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High Catalytic Activity of Heteropolynuclear Cyanide Complexes Containing Co and Pt Ions for Visible-Light Driven Water Oxidation**

Yusuke Yamada, Kohei Oyama, Rachel Gates, and Shunichi Fukuzumi**

Abstract: *Nearly stoichiometric amount of* O_2 *evolution was observed by visible-light irradiation of an aqueous solution containing* $[Ru^{II}(2,2'\text{-bipyridine})_3]^{2+}$, $Na_2S_2O_8$ *and a heteropolynuclear cyanide complex containing Co and Pt as a photosensitizer, a sacrificial electron acceptor and a water oxidation catalyst, respectively. The heteropolynuclear cyanide complexes exhibited higher catalytic activity than a polynuclear cyanide complex solely containing either Co or Pt ions. The origin of synergistic effect between Co and Pt is discussed in relation to electronic and local atomic structures of the complexes.*

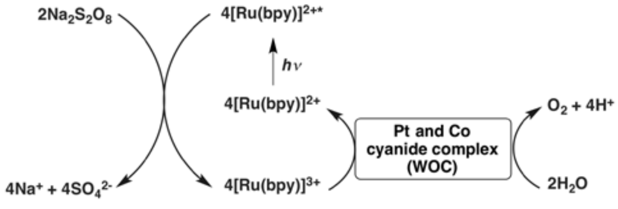
Increasing demand by human beings for energy encourages researchers to realize artificial photosynthesis, in which high-energy compounds are produced from water as an electron donor, utilizing solar energy.[1–3] A bottleneck to realize the artificial photosynthesis is low activity of water oxidation catalysts.[4-5] A wide variety of homogeneous and heterogeneous catalysts have been examined for the water oxidation.[6,7] Metal complexes often used as homogeneous catalysts are advantageous for designing the active species, however their low stability causes a problem about truly active species.[8] Metal oxides have also been extensively studied in heterogeneous systems as robust water oxidation catalysts, although their catalytically active species remain equivocal in multiple component systems.[9] Recently, metal organic frameworks (MOFs) emerged as potential candidates possessing both designable structures in atomic level and robustness under harsh reaction conditions.[10]

Heteropolynuclear cyanide complexes are the simplest class of MOFs. In general, heteropolynuclear cyanide complexes take a cubic structure as far as contained metal ions allow octahedral coordination.[11] Both C and N atoms of cyanide interact with metal ions, however, the C atom tends to coordinate to a metal ion more firmly. When the number of N-bound metal ions is larger than that of C-bound metal ions, the N-bound metal ions need external ligands such as an aqua ligand to fulfill octahedral coordination. In such a case, the aqua ligands can be liberated from the N-bound metal ions in a reaction solution to provide substrate-binding sites.[12] The number of external ligands can be controlled by considering charge compensation in a heteropolynuclear complex.[12] Additionally, the character of the N-bound metal ion can be influenced by the C-bound metal ion through pπ-dπ interaction among a cyanide ligand and the metal ions.[13] Thus, heteropolynuclear cyanide complexes can be designable heterogeneous catalysts for water oxidation.

We report herein visible-light driven water oxidation catalysis of heteropolynuclear cyanide complexes containing both Co and Pt ions, which are superior to polynuclear cyanide complexes solely containing either Co or Pt ions. The heteropolynuclear complexes contain Co^{III} and Pt^{IV} ions as C-bound metal ions and Co^{II} ions as N-bound metal ions. The higher oxidation state of Pt^{IV} than that of Co^{III} can be expected to enhance the oxidation ability of Co^{II} ions. When heteropolynuclear cyanide complexes contain Pt^{II} ions instead of Pt^{IV} ions, the number of defect sites increases in the framework, resulting in increasing the number of active sites accessible by a substrate molecule. Both electronic and structural effects are examined for a series of cyanide complexes by changing content of Pt ion.

The catalysis of the heteropolynuclear cyanide complexes for visible-light driven water oxidation was examined in a reaction solution containing ($[Ru(bpy)_3]^{2+}$: bpy = 2,2'-bipyridine) and $S_2O_8^{2-}$ as a photosensitizer and a sacrificial electron acceptor, respectively. The overall catalytic cycle is shown in Scheme 1, where photoexcited $[Ru(bpy)_3]^{2+}$ initiates the reaction by reducing $Na_2S_2O_8$, and $[Ru(bpy)_3]^{3+}$ thus formed oxidizes a heteropolynuclear cyanide complex which then oxidizes water for O_2 evolution.

Scheme 1. Overall Catalytic Cycle of Visible-light Driven Water Oxidation



A series of the heteropolynuclear cyanide complexes containing Pt^{IV} ions, $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$, were prepared by mixing an aqueous solution containing both $K_3[Co^{III}(CN)_6]$ and $K_2[Pt^{IV}(CN)_6]$ with various Co/Pt ratios ranging from 1:0 to 0:1 and an aqueous solution containing an excess amount of $Co(NO_3)_2$. The formed crystalline powder was collected by filtration. The contents of Co and Pt ions of each powder were determined by X-ray fluorescence measurements. The number of Co^{II} ions in a unit cell decreases by increasing the number of Pt^{IV} ions in a unit cell ($n = 1.5 - 0.5x$). Also, the number of water molecules coordinating to Co^{II} ions decreases from 2 to 0 by increasing the content of Pt^{IV} ions ($m = 3\times(1-x)/n$) (Note in page S2). No peak from K^+ ions was observed

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for all samples, indicating that the content of contaminated K^+ ions was lower than 0.12%. Incorporation of Co^{II} ions in the framework was also confirmed by the higher wavenumber shift of the CN stretching bands [ν(CN)] in IR spectra (Figure S1). Powder X-ray diffraction patterns for the heteropolynuclear cyanide complexes with contents of Pt^{IV} ion ranging from 0 to 1 shown in Figure 1a were assignable to the cubic structure (Figure 1b), which is often called as Prussian blue analogue structure. The gradual decrease of the diffraction peaks in 2θ angle in accordance with increase in the content of Pt^{IV} ions reflects the expansion of a unit cell due to the larger ionic radii of a Pt^{IV} ion (0.77 Å) than that of a Co^{III} ion (0.69 Å).[14] Microporous structures of the series of complexes were also evidenced by the Brunauer-Emmett-Teller (BET) surface areas higher than 400 $m^2\ g^{-1}$ (Figure S2).

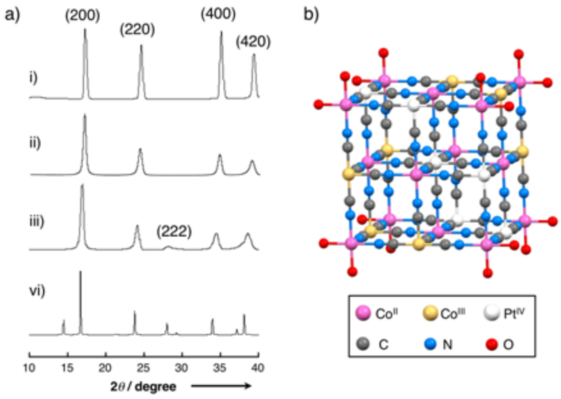

Figure 1. a) Powder X-ray diffraction patterns of a series of heteropolynuclear cyanide complexes, $[Co^{II}(H_2O)_m]_n[Co^{III}_{1-x}Pt^{IV}_x(CN)_6]$. x = i) 0, ii) 0.15, iii) 0.43 and iv) 1. b) A schematic drawing of $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$. Ions are color coded: Co^{II} (pink), N (blue); C (black); O (red); Co^{III} (yellow) and Pt^{IV} (white). Hydrogen atoms of water molecules are omitted.

Replacement of Co^{III} ions in $[Co^{II}(H_2O)_2]_{1.5}[Co^{III}(CN)_6]$ by Pt^{IV} ions enhances the oxidation ability of Co^{II} ions. The oxidation potential of Co^{II} ions in $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$ were examined by differential pulse voltammetry (DPV) in an acetonitrile suspension. The oxidation peak originated from Co^{II} to Co^{III} in $[Co^{II}(H_2O)_2]_{1.5}[Co^{III}(CN)_6]$ (0.67 V *vs*. Ag/Ag^+) was observed in an anodic sweep. The oxidation peak of Co^{II} to Co^{III} was gradually shifted in the positive direction to 0.94 V by increasing the content of Pt^{IV} ions to 1.0 (Figure 2). The positive shift with increasing the content of Pt^{IV} ions evidences the electronic interaction between Pt^{IV} and Co^{II} ions. The electronic interaction between Co^{II} and Pt^{IV} ions also depends on the content of Pt^{IV} ion, evidenced by the shift of absorption maxima originating from the metal-to-metal charge transfer band appearing in the near IR region (Figure S3). The absorption band appeared at around 1165 nm for $[Co^{II}(H_2O)_2]_{1.5}[Co^{III}(CN)_6]$ (x = 0) and was gradually shifted to 1126 nm by increasing the content of Pt^{IV} ions in $[Co^{II}(H_2O)_{1.33}]_{1.29}[(Co^{III}_{0.57}Pt^{IV}_{0.43})(CN)_6]$ (x = 0.43). The near IR bands were assigned to metal-to-metal charge transfer from e_g orbitals of Co^{II} (high spin) to e_g orbitals of Co^{III} or Pt^{IV} (low spin).[15] The positive shift of the oxidation potential of Co^{II} observed in DPV suggests the energy level of the e_g orbital of Co^{II} ions decreases.

Photocatalytic water oxidation was performed by photoirradiation (λ > 420 nm) of a phosphate buffer (2.0 mL, 50 mM, pH 8.0) containing $[Ru(bpy)_3]^{2+}$ (1.0 mM), $Na_2S_2O_8$ (5.0 mM) and $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$ (80 µg). Time courses of O_2

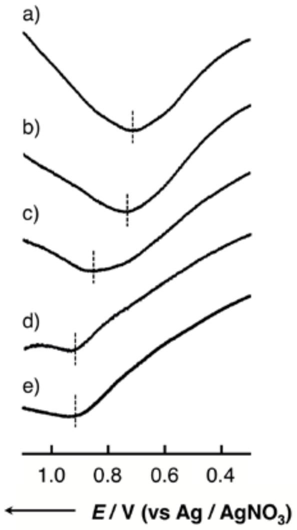

Figure 2. Differential pulse voltammetry of a series of heteropolynuclear cyanide complexes, $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$. x = a) 0; b) 0.15; c) 0.43; d) 0.69 and e) 1. The measurements were performed in an acetonitrile (2.0 mL) suspension of $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$ (10 µmol) using a glassy carbon electrode, a Pt wire and an $Ag/AgNO_3$ electrode as the working electrode, counter electrode and reference electrode, respectively.

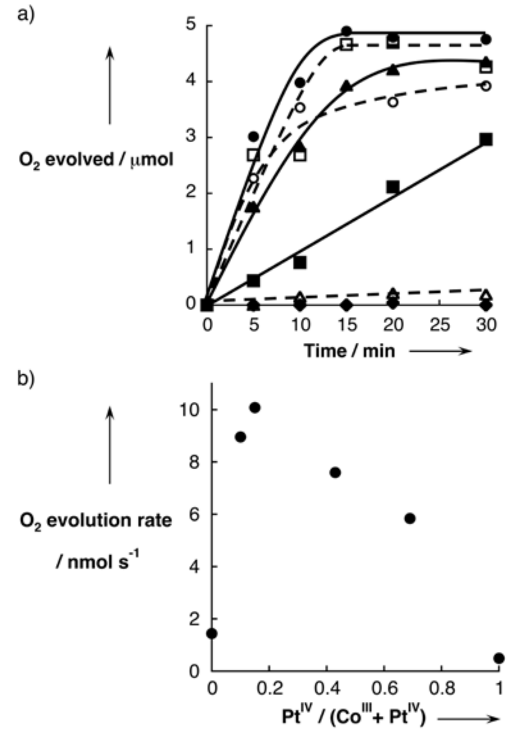

Figure 3. a) Time courses of O_2 evolution by visible-light irradiation (λ > 420 nm) of a phosphate buffer (2.0 mL, 50 mM, pH 8.0) containing $[Ru(bpy)_3]^{2+}$ (1.0 mM), $Na_2S_2O_8$ (5.0 mM) and a heteropolynuclear cyanide complex, $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$ (80 µg). x = 0 (closed square); 0.10 (open square); 0.15 (closed circle); 0.43 (open circle); 0.69 (closed triangle) and 1 (open triangle). Time course of O_2 evolution under dark conditions using the complex with x = 0.15 (open diamond). b) Initial O_2 evolution rates (< 5 min) depending on the content of Pt^{IV} ion in $[Co^{II}(H_2O)_m]_n[(Co^{III}_{1-x}Pt^{IV}_x)(CN)_6]$.

evolution are indicated in Figure 3a. No O_2 evolution was confirmed under dark conditions before photoirradiation. An insignificant amount of O_2 evolution was observed for the reaction solution containing $Co^{II}[Pt^{IV}(CN)_6]$. In contrast, a significant amount of O_2 evolution was observed for the reaction solution containing $[Co^{II}(H_2O)_2]_{1.5}[Co^{III}(CN)_6]$, where the O_2 yield (based on the amount of $Na_2S_2O_8$) reached ~60% after photoirradiation for 30 min. The O_2 yields were further increased to more than 80% by employing $[Co^{II}(H_2O)_m]_n[(Co^{III}{}_{1-x}Pt^{IV}{}_x)(CN)_6]$ (x = 0.15, 0.43 and 0.69) as WOCs. Especially, a nearly stoichiometric amount of O_2 (> 98%) was obtained for the reaction system containing $[Co^{II}(H_2O)_{1.79}]_{1.42}[(Co^{III}{}_{0.85}Pt^{IV}{}_{0.15})(CN)_6]$ (x = 0.15). The initial O_2 evolution rates (< 5 min) were plotted against the content of Pt^{IV} ions in $[Co^{II}(H_2O)_m]_n[(Co^{III}{}_{1-x}Pt^{IV}{}_x)(CN)_6]$ (Figure 3b). The fastest O_2 evolution was observed for $[Co^{II}(H_2O)_{1.79}]_{1.42}[(Co^{III}{}_{0.85}Pt^{IV}{}_{0.15})(CN)_6]$ where the initial O_2-evolution rate exceeds 10 nmol s^{-1}, which is comparable to that reported for the reaction system using IrO_2 nanoparticles, which are known as one of the most active heterogeneous catalysts for the photocatalytic water oxidation, under the condition of pH 5.[16]

The Co^{III} and Pt^{IV} ions are coordinatively saturated, thus, N-bound Co^{II} ions can act as active sites by liberating coordinating H_2O molecules. The number of the H_2O molecules decreases in proportion to the content of Pt^{IV} ions due to charge compensation. On the other hand, the oxidation ability of Co^{II} ions is more enhanced in the presence of Pt^{IV} ions at higher contents by electronic interaction. The lowest activity of $Co^{II}[Pt^{IV}(CN)_6]$ in the O_2 evolution rate suggested that the presence of labile coordination sites on Co^{II} ion is as crucial as oxidation ability.

The robustness of the $[Co^{II}(H_2O)_{1.79}]_{1.42}[(Co^{III}{}_{0.85}Pt^{IV}{}_{0.15})(CN)_6]$ was confirmed by the repetitive addition of an aliquot (100 µL) of $Na_2S_2O_8$ to the reaction solution after ceasing O_2 evolution. O_2 yields higher than 90% were attained up to 3rd run (Figure 4). The used catalyst was collected by centrifugation and used for IR spectrum and powder X-ray diffraction measurements. The IR spectrum measurements of the used sample showed no changes in peak positions and relative intensities of the two ν(CN) peaks at 2236 and 2175 cm^{-1} from those of the fresh sample (Figure S4). $[Co^{II}(H_2O)_2]_{1.5}[Co^{III}(CN)_6]$ has been reported to lose the catalytic activity for water oxidation by binding of bipyridine as evidenced by IR and Raman spectroscopy.[10b] Adsorption of $[Ru(bpy)_3]^{2+}$ or bpy on the $[Co^{II}(H_2O)_{1.79}]_{1.42}[(Co^{III}{}_{0.85}Pt^{IV}{}_{0.15})(CN)_6]$ after the photocatalytic O_2 evolution was also confirmed by the IR spectroscopy, however, deceleration effect of the adsorbent was limited. The XRD peaks of the used sample also contained all the peaks observed for the fresh sample (Figure S5). These results assure the robustness of the $[Co^{II}(H_2O)_{1.79}]_{1.42}[(Co^{III}{}_{0.85}Pt^{IV}{}_{0.15})(CN)_6]$.

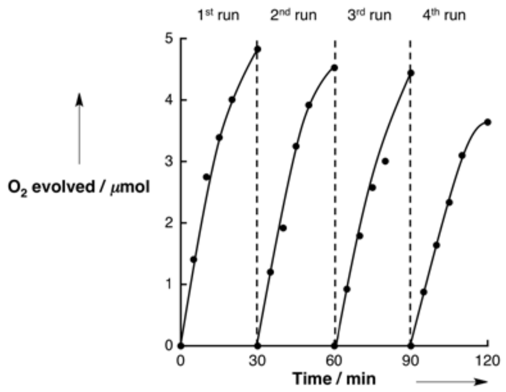

Figure 4. Time courses of O_2 evolution by visible-light irradiation (λ > 420 nm) of a phosphate buffer (2.0 mL, 50 mM, pH 8.0) containing $[Ru(bpy)_3]^{2+}$ (1.0 mM), $Na_2S_2O_8$ (5.0 mM) and $[Co(H_2O)_{1.79}]_{1.42}[(Co_{0.85}Pt_{0.15})(CN)_6]$ (800 µg). A small portion of a concentrated $Na_2S_2O_8$ solution was added to the reaction solution to make a concentration of $Na_2S_2O_8$ 5.0 mM after O_2 evolution ceased.

Effect of structural modification of the frameworks was confirmed by investigating the catalysis of $[Co^{II}(H_2O)_2]_{n'}[\{Co^{III}(CN)_6\}_{1-x}\{Pt^{II}(CN)_4\}_x]$ (n' = 1.5 – 0.5x), which contains Pt^{II} ions with a square planar coordination structure instead of Pt^{IV} ions with an octahedral structure. The Co^{II} ions in the complexes possess two H_2O molecules as external ligands independent of content of Pt^{II} ions (Note in page S3). When no Co^{III} ion was included in a complex, the powder X-ray diffraction pattern indicated that the complex has a planar structure, not a cubic structure. However, complexes containing both Co^{III} and Pt^{II} ions provided the diffraction patterns indicating the cubic structure which is isostructural to Prussian blue (Figure 5a). Also, N_2 adsorption desorption isotherm indicated the presence of micropores with high BET surface area (Figure S2b). A schematic drawing of a typical structure of $[Co^{II}(H_2O)_2]_{n'}[\{Co^{III}(CN)_6\}_{1-x}\{Pt^{II}(CN)_4\}_x]$ is depicted in Figure 5b.

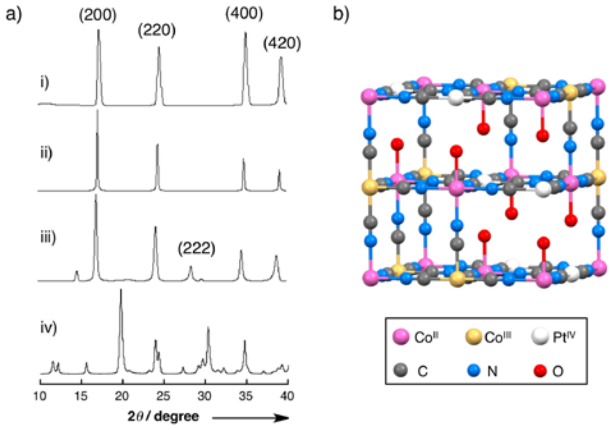

Figure 5. a) Powder X-ray diffraction patterns of a series of heteropolynuclear cyanide complexes, $[Co^{II}(H_2O)_2]_{n'}[\{Co^{III}(CN)_6\}_{1-x}\{Pt^{II}(CN)_4\}_x]$. x = i) 0, ii) 0.37, iii) 0.60 and iv) 1. b) A schematic drawing of $[Co^{II}(H_2O)_2]_{n'}[\{Co^{III}(CN)_6\}_{1-x}\{Pt^{II}(CN)_4\}_x]$. Ions are color-coded: Co^{II} (pink), N (blue); C (black); O (red); Co^{III} (yellow); Pt^{IV} (white). Hydrogen atoms of water molecules are omitted.

Photocatalytic water oxidation was performed by photoirradiation (λ > 420 nm) of a phosphate buffer (2.0 mL, 50 mM, pH 8.0) containing $[Ru(bpy)_3]^{2+}$ (1.0 mM), $Na_2S_2O_8$ (5.0 mM) and $[Co^{II}(H_2O)_2]_{n'}[\{Co^{III}(CN)_6\}_{1-x}\{Pt^{II}(CN)_4\}_x]$ (80 µg) with various contents of Pt^{II} ion (Figure 6). The initial O_2 evolution rate (5 min) of $[Co^{II}(H_2O)_2][Pt^{II}(CN)_4]$ (6.0 nmol s^{-1}) was much higher than that of $Co^{II}[Pt^{IV}(CN)_6]$ (0.50 nmol s^{-1}), resulting from the presence of water molecules coordinating to Co^{II} ions. The initial O_2 evolution rates increased by decreasing the content of Pt^{II} ions up to 0.37, where the initial O_2 evolution rate exceeded 9.9 nmol s^{-1} with a nearly stoichiometric amount of O_2 evolution. An apparent quantum yield determined by using monochromatized light with 450 nm wavelength was calculated to be 50% (Figure S6). The high O_2-evolution rates in accordance with decreasing of content of Pt^{II} ion resulted from a larger number of Co^{II} ions, serving as active sites. The low O_2-evolution rates at low contents of Pt^{II} ions (0.16 and 0) may result due to decreasing available space inside the crystals from increasing the unit with octahedral coordination, $[Co^{III}(CN)_6]^{3-}$.

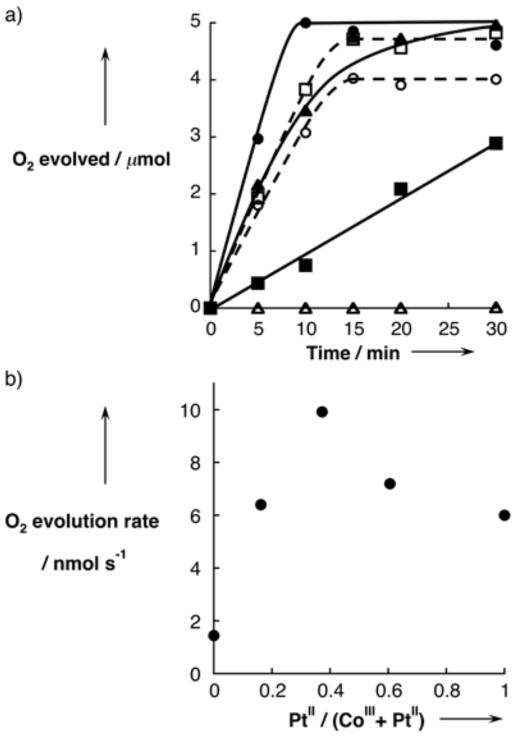

Figure 6. a) Time courses of O_2 evolution by visible-light irradiation (λ > 420 nm) of a phosphate buffer (2.0 mL, 50 mM, pH 8.0) containing $[Ru(bpy)_3]^{2+}$ (1.0 mM), $Na_2S_2O_8$ (5.0 mM) and a heteropolynuclear cyanide complex, $[Co^{II}(H_2O)_2]_n[\{Co^{III}(CN)_6\}_{1-x}\{Pt^{II}(CN)_4\}_x]$ (80 µg). x = 0 (closed square); 0.16 (open square); 0.37 (closed circle); 0.60 (closed triangle) and 1 (open circle). Time course of O_2 evolution under dark conditions using the complex with x = 0.37 (open triangle) b) Initial O_2 evolution rates (< 5 min) depending on the content of Pt^{II} ion in $[Co^{II}(H_2O)_2]_n[\{Co^{III}(CN)_6\}_{1-x}\{Pt^{II}(CN)_4\}_x]$.

Repetitive experiments using $[Co^{II}(H_2O)_2]_{1.31}[\{Co^{III}(CN)_6\}_{0.63}\{Pt^{II}(CN)_4\}_{0.37}]$ (800 µg) as a water oxidation catalyst were performed by the same procedure as the experiments that used $[Co^{II}(H_2O)_{1.79}]_{1.42}[(Co^{III}_{0.85}Pt^{IV}_{0.15})(CN)_6]$. O_2 yields higher than 80% were obtained for 3rd run (Figure S7). The XRD pattern and ν(CN) in IR spectroscopy of $[Co^{II}(H_2O)_2]_{1.31}[\{Co^{III}(CN)_6\}_{0.63}\{Pt^{II}(CN)_4\}_{0.37}]$ after the reaction were the same as those of the fresh catalyst (Figures S8 and S9). IR spectra indicated that strong adsorption of negatively charged SO_4^{2-} on $[Co^{II}(H_2O)_2]_{1.31}[\{Co^{III}(CN)_6\}_{0.63}\{Pt^{II}(CN)_4\}_{0.37}]$, however, no adsorption of positively charged $[Ru(bpy)_3]^{2+}$ or neutral bpy, which adsorbed on $[Co^{II}(H_2O)_{1.79}]_{1.42}[(Co^{III}_{0.85}Pt^{IV}_{0.15})(CN)_6]$, was confirmed. These results may reflect the nature of defect sites of each complex.

In conclusion, a nearly stoichiometric amount of O_2 evolution was observed in visible-light (λ > 420 nm) driven water oxidation efficiently catalyzed by heteropolynuclear cyanide complexes containing both Co and Pt ions. The addition of $Pt^{IV}(CN)_6^{2-}$ units to Co cyanide complexes enhanced the catalysis for water oxidation by increasing the oxidation potential of N-bound Co^{II} ions acting as active sites. When $Pt^{II}(CN)_4^{2-}$ units are introduced to Co cyanide complexes, the hollow structure enables utilization of space inside the crystals. These results suggest that Pt ions irrespective of the valence are effective to enhance catalytic activity of Co cyanide complex by electronic and structural modifications. The strategy to utilize heteropolynuclear cyanide complexes reported in this study provides a convenient way to develop efficient water oxidation catalysts.

Experimental Section

Heteropolynuclear cyanide complexes were prepared by mixing an aqueous solution containing $K_3[Co^{III}(CN)_6]$ and $K_2[Pt^{IV}(CN)_6]$ or $K_2[Pt^{II}(CN)_4]$ with that containing $Co(NO_3)_2$ to form precipitates. The contents of Co^{III} and Pt^{IV} ions in a prepared complex were determined by X-ray fluorescence measurements (Rigaku ZSX 1000/MPS). A typical procedure for a catalysis measurement is as follows: a heteropolynuclear cyanide complex (80 µg) was suspended to a phosphate buffer (pH 8.0, 50 mM, 2.0 mL) containing $[Ru(2,2'\text{-bipyridine})_3]SO_4$ (1.0 mM) and $Na_2S_2O_8$ (5.0 mM) under Ar atmosphere. After photoirradiation (λ > 420 nm) of the suspension with magnetic stirring, an aliquot of a 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). Repetitive reactions were conducted by addition of $Na_2S_2O_8$ to a reaction solution after ceasing O_2 evolution where the pH of the solution was adjusted to a certain value. The experimental details about chemicals and other characterization of complexes are described in the Supporting Information.

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Entry for the Table of Contents

Water Oxidation

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Nearly stoichiometric amount of O_2 evolution was observed by visible-light irradiation of an aqueous buffer (pH 8) containing [Ru^{II}(2,2'-bipyridine)$_3$], $Na_2S_2O_8$ and a heteropolynuclear cyanide complex containing Co and Pt ions as a photosensitizer, a sacrificial electron acceptor, and a water oxidation catalyst, respectively. Synergistic effect between Co and Pt ions was confirmed for the water oxidation catalysis of the heteropolynuclear complexes.