# Electronic Supplementary Information

# Photocatalytic oxidation of benzene to phenol using dioxygen as an oxygen source and water as an electron source in the presence of a cobalt catalyst

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**Table S1** Stern-Volmer quenching constants ($K_{SV}$), exited state lifetimes ($\tau_0$) in the absence of quencher, and rate constants ($k_{et}$) of photoinduced electron transfer from $[Ru^{II}(Me_2phen)_3]^{2+}*$ to $O_2$ in the absence and presence of $Sc(NO_3)_3$ (100 mM) in a solvent mixture of MeCN and $H_2O$ ($v/v$ = 23:2) at 273 K.

|  | without $Sc(NO_3)_3$ | with $Sc(NO_3)_3$ |
|---|---|---|
| $K_{SV}$[a] | $8.2(6) \times 10^2$ $M^{-1}$ | $1.1(1) \times 10^3$ $M^{-1}$ |
| $\tau_0$ | $7.6(6) \times 10^{-7}$ s | $7.1(6) \times 10^{-7}$ s |
| $k_{et}$[b] | $1.1(1) \times 10^9$ $M^{-1}$ $s^{-1}$ | $1.5(1) \times 10^9$ $M^{-1}$ $s^{-1}$ |

[a] The Stern-Volmer quenching constant ($K_{SV}$) was obtained from the slope of the Stern-Volmer plot, $I_0/I - 1$ *vs.* $[O_2]$ (see Figure S5c). Stern-Volmer equation is $I_0/I = 1 + K_{SV}[Q]$, where $I_0$ and $I$ are the emission intensities observed in the absence and presence of quencher, Q.

[b] $K_{SV} = k_q \times \tau_0$, where $k_q$ is bimolecular quenching rate constant and $\tau_0$ is the exited state lifetime in the absence of quencher. Therefore, the observed rate constants ($k_{et}$) were obtained from the $K_{SV}$ and the emission lifetime ($\tau_0$) (*i.e.*, $k_{et} = K_{SV} / \tau_0$).

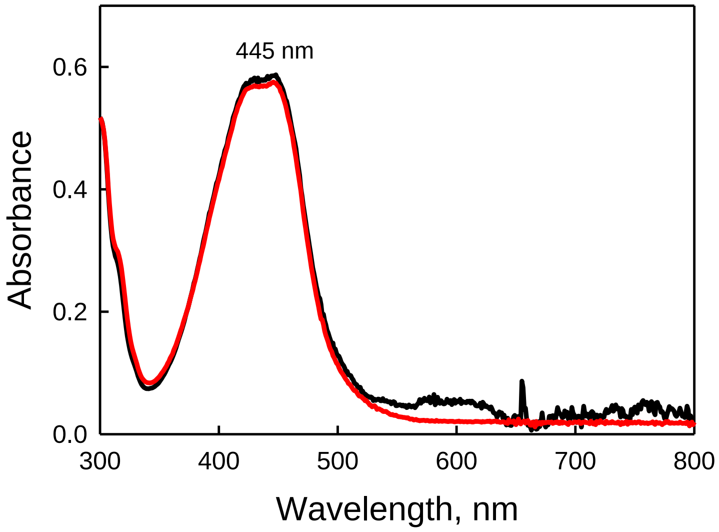

**Fig. S1** UV-visible absorption spectra of the 50 times diluted reaction solution [before reaction (black line) and after reaction for 15 h (red line)] obtained in the photocatalytic oxidation of benzene under photoirradiation (white light) of an $O_2$-saturated solvent mixture of MeCN and $H_2O$ (*v*/*v* = 23:2) containing **1** (0.10 mM), $[Ru^{II}(Me_2phen)_3]^{2+}$ (1.0 mM), $Sc(NO_3)_3$ (100 mM), and benzene (1.0 mM) at 298 K.

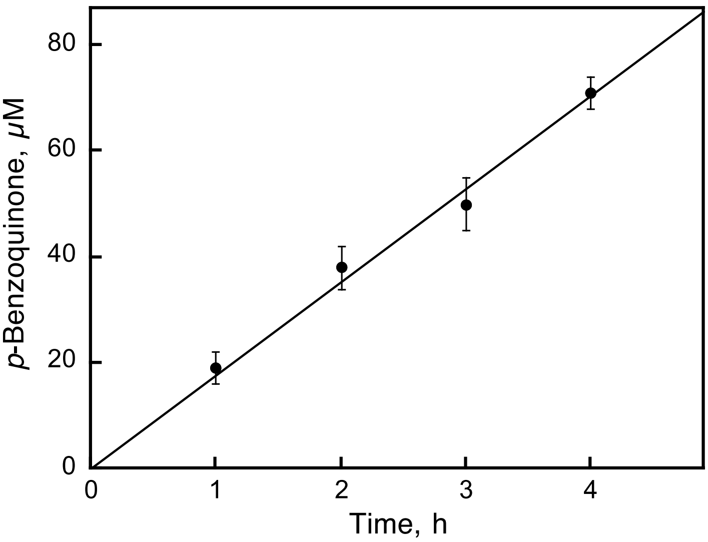

**Fig. S2** Time course of concentration of *p*-benzoquinone produced in the photocatalytic oxidation of phenol (PhOH) by $O_2$ under photoirradiation (white light) of an $O_2$-saturated solvent mixture of MeCN and $H_2O$ ($v/v$ = 23:2) containing **1** (1.0 μM), $[Ru^{II}(Me_2phen)_3]^{2+}$ (1.0 mM), $Sc(NO_3)_3$ (100 mM), and PhOH (1.0 mM) at 298 K.

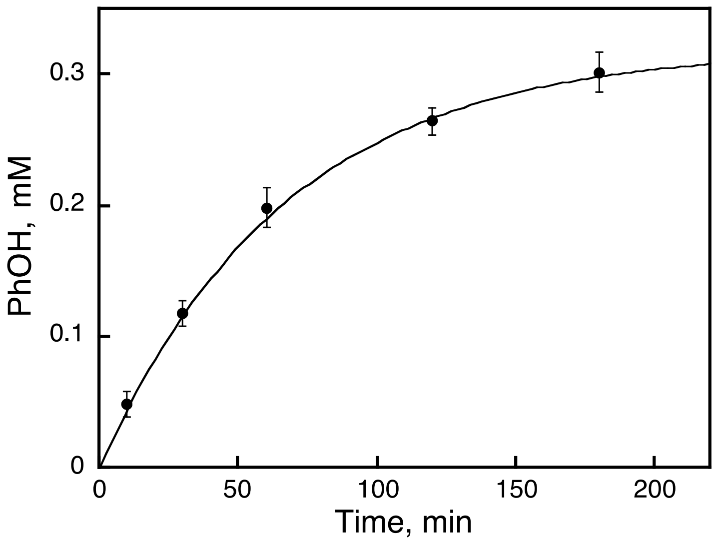

**Fig. S3** Time course of concentration of PhOH produced in the photocatalytic oxidation of benzene under photoirradiation ($\lambda$ = 440 nm with filter) of an $O_2$-saturated solvent mixture of MeCN and $H_2O$ ($v/v$ = 23:2) containing **1** (1.0 mM), $[Ru^{II}(Me_2phen)_3]^{2+}$ (1.0 mM), $Sc(NO_3)_3$ (100 mM), and benzene (2.0 M) at 298 K.

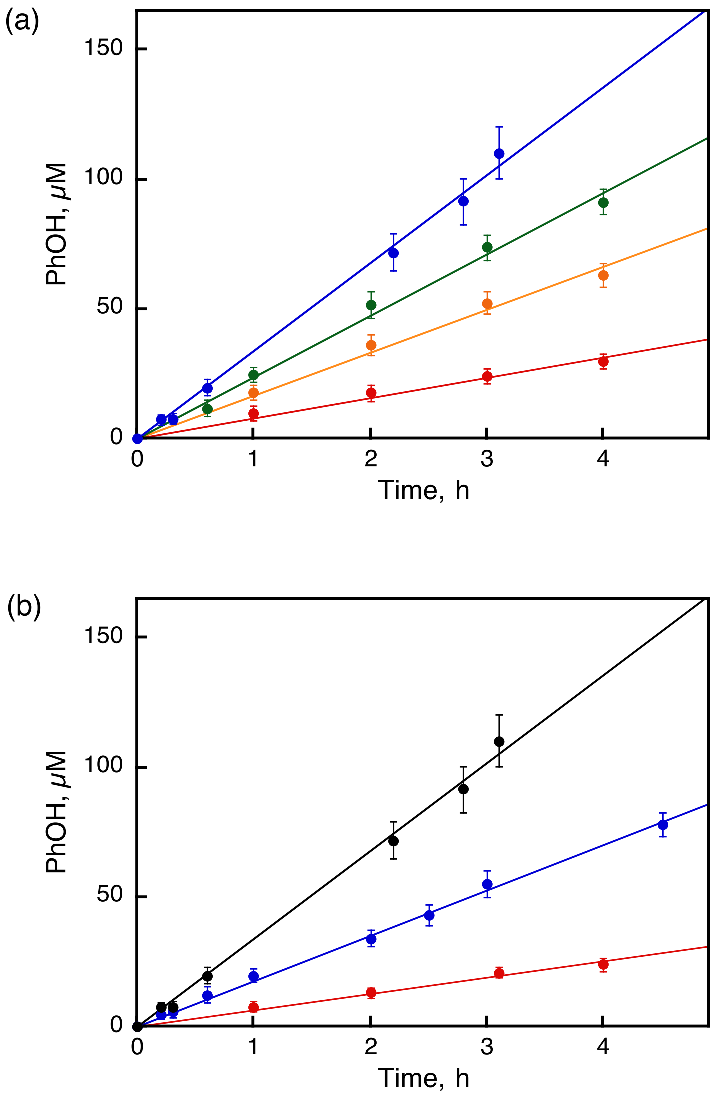

**Fig. S4** (a) Time courses of concentration of PhOH produced in the photocatalytic oxidation of benzene under photoirradiation (white light) of an $O_2$-saturated solvent mixture of MeCN and $H_2O$ (*v*/*v* = 23:2) containing **1** (1.0 μM), $[Ru^{II}(Me_2phen)_3]^{2+}$ (1.0 mM), and benzene [0.25 M (red), 0.50 M (orange), 0.75 M (green), and 1.0 M (blue)] in the presence of $Sc(NO_3)_3$ (100 mM) at 298 K. (b) Time courses of concentration of PhOH produced in the photocatalytic oxidation of benzene under photoirradiation (white light) of an $O_2$-saturated solvent mixture of MeCN and $H_2O$ (*v*/*v* = 23:2) containing **1** (1.0 μM), $[Ru^{II}(Me_2phen)_3]^{2+}$ [0.10 mM (red), 0.50 mM (blue), and 1.0 mM (black)], and benzene (1.0 M) in the presence of $Sc(NO_3)_3$ (100 mM) at 298 K.

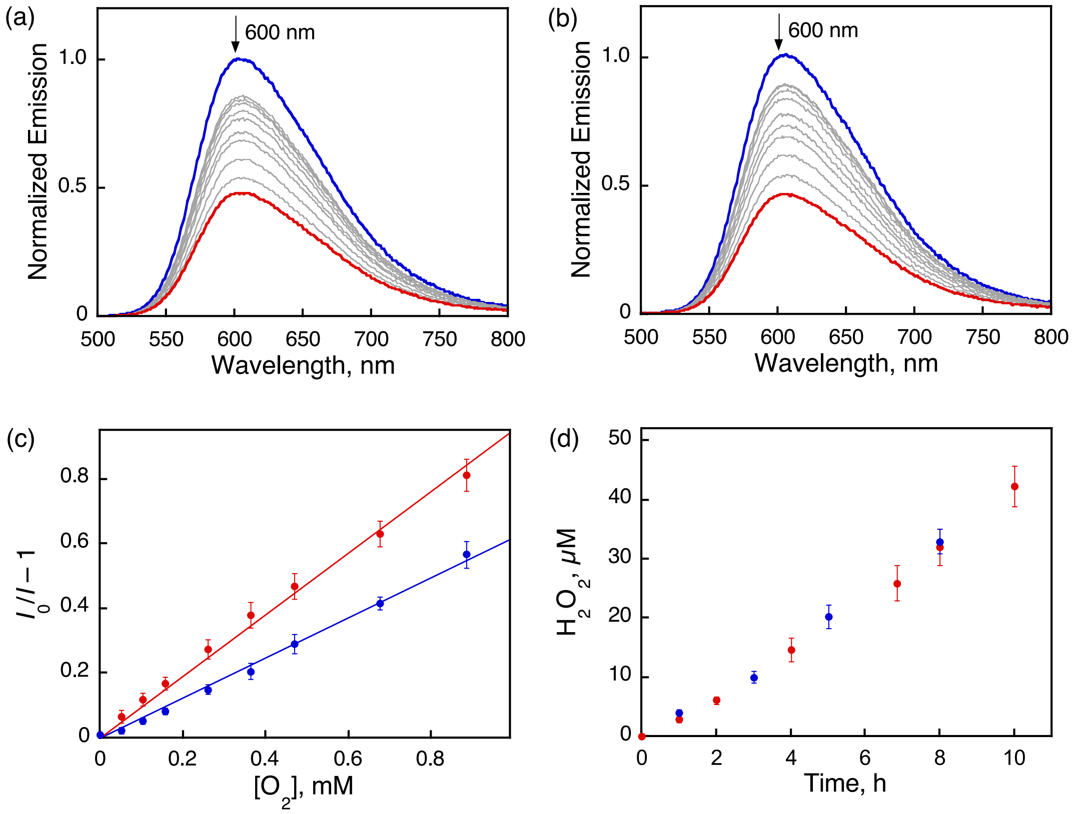

**Fig. S5** (a, b) Emission spectra of $[Ru^{II}(Me_2phen)_3]^{2+}$ (4.0 μM) in the presence of $O_2$ [0 mM (blue) – 1.2 mM (red)] observed under visible light excitation ($\lambda$ = 450 nm) of an $O_2$-saturated solvent mixture of MeCN and $H_2O$ (*v*/*v* = 23:2) containing $[Ru^{II}(Me_2phen)_3]^{2+}$ (4.0 μM) in the absence (a) and presence (b) of $Sc(NO_3)_3$ (100 mM) at 298 K. (c) Stern-Volmer plots for the emission quenching of $[Ru^{II}(Me_2phen)_3]^{2+}$ by $O_2$ determined from emission spectra in the absence (blue) and presence (red) of $Sc(NO_3)_3$ (100 mM) at 298 K. (d) Time courses of concentration of $H_2O_2$ produced from $H_2O$ and $O_2$ for the photocatalytic oxidation of $[Ru^{II}(Me_2phen)_3]^{2+}$ under photoirradiation (white light) of an air-saturated (blue) and $O_2$-satured (red) solvent mixture of MeCN and $H_2O$ (*v*/*v* = 23:2) containing $[Ru^{II}(Me_2phen)_3]^{2+}$ (100 μM) in the presence of $Sc(NO_3)_3$ (100 mM) at 298 K.

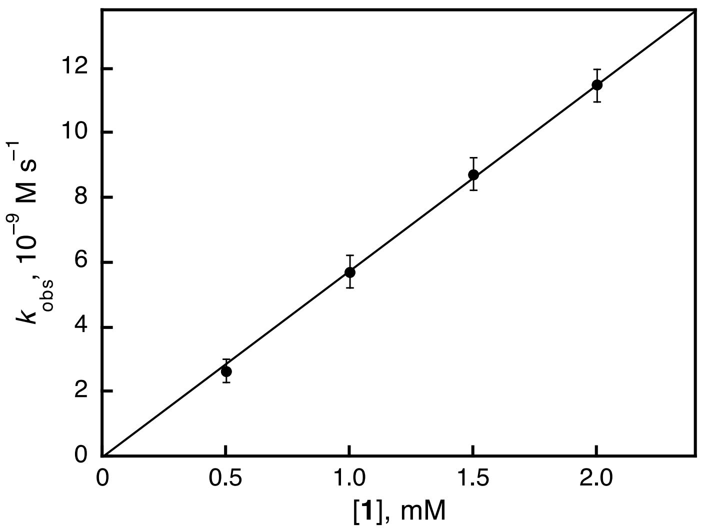

**Fig. S6** Plot of the zeroth-order rate constants ($k_{obs}$) for the $H_2O_2$ production *vs.* the concentration of **1** in the photocatalytic oxidation of $H_2O$ by $O_2$ upon photoirradiation (white light) of an $O_2$-saturated solvent mixture of MeCN and $H_2O$ (*v*/*v* = 23:2) containing **1** (0.50 – 2.0 mM) and $[Ru^{II}(Me_2phen)_3]^{2+}$ (0.10 mM) in the presence of $Sc(NO_3)_3$ (100 mM) at 298 K.

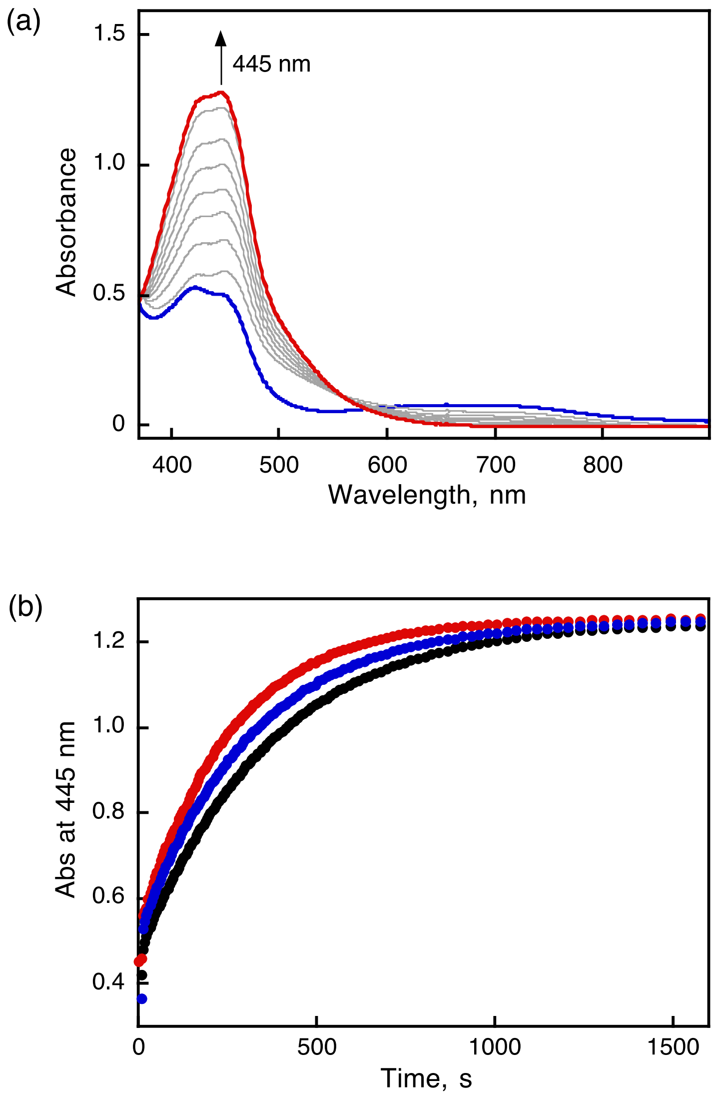

**Fig. S7** (a) Visible spectral change observed in the oxidation of $H_2O$ by $[Ru^{III}(Me_2phen)_3]^{3+}$ (50 μM, blue line) with **1** (0.20 mM) in the presence of $Sc(NO_3)_3$ (100 mM) in a solvent mixture of MeCN and $H_2O$ (*v*/*v* = 23:2) at 298 K. (b) Time courses monitored for the change of absorbance at 445 nm due to the formation of $[Ru^{II}(Me_2phen)_3]^{2+}$ observed in the oxidation of $H_2O$ by $[Ru^{III}(Me_2phen)_3]^{3+}$ (50 μM) with **1** [0.20 mM (black), 0.40 mM (blue), and 0.60 mM (red)] in the presence of $Sc(NO_3)_3$ (100 mM) in a solvent mixture of MeCN and $H_2O$ (*v*/*v* = 23:2) at 298 K.

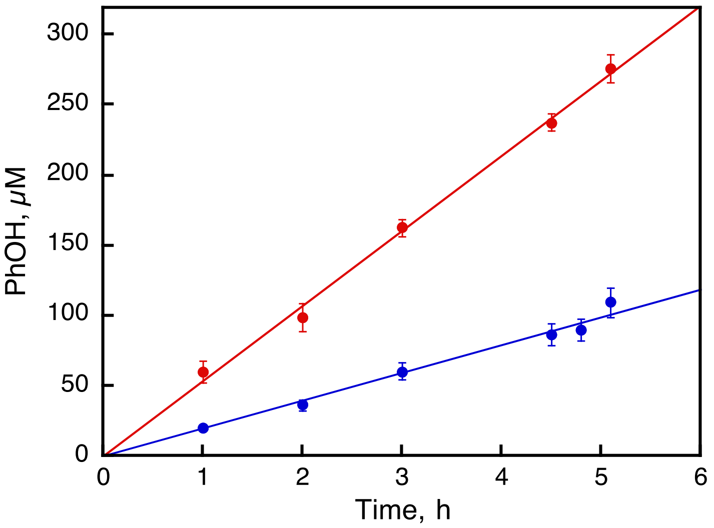

**Fig. S8** Time courses of concentration of PhOH produced in the hydroxylation of benzene (1.0 M) by $H_2O_2$ [100 mM (blue) and 200 mM (red)] with a catalytic amount of **1** (1.0 µM) in an $O_2$-saturated solvent mixture of MeCN and $H_2O$ (*v*/*v* = 23:2) at 298 K.