

## New development of photoinduced electron-transfer catalytic systems\*

Shunichi Fukuzumi

*Department of Material and Life Science, Division of Advanced Science and Biotechnology, Graduate School of Engineering, Osaka University, SORST, Japan Science and Technology Agency, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan*

*Abstract:* As an alternative to conventional charge-separation functional molecular models based on multi-step long-range electron transfer (ET) within redox cascades, simple donor–acceptor dyads have been developed to attain a long-lived and high-energy charge-separated (CS) state without significant loss of excitation energy. In particular, a simple molecular electron donor–acceptor dyad, 9-mesityl-10-methylacridinium ion (Acr<sup>+</sup>–Mes), is capable of fast charge separation but extremely slow charge recombination. Such a simple molecular dyad has significant advantages with regard to synthetic feasibility, providing a variety of applications for photoinduced ET catalytic systems, including efficient photocatalytic systems for the solar energy conversion and construction of organic solar cells.

*Keywords:* electron transfer; redox cascades; donor–acceptor dyads; photoinduced electron transfer; solar energy; photocatalytic.

### INTRODUCTION

Extensive efforts have been devoted to mimic the function of the photosynthetic reaction center of purple bacteria ever since the three-dimensional X-ray crystal structures of reaction centers have been disclosed [1,2]. The importance and complexity of energy- and electron-transfer processes in the photosynthetic reaction center have prompted the design and preparation of a variety of donor–acceptor covalently linked ensembles, including dyads, triads, tetrads, and pentads, which can mimic the energy- and electron-transfer processes in the photosynthetic reaction center [3–10]. However, the multi-step electron-transfer (ET) processes are inevitably accompanied by significant energy loss, because each step should be exothermic to reach the final charge-separated (CS) state. Thus, a specific challenge involves construction of simple donor–acceptor dyads, which can afford long-lived and high-energy CS states.

This article is intended to focus on recent development of simple donor–acceptor dyads, capable of fast charge separation but extremely slow charge recombination with high-energy states, which provide a variety of applications for construction of efficient photoinduced ET catalytic systems.

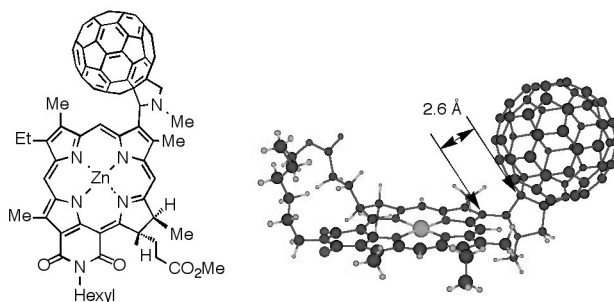
### SIMPLE DONOR–ACCEPTOR DYADS WITH LONG CHARGE-SEPARATED LIFETIMES

A number of multi-step ET processes have so far been developed to attain a long-distance charge separation, mimicking the natural photosynthetic reaction center [3–16]. However, a significant amount of

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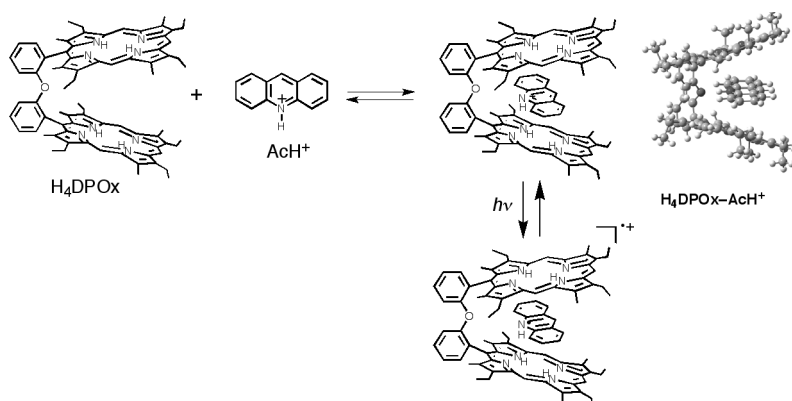
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energy is lost during the multi-step ET processes to reach the final CS state. It is thereby desired to design simple molecular electron donor–acceptor dyads, which are capable of fast charge separation but retain slow charge recombination without the energy loss. Theoretically, it is possible to obtain such electron donor–acceptor dyads, because the CS lifetime increases with increasing the CS energy in the Marcus inverted region [17]. However, the CS energy should be lower than the triplet excited state of one of the components of donor–acceptor dyads. Otherwise, the CS state would decay rapidly to the triplet excited state in the Marcus normal region rather than to the ground state in the Marcus inverted region. A number of simple donor–acceptor dyads have been designed and synthesized to attain a long-lived CS state, where the donor and acceptor molecules are linked with a short spacer to minimize the solvent reorganization energy [18–25]. For example, a closely linked zinc chlorin–fullerene dyad (ZnCh–C<sub>60</sub> in Fig. 1) affords the longer CS lifetime as compared with other zinc chlorin–fullerene dyads with the longer spacers [23–25]. A deoxygenated benzonitrile (PhCN) solution containing ZnCh–C<sub>60</sub> gives rise upon a 388-nm laser pulse to a transient absorption maximum at 460 nm due to the singlet excited state of ZnCh [25]. The decay of absorbance at 460 nm due to <sup>1</sup>ZnCh\* is accompanied by an increase in absorbance at 590 nm due to ZnCh<sup>•+</sup> [23–25]. This indicates that ET from <sup>1</sup>ZnCh\* to C<sub>60</sub> occurs rapidly to form the CS state, ZnCh<sup>•+</sup>–C<sub>60</sub><sup>•-</sup>. The CS state decays via back electron transfer (BET) to the ground state rather than to the triplet excited state, since the CS state is lower in energy (1.26 eV) than both the triplet excited state of C<sub>60</sub> (1.50 eV) and ZnCh (1.36–1.45 eV) [25]. The lifetime of the CS state is determined as 230 μs at 298 K [25]. The large temperature dependence of the CS lifetime is observed, and a remarkably long lifetime of the CS state (120 s) is attained at 123 K [25].

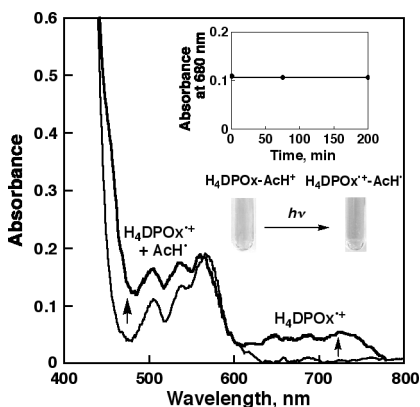


**Fig. 1** Structure of a closely linked ZnCh–C<sub>60</sub> dyad [25].

The use of noncovalent bonding such as hydrogen bond and  $\pi$ – $\pi$  interaction has recently merited increasing attention as a simpler but more elegant way to construct electron donor–acceptor ensembles [26,27]. For example, a free base cofacial bisporphyrin, H<sub>4</sub>DPOx, forms a  $\pi$ -complex with acridinium ion (AcH<sup>+</sup>) by  $\pi$ – $\pi$  interaction in PhCN [28]. Formation of the H<sub>4</sub>DPOx–AcH<sup>+</sup>  $\pi$ -complex was probed by UV–vis and NMR spectra. The binding constant between AcH<sup>+</sup> and H<sub>4</sub>DPOx is determined as  $9.7 \times 10^4 \text{ M}^{-1}$  [28]. Photoinduced ET from the H<sub>4</sub>DPOx to the AcH<sup>+</sup> moiety occurs efficiently in the  $\pi$ -complex to form the ET state (H<sub>4</sub>DPOx<sup>•+</sup>–AcH<sup>•</sup>) as shown in Scheme 1 [28]. The lifetime of the ET state is determined as 18 μs in PhCN at 298 K, and the quantum yield of the ET state is 90 % [28]. The ET state lifetime exhibited large temperature dependence, and 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 [28]. Such an extremely long-lived ET state is even detected by steady-state UV–vis absorption spectroscopy as shown in Fig. 2, together with the color change from the ground state of the H<sub>4</sub>DPOx–AcH<sup>+</sup> complex to the ET state [28]. The observed ET state exhibits no decay for 200 min at 77 K (inset of Fig. 2).

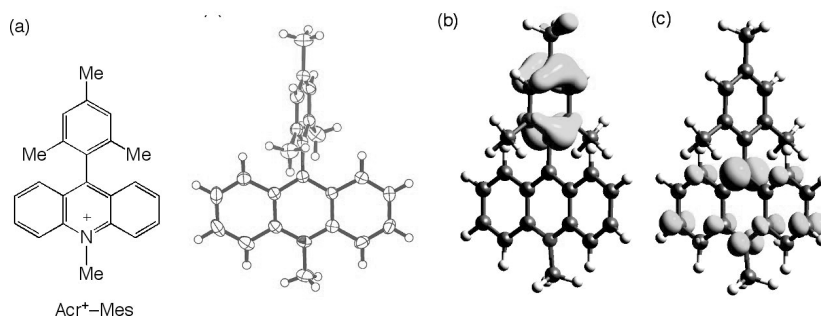


**Scheme 1** Photoinduced ET in a  $\pi$ -complex between a free base cofacial bisporphyrin ( $H_4DPOx$ ) and acridinium ion ( $AcH^+$ ) [28].



**Fig. 2** Visible absorption spectra obtained by photoirradiation with high-pressure mercury lamp of deaerated 2-MeTHF/butyronitrile (9:1 v/v) glasses of  $H_4DPOx$  ( $1.8 \times 10^{-5}$  M) and  $AcH^+$  ( $3.6 \times 10^{-4}$  M) at low temperature and measured in liquid  $N_2$  dewar at 77 K [28]. Inset: Time profile at 680 nm and images before and after photoirradiation at low temperatures measured at 77 K [28].

As long as porphyrins and  $C_{60}$  are used as components of donor–acceptor dyads, however, the low-lying triplet energies of porphyrins and  $C_{60}$  have precluded attempts to attain long-lived CS states with a higher energy than the triplet energies. Acridinium ion can be regarded as the best candidate for such a purpose, since the  $\lambda$  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 [29], and the triplet excited energy is significantly higher than those of porphyrins and  $C_{60}$ . 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 ( $AcR^+-Mes$ ), in which the solvent reorganization of ET is minimized because of the short linkage between the donor and acceptor moieties [30]. The X-ray crystal structure of  $AcR^+-Mes$  is shown in Fig. 3a [30]. The dihedral angle made by aromatic ring planes is perpendicular. Thus, there is no orbital interaction between the donor and acceptor moieties as indicated by the absorption and fluorescence spectra of  $AcR^+-Mes$ , which are superpositions of the spectra of each component, i.e., mesitylene and 10-methylacridinium ion [30]. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) orbitals of  $AcR^+-Mes$  calculated by a density functional theory (DFT) method with Gaussian 98 (B3LYP/6-31G\* basis set) are localized

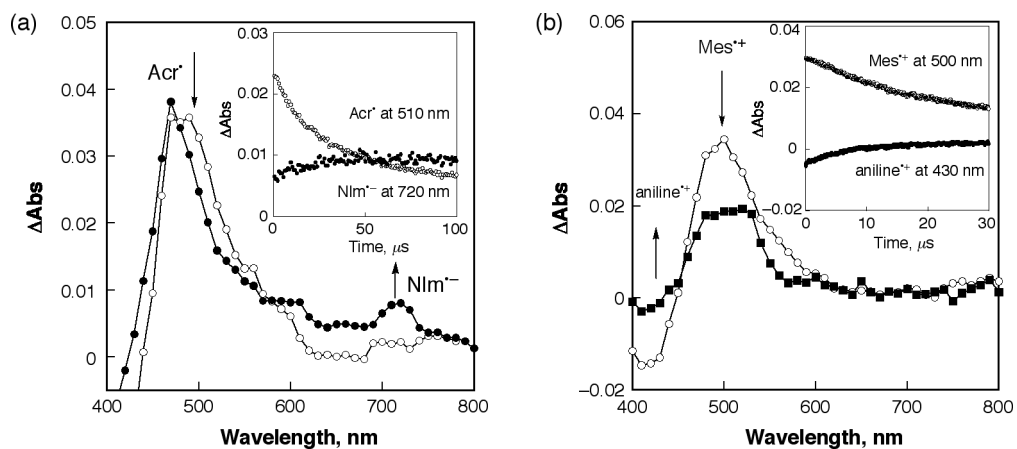


**Fig. 3** (a) X-ray crystal structure of 9-mesityl-10-methylacridinium ion (Acr<sup>+</sup>-Mes) [30]. (b) HOMO and, (c) LUMO orbitals calculated by a DFT method with Gaussian 98 (B3LYP/6-31G\* basis set) [30].

on mesitylene and acridinium moieties (Figs. 3b and 3c), respectively [30]. The energy of the ET state (Acr<sup>•</sup>-Mes<sup>•+</sup>) is determined by the redox potentials of each component of Acr<sup>+</sup>-Mes as 2.37 eV, which is significantly higher than the CS states of electron donor-acceptor dyads containing porphyrins and C<sub>60</sub> (vide supra) [30].

Photoexcitation of a deaerated PhCN solution of Acr<sup>+</sup>-Mes by a nanosecond laser light flash at 430 nm results in the formation of Acr<sup>•</sup>-Mes<sup>•+</sup> with a quantum yield close to unity (98 %) via photo-induced ET from the mesitylene moiety to the singlet excited state of the acridinium ion moiety (<sup>1</sup>Acr<sup>•+</sup>-Mes) [30]. The decay of Acr<sup>•</sup>-Mes<sup>•+</sup> obeyed second-order kinetics rather than first-order kinetics at ambient temperature, when the bimolecular BET predominates due to the slow intramolecular BET [30]. In contrast, the decay of Acr<sup>•</sup>-Mes<sup>•+</sup> obeys first-order kinetics in PhCN at high temperatures (e.g., 373 K) [30]. This indicates that the rate of the intramolecular BET of Acr<sup>•</sup>-Mes<sup>•+</sup> becomes much faster than the rate of the intermolecular BET at higher temperatures, because the activation energy of the former is higher than that of the latter. In such a case, the lifetime of the ET state becomes surprisingly longer with decreasing temperature, to approach a virtually infinite value at 77 K [31]. Such a simple molecular dyad capable of fast charge separation but extremely slow charge recombination has been recognized as clear advantages with regard to synthetic feasibility and the applications [32].

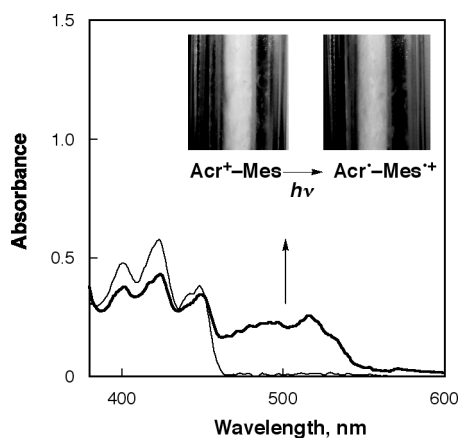
However, Benniston et al. claimed that the triplet excitation energy of Acr<sup>+</sup>-Mes was 1.96 eV based on the phosphorescence spectrum, which is lower than the energy of the ET state (2.37 eV) and that the triplet excited state of the acridinium ion moiety (<sup>3</sup>Acr<sup>•+</sup>-Mes) might be formed rather than the ET state (Acr<sup>•</sup>-Mes<sup>•+</sup>) [33]. If this value were correct, the one-electron oxidation potential ( $E_{\text{ox}}$ ) of <sup>3</sup>Acr<sup>•+</sup>-Mes would be -0.08 V vs. SCE, which is determined from the one-electron oxidation potential of the Mes moiety (1.88 V) and the triplet excitation energy (1.96 V). In such a case, ET from the triplet excited state of Acr<sup>+</sup>-Mes to *N,N*-dihexylnaphthalenediimide (NIm;  $E_{\text{red}} = -0.46$  V vs. SCE) would be energetically impossible judging from the positive free energy change of ET (0.38 eV). However, the addition of NIm ( $1.0 \times 10^{-3}$  M) to a PhCN solution of Acr<sup>+</sup>-Mes and the laser photoexcitation results in the formation of NIm<sup>•-</sup> as detected by the well-known absorption bands at 480 and 720 nm, accompanied by the decay of transient absorption at 510 nm due to the Acr<sup>•</sup> moiety of the ET state as shown in Fig. 4a [31]. Similarly, the addition of aniline ( $3.0 \times 10^{-5}$  M) to a PhCN solution of Acr<sup>+</sup>-Mes results in formation of aniline radical cation ( $\lambda_{\text{max}} = 430$  nm), accompanied by decay of the Mes<sup>•+</sup> moiety at 500 nm as shown in Fig. 4b [31]. The formation rate constant of aniline radical cation is determined as  $5.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , which is close to the diffusion rate constant in PhCN [31]. Thus, the photogenerated state of Acr<sup>+</sup>-Mes has both the reducing and the oxidizing ability: to reduce NIm and to oxidize aniline, respectively. Only the ET state (Acr<sup>•</sup>-Mes<sup>•+</sup>) has such a dual ability. However, this conclusion is contradictory to the triplet energy (1.96 eV), which was reported to be lower in energy than the ET state by Benniston et al. (vide supra) [33]. This contradiction comes from acridine contained as an impurity in the preparation of Acr<sup>+</sup>-Mes by Benniston et al., who synthesized the com-



**Fig. 4** Transient absorption spectra of  $\text{Acr}^+-\text{Mes}$  ( $5.0 \times 10^{-5}$  M) in deaerated acetonitrile (MeCN) at 298 K taken at 2 and 20  $\mu\text{s}$  after laser excitation at 430 nm in the presence of (a) *N,N*-dihexylnaphthalenediimide ( $1.0 \times 10^{-3}$  M) or (b) aniline ( $3.0 \times 10^{-5}$  M) [31]. 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 [31].

pound via methylation of the corresponding acridine [33]. It was confirmed that the phosphorescence maximum of 9-phenylacridine in glassy 2-MeTHF at 77 K afforded virtually the same spectrum as that reported by Benniston et al. [33]. In contrast to the synthetic method that Benniston et al. employed [33], we have prepared  $\text{Acr}^+-\text{Mes}$  by the Grignard reaction of 10-methyl-9(10*H*)-acridone with 2-mesitylmagnesium bromide without involving methylation [30,31]. In this case, there is no acridine impurity in  $\text{Acr}^+-\text{Mes}$ .

In contrast to the photoirradiation of a purified PhCN solution of  $\text{Acr}^+-\text{Mes}$  at 298 K, 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. 5 [31]. When a glassy 2-methyltetrahydrofuran (2-MeTHF) is employed for the photoirradiation of  $\text{Acr}^+-\text{Mes}$  at low temperature, the resulting glassy solution measured at 77 K affords

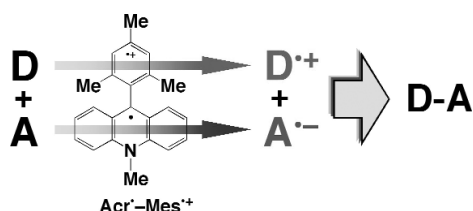


**Fig. 5** UV-vis absorption spectra obtained by photoirradiation with high-pressure mercury lamp of deaerated 2-MeTHF glasses of  $\text{Acr}^+-\text{Mes}$  at 77 K [31]. Inset: images of frozen PhCN solutions of  $\text{Acr}^+-\text{Mes}$  before and after photoirradiation at low temperatures and taken at 77 K [31].

the absorption spectrum due to the ET state, which consists of the absorption bands of the Acr<sup>•</sup> moiety (500 nm) and the Mes<sup>•+</sup> moiety (470 nm), as shown in Fig. 5 [31]. No decay of the absorption due to the ET state in Fig. 5 was observed at 77 K [31]. Any excited state, even triplet, would never have such a nearly infinite lifetime at 77 K.

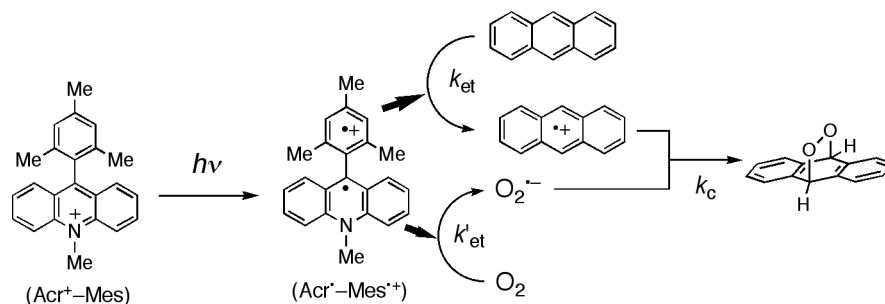
### PHOTOINDUCED ELECTRON-TRANSFER CATALYTIC REACTIONS OF A DONOR–ACCEPTOR DYAD

The long-lived ET state (Acr<sup>•</sup>–Mes<sup>•+</sup>), which has both the high oxidizing and reducing ability (Fig. 4), has been utilized as an efficient photocatalyst for radical coupling reactions between radical cations and radical anions, which can be produced by the ET oxidation and ET reduction of external electron donors and acceptors, respectively (Scheme 2).



**Scheme 2** Photocatalytic reaction of an electron donor (D) and an acceptor (A) with the ET state of Acr<sup>•</sup>–Mes to form D–A via radical coupling between D<sup>•+</sup> and A<sup>•-</sup>.

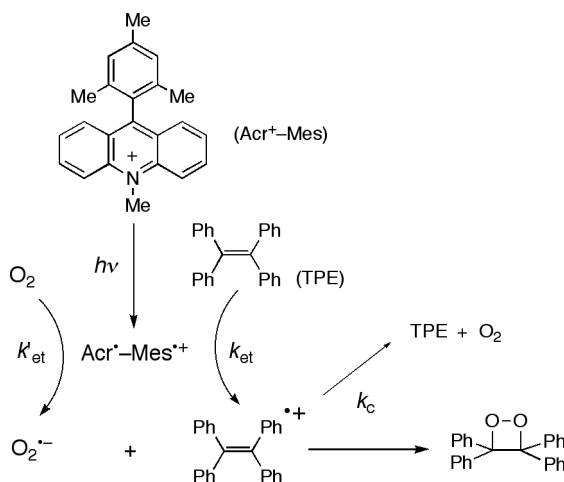
Visible light irradiation ( $\lambda > 430$  nm) of the absorption band of Acr<sup>•</sup>–Mes in an O<sub>2</sub>-saturated MeCN solution containing anthracene derivatives results in formation of the oxygenation products, i.e., epidioxanthracenes via the radical coupling between anthracene radical cations and O<sub>2</sub><sup>•-</sup>, produced by ET from anthracenes to the Mes<sup>•+</sup> moiety and ET from the Acr<sup>•</sup> moiety to O<sub>2</sub>, respectively (Scheme 3) [34]. It is important to note that An–O<sub>2</sub> is formed exclusively by the radical coupling between anthracene radical cation and O<sub>2</sub><sup>•-</sup> rather than the reaction of anthracene and <sup>1</sup>O<sub>2</sub> [34].



**Scheme 3** Photocatalytic oxygenation of anthracene with O<sub>2</sub> using Acr<sup>•</sup>–Mes [34].

The radical coupling reaction between anthracene radical cation and O<sub>2</sub><sup>•-</sup> to produce An–O<sub>2</sub> in Scheme 3 has been expanded to the dioxetane formation from olefins [34]. 1,2-Dioxetanes have been commonly prepared by the formal [2+2] cycloaddition of singlet oxygen (<sup>1</sup>O<sub>2</sub>) to electron-rich alkenes [35]. If alkenes are too electron-poor to react with <sup>1</sup>O<sub>2</sub>, however, no oxygenated products were obtained. For example, it was reported that no products were formed in an oxygen-saturated MeCN solution of

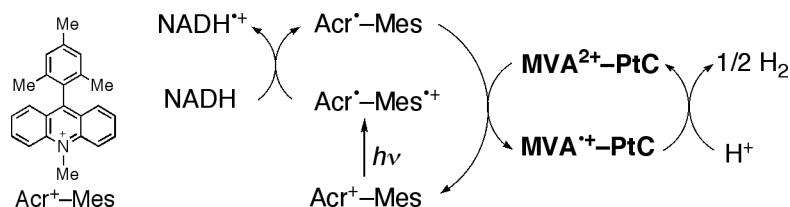
tetraphenylethylene (TPE) in the presence of  $^1\text{O}_2$  sensitizers under photoirradiation [36]. No oxygenation occurred in an  $\text{O}_2$ -saturated solution of TPE containing  $\text{C}_{60}$  or tetraphenylporphyrin as  $^1\text{O}_2$  sensitizers, since the reaction of TPE with  $^1\text{O}_2$  has been reported to be very slow [36,37]. In contrast, when  $\text{Acr}^+-\text{Mes}$  is used as a photocatalyst, oxygenation of TPE with  $\text{O}$  occurs efficiently via ET reactions of TPE and  $\text{O}$  with photogenerated ET state of  $\text{Acr}^+-\text{Mes}$ , followed by the radical coupling reaction between TPE radical cation and  $\text{O}_2^{\bullet-}$  to produce 1,2-dioxetane selectively (Scheme 4) [37].



**Scheme 4** Photocatalytic oxygenation of TPE with  $\text{O}_2$  using  $\text{Acr}^+-\text{Mes}$  [37].

The  $\text{Acr}^+-\text{Mes}$  also acts as an efficient photocatalyst for oxygenation of triphenylphosphine ( $\text{Ph}_3\text{P}$ ) to triphenylphosphine oxide ( $\text{Ph}_3\text{P}=\text{O}$ ) with molecular oxygen ( $\text{O}_2$ ) [38]. Photooxidation of benzylamine ( $\text{PhCH}_2\text{NH}_2$ ) with  $\text{O}_2$  also occurs efficiently under photoirradiation of  $\text{Acr}^+-\text{Mes}$  to yield  $\text{PhCH}_2\text{N}=\text{CHPh}$  and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) [38]. Each photocatalytic reaction is initiated by intramolecular photoinduced ET from the Mes moiety to the singlet excited state of the  $\text{Acr}^+$  moiety to produce the ET state ( $\text{Acr}^+-\text{Mes}^*$ ). Thus, the use of  $\text{Acr}^+-\text{Mes}$  as an ET photocatalyst in the presence of  $\text{O}_2$  provides a convenient methodology to produce radical cations of electron donors and  $\text{O}_2^{\bullet-}$ , which can combine together to yield the oxygenated products selectively in a preparative scale. The  $\text{Acr}^+-\text{Mes}$  can also be used as an effective photocatalyst for the ET oxidation of DNA as well as DNA bases to produce all types of DNA base radical cation, which leads to efficient DNA cleavage in the absence of  $\text{O}_2$  [39].

A highly efficient photocatalytic system for hydrogen evolution with NADH as a sacrificial agent in an aqueous solution has also been constructed by using  $\text{Acr}^+-\text{Mes}$  as a photocatalyst, water-soluble platinum clusters functionalized with methyl viologen-alkanethiol ( $\text{MVA}^{2+}$ ) as a catalyst for hydrogen evolution (Scheme 5) [40]. The hydrogen-evolution rate of the photocatalytic system with  $\text{MVA}^{2+}$ -modified platinum clusters ( $\text{MVA}^{2+}-\text{PtC}$ ) is 10 times faster than the photocatalytic system with the mixture of the same amount of  $\text{MVA}^{2+}$  and platinum clusters as that of  $\text{MVA}^{2+}-\text{PtC}$  under otherwise the same experimental conditions. First, the photoirradiation of  $\text{Acr}^+-\text{Mes}$  results in formation of the ET state ( $\text{Acr}^+-\text{Mes}^*$ ). This undergoes the ET oxidation of NADH and/or the ET reduction of  $\text{MVA}^{2+}$  in  $\text{MVA}^{2+}-\text{PtC}$ . Both processes are thermodynamically feasible, because the one-electron oxidation potential of NADH ( $E_{\text{ox}}^0 = 0.76$  V vs. SCE) [41,42] is less positive than the one-electron reduction potential of the Mes $^{\bullet+}$  moiety of  $\text{Acr}^+-\text{Mes}^*$ , and the one-electron oxidation potential of the  $\text{Acr}^+$  moiety ( $E_{\text{ox}}^0 = -0.57$  V vs. SCE) [30] is more negative than the one-electron reduction potential of the  $\text{MVA}^{2+}$  moiety in  $\text{MVA}^{2+}-\text{PtC}$  ( $E_{\text{red}}^0 = -0.50$  V) [40]. In contrast, however, ET from  $\text{Acr}^+-\text{Mes}^*$  ( $E_{\text{ox}}^0 =$

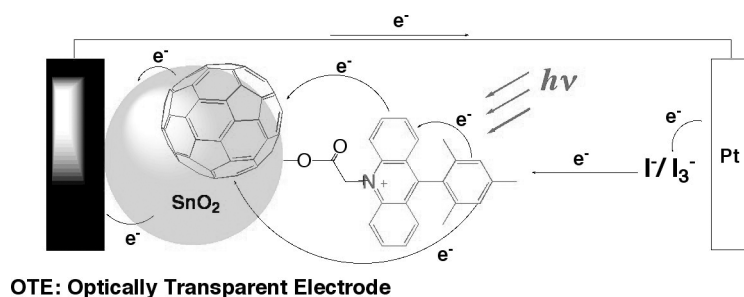


**Scheme 5** Photocatalytic hydrogen evolution with Acr<sup>+</sup>-Mes and NADH [40].

−0.57 V vs. SCE) to MV<sup>2+</sup> ( $E_{\text{red}}^0 = -0.67$  V) is energetically unfavorable, because the  $E_{\text{ox}}^0$  value of Acr<sup>+</sup>-Mes<sup>•+</sup> is more positive the  $E_{\text{red}}^0$  value of MV<sup>2+</sup>. In this case, MV<sup>2+</sup> may be reduced by NAD<sup>•</sup>, which is produced via deprotonation of NADH<sup>+</sup>, since the ET from NAD<sup>•</sup> ( $E_{\text{ox}}^0 = -1.1$  V vs. SCE) [41,42] to MV<sup>2+</sup> ( $E_{\text{red}}^0 = -0.67$  V) is highly exergonic. Thus, Acr<sup>+</sup>-Mes<sup>•+</sup> is more efficiently quenched in the NADH/MVA<sup>2+</sup>-PtC system as compared with the NADH/MV<sup>2+</sup>/Pt-PVP colloid system. In addition, the electron injection from MVA<sup>•+</sup> to Pt clusters is much more efficient in the MVA<sup>2+</sup>-bound Pt clusters as compared with intermolecular ET from MV<sup>•+</sup> to Pt-PVP colloid in solution, leading to the 10 times faster H<sub>2</sub> evolution.

## ORGANIC SOLAR CELLS WITH DONOR-ACCEPTOR DYADS

The requirement to develop inexpensive renewable energy sources has stimulated new approaches for production of efficient, low-cost organic photovoltaic devices [43,44]. A simple molecular dyad (Acr<sup>+</sup>-Mes) capable of fast charge separation but extremely slow charge recombination has allowed to develop a unique organic photovoltaic cell using the dyad. In order to assemble the dyad on an optically transparent electrode (OTE) of nanostructured SnO<sub>2</sub> (OTE/SnO<sub>2</sub>), a carboxyl group was introduced to the dyad to prepare 9-mesityl-10-carboxymethylacridinium ion (Mes-Acr<sup>+</sup>-COOH) [45]. An organic photovoltaic cell composed of Mes-Acr<sup>+</sup>-COOH and fullerene nanoclusters has been constructed as shown in Scheme 6 [45]. Fullerene (C<sub>60</sub>) clusters prepared from C<sub>60</sub> suspension in acetonitrile/toluene (3/1) have been deposited electrophoretically on the OTE/SnO<sub>2</sub>/Mes-Acr<sup>+</sup>-COOH electrode [denoted as OTE/SnO<sub>2</sub>/Mes-Acr<sup>+</sup>-COOH+(C<sub>60</sub>)<sub>n</sub>] in order to improve the light-harvesting and electron-transport efficiency [45].



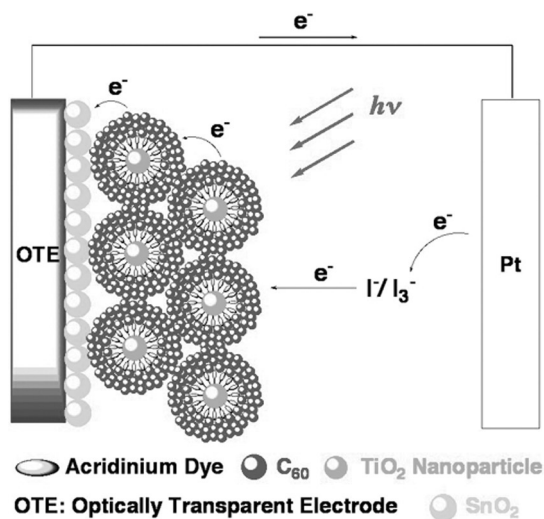
**Scheme 6** The photovoltaic cell composed of fullerene nanoclusters and 9-mesityl-10-carboxymethylacridinium ion [45].

Photoelectrochemical measurements were performed using a standard two-electrode system consisting of a working electrode and a Pt wire gauze electrode in air-saturated acetonitrile containing 0.5 M NaI and 0.01 M I<sub>2</sub> [45]. The maximum IPCE (incident photon-to-photocurrent efficiency) value of OTE/SnO<sub>2</sub>/Acr<sup>+</sup>-Mes-COOH was only 2 % (445 nm), whereas the IPCE value of



OTE/SnO<sub>2</sub>/Acr<sup>+</sup>-Mes-COOH+(C<sub>60</sub>)<sub>n</sub> reaches 15 % (480 nm) [45]. The IPCE value of OTE/SnO<sub>2</sub>/Acr<sup>+</sup>-Mes-COOH+(C<sub>60</sub>)<sub>n</sub> is much higher than the sum of the two individual IPCE values of the individual systems in the visible region [45]. The charge separation in the OTE/SnO<sub>2</sub>/Mes-Acr<sup>+</sup>-COOH+(C<sub>60</sub>)<sub>n</sub> electrode can be further modulated by controlling the applied potential in a standard three-compartment cell with a working electrode along with a Pt wire gauze counterelectrode and a saturated calomel reference electrode (SCE) [45]. The maximum IPCE value is obtained as 25 % at an applied potential of 0.2 V vs. SCE [45]. Such a high IPCE value indicates that photocurrent is initiated via ET between excited Mes-Acr<sup>+</sup>-COOH and C<sub>60</sub> clusters, followed by the charge transport to the collective surface of OTE/SnO<sub>2</sub> electrode. The charge transport is significantly improved under the influence of an applied bias.

In order to improve the photoelectrochemical properties further, TiO<sub>2</sub> nanoparticles have been utilized for three-dimensional control in organization of composite nanoclusters of Mes-Acr<sup>+</sup>-COOH and C<sub>60</sub> [46]. TiO<sub>2</sub> nanoparticles were modified with composite nanoclusters of Mes-Acr<sup>+</sup>-COOH and C<sub>60</sub> in acetonitrile/toluene (3:1, v/v) and then deposited as thin films on nanostructured SnO<sub>2</sub> electrode using an electrophoretic technique (Scheme 7) [46]. In the case of a monolayer system of TiO<sub>2</sub> nanocrystallites modified with Mes-Acr<sup>+</sup>-COOH, no net photocurrent is observed in the photocurrent action spectrum [46]. This indicates that TiO<sub>2</sub> nanoparticles act as materials to organize composite molecules rather than as those to accept electrons. The IPCE value of 37 % has been achieved at an applied bias potential of 0.2 V vs. SCE in the Mes-Acr<sup>+</sup>-COOH/C<sub>60</sub> composite system using TiO<sub>2</sub> nanoparticles [46].



**Scheme 7** Supramolecular photovoltaic cells based on composite molecular clusters of Mes-Acr<sup>+</sup>-COOH and C<sub>60</sub>, which are electrophoretically organized by TiO<sub>2</sub> nanoparticles [46].

## CONCLUSION AND OUTLOOK

As demonstrated in this article, simple molecular dyads, capable of fast charge separation but extremely slow charge recombination of high-energy CS states, provide a variety of applications for photoinduced ET catalytic systems. The scope of the use of simple molecular dyads may be expanded further to develop more efficient ET catalytic systems aiming at solving global energy and environmental problems. There still remains a wealth of important fundamental questions with regard to the design and control of ET processes of donor-acceptor dyads, which have been only partially explored so far, and which certainly deserve a much more attention.

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