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Short communication

Positive and negative photochromism of novel spiro[indoline-phenanthrolinoxazines]

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Abstract

A series of new spirooxazines (SPO) containing phenanthroline were synthesized and their photochromic properties were investigated. Photoisomerization of the spirooxazine was facilitated by electron donating groups in the indole moiety, a polar solvent and metal complexation. Their complexes $(PMC)_3Ni^{2+}$ were very stable at room temperature and exhibited excellent negative photochromism.

Keywords: Spirooxazine; Positive photochromism; Negative photochromism; Complexation; Ni^{2+}

As the application of photochromic compounds in optical devices is of great interests, various photochromic compounds have been prepared and examined [1–4]. Spirooxazine (SPO) derivatives are well-known photochromic compounds that isomerize to the corresponding photomerocyanine (PMC) form upon UV irradiation; the PMC can be reversed to SPO upon visible irradiation or by heating [5–7]. Recently, the coordination of photochromes with metal ions attracted great interests [8–12]; the metal ions were found to influence photochromism of the metal complexes, some of which exhibited negative photochromism, which may bode well for potential new applications for photochromic compounds. However, investigations in this field are few [8–11].

Compared with conventional spiro[indoline-naphthoxazines], spiro[indoline-phenanthrolinoxazines] contain two more nitrogen atoms in the phenanthroline connected to the oxazine moiety; the presence of the nitrogen atoms provides interest from the viewpoint of complexation with metal ions.

For conventional spirooxazine, complexes are formed by the metal ion coordinating with the photomerocyanine form of the dye, leading to a non-photochromic metal complex that exists only transiently [12]. In the case of spiro[indoline-phenanthrolinoxazines], a ligand is incorporated into the spirooxazine framework and the metal ion is, therefore, bound to a ligand-functionalized group in spirooxazine and remains bound in both the opened and the closed forms of the spirooxazine. When the metal complex of the closed form is irradiated with UV light, it can transfer to a colored form (shown in Scheme 1), which differs to that of conventional metal complexes of spirooxazine. Some of the opened form metal complexes of spiro[indoline-phenanthrolinoxazines] are quite stable at room temperature [13], which provides an opportunity for exploring the negative photochromic behaviours of photomerocyanine complexes.

This paper concerns the syntheses of a series of 5-substituted 1,3,3-trimethyl-1,3-dihydrospiro[2*H*-indole-2,2′-[2*H*]bipyrido[3,2-*f*][2,3-*h*][1,4]benzoxazine] (**a**–**f**) and the studies of their photochromic behaviours. UV–vis spectrophotometry revealed that the substituents, solvents and the metal ion Ni^{2+} each had a marked effect on the positive photochromism of the spirooxazines; in addition, the complex was found to exhibit good negative photochromism. Spirooxazines **a**–**f** were prepared by condensation of the corresponding 5-substituted 1,2,3,3-tetramethyl-3*H*-indolenium iodide (Fischer's procedure [14]) and

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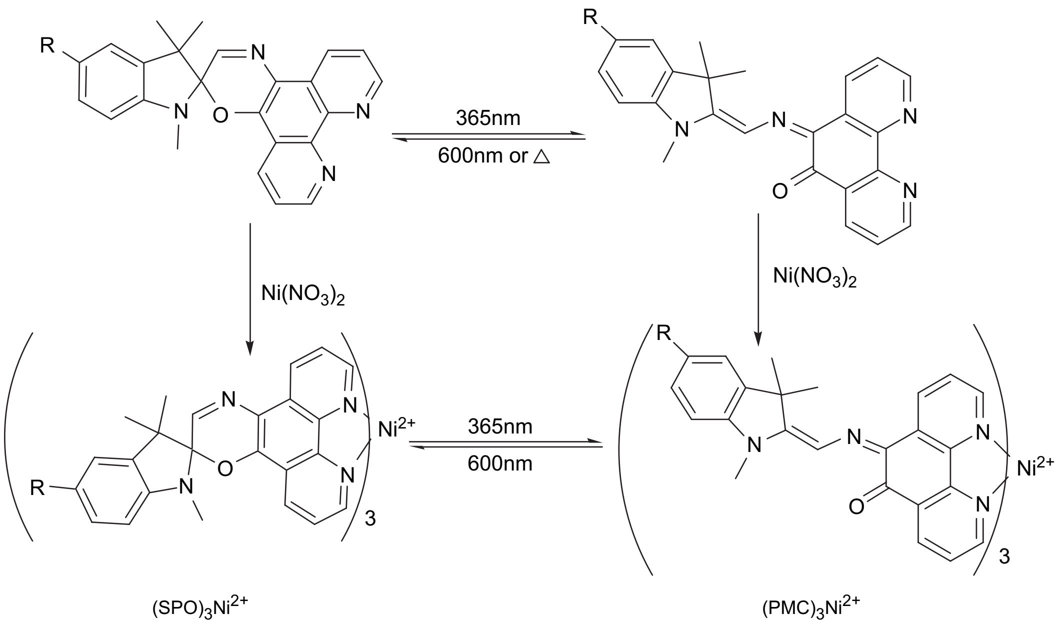

Scheme 1. Isomerization and complexation of the title compounds and their colored form. (a) R = CH_3, (b) R = benzo, (c) R = Br, (d) R = Cl, (e) R = H, (f) R = CH_3O.

the mono-oxime of 1,10-phenanthroline-5,6-quinone (based on Yamada [15] and Hiort [16]) in the presence of triethylamine and anhydrous sodium sulfate. The structures were confirmed by ^{1}H NMR spectroscopy, mass spectroscopy and elemental analysis [17]. Continuous UV irradiation at 254 nm resulted in conversion from the colorless form to the colored form, photomerocyanine (λ_{max}=588 nm). When the PMC was irradiated with 600-nm light, the concentration of the colorless form increased (as shown in Fig. 1).

An electron donating group in the 5 position of the indole moiety and a polar solvent impart 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). The solvents also affected the thermal equilibration between SPO and PMC; polar solvents moved the equilibrium to the colored form (PMC), so that solutions of **a**–**f** in methanol were dark blue while in cyclohexane were colorless. This may be due to the electron donating group having increased the electron density of the nitrogen atom in the indole moiety through the conjugation system, so stabilizing the colored PMC form. The positive solvatochromism indicates the delocalized charge structures of SPO and PMC.

In terms of the influence of metal complexation on photochromism and the equilibrium between the closed and opened forms, Fig. 2 shows that upon addition of the Ni^{2+} ion to the methanolic solution of compound **c** in the dark, the absorption band between 500 and 650 nm increased gradually, indicating that the complexation ability of PMC was stronger than that of SPO and the formation of the PMC complex with Ni^{2+} facilitated the thermoisomerism of the spirooxazine moiety to the photomerocyanine form. No further changes occurred until

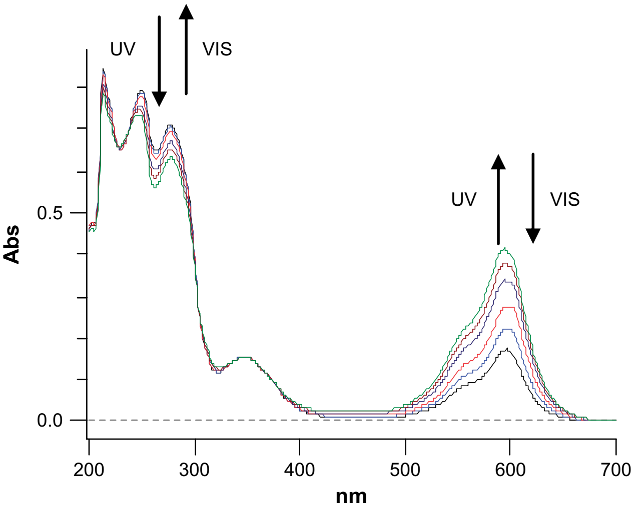

Fig. 1. Absorption spectra change of compound **c** (2.2×10^{-5} M) in methanol under irradiation with 254 and 600-nm light.

Table 1
5-Substituent and solvent effects on the maximum absorption wavelength data and thermal bleaching constant of PMC

Entry	R	λ_{Max} (nm) ($\varepsilon \times 10^4$ cm^{-1} M^{-1})			k ($\times 10^4$ s^{-1})		
		Methanol	Chloroform	Cyclohexane	Methanol	Chloroform	Cyclohexane
a	CH_3	600	603	580	2.40	0.53	157.04
b	Benzo	613	616	588	1.76	0.24	97.86
c	Br	596	598	580	22.87	5.17	–[a]
d	Cl	595	600	580	61.49	2.54	–[a]
e	H	591	597	569	13.81	0.61	207.62
f	CH_3O	610	615	602	0.14	0[b]	11.92

[a] Bleaching rate is too fast to be measured using conventional method.

[b] The opened form is so stable that no ring-closing was observed based on our experimental conditions.

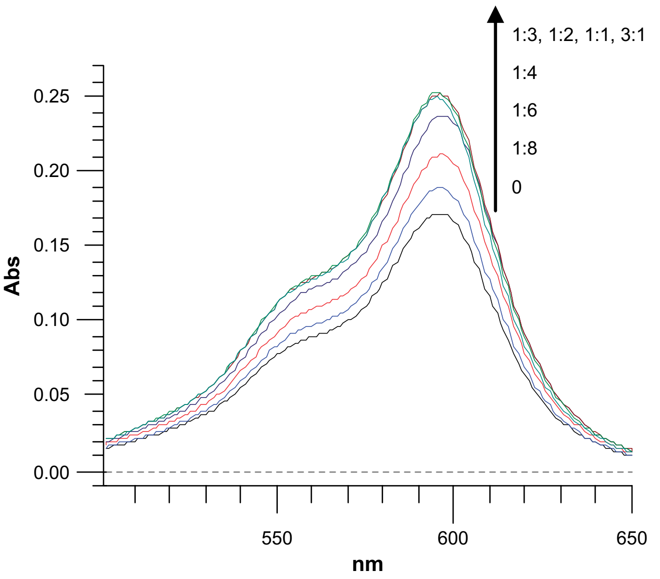

Fig. 2. Absorption spectral changes of **c** in methanol upon addition of Ni^{2+} in dark. The ratio of Ni^{2+}/**c** is 0, 1:8, 1:6, 1:4, 1:3, 1:2, 1:1 and 3:1, with 30 min interval, respectively.

the ratio of Ni^{2+}/**c** increased to 1:3, with the result that compound **c** was completely coordinated to Ni^{2+}, forming a 1:3 $(PMC)_3Ni^{2+}$ complex. The photochemical kinetic parameters k of the complex are summarized in Table 2; thermal bleaching of the complex can be neglected at room temperature under the experimental conditions employed as metal complexation lowered the negative charge density of the indole moiety through inductive effects [18].

As the $(PMC)_3Ni^{2+}$ complex was very stable in the dark at room temperature, this provided the opportunity to explore its negative photochromism. Upon irradiation with 600-nm visible light, the solution of the complex $(PMC)_3Ni^{2+}$ was bleached immediately (shown in Fig. 3). The bleached state of the $(PMC)_3Ni^{2+}$ complex is $(SPO)_3Ni^{2+}$; when the visible light was switched off, the $(SPO)_3Ni^{2+}$ complex reverted to the $(PMC)_3Ni^{2+}$ complex during a 600-s color-forming process. The absorption spectra were identical before and after multiple, visible irradiation cycles. This reversible photoisomerization processes indicated that the $(PMC)_3Ni^{2+}$ complex has excellent negative photochromic properties.

Table 2
Absorption maximum wavelength of complex $(PMC)_3Ni^{2+}$ and photochemical bleaching constant of the complex in methanol solution

Entry	R	$\lambda_{max\ opened\ form}$ (nm) ($\varepsilon \times 10^4\ cm^{-1}\ M^{-1}$)	k ($\times 10^4\ s^{-1}$)
a	CH_3	596	0.71
b	Benzo	611	0.66
c	Br	595	12.34
d	Cl	594	13.26
e	H	590	2.29
f	CH_3O	607	0[a]

[a] The opened form is so stable that no ring-closing happens during visible light irradiation with our experimental conditions.

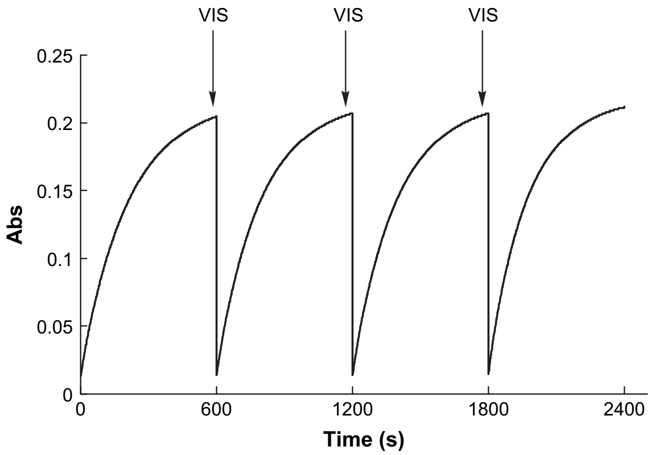

Fig. 3. The color-bleaching and color-forming processes irradiated with 600-nm light and in the dark of $(PMC)_3Ni^{2+}$ in methanol at room temperature.

In summary, we have synthesized a series of spiro[indoline-phenanthrolinoxazines] and studied their positive behaviours and negative photochromic properties of the colored $(PMC)_3Ni^{2+}$ complexes. 5-Substituent in the indole moiety, solvent and metal ion binding affected the positive photochromic behaviours of the spirooxazines combined with phenanthroline. The colored $(PMC)_3Ni^{2+}$ complexes exhibited excellent negative photochromism, which might pave the way for new applications for the spirooxazine. Further studies on their complexation with rare earth metal ions are in progress and the results will be reported later.

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[17] Compound **a**: ^{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). 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. Compound **b**: ^{1}H NMR(δ, $CDCl_3$, 500 MHz): 9.11(dd, 1H, $J = 1.5$, 4.0 Hz), 9.08(dd, 1H, $J = 1.5$, 4.0 Hz), 8.99(dd, 1H, $J = 1.5$, 8.5 Hz), 8.37(dd, 1H, $J = 1.5$, 8.5 Hz), 7.86(d, 1H, $J = 8.5$ Hz), 7.82(d, 2H, $J = 6.0$ Hz), 7.80(d, 1H, $J = 8.5$ Hz), 7.68(dd, 1H, $J = 4.5$,8.0 Hz), 7.55−7.52(m, 2H), 7.30(t, 1H, $J = 8.0$ Hz), 7.01(d, 1H, $J = 8.5$ Hz), 2.86(s, 3H), 1.76(s, 3H), 1.62(s, 3H). MS m/z(%): 430(39), 415(43), 399(9), 222(9), 220(8), 108(100), 194(54), 180(17), 165(13), 152(25), 98(10). Anal. Calcd for $C_{28}H_{22}N_4O$: C, 78.12; H, 5.15; N, 13.01. Found: C, 78.24; H, 5.07; N, 13.12. Compound **c**: ^{1}H NMR(δ, $CDCl_3$, 500 MHz): 9.14(dd, 1H, $J = 1.5$, 4.5 Hz), 9.08(dd, 1H, $J = 1.5$, 4.5 Hz), 8.95(dd, 1H, $J = 1.5$, 8.5 Hz), 8.39(dd, 1H, $J = 1.5$, 8.5 Hz), 7.82(s, 1H), 7.67(dd, 1H, $J = 4.5$, 8.0 Hz), 7.54(dd, 1H, $J = 4.5$, 8.5 Hz), 7.32(dd, 1H, $J = 1.5$, 8.5 Hz), 7.19(d, 1H, $J = 1.5$ Hz), 6.46(d, 1H, $J = 8.5$ Hz), 2.75(s, 3H), 1.40(s, 3H), 1.35(s, 3H). MS m/z(%): 460(94), 458(100), 445(39), 443(40), 364(14), 349(9), 239(95), 237(96), 224(38), 222(58), 209(24), 182(10), 177(19), 159(32), 143(16), 140(21), 128(10), 115(20), 102(13). Anal. Calcd for $C_{24}H_{19}BrN_4O$: C, 62.75; H, 4.17; Br, 17.40; N, 12.20. Found: C, 62.73; H, 4.20; Br, 17.45; N, 12.22. Compound **d**: ^{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), 8.39(dd, 1H, $J = 1.5$, 8.5 Hz), 7.81(s, 1H), 7.66(dd, 1H, $J = 4.5$, 8.5 Hz), 7.53(dd, 1H, $J = 4.5$, 8.5 Hz), 7.17(dd, 1H, $J = 2.0$, 8.0 Hz), 7.05(d, 1H, $J = 2.0$ Hz), 6.49(d, 1H, $J = 8.0$ Hz), 2.74(s, 3H), 1.40(s, 3H), 1.34(s, 3H). MS m/z(%): 416(26), 414(75), 401(14), 399(39), 367(4), 222(11), 209(12), 195(32), 193(100), 180(53), 178(54), 167(10), 140(10), 115(8). Anal. Calcd for $C_{24}H_{19}ClN_4O$: C, 69.48; H, 4.62; Cl, 8.55; N, 13.50. Found: C, 69.56; H, 4.45; Cl, 8.68, N, 13.62. Compound **e**: ^{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. Compound **f**: ^{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.

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