

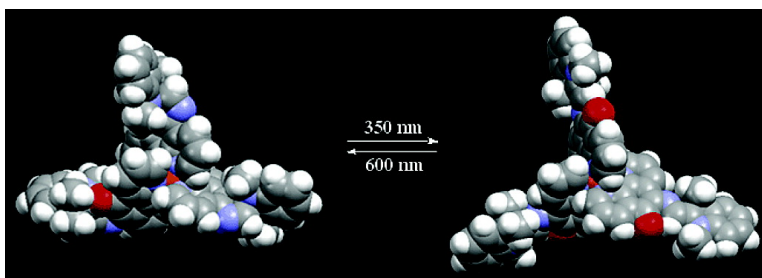
Communication

## Tunable Photochromism of Spirooxazines via Metal Coordination

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## Tunable Photochromism of Spirooxazines via Metal Coordination

Roni A. Kopelman, Sean M. Snyder, and Natia L. Frank\*

Department of Chemistry, University of Washington, Seattle, Washington 98195-1700

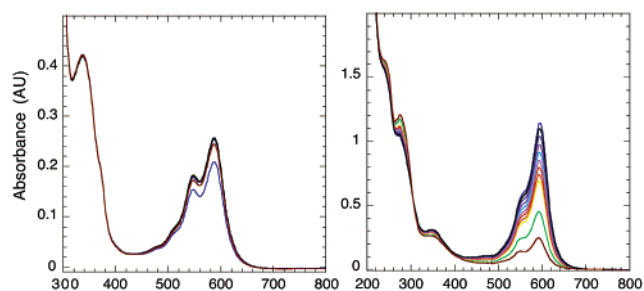
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Photochromic materials are of great interest due to their applications in ophthalmic lenses, display and communications systems, and optical storage and memory devices.<sup>1–4</sup> The coupling of changes in the electronic state accompanying photoisomerization with other physical phenomena would allow development of multifunctional materials.<sup>5–9</sup> Metal coordination of photochromes provides a novel and potentially powerful approach to the development of systems in which changes in the electronic state of the photochrome can induce changes in redox, magnetic, or optical properties of the metal center. This approach, however, has been largely unexplored.<sup>10</sup> Previously investigated spiroopyran-metal complexes have taken advantage of the charge separation present in the merocyanine form, leading to nonphotochromic metal complexes that exist only as transient species.<sup>11–14</sup> These metal complexes involve complexation of the merocyanine form through the oxazine moiety, and hence upon ring closure they dissociate in solution.

Herein, we report the synthesis of a series of stable spiro[indoline-phenanthroline]oxazine-metal (II) complexes in which a ligand moiety has been incorporated into the spirooxazine framework. The metal is therefore bound to a ligand-functionalized spirooxazine and remains bound in both the open and the closed forms. These systems allow the investigation of the effect of metal complexation on the photoresponsivity and thermal stability of the photomerocyanine form and were found to exhibit extremely large photochromic responses relative to the parent spirooxazine. We have found that metal complexation leads to a significant stabilization of the photomerocyanine form, a decrease in thermal fading, and order of magnitude increases in photoresponsivity that are greatly dependent on the nature of the metal center.

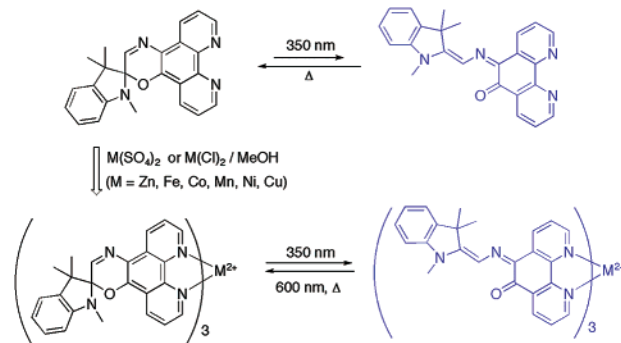
The parent spirooxazine, spiro[indoline-phenanthroline]oxazine (IPSO), was synthesized by condensation of 5-hydroxy-6-nitroso-1,10-phenanthroline with 1,3,3-trimethyl-2-methylene indoline (Fischer's Base)<sup>15</sup> to give a blue microcrystalline solid in 36% yield. Continuous UV irradiation of the unbound photochrome (IPSO) with ultraviolet light results in the reversible, photochemically induced conversion from the colorless spirooxazine form ( $\lambda_{\max}$  350 nm) to the intensely colored photomerocyanine (PMC) form ( $\lambda_{\max}$  588 nm) with first-order kinetics (Figure 1). After generation of the UV photostationary state ( $K_{UV}$ ), thermal reversion leads to an increase in the concentration of the spirooxazine form with first-order kinetics and a rate constant of  $0.2 \text{ s}^{-1}$  in acetonitrile at 293 K. The thermal equilibrium ( $K_T$ ) between closed (spirooxazine) and open (photomerocyanine) forms is 0.06 at 293 K as determined by <sup>1</sup>H NMR spectroscopy, consistent with the greater stability of the closed spirooxazine form in the unbound ligand.<sup>15,16</sup>

The  $M(\text{IPSO})_3(\text{BPh}_4)_2$  metal complexes were prepared by reaction of divalent metal sulfates or chlorides with 3 equiv of ligand in a degassed methanol solution at room temperature (Scheme 1). Anion exchange with sodium tetraphenylborate ( $\text{BPh}_4$ ) led to isolation of a series of dark blue microcrystalline solids in high yield (73–91%). The identity and purity of the complexes after



**Figure 1.** Left: Solution absorption spectra of IPSO ( $8 \times 10^{-5} \text{ M}$ , ACN) as a function of time with constant UV ( $\lambda_{\max}$  350–400 nm) irradiation. Right: Solution absorption spectra of  $\text{Co}(\text{IPSO})_3(\text{BPh}_4)_2$  ( $2 \times 10^{-5} \text{ M}$ , ACN) as a function of time with constant visible ( $\lambda_{\max} > 550 \text{ nm}$ ) irradiation at 5 s intervals.

### Scheme 1



reprecipitation was established by elemental analysis, mass spectroscopy, absorption, and <sup>1</sup>H NMR spectroscopy.

Ultraviolet irradiation of the series of  $M(\text{IPSO})_3(\text{BPh}_4)_2$  complexes at  $\lambda_{\text{exc}}$  350 nm led to an increase in absorption intensity in the visible region corresponding to an increase in the concentration of the photomerocyanine form ( $K_{UV}$ ). A slight bathochromic shift in the  $\lambda_{\max}$  relative to the parent-unbound spirooxazine (see Table 1, Figure 1) was observed. Thermal relaxation in the absence of light led to bleaching and regeneration of the thermal equilibrium state ( $K_T$ ). Visible photoexcitation of this state ( $K_T$ ) led to further photobleaching and generation of a new photostationary state enriched in the spirooxazine form ( $K_{Vis}$ ). Thermal relaxation from this state led to an increase in the photomerocyanine form, as evidenced by an increase in absorption at  $\lambda_{\max}$  600 nm and regeneration of the thermal equilibrium state ( $K_T$ ). The optical spectra for all complexes obtained before and after multiple ultraviolet irradiation cycles were identical, indicating that the photoisomerization processes were reversible.<sup>17</sup>

The rates of photoisomerization under constant ultraviolet (300–350 nm) or visible irradiation (520–600 nm) exhibit first-order kinetics. One isosbestic point is observed in the absorption spectra for spirooxazine-merocyanine conversion, suggesting isomerization without formation of an intermediate state, consistent with

**Table 1.** Equilibrium Constants for IPSO and Metal Complexes<sup>a</sup>

	$\lambda_{\max}$ (nm)	$K_T$	$K_{UV}^b$	$K_{Vis}^c$	$k_{UV}$ ( $10^{-3} \text{ s}^{-1}$ )	$k_T$ ( $10^{-3} \text{ s}^{-1}$ )
IPSO	588	0.06	0.08	n/a	206	227
Mn(II)	592	0.63	1.43	0.26	125	53
Fe(II)	605	0.87	n/a	0.03	n/a	n/a
Co(II)	591	0.56	1.37	0.26	40	4.7
Ni(II)	594	1.29	9.18	0.05	39	4.2
Cu(II)	594	0.60	0.84	0.33	58	27
Zn(II)	592	0.69	0.92	0.15	38	13

<sup>a</sup> The equilibrium constants  $K$  are defined as the ratio of [open]/[closed].

<sup>b</sup> Photostationary state generated with constant UV irradiation ( $\lambda = 350\text{--}400 \text{ nm}$ ). <sup>c</sup> Photostationary state generated with constant visible irradiation ( $\lambda > 550 \text{ nm}$ ). Rates were measured at 293 K at an irradiation power of 6 mW.

kinetic studies of spirooxazine photoisomerization.<sup>18,19</sup> The rates of thermal relaxation ( $k = 10^{-2}$  to  $10^{-3} \text{ s}^{-1}$ ) and photoisomerization for the series of metal complexes are all approximately 1 order of magnitude slower than that of the parent, unbound spirooxazine ( $k = 10^{-1}$ , Table 1).

The photoresponsive factor of photochromes, or photocolability ( $\Delta A$ ), can be defined as the change in long wavelength absorption upon UV irradiation ( $A - A_0$ ,  $A/A_0$ ).<sup>20</sup> Here, we define photocolability as the difference (i.e.,  $\Delta K_{UV} = K_{UV} - K_T$ ) between the thermal equilibrium constant ( $K_T$ ) and the photostationary states as a function of visible ( $K_{Vis}$ ) or UV ( $K_{UV}$ ) irradiation (Table 1). The parent ligand demonstrates a photoresponsivity equal to that of the well-known parent spiro[indole-naphthoxazine], which exhibits superior colorability relative to other spirooxazines.<sup>16</sup> As shown in Table 1, the  $M(\text{IPSO})_3(\text{BPh}_4)_2$  complexes exhibit a significant increase in photochromic activity relative to the parent spirooxazine that is metal dependent. While the change in stationary state for the parent ligand ( $\Delta K_{UV} = 0.02$ ) is quite small, the changes associated with photoisomerization of the metal complexes are all at least an order of magnitude larger and dependent on the metal center. The colorability ( $\Delta K_{UV}$ ) for copper(II) and zinc(II) complexes is an order of magnitude larger ( $\Delta K_{UV} = 0.23$ ) than that of the ligand, whereas the colorability of the nickel (II) complex is over 2 orders in magnitude larger ( $\Delta K_{UV} = 7.89$ ) than that of the parent ligand.

The greatly improved colorability of these metal complexes may be a result of the metal cation stabilization of the photomerocyanine form. The effects of substitution on the kinetic and thermodynamic parameters of spirooxazine ring opening and closing are generally interpreted in terms of steric and electronic effects.<sup>21,22</sup> Consideration of the positions of substitution suggests that steric effects, which typically lead to stabilization of the closed form, are relatively minor in this case. Electronic effects are usually interpreted in terms of their influence on the extent of charge separation in the photomerocyanine form, and thus an increase in charge density in the oxazine or indoline portion of the molecule leads to destabilization of the photomerocyanine form. Metal complexation is expected to decrease the negative charge density of the oxazine moiety through inductive effects and to increase the charge density through  $d\text{-}\pi^*$  donation. The increase in photomerocyanine stability suggests that inductive effects play a dominant role. However, as the inductive effects and back-bonding abilities vary along the series, both are expected to play a significant role in the nature and extent of the electronic stabilization.

In summary, we have synthesized a series of photochromic transition metal spirooxazine complexes in which the photochrome remains bound to the metal center in both the spirooxazine and the photomerocyanine forms during the photoconversion. A significant stabilization of the photomerocyanine form results from metal complexation, as indicated by the shift in thermal equilibrium values. The photoresponsive factors are greatly increased relative to the parent spirooxazines and dependent on the nature of the metal center. The robust photochemical behavior ascribed to spirooxazines is conserved upon formation of the  $M^{\text{II}}(\text{tris-spiro}[\text{indoline-phenanthroline}]\text{oxazine})$  complex. This new class of compounds provides the opportunity to investigate the synergy between changes in electronic structure associated with photoisomerization, and metal-centered functionality. Future work will be aimed at understanding the origins of metal complex effects on photochromic behavior, and the effect of photochromism on metal electronic state through the investigation of complexes in which the ligand field is varied systematically within a given family.

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**Supporting Information Available:** Synthetic details and characterization of the ligand and metal complexes (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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