

**This version published 18/12/2024 replaces the previous version published 23/09/2024. Figure S16 and S17 are replaced with a corrected version.**

## **Electronic supplementary information (ESI)**

### **Enhanced catalytic activity of solubilised species obtained by counter-cation exchange of $\text{K}\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$ for water oxidation**

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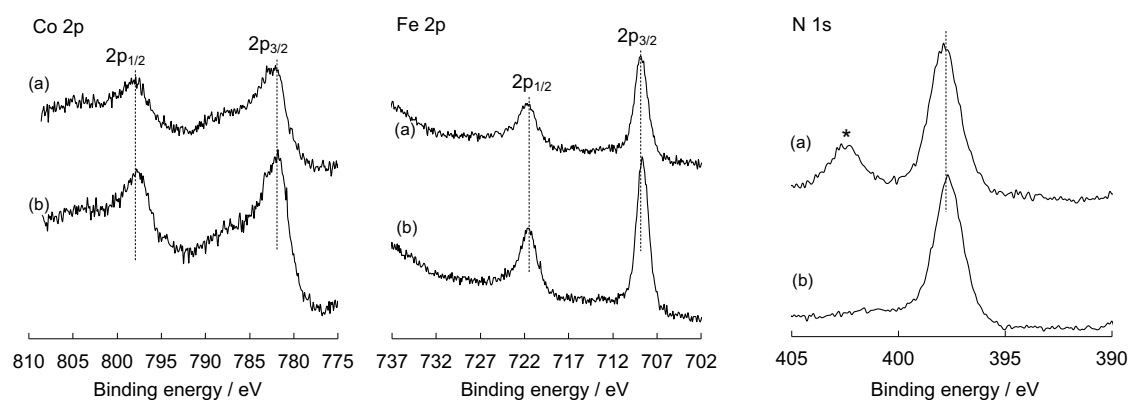
\*E-mail: ymd@omu.ac.jp

### Supporting table

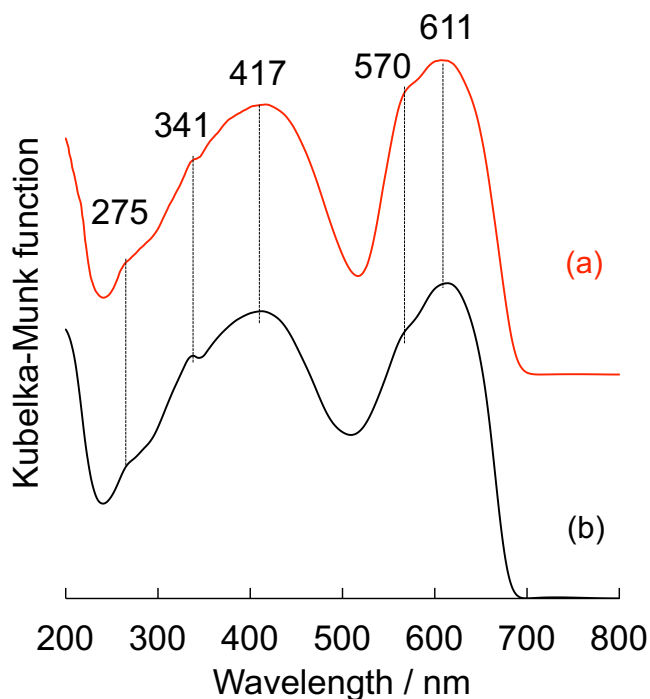
**Table S1.** Chemical compositions of  $(\text{Me}_4\text{N})\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$   $\{(\text{Me}_4\text{N})\text{Co-Fe}\}$  and  $\text{K}\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$   $\{(\text{K})\text{Co-Fe}\}$  determined by X-ray fluorescence (XRF) measurements.

Cyano-bridged coordination polymer	Observed Molar Ratio		
	K/Fe	Co/Fe	Cl/Fe
$(\text{Me}_4\text{N})\text{Co-Fe}$	0.05	1.4	0.07
$(\text{K})\text{Co-Fe}$	0.98	1.4	–

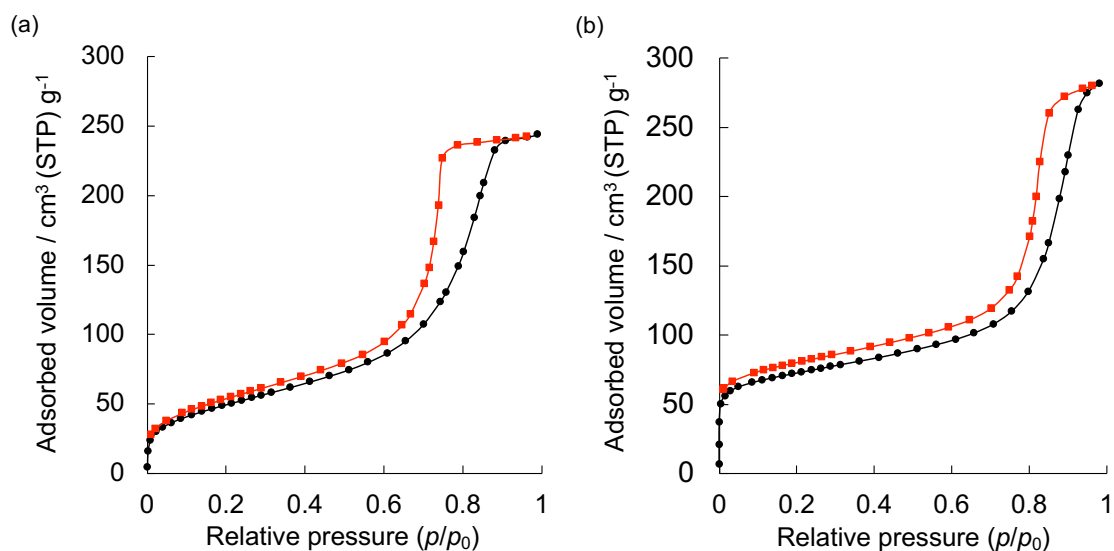
## Supporting figures



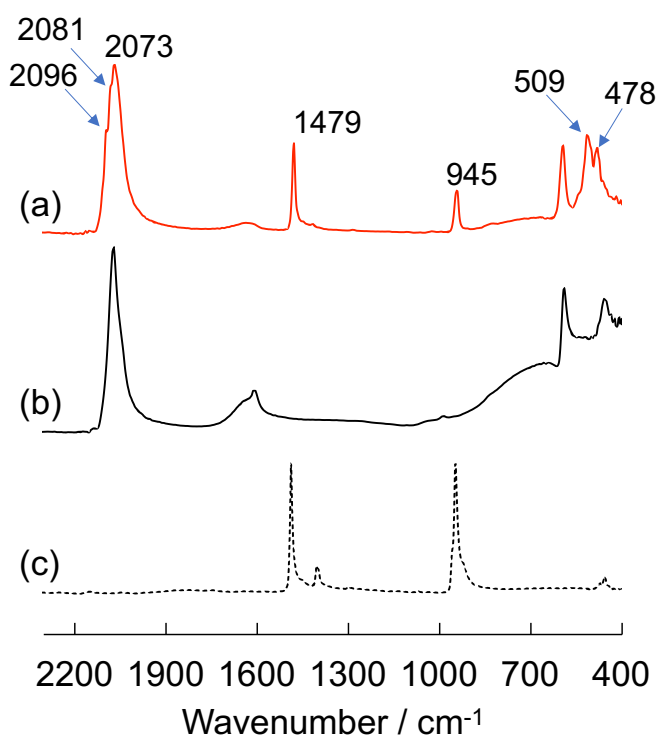
**Fig. S1** X-ray photoelectron spectra of (a)  $(\text{Me}_4\text{N})\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$   $\{(\text{Me}_4\text{N})\text{Co-Fe}\}$  and (b)  $\text{K}\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$   $\{(\text{K})\text{Co-Fe}\}$  in Co 2p, Fe 2p, and N 1s regions. \*Attributed to  $\text{Me}_4\text{N}^+$  ion.



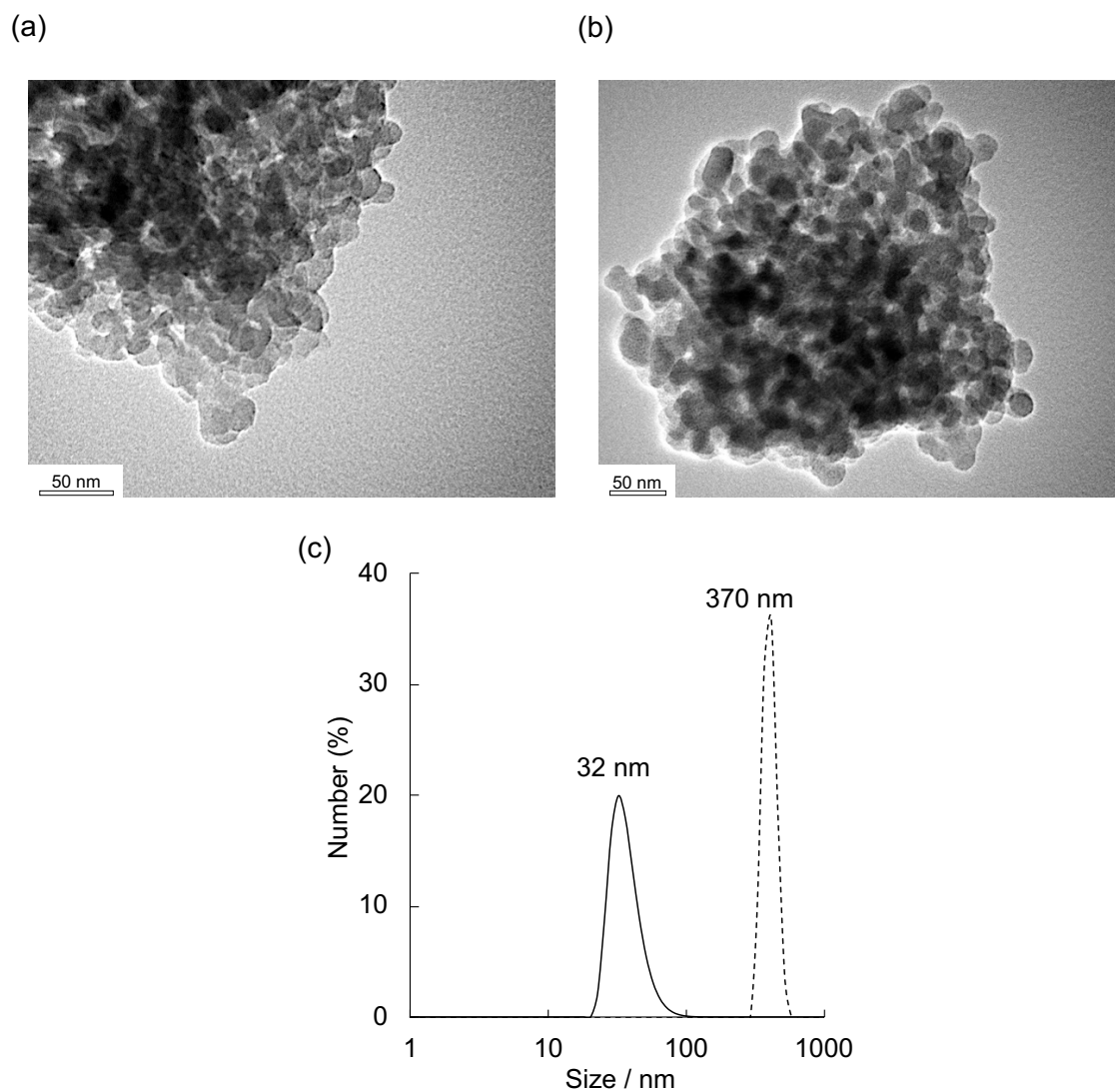
**Fig. S2** Diffused reflectance UV-vis spectra of (a)  $(\text{Me}_4\text{N})\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$   $\{(\text{Me}_4\text{N})\text{Co-Fe}\}$  and (b)  $\text{K}\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$   $\{(\text{K})\text{Co-Fe}\}$ . The numbers indicate the wavelengths of absorption maxima.



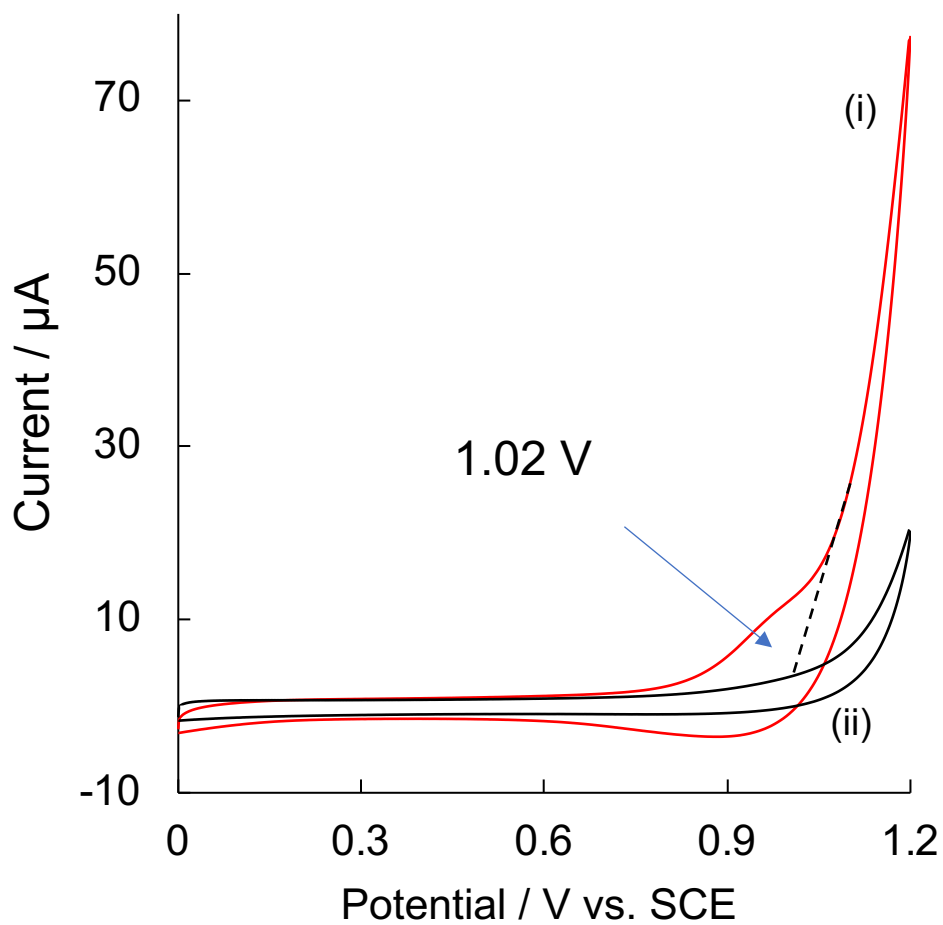
**Fig. S3** Nitrogen adsorption (black circles)-desorption (red squares) isotherms of (a)  $(\text{Me}_4\text{N})\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}\{(\text{Me}_4\text{N})\text{Co-Fe}\}$  and (b)  $\text{K}\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}\{(\text{K})\text{Co-Fe}\}$  at  $-196^\circ\text{C}$ .



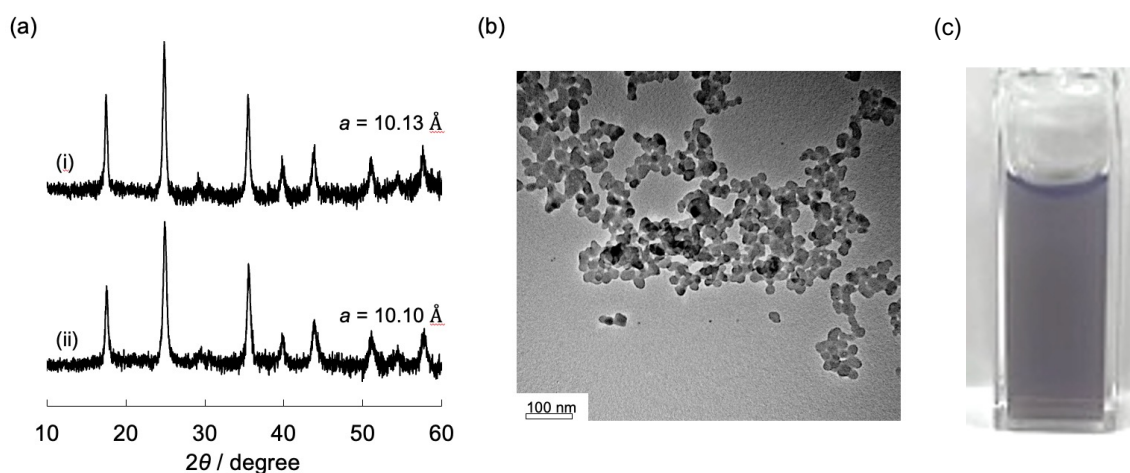
**Fig. S4** Infrared (IR) spectra of (a)  $(\text{Me}_4\text{N})\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}\{(\text{Me}_4\text{N})\text{Co-Fe}\}$ , (b)  $\text{K}\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}\{(\text{K})\text{Co-Fe}\}$ , and (c)  $\text{Me}_4\text{NCl}$ . The spectra were obtained by the IR spectrometer with a diamond ATR attachment.



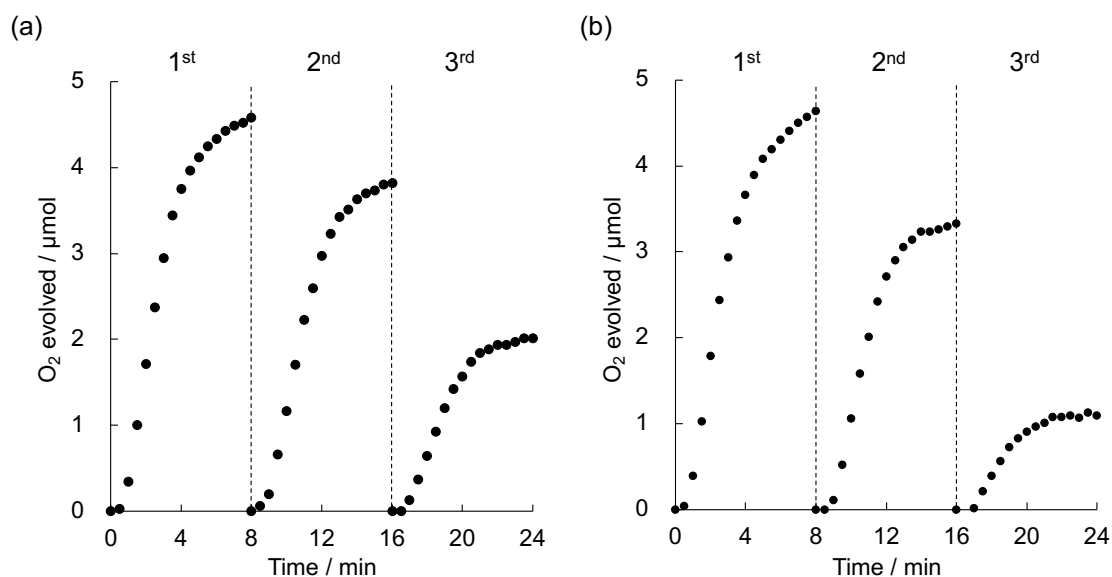
**Fig. S5** (a) Transmission electron microscope (TEM) images of (a)  $(\text{Me}_4\text{N})\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}\{(\text{Me}_4\text{N})\text{Co-Fe}\}$  and (b)  $\text{K}\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}\{(\text{K})\text{Co-Fe}\}$ . (c) Size distribution of  $(\text{Me}_4\text{N})\text{Co-Fe}$  (solid line) and  $(\text{K})\text{Co-Fe}$  (dotted line) determined by dynamic light scattering (DLS).



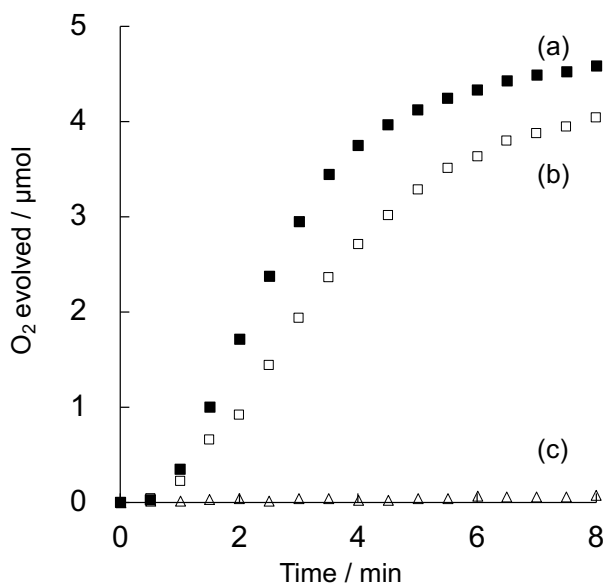
**Fig. S6** Cyclic voltammetry of (i)  $(\text{Me}_4\text{N})\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$   $\{(\text{Me}_4\text{N})\text{Co-Fe}, 1.0 \text{ mM}_{\text{Fe}}\}$  and (ii) blank in a phosphate buffer (pH 7.0, 50 mM, 3.0 mL) recorded at the sweep rate of  $100 \text{ mV s}^{-1}$ . The working, counter, and reference electrodes were a glassy carbon, a Pt wire, and SCE, respectively.



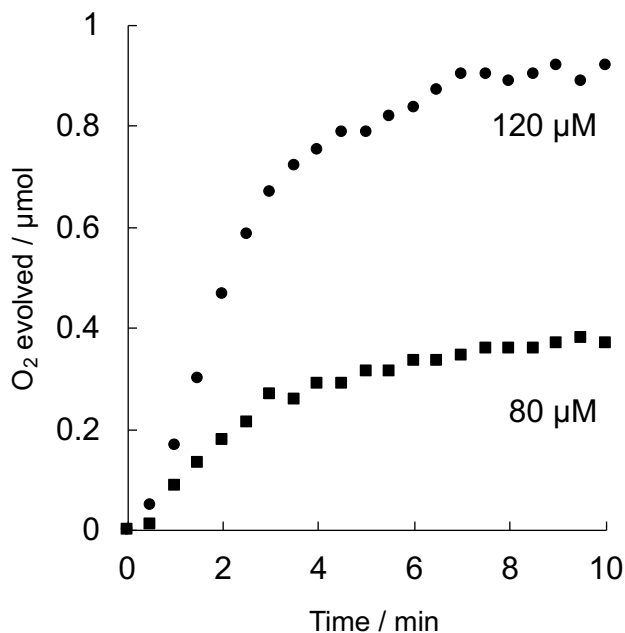
**Fig. S7** (a) Powder X-ray diffraction (PXRD) patterns of (i)  $\text{K}\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$   $\{(\text{K})\text{Co-Fe}\}$  and (ii) water-dispersible  $(\text{K})\text{Co-Fe}$  (modified with  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ ). (b) TEM image of water-dispersible  $(\text{K})\text{Co-Fe}$ . (c) water-dispersible  $(\text{K})\text{Co-Fe}$  (modified with  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ ) in water.



**Fig. S8** Repetitive experiments of photocatalytic water oxidation under photoirradiation of a phosphate buffer (pH 8.0, 50 mM, 2.0 mL) containing  $\text{Na}_2\text{S}_2\text{O}_8$  (5.0 mM, 10  $\mu\text{mol}$ ),  $[\text{Ru}(\text{bpy})_3]\text{SO}_4$  (0.30 mM, 0.6  $\mu\text{mol}$ ) and  $(\text{Me}_4\text{N})\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$   $\{(\text{Me}_4\text{N})\text{Co-Fe}\}$ , 80  $\mu\text{M}_{\text{Fe}}$  with an LED light. A small aliquot (100  $\mu\text{L}$ ) of (a)  $\text{Na}_2\text{S}_2\text{O}_8$  (10  $\mu\text{mol}$ ) and  $[\text{Ru}(\text{bpy})_3]\text{SO}_4$  (0.6  $\mu\text{mol}$ ) and (b)  $\text{Na}_2\text{S}_2\text{O}_8$  (10  $\mu\text{mol}$ ) was added to the reaction solution after each run.

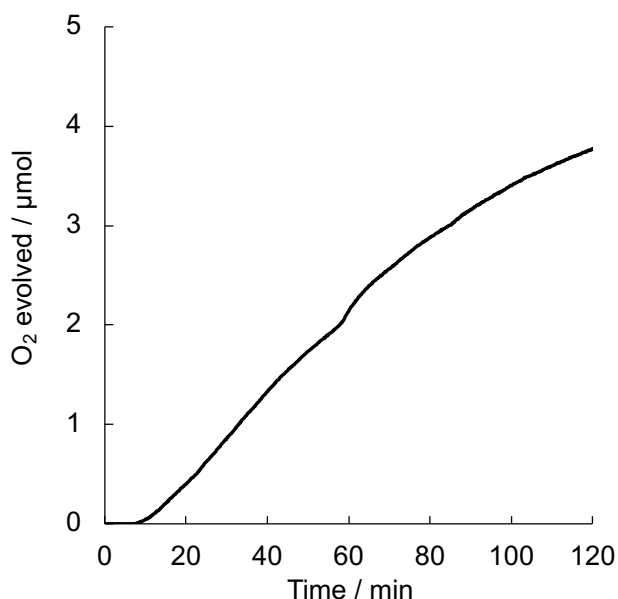


**Fig. S9** Time courses of  $\text{O}_2$  evolution under visible-light irradiation of a phosphate buffer (pH 8.0, 50 mM, 2 mL) containing  $\text{Na}_2\text{S}_2\text{O}_8$  (5.0 mM),  $[\text{Ru}(\text{bpy})_3]\text{SO}_4$  (0.30 mM) and a catalyst ( $80 \mu\text{M}_{\text{Fe}}$ ): (a)  $(\text{Me}_4\text{N})\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$   $\{(\text{Me}_4\text{N})\text{Co-Fe}$ , closed square}, (b)  $\text{Co}^{\text{II}}(\text{NO}_3)_2$  (open square), or (c)  $\text{K}_4[\text{Fe}^{\text{II}}(\text{CN})_6]$  (open triangle) with LED light.

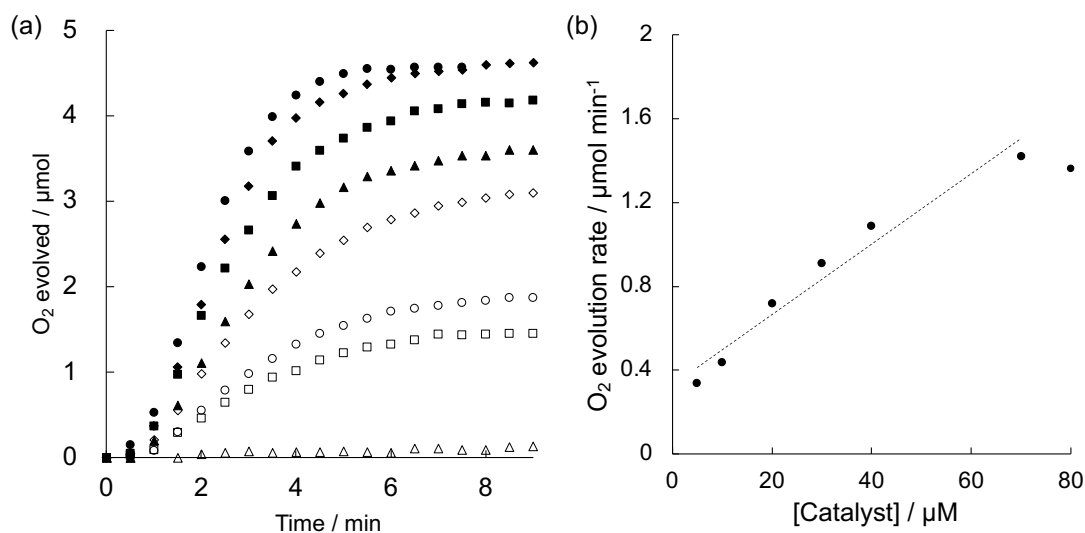


**Fig. S10** Thermal water oxidation using  $(\text{Me}_4\text{N})\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$   $\{(\text{Me}_4\text{N})\text{Co-Fe}$ , 120  $\mu\text{M}_{\text{Fe}}$ } and  $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$  (4  $\mu\text{mol}$ ) in a phosphate buffer (pH 8.0, 50 mM) and  $\text{H}_2\text{SO}_4$  aq. (50 mM) (19:1 (v/v), 2.0 mL).

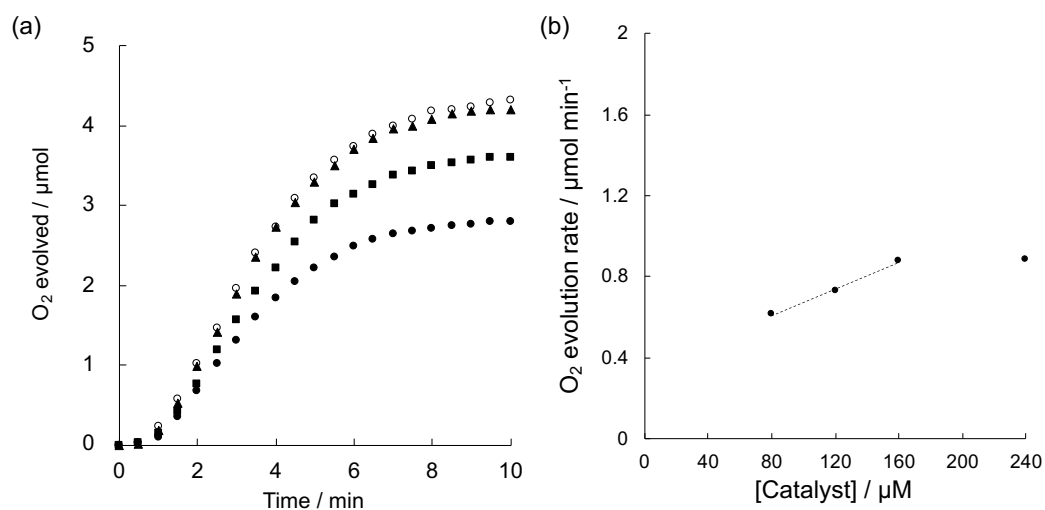




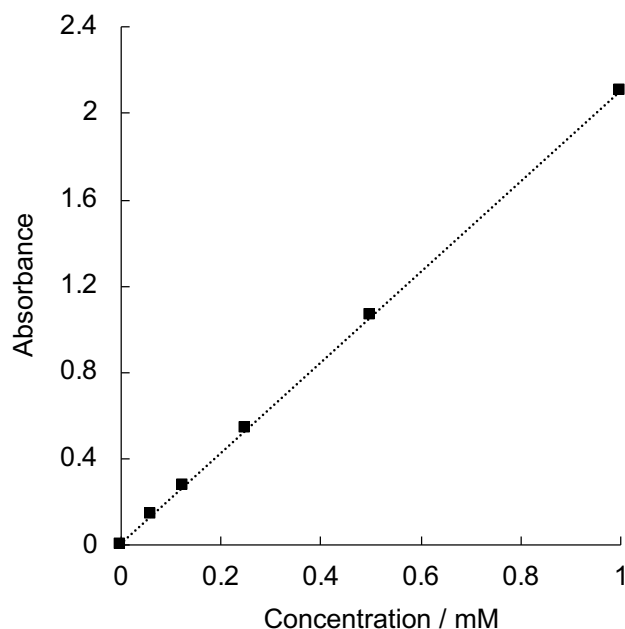
**Fig. S11** Time course of  $O_2$  evolution under visible-light irradiation ( $\lambda = 450$  nm) of a phosphate buffer (pH 8.0, 50 mM, 2 mL) containing  $Na_2S_2O_8$  (5.0 mM),  $[Ru(bpy)_3]SO_4$  (0.30 mM) and  $(Me_4N)\{Co^{II}_{1.5}[Fe^{II}(CN)_6]\}$   $\{(Me_4N)Co-Fe, 80 \mu M_{Fe}\}$  in a quartz cuvette (light path length: 1.0 cm).



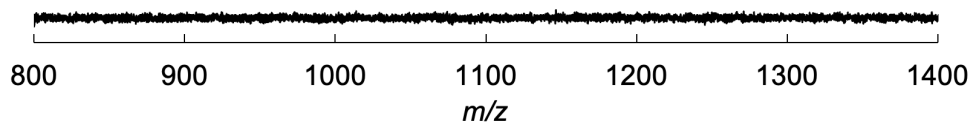
**Fig. S12** (a) Time courses of  $O_2$  evolution under visible-light irradiation of a phosphate buffer (pH 8.0, 50 mM, 2.0 mL) containing  $Na_2S_2O_8$  (5.0 mM),  $[Ru(bpy)_3]SO_4$  (0.30 mM) and  $(Me_4N)\{Co^{II}_{1.5}[Fe^{II}(CN)_6]\}$   $\{(Me_4N)Co-Fe\}$  ( $80 \mu M_{Fe}$ ; closed diamond,  $70 \mu M_{Fe}$ ; closed circle,  $40 \mu M_{Fe}$ ; closed square,  $30 \mu M_{Fe}$ ; closed triangle,  $20 \mu M_{Fe}$ ; closed diamond,  $10 \mu M_{Fe}$ ; open circle,  $5 \mu M_{Fe}$ ; open square, no catalyst; open triangle) with LED light. (b) Plots of initial  $O_2$ -evolution rates at various concentrations of  $(Me_4N)Co-Fe$ . The initial rates were calculated by the slopes of the plots from 1 to 3.5 min.



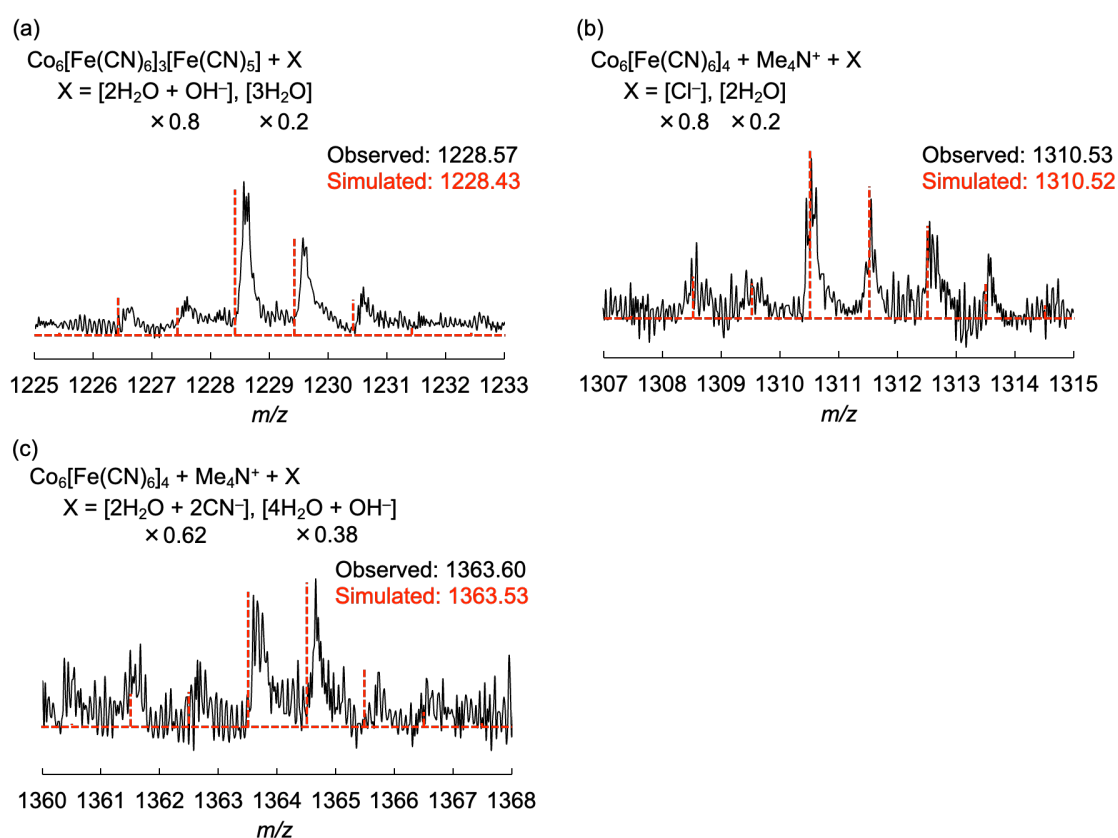
**Fig. S13** (a) Time courses of O<sub>2</sub> evolution under visible-light irradiation of a phosphate buffer (pH 8.0, 50 mM, 2.0 mL) containing Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (5.0 mM), [Ru(bpy)<sub>3</sub>]SO<sub>4</sub> (0.30 mM) and K{Co<sup>II</sup><sub>1.5</sub>[Fe<sup>II</sup>(CN)<sub>6</sub>]} {(K)Co-Fe: 80 μM<sub>Fe</sub>, closed circle; 120 μM<sub>Fe</sub>, closed square; 160 μM<sub>Fe</sub>, closed triangle; 240 μM<sub>Fe</sub>, open circle} with LED light. (b) Initial O<sub>2</sub>-evolution rates depending on the concentrations of (K)Co-Fe. The initial rates were calculated from the slopes of the plots in (a) from 1 to 3.5 min.



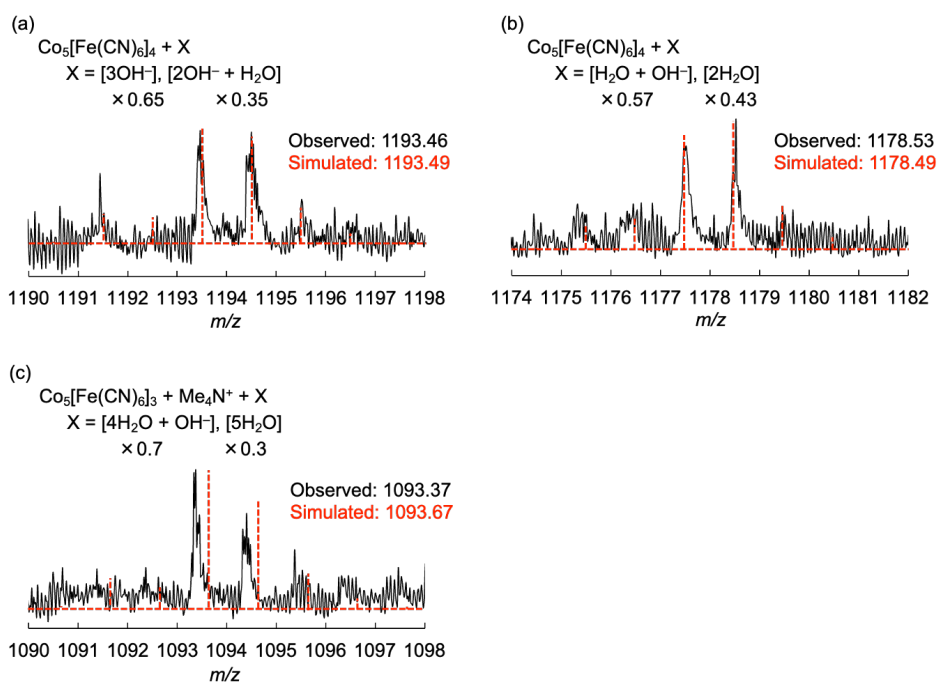
**Fig. S14** Absorbance at 615 nm as a function of the concentrations of (Me<sub>4</sub>N)Co-Fe in the mixed solution of water and acetonitrile [1:39 (v/v)].



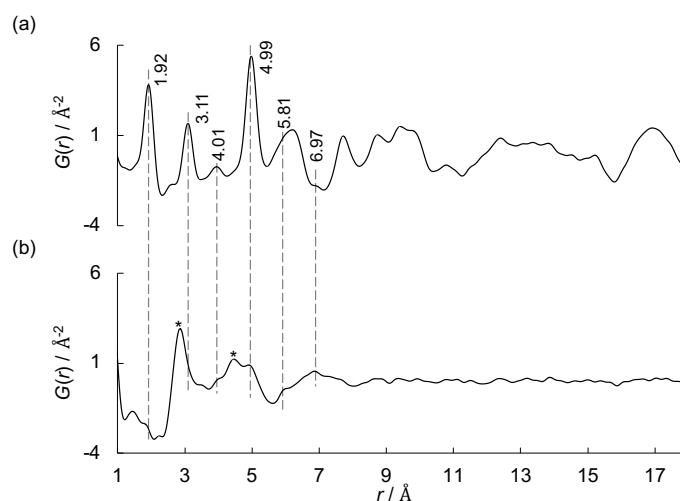
**Fig. S15** Electrospray ionization mass spectrum (ESI-MS) measured for a mixed solution of water and acetonitrile [1:39 (v/v)] without solute (background).



**Fig. S16** Isotope patterns (black solid lines) of ESI-MS peaks (negative mode) appeared around (a) 1228.58, (b) 1310.53, and (c) 1363.60 at the measurements of a mixed solution of water and acetonitrile [1:39 (v/v)] containing  $(\text{Me}_4\text{N})\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\} \{(\text{Me}_4\text{N})\text{Co-Fe}\}$ . The simulated patterns (red dotted lines) were calculated under the assumption that a couple of species containing decanuclear metal complex,  $\text{Me}_4\text{N}^+$ , and extra-ligands such as  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{CN}^-$ , and  $\text{Cl}^-$  ions were concomitantly generated.



**Fig. S17** Isotope patterns (black solid lines) of ESI-MS peaks (negative mode) appeared around (a) 1193.46, (b) 1178.53, and (c) 1093.37 at the measurements of a mixed solution of water and acetonitrile [1:39 (v/v)] containing  $(\text{Me}_4\text{N})\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$   $\{(\text{Me}_4\text{N})\text{Co-Fe}\}$ . The simulated patterns (red dotted lines) were calculated under the assumption that a couple of species containing  $\{\text{Co}_5[\text{Fe}(\text{CN})_6]_4\}^{n-}$  or  $\{\text{Co}_5[\text{Fe}(\text{CN})_6]_3\}^{n-}$  derived from  $\{\text{Co}_6[\text{Fe}(\text{CN})_6]_4\}^{n-}$ ,  $\text{Me}_4\text{N}^+$ , and extra-ligands such as  $\text{H}_2\text{O}$  and  $\text{OH}^-$ , were concomitantly generated.



**Fig. S18** Pair distribution function (PDF) of (a)  $(\text{Me}_4\text{N})\{\text{Co}^{\text{II}}_{1.5}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$   $\{(\text{Me}_4\text{N})\text{Co-Fe}\}$  and (b)  $(\text{Me}_4\text{N})\text{Co-Fe}$  in water. \*Attributed to water.<sup>[S1]</sup>

## References

S1 A. H. Narten and W. E. Thiessen, L. Blum, *Science* 1982, **217**, 1033.