

Bivalent Metal Ion-dependent Photochromism and Photofluorochromism from a Spiroquinoxazine

Michael J. Preigh, Fu-Tyan Lin, Kamal Z. Ismail and Stephen G. Weber*

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, USA

Illumination of solutions of spiroquinoxazine **1** yields both a coloured species and a fluorescent species, both of which are reverse photochromic and both of which are trapped by bivalent metal ion complexation.

When a photosensitive spiro-pyran or -oxazine is combined with a metal-ion coordinating moiety; then light may influence metal binding or metal binding may influence photochromism.^{1–3} We are interested in the design and application of fluorescent, metal-responsive photochromics for applications in sensors. We reasoned that the spiroquinoxazine **1**⁴ would be a good starting point for such a species; it has the fluorophore in the 6-hydroxyquinoline moiety, and the stable oxazin.² Further, the nitrogen near the quinoline ring may lead to nitrogen-lone-pair quenching of fluorescence, which is an excellent means of transduction for metal ion binding.⁵ However, **1** apparently has several potential metal-binding sites (**2–4** among others). Previous demonstrations of light-induced metal binding have relied upon substitution at the 4' position to create a nascent bidentate chelator that becomes active after photoinduced ring opening,⁶ or have augmented a macrocyclic ligand with a photochromic⁷ moiety. The published work has not clarified what goes on in simpler systems such as **1** which, though they do not have a dominant metal binding chelator, nonetheless have the potential for metal ion binding. We have found that the metal binding chemistry of **1** is surprisingly rich: we have convincing evidence for the existence of **2** and **3a**, and indirect evidence for **4**. Compound **2** is formed in the dark; compound **3** is formed thermally (slowly) or photochemically and the resulting complex is reversibly photochromic, but not fluorescent, **4** is accessible only photochemically, and it is fluorescent ($M = Co^{2+}, Zn^{2+}, Cr^{2+}, Cd^{2+}, Ni^{2+}, Fe^{2+}$ and Mg^{2+}). The precursor to **4** is the unstable photoisomer **5b**, which is itself fluorescent. Furthermore, we provide experimental evidence for the relative stabilities of the isomers that are *cis* or *trans* about the oxazine nitrogen–ring carbon bond.

The addition of $Zn(ClO_4)_2$ to a solution of **1** in equimolar proportions leads to downfield shifts in the 1H NMR resonances **8** of all of the quinoline protons, but especially those on C-5', -7' and -8'. There is only a 0.1 ppm shift in the resonance of the proton on C-2'. As the proton on C-2' is a very sensitive indicator of ring opening, we surmise that Zn^{2+} is associating with the quinoline nitrogen, structure **2**. Indeed, the influence of Zn^{2+} on the 1H -NMR spectrum of quinoline itself is similar. The shifts observed are not due to small quantities of water, certainly present in $Zn(ClO_4)_2$, as controls show no shifts in the 1H NMR spectra.

At 10- and 100-fold molar excess of Zn^{2+} , the ring opens as indicated by the new positions of the resonances of protons on C-2', -4 and -7. The thermal reaction is slow ($\approx 1 \times 10^{-3} s^{-1}$) and independent of the $[Zn^{2+}]$ which implies that the ring opening is the rate determining step. We favour **3a** as the

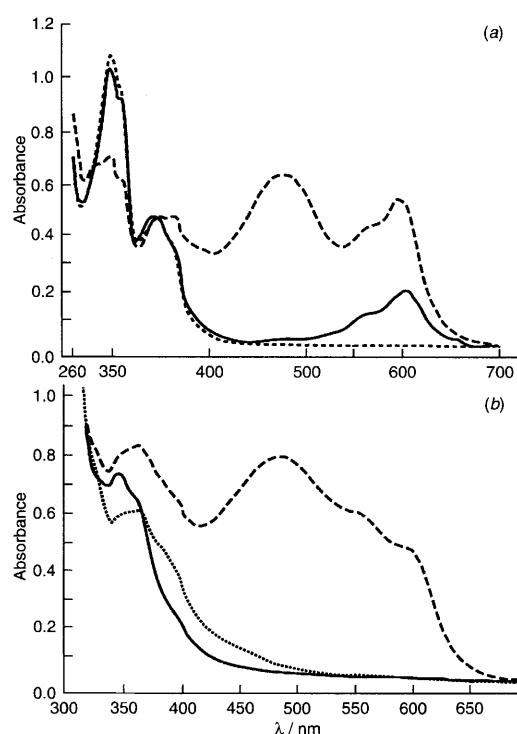
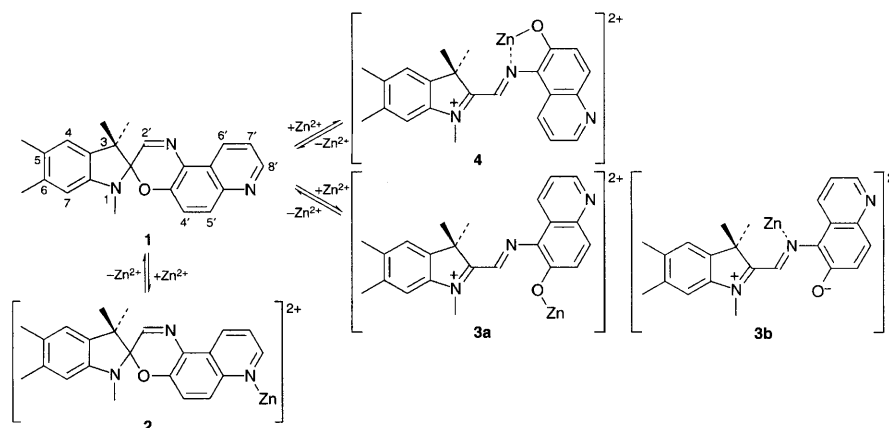


Fig. 1 (a) Electronic absorbance spectra of $1.0 \times 10^{-4} \text{ mol l}^{-1}$ **1** in acetonitrile (short dash), after 300 s illumination with 315–388 nm filtered (Turner 7-60) light from a 150 W Xe arc lamp (solid line), and an equivalent solution also containing $5.0 \times 10^{-3} \text{ mol l}^{-1} Zn(ClO_4)_2$ which had been illuminated as above (long dash). (b) Electronic absorbance spectra of $1.7 \times 10^{-4} \text{ mol l}^{-1}$ **1** and $8.3 \times 10^{-3} \text{ mol l}^{-1} Zn(ClO_4)_2$ in acetonitrile before illumination (solid line), after 300 s illumination with filtered (Turner 7-60) light from a 150 W Xe arc lamp (long dash), and after 120 s illumination with light of wavelength $> 600 \text{ nm}$ from a 150 W Xe arc lamp (short dash).



structure of the species that results. The evidence is as follows. The resonance of the proton on C-2' (δ 10.59) is within tenths of a ppm from where it is in other merocyanine-form oxazines. Monodentate coordination to the oxazine N (**3b**) would engender a significant shift in that resonance. The addition of the Zn^{2+} ion leads to a broad absorbance band in the visible (*vide infra*). A similar visible spectrum is obtained from adding Zn^{2+} to the spiropyrans 1',3',3'-trimethyl-8-nitrospiro-[2H-1-benzopyran-2,2'-indoline] (8-nitroBIPS) and 1',3',3'-trimethyl-6-hydroxyspiro-[2H-1-benzopyran-2,2'-indoline] (6-hydroxyBIPS). The only common ligand of these compounds is the Ar-O⁻ functional group. Finally, preparation of mixed-ligand complexes of transition metals and spiropyrans has led to evidence for the spiropyran acting as a monodentate ligand with the structure shown in **3a**.⁹

UV-VIS and ¹H NMR spectra qualitatively very similar to those mentioned above are recorded if a solution containing **1** and an excess of Zn^{2+} is photolysed (150 W Xe arc lamp through a 315–388 nm filter). The spectra of the illuminated solutions of **1** in the presence and absence of Zn^{2+} are shown in Fig. 1(a). This coloured solution is reverse photochromic [Fig. 1(b)] throughout the visible spectrum, *i.e.* both in the free ligand absorption band and in the zinc complex absorption band. Thus, the 3'-oxyanion moiety of **1** is a photochemically reversible metal ion ligand.

In contrast to the solutions prepared in the dark, solutions of **1** and metal ion perchlorate that have been illuminated (315–388 nm) are fluorescent at room temperature (Fig. 2). The corrected excitation spectrum does not resemble the absorbance spectrum of **3**. In metal-free solutions of **1**, a similar, but transient, fluorescence spectrum is generated by photolysis, thus the compound is photofluorochemical. The fluorescence of the metal-free solutions is diminished by illumination at $\lambda > 400$ nm. Further, in the dark the fluorescence in metal-free solutions decays with a rate that increases linearly with water content in acetonitrile–water mixtures (see inset in Fig. 2). Qualitatively similar results are seen for Co^{2+} , Mg^{2+} , Cr^{2+} ,

Cd^{2+} , Ni^{2+} and Fe^{2+} , but not Na^{+} or K^{+} , as perchlorates in MeCN–H₂O.

As the fluorescent compound is a minor constituent, we must infer its identity from circumstantial evidence. Neither ¹H NMR nor TLC show any signs of new compounds being formed after 30 min of photolysis. We believe that M^{2+} ion has trapped the unstable photoisomer **5b**. During the course of this work, computations and NOE experiments on similar compounds confirmed that isomer **5a** is more stable than **5b**.^{8a} Because of the instability, this isomer has, to our knowledge, never been observed experimentally in spiropyrans, spirooxazines, and related molecules. The luminescence arises because the Zn^{2+} occupies the unshared electron pair on the imine N which otherwise quenches the quinoline fluorescence. The effect of water on the relaxation rate is probably to act as a proton donor, stabilizing the zwitterionic resonance structure of **5** over the quinoidal. As the quinoidal resonance form has a far higher barrier to rotation about the aromatic C–N_{imine} bond than the zwitterionic resonance form, stabilization of the zwitterionic form enhances the rate of relaxation.

If this is actually a trapped photoisomer, it should be possible to remove the metal ion, and thus lose the unstable isomer and the corresponding fluorescence. Addition of a competing ligand, *e.g.* 4,4'-dimethyl-2,2'-bipyridine, to fluorescent, metal-containing solutions liberates **5b** which thermally relaxes, probably to **1**.

Recently, Tsivgoulis and Lehn have prepared a diarylethylene system in which the photoisomer is fluorescent.¹⁰ In that case, the major photoisomer is fluorescent, and thermal reversion negligible. The current compound's properties make it more suitable to, *e.g.* metal ion sensors, while the diarylethylene¹⁰ is more suited for optical memory applications.

The amount of fluorescence depends linearly on $[\text{Zn}^{2+}]$ at low $[\text{Zn}^{2+}]$ (for 5 concentrations plus blank from 100 nmol l⁻¹ to *ca.* 5 $\mu\text{mol l}^{-1}$, $r^2 = 0.9983$). Thus this compound, or compounds like it, may have application in metal ion sensing.

We are grateful to Dr Barry vanGemert and Mr David Knowles of PPG Industries for providing the spirooxazine, and for many helpful discussions. We thank the Office of Naval Research for financial support.

Received, 6th June 1995; Com. 5/03653D

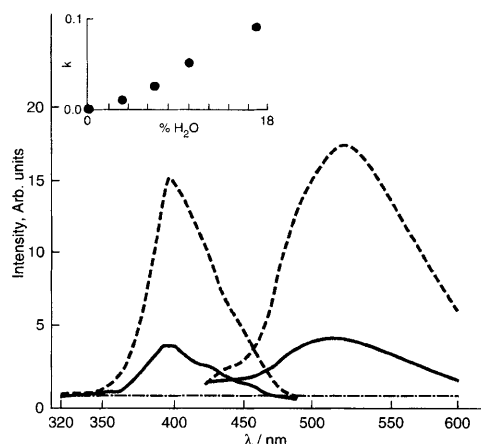
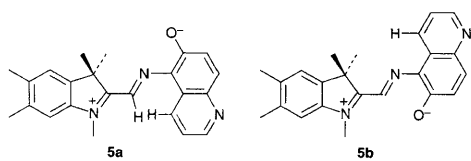


Fig. 2 Fluorescence emission and excitation spectra with and without added Zn^{2+} . Spectra after illumination (Turner 7-60) of $5.0 \times 10^{-4} \text{ mol l}^{-1}$ **1** in acetonitrile (solid) and of a similar solution containing also $3.3 \times 10^{-5} \text{ mol l}^{-1}$ $\text{Zn}(\text{ClO}_4)_2$ (long dash). Before illumination (dash-dot). Inset: fluorescence emission decay rate (s^{-1}) as a function of volume percent water in acetonitrile.



Scheme 2

References

1. R. Guglielmetti, in *Photochromism*, ed. H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990, pp. 855–878.
2. N. Y. C. Chu, in *Photochromism*, ed. H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990, pp. 879–882.
3. Seminal papers: J. D. Phillips, A. Mueller and F. Przystal, *J. Am. Chem. Soc.*, 1965, **87**, 4020; L. D. Taylor, J. Nicholson and K. B. Davis, *Tetrahedron Lett.*, 1967, 1585. Reviews: (a) I. Willner and B. Willner; (b) J. D. Winkler, K. DeShayes and B. Shao, in *Bioorganic Photochemistry V.2: Biological Applications of Photochemical Switches*, ed. H. Morrison, New York, 1993, (a) pp. 1–110; (b) pp. 167–196.
4. W. S. Kwak and R. J. Hurditch, *US Pat.*, 4 637 698, Jan. 20, 1987.
5. A. P. deSilva, H. Q. N. Gunaratne and G. E. M. Maguire, *J. Chem. Soc., Chem. Commun.*, 1994, 1214; A. W. Czarnik, *Acc. Chem. Res.*, 1994, **27**, 302.
6. T. Tamaki and K. Ichimura, *J. Chem. Soc., Chem. Commun.*, 1989, 1477; T. Tamaki, Y. Kawanishi, T. Sehi, M. Sakuragi, K. Ihimura and T. Yamaguchi, *J. Photopolymer Sci. Tech.*, 1990, **3**, 85; K. Kimura, T. Yamashita, M. Kaneshige and M. Yokohama, *J. Chem. Soc., Chem. Commun.*, 1992, 969; H. Oda, *Chem. Express*, 1993, **8**, 629.
7. M. Inouye, Y. Noguchi and K. Isagawa, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1163, and references therein.
8. (a) S. Nakamura, K. Uchida, A. Murakami and M. Irie, *J. Org. Chem.*, 1993, **58**, 5543; (b) N. L. Zaichenko, A. V. Lyubimov, V. S. Marevtsev and M. I. Cherkashin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1040.
9. M. LeBaccon and R. Guglielmetti, *New J. Chem.*, 1988, **12**, 825.
10. G. M. Tsivgoulis and J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1119.