

Selective photocatalytic reactions with organic photocatalysts

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Selective photocatalytic oxygenation of various substrates has been achieved using organic photocatalysts via photoinduced electron-transfer reactions of photocatalysts with substrates and dioxygen under visible light irradiation. Photoinduced electron transfer from benzene to the singlet-excited state of the 3-cyano-1-methylquinolinium ion has enabled the oxidation of benzene by dioxygen with water to yield phenol selectively. Alkoxybenzenes were obtained when water was replaced by alcohols under otherwise the same experimental conditions. Photocatalytic selective oxygenation reactions of aromatic compounds have also been achieved using an electron donor–acceptor linked dyad, 9-mesityl-10-methylacridinium ion (Acr⁺–Mes) acting as a photocatalyst and dioxygen as an oxidant under visible light irradiation. The oxygenation reaction is initiated by intramolecular photoinduced electron transfer from the mesitylene moiety to the singlet-excited state of the acridinium moiety of Acr⁺–Mes to afford an extremely long-lived electron-transfer state. The electron-transfer state can oxidize and reduce substrates and dioxygen, respectively, leading to selective oxygenation and halogenation of substrates. C–C bond formation of substrates has also been made possible by using Acr⁺–Mes as a photocatalyst.

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1 Introduction

The depletion of fossil fuels and the impact of global warming has led to the utilization of solar energy as an abundant and renewable energy resource.^{1–3} The sun has been providing an enormous amount of energy on Earth and life is dependent upon the solar energy, which is converted to chemical energy

by photosynthesis, for its existence. Thus, extensive efforts have been devoted to developing artificial photosynthetic systems including photovoltaics.^{4–14} One area that has yet to be fully developed is chemical reactions using solar energy. In the past, inorganic materials, such as TiO₂^{15–18} and ZnO,^{19,20} have been utilized mainly as photocatalysts. However, poor absorption of visible light by such inorganic photocatalysts has limited their utilization for chemical reactions using solar energy although some modified inorganic photocatalysts can absorb visible light.^{21,22} In particular, no selective photocatalytic oxygenation reactions with dioxygen have been achieved using inorganic materials, because substances were over-oxidized to CO₂ due to the high oxidizing ability of the

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photoexcited state. Unlike inorganic photocatalysts without modification, organic photocatalysts can absorb visible light and the photoredox properties can be finely modified by rational design and synthesis.^{23–25}

In this perspective, we focus first on our recent advancements in the selective oxygenation reactions of substrates with dioxygen and water using organic photocatalysts under visible light irradiation. Photoinduced electron transfer from substrates to the singlet-excited states of organic dyes results in formation of substrate radical cations and one-electron reduced species of organic dyes. The produced radical cations of substrates react with nucleophiles such as water, alcohols and halide anions to yield radical adducts, whereas the one-electron reduced species of organic dyes reduce oxygen to yield hydroperoxyl radicals, which react with the radical adducts to yield the oxidized products and hydrogen peroxide. Besides organic dyes, we describe how organic electron donor–acceptor dyads, which afford long-lived electron-transfer states upon photoexcitation, can also be used as organic photocatalysts for selective oxygenation and bromination of substrates with dioxygen as well as C–C bond formation reactions.

2 Photocatalytic oxygenation reactions

Photoinduced electron transfer from substrates to organic photosensitisers produces substrate radical cations and the sensitizer radical anions, leading to photocatalytic oxygenation of substrates in the presence of dioxygen and water as described below.

2.1 Oxygenation of benzene

Phenol is one of the most important chemicals in industry, being currently produced from benzene by a three-step cumene process.^{26–30} However, the cumene process affords very low yields (~5%), with by-products such as acetone and α -methylstyrene under severe conditions.^{26–30} Thus, extensive efforts have so far been made to develop a one-step oxygenation process of benzene to phenol using heterogeneous inorganic catalysts.^{31–40} In contrast to inorganic catalysts, which afford only low yields of phenol, an organic dye, 3-cyano-1-methylquinolinium ion (QuCN⁺) acts as an efficient photocatalyst for the selective oxygenation of benzene to phenol with dioxygen (O₂) and water (H₂O) under homogeneous and ambient conditions (*vide infra*).⁴¹

Photocatalytic oxygenation of benzene with O₂ and H₂O occurs under photoirradiation of QuCN⁺ClO₄[−] ($\lambda_{\text{max}} = 330 \text{ nm}$), in oxygen-saturated acetonitrile (MeCN) containing benzene and H₂O, with a xenon lamp (500 W) attached with a color-cut glass filter ($\lambda = 290\text{--}600 \text{ nm}$) to yield phenol and hydrogen peroxide [eqn (1)].⁴¹ The time course of the reaction is shown in Fig. 1.⁴¹ The selectivity of formation of phenol was 98% with 16% quantum yield after 1 h irradiation, and then 51% of phenol yield after 5 h irradiation.⁴¹ When H₂¹⁸O was replaced by H₂¹⁶O, the mass number of phenol was increased from $m/z = 94$ to 96.⁴¹ Thus, the origin of phenol oxygen has been confirmed to be H₂O.

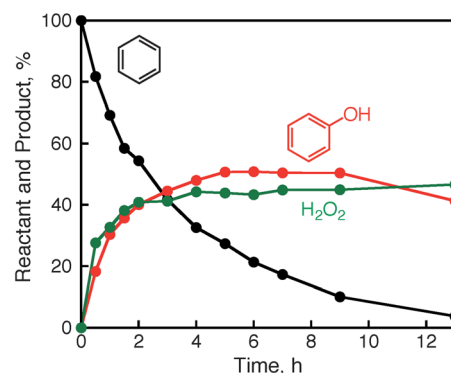
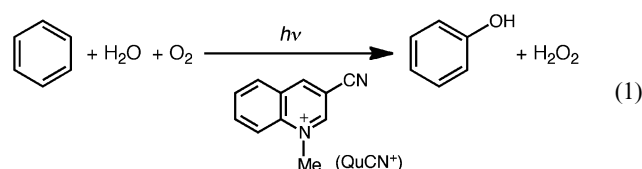
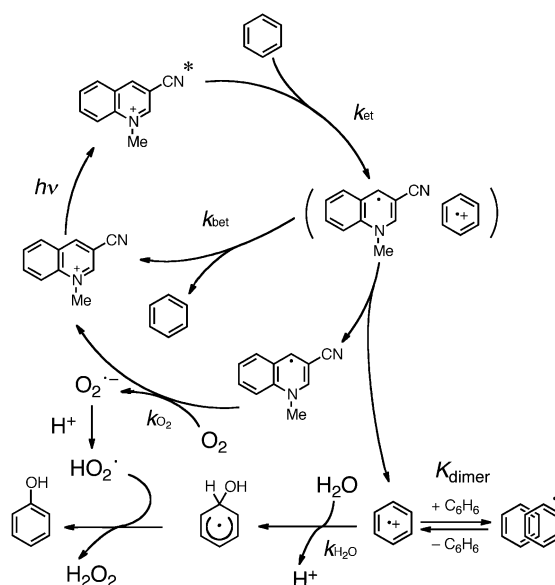


Fig. 1 Irradiation time profile of benzene (black), phenol (red) and H₂O₂ (green) in the photocatalytic oxygenation of benzene by oxygen and water with QuCN⁺ in oxygen-saturated MeCN (1.0 mL) at 298 K: [benzene] = 30 mM; [QuCN⁺] = 2.0 mM; [H₂O] = 2.0 M.⁴¹



The mechanism of the photocatalytic oxygenation of benzene to phenol is shown in Scheme 1.⁴¹ Upon photoexcitation of QuCN⁺, electron transfer from benzene to the singlet excited state of QuCN⁺ (¹QuCN⁺*) occurs to produce 3-cyano-1-methylquinolinyl radical (QuCN) and benzene radical cation, which is in equilibrium with benzene π -dimer radical cation. Both QuCN and benzene π -dimer radical cation were detected from transient absorption spectra as shown in Fig. 2, where the absorption band at 500 nm and near-IR band at 780 nm are assigned to QuCN and benzene π -dimer radical cation,



Scheme 1 Photocatalytic mechanism of oxygenation of benzene with O₂ and H₂O to phenol using QuCN⁺ as an organic photocatalyst.⁴¹

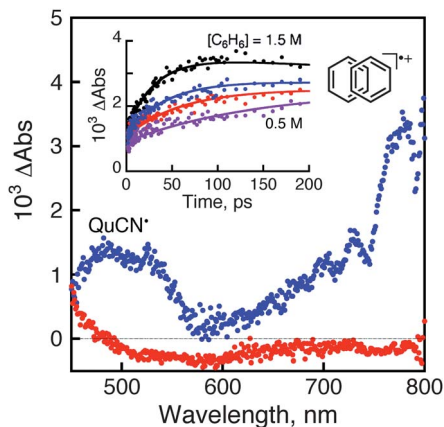


Fig. 2 Transient absorption spectra of QuCN⁺ with benzene (1.5 M, blue) and without benzene (0 M, red) in deaerated MeCN taken at 200 ps after femto-second laser excitation ($\lambda_{\text{ex}} = 355 \text{ nm}$).⁴¹ Inset: the rise time profiles at 760 nm with various concentrations of benzene (0–1.5 M).

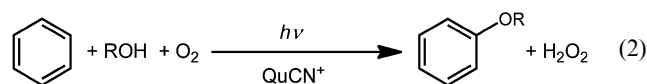
respectively.⁴¹ The formation rate of benzene π -dimer radical cation increased with increasing concentration of benzene (inset of Fig. 2).⁴¹ The second-order rate constant of formation of benzene dimer radical cation was determined to be $2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is close to be the diffusion limited value in MeCN, as expected from the exergonic electron transfer from benzene (E_{ox} vs. SCE = 2.32 V)^{42,43} to $^1\text{QuCN}^{+\ast}$ (E_{red} vs. SCE = 2.72 V).^{44–46} The association constant (K_{dimer}) between benzene and benzene dimer radical cation was determined to be 11 M^{-1} , obtained from the transient absorption intensities at 800 nm with various concentrations of benzene.^{40,41} It is well established that radical cations of aromatic compounds form π -dimer radical cations with neutral aromatic compounds.^{47–50}

The decay rate of QuCN and benzene π -dimer radical cation followed by nanosecond laser flash photolysis measurements without H₂O obeyed second-order kinetics due to the bimolecular back electron transfer.⁴¹ The decay rate constant (k_{bet}) was determined using the molar absorption coefficient of QuCN ($\epsilon_{520} = 2000 \text{ M}^{-1} \text{ cm}^{-1}$)⁵¹ to be $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is also close to the diffusion limited rate constant in MeCN ($2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).⁴¹ Benzene radical cation reacts with H₂O to yield the OH-adduct radical (Scheme 1), as indicated by the acceleration of the decay rate of the benzene π -dimer radical cation with increasing concentration of H₂O.⁴¹ The rate constant for the reaction of benzene radical cation and benzene π -dimer radical cation with H₂O was determined to be $k_{\text{H}_2\text{O}} = 1.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.⁴¹ On the other hand, QuCN reduces O₂ to O₂^{•-} to regenerate QuCN⁺ and this is followed by protonation of O₂^{•-} to afford HO₂[•].⁴¹ The hydrogen abstraction of HO₂[•] from OH-adduct radical affords phenol and H₂O₂ (Scheme 1).⁴¹ The rate constant for electron transfer from QuCN to O₂ was determined to be $k_{\text{O}_2} = 5.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.⁴¹

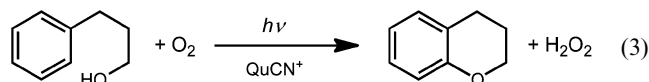
Although the fluorescence of $^1\text{QuCN}^{+\ast}$ was efficiently quenched by electron transfer from phenol to $^1\text{QuCN}^{+\ast}$, back electron transfer from QuCN to phenol radical cation is much faster than that to benzene radical cation, as indicated by no detection of QuCN probably because of the much smaller

driving force of the back electron transfer as compared with the case of benzene radical cation. The large driving force of the back electron transfer from QuCN to benzene radical cation (3.29 eV), which is deeply in the Marcus inverted region, makes it possible to produce free benzene radical cation and QuCN in competition with the back electron transfer within the solvent cage.⁴¹ This may be the reason why benzene was oxidized but phenol was not oxidized in the photocatalytic oxygenation with QuCN⁺, leading to the selective photocatalytic oxygenation of benzene to phenol with O₂ and H₂O. Prolonged photoirradiation of phenol with QuCN⁺ afforded only small amounts of further oxygenated products such as quinones and diphenol derivatives.⁴¹

When H₂O was replaced by alcohols (ROH), photocatalytic alkoxylation of benzene with O₂ and ROH occurred using QuCN⁺ to yield the corresponding alkoxybenzenes [eqn (2)].⁵² When methanol was employed, the yield of methoxybenzene after 4 h photoirradiation of an MeCN solution of benzene (30 mM) with MeOH (30 mM) and QuCN⁺ (5 mM) was 26%.⁵² When methanol was replaced by ethanol, isopropanol or *tert*-butanol, the photocatalytic alkoxylation of benzene also occurred to yield the corresponding alkoxybenzenes (ethoxybenzene, isopropoxybenzene, *tert*-butoxybenzene with 21, 12 and 12% yield, respectively).⁵² Because the conventional synthesis of alkoxybenzenes from benzene requires a 4-step reaction sequence,^{53,54} the one-pot synthesis of alkoxybenzenes from benzene in eqn (2) provides a convenient way to synthesize alkoxybenzenes. The photocatalytic mechanism is virtually the same as for the case of the photocatalytic oxygenation of benzene to phenol in Scheme 1 except for the reaction of benzene radical cation with ROH instead of H₂O.⁵² The rate constants of benzene radical cation with MeOH, EtOH, *i*-PrOH, and *t*-BuOH were determined to be 4.3×10^6 , 4.4×10^6 , 1.5×10^7 , and $1.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively.⁵²



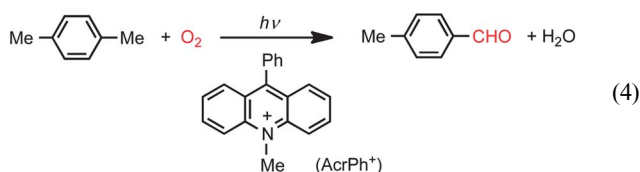
Cyclization of 3-phenyl-1-propanol is known to occur *via* the nucleophilic capture of organic radical cations by tethered OH functions.^{43,44} Interestingly, photocatalytic cyclization occurred under photoirradiation of QuCN⁺ClO₄⁻ (5.0 mM) in oxygen-saturated MeCN containing 3-phenyl-1-propanol to give a cyclization product, chroman [eqn (3)].⁵² The Φ value of formation of chroman was 3% and the yield of chroman after 15 min photoirradiation was 30%.⁵² The photocyclization is initiated by photoinduced electron transfer from 3-phenyl-1-propanol to $^1\text{QuCN}^{+\ast}$ to produce the radical cation in which the cationic charge is localized on the phenyl group and intramolecular attack of the OH group leads to formation of chroman.⁵²



2.2 Oxygenation of ring-substituted toluenes

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 intermolecular photoinduced electron transfer and slow charge recombination.⁵⁵ 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*).⁵⁶

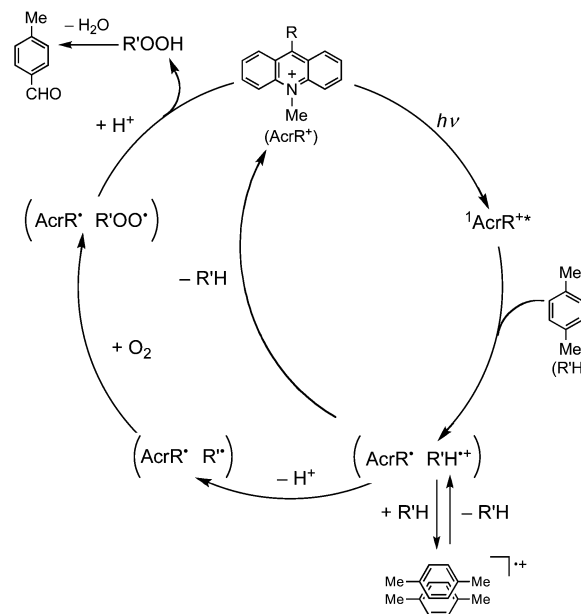
Visible light irradiation of the absorption band of AcrH^+ in oxygen-saturated MeCN containing *p*-xylene with a xenon lamp results in the formation of *p*-tolualdehyde accompanied by disappearance of *p*-xylene.⁵⁶ After 24 h irradiation, the yield of *p*-tolualdehyde is 37%. The product yield is improved to 66%, when MeCN is replaced by a less polar solvent, chloroform, under otherwise the same experimental conditions.⁵⁶ The photooxygenated product yield is further improved to 100% when AcrH^+ is replaced by 9-phenyl-10-methylacridinium ion (AcrPh^+) in chloroform [eqn (4)].^{43,56}



It was confirmed that there was no adduct formation between the photocatalyst, AcrPh^+ and *p*-xylene because of the steric effect of the phenyl group.⁵⁶ 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 h to 10 h when a xenon lamp was replaced by a high-pressure mercury lamp (1000 W).^{43,56}

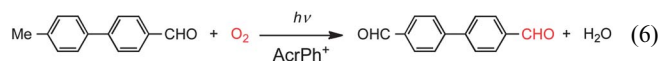
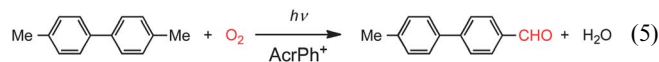
The reaction mechanism for the AcrR^+ -photosensitized oxygenation ($\text{R} = \text{H}$ and Ph) of *p*-xylene is shown in Scheme 2.^{43,56} Photoinduced electron transfer from *p*-xylene to $^1\text{AcrR}^{*+}$ occurs to produce AcrR^+ and *p*-xylene radical cation which is in equilibrium with the dimer radical cation.⁵⁶ 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 absence of O_2 , AcrH^+ is coupled with *p*-methylbenzyl radical to yield the radical coupling product.^{57,58} In the presence of O_2 , however, *p*-methylbenzyl radical is readily trapped by oxygen to give *p*-xylenylperoxyl radical.^{43,56} In the case of AcrPh , the steric effect of the phenyl group prohibits the radical coupling with *p*-methylbenzyl radical.⁵⁷ The *p*-methylbenzyl peroxyl radical is reduced by back electron transfer from AcrR^+ to yield *p*-methylbenzyl hydroperoxide, accompanied by regeneration of AcrR^+ (Scheme 2).^{43,56} The hydroperoxide decomposes to yield *p*-tolualdehyde selectively.^{43,56}

When *p*-xylene is replaced by 4,4'-dimethylbiphenyl, efficient photooxygenation is also achieved in the presence of $\text{AcrPh}^+\text{ClO}_4^-$ under visible light irradiation in O_2 -saturated chloroform (CHCl_3) to yield 4-(4-methylphenyl)benzaldehyde as a main oxygenated product [eqn (5)].⁵⁹ Prolonged



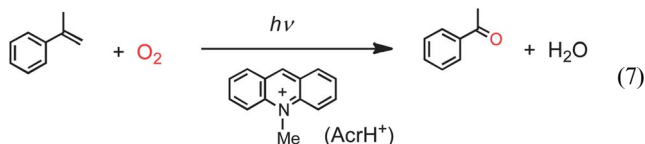
Scheme 2 Reaction mechanism of photocatalytic oxygenation of toluenes ($\text{R}'\text{H}$) with AcrR^+ .⁵⁶

photoirradiation afforded the further oxygenated product, 4,4'-biphenyldicarbaldehyde [eqn (6)].⁵⁹ The photocatalytic mechanism for the oxygenation of 4,4'-dimethylbiphenyl is virtually the same as in Scheme 2. Nanosecond laser flash photolysis measurements have provided evidence of the occurrence of photoinduced electron transfer from 4,4'-dimethylbiphenyl to $^1\text{AcrPh}^{*+}$ and the formation of the peroxyl radical was detected by EPR measurements.⁵⁹

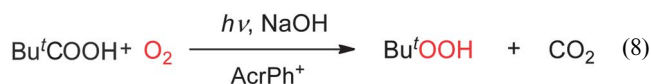


2.3 Oxygenation of other substrates

α -Methylstyrene can also be oxygenated with molecular oxygen in the presence of $\text{AcrH}^+\text{ClO}_4^-$ under visible light irradiation in oxygen-saturated MeCN to yield acetophenone [eqn (7)].⁶⁰ As in the case of the photochemical reaction of AcrH^+ with toluene derivatives, the photochemical reaction of AcrH^+ with alkenes in the absence of O_2 yielded the radical coupling products of AcrH^+ and deprotonated radical cations of alkenes.⁶¹ The photocatalytic oxygenation of α -methylstyrene with O_2 also proceeds *via* photoinduced electron transfer from α -methylstyrene to $^1\text{AcrH}^{*+}$.⁶⁰ The occurrence of the electron transfer has been confirmed by nanosecond laser flash photolysis and EPR measurements.⁶⁰ The quantum yield increased with an increase in concentration of α -methylstyrene to reach the limiting value $\Phi = 0.62$.⁶⁰

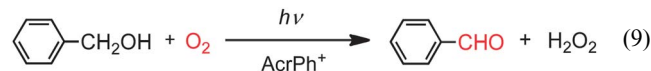


Pivalic acid (Bu^tCOOH) is also oxygenated with O_2 to produce Bu^tOOH by repeated cycles of the photoreduction of 10-methylacridinium ion (AcrH^+) by Bu^tCOO^- to produce the Bu^t adduct, 9-*tert*-butyl-9,10-dihydro-10-methylacridine (AcrHBU^t) and the photooxidation of AcrHBU^t with O_2 in the presence of perchloric acid (HClO_4) to yield *tert*-butyl hydroperoxide (Bu^tOOH), accompanied by regeneration of AcrH^+ .⁶² When AcrH^+ is replaced by the 9-phenyl derivative (AcrPh^+), AcrPh^+ acts as an effective photocatalyst for the photooxygenation of Bu^tCOOH in the presence of less than one equivalent of NaOH relative to Bu^tCOOH with O_2 to yield Bu^tOOH and Bu^tOH [eqn (8)].⁶²



The mechanism of photocatalytic oxygenation of Bu^tCOOH with AcrPh^+ is shown in Scheme 3.⁶² Photoinduced electron transfer from Bu^tCOO^- to $^1\text{AcrPh}^{+\bullet}$ produces the geminate radical pair ($\text{Bu}^t\text{COO}^\bullet \text{AcrPh}$). $\text{Bu}^t\text{COO}^\bullet$ undergoes facile decarboxylation to produce $\text{Bu}^t\cdot$,^{62–64} which is trapped by O_2 to yield $\text{Bu}^t\text{OO}^\bullet$. The radical coupling between $\text{Bu}^t\cdot$ and AcrPh observed in the case of AcrH is prohibited by the steric effect of the phenyl group. Proton-coupled electron transfer from AcrPh to $\text{Bu}^t\text{COO}^\bullet$ yields Bu^tOOH , accompanied by regeneration of AcrPh^+ .

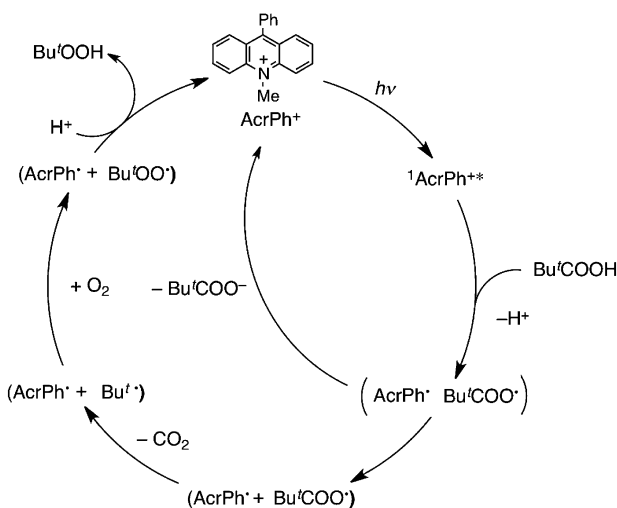
$\text{AcrPh}^+\text{ClO}_4^-$ is soluble in benzyl alcohol, acting as an effective photocatalyst for the selective photocatalytic oxidation of benzyl alcohol to benzaldehyde under visible light irradiation *via* efficient photoinduced electron transfer from benzyl alcohol to the singlet excited state of AcrPh^+ in neat benzyl alcohol [eqn (9)].⁶⁵



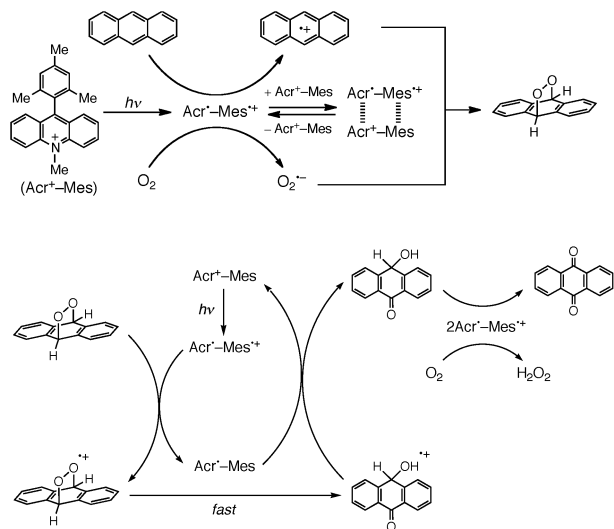
2.4 Photocatalytic oxygenation using 9-mesityl-10-methylacridinium ions

Donor-acceptor linked dyads have been extensively investigated for the formation of long-lived photoinduced charge separation, mimicking the photosynthetic reaction centre.^{4–14} The acridinium ion is the best candidate for the electron acceptors because the reorganization energy of electron transfer between an acridinium ion and its corresponding reduced radical is the smallest (0.3 eV) among the redox active organic compounds.⁵⁵ 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 electron transfer is minimized because the overall charge remains the same in the charge-shift electron transfer with the short linkage between the donor and acceptor moieties.⁶⁶ Photoexcitation of Acr^+-Mes results in formation of the electron-transfer state ($\text{Acr}^+-\text{Mes}^{\bullet+}$), which has an extremely long lifetime (*e.g.*, $\tau = 2$ h at 203 K, $\tau = \infty$ at 77 K) as well as both high oxidizing and reducing ability.^{66,67} Such a simple molecular dyad capable of fast charge separation, but extremely slow charge recombination, has obvious advantages with regard to synthetic feasibility.⁶⁸ It was suggested that the triplet excited state of the AcrH^+ moiety was formed rather than the electron-transfer state.⁶⁹ However, the formation of the electron-transfer state ($\text{Acr}^+-\text{Mes}^{\bullet+}$) has been clearly demonstrated by observation of the near-IR absorption band due to the π -dimer radical cation formed between $\text{Acr}^+-\text{Mes}^{\bullet+}$ and Acr^+-Mes .^{70–72} The long lifetime of the electron transfer state ($\text{Acr}^+-\text{Mes}^{\bullet+}$) has enabled the clarification of the structural changes in which the *N*-methyl group in Acr^+ was bent, and a weak electrostatic interaction between $\text{Mes}^{\bullet+}$ and a counteranion in the crystal (ClO_4^-) was observed upon photoinduced electron transfer by laser pump and X-ray probe crystallographic analysis.⁷³ The high energy and long lifetime of $\text{Acr}^+-\text{Mes}^{\bullet+}$ has also enabled the use of Acr^+-Mes as an efficient electron-transfer photocatalyst for the highly selective oxygenation of various substrates with O_2 *via* selective radical coupling of the donor radical cation and $\text{O}_2^{\bullet-}$ under visible light irradiation (*vide infra*).⁷⁴

Visible light irradiation of the absorption band of Acr^+-Mes ($\lambda_{\text{max}} = 430$ nm) in an O_2 -saturated MeCN solution containing 9,10-dimethylantracene results in formation of oxygenation product, *i.e.*, dimethylepidioxyanthracene ($\text{Me}_2\text{An-O}_2$).⁷⁴ Anthracene and 9-methylantracene also undergo photocatalytic oxygenation with Acr^+-Mes to afford the corresponding epidioxyanthracenes under photoirradiation.⁷⁴ In the case of anthracene, further photoirradiation results in the formation of anthraquinone as the final six-electron oxidation product, *via* 10-hydroxyanthrone, accompanied by generation of H_2O_2 (Scheme 4).⁷⁴ The photocatalytic oxygenation of anthracenes is initiated by photoexcitation of Acr^+-Mes , which results in formation of the electron-transfer state ($\text{Acr}^+-\text{Mes}^{\bullet+}$) and the π -dimer radical cation [$(\text{Acr}^+-\text{Mes}^{\bullet+})(\text{Acr}^+-\text{Mes})$], followed by



Scheme 3 Reaction mechanism of photocatalytic oxygenation of Bu^tCOOH with AcrPh^+ .⁶²



Scheme 4 Photocatalytic oxygenation of anthracene with Acr⁺-Mes.⁷⁴

electron transfer from anthracenes and olefins to the Mes⁺ moiety together with electron transfer from the Acr moiety to O₂.⁷⁴ The resulting anthracene radical cation undergoes radical coupling reactions with O₂^{•-} to produce the epidioxyanthracene (An-O₂).⁷⁴ An-O₂ is known to be formed by the reaction of anthracene with singlet oxygen as well (¹O₂).⁷⁵ However, it was confirmed that no singlet oxygen emission was observed during the photocatalytic oxygenation of anthracenes.⁷⁴ An-O₂ is photoisomerized *via* electron transfer from An-O₂ to the Mes⁺ moiety of Acr⁺-Mes⁺, which results in the O-O bond cleavage of An-O₂, followed by facile intramolecular hydrogen transfer to produce 10-hydroxyanthrone radical cation.⁷⁴ The back electron transfer from the Acr moiety to 10-hydroxyanthrone radical cation affords 10-hydroxyanthrone, accompanied by regeneration of Acr⁺-Mes (Scheme 4).⁷⁴ The electron-transfer oxidation of 10-hydroxyanthrone by the Mes⁺ moiety of Acr⁺-Mes⁺ results in the further two-electron oxidation to yield anthraquinone by releasing two protons, whereas the two-electron reduction of O₂ by the acridinyl radical moiety of Acr⁺-Mes⁺ with two protons yields H₂O₂ (Scheme 4).⁷⁴

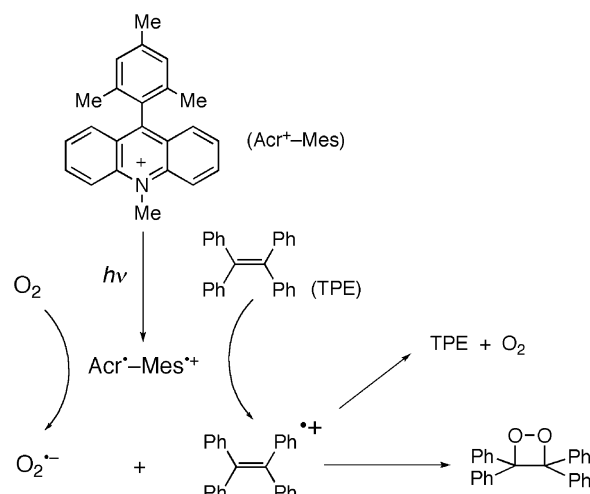
The radical coupling reaction between anthracene radical cation and O₂^{•-} to produce An-O₂ in Scheme 4 has been expanded to dioxetane formation from olefins. 1,2-Dioxetanes have attracted considerable interest because of their broad range of biological, chemical, and medical applications through chemiluminescence and bioluminescence.^{76,77} The most common preparation of 1,2-dioxetanes is through the formal [2 + 2] cycloaddition of singlet oxygen (¹O₂) to electron-rich alkenes.⁷⁵

Diastereoselective formation of dioxetanes has also been achieved by a chiral-axially-induced [2 + 2] cycloaddition of ¹O₂ with a chiral allylic alcohol and enecarbamates.^{78,79} Nelsen and co-workers have reported the isolation and electron-transfer oxidation properties of 1,2-dioxetane of adamantylidene adamantane.⁸⁰ However, 1,2-dioxetane cannot be obtained by the reaction of electron-poor alkenes such as tetraphenylethylene (TPE) with ¹O₂, because of the low nucleophilicity of TPE.^{81,82}

In contrast to the absence of reactivity of TPE toward ¹O₂, the 1,2-dioxetane of TPE is obtained using Acr⁺-Mes as a photocatalyst *via* electron transfer from TPE to the Mes⁺ moiety together with electron transfer from the Acr moiety to O₂, and the subsequent radical coupling between TPE^{•+} and O₂^{•-} as shown in Scheme 5. The dioxetane thus formed was isolated using column chromatography.⁸¹ 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 Acr⁺-Mes⁺ to stilbene derivatives and oxygen.⁸²

Oxygenations of aromatic compounds to produce aromatic aldehydes are key chemical reactions for the production of precursors of a variety of fine or speciality chemicals such as pharmaceutical drugs, dyestuffs, pesticides, and perfume compositions.⁸³⁻⁸⁸ However, their synthetic utility has been limited because of low yields and poor selectivities. Moreover, the use of stoichiometric amounts of inorganic oxidants should be avoided because of environmental problems.⁸⁸ For this reason, catalytic oxygenation processes with molecular oxygen or hydrogen peroxide (H₂O₂), have merited increasing attention.⁸⁹ H₂O₂ is in high demand as a clean and mild oxidant because the by-product in the oxygenation of substrates is only H₂O.^{90,91} There have been extensive studies on the photocatalytic formation of H₂O₂,⁹² or photocatalytic oxygenation of aromatic substrates.⁹³⁻⁹⁷ If valuable aromatic aldehydes are produced together with H₂O₂ in the photocatalytic oxygenation of alkylaromatic compounds by O₂, such a process would be superior as compared to the conventional methods to produce either or both H₂O₂ and aromatic aldehydes.

Such selective photocatalytic oxygenation has been made possible by using Acr⁺-Mes and its derivatives, which act as efficient photocatalysts for the simultaneous production of aromatic aldehydes and H₂O₂ in the photocatalytic oxygenation of alkylaromatic compounds by O₂ under visible light irradiation.⁹⁸ Visible light irradiation of [Acr⁺-Mes]ClO₄⁻ (λ_{max} = 430 nm, 0.20 mM) in oxygen-saturated MeCN containing *p*-xylene



Scheme 5 Photocatalytic oxygenation of tetraphenylethylene with Acr⁺-Mes.⁸¹

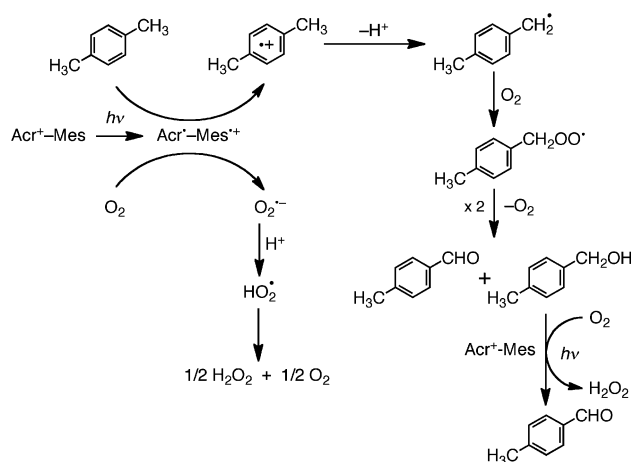
(4.0 mM) with a xenon lamp attached with a colour glass filter ($\lambda = 380\text{--}500\text{ nm}$) for 80 min resulted in formation of an oxygenated product, *p*-tolualdehyde (34%), *p*-methylbenzyl alcohol (10%) and H_2O_2 (30%).⁹⁸

The photocatalytic reactivity was enhanced by the presence of H_2O (0.9 M) and sulfuric acid (1.0 mM) to yield *p*-tolualdehyde (75%), *p*-methylbenzyl alcohol (15%) and H_2O_2 (74%) with a high quantum yield (0.25).⁹⁸ 100% yields of *p*-tolualdehyde and H_2O_2 with a higher quantum yield (0.37) were achieved by using 9-mesityl-2,7,10-trimethylacridinium ion ($\text{Me}_2\text{Acr}^+\text{-Mes}$), where the hydrogens at the 2 and 7 positions of the acridinium ring are replaced by methyl groups.⁹⁸ The reducing ability of the electron-transfer state of $\text{Acr}^+\text{-Mes}$ is improved by the electron-donating methyl substitution of the acridinium ring of $\text{Acr}^+\text{-Mes}$.⁹⁸ The E_{red} value of $\text{Me}_2\text{Acr}^+\text{-Mes}$ (-0.67 V vs. SCE) is 0.1 eV more negative than that of $\text{Acr}^+\text{-Mes}$ (-0.57 V).⁹⁸ The difference in dynamics of the electron-transfer reduction of O_2 by the electron-transfer states of $\text{Acr}^+\text{-Mes}$ and $\text{Me}_2\text{Acr}^+\text{-Mes}$ was determined by nanosecond laser flash photolysis.⁹⁸ The rates of the electron-transfer reduction were determined from the quenching of the transient absorption due to the electron-transfer state by O_2 to be $6.8 \times 10^8\text{ M}^{-1}\text{ s}^{-1}$ for $\text{Acr}^+\text{-Mes}^+$ and $2.0 \times 10^{10}\text{ M}^{-1}\text{ s}^{-1}$ for $\text{Me}_2\text{Acr}^+\text{-Mes}^+$.^{74,98} Thus, the reducing ability of $\text{Me}_2\text{Acr}^+\text{-Mes}^+$ was indeed significantly enhanced by the methyl substitution. This may be the reason why the 100% yield of tolualdehyde and H_2O_2 with a higher quantum yield (0.37) was achieved by using $\text{Me}_2\text{Acr}^+\text{-Mes}$ (*vide infra*).⁹⁸

No further oxygenated product, *p*-toluic acid or *p*-phthalaldehyde, was produced during the photocatalytic reaction. When the concentration of $\text{Me}_2\text{Acr}^+\text{-Mes}$ ($1.0 \times 10^{-4}\text{ M}$) was decreased, the TON increased to 200. A preparative scale photocatalytic reaction with *p*-xylene (0.5 g, 4.7 mmol) and $\text{Me}_2\text{Acr}^+\text{-Mes}$ (60 mg, 0.14 mmol) in MeCN (150 mL) under irradiation with a xenon lamp for 48 h afforded *p*-tolualdehyde (59%), *p*-methylbenzyl alcohol (28%) and H_2O_2 (51%) with 87% conversion of substrate.⁹⁸ The catalyst can be recycled because no decomposition of photocatalyst occurred under the present experimental conditions.⁹⁸

The photocatalytic oxygenation also occurred in the case of durene and mesitylene.⁹⁸ The E_{ox} values of toluene derivatives are lower than the one-electron reduction potential (E_{red}) of the electron-transfer state of $\text{Acr}^+\text{-Mes}$ ($\text{Acr}^+\text{-Mes}^+$: 2.06 V vs. SCE in MeCN).⁹⁸ Thus, electron transfer from toluene derivatives such as *p*-xylene to the Mes^+ moiety of $\text{Acr}^+\text{-Mes}^+$ is energetically feasible, whereas electron transfer from toluene ($E_{\text{ox}} = 2.20\text{ V}$)^{55,98} to the Mes^+ moiety is energetically unfavorable when no photocatalytic oxidation of toluene by O_2 occurred with $\text{Acr}^+\text{-Mes}$ under the same experimental conditions.⁹⁸ The E_{ox} values of the oxygenated products of the corresponding benzaldehydes are also higher than the E_{red} value of $\text{Acr}^+\text{-Mes}^+$ (2.06 V).⁹⁸ This is the reason why the oxygenated product of *p*-xylene was only *p*-tolualdehyde and no further oxygenated product such as *p*-phthalaldehyde was formed.

The photocatalytic reaction is initiated by intramolecular photoinduced electron transfer from the mesitylene moiety to the singlet excited state of the Acr^+ moiety of $\text{Acr}^+\text{-Mes}$, which affords the electron-transfer state ($\text{Acr}^+\text{-Mes}^+$).^{66,98} Electron



Scheme 6 Reaction scheme of photocatalytic oxygenation of *p*-xylene and formation of H_2O_2 catalyzed by $\text{Acr}^+\text{-Mes}$.⁹⁸

transfer from *p*-xylene to the Mes^+ moiety occurs to produce *p*-xylene radical cation, which undergoes deprotonation to afford the deprotonated radical. This is followed by rapid O_2 addition to afford the peroxy radical as shown in Scheme 6.⁹⁸ The disproportionation of the peroxy radical affords *p*-tolualdehyde, *p*-methylbenzyl alcohol and O_2 . *p*-Methylbenzyl alcohol is readily oxygenated to yield *p*-tolualdehyde with $\text{Acr}^+\text{-Mes}^+$.⁹⁸ On the other hand, $\text{O}_2^{\cdot-}$ undergoes disproportionation with a proton to yield H_2O_2 and O_2 (Scheme 6). The radical intermediates involved in Scheme 6 were detected by EPR ($g_{\parallel} = 2.101$, $g_{\perp} = 2.009$ for $\text{O}_2^{\cdot-}$ and $g_{\parallel} = 2.033$, $g_{\perp} = 2.006$ for *p*-methylbenzyl peroxy radical) in frozen MeCN.⁹⁸

Addition of aqueous sulfuric acid enhanced the deprotonation of *p*-xylene radical cations and the disproportionation process of $\text{O}_2^{\cdot-}$, respectively, leading to a remarkable enhancement of photocatalytic reactivity as mentioned above.⁹⁸ The reaction pathway of photocatalytic oxygenation of *p*-xylene by O_2 with $\text{Acr}^+\text{-Mes}$ is not a radical chain process, because there is no dependence of the product quantum yield on the concentration of *p*-xylene and irradiation light intensity.⁹⁸ If a radical chain (autoxidation) process is involved in the photocatalytic reaction, the quantum yield would increase linearly with increasing concentration of *p*-xylene, because the rate-determining step in the radical chain process would be the hydrogen abstraction from *p*-xylene by the peroxy radical. In addition, there is no induction period that is typically observed for an autoxidation process. Thus, disproportionation of *p*-methylbenzyl peroxy radicals and hydrogen peroxy radicals is the major pathway in the photocatalytic oxygenation of *p*-xylene by O_2 with $\text{Acr}^+\text{-Mes}$.

In contrast to the case of $\text{Acr}^+\text{-Mes}$, the photocatalytic oxygenation of *p*-xylene by O_2 with $\text{Acr}^+\text{-Ph}$ that contains no electron donor moiety proceeds *via* electron transfer from *p*-xylene to the singlet excited state of $\text{Acr}^+\text{-Ph}$ (Scheme 2). However, the lifetime of the singlet excited state of $\text{Acr}^+\text{-Ph}$ ($\tau = 1.5\text{ ns}$ in MeCN)⁴³ is much shorter than that of the electron-transfer state of $\text{Acr}^+\text{-Mes}$. A high concentration of substrate is thereby needed to quench the short-lived singlet excited state of $\text{Acr}^+\text{-Ph}$.

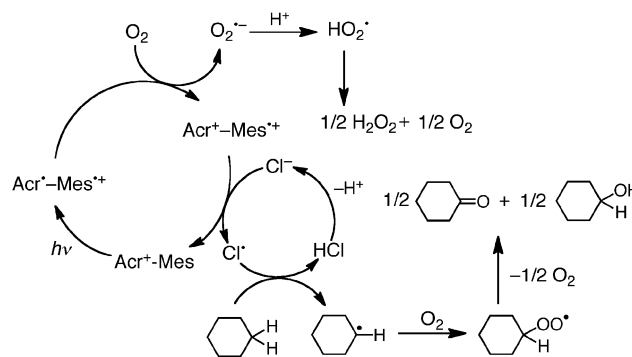
The catalytic durability of Acr^+-Mes is dramatically improved by the addition of $[\{\text{tris}(2\text{-pyridylmethyl})\text{amine}\}\text{Cu}^{\text{II}}](\text{ClO}_4)_2$ ($[(\text{tmpa})\text{Cu}^{\text{II}}]^{2+}$) in the photocatalytic oxygenation of *p*-xylene by O_2 in MeCN.^{99,100} Such an improvement is not observed on the addition of $\text{Cu}(\text{ClO}_4)_2$ in the absence of organic ligands. The addition of $[(\text{tmpa})\text{Cu}^{\text{II}}]^{2+}$ in the reaction solution resulted in more than an 11 times higher turnover number (TON) compared with the TON obtained without $[(\text{tmpa})\text{Cu}^{\text{II}}]^{2+}$.⁹⁹ In the photocatalytic oxygenation, a stoichiometric amount of H_2O_2 formation was observed in the absence of $[(\text{tmpa})\text{Cu}^{\text{II}}]^{2+}$, however, much less H_2O_2 formation was observed in the presence of $[(\text{tmpa})\text{Cu}^{\text{II}}]^{2+}$.⁹⁹ The reaction of O_2 with $[(\text{tmpa})\text{Cu}^{\text{II}}]^{2+}$ in propionitrile at 203 K suggested formation of the dicopper(II) peroxy complex, $[\{(\text{tmpa})\text{Cu}^{\text{II}}\}_2\text{O}_2]^{2+}$, a transformation that is crucial for overall 4-electron reduction of molecular O_2 to water, and key in the observed improvement in the catalytic durability of Acr^+-Mes .^{99,100}

2-Methylnaphthalene that does not react with singlet oxygen (*i.e.*, no conversion under irradiation conditions in the presence of tetraphenylporphyrin as a singlet oxygen photosensitizer) is also efficiently oxygenated by O_2 with Acr^+-Mes acting as a photocatalyst to yield the corresponding naphthaldehyde.¹⁰¹ 9,10-Dicyanoanthracene (DCA) also acts as a photocatalyst for the oxygenation of 2-methylnaphthalene by O_2 as a result of the photoinduced oxidation of 2-methylnaphthalene, followed by deprotonation from the methyl group, and O_2 addition,¹⁰¹ which is similar to the photocatalytic oxygenation of *p*-xylene by O_2 with Acr^+-Mes .

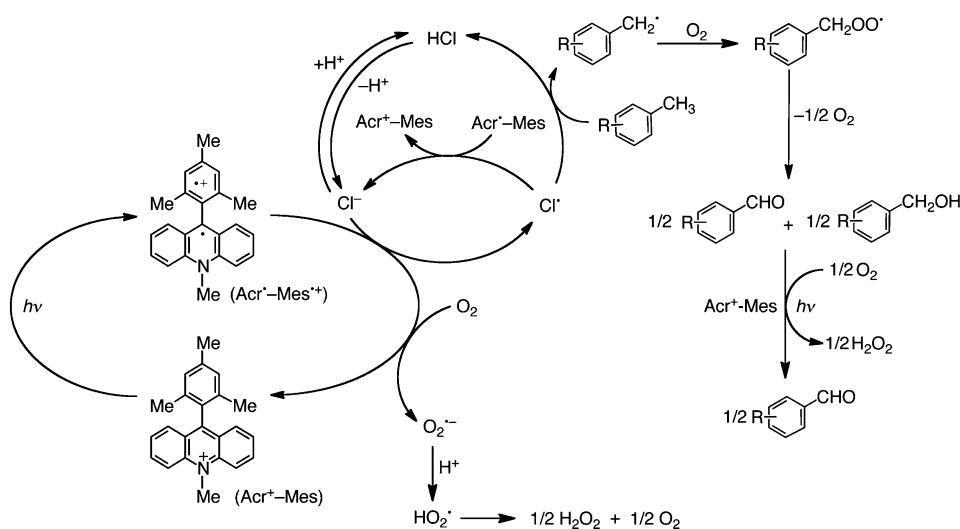
As described above, the electron-transfer state of $\text{Me}_2\text{Acr}^+-\text{Mes}$, which has both a high oxidizing and reducing ability, makes it possible to produce both aromatic aldehydes and H_2O_2 selectively in the photocatalytic oxygenation of alkylaromatic compounds with oxygen. After aromatic aldehydes are formed, no further oxidation takes place because electron transfer from aromatic aldehydes to the Mes^+ moiety is thermodynamically unfavorable. Thus, the use of charge-separation dyads as photocatalysts paves a new way for the selective oxygenation of alkylaromatic compounds with simultaneous formation of H_2O_2 .

We have expanded the scope of the use of Acr^+-Mes as an efficient electron-transfer photocatalyst for the oxidation of organic compounds with O_2 by examining the photocatalytic oxygenation of toluene and cyclohexane with O_2 and hydrochloric acid (Schemes 7 and 8, respectively).^{102,103}

These reactions are initiated by the electron transfer oxidation of Cl^- with the electron-transfer state of Acr^+-Mes to form Cl^\bullet which cleaves a C–H bond of the substrates.^{102,103} The carbon-centred radicals thus produced are readily trapped by O_2 to produce peroxy radicals which undergo disproportionation to produce the alcohols and aldehydes or ketones. The rate-determining step of the photocatalytic oxygenation of substrates described in the previous section is electron-transfer reduction of O_2 because one-electron oxidation potentials of the electron-transfer states of Acr^+-Mes and $\text{Me}_2\text{Acr}^+-\text{Mes}$ are -0.57 and -0.67 V vs. SCE in MeCN, respectively,⁹⁸ which are more positive than the one-electron reduction potential of O_2 (-0.87 V vs. SCE).¹⁰⁴ The free energy changes of electron transfer from the electron-transfer states of Acr^+-Mes and $\text{Me}_2\text{Acr}^+-\text{Mes}$ to O_2 are slightly positive.



Scheme 8 Photocatalytic mechanism of oxygenation of cyclohexane with Acr^+-Mes and HCl .¹⁰³



Scheme 7 Photocatalytic mechanism of oxygenation of toluene derivatives ($\text{R}-\text{C}_6\text{H}_4\text{CH}_3$; $\text{R} = \text{H}, \text{CN}, \text{NO}_2, \text{Br}, \text{Cl}, \text{CH}_3$).¹⁰²

2.5 Photocatalytic production of H₂O₂ using 2-phenyl-4-(1-naphthyl)quinolinium ions

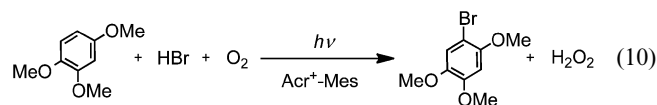
To improve the photocatalytic reactivity, we used a donor-acceptor dyad with much stronger reducing ability at the electron-transfer state as well as a long-lived electron-transfer state. The one-electron reduction potential of the 2-phenyl-4-(1-naphthyl)quinolinium ion (QuPh⁺-NA) is -0.90 V vs. SCE, which is more negative than that of O₂.⁷² Thus, electron-transfer reduction of O₂ with the electron transfer state of QuPh⁺-NA is energetically feasible to produce O₂^{•-}. On the other hand, the one-electron oxidation potential of the naphthalene (NA) moiety of QuPh⁺-NA is 1.87 V vs. SCE, which can also oxidize a variety of substrates.⁷² It is desirable to use oxalate as an electron donor for the photocatalytic production of H₂O₂, because oxalate stored in edible plants is easily extracted with boiling water but disposed of as a waste material.^{105,106} H₂O₂ is also a potential candidate for a clean liquid fuel in the next generation, because H₂O₂ generates electrical power through use of an H₂O₂ fuel cell and emits only water and oxygen after the reaction.^{107,108} Photocatalytic H₂O₂ production has been performed by photoirradiation ($\lambda > 340$ nm) of an oxygen-saturated (1.3 mM) mixed solution (2.0 mL) of a phosphate buffer (300 mM, pH 6.0; pH was adjusted using NaOH) and MeCN [1 : 1 (v/v)] containing QuPh⁺-NA (0.22 mM) and oxalate (1.5 mM).¹⁰⁹ The rate of CO₂ evolution is 0.45 mmol h⁻¹, which is nearly double the H₂O₂ production rate of 0.23 mmol h⁻¹ (Scheme 9).¹⁰⁹ The photocatalytic mechanism is shown in Scheme 9, where oxalate anions are oxidized to CO₂ by the NA⁺ moiety of QuPh⁺-NA⁺ whereas O₂ is reduced by the QuPh moiety to yield H₂O₂ with H⁺.¹⁰⁹ The rate constant of the electron-transfer reduction of O₂ with the QuPh moiety of QuPh⁺-NA⁺ was determined to be 4.6×10^9 M⁻¹ s⁻¹.¹⁰⁹ This value is close to the diffusion-limited value in H₂O and much faster than the case of Acr⁺-Mes (4.6×10^8 M⁻¹ s⁻¹).¹⁰⁹

2.6 Photocatalytic bromination *via* charge-separation

We have further expanded the scope of the use of Acr⁺-Mes as an efficient electron-transfer photocatalyst for the selective bromination of aromatic hydrocarbons and thiophenes with aqueous HBr as a Br source without using a toxic bromine source and O₂ as a green oxidant under visible light

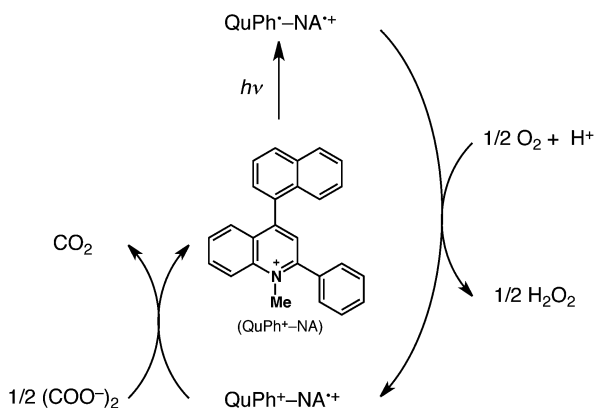
irradiation.¹¹⁰ It should be noted that bromination of thiophenes is particularly important in the preparation of oligothiophenes and polythiophenes,¹¹¹⁻¹²³ which have many applications as conductive, semiconductive, nonlinear optical and liquid crystalline materials.¹²⁴

Visible light irradiation of [Acr⁺-Mes]ClO₄⁻ ($\lambda_{\max} = 430$ nm, 0.20 mM) in an oxygen-saturated MeCN solution containing 1,2,4-trimethoxybenzene (TMB, 4.0 mM), 50% aqueous HBr ([HBr] = 20 mM, [H₂O] = 100 mM) with a xenon lamp attached with a color glass filter ($\lambda < 320$ nm) for 20 min resulted in formation of a brominated product, 2,4,5-trimethoxybromobenzene.¹¹⁰ The overall stoichiometry of the photocatalytic reaction is given by eqn (10). The yield and selectivity of 2,4,5-trimethoxybromobenzene is nearly 100%, because no further brominated product, dibromo- or tribromo-derivative, was produced under these reaction conditions.¹¹⁰ Photocatalytic bromination reactions of various aromatic compounds also occurred as shown in Table 1, where the products and quantum yields are listed. A preparative scale photocatalytic reaction of TMB (200 mg, 1.2 mmol) with 50% aqueous HBr (160 μ L 1.5 mmol) in the presence of Acr⁺-Mes (0.044 mmol) in oxygen-saturated MeCN under photoirradiation by a xenon lamp for 24 h affords the brominated product in 100% selectivity and in 81% yield.¹¹⁰



The photodynamics of the photocatalytic bromination of TMB with HBr in the presence of Acr⁺-Mes were revealed by nanosecond laser flash photolysis.¹¹⁰ A transient absorption spectrum due to the electron-transfer state of Acr⁺-Mes (Acr⁺-Mes⁺) is observed after the laser pulse excitation at 430 nm of a MeCN solution of Acr⁺-Mes.¹¹⁰ The broad absorption band in the near IR region is attributed to the π -dimer of Acr⁺-Mes⁺ with the ground state of Acr⁺-Mes as described earlier.^{70,71} In the presence of TMB, a new band at 450 nm appeared at 12 μ s, which is assigned to TMB radical cation (TMB^{•+}).¹¹⁰ The rate constant for electron transfer from TMB to the Mes⁺ of the electron-transfer state of Acr⁺-Mes was determined from the slope of the linear plot of k_{rise} vs. [TMB] to be $k_{\text{TMB}} = 2.0 \times 10^{10}$ M⁻¹ s⁻¹.¹¹⁰ The rate of disappearance of TMB^{•+} was accelerated on increasing the concentration of HBr. The observed decay rate constant (k_{decay}) increases linearly with increasing concentration of HBr.¹¹⁰ Thus, TMB^{•+} efficiently reacts with Br⁻ to form the Br adduct radical [TMB(Br)]. The rate constant of the addition of Br⁻ was determined from the slope of k_{decay} vs. [HBr] to be $k_{\text{HBr}} = 1.4 \times 10^8$ M⁻¹ s⁻¹.¹¹⁰ The electron-transfer oxidation of Br⁻ in the photocatalytic reaction was also revealed by quenching of Acr⁺-Mes⁺ by HBr. The quenching rate constant of Acr⁺-Mes⁺ with HBr is two orders of magnitude smaller (2.9×10^8 M⁻¹ s⁻¹) than the k_{TMB} value.¹¹⁰ Thus, the electron-transfer oxidation of TMB predominated over the oxidation of Br⁻.

The one-electron oxidation potentials (E_{ox}) of aromatic compounds in deaerated MeCN (0.96 – 1.76 V) listed in Table 1 are



Scheme 9 Photocatalytic production of H₂O₂ with QuPh⁺-NA and oxalate.¹⁰⁵

Table 1 Product and quantum yields for photocatalytic bromination of organic compounds by O₂ and HBr with Acr⁺-Mes in MeCN, and one-electron oxidation potentials of substrates (ref. 101)^a

Entry	Substrate	Product	Conversion, %	Yield, %	Time, h	Quantum yield, %	E _{ox} , V vs. SCE
1			>99	>99	0.3	4.3	0.96
2			>99	>99	0.3	4.8	1.43
3			>99	>99	0.3	3.9	1.49
4			>99	>99	0.5	3.1	1.34
5			>99	>99	1.5	1.1	1.42
6			>99	>99	2	0.26	1.47
7			>99	>99	16	0.01	1.76
8			>99	78	3	0.10	1.45
9			>99	53	2	0.36	1.33
10			100	44	2	0.32	1.47

^a Conditions: [substrate] = 4.0 mM; [Acr⁺-Mes] = 0.20 mM; [HBr] = 20 mM; [H₂O] = 100 mM.

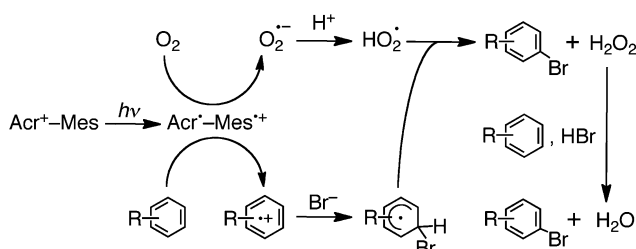
lower than the one-electron reduction potential of the electron-transfer state of Acr⁺-Mes (Acr⁻-Mes⁺; E_{red} = 2.06 V vs. SCE).⁹⁸ Thus, electron transfer from aromatic compounds such as TMB to Acr⁻-Mes⁺ is energetically favorable, whereas electron transfer from toluene (E_{ox} = 2.20 V) and benzene (2.32 V) to the Mes⁺ moiety of Acr⁻-Mes⁺ is energetically unfavorable. In such a case no photocatalytic bromination of benzene or toluene occurs under the same experimental conditions as TMB. The decreased reactivity of methoxybenzene (entry 7 in Table 1) is attributed to the high E_{ox} value (1.76 V). On the other hand, the one-electron reduction of O₂ by the electron-transfer state of Acr⁺-Mes in the presence of an acid is known to occur efficiently, producing HO₂[•] that disproportionates to yield H₂O₂ and O₂.¹¹⁰

The photocatalytic bromination of TMB by HBr with Acr⁺-Mes is initiated by intramolecular photoinduced electron transfer from the Mes moiety to the singlet excited state of the

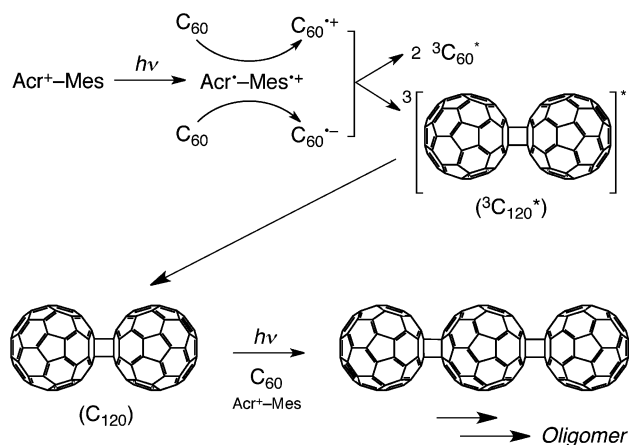
Acr⁺ moiety of Acr⁺-Mes to generate Acr⁻-Mes⁺ as shown in Scheme 10.¹¹⁰ The Mes⁺ moiety of Acr⁻-Mes⁺ can oxidize TMB to produce TMB^{•+}, whereas the Acr⁻ moiety can reduce O₂ to HO₂[•]. The TMB^{•+} thus produced reacts with Br⁻ to form the Br adduct radical, which undergoes dehydrogenation with protonated HO₂[•] to afford the corresponding brominated product and hydrogen peroxide.¹¹⁰ Hydrogen peroxide is known to further react with HBr and substrate to produce another brominated product and H₂O.¹²⁴ The quantum yield remained constant on increasing the concentration of TMB and the light intensity under the present experimental conditions.¹¹⁰ This suggests that no radical chain process is involved in the present photocatalytic aerobic bromination of substrates with HBr.

2.7 Carbon-carbon bond formation *via* radical coupling using an ET state

The photochemical carbon-carbon bond formation of aromatic compounds has been extensively investigated not only for synthetic exploitation, but also for achieving a basic understanding of the photochemical process.¹²⁵ The Acr⁺-Mes catalyzed radical coupling reactions between radical cations and O₂⁻ has been extended to the development of the 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



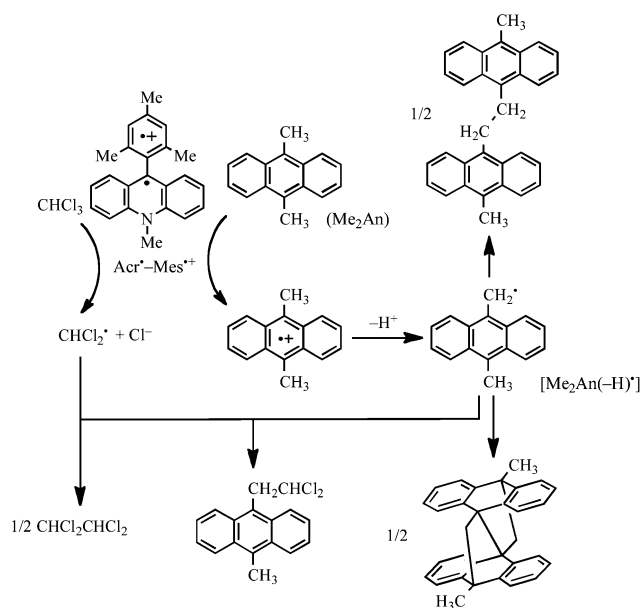
Scheme 10 Photocatalytic mechanism of bromination of benzene derivatives with Acr⁺-Mes, HBr and O₂.¹¹⁰



Scheme 11 Photocatalytic oligomerization of fullerene with Acr^+-Mes .¹²⁶

radical cation and radical anion (Scheme 11).¹²⁶ The photo-products obtained were analyzed by MALDI-TOF-MS. 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.¹²⁶

When the photochemical reaction of 9,10-dimethylanthracene with Acr^+-Mes was carried out without O_2 in CHCl_3 , photocatalytic carbon-carbon bond formation occurred efficiently to give dimethyllepidoptere (5,6,11,12-tetrahydro-5,12-dimethyl-4b,12[1',2']:6,10b[1'',2'']-dibenzochrysenes).¹²⁷ The dimethyllepidoptere is formed *via* deprotonation of dimethylanthracene radical cation (Scheme 12). In this case, CHCl_3 is reduced by the Acr^+ moiety to yield the radical coupling product, $(\text{CHCl}_2)_2$.¹²⁷



Scheme 12 Photocatalytic formation of dimethyllepidoptere with Acr^+-Mes .¹²⁷

3 Conclusions

As described above, a variety of photocatalytic reactions are made possible by using organic photocatalysts *via* photoinduced electron-transfer reactions. Benzene radical cations produced by photoinduced electron transfer from benzene to 3-cyano-1-methylquinolinium ions as a photocatalyst react with nucleophiles such as water and alcohol to form phenol and alkoxybenzenes, respectively. The use of acridinium ion derivatives (AcrH^+ and AcrPh^+), which have small reorganization energies of electron transfer, as photocatalysts has enabled the selective oxygenation of organic substrates to be accomplished. The electron-transfer state of a simple donor-acceptor linked dyad, 9-mesityl-10-methylacridinium ion (Acr^+-Mes), produced upon photoirradiation can oxidize and reduce external electron donors and acceptors to produce the corresponding radical cations and radical anions, respectively. Much smaller concentrations of substrates can be used for the oxidation because of the long lifetime of the electron-transfer state ($\text{Acr}^+-\text{Mes}^*$) as compared with the use of the singlet excited state of AcrH^+ and AcrPh^+ . The substrate radical cations produced by electron transfer from electron donor substrates to the electron-transfer state of Acr^+-Mes efficiently react with electron-acceptor radical anions such as superoxide anion (O_2^-) to form oxygenated products. The reactions of radical cations with nucleophiles such as bromide and chloride can also afford the brominated and chlorinated adducts. In addition, the radical coupling of neutral radicals produced by deprotonation of the produced radical cations is utilized for the C-C bond formation reactions. Thus, photocatalytic reactions *via* photoinduced electron transfer of organic photosensitisers and donor-acceptor dyads provide new ways to design environmentally benign syntheses.

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