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for

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

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Experimental section

Materials

All chemicals commercially available were used without further purification unless otherwise noted. $RuCl_3$ (38.220 wt% Ru) was purchased from Tanaka Kikinzoku Kogyo K.K. $K_3[Co(CN)_6]$ was purchased from Stream Chemicals. 4,7-dimethyl-1,10-phenanthroline (Me_2phen, 98%), Ag_2SO_4 (99.9%), $(NH_4)_2SO_4$ (99.99%), $Ru(bpy)_3Cl_2•6H_2O$, $K_3[Cr(CN)_6]$, $K_4[Mn(CN)_6]$ and $Na_2S_2O_8$ 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). $Sc(NO_3)_3•4H_2O$ (99.9%) was supplied from Mitsuwa Chemicals Co., Ltd. $Co(NO_3)_2$, $FeSO_4$, $Mn(NO_3)_2$, $K_2[Pd(CN)_4]$, $K_4[Fe(CN)_6]$ and $K_2[Ni(CN)_4]$ 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). $[Ru(bpy)_3]SO_4$ was synthesised by a reported method.[S1]

Spectroscopic measurements in solution

^{1}H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer in D_2O 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-d_4 acid sodium salt (TSP) in D_2O 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 $[Ru^{II}(Me_2phen)_3]SO_4$

Tris(4,7-dimethyl-1,10-phenanthroline)ruthenium(II) sulfate ($[Ru^{II}(Me_2phen)_3]SO_4$) complex was synthesised according to the literature.[S2] $RuCl_3$ (40 mg) was refluxed under N_2 overnight in ethanol/water (v/v 80/20) with 6 equiv. of ligand, Me_2phen, to form the red-orange $[Ru^{II}(Me_2phen)_3]Cl_2$ complex. After evaporation of the solvent, the product was readily precipitated from acetone with ether. The precipitate, $[Ru^{II}(Me_2phen)_3]Cl_2$, was added to water to be completely dissolved and Ag_2SO_4 (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 $(NH_4)_2SO_4$ was added to the reaction solution to obtain crystalline product. ^{1}H-NMR (300 MHz, D_2O): 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 ($M_x[M'(CN)_y]_z$, 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 $Co(NO_3)_2$, $FeSO_4 \bullet 7H_2O$, $CuSO_4$, or $Mn(NO_3)_2$ 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 Instruments Ltd., USA). Powder X-ray diffraction (XRD) patterns were recorded by a Rigaku MiniFlex 600 X-Ray diffractometer. IR spectra were measured by a Jasco FT/IR-6200 spectrometer for the samples pelletized with KBr.

Quantification of produced H_2O_2

From spectroscopic titration with an acidic solution of $[TiO(tpypH_4)]^{4+}$ complex (Ti-TPyP reagent), the amount of produced H_2O_2 was determined.[S2] 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 (A_S). 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 A_B. The difference in absorbance was determined by following the equation: $\Delta A_{434} = A_B - A_S$. Based on ΔA_{434} and the volume of the solution, the amount of hydrogen peroxide was determined according to the literature.[S3]

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 $Na_2S_2O_8$ (5.0 mM) under Ar atmosphere. After photoirradiation (λ > 420nm) of the suspension with magnetic stirring, an aliquot of headspace gas was analyzed to determine the amount of evolved O_2 by a gas chromatograph (Shimadzu GC-17A equipped with a molecular sieve 5A column and thermal conductivity detector).

Water Oxidation Reaction Using $[Ru^{III}(Me_2phen)_3]^{3+}$ as an Oxidant

An aqueous solution containing $[Ru(Me_2phen)_3]^{3+}$ was prepared according to the literature.[S4] Excess amount of PbO_2 was added to an H_2SO_4 solution (0.10 M) containing $[Ru^{II}(Me_2phen)_3]^{2+}$ (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 μL of the $[Ru^{III}(Me_2phen)_3]^{3+}$ 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_2 was calculated based on the equation shown in page S15.

Repetitive Photocatalytic H_2O_2 Production

H_2O_2 production was performed by visible light irradiation ($\lambda > 450$ nm) of $[Ru^{II}(Me_2phen)_3]^{2+}$ (100 μM) in the presence of Sc^{3+} (100 mM) and $(Co_{0.25}Fe_{0.75})_3[Co(CN)_6]_2$ (2.5 mg) in O_2-saturated H_2O (5.0 mL). After the reaction,, $(Co_{0.25}Fe_{0.75})_3[Co(CN)_6]_2$ was recovered by centrifugation as a precipitate. To the recovered precipitate, an aqueous solution (5.0 mL) of $[Ru^{II}(Me_2phen)_3]^{2+}$ (100 μM) and Sc^{3+} (100 mM) was added and the resulting solution was used for another cycle of H_2O_2 production.

Table S1 Calculated and experimentally observed ratios of Fe and Co ions in $(Fe_xCo_{1-x})_3[Co(CN)_6]_2$

	Calculated ratio (mol%)		Experimental ratio[a,b] (mol%)	
x	Fe	Co	Fe	Co
0	0	100	0.0	100
0.10	6	94	6.0	94
0.50	30	70	31	69
0.75	45	55	45	55
0.90	54	46	57	43
1	60	40	64	36

[a] Experimentally observed ratios are based on X-ray fluorescence measurements. [b] Four measurements were performed for each samples and then the data were averaged to give the experimental ratios.

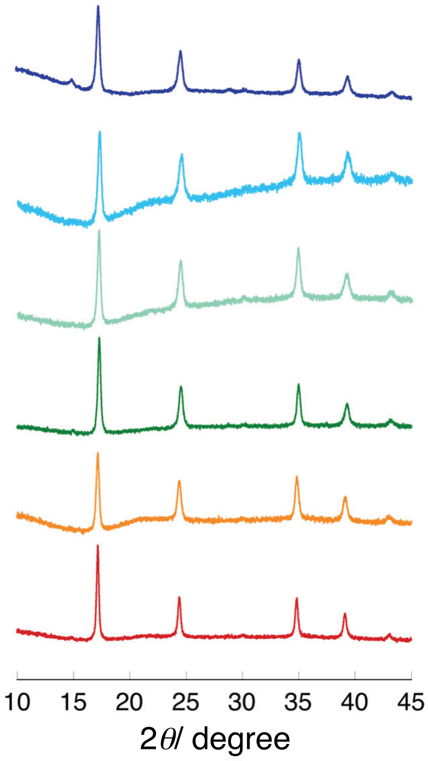

Fig. S1 The powder X-ray diffraction patterns of $(Fe_xCo_{1-x})_3[Co(CN)_6]_2$ [x = 0 (blue), 0.10 (light blue), 0.50 (light green), 0.75 (green), 0.90 (orange) and 1 (red)].

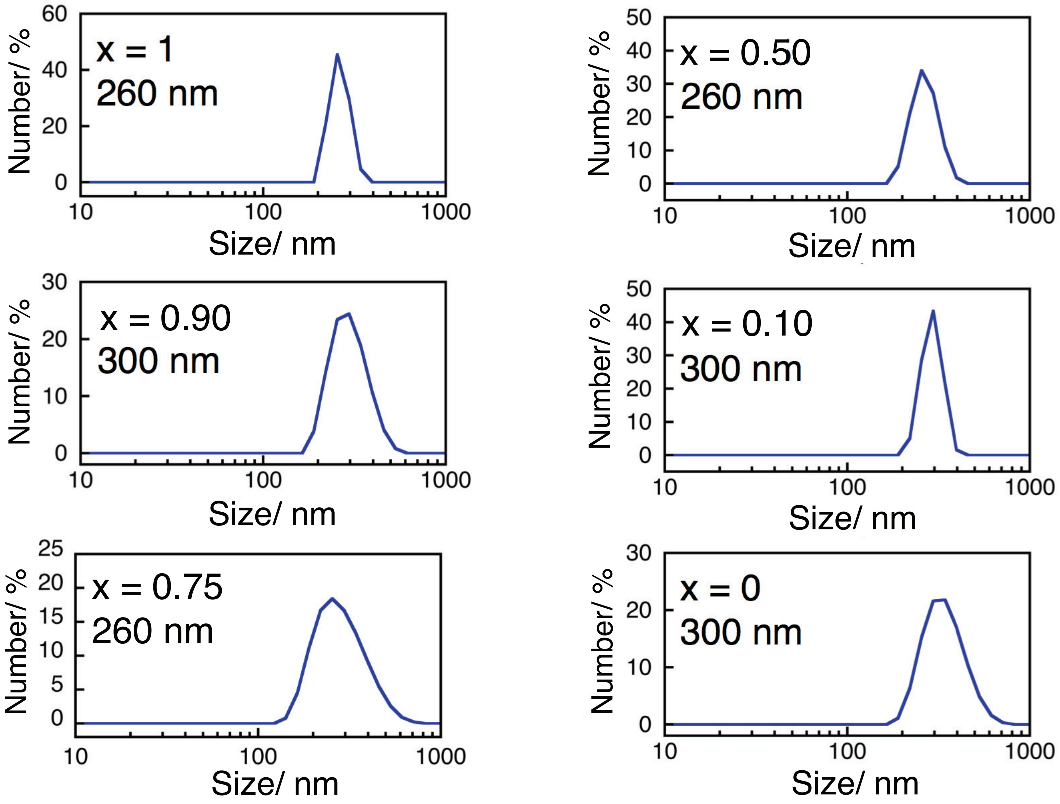

Fig. S2 Size distributions of the $(Fe_xCo_{1-x})_3[Co(CN)_6]_2$ particles obtained by DLS measurements.

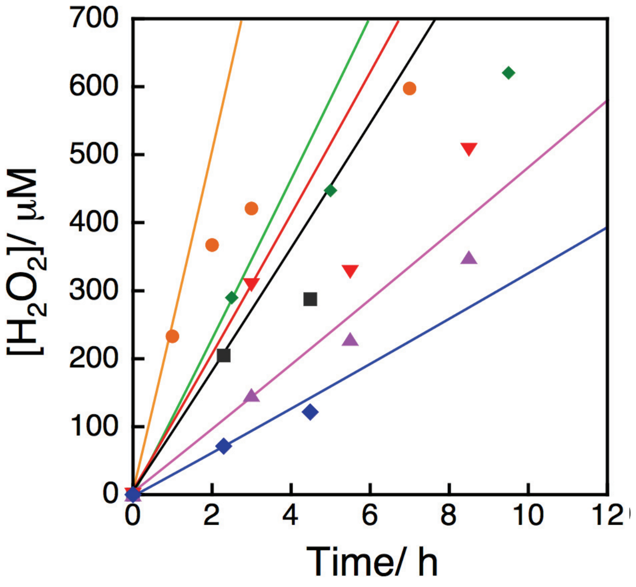

Fig. S3 H_2O_2 production from H_2O and O_2 in an O_2-saturated aqueous solution (2.0 mL) of $[Ru(Me_2phen)_3]^{2+}$ (100 μM), $Sc(NO_3)_3$ (100 mM) and $(Fe_xCo_{1-x})_3[Co(CN)_6]_2$ (1.0 mg), where x = 1 (black square), 0.90 (inverse red triangle), 0.75 (orange circle), 0.50 (green diamond), 0.10 (purple triangle) and 0 (blue diamond) under photoirradiation of visible light with a Xenon lamp using a UV light cut filter ($\lambda > 420$ nm) at room temperature. The initial rates of H_2O_2 production were calculated based on the slopes of the lines in the figure.

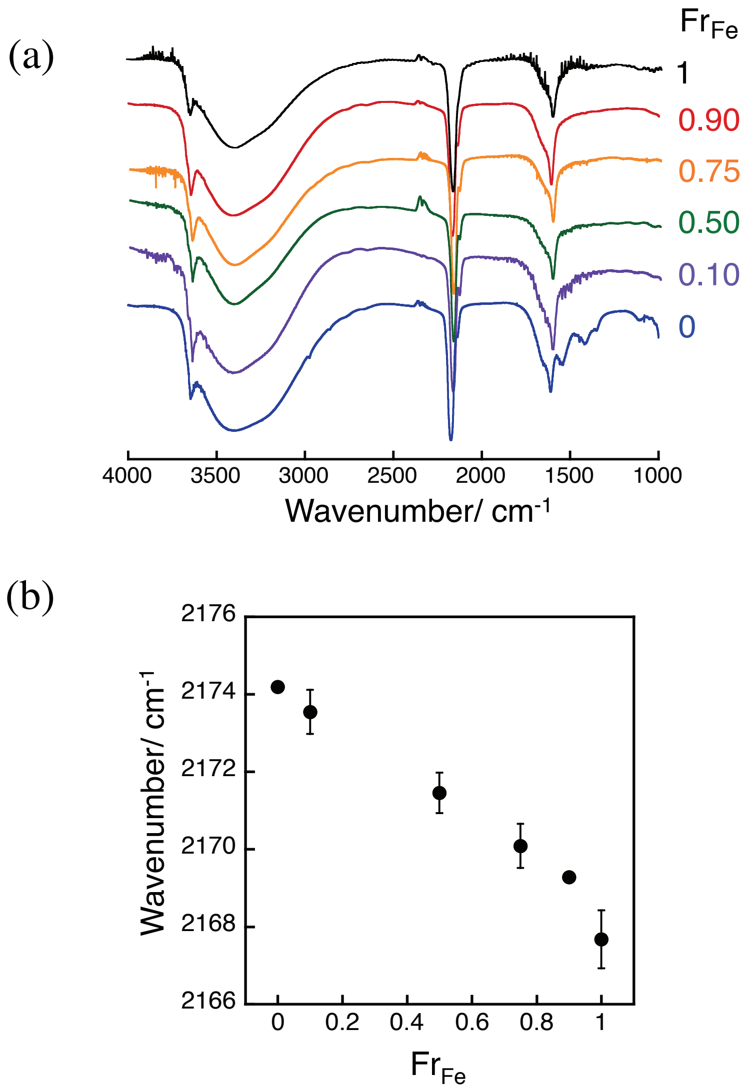

Fig. S4 (a) IR spectra of $(Fe_xCo_{1-x})_3[Co(CN)_6]_2$, where x = 1 (black), 0.90 (red), 0.75 (orange), 0.50 (green), 0.10 (purple) and 0 (blue). (b) Plot of n_{CN} *vs*. the ratio of Fe to Co in the (Fe_xCo_{1-x}) moiety (Fr_{Fe}). The ν_{CN} of the complexes were measured 3 times for each of the complexes.

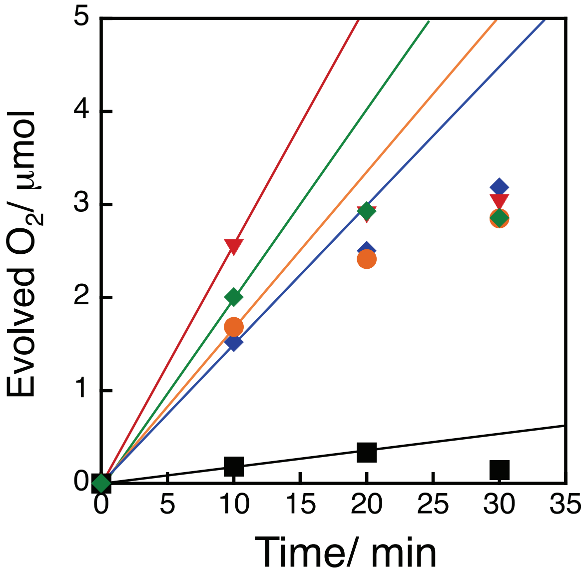

Fig. S5 Time courses of O_2 evolution by photoirradiation of an aqueous phosphate buffer (2.0 mL) containing $Na_2S_2O_8$ (5.0 mM), $Ru[(bpy)_3]^{2+}$ (100 µM) and $(Fe_xCo_{1-x})_3[Co(CN)_6]_2$ (1.0 mg), where x = 1 (black square), 0.90 (green diamond), 0.75 (red inverse triangle), 0.50 (orange circle) 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.

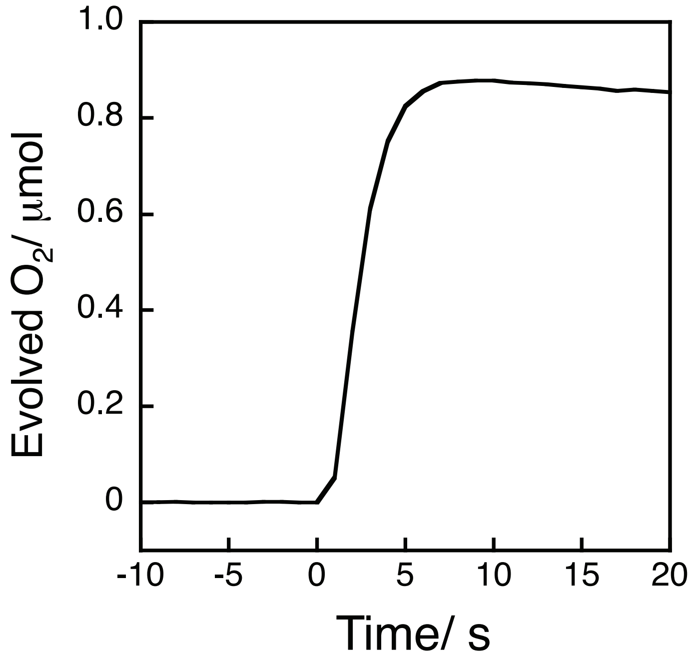

Fig. S6 Time course of O_2 evolution after addition of $[Ru^{III}(Me_2phen)_3]^{3+}$ (1 mM) to an aqueous suspension (4 mL) of $(Fe_{0.75}Co_{0.25})_3[Co(CN)_6]_2$ (0.10 mg) at pH 3 measured using an O_2 sensor.

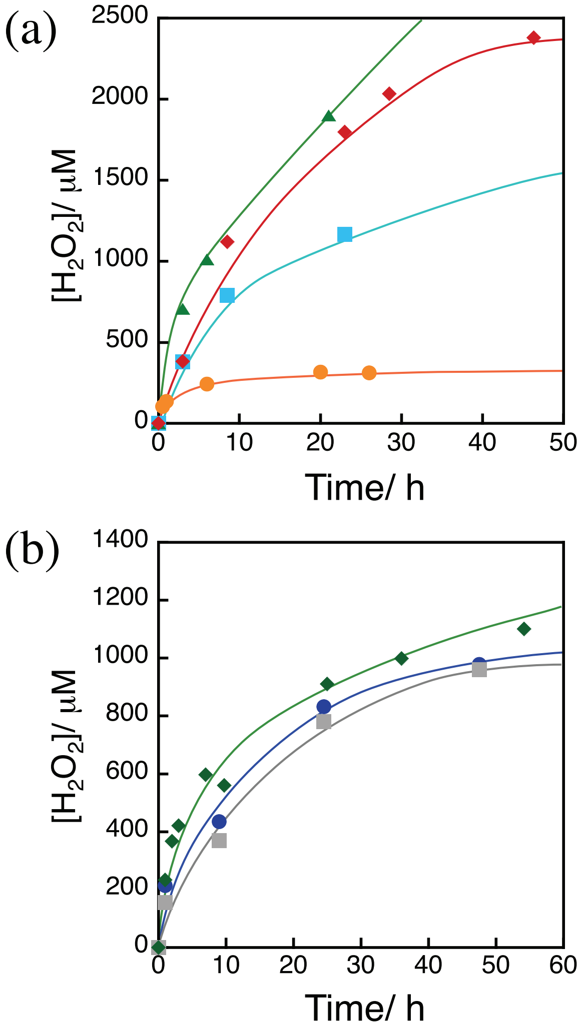

Fig. S7 (a) Time courses of H_2O_2 production at different concentrations of $[Ru^{II}(Me_2phen)_3]^{2+}$ [10 μM (orange circle), 50 μM (blue square), 100 μM (green triangle) and 200 μM (red diamond)] under irradiation of $[Ru^{II}(Me_2phen)_3]^{2+}$ with visible light ($\lambda >$ 420 nm) in the presence 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_2O (2.0 mL) at room temperature. (b) Time courses of production of H_2O_2 from H_2O and O_2 in an O_2-saturated aqueous solution (2.0 mL) of $[Ru(Me_2phen)_3]^{2+}$ (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 ($\lambda >$ 420 nm) irradiation at room temperature.

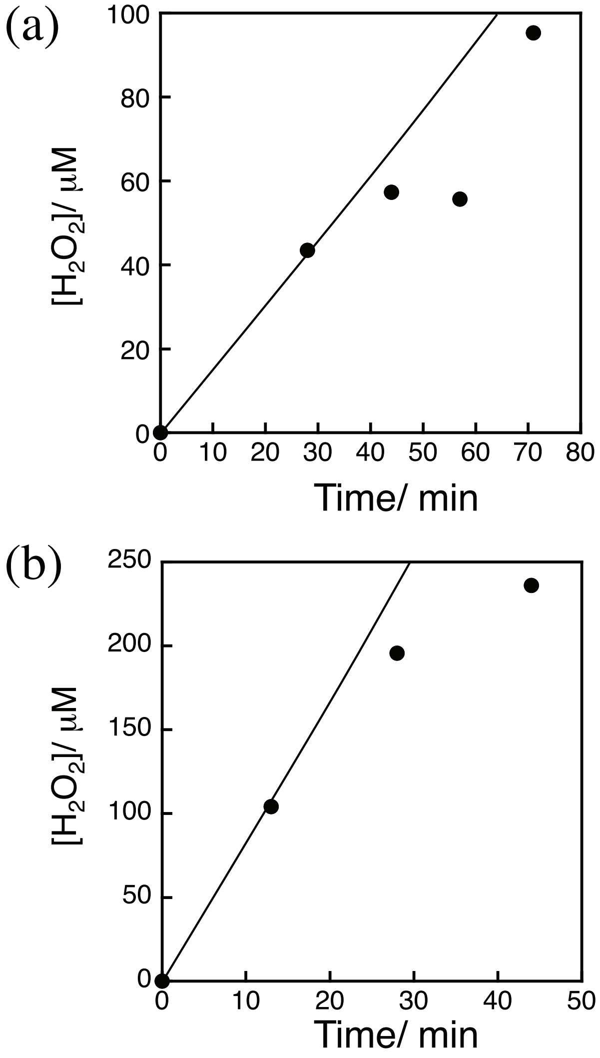

Fig. S8 (a) Time course of H_2O_2 production under visible light irradiation (λ = 450 nm) of $[Ru^{II}(Me_2phen)_3]^{2+}$ (100 µM) in the presence of Sc^{3+} (100 mM) and $(Co_{0.25}Fe_{0.75})_3[Co(CN)_6]_2$ (1.0 mg) in O_2-saturated H_2O (2.0 mL). The quantum efficiency was calculated from the slope of the black line. (b) Time course of H_2O_2 production under photoirradiation of $[Ru^{II}(Me_2phen)_3]^{2+}$ (100 µM) 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_2O (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.

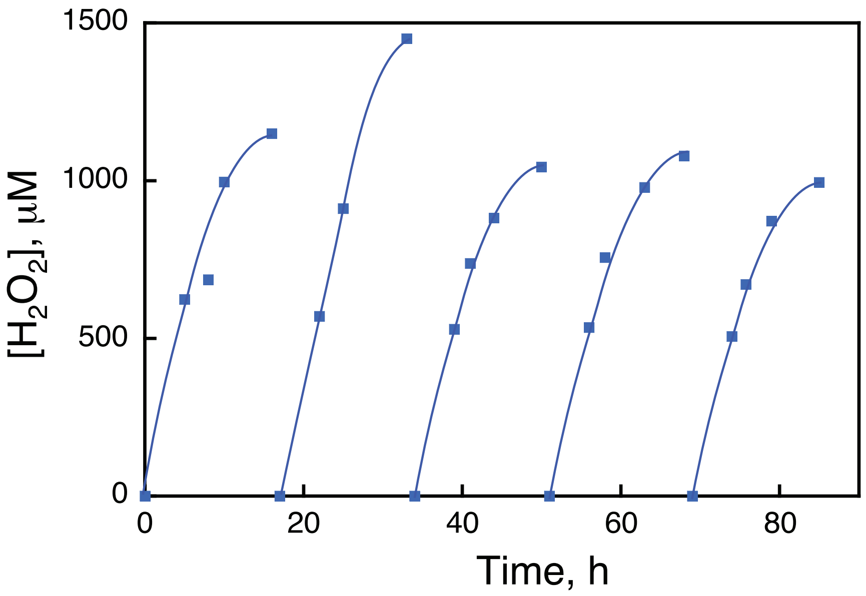

Fig. S9 Time course of H_2O_2 production under visible light irradiation (λ > 450 nm) of $[Ru^{II}(Me_2phen)_3]^{2+}$ (100 μM) in the presence of Sc^{3+} (100 mM) and $(Co_{0.25}Fe_{0.75})_3[Co(CN)_6]_2$ (2.5 mg) in O_2-saturated H_2O (5 mL). $(Co_{0.25}Fe_{0.75})_3[Co(CN)_6]_2$ was recovered by centrifugation at 16 h, 33 h, 50 h, 68 h, and 85 h. To the recovered $(Co_{0.25}Fe_{0.75})_3[Co(CN)_6]_2$, an aqueous solution (5.0 mL) of $[Ru^{II}(Me_2phen)_3]^{2+}$ (100 μM) and Sc^{3+} (100 mM) was added and the resulting solution was used for the next cycle of H_2O_2 production.

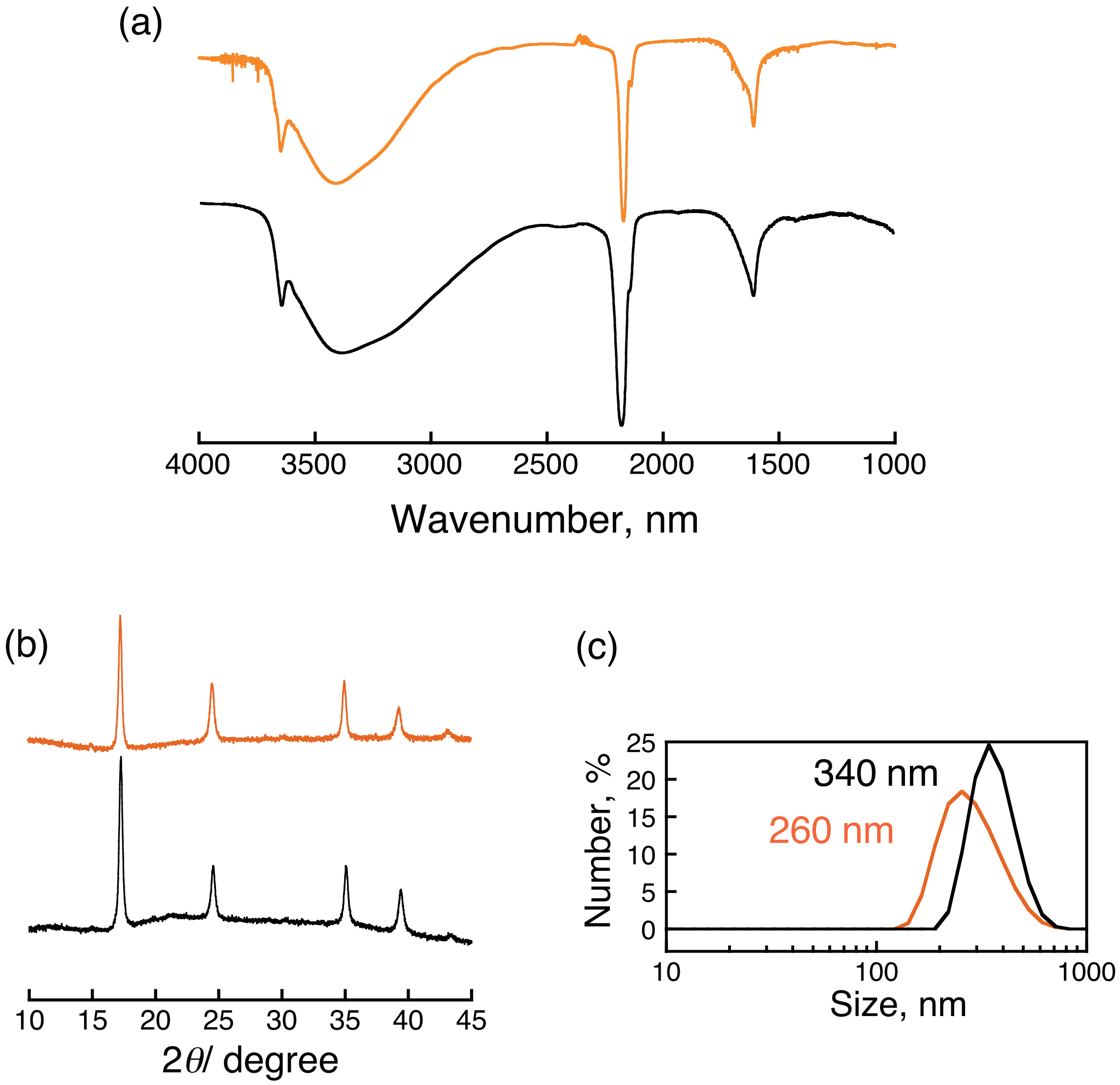

Fig. S10 (a) IR spectra, (b) powder X-ray diffraction patterns, and (c) DLS measurements of $(Co_{0.25}Fe_{0.75})_3[Co(CN)_6]_2$ (orange lines) and the precipitate after centrifugation (black lines) of the reaction solution obtained after the reaction under visible light irradiation (λ > 450 nm) of $[Ru^{II}(Me_2phen)_3]^{2+}$ (100 μM) for 16 h in the presence of Sc^{3+} (100 mM) and $(Co_{0.25}Fe_{0.75})_3[Co(CN)_6]_2$ (8.0 mg) in O_2-saturated H_2O (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 ×10 [L] at 298 K under atmospheric pressure, 1.0×10^4 [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].[S5]

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

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

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

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