

Supporting Information

A Photo-Hydrogen-Evolving Molecular Device Driving Visible-Light-Induced EDTA-Reduction of Water into Molecular Hydrogen

Hironobu Ozawa, Masa-aki Haga[†], and Ken Sakai^{*}

Department of Chemistry, Faculty of Science, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

[†]Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

Syntheses and Characterization

Preparation of [Ru-bpy](PF₆)₂·3H₂O. A suspension of 2,2'-Bipyridine-4,4'-dicarboxylic acid (Case, F. H. *J. Am. Chem. Soc.* **1946**, 68, 2574; Anderson, S.; Constable, E. C.; Seddon, K. R.; Turp, J. E.; Baggott, J. E.; Pilling, M. J. *J. Chem. Soc., Dalton. Trans.* **1985**, 2247.) (0.488 g, 2.00 mmol) in 20 mL of thionyl chloride was refluxed for 3-4 h. The resulting clear yellow solution was evaporated to dryness and the yellow residue was dried in vacuo to give 4,4'-bis(chlorocarbonyl)-2,2'-bipyridine. This was dissolved in anhydrous THF (30 mL). To a solution of [Ru-NH₂](PF₆)₂·H₂O (Ellis, C. D.; Margerum, L. D.; Murray, R. W.; Meyer, T. J. *Inorg. Chem.* **1983**, 22, 1283) (0.917 g, 1.00 mmol) and triethylamine (*ca.* 0.7 mL, *ca.* 5.0 mmol) in anhydrous acetonitrile (100 mL) kept at 0 °C was added the former THF solution over 30 min. After stirring the solution overnight at room temperature, insoluble materials, such as triethylammonium chloride were removed by filtration. Most of the solvent was removed by evaporation followed by addition of water (*ca.* 20 mL). To the solution was added an aqueous saturated NH₄PF₆ solution (*ca.* 0.5 mL) to give an orange precipitate, which was collected by filtration and dried in vacuo. The product was purified on a Sephadex LH-20 column (*ca.* 60 cm) using a mixed solvent consisting of acetonitrile and methanol (1:1 v/v) as eluent. The first brown band was collected and evaporated to dryness to give a brownish orange solid; yield 0.23 g (20 %). Elemental analysis (%): C₄₄H₃₇N₉O₆RuP₂F₁₂ ([Ru-bpy](PF₆)₂·3H₂O) calcd.: C 44.83, H 3.16, N 10.69; Found: C 44.97, H

3.12, N 10.63. ESI-TOF MS (positive ion, CH₃CN): m/z 417.5 ([M-(2PF₆·3H₂O)]²⁺) (see Figure S1). ¹H NMR (500.16 MHz, CD₃CN, ppm): δ 9.95 (d, J = 9.1 Hz, 1H), 8.58-8.49 (m, 7H), 8.29 (d, J = 5.5 Hz, 1H), 8.14-8.11 (m, 4H), 8.10-7.99 (m, 4H), 7.87 (m, 3H), 7.75-7.72 (m, 3H), 7.60-7.59 (m, 1H), 7.50-7.44 (m, 3H), 7.27-7.25 (m, 3H). UV/vis (H₂O): λ_{\max}/nm ($\epsilon/10^2 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) 235 (410), 285 (646), 450 (157).

Preparation of [RuPt](PF₆)₂ and [RuPt]Cl₂·3H₂O. [Ru-bpy](PF₆)₂·3H₂O (0.118 g, 0.10 mmol) was dissolved in a minimum amount of mixed solvent consisting of ethanol and water (1:1 v/v), and the solution was treated with Amberlite IRA-400 ion exchange resin in the Cl form to give a solution of the dichloride salt of the complex. After most of ethanol was removed by evaporation, the aqueous solution was further evaporated to a total volume of *ca.* 10 mL followed by addition of 1.1 equivalents of K₂PtCl₄ (0.05 g, 0.12 mmol). The solution was stirred at 80 °C for 2-3 h. After the solution was cooled down to room temperature, an aqueous saturated NH₄PF₆ solution (*ca.* 0.2 mL) was added to the solution to give a brown precipitate of [RuPt](PF₆)₂, which was washed with water, air-dried by suction, and dried in vacuo; yield 0.13 g (90 %). Elemental analysis (%): C₄₄H₃₁N₉O₃Cl₂RuPtP₂F₁₂ ([RuPt](PF₆)₂) calcd.: C 38.00, H 2.25, N 9.06; Found: C 37.92, H 2.28, N 9.11. ESI-TOF MS (positive ion, CH₃CN): m/z 550.5 ([M-2(PF₆)]²⁺) (see Figure S2). ¹H NMR (500.16 MHz, CD₃CN, ppm): δ 9.94 (d, J = 8.2 Hz, 1H), 8.58-8.50 (m, 6H), 8.28 (d, J = 6.1 Hz, 1H), 8.19-8.15 (m, 4H), 8.07-7.95 (m, 4H), 7.87-7.82 (m, 3H), 7.75- 7.72 (m, 2H), 7.61-7.55 (m, 2H), 7.50-7.41 (m, 4H), 7.27-7.25 (m, 3H). The brown solid ([RuPt](PF₆)₂) was dissolved in a minimum amount of mixed solvent consisting of ethanol and water (1:1 v/v), and the solution was treated with Amberlite IRA-400 ion exchange resin in the Cl form to give a solution of the dichloride salt of the complex. After most of ethanol was removed by evaporation, the solution was freeze-dried to give the dichloride salt of the complex [RuPt]Cl₂·3H₂O. Elemental analysis (%): C₄₄H₃₇N₉O₆Cl₄RuPt ([RuPt]Cl₂·3H₂O) calcd.: C 43.11, H 3.04, N 10.28; Found: C 43.39, H 3.17, N 10.03. UV/vis (H₂O): λ_{\max}/nm ($\epsilon/10^2 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) 285 (618), 450 (143).

Preparation of PtCl₂(dcbpy)·H₂O. A suspension of 2,2'-Bipyridine-4,4'-dicarboxylic acid (0.049 g, 0.20 mmol) and *cis*-PtCl₂(dmsO)₂ (J. H. Price, A. N. Williamson, R. F. Schramm, B. B. Wayland, *Inorg. Chem.* **1972**, *11*, 1280) (0.106 g, 0.25 mmol) in 20 mL of methanol

was sealed in a pressure-resistant vial and was reacted at 120 °C for 6 h. After the vial was cooled down to room temperature, the yellow precipitate was collected by filtration, air-dried by suction, and dried in vacuo; yield 0.06 g (85 %). Elemental analysis (%): $C_{12}H_{10}N_2O_5Cl_2Pt$ ($C_{12}H_8N_2O_4Cl_2Pt \cdot H_2O$) calcd.: C 27.29, H 1.91, N 5.30; Found: C 27.56, H 1.72, N 5.11. 1H NMR (270.17 MHz, $(CD_3)_2SO$, ppm): δ 9.71 (d, $J = 4.1$ Hz, 2H), 9.03 (s, 2H), 8.23 (d, $J = 5.9$ Hz, 2H).

Measurements. 1H NMR spectra were acquired on a JEOL JNM-EX500 (500.16 MHz) and a JNM-EX270 (270.17 MHz) spectrometer, where chemical shifts in $(CD_3)_2SO$ and CD_3CN were referenced to internal tetramethylsilane. Electrospray ionization time-of-flight mass spectra (ESI-TOF MS) were obtained for acetonitrile solutions of the complexes using a Micromass LCT spectrometer. Elemental analyses were carried out on a Perkin-Elmer 2400II CHN elemental analyzer using acetanilide as a standard material. Absorption spectra were recorded on a Shimadzu MutiSpec-1500 UV-visible spectrophotometer. Emission spectra were recorded on a Shimadzu RF-5300PC spectrofluorophotometer, equipped with a Hamamatsu R928 photomultiplier tube. All the sample solutions were thermostated at 20 °C during the spectrophotometric investigations.

Photolysis Experiments. Photochemical hydrogen production from water was analyzed by using an automatic H_2 monitoring system developed in our group. In this system, continuous flow of Ar (10.0 mL/min, controlled by a STEC SEC-E40/PAC-D2 digital mass flow controller) was bubbled through a photolysis solution (10 mL) contained in a Pyrex vial (*ca.* 20 mL). The vent gas from the vial was introduced into a 6-way valve which allowed the automatic injection of the sample gas onto a gas chromatograph (Shimadzu GC-14A equipped with a molecular sieve 5A column of 2 m x 3 mm i.d., thermostated at 30 °C). The injection of the sample gas and the output signal from the thermal conductivity detector of the gas chromatograph were both controlled by a control software operating on a Windows system. Photolysis solutions were deaerated with Ar for at least 30 min prior to the photolysis. The photoirradiation was carried out by an Ushio xenon short arc lamp UXL500D-O (operated at 350 W). Photolysis vial was immersed in a water bath thermostated at 20 °C to remove IR radiation and to eliminate the temperature effect. In some experiments, an UV cut-off filter (HOYA L39 filter; transmittance at 390 nm is 50 %) was used to examine the effect of UV irradiation.

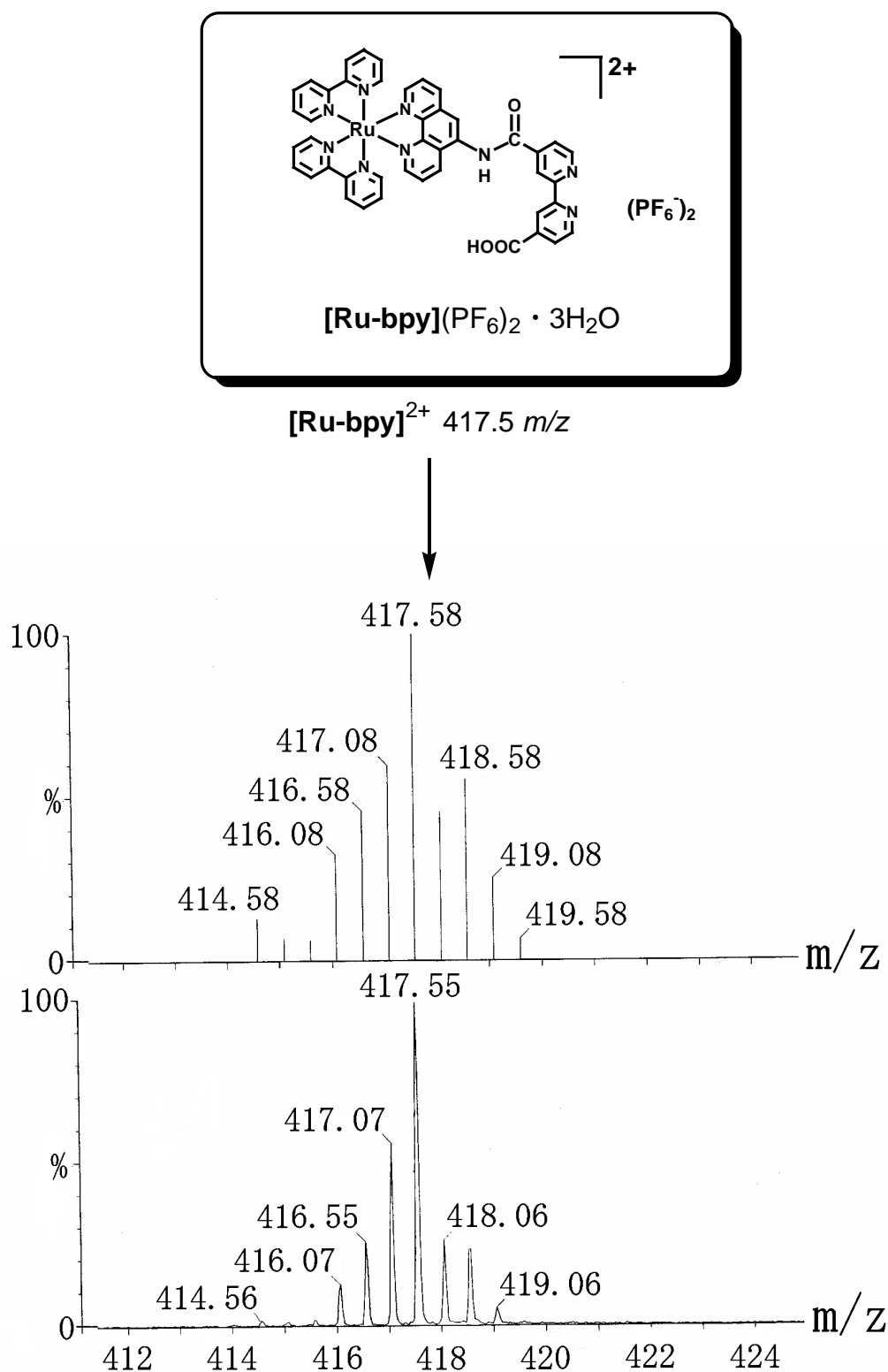


Figure S1. The observed (bottom) and calculated (top) positive-ion ESI-TOF mass spectra obtained for a solution of $[\text{Ru-bpy}](\text{PF}_6)_2 \cdot 3\text{H}_2\text{O}$ in CH_3CN (Micromass LCT), in which a divalent cation $[\text{Ru-bpy}]^{2+}$ ion is detected.

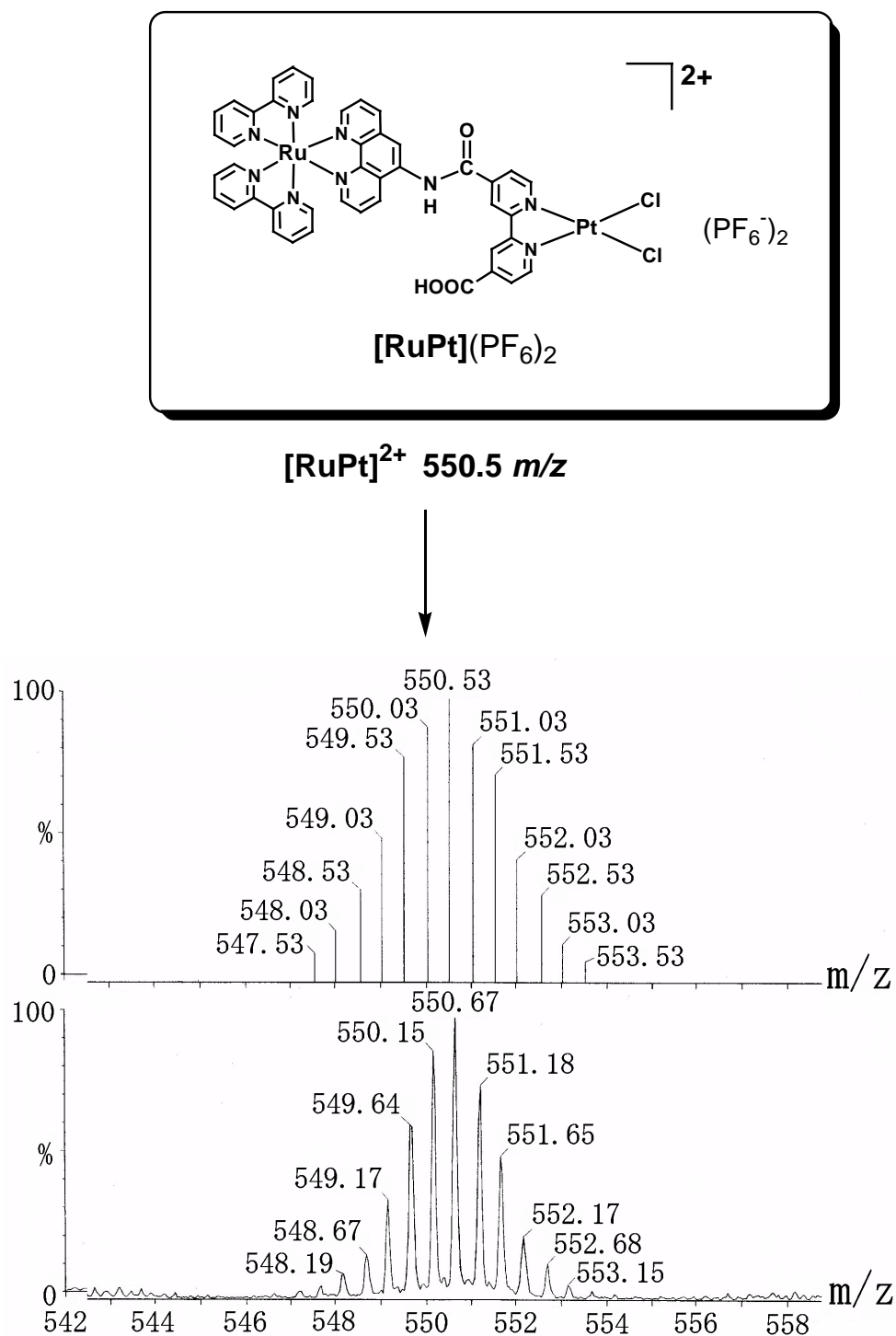


Figure S2. The observed (bottom) and calculated (top) positive-ion ESI-TOF mass spectra obtained for a solution of $[\text{RuPt}](\text{PF}_6)_2 \cdot 3\text{H}_2\text{O}$ in CH_3CN (Micromass LCT), in which a divalent cation $[\text{RuPt}]^{2+}$ ion is detected.

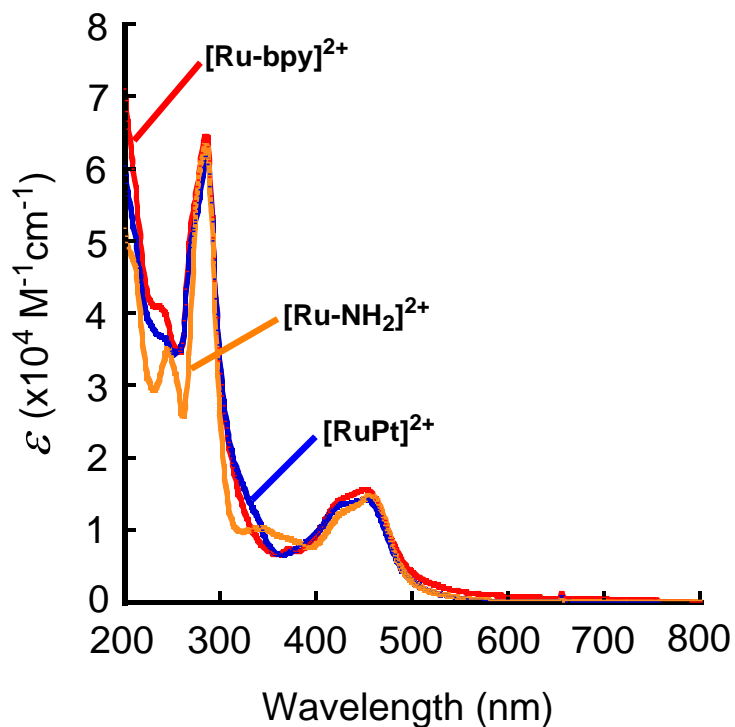


Figure S3. Molar absorptivity (ϵ) spectra of $[\text{Ru-NH}_2](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$, $[\text{Ru-bpy}](\text{PF}_6)_2 \cdot 3\text{H}_2\text{O}$, and $[\text{RuPt}]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ in water, in air, at 20 °C.

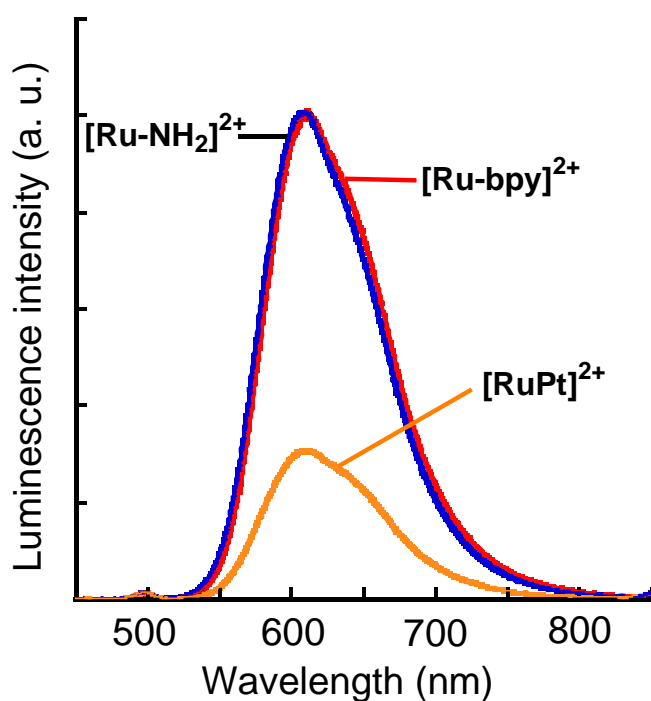


Figure S4. Uncorrected luminescence spectra of $[\text{Ru-NH}_2](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$, $[\text{Ru-bpy}](\text{PF}_6)_2 \cdot 3\text{H}_2\text{O}$, and $[\text{RuPt}]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ in water, in air, at 20 °C, where the excitation wavelength was fixed at 425 ± 2.5 nm and all the solutions had an equal absorbance of 0.1 at 425 nm.

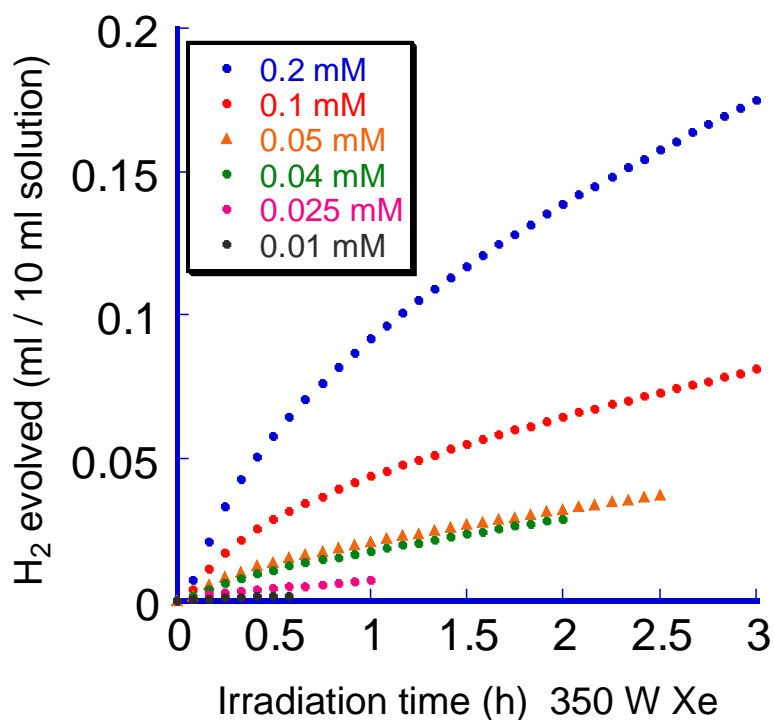


Figure S5. Concentration dependence of photochemical H_2 production from aqueous acetate buffer solutions (0.03 M $\text{CH}_3\text{CO}_2\text{H}$ and 0.07 M $\text{CH}_3\text{CO}_2\text{Na}$; pH 5.0, 10 mL) containing 30 mM EDTA in the presence of $[\text{RuPt}]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ at various concentrations (the original H_2 evolution curves of Figure 3). The irradiation was carried out using 350 W Xe lamp, under the continuous flow of Ar (10.0 mL/min), where the vent gas was automatically analyzed by gas chromatography every 5 min. The photolysis solutions were immersed in a water bath thermostated at 20 °C.