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Electronic Supplementary Information

for

Efficient photocatalytic proton-coupled electron-transfer reduction of O_2 by a saddle-distorted porphyrin as a photocatalyst

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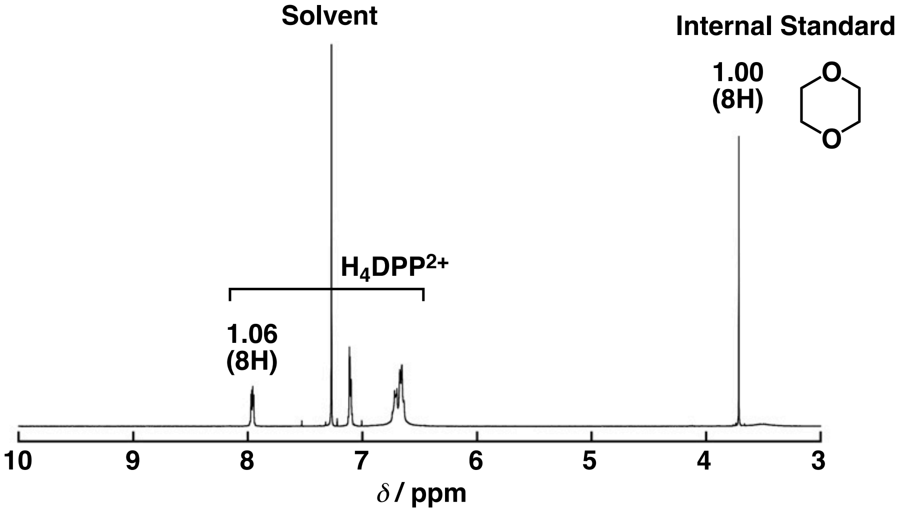
Contents

Experimental Section

General. Spectroscopic grade acetonitrile (MeCN) were used as a solvent without further purification. Chemical reagents were purchased from commercial sources and used without further purification. $AcrH_2$ and $H_4DPP^{2+}(Cl^-)_2$ were synthesized according to the previous reports.[1,2] ^1H NMR spectra were measured on a Bruker AVANCEHD400 spectrometer at 298 K.

^1H NMR spectrum of $H_4DPP^{2+}(Cl^-)_2$ (1.16 mM) used in the study in $CDCl_3$ with dioxane (1.13 mM)



Spectroscopic Measurements. UV-Vis measurements were performed on Shimadzu UV-3600 and Agilent 8454 spectrometers at room temperature. The cell length (*l*) of a quartz cuvette was typically 10 mm unless otherwise noted. The amount of hydrogen peroxide (H_2O_2) formed was determined by titration with iodide ion: A diluted MeCN solution (3.0 mL) of a reaction mixture (100 μL) was treated with an excess NaI (0.1 M), and the amount of I_3^- formed was determined by the absorption spectrum (λ_{max} = 361 nm, $\varepsilon = 2.8 \times 10^4$ M^{-1} cm^{-1}).[3]

ns-Laser Flash Photolysis Measurements. Nanosecond transient absorption measurements were carried out using an Unisoku TSP-2000 flash spectrometer. A Surelite-I Nd-YAG (Continuum, 4–6 ns fwhm) laser with the second harmonic at 532 nm was employed for the flash photoirradiation. The photodynamics was monitored by continuous exposure to a xenon lamp (150 W) as a probe light and a photomultiplier tube (Hamamatsu R-2949) as a detector. Each sample solution was purged with Ar for at least 20 min prior to the measurement. All experiments were performed at room temperature.

Electrochemical Measurements. Cyclic voltammetric and differential pulse voltammetric measurements were carried out in MeCN containing 0.1 M $TBAPF_6$ as an electrolyte at room temperature under Ar. All measurements were made using a BAS ALS-710D electrochemical analyzer with a glassy carbon as a working electrode, a platinum wire as a counter electrode, and $Ag/AgNO_3$ as a reference electrode.

Photocatalytic ORR by H_4DPP^{2+}.

Typically, photocatalytic ORR were performed in a quartz cuvette (path length = 10 mm) containing a MeCN solution of H_4DPP^{2+}, $AcrH_2$, O_2, and acids. The solution was irradiated with an ASAHI Spectra Co. Xe lamp MAX-300 (300 W), equipped with a band pass filter centred at 480 (ASAHI Spectra MX0480). Typically, the concentration of O_2 (0.29 mM) in MeCN was controlled by mixing air-saturated MeCN ($[O_2]$ = 2.6 mM) and Ar-saturated MeCN with the ratio (1:8 v/v).

Determination of the Quantum Yield for Photocatalytic ORR.

A standard actinometer (potassium ferrioxalate)[4] was used for the quantum yield determination. Under the conditions of actinometry experiments, the actinometer absorbed essentially all the incident light of $\lambda = 480$ nm. The fraction of light absorption of H_4DPP^{2+} was estimated by considering the absorbance at 480 nm. The light intensity of monochromatized light of $\lambda = 480$ nm was determined to be 5.8×10^{-8} einstein s^{-1}. Then, Φ was defined as {100% × [product / mol]/[absorbed photon / einstein]} as an internal quantum yield (maximum is 100%).

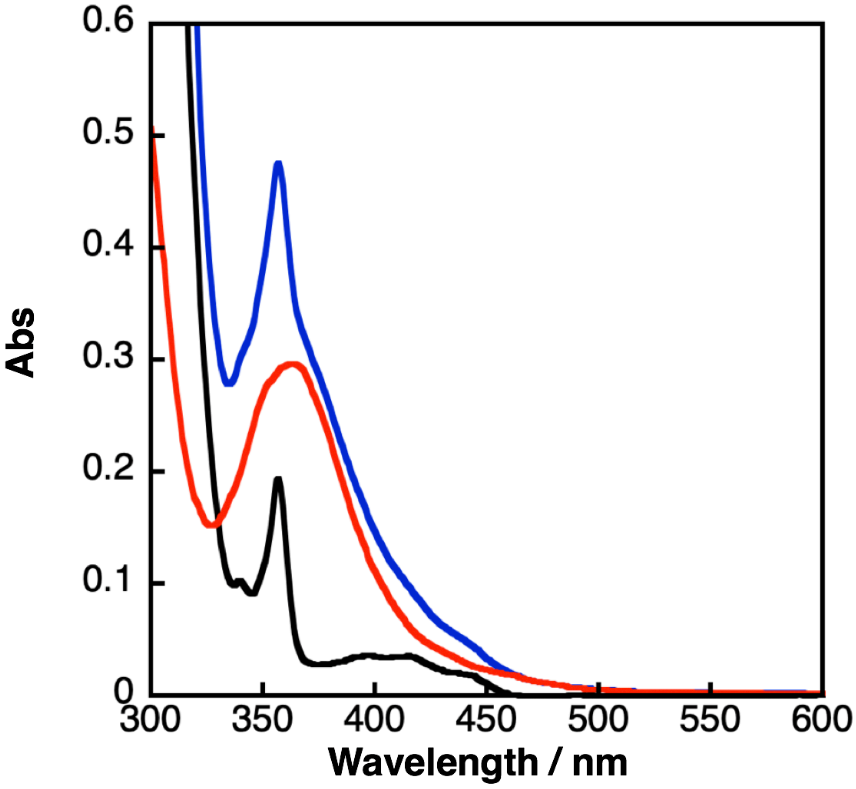


Fig S1. Iodometry titration of H_2O_2 in the resulting solution after 20 min photocatalytic ORR before (a black line) and after addition of 0.1 M NaI (a blue line) and the differential spectrum (a red line). Conditions: [H_4DPP^{2+}] = 10 μM, [$AcrH_2$] = 5 mM, [MCA] = 0.1 M, and [O_2] = 0.29 mM in MeCN at 298 K.

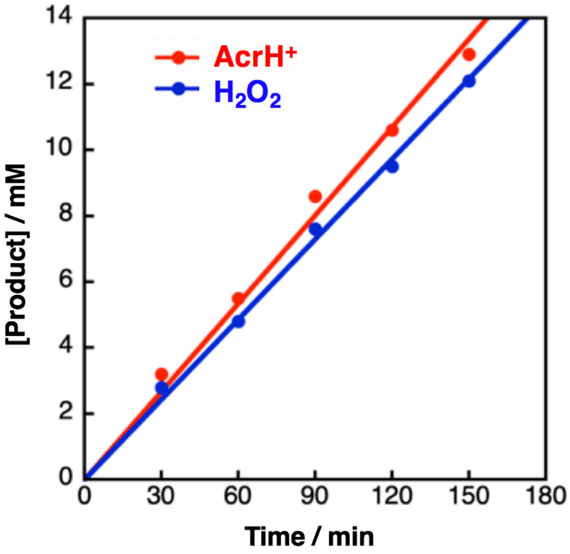


Fig S2. Time profiles of [$AcrH^+$] and [H_2O_2] during photocatalytic ORR. Conditions: H_4DPP^{2+} (10 μM), $AcrH_2$ (50 mM), and MCA (0.1 M) in O_2-saturated MeCN at 298 K.

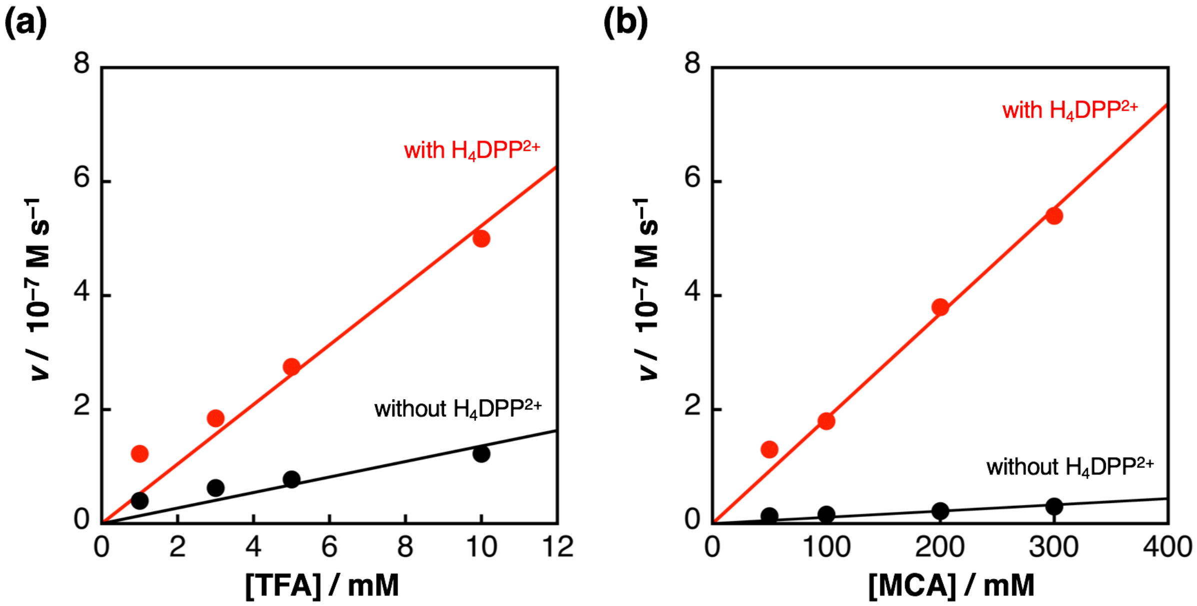


Fig S3. Acid concentration dependence ((a) TFA and (b) MCA) of v values during photocatalytic ORR with or without H_4DPP^{2+} in MeCN containing $AcrH_2$ (5 mM) and O_2 (0.29 mM) at 298 K.

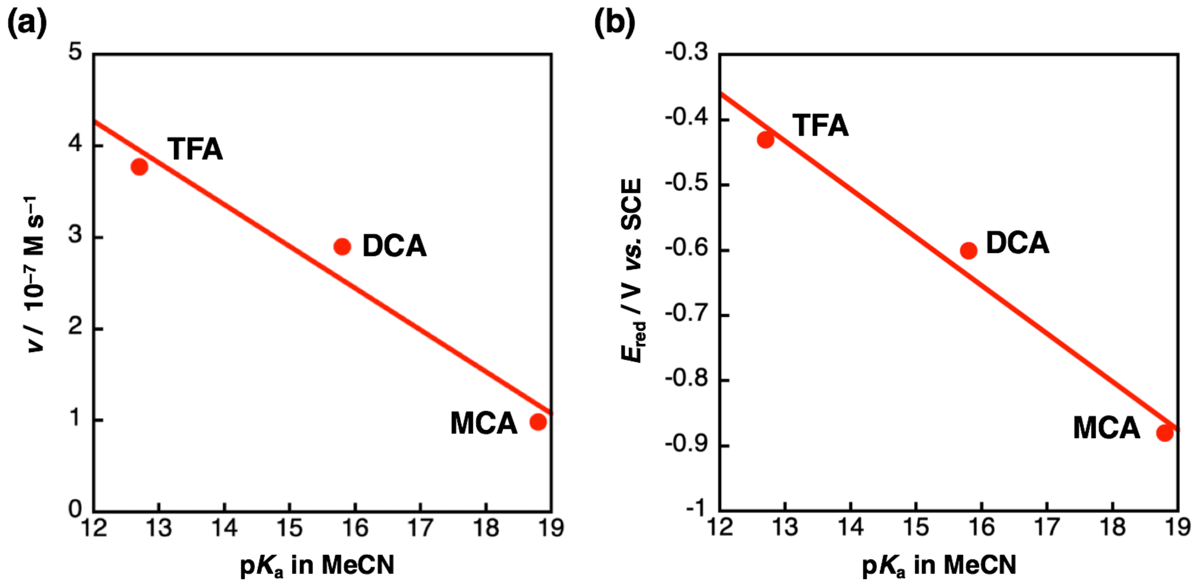


Fig S4. (a) The plots of v values *vs*. pK_a of acids.[5] Conditions: [H_4DPP^{2+}] = 10 μM, [$AcrH_2$] = 5 mM, [acids] = 10 mM, and [O_2] = 0.29 mM in MeCN at 298 K. (b) E_{red} values of O_2 *vs*. pK_a value. Conditions: [acids] = 10 mM, and [O_2] = 0.13 mM in MeCN at 298 K.

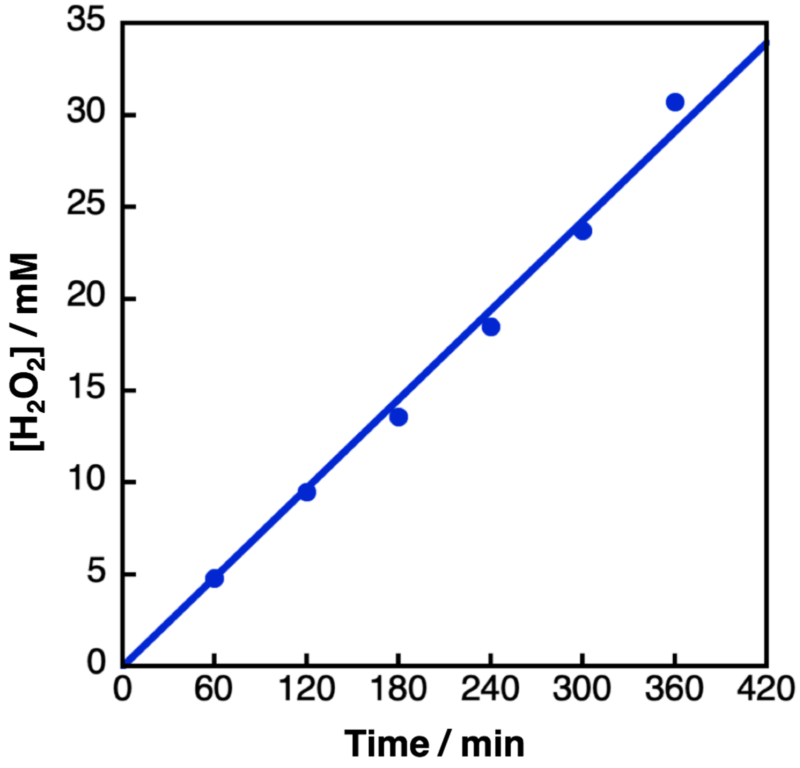


Fig S5. A time profile of [H_2O_2] in photocatalytic ORR. Conditions: [H_4DPP^{2+}] = 10 μM, [$AcrH_2$] = 50 mM, and [MCA] = 0.1 M in O_2-saturated MeCN at 298 K.

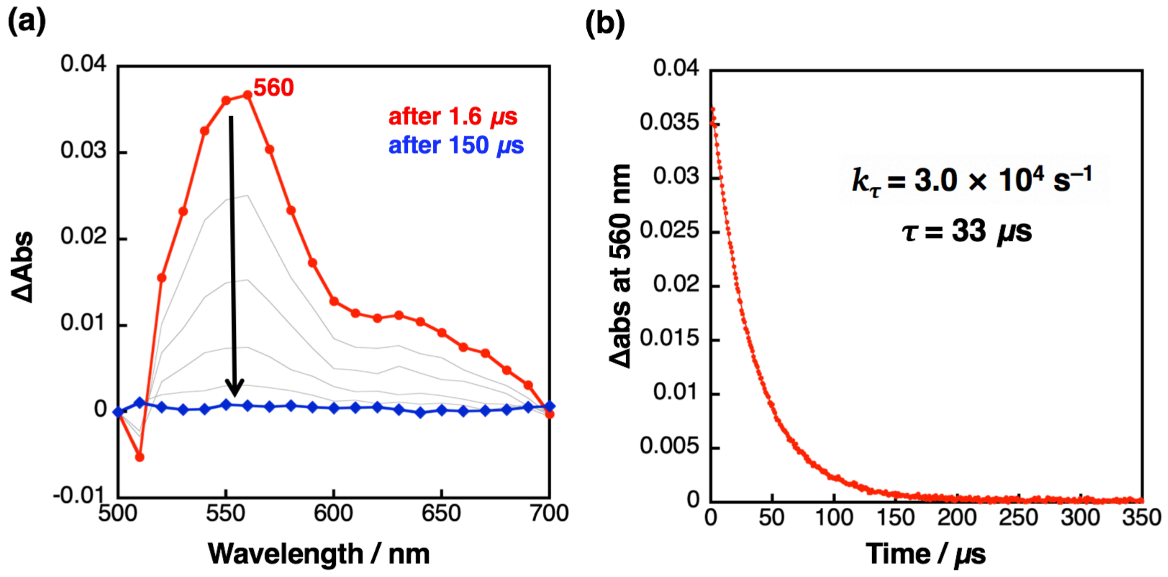


Fig S6. (a) Transient absorption spectra of H_4DPP^{2+} (50 μM) with TFA (0.1 M) in deaerated MeCN at 298 K taken at 1.6 μs (red) and 150 μs (blue) after nano-second laser excitation at 532 nm. (b) The decay time profile at 560 nm.

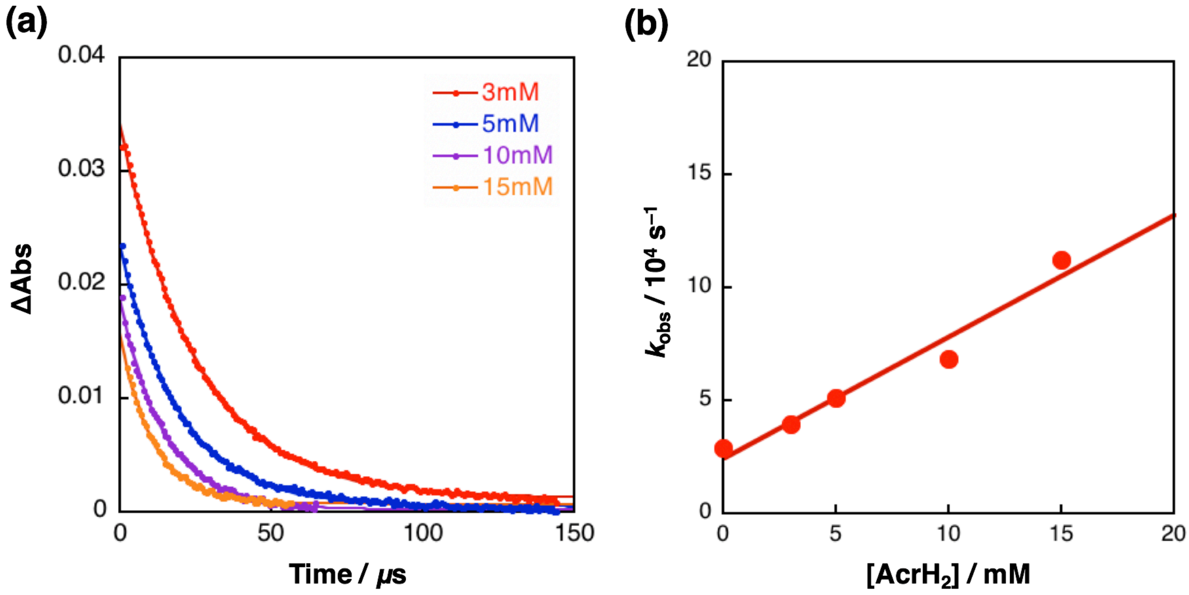


Fig S7. (a) The decay time profiles at 560 nm in the presence of various concentrations of $AcrH_2$ and TFA (0.1 M) in deaerated MeCN at 298 K. (b) A plot of k_{obs} *vs.* [$AcrH_2$].

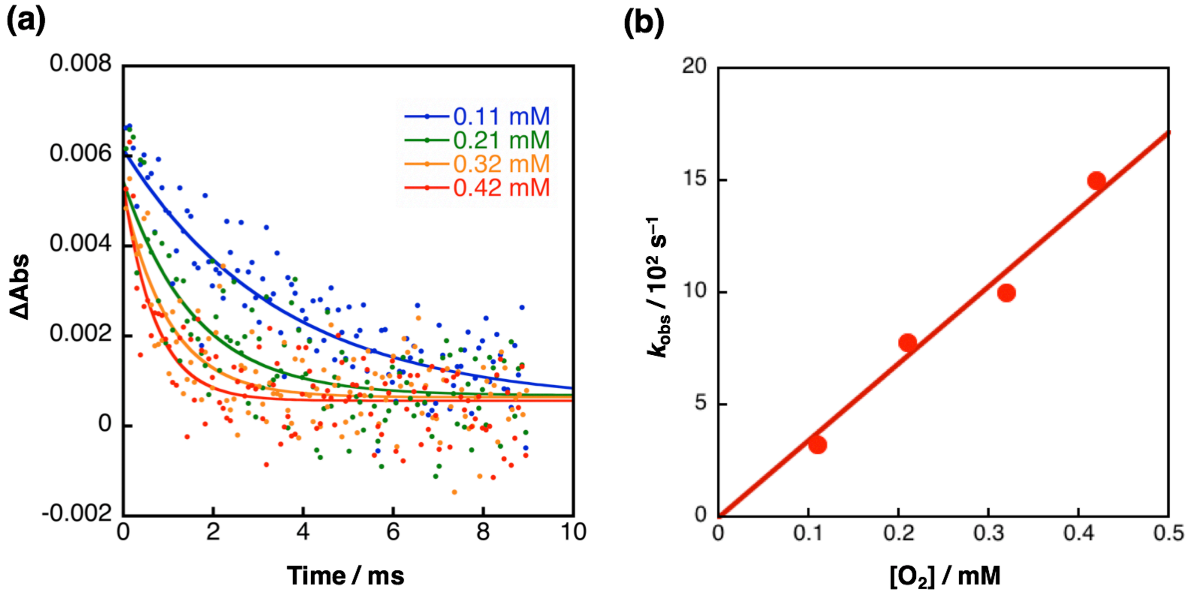


Fig S8. (a) The decay time profiles at 520 nm in the presence of various concentrations of O_2, $AcrH_2$ (15 mM) and TFA (0.1 M) in MeCN at 298 K. (b) A plot of k_{obs} *vs*. [O_2].

References

1 S. Fukuzumi, Y. Tokuda, T. Kitano, T. Okamoto and J. Otera, *J. Am. Chem. Soc.,* 1993, **115**, 8960-8968.

2 C. J. Medforth, M. O. Senge, K. M. Smith, L. D. Sparks and J. A. Shelnutt, *J. Am. Chem. Soc.,* 1992, **114**, 9859-9869.

3 K. Mase, K. Ohkubo and S. Fukuzumi, *J. Am. Chem. Soc.,* 2013, **135**, 2800-2808.

4 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A* 1956, **235**, 518-536.

5 K. Izutsu, in *Acid–Base Dissociation Constants in Dipolar Aprotic Solvents*, Blackwell Scientific Publications, Oxford, 1990.