Optical Switching of the Redox Activity of a Hydroxychromene

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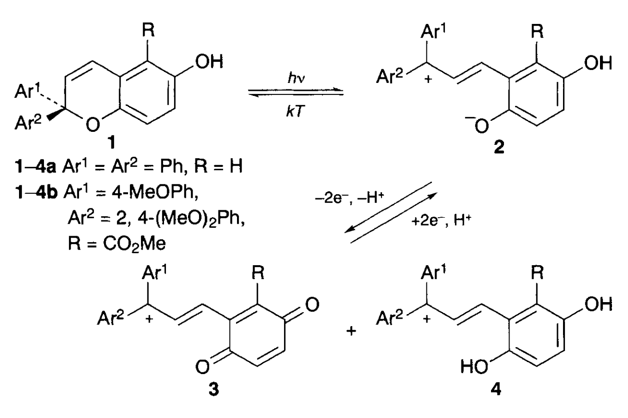
Simultaneous illumination and oxidation allows the transient photoisomer of a hydroxychromene to be held open or 'trapped', with subsequent liberation of the trapped quinone by dark cathodic reduction.

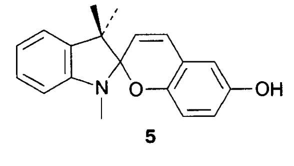
An approach to exerting control over the light-induced switching capability of chromenes[1] is the combined use of photochemistry and electrochemistry. Potential applications in optical memory,[2] imaging,[3] and control over binding to biomolecules,[4] will require the ability to switch at will between two or more states upon application of external stimuli. Recently, Kawai *et al.*[5] described a dithienylethene derivative in which a photochemical ring closure brought two phenols into contact through conjugation to yield hydroquinone–quinone-like redox electrochemistry. Prior to that, Liu *et al.*[6] found that a liquid crystalline azobenzene could be reduced more easily in the photoisomeric *cis* than the *trans* form. Newell and Utley[7] described an arylvinylanthraquinone in which the electrochemistry and photochemistry function independently of each other.

We have endeavoured to trap electrochemically the transient, merocyanine-like photoisomers of chromenes, indolinospiropyrans and indolinooxazines, which undergo thermal relaxation faster than azobenzenes[1a] ($< 10^{-3}$ *vs.* 10^{-5} s^{-1}) and much faster than the thermally irreversible dithienylethenes.[1f] The ability to trap the photoisomer, lending a permanence to the switching that the chromenes, indolinospiropyrans and indolinooxazines do not naturally possess, is important for molecular-level control in applications. Our approach, as applied to 6-hydroxy-2,2-diphenylchrom-3-enes, is postulated in Scheme 1. We take advantage of the difference in redox potentials between the pyran form **1**, an alkoxyphenol analogue, and the merocyanine form **2**, a hydroquinone monoanion analogue.

Our initial attempts at reversible electrochemical trapping of a photochromic species, involving a chromene **1a** (Scheme 1) and the analogous 6-hydroxy-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] **5**,[8] failed. In the case of **5**, oxidation at the indoline nitrogen of the closed form occurs at a potential near the oxidation of the hydroquinone of the open form. In the case of **1a**, electrochemical trapping is irreversible; this is attributed to the electrophilicity of the trapped species **3a**. By analogy with previous work by Padwa *et al.*,[9] ^1H NMR showed that when **1a** was photoisomerized in the presence of nucleophiles, *e.g.* OMe^-, OH^- and OAc^-, the photoproducts relaxed very slowly, or not at all, back to **1a**. We hypothesized that the cationic **3a**, containing only the positive centre, would be even more susceptible to attack by *e.g.* adventitious water. The results of the above experiments suggest that for a chromene to undergo reversible electrochemical trapping, it must possess electron-donating groups that can stabilize the positive charge that forms upon photoinduced cleavage of the pyran ring. At the same time, the electron-donating system must not be too electron-rich, otherwise it will undergo anodic oxidation (*e.g.* the indolino group of the indolinospiropyrans).



Scheme 1



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The electrode was reticulated vitreous carbon (RVC, 254 pores cm^{-1}. Electrochemistry, photochemistry and UV–VIS spectroscopy were carried out in the same RVC-containing 1 mm cuvette oriented at 45° to the spectroscopic and photoillumination light paths, which were orthogonal.

Compound **1b** (λ_{max} 372 nm, ε_{372} = 5.1×10^3 $dm^3\ cm^{-1}\ mol^{-1}$) exhibits typical photochromism.[1] Irradiation of a solution of **1b** (5.57×10^{-4} $mol\ dm^{-3}$, MeCN) with 300–400 nm light yielded a visible absorption band (λ_{max} 504 nm, ε_{504} = 1.1×10^4 $dm^3\ cm^{-1}\ mol^{-1}$). Thermal relaxation follows in the dark ($k = 2.2 \times 10^{-3}\ s^{-1}$).

We found that, as planned, anodic oxidation of **1b** and **2b** occurs at distinctly separate peak potentials (+0.92 and +0.33 V, respectively, *vs.* Fc^+/Fc, by CV). Cyclic voltammetry of **1b** (Fig. 1) in the absence and presence of 300–400 nm light, shows that electrochemistry occurs during UV irradiation [E_{pa} = +0.33 V (*vs.* Fc^+/Fc)] [Fig. 1(*a*)], and no electrochemistry occurs in the dark [Fig. 1(*b*)]. The trapping and reversal were achieved with illumination at the potentiostated RVC electrode [Fig. 2(*a*)] while monitoring the UV-VIS spectra [Fig. 2(*b*)]. The photochronoamperometry [Fig. 2(*a*)] clearly shows that **1b** undergoes no electrochemistry in the dark at +0.47 V (*vs.* Fc^+/Fc). The simultaneously obtained spectra show that the solution is unchanged in the dark at +0.47 V (*vs.* Fc^+/Fc) for 10 s [Fig. 2(*b*),——]. Upon simultaneous irradiation with 300–400 nm light and application of +0.47 V (*vs.* Fc^+/Fc) for 15 s, there is a significant photocurrent and a large change in the visible spectrum. New absorption bands at 520 and 580 nm

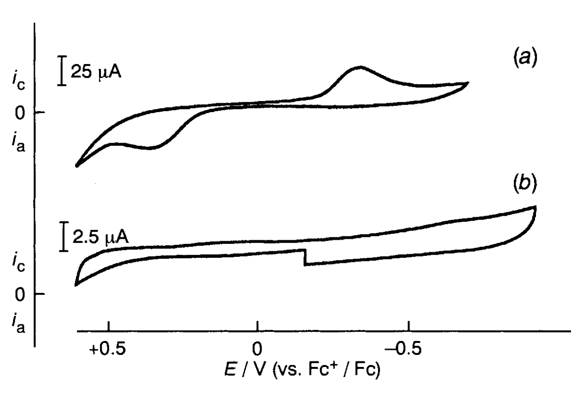

Fig. 1 CV of **1b** (1.06×10^{-3} $mol\ dm^{-3}$) in Me_3CN containing 0.1 $mol\ dm^{-3}$ TEAP (tetraethylammonium perchlorate) supporting electrolyte, (*a*) under 300–400 nm irradiation (25 $\mu A\ cm^{-1}$) and (*b*) in the dark (2.5 $\mu A\ cm^{-1}$). Scan rate 7 $mV\ s^{-1}$

appear [Fig. 2(*b*), – – –]. The photoanodic trapping step is then reversed by application of −0.58 V (*vs.* Fc^+/Fc) [Fig. 2(*a*), t = 37 s] in the dark for 20 s. There is a large cathodic current, and the visible absorption spectrum returns nearly to its original appearance. UV photolysis of the cathodic reduction product [Fig. 2(*b*), - - -] at open circuit for 10 s yielded the spectrum of **2b** [Fig. 2(*b*), – – –], verifying the return to **1b**. Successive photoanodic/dark cathodic cycling of **1b** revealed that the amount of **1b** recovered after the first cycle decreased by roughly 10%, with smaller decreases after successive cycles. This may be photochemical or electrochemical degradation, it may be due to lack of buffering (oxidation produces H^+), or it may simply be diffusion out of the observation volume.

We identified two absorption bands in the electronic spectrum following illumination at +0.47 V [Fig. 2(*b*), – – –], one at 520 nm and one at 580 nm. In independent experiments we confirmed that the 580 nm band is due to protonation of the merocyanine form **4b**. We suggest that the 520 nm band is due to **3b**. We carried out anodic oxidation of **1b** in the dark as a control. UV-VIS spectroscopic monitoring of the dark anodic oxidation of **1b** revealed the appearance of two large absorption bands at 410 and 550 nm. These bands are completely different from those observed during the photoanodic oxidation.

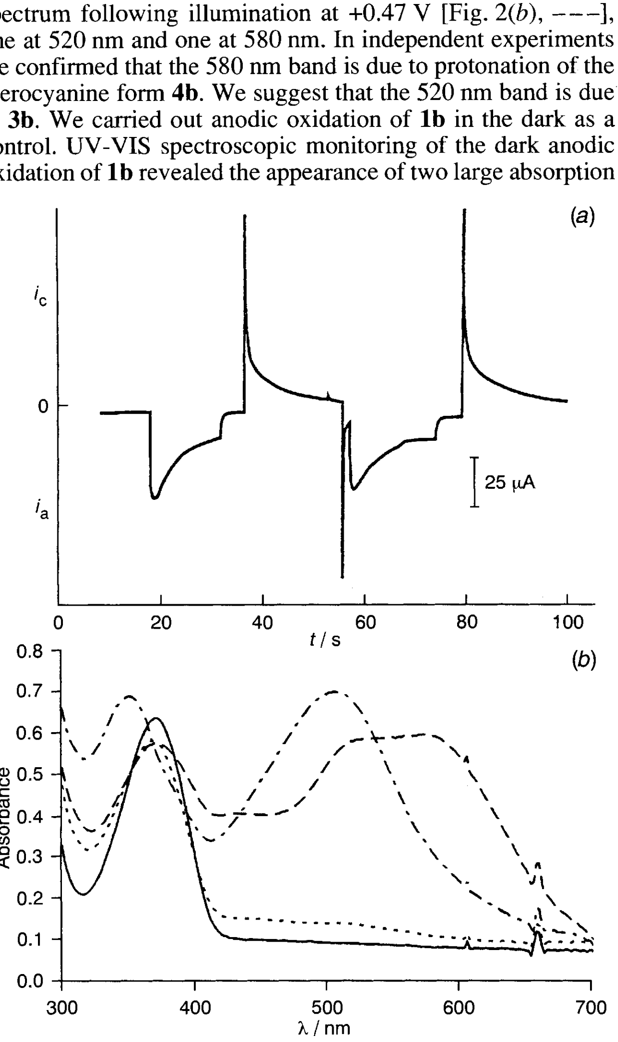

Fig. 2 (*a*) Photochronoamperometry of **1b**, two-cycle photoanodic oxidation/dark cathodic reduction: t = 8 s, start of experiment, +0.47 V; t = 18 s, +0.47 V, UV on; t = 32 s, +0.47 V, UV off; t = 37 s, −0.58 V, UV off; t = 56 s, +0.47 V, UV off; t = 57 s, +0.47 V, UV on; t = 73 s, +0.47 V, UV off; t = 79 s, −0.58 V, UV off; t = 100 s, potential off, UV off. (*b*) Electronic spectroscopic monitoring of the photoanodic oxidation/dark cathodic reduction of **1b**; (——) +0.47 V, dark, t = 5 s; (– – –) +0.47 V and 300–400 nm irradiation, t = 25 s; (- - -) −0.58 V, dark, t = 50 s; (– – –) 300–400 nm irradiation, open circuit, t = 110 s. All potentials are *vs.* Fc^+/Fc. λ_{max} (nm): (——), 370; (– – –), 520, 580; (- - -), 370; (– – –), 350, 504.

If the scheme proposed is correct, then we ought to be able to trap the photoisomer with a *homogeneous* electron transfer reaction. We have found that small amounts of water considerably diminish the redox potential for Fe^{III}/Fe^{II} in MeCN–H_2O solvents. Thus, when a solution of **1b** (0.37 mmol dm^{-3}, MeCN) and Fe^{III} [$Fe(ClO_4)_3$, 0.75 mmol dm^{-3}, MeCN] is prepared with 1.25% H_2O, we found that, in the dark, little or no reaction of **1b** with Fe^{III} occurred. Upon irradiation with 300–400 nm light, the 520 and 580 nm absorptions observed for the photoanodic oxidation appeared. On the other hand, when only 0.25% H_2O was added to the solvent, the Fe^{II}/Fe^{III} couple is a more powerful oxidant. We observed oxidation of **1b** in the dark. The 410 and 550 nm absorption bands observed for the dark anodic oxidation of **1b** were also observed in the presence of 0.25% H_2O. Irradiation of this solution with 300–400 nm light caused further oxidation as evidenced by an increase in A_{520} and a shoulder at *ca.* 580 nm.

In summary, by using light to switch the redox potential of the electron-donor moiety of a hydroxychromene, we have demonstrated the ability to trap photoisomerized **1b** by anodic oxidation of **2b**, and then reverse the trapping by dark cathodic reduction of the trapped form back to **1b**. Homogeneous trapping adds a new dimension to potential applications while confirming the simple 'electron sink' role of the electrode.

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