Electronic Supporting Information (ESI)

Dual function photocatalysis of cyano-bridged heteronuclear metal complexes for water oxidation and two-electron reduction of dioxygen to produce hydrogen peroxide as a solar fuel

Yusuke Aratani,¹ Tomoyoshi Suenobu,¹ Kei Ohkubo,¹ Yusuke Yamada,*b and Shunichi Fukuzumi,*c,d

¹ Department of Material and Life Science, Graduate School of Engineering, Osaka University, SENTAN, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan
b Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, Osaka 558-8585, Japan
c Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea
d Faculty of Science and Engineering, Meijo University, SENTAN, Japan Science and Technology Agency (JST), Nagoya, Aichi 468-8502, Japan

* To whom correspondence should be addressed.
E-mail: ymd@a-chem.eng.osaka-cu.ac.jp; fukuzumi@chem.eng.osaka-u.ac.jp
**Experimental section**

**Materials.** All chemicals used for synthesis were obtained from chemical companies and used without further purification. Purified water was provided by a water purification system, Millipore Direct-Q3 UV, where the electronic conductance was 18.2 MΩ cm. Nickel(II) sulphate, copper(II) sulphate, cobalt(II) chloride, 2,2'-bipyridyl and sodium iodide were purchased from Wako Pure Chemical Industries. Iron(II) perchlorate hydrate, manganese(II) perchlorate hydrate and potassium hexacyanoruthenate(II) hydrate were delivered by Sigma-Aldrich. Methanol was obtained from Nacalai tesque. Scandium(III) nitrate was supplied by Mitsuwa Chemicals Co., Ltd.

**Synthesis of K₂[Ru²⁺(CN)₄(bpy)].** S¹ H₂SO₄ was added to a solution (50 mL, pH 4) of water and methanol [3 : 1 (v/v)] containing K₄[Ru²⁺(CN)₆] (0.97 mmol) and 2,2'-bipyridyl (0.96 mmol). The reaction mixture was refluxed for 20 h and the obtained orange solution was purified with Sephadex G10 column. The main fraction was concentrated and precipitated with excess acetone as K₂[Ru²⁺(CN)₄(bpy)].

**Synthesis of K₂[Ru²⁺(CN)₄(Me₂phen)] and K₂[Ru²⁺(CN)₄{(MeO)₂bpy}].** S² A mixed solution (4.0 mL) of water and methanol [3 : 1 (v/v)] containing potassium hexacyanoruthenate(II) hydrate (0.12 mmol) and 2,9-dimethyl-1,10-phenanthroline or 2,2’-bi(5-methoxypyridine) (0.12 mmol) was irradiated for 48 h using an Hg lamp. The irradiated solution was evaporated and the residue was dissolved in water. Excess methanol was added to remove unreacted K₄[Ru²⁺(CN)₆] as a precipitate and the solution was evaporated. The obtained solid was dissolved in water and precipitated with excess amount of acetone as K₂[Ru²⁺(CN)₄(L)] (L = Me₂phen or (MeO)₂bpy).

**Synthesis of [Mn²⁺(H₂O)₂][Ru²⁺(CN)₄(bpy)], [Fe²⁺(H₂O)₂][Ru²⁺(CN)₄(bpy)], [Co²⁺(H₂O)₂][Ru²⁺(CN)₄(bpy)], [Cu²⁺(H₂O)₂][Ru²⁺(CN)₄(bpy)], [Ni²⁺(H₂O)₂]-[Ru²⁺(CN)₄(bpy)], [Fe²⁺(H₂O)₂][Ru²⁺(CN)₄(Me₂phen)] and [Fe²⁺(H₂O)₂]-[Ru²⁺(CN)₄{(MeO)₂bpy}].** An aqueous solution (10 mL) of manganese(II) perchlorate hydrate, iron(II) perchlorate hydrate, cobalt(II) chloride, copper(II) sulphate or nickel(II) sulphate (0.083 mmol) was slowly added to an aqueous solution (10 mL) of K₂[Ru²⁺(CN)₄(bpy)] (0.023 mmol), K₂[Ru²⁺(CN)₄(Me₂phen)] or K₂[Ru²⁺(CN)₄{(MeO)₂bpy}] for 2 h with stirring magnetically. The formed precipitate was collected by filtration, washed with water and dried \textit{in vacuo}. 

S2
Physical measurements. UV-vis absorption spectrum of a solution was recorded on a Hewlett Packard 8453 diode array spectrometer. Diffuse reflectance UV-vis spectrum was taken by a JASCO V-770 equipped with an integrating sphere attachment. IR spectra were recorded on a Jasco FT/IR-6200 spectrometer for the samples pelletised with KBr. The EPR spectra were taken on a JEOL X-band spectrometer (JES-REIXE) with a quartz EPR tube (4.5 mm) at 100 K or 298 K. The g values were calibrated using an Mn\(^{2+}\) marker. Emission spectroscopy was carried out on a Shimadzu RF-5300PC fluorescence spectrometer at room temperature using quartz cells (light path length = 1.0 cm). Sub-nanosecond to microsecond transient absorption spectra were collected using recently developed RIPT method. The pump source is a passively Q-switched microchip laser, (PowerChip PNV-M02510, Teem Photonics, 1 kHz, 350 ps, 355 nm, 25 mJ), and the probe source is a supercontinuum radiation source (SC-450, Fianium, 20 MHz, 50–100 ps, 450–2000 nm). The monochromatized probe pulses with a pre-dispersive monochromator (MD200, Unisoku) which is asynchronous with a pump pulse were irradiated on the sample and the beams transmitted through the sample and its reference beam were detected by InGaAs-photodiodes (G10899-01K, 400-1600 nm, Hamamatsu). A post-dispersive monochromator (CM110, Spectral Products) were positioned before the detector to minimize fluorescence signals from the sample. Si PIN photodiodes (S5972, Hamamatsu) were used to pick up the pump pulse and the probe pulses and to evaluate delay-times between them in a shot-by-shot manner. All photodiodes’ outputs are recorded with a digitizing oscilloscope (HDO8038, Teledyne Lecroy) then transferred to a PC to construct the TA temporal profile. Time resolution of the system was estimated at 400 ps from the 10-90% rise time.

Photocatalytic production of \(\text{H}_2\text{O}_2\). Typical reaction conditions are as follows: [Ni\(^{II}\)(H\(_2\)O)\(_2\)][Ru\(^{II}\)(CN)\(_4\)(bpy)] (10 \(\mu\)g, 9.6 \(\mu\)M) was suspended to an O\(_2\)-saturated mixed solution (3.0 mL) composed of methanol and water [5:1 (v/v)] containing Sc(NO\(_3\))\(_3\) (67 mM). The suspension was gently stirred by a magnetic stirrer under photoirradiation with an Xe lamp (Ushio Optical, Model X SX-UID 500X AMQ) using a UV cut filter (Asahi Techno Glass) transmitting \(\lambda > 390 \text{ nm}\) at room temperature. The amount of produced H\(_2\)O\(_2\) at each reaction time was determined by the titration by iodide ion.

\(^{18}\text{O}_2\)-Labeling experiment for photocatalytic production of \(\text{H}_2\text{O}_2\). Typical reaction conditions are as follows: Ni\(^{II}\)[Ru\(^{II}\)(CN)\(_4\)(bpy)] (10 \(\mu\)g, 9.6 \(\mu\)M) was suspended to an \(^{18}\text{O}_2\)-saturated mixed solution (3.0 mL) composed of methanol and water [5:1 (v/v)]
containing Sc(NO$_3$)$_3$ (67 mM). The suspension was gently stirred by a magnetic stirrer under photoirradiation with an Xe lamp (Ushio Optical, Model X SX-UID 500X AMQ) using a UV cut filter (Asahi Techno Glass) transmitting $\lambda > 390$ nm at room temperature. After 9h, $^{18}$O$_2$ was removed by bubbling of He gas, then MnO$_2$ was added to decompose the produced H$_2$O$_2$ to O$_2$. The evolved O$_2$ was analysed by a Shimadzu GC-17A gas chromatograph [He carrier, TC-FFAP column (GL Science) at 313 K] equipped with a mass spectrometer (Shimadzu, QP-5000).

**Photocatalytic water oxidation.** Typical reaction conditions are as follows: [Ni$^{II}$($H_2$O)$_2$][Ru$^{II}$($CN$)$_4$(bpy)] (0.24 mM) was suspended to an Ar-saturated mixed solution (3.0 mL) composed of methanol and water [5:1 (v/v)] containing Sc(NO$_3$)$_3$ (67 mM) and Na$_2$S$_2$O$_8$ (10 mM). The solution was then irradiated with a xenon lamp through a colour filter glass transmitting $\lambda > 390$ nm at room temperature. The concentration of oxygen gas in a headspace was quantified by a Shimadzu GC-17A gas chromatograph [Ar carrier, a capillary column with molecular sieves (Agilent Technologies, 19095PMS0, 30 m × 0.53 mm) at 313 K] equipped with a thermal conductivity detector at a certain reaction time.

**$^{18}$O$_2$-Labeling experiment for photocatalytic water oxidation.** Typical reaction conditions are as follows: Ni$^{II}$[Ru$^{II}$($CN$)$_4$(bpy)] (1.0 mg 1.2 mM) was suspended to an He-saturated mixed solution (2.0 mL) composed of methanol and H$_2^{18}$O [1:1 (v/v)] containing Na$_2$S$_2$O$_8$ (5.0 mM). The solution was then irradiated with a xenon lamp through a colour filter glass transmitting $\lambda > 390$ nm at room temperature. After photoirradiation for 18 h, the concentration of oxygen gas in the headspace was analysed 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).

**References**


Fig. S1 Powder XRD spectra of Mn$^{II}$[Ru$^{II}$(CN)$_4$(bpy)], Fe$^{II}$[Ru$^{II}$(CN)$_4$(bpy)], Co$^{II}$[Ru$^{II}$(CN)$_4$(bpy)], Cu$^{II}$[Ru$^{II}$(CN)$_4$(bpy)] and Ni$^{II}$[Ru$^{II}$(CN)$_4$(bpy)].
Fig. S2  IR spectra of (a) Mn$^{II}$[Ru$^{II}$(CN)$_4$(bpy)], Fe$^{II}$[Ru$^{II}$(CN)$_4$(bpy)], Co$^{II}$[Ru$^{II}$(CN)$_4$(bpy)], Cu$^{II}$[Ru$^{II}$(CN)$_4$(bpy)], Ni$^{II}$[Ru$^{II}$(CN)$_4$(bpy)] and K$_2$[Ru$^{II}$(CN)$_4$(bpy)], (b) K$_2$[Ru$^{II}$(CN)$_4$(Me$_2$phen)] (black dotted line) and Fe$^{II}$[Ru$^{II}$(CN)$_4$(Me$_2$phen)] (red solid line), (c) K$_2$[Ru$^{II}$(CN)$_4$(MeO)$_2$(bpy)] (black dotted line) and Fe$^{II}$[Ru$^{II}$(CN)$_4$(MeO)$_2$(bpy)] (red solid line).
Fig. S3 UV-vis spectra of $K_2[Ru^{II}(CN)_4(bpy)]$ (black dashed line) in water and diffused reflectant UV-vis spectrum of $Ni^{II}[Ru^{II}(CN)_4(bpy)]$ (red solid line).

Fig. S4 The observed ratio of $^{16}O^{16}O : ^{16}O^{18}O : ^{18}O^{18}O$ which was evolved by MnO$_2$-catalysed disproportionation of H$_2$O$_2$ produced by photoirradiation of the $^{18}O_2$ saturated mixed solution of CH$_3$OH/H$_2$O (3.0 mL; 5:1, v/v) containing Ni$^{II}[Ru^{II}(CN)_4(bpy)]$ (9.6 mM) and Sc(NO$_3$)$_3$ (67 mM) with a Xe lamp ($\lambda > 390$ nm) for 9 h.
**Fig. S5** Time course of H$_2$O$_2$ generation by visible light irradiation ($\lambda > 390$ nm) of an O$_2$-saturated solution containing K$_2$[Ru$^{II}$(CN)$_4$(bpy)] (10 mM) and Sc(NO$_3$)$_3$ (67 mM).
**Fig. S6** Size distributions of particles during the production of H₂O₂ from H₂O and O₂ with Ni^{II}[Ru^{II}(CN)₄(bpy)] (9.6 µM) in the presence of Sc(NO₃)₃ (67 mM) in O₂-saturated CH₃OH/H₂O (3.0 mL, 5:1 v/v) under visible light irradiation for (a) 0 h, (b) 3 h and (c) 24 h with a Xenon lamp using a UV cut-off filter (λ > 390 nm) at 298 K obtained by DLS measurements.
Fig. S7 EPR spectra observed under dark (black dotted line) and photoirradiation with an Hg lamp ($\lambda > 310$ nm; red solid line) of an O$_2$-saturated CH$_3$OH/H$_2$O (5:1, v/v) solution (2.0 mL) containing Ni$^{II}$[Ru$^{II}$(CN)$_4$(bpy)] (0.50 mM) and Sc(NO$_3$)$_3$ (0.10 M) at 100 K.
Fig. S8 (a) Emission spectra observed in the mixture solution of CH₃OH/H₂O (5:1, v/v) containing K₂[Ruᴵᴵ(CN)₄(bpy)] (0.37 mM) and various concentration of O₂ (0-7.6 mM). (b) Stern-Volmer plots for the emission quenching of [Ruᴵᴵ(CN)₄(bpy)]²⁺ by O₂.
Fig. S9 The observed ratio of $^{18}$O-labeled and unlabelled oxygen evolved during photoirradiation for 18 h of the He saturated mixed solvent of $H_{2}^{18}$O/CH$_3$OH (2.0 mL; 1:1, v/v) containing Ni$^{II}$[Ru$^{II}$(CN)$_4$(bpy)] (1.0 mg, 1.2 mM) and Na$_2$S$_2$O$_8$ (5.0 mM) with a Xe lamp ($\lambda > 390$ nm).