Illumination of the 9-mesityl-10-methylacridinium ion does not give a long-lived photoredox state

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Photolysis of the 9-mesityl-10-methylacridinium cation in benzonitrile forms an acridinyl radical, detected by EPR and UV–visible spectroscopy, by way of a sacrificial process.

Light-induced electron transfer across a bilayer lipid membrane takes place in natural photosynthesis by way of a cascade of short range steps.[1] Each individual electron transfer event has to compete with exoergonic charge recombination within the relevant radical ion pair. As such, the thermodynamics are optimised to favour charge separation over charge recombination. When seeking to construct artificial photosystems that display unusually long-lived charge-transfer states, it has also been necessary to use the multi-step approach. Thus, certain molecular triads,[2] tetrads,[3] pentads,[4] *etc.*, have been shown to form increasingly long-lived (*e.g.*, μs to s), charge-separated states at ambient temperature. All such systems operate by long range charge separation and by ensuring that the redox state lies at a lower energy than the localised triplet excited states.

The alternative strategy of using a simple molecular dyad to produce a long-lived, charge-separated state seems not to be viable[5] because of the inherent problem caused by charge recombination. The full impact of the Marcus inverted region is rarely seen, due to quantum mechanical effects and/or nuclear tunnelling.[6] Molecular dyads seldom provide charge-separated states living for longer than a few tens of ns. However, a recent report by Fukuzumi *et al.*[7] challenges this general viewpoint by describing a simple 9-mesityl-10-methylacridinium dyad, of which the photoredox state remains for 2 h at −70 °C. This is an astonishing claim, contrary to all expectations, that, if correct, could lead to the construction of novel molecular photonic devices without recourse to elaborate synthesis. A crucial part of the experimental proof of the existence of long-lived photoredox states with strongly temperature-dependent lifetimes comes from low temperature EPR studies made in deoxygenated benzonitrile.[7,8] We have confirmed that illumination of the dyad under these conditions can indeed form an exceptionally long-lived radical, but our interpretation of the results differs markedly from that given by Fukuzumi *et al.*[7]

9-Mesityl-10-methylacridinium hexafluorophosphate (**1**) could not be prepared by the Bernthsen reaction of condensing diphenylamine and 2,4,6-trimethylbenzoic acid with $ZnCl_2$ at a high temperature. It was eventually prepared in three steps from 9(10*H*)-acridone, firstly by protecting the N atom, followed by reaction with 2-mesitylmagnesium bromide and hydrolysis with aqueous Na_2CO_3. The resultant 9-mesitylacridine was methylated using CH_3I or dimethylsulfate and converted to its hexafluorophosphate salt. Multiple recrystallisations from CH_3OH–Et_2O and CH_3CN–Et_2O solutions finally produced a sample of **1** which, as evidenced by electrospray mass spectrometry (ES–MS), showed minute traces ($\ll$1%) of an impurity. Very pure samples of **1** were obtained from preparative TLC (silica gel) using an acetone–water–KPF_6 solution. The authenticity of **1** was confirmed by high field ^{1}H-NMR spectroscopy, ES–MS and elemental analysis.† Benzonitrile (Aldrich HPLC grade) was redistilled from either CaH_2, P_2O_5, or eluted through activated alumina.

Spectroelectrochemical studies made in deoxygenated acetonitrile containing 0.1 mol dm^{-3} tetra-*N*-butylammonium hexafluorophosphate gave a UV–visible absorption spectrum of the resultant acridinyl radical (Fig. 1). This latter species shows pronounced absorption around 520 nm and weaker transitions that stretch towards the far red region. There is also a strong absorption band centred around 360 nm. The radical was stable on standing at rt in the absence of oxygen but was quickly oxidised upon aeration of the solution. Electrochemical reduction in benzonitrile also gave the acridinyl radical. The EPR spectrum recorded at 20 °C is shown in Fig. 2 and gives a *g*-factor of 2.0035. Confirmation of the assignment to this species was obtained by computer simulation of the spectrum. Somewhat similar EPR spectra have also been reported for the related 9-phenyl-10-methylacridinyl radical.[9,10]

A solution of **1** in deoxygenated benzonitrile was illuminated ($\lambda > 350$ nm, 150 W quartz–halogen) in the cavity of a Varian X-band EPR spectrometer at temperatures between 170 and 243 K. A weak signal began to appear after a few min
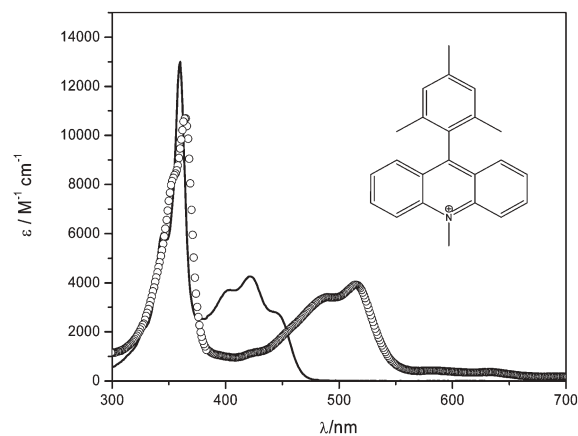

Fig. 1 Absorption spectra recorded for **1** before (solid line) and after (open circles) reduction at −0.6 V *vs.* Ag–AgCl in acetonitrile.
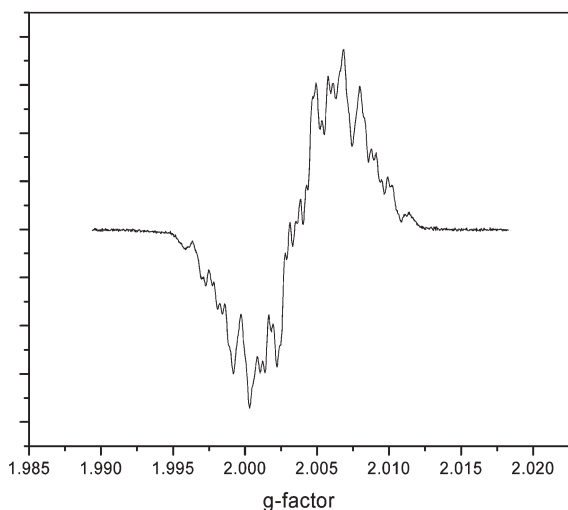
Fig. 2 EPR spectrum recorded after the *in situ* electrochemical reduction of **1** in benzonitrile at 20 °C.

illumination. The intensity of this signal increased progressively with illumination time, until reaching a steady-state value after about 10 min. The signal disappeared upon melting of the solvent and recooling to 200 K in the dark. No signal was observed prior to illumination, and prolonged irradiation of the solvent alone failed to give an EPR signal. These results were reproducible with different samples of **1**. Upon extinguishing the light source, the signal was found to be stable for at least 30 min at 243 K. As no obvious sign of decay was observed, our conclusion is that a stable radical is generated upon photolysis under these conditions.

The observed EPR spectrum is symmetrical and centred at $g = 2.0036$ (Fig. 3 (inset)). This signal cannot be attributed to either a triplet state or a superposition of two doublet radicals, unless the latter have exactly the same *g* values. A comparison with the electroreduction studies suggests that the photoproduct is the corresponding acridinyl radical, formed by one-electron reduction.

These experimental findings are in general agreement with those reported previously, except that whereas we see a stable radical, Fukuzumi *et al.*[7] were able to measure decay kinetics. Their results indicate a lifetime of *ca.* 36 min at 200 K and an activation energy

of *ca.* 48 kJ mol^{-1} for the decay process. Fukuzumi *et al.*[7] also describe the EPR spectrum as being a superposition of signals for the mesityl radical cation and the 10-methylacridinyl radical—as formed by a light-induced charge shift across the dyad. The spectral profile was not shown.

Steady-state irradiation of **1** in deoxygenated benzonitrile at rt, under conditions similar to those used for the EPR studies, gave rise to the absorption spectral changes shown in Fig. 3. During the first few minutes, there is a progressive build up of a product having an absorption spectrum remarkably similar to that of the acridinyl radical. The radical decays slowly by second-order kinetics under these conditions (Fig. 4 (inset)). Addition of oxygen greatly increases the rate of decay but recovery of **1** is limited to about 50% (Fig. 4), and a further coloured product remains. It is interesting to note that the acridinium–acridan system has been studied as a model for the NAD$^+$–NADH redox couple.[9] It has also been reported that the presence of a 9-phenyl group stabilises the intermediate species involved in this cycle.[9,11]

In summary, our studies show that illumination of **1** in deoxygenated benzonitrile gives rise to a species that appears to be the one-electron reduced acridinyl radical. This species is not a long-lived, charge shift or photoredox product. It is clear that it arises from a sacrificial photoreaction, but the source of electrons remains to be identified. Since different batches of **1** react identically, it is unlikely that an impurity in the sample is responsible for photochemical breakdown. This leaves the solvent to be considered. For the above studies, the benzonitrile was redistilled from CaH$_2$ and its purity checked by cyclic voltammetry. There is a possibility that this treatment introduces trace amounts of amine into the system;[12] it is well known that certain amines act as sacrificial electron donors in photochemical processes.[13] Treating the solvent with activated alumina resulted in a significant decrease in the level of photoactivity, but did not totally inhibit formation of the acridinyl radical under illumination. However, redistillation from P$_2$O$_5$ had the effect of curtailing photochemical production of the acridinyl radical under steady-state conditions. Since P$_2$O$_5$ will remove amines from the solvent, it is reasonable to assume that the build up of acridinyl radical under illumination is a direct consequence of trace amounts of amine present in the solvent. Indeed, photolysis of **1** in P$_2$O$_5$-treated benzonitrile containing benzylamine (1 mM) led to formation of the acridinyl radical.
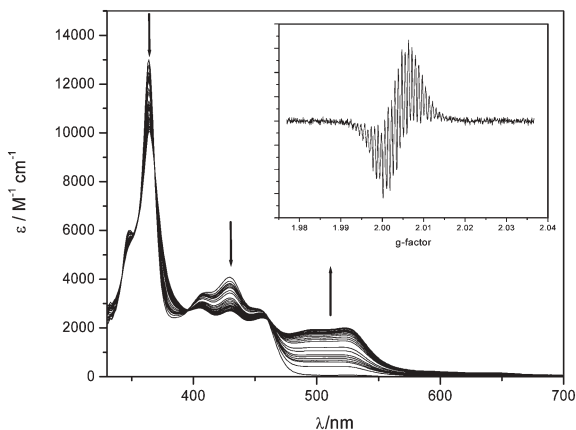

Fig. 3 Absorption spectral changes observed following the illumination of **1** in deoxygenated benzonitrile at 20 °C and the EPR spectrum (inset) recorded following the *in situ* illumination of **1** in benzonitrile at 243 K.
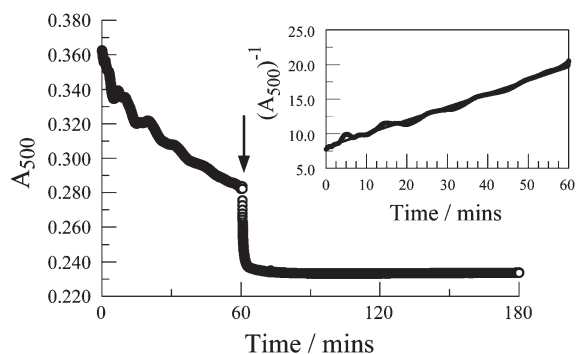

Fig. 4 Decay of the radical produced by photolysis of **1** in deoxygenated benzonitrile at 20 °C. The arrow denotes when air was admitted. The insert shows a fit to second-order kinetics.
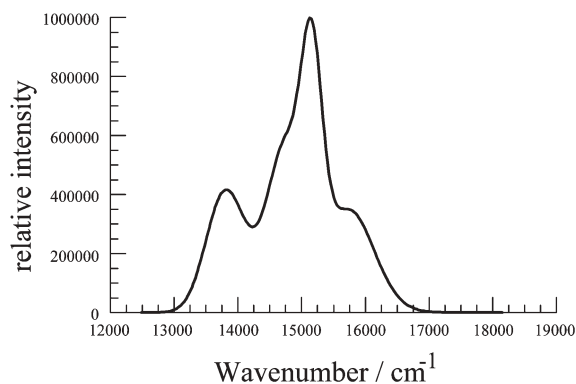
Fig. 5 The phosphorescence spectrum recorded for **1** in deoxygenated ethanol at 77 K.

A set of EPR studies carried out using HPLC-grade benzonitrile gave rise to a very small signal that retained the appearance of the acridinyl radical. Repeating the low temperature EPR studies with benzonitrile redistilled from P_2O_5 gave a barely detectable signal that developed over a few min illumination. This latter signal was difficult to resolve from the baseline. The signal was tiny over the 200–243 K range and disappeared upon melting of the solvent. In this case, refreezing the solvent under continued illumination did not lead to the reappearance of the signal, indicating that the supply of electrons had been extinguished. The EPR signal was too small to be identified, although the g value was around 2.004, and did not decay during 30 min of standing at 240 K.

We can consider two modes of formation for the acridinyl radical. Firstly, illumination of **1** in a polar solvent promotes rapid charge-transfer from the mesityl group to the acridinium cation.[7,8] The fate of the resultant photoredox state is uncertain,[14] but it is possible that a small fraction of the strongly oxidising mesityl cation reacts with an amine impurity.‡ This would result in the sacrificial build up of acridinyl radical, providing that the amine radical cation eliminates a proton and forms a reducing radical. Secondly, charge recombination within the photoredox state might lead to the formation of a triplet excited state, localised on the acridinium cation.[14,15] This latter species, which is likely to be long-lived under steady-state conditions, could enter into bimolecular reactions. Indeed, **1** exhibits phosphorescence at 77 K (Fig. 5), showing clearly that the energy of the π,π^* triplet state ($E_T =$ 1.96 eV) is below that of the reported energy of the redox state ($E_{CT} = 2.37$ eV).

Our experimental results are quite inconsistent with the concept of charge recombination in **1** being exceptionally slow. The observed EPR signal is not due to the photoredox state, but results from a sacrificial photoreaction. The electron donor is probably an amine impurity in the solvent. The yield of the acridinyl radical formed at low temperatures in highly purified benzonitrile is far too low for it to have arisen from anything other than a sacrificial photoreaction, driven by a trace (*i.e.* ppb quantities) impurity. It is notable that the corresponding 9-naphthyl-10-methyl-acridinium cation also gives a long-lived radical under steady-state illumination in CaH_2-distilled benzonitrile. Prior work has shown that charge recombination in this latter system occurs within 10 ns.[14,16] Furthermore for **1**, there is a low energy π,π^* triplet state that acts as an energy sink. These observations cast doubt on the earlier claims.[7] It seems prudent to reinvestigate the spectroscopic studies and provide a full kinetic balance for the events that follow from the illumination of **1**. The outcome of such an investigation will be of extreme importance to the future design of molecular electronic components.

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Notes and references

† Full synthetic details will be reported in due course.
‡ The mesityl group in **1** and mesitylene display irreversible oxidation peaks in cyclic voltammograms due to the fast chemical breakdown of the mesityl radical cation.

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