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Photochemical Properties of a Photochromic Naphthoxazine upon UV Irradiation in the Presence of Transition Metal Ions

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ABSTRACT

1,3,3-Trimethylspiro[indoline-2,3'-[3H]-naphth-[2,1-b][1,4]oxazine] was synthesized in order to study its photochromic activity in the presence of transition metal ions. Its photochemistry and irreversible phototransformation were studied on UV-irradiation in the presence of 10^{-5}–10^{-6} *M concentrations of transition metal ions in methanol, ethanol and acetonitrile. A new, stable strongly luminescent product appeared, giving rise to broad and unstructured luminescence. The obtained absorption and emission spectra were used to calculate the fluorescence quantum yields. © 1998 Elsevier Science Ltd. All rights reserved*

Keywords: absorption and fluorescent spectra, naphthoxazine, metal complex.

1. INTRODUCTION

Most photochromic compounds change their colour on photoirradiation and return to their initial state while kept in the dark. Colour changes of the compounds are only slightly induced when the light intensity is weak, while photoreactions readily occur on illumination with high intensity light. Photochromism is an area which has been continuously growing in importance particularly with respect to potential application of photochromic materials in electronic and other devices. The most intensively studied class of photochromic materials are the spiropyrans [1–5]. Their photochemical kinetics, spectra, and photoinduced structural transformations have been described in some detail. The photochemistry and spectroscopy of photochromic

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naphthoxazines has been studied much less than that of spiropyranes, and the synthesis and luminescence spectra of only a few photochromic naphthoxazines have been published [6–9]. There is very little information regarding this interesting class of photoactive materials which have the potential ability for many applications owing to additional characteristics, such as fatigue resistant, since naphthoxazines continue to display this phenomenon even after 10^4 times of the coloration/decoloration operations shown in Scheme 1.

Herein we describe the synthesis, electronic absorption and emission spectra obtained upon UV-irradiation of the title compound when dissolved in methanol, ethanol and acetonitrile in the presence of low concentrations (10^{-4}–10^{-5} M) of transition metal ions.

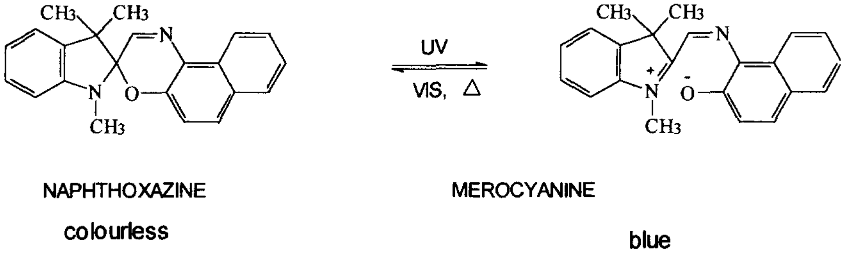
2. EXPERIMENTAL

2.1 Materials

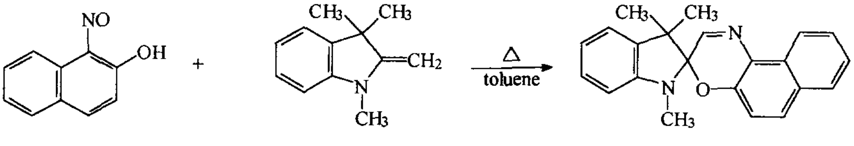
All starting materials for synthesis were purchased from commercial sources and were used without further purification. Reagent grade metal salts were used for preparations and the solvents were of analytical grade.

2.2 Preparation of compound

1′,3′,3′-Trimethyl[indoline-2,3′-[3H]-naphth-[2,1-b] [1, 4] oxazine (**3**) was synthesized by condensation of 1,3,3-trimethyl-2-methylene-indoline (2) with 1-nitroso-2-naphthol (1) [10] in toluene according to Scheme 2. Compound



Scheme 1. Photochromic transformation of naphthoxazine.



1 2 3

Scheme 2. Synthesis of compound 3.

(**1**) was dissolved by heating in toluene and (**2**) was then added. The reaction mixture was refluxed for 1 h and the solution cooled, filtered, and the precipitate washed with methanol and recrystallized from acetone (m.p. 124–125°C) [10].

2.3 Instrumentation

Absorption and fluorescence spectra were measured on a Specord UV-Vis (Carl Zeiss, Jena) spectrophotometer or a Shimadzu UV 160 U spectrophotometer, and a Shimadzu FR 5000 U spectrofluorometer.

2.4 Photolysis experiments

Photolysis experiments were performed with a 250 W medium-pressure mercury lamp under steady irradiation. A measured volume of the appropriate solution at a concentration sufficient to absorb all the incident radiation was exposed to UV light. This solution was placed in a 1-cm optical path quartz cell and irradiated with the full spectrum of the mercury lamp for an accurately known period of time, *t*. After time *t*, the increase in absorption was spectrophotometrically recorded.

2.5 Fluorescence quantum yields

All fluorescence spectra were corrected for detector sensitivity. The emission spectral profiles were similar for all samples and independent of excitation wavelength.

The determination of emission quantum yields relative to fluoresceine as an external standard was calculated by using eqn (1), in which A_S and A_r are the absorbance of the sample and of the reference at the excitation wavelength, respectively, I_S and I_R are the integrated intensity of the emission band of the sample and of the reference, and Φ_r is the emission quantum yield of the reference.

$$\Phi_{em} = \frac{[Ar.I_S]}{[A_S.I_r]}\Phi_r \qquad (1)$$

3. RESULTS AND DISCUSSION

3.1 Absorption spectra

When 1.6×10^{-4} M ethanol solutions of naphthoxazine were photolysed from 5 to 30 min with UV light at 20°C in the presence of an equimolar quantity of Cu(II), the UV band of the naphthoxazine at about 300 nm decreased in intensity with a corresponding increase in absorption at 440 nm (Fig. 1). Reaction was quite clean with an isosbestic point at 385 nm. After irradiation, the solutions were kept for 24 h in the dark in order to check whether the photoreaction proceeded reversibly. The absorption spectra were then measured and the resulting spectra clearly showed that the naphthoxazine underwent an irreversible photo-transformation in the presence of Cu(II).

Figure 2 illustrates the electronic absorption spectral changes when irradiation of 1.6×10^{-4} M ethanol solutions of naphthoxazine was carried out for 5 to 30 min in the presence of an equimolar quantity of Fe(III). The data in Fig. 2 are similar to the spectral changes observed in Fig. 1 for the Cu(II)-naphthoxazine mixture (1:1). On keeping the irradiated solutions for 24 h in the dark, their absorption spectra remain unchanged, suggesting irreversible photo-transformation of naphthoxazine in the presence of Fe(III).

The changes in the visible absorption spectrum of 1.6×10^{-4} M ethanol solutions of the naphthoxazine during a 5 to 15 min irradiation with UV light at 20°C in the presence of an equimolar quantity of Cr(III) are given in Fig. 3. This experiment confirmed the formation of a new product with λ_{max} at 440 nm and isosbestic point at 385 nm. When the irradiated solutions containing the new product were kept for 24 h in the dark, and the absorption

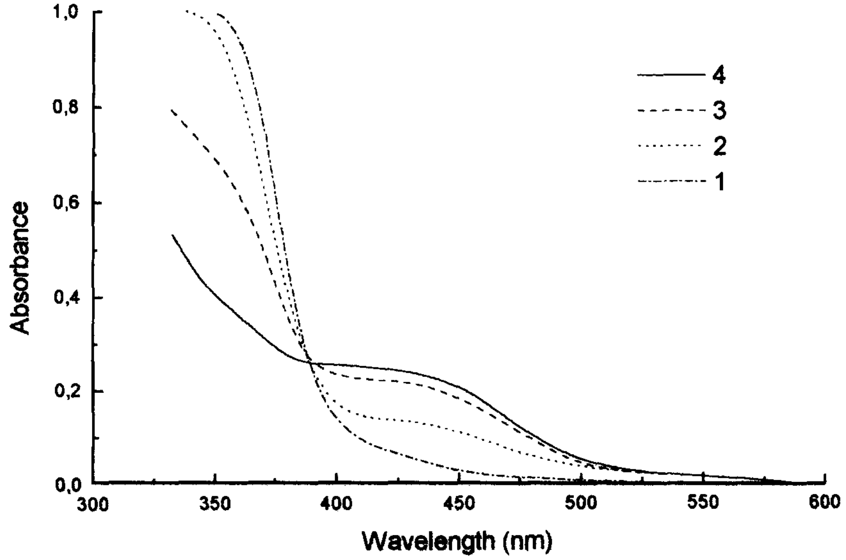


Fig. 1. Visible absorption spectra taken (1) before, and after consecutive (2) 5; (3) 15 and (4) 30 min UV-irradiations of 3.3×10^{-4} M ethanol solutions of naphthoxazine in the presence of an equimolar quantity of Cu(II).

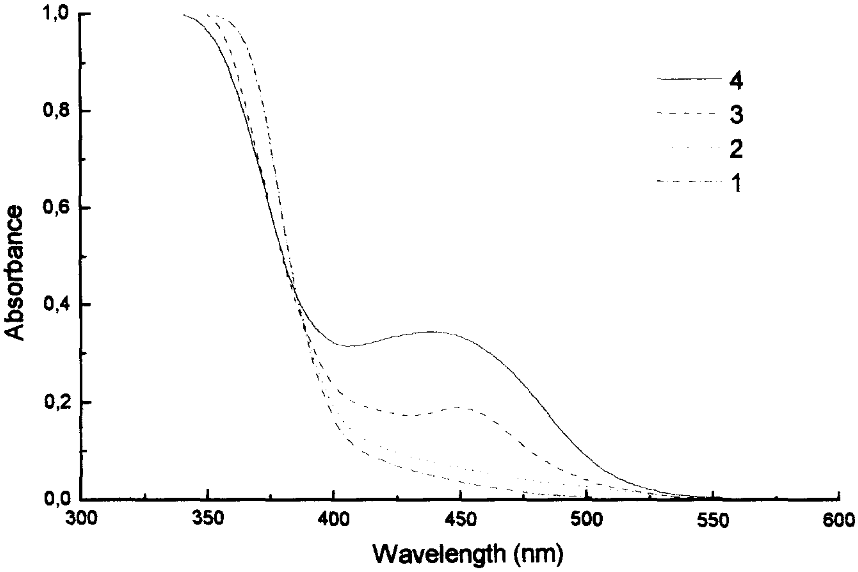


Fig. 2. Visible absorption spectra taken (1) before and after consecutive (2) 5; (3) 15 and (4) 30 min UV-irradiations of 3.3×10^{-4} M ethanol solutions of naphthoxazine in the presence of an equimolar quantity of Fe(III).

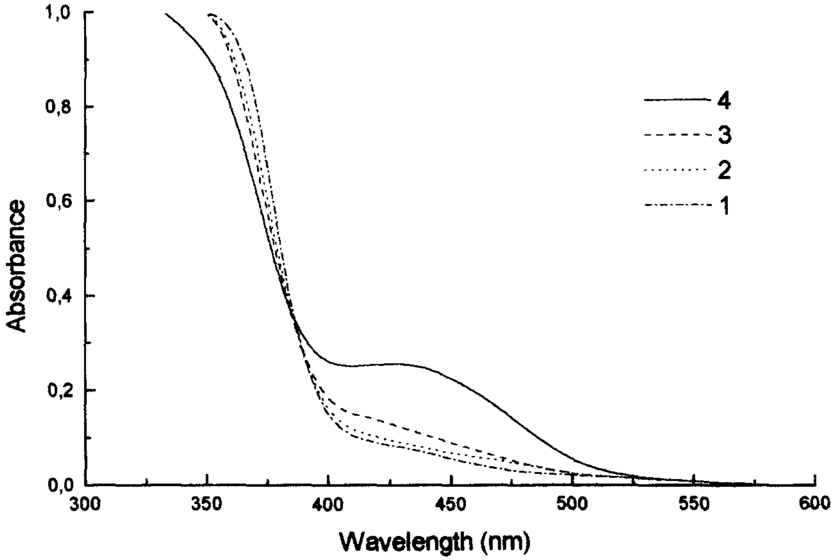


Fig. 3. Visible absorption spectra taken (1) before and after consecutive (2) 5; (3) 10 and (4) 15 min UV-irradiations of 3.3×10^{-4} M ethanol solutions of naphthoxazine in the presence of an equimolar quantity of Cr(III).

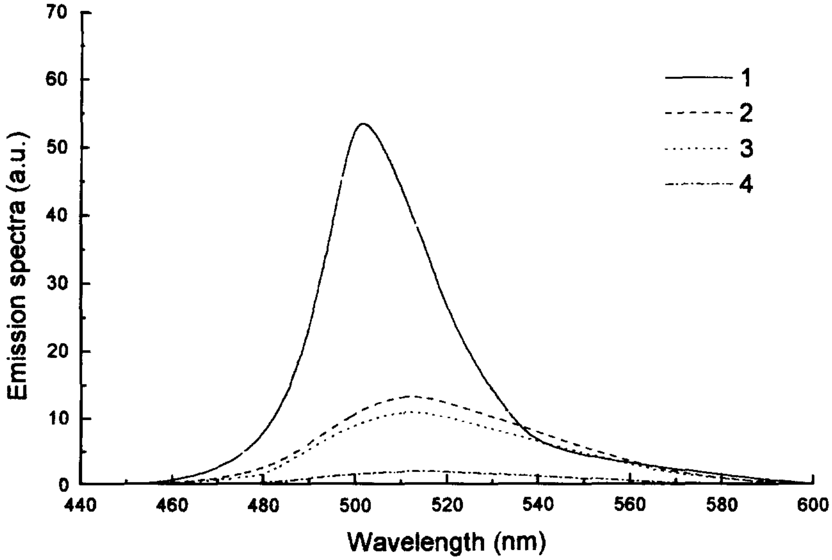


Fig. 4. Emission spectra of 4×10^{-5}M methanol solution of (1) Fluoresceine (1) and UV-irradiated samples of naphthoxazine in the presence of an equimolar quantity of: (2) Fe^{3+} (2.8×10^{-5}M), (3) Cu^{2+} (7.7×10^{-5}M) and (4) Cr^{3+} (3.3×10^{-5}M) in methanol.

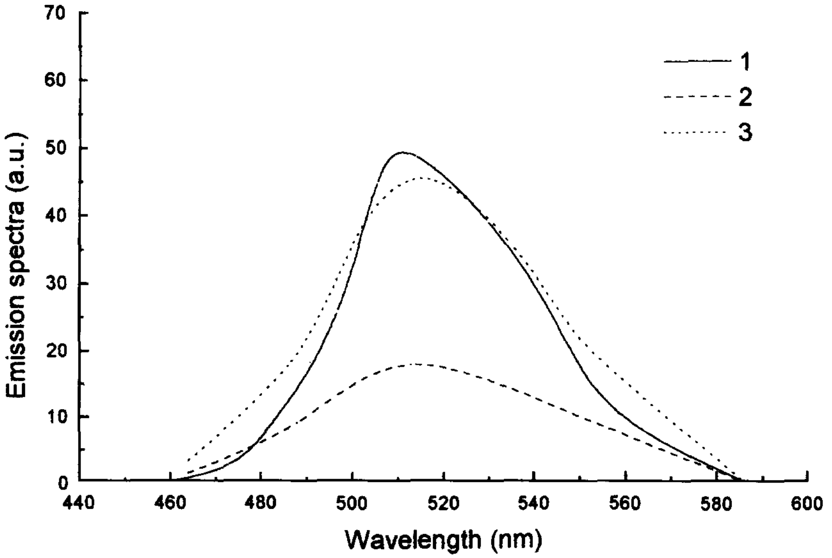


Fig. 5. Emission spectra of UV-irradiated samples of 1.3×10^{-5}M ethanol solution of naphthoxazine in the presence of an equimolar quantity of (1) Fe^{3+}, (2) Cu^{2+} and (3) Cr^{3+}.

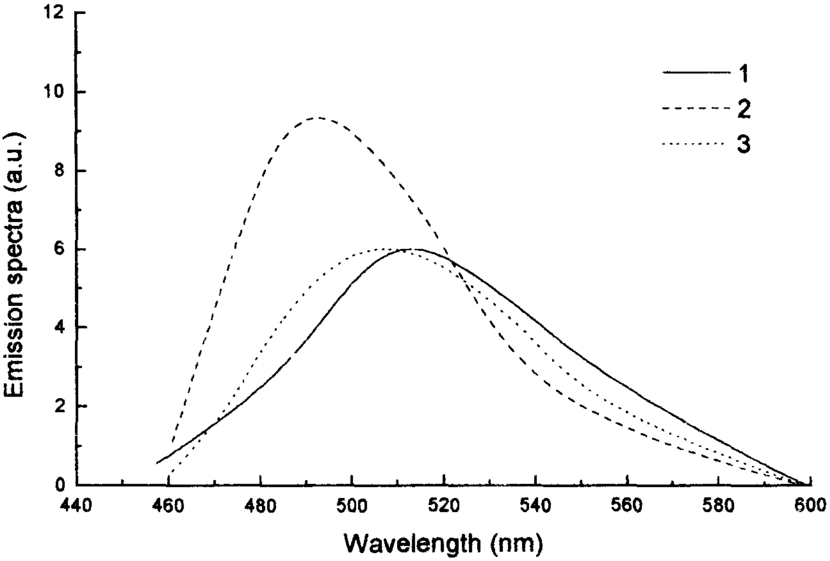


Fig. 6. Emission spectra of UV-irradiated samples of naphthoxazine in the presence of an equimolar quantity of: (1) Fe^{3+} (1.1×10^{-5} M), (2) Cu^{2+} (1.1×10^{-5} M) and (3) Cr^{3+} (5.5×10^{-6} M) in acetonitrile.

spectra then measured again, the obtained spectra remained unchanged because of the irreversible photo-transformation of naphthoxazine in the presence of Fe(III).

Irradiation of the same systems in methanol and acetonitrile confirmed the irreversible character of the phototransformations of naphthoxazine. Completely analogous photochemical reactions took place in these solvents as shown by characterization of their absorption spectra. The electronic absorption spectra showed the same band at 440 nm with an isosbestic point at 380 nm upon 5 to 15 min UV-irradiation of naphthoxazine at 20°C in methanol in the presence of an equimolar quantity of Cu(II).

Similar spectral changes were observed as a result of the thermal reaction of 1.6×10^{-4} M naphthoxazine with Cu(II) in acetonitrile, and with Fe(III) in methanol.

The photo-transformation was not observed in the presence of Zn(II), and the photochromic behaviour of the net compound was preserved in all solvents used.

3.2 Fluorescence spectra

A quite interesting property of the product above is the ability to give a strong yellow luminescence. The products of previously reported

TABLE 1
Values of λ_{ex} in All Experiments with Fe^{3+}, Cu^{2+}, Cr^{3+} and Fluorescein

Solvent	*FeL*	*CuL*	*CrL*	*Fl*
C_2H_5OH	439	438.5	439	490.5
CH_3OH	434	433	427	496
CH_3CN	440.5	450	452.5	—

TABLE 2
Quantum Yields of the Fluorescing Products in Different Solvents, Calculated with Fluorescein as a Reference

Solvent	*FeL*	*CuL*	*CrL*
C_2H_5OH	0.23	0.15	0.21
CH_3OH	0.25	0.53	0.07
CH_3CN	0.23	0.05	0.58

naphthoxazine photo-transformations do not exhibit this property [6–8], and to our knowledge the compounds discussed in the present paper constitute the first example of stable luminescent products obtained upon UV-irradiation of naphthoxazine, provided transition metal ions are present. The emission spectra of the species obtained in ethanol, methanol and acetonitrile solutions are strong, and we have succeeded in determining the quantum yields of these solutions relative to Fluorescein.

The emission spectra of the UV-irradiated samples of naphthoxazine in the presence of 10^{-5}–10^{-6} M Fe^{3+}, Cu^{2+} and Cr^{3+} in methanol are depicted in Fig. 4, together with the emission spectrum of Fluorescein used as a standard. Figure 5 illustrates the fluorescence spectra obtained under the same conditions in ethanol. The corresponding spectra in acetonitrile are depicted in Fig. 6.

The excitation wavelength (λ_{ex}) values are given in Table 1. Table 2 summarizes all calculated values of the fluorescence quantum yields relative to Fluorescein.

The data reported in Table 2 reflect the influence of the solvent on the quantum yields and indicate that the nature of the metal ions affects the quantum yield in solution, but does not strongly modify the emission properties of the species.

4. CONCLUSIONS

1,3,3-Trimethylspiro(indoline-2,3′-(3H)naphth(2,1-6)(1,4) oxazine) underwent photochromic reaction and irreversible photo-transformation upon

UV-irradiation in the presence of 10^{-5}–10^{-6} M concentrations of Cu(II), Cr(III), and Fe(III), displaying an intense yellow emission. The compound also showed a similar thermal reaction with Cu(II) in acetonitrile, and with Fe(III) in methanol. The photo-transformation was not observed in the presence of Zn(II), and the photochromic behaviour of the net compound was preserved in all solvents used.

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