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Short communication

Synthesis and complexation mechanism of europium ion (Eu^{3+}) with spiro[indoline-phenanthrolineoxazine]

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Abstract

A series of spirooxazines containing phenanthroline were synthesized; the opened forms of such molecules have two potential metal-binding sites. By studying the photochromic and thermochromic properties of the complexes of europium ion (Eu^{3+}) with the photomerocyanine of spirooxazine, the complexation mechanism and metal-binding site of Eu^{3+} were determined.

Keywords: Complexation; Spirooxazine; Spiro[indoline-phenanthrolineoxazine]; Photochromism; Thermochromism; Europium ion (Eu^{3+})

1. Introduction

Organic photochromic molecules, including spiropyran [1–3] and spirooxazine [4,5], are the subjects of intense research due to their application as memories in optical systems [6–8]. In recent years, much attention has been given to the isomerization of spiropyran and spirooxazine that occurs under the action of certain substrates, for example, metal ions [9–18].

Compared with conventional spiro[indoline-naphthooxazine] and spiro[indoline-benzooxazine] derivatives, spiro[indoline-phenanthrolineoxazines] contain two more nitrogen atoms in the phenanthrolineoxazine connected to the oxazine moiety which is of interest from the viewpoint of complexation with metal ions.

Previous investigations have shown that in the case of conventional spirooxazines, metal ion complexes were formed by the metal ion coordinating with the photomerocyanine form of the dye. In the case of spiro[indoline-phenanthrolineoxazines], a ligand is incorporated into the spirooxazine framework and the metal ion can, therefore, become bound to a ligand-functionalized group in spirooxazine. Hence, the photomerocyanine (PMC) could have two potential metal-binding sites, as shown in Scheme 1, and the binding sites of the PMC may differ, depending on the particular metal ion.

In this paper, a series of spirooxazines (SPO) containing the phenanthroline-functional group (as shown in Scheme 2) have been synthesized. The opened forms of such molecules have two potential metal-binding sites. By studying the photochromic and the thermochromic properties of the complexes formed by europium ion (Eu^{3+}) coordinated with PMC, the complexation mechanism and metal-binding sites were determined.

2. Experimental

2.1. Materials

2.1.1. General procedure for the preparation of spirooxazines *1–4*

5-Hydroxy-6-nitroso-1,10-phenanthroline [19,20] (2.3 g, 10 mmol) was dissolved in anhydrous EtOH (180 mL) and refluxed for 30 min. The corresponding substituted 1,2,3,3-tetramethyl-3*H*-indolium iodide [21] (12 mmol) in anhydrous

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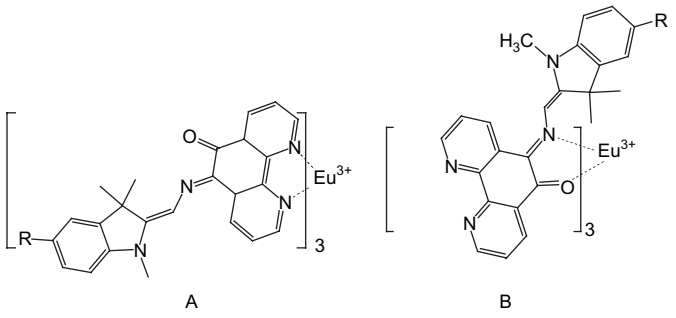
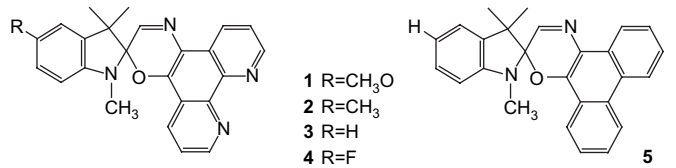


Scheme 1. Complexation species in PMC of spiro[indoline-phenanthrolineoxazines].

EtOH (30 mL) was mixed with triethylamine (6.1 g, 60 mmol) and the mixture was then added over a period of 30 min to the above solution of 5-hydroxy-6-nitroso-1,10-phenanthroline. After refluxing for 20 h, the reaction mixture was cooled and filtered; the ensuing solution was condensed under reduced pressure. The residue was purified twice using column chromatography on silica gel, firstly using petroleum/ethyl acetate (5:2) and secondly using chloroform as eluents. Compounds **1**–**4** were produced by recrystallization from EtOH. The structures were confirmed by ^{1}H NMR spectroscopy, mass spectroscopy, and elemental analysis.

*2.1.1.1. Compound **1***. ^{1}H NMR (δ, $CDCl_3$, 500 MHz): 9.14 (dd, 1H, $J = 1.5$, 4.5 Hz), 9.08 (dd, 1H, $J = 1.5$, 4.0 Hz), 8.96 (dd, 1H, $J = 1.5$, 8.5 Hz), 8.41 (dd, 1H, $J = 1.5$, 8.5 Hz), 7.84 (s, 1H), 7.67 (dd, 1H, $J = 4.5$, 8.5 Hz), 7.53 (dd, 1H, $J = 4.5$, 8.0 Hz), 6.76 (dd, 1H, $J = 2.5$, 8.0 Hz), 6.75 (d, 1H, $J = 2.5$ Hz), 6.50 (d, 1H, $J = 8.0$ Hz), 3.82 (s, 3H), 2.72 (s, 3H), 1.41 (s, 3H), 1.36 (s, 3H). MS *m/z* (%) 410 (55), 395 (30), 379 (7), 281 (12), 267 (7), 249 (8), 222 (7), 221 (8), 203 (35), 191 (35), 189 (42), 188 (100), 174 (63), 160 (27), 145 (18), 132 (27), 115 (16), 102 (15) .Anal. Calcd for $C_{25}H_{23}N_4O_2$: C, 75.77; H, 5.30; N, 14.73; found: C, 75.85; H, 5.20; N, 14.61.

*2.1.1.2. Compound **2***. ^{1}H NMR (δ, $CDCl_3$, 500 MHz): 9.12 (dd, 1H, $J = 1.5$, 4.5 Hz), 9.07 (dd, 1H, $J = 1.5$, 4.5 Hz), 8.96 (dd, 1H, $J = 1.5$, 8.5 Hz), 8.41 (dd, 1H, $J = 1.5$, 8.5 Hz), 7.83 (s, 1H), 7.66 (dd, 1H, $J = 4.5$, 8.5 Hz), 7.51 (dd, 1H, $J = 4.5$, 8.5 Hz), 7.02 (d, 1H, $J = 7.5$ Hz), 6.92 (s, 1H), 6.49 (d, 1H, $J = 8.0$ Hz), 2.74 (s, 3H), 2.35 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H). MS *m/z* (%): 394 (56), 379 (22), 222 (5), 209 (9), 183 (8), 173 (100), 158 (46), 115 (11).



Scheme 2. Structures of spirooxazines containing phenanthroline **1**–**4** and spirooxazine containing phenanthrene **5**.

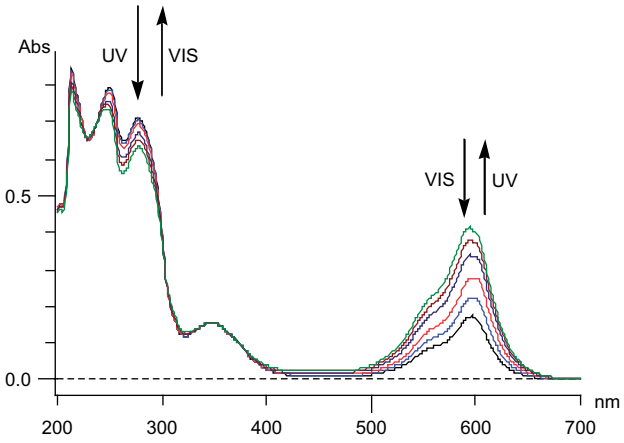


Fig. 1. Absorption spectral changes of compound **3** (2.2×10^{-5} M) in methanol under irradiation with 254-nm and 600-nm light.

Anal. Calcd for $C_{25}H_{22}N_4O$: C, 79.12; H, 5.62; N, 14.20; found: C, 79.01; H, 5.70; N, 14.28.

*2.1.1.3. Compound **3***. ^{1}H NMR (δ, $CDCl_3$, 500 MHz): 9.11 (dd, 1H, $J = 1.5$, 4.5 Hz), 9.06 (dd, 1H, $J = 1.5$, 4.0 Hz), 8.95 (dd, 1H, $J = 1.5$, 8.5 Hz), 8.39 (dd, 1H, $J = 1.5$, 8.5 Hz), 7.83 (s, 1H), 7.65 (dd, 1H, $J = 4.5$, 8.5 Hz), 7.49 (dd, 1H, $J = 4.0$, 8.5 Hz), 7.23 (t, 1H, $J = 7.5$ Hz), 7.09 (d, 1H, $J = 7.0$ Hz), 6.92 (t, 1H, $J = 7.5$ Hz), 6.58 (d, 1H, $J = 7.5$ Hz), 2.76 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H), MS *m/z* (%): 380 (35), 365 (20), 222 (5), 209 (8), 169 (6), 159 (100), 144 (37), 115 (9), 103 (5), 77 (5). Anal. Calcd for $C_{24}H_{20}N_4O$: C, 75.77; H, 5.30; N, 14.73; found: C, 75.86; H, 5.43; N, 14.60.

*2.1.1.4. Compound **4***. ^{1}H NMR (δ, $CDCl_3$, 500 MHz): 9.13 (dd, 1H, $J = 1.5$, 4.5 Hz), 9.07 (dd, 1H, $J = 1.5$, 4.5 Hz), 8.95 (dd, 1H, $J = 1.5$, 8.0 Hz), 8.38 (dd, 1H, $J = 1.5$, 8.5 Hz), 7.83 (s, 1H), 7.67 (dd, 1H, $J = 4.5$, 8.5 Hz), 7.48 (dd, 1H, $J = 4.5$, 8.5 Hz), 6.91 (td, 1H, $J = 2.5$ Hz), 6.63 (dd, 1H, $J = 2.5$, 8.0 Hz), 6.47 (dd, 1H, $J = 4.0$, 8.5 Hz), 2.73 (s, 3H), 1.40 (s, 3H), 1.34 (s, 3H) MS *m/z* (%) 398

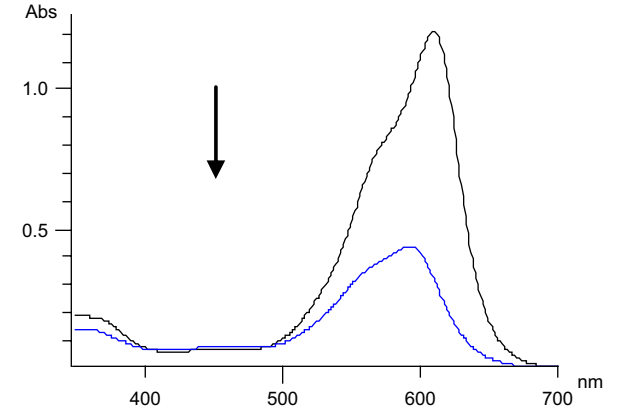


Fig. 2. Absorption spectra of compound **1** (2.2×10^{-5} M) in methanol before (black) and after (blue) addition of Eu^{3+} in 1 min.

Table 1
Absorption spectral and kinetic data of compounds **1**–**4** with and without addition of Eu^{3+} in methanol with UV light irradiation

Entry	R	$\lambda_{max\ opened\ form}$ (nm)		k ($\times 10^4\ s^{-1}$)	
		Without Eu^{3+}	With Eu^{3+}	Without Eu^{3+}	With Eu^{3+}
1	CH_3O	610	593	41	13
2	CH_3	601	584	60	28
3	H	591	579	98	38
4	F	591	578	170	42

(90), 383 (39), 367 (4), 222 (8), 209 (12), 188 (8), 177 (100), 162 (s, 3H), 140 (7) FT/IR (cm^{-1} KBr): 3417, 3017, 2948, 2866, 2816, 1618, 1599, 1560, 1489, 1433, 1409, 1360, 1319, 1267, 1198, 1109, 1077, 1036, 1005, 929, 871, 808, 740. Anal. Calc.: $C_{24}H_{19}FN_4O$: C, 72.35; H, 4.81; F, 4.77; N, 14.06; found: C, 72.52; H, 4.96; N, 14.51.

Compound **5** was purchased from Aldrich, and was used without further purification.

2.2. Absorption spectral measurements

For spectral measurements, solutions of spirooxazines **1**–**5** were prepared in methanol at a concentration of 2×10^{-5} mol/L. Absorption spectra were recorded using a Hitachi U-3010 spectrophotometer at room temperature (298 K).

3. Results and discussion

For compound **3**, continuous UV irradiation at 254 nm resulted in the conversion of the colorless form to the colored photomerocyanine ($\lambda_{max} = 591$ nm). When the PMC was irradiated with 600 nm light, the concentration of the spirooxazine form increased (Fig. 1). In the case of compound **1**, under UV irradiation, the addition of Eu^{3+} caused the intensity of the absorption centered at 610 nm, which was the absorption of PMC, to decrease immediately and to shift from 610 nm to 593 nm (Fig. 2), a blue shift of 17 nm. The new band can be

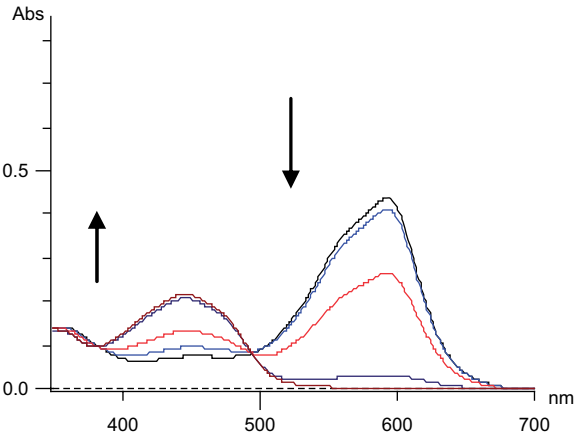


Fig. 3. Absorption spectral changes of 2.2×10^{-5} M compound **1** in methanol after UV irradiation in the presence of Eu^{3+} with time (min): 0, 120, 330, 1030, 1710.

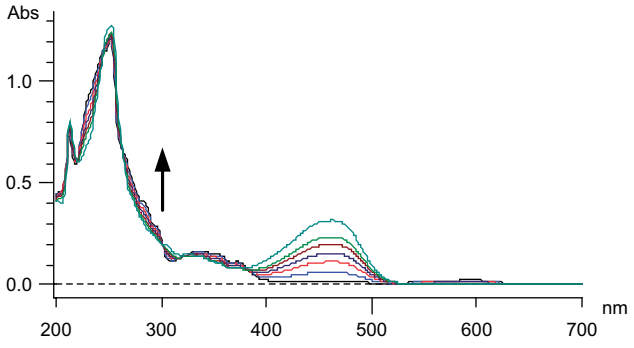


Fig. 4. Absorption spectral changes of 2.2×10^{-5} M compound **5** in methanol in the presence of Eu^{3+} with time (min): 20, 45, 60, 80, 100 and 300 min.

attributed to the absorption of the complex formed by PMC having coordinated with Eu^{3+}**A** (PMC–Eu^{3+}).

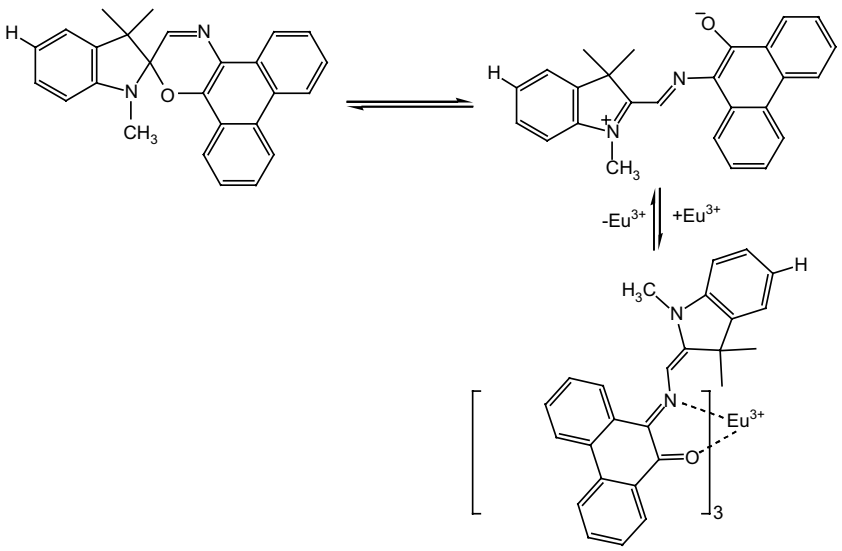
Similar findings were obtained for the other compounds used; the data are summarized in Table 1.

A polar solvent and an electron donating group at the 5 position of the indole moiety imparted a bathochromic shift of the λ_{max} of PMC and resulted in stabilization of the PMC, as shown by reduced thermal fading rate (Table 1). This may be due to the electron donating group increasing the electron density of the nitrogen atom of the indole moiety through the conjugated system, which thus stabilized the colored form of the PMC and the complex **A**.

However, the complex thus formed is unstable and can be thermally transformed to another stable form in the dark, as evidenced by the appearance of a new absorption band centered at ~450 nm (Fig. 3), indicating the formation of the new complex, **B** (PMC–Eu^{3+}). In order to further determine the metal-binding sites and the complexation mechanism, the phenanthrene-containing spirooxazine **5**, which has only one site for metal coordination, was used for comparison. Under UV irradiation, the addition of $EuCl_3$ imparted to compound **5** an intense absorption band centered at ~460 nm (Fig. 4), which was similar to the absorption of the new complex **B**. Since compound **5** has only one metal-binding site, the complex was the only product. It is reasonable to assign the band centered at ~460 nm to the complex in which the N atom and the O atom of the PMC moiety act as coordination sites (as shown in Scheme 3).

Comparing the absorption spectra of the **B** complexes of compounds **1**–**4** with that of compound **5**, similar, new absorption bands centered at ~450 nm appeared. Therefore the complexation mechanism of compounds **1**–**4** is as follows.

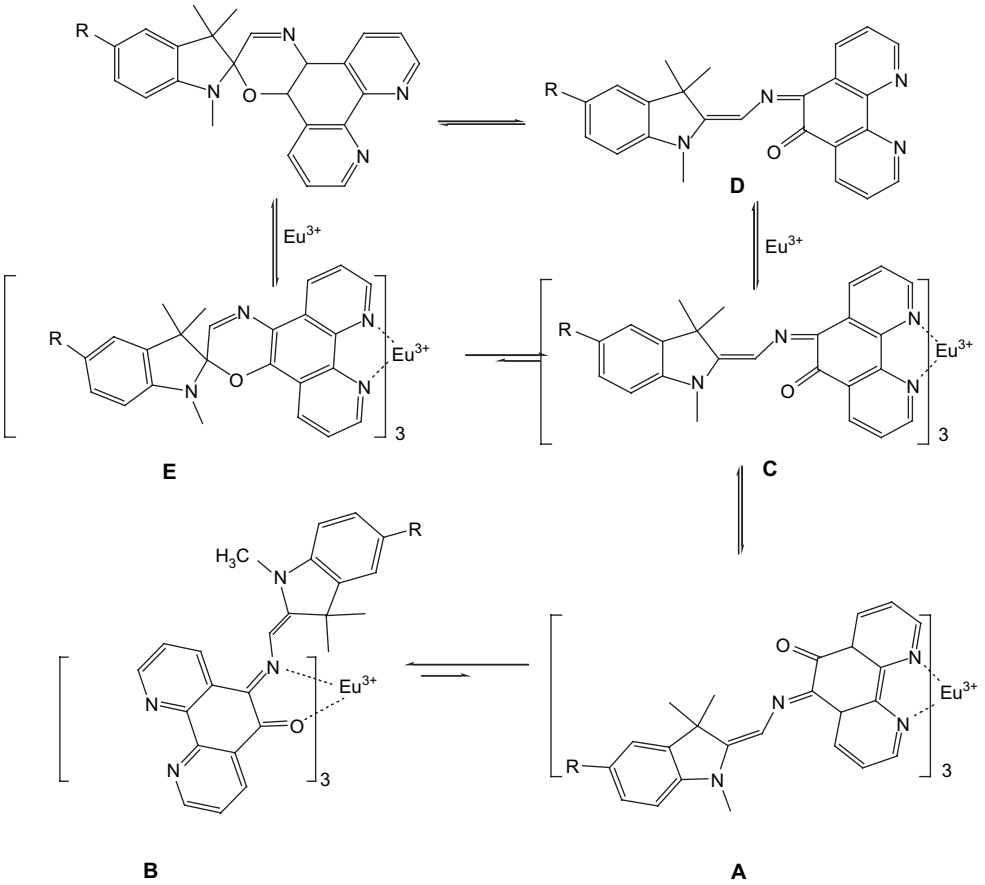
Under UV irradiation, the addition of Eu^{3+} caused the phenanthroline nitrogen atoms of the opened form of PMC to coordinate with Eu^{3+}, and formed the complex **A**, the absorption of which was around ~590 nm. The complex **A** was unstable and could transform to another stable complex **B** in the dark, as evidenced by the appearance of an absorption band centered at ~450 nm and a decrease of the absorption around ~590 nm. The reason may be that before the addition of Eu^{3+}, the closed form of the SPO and the most stable opened form **D** (PMC) equilibrated in the solution. The



Scheme 3. Complexation mechanism of compound **5**.

position of the lone electron pairs of the oxygen and nitrogen atoms of the opened form **D** (PMC) did not permit coordination with the metal ion. Thus, when added to the solution of compound **1**, the metal ion Eu^{3+} first coordinated with the phenanthroline nitrogen atoms and formed complex **C** (the dynamic product).

The space between the N atoms of the phenanthroline moiety is rigid and suitable for the metal ion of smaller radius, for example a transitional metal ion [16]. While for the rare earth metal ion, Eu^{3+}, the radius is 1.03 Å, this being larger than that of transitional metal ions, which is ~0.65 Å. Hence, the space between the nitrogen atoms of the phenanthroline



Scheme 4. Complexation mechanism of compound **1**–**4**.

moiety is not suitable for the large radius metal ion Eu^{3+}. Thus the complex **C** formed between them was not stable.

The chain between the oxygen and nitrogen atoms of the opened PMC is flexible, and the complex **B** of Eu^{3+} with the lone electron pairs of oxygen and nitrogen atoms of the opened form PMC is more stable than complex **A**. Hence, the complex **C** could transform via complex **A** to the stable complex **B** (the thermodynamic product) slowly (Scheme 4). Because of the coordination of metal ions with the lone electron pairs of oxygen and nitrogen atoms of the opened form PMC, the extension of the π-conjugation system was slightly distorted, which is why the absorption of complex **B** was ~450 nm, and blue shifted from that of the complex **A**, which was ~590 nm.

Upon the addition of Eu^{3+}, the phenanthroline nitrogen atoms of the closed form SPO could also coordinate with $Eu^{3+}$and form the complex **E** (SPO–Eu^{3+}). While for the opened form PMC, extension of the π-conjugation system resulted in the positive electrical charge of Eu^{3+} being distributed throughout the whole molecule, which improved the stability of the **C** (PMC–Eu^{3+}) complex greatly. Consequently, the complexation ability of PMC is much stronger than that of SPO. When added to a solution of compound **1**, the Eu^{3+} metal ion mainly coordinated with the phenanthroline nitrogen atoms of the opened form of PMC and absorption of the SPO–Eu^{3+} complex was not observed.

4. Conclusions

A series of phenanthroline-containing spirooxazines were prepared. The photochromic and thermochromic behaviour of phenanthroline-containing spirooxazines and their colored form, in the presence of the Eu^{3+} metal ion were also studied. It was found that in the presence of Eu^{3+}, the nitrogen atoms in the phenanthroline moiety of the opened form PMC first coordinated with $Eu^{3+}$and formed complex **A**, which had an absorption band ~590 nm. Complex **A** was not stable and could be transformed to another stable complex **B** with an absorption band at ~450 nm. In addition, the **R** substituent has a remarkable effect on the absorption spectra of both PMC and PMC–Eu^{3+}. An electron-donating group in the indole moiety induced a bathochromic shift of the absorption maximum and an electron-withdrawing group caused a blue shift.

Acknowledgement

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