Electronic Supporting Information

Factors influencing the photoelectrochemical device performance sensitized by ruthenium polypyridyl dyes

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1. General

UV-Vis and fluorescence spectra were recorded on a Shimadzu UV-3600 UV-Vis spectrophotometer and JASCO FP-6300 spectrofluorometer, respectively. $^1$H NMR and $^{13}$C NMR spectra were collected at 298 K using Bruker instrument (500 MHz). Electro spray ionization mass spectrometry (ESI-MS) spectra were measured on a Bruker micrOTOF II. Elemental analysis was carried out on an Exeter Analytical, Inc. CE-440F elemental analyzer.

2. Materials

Transparent titania paste and RuCl$_3$ hydrate were purchased from Sigma Aldrich. 4,4’-Di-tert-butyl-2,2’-bipyridyl 1 was purchased from Tokyo Chemical Industry Co., Ltd. Other chemicals were purchased from Kanto Chemical and Wako. Organic solvents were dried and distilled according to the standard methods when necessary. The organic syntheses were carried out under a N$_2$ atmosphere using Schlenk techniques. Ruthenium complex P1 and P2 were
prepared according to the previous report\textsuperscript{1} with slight modification using methanol for the reaction and acetonitrile for the hydrolysis. P4\textsuperscript{2} and 4,4'-bis(diethylphosphonate)-2,2'-bipyridine 3\textsuperscript{3} were prepared according to the procedure described in the literature.

3. Synthesis and characterization of P3

*Synthesis of complex 2.* The synthesis of complex 2 follows the “ruthenium blue” method reported previously.\textsuperscript{4} Compound 1 (1.06 g, 3.95 mmol) in 10 mL EtOH along with HCl (2 mL) was added to the prepared “ruthenium blue” solution (RuCl\textsubscript{3}, 396 mg, 1.91 mmol) in 30 mL EtOH/H\textsubscript{2}O (2:1) while the temperature was maintained at 80 °C.\textsuperscript{4} This mixture was refluxed for 0.5 hr under nitrogen, after which the color of the solution turned dark brown. After evaporating the solvent using a rotary evaporator, the deep brown crystals were deposited, collected by filtration and washed with water. The formed ruthenium(III) complex was suspended in 30 mL 2M HCl and 0.24 g of SnCl\textsubscript{2}.2H\textsubscript{2}O solid was added followed by heating at 90 °C while stirring until the dark precipitate was formed. The solid material 2 was collected by filtration, washed with water, and dried without further purification.
Synthesis of complex 4. A mixture of complex 2 (300 mg) and compound 3 (108 mg, 0.25 mmol) in a 15 mL mixed solution of EtOH/H₂O (2:1) was refluxed for 6 h under nitrogen. The solvents were removed by rotary evaporator and the product was isolated by column chromatography on silica gel. The main fraction was collected and eluted by 10% CH₃OH in
acetone (10 drops of saturated KPF₆ in CH₃OH was added to 100 mL solution) to afford complex 4. The pure fractions were collected to yield 42.9% (123 mg) of the complex. ¹H NMR (500 MHz, CD₃CN): 1.32 (12H, t, J= 7.05 Hz), 1.41 (18H, s), 1.42 (18H, s), 4.19 (8H, p, J= 7.06 Hz ), 7.37 (2H, dd, J= 2.07 Hz, 6.02 Hz), 7.42 (2H, dd, J= 2.12 Hz, 6.08 Hz), 7.54 (4H, dd, J= 6.00 Hz, 11 Hz), 7.62 (2H, dd, J= 5.73 Hz, 12.4 Hz); 7.87 (2H, dd, J= 4.12 Hz, 5.50 Hz), 8.58 (4H, dd, J= 1.85 Hz, 7.05 Hz), 8.78 (2H, d, J= 13.4 Hz)

Synthesis of P3. Complex 4 (116 mg, 0.1 mmol) was dissolved in dry CH₃CN (25 mL) and Si(CH₃)₃Br (0.13 mL, 1.0 mmol) was added dropwise at room temperature under a N₂ atmosphere. The mixture was heated to 45°C for 48 h and then cooled to room temperature. Dry CH₃OH (25 mL) was then added and the solution was stirred for another 3 h. The solvent was then removed under reduced pressure and the product was obtained after recrystallization from diethyl ether to yield 94.8% of the complex. ¹H NMR (500 MHz, CD₃OD): 1.44 (18H, s), 1.45 (18H, s), 7.51 (2H, dd, J= 1.98 Hz, 6.08 Hz), 7.55 (2H, dd, J= 2.02 Hz, 6.03 Hz), 7.65 (4H, dd, J= 6.62 Hz, 6.50 Hz), 7.74 (2H, dd, J= 5.50 Hz, 12.0 Hz); 7.96 (2H, dd, J= 3.60 Hz, 5.50 Hz), 8.73 (4H, dd, J= 2.20 Hz, 2.20 Hz), 8.88 (2H, d, J= 13.3Hz). ESI-MS: 951.29 [M-3H]. Calcd: 951.30. Elemental analysis: Calcd for C₄₆H₅₈F₁₂N₆O₆P₄Ru.H₂O: C, 43.44; H, 4.83; N, 6.61. Found: C, 43.47; H, 4.84; N, 6.64.

4. Film Preparation
Transparent TiO₂ films of 9 mm x 9 mm size with 7 µm thickness printed on FTO (Fluorine-doped Tin Oxide) glass were made according to the previous report. The mesoporous films were cast through doctor blading onto an ethanol cleaned FTO substrate using tape as a spacer for consistent thickness. The films were first dried while covered for 30 min and then sintered at 450 °C for 30 min. Film thicknesses (~7 µm) were determined using a Mitutoyo 156-101 micrometer stand. Titania films were submerged into concentrated CH₃OH solutions of P1, P2, P3 or P4 to allow the molecules to anchor to the nanocrystallite surface. The films were submerged for 4 h to achieve the optimum dye loading as monitored by UV-Vis spectroscopy. The amount of the dyes on TiO₂ surface (dye loading cₒ in cm⁻³) were estimated according to the previously reported calculations and presented in Table 2 and Table S1. Prior to use, the films were soaked for ~30 m in neat CH₃OH to remove any weakly adsorbed molecules from the film.

5. Electrochemistry and photoelectrochemistry
Electrochemical and photoelectrochemical measurements of the dyes on TiO$_2$ were performed on a VersaSTAT 3 potentiostat (Princeton Applied Research), using FTO/TiO$_2$/dye as working electrode, Ag/AgCl reference electrode and platinum counter electrode, measured in a custom-made cell as shown in Figure S2 using 0.1 M acetate buffer pH 5 containing 0.1 M NaClO$_4$ as the supporting electrolyte. A Max-303 Xenon lamp (Asahi Spectra) 300 W with 400 nm long pass filter was used to irradiate the photoanodes from the FTO side. The light intensity 160 mW/cm$^2$ was used for irradiating the photoanode in photoelectrochemical experiments. For cyclic voltammetry measurements in solution, the dyes were dissolved in 0.1 M acetate buffer pH 5 and methanol (1:3) containing 0.1 M NaClO$_4$ supporting electrolyte. The potential values were converted to NHE ($E_{NHE} = E_{Ag/AgCl} + 0.207$).  

For the determination of Ru$^{III}$/Ru$^{II}$ self-exchange energy (reorganization energy), variable-temperature cyclic voltammetry of FTO/TiO$_2$/dye electrodes was performed in 0.1 M acetate buffer pH 5 containing 0.1 M NaClO$_4$ and in dry acetonitrile containing 0.1 M TBAPF$_6$. The modeling to obtain the reorganization energies from the CV data was performed using Origin 9.0 software with the least-squares error minimization and Levenberg–Marquardt iteration method.

6. Measurements of H$_2$

Hydrogen measurements were performed on a Shimadzu 2010 Plus with a BID detector. The evolved gas in the headspace of the DSPEC was withdrawn using a Vici pressure lock gas syringe and injected to the GC. The gas mixture was separated using a miropacked ST column at oven temperature 35 °C using helium gas carrier. Hydrogen quantification was determined using 5% H$_2$ in argon and 5% O$_2$ in helium reference gases, purchased from Taiyo Nippon Sanso Co., Ltd. The Faradaic efficiency for the hydrogen production was calculated according to equation 1:

$$\eta H_2 = \frac{2nH_2}{Q}$$

where $nH_2$ is the mole of gas observed from the experiments and $Q = \text{charge} / 96485$.

7. IPCE measurements

The incident photon-to-charge carrier efficiencies (IPCE) of each dye on TiO$_2$ were measured manually in a custom-made two-electrode cell comprising of FTO/TiO$_2$/dye working electrode and Pt counter electrode loaded with 0.1 M acetate buffer pH 5 containing 0.1 M NaClO$_4$. 

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electrolyte in the absence and presence of EDTA. Xenon light irradiation is filtered with appropriate bandpass filters to obtain monochromatic lights at the wavelengths between 460 and 670 nm. The light intensity was measured by ADCMT 8230E Optical Power Meter (ADC Corporation). The measurement was performed at 0.05 V vs. NHE external bias. The data parameters were collected and calculated according to equation 2.

\[
\text{IPCE} \, (\%) = \frac{I(mA)}{P(mW)} \times \frac{1240}{\lambda(nm)} \times 100
\]  

(2)

8. Lifetime phosphorescence

The phosphorescence lifetime of the photoluminescence of the dyes in solution and in film was measured on a Quantaurus-Tau Fluorescence Spectrometer C11367. For solution, 14 µM of dye solution in methanol/acetate buffer pH 5 containing 0.1 M NaClO₄(3:1) was purged by N₂ for 20 mins prior to measuring the phosphorescence decay. For films, FTO/TiO₂/dye was inserted in the cell at 45° position and purged by N₂ for 20 mins before the measurement. The cell is kept deaerated throughout the measurement.

9. Theoretical calculation

Theoretical energy levels were obtained using B3LYP functional, which uses Stuttgart ECP (SDD) basis set for Ru and 6-31G** for all other atoms (C, H, O, N, P), calculated in the polarizable continuum model (PCM) of methanol using Gaussian 09 package. The molecular orbitals were visualized using the Gauss view 5.0.8 program.

10. References


![Figure S1](image.png)

**Figure S1** Absorption (solid) and emission (dashed) spectra of **P1** (red) **P2** (blue) **P3** (green) and **P4** (purple) measured in (a) 0.1 M acetate buffer pH 5 and methanol (1:3) containing 0.1 M NaClO₄ and in (b) FTO/TiO₂.
**Figure S2** A photograph of the custom-made DSPEC containing FTO/TiO$_2$/dye working electrode, Ag/AgCl reference electrode and platinum wire counter electrode that are connected to a potensiostat.

**Figure S3** (a) Cyclic voltammograms of P1 (red), P2 (blue), P3 (green), P4 (purple) immobilized in FTO/TiO$_2$ electrode using 0.1 M acetate buffer pH 5 containing 0.1 M NaClO$_4$ electrolyte solution at the scan rate 0.1 V sec$^{-1}$; (b) The CV of the dye solutions (0.6 mM) in 1:3 methanol/0.1 M acetate buffer pH 5 and methanol containing 0.1 M NaClO$_4$. The assignments of the redox potentials are presented in Table 1.
Figure S4 Cyclic voltammogram of EDTA acetate buffer pH 5 solution at the scan rate 0.1 V sec⁻¹. The $E_{1/2}$ was determined from the $E_{pa}$ value.

Figure S5 Linear sweep voltammograms of the FTO/TiO₂/P₁ (red) FTO/TiO₂/P₂ (blue) FTO/TiO₂/P₃ (green) FTO/TiO₂/P₄ (purple) (a) under continuous photoirradiation (b) under chopped illumination at a scan rate 0.01 V sec⁻¹. Xenon light (160 mW cm⁻²) with 400 nm long pass filter was used to irradiate the electrodes from the FTO side.

Table S1 Reorganization energies of the dyes on TiO₂ measured in acetonitrile

<table>
<thead>
<tr>
<th>Dye</th>
<th>$c₀$ [10¹⁹ cm⁻³]</th>
<th>$D_{app}$ at 300 K [10⁻¹⁰ cm² s⁻¹]</th>
<th>$E_{act}$ [meV]</th>
<th>$λ$ [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₁</td>
<td>13.0 ± 0.5</td>
<td>0.5 ± 0.1</td>
<td>495 ± 28</td>
<td>1916 ± 134</td>
</tr>
<tr>
<td>P₂</td>
<td>13.0 ± 1.2</td>
<td>1.2 ± 0.2</td>
<td>424 ± 32</td>
<td>1879 ± 183</td>
</tr>
<tr>
<td>P₃</td>
<td>11.2 ± 0.5</td>
<td>0.2 ± 0.04</td>
<td>548 ± 16</td>
<td>2422 ± 173</td>
</tr>
<tr>
<td>P₄</td>
<td>8.2 ± 0.2</td>
<td>0.2 ± 0.1</td>
<td>644 ± 24</td>
<td>2874 ± 176</td>
</tr>
</tbody>
</table>
Figure S6 The IPCE value of (a) FTO/TiO$_2$/P1 (b) FTO/TiO$_2$/P2 (c) FTO/TiO$_2$/P3 (d) FTO/TiO$_2$/P4 in absence of EDTA (×) and presence of EDTA (■) in comparison with their absorption spectra given as dotted lines.
Figure S7 Lifetime decay profiles of (a) P1 (b) P2 (c) P3 and (d) P4 in FTO/TiO$_2$ film

Figure S8 Lifetime decay profiles of P1 (red) P2 (blue) P3 (green) and P4 (purple) in solution

Figure S9 Time-course photocurrent density generated by the FTO/TiO$_2$/P1 (red)
FTO/TiO$_2$/P2 (blue) FTO/TiO$_2$/P3 (green) FTO/TiO$_2$/P4 (purple) electrodes under continuous irradiation at 0.05 V NHE performed in 0.1 M acetate buffer pH 5 containing 0.1 M NaClO$_4$ electrolyte solutions (a) in the absence of EDTA for 30 min photolysis; (b) in the presence of 30mM EDTA for 5.5 h photolysis.

**Figure S10** The amount of H$_2$ evolved after 30 min photolysis under the conditions described in Fig. S7a, where faradaic efficiency were 40, 41, 42, and 51% for P1, P2, P3, and P4 respectively.

**Figure S11** (a) Gas chromatograms showing the hydrogen peak at the retention time 0.42 min for the gas sample taken from FTO/TiO$_2$/P1 (red), FTO/TiO$_2$/P2 (blue), FTO/TiO$_2$/P3 (green), and FTO/TiO$_2$/P4 (purple) after 5.5 h photolysis; (b) The increase in the hydrogen peak over time is shown for the photolysis of FTO/TiO$_2$/P2.
Figure S12 $^1$H NMR spectrum of P1 in Methanol-$d_4$
Figure S13 ESI-MS spectrum (negative mode) of P1, showing m/z 727.0 ([M-3H]−)
Figure S14 $^1$H NMR spectrum of P2 in Methanol-$d_4$
Figure S15 ESI-MS spectrum (negative mode) of P2 showing m/z 783.1 ([M-3H]⁻)
Figure S16 $^1$H NMR spectrum of P3 in Methanol-$d_4$
Figure S17 $^{13}$C NMR spectrum of P3 in Methanol-$d_4$
Figure S18 ESI-MS spectrum (negative mode) of P3, showing m/z 951.3 ([M-3H]⁻)
Figure S19 $^1$H NMR spectrum of P4 in Methanol-d4
Figure S20 ESI-MS spectrum (negative mode) of P4, showing m/z 1230.5 ([M-3H]^−)