

Research Letter

The Effect of Tb and Sm Ions on the Photochromic Behavior of Two Spiropyrans of Benzoxazine Series in Solution

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The photochromism of [7'-hydroxy-8'-formyl-3-methyl-4-oxospiro[1,3-benzoxazin-2,2'-[2H-1]benzopyran], SP(I), [7'-hydroxy-8'-formyl-3-benzyl-4-oxospiro[1,3-benzoxazin-2,2'-[2H-1]benzopyran] SP(II) and their coordination with Tb³⁺ and Sm³⁺ ions have been studied in DMF. UV/vis induced-color development due to heterolytic bond cleavage of SP(I) and SP(II) is greatly influenced by complexation with the lanthanide ions. The irradiation-induced color enhancement due to ring opening and thermal decoloration of the open forms of SP(I), SP(II) follows first-order kinetics. Physical characteristics of the studied systems such as colorability and relaxation time of thermal bleaching parameters were determined. Moreover, light-energy transfer-induced luminescence of lanthanide ions via coordination with the two spirobenzoxazines was monitored.

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1. INTRODUCTION

Recently, many profitable applications of photochromic dyes, particularly spirooxazines, either as passive or active devices, have been proposed [1–13].

In some cases, it has been reported that thermal equilibrium between the closed (colorless form) and opened form (colored merocyanine quinonoid form) is affected by the change in solvent polarity [14, 15], since polar solvents promote the formation of the colored form at room temperature in the absence of light. The equilibrium between both forms is strongly displaced upon irradiation to the side of open-chain colored photomerocyanine and spontaneously converts to the colorless spiro form to reach thermal equilibrium immediately after removing the light [15]. The metal-ion coordination ability of photochromic spirocyclic compounds adequately substituted is of a great interest and is being the topic of several recent studies [12, 13]. Search for molecules possessing better performances is valuable and it is important to continue to explore this subject. Here, we report on the possibility to stabilize the colored open forms of the recently synthesized spirobenzoxazines SP(I) and SP(II) toward thermal bleaching by coordination with Tb³⁺ and Sm³⁺ ions in polar DMF solvent. Moreover, the expected light-energy transfer-induced characteristic lumines-

cence of lanthanide ions via complexation with the merocyanine quinonoid open forms of the two spirobenzoxazines will be explored.

2. EXPERIMENTAL

2.1. Materials

The metal chlorides (Sigma-Aldrich, 99.99%) were used as received. The synthesis of [7'-hydroxy-8'-formyl-3-methyl-4-oxospiro [1,3-benzoxazin-2,2'-[2H-1]benzopyran], SP(I), [7'-hydroxy-8'-formyl-3-benzyl-4-oxospiro [1,3-benzoxazin-2,2'-[2H-1] benzopyran] SP(II) were described previously [16, 17]. Spectroscopic pure grade solvents were used.

2.2. Instruments

UV-visible absorption spectra were recorded on a range (200–650 nm) using λ -Helios SP Pye-Unicam spectrophotometer and/or Ocean Optics US4000 fiber optics spectrophotometer. Continuous irradiation experiments were performed using a 150 W xenon arc lamp (PTI-LPS-220 Photon Technology International, USA) operated at 70 W. Photochemical reactions were carried out in the spectrophotometric quartz cell with a homogeneously spread light on

TABLE 1: The experimental values of absorption maxima of SP and its open form (λ_{SP} , λ_{open}), SP ring opening rate constant (k_1), thermal open form ring closure rate constant (k_{-1}), equilibrium constant of the reversible reaction (K_e), relaxation time of open form ($\tau_{open-SP}$), and colorability in DMF at 295 ± 1 K. Error limits of the kinetics parameters are in the order of about 5%.

Compound	λ_{SP} (nm)	λ_{open} (nm)	$k_{-1} \times 10^3$ (min ⁻¹)	$k_1 \times 10^3$ (min ⁻¹)	$\tau_{open-SP}$ (min)	K_e	Colorability M ⁻¹ cm ⁻¹ × 10 ⁻²
SP(I)	276	409	3.16	192	316	60	7.36
	370						
SP(II)	276	404	7.96	529	125	66	1.30
	370						

the cell window to avoid stirring. Measurements were made on aerated solutions.

Fluorescence spectra were measured in the range (290–750 nm) using Shimadzu RF5301 (PC) spectrofluorophotometer.

2.3. Kinetics measurements

The ring-closure reaction after photocoloration was monitored directly after removal of light at room temperature. First-order rate constants were obtained from the linear $\ln A$ versus time descending curves. By extrapolation of the obtained $\ln A/t$ plots to zero time, the absorbance A_0 of the open form or its complexes at $t = 0$ was related to their “colorabilities” [18–21] using the expression ($A_0/c_{SP}b$), where c_{SP} is the initial concentration of SP and b is the optical path length.

3. RESULTS AND DISCUSSION

3.1. Absorption spectra

The absorption spectrum of SP(I) and SP(II) displayed two bands at 276 and 370 nm, Table 1, which are solvent independent (methanol, ethanol, and DMF solvents were tried). UV light-induced color development of both compounds was only remarkably observed in DMF solution.

Upon irradiation of 60 μ M SP(I) solutions, the absorption spectra at 276 nm and 370 nm decreased and a new band at 409 nm appeared and its intensity increased by increasing the irradiation time. Addition of lanthanide chloride solution in DMF showed no change in the absorption band of SP(I) in the dark. However, irradiation of the (1 : 1 molar ratio) solution of SP(I) in presence of Tb³⁺ and Sm³⁺, respectively, led to a new band at 412 nm and 414 nm, Figure 1. Similar behavior observed for SP(II) in presence of lanthanide ions (Tb³⁺, Sm³⁺) in DMF, Table 1. Thermal bleaching was monitored spectrophotometrically. First-order kinetics rate constants of the reversible close \rightleftharpoons open reactions (see Scheme 2) were determined graphically (Figure 2, as an example) and data are collected in Tables 1 and 2.

Color development rate constant (k_1) of the photomercyanine form and the thermal bleaching rate constant (k_{-1}) are used to estimate the equilibrium constant ($K_e = k_1/k_{-1}$) of the forward photochemical ring opening reaction and the backward thermal bleaching one. The results of K_e are summarized in Table 1 for the SP(I) and SP(II). Data for Ln³⁺-SP (I and II) appear in Table 2. The relaxation time of the open

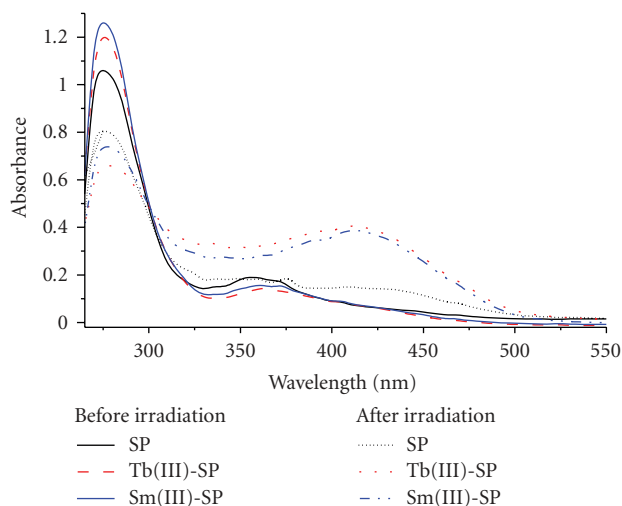
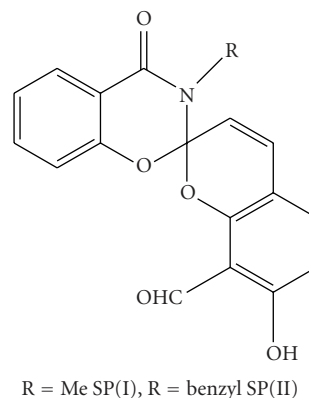
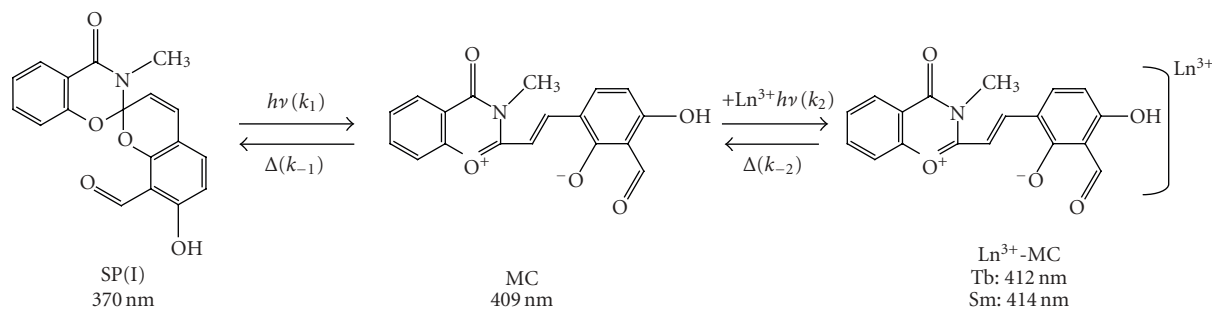


FIGURE 1: UV/vis absorption spectra of SP(I) and its complexes with Tb³⁺ and Sm³⁺ ions in DMF before and after light irradiation ([SP(I)] = [Ln³⁺] = 60 μ M) (at 295 ± 1 K).



SCHEME 1

form ($\tau_{open-SO}$) given in Table 1 was obtained from the first-order rate constant using the expression $\tau = 1/k_{-1}$ [18–21]. The obtained relaxation time of SP and its complexes with lanthanide ions are relatively high [22], reflecting highly stabilized color form. The colored open MC form of the methyl-substituted SP(I) is more stable than that of the bulky benzyl derivative reflecting the influence of the constituent’s nature and size. Moreover, the presence of the lanthanide ions



SCHEME 2: Illustration of the reversible structural transformation of SP to the MC form in response to light in the absence and presence of Ln^{3+} metal ion.

TABLE 2: The experimental values of absorption, M(III)-SP formation rate constant (k_2), thermal ring closure rate constant (k_{-2}), equilibrium (K_e) constant of the reversible reaction, relaxation time $\tau_{\text{M(III)-open-SP}}$, and colorability in DMF at 295 ± 1 K. Error limits of the kinetics parameters are in the order of about 5%.

Complexes	$\lambda_{\text{open-M(III)}} \text{ (nm)}$	$k_{-2} \times 10^3 \text{ (min}^{-1}\text{)}$	$k_2 \times 10^3 \text{ (min}^{-1}\text{)}$	$\tau_{\text{M(III)-open-SP}} \text{ (min)}$	K_e	Colorability $\text{M}^{-1}\text{cm}^{-1}10^{-2}$
Tb(III)-SP(I)	412	4.04	661	247	163	7.02
Sm(III)-SP(I)	414	4.55	258	219	56	7.85
Tb(III)-SP(II)	412	8.16	327	122	40	7.73
Sm(III)-SP(II)	414	4.77	225	209	47	7.72

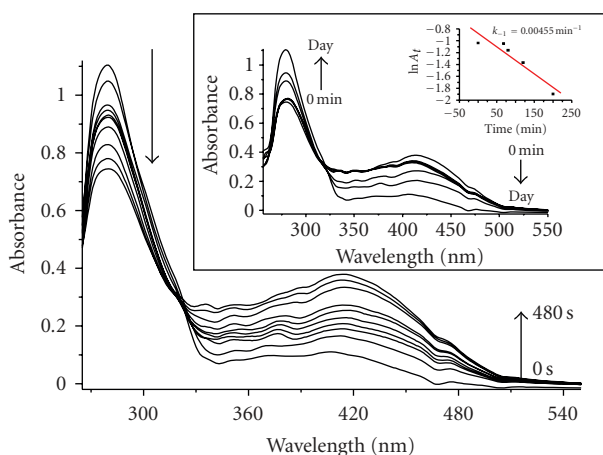


FIGURE 2: Effect of time of irradiation on the UV/vis absorption spectra of DMF solution of a mixture of $60 \mu\text{M}$ Sm^{3+} and $60 \mu\text{M}$ SP(II) (inset back ring closure reaction and the first-order plots of thermal decoloration of SP in dark) after UV irradiation at 295 ± 1 K.

generally enhances the colorability of both SP derivatives reflecting the result of coordination with the MC forms.

Benzyl group substituent in SP(II) relative to the smaller methyl group substituent in SP(I) accelerates both rates of photocoloration and thermal bleaching as reflected in the higher values of the rate constants for SP(II) shown in Table 1. A significant decrease in relaxation time and colorability of the open form (MC quinonoid form) of the SP(II) was also induced due to the effect of more bulky benzyl group. Generally speaking, the presence of Ln^{3+} metal ions induced more bathochromic shift in the absorption band of

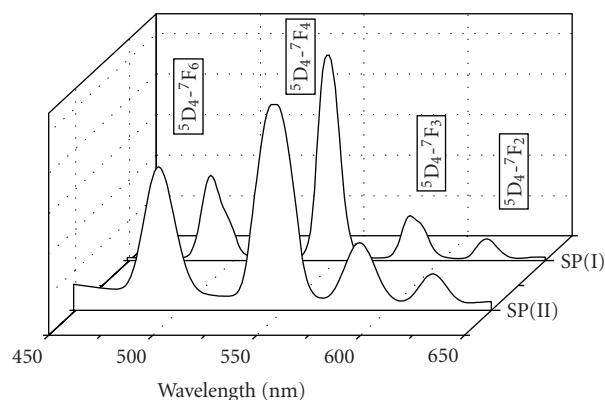


FIGURE 3: The sensitized luminescence spectra of $60 \mu\text{M}$ Tb^{3+} in the presence of $60 \mu\text{M}$ SP(I,II) in DMF at room temperature.

the MC form, enhance colorability and relaxation time. Exception is the case of Tb^{3+} -SP(I) complexes, where colorability and relaxation time slightly decrease.

3.2. Luminescence spectra of lanthanide complexes

The ligand-centered luminescence was not observed in Tb^{3+} and Sm^{3+} complexes, whereas the typical characteristic narrow emission bands of the Tb^{3+} ($^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^7\text{F}_5$, $^7\text{F}_4$, and $^7\text{F}_3$) and Sm^{3+} ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$, $^6\text{H}_{7/2}$, $^6\text{H}_{9/2}$, and $^6\text{H}_{11/2}$) (at $\lambda_{\text{ex}} = 360 \text{ nm}$) ions can be detected in polar protic solvents upon excitation of the SP absorption band (see Figure 3). This indicates efficient energy transfer from the excited open MC form to the Ln^{3+} ions having lower energy levels [23].

3.3. Conclusion

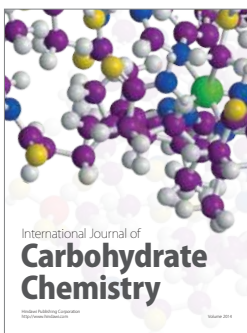
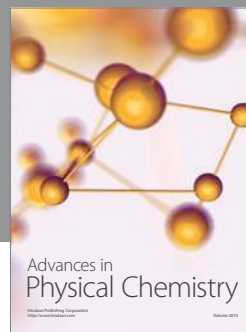
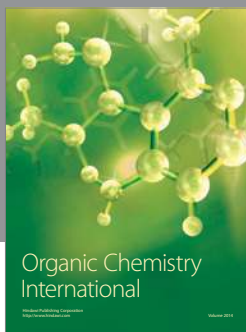
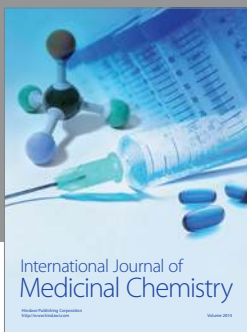
The substituent nature and the presence of lanthanide metal ions in solution of recently synthesized photochromic spirobenzopyrans of benzoxazine series induced significant changes in its photochromic parameters. It could be generally concluded that the presence of lanthanide ions significantly enhances the rate constants of both color development of the light-induced formation of the open merocyanine-like quinonoid species and the rate constant of its thermal bleaching. In most cases, colorability is enhanced. Moreover, strong characteristic sensitized luminescence of the lanthanide ions was observed due to efficient population of its emissive states via energy transfer from the open forms of the spirobenzoxazines.

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