Modulation of the Spiropyran−Merocyanine Reversion via Metal-Ion Selective Complexation: Trapping of the "Transient" *cis*-Merocyanine

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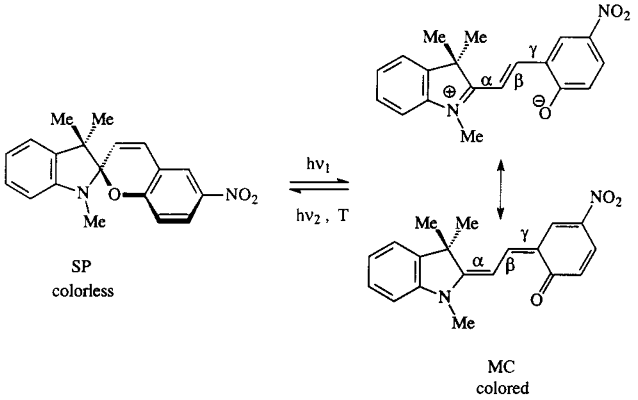
The effects of molecular structure and metal-ion complexation on the photochromic and thermochromic properties of N-functionalized carboxyl ligands of 6′-nitrobenzoindolinospiropyrans (6-nitroBIPS) with varying methylene spacers ($n = 2$, 4, and 5) were examined. Irradiation of this series of molecules in the presence of Cu^{2+} and Zn^{2+} produced two species that were spectroscopically distinguishable based on their absorption characteristics and stable toward the thermal reversion process. The two bands were diagnostic of the *cis*- and *trans*-MC−M^{2+} complexes, with $\lambda_{cis} = 410$ nm and $\lambda_{trans} = 490$ nm, respectively. It was found that lengthening the N-moiety spacer produced no perturbations in the metal-ion complexation behavior. Addition of an equimolar amount of the chelating agent, EDTA, to these solutions resulted in the disappearance of the *cis*-MC−M^{2+} and *trans*-MC−M^{2+} complex absorptions and a simultaneous increase in free *trans*-MC which could then be observed to revert back to the SP form by a first-order rate decay process. Thus it is shown that Cu^{2+} and Zn^{2+} function as traps of the "transient" *cis*-merocyanine stereoisomer formed upon irradiation of spiropyrans functionalized with carboxyl ligands having two, four, and five methylene spacer units, with the potential to modulate this molecular switch by selection of the appropriate metal.

Introduction

Thermo- and photochromic compounds have provided a number of interesting dye molecules due to their inherent transformation to colored species on exposure to heat or UV irradiation (Scheme 1).[1]

Thus, the interconversion of spiropyran (SP)−merocyanine (MC) systems, SP⇄MC, has been extensively investigated due to their potential applications in molecular devices and uses in nanotechnology.[2] However, application of this system is hindered by the spontaneous thermal reversion process (MC → SP) and photodegradation that destroys switchability of the system.[3] Numerous studies have attempted to shed light on the nature of the intermediates (*cis/trans*) and toward establishing the mechanisms of the thermal and photochemical transformations in the ring opening/closure pathways.[4] Knowledge of the intermediate structures in these pathways is important to circumvent existing problems of thermal reversion and photodegradation. Previous studies for detection of these intermediates have included laser flash photolysis[5] and transient spectroscopy on the nano- and picosecond time scales.[6]

Scheme 1



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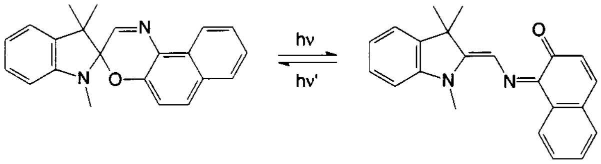
10.1021/cm010038q CCC: $20.00

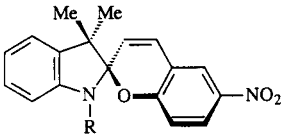
Scheme 2



The studies have included a number of structurally modified photochromic spiro structures, including the spirooxazine system illustrated in Scheme 2. Interestingly, this study showed that the photochromism of spirooxazines is very dependent on solvent and on substitution which decreases the rotational freedom after cleavage of the C−O bond.[5]

In our laboratories, the thermal reversion, MC → SP, was examined via a solvatochromic, solvatokinetic, and semiempirical study.[7] The latter simulates the lowest energy pathway for conversion of the *trans*-MC to a *cis*-MC form (the immediate precursor of the SP form), via sequential bond rotation of the three central dihedral angles (α, β, γ). The calculations support the observed solvatokinetic behvaior and lead to the assignment of the *trans/cis* isomerization (β dihedral rotation) as the rate-determining step in the overall process.

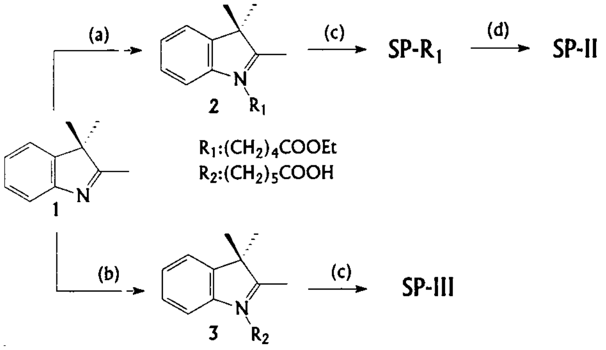
We have recently developed a thermally stable SP−MC photoswitch via intramolecular bidentate metal ion chelation.[8] Functionalization of the indolino moiety with a chelating ligand produces on irradiation a bidentate chelator that is thermally stable and photoswitchable at two different light energies. In the previous study, the effect of added $CaCl_2$ and $ZnCl_2$ on the SP$\rightleftarrows$MC interconversion, with stabilization of the *trans*-MC−M^{2+} complex, was described.[8] As an extension of that study, we report herein the stabilization and UV/vis characterization, of *two* geometric isomers of the merocyanine, *cis*- and *trans*-MC, via intramolecular bidentate chelation of COOH-containing SP ligands (I−III) with increasing methylene spacer units, in the presence of fully dissociated $Zn(ClO_4)_2$ and $Cu(ClO_4)_2$.



SP	R
I	$(CH_2)_2COOH$
II	$(CH_2)_4COOH$
III	$(CH_2)_5COOH$

The present study provides the first evidence of the *cis*-MC form as a species observable by UV/vis spectrophotometry over a time scale of hours/days, contrasting with the nano- and picosecond time scale in laser flash photolysis studies.[5,6]

Scheme 3. (a) Ethyl 5-Bromovalerate; (b) 6-Bromohexanoic Acid; (c) 5-Nitrosalicaldehyde, Et_3N; (d) THF/NaOH



Experimental Section

Synthesis. The synthesis of SP-I used in this study has been reported previously.[9] The synthesis of SP-II and SP-III is outlined in Scheme 3.

Synthesis of SP-II. A two-necked 50 mL round-bottomed flask equipped with a magnetic stir bar and an argon inlet was charged with redistilled **1** (7.95 g, 50.0 mmol) and ethyl 5-bromovalerate (2.09 g, 10 mmol). The mixture was heated to 80 °C for 12 h, during which time the product came out of solution in a highly viscous form. Upon cooling, the reaction mixture was extracted with 3 × 200 mL of Et_2O to remove all of the unreacted starting material. The remaining crystalline solid was dissolved in 10 mL of water and extracted with 3 × 50 mL of Et_2O and 3 × 25 mL of $CHCl_3$. The aqueous layer was separated and concentrated under vacuum (1.0 mmHg, 24 h) to dryness. The resulting amorphous solid **2** was recrystallized from toluene/$CHCl_3$ to a yellow solid: 2.65 g (yield 78%).

Into a 50 mL round-bottomed flask equipped with a water condenser topped with a pressure-equalized dropping funnel was added **2** (1.0 g, 2.78 mmol) and 5-nitrosalicaldehyde (0.50 g, 3.0 mmol). The mixture was heated to reflux and ethanol was added until the solids dissolved, followed by addition of triethylamine (0.280 g, 2.78 mmol) in 5 mL of EtOH via the dropping funnel over 20 min. Addition of the base resulted in an immediate color change to purple, signifying that spiropyran formation was occurring. The mixture was refluxed for 6 h and then cooled to room temperature. The solution was concentrated to 5 mL, and the flask was allowed to stand in a refrigerator for 24 h. The spiropyran precipitate was filtered under vacuum and recrystallized from ethanol to give yellow crystals of SP−R_1, yield = 0.763 g (72.2%).

A 50 mL round-bottom flask equipped with a magnetic stir bar and an argon inlet was charged with finely ground SP−R_1 (1.0 g, 2.28 mmol) which was dissolved in 10 mL of THF. After addition of aqueous NaOH (25 mL, 1 M), the solution was stirred for 24 h. The solution was evaporated at room temperature under high vacuum, the solids were dissolved in a minimum amount of water, and the product was precipitated through neutralization with 1 M HCl. The filtered solid was recrystallized from EtOH to give yellow red crystals: 0.962 g (94%), of SP-II, mp 139−141 °C.

^1H NMR (400.1 MHz) in DMSO-d_6: δ 8.19 (1H, d, J = 2.8), 7.97 (1H, d, J = 9.0), 7.19 (1H, d, J = 10.4), 7.08 (2H, m), 6.84 (1H, d, J = 7.2), 6.76 (1H, t, J = 7.2), 6.57 (1H, d, J = 7.8), 5.98 (1H, d, J = 10.4), 3.10 (2H, m, N−CH_2), 2.16 (2H, t, J = 6.8, CH_2CO), 1.55 (4H, m, −CH_2−), 1.18 (3H, s, CH_3), 1.09 (3H, s, CH_3).

^{13}C NMR: 174.4, 159.2, 146.7, 140.4, 135.6, 128.1, 127.6, 125.7, 122.8, 121.6, 118.9, 118.7, 115.4, 106.4, 52.2, 33.5, 28.0, 26.1, 24.2, 19.5.

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IR (cm^{-1}): 3030, 3000, 2971, 1709, 1654, 1610, 1575, 1510, 1483, 1457, 1441, 1360, 1330, 1270, 1141, 1088, 1020, 915, 803.

UV−visible (DMSO, λ_{max} (ϵ)): 338 nm, 7800 M^{-1} cm^{-1}.

Anal. Calcd for $C_{23}H_{24}O_5N_2$: C, 67.61; H, 5.89; N, 6.82. Found: C, 67.31; H, 5.92; N, 6.60.

Synthesis of SP-III. The synthesis of **3** was effected by following the above illustrative procedure with **1** and 6-bromohexanoic acid to produce 2.43 g (71.2%) of yellow crystals.

^{1}H NMR (400.1 MHz) in DMSO-d_6: δ 7.98 (1H, m), 7.86 (1H, m), 7.60 (2H, m), 4.46 (2H, t, $J = 6$, N−CH$_2$), 2.85 (3H, s, CH$_3$), 2.21 (2H, t, $J = 7$, C*H*$_2$CO), 1.83 (2H, m, −CH$_2$), 1.52 (6H, s, CH$_3$), 1.46 (4H, s, −CH$_2$−).

^{13}C NMR (100.1 MHz) in DMSO-d_6: 196.9, 174.7, 142.3, 141.5, 129.6, 129.4, 123.9, 115.9, 54.6, 47.9, 33.8, 27.4, 25.8, 24.5, 22.4, 14.6.

SP-III was synthesized by condensation of 5-nitrosalicaldehyde with **3** using the illustrative procedure for SP−R$_1$, to produce 1.23 g (48%) of yellow-red crystals, mp 80−82 °C.

^{1}H NMR (400.1 MHz) in DMSO-d_6: δ 8.19 (1H, d, $J = 3.2$), 8.00 (1H, d, $J = 9.0$), 7.21 (1H, d, $J = 10.5$), 7.08 (2H, m), 6.80 (2H, m), 6.57 (1H, d, $J = 7.8$), 5.98 (1H, d, $J = 10.5$), 3.10 (2H, m, N−CH$_2$), 2.13 (2H, m, CH$_2$CO), 1.45 (4H, m, −CH$_2$−), 1.20 (2H, m, −CH$_2$−), 1.18 (3H, s, CH$_3$), 1.07 (3H, s, CH$_3$).

^{13}C NMR: 174.4, 159.2, 146.7, 140.4, 135.6, 128.1, 127.6, 125.7, 122.8, 121.6, 118.9, 118.7, 115.4, 106.4, 52.2, 33.5, 28.0, 26.1, 25.8, 24.2, 19.5.

IR (cm^{-1}): 3030, 3000, 2971, 1709, 1654, 1610, 1575, 1510, 1483, 1457, 1441, 1360, 1330, 1270, 1141, 1088, 1020, 915, 803.

UV−visible (DMSO, λ_{max} (ϵ)): 342 nm, 8400 M^{-1} cm^{-1}.

Anal. Calcd for $C_{24}H_{25}O_5N_2$: C, 68.20; H, 6.16; N, 6.70. Found: C, 68.30; H, 6.09; N, 6.52.

Spectrophotometric Method and Procedures. All glassware was washed with ethanol and acetone and soaked in an acid bath (2 M HCl) for 24 h before being dried under vacuum at 150 °C. Solvents purified on a bulk scale were DMSO, acetone, DMF, and acetonitrile using literature procedures.[10]

Stock solutions of SPs (1 × 10^{-2} M) in DMSO or DMF were made up in 5 mL volumetric flasks in an inert atmosphere, capped with a rubber septum, wrapped in aluminum foil, and stored at 0 °C. The metal salts, Zn(ClO$_4$)$_2$ and Cu(ClO$_4$)$_2$, were commercially available (Acros) and used without further purification. Stock solutions of metal salts (0.02 M) were prepared by the following procedure. Metal salts were weighed and transferred into dry 100 mL volumetric flasks that were then stored under nitrogen. Dry CH$_3$CN (VWR, HPLC grade, distilled over P$_2$O$_5$ and stored over 3 Å molecular sieves that were activated at 290 °C for 24 h) was added to the volumetric flask to dissolve the salts. The solutions were allowed to stand in the drybox for 12 h to ensure complete dissolution before 20 g of activated 3 Å molecular sieves was added to remove the trace amounts of water present. The flasks were then cooled and sealed with a rubber septum under the inert atmosphere and used over a period of 1 month.

The EDTA (Aldrich) was recrystallized prior to use. The stock solution of EDTA (0.01 M) was made up in dry DMF.

Reproducible results of the photochromic transformation of spiropyran to merocyanine were obtained through the development of a protocol that maximized the formation of the colored form. Briefly, 2.00 mL of acetone was injected into a 1.0 cm path length quartz cuvette via a 2.50 mL syringe. An aliquot of the metal/acetonitrile solution was injected into the cuvette which was inserted into a HP 8452 diode array spectrophotometer equipped with a thermostated cell compartment at 25 °C. After acquiring the "blank" spectrum, a 10 μL aliquot of the spiropyran dye stock solution was injected into the cuvette, which was placed in a Spectroline ultraviolet irradiation chamber equipped with two 150 W, 365 nm light sources. The cuvette was irradiated with 365 nm light for 90 s to obtain the maximum concentration of colored merocyanine form. The cuvette was then transferred immediately to the cell compartment of the cell spectrophotometer, which was covered to ensure there was no exposure to ambient light. The absorption spectrum of the complexed merocyanine sample was monitored at constant intervals over a 3 day period to follow the thermal reversion reaction.

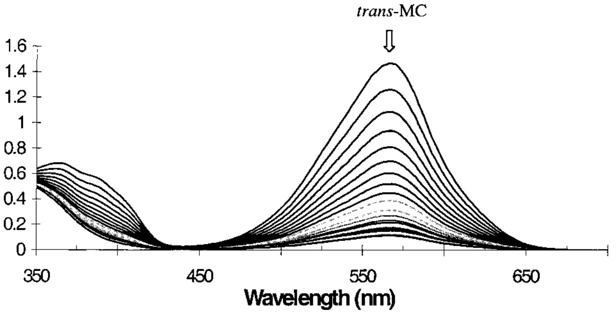

Figure 1. Overlay spectra illustrating the first-order thermal decay of *trans*-MC-I to SP-I form at 25 °C in acetone (scanning at 10 s intervals).

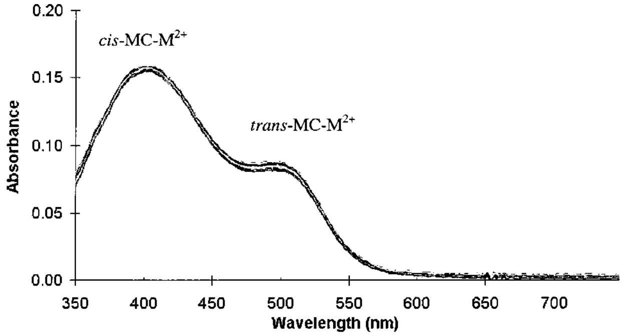

Figure 2. Overlay spectra (900 s intervals) displaying inhibition of thermal decay for the *cis* ($\lambda_{cis} = 405$ nm) and *trans* ($\lambda_{trans} = 496$ nm) complexed forms of MC-I ([SP] = 5 × 10^{-5} M) with Zn(ClO$_4$)$_2$ (or Cu(ClO$_4$)$_2$), [M(ClO$_4$)$_2$] = 5 × 10^{-5} M with SP as the reference spectrum. Similar results are observed with MC-II and MC-III in the presence of Zn(ClO$_4$)$_2$ or Cu(ClO$_4$)$_2$ over the 3 day monitoring period.

The EDTA experiment was performed on solutions of SP-I−SP-III that were irradiated in the presence of a 1:1 molar ratio of SP:metal salt. The absorption spectrum was monitored immediately after injection of an equimolar amount of EDTA relative to the SP, over a period of 10 half-lives.

Results and Discussion

Studies of the effects of Zn(ClO$_4$)$_2$ and Cu(ClO$_4$)$_2$ on solutions of SP-I, -II, and -III (5 × 10^{-5} M) were conducted in acetone. Irradiation of each SP in the absence of metal perchlorate produced spectra with similar absorption characteristics (Figure 1) corresponding to the *trans*-MC ($\lambda_{MC} = 560$ nm) and exhibited first-order rate decay to the SP: k_{obs}(MC-I) = 22.8 × 10^{-3} s^{-1}; k_{obs}(MC-II) = 1.13 × 10^{-3} s^{-1}; k_{obs}(MC-III) = 2.99 × 10^{-3} s^{-1}. Injection of 1 molar equivalent of M(ClO$_4$)$_2$ into a cuvette containing the SP in acetone produced no distortion of the SP spectrum ($\lambda_{SP} = 320$ nm, ϵ = 8000 M^{-1} cm^{-1}). However, irradiation of the M(ClO$_4$)$_2$-containing solution for 90 s ($\lambda_{irr} = 365$ nm) yielded a spectrum having two partially overlapped absorptions: (1) $\lambda_{max} = 496$ nm, assignable to the previously characterized[8] *trans*-MC−M^{2+} complex, and (2) a new absorption at ∼410 nm; no free MC was observed (Figure 2). There was no apparent change in the absorption properties of the complexed form at 410 and 496 nm on increasing the concentration of metal perchlorate. When the concentration of metal perchlorate was decreased,

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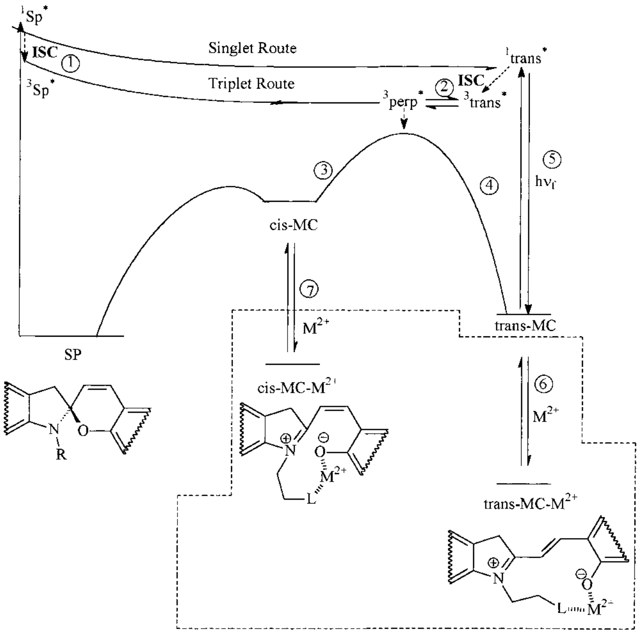


Figure 3. Energy-reaction coordinate diagram for the chelation of SPs I–III in the presence of Zn^{2+} and Cu^{2+}. Irradiation of SP produces the *cis*- and *trans*-MC isomers (steps 1–5) capable of chelation with M^{2+} (steps 6 and 7). Chelation is reversible upon addition of EDTA. Boxed-in portion (dashed) pertains to the processes during irradiation in the presence of metal salts.

the absorption intensities of both *cis*- and *trans*-MC–M^{2+} complexes decreased while a peak corresponding to the unbound MC steadily increased. The unbound *trans*-MC decreased with its usual first-order decay while the metal–MC complexes exhibited no decay over the 3 day monitoring period.

On the basis of evidence described below, the two peaks are assigned to two different isomeric forms that occur upon photochemical ring opening of the SP, i.e., *cis*-MC–M^{2+} and *trans*-MC–M^{2+}. The planarity of the *trans*-MC–metal complex optimizes the conjugation of the two π-electron systems which gives rise to a longer wavelength absorption ($\lambda_{trans} = 490-520$). On the other hand, in the *cis*-MC form the two chromophore systems are nonplanar, inducing a blue shift ($\lambda_{cis} = 405$ nm) relative to the *trans*-MC form (Figure 2). *This is the first evidence of the cis-MC isomeric form being observable by UV/vis spectrophotometry over a significant time period.*

Previous laser flash photolysis spectroscopic studies have shown that the photochemical pathway can produce two isomeric forms of the merocyanine, *cis*-MC and *trans*-MC, via steps 1–5 (Figure 3, omitting the dashed boxed-in portion).[5,11,12] The *trans*-MC isomer is thermodynamically more stable due to a minimum of steric repulsions between the indoline and benzopyran ring systems. The intersystem crossing (ISC; step 1) of the ^{1}SP* state to ^{3}SP* is enhanced by the nitro group in the SP ring.[6] Decay of the excited state along the triplet route forms an equilibrium of two excited species, ^{3}perp-MC* and ^{3}*trans*-MC* (step 2). Transition of this excited state to the ground state produces both the *cis* and *trans* isomers (steps 3 and 4). Thus, ISC increases the probability of *cis*-MC formation since relaxation via the singlet energy pathway will primarily occur through ^{1}*trans** → *trans*-MC (step 5). Furthermore, lifetimes of the *cis*-MC for 6-NO_2-BIPS ranging from micro- to milliseconds were observed.[11]

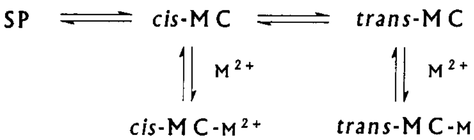
In contrast, studies by conventional UV–vis spectroscopy, as in the present work, only detect the *trans*-MC and its decay back to the SP. The thermal decay process must proceed via the *cis*-MC species, which will be present as a transient intermediate (see Figure 3), i.e., the sequence step 4 → step 3 → SP.

The design of the present experiments, as noted above, was to irradiate an SP containing an appended chelating moiety, and to study the effect of added metal ions (M^{2+}) on the MC→SP thermal reversion. As is apparent from Figure 3, M^{2+} can undergo complexation not only with the *trans*-MC species but also with the transient *cis*-MC; i.e., trapping of the transient *cis*-MC form can result. In the present system, the ground-state energies following complexation as a result have been lowered to such an extent that reversion to the SP has been effectively impeded.

Importantly, as noted above, addition of M^{2+} to the SP solution does not change the absorption spectrum, which signifies that a SP–metal complex is not formed. Furthermore, injection of the metal solution to an irradiated SP solution after a few seconds produces a spectrum identical with that shown in Figure 2. Thus, the time frame of this experiment allows for equilibration for the *trans*-MC species with the *cis*-MC and the SP. These results demonstrate that the trapping of the transient *cis*-MC species occurs from the *trans*-MC and is indeed consequent to the photochemical ring opening of the SP as shown in the boxed-in portion of Figure 3 (steps 6 and 7).

Overall, the design of the SPs enabling intramolecular bridging of the two ligands following ring opening has allowed for the *cis*-MC isomer to be observed spectroscopically, together with *trans*-MC, following complexation by M^{2+}, according to Scheme 4.

Scheme 4



Our work is complementary to that of Gorner et al.,[11] who investigated complexation of 8-methoxy-substituted BIPS with transition and rare-earth metal ions, through laser flash photolysis. It is noteworthy that in this system the primary mechanism is ortho chelation (Scheme 5), which contrasts with our study.

Following the above studies, the question was posed whether introduction into the MC–metal system of a competitive metal chelator would disturb the equilibrium set up in Scheme 3. The chelator of choice was ethylenediaminetetraacetic acid (EDTA), which has widespread use as a chelating agent in both medicinal and kinetic studies, due to its strong affinity for metal ions. Spectrophotometric monitoring of the solution

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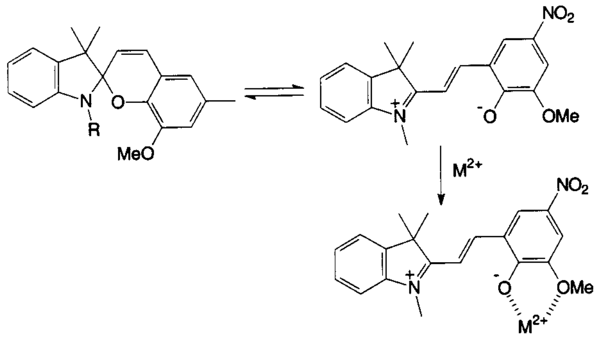
Scheme 5



containing both MC–M^{2+} complexes after addition of an equimolar amount of EDTA resulted in the disappearance of both metal-complex absorptions (λ_{cis} = 410 nm; λ_{trans} = 500 nm), with a simultaneous increase in the absorption intensity centered at ~560 nm corresponding to the free *trans*-MC (Figure 4). This absorption was observed to thermally decay back to the SP form via a first-order process, diagnostic of the free MC in the absence of metal ion.

Interestingly, while the thermal reversion rates for the free *trans*-MC generated immediately after EDTA injection are similar to those in the absence of metal ion, the concentration of *trans*-MC in solution was almost an order of magnitude smaller based on the absorption intensity (Figure 4, dashed line). This observation can be explained as being due to the relative concentrations of *cis*- and *trans*-MC complexes. Based on the spectrum in Figure 2, there is a much larger concentration of *cis*-MC complex relative to the *trans*-MC complex. On capture by EDTA of the metal from the *cis*-MC–M^{2+} complex, the free *cis*-MC form is produced (step 7) and the energetically favored pathway available to this species is reformation of the SP form.

Previously, we examined the energetics of the MC → SP thermal reversion by means of semiempirical calculations.[7] Evaluation of the relative energy barriers for different pathways in the absence of M^{2+} showed that the highest energy barrier corresponds to rotation about the central bond, i.e., *trans* → *cis* isomerization. In the EDTA experiment, therefore, any *cis*-MC generated on abstraction of M^{2+} from the *cis*-MC–M^{2+} complex will necessarily undergo spontaneous reversion to the SP form. This accounts for the overall diminution of the *trans*-MC form in the EDTA experiment and corroborates the validity of Scheme 3 for trapping of the two MC forms by M^{2+}.

The experimental results in the present study, for the addition of M^{2+}, point to the importance of carrying out corresponding calculations, energies, and barriers, for metal-complexed merocyanines. Clearly, the relative amounts of metal-complexed species will be dependent on the manner in which the metal influences the nature of the hypersurface. Such calculations would provide a more quantitative basis for the energy diagram presented in Figure 3.

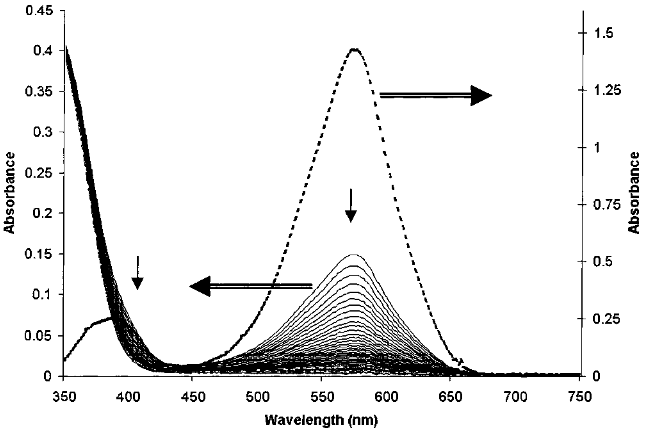


Figure 4. Overlay spectra (30 s intervals) illustrating the thermal decay of *trans*-MC-III to SP and the appearance of SP after injection of an equimolar amount of EDTA to a solution containing *cis*- (λ_{cis} = 410 nm) and *trans*- (λ_{trans} = 496 nm) MC-III complexed forms. The dashed line corresponds to the spectrum associated with the appearance of *trans*-MC-III in the absence of metal ion. Vertical arrows correspond to the spectral trend at the $\lambda_{\max}$ and in the area below 400 nm.

Conclusions

A mechanism based on the ring-opening and ring-closing processes in the presence and absence of metal salts has been developed. Importantly, our study has shown that it is possible to modulate the ground-state properties of the *cis*-MC and *trans*-MC isomers through metal chelation, forming relatively stable metal complexes that are blue-shifted, depending on the geometry that is enforced in the complex. The synthesis of novel SPs with COOH ligating groups attached to the indolino ring takes advantage of the negatively charged phenolic oxygen in the zwitterionic MC form to bind with a metal in cooperation with the *N*-indolino ligating group. Irradiation of 6-NO_2–SPs with UV light produces *cis*- and *trans*-MC isomers which complex with Zn^{2+} and Cu^{2+} to stabilize each form from subsequent thermal processes. This allows each isomeric form to be discerned spectroscopically through complex formation. Addition of EDTA captures the metal from the *cis* and *trans* bidentate MC–M^{2+} complexes to reform the SP and the free *trans*-MC. Since geometrical changes in the complex are readily detected spectrally, comparison of the spectral behavior delineates metals that can be classified as *cis* and *trans* complex stabilizers. Ongoing work will determine whether the spectral properties and the thermal reversion rate are sensitive to the nature of the metal ion and the chelating ligand, and further kinetic studies will aim at determining the lifetime of the *cis*-MC intermediate in this and related systems.

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