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Two-phase photocatalytic oxidation of toluene derivatives by dioxygen with 3-cyano-1-decylquinolinium ion[†]

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Two-phase photocatalytic oxidation of toluene and *p*-xylene by dioxygen occurred efficiently using 3-cyano-1-decylquinolinium hexafluorophosphate (DeQuCN⁺PF₆⁻) as an organic photocatalyst in toluene and *p*-xylene used as solvent with H₂O (2%) to produce the oxygenated products in the organic phase and hydrogen peroxide (H₂O₂) in an aqueous phase with high turnover numbers.

Photocatalytic oxidation of toluene and its derivatives by dioxygen with organic photocatalysts under light irradiation has merited increasing attention as atom-economic and environmental benign alternative to classical oxidation methods with inorganic oxidants.¹⁻⁴ Hydrogen peroxide (H₂O₂) produced as the reduced product of dioxygen often degrades organic photocatalysts under light irradiation, precluding to obtain the high turnover numbers.^{5,6} The stability of riboflavin tetraacetate used as an organic photocatalyst was much enhanced by combination with a non-heme iron catalyst which disproportionates H₂O₂.⁶ On the other hand, H₂O₂ has merited increasing attention as an ideal energy carrier alternative to hydrogen, because an aqueous solution of H₂O₂ instead of gaseous hydrogen can be used as a fuel in a one-compartment fuel cell to generate electricity.⁸⁻¹⁰ If H₂O₂ can be separated from the reactant solution as soon as it is formed, the degradation of organic photocatalysts would be avoided. However, such separation of H₂O₂ during photocatalytic oxygenation of substrates has yet to be achieved.

We report herein two-phase photocatalytic oxidation of toluene

by dioxygen with 3-cyano-1-decylquinolinium hexafluorophosphate (DeQuCN⁺PF₆⁻) as an organic photocatalyst in toluene used as a solvent with H₂O (2%) to produce the oxygenated products in toluene and hydrogen peroxide (H₂O₂) in an aqueous phase with high turnover numbers (Fig. 1).¹¹ Toluene can be replaced by

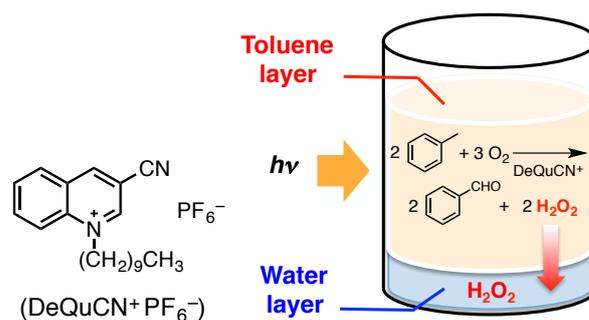


Fig. 1 Chemical structure of DeQuCN⁺PF₆⁻; Two-phase photocatalytic oxidation of toluene by O₂ with DeQuCN⁺. The oxygenated products are accumulated in an organic phase, whereas H₂O₂ is accumulated in an aqueous phase.

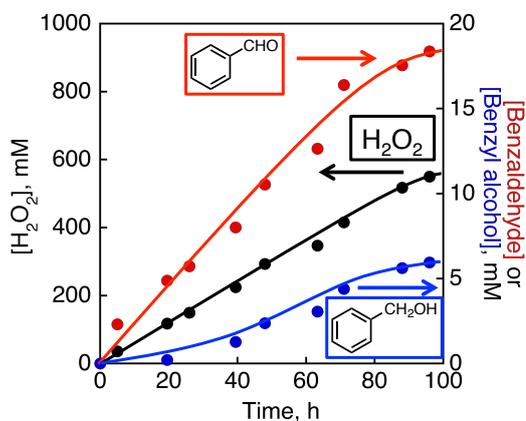


Fig. 2 Time courses of two-phase photocatalytic oxidation of toluene by O₂ with DeQuCN⁺PF₆⁻ (50 μM) in toluene with H₂O (2%) under photoirradiation with a high-pressure mercury lamp (1000 W) (λ > 310 nm).

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[†] Electronic Supplementary Information (ESI) available: Experimental details spectral data. See DOI:

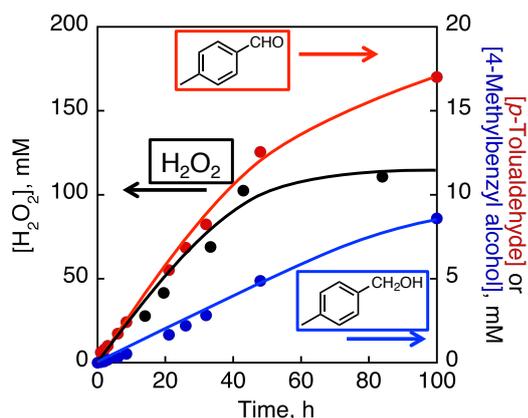


Fig. 3 Time courses of two-phase photocatalytic oxidation of *p*-xylene by O_2 with $DeQuCN^+PF_6^-$ (50 μM) in *p*-xylene with H_2O (10%) under photoirradiation with a xenon lamp (500 W) ($\lambda > 310$ nm).

p-xylene when higher concentrations of H_2O_2 were obtained in an aqueous phase. Such a two-phase system was reported for the catalytic O_2 reduction to produce H_2O_2 .¹²⁻¹⁴ However, no two-phase photocatalytic oxidation of substrates was reported for production of H_2O_2 in an aqueous phase.

Synthesis of $DeQuCN^+PF_6^-$ was carried out by alkylation of quinoline with decyl triflate. The product was obtained by salt exchange with potassium hexafluorophosphate, characterised by 1H NMR, HR-MS spectroscopies (Fig. S1 in the electronic supplementary information (ESI) \dagger). The detailed synthetic procedures are shown in the experimental section of ESI \dagger .

The oxygenation of toluene and *p*-xylene, by molecular oxygen (O_2) was achieved by use of $DeQuCN^+$ as a photocatalyst. Photoirradiation of the absorption band ($\lambda_{max} = 330$ nm, see Fig. S2 in ESI \dagger) of $DeQuCN^+$ (50 μM) in an oxygen-saturated toluene/aqueous bilayer solution (36 mL / 0.72 mL) with a high-pressure mercury lamp (1000 W) through a UV cutoff filter ($\lambda < 310$ nm) results in formation of benzaldehyde and benzyl alcohol (Fig. 1). The products were identified by the gas-chromatographic (GC) analyses (see experimental section and data as shown in Fig. S3 in ESI \dagger). After 96 h of irradiation, the production amounts of benzaldehyde and benzyl alcohol were 18 mM (0.66 mmol) and 6.0 mM (0.22 mmol) in the toluene layer (Fig. 2). Hydrogen peroxide was accumulated in the aqueous layer, quantitated by spectroscopic titration with $[TiO(tpypH_4)]^{4+}$ complex (Ti-TPyP reagent; oxo[5,10,15,20-tetra(4-pyridyl)porphyrinato titanium(IV)] in an acidic solution (see the experimental section in ESI \dagger).¹⁵ The final concentration of H_2O_2 was reached to 550 mM (0.40 mmol). The catalytic turnover numbers (TONs) were 490 for toluene and 510 for *p*-xylene based on the initial concentration of $DeQuCN^+$.¹⁶ Most of $DeQuCN^+$ was still remaining after photoirradiation for 96 h. However, the reaction rate decreased at prolonged photoirradiation time due to the photooxidation of the catalyst with H_2O_2 . Because H_2O_2 in H_2O is separated from the organic catalyst in MeCN, the photodegradation of the catalyst is avoided in the present catalytic system.

When toluene was replaced by *p*-xylene, formation of *p*-tolualdehyde and *p*-methylbenzyl alcohol was also observed with production of H_2O_2 as shown in Fig. 3 (GC data are shown in ESI \dagger , Fig. S4).¹⁷ The quantum yields of H_2O_2 formation were determined from the initial rate of the photocatalytic reaction to be 5.6% in

toluene and 12% in *p*-xylene (Fig. S5 in ESI \dagger). The TONs and quantum yields of photocatalytic oxidation of toluene and *p*-xylene by O_2 with $DeQuCN^+$ are summarized in Table 1.

Irradiation of the absorption band of $DeQuCN^+$ ($\lambda_{max} = 330$ nm) results in strong fluorescence at 432 nm in acetonitrile (MeCN). On the other hand, the fluorescence was significantly quenched in toluene and *p*-xylene. The quenching rate constants were determined in MeCN from the slopes of the Stern-Volmer plots (Fig. 4) and lifetimes of the singlet excited state of $DeQuCN^+$ ($\tau = 34$ ns, Fig. S6 in ESI \dagger). The k_q values thus obtained from eqn (1) to be 1.6

$$k_q = K_{SV} \tau^{-1} \quad (1)$$

Table 1 TONs and quantum yields of photocatalytic oxidation of toluene and *p*-xylene by O_2 with $DeQuCN^+PF_6^-$ (50 μM)

| Substrate | Product (TON) | quantum yield (%) |
|------------------|--------------------------------------|-------------------|
| toluene | benzyl alcohol (120) | 5.6 |
| | benzaldehyde (370) | |
| <i>p</i> -xylene | <i>p</i> -methylbenzyl alcohol (170) | 12 |
| | <i>p</i> -tolualdehyde (340) | |

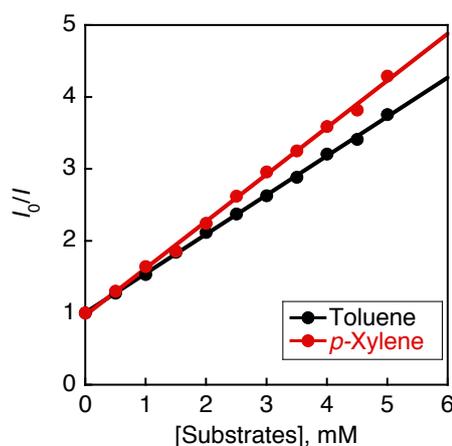
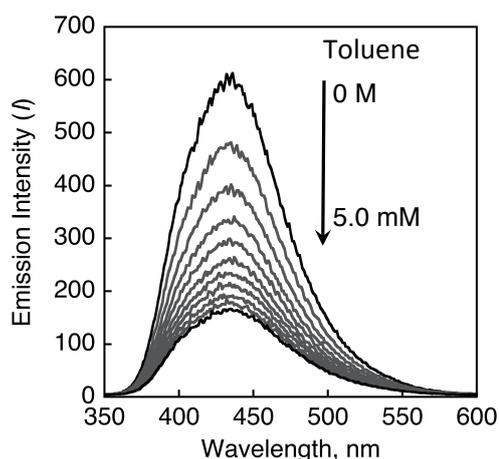


Fig. 4 (a) Emission spectra of $DeQuCN^+PF_6^-$ (20 μM) in the presence of toluene (0–5.0 mM) in MeCN at 298 K; (b) Stern-Volmer plots for the electron-transfer quenching of $DeQuCN^+$ by toluene and *p*-xylene in MeCN.

$\times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for toluene and $1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for *p*-xylene, which are close to the diffusion rate constant in MeCN ($2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). The free energy change of photoinduced electron transfer (ΔG_{et} in electron volts) from toluene to the singlet excited states of DeQuCN⁺ is given by eqn (2),

$$\Delta G_{\text{et}} = e(E_{\text{ox}} - E_{\text{red}}^*) \quad (2)$$

where e is elementary charge, and E_{ox} and E_{red}^* are the one-electron oxidation potential of toluene ($E_{\text{ox}} = 2.20 \text{ V vs. SCE}$)^{5,18} and the one-electron reduction potential of the singlet excited state of DeQuCN⁺ ($E_{\text{red}}^* = 2.72 \text{ V vs. SCE}$)¹⁹ respectively. The ΔG_{et} values were -0.52 eV for toluene and -0.79 eV for *p*-xylene ($E_{\text{ox}} = 1.93 \text{ V vs. SCE}$)⁴, indicating that the photoinduced electron-transfer reactions are energetically favourable.²⁰

The occurrence of photoinduced electron transfer from substrates to DeQuCN⁺ is confirmed by laser flash photolysis experiments (see the experimental section in ESI †). Laser excitation ($\lambda = 355 \text{ nm}$ from a Nd:YAG laser) of DeQuCN⁺ ($3.0 \times 10^{-4} \text{ M}$) in a deaerated toluene solution affords a transient absorption spectrum at $1 \mu\text{s}$ with appearance of new absorption bands at 540, and 950 nm as shown in Fig. 5. Similar transient absorption spectra are also observed in *p*-xylene (see ESI †, Fig. S7). The transient absorption band at $\lambda_{\text{max}} = 540 \text{ nm}$ is assigned to DeQuCN⁺.¹⁹ The broad absorption band at near-IR region ($\lambda_{\text{max}} = 950 \text{ nm}$) can be assigned to toluene π -dimer radical cation, because similar broad transient absorption bands at a long-wavelength region have been reported for the radical cations of toluene and other aromatic compounds.^{19,21,22} The decay of the absorbances due to the radical ion pair obeyed second-order kinetics, indicating the bimolecular back electron transfer between DeQuCN⁺ and toluene radical cation.

The photocatalytic reaction is initiated by photoinduced electron transfer from toluene to the singlet excited state of DeQuCN⁺ as shown in Scheme 1. The toluene radical cation, which is in equilibrium with the π -dimer toluene radical cation, formed by photoinduced electron transfer gives a benzyl radical via deprotonation. This is followed by rapid O₂ addition to afford the peroxy radical, leading to the final oxygenated product, benzaldehyde and benzyl alcohol.²³ On the other hand,

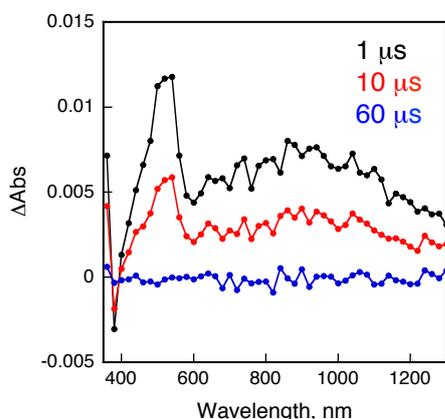
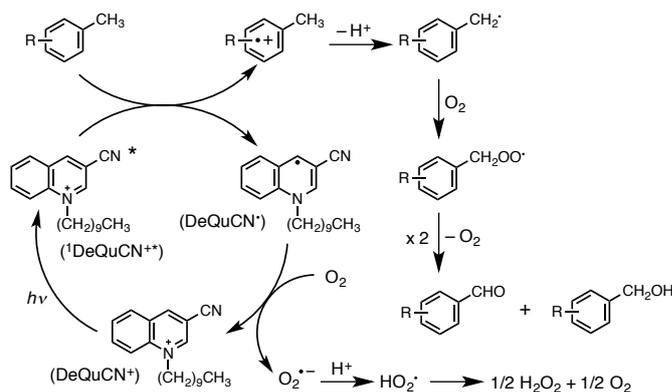
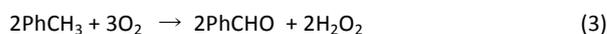


Fig. 5 Transient absorption spectra of DeQuCN⁺PF₆⁻ (100 μM) in deaerated toluene at 298 K taken at 1, 10, 60 μs after nanosecond laser excitation at 355 nm.



Scheme 1 Reaction mechanism of photocatalytic oxygenation of toluene derivatives and formation of H₂O₂ catalysed by DeQuCN⁺

DeQuCN⁺ produced by electron transfer reacts with O₂ to form O₂^{•-}. O₂^{•-} disproportionates in the presence of proton to yield H₂O₂. The overall stoichiometry of the photocatalytic reaction is given by eqn (3).



In conclusion, DeQuCN⁺ acts as an efficient organic photocatalyst for the two-electron reduction of O₂ to produce H₂O₂ as well as the oxygenation of organic substrates in a two-phase solution. The photochemical reaction is initiated by photoinduced electron transfer to produce radical ion pair. The reaction intermediates were detected by the time-resolved transient absorption measurements. The present study provides a valuable method for the selective oxygenation of organic substrates with simultaneous formation of high concentrations of H₂O₂.

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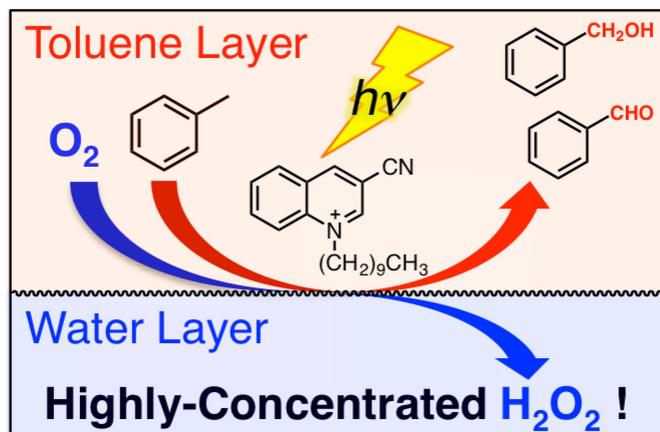
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- 23 The yield of benzaldehyde is higher than that of benzyl alcohol (Fig. 2). Further oxidation of benzyl alcohol with photoexcited DeQuCN⁺ occurred to give benzaldehyde.

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Two-phase photocatalytic oxidation of toluene by O_2 occurred efficiently using 3-cyano-1-decylquinolinium ion in toluene with H_2O to produce the oxygenated products in the organic phase and H_2O_2 in an aqueous phase.