Electronic Supplementary Information for

Water-soluble mononuclear cobalt complexes with organic ligands acting as precatalysts for efficient photocatalytic water oxidation

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Synthesis of Tris(*N, N'*-(dimethylamino)ethyl)amine (Me_6tren). Me_6tren was prepared according the reported procedure.[S1] ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.16 ppm (s, 18H), 2.30 (m, 6 H), 2.54 (m, 6 H).

Synthesis of [Co(Me_6tren)(OH_2)](ClO_4)$_2$ (1). $Co(ClO_4)_2 \cdot 6H_2O$ (1.83 g) was dissolved in a 30 mL of CH_3CN solution containing Me_6tren (1.15 g). The solution was stirred for 2 h at room temperature. Et_2O (150 mL) was added to the mixture to yield pale purple precipitate, which was filtered and dried *in vacuo*. The purple powder was recrystallized from CH_3CN-Et_2O. Yield: 72% (1.89 g). ESI-MS in CH_3CN: *m*/*z* 342.2 for $[Co(Me_6tren)Cl]^+$ and *m*/*z* 388.1 for $[Co(Me_6tren)(ClO_4)]^+$.

Synthesis of [Co(Cp*)(bpy)(OH_2)](PF_6)$_2$ (2). Pentamethylcyclopentadiene (Cp*, 25 mL) and *tert*-butyllithium (~1.7 M in *n*-pentane, 90 mL) were combined in an equimolar amount (1:1) in *n*-pentane at 203 K. The solution was stirred and slowly allowed to warm up to room temperature. After stirring for further 24 h at room temperature, a white suspension was filtered as pentamethylcyclopentadienyllithium (Cp*Li) by an inert gas frit. The anhydrous $CoCl_2$ (1.32 g) was added to the solution of Cp*Li (1.42 g) in 20 mL of tetrahydrofuran. The mixture was stirred for 3 h at room temperature until the brown solution became green-brown. Afterwards the solution was concentrated to a smaller volume under reduced pressure and extracted with 100 mL of *n*-pentane. The brown extractions were bubbled by CO gas for 30 min through the solution. Di-μ-chloro-bis[chloro(pentamethylcyclopentadienyl)cobalt] ([(μ-Cl)(CoCp*Cl)]$_2$) was obtained as green powder. The [(μ-Cl)(CoCp*Cl)]$_2$ (100 mg) in 20 mL of water was stirred with the stoichiometric amount of $AgPF_6$ (191 mg) for 4 h at the room temperature. After filtering off AgCl as precipitates, 2,2'-bipyridine (65 mg) was added to the filtrate. The reaction was completed in 15 min at 313 K. An aqueous solution of NH_4PF_6 was added to the reaction solution to obtain crystalline product. ^{1}H-NMR (300 MHz, D_2O): δ = 1.27 ppm (s, 15H), 8.04 (t, 2 H), 8.36 (t, 2 H), 8.44 (d, 2 H), 9.78 (d, 2 H).

Isotope-Labelling Experiments

An $H_2{}^{18}O$ (44.9% ^{18}O) solution of phosphate buffer (25 mM, pH 8.0) containing **1** (50 mM), $[Ru(bpy)_3](ClO_4)_2$ (0.25 mM) and $Na_2S_2O_8$ (5.0 mM) was irradiated by a Xe lamp (*l* > 420 nm) in a vial sealed with a rubber septum after bubbling He gas. After 10 min, a small portion

(50 mL) of the gas in a headspace was sampled by using a gas-tight syringe for gas analysis. The ratio of $^{16}O^{16}O$, $^{16}O^{18}O$ and $^{18}O^{18}O$ was determined based on the intensity of mass spectra (m/z = 32, 34, and 36) obtained by a Shimadzu GC-17A gas chromatograph [He carrier, TC-FFAP column (GL Science, 1010-15242) at 313 K] equipped with a mass spectrometer (Shimadzu, QP-5000).

Reference

S1. M. Ciampoli, and N. Nardi, *Inorg. Chem.* 1966, **5**, 41.

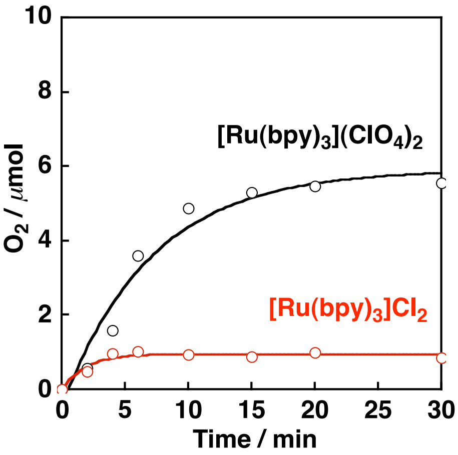

Fig. S1 Time courses of O_2 evolution by using [Ru(bpy)$_3$](ClO$_4$)$_2$ (black, 0.50 mM) or [Ru(bpy)$_3$]Cl$_2$ (red, 0.50 mM) in 2.0 mL of phosphate buffer containing **1** **(**50 μM) and $Na_2S_2O_8$ (10 mM) at initial pH 8.0 to clarify the coexistence effect of Cl$^-$ ion on O_2 evolution.

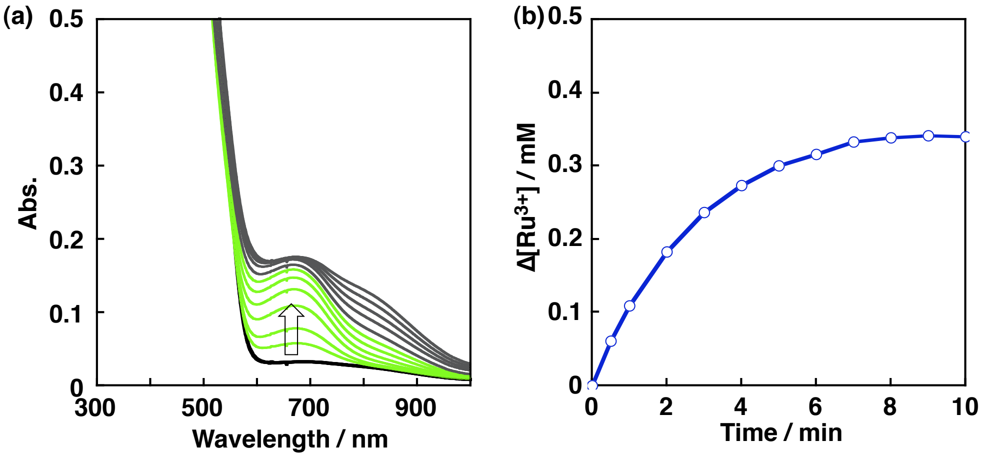

Fig. S2 (a) UV-vis spectral change of [Ru(bpy)$_3$]$^{2+}$ (0.50 mM) to produce [Ru(bpy)$_3$]$^{3+}$ in 2.0 mL of phosphate buffer (50 mM, pH 8) containing with $Na_2S_2O_8$ (10 mM) by photoirradiation with a Xe lamp using a band pass filter (440 – 460 nm). (b) Time course of [Ru(bpy)$_3$]$^{3+}$ concentration under the photoirradiation determined from the absorbance change at 670 nm under the conditions of (a).

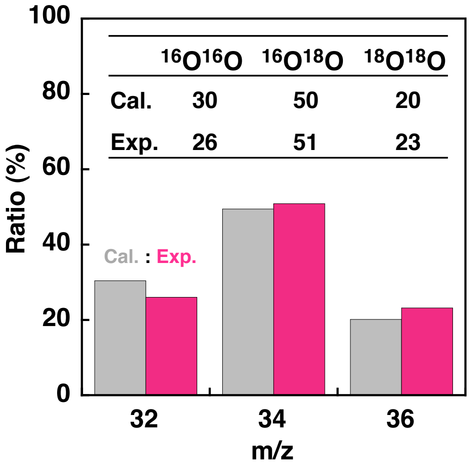

Fig. S3 Comparison of relative abundance of ^{18}O-labelled and unlabelled O_2 evolved in the photocatalytic oxidation of a buffer solution (1.0 mL) prepared with ^{18}O-enriched water (44.9% $H_2{}^{18}O$) containing precatalyst **1** (50 μM), $[Ru(bpy)_3]^{2+}$ (0.50 mM) and $Na_2S_2O_8$ (10 mM) (pink, observed mass intensity; grey, calculated values assuming that evolved O_2 results exclusively from water).

Comments: Isotope-labelling experiments using ^{18}O-enriched water (44.9%) instead of $H_2{}^{16}O$ were conducted with precatalyst **1** to obtain direct evidence for the water oxidation in which the source of evolved O_2 was water [eqn (1)]. After the reaction, evolved O_2 in a headspace of a reaction vial was separated by a gas chromatograph equipped with a molecular sieve column and quantified by a mass spectrometer. Fig. S2 compares the relative mass intensities of ^{18}O-labelled and unlabelled O_2 with calculated intensities assuming that all evolved O_2 molecules derive from water. If O_2 was derived from the ^{18}O-enriched water (44.9%), the ratio of $^{16}O^{16}O$: $^{16}O^{18}O$: $^{18}O^{18}O$ should be 30:50:20. The observed ratio of $^{16}O^{16}O$: $^{16}O^{18}O$: $^{18}O^{18}O$ was indeed 26:51:23, which is virtually the same as the calculated ratio within experimental errors, indicating that evolved O_2 comes exclusively from water.

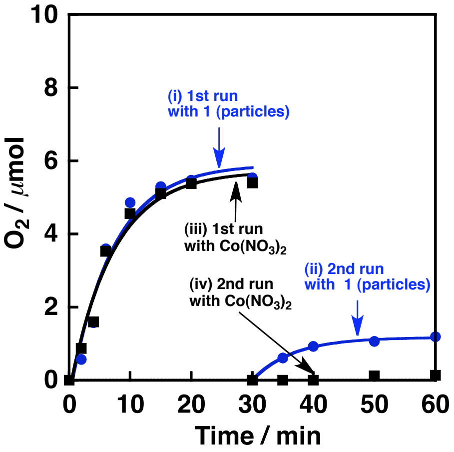

Fig. S4 Time courses of O_2 evolution under photoirradiation (Xe lamp, $\lambda > 420$ nm) of a buffer solution (pH 8.0, 2.0 mL) containing $[Ru(bpy)_3]^{2+}$ (0.50 mM) and $Na_2S_2O_8$ (10 mM) with a precatalyst (i and ii) **1** (50 μM) and (iii and iv) $Co(NO_3)_2$ (50 μM). 2nd runs were performed by adding $Na_2S_2O_8$ (5.0 μmol) to the solutions after 1st run and adjusted pH to 8.0 by NaOH (1M, 40 μL).

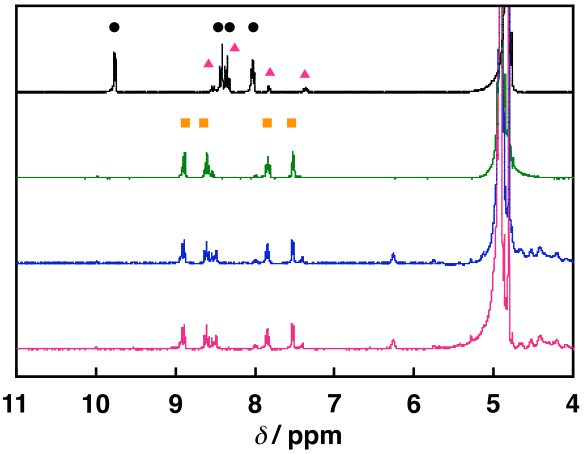

Fig. S5 ^{1}H NMR spectra in a D_2O buffer (pD 10) (a) containing 2 (2.0 mM) with $[Ru(bpy)_3]^{2+}$ (0.20 mM) and $Na_2S_2O_8$ (10 mM), (b) after photoirradiation of the solution for 30 min, (c) with addition of NADH (1.0 mM) to the photoirradiated solution and (d) after exposure of the solution containing NADH to air for 1 h (black circles, bpy of **2**; pink triangles, bpy from $[Ru(bpy)_3]^{2+}$; yellow squares, free bpy).

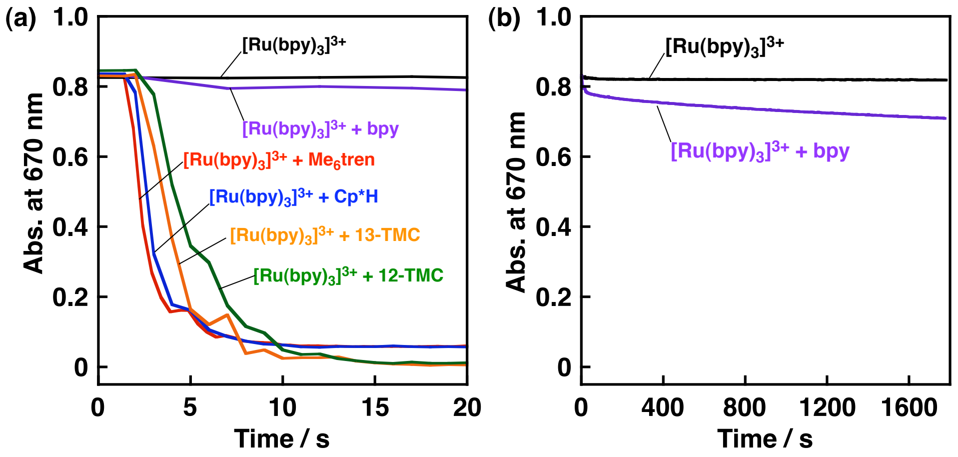

Fig. S6 (a) Time courses of absorbance decay at 670 nm of a CH_3CN solution containing $[Ru^{III}(bpy)_3]^{3+}$ (2.0 mM) (black line) with addition of the ligands of complexes **1-4** (2.0 mM); bpy (purple line), Cp*H (2.0 mM) (blue line), 13-TMC (yellow line), 12-TMC (green line) and Me_6tren (red line). (b) Prolonged reaction time for (a).

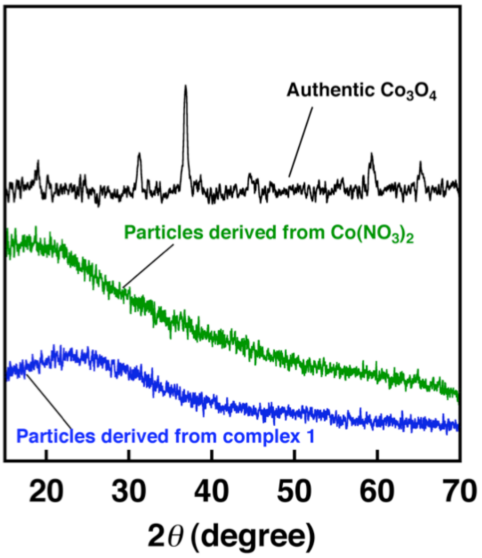

Fig. S7 Powder XRD patterns of authentic Co_3O_4 (black), particles derived from $Co(NO_3)_2$ (green) and particles derived from complex **1** (blue).

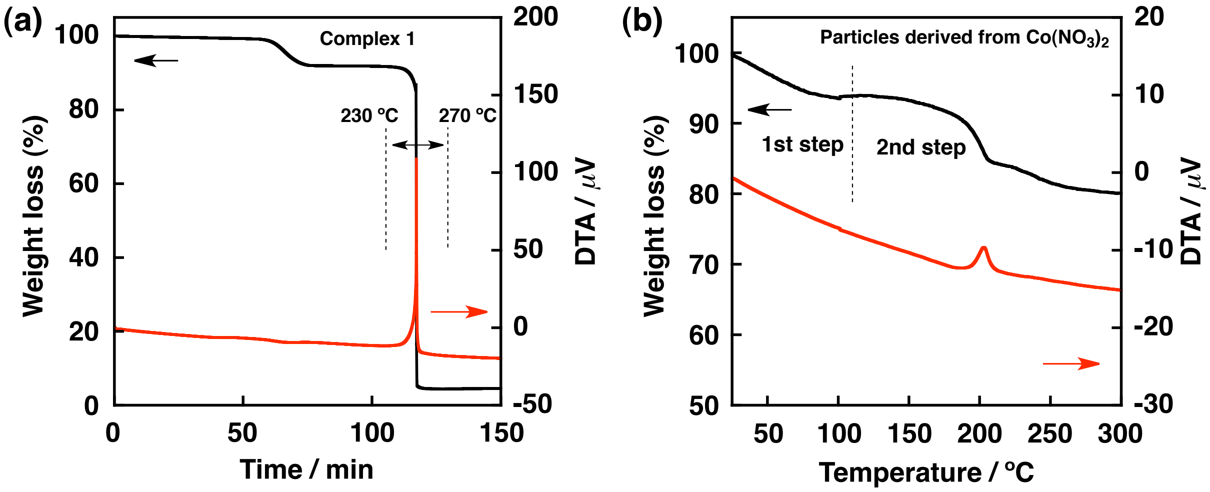

Fig. S8 TG/DTA data for (a) complex **1** and (b) nanoparticles derived from $Co(NO_3)_2$ (TG curve: black, DTA curve: red). The temperature increased from 25 ºC to 600 ºC with a ramp rate of 2 °C/min.

Comments: The particles derived from $Co(NO_3)_2$ contains carbonaceous residue less than 8.7%, which is originated from the ligand of $[Ru(bpy)_3]^{2+}$ in the reaction solution.

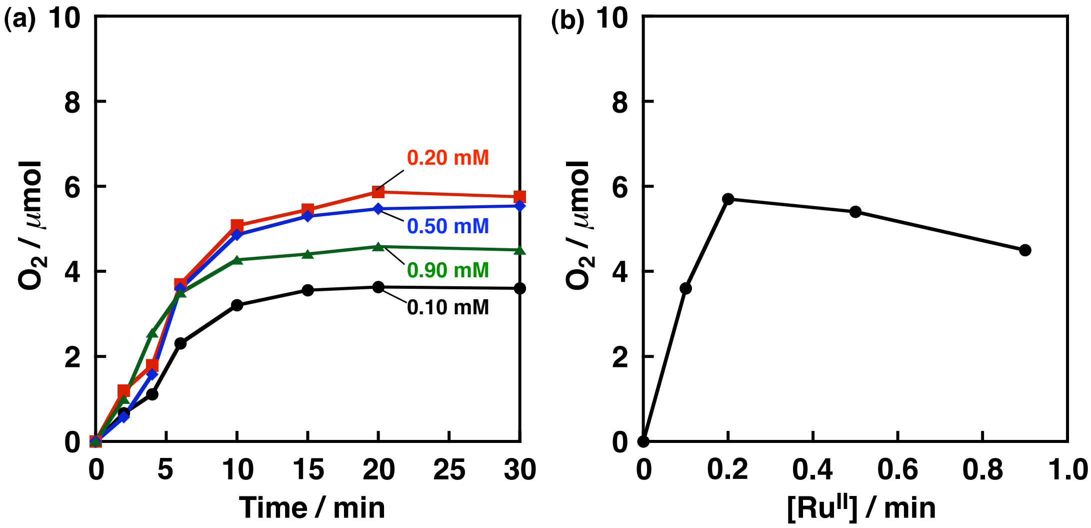

Fig. S9 (a) Time courses of O_2 evolution under photoirradiation (Xe lamp, $\lambda > 420$ nm) of a buffer solution (pH 8.0, 2.0 mL) containing precatalyst **1** (50 μM), $Na_2S_2O_8$ (10 mM) and $[Ru(bpy)_3](ClO_4)_2$ [0.10 mM (black cycle), 0.20 mM (red square), 0.50 mM (blue diamond), 0.90 mM (green triangle)]. (b) Dependence of O_2 evolution on concentrations of $[Ru(bpy)_3](ClO_4)_2$ after 20 min photoirradiation (Xe lamp, $\lambda > 420$ nm) of the solution (pH 8.0).