

Electron-Transfer State of 9-Mesityl-10-methylacridinium Ion with a Much Longer Lifetime and Higher Energy Than That of the Natural Photosynthetic Reaction Center

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The natural photosynthetic reaction center utilizes sequential multistep electron transfer from the excited chromophore to the terminal electron acceptor via electron mediators, which are well-organized in a protein matrix, to attain a lifetime of the final charge-separated (CS) state as long as seconds.¹ However, a significant amount of energy is lost during the multistep electron-transfer processes to reach the final CS state (0.50 eV).¹ Despite extensive efforts to mimic the photosynthetic reaction center,^{2–12} an artificial system which exceeds both the lifetime and the energy of the CS state of the natural system has yet to be developed. We report herein an electron donor–acceptor linked compound which affords the electron-transfer (ET) state upon photoexcitation with 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 the natural system.¹³

According to the Marcus theory of electron transfer (ET),¹⁴ the ET rate is expected to decrease and thereby the lifetime of the ET state increases as the ET driving force ($-\Delta G_{ET}^0$) increases in the strongly exergonic region where $-\Delta G_{ET}^0 < \lambda$; λ is the reorganization energy required to structurally reorganize the donor, acceptor, and their solvation spheres upon ET. Such a strongly exergonic regime is generally referred to as the Marcus inverted region, which in principle allows an increase in the lifetime of the ET state with an increase in the driving force of the back electron transfer.

We have designed and synthesized an electron donor–acceptor linked molecule with a small λ value and a high-lying triplet excited state. Acridinium ion is the best candidate for such a purpose, because the λ value for the electron self-exchange between the acridinium ion and the corresponding one-electron reduced radical is the smallest (0.3 eV) among the redox active organic compounds.¹⁵ An electron donor moiety (mesityl group) is directly connected at the 9-position of the acridinium ion to yield 9-mesityl-10-methylacridinium ion (Acr⁺–Mes), in which the solvent reorganization of ET is minimized because the overall charge remains the same in the charge-shift ET with the short linkage between the donor and acceptor moieties.

The X-ray crystal structure of Acr⁺–Mes is shown in Figure 1.¹⁶ The dihedral angle made by aromatic ring planes was found to be approximately perpendicular. This indicates that there is no π conjugation between the donor and acceptor moieties. Indeed, the absorption and fluorescence spectra of Acr⁺–Mes are superpositions of the spectra of each component, that is, mesitylene and 10-methylacridinium ion.

The HOMO and LUMO orbitals of Acr⁺–Mes calculated by a DFT method with Gaussian 98 (B3LYP/6-31G* basis set) are localized on mesitylene and acridinium moieties, respectively.

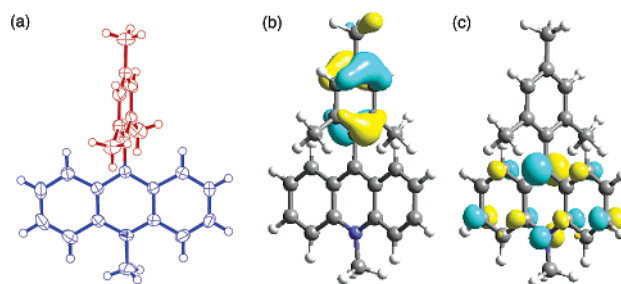


Figure 1. (a) X-ray crystal structure of Acr⁺–Mes. (b) HOMO and, (c) LUMO orbitals calculated by a DFT method with Gaussian 98 (B3LYP/6-31G* basis set).

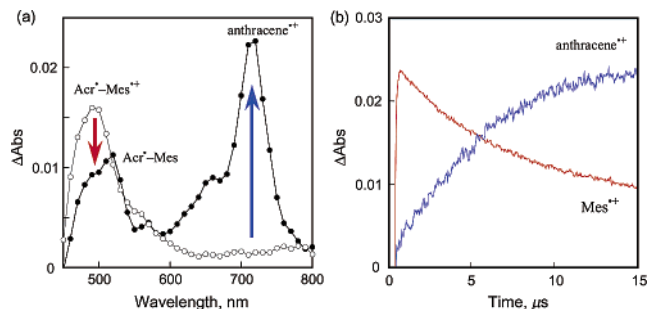


Figure 2. (a) Transient absorption spectra of Acr⁺–Mes (5.0×10^{-5} M) in deaerated MeCN at 298 K taken 15 μ s after laser excitation at 430 nm in the absence (○) and presence (●) of anthracene (5.0×10^{-5} M). (b) Time profiles of the absorbance decay at 480 nm and the rise at 720 nm.

The one-electron oxidation and reduction potentials of Acr⁺–Mes in benzonitrile (PhCN) were determined by the cyclic voltammetry and second harmonic AC voltammetry as 1.88 and -0.49 V vs SCE, respectively. It is important to note that the oxidation potential of 1.88 V is high enough to oxidize water. The ET state energy of Acr⁺–Mes is determined as 2.37 eV, which is much higher than the ET state energy of the natural system (0.50 eV).

Irradiation of a deaerated acetonitrile (MeCN) solution of Acr⁺–Mes by nanosecond laser excitation at 430 nm results in formation of the ET state (Acr⁺–Mes^{•+}) via photoinduced ET from the mesitylene moiety to the singlet excited state of the acridinium ion moiety (¹Acr⁺–Mes) at 298 K. The absorption band of the radical cation of the mesitylene moiety ($\lambda_{max} = 480$ nm)¹⁷ overlaps with that of the acridinyl radical moiety ($\lambda_{max} = 520$ nm)¹⁵ as shown in Figure 2. The quantum yield of the ET state was determined as 98%.¹⁸ The addition of anthracene to an MeCN solution of Acr⁺–Mes and laser photoirradiation result in the formation of anthracene radical cation ($\lambda_{max} = 720$ nm)¹⁹ with a concomitant decrease in

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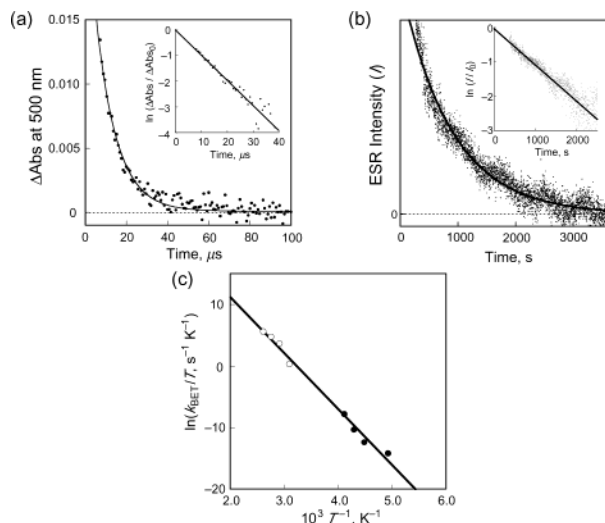


Figure 3. (a) Decay time profile of the transient absorption spectrum of $\text{Acr}^+-\text{Mes}^{*+}$ in PhCN solution at 383 K. (b) ESR decay time profile of the ESR signal intensity of $\text{Acr}^+-\text{Mes}^{*+}$ in frozen PhCN at 223 K. Insets: First-order plots. (c) Plot of $\ln(k_{\text{BET}}/T)$ versus T^{-1} for the intramolecular BET in $\text{Acr}^+-\text{Mes}^{*+}$ in PhCN determined by laser flash photolysis (○) and ESR (●) measurements.

the absorption band due to the radical cation of the mesitylene moiety (Figure 2b), whereas the absorption band due to the acridinyl radical moiety remains virtually the same (Figure 2a).

The intramolecular back electron transfer of the ET state was too slow to compete with the intermolecular back electron-transfer reaction because the decay time profile of $\text{Acr}^+-\text{Mes}^{*+}$ obeyed second-order kinetics.¹⁰ In contrast, the decay of the ET state obeys first-order kinetics in PhCN at high temperatures as shown in Figure 3a (the data at 383 K). This indicates that the rate of the intramolecular back electron transfer (BET) of the ET state becomes much faster than the rate of the intermolecular BET at higher temperatures because of the larger activation energy of the former than the latter. Such a large temperature dependence of k_{BET} is expected by the Marcus equation (eq 1) for adiabatic electron transfer,¹⁴ and the plot of $\ln(k_{\text{BET}}T^{-1})$ versus T^{-1} in the temperature range from 323 to 383 K gives a linear correlation as shown in Figure 3c (○).

$$\ln(k_{\text{BET}}T^{-1}) = \ln\left(\frac{k_{\text{B}}}{h}\right) - \frac{(\Delta G_{\text{BET}}^0 + \lambda)^2}{4\lambda k_{\text{B}}T} \quad (1)$$

The formation of the ET state is also detected by ESR under photoirradiation of Acr^+-Mes in frozen PhCN. The resulting spectrum consists of the superposition of the ESR signals of the radical cation of the mesitylene moiety and the acridinyl radical moiety, although the line broadening was observed because of the spin–spin interaction. The disappearance of the ESR signal intensity obeyed first-order kinetics (Figure 3b). The temperature dependence of the decay rate constant (k_{BET}) was also examined in frozen PhCN at 203–243 K. The temperature dependence of k_{BET} in frozen PhCN at 203–243 K (Figure 3c, ●) falls on the single linear line with that in PhCN solution at 323–383 K (Figure 3c, ○). The intercept value (29 ± 4) in Figure 3c agrees reasonably well with the value expected from eq 1 (24). Such an agreement indicates that the electron transfer is indeed adiabatic because of the short linkage between the electron donor and acceptor moieties in Acr^+-Mes .

However, the donor–acceptor interaction may not be so strong due to the orthogonal geometry in that the electron transfer remains outer-sphere rather than inner-sphere.¹⁴ From the slope of Figure 3c, the λ value was determined as 0.79 eV.

The k_{ET} value of the forward intramolecular photoinduced ET from the mesitylene moiety to the singlet excited state of the acridinium ion moiety is estimated as $3.6 \times 10^{11} \text{ s}^{-1}$ using eq 1, provided that the λ value is the same as that for BET. The driving force of the photoinduced electron transfer is determined as 0.31 eV from the ET energy (2.37 eV) and the singlet excitation energy of Acr^+-Mes (2.68 eV). The fluorescence lifetime of $^1\text{Acr}^{*+}-\text{Mes}$ was determined by an up-conversion method as 4.2 ps which corresponds to $k_{\text{ET}} = 2.4 \times 10^{11} \text{ s}^{-1}$.²⁰ This value agrees reasonably well with that expected from eq 1. Thus, the present system is well analyzed by the classical form of electron transfer (eq 1) without introducing quantum effects.²¹

In conclusion, we have successfully achieved the ET state of Acr^+-Mes produced by a single step photoinduced ET, which has a much longer lifetime and higher energy than the natural system, by minimizing the reorganization energy of ET without loss of energy due to multistep electron-transfer processes.

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Supporting Information Available: Crystallographic information (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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