DOI: 10.1002/ejoc.200800806

On the Photochemical Stability of the 9-Mesityl-10-methylacridinium Cation

Andrew C. Benniston,*[a] Kristopher J. Elliott,[a] Ross W. Harrington,[b] and William Clegg[b]

Keywords: Acridinium cation / Degradation / Oxidation / Photochemistry / NMR spectroscopy

The 9-mesityl-10-methylacridinium cation in aerated deuterated/normal acetonitrile decomposes to give several side products when continuously exposed to white light. The main breakdown product isolated by column chromatography is identified as 3,5-dimethyl-4-(10-methylacridinium)-benzaldehyde. This assignment was confirmed by single-crystal X-ray crystallography. In light of these findings it appears that decomposition pathways also need to be considered when discussing the photochemical properties of the 9-mesityl-10-methylacridinium cation, especially in the presence of dioxygen.

Introduction

The huge carbon footprint left behind by the continued burning of fossil fuels is well recognised, and it is generally accepted that the time has arrived to find a real solution to the problem.[1] Over the past few years we have witnessed a major effort to find alternative energy-producing methods that are both non-polluting and can meet the high-energy demand of consumers. Amongst the many solutions to the challenge, usage of solar energy has been targeted because its supply is virtually never-ending.[2] Considering that photosynthesis in plants sustains the cycle of O_2 generation and CO_2 fixation to organic fuel, the successful mimicking of these two processes in an abiotic system is of considerable importance if artificial photosynthesis is to be a viable way forward.[3] The one key process is charge separation as a means to generate redox equivalents that can drive chemical transformations.[4] Many attempts have been made to create artificial systems that are proficient in sustaining long-lived charge-transfer states.[5] Lifetimes tend to be limited to several hundred nanoseconds,[6] though some reports of timescales reaching microseconds have been reported recently.[7] The most impressive claim relates to the cation 9-mesityl-10-methylacridinium (mes-acr$^+$) (Figure 1) that purportedly forms a charge-shift state (CSS) that lives in fluid solution at 200 K for some 2 h, and even more incredibly does not decay at 77 K.[8] This finding has been challenged on the grounds that the triplet state localised on the acridinium cation is in fact lower in energy than the CSS and is populated during charge recombination.[9] Additionally, the mesityl radical cation is unstable to side reactions[10] and opens up the possibility of sacrificial reactions. Despite this controversy, if mes-acr$^+$ were to fulfil a leading role in artificial photosynthesis its stability under mild conditions (i.e., water, O_2) and visible-light illumination for prolonged periods would have to be high. In particular, because the mesityl group is the electron donor, any change in its ability to function in this manner would have severe detrimental effects in the performance of mes-acr$^+$. Here, it is shown that white light (and even sunlight) illumination of a solution of mes-acr$^+$ in aerated CD_3CN leads to compound degradation. The main breakdown product, as evidenced by ^{1}H NMR, FT-IR spectroscopy, electrospray mass spectrometry and X-ray crystallography, is assigned to the oxidised species in which a methyl group has been converted to an aldehyde (dmb-acr$^+$) (Figure 1). Competing decomposition pathways involving the unstable mesityl radical cation of the CSS can account for this side product.

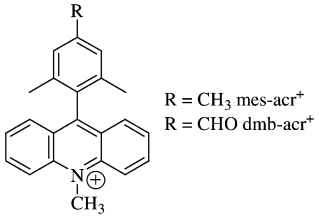


Figure 1. Structural formulae of compounds discussed in text.

Results and Discussion

Purified mes-acr$^+$ dissolved in aerated CD_3CN was irradiated by using unfocussed white light for several hours, and the corresponding ^{1}H NMR spectra were recorded.

[a] Molecular Photonics Laboratory, School of Chemistry, Newcastle University,
Newcastle upon Tyne, NE1 7RU, UK
Fax: +44-191-222-6929
E-mail: a.c.benniston@ncl.ac.uk
[b] Crystallography Laboratory, School of Chemistry, Newcastle University,
Newcastle upon Tyne, NE1 7RU, UK

Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

The initial spectrum (Figure 2) is fully consistent with the chemical structure of mes-acr$^+$ and in particular shows no discernible peaks due to 9-mesitylacridine impurity. Because this would presumably form singlet oxygen via its well-characterised triplet state, its absence is important because any feasible $^1O_2$ decomposition pathways would have to originate from the triplet state localised on mes-acr$^+$. After 12 h of irradiation, it is evident that the ^{1}H NMR spectrum is significantly different. There are clear signs of new, almost equal-intensity, downfield resonances at δ = 9.6 and 10.2 ppm. The chemical shifts are very much indicative of deshielded protons, associated with groups such as aldehydes, carboxylic acids or intramolecular hydrogen-bonded phenols.[11] As well as these obvious changes to the spectrum, new resonances appear in the region at $\delta \approx 8$ ppm. Furthermore, the upfield region between δ = 3 and 1.5 ppm becomes more complex as new resonances appear for the methyl protons of the mesityl group. It should be noted that the *N*-methyl resonance remains relatively unaffected, which would suggest that the acridinium group remains intact. After prolonged illumination of the NMR sample, the new resonances are further enhanced, whereas the singlet (δ = 7.2 ppm) associated with the α-protons of the mesityl group appears diminished. This signal, after 48 h of irradiation, completely disappears (Supporting Information) and is located in the region at $\delta \approx 8$ ppm. Such an observation is consistent with introduction of electron-withdrawing group(s) into the aromatic ring; that is, oxidation of methyl group(s) in the mesityl unit. An FT-IR spectrum recorded for the solid sample after solvent removal, when compared to pure mes-acr$^+$, shows three new peaks at 1692, 1277 and 1001 cm^{-1} (Supporting Information). It is known that benzaldehydes absorb in the 1710–1685 cm^{-1} region, and peaks in the fingerprint region around 1200–1350 cm^{-1} are also in fitting with aromatic aldehydes.[12]

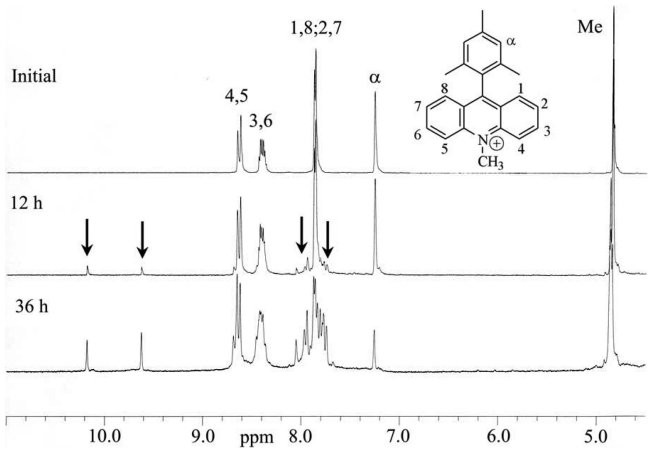


Figure 2. Selected region of the ^{1}H NMR (300 MHz) spectra recorded at room temperature for mes-acr$^+$ in aerated CD_3CN at various times after illumination with white light. Arrows show regions where clear new resonances emerge.

A somewhat similar NMR picture to that presented above could be seen when a fresh sample of mes-acr$^+$ in CD_3CN was left in normal sunlight for two weeks (Supporting Information). Even though the reaction time is very much longer, the distinctive alterations in the spectra are again fully consistent with the compound degrading.

A further identification of the photochemical breakdown products was performed on the irradiated samples of mes-acr$^+$ by using electrospray mass spectrometry (Supporting Information). Samples from the two NMR experiments were analysed in an identical manner. Both the analysed samples show in their respective mass spectrum a main cluster of peaks at *m*/*z* = 312.2 that are assigned to the [M – PF_6]$^+$ ion ($C_{23}H_{22}N^+$). Two more main peaks are also observed at *m*/*z* = 326.2 and 342.2, respectively. An expansion of the baseline also revealed other minor peaks, and in particular a small cluster of peaks at *m*/*z* = 767.3. The peak cluster at *m*/*z* = 326.2 fits well to a theoretical isotope model for the formula $C_{23}H_{20}NO^+$, whereas the ion at *m*/*z* = 342.2 is consistent with an isotope pattern for $C_{23}H_{20}NO_2^+$. The high-mass ion can be tentatively assigned to $C_{46}H_{42}N_2PF_6^+$, containing a dimer with the loss of two protons. Considering the starting-material formula, the first ion (*m*/*z* = 326.2) represents the loss of two protons and introduction of an oxygen atom. This can be interpreted as conversion of a methyl group into a CHO unit. The second peak (*m*/*z* = 342.2) represents loss of two protons and introduction of two oxygen atoms. Again, this could represent the alteration of a methyl group into a CO_2H group. Alternatively, a CHO group with an adjacent OH group also fits the proposed formula.

In order to understand, at a deeper level, the NMR and mass spectrometry findings, a sample of mes-acr$^+$ in aerated CH_3CN was irradiated and the crude material purified. A thin-layer chromatography separation of the crude material (silica gel, acetone) showed multiple overlapping spots. Column chromatography of the crude product on silica gel, eluting firstly with ethyl acetate/petroleum ether (2:1), afforded a very minor fraction. Upon changing the solvent mixture to ethyl acetate/MeOH (80:20) a series of close-running fractions eluted, but these were not analysed because of the difficulty encountered in their complete separation. The main readily isolated fraction was eluted by using a mixture of CH_3CN/satd. KPF_6 (aq.) (99:1) to afford a yellow solid. The ^{1}H NMR spectrum of this material (Supporting Information) is somewhat more simplified than the final spectrum shown in Figure 2. The resonance corresponding to the α-protons of the starting material is missing and is now located at δ = 7.92 ppm. In addition, only the most downfield resonance at δ = 10.2 ppm is associated with the product. The ^{13}C NMR spectrum (Supporting Information) shows a clear downfield resonance at $\delta \approx$ 193 ppm and eleven other peaks in the aromatic region, of which six are quaternary. The aromatic-region spectrum is very similar in appearance to that of simple mes-acr$^+$ (Supporting Information); the chemical shifts of resonances are different. It can be concluded that there is no overall loss of symmetry in the product. The ES mass spectrum is dominated by a peak at *m*/*z* = 326. In order to identify the product completely, single crystals were grown (CH_3CN/Et_2O) and subjected to analysis by X-ray crystallography. The ^{1}H

NMR spectrum of the crystalline material was identical to the main powder-like sample (Supporting Information). Thus, the crystals represent a true picture of the main sample. The molecular structure of the product is illustrated in Figure 3. It is clear from the structure determination that the terminal methyl group of the mesityl group has been converted to an aldehyde group to produce the 9-(4-formyl-2,6-dimethylphenyl)-10-methylacridinium cation (dmb-acr$^+$). A selection of bond lengths and torsion angles for this compound is collected in Table 1. It is interesting to note that, similar to the structure of mes-acr$^+$, the aromatic group is almost orthogonal to the acridinium subunit.[8] However, a view along the C16–C5 bond for dmb-acr$^+$ (Supporting Information) clearly shows that the dimethylbenzaldehyde group is bent over to one side; this bond is inclined at only 1.3° to the acridinium mean plane but at 8.6° to the substituent ring plane. Probably crystal packing effects account for this observation, i.e., intermolecular rather than intramolecular interactions; the most significant of these seem to be two intermolecular CH···O contacts with d(H···O) = 2.52 Å giving an essentially planar environment for the O atom consistent with weak CH···O hydrogen bonding to the O atom electron lone pairs, and two CH···F contacts with d(H···F) = 2.43 and 2.46 Å. All four of these interactions involve H atoms of the acridinium system and are roughly coplanar with the acridinium mean plane. The acridinium fused-ring system is slightly bowed, the two benzene rings making dihedral angles of 3.2 and 2.4° with the central pyridine ring. The crystal structure has no significant π–π stacking interactions.

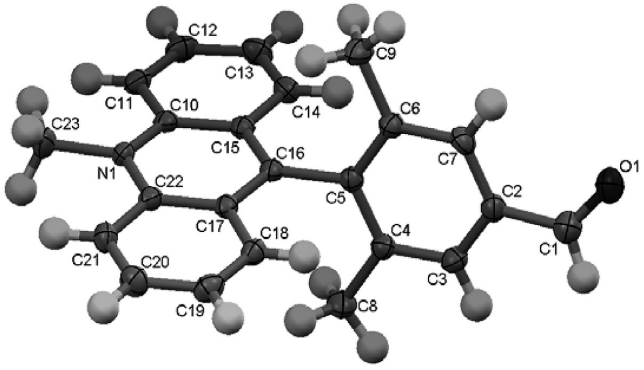


Figure 3. Molecular structure of the isolated product, dmb-acr$^+$, following light-induced degradation of mes-acr$^+$. Hexafluorophosphate anion omitted for clarity.

Table 1. Selected bond lengths and torsion angles for the dmb-acr$^+$ cation.

Selected atoms	Bond length [Å][a]	Selected atoms	Torsion angle [°]
C1–O1	1.201(3)	C15–C16–C5–C6	84.5(3)
C1–C2	1.480(4)	C17–C16–C5–C4	76.3(3)
C5–C16	1.498(3)	O1–C1–C2–C7	–8.6(4)

[a] Standard uncertainty in parentheses.

Having established unequivocally the identity of the main breakdown product, the basic photophysical and electrochemical properties of crystals of dmb-acr$^+$ were measured. The electrochemical behaviour of dmb-acr$^+$ in dry CH_3CN containing tetra-*n*-butylammonium tetrafluoroborate (0.2 M) background electrolyte was measured by using standard cyclic voltammetry. Upon oxidative scanning, no clear-cut wave could be seen up to the solvent cut-off at around +2.1 V vs. Fc/Fc$^+$. The irreversible oxidation of the mesityl group in mes-acr$^+$ in CH_3CN occurs at around +1.6 V vs. Fc/Fc$^+$. It is expected that the electron-withdrawing nature of the aldehyde group would push this potential more anodic, thus accounting for the difficulty in observing the aryl oxidation wave for dmb-acr$^+$. The reductive scan portion of the cyclic voltammogram contains a reversible one-electron wave at E_1 = –0.88 V (ΔE = 60 mV) vs. Fc/Fc$^+$, and a further one-electron wave at E_2 = –1.82 V (ΔE = 70 mV) vs. Fc/Fc$^+$. By comparison with literature data,[13] the first wave can be assigned to reduction of the acridinium unit to produce the acridinyl radical. The second reduction wave is presumably addition of an electron to the radical to generate the anion.

The electronic spectrum recorded for a dilute solution of dmb-acr$^+$ in dry CH_3CN (Figure 4) displays, as well as an intense absorption profile at 362 nm, the characteristic slightly structured band centred at λ_{ABS} = 422 nm. The bandshape of the latter is very similar to those reported previously for acridinium-based compounds such as the 10-methyl-9-*o*-tolylacridinium cation (Supporting Information). Selective illumination into the long-wavelength band at 395 nm affords strong fluorescence, corresponding to a partially structured profile centred at λ_{FLU} = 499 nm (Figure 4); the bandshape and λ_{FLU} are independent of the excitation wavelength. The excitation spectrum matches very well to the absorption spectrum. The fluorescence quantum yield (ϕ_F) = 0.88, is very similar to values reported for acridinium compounds in which the 9-aryl substituent is rotationally hindered.[14] Decay of fluorescence, as measured by single-photon-counting, was strictly mono-exponential corresponding to a singlet lifetime (τ_S) of 27 ns. The radiative rate ($k_{RAD} = \phi_F/\tau_S$) of 3.3×10^7 s^{-1} and non-radiative rate [$k_{NR} = (1/\tau) - k_{RAD}$] of 4.0×10^6 s^{-1} are consistent with reported data for the 10-methyl-9-*o*-tolylacridinium cation.[15] It is worth emphasising that the fluorescence properties of dmb-acr$^+$ are very different from those reported for pure mes-acr$^+$. In particular, the latter compound shows a broad weak fluorescence profile centred at ca. 600 nm with a lifetime of 6 ns, which is associated with the intramolecular CSS.[9] This feature is understandably missing for dmb-acr$^+$ because the aromatic group is no longer a suitable electron donor, because of introduction of the electron-withdrawing aldehyde group. It is worth stressing that, because dmb-acr$^+$ is so strongly fluorescent, any trace amount in mes-acr$^+$ would overshadow the weak fluorescence previously discussed. Overall, the photophysical properties of dmb-acr$^+$ are dominated by the acridinium unit, and in fact very similar to those of the simple 10-methylacridiunium cation.[9]

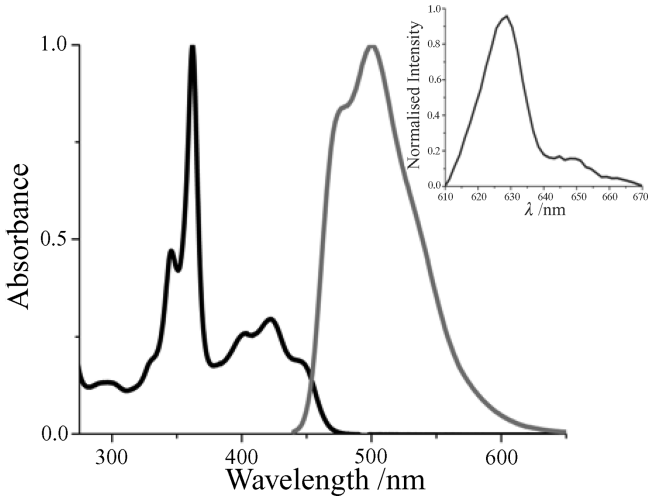
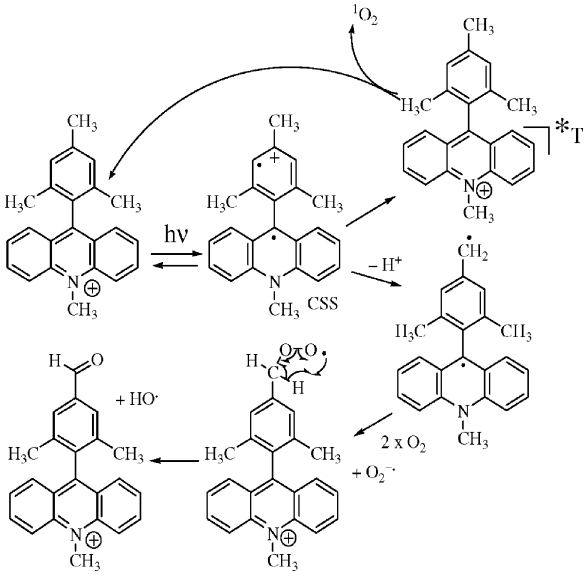


Figure 4. Absorption spectrum for dmb-acr$^+$ in CH_3CN (black line) and fluorescence spectrum (grey line). The inset depicts the phosphorescence spectrum in deoxygenated butyronitrile glass containing EtI (10%) at 77 K.

Weak phosphorescence at λ_{PHOS} = 629 nm could be observed from dmb-acr$^+$ in deoxygenated butyronitrile glass at 77 K containing 10% EtI (Figure 4). The overall profile is somewhat similar to that found for mes-acr$^+$ under similar conditions.[9] It has been argued that phosphorescence observed for mes-acr$^+$ is from impurity of the unmethylated derivative, 9-mesitylacridine.[16] Clearly, this cannot be the case on two grounds: namely, no 9-mesitylacridine could be detected in the starting material (Figure 2), and the likelihood is low of carrying through an extensive purification procedure the identical impurity, especially to a crystalline material analysed by X-ray crystallography. In fact, the observation of phosphorescence from dmb-acr$^+$ is fully consistent with previous findings.[17] For example, Kikuchi and co-workers[18] reported the triplet energies for protonated versions of acridine, 9-phenylacridine, 9-methylacridine and 9-aminoacridine to be 2.01 eV, 1.91 eV, 1.97 eV and 2.32 eV, respectively. *All these triplet energies are lower than the reported CSS energy obtained by spectroscopic (2.57 eV)*[9] *and electrochemical (2.37 eV)*[8] *means for mes-acr$^+$.* The conclusions here again reinforce the point made previously for mes-acr$^+$, that the lowest energy state in this acridinium-based system is the triplet state.[9,19]

Conclusions

It has been shown that the 9-mesityl-10-methylacridinium cation in fluid solution is unstable under conditions of white light and dioxygen. That a decomposition pathway is available to the CSS of the compound begs the question: could such a highly energetic excited-state species live for a long time under practical working conditions necessary in artificial photosynthesis? Considering the probability is high for an energetic species to find pathways to decay, the prospect must surely be very unlikely. In view of the findings outlined here it appears that decomposition pathways also need to be considered when discussing the photophysical properties of the 9-mesityl-10-methylacridinium cation in solution, especially in the presence of dioxygen.[19] A very much simplified picture of probable processes following light activation are depicted in Scheme 1, where the oxidation product is formed via the mesityl radical created by proton loss from the CSS. That oxidised mesitylene is known to be unstable to this proton loss process[20] is fully consistent with the proposed first step. It is worth noting that, if the CSS were exceptionally long-lived, then proton loss would easily compete with charge recombination. Because degradation of mes-acr$^+$ is relatively slow, this can be accounted for by the fact that triplet formation and ground state restoration can more than compete with proton loss from oxidised mesitylene.[9] The follow-on reactions from the radical are again fully consistent with known chemical reactions to produce the aldehyde group.[21] Clearly, other sideproducts must be produced as evidenced by TLC of the crude material. These may arise from singlet-oxygen reactions, especially because mes-acr$^+$ has been shown to be a good $^1O_2$ sensitizer,[22] and formation of a dioxetane at the acridine group has been reported.[23] A more detailed analysis of the oxygen uptake kinetics is underway to shed more light on the breakdown reactions, and these findings will be reported at a later date.



Scheme 1. Simplified picture of the possible processes that occur after initial formation of the CSS, following light activation of mes-acr$^+$ in solution containing dioxygen.

Experimental Section

General: The target compound, 9-mesityl-10-methylacridinium hexafluorophosphate, was synthesised and purified extensively by using methods published previously.[9] ^{1}H NMR spectra were obtained by using either a Bruker Avance 300 MHz, Jeol ECS

400 MHz or Jeol Lambda 500 MHz spectrometers, using air-equilibrated solutions of the compound in CD_3CN (99.8%) purchased from Aldrich Chemical Co. The solvent was used as received without further purification. A typical sample consisted of ca. 5 mg of mes-acr$^+$ in 0.7 mL of solvent. The NMR spectra were referenced to the residual protiated solvent peak (δ = 1.93 ppm). Irradiation experiments were performed either by exposing the sample tube to direct sunlight on a window ledge, or with long-wavelength ($\lambda >$ 400 nm) light from a Dolan-Jenner Industries Fibre-Lite PL 900 lamp. The ^{1}H NMR spectra were recorded at various times and processed by using the commercial package MestReC. The solvent was removed at the end of the irradiation run, and the solid dried under vacuum and analysed by FT-IR spectroscopy and electrospray mass spectrometry.

Photochemical Degradation of mes-acr$^+$: A sample of pure mes-acr$^+$ PF_6^- (70 mg, 0.15 mmol) was dissolved in dry aerated CH_3CN (10 mL) and irradiated with white light for 5 d. The solvent was removed and the crude material chromatographed on silica gel by using firstly ethyl acetate/petroleum ether (2:1) to afford a yellow solid (4 mg). The eluant was changed to ethyl acetate/MeOH (80:20) to remove any remaining organic residues. The main fraction was eluted by using acetonitrile/satd. KPF_6 (aq.) (99:1) to afford a yellow solid (24 mg, 34% yield), which was recrystallised from CH_3CN/diethyl ether. ^{1}H NMR (CD_3CN, 300 MHz): δ = 10.16 (s, 1 H); 8.65 (d, J = 9.2 Hz, 2 H), 8.41 (ddd, J = 9.2, J' = 6.4, J'' = 1.8 Hz, 2 H), 7.92 (s, 2 H), 7.82 (m, 4 H), 4.85 (s, 3 H), 1.83 (s, 6 H) ppm. ^{13}C NMR (CD_3CN, 125 MHz): δ = 192.7 (CO), 160.0, 141.9, 139.2, 138.6, 137.9, 137.8, 129.0, 128.8, 128.5, 125.3, 119.2, 41.2, 21.9 ppm. ES-MS: *m*/*z* calcd. for $C_{23}H_{20}NO$ 326.2; found 326.2. UV (CH_3CN): λ_{ABS} (ε [mol^{-1} dm^3 cm^{-1}]) = 345 (5465), 362 (11,614), 422 nm (3486).

X-ray Crystallography: Yellow crystals of the title compound were grown by slow vapour diffusion of Et_2O into a solution of dmb-acr$^+$$PF_6^-$ in CH_3CN. Data from a single crystal were collected with Mo-K_α radiation by using an Oxford Diffraction Gemini A Ultra diffractometer at 150 K. CCDC-698936 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Absorption and Fluorescence Spectroscopy: Absorption spectra were recorded with a Hitachi U3310 spectrophotometer, whereas all fluorescence studies were made with a Hitachi F4500 spectrometer. Measurements were made by using optically dilute solutions. Fluorescence quantum yields were measured with respect to the 9-methylacridinium cation.[9] Fluorescence lifetimes were measured by time-correlated, single-photon counting conditions following excitation with an ultrashort laser diode emitting at 440 nm. After deconvolution of the instrumental response function, the temporal resolution of this setup was ca. 50 ps.

Cyclic Voltammetry: Cyclic voltammetry experiments were performed by using a fully automated HCH Instruments Electrochemical Analyzer and a three-electrode setup consisting of a platinum working electrode, a platinum wire counter electrode and a silver wire reference electrode. Ferrocene was used as an internal standard. Studies were performed in deoxygenated CH_3CN containing tetra-*n*-butylammonium tetrafluoroborate (TBATFB) (0.2 M) as background electrolyte.

Supporting Information (see footnote on the first page of this article): Additional ^{1}H and ^{13}C NMR spectra, FT-IR spectra, electrospray mass spectra of samples after irradiation experiments, X-ray data and comparison of absorption/fluorescence spectra.

Acknowledgments

This work was supported by Newcastle University, and the EPSRC-sponsored Mass Spectrometry Service at Swansea is thanked for obtaining the electrospray mass spectra. We also thank the EPSRC for funding the crystallographic equipment.

[1] a) M. S. Dresselhaus, I. L. Thomas, *Nature* **2001**, *414*, 332–337; b) K. Kleiner, *Nature Rep.* **2007**, *3*, 40–43; c) D. L. Royer, R. A. Berner, J. Park, *Nature* **2007**, *446*, 530–532.
[2] a) N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Soc. USA* **2006**, *103*, 15729–15735; b) V. Balzani, A. Credi, M. Venturi, *ChemSusChem* **2008**, *1*, 26–58.
[3] A. J. Esswein, D. G. Nocera, *Chem. Rev.* **2007**, *107*, 4022–4047.
[4] M. Wasielewski, *Chem. Rev.* **1992**, *92*, 435–461.
[5] a) J. W. Verhoeven, *J. Photochem. Photobiol.* **2006**, *7*, 40–60; b) H. Imahori, K. Tamaki, D. M. Guldi, C. Luo, M. Fujitsuka, O. Ito, Y. Sakata, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 2607–2617; c) H. Imahori, D. M. Guldi, K. Tamaki, Y. Yoshida, C. Luo, Y. Sakata, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 6617–6628; d) Y. Kobori, S. Yamaguchi, K. Akiyama, S. Tero-Kubota, H. Imahori, S. Fukuzumi, J. R. Norris Jr, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 10017–10022.
[6] a) U. Werner, Y. Sakaguchi, H. Hayashi, G. Nohya, R. Yoneshima, S. Nakjima, A. Osuka, *J. Phys. Chem.* **1995**, *99*, 13930–13937; b) R. E. Palacios, S. L. Gould, C. Herrero, M. Hambourger, A. Brune, G. Kodis, P. A. Liddell, J. Kennis, A. N. Macpherson, D. Gust, T. A. Moore, A. L. Moore, *Pure Appl. Chem.* **2005**, *77*, 1001–1008.
[7] a) J. W. Verhoeven, H. J. van Ramesdonk, M. M. Groeneveld, A. C. Benniston, A. Harriman, *ChemPhysChem* **2005**, *6*, 2251–2260; b) H. Imahori, Y. Sekiguchi, Y. Kashiwagi, T. Sato, Y. Araki, O. Ito, H. Yamada, S. Fukuzumi, *Chem. –Eur. J.* **2004**, *10*, 3184–3196; c) K. Ohkubo, J. R. Reimers, S. Fukuzumi, M. J. Crossley, *Phys. Chem. Chem. Phys.* **2007**, *9*, 5260–5266.
[8] S. Fukuzumi, H. Kotani, K. Ohkubo, S. Ogo, N. V. Tkachenko, H. Lemmetyinen, *J. Am. Chem. Soc.* **2004**, *126*, 1600–1601.
[9] a) A. C. Benniston, A. Harriman, P. Li, J. P. Rostron, H. J. van Ramesdonk, M. M. Groenveld, H. Zhang, J. W. Verhoeven, *J. Am. Chem. Soc.* **2005**, *127*, 16054–16064; b) A. C. Benniston, A. Harriman, P. Li, J. P. Rostron, J. W. Verhoeven, *Chem. Commun.* **2005**, 2701–2702.
[10] a) K. Nyberg, *Acta Chem. Scand.* **1971**, *25*, 534–542; b) M. Mellah, J. Zeitouny, S. Gmouh, M. Vaultier, V. Jouikov, *Electrochem. Commun.* **2005**, *7*, 869–874; c) P. M. Reis, J. A. L. Silva, J. J. R. Frausto da Silva, A. J. L. Pombeiro, *J. Mol. Catal. A* **2004**, *224*, 189–195.
[11] R. M. Silverstein, F. X. Webster, *Spectroscopic Identification of Organic Compounds*, 6th ed., John Wiley & Sons, NJ, USA, **1998**, p. 211.
[12] D. H. Williams, I. Fleming, *Spectroscopic Methods in Organic Chemistry*, 3rd ed., McGraw-Hill, Maidenhead, Berkshire, UK, **1980**, p. 46.
[13] a) S. Fukuzumi, K. Ohkubo, T. Suenobu, K. Kato, M. Fujitsuka, O. Ito, *J. Am. Chem. Soc.* **2001**, *123*, 8459–8467; b) P. Hapiot, J. Moiroux, J. M. Saveant, *J. Am. Chem. Soc.* **1990**, *112*, 1337–1343.
[14] G. Jones II, M. S. Farahat, S. R. Greenfield, D. J. Gosztola, M. R. Wasielewski, *Chem. Phys. Lett.* **1994**, *229*, 40–46.
[15] S. A. Jonker, F. Ariese, J. W. Verhoeven, *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 109–115.
[16] K. Ohkubo, H. Kotani, S. Fukuzumi, *Chem. Commun.* **2005**, 4520–4522.
[17] H. van Willigen, G. Jones II, M. S. Farahat, *J. Phys. Chem.* **1996**, *100*, 3312–3316.
[18] K. Kikuchi, C. Sato, M. Watabe, H. Ikeda, Y. Takahashi, T. Miyashi, *J. Am. Chem. Soc.* **1993**, *115*, 5180–5184.
[19] A. C. Benniston, A. Harriman, J. W. Verhoeven, *Phys. Chem. Chem. Phys.* **2008**, *10*, 5156–5158.

[20] K. Sehested, J. Holcman, *J. Phys. Chem.* **1978**, *82*, 651–653.
[21] a) I. Saito, K. Tamoto, T. Matsura, *Tetrahedron Lett.* **1979**, *31*, 2889–2892; b) J. Santamaria, R. Jroundi, *Tetrahedron Lett.* **1991**, *32*, 4291–4294; c) *Active Oxygen in Chemistry: Search Series*, vol. 2 (Eds.: C. S. Foote, J. Selverstone Valentine, A. Greenberg, J. F. Liebman), Chapman and Hall, London, UK, **1995**.
[22] A. G. Griesbeck, M. Cho, *Org. Lett.* **2007**, *9*, 611–613.
[23] I. Negrón-Encarnación, R. Arce, *Atmos. Environ.* **2007**, *41*, 6771–6783.

Received: August 20, 2008
Published Online: December 3, 2008

