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 (Me₆tren). Me₆tren was prepared according the reported procedure.S¹ ¹H-NMR (300 MHz, CDCl₃): δ = 2.16 ppm (s, 18H), 2.30 (m, 6 H), 2.54 (m, 6 H).

Synthesis of [Co(Me₆tren)(OH₂)](ClO₄)₂ (1). Co(ClO₄)₂·6H₂O (1.83 g) was dissolved in a 30 mL of CH₃CN solution containing Me₆tren (1.15 g). The solution was stirred for 2 h at room temperature. Et₂O (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 CH₃CN-Et₂O. Yield: 72% (1.89 g). ESI-MS in CH₃CN: m/z 342.2 for [Co(Me₆tren)Cl]⁺ and m/z 388.1 for [Co(Me₆tren)(ClO₄)]⁺.

Synthesis of [Co(Cp*)(bpy)(OH₂)](PF₆)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 CoCl₂ (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 AgPF₆ (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 NH₄PF₆ was added to the reaction solution to obtain crystalline product. ¹H-NMR (300 MHz, D₂O): 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 H₂¹⁸O (44.9% ¹⁸O) solution of phosphate buffer (25 mM, pH 8.0) containing 1 (50 mM), [Ru(bpy)₃](ClO₄)₂ (0.25 mM) and Na₂S₂O₈ (5.0 mM) was irradiated by a Xe lamp (λ > 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 $^{16}\text{O}^{16}\text{O}$, $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}^{18}\text{O}$ 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

Fig. S1 Time courses of O₂ evolution by using [Ru(bpy)₃](ClO₄)₂ (black, 0.50 mM) or [Ru(bpy)₃]Cl₂ (red, 0.50 mM) in 2.0 mL of phosphate buffer containing 1 (50 μM) and Na₂S₂O₈ (10 mM) at initial pH 8.0 to clarify the coexistence effect of Cl⁻ ion on O₂ evolution.

(a) (b)

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 Na₂S₂O₈ (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$_2$S$_2$O$_8$ (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 $\text{O}_2$ evolution under photoirradiation (Xe lamp, $\lambda > 420$ nm) of a buffer solution (pH 8.0, 2.0 mL) containing $[\text{Ru(bpy)}_3]^{2+}$ (0.50 mM) and Na$_2$S$_2$O$_8$ (10 mM) with a precatalyst (i and ii) 1 (50 $\mu$M) and (iii and iv) Co(NO$_3$)$_2$ (50 $\mu$M). 2$^{\text{nd}}$ runs were performed by adding Na$_2$S$_2$O$_8$ (5.0 $\mu$mol) to the solutions after 1$^{\text{st}}$ run and adjusted pH to 8.0 by NaOH (1M, 40 $\mu$L).

Fig. S5 $^1$H NMR spectra in a D$_2$O buffer (pD 10) (a) containing 2 (2.0 mM) with $[\text{Ru(bpy)}_3]^{2+}$ (0.20 mM) and Na$_2$S$_2$O$_8$ (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 $[\text{Ru(bpy)}_3]^{2+}$; yellow squares, free bpy).
Fig. S6 (a) Time courses of absorbance decay at 670 nm of a CH$_3$CN solution containing [Ru$^{II}$(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$_6$tren (red line). (b) Prolonged reaction time for (a).

Fig. S7 Powder XRD patterns of authentic Co$_3$O$_4$ (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(NO₃)₂ (TG curve: black, DTA curve: red). The temperature increased from 25 °C to 600 °C with a ramp rate of 2 °C/min.

Comments: The particles derived from Co(NO₃)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 O₂ evolution under photoirradiation (Xe lamp, λ > 420 nm) of a buffer solution (pH 8.0, 2.0 mL) containing precatalyst 1 (50 μM), Na₂S₂O₈ (10 mM) and [Ru(bpy)₃](ClO₄)₂ [0.10 mM (black cycle), 0.20 mM (red square), 0.50 mM (blue diamond), 0.90 mM (green triangle)]. (b) Dependence of O₂ evolution on concentrations of [Ru(bpy)₃](ClO₄)₂ after 20 min photoirradiation (Xe lamp, λ > 420 nm) of the solution (pH 8.0).