Supporting information

Production of hydrogen peroxide as a sustainable solar fuel from water and dioxygen

Satoshi Kato,[a] Jieun Jung,[a] Tomoyoshi Suenobu[a] and Shunichi Fukuzumi*[a,b]

[a] *Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan*

[b] *Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea*

*To whom correspondence should be addressed.
E-mail: fukuzumi@chem.eng.osaka-u.ac.jp

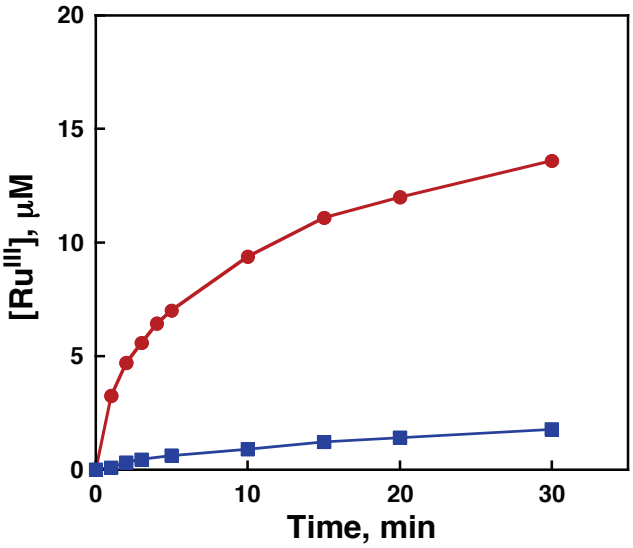

Fig. S1 Time courses of ruthenium(III) complex generation under irradiation of a ruthenium(II) complex (20 μM), i.e., $[Ru^{II}(Me_2phen)_3]^{2+}$ (red circle) or $[Ru^{II}(bpy)_3]^{2+}$ (blue square) with visible light (λ = 450 nm) in an O_2-saturated H_2SO_4 aqueous solution (2.0 M, 3.0 mL, $[O_2]$ = 1.2 mM).

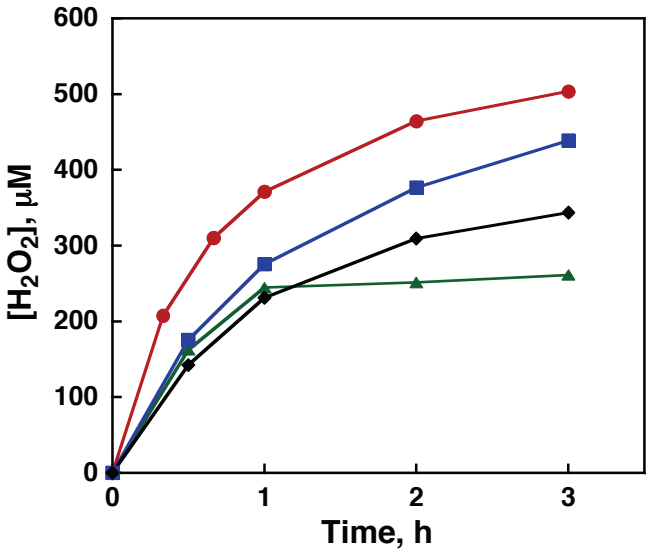

Fig. S2 Time courses of H_2O_2 production at different concentrations of H_2SO_4 [3.0 M (green triangle), 2.0 M (red circle), 1.0 M (blue square) and 0.5 M (black diamond)] under visible light (λ > 420 nm) irradiation of $[Ru^{II}(Me_2phen)_3]^{2+}$ (20 μM) in the presence of $Ir(OH)_3$ (3.0 mg) in an O_2-saturated H_2SO_4 aqueous solution (3.0 mL, $[O_2]$ = 1.2 mM).

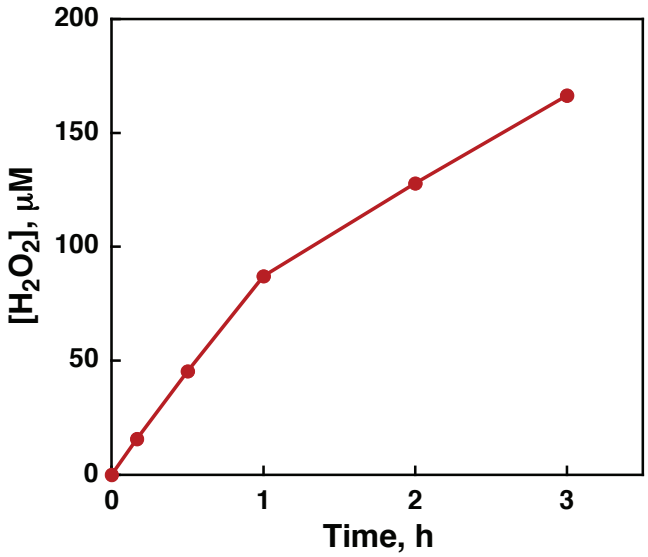

Fig. S3 Time course of H_2O_2 production under visible light (λ = 450 nm) irradiation of $[Ru^{II}(Me_2phen)_3]^{2+}$ (20 μM) in the presence of $Ir(OH)_3$ (3.0 mg) in an O_2-saturated H_2SO_4 aqueous solution (2.0 M, 3.0 mL, $[O_2]$ = 1.2 mM).

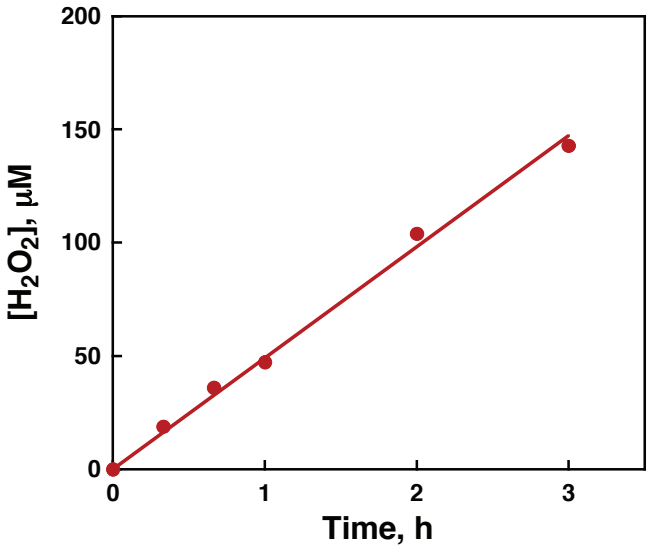

Fig. S4 Time course of H_2O_2 production under visible light (λ = 450 nm) irradiation of $[Ru^{II}(Me_2phen)_3]^{2+}$ (20 μM) in the presence of $Ir(OH)_3$ (3.0 mg) and $Sc(NO_3)_3$ (100 mM) in O_2-saturated H_2O (3.0 mL, $[O_2]$ = 1.2 mM).

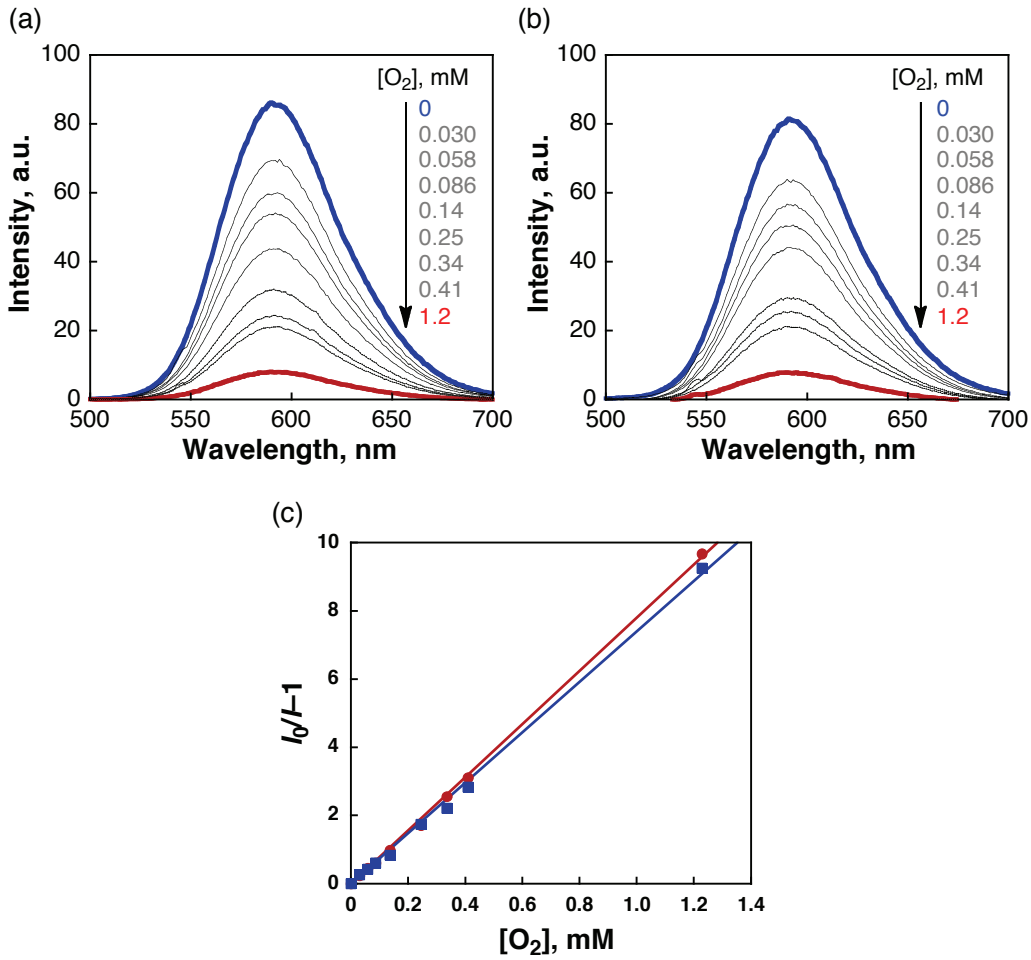

Fig. S5 Emission spectra of $[Ru^{II}(Me_2phen)_3]^{2+}$ (20 μM) in the absence and presence of O_2 (blue: 0 mM and red: 1.2 mM) taken in H_2O under irradiation of monochromatised light at λ = 450 nm (a) in the absence of $Sc(NO_3)_3$ and (b) in the presence of $Sc(NO_3)_3$ (10 mM). (c) Stern-Volmer plots for the emission quenching of $[Ru^{II}(Me_2phen)_3]^{2+}$ by O_2 in H_2O in the absence of $Sc(NO_3)_3$ (red circle) and in the presence of $Sc(NO_3)_3$ (10 mM) (blue square).

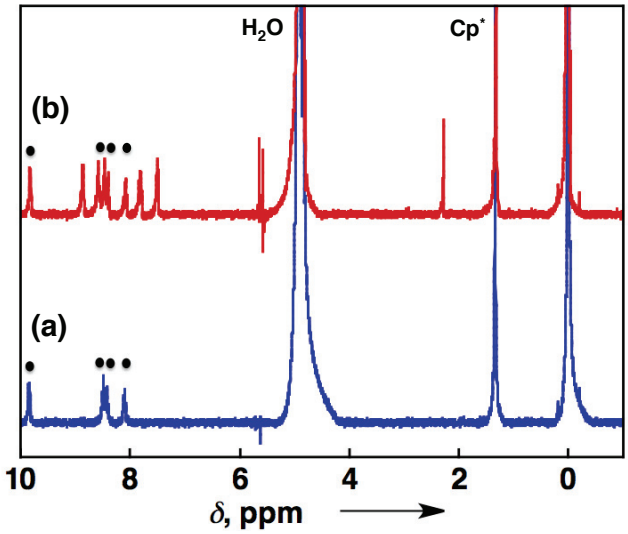

Fig. S6 ^{1}H NMR spectra of (a) an aqueous solution containing $[Co^{III}(Cp^{*})(bpy)(H_2O)]^{2+}$ (4.0 mM), $[Ru^{II}(Me_2phen)_3]^{2+}$ (20 μM) and $Sc(NO_3)_3$ (10 mM) in the dark and (b) after visible light ($\lambda > 420$ nm) irradiation of the solution for 3 h. Black circles indicate bpy signals of $[Co^{III}(Cp^{*})(bpy)(H_2O)]^{2+}$ in D_2O.

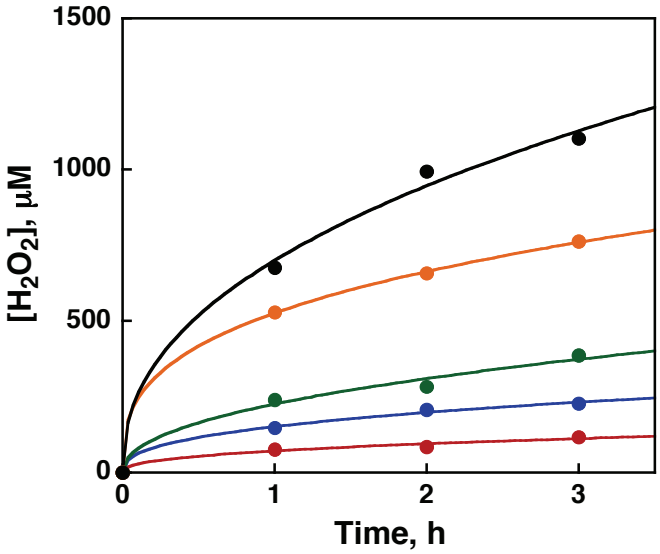

Fig. S7 Time courses of H_2O_2 production at different concentrations of $[Co^{III}(Cp^*)(bpy)(H_2O)]^{2+}$ [0.1 mM (red line), 0.5 mM (blue line), 1.0 mM (green line), 4.0 mM (orange line) and 10 mM (black line)] under irradiation of $[Ru^{II}(Me_2phen)_3]^{2+}$ (20 μM) with visible light ($\lambda > 420$ nm) in the presence of $[Co^{III}(Cp^*)(bpy)(H_2O)]^{2+}$ and $Sc(NO_3)_3$ (100 mM) in O_2-saturated H_2O (3.0 mL, $[O_2] = 1.2$ mM).

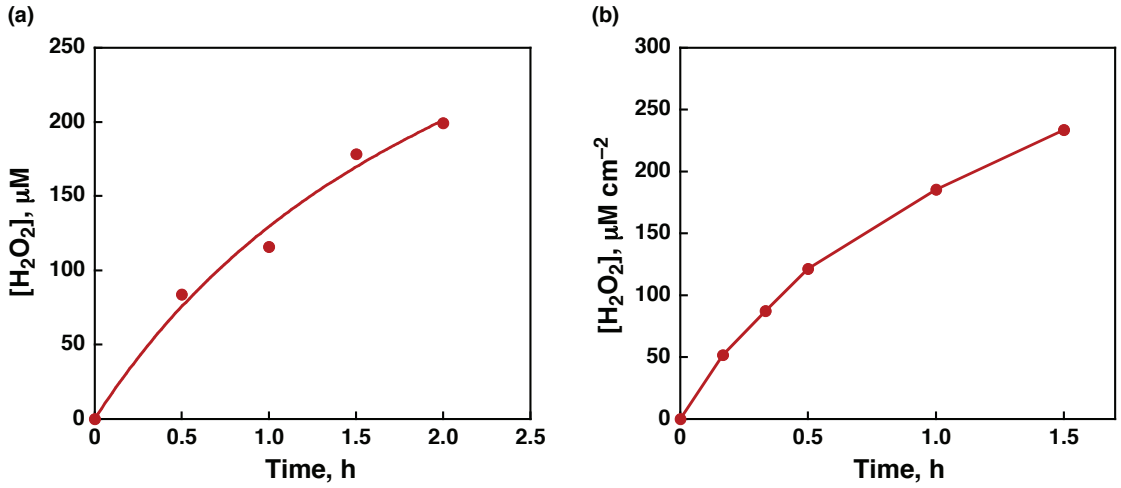

Fig. S8 (a) Time course of H_2O_2 production under visible light (λ = 450 nm) irradiation of $[Ru^{II}(Me_2phen)_3]^{2+}$ (20 μM) in the presence of $[Co^{III}(Cp^*)(bpy)(H_2O)]^{2+}$ (10 mM) and $Sc(NO_3)_3$ (100 mM) in O_2-saturated H_2O (3.0 mL, $[O_2]$ = 1.2 mM). (b) Time course of H_2O_2 production under photoirradiation of $[Ru^{II}(Me_2phen)_3]^{2+}$ (100 μM) in the presence of $[Co^{III}(Cp^*)(bpy)(H_2O)]^{2+}$ (10 mM) and $Sc(NO_3)_3$ (100 mM) in O_2-saturated H_2O (3.0 mL, $[O_2]$ = 1.2 mM). A solar simulator was used as the light source. The light intensity was adjusted to 10 mJ cm^{-2} s^{-1} (AM1.5) at the sample position for whole irradiation area (1.0 × 3.0 cm^2).

Table S1 BET surface area of $Ir(OH)_3$ and commercially available IrO_2

	$Ir(OH)_3$	IrO_2
BET, $m^2\ g^{-1}$	22.1	0.8

Table S2 Dependence of the quantum yield of the generation of $[Ru^{III}(Me_2phen)_3]^{3+}$ on the concentration of H_2SO_4 under irradiation of $[Ru^{II}(Me_2phen)_3]^{2+}$ (20 μM) with visible light (λ = 450 nm) in an O_2-saturated H_2SO_4 aqueous solution (3.0 mL, $[O_2]$ = 1.2 mM) for 1 min

$[H_2SO_4]$, M	Quantum yield, %
4.0	72
3.0	47
2.0	21
1.0	4.9

Table S3 Rate constants (k_{et}) of photoinduced electron transfer from $[Ru^{II}(Me_2phen)_3]^{2+*}$ to O_2 in H_2O in the absence and presence of $Sc(NO_3)_3$

$[Sc(NO_3)_3]$, mM	k_{et}, $M^{-1}\ s^{-1}$
0	6.1×10^9
10	6.3×10^9