

## Electronic Supporting Information

### **Photocatalytic production of hydrogen peroxide by two-electron reduction of dioxygen with carbon-neutral oxalate using 2-phenyl-4-(1-naphthyl)-quinolinium ion as a robust photocatalyst**

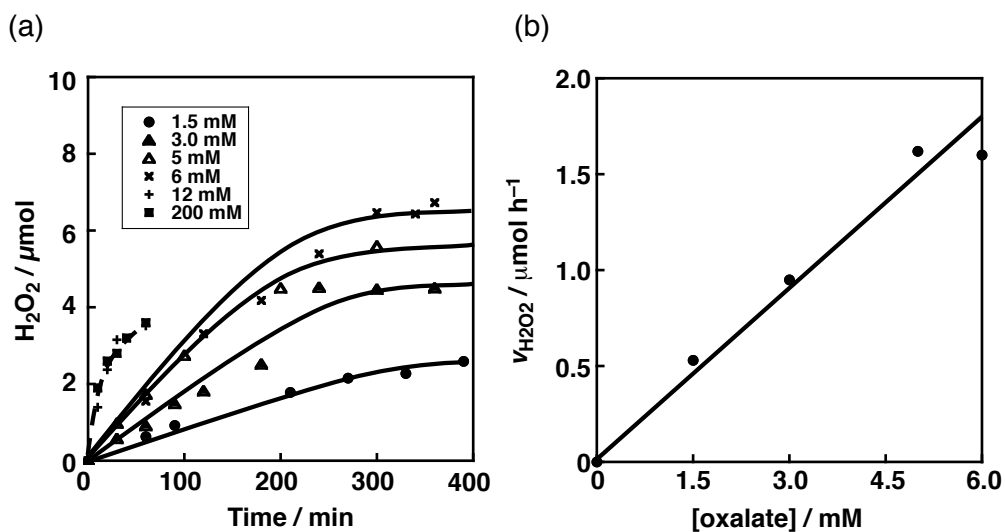
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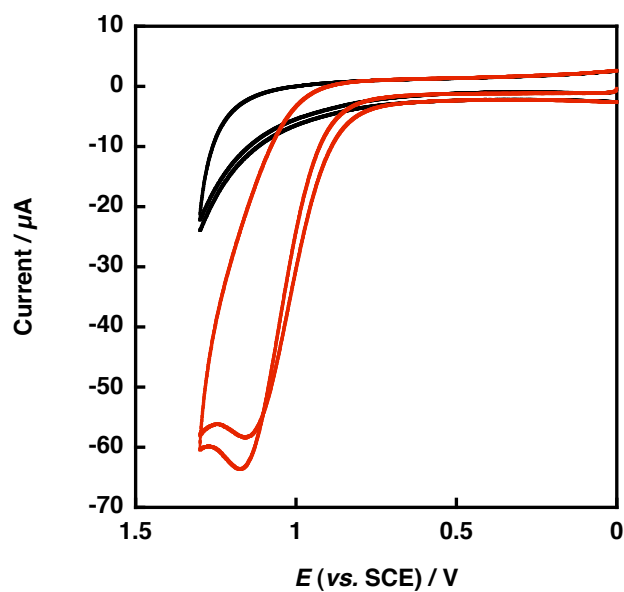
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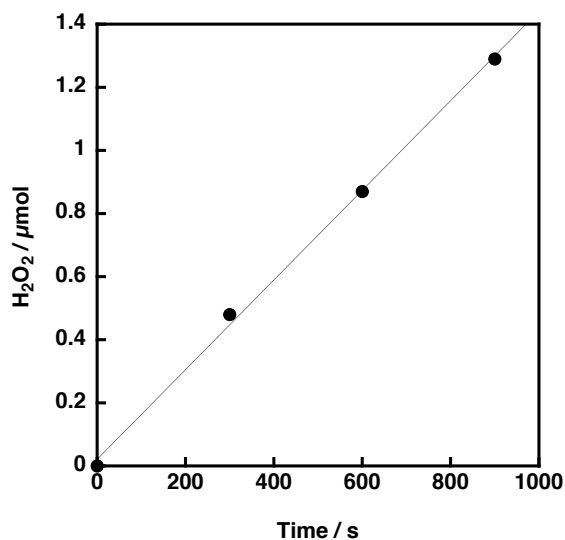
E-mail: fukuzumi@chem.eng.osaka-u.ac.jp



**Fig. S1** (a) Time courses of H<sub>2</sub>O<sub>2</sub> production under photoirradiation of an oxygen-saturated mixed solution of an phosphate buffer (200 mM, pH 7.0 for 1.5-6.0 mM oxalate) or pure water (for 12 mM and 200 mM oxalate) and MeCN [1:1 (v/v)] containing QuPh<sup>+</sup>-NA (0.22 mM) and oxalate (1.5 mM, closed circle; 3.0 mM, closed triangle; 5.0 mM, open triangle; 6.0 mM, x; 12 mM, + and 200 mM, rectangle). (b) H<sub>2</sub>O<sub>2</sub> production rate determined from the initial (90 min) slope of the time courses vs. concentration of oxalate in an oxygen-saturated mixed solution of an aqueous phosphate buffer (200 mM, pH 7.0) and MeCN.

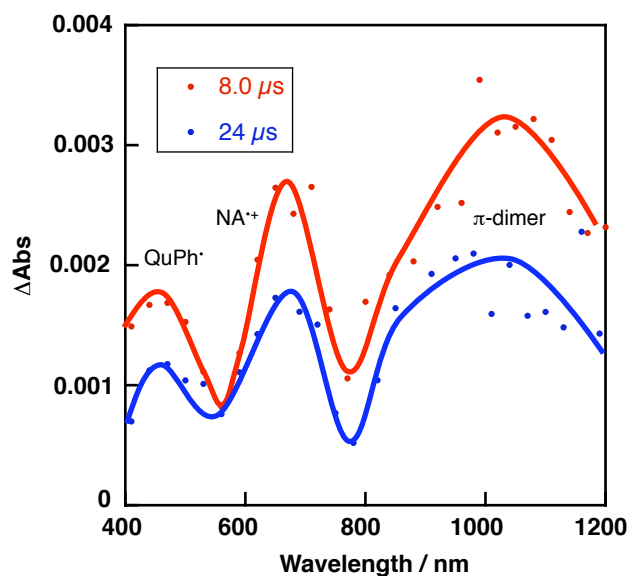


**Fig. S2** Cyclic voltammograms of oxalate in a deaerated mixed solution of a phosphate buffer (200 mM, pH 7.0) and MeCN [1:1 (v/v)]. The concentration of oxalic acid was 0 mM (black) or 2.5 mM (red) and the scan rate was 100 mV/sec.



**Fig. S3** (a) Time courses of hydrogen peroxide production under photoirradiation ( $\lambda = 334$  nm) of an oxygen saturated mixed solution (2.0 mL) of pure water and MeCN [1:1 (v/v)] containing oxalate ions (200 mM) and QuPh<sup>+</sup>-NA (0.0596 mM). The total mole (einstein) number of incident photons was measured by a standard method using an actinometer (potassium ferrioxalate, K<sub>3</sub>[Fe<sup>III</sup>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]) in an aqueous solution at room temperature where photon flux was determined to be  $1.15 \times 10^{-8}$  einstein s<sup>-1</sup>. The absorbance of the solution at 334 nm was 1.028, indicating transmittance of 0.094.

$$\Phi = \{1.42 \times 10^{-9} / (1.15 \times 10^{-8} \times 0.906)\} = 0.136 \text{ (0.14)}$$



**Fig. S4** Transient absorption spectra of QuPh<sup>+</sup>-NA (0.056 mM) in a mixed solution of a deaerated phosphate buffer (pH 7.0) and MeCN [1:1 (v/v)] at 298 K taken at 8.0  $\mu s$  (red) and 24  $\mu s$  (blue) after nanosecond laser excitation at 355 nm in the presence of oxygen (0.024 mM).

**Comment:** The absorption ascribed to NA<sup>+</sup> moiety decayed depending on the time perhaps due to back electron transfer from O<sub>2</sub><sup>•-</sup> to NA<sup>+</sup>.