An artificial model of photosynthetic photosystem II: visible-light-derived O_2 production from water by a di-μ-oxo-bridged manganese dimer as an oxygen evolving center†

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Visible-light-derived O_2 production was yielded by conjugating water oxidation catalysis by $[(OH_2)(terpy)Mn(\mu\text{-}O)_2Mn(terpy)(OH_2)]^{3+}$ as an *oxygen evolving center* model and photo-sensitization of $[Ru(bpy)_3]^{2+}$ as a photoexcitation center model at an interlayer of mica.

Light absorption of the chlorophyll photoexcitation center so-called P_{680} induces electron transfer from P_{680} to pheophytin as a primary electron acceptor and subsequently to two quinones at photosystem II (PS II) in photosynthesis.[1] To the formed $P_{680}{}^{\bullet+}$ radical cation, an electron is donated from an oxo-bridged tetra-manganese cluster so-called *oxygen evolving complex* (OEC) through a Tyr_Z residue as an electron mediator. Water oxidation to evolve O_2 occurs upon accumulating four oxidizing equivalents on OEC by the successive photo-induced electron-transfer process. Development of a functional PS II model is a challenging task in the related fields to provide mechanistic insight into photosynthetic O_2 production and shed light on the promising way towards an artificial photosynthetic model.[2–5] The most functional OEC models capable of catalyzing water oxidation to O_2 have been synthesized based on ruthenium and iridium complexes.[6–13] Synthetic manganese-oxo complexes reported as a functional OEC model are few, though OEC is composed of oxo-bridged manganese clusters.[14–18] The extension of manganese-oxo complex-based OEC models to a photochemical system is expected to yield a strikingly similar PS II model.

We previously reported that $[(OH_2)(terpy)Mn(\mu\text{-}O)_2Mn(terpy)(OH_2)]^{3+}$ (**1**) (terpy = 2,2′:6′,2″-terpyridine) works as a catalyst for water oxidation when it is adsorbed on layer compounds of kaolin, montmorillonite and mica.[15,19] This encourages us to develop a functional PS II model using the layer compound/**1** adsorbate as an OEC model. It is well-defined that with a metal-to-ligand charge transfer (MLCT) photoexcited state of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) it is thermodynamically possible to split water to O_2 and H_2. Herein we report that visible-light-derived O_2 production is yielded by conjugating water oxidation catalysis by **1** and photo-sensitization of $[Ru(bpy)_3]^{2+}$ at an interlayer of mica.

Mica is able to adsorb cationic **1** and $[Ru(bpy)_3]^{2+}$ by cation exchange with Na^+ (cation exchange capacity: CEC = 1.2 meq g^{-1}). **1** was adsorbed onto mica from an aqueous solution of **1**, followed by similar adsorption of $[Ru(bpy)_3]^{2+}$ to yield the mica adsorbate of **1** and $[Ru(bpy)_3]^{2+}$ (mica/**1**/$[Ru(bpy)_3]^{2+}$). The X-ray diffraction (XRD) data indicate that either **1** or $[Ru(bpy)_3]^{2+}$ is intercalated into an interspace between mica layers (Fig. S1, ESI†). For the diffuse reflectance (DR) spectra of the mica/**1**/$[Ru(bpy)_3]^{2+}$ adsorbate, the absorption at λ_{max} = 475 nm assigned to MLCT transition of $[Ru(bpy)_3]^{2+}$ was 5.2 times more intense than that for the mica/$[Ru(bpy)_3]^{2+}$ adsorbate with the identical $[Ru(bpy)_3]^{2+}$ concentration (w_{Ru} = 20 μmol g^{-1}) (Fig. S2†). The specifically intense absorption of the mica/**1**/$[Ru(bpy)_3]^{2+}$ adsorbate can be explained by localization of $[Ru(bpy)_3]^{2+}$ close to the mica surface. This means that $[Ru(bpy)_3]^{2+}$ is shallowly-intercalated outside **1** in an interlayer of mica.

The mica/**1**/$[Ru(bpy)_3]^{2+}$ adsorbate (3.3 μmol **1**, 0.4 μmol $[Ru(bpy)_3]^{2+}$, 20 mg mica) was suspended in an acetate buffer solution (pH = 6.2, 2.0 ml) containing 15 mM $S_2O_8{}^{2-}$. When visible light (λ > 420 nm) irradiated the suspension with stirring, O_2 was significantly evolved, as shown in Fig. 1a. In the absence of a component of **1**, $[Ru(bpy)_3]^{2+}$ and $S_2O_8{}^{2-}$, O_2 was not evolved (Fig. 1b–e), showing that these three components are essential for the photoinduced O_2 evolution. Nor was O_2 evolved in the homogeneous solution containing the same amounts of **1**, $[Ru(bpy)_3]^{2+}$ and $S_2O_8{}^{2-}$ (Fig. 1f). This result suggests that **1** and $[Ru(bpy)_3]^{2+}$ adsorbed on mica are effective for O_2 evolution, which is consistent with the conclusion for a chemical water oxidation system.[19] 5.5 μmol of O_2 was evolved by light irradiation of the suspension (pH = 6.2, 2.0 ml) containing the mica/**1**/$[Ru(bpy)_3]^{2+}$ adsorbate for 17 h under the conditions (1.6 μmol (164 μmol g^{-1}) **1**, 0.25 μmol (25 μmol g^{-1}) $[Ru(bpy)_3]^{2+}$, 10 mg mica, 15 mM $S_2O_8{}^{2-}$). The turnover numbers (TN) of **1** and $[Ru(bpy)_3]^{2+}$ were 3.4 and 88 during the 17 h catalysis, respectively. This result corroborates that **1** and $[Ru(bpy)_3]^{2+}$ works as a catalyst and a photocatalyst in photochemical water oxidation, respectively, because the TN numbers are more than unity. Nevertheless, TN of **1** is considerably lower compared with TN = 15–17 for a chemical water oxidation system.[19] Instability of $[Ru(bpy)_3]^{2+}$ is supposed to be responsible for the lower TN of **1**. Most likely, $[Ru(bpy)_3]^{2+}$ might be decomposed by oxidized **1** during the photochemical reaction.

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† Electronic supplementary information (ESI) available: Experimental details, X-ray diffraction (XRD) spectroscopic data of mica adsorbate, UV-visible diffuse reflectance (DR) spectroscopic data of mica adsorbates, electron-impact-ionization mass spectra (EI-MS) in ^{18}O-labeling experiments, kinetic data of photochemical O_2 evolution. See DOI: 10.1039/c0cc03114c

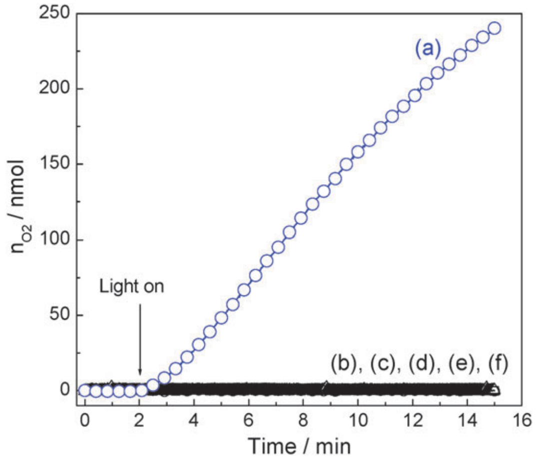

Fig. 1 Time courses of the amount (n_{O_2}/mol) of O_2 evolved in photochemical water oxidation in an aqueous suspension (2.0 ml, pH = 6.2) of 0.2 M acetate buffer and 15 mM $S_2O_8^{2-}$ (a) containing the mica/**1**/$[Ru(bpy)_3]^{2+}$ adsorbate, (b) the mica/**1** adsorbate, (c) the mica/$[Ru(bpy)_3]^{2+}$ adsorbate, (d) neat mica. (mica, 20 mg; **1**, 3.3 µmol (164 µmol g^{-1}); $[Ru(bpy)_3]^{2+}$, 0.4 µmol (20 µmol g^{-1})). (e) In the absence of $S_2O_8^{2-}$ under the conditions of (a). (f) In a homogenous solution (pH = 6.2, 2.0 ml) containing 3.3 µmol (1.6 mM) **1** and 0.4 µmol (0.2 mM) $[Ru(bpy)_3]^{2+}$ and 15 mM $S_2O_8^{2-}$.

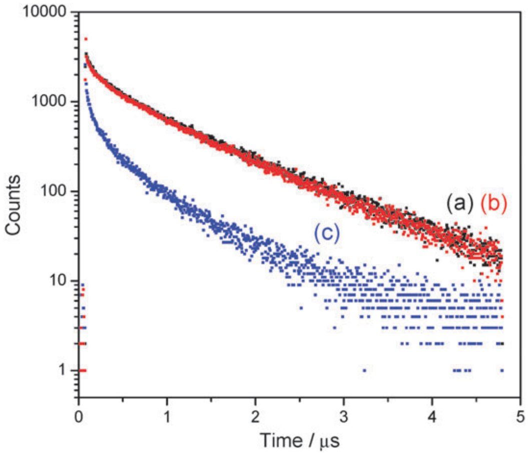

Fig. 2 Emission decays of photoexcited $[Ru(bpy)_3]^{2+}$ intercalated in mica in water using a single-photon counting technique. (a; black) mica/$[Ru(bpy)_3]^{2+}$, (b; red) mica/$[Ru(bpy)_3]^{2+}$ in the presence of $S_2O_8^{2-}$ in a liquid phase, (c; blue) mica/**1** (8 eq.)/$[Ru(bpy)_3]^{2+}$. 0.08 µmol (20 µmol g^{-1}) $[Ru(bpy)_3]^{2+}$, 4 mg mica, acetate buffer (3.0 ml, pH = 6.2), 25 °C, Ar atmosphere.

In order to identify an oxygen atom source for O_2 evolution, ^{18}O-isotope labeling experiments for photochemical water oxidation were carried out in a $H_2{}^{18}O$ medium, and the evolved gas was analyzed using an electron-impact-ionization mass spectroscopic (EI-MS) technique. In a 99% $H_2{}^{18}O$ medium, EI-MS spectra gave a main peak at m/z = 36 assigned to $^{18}O_2$ and a minor peak (4.3%) at m/z = 34 assigned to $^{18}O^{16}O$ in a range of m/z = 25–40, in contrast to a single peak at m/z = 32 for $^{16}O_2$ observed for the experiment in an abundant water medium (Fig. S3†). This result corroborates that the oxygen atoms in O_2 evolved are originated exclusively from water.

The initial O_2 evolution rate (v_{O_2}/mol s^{-1}) was given from the initial slope of the time course of the amount (n_{O_2}/mol) of O_2 evolved. v_{O_2} increased linearly with the light intensity and deviated downward above 95 mW cm^{-2}. This result indicates that the O_2 evolution is rate-determined by the subsequent reactions rather than the photochemical process above 95 mW cm^{-2} under the conditions employed (Fig. S4†). The following experiments were conducted under the light intensity of 127 mW cm^{-2}. The second order dependency of v_{O_2} with respect to the concentration of **1** (w_{Mn}/mol g^{-1}) was given (Fig. S5†), suggesting that two equivalents of **1** are required for photochemical O_2 production. This is consistent with the cooperative catalysis reported in the chemical water oxidation system.[19] Although O_2 was hardly evolved below w_{Ru} = 5 µmol g^{-1} under the constant w_{Mn} (164 µmol g^{-1}) conditions, v_{O_2} critically increased at more than w_{Ru} = 7.5 µmol g^{-1} (Fig. S6†). Light harvesting by $[Ru(bpy)_3]^{2+}$ should be an important factor to yield photochemical O_2 evolution. However, it can not explain the critical v_{O_2} increase with w_{Ru} reasonably, because the light absorption by $[Ru(bpy)_3]^{2+}$ increases linearly with w_{Ru} for the mica/**1**/$[Ru(bpy)_3]^{2+}$ adsorbate.

The photoexcited state of $[Ru(bpy)_3]^{2+}$ is well-known to be sufficiently quenched by $S_2O_8^{2-}$ in a homogeneous aqueous solution. Nevertheless, the emission decay from the photoexcited state did not change if 15 mM $S_2O_8^{2-}$ is contained in an aqueous suspension of the mica/$[Ru(bpy)_3]^{2+}$ adsorbate,[20] showing that the photoexcited state in mica is not quenched by $S_2O_8^{2-}$ in the liquid phase (Fig. 2b). $S_2O_8^{2-}$ anions in the liquid phase can not be allowed to come close to $[Ru(bpy)_3]^{2+}$ in an anionic interspace between mica layers for quenching due to electrostatic repulsion. In contrast, the emission decay is significantly fast for the mica/**1**/$[Ru(bpy)_3]^{2+}$ adsorbate, as shown in Fig. 2c. This indicates that the photoexcited state is quenched by **1** in mica. The electron transport for photochemical O_2 evolution in the mica/**1**/$[Ru(bpy)_3]^{2+}$ adsorbate is initiated from the photoexcitation of $[Ru(bpy)_3]^{2+}$, followed most probably by electron transfer from **1** to the excited $[Ru(bpy)_3]^{2+}$ to form oxidized **1** and $[Ru(bpy)_3]^{+}$. The reductive quenching of the excited $[Ru(bpy)_3]^{2+}$ is well-known from previous reports,[21,22] though we do not have any spectroscopic evidence for $[Ru(bpy)_3]^{+}$ formation yet. The successive photoinduced electron-transfer processes could generate oxidizing equivalents that are used for water oxidation catalysis. On the other hand, $[Ru(bpy)_3]^{+}$ could be re-oxidized to $[Ru(bpy)_3]^{2+}$ by $S_2O_8^{2-}$ in a liquid phase to suppress a back electron transfer from $[Ru(bpy)_3]^{+}$ to the oxidized **1**, as reported in the literature.[23] However, since $[Ru(bpy)_3]^{+}$ formed close to **1** in mica can not react directly with $S_2O_8^{2-}$, an electron on $[Ru(bpy)_3]^{+}$ must be relayed to $[Ru(bpy)_3]^{2+}$ close to the mica surface for the re-oxidation by $S_2O_8^{2-}$ possibly by a successive self-exchange electron-transfer reaction between $[Ru(bpy)_3]^{+}$ and $[Ru(bpy)_3]^{2+}$ (electron hopping) in mica (Fig. 3). The electron relay by electron hopping could occur efficiently at the higher w_{Ru} conditions to achieve photochemical O_2 evolution. This could be a possible explanation for the critical v_{O_2} increase with w_{Ru}.

For preliminary experiments, photochemical O_2 production was not yielded under the same conditions (164 µmol g^{-1} **1**, 20 µmol g^{-1} $[Ru(bpy)_3]^{2+}$, 20 mg mica, 15 mM $S_2O_8^{2-}$) using two control adsorbates: (i) the mica/$[Ru(bpy)_3]^{2+}$/**1** adsorbate

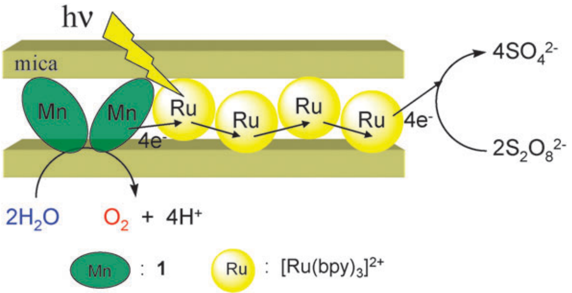

Fig. 3 Illustration of possible vectorial electron transport for photochemical O_2 production. Electrons are relayed from **1** to $[Ru(bpy)_3]^{2+}$ close to the mica surface by a successive self-exchange electron-transfer reaction between $[Ru(bpy)_3]^{+}$ and $[Ru(bpy)_3]^{2+}$ (electron hopping) in mica, further transferring to $S_2O_8^{2-}$ in a liquid phase.

prepared by an opposite adsorption order: $[Ru(bpy)_3]^{2+}$ followed by **1**, and (ii) the mica/(**1**+$[Ru(bpy)_3]^{2+}$) adsorbate prepared by co-adsorption from the mixed solution of **1** and $[Ru(bpy)_3]^{2+}$. The DR spectra for these control adsorbates did not exhibit the specifically intense absorption at 475 nm due to $[Ru(bpy)_3]^{2+}$ in contrast to the case for the mica/**1**/$[Ru(bpy)_3]^{2+}$ adsorbate, implying that $[Ru(bpy)_3]^{2+}$ is not shallowly-intercalated outside **1** in an interlayer for these control adsorbates (Fig. S2†). These results suggest that the arrangement of **1** and $[Ru(bpy)_3]^{2+}$ in an interlayer is important for photochemical O_2 evolution. The arrangement of inside **1** and outside $[Ru(bpy)_3]^{2+}$ could allow for efficient vectorial electron transport from **1** to $S_2O_8^{2-}$. The present work demonstrates the illustration of artificial PS II model for **1** and $[Ru(bpy)_3]^{2+}$ to act as OEC and P_{680} models, respectively. We are undertaking an advanced project to build up the artificial photosynthetic model by assembling the PS II model and a H_2 production catalyst system.

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