Functionalized Photochromics for Molecular Switching: The Multistabilities of a Dihydroazulene–Anthraquinone System

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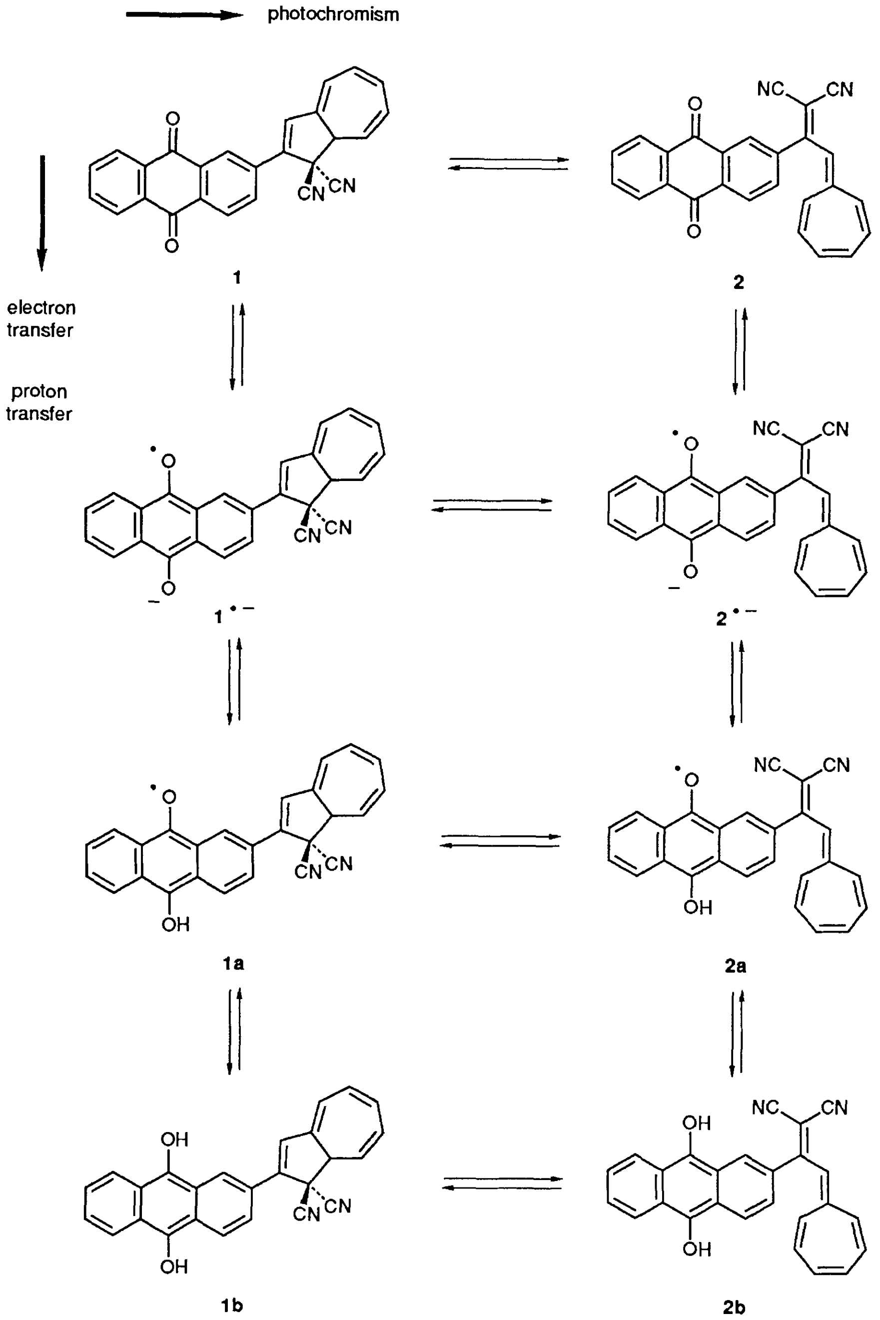
Addressability and multimode activity of the dihydroazulene–anthraquinone conjugate **1** are investigated by photochemical and electrochemical techniques, establishing pH-dependent redox behaviour and dihydroazulene–vinylheptafulvene photochromism (**1**⇆**2**), enabling an electric current to be modulated by light-pulse-irradiation.

Functionalized dye compounds are receiving increased attention as organic molecular units for energy and information storage and processing.[1] Of special interest within this class of compounds are dynamic systems with photochromic behaviour due to their potential as bistable or oligostable optical devices.[2] Functionalized photochromics therefore provide access to multifold switching. In preceding work using photomodulation amperometry we have demonstrated that the dihydroazulene–vinylheptafulvene couple[3] covalently attached to electron-transfer-active substructures, enables chemical and physical switching caused by a photochemically induced rearrangement accompanied by a change of the redox potential.[4]

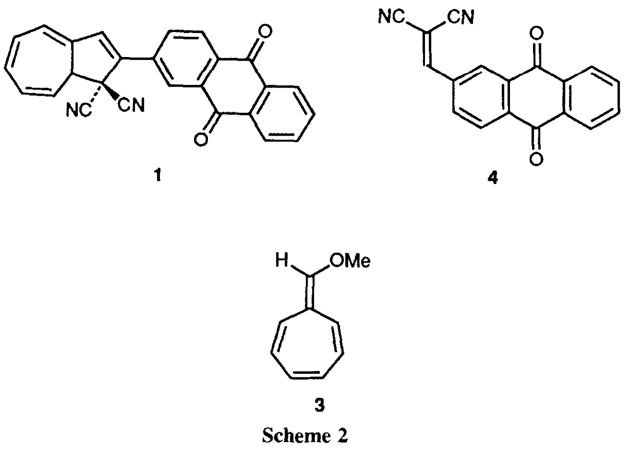
This report extends these investigations to compound **1** containing a dihydroazulene and a covalently linked anthraquinone subunit offering the following functionalities for switching: (*i*) photochromism (photochemical **1** → **2** reaction and thermal back-reaction **2** → **1**), (*ii*) reversible electron-



Scheme 1 Light-driven multimode molecular switching of the electrontransfer active dihydroazulene 1

transfer and (*iii*) protonation–deprotonation (Scheme 1). In this preliminary account the general features of multifold processes are outlined and characterized by electrochemical and optical methods and by photomodulation amperometry.[5]

A convenient synthetic route to the dihydroazulene–anthraquinone conjugate **1** is employed starting from 2-(dicyanovinyl)-9,10-anthraquinone **4**† and 8-methoxyheptafulvene **3**.[3,6]‡



Scheme 2

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† 2-(Dicyanovinyl)-9,10-anthraquinone **4** was synthesized from 2-formyl-9,10-anthraquinone and malonodinitrile, yellow crystals from dimethylformamide (DMF), m.p. 260–270 °C (decomp.); IR (KBr): ν/cm^{-1} 3030w, 2220m (C≡N), 1670s (C=O).

‡ 2-(1,1-Dicyano-1,8a-dihydroazulen-2-yl)-9,10-anthraquinone **1**, yellow crystals, m.p.: 215–216 °C, 78% yield; IR (KBr): 2930, 1670, (C=O), 1590, 1330 and 1300 cm^{-1}.

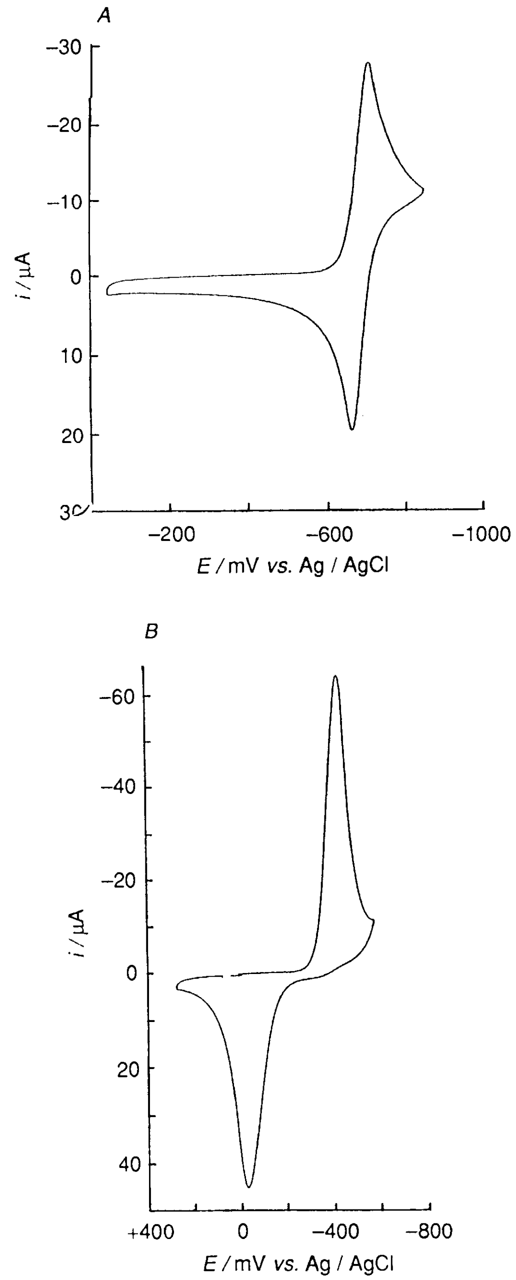

Fig. 1 Cyclic voltammetry of **1** in acetonitrile depending on pH: (*A*) under neutral conditions, (*B*) at pH 5.6 (ammonium acetate–acetic acid)

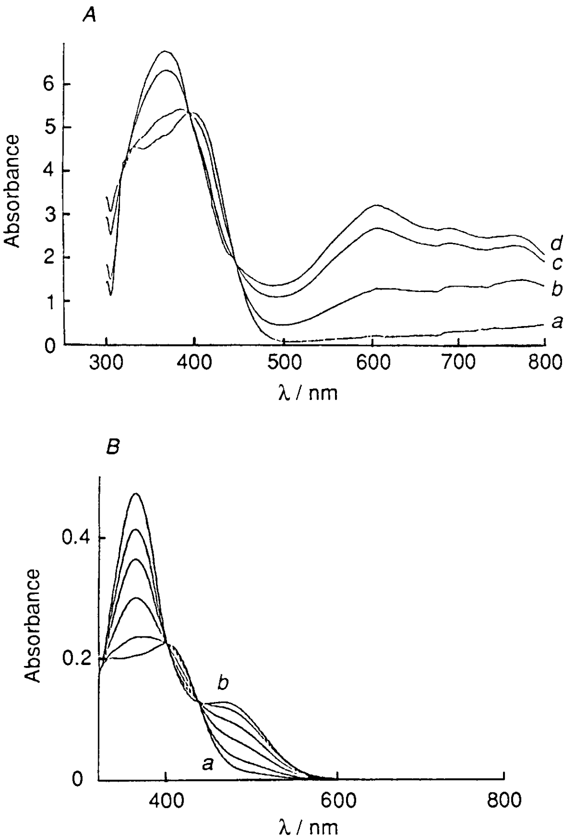

Fig. 2 Spectra obtained by multisweep voltammetry of **1** depending on pH, (*A*) in acetonitrile, (*a*) 0 mV, (*b*) −800 mV, (*c*) −900 mV, (*d*) −950 mV; (*B*) in acetonitrile at pH 5.6 (buffer trimethylammonium acetate–acetic acid), (*a*) 0 mV; (*b*) −700 mV

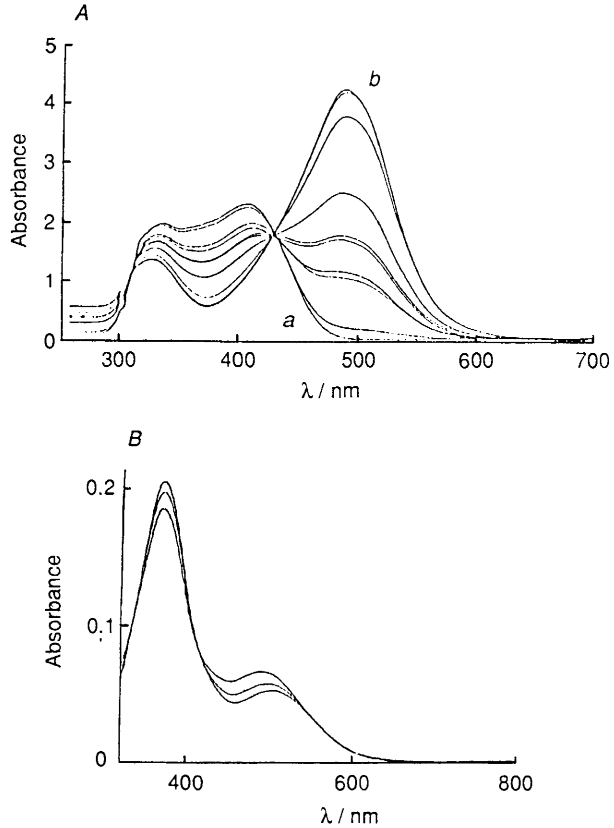

Fig. 3 Spectral changes on irradiation. (*A*) in dichloromethane, (*a*) before irradiation, (*b*) after 1 min irradiation with an Osram HWLS 500 W lamp. (*B*), in dichloromethane at pH 4–5, irradiation with the daylight lamp after reduction to hydroquinone **1b**.

Redox-active dye compound **1** in acetonitrile is reversibly reduced to the quinone radical anion ($E_{1/2}$ = −780 mV *vs.* Ag/AgCl) (Fig. 1*A*) at slightly less negative potential than 9,10-anthraquinone **5** under the same conditions (**5**: $E_{1/2}$ = −925 mV *vs.* Ag/AgCl).[7] Extended reduction of $\mathbf{1}^{\bullet-}$ to the dianion $\mathbf{1}^{2-}$ occurs irreversibly at $E_{1/2}$ = −1295 mV *vs.* Ag/AgCl, scan 250 mV, with the formation of a new species identified by an oxidation peak at E_p = ±90 mV *vs.* Ag/AgCl. The reduction of **1** depends on the solvent and pH. Cyclic voltammetry (Fig. 1*B*), of **1** in acetonitrile at pH 5.6 (buffer tetramethylammonium acetate–acetic acid) reveals a complex electron- and proton-transfer mechanism with EC-characteristics originating from two one-electron-transfer steps accompanied by fast protonation and leading to hydroquinone **1b** *via* semiquinone **1a** as the intermediate.

Spectroelectrochemistry underlines the reversibility of the individual processes demonstrated by cyclic voltammetry (Fig. 2). Under neutral conditions (Fig. 2*A*), the formation of

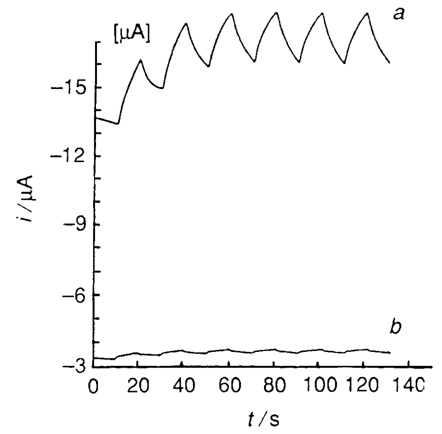

Fig. 4 Pulsed irradiation of a homogeneous solution of anthraquinone **1**, in acetonitrile (*c* 8.9 10^{-4} mol l^{-1}), at room temp. working potential: (*a*) −800 mV, (*b*) −700 mV. Switching sequence, light on: 10 s, light off: 10 s.

radical anion $\mathbf{1}^{\bullet -}$ is indicated by long-wavelength absorptions originated from the anthraquinone radical anion.[7,8] On reduction at pH 5.6 isosbestic points at 400 and 437 nm and new absorption maxima at λ_{max} = 363 and 465 nm appear, which clearly prove the formation of hydroquinone **1b** (Fig. 2*B*).[9]

Dihydroazulene conjugate **1** on irradiation in dichloromethane or chloroform with a daylight lamp (Osram HWLS, 500 W) rearranges to vinylheptafulvene **2** accompanied by a red-shift of the long-wavelength absorption.§ In the dark at room temperature **2** is reconverted completely to the dihydroazulene **1** (Fig. 3*A*). It is noteworthy that in acetonitrile under the same irradiation conditions the photochemical rearrangement could not be observed by UV–VIS-spectroscopy, presumably because of a fast thermal back-reaction **2** → **1**, which was found to be faster in acetonitrile than in dichloromethane.

The photochromism depends on the oxidation state of the quinone group as shown in Fig. 3*B*.[10] Even extended irradiation of the hydroquinone **1b** formed from **1** by electrochemical reduction at pH 4–5 leads to only a minor decrease of the long-wavelength absorption of dihydroazulene **1b** with a new signal appearing λ_{max} = 473 nm as demonstrated by difference spectroscopy. This proves a slight shift of the **1b**/**2b** equilibrium to isomer **2b** with a vinylheptafulvene residue.

Compound **1** was subjected to photomodulation amperometry, an electrochemical–photochemical combination-technique specially devised to investigate photolabile functional dyes which change their redox potential on photochemical rearrangement. In a photoelectrochemical cell, a solution of **1** in acetonitrile was irradiated with a pulsed light-beam under constant potential conditions set at a slightly less negative potential than that required for the reduction of **1** to $\mathbf{1}^{\bullet -}$. The resulting response signal yields the switching pattern given in Fig. 4. By light induced rearrangement of **1** into **2** the reduction potential decreases and a fast e^--transfer takes place reducing **2** to $\mathbf{2}^{\bullet -}$ leading to a cathodic current which retreats after interrupting the light source. Obviously owing to the fast electron-transfer even a small amount of vinylheptafulvene–anthraquinone conjugate **2** photochemically generated in acetonitrile is sufficient to create the photomodulation pattern shown in Fig. 4.

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§ Absorption spectra λ_{max}/nm (lg ε): **1**, 405 (4.22) nm; **2**, 488 nm.

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