Misleading effects of impurities derived from the extremely long-lived electron-transfer state of 9-mesityl-10-methylacridinium ion

Kei Ohkubo, Hiroaki Kotani and Shunichi Fukuzumi*

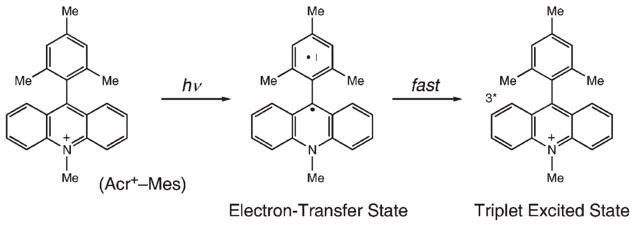
Received (in Cambridge, UK) 11th May 2005, Accepted 7th June 2005
First published as an Advance Article on the web 1st July 2005
DOI: 10.1039/b506479a

9-Mesityl-10-methylacridinium ion has an extremely long-lived electron-transfer state, which results in the misleading effects of electron donor impurities contained in benzonitrile to produce the stable acridinyl radical.

Extensive efforts have been devoted to mimic the photosynthetic reaction center,[1–11] leading to development of artificial systems which exceed both the lifetime and energy of the CS state of the natural system.[9–11] In particular, 9-mesityl-10-methylacridinium ion (Acr$^+$–Mes) exhibits the best performance: the electron-transfer (ET) state upon photoexcitation has not only a much longer lifetime (*e.g.*, 2 h at 203 K) but also a much higher energy (2.37 eV) than that of other donor–acceptor linked compounds.[11] However, Benniston *et al.* have recently claimed that the triplet excited state of the acridinium ion moiety may be formed rather than the ET state and that the energy of the triplet excited state of the acridinium ion moiety is lower than that of the ET state (Scheme 1).[12]

We report herein that the data reported by Benniston *et al.* result from the misleading effects of impurities which are actually derived from the extremely long-lived ET state of Acr$^+$–Mes in benzonitrile (PhCN).

Fig. 1(a) shows the UV-visible spectra in deaerated PhCN solution containing Acr$^+$–Mes (3.3×10^{-5} mol dm^{-3}) after photoirradiation with a 1000 W high-pressure mercury lamp through a UV light cutting filter (>390 nm). No decay of the absorption band due to Acr$^+$–Mes at 360 and 430 nm was observed after 30 min photoirradiation. In contrast to this result, the addition of a small amount of aniline (5.0×10^{-5} mol dm^{-3}) resulted in a significant change in the absorption band of Acr$^+$–Mes, which decreased, accompanied by a concomitant increase in the absorption band due to the acridinyl radical as reported by Benniston *et al.* when unpurified PhCN was employed as a solvent.[12] In general, benzonitrile (PhCN) obtained commercially contains electron donor impurities such as aromatic amines.[13] Benzonitrile used in Fig. 1(a) was distilled from P_2O_5 *in vacuo* at 333 K very carefully to remove any aromatic amines.[13]



Scheme 1

When a small amount of impurity of an electron donor is contained in PhCN, electron transfer would occur from an electron donor to the mesitylene radical cation moiety in the ET state (Acr$^•$–Mes$^{•+}$) to give the stable radical, Acr$^•$–Mes (λ_{max} = 505 nm),[12,14] since electron transfer from aromatic amines to the Mes$^{•+}$ moiety (the one-electron reduction potential: E^0_{red} = 1.88 V *vs.* SCE) of the ET state (Acr$^•$–Mes$^{•+}$) is energetically feasible and the lifetime of the ET state is long enough to be quenched by a small concentration of an electron donor.[11,15] Thus, the formation of the stable radical, Acr$^•$–Mes results from a long-lived ET state which can quench the Mes$^{•+}$ moiety by electron transfer.

We have previously reported that the ET state of Acr$^+$–Mes in solution disproportionates in fluid solution because the intramolecular back electron transfer is too slow.[11] The rate of intramolecular electron transfer from the Acr$^•$ moiety to the Mes$^{•+}$ moiety in the same Acr$^•$–Mes$^{•+}$ molecule is highly temperature dependent and the lifetime of the ET state becomes almost infinite at 77 K in the solid state (*vide infra*).[11]

In contrast to the photoirradiation of a purified PhCN solution of Acr$^+$–Mes at 298 K, which results in no change in the absorption spectrum (Fig. 1(a)), when the photoirradiation of the same solution was performed at low temperatures (213–243 K) with a 1000 W high-pressure mercury lamp through the UV light cutting filter (>390 nm) and the sample was cooled to 77 K, the color of the frozen sample at 77 K was clearly changed from green to brownish as shown in the inset of Fig. 1(b). When glassy 2-methyltetrahydrofuran (2-MeTHF) is employed for the photoirradiation of Acr$^+$–Mes at low temperature, the resulting glassy solution measured at 77 K affords the absorption spectrum due to the ET state, which consists of the absorption bands of the Acr$^•$ moiety (510 nm) and the Mes$^{•+}$ moiety (470 nm) as shown in Fig. 1(b).[11] No decay of the absorption due to the ET state in Fig. 1(b) was observed until liquid nitrogen ran out, as the case of the ESR detection of the ET state, which was reported previously.[11]

Benniston *et al.* reported the triplet excitation energy of Acr$^+$–Mes is 1.96 eV.[12] If this value were correct, the one-electron oxidation potential (E^0_{ox}) of the triplet excited state of Acr$^+$–Mes would be −0.08 V *vs.* SCE, which is determined from the one-electron oxidation potential of the Mes moiety (1.88 V)[11] and the triplet excitation energy (1.96 V). In such a case, electron

---

Department of Material and Life Science, Graduate School of Engineering, Osaka University, SORST, Japan Science and Technology Agency (JST), Suita, Osaka, 565-0871, Japan.
E-mail: fukuzumi@chem.eng.osaka-u.ac.jp; Fax: +81-6-6879-7370;
Tel: +81-6-6879-7368

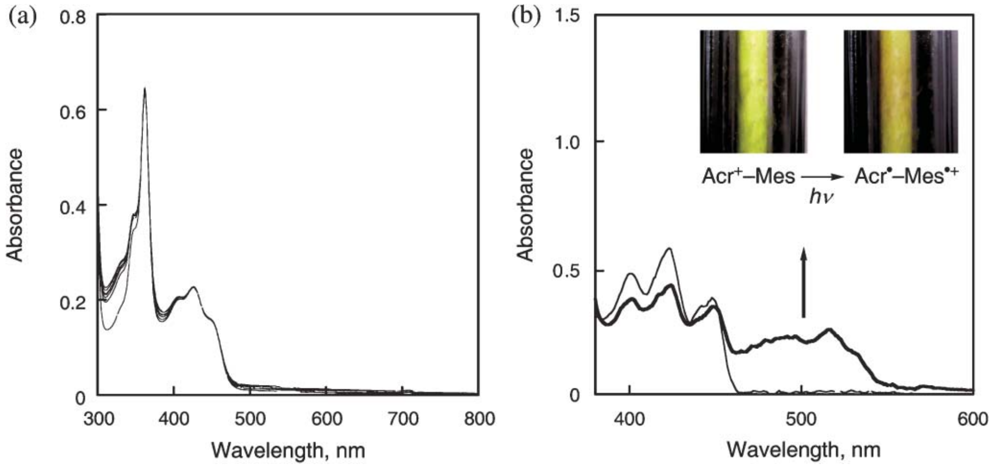


Fig. 1 (a) UV-vis spectral change in the steady-state photolysis of a deaerated PhCN solution of Acr^+–Mes (3.3×10^{-5} mol dm^{-3}). Spectra were recorded at 90 s intervals. (b) UV-vis absorption spectra obtained by photoirradiation with a high-pressure mercury lamp of deaerated 2-MeTHF glasses of Acr^+–Mes at 77 K. Inset: images of frozen PhCN solutions of Acr^+–Mes before and after photoirradiation at low temperatures and taken at 77 K.

transfer from the triplet excited state of Acr^+–Mes to *N*,*N*-dihexylnaphthalene diimide (NIm: $E^0_{red} = -0.46$ V *vs.* SCE) would be energetically impossible judging from the positive free energy change of electron transfer (0.38 eV). However, the addition of NIm (1.0×10^{-3} M) to a PhCN solution of Acr^+–Mes and laser photoirradiation, results in the formation of $NIm^{•-}$ as detected by the well-known absorption bands at 480 and 720 nm,[16] accompanied by the decay of the transient absorption at 510 nm due to the $Acr^•$ moiety of the ET state, as shown in Fig. 2(a).

Similarly, the addition of aniline (3.0×10^{-5} mol dm^{-3}) to a PhCN solution of Acr^+–Mes results in formation of the aniline radical cation ($\lambda_{max} = 430$ nm),[17] accompanied by decay of the $Mes^{•+}$ moiety at 500 nm, as shown in Fig. 2(b). The formation rate constant of the aniline radical cation is determined as 5.6×10^9 mol^{-1} dm^3 s^{-1}, which is close to the diffusion rate constant in PhCN. Thus, the ET state Acr^+–Mes has both the reducing and oxidizing ability to reduce NIm and to oxidize aniline, respectively. This conclusion is contradictory to the triplet energy (1.96 eV), which is reported to be lower in energy than the ET state by Benniston *et al.*[12]

Benniston *et al.* prepared Acr^+–Mes *via* methylation of the corresponding acridine.[12] However, the yield of acridinium ion is about 50–70% after reflux at high temperature for a few days. In such a case, acridine may remain as an impurity even after purification of acridinium ion by recrystallization. In contrast to the synthetic method that Benniston *et al.* employed, we have prepared Acr^+–Mes by the Grignard reaction of 10-methyl-9(10*H*)acridone with 2-mesitylmagnesium bromide, without involving methylation.[11,15] Our purified Acr^+–Mes has afforded no phosphorescence spectrum in either deaerated glassy 2-MeTHF or ethanol at 77 K. It is well known that acridine derivatives exhibit phosphorescence at 15650–15850 cm^{-1}.[18] We have confirmed that the phosphorescence maximum of 9-phenylacridine in glassy 2-MeTHF at 77 K afforded a quite similar spectrum to that reported by Benniston *et al.*[12] Thus, the reported low triplet energy of Acr^+–Mes, which contradicts to our results on the long-lived ET state, results from the acridine impurity contained in Acr^+–Mes used by Benniston *et al.*

In conclusion, we have reconfirmed that the 9-mesityl-10-methylacridinium ion affords an extremely long-lived electron

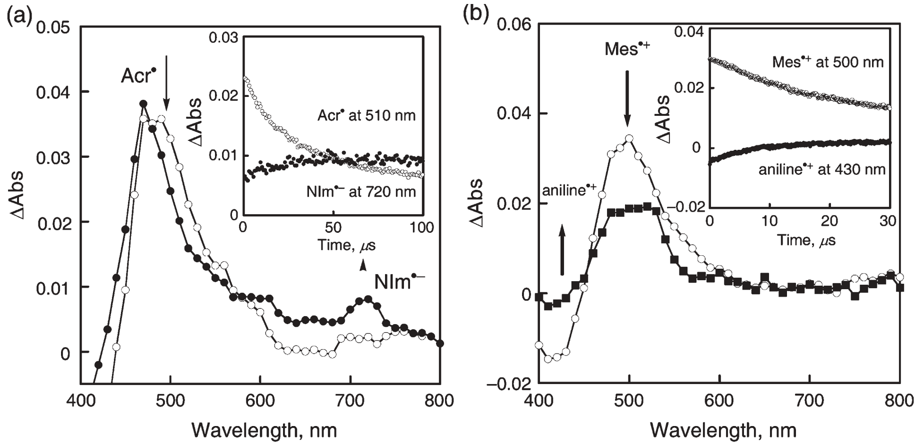


Fig. 2 Transient absorption spectra of Acr^+–Mes (5.0×10^{-5} mol dm^{-3}) in deaerated MeCN at 298 K taken at 2 and 20 μs after laser excitation at 430 nm in the presence of (a) *N*,*N*-dihexylnaphthalene diimide (1.0×10^{-3} mol dm^{-3}) or (b) aniline (3.0×10^{-5} mol dm^{-3}). Inset: Time profiles of the absorbance decay at 510 and the rise at 720 nm and (b) the decay at 500 nm and the rise at 430 nm.

transfer state. A small amount of donor impurities contained in solvent results in formation of a stable radical (Acr$^•$–Mes), because the lifetime of the ET state is long enough to quench the Mes$^{•+}$ moiety of the ET state by electron transfer from the donor impurity.

This work was partially supported by a Grant-in-Aid (No. 16205020) from the Ministry of Education, Culture, Sports, Science and Technology, Japan

Notes and references

1 *The Photosynthetic Reaction Center*, ed. J. Deisenhofer and J. R. Norris, Academic Press, San Diego, CA, 1993.

2 (*a*) D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 2001, **34**, 40; (*b*) D. Gust, T. A. Moore and A. L. Moore, in *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley-VCH, Weinheim, 2001, vol. 3, p. 272; (*c*) M. N. Paddon-Row, *Acc. Chem. Res.*, 1994, **27**, 18; (*d*) J. W. Verhoeven, in *Electron Transfer-From Isolated Molecules to Biomolecules*, ed. J. Jortner and M. Bixon, John Wiley & Sons, New York, 1999, part 1, p. 603.

3 (*a*) M. R. Wasielewski, *Chem. Rev.*, 1992, **92**, 435; (*b*) F. D. Lewis, R. L. Letsinger and M. R. Wasielewski, *Acc. Chem. Res.*, 2001, **34**, 159.

4 J. W. Verhoeven, *Adv. Chem. Phys.*, 1999, **106**, 603.

5 (*a*) M.-J. Blanco, M. C. Jiménez, J.-C. Chambron, V. Heitz, M. Linke and J.-P. Sauvage, *Chem. Soc. Rev.*, 1999, **28**, 293; (*b*) A. Harriman and J.-P. Sauvage, *Chem. Soc. Rev.*, 1996, **25**, 41.

6 (*a*) H. Imahori, K. Tamaki, D. M. Guldi, C. Luo, M. Fujitsuka, O. Ito, Y. Sakata and S. Fukuzumi, *J. Am. Chem. Soc.*, 2001, **123**, 2607; (*b*) H. Imahori, D. M. Guldi, K. Tamaki, Y. Yoshida, C. Luo, Y. Sakata and S. Fukuzumi, *J. Am. Chem. Soc.*, 2001, **123**, 6617.

7 (*a*) S. Fukuzumi, K. Ohkubo, H. Imahori, J. Shao, Z. Ou, G. Zheng, Y. Chen, R. K. Pandey, M. Fujitsuka, O. Ito and K. M. Kadish, *J. Am. Chem. Soc.*, 2001, **123**, 10676; (*b*) K. Ohkubo, H. Imahori, J. Shao, Z. Ou, K. M. Kadish, Y. Chen, G. Zheng, R. K. Pandey, M. Fujitsuka, O. Ito and S. Fukuzumi, *J. Phys. Chem. A*, 2002, **106**, 10991.

8 Y. Kashiwagi, K. Ohkubo, J. A. McDonald, I. M. Blake, M. J. Crossley, Y. Araki, O. Ito, H. Imahori and S. Fukuzumi, *Org. Lett.*, 2003, **5**, 2719.

9 S. Fukuzumi, K. Ohkubo, W. E, Z. Ou, J. Shao, K. M. Kadish, J. A. Hutchison, K. P. Ghiggino, P. J. Sintic and M. J. Crossley, *J. Am. Chem. Soc.*, 2003, **125**, 14984.

10 K. Ohkubo, H. Kotani, J. Shao, Z. Ou, K. M. Kadish, G. Li, R. K. Pandey, M. Fujitsuka, O. Ito, H. Imahori and S. Fukuzumi, *Angew. Chem., Int. Ed.*, 2004, **43**, 853.

11 S. Fukuzumi, H. Kotani, K. Ohkubo, S. Ogo, N. V. Tkachenko and H. Lemmetyinen, *J. Am. Chem. Soc.*, 2004, **126**, 1600.

12 A. C. Benniston, A. Harriman, P. Li, J. P. Rostron and J. W. Verhoeven, *Chem. Commun.*, 2005, 2701.

13 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, in *Purification of Laboratory Chemicals*, Pergamon Press, Elmsford, NY, 4th edn., 1996.

14 K. Ohkubo, K. Suga, K. Morikawa and S. Fukuzumi, *J. Am. Chem. Soc.*, 2003, **125**, 12850.

15 H. Kotani, K. Ohkubo and S. Fukuzumi, *J. Am. Chem. Soc.*, 2004, **126**, 15999.

16 (*a*) X. Guo, Z. Gan, H. Luo, Y. Araki, D. Zhang, D. Zhu and O. Ito, *J. Phys. Chem. A*, 2003, **107**, 9747; (*b*) K. Okamoto, Y. Mori, H. Yamada, H. Imahori and S. Fukuzmi, *Chem. Eur. J.*, 2004, **10**, 474.

17 T. Shida, *Electronic Absoption Spectra of Radical Ions*, Elsevier, Amsterdam, 1988.

18 O. Morawski and J. Prochorow, *Chem. Phys. Lett.*, 1995, **242**, 253.