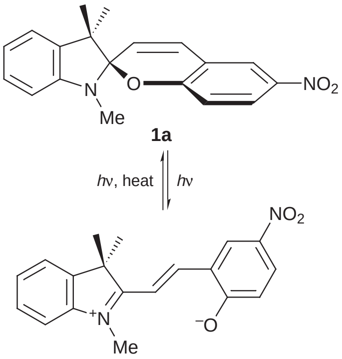
Effects of metal ion complexation on the spiropyran–merocyanine interconversion: development of a thermally stable photo-switch

James T.C. Wojtyk,[a] **Peter M. Kazmaier**[b] **and Erwin Buncel***[a]†

[a] *Department of Chemistry, Queen's University, Kingston, Canada K7L 3N6*
[b] *Xerox Research Center of Canada, Mississauga, Canada L5K 2A1*

Spectrophotometric absorption and fluorescence measurements of spiropyrans 2 and 3 modified with chelating functionalities, in the presence of Ca^{2+} and Zn^{2+}, provide evidence of a thermally stable spiropyran–merocyanine photoswitch that is modulated by the metal cations.

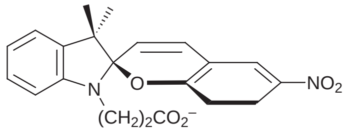
The potential application of spiropyran–merocyanine equilibria (SP⇌MC), *e.g.* **1a**⇌**1b**, in molecular devices (sensors, switches, signal transducers) has led to burgeoning activity aimed at exploitation of these systems.[1] A conceptually attractive possibility is the modification of the spiropyran moiety to enable chelation by metal ions and preferentially, stabilize the open MC form.[2] Other approaches to a molecular switch exploit the photoactive anthracene moiety bound to an aza crown ether which upon irradiation undergoes photocyclisation to form a cryptand, with the forward and the thermal reverse reactions strongly affected by metal cations.[3] One can thus envisage a photosensitive molecular switch with selectivity for particular metal cations. However, none of the studies reported to date have provided the necessary requirements[4] of a molecular switch: two thermodynamically stable states, or bistability, with facile interconversion between the two states.



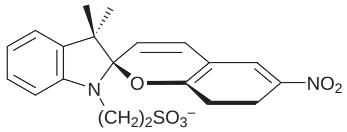
1b

Following our previous studies of SP⇌MC systems and structural/solvent changes thereupon,[5] here we report our results on intramolecular electrostatic bridging in molecules **2** and **3**, *via* addition of a divalent metal ion to stabilize the MC form from thermal decay. Furthermore, the open MC forms of these molecules undergo the ring closure back-reaction through photo-activation at wavelengths appreciably different from the SP→MC light irradiation. Evidence for a dual wavelength photoactivation molecular switch is presented.

Spiropyrans **2** and **3** were synthesized by reaction of 2,3,3-trimethylindolenine with β-iodopropionic acid[6] and γ-sultone, respectively, followed by condensation with 5-nitrosalicaldehyde in the presence of Et$_3$N and were fully characterized. Studies on the effects of CaCl$_2$ and ZnCl$_2$ on the SP⇌MC process for **2**, **3** and **1a** as a control were conducted in acetone. Following the injection of 1, 2, 5 and 10 equiv. of the dry metal halide salt in acetone into the cuvette containing an acetone solution of the SP (1×10^{-5} M), the cuvette was irradiated with a 15 W UV lamp (λ = 254 nm) for 1 min; the MC→SP reaction was monitored spectrophotometrically, scanning at 1 min intervals over a period of 30 min at 25 °C.



2



3

A control experiment on the decay of the MC form (λ_{max} = 572 nm) of **1** showed a first-order process, $k_{obs} = 7.30\times 10^{-3}$ s^{-1} [Fig. 1(*a*)], and addition of CaCl$_2$ had no effect on the rate or on the nature of the spectra. However, addition of ZnCl$_2$ resulted in the appearance of two distinct photo-reversible species: one corresponding to the free MC (λ_{max} = 566nm) and the other to a MC–Zn^{2+} complex (λ_{max} = 502 nm). Spectra [Fig. 1(*b*)] generated in the presence of 10:1 ratio of ZnCl$_2$:**1** showed that the amount of the MC–Zn^{2+} complex depended on the ZnCl$_2$:SP ratio. Furthermore, there was a significant decrease in the rate constant for MC decay, from $k_{obs} = 7.3\times 10^{-3}$ s^{-1} when [Zn^{2+}] = 0 to $k_{obs} = 3.3\times 10^{-3}$ s^{-1} when ZnCl$_2$:**1** = 10:1. A similar hypsochromic shift was observed upon addition of ZnCl$_2$ or CaCl$_2$ to sodium *p*-nitrophenoxide in acetone, with λ_{max} shifting from 428 nm when [M^{2+}] = 0, to 310 nm upon addition of 1 equiv. of MCl$_2$. Addition of either

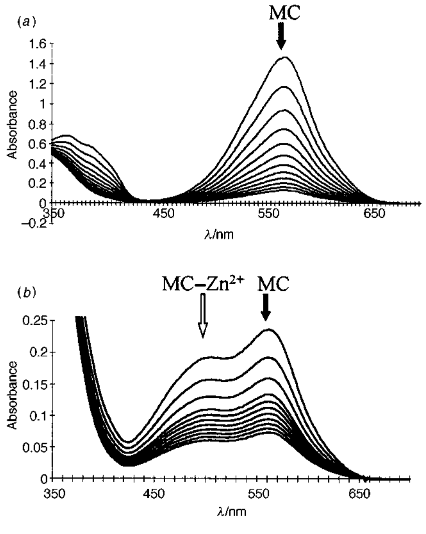


Fig. 1(*a*) Spectra illustrating the first order thermal reversion of the MC form **1b** at 25 °C in acetone (scanning at 1 min intervals). (*b*) Thermal reversion of the free and complexed forms of **1b** (MC and MC–Zn^{2+}) in the presence of ZnCl$_2$:**1** = 10:1.

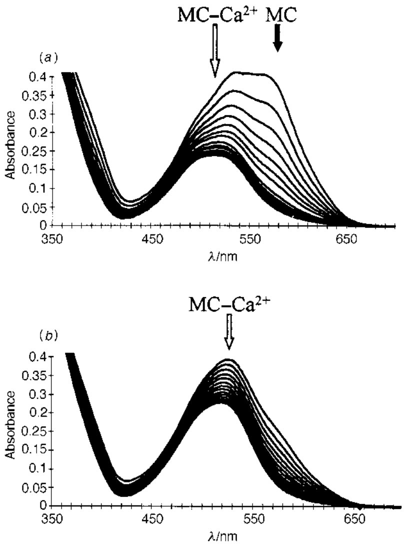


Fig. 2 Illustration of the thermal reversion of the MC and MC–Ca^{2+} forms of **2** in the presence of (*a*) 1 and (*b*) 10 equiv. $CaCl_2$

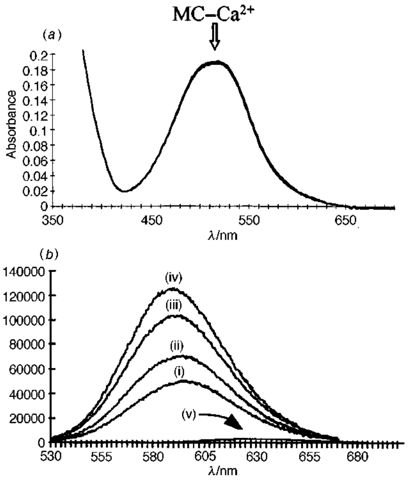


Fig. 3 (*a*) Overlay spectra illustrating the stabilization of the MC–Ca^{2+} form of **3** to thermal reversion in the presence of $CaCl_2$:**3** = 1:1. (*b*) Emission spectra (λ_{ex} = 520 nm) of the MC–Ca^{2+} form of **2** with increasing Ca^{2+}:SP ratios of (i) 1:1, (ii) 2:1, (iii) 5:1 and (iv) 10:1 compared to (v) MC.

metal salt to *p*-nitrophenol had no effect on the absorption spectra, which points to complexation of M^{2+} to the phenoxide moiety in the case of **1b** as the cause of the spectral changes.

For **2** in the absence of metal ion, the first-order decay of the MC form (λ_{max} = 572 nm) occurred with k_{obs} = 20.0× 10^{-3} s^{-1} . Addition of Zn^{2+} generated a new photo-reversible peak (λ_{max} = 502 nm) with peak intensity and k_{obs} both being dependent on added [$ZnCl_2$]: k_{obs} = 9.70× 10^{-3} s^{-1} for a 5:1 ratio of $ZnCl_2$:**2.** Addition of Ca^{2+} similarly generated a new photo-reversible peak at λ_{max} = 520 nm, the intensity and k_{obs} being dependent on added Ca^{2+} [Fig. 2(*a*),(*b*)]: k_{obs} = 9.03 × 10^{-3} s^{-1} for $CaCl_2$:**2** = 5:1, *i.e.* half the initial value.

The above results show that introduction of a chelating moiety onto the SP indoline ring results in an electrostatic bridge being formed that inhibits the thermal reversion of the MC form to the SP. In contrast to the lack of effect of Ca^{2+} on ring closure with control SP **1,** Ca^{2+} had a significant effect on the ring-closure of **2**. In addition, the contrasting k_{obs} values and λ_{max} for MC–Ca^{2+} and MC–Zn^{2+} complexes of **2** and the free MC forms demonstrate that stabilization of the MC form to thermal reversion through complexation is metal-dependent.

Similar experiments with **3** showed totally different behaviour. With a 1:1 ratio of Ca^{2+} and Zn^{2+}, complete stabilization of the MC form towards thermal decay was observed [Fig. 3(*a*)], no free MC being detected. The photo-stable form was found to persist for at least three days in the dark but exposure to visible light resulted in rapid decay of the spectrum of the complex.

Fluorescence measurements provided further information on the roles of Ca^{2+} and Zn^{2+} complexation with the MC form of **2** and **3**. As shown in Fig. 3(*b*), the fluorescence intensity increased on increasing the metal halide concentration. Moreover, Fig. 3(*b*) illustrates the overlapped emission spectra using excitation wavelengths of 520 nm for the MC–Ca^{2+} complex (for the MC–Zn^{2+} complex, λ_{oxc} = 502 nm). These observations reveal two main features which inherently facilitate application of these MC–M^{2+} complexes to optical data storage. The first is that fluorescence of the complexed forms is more intense compared to the free MC form, which fluoresces only weakly at these wavelengths. Secondly, the fact that fluorescence occurs at 587 nm for both Ca^{2+} and Zn^{2+} complexed forms, and that the absorption and fluorescence envelopes do not overlap, eliminates the possibility of 'cross-talk' and points to the suitability of fluorescence as the method of choice for 'reading' data that has been 'written' into these systems.

In order to investigate the light-induced reversion of the metal-complexed MC form to SP, a solution of **3**–Ca^{2+} was irradiated continuously with a 520 nm light source. The measured fluorescence intensity decreased gradually over a 30 min period, signifying reversion to the closed SP form. Since the above UV–VIS measurements have shown that the MC form of **3** does not decay over a three day period, this reversion of the complexed MC to the SP form must be a photo-induced process. Clearly, the reversion would be more efficient upon irradiation at shorter wavelengths. Hence switching between the colorless SP and the colored MC–M^{2+} forms can be modulated *via* irradiation at two wavelengths: SP→MC–M^{2+}, 254 nm; MC–M^{2+}→SP, 520 nm (or lower λ).

The results of this work have shown that the MC form of **3** has been stabilized towards thermal reversion, a key requirement of optical data storage systems.[4] Importantly, this system exhibits bistability at room temperature and is photo-switchable with two different light energies.

In conclusion, this report documents the first thermally stable SP–MC photo-switch *via* intramolecular bidentate metal ion chelation. Further investigations are ongoing into the effects of alkyl chain length and metal ion complexation ability in stabilizing the MC form. Optimization, *via* molecular modeling, enforcing ligand conformation and varying the heteroatom substitution and the nature of the metal, may lead to a prototypical device based on these systems.

The authors thank the Natural Sciences and Engineering Research Council of Canada for support of this research.

Notes and References

† E-mail: buncele@chem.queensu.ca

1 *Photochromism: Molecules and Systems*, ed. H. Durr and H. Bouas-Laurent, Elsevier, London, 1992; B. L. Feringa, W. F. Jager and B. de Lange, *Tetrahedron*, 1993, **49**, 37 and 8267; A. S. Dvornikov, J. Malkin and P. M. Rentzepis, *J. Phys. Chem.*, 1994, **98**, 6746.

2 T. Tamaki and K. Ichimura, *J. Chem. Soc., Chem. Commun.*, 1989, 1477; M. Priegh, F.-Y. Lin, K. Z. Ismail and S. G. Weber, *J. Chem. Soc., Chem. Commun.*, 1995, 2091; M. Inouye, K. Akamatsu and H. Nakazumi, *J. Am. Chem. Soc.*, 1997, **119**, 9160.

3 J. H. R. Tucker, H. Bouas-Laurent, P. Marsau, S.W. Riley and J.-P. Desvergne, *Chem. Commun.*, 1997, 1165.

4 D. Rouvary, *Chem. Br.*, 1998, **34**, 26; S. Janicki and G. B. Schuster, *J. Am. Chem. Soc.*, 1995, **117**, 8524; F. Pina, M. J. Melo, M. Maestri, R. Ballardini and V. Balzani, *J. Am. Chem. Soc.*, 1997, **119**, 5556.

5 S.-R. Keum, M.-S. Hur, P. M. Kazmaier and E. Buncel, *Can. J. Chem.*, 1991, **69**, 1940; S.-R. Keum, K.-B. Lee, P. M. Kazmaier and E. Buncel, *Tetrahedron Lett.*, 1994, **35,** 1015.

Received in Cambridge, UK, 28th April 1998; revised manuscript received, 22nd June 1998; 8/04908D