Photo- and electro-chromism of a 1,4-anthraquinone derivative. A multi-mode responsive molecule

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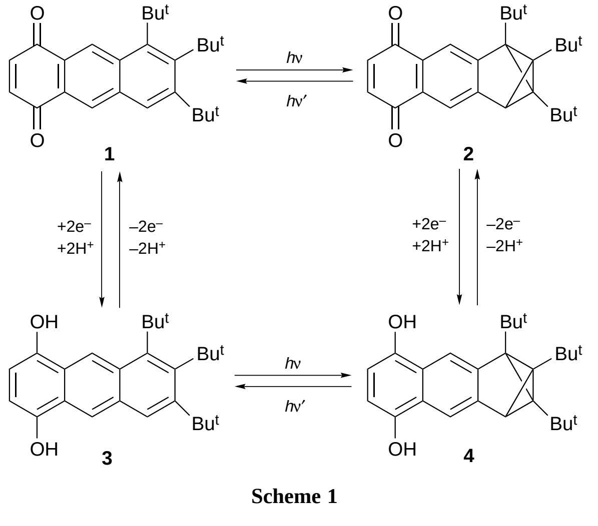
5,6,7-Tri-*tert*-butyl-1,4-anthraquinone shows electro- and photo-chromism, independently based on the electrochemical redox reaction of the carbonyl groups and the χ[2 + 2]-type photo-valence isomerization of the aromatic ring.

In the context of the importance of multi-mode responsive molecules in chemionics,[1] optical–electrical dual-mode responsive molecular devices have been the subject of much recent interest.[2–4] It is desirable that such a device can be reversibly converted between all of the four possible states,[2] and that the photo- and electro-chromic properties are completely integrated within a single structure.[4] However, among the examples reported so far, the number of molecular systems possessing these characteristics is very limited. Here, we report that 5,6,7-tri-*tert*-butyl-1,4-anthraquinone **1** shows electro- and photo-chromism independently and can be converted reversibly between all of the four possible states (Scheme 1). The 1,4-anthraquinone derivative **1** was synthesized by the thermal decarbonylation of 5,6,7-tri-*tert*-butyl-5,8-oxomethano-5,8-dihydro-1,4-anthraquinone prepared previously by us.[5]

Steady-state photolysis of **1** was performed with a degassed solution of **1** (5.6×10^{-4} m) in hexane at room temperature with 460 nm light from a xenon lamp using a monochromator. As shown in Fig. 1, the absorption spectral changes upon photolysis revealed isobestic points indicating that the photoreaction proceeded without forming by-products. Spectroscopic and analytical data for the product were compatible with the valene-type isomer **2**. The photo-valence isomerization of **1** was photochemically reversible. Upon irradiation of the solution of **2** with 402 nm light (one of the isobestic points), absorption bands for **1** were recovered, reaching a photostationary state with a composition of **1**:**2** = 7.2:1. Spectral changes for the reverse reaction were also accompanied by distinct isobestic points. Thus, the 1,4-anthraquinone derivative **1** shows photochromism based on χ[2 + 2]-type photo-valence isomerisation similar to other tri-*tert*-butyl-substituted polyacenequinones.[5,6]

It is well known that 9,10-anthraquinone undergoes a reversible two-step redox reaction to the hydroanthraquinone dianion *via* a semiquinone radical in aprotic solvents, and correspondingly its polarograph in DMF shows two reduction waves at $E_{1/2} = -0.98$ and -1.74 V (*vs.* SCE).[7] 1,4-Anthraquinone derivative **1** showed electrochemical behaviour similar to that of 9,10-anthraquinone, and the cyclic voltammogram of **1** in dry DMF containing Bu_4NClO_4 revealed two reversible redox waves at $E_{1/2} = -0.71$ V (*vs.* SCE), assignable to the redox between **1** and its semiquinone radical, and at -1.43 V, for the redox between the semiquinone radical and hydroanthraquinone dianion. Spectral changes upon electrolysis were measured using a thin-layer cell (*ca.* 0.3 mm thickness) made of transparent indium–tin oxide coated glass (ITO glass) and using the indium film on the glass as the working electrode. The spectral changes for the cathodic reduction of **1** in dry DMF (containing Bu_4NClO_4) were not simple because of the simultaneous formation of the semiquinone radical and the hydroanthraquinone dianion. Therefore, Fig. 2 shows the time scanning spectral changes for the reduction of **1** at -1.0 V (*vs.* SCE), where most of **1** could be reduced to semiquinone radical, in the presence of acetic acid (0.03 m) as a proton source. The spectral changes showed a simple decrement of the bands (474 and 333 nm) due to **1** and the appearance of a new band (400 nm) and its increment accompanied by distinct isobestic points. In the presence of the proton source, the semiquinone radical of **1** will be protonated rapidly to give monohydroanthraquinone radical, and successive disproportionation of the radical will form 5,6,7-tri-*tert*-butyl-1,4-hydroanthraquinone **3** and **1**. The product responsible for the new absorption was assigned to **3** based on the fact that the new absorption spectrum was in good agreement with that obtained for **3** chemically synthesized from **1** as follows. A diethyl ether solution of **1** and aq. $Na_2S_2O_4$ were mixed together in an optical cell, and after degassing by freeze-thaw cycles the contents were sonicated. In the absorption spectrum of the



Scheme 1

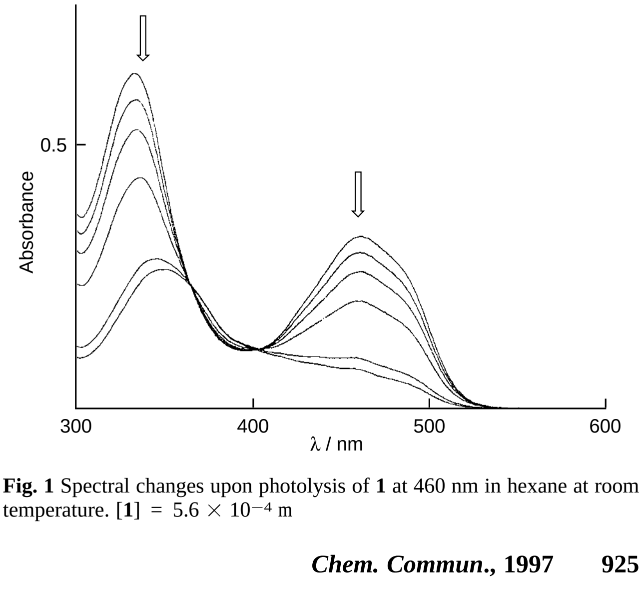


Fig. 1 Spectral changes upon photolysis of **1** at 460 nm in hexane at room temperature. [**1**] = 5.6×10^{-4} m

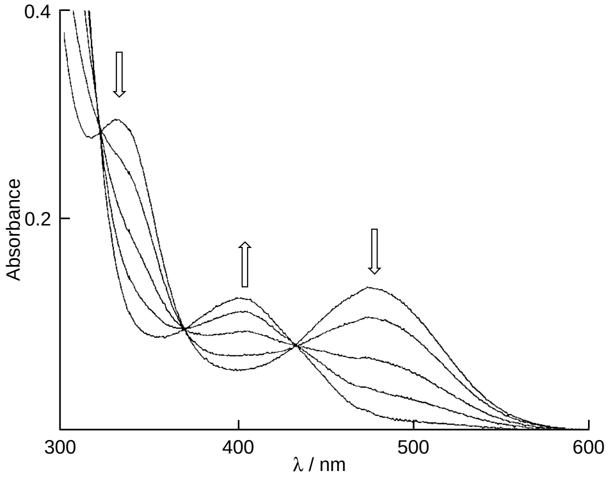


Fig. 2 Spectral changes upon cathodic reduction of **1** at -1.0 V *vs.* SCE in DMF containing acetic acid (0.03 m) and Bu$_4$NClO$_4$ (0.1 m)

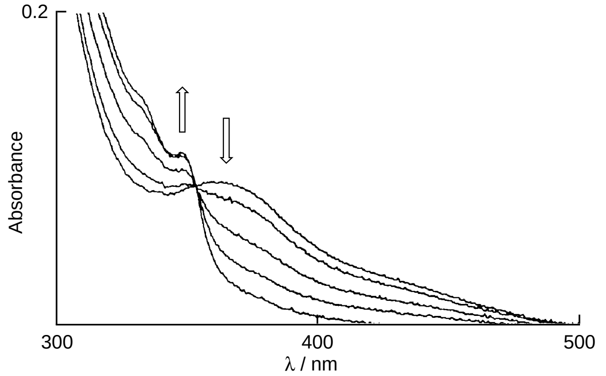


Fig. 3 Spectral changes upon cathodic reduction of **2** at -1.0 V *vs.* SCE in DMF containing acetic acid (0.03 m) and Bu$_4$NClO$_4$ (0.1 m)

ethereal layer, the bands due to **1** were not observed and a band at 398 nm appeared. Upon exposure of the ethereal solution to air, the band at 398 nm disappeared and the bands for **1** were recovered completely. ^{1}H NMR spectroscopy of the product obtained by Na$_2$S$_2$O$_4$ reduction of **1** was consistent with the structure of **3** (*vide infra*).

The electrochemical reaction of **1** was reversible. After cathodic reduction of **1** in the thin-layer cell, the polarity of the electrode was changed and the spectral changes were followed for anodic oxidation at +0.2 V (*vs.* SCE). The band at 400 nm due to **3** decreased with concomitant increases of the bands due to **1** finally giving the complete recovery of the latter.

The electrochemical behaviour of the valene isomer **2** was similar to that of **1**, and its cyclic voltammogram also revealed two reversible redox waves at -0.65 and -1.42 V (*vs.* SCE). Fig. 3 shows the spectral changes that occurred during the cathodic reduction (-1.0 V *vs.* SCE) of **2** in dry DMF containing acetic acid and Bu$_4$NClO$_4$. The new absorption spectrum was in good agreement with that of the hydronaphthoquinone derivative **4** obtained by Na$_2$S$_2$O$_4$ reduction of **2**. The electrochemical reaction was also reversible, and upon anodic oxidation at +0.5 V (*vs.* SCE), **4** disappeared and **2** was recovered completely.

A diethyl ether solution of **3** (1.06×10^{-4} m) was prepared by the method described above. In the spectral changes following the photolysis (436 nm) of the solution (Fig. 4), the band at 398 nm for **3** decreased and new bands at 347 nm and 330 nm appeared and increased. The new absorption spectrum was in good agreement with the spectrum of **4** obtained by Na$_2$S$_2$O$_4$ reduction or cathodic reduction of **2**. The reaction was photochemically reversible, and upon photolysis of the photolysate at 347 nm, the absorption bands for **4** decreased and the bands for **3** were recovered. Spectral changes for both of the forward and the reverse reactions revealed distinct isobestic points. The photochemical interconversion between **3** and **4** was followed also by ^{1}H NMR spectroscopy as follows. A solution of **1** in CDCl$_3$ was put in an NMR sample tube and a solution of Na$_2$S$_2$O$_4$ in D$_2$O was added. In the ^{1}H NMR spectrum measured after sonication, signals due to **1** disappeared and a set of signals for **3** appeared [δ 8.99 (s, 1 H), 8.32 (s, 1 H), 7.51 (s, 1 H), 6.52 (s, 2 H), 1.76 (s, 9 H), 1.48 (s, 9 H) and 1.37 (s, 9 H)]. After irradiation at 436 nm, the signals for **3** disappeared and a new set of signals for **4** appeared [δ 7.90 (s, 1 H), 7.58 (s, 1 H), 6.50 (ABq, 2 H), 2.36 (s, 1 H, benzylic H), 1.58 (s, 6 H, two methyl groups of the *tert*-butyl group on benzylic carbon) and 1.22 (s, 21 H, two *tert*-butyl groups and one methyl group); the *tert*-butyl group on the benzylic carbon gave split signals due to restricted rotation]. It was confirmed that the changes in the ^{1}H NMR spectra were photochemically reversible.

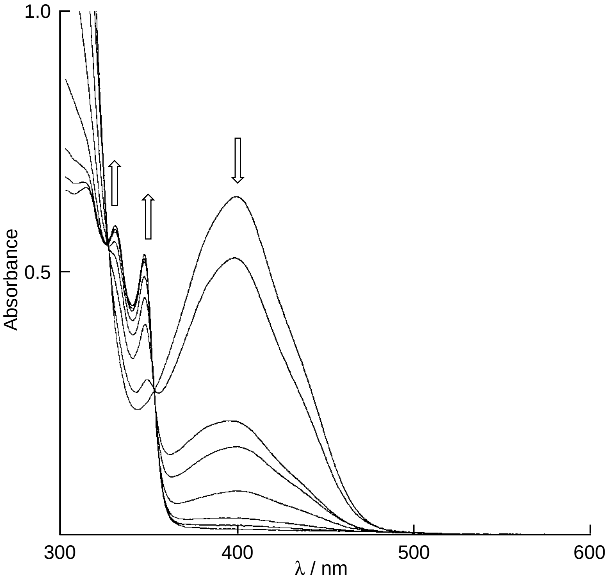


Fig. 4 Spectral changes upon photolysis of **3** at 436 nm in diethyl ether at room temperature. [**3**] = 1.06×10^{-4} m

The present system is considered to be an example of a multi-mode chemical transducer. All of the four states (**1**, **2**, **3** and **4**) have infinite thermal stability, while in the reported case of phenylazoquinones, the *cis*-phenylazo isomers are kinetically unstable.[2]

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