 10 min. Absorption spectra of each time interval were measured using UV-Vis spectrometer. In addition, thin film fabrication of **SP-1**-PMMA polymer matrix was prepared following the procedure in [Natali et al. 2010]. The switching between two different states of **SP-1** film was also accomplished by UV light irradiation.

## RESULTS

### 3.1 Ionochromic properties of SP-1

The effects of the three different pH solutions on the **SP-1** were investigated. The **SP-1** isomerisation of spiropyran to MC occurred in acidic condition. The presence of  $H^+$  led to the protonation of SP moieties, and formed the MC species<sup>14</sup>. In acidic condition (pH 1), the strong formation of absorption peak at 490 nm (see Figure 1) corresponded to the open MC form, suggesting the acid-catalysed ring opening of **SP**<sup>13</sup>. Addition of

NaOH resulted in disappearance of the absorption peak at 490 nm. Addition of  $\text{OH}^-$  neutralised the protonated MC species, followed by the isomerisation of MC to the closed  $\text{SP}^{10}$ .

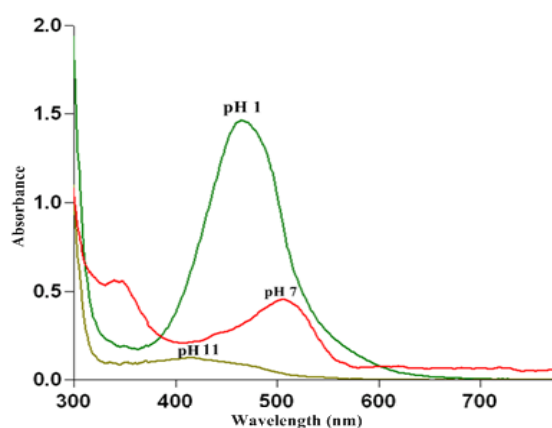


Figure 1. Absorption spectra of SP-1 in different pH solutions.

### 3.2 Metallochromic study

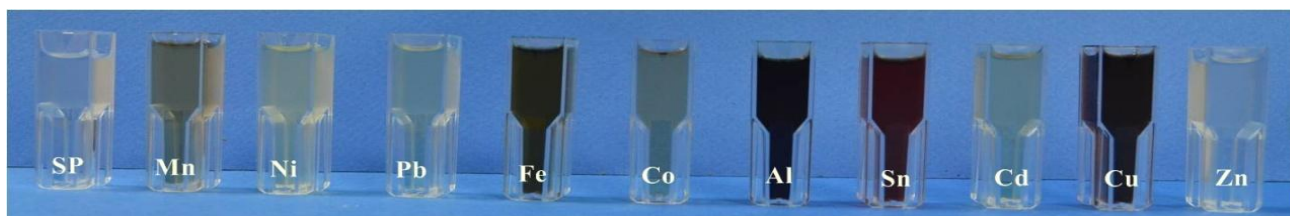


Figure 2. The visual colour changes of different metal ion complexes (MC-M) formed upon

The binding interaction of **SP-1** with ten various metal ions was studied using UV-Vis spectroscopy. **SP-1** solution produced colour changes from colourless to colour upon interaction with different metal ions ( $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Al}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$ ), as presented in Figure 2. The absorption spectrum of each mixture was measured and bathochromic (red) or hypsochromic (blue) shift of the absorbance band (350-550 nm) was observed (see Figure 3).

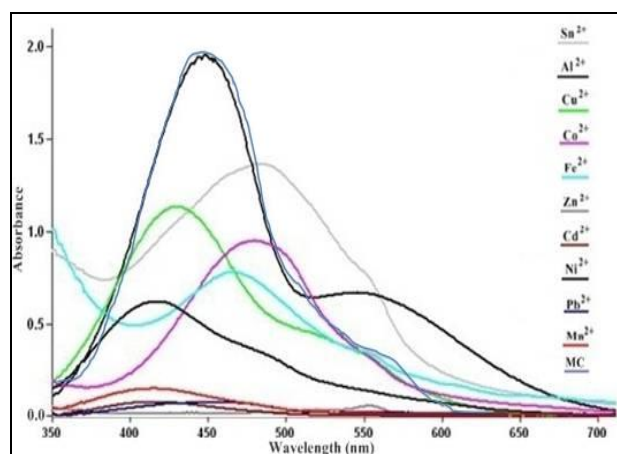
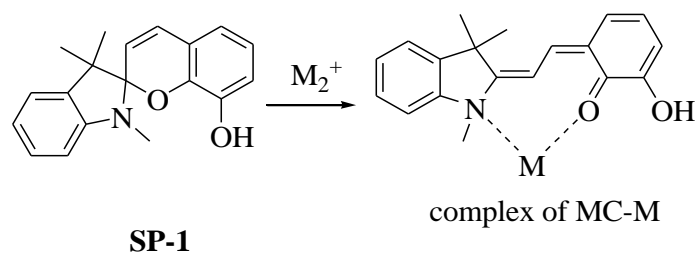


Figure 3. UV-Vis absorbance spectra of SP in the presence of different divalent metal ions namely  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Al}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$  (10 Mm).

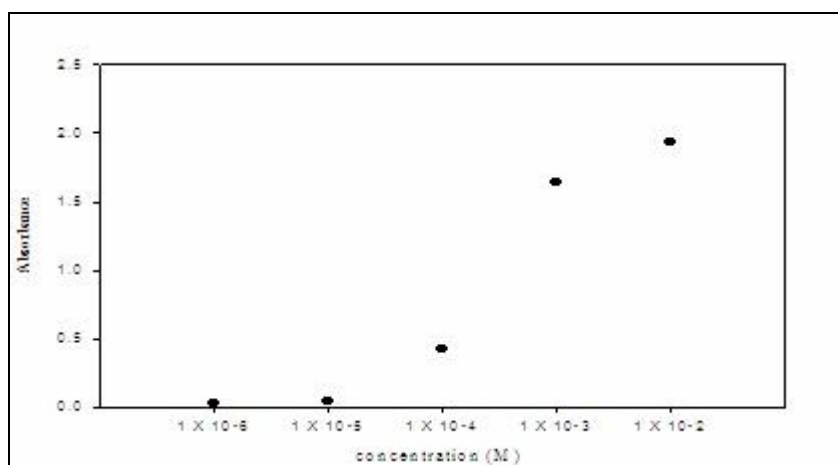
Most of metal ions successfully interacted with **SP-1** form. As an example,  $\text{Al}^{2+}$  caused the most appreciable colour change with the highest absorbance (1.92) at  $\lambda_{\text{max}}$  of 430 nm. Hence, the absorption peak was

due to the formation of MC-Al complex as the MC absorption band also appears at the same  $\lambda_{\text{max}}$  (430 nm). It is envisaged that  $\text{Al}^{2+}$  binds at two different binding sites namely a phenolate anion and an indolic nitrogen possibly involved (see Figure 4). This binding interaction was significant with the previous report<sup>15</sup>. The interaction involved two electron donating moieties that offered sufficient conformational flexibility with both acting as a strong coordinating moiety for binding interaction between **SP-1** and divalent metal ions.



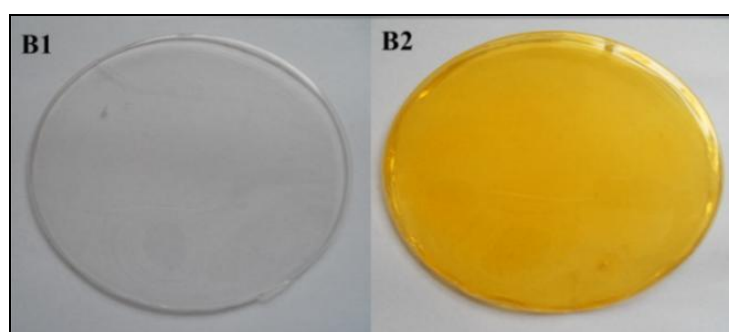
**Figure 4. Schematic diagram of metal-induced conversion of SP after being treated with metal ion, and formation of MC-M complex.**

One of the novel approach using a responsive compound (which acts as smart dye) is that UV irradiation essentially transforms the properties and stability rapidly and noninvasively. As previously discussed, when the **SP-1**-metal was subjected to the UV irradiation, the samples turned to be coloured from colourless. Due to that, extension was made to determine the detection limitation. All samples have been tested and an equal results were obtained. Herein, only Al was presented due to interesting results obtained. As shown in Figure 5, the chemisensor exhibited a good response towards  $\text{Al}^{2+}$  ion with linear working range from 10 to 0.1 mM. It is clear the findings suggest that **SP-1** able to respond to the  $\text{Al}^{2+}$  with the lowest detection limit until  $1 \times 10^{-5}$  M.

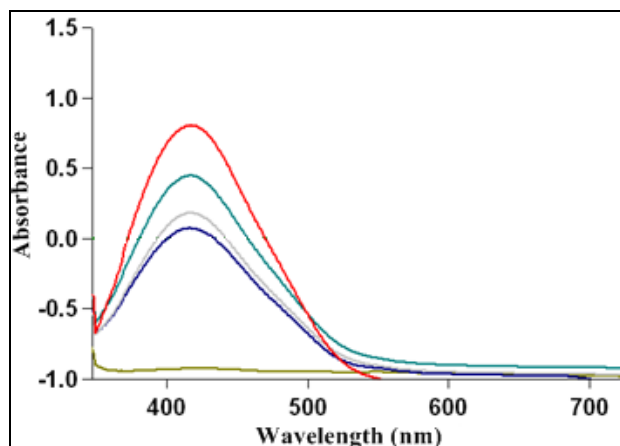


**Figure 5. Absorbance changes of SP-1 in the presence of different concentrations of  $\text{Al}^{2+}$  at 430 nm.**

### 3.4 Photochromic study



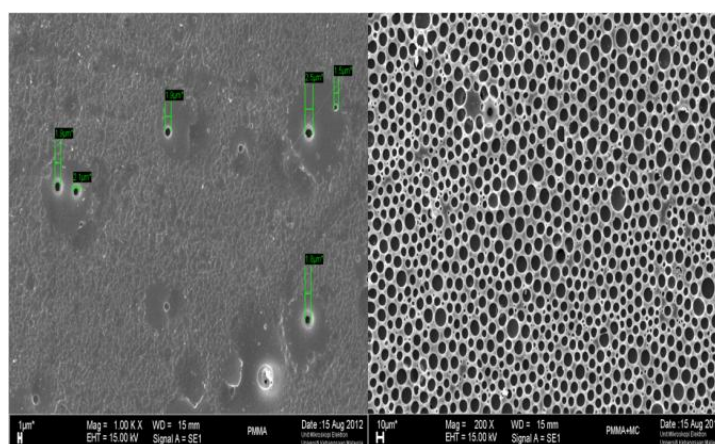
**Figure 6. Colour changes of SP film before (B1) and after 120 min (B2) UV light exposure.**



**Figure 7.** UV absorption spectra of immobilised SP-1-PMMA polymer matrix.

The effect of UV light on **SP-1** in both liquid and solid state was measured. The **SP-1** solution, **SP-1** was converted to MC after 10 min. On the other hand, the colouration on **SP-1** film (see Figure 6) was only observed after 120 min. This change was attributed to the polymer functionalised with spiropyran through an amide and carboxyl group<sup>11</sup>. The spectral absorbance at 430 nm was also in accordance to the solution work (see Figure 7).

Morphological differences between SP embedded within PMMA matrix before and after UV exposure were investigated. The SEM images (see Figure 8) showed the film produced uniform honeycomb-like pores after 120 min of UV irradiation exposure, with average pores diameter between 14.0 and 2.6  $\mu\text{m}$ . Upon irradiation, destabilisation of **SP-1** occurred. Consequently the molecules absorbed/adsorbed into and onto the PMMA networks. The association between **SP-1** and **PMMA** showed physical alteration, hence producing honeycomb-like pores<sup>12</sup>.



**Figure 8.** The SEM micrograph shows honeycomb-like pores of SP-1-PMMA film before (left) and after (right) irradiation.

## Conclusion

The overall analysis in the present study demonstrated that the on-switching response of SP synthesised can be elicited with alternating responses such as pH and metal ions. The SP was able to demonstrate the photochromism by successfully undergoing conversion to merocyanine (MC) form. The structural differences between two states were confirmed through UV analysis. The ionochromic behaviour of SP was able to be induced in the acidic environment that assisted the ring opening reaction. The metallochromic behaviour of SP demonstrated that the ion complexation and spectral changes occurred when divalent metal ion was added into the SP solution. The photochrome was highly sensitive as it was able to detect as low as  $1 \times 10^{-5}$  M of metal ion

concentration. Another concept of immobilisation organic indicator SP was introduced as it was able to be encapsulated in polymer matrix (PMMA). Interesting morphology was successfully observed where honeycomb-like film was produced after exposure under UV light.

## Acknowledgement

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