

# Photoinduced switching of metal complexation by quinolinospiropyranindolines in polar solvents

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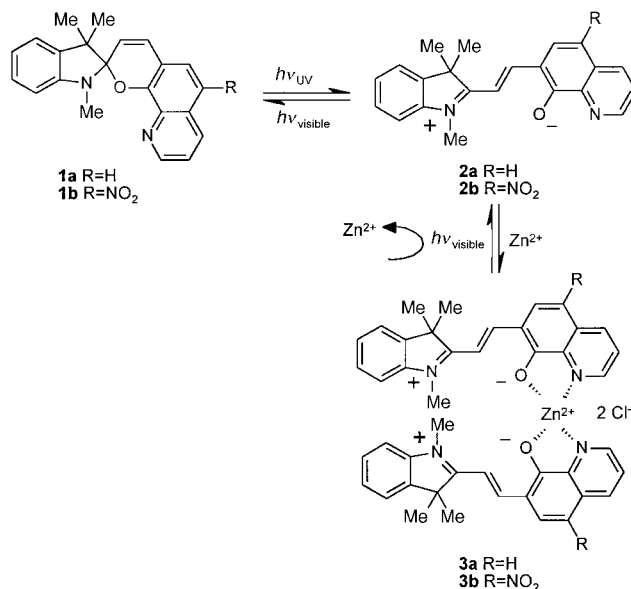
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The first demonstration of rapid and reversible, photo-induced switching of metal complexation from a quinolinospiropyranindoline–metal complex in aqueous solution is presented.

The design and synthesis of functional molecules with molecular switching characteristics is currently an area of intense activity and tremendous potential significance to the fields of molecular electronics and sensor device fabrication.<sup>1</sup> The development of new materials for application in sensing transducers has traditionally been plagued by non-reversible interactions between the analyte and sensing receptor, a factor resulting in one-time use sensors. Innovative efforts to overcome this problem have typically relied upon the incorporation of both the complexation or recognition site and a light- or potential induced rejection mechanism into a single sensing molecule.<sup>2,3</sup> Spiropyrans<sup>4,5</sup> and spirooxazines<sup>6,7</sup> have shown particular promise in this regard due to the photochemically-mediated interconversion of ‘open’ and ‘closed’ forms (*e.g.* **1** ⇌ **2**) upon exposure to UV or visible light, respectively. The introduction of metal ion complexation sites to take advantage of the spiropyranindoline ⇌ merocyanine interconversion leads to the photoreversible ejection of complexed metal ions.<sup>4</sup> To our knowledge, there are no published accounts of photoreversible metal ion complexation by these compounds in aqueous media. The reason for this is simple: stabilization of the merocyanine isomer in water prevents the photoinduced ejection of trapped metal ions. Photoreversible metal complexation in water is critical to the eventual application of these materials to sensor transducers operated in aqueous systems for environmental monitoring. Here we describe the molecular design issues critical to promoting photoreversible metal complexation for spirobenzopyrans in polar solvents, and present the first demonstration of rapid and reversible, photoinduced switching of metal complexation from a quinolinospiropyranindoline–metal complex in aqueous solution.

Two 8-hydroxyquinoline-derived spiropyranindolines **1a** (R = H)<sup>4,8</sup> and **1b** (R = NO<sub>2</sub>),<sup>4</sup> which differ only by the addition of a nitro group *para* to the pyran oxygen, are shown in Scheme 1.

While the denticity of 8-hydroxyquinoline for metal ions is well precedented, our initial expectation was that the stability of the metal/merocyanine complex **3a** would prevent photoisomerization to **1a** with concomitant release of metal ion. Spirobenzopyran **1b** was, therefore, prepared to promote photoreversibility of metal complexation by withdrawing electron density away from the phenolate oxygen and decreasing the denticity of **2b**. Spirobenzopyran **1b** does indeed exhibit significant, photoreversible metal complexation in organic solvents with low polarity, such as tetrahydrofuran. Unfortunately, there is little to no observable reversibility in solvents of higher polarity, such as acetonitrile. The inability to achieve the conversion of **3b** to **1b** *via* irradiation can be explained by the enhanced stabilization of the zwitterionic merocyanine form, **2b**, by the nitro group which serves to

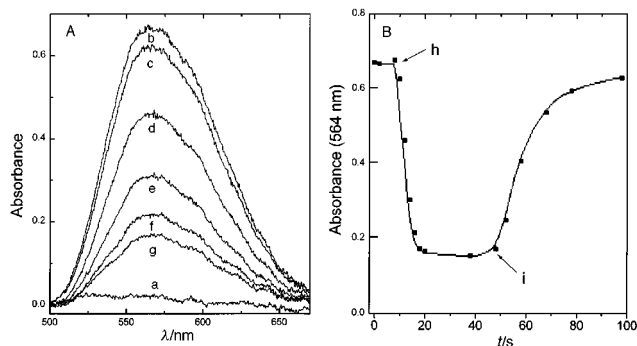


**Scheme 1** Photoreversible equilibria of quinolinospiropyranindoline (**1a**, R = H) and nitroquinolinospiropyranindoline (**1b**, R = NO<sub>2</sub>).

delocalize the phenoxide anion in **2b**.<sup>9</sup> This stabilizing effect of the nitro group in **2b** is underscored by the rapid conversion of **1b** in the dark to the colored, merocyanine form **2b** in solvents with dielectric constants higher than that of tetrahydrofuran. Note from Scheme 1 that in addition to the solvent dependent generation of **2** under dark conditions, the concentration of **2** is further enhanced under UV light illumination. Ultimately, the lifetime of any free zinc ions ejected into solution is significantly attenuated due to the rapid recomplexation event, **2b** → **3b**.

The thermodynamic stability of the closed quinolinospiropyranindoline, **1**, must be enhanced to promote photoreversibility of metal complexation of **3** in polar solvents. The simplest way of doing this is to remove the nitro group *para* to the phenoxide anion, as in **1a**. Evidence for the improved stability of **1a** relative to **1b** is apparent from the colorless solution, indicative of the closed spiropyran, obtained for **1a** in acetonitrile ( $2.4 \times 10^{-5}$  M; Fig. 1A, spectrum a). The dark addition of 0.5 equivalents of Zn<sup>2+</sup> to this solution of **1a** in acetonitrile (Fig. 1A, spectrum b) results in the formation of a bright red complex **3a**, with Zn<sup>2+</sup> in a 2 : 1 ligand : metal ratio, based upon stoichiometric determinations using the molar ratio absorbance method.

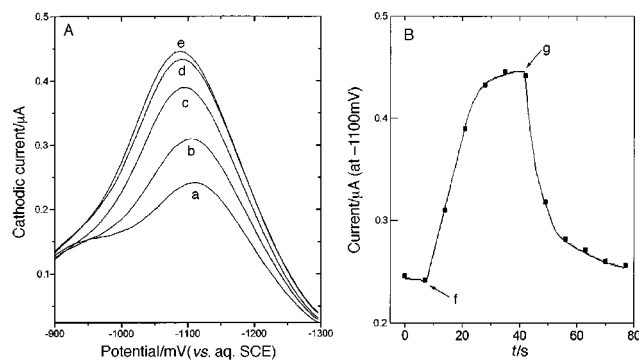
Exposure of a solution of **3a** in acetonitrile to visible light (150 W tungsten flood lamp) causes the temporary ejection of the complexed metal ion, and a transition to the colorless, closed form of the quinolinospiropyranindoline (**3a** → **1a**). Evidence for this shift is shown in Fig. 1A, which shows the effect of exposure of a solution of **3a** to visible light as a function of time.



**Fig. 1** (A) UV-VIS spectra of  $2.4 \times 10^{-5}$  M **1a** in acetonitrile with (a) no  $\text{Zn}^{2+}$  added; (b)  $1.2 \times 10^{-5}$  M  $\text{Zn}^{2+}$  added; and solution (b) after exposure to visible light for (c) 2, (d) 12, (e) 14, (f) 16, (g) 20 s. (B) Switching behavior observed in the absorbance intensity at 564 nm with visible light on at 8 s (h) and off at 48 s (i).

This amazing effect can be monitored visually without the aid of a spectrometer, the transition from a strongly colored, red complex to a nearly colorless solution (78% reduction in absorbance at 564 nm, Fig. 1A) indicating that the complex **3a** is undergoing photoisomerization to the closed spirobenzopyran form **1a** and ejecting the complexed  $\text{Zn}^{2+}$  ion in the process. The photochemically mediated ejection of the metal ion from **3a** is fast, with an 8 s response time following the onset of visible light irradiation (Fig. 1B). Immediately following the cessation of light, the free metal ion is quickly recomplexed (50 s time response) as the equilibrium shifts back to its original state (**1a**  $\rightarrow$  **3a**). In contrast, ejection of  $\text{Zn}^{2+}$  ion from a solution of **3b** in acetonitrile upon irradiation with visible light is minimal (14%), a result which can be ascribed to the enhanced stability of **2b** in polar solvents, as described above. This rapid switching behavior in the metal complexation properties of spiropryanindoline **1a** is an important step toward the development of molecular devices and sensors.<sup>10</sup>

While UV-VIS spectroscopy monitors equilibria pertaining to the ligand, electrochemistry can be used to monitor equilibria associated with the metal ion. Square wave voltammetry was utilized (1) as a complementary technique to confirm the ejection of metal ions from the merocyanine complex, and (2) to assess the extent of reversible rejection of complexed zinc from both **3a** and **3b** in aqueous solution (a 4:1 water-acetonitrile solution was utilized due to solubility constraints). Initially, a control experiment was run on a solution of  $1.2 \times 10^{-5}$  M  $\text{Zn}^{2+}$  in order to identify the peak position and intensity of the  $\text{Zn}^{2+}$  cathodic wave ( $-1100$  mV vs. aq. SCE). Exposure of the control solution to visible light had no effect on the voltammogram prior to the addition of the spiropryanindolines. Both **1a** and **1b** ( $2.4 \times 10^{-5}$  M) led to rapid complexation of  $\text{Zn}^{2+}$ , resulting in the near elimination of the free  $\text{Zn}^{2+}$  potential peak. Because of the rapid increase in current associated with the reduction of water, we were unable to identify any cathodic waves corresponding to the reduction of **3a** or **3b**. Unlike the irradiation of **3b** with visible light, which resulted in no change in the free  $\text{Zn}^{2+}$  cathodic wave at  $-1100$  mV, complex **3a** exhibited an ejection of 8% of the complexed  $\text{Zn}^{2+}$  ions into the aqueous solution (Fig. 2A). The rate of recomplexation of ejected  $\text{Zn}^{2+}$  ions in water (Fig. 2B) was nearly twice as fast as



**Fig. 2** (A) Cathodic reduction of free  $\text{Zn}^{2+}$  ions in a 4:1 water-acetonitrile solution containing  $2.4 \times 10^{-5}$  M **1a** and  $1.2 \times 10^{-5}$  M  $\text{Zn}^{2+}$  after exposure to visible light for (a) 0, (b) 7, (c) 14, (d) 21, (e) 28 s. (B) Switching behavior observed in the cathodic reduction of free  $\text{Zn}^{2+}$  ions in solution with visible light on at 7 s (f) and off at 42 s (g).

that observed in acetonitrile (light on, 14 s response time; light off, 28 s response time, both in an unstirred solution). The attenuation in the extent of photoreversible metal ejection and the more rapid metal ion recomplexation are both indicators of the enhanced stabilization effect water has on the merocyanine form, **2a**, when compared to the solvent, acetonitrile.

In conclusion, we have demonstrated a rapid, switching type mechanism for photoreversible metal complexation by quinolino-spiropyranindoline **1a** in aqueous solution. Modifications of these systems designed to enhance the photoreversibility in aqueous media are currently under investigation in our laboratories.

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## Notes and references

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- 9 T. Bercovici, R. Heiligman-Rim and E. Fischer, *Mol. Photochem.*, 1969, **1**, 23.
- 10 In addition to  $\text{Zn}^{2+}$ , the photoreversibility of complexation by NQSP and QSP was examined using UV-VIS spectroscopy for the following metals:  $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ . NQSP in THF exhibited photoreversibility for  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ , while QSP in THF and MeCN exhibited photoreversibility for only  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$ .

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