Bivalent Metal Ion-dependent Photochromism and Photofluorochromism from a Spiroquinoxazine

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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 photochromic[7] 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

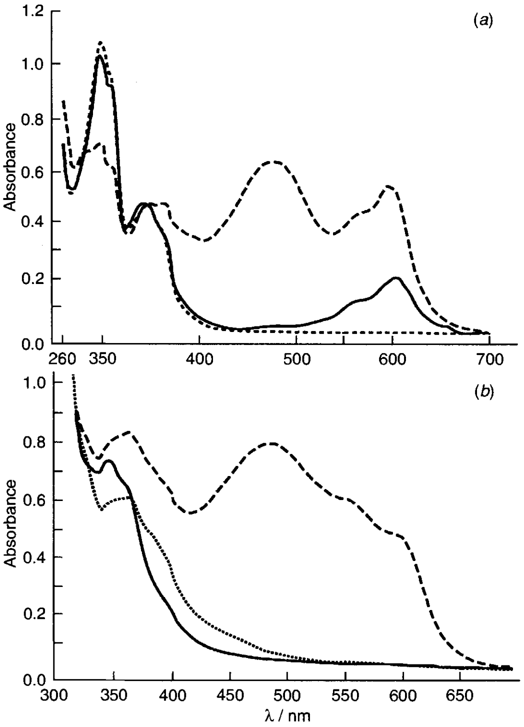
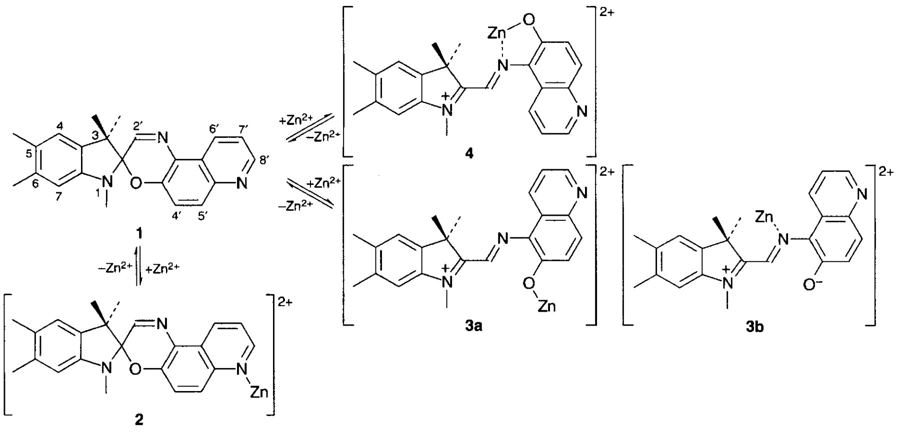


Fig. 1 (*a*) Electronic absorbance spectra of 1.0×10^{-4} mol l^{-1} **1** in acetonitrile (short dash), after 300 s illumination with 315–388 nm filtered (Turner 7-60) light from a 150 W Xe arc lamp (solid line), and an equivalent solution also containing 5.0×10^{-3} mol l^{-1} $Zn(ClO_4)_2$ which had been illuminated as above (long dash). (*b*) Electronic absorbance spectra of 1.7×10^{-4} mol l^{-1} **1** and 8.3×10^{-3} $Zn(ClO_4)_2$ 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 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 oxaxines. 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-[2*H*-1-benzopyran-2,2′-indoline] (8-nitroBIPS) and 1′,3′,3′-trimethyl-6-hydroxyspiro-[2*H*-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 ^{1}H 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 photofluorochromic. The fluorescence of the metal-free solutions is diminished by illumination at $\lambda >$ 400 nm. Further, in the dark the fluoresence 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 $MeCN–H_2O$.

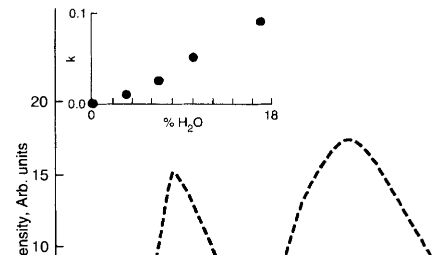
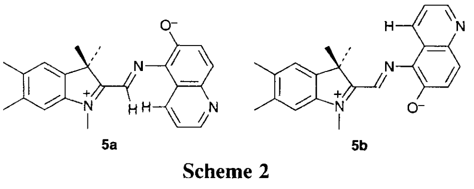


Fig. 2 Fluorescence emission and excitation spectra with and without added Zn^{2+}. Spectra after illumination (Turner 7-60) of 5.0×10^{-4} mol l^{-1} **1** in acetonitrile (solid) and of a similar solution containing also 3.3×10^{-5} mol l^{-1} $Zn(ClO_4)_2$ (long dash). Before illumination (dash-dot). Inset: fluorescence emission decay rate (s^{-1}) as a function of volume percent water in acetonitrile.



5a **5b**

Scheme 2

As the fluorescent compound is a minor constituent, we must infer its identity from circumstantial evidence. Neither ^{1}H 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 diarylethylene[10] is more suited for optical memory applications.

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

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