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SUPPLEMENTARY INFORMATION FOR

A Ruthenium Complex as a Single-Component Redox Shuttle for Electrochemical Photovoltaics

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Section S1. Materials and Methods

Materials. All reagents were obtained from commercial sources (Sigma Aldrich, TCI, Fluka, Daejung, or Ducksan) and were used without further purification. Methanol (MeOH, 99.8%, Aldrich), ethanol (EtOH, 96%, Daejung), isopropyl alcohol (IPA, 99.5%, Ducksan), acetonitrile (MeCN, 99.8%, Aldrich), and diethyl ether (ACS grade, >99.0%, Aldrich) were purchased from the noted chemical suppliers. Titanium(IV) isopropoxide (TIP, 97%, Aldrich), tetrabutylammonium hydroxide (TBAOH, 40 wt%, Aldrich), hydroxypropylcellulose (HPC, M_w \approx 80,000, Aldrich), and α -terpineol (>80%, TCI) were used to synthesize 10-nm size TiO₂ nanoparticles or to prepare the TiO₂ paste. Iodine (I₂, 99.8%, Aldrich), lithium iodide (Lil, 99.9%, Aldrich) guanidine thiocyanate (G⁺SCN⁻, 99%, Aldrich), 4-tert-butylpyridine (TBP, 96%, Aldrich), valeronitrile (99.5%, Aldrich), and 1-butyl-3-methylimidazolium iodide (BMII, >95%, TCI) were used to prepare the iodine-based redox shuttle. Tris(2,2'-bipyridyl)ruthenium(II) hexafluorophosphate $[Ru(bpy)_3:2PF_6, 97\%, Aldrich]$ was used as received for the single-redox shuttle with an additive of TBP. Lithium perchlorate (LiClO₄, 99.99%, Aldrich) and tetrabutylammonium tetrafluoroborate (TBABF₄, 99%, Aldrich) were used as additives for the cyclic voltammetric analysis. Fluorine-doped tin-oxide glasses (FTO, 7 $\Omega \cdot \text{cm}^{-2}$, Philkington), Alconox detergent, TiO₂ paste for the transparent layer (containing TiO₂ NPs with an average size of ca. 18 nm, 18NR-T, Dyesol), TiO₂ paste for the scattering layer (containing TiO₂ particles with an average size of ca. 200 nm, WER2-O Reflector paste, Dyesol), titanium(IV) chloride (90 mM in 20% HCl solution, Aldrich), and chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, ACR grade, Aldrich) were used to prepare the photoanodes or counter electrodes of the cells. Cells were assembled using thermoplastic Surlyn-1702 film (thickness = 25 μ m, DuPont), tin-coated copper wire (diameter = 0.25 mm, Arcor), conductive silver epoxy (types A and B, Circuitworks), and micro-cover glasses ($18 \times 18 \text{ mm}^2$, Duran).

Synthesis of TiO₂ NPs with an average size of 10 nm. We synthesized TiO₂ nanoparticles with an average size of 10 nm and prepared a paste using these nanoparticles according to the procedure reported previously.^{S1,S2}

Synthesis of JK2 dye. We synthesized a batch of JK2 dye according to the procedure reported previously.^{S2}

Synthesis of tris(2,2'-bipyridyl)ruthemium(III) hexafluorophosphate compounds. We have synthesized tris(2,2'-bipyridyl)ruthenium(III) complexes modifying the procedure described in reports.^{S3-S6} То tris(2,2'-bipyridyl)ruthenium(III) synthesize complexes, first, tris(2,2'bipyridyl)ruthenium(II) hexafluorophosphate powder (0.3 g) was dissolved in acetonitrile (130 g) and subsequently, a little amount of NOBF₄ (0.07 g) was added into the solution. After continuous stirring for 3 h, we removed the solvent using rotary evaporator. The obtained powder was again dissolved in acetonitrile (80 g) and then, an excess amount of NH₄PF₆ (0.16 g) was added into the solution. After the unreacted NH_4PF_6 was removed by filtration, diethyl ether was added into the solution until crystallization was formed. Eventually, green crystallites were collected by sedimentation and washed with a mixed solvent of acetonitrile and diethyl ether (2:1 volume ratio). The collected green powder was dried under vacuum at room temperature and move into a glove box prior to use.

Preparation of the iodine-based electrolyte. An admixture of 600 mM BMII, 100 mM LiI, 30 mM I_2 , 100 mM G⁺SCN⁻, and 500 mM TBP in a mixed solvent of acetonitrile (85 vol%) and valeronitrile (15 vol%) was used as the iodine-based electrolyte.

Preparation of the Ru(bpy)₃²⁺ **electrolyte.** An acetonitrile solution of 8 mM tris(bipyridyl)ruthenium(II) bis(hexafluorophosphate) [Ru(bpy)₃·2PF₆] and 500 mM TBP was used as a ruthenium-based electrolyte. We also prepared 4 mM and 6 mM ruthenium electrolyte solutions for optimization of the cell performance.

Preparation of the mixed $Ru(bpy)_3^{2+/3+}$ **electrolyte.** An acetonitrile solution of 8 mM tris(bipyridyl)ruthenium(II) bis(hexafluorophosphate) [Ru(bpy)_3·2PF_6], 3 mM tris(bipyridyl)ruthenium(III) bis(hexafluorophosphate) [Ru(bpy)_3·3PF_6], and 100 mM LiClO₄ was used for a ruthenium-based mixed electrolyte.

Preparation of TiO₂ films. FTO glass plates (10 $\Omega \cdot \text{cm}^{-2}$) were cut into 15 mm × 15 mm squares. Contaminants were removed from the plates by sonicating them in a 10% aqueous solution of Alconox detergent for 30 min. After being washed with copious amounts of distilled deionized water, the FTO plates were refluxed in a 40 mM TiCl₄/IPA solution for 30 min and removed from the solution and then placed in an oven at 420 °C for 30 min. For the fabrication of porous TiO_2 films, the commercial (ca. 20 nm) TiO₂ paste was deposited onto the FTO squares using the doctor-blade method, using parallel single layers of Scotch Magic tape as a mask. After the films were dried at 110 °C for 60 min, the tape was removed. The films were subsequently calcined at 400 °C for 30 min. The TiO₂-coated FTO glass plates were refluxed in a 40 mM TiCl₄/IPA solution and then calcined again at 400 °C for 30 min. The thickness of the fabricated films was ca. 7.0 μm (see Fig. S9). To prepare thicker films (13 μm), we have used parallel double layers of the Scotch tape instead of single layers. For preparation of 2.4- and 3.2- μ m-thick films, we diluted the commercial paste with α -terpineol by 2.0- and 1.5-fold by weight, respectively, and deposited the diluted paste between parallel single layers of the Scotch tape using the doctor-blade method (see Fig. S9). To prepare 2.6-µm-thick films of 10-nm TiO₂ NPs, we deposited the homemade paste using parallel single layers of the Scotch tape (see Section S12). For all of the films, the dimensions were reduced to approximately 3×3 mm² by a razor blade after calcination.

Dye loading. The films were soaked in a dichloromethane/ethanol (3:2 v/v) solution containing 0.5 mM JK2. After 4 h, the films were washed with copious amounts of the aforementioned mixed solvent and dried under flowing nitrogen.

Preparation of Platinized Cathodes. FTO glass plates were cut into 20 mm × 20 mm squares. A 0.3mm-diameter hole was drilled into each glass plate. Contaminants on the FTO glass plates were removed using the same method previously described. A 5 mM $H_2PtCl_6/EtOH$ solution was drop-cast (1 drop = ca. 10 µL) onto each square and allowed to dry in a capped polycarbonate Petri dish. Finally, the platinized squares were calcined at 380 °C for 30 min.

Assembly of Photovoltaic Cells. Dye-coated photoanodes and platinized FTO glass plates were sealed together by melting a ca. 25- μ m-thick Surlyn polymer film on a hotplate at 170 °C. Tin-coated copper wires were connected to each electrode using silver epoxy. The epoxy was then dried at approximately 80 °C for 40 min. The electrolyte solution (ca. 30 μ L) was dropped onto the drilled hole, and the electrolyte was then vacuum-loaded into the cell. After the residual electrolyte on the hole was removed, the hole was sealed by melting a sheet of Surlyn polymer film that was inserted between the backside of the FTO and a micro-cover glass slide. Finally, a photo-mask with an aperture was applied on top of the active area of each cell.^{S7,S8} The gap interval of electrolyte layer was modulated, varying the number of 25- μ m-thick Surlyn films that are inserted between photoelectrode and counter electrode.

Instrumentation. Distilled and deionized water was obtained from a water purification system (Merck Millipore, MQ Direct 8). Scanning electron microscopy (SEM) images were obtained from a FE-SEM (Hitachi S-4800) operated at an acceleration voltage of 3 kV, after samples were coated by Au-Pt alloys with the thickness of 3 nm. Transmission electron microscopy (TEM) images were obtained from a field-emission transmission electron microscope (Hitachhi HF-3300) operated at an acceleration voltage of 300 kV. The UV-Vis spectra of samples were recorded on an Agilent Cary 5000 UV-VIS-NIR spectrophotometer. The JV curves of photovoltaic cells were obtained using a homemade setup consisting of an electrochemical potentiostat (CHI 604E, CH Instruments) and a solar simulator (3A solar system, model 94023A, Newport). The light intensities in the range from 10 to 100 mW·cm⁻² were calibrated using a reference solar cell (a monocrystalline silicon solar cell calibrated with NIST traceability, model 91150-KG1, Newport). Incident photon-to-electron conversion efficiency (IPCE) tests of the cells were performed using a home-made setup which consists of xenon lamp, an AM 1.5 light filter, a monochromator, and an electrochemical potentiostat (CHI 604E, CH Instruments). Cyclic voltammetry (CV) was performed on a potentiostat (CHI 604E). For cyclic voltammetric analyses, we employed a platinum disk working electrode (CH Instruments, CHI 102), a platinum wire counter electrode (Bioanalytical Systems, Inc.), and an Ag/Ag⁺ reference electrode (ALS, RE-7). The instruments used for FE-SEM and TEM analyses are located at the Center for Core Research Facilities (CCRF) in DGIST.

Section S2. Instability of Ru(bpy)₃·3PF₆ Compound

We have wondered if addition of an oxidized form of $Ru(bpy)_3^{2+}$ into the electrolyte can engender higher photovoltaic performance. With this in our mind, we have synthesized $Ru(bpy)_3 \cdot 3PF_6$ from $Ru(bpy)_3 \cdot 2PF_6$ using an oxidant, NOBF_4. See details for synthesis in Section S1. The color of the obtained $Ru(bpy)_3 \cdot 3PF_6$ compound was green (See the absorption spectrum and photograph image in Fig. S1 and S2, respectively). However, we have observed that the color of the compound is readily changed from green to red especially in moisture-containing solvent or moist atmosphere, indicating that it is not so stable in contrast to its reduced form, $Ru(bpy)_3 \cdot 2PF_6$ (See Fig. S1). The addition of trace amount of water into the $Ru(bpy)_3^{3+}/MeCN$ solution leads to its reduction to $Ru(bpy)_3^{2+}$. Thus, we have handled the compound very carefully from synthesis through fabrication of cells in a moist-free, argoncharged glove box.

Meanwhile, we have used TBP for $Ru(bpy)_3^{2+}$ electrolyte as an additive to maximize the photovoltaic performance of the cells. However, we have found that TBP also chemically reduces the $Ru(bpy)_3^{3+}$ to $Ru(bpy)_3^{2+}$. See color changes and spectral changes in Fig. S2 and Fig. S4, respectively. Instead, we have used LiClO₄ salt as an additive in electrolyte (to avoid its reduction). The photograph images in Fig. S3 and absorption spectra in Fig. S4 show that the $Ru(bpy)_3^{3+}$ compound is stable in LiClO₄-containing medium in contrast to that in TBP.



Fig. S1 Intensity-normalized UV-vis absorption spectra of (a) $Ru(bpy)_3 \cdot 2PF_6/MeCN$ and (b) $Ru(bpy)_3 \cdot 3PF_6/MeCN$ solutions. The spectra show the changes of $Ru(bpy)_3^{3+}$ to $Ru(bpy)_3^{2+}$ after addition of 300 μ L H₂O.



Fig. S2 Sequential photograph images of a $Ru(bpy)_3$ ·3PF₆/MeCN solution after addition of a drop of 500 mM TPB/MeCN solution.



Fig. S3 Photograph images of a $Ru(bpy)_3 \cdot 3PF_6/MeCN$ solution after addition of several drops of 100 mM LiClO₄/MeCN solution.



Fig. S4 Intensity-normalized UV-vis absorption spectra of $Ru(bpy)_3$ ·3PF₆/MeCN solution before (green curve) and after addition of a drop of 500 mM TBP/MeCN (red curve) and several tens drops of 100 mM LiClO₄/MeCN solutions (blue curve).

Section S3. Photovoltaic Performance of Cells Assembled with a paired $Ru(bpy)_3^{2+/3+}$ Shuttle

As commented in Section S2, LiClO₄ salt has allowed us to fabricate cells containing Ru(bpy)₃³⁺ without its reduction. We expected that addition of Ru(bpy)₃³⁺ can increase the photovoltaic performance of the cells, boosting the supply of the oxidized component, Ru(bpy)₃³⁺, and thereby, enhancing the overall electrochemical rate for dye-regeneration. In contrast to our expectation and other electrolyte systems, however, we found that the addition substantially suppressed its photovoltaic performance. See JV and IPCE curves in Fig. S5. Although we need more comprehensive studies, we speculate that the factors such as the ligands of shuttle complexes, the content ratio of oxidized to reduced components, additives in electrolyte, and their concentration can be influential in both photocurrent densities and photovoltages of the cells.



Fig. S5 (a, c) JV curves and (b, d) IPCE spectra of the cells comprised of (a, b) only $Ru(bpy)_3^{2+}$ and (c, d) paired $Ru(bpy)_3^{2+/3+}$ electrolytes. Note that LiClO₄ was co-dissolved in the electrolyte solution as an additive.

Section S4. Redox Potential of the Ru(bpy)₃²⁺ Shuttle

Electrochemical redox potentials of Ru(bpy)₃²⁺ and quasi-HOMO potential of JK2 were obtained using the CV technique. The CV curve of Ru(bpy)₃²⁺ was measured at a concentration of 1 mM and at a scan rate of 100 mV·s⁻¹, whereas the curve of JK2 was measured at 0.1 mM and 20 mV·s⁻¹ (see Fig. S6). The quasi-HOMO potentials of JK2 was determined at the inflection points of its oxidation curves (because the inflection point should be the highest value in HOMO band which can be formed by broad energy distribution of molecular population) and the redox potential of Ru(bpy)₃²⁺ was decided at the average potential of reduction and oxidation reactions. The determined quasi-HOMO potential of JK2 and redox potential of Ru(bpy)₃²⁺ were 1.78 and 1.58 V, respectively, vs. the normal hydrogen electrode (NHE) potential. We observed that these values are comparable or quite similar to the values previously reported in the literature.^{S9,S10} The quasi-LUMO potential of the JK2 dye was also determined by adding the minimum energy required for the first excitation to the quasi-HOMO level. The excitation energy of the JK2 dye was obtained from its UV-vis absorption spectrum (see Fig. S8).

Fig. S6 Cyclic voltammograms of acetonitrile solutions containing (a) 0.1 mM JK2 and (b) 1 mM Ru(pby)₃²⁺; TBABF₄ was codissolved in the solutions as an additive. The scan rates were 20 mV·s⁻¹ for JK2 and 100 mV·s⁻¹ for Ru(pby)₃²⁺.

Section S5. Theoretical Studies for the HOMO Potential of the Ru(bpy)₃²⁺ Shuttle

To gain better understanding of the HOMO potential of the Ru(bpy)²⁺ molecule, we simulated its molecular orbital (MO) and charge density distributions. The simulation was performed using density functional theory (DFT) with projector augmented wave (PAW)^{S11,S12} pseudopotentials, as implemented in the Vienna *ab initio* simulation package (VASP) code.^{S13} To incorporate an effect of exchange-correlation into the calculation, we used the hybrid B3LYP functional.^{S14,S15} Prior to the simulation, we placed the molecule into a cubic supercell that was surrounded by a vacuum space of at least 10 Å in all Cartesian directions. The calculations were repeatedly executed until the residual force for atomic relaxation reached 0.01 eV·Å⁻¹ or less. The resulting HOMO potential was -6.4 eV (see Fig. S7). We note that this value is quite close to the aforementioned experimental result (-6.08 eV).

Fig. S7 Simulated MO energy diagrams and the charge density distribution of $Ru(bpy)_3^{2+}$. The magenta-, cyan-, black-, and white-colored spheres indicate Ru, N, C, and H atoms, respectively. The isosurface (blue) of the charge density distribution is ca. $5 \times 10^{-3} e^{\text{Å}-3}$.

Fig. S8 Uv-vis absorption spectrum of JK2 that is coated in 2.4- μ m-thick transparent TiO₂ film.

Section S7. Optimization of TiO₂ Film Thickness and Ru(bpy)₃²⁺ Concentration

We optimized the cells by varying the thickness of the TiO₂ photoelectrode and the concentration of the Ru(bpy)₃²⁺ electrolyte. (See Fig. S9 and S10; Table S1 and S2) At the end of the experiment, we obtained the maximized J_{SC} and V_{OC} of the cells composed of a 2.4- μ m-thick TiO₂ film and an 8 mM Ru(bpy)₃²⁺ electrolyte solution. To gain greater current and voltage outputs, we attempted to increase the concentration of the electrolyte; however, the solubility of Ru(bpy)₃²⁺ in acetonitrile limited its maximum concentration to 8 mM.

Fig. S9 Cross-sectional scanning electron microscopy (SEM) images of The TiO₂ films with thicknesses of (a) 2.4, (b) 3.2, (c) 7.0, and (d) 13.0 μ m.

Fig. S10 (a) JV curves of the cells comprised of 2.4- (red), 3.2- (green), 7.0- (blue), and $13.0-\mu$ m-thick (black) TiO₂ films. The concentration of electrolyte was fixed at 8 mM. (b) JV curves of the cells containing 4 mM (blue), 6 mM (green), and 8 mM (red) Ru(bpy)₃²⁺ electrolyte. The thickness of the TiO₂ film of the cells was fixed at 2.4 μ m.

Table S1 Photovoltaic Parameters of the Cells with TiO ₂ Fi	ilms of Various Thickness
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Film Thickness (µm)	J _{sc} (mA⋅cm ⁻²)	V_{oc} (V)	FF	η (%)
2.4	1.41	0.94	0.63	0.83
3.2	1.32	0.94	0.65	0.80
6.9	1.19	0.92	0.66	0.72
13.0	1.05	0.93	0.67	0.66

Table	S2	Photovoltaic	Parameters	of	the	Cells	Containing	Different
Concer	ntrati	ions of Ru(bpy)	²⁺ Electrolyte					

Electrolyte Conc. (mM)	J _{sc} (mA⋅cm ⁻²)	V _{oc} (V)	FF	η (%)
4	0.98	0.89	0.51	0.44
6	1.39	0.89	0.48	0.59
8	1.41	0.94	0.63	0.83

Section S8. Examination of Whether Ru(bpy)₃²⁺ Shuttle Harvests Light

Ru(bpy)₃²⁺ shuttle contained in 25 μ m-thick electrolyte gap space absorbs visible light, although its strength is weak relative to that of JK2 dye loaded in 2.4 μ m-thick TiO₂ film. (See Fig. S11) To examine whether the absorption of this Ru(bpy)₃²⁺ shuttle contributes to photocurrent generation, first we have checked IPCE spectra of the cells with variation of the electrolyte concentration from 4 to 8 mM. Our postulation was that increasing absorptivity by Ru(bpy)₃²⁺ can induce peaky IPCE curve in 400-500 nm range if the shuttle harvests the corresponding visible light and contributes to generation of photocurrent. The IPCE results, however, have not shown these phenomena, indicating that the ruthenium shuttle does not contribute to photocurrent. (See Fig. S12)

To make sure this again, we have made cells without dye and tested JV and IPCE curves with the cells. (See Fig. S13) The dye-free cell exhibited the short-circuit current density of 0.04 mA·cm⁻² (0.02-folds) which value is quite small compared to that of dye-loaded cells (ca. 1.4 mA·cm⁻²). IPCE spectrum of the dye-free cell proves that the small photocurrent comes from the absorption of semiconducting TiO₂. Therefore, we tentatively conclude that the ruthenium shuttle absorbs visible light a little but does not contribute to photocurrent generation.

Fig. S11 (a) UV-vis Absorption spectra and (b) light harvesting efficiencies (LHEs) spectra of JK2 coated in 2.4 μ m-thick transparent TiO₂ film (red curves) and 8 mM Ru(bpy)₃²⁺/MeCN electrolyte solution contained in 25 μ m-thick electrolyte gap space (blue curves). LHEs, magnitude of light absorptivity versus unity, are calculated with a simple equation, 1-10^{-A}.

Fig. S12 IPCE spectra of the cells containing 4 mM (blue), 6 mM (green), and 8 mM (red) $Ru(bpy)_{3}^{2+}$ electrolyte. The TiO₂ film thickness of the cells was fixed with 2.4 μ m.

Fig. S13 (a) JV curves and (b) IPCE spectra of the cells with (red curves) and without (blue curves) JK2 dye. The cells were commonly comprised of 2.4 μ m-thick transparent TiO₂ films and 8 mM Ru(bpy)₃²⁺ electrolyte.

Section S9. Photocurrent Changes with Variation of the Longitudinal Gap Intervals of the Electrolyte Layer in Ru(bpy)₃²⁺ Cells

We hypothesized that the low photocurrent was due to the slow dye-regeneration resulting from the low mass-transfer rate and low concentration of the Ru(bpy)₃²⁺ shuttle. To examine this hypothesis, we modulated the cross-sectional electrolyte gap interval from 25 to 175 μ m. As expected, the photocurrent densities decreased as the interval increased (see Fig. S14 and Table S3).

Fig. S14 (a) JV curves of the cells assembled with electrolyte gap intervals of 25, 50, 75, 125, and 175 μ m and (b) their photocurrent density plotted as a function of the gap interval.

Gap Interval (µm)	J _{SC} (mA⋅cm ⁻²)	V _{oc} (V)	FF	η (%)
25	1.41	0.94	0.63	0.83
50	0.70	0.89	0.68	0.42
75	0.38	0.86	0.70	0.23
125	0.24	0.77	0.42	0.08
175	0.11	0.76	0.47	0.04

Table S3 Photovoltaic Parameters of the Cells Assembled with Various Electrolyte Gap Intervals

Section S10. Photocurrent Changes with Variation of the Longitudinal Gap Interval of the Electrolyte Layer in Iodine Cells

We tested a standard iodine-based electrolyte in the same manner used to test $Ru(bpy)_3^{2+}$ (see Section S9) to examine whether the aforementioned observations related to photocurrent density were common to all electrochemical photovoltaics. However, we did not observe significant changes in the photocurrent densities of the I^{-}/I_3^{-} -based cells (see Fig. S15).

Fig. S15 (a) JV curves and (b) IPCE spectra of I^{-}/I_{3}^{-} -based cells assembled with electrolyte gap intervals of 25, 50, 75, 125, and 175 μ m.

Section S11. Diffusion Limit of the Ru(bpy)₃²⁺ Shuttle in TiO₂ Films with Smaller Nanopores

To see the effect of the diffusion rate of Ru(bpy)₃²⁺ molecules on dye regeneration, we examined their diffusion through TiO₂ films with smaller nanopores. For these experiments, we synthesized smaller TiO₂ particles according to the procedure reported previously.^{S1,S2} Whereas the average size of the commercial TiO₂ nanoparticles is ca. 20 nm, the average size of the home-made TiO₂ nanoparticles was ca. 10 nm along the [100] or [110] directions (see Fig. S16). Using this homemade TiO₂, we fabricated films with a thickness of 2.6 μ m to bring the thickness quite close to that of commercial TiO₂ films (2.4 μ m; see Fig. S17). As described in our previous report, the average pore size of the homemade films was determined to be 14 nm.^{S1} This pore size is approximately half that of the commercial films.^{S1}

Fig. S16 TEM images of (a) commercial and (b) homemade TiO_2 nanoparticles. Their average sizes are 20 and 10 nm, respectively, along the [100] axis.

Fig. S17 Cross-sectional SEM image of a film fabricated with the homemade 10-nm TiO₂ nanoparticles.

As expected, the J_{SC} value of a cell made with smaller TiO₂ nanoparticles was lower than that of the cells made with bigger commercial TiO₂. (See Fig. S18) Here, we suspected whether such a decrease may come from lower dye-loading amount that can lead lower light harvesting. To confirm this, we have examined UV-vis absorption of dye-loaded films with transmittance-mode. The films made with smaller and larger TiO₂, respectively, exhibited the absorbance of ca. 3.30 and 1.74, showing the ratio of ca. 1.90. (See Fig. S19) On the basis of this result, we tentatively concluded that the amount of dye in smaller TiO₂ film is approximately double that in larger TiO₂ film. We note that this "double" is quite close to the ratio of surface areas.

To make sure this, we have conducted dye-desorption experiments. To obtain extinction coefficient of JK2, first, we have taken absorption spectra of JK2, dissolving it in 0.1 M TBAOH/EtOH solution to several concentrations. (See Fig. S20) The obtained extinction coefficients at 365 and 455 nm were, respectively, 65,900 and 56,500. Next, we have detached JK2 dye from the films (made with

smaller and larger TiO_2) by soaking them into 5 mL of 0.1 M TBAOH/EtOH solution and then, taken absorption spectra with the solutions. Consistent with the apparent similarity of the above ratios, the amounts of desorbed-dye showed two-fold difference. (See Fig. S21 and Table S4)

Fig. S18 (a) JV curves and (b) IPCE spectra of the cells with photoanodes prepared using commercial 20-nm (blue curves) or homemade 10-nm (red curves) TiO₂ nanoparticles. The thicknesses of the anodes were 2.4 and 2.6 μ m, respectively.

Fig. S19 Transmittance-mode UV-vis absorption spectra of JK2-coated transparent TiO_2 film made with average 10-nm (red curve) and 20-nm (blue curve) size nanoparticles. The thicknesses of the films were, respectively, 2.6 and 2.4 μ m.

Fig. S20 (a) UV-vis absorption spectra of 0.5, 5.0, 10, 13, 15, 17, 25, and 50 μ M JK2 solution dissolved in 0.1 M TBAOH/EtOH. (b) plots of absorbance of JK2 at λ_{max} s of 365 and 455 nm with respect to its concentration and their least-square fits.

Fig. S21 UV-vis absorption spectra of 0.1 M TBAOH/EtOH solution containing JK2 desorbed from the TiO_2 film which were made with average 10-nm (red curve) and 20-nm (blue curve) size nanoparticles. The thicknesses of the films were, respectively, 2.6 and 2.4 μ m.

Table S4 Input and Output Parameters in Dye-Desorption Experiments

TiO ₂ size	wavelength	А	٤ (M ⁻¹ .cm ⁻¹)	conc.	film area	film thickness	mole of JK2	ratio of moles
10	365	1 30	65900	1.08×10-5	1 28	2 60	2.76×10^{-8}	2.03
		1.30	5500	1.98×10	1.38	2.00	2.70×10*	2.03
	455	1.12	56500	1.99×10-3	1.38	2.60	2.77×10**	2.02
20 -	365	0.71	65900	1.07×10 ⁻⁵	1.64	2.40	1.36×10 ⁻⁸	1.00
	455	0.61	56500	1.08×10 ⁻⁵	1.64	2.40	1.37×10 ⁻⁸	1.00

*The volume of 0.1 M TBAOH/EtOH solution was 5 mL.

Section S12. JV Curves of a Typical I⁻/I₃⁻ Cell under Various Illumination Powers

The typical I^{-}/I_{3}^{-} cells were assembled with a 13-µm-thick film fabricated from a commercial 20nm source and an electrolyte solution that comprised of 600 mM BMII, 100 mM LiI, 30 mM I_{2} , 100 mM G⁺SCN⁻, and 500 mM TBP in a mixed solvent of acetonitrile (85 vol%) and valeronitrile (15 vol%). The details are presented in Section S1.

Fig. S22 JV curves of a typical I^{-}/I_{3}^{-} cell measured under illumination powers of 10, 30, 50, and 100 mW·cm⁻².

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