

## Supporting Information

### **Highly Stable Chemisorption of Dyes with Pyridyl Anchors over TiO<sub>2</sub>: Application in Dye-Sensitized Photoelectrochemical Water Reduction in Aqueous Media**

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## Materials and general measurements

4,4':2',2'':4'',4'''-quaterpyridine (qpy),<sup>S1</sup> *cis*-RuCl<sub>2</sub>(dmbpy)<sub>2</sub>,<sup>S2</sup> [Ru(dmbpy)<sub>2</sub>(dcbpy)](PF<sub>6</sub>)<sub>2</sub> (**Ru-C**),<sup>S3</sup> and [Ru(dmbpy)<sub>2</sub>(dpbpy)](PF<sub>6</sub>)<sub>2</sub> (**Ru-P**),<sup>S4</sup> were prepared according to the previously reported procedures. All other reagents were purchased from Tokyo Chemical Industry Co., Ltd, and were used without further purification.

<sup>1</sup>H NMR spectra of the polypyridyl ruthenium dyes were acquired on a JEOL JNM-ESA 600 spectrometer. The ESI-TOF mass spectra were recorded on a JEOL JMS-T100CS spectrometer. The spectral changes in the IR region upon adsorption of the dyes over TiO<sub>2</sub> were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer, equipped with a Diamond ATR Crystal, where each FTO/TiO<sub>2</sub>/Ru-dye electrode was directly located on the ATR system. UV-vis-NIR spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Transmittance and reflectance spectra of the FTO/TiO<sub>2</sub>/Ru-dye electrodes were recorded on a Shimadzu UV-3600 spectrophotometer, equipped with an integrated sphere attachment. Luminescence spectra were recorded on a Shimadzu RF-5300PC spectrofluorophotometer equipped with a Hamamatsu R928 photomultiplier tube. Cyclic voltammograms were recorded on a BAS ALS Model 602DKM electrochemical analyzer, using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag<sup>+</sup> reference electrode (-0.11 V vs. Fc/Fc<sup>+</sup>). The electrolysis was carried out using an acetonitrile solution containing 0.1 M TBAP (tetra(*n*-butyl)ammonium perchlorate) as a supporting electrolyte, where the scan rate was always 50 mV/s.

## Synthesis of [Ru(dmbpy)<sub>2</sub>(qpy)](PF<sub>6</sub>)<sub>2</sub>·2H<sub>2</sub>O (**Ru-py**)

*cis*-RuCl<sub>2</sub>(dmbpy)<sub>2</sub> (52 mg, 96 μmol) and qpy (29 mg, 94 μmol) were dissolved in 10 mL of ethylene glycol, and this mixture was refluxed for 1 h. After the solution was cooled to room temperature, 3 mL of H<sub>2</sub>O and 0.5 mL of aqueous saturated NH<sub>4</sub>PF<sub>6</sub> solution were added to afford a brown powder, which was collected by filtration, and washed with water. This crude product was purified by a silica gel column chromatography using a mixed solvent of CH<sub>3</sub>CN, H<sub>2</sub>O, and aqueous saturated KNO<sub>3</sub> (10:3:3, v/v) as an eluent. The second brown band was collected, and then most of CH<sub>3</sub>CN was removed by evaporation to give a dark red powder, which was collected by filtration, washed with water, and dried in vacuo. Yield: 42 mg (38 μmol, 40%). <sup>1</sup>H NMR (600 MHz, acetone-d<sub>6</sub>): δ = 9.44 (d, *J* = 1.4 Hz, 2H), 8.79 (d, *J* = 6.2 Hz, 4H), 8.73 (d, *J* = 6.2 Hz, 4H), 8.24 (d, *J* = 5.5 Hz, 2H), 7.97 (d, *J* = 6.2 Hz, 4H), 7.91-7.89 (m,

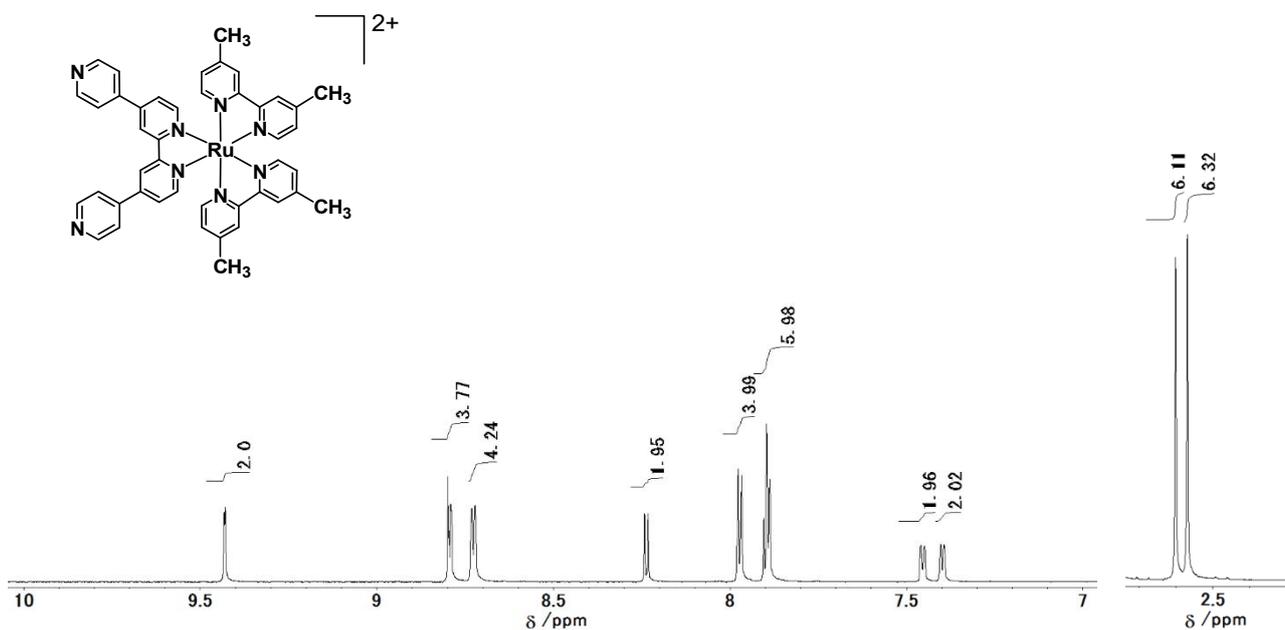
6H), 7.46 (d,  $J = 4.8$  Hz, 2H), 7.40 (d,  $J = 4.8$  Hz, 2H), 2.60 (s, 6H), 2.57 (s, 6H). ESI-TOF MS (positive ion, CH<sub>3</sub>CN) 390.12  $m/z$  ([**M**]<sup>2+</sup>). Anal. Calcd. for C<sub>44</sub>H<sub>42</sub>N<sub>8</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>Ru ([**M**](PF<sub>6</sub>)<sub>2</sub>·2H<sub>2</sub>O): C, 47.79; H, 3.83; N, 10.13. Found: C, 47.91; H, 3.65; N, 10.04.

### Preparation of dye-adsorbed TiO<sub>2</sub> electrodes

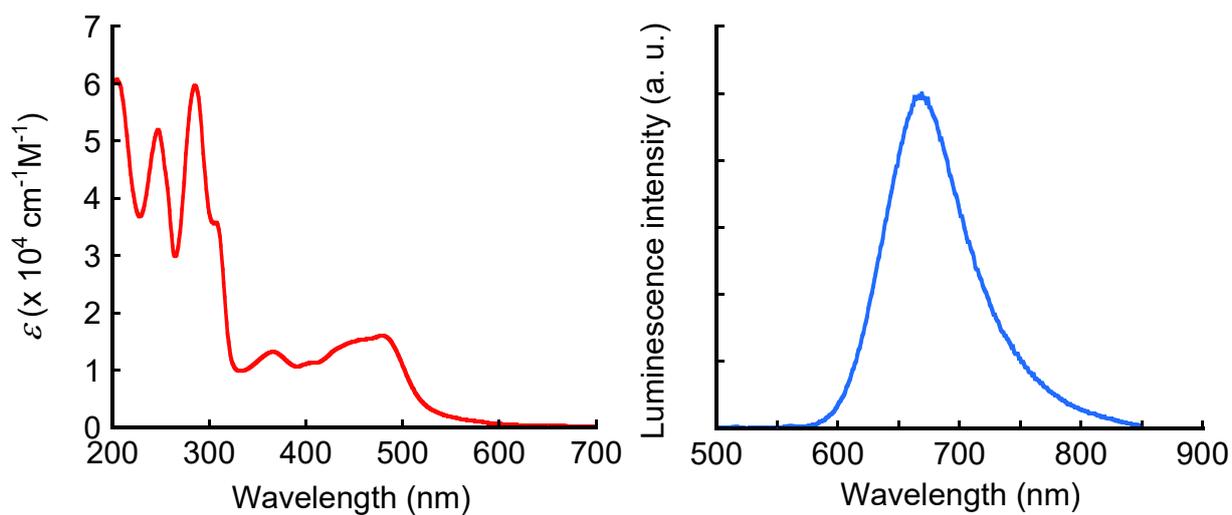
Single or multi-layered mesoporous TiO<sub>2</sub> thin film on the FTO glass substrate (FTO/TiO<sub>2</sub> electrode) was fabricated by screen-printing and high-temperature sintering technique.<sup>S5</sup> Film thickness of the single and multi-layered TiO<sub>2</sub> films were ca. 7 and ca. 25  $\mu\text{m}$ , respectively. Active area of each TiO<sub>2</sub> film was 1.0 cm<sup>2</sup>. Typically, a pristine FTO/TiO<sub>2</sub> electrode was immersed into a dye bath for 24 h at 20 °C to uptake each dye. The amount of the dye adsorbed was spectrophotometrically determined by observing the absorption change in the dye bath. After the FTO/TiO<sub>2</sub> electrode was removed from the dye bath, it was rinsed, and dried in air at room temperature.

### Photoelectrochemical measurements

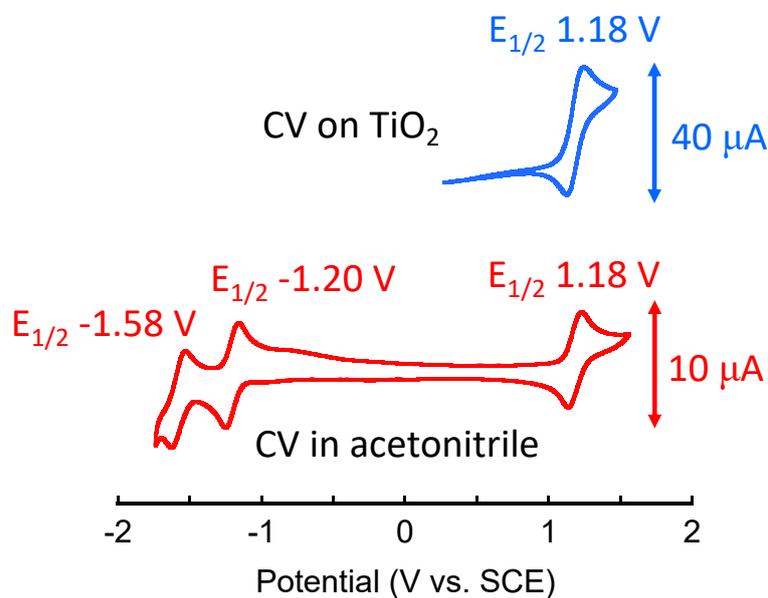
Linear sweep voltammetry (LSV) was carried out using a BAS ALS Model 602DKM electrochemical analyzer in a three-electrode PEC with a dye-adsorbed TiO<sub>2</sub> electrode as a working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode (-0.02 V vs. SCE). Scan rate was 10 mV/s. The electrolyte solution used was an aqueous acetate buffer (0.1 M, pH 5.0) containing 30 mM EDTA as a sacrificial reagent and 0.1 M NaClO<sub>4</sub> as a supporting electrolyte. Photoirradiation was carried out by an ILC Technology CERMAX LX-300 Xe lamp (300 W), equipped with a cutoff filter (L-42, HOYA) and a cold filter (SC1201, Asahi Spectra) (ca. 410 <  $\lambda$  < 770 nm). The whole PEC system was deaerated with Ar at least 30 min prior to the measurements. Amperometry was performed using the same three-electrode PEC with the potential held at -0.17 V vs. SCE, which corresponds to the open circuit potential of the FTO/TiO<sub>2</sub>/**Ru-py** electrode in the dark. The amount of H<sub>2</sub> evolved was measured by a Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector and a Molecular Sieve 5A column (3 mm  $\times$  2.5 m; Ar as a carrier).



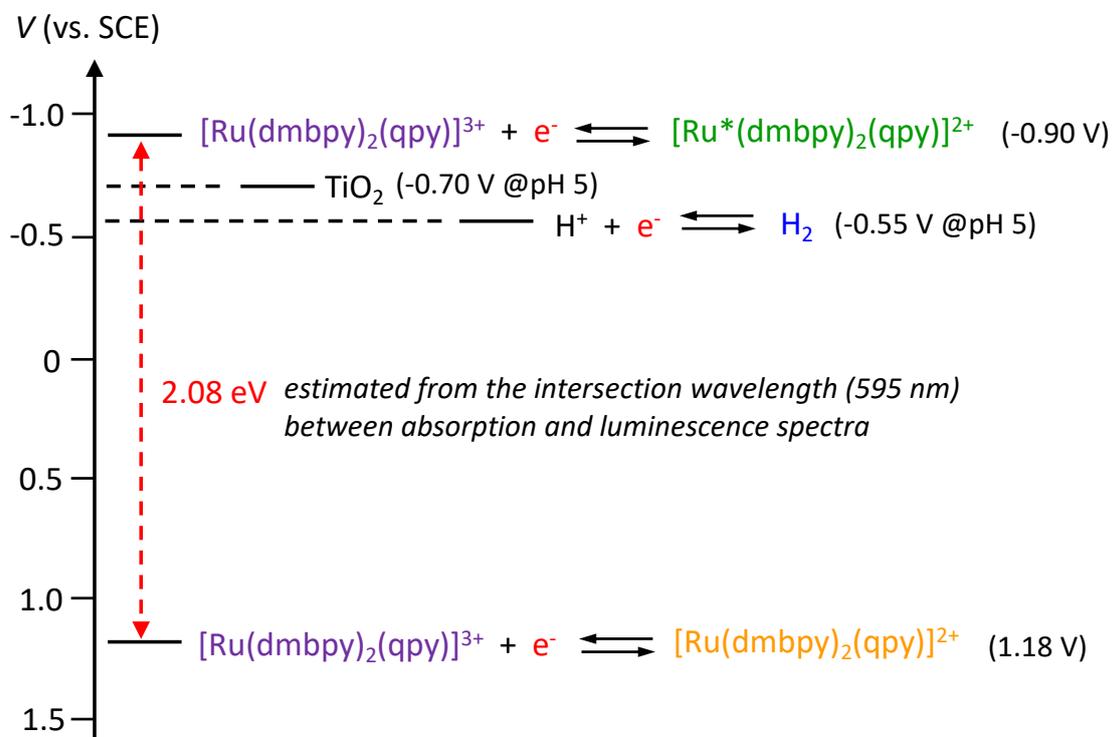
**Figure S1.**  $^1\text{H}$  NMR spectrum of **Ru-py** in acetone.



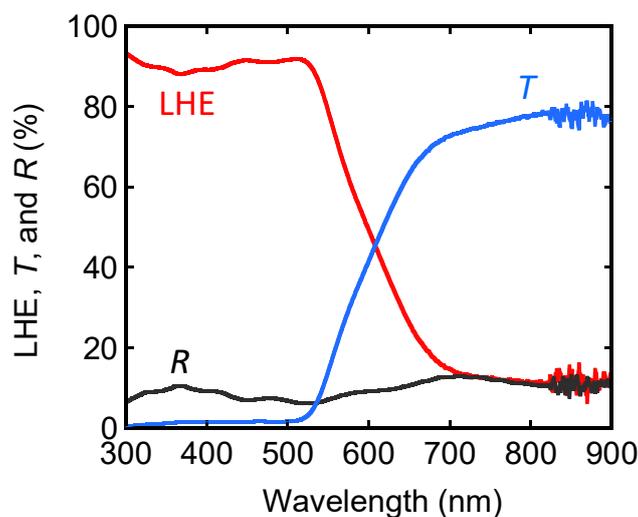
**Figure S2.** Absorption and uncorrected luminescence spectra of **Ru-py** in acetonitrile. Excitation wavelength is 480 nm. The intersection wavelength between normalized absorption and normalized luminescence spectra is 595 nm.



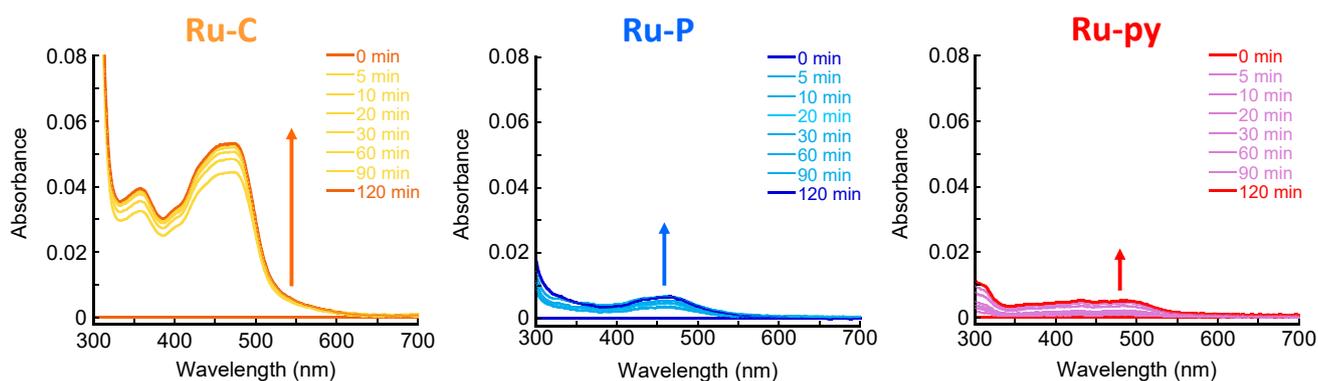
**Figure S3.** Cyclic voltammograms of 0.1 mM acetonitrile solution of **Ru-py** (bottom, red), and FTO/TiO<sub>2</sub>/**Ru-py** electrode in acetonitrile (top, blue) under Ar at room temperature. The electrolyte solution contained 0.1 M TBAP. Scan rate was 50 mV/s. Film thickness of the mesoporous TiO<sub>2</sub> thin film was ca. 7  $\mu\text{m}$ , and the amount of **Ru-py** adsorbed was estimated as  $5.6 \times 10^{-8}$  mol/cm<sup>2</sup>.



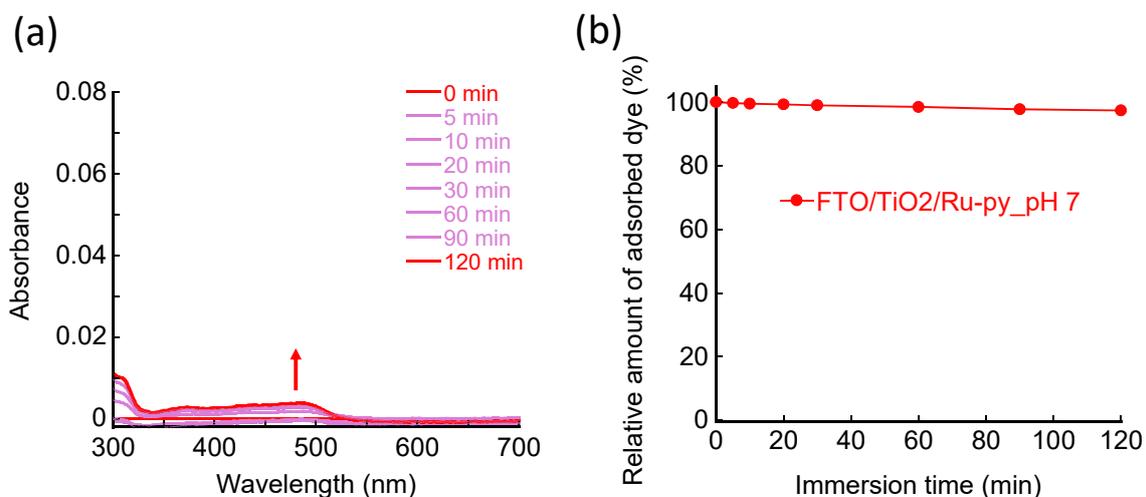
**Figure S4.** Schematic representation of the energy diagram for the relevant redox processes of **Ru-py**, together with the conduction band edge potential of  $\text{TiO}_2$  and the  $\text{H}_2$  evolution potential at pH 5. The edge potential of  $\text{TiO}_2$  was calculated based on the reported value of -0.4 V vs. SCE at pH 0.<sup>S6</sup>



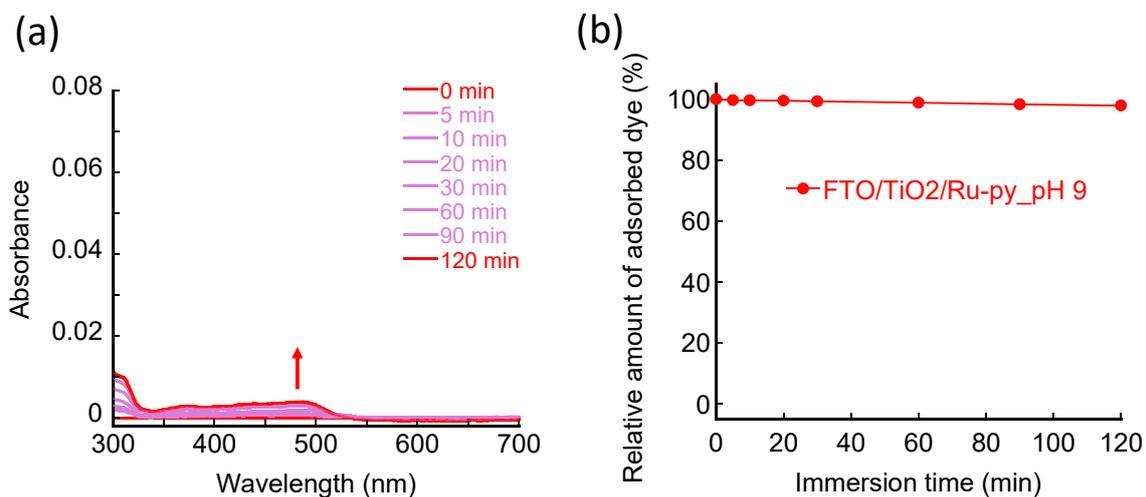
**Figure S5.** Light harvesting efficiency (LHE; red), transmittance ( $T$ ; blue) and reflectance ( $R$ ; gray) of the FTO/TiO<sub>2</sub>/Ru-py electrode. The film thickness of the mesoporous TiO<sub>2</sub> thin film was ca. 25  $\mu\text{m}$ , and the amount of Ru-py adsorbed was  $1.3 \times 10^{-7}$  mol/cm<sup>2</sup>. LHE was calculated by using following equation;  $\text{LHE (\%)} = 100 - T - R$ .<sup>S7</sup>



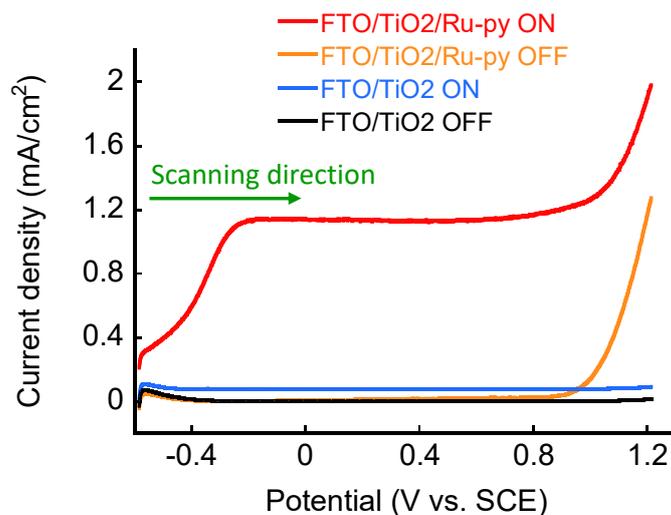
**Figure S6.** (a) Changes in the absorption spectrum of an aqueous acetate buffer solution (0.1 M, pH 5.0) containing 30 mM EDTA and 0.1 M NaClO<sub>4</sub> over time while the FTO/TiO<sub>2</sub>/Ru-dye electrode was submerged in the dark (the raw date of Figure 2). The amount of dye adsorbed on the TiO<sub>2</sub> surface was  $1.9 \times 10^{-7}$ ,  $1.0 \times 10^{-7}$  and  $1.3 \times 10^{-7}$  mol/cm<sup>2</sup> for Ru-C, Ru-P and Ru-py, respectively.



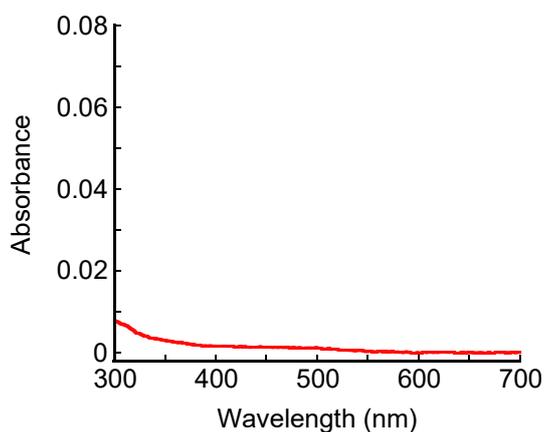
**Figure S7.** (a) Changes in the absorption spectrum of an aqueous borate buffer solution (0.1 M, pH 7.0) containing 0.1 M NaClO<sub>4</sub> over time while the FTO/TiO<sub>2</sub>/Ru-py electrode was submerged in the dark. (b) Plots of the relative amount of Ru-py adsorbed on the TiO<sub>2</sub> electrode as a function of immersion time. The amount of Ru-py adsorbed on the TiO<sub>2</sub> surface was  $1.0 \times 10^{-7}$  mol/cm<sup>2</sup>.



**Figure S8.** (a) Changes in the absorption spectrum of an aqueous phosphate buffer solution (0.1 M, pH 9.0) containing 0.1 M NaClO<sub>4</sub> over time while the FTO/TiO<sub>2</sub>/Ru-py electrode was submerged in the dark. (b) Plots of the relative amount of Ru-py adsorbed on the TiO<sub>2</sub> electrode as a function of immersion time. The amount of Ru-py adsorbed on the TiO<sub>2</sub> surface was  $1.0 \times 10^{-7}$  mol/cm<sup>2</sup>.



**Figure S9.** Linear sweep voltammograms of the FTO/TiO<sub>2</sub> and FTO/TiO<sub>2</sub>/Ru-py electrodes with or without continuous photoirradiation at a scan rate of 10 mV/s. Measurements were carried out in a three-electrode PEC with a Pt wire counter electrode and an Ag/AgCl reference electrode in an aqueous acetate buffer solution (0.1 M, pH 5.0) containing 30 mM EDTA and 0.1 M NaClO<sub>4</sub>. Photoirradiation was carried out using a 300 W Xe lamp equipped with a cutoff filter (L-42, HOYA) and a cold filter (SC1201, Asahi Spectra).



**Figure S10.** Absorption spectrum of the electrolyte solution (0.1 M aqueous acetate buffer solution containing 30 mM EDTA and 0.1 M NaClO<sub>4</sub>; pH 5.0) after 100 min photoelectrochemical measurement for the FTO/TiO<sub>2</sub>/Ru-py electrode. The experimental conditions were same to those for Fig. 3b. The relative amount of Ru-py desorbed from the TiO<sub>2</sub> surface after measurement was estimated to be ca. 2%.

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