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Efficient photocatalytic proton-coupled electron-transfer reduction of O₂ by a saddle-distorted porphyrin as a photocatalyst

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Photocatalytic O₂ reduction reactions proceeded to produce H₂O₂ by a diprotonated saddle-distorted dodecaphenylporphyrin as a photocatalyst. The quantum yield (12%), the turnover number (3000 for 6 h), and the turnover frequency (500 h⁻¹) are achieved in photocatalytic systems based on free-base porphyrins for the first time. The photocatalytic reaction mechanism has been revealed by ns-laser flash photolysis and the kinetic analysis.

Oxygen reduction reaction (ORR) has been recognized as one of the most fundamental reactions in biological processes as performed by cytochrome *c* oxidase in respiration¹ and chemical technologies such as fuel cells.² In addition, hydrogen peroxide (H₂O₂) is a promising candidate for environmentally benign oxidizing reagents, bleaching, and an energy source of fuel cells as a two-electron reduced product in ORR (eqn 1).³ In industry, H₂O₂ is manufactured by the anthraquinone process, which requires a hydrogen gas to reduce anthraquinone in the presence of a palladium catalyst.⁴ Instead of the energy-consuming process using precious resources, alternative ORR catalysis for H₂O₂ production should be required to be constructed on the basis of photon energy without using precious metals.



Toward this goal, extensive efforts have been devoted to the development of ORR catalysts for selective H₂O₂ production thermally⁵ or photochemically⁶ in the presence of acids without using noble metals. Especially, organocatalysts should be good candidates for proton-coupled O₂ reduction because of involvements of protons in the course of their redox reactions.⁷ In addition, utilization of the visible light should be advantageous in terms of sustainable and environmental benign catalytic reactions.^{3,6} Among organic

photocatalysts, porphyrins are good candidates because of their rich redox-active properties and photochemical properties including strong absorption in a wide range of visible region.⁸ However, there is no report on the use of a free-base porphyrin as a photocatalyst for ORR due to the high efficiency of energy transfer from the triplet excited state to molecular oxygen (O₂) to afford the singlet oxygen (¹O₂).⁹ To avoid energy transfer to O₂, introduction of saddle-distortion to the porphyrin core should be effective because of the destabilization of the HOMO level, resulting lower triplet excited energy.^{9,10} Among saddle-distorted porphyrins, a diprotonated saddle-distorted dodecaphenylporphyrin¹¹ (H₄DPP²⁺) has been selected as a photocatalyst in this study because the photodynamics and electron-transfer properties of H₄DPP²⁺ have been well understood.¹² Recently, we have reported that a water-soluble H₄DPP²⁺ derivative works as a photosensitizer for photocatalytic oxidation reactions in water.¹³ Besides a role of photosensitizer, H₄DPP²⁺ has also acted as an electron acceptor to afford one-electron-reduced species (H₄DPP^{•+}) due to the high reduction potential ($E_{\text{red}} = -0.37$ V vs. SCE)¹², which allows us to expect that H₄DPP^{•+} acts as a reducing agent for ORR. Judging from the characteristic properties of saddle-distorted porphyrins, photocatalytic ORR could be achieved by employing H₄DPP²⁺ as an ORR photocatalyst. Herein, we have developed a metal-free photocatalytic ORR system based on (H₄DPP²⁺)(Cl⁻)₂ (Fig. 1)^{11b,14} in the presence of an electron donor and Brønsted acids to afford H₂O₂ efficiently and selectively.

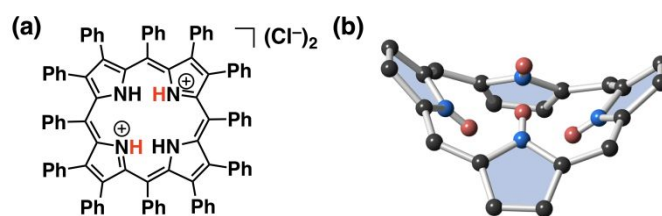


Fig. 1 (a) A chemical structure of H₄DPP²⁺(Cl⁻)₂ and (b) the structural model of H₄DPP²⁺ without peripheral phenyl groups.

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Photocatalytic ORR by $\text{H}_4\text{DPP}^{2+}$ was performed in the presence of 10-methyl-9,10-dihydroacridine (AcrH_2) as a two-electron donor and carboxylic acids as a proton source in acetonitrile (MeCN) at 298 K. Upon photoirradiation ($\lambda_{\text{ex}} = 480$ nm) to a MeCN solution containing $\text{H}_4\text{DPP}^{2+}$, O_2 , AcrH_2 , and monochloroacetic acid (MCA), UV-vis spectral changes were observed as shown in Fig. 2. Absorption bands rised at 358 nm and 400 nm, which were derived from AcrH^+ as a two-electron-oxidized product of AcrH_2 ,¹⁵ although the spectrum of $\text{H}_4\text{DPP}^{2+}$ exhibiting the absorption maxima at 490 nm and 730 nm was almost intact. We quantified the amount of H_2O_2 as a two-electron reduced product of O_2 in ORR to be 99% yield based on AcrH_2 by an iodometry method, in which a reaction between I_2 and H_2O_2 occurs to form I_3^- ion^{5c,16} (Fig. S1 in the ESI[†]). In addition, the amount of AcrH^+ formed was consistent with that of H_2O_2 as shown in Fig. S2 in the ESI[†]. Therefore, the stoichiometry of photocatalytic ORR indicates that two-electron reduction of O_2 to form H_2O_2 proceeds quantitatively by eqn 2. It should be noted that thermal ORR without $\text{H}_4\text{DPP}^{2+}$ proceeded slightly¹⁷ as a background reaction depending on acids used as shown in Fig. S3 in the ESI[†] (also see below).

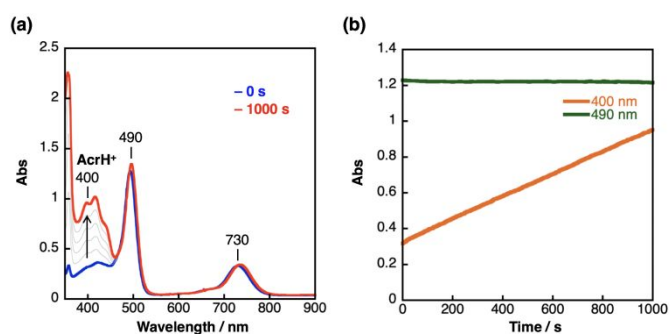
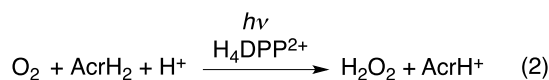


Fig. 2 (a) UV-vis spectral changes in photocatalytic ORR ($\lambda_{\text{ex}} = 480$ nm). Conditions: $[\text{H}_4\text{DPP}^{2+}] = 10 \mu\text{M}$, $[\text{AcrH}_2] = 5 \text{ mM}$, $[\text{MCA}] = 0.1 \text{ M}$, and $[\text{O}_2] = 0.29 \text{ mM}$ in MeCN at 298 K. (b) The time profiles at 400 nm and 490 nm.

The time profile at 400 nm owing to AcrH^+ formation obeyed zero-order kinetics under the photocatalytic conditions (Fig. 2b). Thus, the observed zero-order rate (v , M s^{-1}) of AcrH^+ formation was determined from the linear slope of the plot at 400 nm. The zero-order-kinetics in AcrH^+ formation was also observed employing other acids such as trifluoroacetic acid (TFA), and dichloroacetic acid (DCA) with different values of v . The v values depend on the pK_a value of acids in MeCN¹⁸ (Fig S4a in the ESI[†]), which is correlated with the positive shift of one-electron reduction potential of O_2 (Fig S4b in the ESI[†]). In addition, a linear-proportional relationship between v and the concentration of acids was also observed in the case of MCA as a proton source (Fig. 3a). Judging from these results, one proton is involved to accelerate ORR through proton-coupled electron transfer (PCET). When we changed the concentration of AcrH_2 ($[\text{AcrH}_2]$), the v value increased proportionately with increasing $[\text{AcrH}_2]$ as shown in Fig. 3b. Such a linear-

proportional relationship was also observed by changing light intensity (Fig. 3c).¹⁹ In contrast, there is no dependence of v on $[\text{O}_2]$ ¹⁵ (Fig. 3d), which indicates that the ORR rate law depends on light intensity, $[\text{AcrH}_2]$, and $[\text{H}^+]$. In this case, the kinetic equation was given by eqn 3.

$$v = \frac{d[\text{AcrH}^+]}{dt} = k_{\text{cat}}[\text{H}_4\text{DPP}^{2+}]^*[\text{AcrH}_2][\text{H}^+] \quad (3)$$

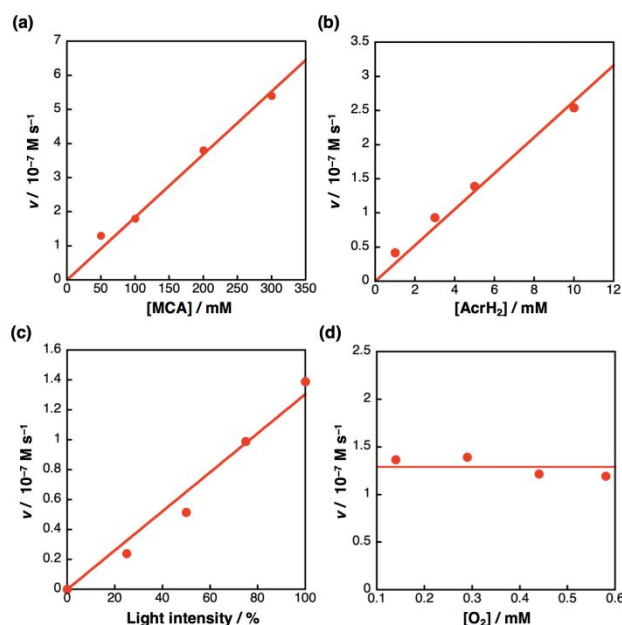


Fig. 3 Plots of rates (v) of AcrH^+ formation vs. (a) $[\text{MCA}]$ in the presence of 5.0 mM AcrH_2 and 0.29 mM O_2 , (b) $[\text{AcrH}_2]$ in the presence of 0.1 M MCA and 0.29 mM O_2 , (c) light intensity at 480 nm in the presence of 5.0 mM AcrH_2 , 0.1 M MCA and 0.29 mM O_2 , and (d) $[\text{O}_2]$ in the presence of 0.1 M MCA and 5.0 mM AcrH_2 , under photocatalytic ORR conditions ($\lambda_{\text{ex}} = 480$ nm) in MeCN containing $\text{H}_4\text{DPP}^{2+}$ (10 μM) at 298 K.

Under the optimized ORR conditions, the quantum yield (Φ) is determined using a ferrioxalate actinometer to be 12% and the turn-over number (TON) and the turnover frequency (TOF) of H_2O_2 production is also determined to be over 3000 for 6 h and 500 h^{-1} based on the amount of $\text{H}_4\text{DPP}^{2+}$, $[\text{H}_4\text{DPP}^{2+}]$, as shown in Fig S5 in the ESI[†]. Photocatalytic ORR using free-base porphyrins has been achieved for the first time.²⁰ In order to obtain a strong evidence for the photocatalytic performance, the requirement of visible light irradiation for H_2O_2 production was examined by repeating on/off cycles of the visible light irradiation. Fig. 4 clearly demonstrates that the photocatalytic ORR only proceeds during visible-light irradiation and stopped in the dark alternately. Thus, the possibility of thermal radical-chain mechanisms¹⁵ could be ruled out based on the determination of the Φ value²¹ and the light on-off experiments, confirming the indispensable role of visible light for the photocatalytic H_2O_2 production.

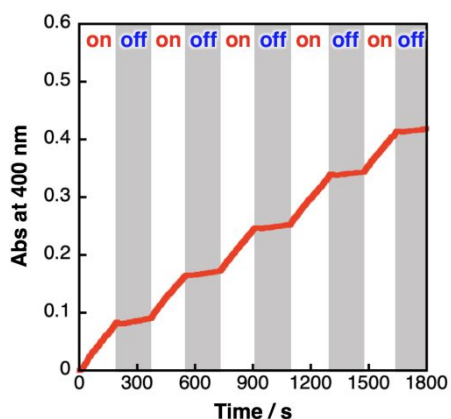


Fig. 4 Repeated experiments with or without photoirradiation under photocatalytic ORR conditions ($\lambda_{\text{ex}} = 480$ nm) in MeCN containing $10 \mu\text{M}$ $\text{H}_4\text{DPP}^{2+}$, 50 mM MCA, 3.0 mM AcrH_2 , and 3.0 mM O_2 at 298 K.

To investigate the photocatalytic ORR mechanism by $\text{H}_4\text{DPP}^{2+}$, we performed nano-second laser flash photolysis (ns-LFP) under the similar reaction conditions to those described above. Upon photoirradiation at 532 nm to a deaerated MeCN solution of $\text{H}_4\text{DPP}^{2+}$ containing trifluoroacetic acid (TFA) as a proton source, the transient absorption spectra of $\text{H}_4\text{DPP}^{2+}$ showed an absorption band at 560 nm at $1.6 \mu\text{s}$ after laser excitation, indicating the formation of the triplet excited state of $\text{H}_4\text{DPP}^{2+}$ ($^3(\text{H}_4\text{DPP}^{2+})^*$) via fast intersystem crossing from the singlet excited state of $\text{H}_4\text{DPP}^{2+}$ ($^1(\text{H}_4\text{DPP}^{2+})^*$) (Fig. S6 in the ESI†).¹² Then, transient absorption spectra of $\text{H}_4\text{DPP}^{2+}$ were measured in the presence of AcrH_2 to examine photoinduced electron transfer (ET) from AcrH_2 to $^3(\text{H}_4\text{DPP}^{2+})^*$ (Fig. 5). In contrast to the result in Fig. S6, transient absorption spectrum derived from $^3(\text{H}_4\text{DPP}^{2+})^*$ at $0.8 \mu\text{s}$ after laser excitation changed to a spectrum with a new absorption band at 520 nm (blue trace in Fig. 5), suggesting the photoinduced ET from AcrH_2 to $^3(\text{H}_4\text{DPP}^{2+})^*$ to form the one-electron reduced $\text{H}_4\text{DPP}^{2+}$ (H_4DPP^{+}).¹² The decay time profile at 560 nm assigned to $^3(\text{H}_4\text{DPP}^{2+})^*$ coincides with the rise time profile at 520 nm due to H_4DPP^{+} as shown in Fig. 5b. The second-order rate constant (k_{et}) of photoinduced ET from AcrH_2 to $^3(\text{H}_4\text{DPP}^{2+})^*$ was determined to be $5.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ by changing $[\text{AcrH}_2]$ (Fig. S7 in the ESI†).

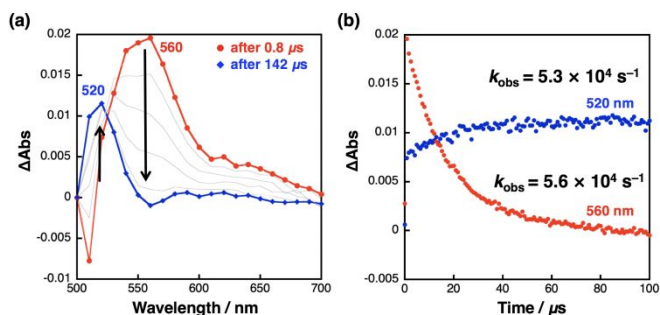
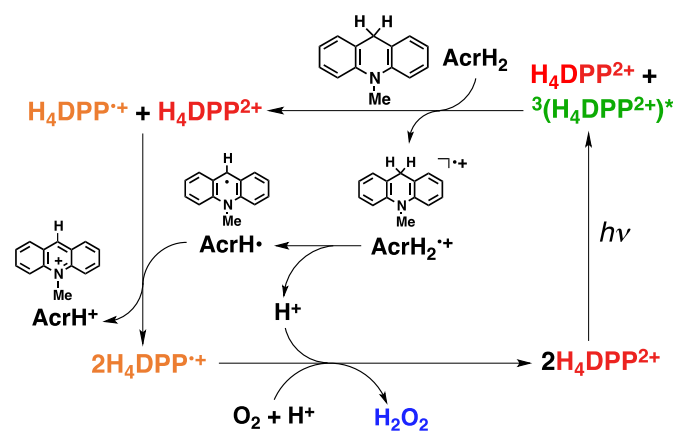


Fig. 5 (a) Transient absorption spectra of $\text{H}_4\text{DPP}^{2+}$ ($50 \mu\text{M}$) in the presence of AcrH_2 (15 mM) and TFA (0.1 M) in deaerated MeCN at 298 K taken at $0.8 \mu\text{s}$ (red) and $142 \mu\text{s}$ (blue) after nano-second laser excitation at 532 nm. (b) The decay and rise time profiles at 520 nm (blue) and 560 nm (red) in photoinduced ET from AcrH_2 to $^3(\text{H}_4\text{DPP}^{2+})^*$.

The rate constant (k_{O_2}) of ET from H_4DPP^{+} to O_2 was also determined by changing $[\text{O}_2]$ as shown in Fig. S8 in the ESI†. The rate constant (k_{O_2}) is calculated to be $3.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, which is almost the same value in comparison to k_{et} ($= 5.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$). The driving forces of ET ($-\Delta G_{\text{et}}$) for k_{et} ($-\Delta G_{\text{et}} = 0.30$ eV) and k_{O_2} ($-\Delta G_{\text{et}} = -0.06$ eV) were determined from the difference between one-electron oxidation potential (E_{ox}) of AcrH_2 ($E_{\text{ox}} = 0.81$ V vs. SCE)²² and one-electron reduction potential (E_{red}) of $^3(\text{H}_4\text{DPP}^{2+})^*$ ($E_{\text{red}} = 1.11$ V vs. SCE in MeCN), and that between E_{ox} of H_4DPP^{+} ($E_{\text{ox}} = -0.37$ V) and O_2 in the presence of 10 mM TFA ($E_{\text{red}} = -0.43$ V). Judging from these $-\Delta G_{\text{et}}$ values, the k_{O_2} value is larger than the expected value ($\sim 10^4 \text{ M}^{-1} \text{ s}^{-1}$) from the Marcus parabola as described in the previous paper.¹² This large rate constant indicates that the O_2 reduction process is accelerated by the subsequent protonation of $\text{O}_2^{\cdot-}$ concertedly. This hypothesis is well consistent with the result of $\text{p}K_{\text{a}}$ dependence on the photocatalytic ORR rate as described above (Fig S4 in the ESI†).

The proposed ORR mechanism has been shown in Scheme 1. Upon photoexcitation of $\text{H}_4\text{DPP}^{2+}$ in the presence of AcrH_2 as an electron donor, photoinduced ET occurs to produce H_4DPP^{+} with the expected k_{et} value determined by ns-LFP. Subsequently, PCET from H_4DPP^{+} to O_2 is also observed in the presence of a proton source with a similar k_{O_2} value in spite of the uphill $-\Delta G_{\text{et}}$ value estimated from the redox potentials of $\text{H}_4\text{DPP}^{2+}$ and O_2 . Thus, we can conclude that the fast ET and PCET processes performed by $\text{H}_4\text{DPP}^{2+}$ allows us to construct the efficient photocatalytic ORR system.



Scheme 1. Proposed photocatalytic ORR mechanism

In summary, we have succeeded in the development of the photocatalytic ORR system based on a diprotonated saddle-distorted porphyrin ($\text{H}_4\text{DPP}^{2+}$). The quantum yield of the photocatalytic system reaches 12% and the turnover number is determined to be over 3000 for 6 h. The reaction mechanism was clarified by nanosecond laser flash photolysis involving the formation of H_4DPP^{+} as the key intermediate. The present study provides not only a new standard for photocatalytic ORR systems by porphyrin derivatives but also an application of a diprotonated porphyrin species as a reducing photocatalyst. Further applications of $\text{H}_4\text{DPP}^{2+}$ derivatives are ongoing in our laboratory.

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Conflicts of interest

There are no conflicts to declare.

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