Electronic Supplementary Information

for

Photocatalytic production of hydrogen peroxide from water and dioxygen using cyano-bridged polynuclear transition metal complexes as water oxidation catalysts

Yusuke Isaka,a Kohei Oyama,a Yusuke Yamada,*b Tomoyoshi Suenobu a and Shunichi Fukuzumi*a,c,d

a Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA and SENTAN, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan. E-mail: fukuzumi@chem.eng.osaka-u.ac.jp
b Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, Osaka 558-0022, Japan
c Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea
d Faculty of Science and Technology, Meijo University, ALCA and SENTAN, Japan Science and Technology Agency (JST), Nagoya, Aichi 468-8502, Japan
# Table of contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental details</td>
<td>S3 – S5</td>
</tr>
<tr>
<td>Table S1</td>
<td>S6</td>
</tr>
<tr>
<td>Figs. S1 – S10</td>
<td>S7 – S16</td>
</tr>
<tr>
<td>Estimation of the total amount of evolved O₂</td>
<td>S17</td>
</tr>
<tr>
<td>References</td>
<td>S17</td>
</tr>
</tbody>
</table>
Experimental section

Materials

All chemicals commercially available were used without further purification unless otherwise noted. RuCl₃ (38.220 wt% Ru) was purchased from Tanaka Kikinzoku Kogyo K.K. K₃[Co(CN)₆] was purchased from Stream Chemicals. 4,7-dimethyl-1,10-phenanthroline (Me₂phen, 98%), Ag₂SO₄ (99.9%), (NH₄)₂SO₄ (99.99%), Ru(bpy)₃Cl₂•6H₂O, K₃[Cr(CN)₆], K₄[Mn(CN)₆] and Na₂S₂O₈ were supplied from Aldrich Chemicals. Oxo[5,10,15,20-tetra(4-pyridyl)porphinato]titanium(IV) ([TiO(tpyp)]) was supplied from Tokyo Chemical Industry Co., Ltd. (TCI). Sc(NO₃)₃•4H₂O (99.9%) was supplied from Mitsuwa Chemicals Co., Ltd. Co(NO₃)₂, FeSO₄, Mn(NO₃)₂, K₂[Pd(CN)₄], K₄[Fe(CN)₆] and K₂[Ni(CN)₄] were supplied from Wako Pure Chemical Industries. Purification of water (18.2 MΩ cm) was performed with a Milli-Q system (Millipore, Direct-Q 3 UV). [Ru(bpy)₃]SO₄ was synthesised by a reported method. S1

Spectroscopic measurements in solution

¹H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer in D₂O solutions. The chemical shifts and relative integration signals were referenced by an external standard solution of 5.0 mM 3-(trimethylsilyl)propanoate-2,2,3,3-d₄ acid sodium salt (TSP) in D₂O sealed in a glass capillary. The UV-visible absorption spectra were recorded using a Hewlett Packard 8453 diode array spectrophotometer with a quartz cuvette (light-path length = 1.0 cm) at 298 K.

Synthesis of [RuII(Me₂phen)₃]SO₄

Tris(4,7-dimethyl-1,10-phenanthroline)ruthenium(II) sulfate ([RuII(Me₂phen)₃]SO₄) complex was synthesised according to the literature. S2 RuCl₃ (40 mg) was refluxed under N₂ overnight in ethanol/water (v/v 80/20) with 6 equiv. of ligand, Me₂phen, to form the red-orange [RuII(Me₂phen)₃]Cl₂ complex. After evaporation of the solvent, the product was readily precipitated from acetone with ether. The precipitate, [RuII(Me₂phen)₃]Cl₂, was added to water to be completely dissolved and Ag₂SO₄ (61 mg) solubilised in water was added to the solution. After stirring for 12 h, AgCl as precipitate was filtered off. An aqueous solution of (NH₄)₂SO₄ was added to the reaction solution to obtain crystalline product. ¹H-NMR (300 MHz, D₂O): δ (ppm) 2.88 (s, 6H), 7.41 (d, J = 5.12 Hz, 2H), 7.90 (d, J = 5.12 Hz, 2H), 8.39 (s, 2H).

Synthesis of heteropolynuclear cyanide complexes
Heteropolynuclear cyanide complexes (M₄[M'(CN)]₂, where x = 3, y = 6, z = 2 when M' = Fe, Co, Cr, Fe and Mn; and x = 1, y = 4, z = 1 when M' = Ni, Pd and Pt) were prepared by mixing an aqueous solution containing K(2x/z)[M'(CN)y] with another aqueous solution of Co(NO₃)₂, FeSO₄•7H₂O, CuSO₄, or Mn(NO₃)₂ to form precipitates.

Characterization of the heteropolynuclear cyanide complexes
The concentrations of Fe and Co ions in heteropolynuclear cyanide complexes were determined by X-ray fluorescence measurements (Rigaku ZSX 1000/MPS). The dynamic light scattering (DLS) data were obtained by Zeta Sizer Nano ZS (Malvern 20 Instruments Ltd., USA). Powder X-ray diffraction (XRD) patterns were recorded by a Rigaku MiniFlex 600 X-Ray 21 diffractometer. IR spectra were measured by a Jasco FT/IR-6200 spectrometer for the samples pelletized with KBr.

Quantification of produced H₂O₂
From spectroscopic titration with an acidic solution of [TiO(tpypH₄)]⁴⁺ complex (Ti-TPyP reagent), the amount of produced H₂O₂ was determined.² The [TiO(tpyp)] complex (34 mg) was dissolved in 1.0 L of 50 mM hydrochloric acid and the solution was used as a Ti-TPyP reagent. An aliquot (e.g., 10 μL) of the reaction solution was diluted with water and 0.25 mL of the sample solution was mixed with 0.25 mL of 4.8 M perchloric acid and 0.25 mL of the Ti-TPyP reagent. After 5 min at room temperature, the mixture was diluted to 2.5 mL with water and used for the spectroscopic measurement. The absorbance at λ = 434 nm was measured by using a Hewlett Packard 8453 diode array spectrometer (Aₘ). In the similar manner, a blank solution was prepared by adding distilled water in place of the sample solution in the same volume with its absorbance designated as A₆. The difference in absorbance was determined by following the equation: ΔA₄₃₄ = A₆ – Aₘ. Based on ΔA₄₃₄ and the volume of the solution, the amount of hydrogen peroxide was determined according to the literature.³

Photocatalytic Water Oxidation Reaction
A typical procedure for water oxidation reactions is as follows: a heteropolynuclear cyanide complex (1.0 mg) was suspended to a phosphate buffer (pH 8.0, 50 mM, 2.0 mL) containing [Ru(bpy)₃]²⁺ (100 μM) and Na₂S₂O₈ (5.0 mM) under Ar atmosphere. After photoirradiation (λ > 420 nm) of the suspension with magnetic stirring, an aliquot of headspace gas was analyzed to determine the amount of evolved O₂ by a gas chromatograph (Shimadzu GC-17A equipped with a molecular sieve 5A column and thermal
Water Oxidation Reaction Using [Ru\textsuperscript{III}(Me\textsubscript{2}phen)\textsubscript{3}]\textsuperscript{3+} as an Oxidant

An aqueous solution containing [Ru(Me\textsubscript{2}phen)\textsubscript{3}]	extsuperscript{3+} was prepared according to the literature.\textsuperscript{S4} Excess amount of PbO\textsubscript{2} was added to an H\textsubscript{2}SO\textsubscript{4} solution (0.10 M) containing [Ru\textsuperscript{II}(Me\textsubscript{2}phen)\textsubscript{3}]	extsuperscript{2+} (200 mM). Heteropolynuclear cyanide complex (0.075 mg) was dispersed in water (4.0 mL) and sealed with a rubber septum in a glass tube (4.9 mL). 20 \( \mu \)L of the [Ru\textsuperscript{III}(Me\textsubscript{2}phen)\textsubscript{3}]\textsuperscript{3+} aqueous solution was filtered with a membrane filter and injected into the tube using a syringe. The amount of evolved oxygen gas in the headspace was analysed by an oxygen sensor (FOXY Fibre Optic Oxygen Sensor, Ocean Optics). The total amount of evolved O\textsubscript{2} was calculated based on the equation shown in page S15.

Repetitive Photocatalytic H\textsubscript{2}O\textsubscript{2} Production

H\textsubscript{2}O\textsubscript{2} production was performed by visible light irradiation (\( \lambda > 450 \) nm) of [Ru\textsuperscript{II}(Me\textsubscript{2}phen)\textsubscript{3}]	extsuperscript{2+} (100 \( \mu \)M) in the presence of Sc\textsuperscript{3+} (100 mM) and (Co\textsubscript{0.25}Fe\textsubscript{0.75})\textsubscript{3}[Co(CN)\textsubscript{6}]\textsubscript{2} (2.5 mg) in O\textsubscript{2}-saturated H\textsubscript{2}O (5.0 mL). After the reaction, (Co\textsubscript{0.25}Fe\textsubscript{0.75})\textsubscript{3}[Co(CN)\textsubscript{6}]\textsubscript{2} was recovered by centrifugation as a precipitate. To the recovered precipitate, an aqueous solution (5.0 mL) of [Ru\textsuperscript{II}(Me\textsubscript{2}phen)\textsubscript{3}]	extsuperscript{2+} (100 \( \mu \)M) and Sc\textsuperscript{3+} (100 mM) was added and the resulting solution was used for another cycle of H\textsubscript{2}O\textsubscript{2} production.
Table S1 Calculated and experimentally observed ratios of Fe and Co ions in (Fe<sub>x</sub>Co<sub>1-x</sub>)<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub>

<table>
<thead>
<tr>
<th>x</th>
<th>Calculated ratio (mol%)</th>
<th>Experimental ratio&lt;sup&gt;a,b&lt;/sup&gt; (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Co</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>0.10</td>
<td>6</td>
<td>94</td>
</tr>
<tr>
<td>0.50</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>0.75</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>0.90</td>
<td>54</td>
<td>46</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>40</td>
</tr>
</tbody>
</table>

<sup>a</sup> Experimentally observed ratios are based on X-ray fluorescence measurements. <sup>b</sup> Four measurements were performed for each samples and then the data were averaged to give the experimental ratios.
Fig. S1 The powder X-ray diffraction patterns of (FeₓCo₁₋ₓ)₃[Co(CN)₆]₂ [x = 0 (blue), 0.10 (light blue), 0.50 (light green), 0.75 (green), 0.90 (orange) and 1 (red)].
Fig. S2 Size distributions of the $(\text{Fe}_{x}\text{Co}_{1-x})_3[\text{Co(CN)}_6]_2$ particles obtained by DLS measurements.
Fig. S3 H$_2$O$_2$ production from H$_2$O and O$_2$ in an O$_2$-saturated aqueous solution (2.0 mL) of [Ru(Me$_2$phen)$_3$]$^{2+}$ (100 μM), Sc(NO$_3$)$_3$ (100 mM) and (Fe$_x$Co$_{1-x}$)$_3$[Co(CN)$_6$]$_2$ (1.0 mg), where x = 1 (black square), 0.90 (inverse red triangle), 0.75 (orange circle), 0.50 (green diamond), 0.10 (purple triangle) and 0 (blue diamond) under photoirradiation of visible light with a Xenon lamp using a UV light cut filter (λ > 420 nm) at room temperature. The initial rates of H$_2$O$_2$ production were calculated based on the slopes of the lines in the figure.
Fig. S4 (a) IR spectra of (Fe<sub>x</sub>Co<sub>1-x</sub>)<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub>, where x = 1 (black), 0.90 (red), 0.75 (orange), 0.50 (green), 0.10 (purple) and 0 (blue). (b) Plot of <i>n</i><sub>CN</sub> vs. the ratio of Fe to Co in the (Fe<sub>x</sub>Co<sub>1-x</sub>) moiety (Fr<sub>Fe</sub>). The <i>ν</i><sub>CN</sub> of the complexes were measured 3 times for each of the complexes.
Fig. S5 Time courses of O$_2$ evolution by photoirradiation of an aqueous phosphate buffer (2.0 mL) containing Na$_2$S$_2$O$_8$ (5.0 mM), Ru[(bpy)$_3$]$_2^{2+}$ (100 μM) and (Fe$_x$Co$_{1-x}$)$_3$[Co(CN)$_6$]$_2$ (1.0 mg), where x = 1 (black square), 0.90 (green diamond), 0.75 (red inverse triangle), 0.50 (orange circle) and 0 (blue diamond), at pH 8.0 at room temperature. The rates of O$_2$ production shown in Fig. 4 were calculated from the slopes of the lines.
**Fig. S6** Time course of O$_2$ evolution after addition of [Ru$^{III}$Me$_2$phen)$_3$$^{3+}$ (1 mM) to an aqueous suspension (4 mL) of (Fe$_{0.75}$Co$_{0.25}$)$_3$[Co(CN)$_6$]$_2$ (0.10 mg) at pH 3 measured using an O$_2$ sensor.
Fig. S7 (a) Time courses of H$_2$O$_2$ production at different concentrations of [Ru$^{II}$(Me$_2$phen)$_3$]$^{2+}$ [10 μM (orange circle), 50 μM (blue square), 100 μM (green triangle) and 200 μM (red diamond)] under irradiation of [Ru$^{II}$(Me$_2$phen)$_3$]$^{2+}$ with visible light (λ > 420 nm) in the presence of (Co$_{0.25}$Fe$_{0.75}$)$_3$(Co(CN)$_6$)$_2$ (1.0 mg) and Sc$^{3+}$ (100 mM) in O$_2$-saturated H$_2$O (2.0 mL) at room temperature. (b) Time courses of production of H$_2$O$_2$ from H$_2$O and O$_2$ in an O$_2$-saturated aqueous solution (2.0 mL) of [Ru(Me$_2$phen)$_3$]$^{2+}$ (100 μM), Sc(NO$_3$)$_3$ (100 mM) and various amounts of (Co$_{0.25}$Fe$_{0.75}$)$_3$(Co(CN)$_6$)$_2$ [0.5 mg (gray square), 1.0 mg (green diamond) and 2.0 mg (blue circle)] under visible light (λ > 420 nm) irradiation at room temperature.
**Fig. S8** (a) Time course of H$_2$O$_2$ production under visible light irradiation ($\lambda = 450$ nm) of [Ru$^{II}$(Me$_2$phen)$_3$]$^{2+}$ (100 $\mu$M) in the presence of Sc$^{3+}$ (100 mM) and (Co$_{0.25}$Fe$_{0.75}$)$_3$[Co(CN)$_6$]$_2$ (1.0 mg) in O$_2$-saturated H$_2$O (2.0 mL). The quantum efficiency was calculated from the slope of the black line. (b) Time course of H$_2$O$_2$ production under photoirradiation of [Ru$^{II}$(Me$_2$phen)$_3$]$^{2+}$ (100 $\mu$M) in the presence of Sc$^{3+}$ (100 mM) and (Co$_{0.25}$Fe$_{0.75}$)$_3$[Co(CN)$_6$]$_2$ (1.0 mg) in O$_2$-saturated H$_2$O (2.0 mL). A solar simulator, in which the intensity was adjusted to 10 mJ cm$^{-2}$ s$^{-1}$ (AM1.5), was used as the light source. The solar energy conversion efficiency was determined from the slope of the black line.
Fig. S9  Time course of H\textsubscript{2}O\textsubscript{2} production under visible light irradiation (\(\lambda > 450\) nm) of [Ru\textsuperscript{II}(Me\textsubscript{2}phen)\textsubscript{3}]\textsuperscript{2+} (100 \(\mu\)M) in the presence of Sc\textsuperscript{3+} (100 mM) and (Co\textsubscript{0.25}Fe\textsubscript{0.75})\textsubscript{3}[Co(CN)\textsubscript{6}]\textsubscript{2} (2.5 mg) in O\textsubscript{2}-saturated H\textsubscript{2}O (5 mL). (Co\textsubscript{0.25}Fe\textsubscript{0.75})\textsubscript{3}[Co(CN)\textsubscript{6}]\textsubscript{2} was recovered by centrifugation at 16 h, 33 h, 50 h, 68 h, and 85 h. To the recovered (Co\textsubscript{0.25}Fe\textsubscript{0.75})\textsubscript{3}[Co(CN)\textsubscript{6}]\textsubscript{2}, an aqueous solution (5.0 mL) of [Ru\textsuperscript{II}(Me\textsubscript{2}phen)\textsubscript{3}]\textsuperscript{2+} (100 \(\mu\)M) and Sc\textsuperscript{3+} (100 mM) was added and the resulting solution was used for the next cycle of H\textsubscript{2}O\textsubscript{2} production.
Fig. S10 (a) IR spectra, (b) powder X-ray diffraction patterns, and (c) DLS measurements of (Co0.25Fe0.75)3[Co(CN)6]2 (orange lines) and the precipitate after centrifugation (black lines) of the reaction solution obtained after the reaction under visible light irradiation ($\lambda > 450$ nm) of $[\text{Ru}^{II}(\text{Me2phen})_3]^2^+ \ (100 \ \mu\text{M})$ for 16 h in the presence of $\text{Sc}^{3+} \ (100 \ \text{mM})$ and $(\text{Co0.25Fe0.75})_3[\text{Co(CN)}_6]_2 \ (8.0 \ \text{mg})$ in O$_2$-saturated H$_2$O (16 mL).
Estimation of the total amount of evolved O$_2$ by measuring the O$_2$ amount in the headspace in equilibrium with that dissolved in solution

The total amount of evolved O$_2$ ($T$ [μmol]) was calculated based on the following equations where $G$ [μmol] is the O$_2$ amount in the headspace in equilibrium with O$_2$ dissolved in solution (amount: $L$ [μmol]) as expressed in eqn (S1). The $G$ value can be expressed by eqn (S2) using volume of the headspace ($x$ [mL]) and O$_2$ molar fraction ($z$ %) in the headspace where the volume of O$_2$ gas is $2.5 \times 10^2$ [L] at 298 K under atmospheric pressure, $1.0 \times 10^4$ [Pa]. The $L$ value can be expressed by eqn (S3) using the volume of the reaction solution ($y$ [mL]) and $z$ where the concentration O$_2$ in an O$_2$-saturated water is $1.2$ [mM].

$$T \ [\mu \text{mol}] = G \ [\mu \text{mol}] + L \ [\mu \text{mol}] \quad (S1)$$

$$G \ [\mu \text{mol}] = \frac{x \ [\text{mL}]}{2.5 \times 10^2 \ [\text{L} \text{mol}^{-1}]} \times \frac{z \ [%]}{100} \times 1000 \quad (S2)$$

$$L \ [\mu \text{mol}] = 1.2 \ [\text{mM}] \times y \ [\text{mL}] \times \frac{z \ [%]}{100} \quad (S3)$$

References