

Full Research Paper

Thermally Stable Merocyanine Form of Photochromic Spiropyran with Aluminum Ion as a Reversible Photo-driven Sensor in Aqueous Solution

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Abstract: A reversible photo-driven sensor for aluminum ions based on photochromic spiropyran was reported with rapid response time. The detection of aluminum was performed via the chelation of aluminum ions with the merocyanine form (MC) of photochromic spiropyran. ^1H NMR studies confirmed the conversion from the MC form into the Al^{3+} -MC form. Addition of aluminum ions to the spiropyran (SP) in a MeCN/ H_2O mixture results in obvious color changes with a loss in absorbance at 539 nm and an enhancement in absorbance at about 420 nm after irradiation at 365 nm. The metal chelation complex (Al^{3+} -MC) can also be converted into the original SP form by irradiation with visible light. Aluminum ions can be detected down to 0.5 μM levels in a fast response of less than 5 seconds with no interference from other ionic species.

Keywords: photo-driven, photochromic spiropyran, sensor, aluminum ion.

1. Introduction

Aluminum is the third most abundant element and widely used for industrial and domestic purposes. However, the toxicity of aluminum towards fish, algae, and plant roots in acidic media is well documented [1]. Toxic concentrations of Al are supposed to have ethological significance in primary

degenerative dementia (Alzheimer's disease or senile dementia), in dialysis dementia, and in dialysis-related osteomalacia [2, 3].

A number of methods such as spectrometry (including graphite furnace atomic absorption spectrometry and inductively coupled plasma-atomic emission spectrometry) [4-6], chromatography [7-9], electrochemistry [10-12], spectrophotometry [13-15] and flow-injection [16-18] have been used to determine aluminum ions.

Though these methods provide accurate results they are not very convenient for the analysis of large numbers of environmental samples as they require sample pretreatment and sufficient infrastructure back-up. On the other hand, analytical procedures involving ion sensors are most appropriate for such determinations as they require no or minimum sample pretreatment and are fast, convenient and observable by the naked eye. However, these sensors suffer from the disadvantages of poor selectivity and significant interference from some cations (e.g. Hg^{2+} , Cu^{2+} , Ga^{3+} , In^{3+} , Pb^{2+} , Mg^{2+} , Fe^{2+} and Fe^{3+}), and also a very slow response time. A selective, sensitive and fast responding aluminum sensor with a long life time is required.

It is well-known that an important characteristic of a good sensor is that it performs reversibly, and the literature shows that a few sensors (e.g. Zn^{2+} , Hg^{2+} and Cu^{2+}) have been reported with good reversibility by addition of external metal ion chelators [19-21], then exhibit decreased stability and reproducibility after several reversible cycles. The development of optical methods to detect and monitor clinically and environmentally important species, such as metal ions, is an important area of contemporary sensor research [22, 23]. Therefore we proposed that an aluminum ion selective sensor can be reversibly photo-driven without any external influences.

Spiropyran molecules, one of promising families of photochromic compounds, can undergo reversible structural transformation in response to external inputs such as light, protons, and metal ions [24-29]. The spirocyanine converts from closed form to open form (merocyanine) after ultraviolet light irradiation. The merocyanine form is thermally unstable and turns back to closed form in several minutes, however; the former displays a high tendency to coordinate with metal ions, and forms a thermally stable chelation complexes with metal ions, which lead to changes in the fluorescence or absorbance wavelength on metal ion binding. Several groups have reported that suitably substituted spiropyran could be used to bind metal ions in the open merocyanine form [30-35]. Based on the reversible changes of the fluorescence or absorption spectra of spiropyran responding to different external stimulations, the development of devices, such as sensors dependent on different wavelengths of light, would be inherently easier, and offer distinct advantages over those that employ other signaling mechanisms in terms of sensitivity and selectivity. As a result, photoreversibility of the photochromic spirocyanine would be required to apply this strategy to metal ion sensors [36-37].

Towards this objective, we describe herein the extension of this spirocyanine-based system to the design and synthesis of a photoreversible spirocyanine "real-time" aluminum ion sensor with considerably great sensitivity (in the micromole range) and good selectivity.

2. Experimental Section

2.1. Reagents

3,3-Dimethyl-1-(2'-methylenepyridine)-5'-nitrospiropyrans were synthesized based on the established method [38] via the reaction of indoline derivatives and 5-nitrosalicylaldehyde.

Acetonitrile was of HPLC grade, and water was doubly distilled in quartz apparatus. The other commercially available chemicals used were of analytical grade. A standard aluminum ion solution was prepared using 0.002 mol/L of aluminum sulfate solution unless noted otherwise and stored in the dark. All metal ion solutions used in interference testing were prepared by dilution from their aqueous solutions of acetate or chloride salts to a concentration of 1.0×10^{-5} mol/L, and all anionic solutions used in interference testing were prepared by dilution from their aqueous solutions of sodium salts to a concentration of 1.0×10^{-5} mol/L.

2.2. Instrumentation

^1H NMR spectra were measured on a Bruker AM 400 spectrometer. UV/Vis spectra were done on a Varian Cary 500 spectrophotometer with 1 cm quartz cell at 25°C. The photo-irradiation was carried on a CHF-XM 500 W high-pressure mercury lamp with suitable filters (365 nm, half width 30 nm, FAL type made in Germany) in a sealed 1 cm quartz cell. The distance between the lamp and the sample cell is 10 cm. Cyclic voltammetry measurements were performed using a platinum disk working electrode, a platinum wire counter electrode, an Ag/AgCl (in a saturated KCl solution) reference electrode and tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte.

2.3. Photochromic experiments

The spectroscopic measurements were performed with a UV/Vis absorption spectrophotometer. The ultraviolet source of irradiation was a high-pressure mercury lamp obtained with a maximum at 365 nm. First, the spiropyran solution was irradiated with the Hg lamp for 10 min, the absorption spectra were recorded until the maximum absorbance decreased to that of the nonirradiated SP, and the variation of maximum absorbance was plotted against time. Then the SP was irradiated for subsequent times until no change in the photochromic properties of the SP was recorded. Again the plots of maximum absorbance with time were reported. The spectral region for the examined photochromic spiropyran was between 200 and 700 nm in order to follow the photo transformations between spiropyran and merocyanine.

3. Results and Discussion

3.1. Photochromic characteristics

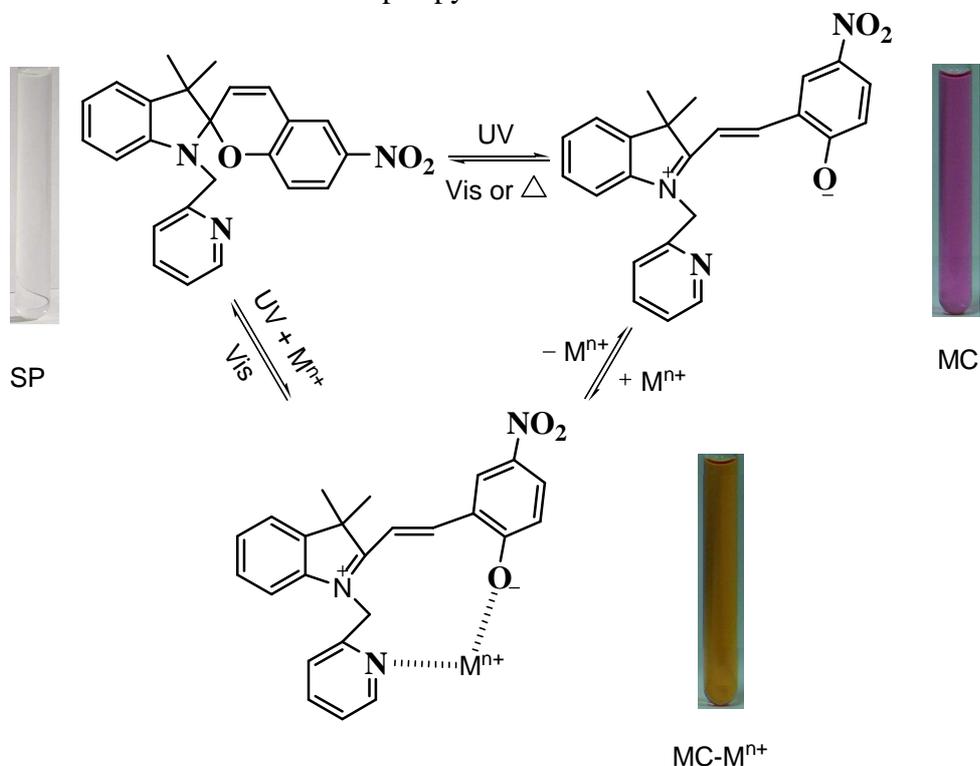
The photochromic spiropyran was excited by irradiation (365 nm light) for various time periods in order to follow the coloration. The result was the cleavage of the spiro carbon-oxygen bond, whereupon the molecule becomes a metastable amphoteric merocyanine ion, and the coloration of the spiropyran was due to the formation of this metastable ion. The latter may exist in different geometrical

isomers, *cis* or *trans*, the *cis* isomer being unstable and transforming into the *trans* isomer. The spiropyran solutions were colorless before the irradiation and turned to red under irradiation at 365 nm, and then the solution color was changed to colorless upon fading. In Figure 1 the absorption spectra of the spiropyran was depicted after the irradiation from 15 s to 1.5 h. The spectra of the spiropyran revealed that no absorption peak was observed in the range of 450-650 nm before irradiation. On the contrary, a well-formed peak at 539 nm was obtained with irradiation at 365 nm light. The peaks between 200 and 400 nm were attributed to the superposition of absorption bands of the spiropyran form and the merocyanine form. After 10 min of total irradiation time, the spiropyran solutions turned red and their photochromic properties were very stable.

Besides the changes caused in the absorption spectra of spiropyran by irradiation at different times, the decoloration rate of these films was also studied after irradiation with 365 nm light for 10 min. In order to follow the decoloration rate, the spectra were taken after each 3 s at 539 nm for the MC. As indicated, the decoloration rate was much quicker as shown by the maximum absorption intensity decrease. This can be clearly followed from the time dependence of the maximum absorption intensity. Considering the decoloration rate of the spiropyran as a first order reaction, then in the plot of the $\ln(A_t - A_\infty)$ of the maximum absorbance against time a linear dependence must be observed. Indeed, a near linear dependence between $\ln(A_t - A_\infty)$ and time (t) for spiropyran can be found by using equation [39].

$$\ln(A_t - A_\infty) = -kt + C$$

This linearity in the dependence of the nature logarithmic of maximum absorption intensity against time shows the decoloration mechanism of spiropyran to be a first order reaction.



Scheme 1. Reversible photochromic reactions of spiropyran.

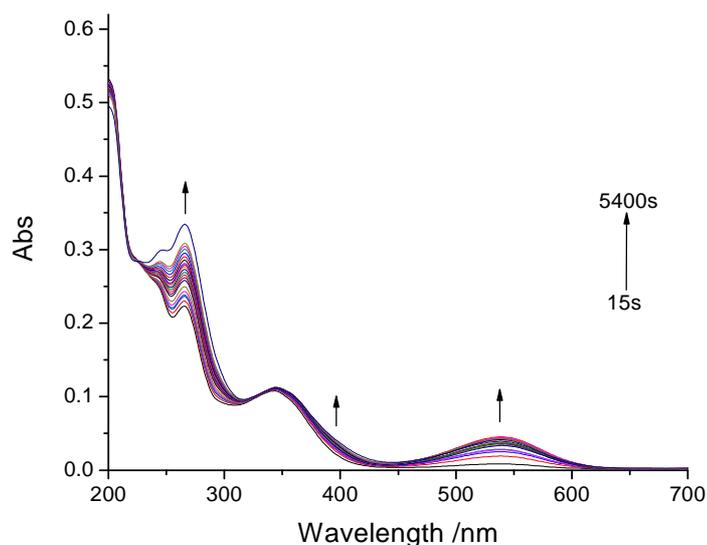


Figure 1. Absorbance spectra of spiropyran (1×10^{-5} mol/L, 298 K, MeCN/H₂O = 6:4) upon irradiation at 365 nm light from 15 s to 5400 s.

3.2. Recognition mechanism

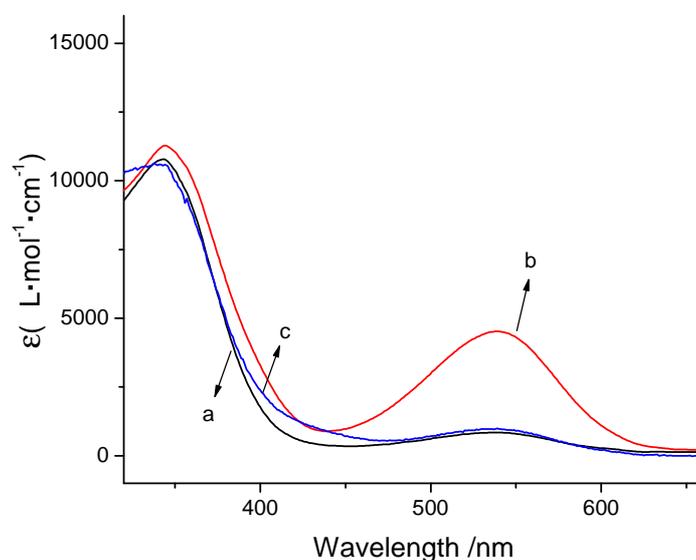


Figure 2. Absorbance spectra of spiropyran sensor (298 K, MeCN/H₂O = 6:4, V/V) after irradiation for 10 min at 365 nm light with addition of Al³⁺ (c), without addition of Al³⁺ (b), and with addition of Al³⁺ after irradiation by visible light for 10 min (a)

Figure 2 shows the visible absorption spectra of spiropyran upon irradiation at 365 nm light for 10 min before and after addition of aluminum ions. As a result, the absorption band in the visible region (539 nm) was enhanced, and attributed to the appearance of the MC after irradiation for 10 min. After addition of aluminum ions, this band disappeared immediately, and a new peak detected at about 420 nm, which was attributed to the metal-ion complexation with MC (Al³⁺-MC) [28]. The phenoxide and

pyridine groups of the merocyanine fragment may be involved in the formation of the coordination bonds between the merocyanine and aluminum ion. ^1H NMR (Figure 3) studies gave strong proof consistent with the above analysis. ^1H NMR spectrum of spiropyran changes dramatically after the addition of aluminum ion upon irradiation at 365 nm light for 10 min. Moreover, the characteristic Ha, Hb and Hc of pyridine signals exhibited a remarkable downfield shift attributed to the interconversion from the MC form to aggregation forms by irradiation [24, 25].

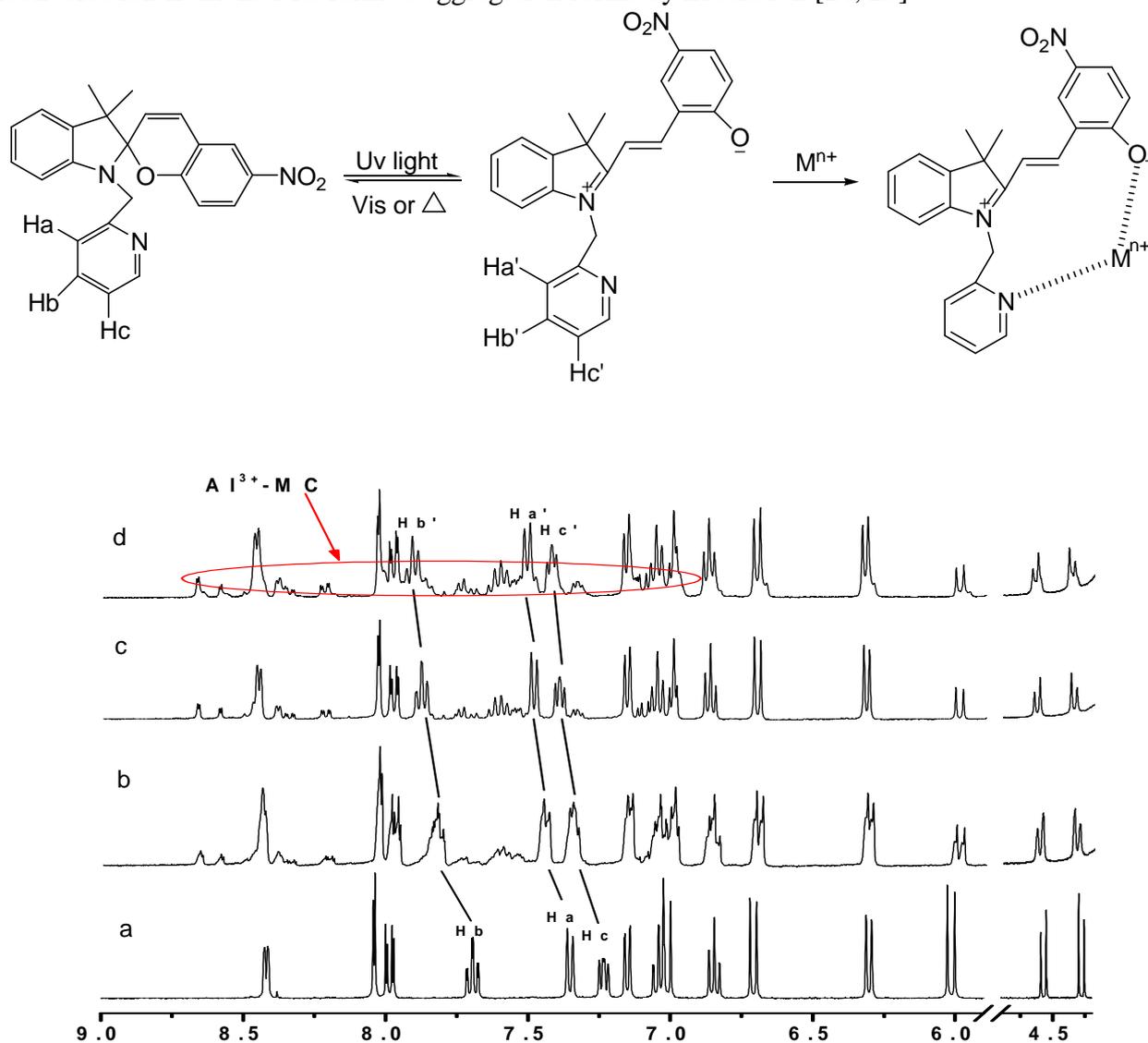


Figure 3. Partial ^1H NMR spectra (400 MHz, $\text{CD}_3\text{CN}/\text{D}_2\text{O} = 8:2$, V/V) of spiropyran without Al^{3+} (a), and by irradiation at 365 nm for 10 min with adding Al^{3+} of different concentration of 0.3 eq (b), 0.5 eq (c), and 1 eq (d).

Furthermore, after irradiation for 10 min by visible light, a decrease occurred at about 420 nm (Figure 2), and the Al^{3+} -MC released the aluminum ion and MC; the latter was simultaneously converted into the SP form. The reversible process (also shown in Scheme 1) provides a reversible detection of aluminum ion by photo controls.

According to the spectra reported in Figure 3, addition of the spiropyran solution (1.0×10^{-5} mol/L) after irradiation for 10 min was carried out by the addition of microliter amounts of a concentrated

standard solution of the aluminum ion in MeCN/H₂O solution (2.0×10^{-3} mol/L) using a precalibrated micropipette, followed by absorption intensity reading at the $\lambda_{\text{max}} = 539$ nm. Since the volume of titrant added during titration was negligible (at the most 0.01 mL) as compared with the initial volume of the ligand (2 mL), no volume correction was carried out. The absorption spectrum of MC showed a decrease of the band at 539 nm upon addition of increasing quantities of aluminum ions to MC, whereas the absorption intensity changes as a function of the $[\text{Al}^{3+}]/[\text{MC}]$ molar ratio (Figure 4). These changes could be attributed to the complexation between the MC and Al^{3+} . From the inflection point in the absorbance/molar ratio plot at $[\text{Al}^{3+}]/[\text{MC}]$ values between 0.4 to 0.7, it can be inferred that 1:3 ($[\text{Al}(\text{MC})_3]^{3+}$), 1:2 ($[\text{Al}(\text{MC})_2]^{3+}$) and 1:1 ($[\text{Al}(\text{MC})]^{3+}$) complexes were formed in MeCN/H₂O solution.

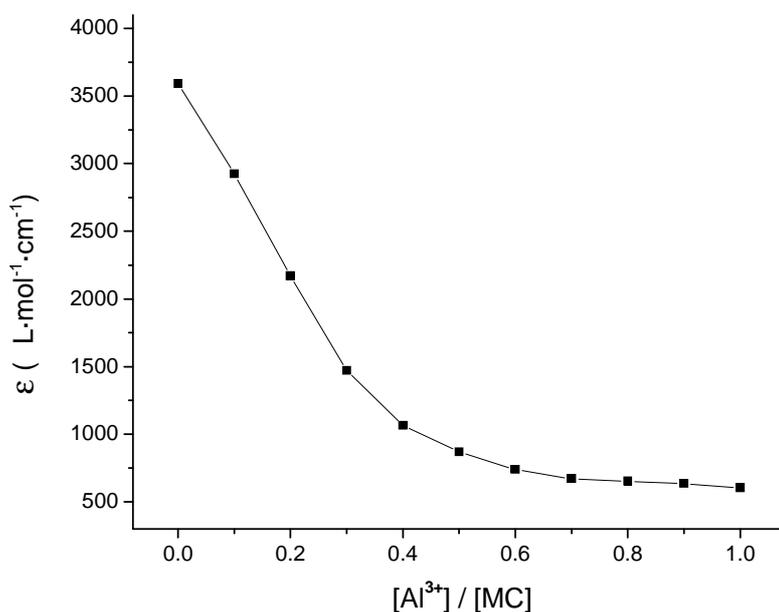


Figure 4. Absorption intensity / mole ratio data of spiropyran (1×10^{-5} mol/L, 298 K, MeCN/H₂O = 6:4, V/V) after irradiation for 10 min at 365 nm light with titration of Al^{3+} at different concentrations.

3.3. Optimization of experimental parameters

The performance of the spiropyran sensor was further assessed in partially non-aqueous media, i.e. acetonitrile–water mixtures. The influence of the rates between MeCN and H₂O was studied. The spiropyran of concentration at 1.0×10^{-5} mol/L was irradiated for 10 min at 365 nm, the maximum absorption wavelength in the visible region was recorded, and the results showed that the maximum wavelength was hypsochromically shifted with decrease in non-aqueous content, and the absorption spectrum in pure water was very similar to which in the MeCN/H₂O mixture solution at 6:4. Therefore, in order to improve the sensitivity, the spiropyran sensor can be used for further studies in mixtures containing only up to 60% MeCN content.

3.4. Response time

An important analytical feature of the spiropyran sensor is its response time for a sample solution of low Al^{3+} concentration. But chemsensors always have the problem of a long response time. In 2001

Mousavi reported a chemosensor based on an Al^{3+} - selective electrode method with a response time of 70 s [12], later lowered to 5 s by Gupta in 2007 [40]. Unexpectedly, the spiropyran sensor responded very fast. The spiropyran in MeCN/ H_2O mixture solution was irradiated for 10 min at 365 nm light, and when titrated with aluminum ion, the band at 539 nm disappeared, and a new weak band was detected very rapidly at about 420 nm within 5 s, remaining quite stable from 5 s to 30 min. As a consequence, the interconversion from MC to Al^{3+} -MC was an immediate response, thus providing a new real-time method for aluminum detection.

3.5. Detection limits

As mentioned above, the C-O bond of spiropyran at the spiro center can be cleaved upon irradiation and converted into merocyanine form, which chelated with aluminum ions, resulting in obvious color changes from red to pale yellow. Thus for spiropyran a highly sensitive colorimeter based on absorbance changed at 539 nm can be proposed as aluminum chemosensor. As shown in Figure 5, the chemosensor exhibited a good response for the aluminum ion with a linear working range from 0 to 4×10^{-6} mol/L. Thus micromolar concentrations of aluminum ion were sufficient to impose a detectable change on the absorption intensity, and the lowest detection limit was 5.0×10^{-7} mol/L.

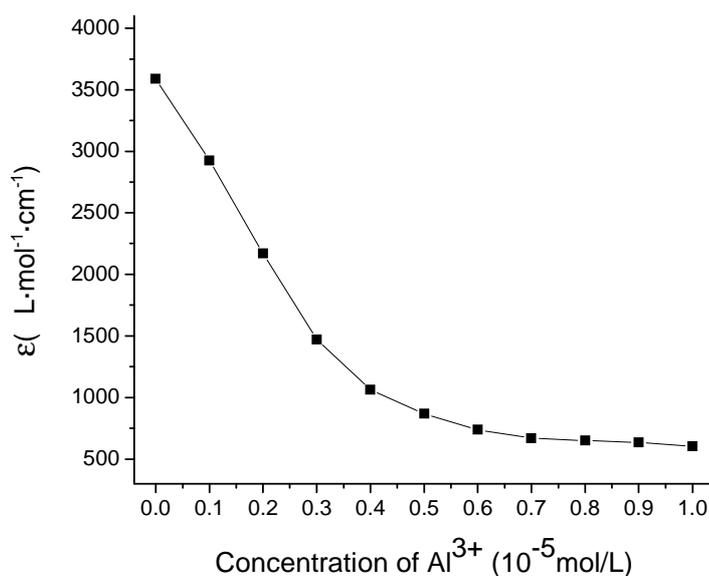


Figure 5. Absorbance changes at 539 nm for spiropyran (1.0×10^{-5} mol/L, 298 K MeCN/ H_2O = 6:4, V/V) with irradiation for 10 min at 365 nm light in the presence of different concentrations of Al^{3+} .

3.6. Reversibility and stability

The long term stability was tested by setting the system in the dark, and the signal recorded at wavelength of 539 nm over a period of about 90 min. The results showed that no significant changes occurred during this time after the merocyanine chelated with aluminum ion. The spiropyran sensor preserved their performance characteristics unchanged for 90 min.

Furthermore, the reversibility of spiropyran sensor was tested by irradiation at a difference wavelength. As shown in Scheme 1, after irradiation for 10 min at 365 nm, the band at 539 nm was

enhanced, then with addition of aluminum ions, a decrease of the absorption spectrum at 539 nm occurred, and the band at about 420 nm appeared simultaneously. Also after irradiation by visible light, a loss of the absorption spectrum at 420 nm occurred and came back to the initial spectrum before irradiation at 365 nm (Figure 2). As a result, the sensor gave good reproducibility of the reversible process. The merocyanine was in the thermally unstable open form, and converted into the original closed form within several minutes in the dark or by irradiation at visible light. With addition of aluminum ions, the metal-ion complexation with MC showed extraordinary thermal stability, resulting in a difference in the color fading to that of the open form of spiropyran. Thus aluminum ions can also control the merocyanine returning to the closed form by thermal fading.

3.7. Selectivity

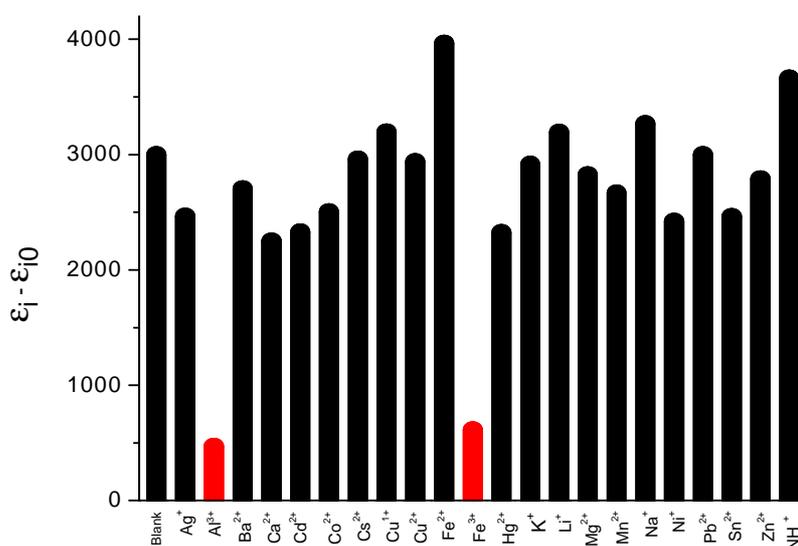


Figure 6. Absorbance changes at 539 nm for spiropyran (1.0×10^{-5} mol/L, 298 K, MeCN/H₂O = 6:4, V/V) with irradiation for 10 min at 365 nm light (blank sample), and in the presence of different metal ions (1 eq). Note: ϵ_{i0} was the absorption intensity at 539 nm with different ions without irradiation; ϵ_i was the absorption intensity at 539 nm with different ions with irradiation for 10 min at 365 nm.

Selectivity is the sensor's most important characteristic as it determines the extent of its utility in real sample measurement. The colorimetric detection of Al³⁺ in a mixture of MeCN and H₂O was generally complicated by the interference from some metal ions. Figure 6 illustrated the spectroscopic response of the spiropyran sensor following addition of a variety of metal ions in aqueous solution (including 10-fold excess Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Cu²⁺, Ba²⁺, Fe²⁺, Hg²⁺, Cd²⁺, Cr²⁺, Pb²⁺, Co²⁺, Ni²⁺, Cs⁺, Ag⁺, NH₄⁺ and 1-fold excess Sn²⁺), which indicated that the spiropyran chemosensor was essentially unaffected by the presence of these common ions except for the Fe³⁺ ion. Notably, the characteristic absorption peak at 539 nm for the MC form only disappeared in the presence of Al³⁺ and Fe³⁺, and was virtually insensitive to other cations. Differential pulse voltammetric experiment was performed in the MeCN/H₂O mixture of the spiropyran with irradiation and addition of Al³⁺, Fe³⁺. Redox potentials of the spiropyran upon irradiation at 365 nm for 10 min and addition of Al³⁺ was

found to be 1.16 V, and 1.07 V for Fe^{3+} , respectively. The oxidation peak was shifted anodically by 90 mV. Therefore, the ability of the spiropyran sensor to electrochemically distinguish Al^{3+} from Fe^{3+} provided high efficiency and good selectivity.

Also, the interference of foreign anions on the determination of Al^{3+} in MeCN/ H_2O was investigated experimentally, and the results (Figure 7) show that the presence of 10-fold excesses of Cl^- , Br^- , I^- , NO_2^- , NO_3^- , SCN^- , SO_3^{2-} and $\text{S}_2\text{O}_3^{2-}$ did not interfere in the determination of Al^{3+} at 1×10^{-5} mol/L.

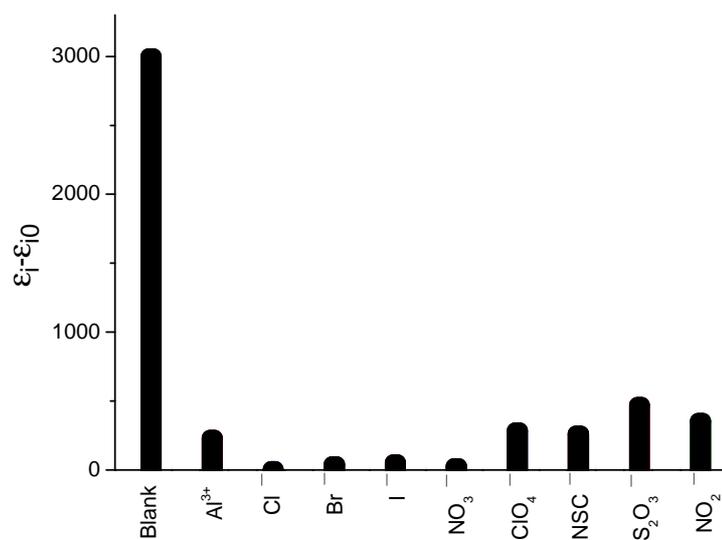


Figure 7. Absorbance changes at 539 nm for spiropyran (1.0×10^{-5} mol/L, 298 K, MeCN/ H_2O = 6:4, V/V) with irradiation for 10 min at 365 nm light in the absence of Al^{3+} (blank sample), and in the presence of Al^{3+} (Al^{3+}) or with other common anions (1 eq). Note: ϵ_{i0} was the absorption intensity at 539 nm with different anions without irradiation in the presence of Al^{3+} ; ϵ_i was the absorption intensity at wavelength 539 nm with different anions with irradiation for 10 min at 365 nm in the presence of Al^{3+} .

4. Conclusion

A highly sensitive and selective sensor for the aluminum ion based upon a photochromic spiropyran has been synthesized and studied. This spiropyran showed photochromic characteristics. After irradiation at 365 nm, the SP form transformed into the MC form, which chelated with Al^{3+} , resulting in obvious changes in color. It showed a very fast response within 5 sec and could be detected by the naked eye. The metal ion chelated complex (Al^{3+} -MC) can be converted into original SP form by irradiation at visible light. Thus, the spiropyran sensor provided a new, reversible real-time photodriven method for Al^{3+} detection, with the aluminum ion controlling the fading process of spiropyran by thermal fading. The detection limit of this sensor is 5.0×10^{-7} mol/L. It fully meets the sensitivity standard by National Secondary Drinking Water Regulations (0.05 to 0.2 mg/L). Notably, the characteristic absorption peak changes for the spiropyran sensor can be observed only in the presence of Al^{3+} , virtually insensitive to other cations or anions. The results clearly demonstrate that a

highly selective detection system for an analyte can be developed with potential applications in a variety of settings requiring rapid and accurate analysis for the aluminum ion.

Acknowledgements

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Supplementary data

The experimental details, synthetic, spectroscopic and electrochemical data are available in supplementary data.

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