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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

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Photocatalytic production of hydrogen peroxide from water and dioxygen under visible light irradiation was made possible by using polymeric cyano-bridged heteronuclear metal complexes ($M^{II}[Ru^{II}(CN)_4(bpy)]$; M^{II} = Ni^{II}, Fe^{II} and Mn^{II}), where the photocatalytic two-electron reduction of O_2 and water oxidation were catalysed by the Ru and M^{II} moieties, respectively.

The production of solar fuel through artificial photosynthesis has attracted considerable attention because of the global energy shortage and growing environmental concerns.[1-3] Artificial photosynthesis is composed of several processes such as light-harvesting, charge-separation, water oxidation and proton or CO_2 reduction, which require hybrid catalytic systems possessing multi-catalytic functions.[4-7] Metal complexes often used as homogeneous catalysts are advantageous for designing and synthesising heteronuclear metal complexes to exhibit the multifunctional catalysis. However, the synthesis of such multifunctional catalysts has been very difficult and the low stability of homogeneous catalysts often causes a problem about truly active species.[8] On the other hand, heterogeneous metal and metal oxide nanoparticles have been extensively studied as robust photocatalysts as well as catalysts for water reduction and oxidation.[8] However, the difficulty to clarify the mechanism of the heterogeneous catalysis has precluded rational design for heterogeneous multifunctional catalysts.[9,10] Recently, coordination polymers including metal organic frameworks have emerged as a class of heterogeneous catalysts possessing the advantage of homogeneous catalysts.[11] The highly designable nature of the coordination polymers allow to design dual function catalysts used for solar fuel production with energy input from sunlight.[12]

We report herein that polymeric cyano (CN)-bridged heteronuclear metal complexes ($M^{II}[Ru^{II}(CN)_4(bpy)]$; M^{II} = Ni^{II}, Fe^{II} and Mn^{II}) act as dual function catalysts. The catalysts incorporate both a visible-light responsible photosensitiser and catalysis units for photocatalytic reduction of O_2 to H_2O_2 and for H_2O oxidation. H_2O_2 has merited increasing attention as an ideal solar fuel alternative to gaseous hydrogen, because an aqueous solution of H_2O_2 can be used as a fuel in a one-compartment fuel cell to generate electricity.[13-15] In this context, photocatalytic production of H_2O_2 by reduction of O_2 with water, both of which are earth abundant, has been studied.[16-18] Reported photocatalytic H_2O_2 production systems usually employed a water oxidation catalyst together with a soluble photosensitiser, which also acts as an O_2 reduction catalyst, to utilise visible light efficiently.[18] Incorporation of such a photosensitiser acting as an O_2 reduction catalyst to a water oxidation catalyst can construct efficient photocatalysts by facilitating electron transfer.

$K_2[Ru^{II}(CN)_4(bpy)]$ (bpy = 2,2'-bipyridine) was synthesised and characterised as reported in the literature.[19] The K^+ ion was replaced by Fe^{2+} ion to produce $Fe^{II}[Ru^{II}(CN)_4(bpy)]$.[20] Similarly $Ni^{II}[Ru^{II}(CN)_4(bpy)]$, $Mn^{II}[Ru^{II}(CN)_4(bpy)]$, $Co^{II}[Ru^{II}(CN)_4(bpy)]$, $Cu^{II}[Ru^{II}(CN)_4(bpy)]$, $Fe^{II}[Ru^{II}(CN)_4(Me_2phen)]$ and $Fe^{II}[Ru^{II}(CN)_4\{(MeO)_2bpy\}]$ were synthesised and characterised by powder X-ray diffraction patterns, IR and diffused reflectance UV-vis spectra (see Figs. S1-S3†). Powder XRD patterns show that the structure of the complexes is 4,2-ribbon like chain (Fig. 1).[21] IR spectra shifting to higher wavenumber indicate the incorporation of divalent metal ions into the frameworks. $Fe^{II}[Ru^{II}(CN)_4(bpy)]$ acts as an effective photocatalyst for production of H_2O_2 from H_2O and O_2 in the presence of $Sc(NO_3)_3$, which is expected to enhance H_2O_2 yield by stabilising a reactive intermediate, $O_2^{\bullet -}$ and thus, by

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† Electronic Supplementary Information (ESI) available: Experimental details, Powder XRD (Fig. S1), IR (Fig. S2), DRS (Fig. S3), O_2-labeling experiment (Figs. S4 and S9), Time course of H_2O_2 generation (Fig. S5), DLS (Fig. S6), EPR (Fig. S7), Emission spectra and Stern-Volmer plots (Fig. S8) and. See DOI: 10.1039/x0xx00000x

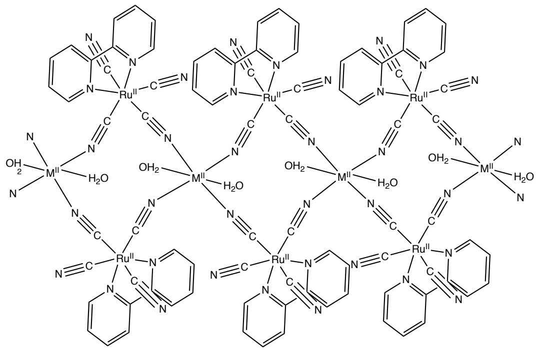

Fig. 1. Schematic drawing of 4,2-ribbon like chain structure.

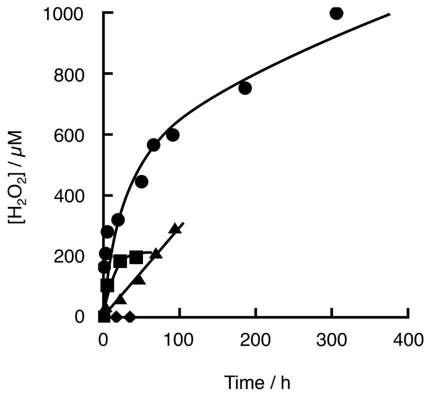

Fig. 2 Time profiles of production of H_2O_2 from H_2O and O_2 with $Fe^{II}[Ru^{II}(CN)_4(bpy)]$ (1.2 mM, ●), $Fe^{II}[Ru^{II}(CN)_4(Me_2phen)]$ (1.1 mM, ▪), $Fe^{II}[Ru^{II}(CN)_4\{(MeO)_2bpy\}]$ (1.0 mM, ▲) and $Fe^{II}_2[Ru^{II}(CN)_6]$ (1.4 mM, ◆), in the presence of $Sc(NO_3)_3$ (0.10 M) in O_2-saturated H_2O (2.0 mL) under visible light irradiation with a Xenon lamp using a UV cut-off filter (λ > 390 nm) at 298 K.

prohibiting back electron transfer,[18a] in H_2O under irradiation of visible light ($\lambda > 390$ nm) as shown in Fig. 2 [Eq. (1)]. The

$$2H_2O + O_2 \xrightarrow[\text{Fe}^{\text{II}}[\text{Ru}^{\text{II}}(\text{CN})_4(\text{bpy})]]{h\nu} 2H_2O_2 \tag{1}$$

origin of oxygen in the produced H_2O_2 was confirmed by labelling experiments using gaseous $^{18}O_2$ (Fig. S4†). It was confirmed that no H_2O_2 was produced when $Fe^{II}[Ru^{II}(CN)_4(bpy)]$ was replaced by $Fe^{II}_2[Ru^{II}(CN)_6]$, which does not absorb visible light (Fig. 2).[22]

Among various metal-substituted $M^{II}[Ru^{II}(CN)_4(bpy)]$, $Ni^{II}[Ru^{II}(CN)_4(bpy)]$ exhibited the highest catalytic reactivity for the production of H_2O_2 from H_2O and O_2 as shown in Fig. 3. No H_2O_2 formation was observed when $K_2[Ru^{II}(CN)_4(bpy)]$ was used as a homogeneous catalyst (Fig. S5†). The catalytic activity highly influenced by N-bound M^{II} species suggests that M^{II} ions offer the active sites for the photocatalytic water oxidation as reported for conventional Prussian blue analogues used as water oxidation catalysts.[23] Thus, a Ni ion in the 4,2-ribbon like structure may have a coordination structure or bonds with aqua ligands suitable for water oxidation.

When H_2O was replaced by a mixed solvent of CH_3OH/H_2O (5:1, v/v), the amount of H_2O_2 produced in the photocatalytic oxidation of H_2O by O_2 with $Ni^{II}[Ru^{II}(CN)_4(bpy)]$ increased significantly as compared with those in only H_2O to afford the apparent turnover number (TON) of 247 based on the number of the monomer unit after 70 h (Fig. 4). The particle sizes of $Ni^{II}[Ru^{II}(CN)_4(bpy)]$ have not been significantly changed during the reaction (Fig. S6†). The better photocatalytic performance in the mixed solvent than that in pure water can be explained by the lower dielectric constant of the mixed solvent. The lower dielectric constant is beneficial to elongate the lifetime of $O_2^{\bullet-}$ by enhancing electrostatic interaction between Sc^{3+} and $O_2^{\bullet-}$, resulting in increasing H_2O_2 yields. No H_2O_2 production in pure CH_3OH as shown in Fig. 4 manifested that water is the electron source of O_2 reduction.

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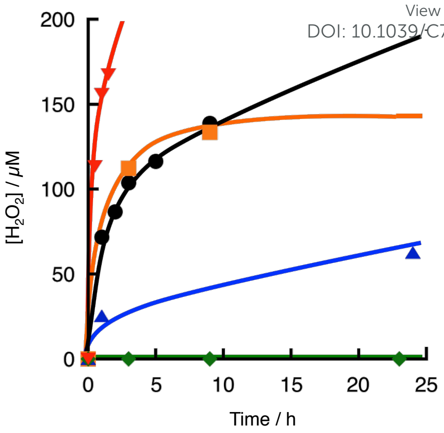

Fig. 3 Time profiles of production of H_2O_2 from H_2O and O_2 with $M^{II}[Ru^{II}(CN)_4(bpy)]$ (0.12 mM; M = Ni (▼), Mn (■), Fe (●), Co (▲) and Cu (◆)) in the presence of $Sc(NO_3)_3$ (0.10 M) in O_2-saturated H_2O (2.0 mL) under visible light irradiation with a Xenon lamp using a UV cut-off filter (λ > 390 nm) at 298 K.

Nanosecond laser-induced transient absorption spectra of $K_2[Ru^{II}(CN)_4(bpy)]$ in CH_3OH/H_2O (5:1, v/v) were measured for $[Ru^{II}(CN)_4(bpy)]^{2-}$ moiety. The lifetime of the excited state of $[Ru^{II}(CN)_4(bpy)]^{2-}$ was determined to be 0.23 μs in CH_3OH/H_2O (5:1, v/v) (Fig. 5a). The lifetime of the excited state of $[Ru^{II}(CN)_4(bpy)]^{2-}$ was shortened by increasing concentration of

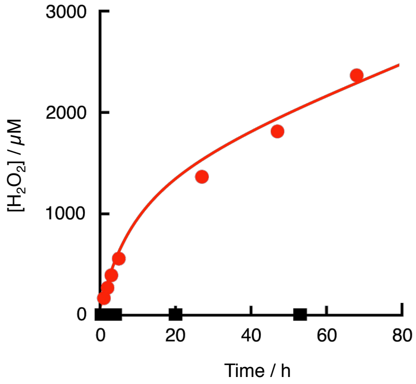

Fig. 4 Time profile of production of H_2O_2 from H_2O and O_2 with $Ni^{II}[Ru^{II}(CN)_4(bpy)]$ (9.6 mM) in the presence of $Sc(NO_3)_3$ (67 mM) in O_2-saturated CH_3OH/H_2O (3.0 mL; 5:1, v/v) under visible light irradiation with a Xenon lamp using a UV cut-off filter (λ > 390 nm) at 298 K (●). Time profile in CH_3OH without H_2O under otherwise the same experimental conditions is also shown for comparison (▪).

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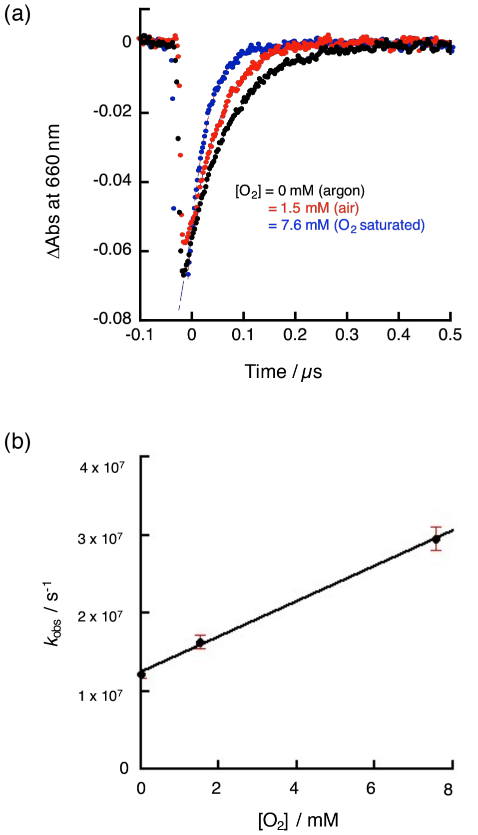


Fig. 5 (a) Decay time profiles of absorbance at 660 nm observed in CH_3OH/H_2O (5:1, v/v) containing $K_2[Ru^{II}(CN)_4(bpy)]$ (0.29 mM) and various concentrations of O_2 ($[O_2]$: 0 (black), 1.5 (red) and 7.6 (blue) mM). (b) Plot of the decay rate constant *vs.* concentration of O_2.

O_2 (Fig. 5b). This suggests that electron transfer from the excited state of $[Ru^{II}(CN)_4(bpy)]^{2-}$ to O_2 occurs to produce $[Ru^{III}(CN)_4(bpy)]^-$ and $O_2^{\bullet-}$. In the presence of Sc^{3+} ions, $O_2^{\bullet-}$ is bound to a Sc^{3+} ion to afford the $O_2^{\bullet-}$–Sc^{3+} complex, which was detected by EPR after photoirradiation of an O_2-saturated CH_3OH/H_2O (5:1, v/v) solution of $Ni^{II}[Ru^{II}(CN)_4(bpy)]$ as shown in Fig. 6 and Fig. S7†, where the superhyperfine due to Sc nucleus (8 lines, $I = 7/2$) is observed.[24] The rate constant of electron transfer from the excited state of $[Ru^{II}(CN)_4(bpy)]^{2-}$ to O_2 was determined from the linear plot of the decay rate constant *vs.* concentration of O_2 to be $2.3(\pm 0.2) \times 10^9$ M^{-1} s^{-1}, which is diffusion-limited and consists the rate constant of electron transfer determined from a slope of Stern–Volmer plot and the lifetime of $[Ru^{II}(CN)_4(bpy)]^*$ (Fig. S8†).

The capability of H_2O oxidation of $Ni^{II}[Ru^{III}(CN)_4(bpy)]^+$ was confirmed in the photocatalytic oxidation of H_2O by persulphate with $Ni^{II}[Ru^{II}(CN)_4(bpy)]$ in the presence of $Sc(NO_3)_3$ in CH_3OH/H_2O (5:1, v/v), where O_2 evolution was observed under visible light irradiation ($\lambda > 390$ nm). Water oxidation using $H_2{}^{18}O$ instead of $H_2{}^{16}O$ was also conducted to confirm whether evolved oxygen comes from water. After the reaction, the evolved oxygen was analysed by GC-MS (Fig. S9†). The observed O_2 was $^{18}O^{18}O$ (>99%), indicating that $Ni^{II}[Ru^{II}(CN)_4(bpy)]$ oxidises water even in the presence of methanol. The photocatalytic cycle is given in Scheme 1, where the excited state of $Ni^{II}[Ru^{II}(CN)_4(bpy)]$ was oxidatively quenched by $Na_2S_2O_8$ to produce $Ni^{II}[Ru^{III}(CN)_4(bpy)]^+$ and, then, $\{Ni^{III}[Ru^{II}(CN)_4(bpy)]\}^+$ that oxidises water to evolve O_2.

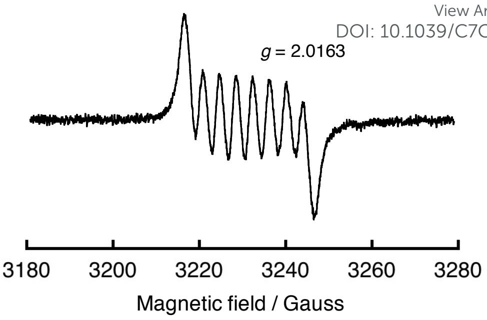
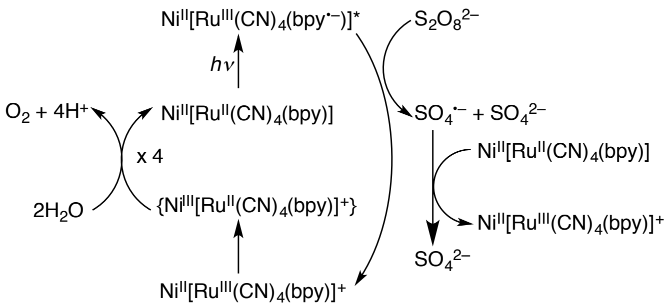


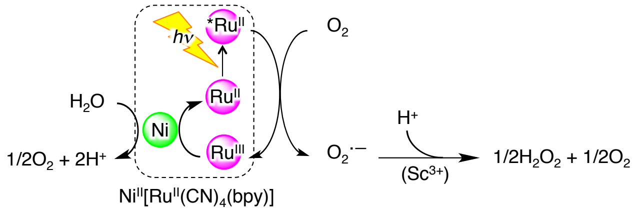
Fig. 6 EPR spectrum observed under photoirradiation of an O_2-saturated CH_3OH/H_2O (5:1, v/v) solution (2.0 mL) containing $Ni^{II}[Ru^{II}(CN)_4(bpy)]$ (0.50 mM) and $Sc(NO_3)_3$ (0.10 M) with an Hg lamp ($\lambda > 310$ nm) at 298 K.



Scheme 1 Catalytic cycle of visible-light driven water oxidation by persulphate with $Ni^{II}[Ru^{II}(CN)_4(bpy)]$

The mechanism of photocatalytic production of H_2O_2 from H_2O and O_2 with $Ni^{II}[Ru^{II}(CN)_4(bpy)]$ in the presence of Sc^{3+} is shown in Scheme 2. Photoexcitation of $Ni^{II}[Ru^{II}(CN)_4(bpy)]$ resulted in electron transfer from the excited state of $Ni^{II}[Ru^{II}(CN)_4(bpy)]$ to O_2 in the presence of Sc^{3+} to produce $Ni^{II}[Ru^{III}(CN)_4(bpy)]^+$ and $O_2^{\bullet-}$–Sc^{3+}. The $O_2^{\bullet-}$–Sc^{3+} complex disproportionates in the presence of H^+ to produce H_2O_2.[12] On the other hand, four equivalents of $Ni^{II}[Ru^{III}(CN)_4(bpy)]^+$ oxidises water to produce O_2 and four equivalents of H^+.

In conclusion, polymeric cyano-bridged heteronuclear metal complexes ($M^{II}[Ru^{II}(CN)_4(bpy)]$; M^{II} = Ni^{II}, Fe^{II} and Mn^{II}) exhibited dual function photocatalysis for H_2O oxidation and O_2 reduction to H_2O_2 in photocatalytic production of H_2O_2 from H_2O and O_2. The highest apparent TON of 247 based on the number of monomer unit was obtained with $Ni^{II}[Ru^{II}(CN)_4(bpy)]$ for production of H_2O_2 from H_2O and O_2 in



Scheme 2 Catalytic cycle of visible-light driven water oxidation by O_2 with $Ni^{II}[Ru^{II}(CN)_4(bpy)]$

the presence of $Sc(NO_3)_3$ in CH_3OH/H_2O (5:1, v/v) under visible light irradiation (λ > 390 nm). The dual function photocatalysis of $M^{II}[Ru^{II}(CN)_4(bpy)]$ in a single catalyst provides a very efficient integrated process for the photocatalytic production of H_2O_2 as a promising solar fuel from H_2O and O_2 using solar energy.

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