

Spectral Properties of a pH Responsive Water Soluble Spironaphthoxazine and Its Multi-Switching Property

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Abstract: A water soluble spironaphthoxazine (SPO) was synthesized, and its spectral properties were determined. Under UV irradiation, colorless SPO shows intensive blue color while the intensity of its initial fluorescence decreased. In addition, SPO also exhibited high sensitivity to pH stimuli both in colorimetry and fluorometry distinguishing from the spectral appearance observed under UV irradiation. Further, integrating these two optical characteristics a three-state switching system can be established, and all interconversions can be observed by naked-eye.

Keywords: water soluble spironaphthoxazine, colorimetric, fluorometric, pH stimulation, multi-switching

1. Introduction

Spironaphthoxazines (SPO), a promising family of photochromic compounds, has already been gained continuous attention for last three decades due to their supereminent fatigue-resistance properties¹⁻³. Many systematic studies on SPO have been reported⁴⁻⁷, and following that ten thousands of SPO derivatives were synthesized and published aiming on the improvement of chemical or physical natures of parent SPO^{8,9} or the extension of application¹⁰. Among these works, water soluble SPO is an interesting series of SPO derivatives from manufacture of photochromic LBL (layer-by-layer) film which is a kind of organic ultrathin film applying in various fields^{11,12}. However, for other application few papers of ionic SPO have been reported.

We herein reported a novel cationic SPO showing reversibly spectral changes by modulation with pH stimuli both in colorimetry and fluorometry. The colorless SPO showed an intensive blue color when upon UV irradiation accompanied with the decrease of initial intensity of fluorescence. In order to improve an essential demerit of SPO as lacking water-solubility which strictly limits its application in

some extent, SPO molecule was converted into ionic configuration by anchoring two quaternary ammonium groups to SPO matrix with a triazinyl. And as we expected, this transformation dramatically enhance the solubility of SPO in water phase.

In this paper, we described the synthesis of cationic SPO and determined its spectral properties when under UV-Vis. irradiation as well as pH stimuli. And multi-switching behavior was also expatiated.

2. Experimental

2.1 Materials and Instruments

1,3,3-trimethyl-2-methyleneindoline (Fisher's base), 2,7-dihydroxynaphthlene, cyanuric chloride, *N,N,N',N'*-tetramethyl-1,3-propanediamine, were purchased from Aldrich Chemical Company. Compound 1 was obtained by synthesis according to the literature methods^{13,14}. Compound 4 was synthesized by following the method reported previously^{11,12}. All chemicals were of the highest grade available and were used without further purification. Melting points were determined to use an Electrothermal IA 900 and are uncorrected.

Absorption spectra were measured with an Agilent 8453 spectrophotometer. Fluorescence spectra were measured on a Shimadzu RF-5310PC fluorescence spectrophotometer. IR spectra were measured with a Spectrum GX & Auto Imaging IR Spectrometer. A

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high pressure mercury lamp (Ushio, SP3-250D) was used as the UV irradiation source and calibrated with a monochromator at 366 nm.

2.2 Synthesis

2.2.1 Synthesis of compound 3

Cyanuric chloride **2** (6.61g, 35.85mmol) was dissolved in 120ml of acetone. Temperature of the solution was maintained at 0 - 5°C. The prepared compound **1** (12.33g, 35.85mmol) was added into the solution, which was then stirred for 2.5h. Na₂CO₃ (40ml, 0.98N) was added into the solution and stirred for 1.5h. After completion of reaction, the solution was poured into 500 ml of H₂O. The resulting solid **3** was filtered and obtained.

Yield: 13.3g(75%); m.p.: 140°C; MS m/z (M⁺) 492; Anal. calc. for C₂₅H₁₉Cl₂N₅O₂ : C, 60.99; H, 3.89; N, 14.22; Found: C, 60.01; H, 3.76; N, 14.13.

2.2.2 Synthesis of SPO

The compound **3** (0.5g, 1mmol) and compound **4** (0.27g, 2mmol) were dissolved in acetonitrile solution (20ml). The mixture solution was stirred for 5h at room temperature. After the reaction finished, the mixture solution was poured into 100 ml ether and precipitated; then filtered and washed with ether and

ethyl acetate by 3 times, respectively. The SPO was obtained and dried at 60°C in vacuum for 12h.

Yield: 33%; m.p.: 256°C

IR (KBr, disc): ν =3420, 2958, 2596, 2481, 1616, 1484, 1387, 1304, 1253, 1208, 1085, 957, 821, 743.

TGA: 346.47°C

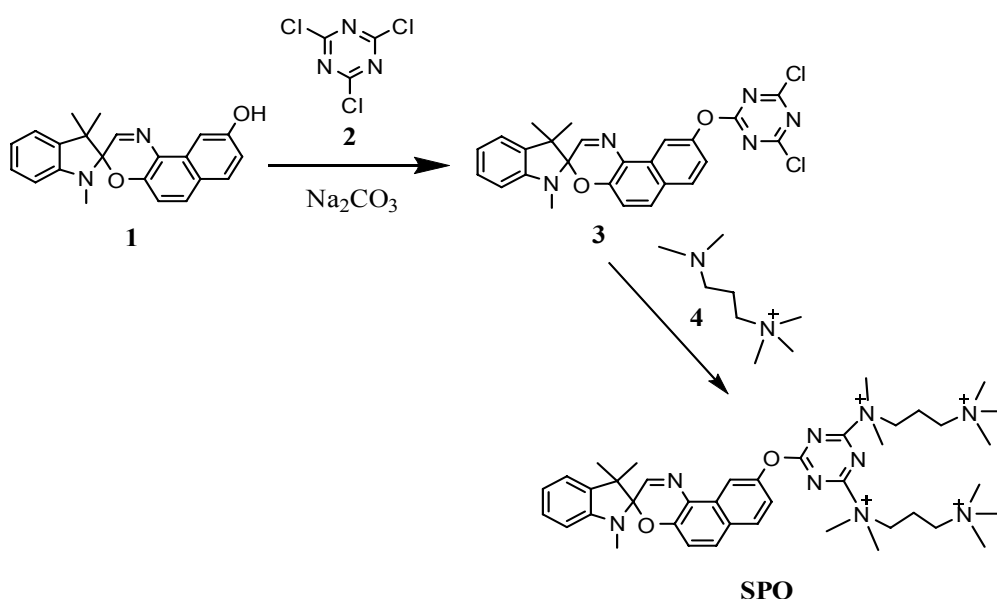
3. Results and Discussions

3.1 Spectral properties of SPO

The photochromic reaction was caused by the reversible heterolytic cleavage of the C(spiro)-O bond under UV irradiation, yielding the colored form that can return to the colorless form by ring closure under visible light irradiation or in the dark^{15,16}. Photochromic behavior of SPO in water is depicted as Figure 1.

Under UV irradiation, the SPO showed an intensive absorption band centered at 598 nm referring to the heterolytic dissociation of C-N from the photochromic component, producing colored open merocyanine^{17,18}.

Comparing to parent compound **1**, the open form of SPO presented a slight bathochromic shift arising from electron-withdrawing property of two quaternary ammonium groups at tetramethylpropanediamine moiety¹⁹. After removing the irradiation source, the absorption maximum decreased as the open merocyanine reversibly



Scheme 1. Synthesis of SPO

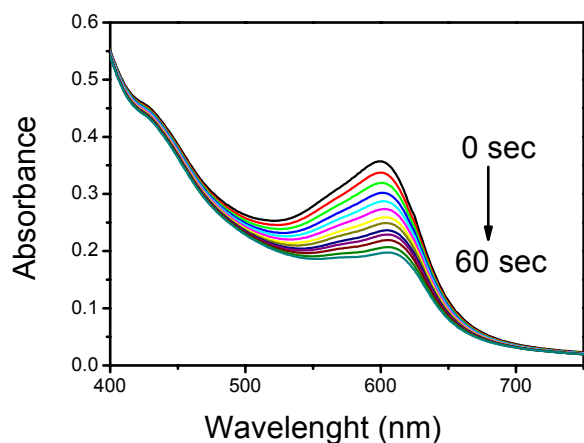


Figure 1. Spectral changes of SPO after UV irradiation for 1 min in water (1×10^{-5} mol/L).

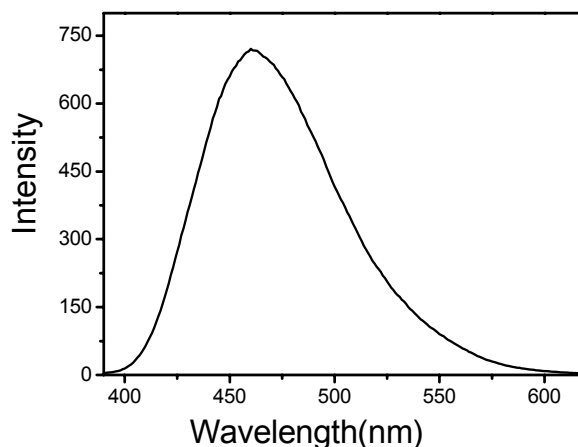


Figure 2. Emission spectrum of SPO when excited with wavelength of 370 nm.

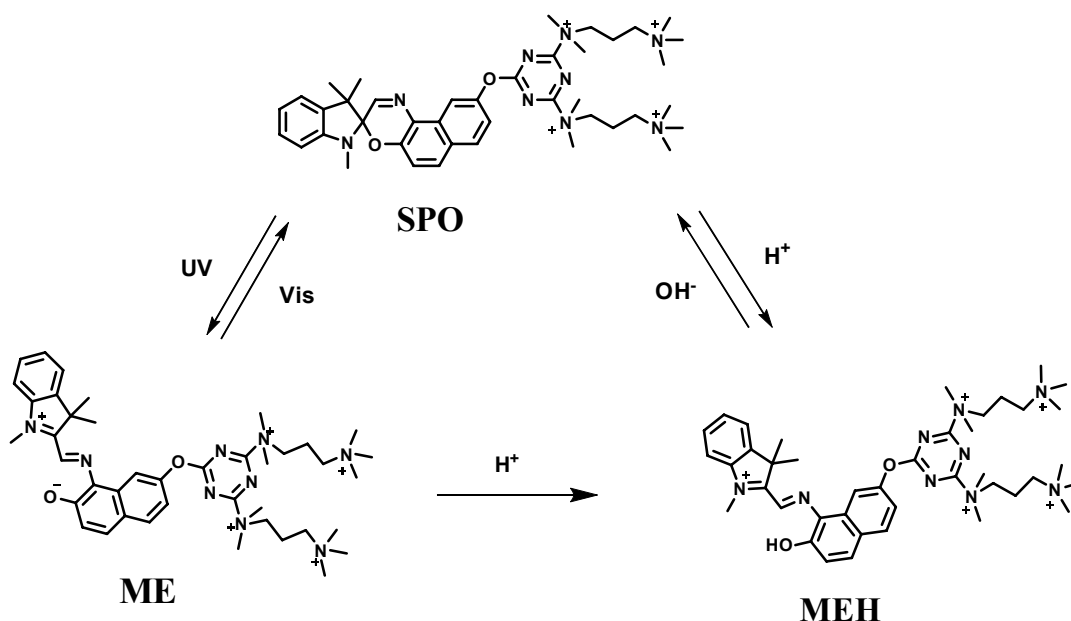
convert into closed spiro form. The spectral measurements after UV irradiation are at any time proportional to each other in the visible region, indicating that only one species was formed. Meanwhile initial SPO showed a broad emission band ranged from 400 to 600 nm (see Figure 2).

3.2 Acid–base switchable behavior of SPO

3.2.1 Acid–base effects on absorption spectra

Upon the addition of H^+ , a distinct absorption band appeared in the visible region.

The measurement was performed in SPO dissolved water solution titrating with hydrogen chloride. The absorbance gradually increased along with increasing the concentration of hydrogen chloride. Distinct from photoinduced course, the new absorption bands arose round 430nm (see Figure 3), leading to a yellow color. This change related to the intrinsic nature of SPO, namely heterolytic cleavage in acidic environment and the subsequent protonation of the merocyanine MEH^{20} (see Scheme 2). After addition of equivalent *n*-tetrabutylammonium hydroxide, the spectral pattern recovered due



Scheme 2. The reversible interconversion of three states of SPO

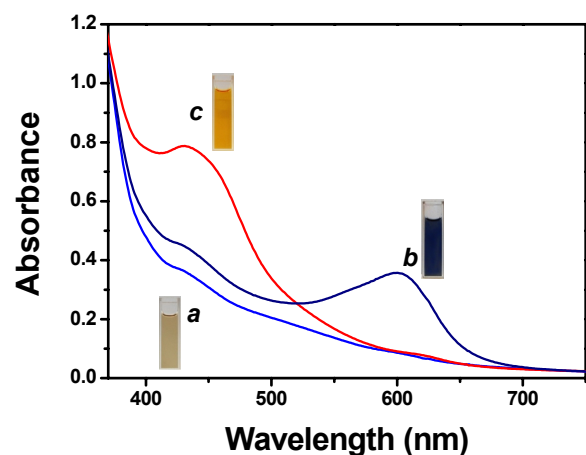


Figure 3. (a) Absorption spectra of SPO, (b) ME, (c) MEH.

to the reversion from the protonated open merocyanine MEH to initial spiro form SPO.

Meigong Sun *et al.*²⁰ reported that parent photochromic spiroanthoxazines also exhibit acidichromic behaviors, where in the protonated open merocyanine gradually discolored when the solution were stored in the dark. The intensity of the absorbance of colored merocyanine MEH, however, was found with no variation in the dark condition. Moreover, the protonated MEH did not only show no sensitivity to photoirradiation, but also to thermal change, indicating that form MEH offers good photostability and thermostability. The interconversion from SPO to MEH can only be modulated by the adjustment of the concentration of H^+ .

3.2.2 Multi-switching system

Associating with change induced by UV/vis irradiation, a three-state switching system can be developed on the basis of reversible interconversion of SPO.

SPO ring opens upon ultraviolet irradiation to generate the merocyanine ME. This transformation is accompanied with the appearance of an intensive absorption band in the visible region (Figure 3). There transformation of merocyanine ME to the original spiro form is thermodynamically forbidden when only treated with heating, indicating that the open form ME offers a good thermostability. In the presence of acid, however, ME switches to MEH

with remarkable changes on the absorption spectra (Figure 3). The protonated merocyanine MEH can also be generated directly from SPO after the addition of acid. Furthermore, the protonated species MEH switches to SPO only upon addition of base, providing good thermo- and photostability. Thus, the reversible interconversion of the three states SPO, ME and MEH can be established by cooperating UV-vis irradiation and pH stimuli.

3.2.3 Acid-base effects on fluorescent spectra

The interconversion from SPO to MEH also resulted in changes on emission spectra illustrated in Figure 4.

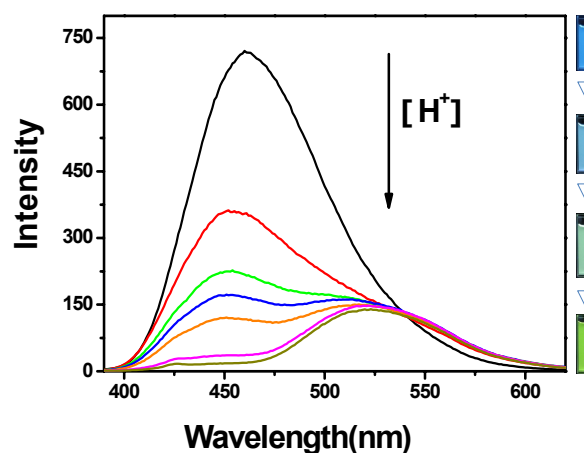


Figure 4. Emission spectral changes of SPO upon addition of HCl and *n*-tetrabutylammonium hydroxide in turn (in water).

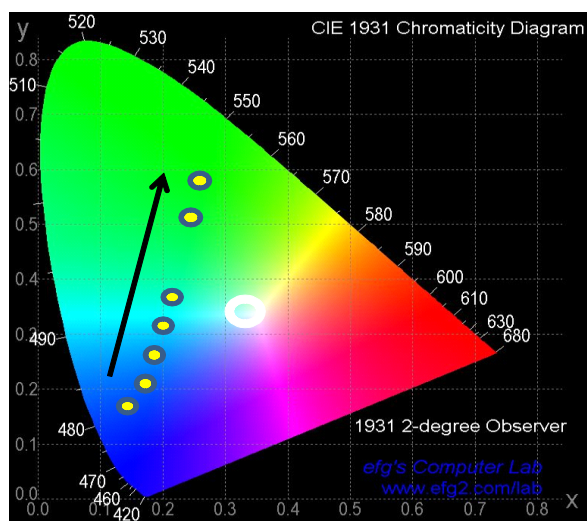
As the data shown in Table 1, in the presence of low concentration of H^+ ($3 \times 10^{-2} M$) the intensity of fluorescence approximately decreases to a half and the emission bands slightly shift to short wavelength region, referring to the heterolytic cleavage of photochromic component (Scheme 2). When the concentration of H^+ increased to $6 \times 10^{-2} M$, the decrease of intensity round 452nm was accompanied with the appearance of a new emission band centered round 525nm, indicating that the open MEH was protonated. Subsequently increasing the ratio, the intensity of former emission bands declined and totally disappeared in a high concentration of H^+ ($> 30 \times 10^{-2} M$) as well as the intensity of new one almost presented no more ascents.

Table 1. Emission spectra changes with addition of H^+ into water solution of SPO (dye= 3×10^{-5} mol)

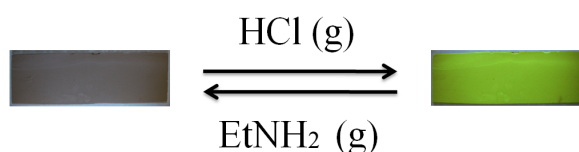
Concentration of H^+ (M)	λ_{em} (nm)	Intensity
0	$\lambda_{em}=460$	I=720
3×10^{-2}	$\lambda_{em}=452$	I=362.16
6×10^{-2}	$\lambda_{em1}=452; \lambda_{em2}=522$	$I_1=225; I_2=154.8$
9×10^{-2}	$\lambda_{em1}=452; \lambda_{em2}=522$	$I_1=171; I_2=155.7$
12×10^{-2}	$\lambda_{em1}=452; \lambda_{em2}=522$	$I_1=119.3; I_2=1477.7$
30×10^{-2}	$\lambda_{em}=522$	I=148
45×10^{-2}	$\lambda_{em}=522$	I=140

* $\lambda_{ex}=370$ nm

The emission response of SPO to H^+ over a wide concentration range is shown in Figure 5. The original blue emission of SPO is changed to light blue in the presence of low concentrations of H^+ ($3 \times 10^{-2} \sim 9 \times 10^{-2}$ M), and in turn subsequently changed to cyan to green in the high concentration region (3.0×10^{-2} M). The CIE chromaticity diagram (CIE=International Commission on Illumination) for the emission of SPO at various concentrations of H^+ demonstrates the fine-tuning of the emission color from blue to green in response to H^+ concentration (Figure 5).

**Figure 5.** CIE chromaticity diagram for the emission of SPO (3.0×10^{-5} mol) in the presence of H^+ in water at 293K.

In the context of the ability of SPO to function as a gas detector, when a TLC plate adsorbed with SPO was exposed to HCl and ethylamine vapour in turn, marked change of fluorescence emission occurred (Figure 6).

**Figure 6.** Fluorescence changes observed for SPO imparted by exposure to HCl/EtNH₂ vapour.

It is apparent that upon exposure to HCl vapour, the change in fluorescent color obtained was visually noticeable; when the TLC plate which had been exposed to the HCl vapour was exposed to ethylamine vapour, the original state was regenerated within 1 s as response time of fluorescent reversal. These reversible phenomena were repeated several times for a given TLC plate adsorbed with SPO.

4. Conclusion

The emission spectra and acid-base switchable behavior of SPO were investigated. The SPO exhibited blue fluorescence in water solution. In the presence of H^+ the SPO underwent heterolytic cleavage converting to an open merocyanine form, resulting in generating a distinct absorption bands from those observed by UV irradiation. And their intensity of fluorescence of SPO can be modulated by either photochromism or acidochromism. Fluorescence in turns changed from cyan to green. Both absorption and emission spectral changes can be restored by addition equivalent *n*-tetrabutylammonium hydroxide. Thus, three-states molecular switching modulated by acid-base and electromagnetic irradiation is realized and expected to show its potential in application.

Acknowledgement

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Reference

1. H. Durr and H. Bouas-Laurent, "Photochromism, Molecules and Systems", Elsevier, Amsterdam, 1990.
2. C. Bohne, M. G. Fan, Z. J. Li, Y. C. Liang, J. Luszyk and J. C. Scaiano, Laser Photolysis Studies of Photochromic Processes in Spirooxazines : Solvent Effects on Photomerocyanine Behavior, *Journal of Photochemistry and Photobiology A: Chemistry*, **66**(1), 79(1992).
3. X. Y. Zhang, S. Jin, Y. F. Ming, Y. C. Liang, L. H. Yu, M. G. Fan, J. Luo, Z. H. Zuo and S. D. Yao, Substituent Effect on Photochromism of Indolinospirooxazines, *Journal of Photochemistry and Photobiology A: Chemistry*, **80**(3), 221(1994).
4. R. J. Hovey, N. Y. C. Chu, P. G. Piusz and C. H. Fuchsman, US Pat. 4215010(1980).
5. J. Hopley and F. Wilkinson, Photochromism of Naphthoxazine-spiro-indolines by Direct Excitation and Following Sensitization by Triplet-energy Donors, *Journal of the Chemical Society, Faraday Transactions*, **92**(8), 1323(1996).
6. N. Y. C. Chu, US Pat. 4699473(1987).
7. M. Rickwood, S. D. Marsden, M. E. Ormsby, A. L. Staunton and D. W. Wood, Red Coloring Photochromic 6'-substituted Spiroindolinonaphth[2,1-b][1,4] Oxazines, *Molecular Crystals and Liquid Crystals Science and Technology Section A: Molecular Crystals and Liquid Crystals*, **246**(1), 17(1994).
8. X. L. Meng, W. H. Zhu, Z. Q. Guo, J. Q. Wang and H. Tian, Highly Stable and Fluorescent Switching Spirooxazines, *Tetrahedron*, **42**(6), 9840(2006).
9. C. R. Zhang, Z. B. Zhang, M. G. Fan and W. P. Yan, Positive and Negative Photochromism of Novel Spiro[indoline-phenanthrolineoxazines], *Dyes and Pigments*, **76**(3), 832(2008).
10. H. Tian, B. Qin, R. X. Yao, X. L. Zhao and S. J. Yang, A Single Photochromic Molecular Switch with Four Optical Outputs Probing Four Inputs, *Advanced Materials(Weinheim, Germany)*, **15**(24), 2104(2003).
11. S. H. Kim, C. J. Shin, S. R. Keum and K. N. Koh, Layer-by-layer self-assembled Multilayer of Cationic Spiroxazine and Polystyrenesulfonate, *Dyes and Pigments*, **72**(3), 378(2007).
12. S. H. Kim, C. Y. Yu, C. J. Shin and M. S. Choi, Photochromic layer-by-layer films of Spiroxazine Polymer, *Dyes and Pigments*, **75**(1), 250(2007).
13. T. Kakishita, K. Matsumoto, T. Kiyotsukuri, K. Matsumura and M. Hosoda, Synthesis and NMR Study of 9'-substituted Spiroindolinonaphthoxazine Derivatives, *Journal of Heterocyclic Chemistry*, **29**(7), 1709(1992).
14. H. Durr, Y. M. Ma and G. Cortellaro, Preparation of Photochromic Molecules with Polymerizable Organic Functionalities, *Synthesis*, **3**, 294(1995).
15. Y. Son and J. Park, Rhodamine 6G Based New Fluorophore Chemosensor Toward Hg²⁺, *Textile Coloration and Finishing*, **24**(3), 158(2012).
16. H. Kim and Y. Son, Synthesis and Optical Properties of Novel Chemosensor Based on Rhodamine 6G, *Textile Coloration and Finishing*, **24**(4), 233(2012).
17. H. Nishikiori, N. Tanaka, K. Takagi and T. Fujii, Solvent Effect on Fluorescence Spectra of a Spirooxazine, *Research on Chemical Intermediates*, **29**(5), 485(2003).
18. S. Kawauchi, H. Yoshida, N. Yamashina, M. Ohira, S. Saeda and M. Irie, A New Photochromic Spiro [3H-1,4-oxazine], *Bulletin of Chemical Society of Japan*, **63**(1), 267(1990).
19. H. H. Tang, H. Xing, W. H. Huang and F. Zhang, Two-photon Three-dimensional Optical Data Storage with Equal Exposure Energy and Time Increase, *Guangxue Xuebao*, **29**(5), 134751(2009).
20. X. D. Sun, M. G. Fan, X. J. Meng and E. T. Knobbe, Acidichromic Effects in Spiro(1,3,3-trimethyl

lindolo-2,3'-naphth[1,2-b]-1,4-oxazine), a Photochromic Compound I: Absorption Characteristics, *Journal*

of Photochemistry and Photobiology A: Chemistry, **102**(3), 213(1997).