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

Masayuki Yagi[1, 2]*, Mayuu Toda[1], Satoshi Yamada[1], Hirosato Yamazaki[1]

[1] Department of Materials Science and Technology, Faculty of Engineering & Center for Transdisciplinary Research, Niigata University, 8050 Ikarashi-2, Niigata, 950-2181, Japan.

[2] PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012 Japan. (PRESTO: Precursory Research for Embryonic Science and Technology)

Supporting Information

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1. Experimental details.

Materials. $[(OH_2)(terpy)Mn^{III}(\mu\text{-}O)_2Mn^{IV}(terpy)(OH_2)](NO_3)_3$ (**1**$(NO_3)_3$) (J. Phys. Chem. B, **2006**, 110, 23107.) was synthesized as described elsewhere. $[Ru(bpy)_3]Cl_2$ (Aldrich Chemical Co. Inc.) and $Na_2S_2O_8$ (Wako Pure Chemical Industries, Ltd.) were purchased and used as received. Somasif (ME-100) of mica was given from Co-op Chemical Co., Inc. and used without further purification.

Preparations of a mica / 1 / $[Ru(bpy)_3]^{2+}$ adsorbate. An aqueous solution (~ 5.7 mM, 10 ml, pH = 4.0) of **1** was added to an aqueous suspension (10 ml, pH = 4.0) of mica (~ 230 mg). The resulting suspension was filtrated after stirring for 30 min, and then dried at 65 ˚C under vacuum for 3 h to yield a mica / **1** adsorbate. An aqueous solution of $[Ru(bpy)_3]^{2+}$ (~0.3 mM, 2 ml) was added to the aqueous suspension of a mica / **1** adsorbate (210 mg, 20 ml), followed by filtration to yield a mica / **1** / $[Ru(bpy)_3]^{2+}$ adsorbate. The amounts of **1** and $[Ru(bpy)_3]^{2+}$ adsorbed were measured by the visible absorption spectral change of the aqueous solution of **1** and $[Ru(bpy)_3]^{2+}$ before and after mica adsorption, respectively. A control sample (i), a mica / $[Ru(bpy)_3]^{2+}$ / **1** adsorbate was prepared by an opposite adsorption order: $[Ru(bpy)_3]^{2+}$ adsorption followed by **1** adsorption under the same conditions as the preparation of the mica / **1** / $[Ru(bpy)_3]^{2+}$ adsorbate. A control sample (ii), the mica / (**1** + $[Ru(bpy)_3]^{2+}$) adsorbate was prepared by co-adsorption **1** and $[Ru(bpy)_3]^{2+}$ from their mixed solution.

Spectroscopic measurements. UV-visible spectra of solutions were measured using a photodiode array spectrophotometer (Shimadzu, Multispec-1500). UV-visible diffuse reflectance (DR) spectra of mica adsorbates were measured using an UV-visible spectrophotometer (JASCO V-550) in a diffuse reflectance mode. X-ray diffraction (XRD) patterns of mica adsorbate were taken in an X-ray diffractometer (MAC Science, MX-Labo). Lifetime of photoexcited state of $[Ru(bpy)_3]^{2+}$ was analyzed from the phosphorescence decay (at 590 nm) measured by a time-correlated single-photon counting apparatus (IBH, 5000F) equipped with nano-flash lamp.

Photochemical O_2 evolution experiments. Typically, the mica / **1** / $[Ru(bpy)_3]^{2+}$ adsorbate (3.3 μmol (164 μmol g^{-1}) **1**, 0.4 μmol (20 μmol g^{-1}) $[Ru(bpy)_3]^{2+}$, 20 mg mica) was suspended to the acetate buffer solution (pH = 6.2, 2.0 ml) containing 30 μmol (15 mM) $Na_2S_2O_8$. The suspension was deaerated by bubbling argon gas for 20 min before light irradiation. Visible light ($\lambda > 420$ nm, 127 mW cm^{-2}) from a filtered halogen lamp (150 W) was irradiated to the suspension with stirring at 25 ^{o}C. The amount of O_2 evolved was monitored using a Clark type oxygen electrode (Hansatech Instruments, Oxygraph OXYG1 and DW1/AD unit). For the experiment on a longer time scale, gas chromatograph (Shimadzu, GC-8A) with equipped with a 5 Å molecular sieve column (argon carrier gas) was used to analyze the amount of O_2 in a head-space in a gas-tight vassal. For ^{18}O-labeling experiments using $H_2{}^{18}O$, the gas in the head-space was analyzed on an electron-impact-ionization mass spectrometer (JEOL, JMS-GCMATE) under the ionization conditions at vacuum of 14 Torr and 200 V.

2. X-ray diffraction (XRD) spectroscopic data of mica adsorbates.

In Figure S1, the XRD pattern of mica gives a peak at 2θ = 7.18 degree, corresponding to an interlayer distance (12.3 Å) of mica intercalating hydrated Na^+ ions. (spectrum (b)) The peak shifted from to 2θ = 7.02 degree and 7.12 degree for the mica / **1** (spectrum (c)) and mica / $[Ru(bpy)_3]^{2+}$ adsorbates (spectrum (d)), respectively. This shows that either **1** or $[Ru(bpy)_3]^{2+}$ are intercalated into an interspace between mica layers. It also suggests that the intercalation of **1** rather than $[Ru(bpy)_3]^{2+}$ makes the interlayer distance slightly wider under the typical conditions employed. (w_{Mn} = 164 μmol g^{-1}, w_{Ru} = 20 μmol g^{-1}) The XRD pattern of the mica / **1** / $[Ru(bpy)_3]^{2+}$ (spectrum (e)) is very close to that of the mica / **1** (spectrum (c)), and the peak (2θ = 7.02 degree) is the same between both the spectra. This in interpreted by less significant influence of the intercalation of $[Ru(bpy)_3]^{2+}$ into the mica / **1** adsorbate on its layer structure under the conditions employed. It is consistent with the fact that the intercalation of **1** rather than $[Ru(bpy)_3]^{2+}$ makes the interlayer distance slightly wider.

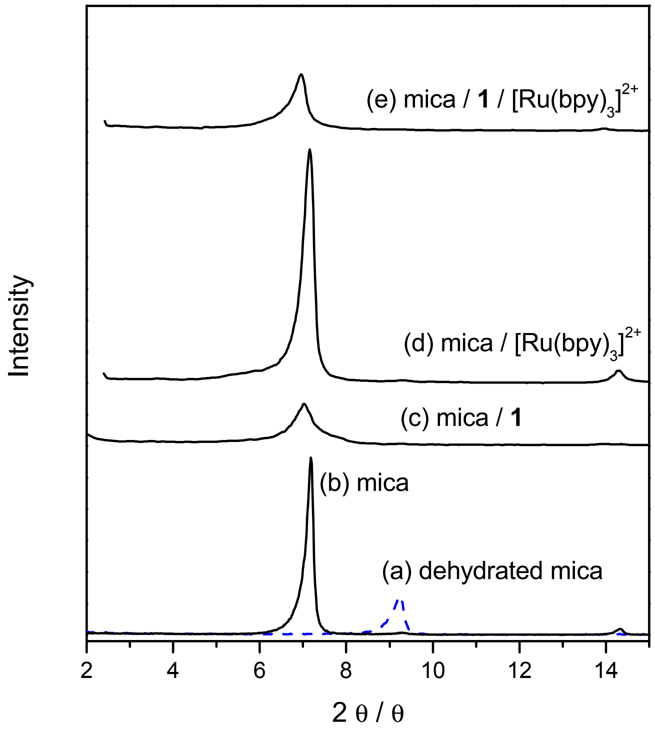

Figure S1 X-ray diffraction (XRD) spectra of (a) dehydrated mica, (b) mica, (c) mica / **1** adsorbate, (d) mica / $[Ru(bpy)_3]^{2+}$ adsorbate and (e) mica / **1** / $[Ru(bpy)_3]^{2+}$ adsorbate. $w_{Mn} = 164$ μmol g^{-1}, $w_{Ru} = 20$ μmol g^{-1}.

3. UV-visible diffuse reflectance (DR) spectroscopic data of mica adsorbates.

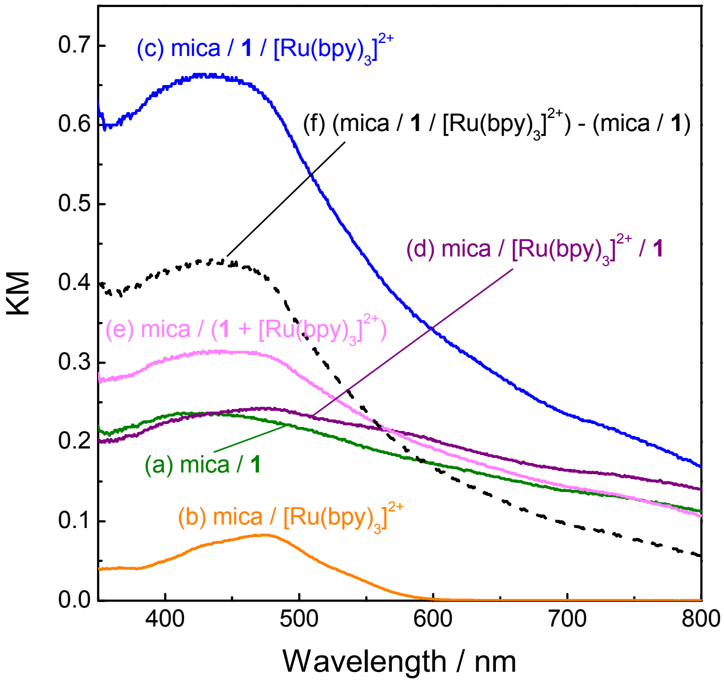

Figure S2 UV-visible diffuse reflectance (DR) spectra of (a) mica / **1** adsorbate, (b) mica / [Ru(bpy)$_3$]$^{2+}$ adsorbate, (c) mica / **1** / [Ru(bpy)$_3$]$^{2+}$ adsorbate, (d) mica / [Ru(bpy)$_3$]$^{2+}$ / **1** adsorbate and (e) mica / (**1** + [Ru(bpy)$_3$]$^{2+}$) adsorbate. w_{Mn} = 164 μmol g^{-1}, w_{Ru} = 20 μmol g^{-1}. The dashed line indicates the spectrum (f) simulated by linear subtraction of (a) mica / **1** from (c) mica / **1** / [Ru(bpy)$_3$]$^{2+}$ adsorbates. The spectrum of mica was used as a reference spectrum. The simulated spectrum (f) gave 5.2 times more intense absorption band at 475 nm than that for the mica / [Ru(bpy)$_3$]$^{2+}$ adsorbate at the identical w_{Ru} conditions.

4. Electron-impact-ionization mass spectra (EI-MS) in ^{18}O-labeling experiments.

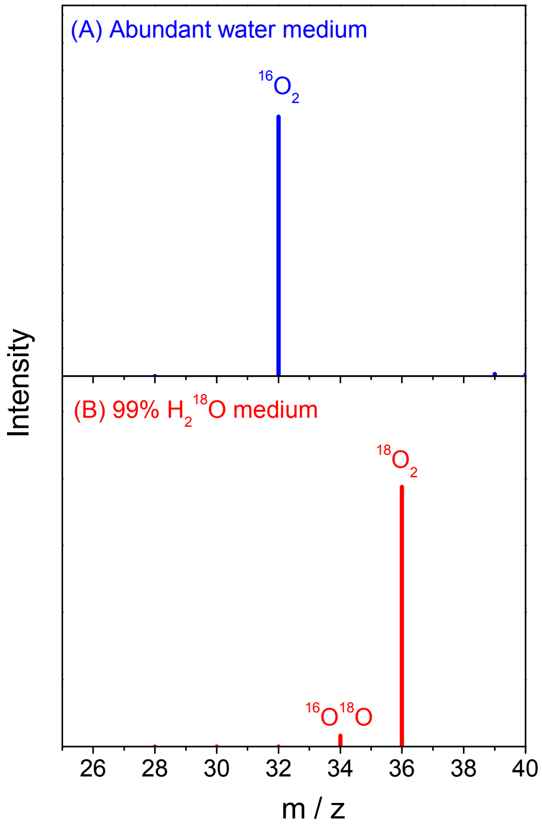

Figure S3 Electron-impact-ionization mass spectra (EI-MS) in ^{18}O-labeling experiments for photochemical water oxidation in an aqueous suspension (1.0 ml, pH = 6.7) of 0.2 M acetate buffer and 15 mM $S_2O_8^{2-}$ containing a mica / **1** / $[Ru(bpy)_3]^{2+}$ adsorbate (3.3 μmol (164 μmol g^{-1}) **1**, 0.4 μmol (20 μmol g^{-1}) $[Ru(bpy)_3]^{2+}$, 20 mg mica). (A) in an abundant water medium, (B) in a 99% $H_2{}^{18}O$ medium. The photochemical reaction time is 8 h. The spectra are given by subtracting the constant background data.

5. Kinetic data of photochemical O_2 evolution.

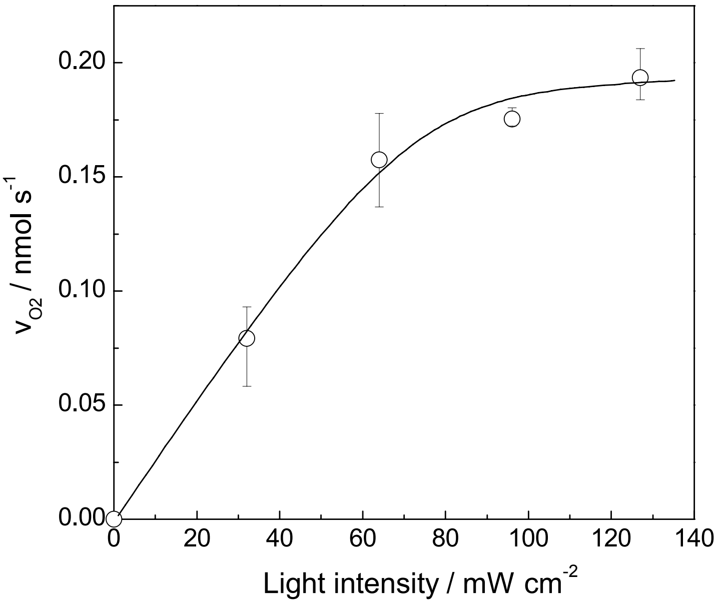

Figure S4 Dependence of v_{O2} on light intensity.

3.3 μmol (164 μmol g^{-1}) **1**, 0.4 μmol (20 μmol g^{-1}) $[Ru(bpy)_3]^{2+}$, 20 mg mica, 15 mM $S_2O_8^{2-}$, 2.0 ml acetate buffer.

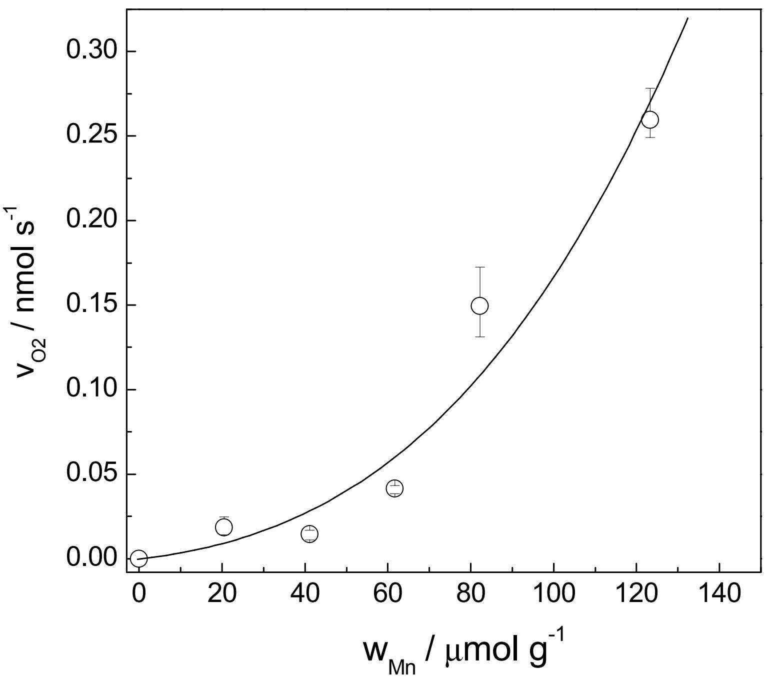

Figure S5 Dependence of v_{O2} on w_{Mn}.

0.4 µmol (20 µmol g^{-1}) $[Ru(bpy)_3]^{2+}$, 20 mg mica, 15 mM $S_2O_8^{2-}$, 2.0 ml acetate buffer.

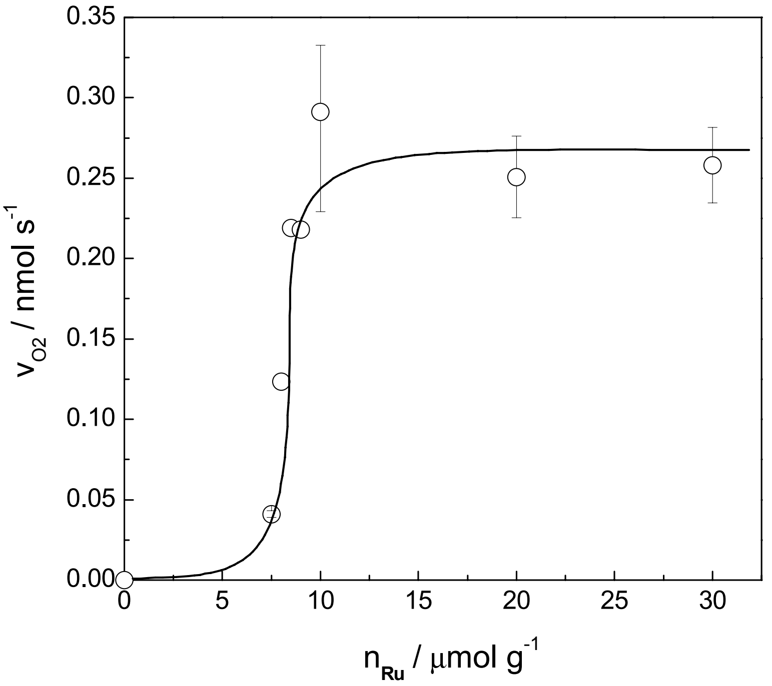

Figure S6 Dependence of v_{O2} on w_{Ru}.

3.3 µmol (164 µmol g^{-1}) **1**, 20 mg mica, 15 mM $S_2O_8^{2-}$, 2.0 ml acetate buffer.