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Rational Design and Functions of Electron Donor–Acceptor Dyads with Much Longer Charge-Separated Lifetimes than Natural Photosynthetic Reaction Centers

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The natural photosynthetic reaction center utilizes sequential multi-step electron transfer from the excited chromophore to the terminal electron acceptor via electron mediators to attain a long lifetime of the final charge-separated (CS) state. Contrary to natural systems, simple electron donor–acceptor dyads have been developed to attain a long-lived CS state, where the donor and acceptor molecules are linked with a short spacer. In the case of a directly linked zinc chlorin–fullerene dyad, the lifetime of the CS state at −150 °C is as long as 120 s. This value is the longest CS lifetime ever reported for porphyrin-based donor–acceptor linked systems. The use of 9-mesityl-10-methylacridinium ion, which has an extremely long-lived CS state, enables the construction of highly efficient photocatalytic systems such as oxygenation of aromatic compounds and hydrogen evolution.

1. Introduction

Photosynthesis is certainly the most important biological process on earth with respect to light energy conversion, since there would be no food or living creatures without photosynthesis. The primary event of photosynthesis at the bacterial photosynthetic reaction center is rapid initial photoinduced electron transfer from a bacteriochlorophyll dimer [$(BChl)_2$] to bacteriopheophytin (Bphe) on a time scale of 3 ps to produce the primary charge-separated (CS) state.[1–3] After the primary charge separation, the electron is transferred to a secondary electron acceptor, ubiquinone (Q_A) in about 200 ps.[4] When Q_A is pre-reduced or removed, the primary CS state decays with a lifetime between 3 and 20 ns depending on the species and conditions,[5,6] which is much longer than the time order of electron transfer to Q_A despite the much larger driving force ($-\Delta G_{ET} = 1.2$ eV) for electron transfer to the ground state than to Q_A ($-\Delta G_{ET} = 0.2$ eV).[1,2] Further charge separation occurs to achieve a nearly quantitative quantum yield of the final CS state with an extremely long lifetime (ca. 1 s).[1] According to the Marcus theory of electron transfer (eq 1),[7,8]

$$k_{ET} = \left(\frac{4\pi^3}{h^2 \lambda k_B T}\right)^{1/2} V^2 \exp\left[-\frac{(\Delta G_{ET} + \lambda)^2}{4\lambda k_B T}\right] \qquad (1)$$

the electron-transfer rate (k_{ET}) is expected to decrease rather than to increase as the driving force of electron transfer ($-\Delta G_{ET}$) increases in the region where the driving force of electron transfer ($-\Delta G_{ET}$) exceeds the reorganization energy (λ), which is the energy required to structurally reorganize the donor, acceptor, and their solvation spheres upon electron transfer: $-\Delta G_{ET} > \lambda$. This region ($-\Delta G_{ET} > \lambda$) is generally referred to the inverted region.[9] In the normal region ($-\Delta G_{ET} < \lambda$), the electron-transfer rate increases with increasing driving force.[7,8] Without the inverted region, no long-lived CS state would be obtained and the inverted region is thereby a prerequisite to the charge-separation processes in photosynthesis. In the inverted region, the smaller the λ value, the slower the electron-transfer rate. Thus, it is important to choose components that have small λ values for mimicking charge-separation processes in photosynthesis.

Earlier efforts were focused to develop multi-step electron-transfer systems involving the initial photoinduced electron transfer using electron donor–acceptor (D–A) linked multi-component systems, which can mimic multi-step charge-separation processes in photosynthesis.[9–19] However, a significant amount of energy is lost during the multi-step electron-transfer processes in both the natural and model systems. Thus, it is highly desired to develop donor–acceptor dyad systems which have long CS state lifetimes without loss of energy by sequential electron transfer.

This account article describes the recent development of a number of simple electron donor–acceptor dyads to attain long-lived CS states, where the donor and acceptor molecules are covalently linked with a short spacer. Our study is intended to attain the long-lived CS state via completely opposite approach from conventional approaches mentioned above. Even one-step electron-transfer process in a simple electron donor–acceptor dyad results in the generation of long-lived and high energy CS

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state, provided that the distance and interaction between electron donor and acceptor moieties are rationally designed to minimize λ value based on the Marcus theory of electron transfer.

The specific objectives are to attain long-lived charge-separated states in electron donor–acceptor directly linked dyads by one-step photoinduced electron transfer and also to apply such simple dyads to photocatalytic reactions.

2. Long-Lived CS State in Donor–Acceptor Dyads

2.1 Directly Linked Porphyrin Dyads. Porphyrins have frequently been used as useful components of such systems because of their resemblance to natural components.[9–19] Porphyrins contain an extensively conjugated two-dimensional π-system and such a highly delocalized π-system is suitable for efficient electron-transfer reactions, because the uptake or release of electrons results in minimal change with respect to the structure and solvation upon electron transfer to afford a small λ value of electron transfer.[20] In general, porphyrins and metalloporphyrins in donor–acceptor dyads have been used as electron donors.[9–19] However, gold(III) porphyrins act as electron acceptors for porphyrin–porphyrin dyads because cationic gold(III) porphyrin are easier to reduce than free-base or zinc porphyrins.[21–24] Both the central metal and porphyrin ligand can be redox active for gold(III) porphyrins.[21] In the case of gold(III) quinoxalinoporphyrins, one-electron reduction occurs at the metal center.[21] We have found that a directly linked donor–acceptor dyad composed of Zn^{II} and Au^{III} quinoxalinoporphyrins ($ZnPQ–AuPQ^+PF_6^-$ in Figure 1) affords a long-lived charge-shifted (CS) state in nonpolar solvents (vide infra).[25]

Time-resolved transient absorption spectra of $ZnPQ–AuPQ^+$ were measured by nanosecond laser photolysis in toluene and cyclohexane. The observed transient absorption bands at 600–800 nm are assigned to the CS state ($ZnPQ^{\bullet+}–AuPQ$) by photoinduced electron transfer from the singlet excited state of ZnPQ to $AuPQ^+$.[26] The CS state decays via back electron transfer (BET) to the ground state rather than to the triplet excited state. The back electron-transfer (BET) rate was determined from the disappearance of the absorption band at 750 nm due to $ZnPQ^{\bullet+}$ in $ZnPQ^{\bullet+}–AuPQ$. The decay of the absorption band obeys first-order kinetics, which indicates the intramolecular BET in the dyad. The k_{BET} value in cyclohexane is determined as $1.0 \times 10^5\,s^{-1}$, which corresponds to a lifetime of 10 μs.[25] This is the longest CS lifetime ever reported for porphyrin–porphyrin dyads.

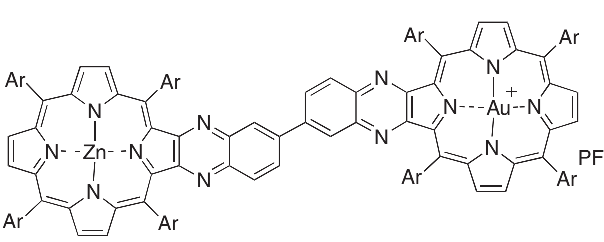


Figure 1. $ZnPQ–AuPQ^+$ dyad. Ar = 3,5-di-*tert*-butylphenyl.[25]

2.2 Chlorin–Fullerene Dyads. Fullerenes have a three-dimensional π-system which has extremely small reorganization energy of electron transfer because of no structural change occurs before and after electron transfer.[27,28] Thus, most fullerene-based donor–acceptor systems synthesized to date have utilized porphyrins as an antenna for efficient light capture in the visible region of the spectrum.[29–36] Although natural photosynthesis utilizes chlorophylls as antenna molecules, relatively few model compounds have been synthesized where a chlorophyll-like donor (a chlorin) is linked with fullerene as compared with porhyrins.[37] We have reported the formation of photoinduced charge-separated (CS) state using bacteriochlorin–C_{60} and chlorin–C_{60} dyads, which afforded long lifetimes as compared to porphyrin–C_{60} dyads.[38,39] The dyads contain the same short methylene spacer, where the edge-to-edge distance (R_{ee}) is 5.9 Å (Figure 2). The rate constants for the charge-separation processes in these dyads were determined by fluorescence lifetime measurements of the dyads. The charge-recombination (CR) rate constants of the dyads were determined using laser flash photolysis. The photoexcitation of the zinc chlorin–C_{60} dyads results in formation of the long-lived CS states, which have absorption maxima at 790 and 1000 nm due to the zinc chlorin radical cation and the C_{60} radical anion, respectively.[38]

Photoexcitation of the free-base bacteriochlorin–C_{60} dyad with the same short methylene linkage leads to formation of a radical ion pair which decays quickly to the triplet excited state of the bacteriochlorin moiety.[38] The driving force dependence of the electron transfer rate constants of these dyads with a short spacer affords a small reorganization energy ($\lambda = 0.51$ eV) as compared with the λ value (0.66 eV) of zinc porphyrin–C_{60} dyads with a longer amide spacer (Figure 2).[18,38–40]

We also developed a directly linked ZnCh–C_{60} dyad which has an extremely short donor–acceptor distance (Figure 3a).[40] The driving force of back electron transfer ($-\Delta G_{BET}$) is the largest (1.26 eV) in the series of bacteriochlorin–, chlorin–, and porphyrin–C_{60} dyads in Figure 2. The lifetime of the CS state is 230 μs at 298 K, which is the longest CS lifetime in the series of dyads shown in Figure 2.[40] The reorganization of electron transfer (λ) value is the smallest for a directly linked ZnCh–C_{60} (0.42 eV).[40] The temperature dependence of the decay rate constant (k_{BET}) was examined in PhCN solution observed by laser flash photolysis (25–65 °C) and also in frozen PhCN observed by the ESR signal decay (−150–−100 °C) as shown in Figure 3b.[40] The CS lifetime at −150 °C is as long as 120 s, which is the longest CS lifetime ever reported for porphyrin-based donor–acceptor-linked systems.[40]

2.3 9-Mesityl-10-methylacridinium Ion. On the basis of the Marcus parabola shown in Figure 2, a larger driving force of back electron transfer ($-\Delta G_{BET}$) gives a long CS state lifetime. When the value of $-\Delta G_{BET}$ is larger than that of the triplet excited state of the chromophores of a donor–acceptor dyad, the charge recombination of CS state goes to the triplet excited state instead of the ground state. Porphyrin, chlorin, and fullerene are useful molecules for electron transfer because of their small reorganization energy of electron transfer as described in the previous section. However, the energies of the triplet excited states are rather low (1.4–1.6 eV).[38] In order to attain a longer CS lifetime, a chromophore that has a small

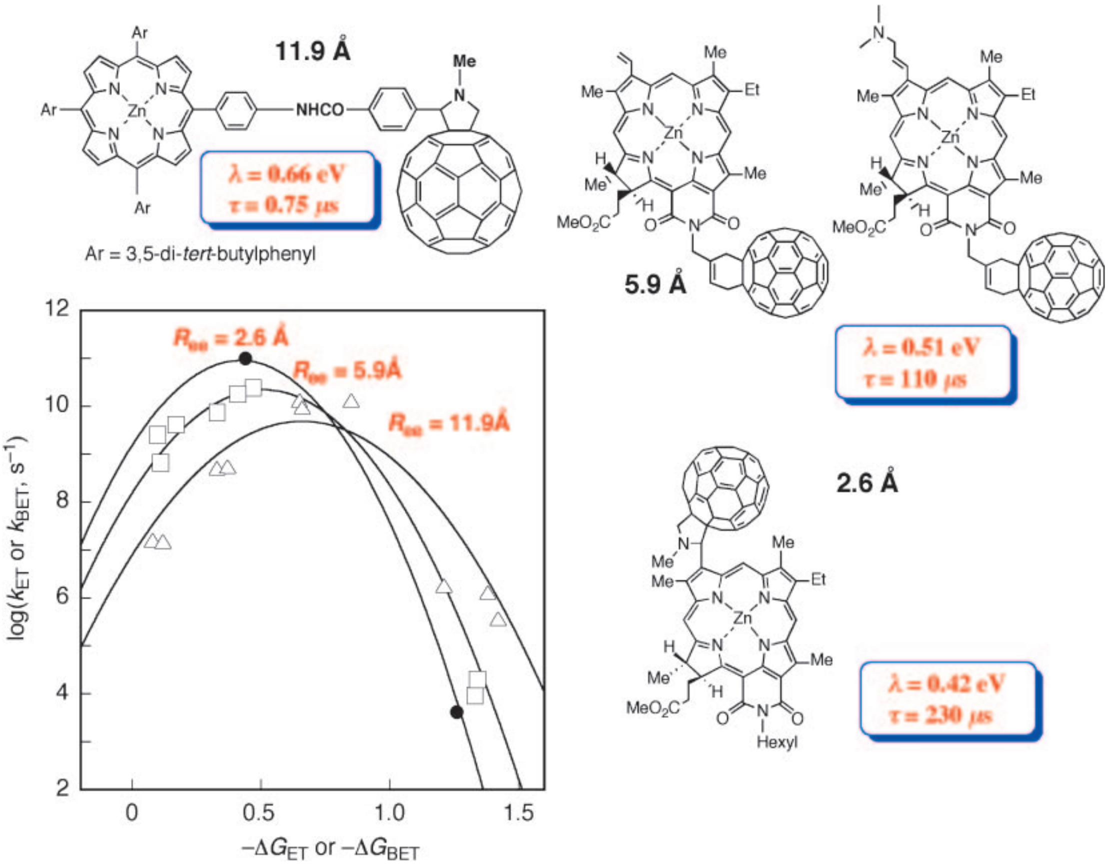


Figure 2. Driving force dependence of $k_{\rm ET}$ and $k_{\rm BET}$ rates for porphyrin–, chlorin–, and bacteriochlorin–fullerene dyads in PhCN linked with various spacers.[18,38–40]

reorganization energy of electron transfer should be chosen to be connected to an electron-donor moiety with a lower CS energy than that of the triplet excited state. In this context, acridinium ion is the best candidate, since 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 and the high-lying triplet excited state.[41] Thus, an electron donor moiety (mesityl group) is directly connected at the 9-position of the acridinium ion to yield 9-mesityl-10-methylacridinium ion ($\rm Acr^+$–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 $\rm Acr^+$–Mes is shown in Figure 4.[42] The dihedral angle made by aromatic ring planes was found to be approximately perpendicular.[42] This indicates that there is no π-conjugation between the donor and acceptor moieties. Indeed, the absorption and fluorescence spectra of $\rm Acr^+$–Mes are superpositions of the spectra of each component, i.e., mesitylene and 10-methylacridinium ion.[42]

The one-electron oxidation and reduction potentials of $\rm Acr^+$–Mes in benzonitrile (PhCN) were determined by cyclic voltammetry and second harmonic AC voltammetry as 1.88 and −0.49 V vs. SCE, respectively.[42] It is important to note that the oxidation potential of 1.88 V is high enough to oxidize water. The ET state energy of $\rm Acr^+$–Mes is determined as 2.37 eV, which is much higher than the ET state energy of the natural system (0.50 eV).[42]

Irradiation of a deaerated MeCN solution of $\rm Acr^+$–Mes by nanosecond laser excitation at 430 nm results in formation of the ET state via photoinduced ET from mesitylene moiety to the singlet excited state of the acridinium ion moiety ($\rm ^1Acr^{+*}$–Mes) at 298 K.[42] The ET state forms the π-dimer with $\rm Acr^+$–Mes due to the π–π interaction in solution as described later. The quantum yield of the ET state was determined as 98%.[42]

The formation of the ET state is also detected by ESR under photoirradiation of $\rm Acr^+$–Mes in frozen PhCN.[42] The resulting spectrum consists of the superposition of the ESR signals of the radical cation of the mesitylene moiety and the acridinyl radical. The disappearance of the ESR signal intensity obeyed first-order kinetics in frozen PhCN.[42] The lifetime of the ET state is determined to be 2 h at 203 K.[42] The rate of intramolecular electron transfer from the $\rm Acr^\bullet$ moiety to the $\rm Mes^{\bullet+}$ moiety in the same $\rm Acr^\bullet$–$\rm Mes^{\bullet+}$ molecule is highly temperature dependent and the lifetime of the ET state becomes almost infinite (10^{29} year extrapolated from the Arrhenius plot for BET rates) at 77 K in solid state.[42,43]

In contrast to the photoirradiation of a purified PhCN solution of $\rm Acr^+$–Mes at 298 K, which results in no change in the absorption spectrum (Figure 5a), when the photoirradiation of the same solution was performed at low temperatures (213–243 K) with a 1000 W high-pressure mercury lamp through a UV light cutting filter (>390 nm) and the sample was cooled to

77 K, the color of the frozen sample at 77 K clearly changed from green to brownish as shown in the inset of Figure 5.

When a glassy 2-methyltetrahydrofuran (2-MeTHF) is employed for 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 $Acr^\bullet$ moiety and the $Mes^{\bullet+}$ moiety as shown in Figure 5b. No decay of the absorption due to the ET state in Figure 5b was observed until liquid nitrogen was exhausted as in the case of the ESR detection of the ET state.[43] 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 multi-step electron-transfer processes.[43]

2.4 Dimerization of ET State of Acr^+–Mes by Strong π-Interaction. The ET state of Acr^+–Mes has both strong oxidizing and reducing ability that would never be attained by the excited state of the electron-acceptor moiety as discussed later. However, Benniston et al. repeatedly questioned the formation of such a long-lived ET state by claiming that the photoexcitation of donor-substituted acridinium ions results in formation of the triplet excited state of the acridinium ion moiety rather than the ET state.[44] In the case of Acr^+–Mes, the overlap of the absorption due to the radical cation of the Mes moiety with that due to the $Acr^\bullet$ moiety has precluded the clear-cut assignment of the formation of the ET state. The photoexcitation of 9-(1-naphthyl)-10-methylacridinium ion (Acr^+–1NA) was also reported to result in formation of the triplet excited state, because of the absence of the transient absorption due to the radical cation at 700 nm.[45] The reason the ET state of Acr^+–1NA was overlooked has recently been shown by clear cut evidence of the formation of the ET state (NOT the

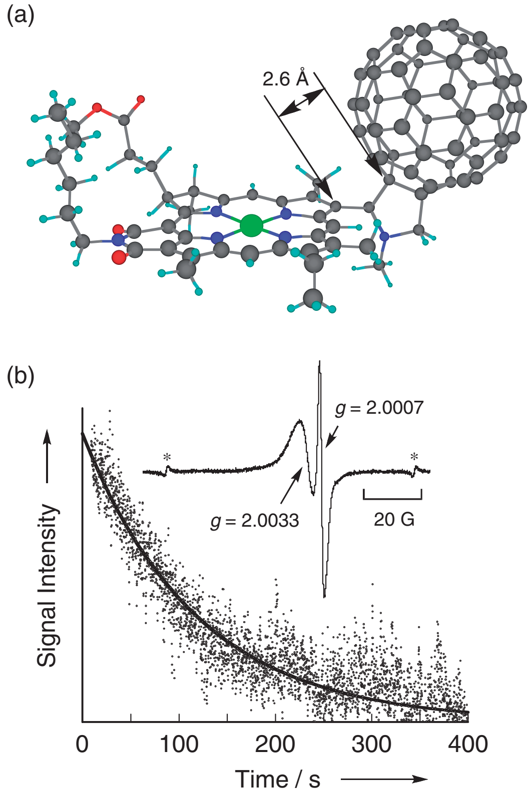


Figure 3. (a) Structure of ZnCh–C_{60} dyad calculated by PM3. (b) ESR spectrum and the decay time profile of the ESR signal intensity of $ZnCh^{\bullet+}$–$C_{60}{}^{\bullet-}$ in frozen PhCN at −150 °C.[40]

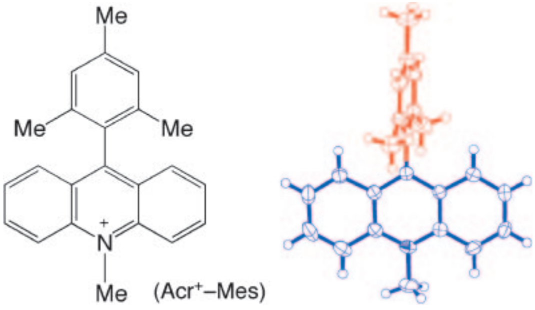


Figure 4. ORTEP drawing of Acr^+–Mes.[42]

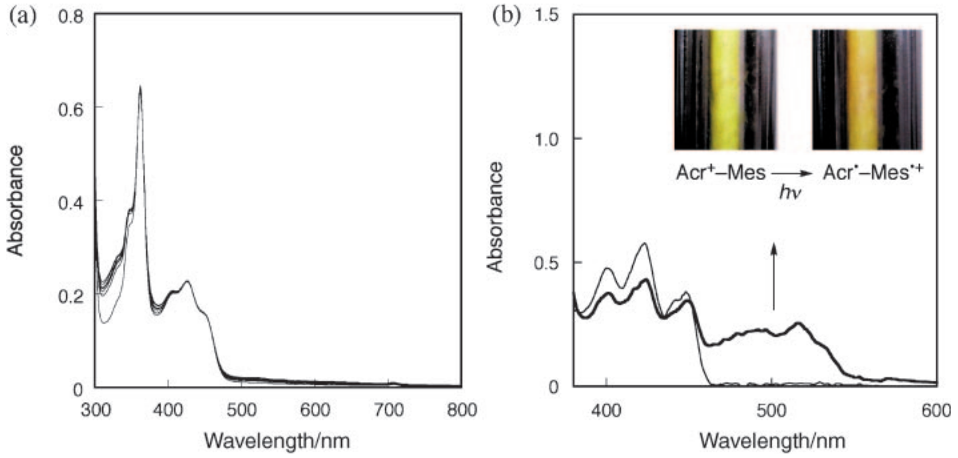
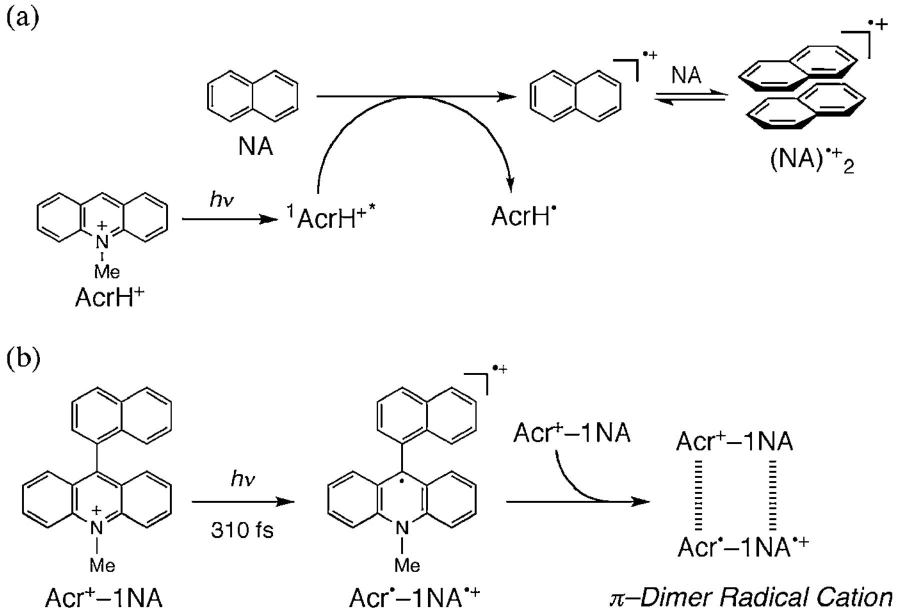


Figure 5. a) UV–vis spectral change in the steady-state photolysis of a deaerated PhCN solution of Acr^+–Mes (3.3×10^{-5} mol dm^{-3}). Spectra were recorded at 90 s interval. b) UV–vis absorption spectra obtained by photoirradiation with a high-pressure mercury lamp of deaerated 2-MeTHF glasses of Acr^+–Mes at 77 K. Inset: picture images of frozen PhCN solutions of Acr^+–Mes before and after photoirradiation at low temperatures and taken at 77 K.[34]



Scheme 1. (a) Dimerization of naphthalene in electron-transfer oxidation with AcrH$^+$. (b) Formation of dimer of electron-transfer state of Acr$^+$–1NA.[46]

triplet excited state) of Acr$^+$–1NA, which forms a π-dimer radical cation complex with Acr$^+$–1NA (vide infra).[46]

The nanosecond laser excitation of a deaerated acetonitrile (MeCN) solution of 9-naphthyl-10-methylacridinium perchlorate [(Acr$^+$–1NA)ClO$_4$$^-$] results in appearance of a new absorption band at 1050 nm in the near-IR region due to formation of a naphthalene π-dimer radical cation. The equilibrium between monomer naphthalene radical cation and dimer naphthalene radical cation is observed in intermolecular photoinduced electron transfer from naphthalene (NA) to the singlet excited state of 10-methylacridinium ion (^{1}AcrH^{+*}) as shown in Scheme 1a. The formation constant of the π-dimer radical cation is determined as 160 dm^3 mol^{-1}.[46]

In the case of Acr$^+$–1NA, the formation constant of π-dimer radical cation is estimated to be larger than 2.0×10^4 dm^3 mol^{-1}. Such a large formation constant in the case of Acr$^+$–1NA results from the π-dimer formation not only in the naphthalene moiety and but also in the acridinium ion moiety (Scheme 1b). The absorption band in the near-IR region due to the π-dimer radical cation was also clearly observed in the case of Acr$^+$–Mes.[46]

The extremely long-lived ET state of Acr$^+$–1NA was also detected by UV–vis absorption spectroscopy. Photoirradiation of glassy 2-methyltetrahydrofuran (2-MeTHF) containing Acr$^+$–1NA by a 1000 W high-pressure mercury lamp at low temperatures at 213 K results in formation of the ET state, which exhibits no decay at 77 K until liquid nitrogen runs out. The absorption bands due to the Acr$^\bullet$ moiety (520 nm) and 1NA$^{\bullet+}$ moiety were clearly observed as shown in Figure 6. The frozen medium at low temperature allowed us to observe the monomer radical cation of 1NA moiety of the ET state that cannot form the π-dimer radical cation via intermolecular reaction. The color change from the ground state of Acr$^+$–1NA to the ET state (Acr$^\bullet$–1NA$^{\bullet+}$) was also clearly observed as shown in the inset of Figure 6.[46]

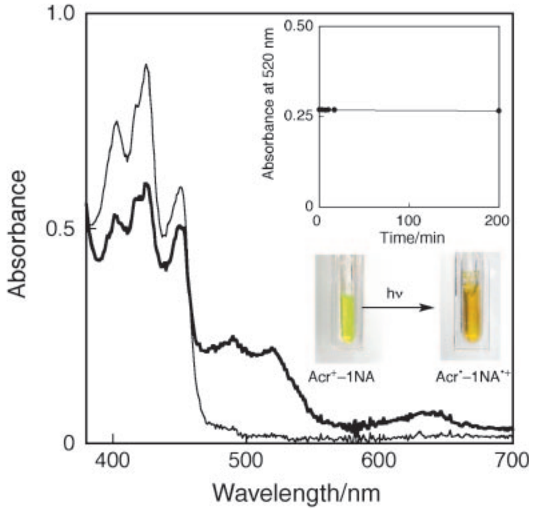
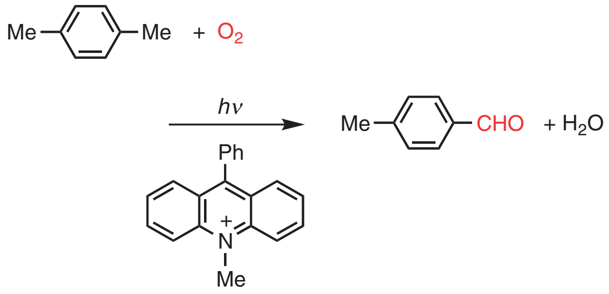


Figure 6. UV–vis absorption spectra obtained by photoirradiation with a high-pressure mercury lamp of a deaerated 2-MeTHF glass of Acr$^+$–1NA at 77 K. Inset: Time profiles at 520 nm, and photographs of a 2-MeTHF glass of Acr$^+$–1NA before and after photoirradiation at low temperature and taken at 77 K.[46]

3. Efficient Photocatalytic Reaction Using Acridinium Ion

3.1 Selective Oxygenation of Ring-Substituted Toluenes with Electron-Donating and -Withdrawing Substituents by Molecular Oxygen via Photoinduced Electron Transfer. The small reorganization of electron transfer of 10-methylacridinium ion (AcrH$^+$), which is the key factor for intramolecular fast charge separation and slow charge recombination of AcrH$^+$–Mes (vide supra) also results in fast intermolecuar photoinduced electron transfer and slow charge recombination.[41] This enables us to use AcrH$^+$ as an efficient photocatalyst for oxygenation of a ring-substituted toluene with an electron-donating substituent, *p*-xylene, by molecular oxygen (vide infra).[47]

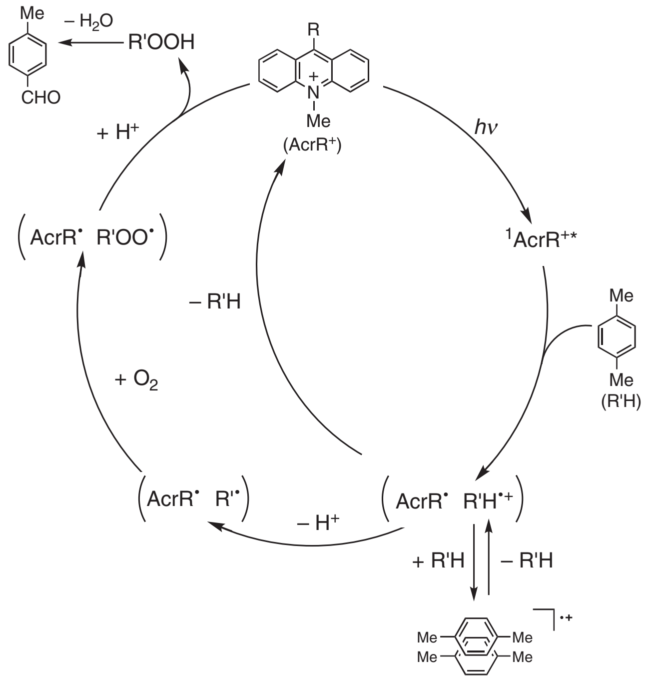
Visible light irradiation of the absorption band of AcrH$^+$ in oxygen-saturated MeCN containing *p*-xylene with a xenon lamp results in formation of *p*-tolualdehyde accompanied by disappearance of *p*-xylene. After 24 h irradiation, the yield of *p*-tolualdehyde was 37%. The product yield is improved to 66%, when MeCN is replaced by a less polar solvent, chloroform, under otherwise the same experimental conditions. The photooxygenated product yield is further improved to 100% when AcrH$^+$ is replaced by AcrPh$^+$ in chloroform (eq 2).[47]



(2)

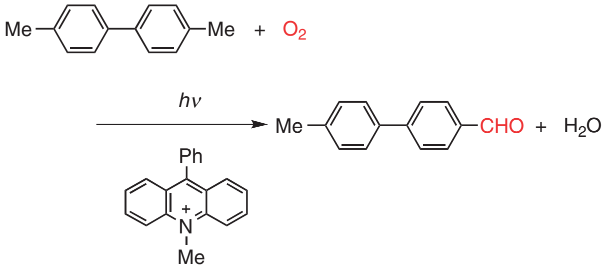
There was no deoxygenated product after prolonged photoirradiation. It was confirmed that there was no adduct formation between the photocatalyst, AcrPh$^+$ and *p*-xylene. Thus, the 100% selective photooxygenation of *p*-xylene to *p*-tolualdehyde has been accomplished by using AcrPh$^+$ as a photocatalyst in chloroform. The photoirradiation time to obtain 100% yield *p*-tolualdehyde was reduced from 24 to 10 h when a xenon lamp was replaced by a high-pressure mercury lamp (1000 W).[47]

The reaction mechanism for the AcrR$^+$-photosensitized oxygenation (R = H and Ph) of *p*-xylene is shown in Scheme 2.[47] Photoinduced electron transfer from *p*-xylene to ^{1}AcrR^{+*} occurs to produce AcrR$^\bullet$ and *p*-xylene radical cation which is in equilibrium with the dimer radical cation. This is followed by deprotonation of *p*-xylene radical cation to give *p*-methylbenzyl radical in competition with the back electron transfer to the reactant pair. In the presence of oxygen, *p*-methylbenzyl radical is readily trapped by oxygen to give *p*-xylenylperoxyl radical. The *p*-methylbenzylperoxyl radical is reduced by back electron transfer from AcrR$^\bullet$ to yield *p*-methylbenzyl hydroperoxide, accompanied by regeneration of AcrR$^+$ (Scheme 2). The hydroperoxide decomposes to yield *p*-tolualdehyde selectively.[47]



Scheme 2. Reaction course of photocatalytic oxygenation of toluenes (R′H) with AcrR$^+$.[47]

When 4,4′-dimethylbiphenyl is replaced by *p*-xylene, efficient photooxygenation is also achieved in the presence of AcrPh$^+$ClO$_4^-$ under visible light irradiation in O$_2$-saturated chloroform (CHCl$_3$) to yield 4-(4-methylphenyl)benzaldehyde as a main oxygenated product (eq 3). Prolonged photoirradiation afforded the further oxygenated product, 4,4′-biphenyldicarbaldehyde (eq 4).[48]



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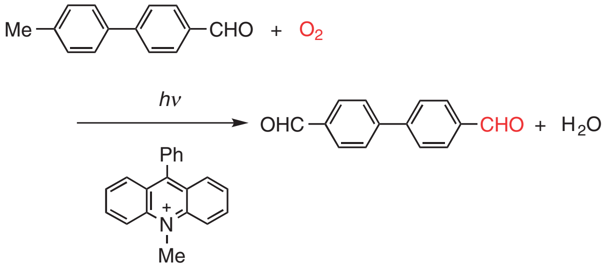
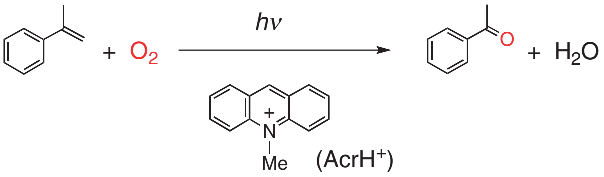


(4)

The reactive radical intermediates involved in the photocatalytic cycle have successfully been detected by laser flash photolysis and ESR measurements. The photocatalytic mechanism for the oxygenation of 4,4′-dimethybiphenyl via photoinduced electron transfer from 4,4′-dimethylbiphenyl to the singlet excited state of AcrPh$^+$ is clarified based on the dependence of quantum yields on concentrations of substrates and the detected radical intermediates.[48]

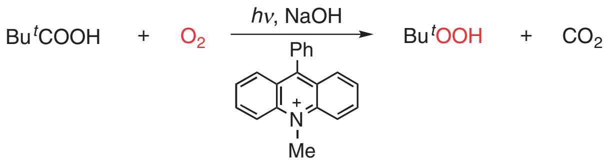
α-Methylstyrene can also be oxygenated with molecular oxygen in the presence of 10-methylacridinium perchlorate (AcrH$^+$ClO$_4^-$) under visible light irradiation in oxygen-saturated MeCN to yield acetophenone (eq 5).[49]



(5)

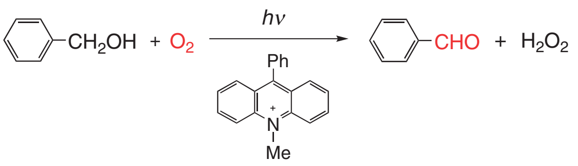
The photocatalytic oxygenation of α-methylstyrene with oxygen proceeds via photoinduced electron transfer from α-methylstyrene to the singlet excited state of AcrH^+ ($^1\mathrm{AcrH}^{+*}$) based on the fluorescence quenching of $^1\mathrm{AcrH}^{+*}$ by α-methylstyrene.[49]

Pivalic acid ($\mathrm{Bu}^t\mathrm{COOH}$) is also oxygenated with O_2 to produce *t*-butyl hydroperoxide ($\mathrm{Bu}^t\mathrm{OOH}$) by repeated cycles of the photoreduction of 10-methylacridiniun ion (AcrH^+) by $\mathrm{Bu}^t\mathrm{COO}^-$ to produce the Bu^t adduct, 9-*t*-butyl-9,10-dihydro-10-methylacridine (AcrHBu^t) and the photooxidation of AcrHBu^t with O_2 in the presence of perchloric acid (HClO_4) to yield $\mathrm{Bu}^t\mathrm{OOH}$, accompanied by regeneration of AcrH^+.[50] When AcrH^+ is replaced by the 9-phenyl derivative (AcrPh^+), AcrPh^+ acts as an effective photocatalyst for the photooxygenation of $\mathrm{Bu}^t\mathrm{COOH}$ in the presence of less than one equivalent of NaOH relative to $\mathrm{Bu}^t\mathrm{COOH}$ with O_2 to yield $\mathrm{Bu}^t\mathrm{OOH}$ and $\mathrm{Bu}^t\mathrm{OH}$ (eq 6).[50]



(6)

$\mathrm{AcrPh}^+\mathrm{ClO}_4^-$ is soluble in benzyl alcohol, acting as an effective photocatalyst for selective photocatalytic oxidation of benzyl alcohol to the benzaldehyde under visible light irradiation via efficient photoinduced electron transfer from benzyl alcohol to the singlet excited state of AcrPh^+ in neat benzyl alcohol (eq 7).[51]



(7)

Thus, we have successively developed selective and efficient photooxidation of aromatic hydrocarbons by molecular oxygen using acridinium ion as an effective photocatalyst under visible light irradiation.

3.2 Photocatalytic Oxygenation of Anthracenes and Olefins with Dioxygen via Selective Radical Coupling Using 9-Mesityl-10-methylacridinium Ion as an Effective Electron-Transfer Photocatalyst. As described in Section **2.3**, photoexcitation of Acr^+–Mes results in formation of the electron-transfer state ($\mathrm{Acr}^\bullet$–$\mathrm{Mes}^{\bullet+}$), which has an extremely long lifetime (e.g., 2 h at 203 K) as well as both high oxidizing and reducing ability.[42] In such case, Acr^+–Mes acts as an efficient electron-transfer photocatalyst for highly selective oxygenation of various substrates with O_2 via selective radical coupling of the donor radical cation and $\mathrm{O}_2^{\bullet-}$ under visible light irradiation (vide infra).[52]

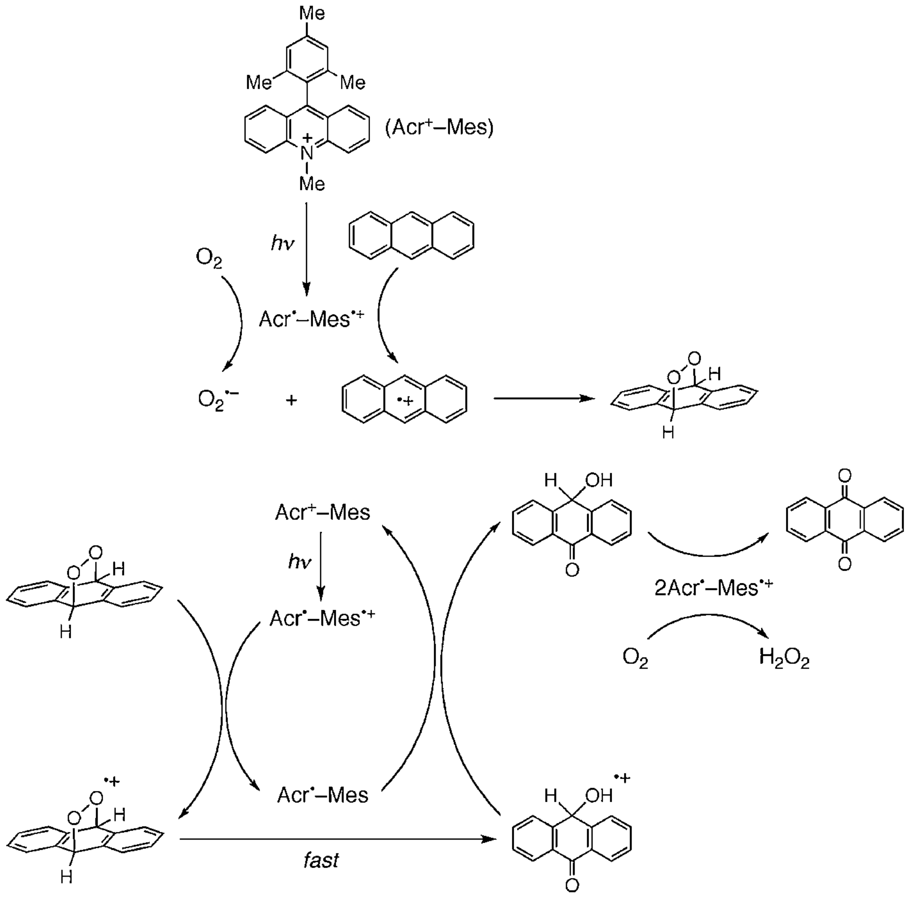
Visible light irradiation of the absorption band of Acr^+–Mes in an O_2-saturated MeCN solution containing 9,10-dimethylanthracene results in formation of oxygenation product, i.e., dimethylepidioxyanthracene ($\mathrm{Me_2An}$–O_2).[53] Anthracene and 9-methylanthracene also undergo photocatalytic oxygenation with Acr^+–Mes to afford the corresponding epidioxyanthracenes under photoirradiation. In the case of anthracene, further photoirradiation results in formation of anthraquinone as the final six-electron oxidation product, via 10-hydroxyanthrone, accompanied by generation of $\mathrm{H_2O_2}$ (Scheme 3). The photocatalytic oxygenation of anthracenes is initiated by photoexcitation of Acr^+–Mes, which results in formation of the electron-transfer state: $\mathrm{Acr}^\bullet$–$\mathrm{Mes}^{\bullet+}$, followed by electron transfer from anthracenes and olefins to the $\mathrm{Mes}^{\bullet+}$ moiety together with electron transfer from the $\mathrm{Acr}^\bullet$ moiety to O_2.[53,54] The resulting anthracene radical cation undergoes radical coupling reactions with $\mathrm{O}_2^{\bullet-}$ to produce the epidioxyanthracene (An–O_2), respectively.[53]

1,2-Dioxetanes have attracted considerable interest because of the key roles played in chemiluminescence and bioluminescence, which have a broad range of biological, chemical, and medical applications. The most common preparation of 1,2-dioxetanes is through the formal [2 + 2] cycloaddition of singlet oxygen ($^1\mathrm{O}_2$) to electron-rich alkenes.[55] Diastereoselective formation of dioxetanes has also been achieved by a chiral-auxially-induced [2 + 2] cycloaddition of $^1\mathrm{O}_2$ with a chiral allylic alcohol and enecarbamates. Nelsen and co-workers have reported the isolation and electron-transfer oxidation properties of 1,2-dioxetane such as adamantylidene adamantane. However, there has been no report of an aromatic 1,2-dioxetane.[56] However, 1,2-dioxetane cannot be obtained by the reaction of electron-poor alkenes such as tetraphenylethylene (TPE) with $^1\mathrm{O}_2$, because of the low nucleophilicity of TPE.[57]

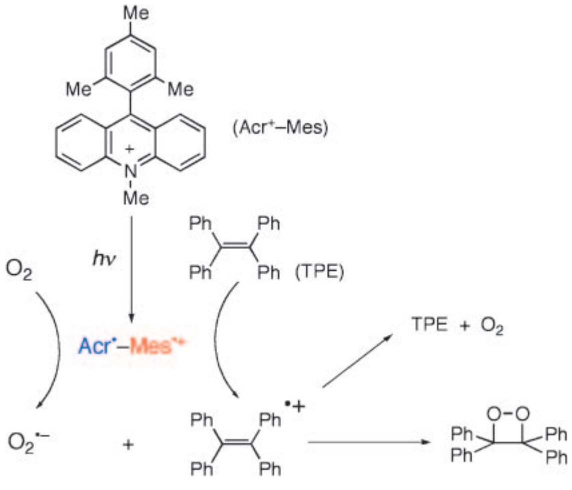
In contrast to no reactivity of TPE toward $^1\mathrm{O}_2$, the 1,2-dioxetane of TPE is obtained using Acr^+–Mes as a photocatalyst via electron transfer from TPE to the $\mathrm{Mes}^{\bullet+}$ moiety together with electron transfer from the $\mathrm{Acr}^\bullet$ moiety to O_2, and the subsequent radical coupling between $\mathrm{TPE}^{\bullet+}$ and $\mathrm{O}_2^{\bullet-}$ as shown in Scheme 4. The dioxetane thus formed was isolated using column chromatography.[57] Photooxygenation of stilbene derivatives is also efficiently catalyzed by Acr^+–Mes, accompanied by efficient cis–trans isomerization, to afford the corresponding benzaldehydes via electron transfer from $\mathrm{Acr}^\bullet$–$\mathrm{Mes}^{\bullet+}$ to stilbene derivatives and oxygen.[58]

3.3 Carbon–Carbon Bond Formation via Radical Coupling Using ET State. The photochemical carbon–carbon bond formation of aromatic compounds has been extensively investigated not only for synthetic exploitation, but also for basic understanding of the photochemical process.[59] The Acr^+–Mes-catalyzed radical coupling reactions between radical cations and $\mathrm{O}_2^{\bullet-}$ has been extended to the development of oligomerization of fullerene with formation of carbon–carbon bonds. Photocatalytic oligomerization of fullerene in toluene/MeCN solution occurs efficiently via electron-transfer reactions with the photogenerated electron-transfer state of Acr^+–Mes, followed by the radical coupling reaction between fullerene radical cation and radical anion (Scheme 5).[60] The photoproducts obtained were analyzed by MALDI-TOFMS. Several peaks were observed from a crude mixture solution after photoirradiation. The peaks at 1440, 2160, and 2880 were clearly assigned to fullerene oligomers, C_{120}, C_{180}, and C_{240}, respectively.[60]

When the photochemical reaction of 9,10-dimethylanthracene with Acr^+–Mes was carried out without O_2 in CHCl_3, photocatcalytic carbon–carbon bond formation occurred efficiently to give dimethyllepidopterene (5,6,11,12-tetrahydro-5,12-dimethyl-4b,12[1′,2′]:6,10b[1″,2″]-dibenzochrysene).[61]



Scheme 3. Photocatalytic oxygenation of anthracene with Acr$^+$–Mes.[53]

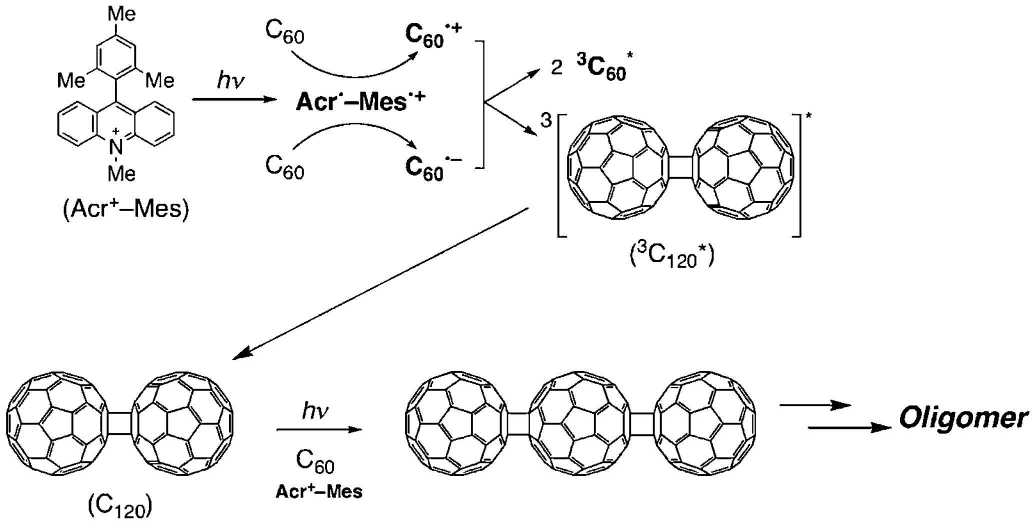


Scheme 4. Photocatalytic oxygenation of tetraphenylethylene with Acr$^+$–Mes.[57]

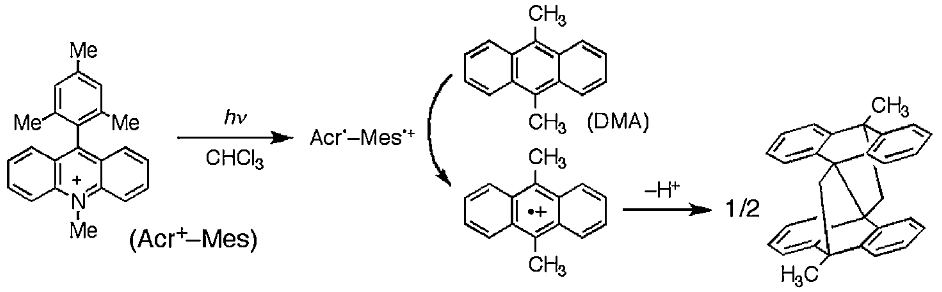
The dimethyllepidopterene is formed via deprotonation of dimethylanthracene radical cation (Scheme 6). In this case, $CHCl_3$ is reduced by the Acr$^\bullet$ moiety to yield the radical coupling product, $(CHCl_2)_2$.[61]

3.4 Efficient Photocatalytic Hydrogen Evolution without an Electron Mediator Using a Simple Electron Donor–Acceptor Dyad. A number of photocatalytic hydrogen-evolution systems have been developed over the past decades.[62,63] Such systems usually consist of an electron donor, a photosensitizer, an electron mediator such as methyl viologen (MV^{2+}), and a hydrogen-evolution catalyst. Photosensitizers have been linked covalently or noncovalently with MV^{2+} in order to improve the charge-separation efficiency in the hydrogen-evolution photocatalytic system.[64] However, the lifetime of the charge-separated state is relatively short and the catalytic activity of hydrogen production with MV$^{\bullet+}$ is also low and thereby it takes a long time to obtain an appreciable amount of hydrogen. In contrast to conventional photosensitizers, the photoinduced ET state of Acr$^+$–Mes has a long-lifetime, which can inject an electron to a hydrogen-evolution catalyst directly without an electron mediator (vide infra).

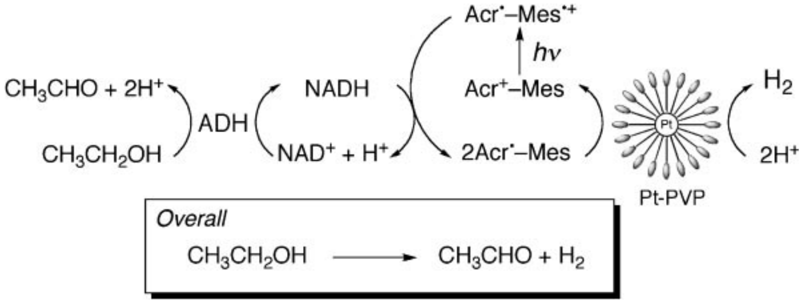
A highly efficient photocatalytic hydrogen-evolution system without an electron mediator such as MV^{2+} has been constructed using Acr$^+$–Mes, poly(*N*-vinyl-2-pyrrolidone)-protected platinum nanoclusters (Pt–PVP) and NADH (β-nicotinamide adenine dinucleotide, reduced form), used as a photocatalyst, a hydrogen-evolution catalyst and an electron donor, respectively.[65] The photocatalyst (Acr$^+$–Mes) undergoes photoinduced electron transfer from the Mes moiety to the singlet excited state of the Acr$^+$ moiety to produce an extremely long-lived ET state, which is capable of oxidizing NADH and reducing Pt–PVP, leading to efficient hydrogen evolution. The hydrogen-evolution efficiency is 300 times higher than that in the presence of MV^{2+} because of the much faster reduction rate of Pt–PVP by Acr$^\bullet$–Mes as compared with



Scheme 5. Photocatalytic oligomerization of fullerene with Acr$^+$–Mes.[60]



Scheme 6. Photocatalytic formation of dimethyllepidopterene with Acr$^+$–Mes.[61]



Scheme 7. Acr$^+$–Mes-catalyzed photocatalytic hydrogen-evolution system using alcohol dehydrogenase and Pt–PVP.[65]

that by $\text{MV}^{\bullet+}$. The electron donor (NADH) is replaced by ethanol in the presence of an alcohol dehydrogenase (ADH) with which NADH is reproduced in the photocatalytic hydrogen evolution (Scheme 7).[65] Thus, the overall catalytic reaction shows the formation hydrogen from ethanol using enzymatic, photochemical, and metal catalysts.

3.5 Direct Detection of Nucleotide Radical Cations Produced by Electron-Transfer Oxidation of DNA Bases with the Electron-Transfer State of 9-Mesityl-10-methylacridinium Ion and Resulting Efficient DNA Cleavage without Oxygen. Acr$^+$–Mes is also soluble in aqueous solution. Acr$^\bullet$–Mes$^{\bullet+}$ can act as a strong oxidant ($E_{\text{red}} =$ 1.88 V vs. SCE), being capable of oxidizing DNA bases, as well as a reductant ($E_{\text{ox}} = -0.49$ V vs. SCE), which can reduce O_2.[42] Photoinduced electron transfer of DNA as well as DNA bases with Acr$^+$–Mes results in formation of all types of DNA base radical cations, which have been detected as the transient absorption spectra in laser flash photolysis measurements. Calf thymus DNA was also efficiently oxidized by the ET state of Acr$^+$–Mes. Transient absorption spectra of oxidized DNA were similar to those of DNA base radical cations.

We also examined the DNA-cleavage activity of Acr$^+$–Mes in the presence of O_2 using the widely used assay with the double-stranded plasmid DNA, pBR322, since $O_2^{\bullet-}$ is formed in the ET reaction from the Acr$^\bullet$ moiety ($E_{\text{ox}} = -0.49$ V vs. SCE) to oxygen ($E_{\text{red}} = -0.40$ V vs. SCE).[53] The retarding effect of O_2 may result from more efficient back ET from $O_2^{\bullet-}$ to DNA radical cation as compared with that from the Acr$^\bullet$ moiety to DNA radical cation before oxidizing DNA as shown in Scheme 8.[66] Although all DNA bases can be oxidized by the

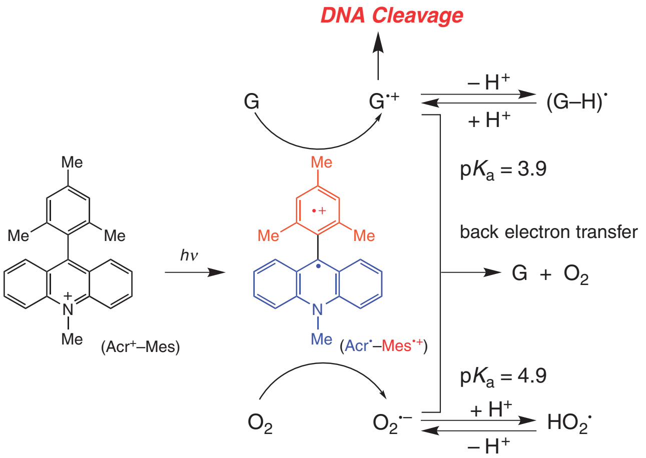
$Mes^{\bullet+}$ moiety of $Acr^{\bullet}$–$Mes^{\bullet+}$, the largest rate constant of the ET oxidation of GMP together with the lowest oxidation potential of GMP among DNA bases indicate that guanine is eventually oxidized in ET from DNA to the $Mes^{\bullet+}$ moiety of $Acr^{\bullet}$–$Mes^{\bullet+}$, leading to the efficient DNA cleavage.[66] The higher DNA cleavage activity at pH 5.0 as compared with that at pH 7.0 suggests that guanine radical cation has a higher reactivity for the DNA cleavage than the deprotonated radical (Scheme 8) judging from the pK_a value of guanine radical cation ($pK_a = 3.9$).[66,67]

4. Formation of a Long-Lived Charge-Separated State by Non-Covalently Linked Dyad

We have tried to produce a much longer-lived charge-separated state than that of natural photosynthetic reaction center using a non-covalent bonding donor–acceptor dyad since it is very easy to prepare such a donor–acceptor ensemble. As mentioned above, acridinium ion is suitable as a component of artificial photosynthetic reaction centers because of the small reorganization energy (λ) of electron transfer, which results in fast photoinduced electron transfer but extremely slow back electron transfer. On the other hand, a bisporphyrin has been known to form a π-complex with fullerene,[67] which is inserted between two porphyrin rings. We have found the formation of a π-complex between a free-base cofacial bisporphyrin (H_4DPOx) and acridinium ion (AcH^+), and also examined the photodynamics in PhCN as shown in Scheme 9.[69] H_4DPOx is regarded as a model compound of a special pair, which has two cofacial porphyrin rings and flexible spacer. The occurrence of photoinduced ET in the π-complex was confirmed by nanosecond laser flash photolysis. The lifetime of the ET state was determined to be 18 µs at 298 K. The decay of the ET state is highly temperature dependent. As a result, a remarkably long-lived ET state has been attained at low temperature and virtually no decay of the ET state was observed at 77 K. Such an extremely long-lived ET state is indeed detected by the steady-state photoirradiation of glassy 2-MeTHF containing a 10% butyronitrile glass of H_4DPOx–AcH^+ by a 1000 W high-pressure mercury lamp at low temperature. The new absorption bands due to $H_4DPOx^{\bullet+}$ and $AcH^{\bullet}$ are clearly observed as shown in Figure 7. The observed ET state exhibits no decay for 200 min at 77 K (inset of Figure 7).[69] The color change on going from the ground state of the H_4DPOx–AcH^+ complex to the ET state is also shown in the inset of Figure 7. The color and the absorption spectrum of the ET state go back to the original ones when the temperature is increased to 298 K. The large temperature dependence of the rate constant of BET results from the small λ value in the π-complex, when the BET is deeply in the Marcus inverted region.[69,70]

5. Summary

This account article has provided a totally opposite strategy from conventional approaches to attain a long-lived CS state with high energy; that is the use of a simple electron donor–



Scheme 8. Scavenging reaction of guanine radical cation by superoxide anion.[66]

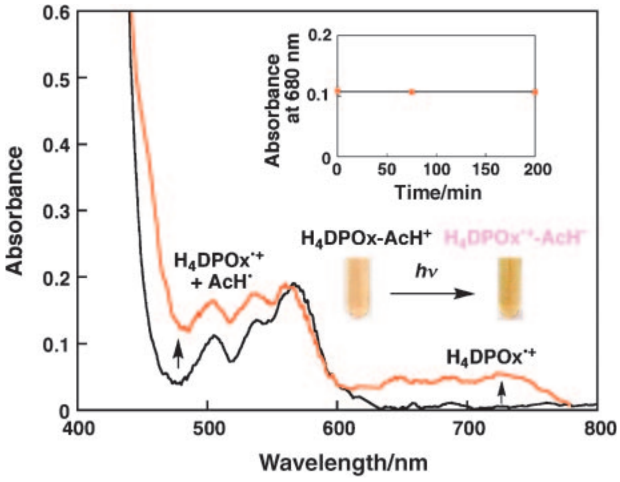
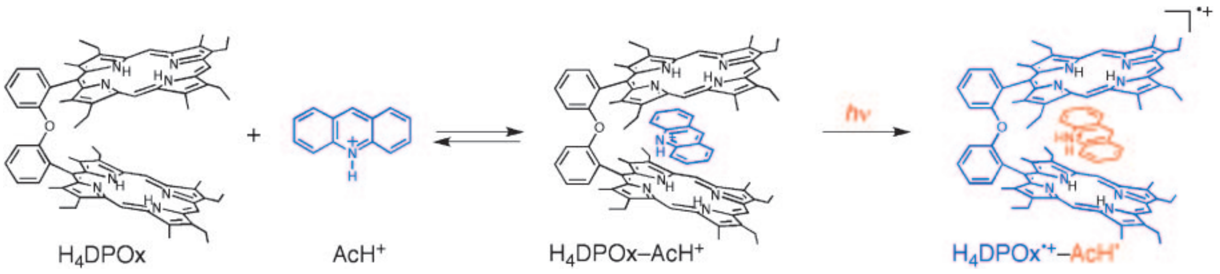


Figure 7. UV–vis absorption spectra obtained by photoirradiation with a high-pressure mercury lamp of deaerated 2-MeTHF glasses containing 10% butyronitrile of H_4DPOx and AcH^+ at 77 K. Inset: Time profile at 680 nm and picture images before and after photoirradiation at low temperatures measured at 77 K.[69]



Scheme 9. Photoinduced charge separation in a π-complex between acridinium ion and bisporphyrin.[69]

acceptor dyad with a short linkage rather than the use of multicomponent systems composed of an electron donor, acceptor, and electron mediator molecules. Rational design of such an electron donor–acceptor dyad based on the Marcus theory of electron transfer has enabled development of a zinc chlorin–fullerene dyad and 9-mesityl-10-methylacridinium ion (Acr^+–Mes) as the best compound capable of fast charge separation and extremely slow charge recombination. Especially Acr^+–Mes has successfully been applied to develop efficient photocatalytic oxygenation reactions of anthracenes, olefins, and other substrates as well as photocatalytic reactions of carbon–carbon bond formation. An efficient photocatalytic hydrogen evolution system has also been developed by combining Acr^+–Mes with platinum nanoclusters. Electron donor–acceptor dyads with long-lived CS states or ET states have been proven to be useful and unique photocatalysts or photosensitizers for organic synthesis and organic devices.[71]

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