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PREPARATION AND ACTIVATION OF SPIROPYRAN-MEROCYANINE SYSTEM

(Penyediaan dan Pengaktifan bagi Sistem Spiropiran-Merosianin)

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Abstract

A benzospiropyran derivative has been prepared by the condensation of the precursor, methylene indoline derivative with 2,3-dihydroxylbenzaldehye in 1:1 mole ratio. The product, spiro [2H-1-benzopyran-2, 2’-(8’-hydroxy-1’, 3’, 3’-trimethylindoline)] was able to undergo molecular rearrangement when exposed to UV light, producing an open form merocyanine. Both opened (MC) and closed form (SP) of benzospiropyran were characterized and distinguished by NMR spectroscopy, ATR Infrared and UV-vis absorption. In addition, complexation of metal ions with benzospiropyran in ethanol solution gives rise to colour changes that are visible to the naked eye. Hence, hypsochromic shift in the absorption bands were observed due to the metal ion binding (MC-M).

Keywords: benzospiropyran, photochromic, merocyanine and hypsochromic shift

Abstrak

Terbitan baru benzospiropiran telah berjaya disediakan melalui kondensasi bahan-bahan pemula metilena indolin dan kumpulan aldehid dengan nisbah 1:1. Penghasilan produk, spiro[2H-1-benzopiran-2,2’-(8’-hidroksi-1’,3’,3’-trimetilindolin)] mampu mengalami perubahan kedudukan molekul apabila diradisi oleh cahaya UV dengan menghasilkan komponen terbuka iaitu merosianin.Pencirian benzospiropiran dalam keadaan tertutup (SP) dan terbuka (MC) dijalankan melalui spekstroskopi NMR, ATR IR dan spektroskopi cahaya ampai (UV). Tambahan pula, pengkompleksanion logam dan benzospiropiran dalam larutan etanol dapat menghasilkan perubahan warna yang dapat dilihat dengan mata kasar. Oleh yang sedemikian, anjakan hipsokromik dalam jalur serapan juga dapat dilihat disebabkan tindak balas bersama ion logam (MC-M).

Kata kunci: benzospiropiran, fotokromik, merosianin dan anjakan hipsokromik

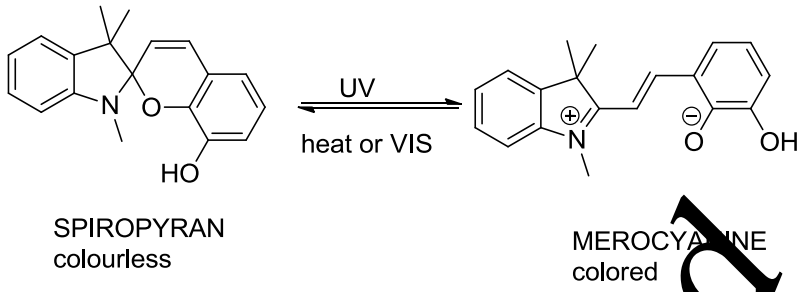
Introduction

Stimuli-responsive polymer is reported to be as the most studied field since decades ago. It has a tremendous demand in sensory [1] as well as biomedical field [2]. This ‘smart’ polymer is able to elicit responsive behaviour on changes in the environment [3]. Light is one of the stimuli that are capable in performing those conformational and chemical changes in particular system [4].

Light-responding polymer present a fine molecular switch as it is known to be non-destructive, non-contact mode [5], with controlled wavelength, intensity, illuminated specific area and direction [6]. All of these have been observed in nature and the same concept was applied for molecular design of synthetic photoresponsive system [7].

There are few photoreaction compounds that are extensively being investigated in photochromic system such as azobenzene [8], spiropyran [9], fulgides [10], triphenylmethane [11] and their derivatives. Among the structurally diverse photochromic compounds, spiropyrans and spiroozanines have attracted much interest due to their potential application for optical devices and sensors [12].

Spiropyrans (SP) is one of the well-known groups of light-responsive compound, which their properties have been studied extensively. They are able to undergo photo-transformation from closed spiropyran to open- zwitterions merocyanine (MC) when exposed to the UV- light as shown in Scheme 1. The current concept of applying the SP as molecular switch is based on the overall consistency of reversibility [13], rapid response time [14] and reasonably stable [15]. The adherence to those properties therefore leads to a potential molecular devices, sensors and fluorescent switches. However, many suffer from the above characteristics that hinder their wider application [16].



Scheme 1. Photochromism of typical spiropyran

Identification of the above problems has led to the search of new spiropyran derivatives to improve light fatigue resistance for sensory devices system. Hence, this study reports the synthesis and activation in photochromic system by employing metal ions to overcome the problem of stability and selectivity issues. Finally, their photochromic behavior will be investigated with the aid of absorption spectral measurements

Experimental

All the chemicals were purchased from Sigma Aldrich and were used without further purification.NMR spectra were recorded on a Bruker Avance MHz instrument (^{1}H NMR MHz) in deuterated chloroform and tetramethylsilane was used as an internal reference. The observation of functional group for spiropyran was recorded by FT-IR/FT-NIR spectrometer (Perkin Elmer, UK) in nitrogen gas purged environment using the attenuated total reflection (ATR) method for sample preparation technique in the range of 400-4000 cm^{-1}. Purification was performed using flash column chromatography on gradle silica gel (Merck, 70-230 mesh). Thin layer chromatography (Merck DC Kieselgel 60 F_{254} plates) was used for detection of all compounds using appropriate solvent system.

Synthesis of benzospiropyran (SP)

Spiro [2H-1-benzopyran-2, 2’(8’-hydroxy-1’, 3’, 3’-trimethylindoline)] abbreviated as (SP). SP was prepared by following the procedure of [17]. 2,3-dihydroxybenzaldehyde (0.7g, 5mmol) and 1,3,3-trimethyl-2-methyleneindoline (0.87g, 5mmol) were mixed together and dissolved into 50ml anhydrous ethanol. The mixture was refluxed for 5 hours and checked by TLC for confirmation of final product. The resulting solution was filtered by vacuum filter and crude compound was obtained after purification using flash column chromatography with petroleum – ethyl acetate (4:1) as eluent. Final product (SP) was afforded in purple powder with 70% yield.

^{1}H NMR ($CDCl_3$) : δ 7.19 (t, J_1= 6.6 Hz, J_2= 6.6 Hz, 1H), 7.08 (d, J=6.6 Hz, 1H), 6.8 (d, J= 10.2 Hz, 2H), 6.87 (d, J=6.6 Hz, 1H), 6.75 (t, J_1= 7.2 Hz, J_2=7.8 Hz, 1H), 6.64 (d, =6.0 Hz, 1H), 6.54 (d, J=7.8Hz, 1H), 5.69 (d, J=10.2 Hz, 1H), 5.59 (s, 1H), 2.76 (s, 3H), 1.31 (s, 3H), 1.19 (s, 3H). IR (ATR, cm^{-1}): 3571, 3206, 1605, 1463, 1246, 1075, 933.

Photochromic Study

The spectroscopic measurements were performed with a UV/Vis absorption spectrophotometer. The spiropyran was dissolved in dichloromethane (10μM) and irradiated by high-pressure mercury lamp for 10 minutes. UV-vis spectra were recorded with subsequent times until no change in the maximum absorption of irradiated SP was recorded.

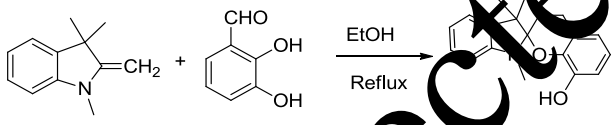
Metal-induced activation of spiropyran

In metal ion activation, standard solution of Zn(II), Cu(II), Co(II), Sn(II) and Fe(II) were prepared in five different concentration (1 x 10^{-2} M, 1 x 10^{-3}M, 1 x 10^{-4}M, 1 x 10^{-5} M and 1 x 10^{-6} M) and dissolved in ethanol and stored in the dark room temperature. The standard solution of SP was prepared in ethanol with fixed concentration of 1 x 10^{-4}M. Solution studies were followed by adding 300µl prepared metal chlorides into 6ml of standard solution of SP. The mixture was placed into a 1cm path length cuvette and the absorption spectra of SP activated in each metals ion were taken.

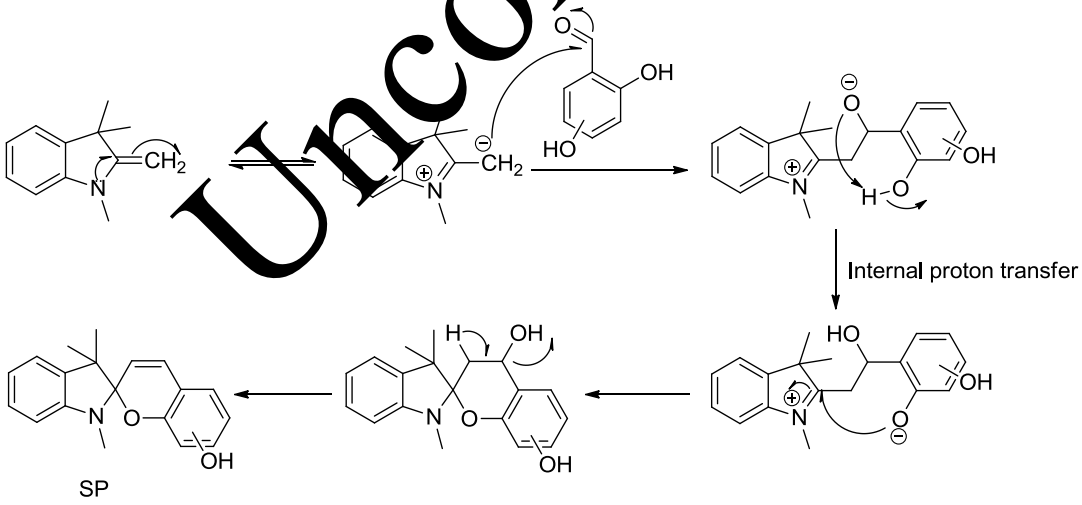
Results and Discussion

Synthesis of benzospiropyran (SP)

Preparation of common benzospiropyran usually dealt with bromination reaction [18] in two consecutive steps. However, the SP prepared in this study is synthesized from the condensation of precursor fisher base and 2, 3-dihydroxylbenzaldehyde in 1:1 mole ratio in one pot reaction (Scheme 2). The reaction mechanism took place when the fisher base formed a carbanion through the mesomeric effect [19]. Thus, the nucleophilic species of fisher base attack to the carbonyl group on the 2,3-dihydroxylbenzaldehyde. This allowed the internal proton transfer of hydroxyl group in the ring [20]. Ring closure was followed through intramolecular addition of the phenolic oxygen to the ammonium group which was formed in the spiro-compound with an elimination of water (Scheme 3).



Scheme 2. Synthesis of spiropyran



Scheme 3. Proposed mechanism of SP compound

Spectroscopic studies of benzospiropyran

The chemical structure of both SP and MC were successfully elucidated with the aid of ^{1}H-NMR and IR spectroscopies. Infrared spectroscopy was employed to confirm the structural changes of before and after the irradiation took place of spiropyran compound. The ring opening process of SP is believed to take place after the irradiation which will result in breaking down of C-O bond and appearing of C=O bond in the merocyanine state

[21]. The IR spectrum from 4000 cm^{-1} to 650 cm^{-1} for both SP and MC are presented in Figure 1 and the overall bands observed were simplified in Table 1. The spectrum of SP shows bands around 3296.88 cm^{-1}which assigned to an OH frequency of intramolecular H-band in the salicyldehydes [22]. Approximate stretching ranging from 3100 to 2800 cm^{-1} correspond to the C-H stretching vibration and the C-O-C stretching vibration is assigned at 1246 cm^{-1} and 1075 cm^{-1} respectively [23]. Furthermore, the C-O_{spiro} stretching frequencies were noticed at 990 cm^{-1} - 934 cm^{-1} that signifies the indolinobenzospiropyrans compounds [24]. In despite, the C-O_{spiro} vibration were not visible and strong band exhibited at 1722.85 cm^{-1} associated to the C=O bond that only appears in merocyanine state. These indicate a significant difference in both open and closed state.

Table 2 summarized the ^{1}H NMR of the SP before and after isomerization to the (coloured) MC form. The SP shows signals of the two geminal methyl groups at 1.19 ppm and 1.3 ppm and *N*-methyl peak at 2.97 ppm due to the ring-closed form consisting of orthogonal nature of both indoline and benzopyran halves [25]. Olefinic protons appear at 5.77 and 6.9 ppm for H_3 and H_4, respectively with large coupling constants J=10 Hz indicates for the *cis* configuration. The J value within 7-10Hz is described for *cis* double bond [26]. In contrast, after SP was irradiated under UV light, the corresponding peaks of germinal methyl groups had shifted downfield because of the effect of the positively charged N in the opened form [25]. This effect is attributed to the cleavage C-O bond and observed mainly at the peaks of NCH_3 which newly appeared at 3.41 ppm. Moreover, the conversion to the new species MC also collapsing the *gem*-dimethyl group signals into single peak at 2.08ppm [25]. However, the rest of C-H aromatic peak assignment of merocyanine form was rather complex hence it has not been assigned.

Table 1. Infrared spectral data of both spiropyran and merocyanine

Sample	Frequency (cm^{-1})				
	OH	C=C	C-O-C	C=O	Cspiro-O
Spiropyran	3206	1605 and 1463	1246 and 1075	-	933
Merocyanine	-	1491	-	1708	-

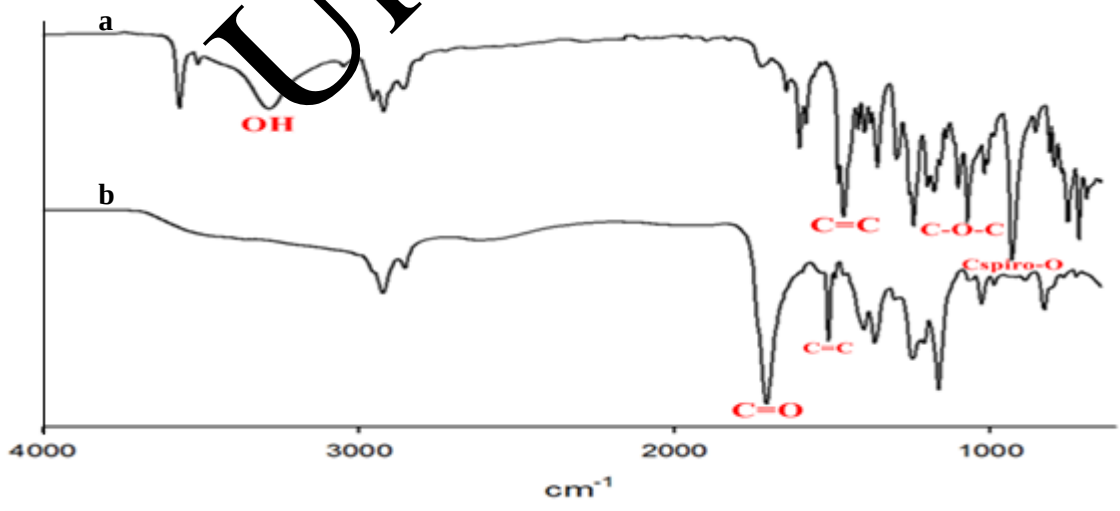


Figure 1. Infrared spectra of (a) spiropyran form (b) merocyanine form

Table 2. Significant ^{1}H NMR spectral data for both SP and MC

Sample	Assignment (ppm)			
	H-C aromatic$^{(m)}$	$CH_3^{(s)}$	N-$CH_3^{(s)}$	C-OH$^{(s)}$
Spiropyran	5.69 – 7.19	1.31 and 1.19	2.76	N.D
Merocyanine	8.3	2.0812	3.417	N.D

s, singlet; m, multiplet; and N.D., Not Detected

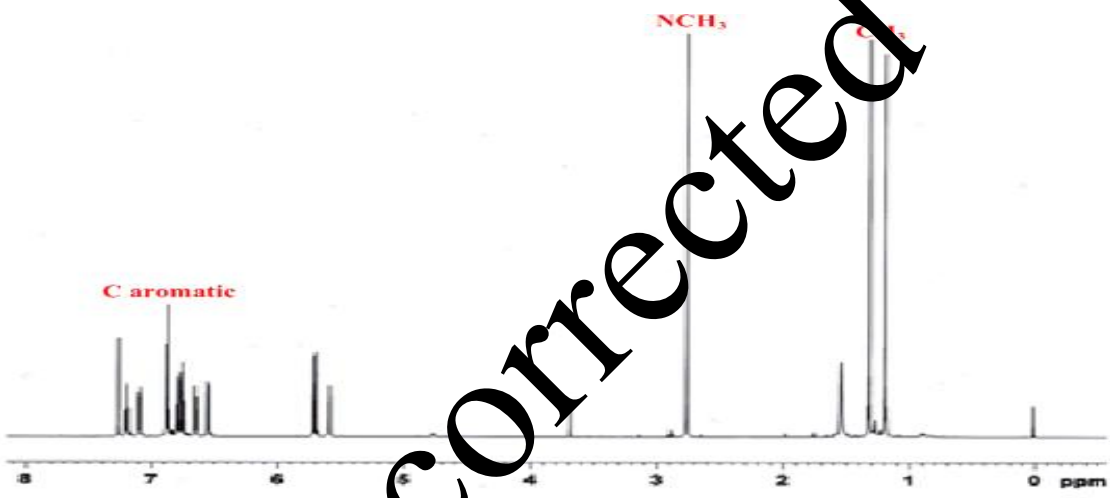


Figure 2. ^{1}H NMR spectrum of spiropyran in $CDCl_3$

Photochromic study

SP prepared which appeared to be colourless after dissolution in dichloromethane was able to exhibit a strong "positive photochromism" and lead to the formation of colored merocyanine. This correspond to the irradiation of spiropyran under UV light for a certain time and triggered the isomerisation to merocyanine form via the photochemical cleavage of the C-O bond [9]. At times zero, there was almost no absorption appears at >430nm, indicating the compound to be at closed form. By contrast, the increase time of UV exposure manifest a build-up of prominent band in the absorption spectrum peaking at 430nm due to hyperchromic effect (Figure 3). Hence, this proved that the conversion of SP → MC in aqueous media can be accelerated in longer time [27].

Metal-induced activation of spiropyran

Upon the addition of various metal cations: Zn^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+} and Sn^{2+}, the colourless spiropyran solution switched to coloured merocyanine metal complex.This binding interaction is in agreement with the previous report [26], that the new absorption peaks observed in the visible region in the presence of metal cations are due to the formation of spiropyran-metal complexes where two different binding sites, a hydroxyl group (position 8') and phenolate anion may be involved (Figure 4). The shifts of the absorption bands were observed in the visible region due to the formation of metal complexes (Figure 5). There is less variation in the response between different ions although the position of the absorption maxima depends on the nature of the metal ions [28]. For example, MC-Cu

complex obtained absorption maxima at 490nm, with MC-Co at 470nm and with MC-Fe at 480nm. These absorption bands are hypsochromically shifted with respect to the free merocyanine absorption. However, there were no difference between MC-Sn complexes and MC absorption maxima occurred only increase by intensity, suggesting the same kinetic energy in both cases.

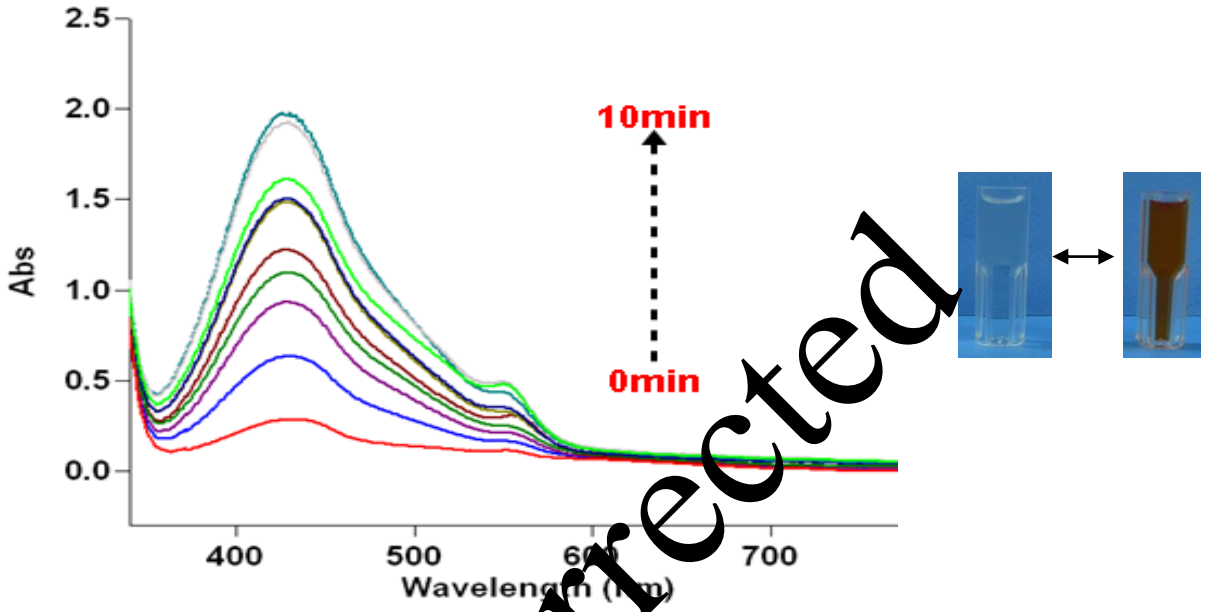


Figure 3. Absorption spectrum of spiropyran after irradiation leads to an increase in absorption at 430nm

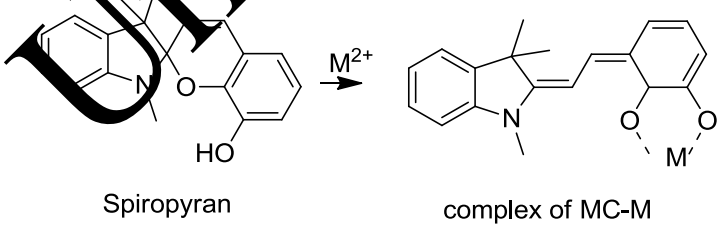


Figure 4. Metal-induced conversion of SP to MC

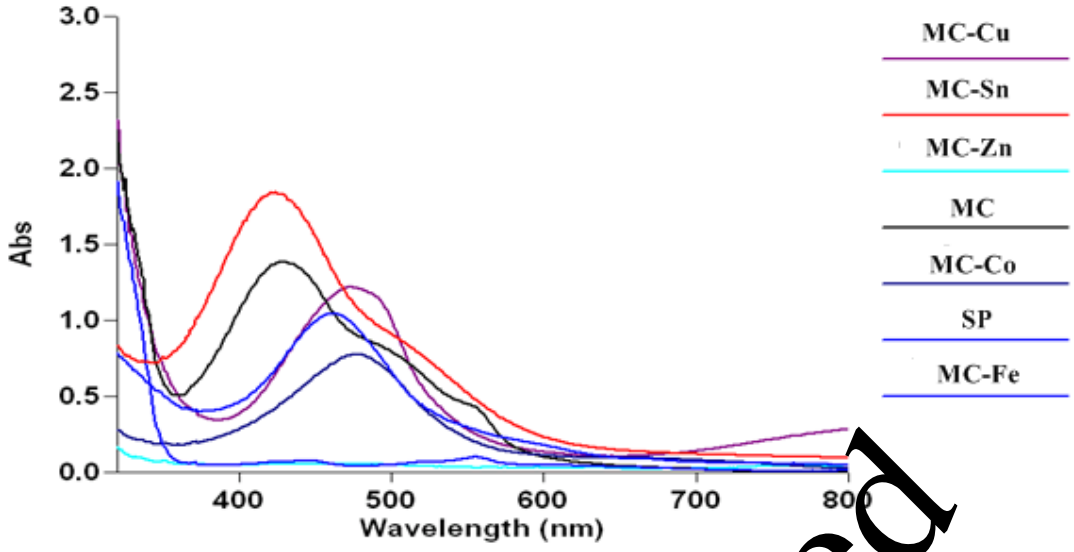


Figure 5. UV-vis absorbance spectra of SP in the presence of different divalent metal ions: Cu, Sn, Fe, Zn, and Co.

Conclusion

New photochromic spiropyrans containing a hydroxyl group were able to undergo cleavage of the weak spiro carbon-oxygen bond and formed a coloured photomerocyanine structure. The interaction between divalent ions Cu^{2+}, Fe^{2+}, Zn^{2+}, Co^{2+} and Sn^{2+} also showed strong spectral and visual changes in all five divalent metal ions. Thus, study proved on the presence of external stimuli such as metal ions can also act as an important factor in heterolytic bond cleavage and ring opening of SP compound. The spectra of all forms are able to exhibit a strong absorption and stabilization with coordination to the metal ions. Lastly, this ionochromic compound is necessary for the basic design of simple and cost-effective chemisensor.

Acknowledgement

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