

Supplementary Information for

# Effective Panchromatic Sensitization of Electrochemical Solar Cells: Strategy and Organizational Rules for Spatial Separation of Complementary Light Harvesters on High-area Photo-electrodes

Nak Cheon Jeong<sup>1,2,\*</sup>, Ho-Jin Son<sup>1</sup>, Chaiya Prasittichai<sup>1</sup>, Chang Yeon Lee<sup>1,3</sup>, Rebecca A. Jensen<sup>1</sup>, Omar K. Farha<sup>1</sup>, and Joseph T. Hupp<sup>1,4,\*</sup>

<sup>1</sup>Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208 U.S.A., <sup>2</sup>Department of Emerging Materials Science, DGIST, Daegu 711-873, Korea, <sup>3</sup>Department of Energy and Chemical Engineering, University of Incheon, Incheon 406-772, Korea, and <sup>4</sup>Argonne National Laboratory, Argonne, IL, 60439 U.S.A.

\*To whom correspondence should be addressed. E-mail: [nc@dgist.ac.kr](mailto:nc@dgist.ac.kr); [j-hupp@northwestern.edu](mailto:j-hupp@northwestern.edu)

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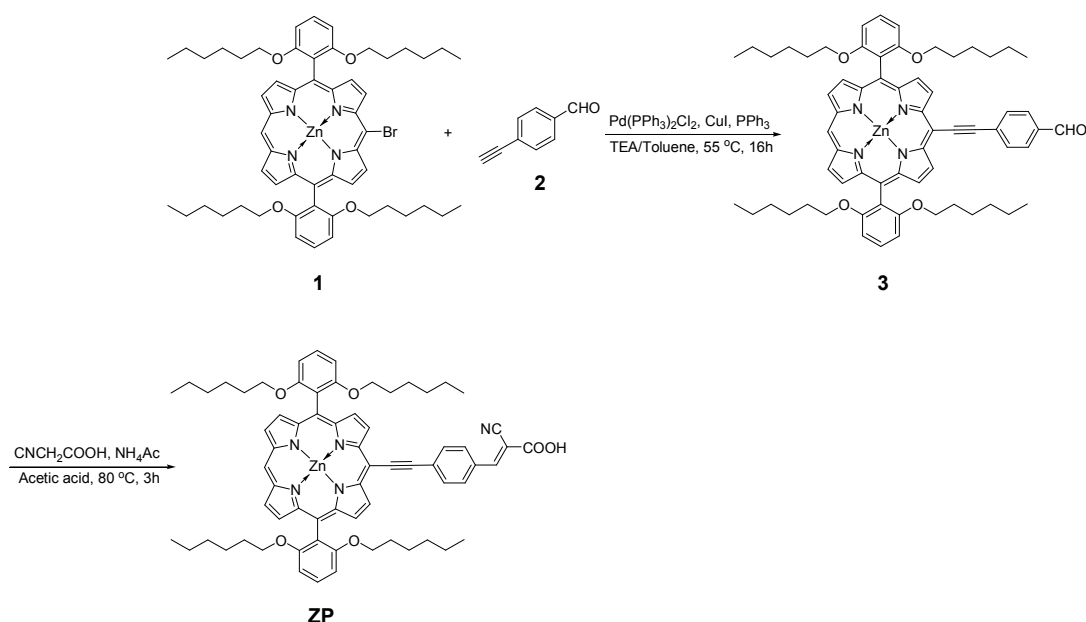
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## Section S1. Syntheses and characterization of ZP and ZPS.

Chemicals for syntheses of JK2, **ZP**, and **ZPS** were used as received from Sigma-Aldrich and Strem chemical company. Solvents were dried following standard procedures prior to use and all chemicals were manipulated under nitrogen atmosphere.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **ZP** and **ZPS** were recorded on a Agilent 400-MR NMR spectrometer and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometric data were performed by a PE Voyager DE-Pro MALDI-TOF mass spectrometer (Bruker) in positive, reflector ionization mode, using dithranol as a matrix.

**Synthesis of JK2.** JK2 were synthesized according to a published procedure<sup>1</sup>.

**Scheme for Synthesis of ZP.** **ZP** was synthesized from 4-(2-(10,20-bis(2,6-di(n-hexoxy)phenyl)porphyrinato zinc(II)-5-yl)ethynyl) benzaldehyde (**3**) which was synthesized with [5-bromo-10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc (**1**) and 4-ethynylbenzaldehyde (**2**), following the synthetic procedure illustrated in Scheme S1. Compounds, (**1**)<sup>2</sup> and (**2**)<sup>3</sup> were synthesized according to literature procedures.

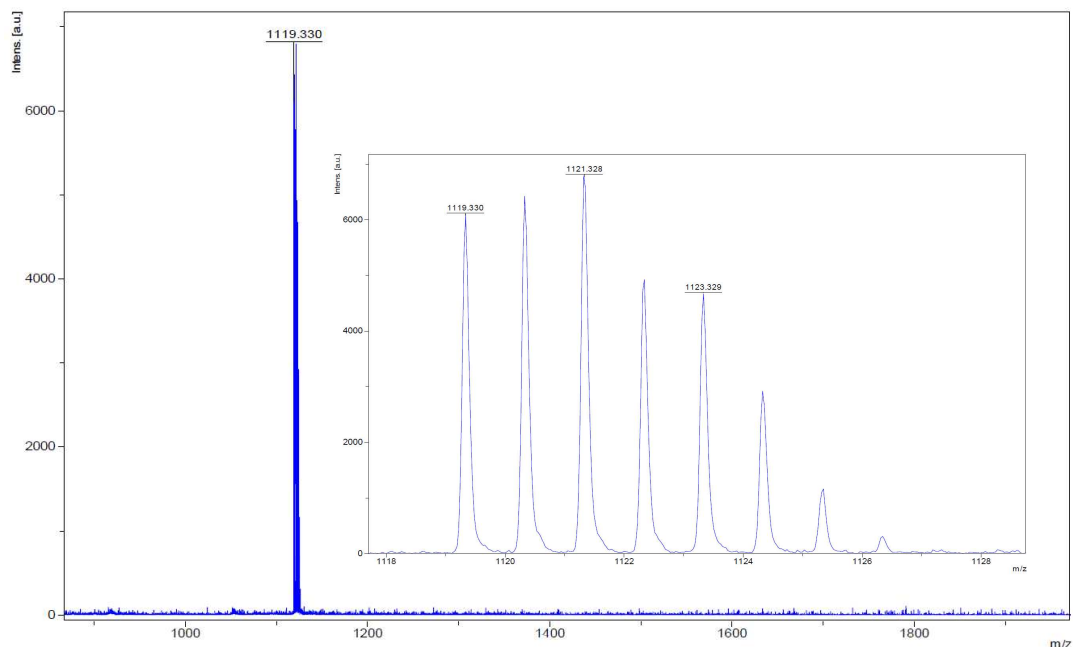


**Scheme S1.** Synthesis of **ZP**.

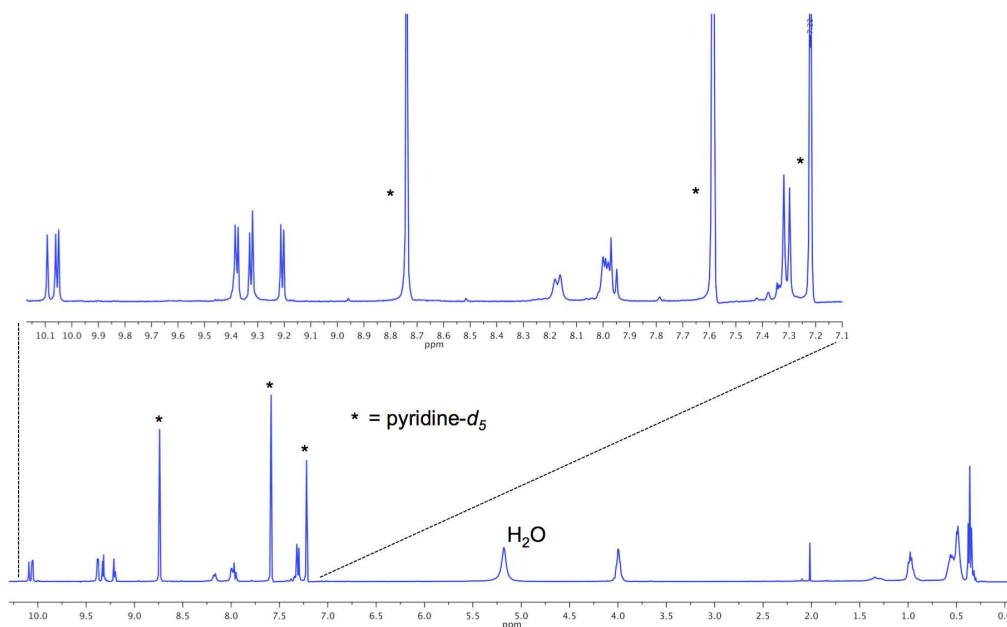
**Synthesis of 4-(2-(10,20-bis(2,6-di(n-hexoxy)phenyl) porphyrinato zinc(II)-5-yl)ethynyl) benzaldehyde (**3**).** To a stirring, mixed solution of **1** (188 mg, 0.187 mmol) and **2** (48.7 mg, 0.374 mmol) in toluene (21.0 mL) and triethylamine (3.7 mL), Triphenylphosphine (6.3 mg, 0.024 mmol),  $\text{CuI}$  (8.6 mg, 0.045 mmol), and bis(triphenylphosphine) palladium(II) dichloride (17 mg, 0.024 mmol) were added after the mixed solution was degassed for 10 min. Then, the solution was heated to  $55^\circ\text{C}$  and maintained for 16 h. After the solution was cooled to room temperature, crude compound was obtained by drying the solution under vacuum. The resulting crude compound was purified using silica-gel column chromatography (hexanes/dichloromethane (2:3 v/v)). Compound **3** was isolated as a green

solid (131 mg, 67% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 10.04 (s, 1 H), 9.73 (s, 1 H), 9.71 (d,  $J = 4.3$  Hz, 2H), 9.23 (d,  $J = 4.3$  Hz, 2H), 9.01 (d,  $J = 4.3$  Hz, 2H), 8.94 (d,  $J = 4.3$  Hz, 2H), 7.75 (br s, 2H), 7.73 (t,  $J = 8.3$  Hz, 2H), 7.62 (br s, 2H), 7.04 (d,  $J = 8.3$  Hz, 4H), 3.87 (t,  $J = 6.2$  Hz, 8H), 0.94 (m, 8H), 0.55 (m, 16H), 0.45 (m, 8H), 0.28 (t,  $J = 6.6$  Hz, 12H). MS (MALDI-TOF)  $m/z$  1052.1 (Calcd  $m/z$  1053.5 for  $(\text{M}+\text{H})^+$ ).

**Synthesis of 2-cyano-3-trans-(4-(2-(10,20-bis(2,6-di(*n*-hexoxy)phenyl) porphyrinato zinc(II)-5-yl)ethynyl)phenyl)acrylic acid (ZP).** A mixture of **3** (100 mg, 0.095 mmol), cyanoacetic acid (160 mg, 1.88 mmol), and piperidine (0.5 mL) in methanol (10 mL) was heated up to 65 °C and kept for 16 h. After the solution was diluted with dichloromethane (10.0 mL), it was washed with water ( $3 \times 20.0$  mL). Crude material was obtained by evaporating the organic solvent. It was purified via silica-gel column chromatography (4% methanol and 0.5% acetic acid in dichloromethane). **ZP** was isolated as a dark green solid (133 mg, 98.0% yield).  $^1\text{H}$  NMR (400 MHz, pyridine- $d_5$ ): 10.09 (s, 1H), 10.06 (d,  $J = 4.5$  Hz, 2H), 9.38 (d,  $J = 4.5$  Hz, 2H), 9.32 (d,  $J = 4.4$  Hz, 2H), 9.21 (d,  $J = 4.3$  Hz, 2H), 8.17 (d,  $J = 7.6$  Hz, 2H), 8.03–7.92 (m, 5H), 7.31 (d,  $J = 8.5$  Hz, 4H), 3.99 (br s, 8H), 1.05–0.85 (m, 8H), 0.64–0.41 (m, 24H), 0.36 (t,  $J = 6.9$  Hz, 12H).  $^{13}\text{C}$  NMR (101 MHz, pyridine- $d_5$ ): 161.01, 152.58, 152.28, 151.30, 133.04, 132.77, 132.49, 132.33, 132.20, 131.41, 131.02, 130.98, 128.92, 128.68, 128.44, 122.12, 115.07, 106.24, 99.95, 99.21, 98.73, 97.78, 97.58, 95.90, 84.70, 69.22, 31.49, 29.53, 25.68, 22.79, 14.22. MS (MALDI-TOF)  $m/z$  1119.33 (Calcd  $m/z$  1119.49 for  $(\text{M})^+$ ).

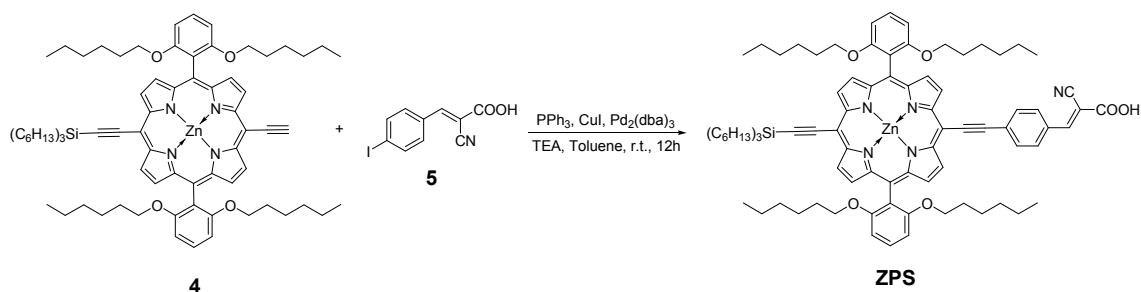


**Figure S1.** MALDI-TOF mass spectrometry of **ZP**



**Figure S2.**  $^1\text{H}$ -NMR spectrum of **ZP**

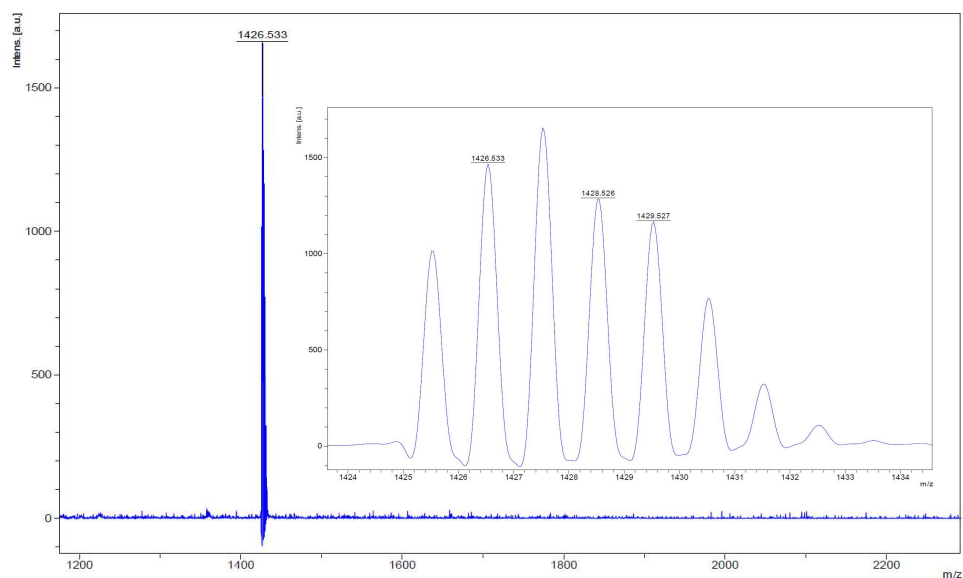
**Scheme for Synthesis of ZPS.** **ZPS** was synthesized following the synthetic procedure (Scheme S2) from [5-Ethynyl-15-(tri-iso-propylsilanyl)ethynyl-10,20-bis[2,6-di(n-hexoxy)phenyl]porphinato]zinc (**4**)<sup>4</sup> and 2-Cyano-3-(4-iodophenyl)acrylic acid (**5**)<sup>5</sup>, which were synthesized according to literature procedures.



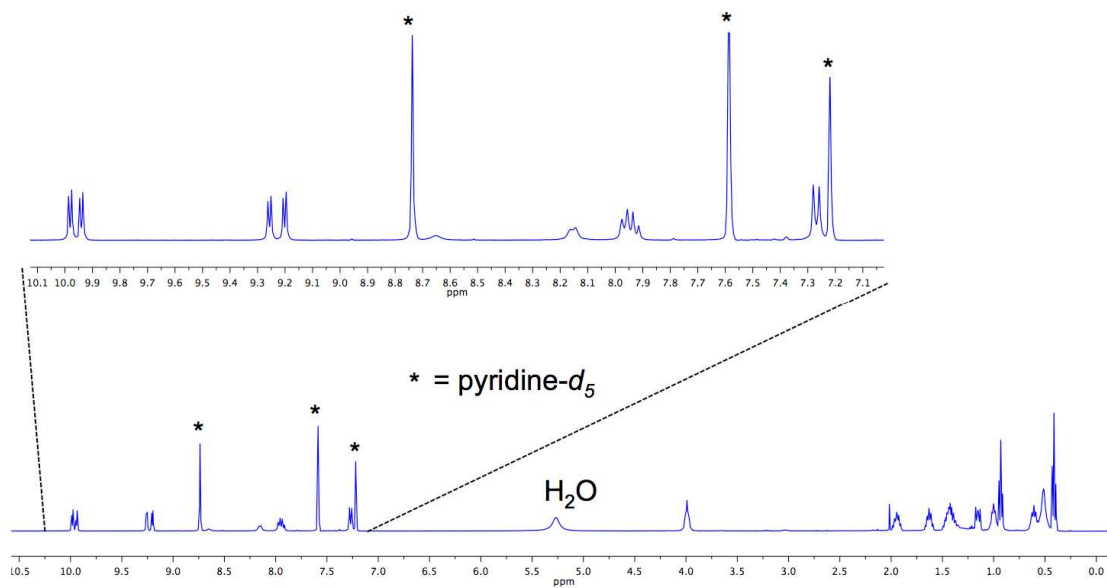
**Scheme S2.** Synthesis of **ZPS**.

**Synthesis of 2-cyano-3-trans-(4-(2-(10,20-bis(2,6-di(n-hexoxy)phenyl)-15-(tri-iso-propylsilanyl)ethynyl-porphyrinato zinc(II)-5-yl)ethynyl)phenyl)acrylic acid (ZPS).** To a stirring mixture of **4** (8 mg, 0.070 mmol), **5** (21 mg, 0.070 mmol), CuI (7 mg, 0.037 mmol), and PPh<sub>3</sub> (18 mg, 0.069 mmol) in 10 mL of TEA/toluene (1:5 v/v), Pd<sub>2</sub>(dba)<sub>3</sub> (16 mg, 0.017 mmol) was added after 10 min. of deoxygenation. The solution was then stirred for 12 h. Crude compound was collected after solvent evaporation and then purified using silica-gel column chromatography (dichloromethane/methanol (95:5 v/v)). Subsequently, pure **ZPS** was obtained (60 mg, 60% yield).  $^1\text{H}$  NMR (400 MHz, Pyridine-*d*<sub>5</sub>): 9.98 (d, *J* = 4.5 Hz, 2H), 9.94 (d, *J* = 4.4 Hz, 2H), 9.26 (d, *J* = 4.4 Hz, 2H), 9.20 (d, *J* = 4.4 Hz, 2H), 8.15 (d, *J* = 7.4 Hz, 2H), 8.00–7.90 (m, 4H), 7.27 (d, *J* = 8.5 Hz, 4H), 4.00 (br s, 8H), 2.00–1.88 (m, 6H), 1.63 (p, *J* = 7.4 Hz, 6H), 1.51–1.32 (m, 12H), 1.19–1.10 (m, 6H), 1.00 (p, *J* = 6.5 Hz, 8H), 0.93 (t, *J* = 7.0 Hz, 9H), 0.68–0.45 (m, 24H), 0.41 (t, *J* = 7.1 Hz, 12H).  $^{13}\text{C}$  NMR (101 MHz, pyridine-*d*<sub>5</sub>): 160.89, 152.78, 152.53, 151.99, 151.81, 133.00, 132.78, 132.31, 131.58, 131.39, 131.30, 131.15, 128.92, 128.67, 128.44,

121.75, 116.70, 106.17, 101.07, 99.72, 99.19, 69.22, 34.12, 32.38, 31.53, 29.54, 25.75, 25.26, 23.45, 22.86, 14.83, 14.74, 14.30. MS (MALDI-TOF)  $m/z$  1426.52 (Calcd  $m/z$  1426.76 for  $(M+H)^+$ ).



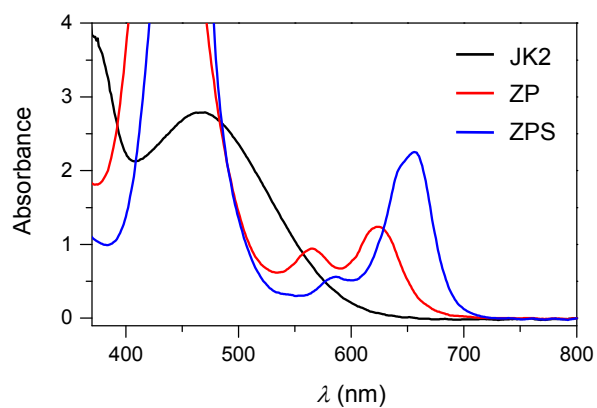
**Figure S3.** MALDI-TOF mass spectrometry of ZPS



**Figure S4.**  $^1\text{H}$ -NMR spectrum of ZPS

## Section S2. Absorption spectra of JK2, ZP, and ZPS.

Absorption spectra of JK2, ZP, and ZPS on 4.5  $\mu\text{m}$  thick nano-porous  $\text{TiO}_2$  films. Films were fabricated with homemade  $\text{TiO}_2$  paste as described by previous report.<sup>6</sup>



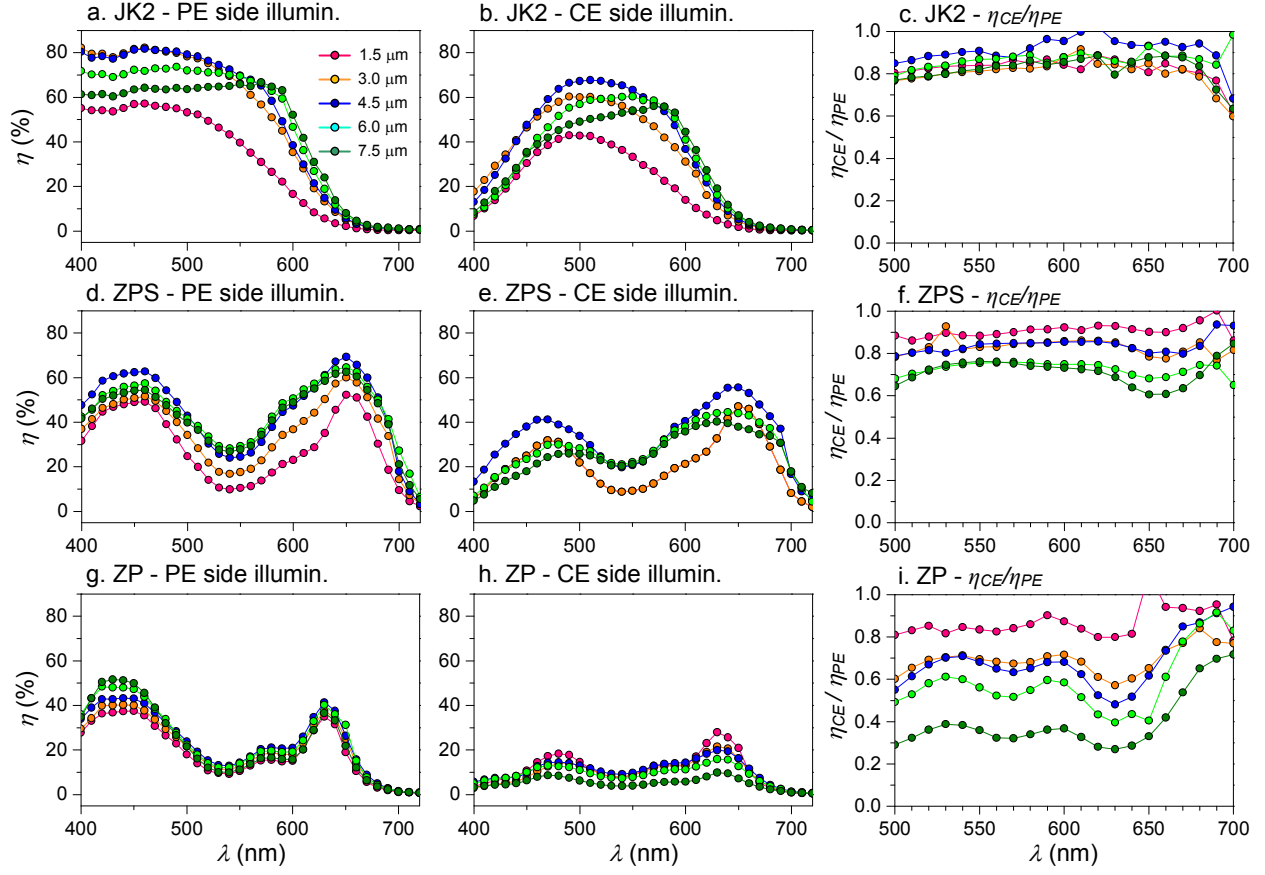
**Figure S5.** Absorption spectra of JK2 (black), ZP (red), and ZPS (blue) adsorbed on nano-porous  $\text{TiO}_2$  films.

### Section S3. IPCEs of JK2, ZP, and ZPS obtained from both PE- and CE-side illumination.

IPCE plots for DSCs containing JK2-, ZPS-, and/or ZP-loaded TiO<sub>2</sub> films of various thicknesses (1.5, 3.0, 4.5, 6.0, 7.5  $\mu\text{m}$ ) were recorded based on either PE-side or CE-side illumination (see Fig. S6). The IPCE values from CE-side illumination are generally less than those from PE-side illumination. This is due, in part, to competitive light absorption by I<sub>3</sub><sup>-</sup> and by the Pt-coated cathode. For JK2, we observed similar IPCE trend from both sides with regard to dependence on electrode thickness. However, CE-side IPCEs from ZP and ZPS preferentially decreased as the thicknesses of the films increased. We evaluated the ratio between CE-side and PE-side IPCEs,  $\eta_{CE}/\eta_{PE}$ , at the wavelength 500-700 nm. We neglected the blue part of the spectrum since IPCE values in the region are complicated by absorption by the iodine-based electrolyte. Fig. S6 shows that while JK2-loaded cells yield ratios near unity regardless of the film thickness and the ratios for ZPS-loaded cells slightly decrease as the film thickness increase, the ratios for ZP-loaded cells drop dramatically as the film thickness increase. These results implied that the effective electron collection lengths of the three chromophores are in this order JK2>ZPS>ZP. We also plotted this ratio at the maximum absorption of each chromophore (JK2 at 570, ZPS at 650, and ZP at 630 nm) and, therefore, determined the electron collection length as shown in (Fig. 1c).

Additionally, PE-side IPCE plots were integrated and weighted relative to the wavelength-dependent intensity of the solar spectrum. This was done as a cross-check on the validity of white-light  $J_{sc}$  measurements. While good agreement is seen (Table 1), the directly measurement current densities do tend to exceed slightly the values derived from IPCE integration. We tentatively ascribe the differences to neglect (in the IPCE integrations) of contributions below 400 nm.

Unfortunately, after experimental studies had been completed a lamp-intensity calibration error was uncovered. Measurements were unintentionally made at an intensity of 1.30 sun, rather than 1 sun. In view of the error, current densities were adjusted downward by a factor of 1.30. The data included in the text, table, and figures include this correction. In principle, small additional corrections should also be introduced for cell voltages (perhaps several millivolts) and overall efficiencies. However, because we lack sufficient information to implement voltage corrections precisely, and because we are not investigating champion cells, we have not attempted to make these additional corrections.



**Figure S6.** IPCEs obtained by PE-side and CE-side illumination and their ratios,  $\eta_{CE}/\eta_{PE}$ , as indicated.



## Section S4. Methods for fabrication of photoanodes and measurement of DSCs.

**Materials.** Titanium (IV) tetrachloride (90 mM in 20% of HCl solution, Aldrich), tetraethyorthsilicate (TEOS, >99%, Aldrich), ethanol (EtOH, 96%, Mallinckrodt), isopropyl alcohol (IPA, 99.5%, Mallinckrodt), acetonitrile (99%, Mallinckrodt), TiO<sub>2</sub> paste for scattering layers (400-nm average-size TiO<sub>2</sub> NPs, WER4-0, Dyesol), and Alconox detergent were used as received. Fluorine-doped tin-oxide glasses (FTO, 10  $\Omega\text{cm}^{-2}$  for anodes and 15  $\Omega\text{cm}^{-2}$  for cathodes) for the photoelectrode were purchased from Hartford glass. Chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, ACR grade, Aldrich) was used for cathode. Iodine (I<sub>2</sub>, 99.8%, Aldrich), guanidine thiocyanate (99%, Aldrich), 4-tert-butylpyridine (99%, Aldrich), valeronitrile (99.5%, Aldrich), and 1-butyl-3-methylimidazolium iodide (BMIT<sup>+</sup>I<sup>-</sup>, 98%, TCI) for preparation of electrolyte solutions were used as received. Cells were assembled using thermoplastic Surlyn-1702 film (thickness = 60  $\mu\text{m}$ , Dupont), tin-coated copper wire (diameter = 0.25 mm, Arcor), conductive silver epoxy (type A and B, Chemtronix), and micro cover glasses (18 × 18 mm<sup>2</sup>, VWR).

**Preparation of TiO<sub>2</sub> paste for transparent photoanodes.** For preparation of transparent photoanodes, we have used homemade TiO<sub>2</sub> paste which was prepared according to the procedure reported earlier<sup>6</sup>.

**Preparation of double TiO<sub>2</sub> films.** FTO glass plates (10  $\Omega\text{cm}^{-2}$ ) were cut into 15 mm x 15 mm squares. Contaminants were removed by sonicating them in a 10% aqueous solution of Alconox detergent for 30 min. After washing with copious amount of distilled water, the FTO were refluxed in a 40 mM solution of TiCl<sub>4</sub>/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<sub>2</sub> films, the homemade TiO<sub>2</sub> paste was deposited on FTO squares by the doctor blade method, using parallel triple layers of Scotch Magic tape as a mask. After drying the films for 60 min at 110 °C, the tape was removed. Films were then calcined at 400 °C for 30 min. The film thickness was ~4.5  $\mu\text{m}$  as shown in Fig. 2b. The TiO<sub>2</sub> coated FTO glasses were refluxed in a 40 mM solution of TiCl<sub>4</sub> in IPA and calcined at 400 °C for 30 min. We used these films for single layer. In order to make double TiO<sub>2</sub> films, we keep fabricating with more step by following below. The TiO<sub>2</sub> films were again refluxed in concentrated TEOS solution for 20 min, washed with ethanol, and placed in an oven at 400 °C for 30 min. SiO<sub>2</sub> on top surface of TiO<sub>2</sub> film was removed by sweeping a cotton wetted with 0.2% HF/EtOH solution. For the fabrication of double TiO<sub>2</sub> film, the TiO<sub>2</sub> paste was deposited on the above TiO<sub>2</sub> film by the doctor-blade method, using parallel triple-layers of tape as a mask. After drying the films for 60 min at 110 °C, the tape was removed. Films were then calcined at 400 °C for 30 min. The film thickness was ~9  $\mu\text{m}$  as shown in Fig. 2b. For

films used to for UV-Vis spectral measurements and usual photovoltaic studies, no additional processing was applied. For films destined to maximize photovoltaic performance, a TiO<sub>2</sub> scattering layer was deposited on top of the above TiO<sub>2</sub> layer using ~400 nm size TiO<sub>2</sub> particles prior to the above-described second calcination step. After calcination, the dimensions of each TiO<sub>2</sub> film were reduced to ~3 × 3 mm by a razor blade.

**Dyes loading.** Dyes adsorption onto the above double TiO<sub>2</sub> layers was accomplished by following method. The films were soaked in a 0.5 mM solution of JK2 in dichloromethane/ethanol (3:2 v/v). After 90 min, the films were washed with copious amount of the above solvent and dried with a nitrogen stream. Then, the films were soaked in 0.5% HF/water solution for 10 seconds for removal of SiO<sub>2</sub> covering TiO<sub>2</sub> surface and washed with water, and then again dried with a nitrogen stream. This was repeated one more. To stabilize JK2, the film was placed in a chamber for atomic layer deposition and coated with TiO<sub>2</sub> thin layer (8 cycles, 7 Å) at 105 °C. Finally, the JK2 coated films were soaked in a 0.5 mM solution of ZP in ethanol for 90 min. The procedure for other combination of dyes was same to the above except type of dyes.

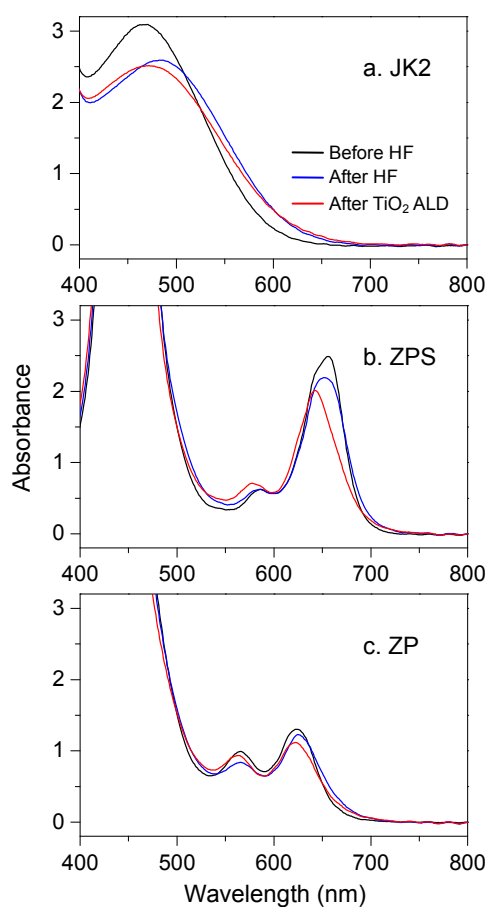
**Preparation of Platinized Cathodes.** FTO glass plates were cut into 20 mm x 20 mm squares. A 0.3 mm diameter hole was drilled in each glass. Contaminants on the FTO glasses were also removed using the above method. A 5 mM solution of H<sub>2</sub>PtCl<sub>6</sub> in EtOH solution was dropcast (1 drop; ca. 10 microliters) on each square and allowed to be dry in a capped polycarbonate Petri dish. Finally, the platinized squares were calcined at 380 °C for 30 min.

**Assembly of Photovoltaic Cells.** dye-adsorbed photoanodes and platinized FTO glass were sealed together by melting a 60-μm-thick Surlyn polymer film on a hotplate at 170 °C. Indium-coated copper wires were connected on each electrode with silver epoxy. Then, the epoxy was dried at 110 °C for 40 min. 0.45 M 1-Butyl-3-methylimidazolium iodide, 0.023 M I<sub>2</sub>, 0.075 M guanidine thiocyanate, and 0.38 M 4-tert-butylpyridine in 3 mL of the mixture of acetonitrile (85 Vol%) and valeronitrile (15 Vol%) were uses as electrolyte. ~30 μL of the electrolyte was dropped onto the drilled hole and then, the electrolyte was vacuum-loaded into the cell. After 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<sup>7-8</sup>.

**Instrumentation.** Scanning electron microscopy (SEM) images were obtained from a FE-SEM (Hitachi S-4800) operated at an acceleration voltage of 5 kV, after samples were coated by Au-Pt alloys with the thickness of 3 nm. UV-Vis spectra of samples were recorded on a Varian Cary 5000 UV-VIS-

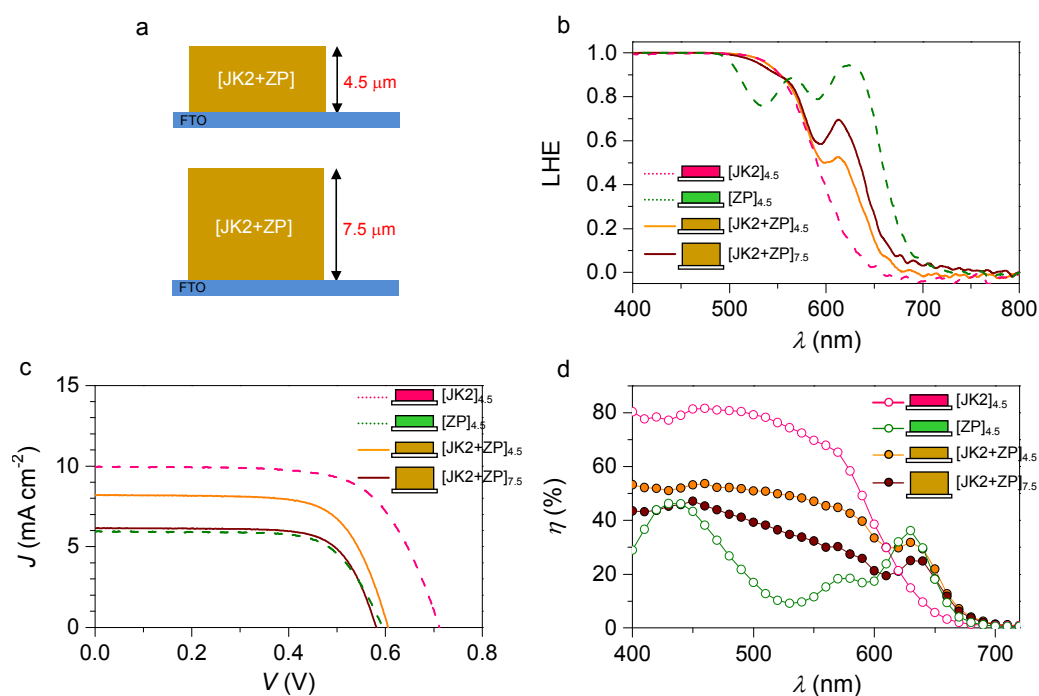
NIR spectrophotometer. The photocurrent-density-to-applied-voltage ( $J$ - $V$ ) curves and IPCE curves of photovoltaic cells were obtained using a homemade setup which consists of xenon lamp, an AM 1.5 light filter, and a CHI 1202 Electrochemical Analyzer (CHI instruments). The power of filtered light was calibrated by optical power meter (OPM) to 100 mWcm<sup>-2</sup>. Electrochemical Impedance Spectroscopy (EIS) was performed by Solartron 1286 chemical interface coupled with Solartron 1260A frequency response analyzer. Cells were measured in the dark with a 10mV AC perturbation under forward bias range from -0.5V to -0.7V. Samples were scanned over the frequency of 0.05Hz to 500,00Hz. Z-view equivalent circuit model (Bisquert #2) was used to fit the data.

## Section S5. UV-Vis absorption spectra changes of JK2, ZPS, and ZP.

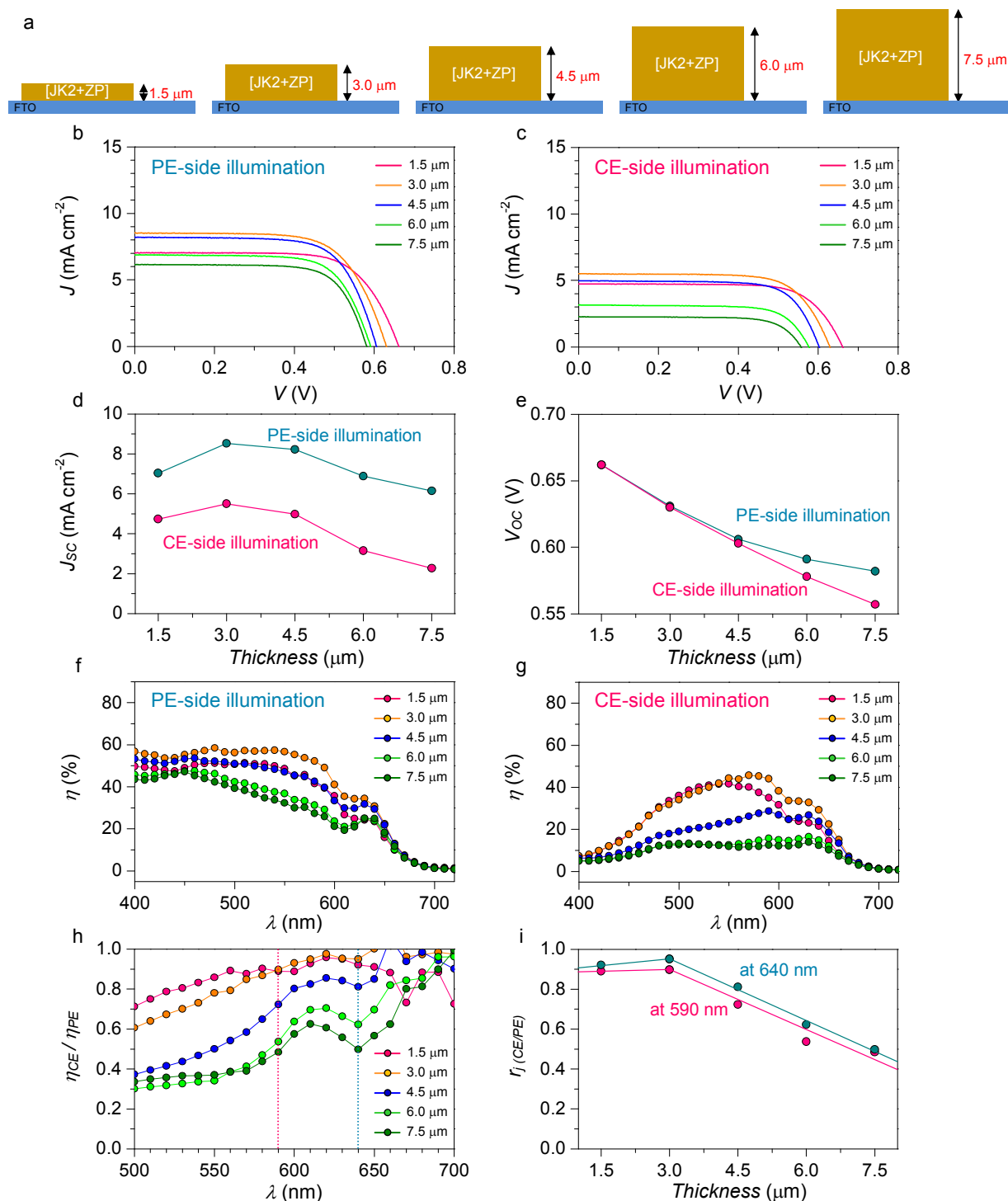


**Figure S7.** Absorption spectra of (a) JK2, (b) ZPS, and (c) ZP before (black curve) and after (blue curve) HF treatment for removing SiO<sub>2</sub>, and after stabilizing sensitizers with a method of TiO<sub>2</sub> atomic layer deposition (ALD).

## Section S6. Mixed co-sensitization of [JK2+ZP] on various thick TiO<sub>2</sub> film.

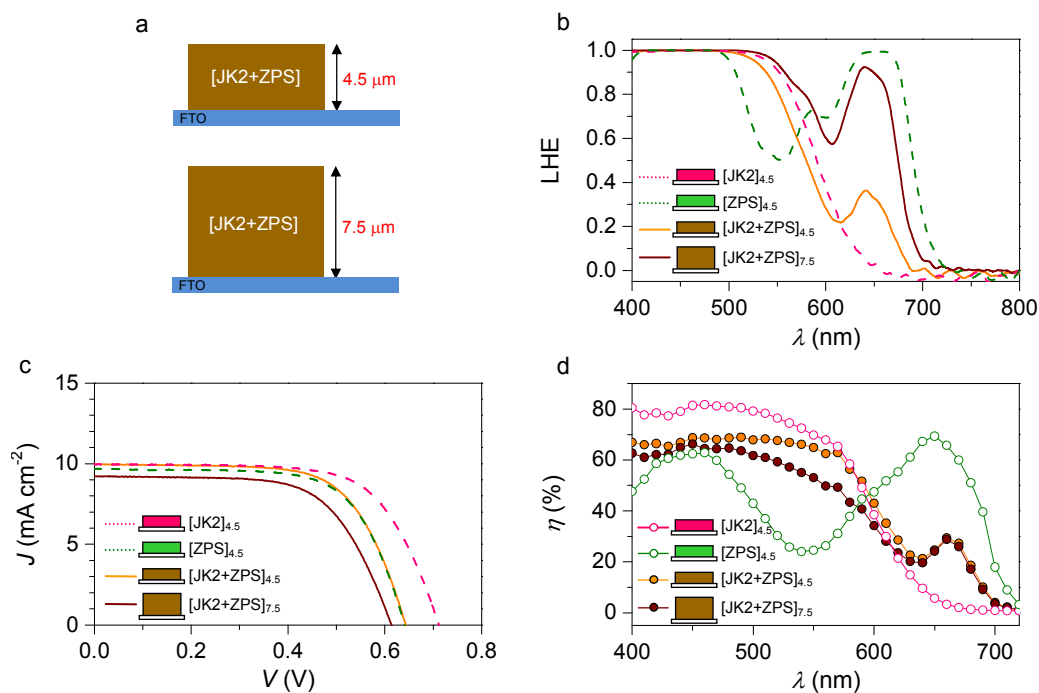


**Figure S8.** (a) Simple illustration of two-different thick TiO<sub>2</sub> film for mixed co-sensitization with JK2 and ZP. Light harvesting efficiencies (b), JV curves (c), and IPCEs (d) of the mixed co-sensitization. Pink and green (dashed and open-circle curves) are, respectively, of only JK2 and only ZP for comparison.

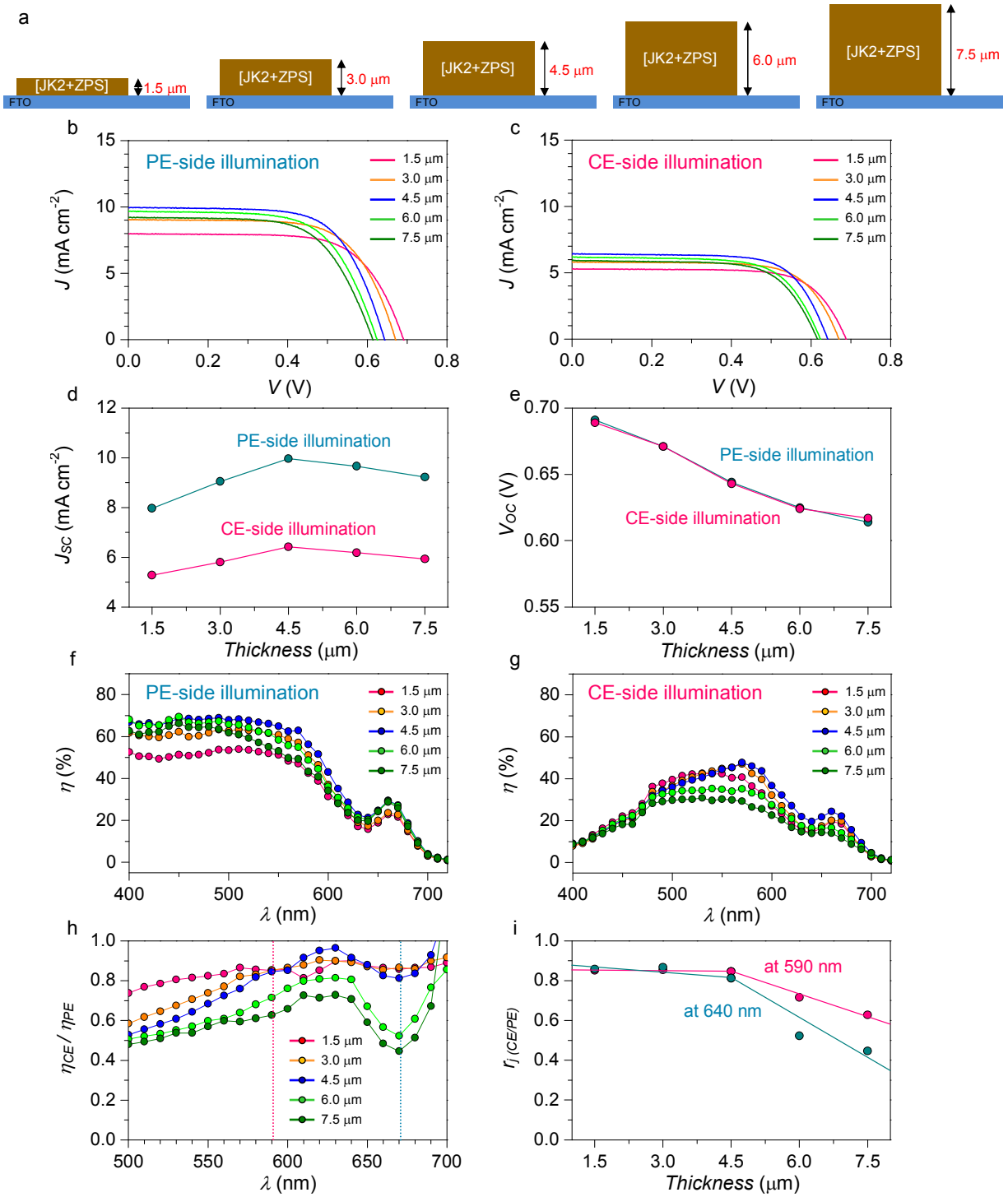


**Figure S9.** (a) Schematic illustration of thickness control for mixed co-sensitization with JK2 and ZP. JV (b, c) and IPCE (f, g) curves of the mixed co-sensitization obtained from PE-side (b, f) and CE-side illumination (c, g) with various film thicknesses as indicated.  $J_{\text{sc}}$  (d) and  $V_{\text{oc}}$  (e) changes versus film thickness. (h) The ratio between IPCEs obtained from CE-side and PE-side illumination in 500-700 nm regions and (i) plot of the ratios at 590 nm and 640 nm with respect to film thickness.

## Section S7. Mixed co-sensitization of [JK2+ZPS] on various thick TiO<sub>2</sub> film.



**Figure S10.** (a) Simple illustration of two-different thick TiO<sub>2</sub> film for mixed co-sensitization with JK2 and ZPS. Light harvesting efficiencies (b), JV curves (c), and IPCEs (d) of the mixed co-sensitization. Pink and green (dashed and open-circle curves) are, respectively, of only JK2 and only ZPS for comparison.

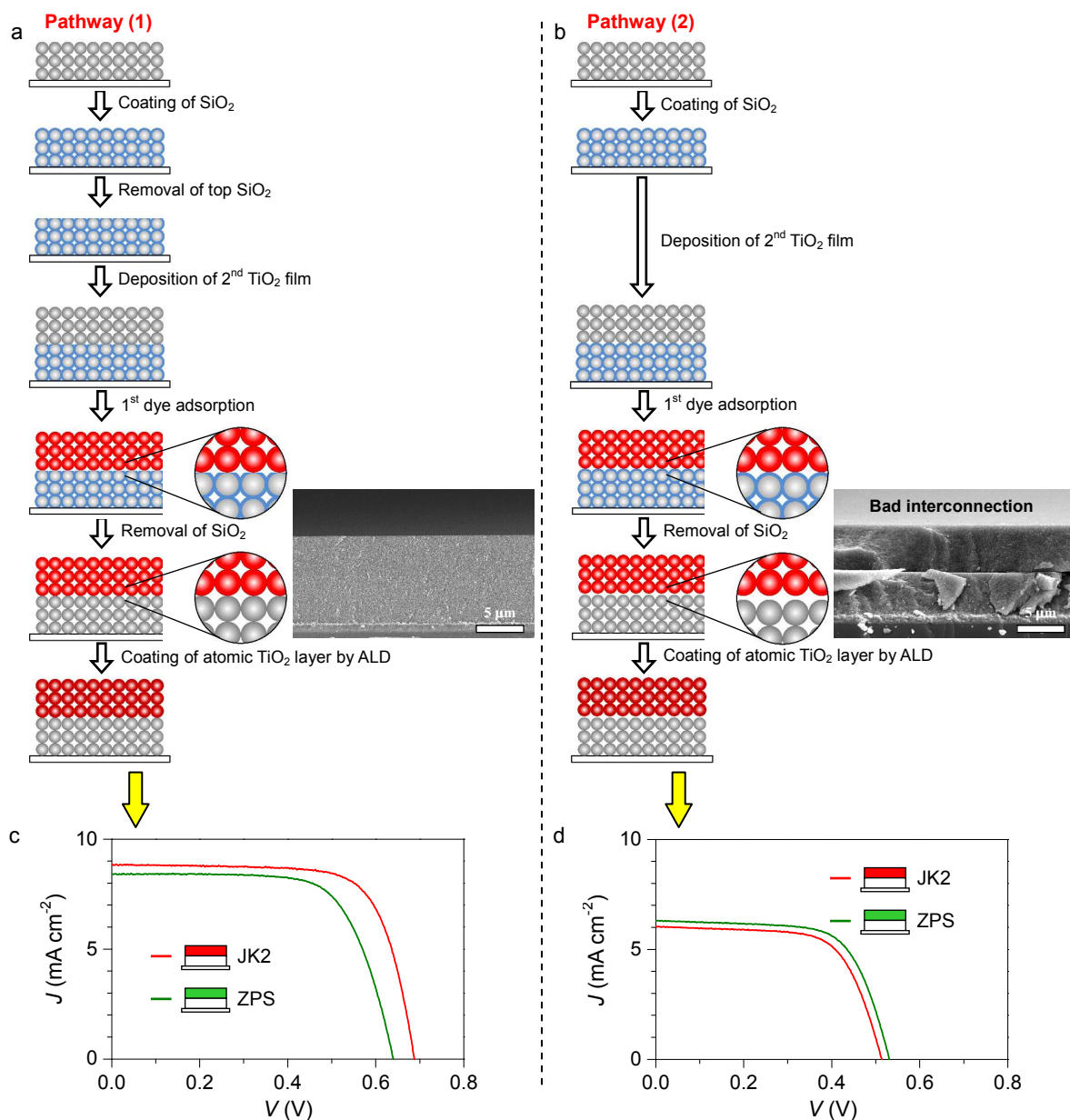


**Figure S11.** (a) Schematic illustration of thickness control for mixed co-sensitization with JK2 and ZPS. JV (b, c) and IPCE (f, g) curves of the mixed co-sensitization obtained from PE-side (b, f) and CE-side illumination (c, g) with various film thicknesses as indicated.  $J_{sc}$  (d) and  $V_{oc}$  (e) changes versus film thickness. (h) The ratio between IPCEs obtained from CE-side and PE-side illumination in 500-700 nm regions and (i) plot of the ratios at 590 nm and 640 nm with respect to film thickness.



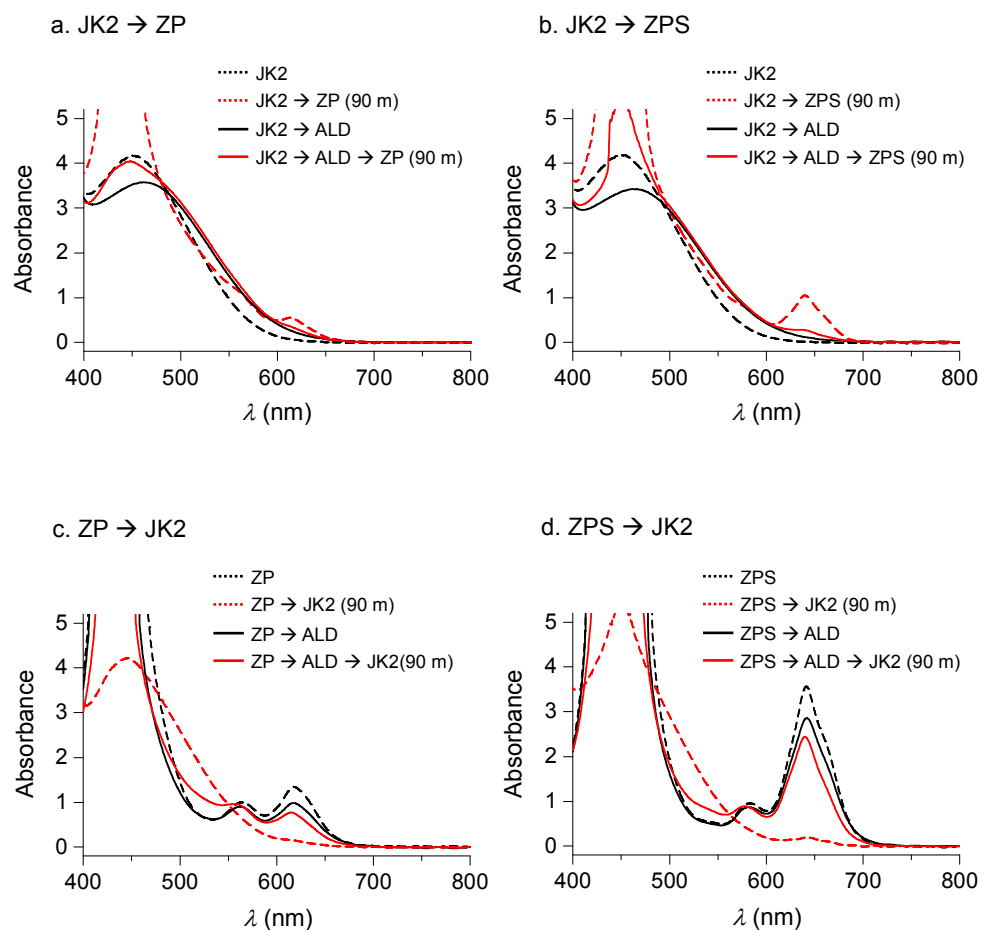
## Section S8. Interconnection between upper and lower layers.

Two schemes are presented below and reveal the importance of removing the  $\text{SiO}_2$  on top of the bottom layer of  $\text{TiO}_2$ . In case that  $\text{SiO}_2$  was not properly removed, the performance of the cells was rather low due to the poor electrical connection between the two  $\text{TiO}_2$  layers. (see Fig. S8, c and d).



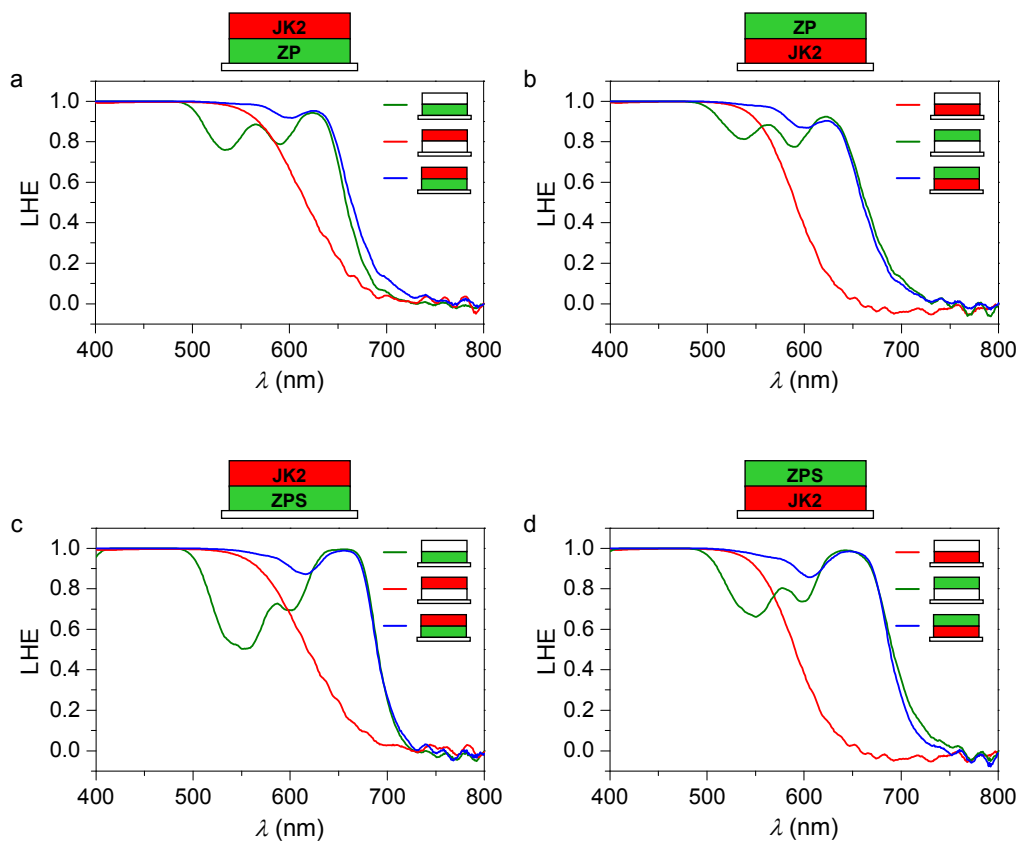
**Figure S12.** Illustration about the procedure for TCPs including the step, “removing top  $\text{SiO}_2$ ” (a) and excluding the step (b), and the corresponding I-V curves with the step (c) and without the step (d).

## Section S9. Dye displacement and stabilization.



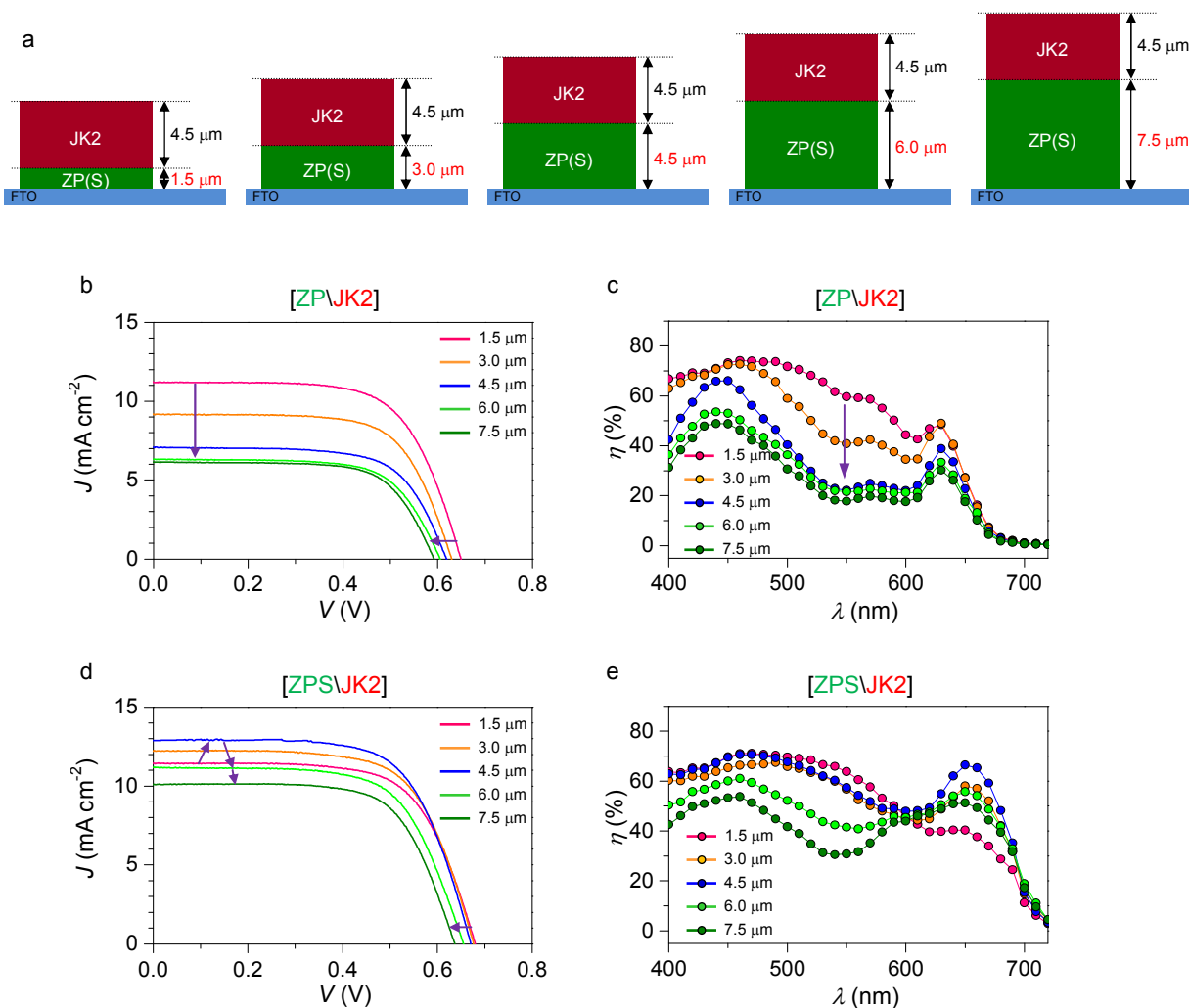
**Figure S13.** Absorption spectra for dye-displacement of JK2 by ZP (a), JK2 by ZPS (b), ZP by JK2 (c), and ZPS by JK2 (d). All of spectra are assigned as indicated.

## Section S10. LHEs of separated co-sensitizations.



**Figure S14.** Light harvesting efficiencies of the separated co-sensitization with JK2/ZP (a), ZP/JK2 (b), JK2/ZPS (c), and ZPS/JK2 (d). Red, green, and blue curves are, respectively, of JK2 only, porphyrin only, and co-sensitization as indicated.

# Section S11. Thickness-controlling experiments with [ZP\JK2] and [ZPS\JK2].



**Figure S15.** (a) Schematic illustration for photoelectrode configuration and for control of bottom layer thickness in separated co-sensitization. JV (b, d) and IPCE (c, e) curves of the photoelectrodes configured as indicated.

**Table S1. Parameters of photovoltaic performance measured at simulated (AM 1.5) one sun.**

<b>Samples</b> ([bottom\top]Thickness ( $\mu\text{m}$ ))	<b><math>J_{\text{SC}}</math> (<math>\text{mA cm}^{-2}</math>)</b>	<b><math>V_{\text{OC}}</math> (mV)</b>	<b><math>FF</math></b>	<b><math>\eta</math> (%)</b>
[ZP\JK2] <sub>1.5\4.5</sub>	11.20 (10.2)	650	0.66	4.80
[ZP\JK2] <sub>3.0\4.5</sub>	9.17 (8.4)	630	0.68	3.93
[ZP\JK2] <sub>4.5\4.5</sub>	7.08 (6.2)	619	0.67	2.94
[ZP\JK2] <sub>6.0\4.5</sub>	6.32 (5.5)	606	0.67	2.57
[ZP\JK2] <sub>7.5\4.5</sub>	6.13 (5.2)	593	0.68	2.47
[ZPS\JK2] <sub>1.5\4.5</sub>	11.44 (10.6)	681	0.67	5.22
[ZPS\JK2] <sub>3.0\4.5</sub>	12.22 (11.3)	677	0.67	5.54
[ZPS\JK2] <sub>4.5\4.5</sub>	12.89 (11.8)	671	0.67	5.79
[ZPS\JK2] <sub>6.0\4.5</sub>	11.18 (10.2)	656	0.65	4.77
[ZPS\JK2] <sub>7.5\4.5</sub>	10.09 (9.0)	637	0.68	4.37

The numbers in parenthesis are estimated values of  $J_{\text{SC}}$  obtained by integrating IPCEs.

## References

- (1) Kim, S.; Lee, J. K.; Kang, S. O.; Ko, J.; Yum, J. H.; Fantacci, S.; De Angelis, F.; Di Censo, D.; Nazeeruddin, M. K.; Gratzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 16701-16707.
- (2) Jensen, R. A.; Kelley, R. F.; Lee, S. J.; Wasielewski, M. R.; Hupp, J. T.; Tiede, D. M. *Chem. Commun.* **2008**, 1886-1888.
- (3) Teng, C.; Yang, X. C.; Yang, C.; Li, S. F.; Cheng, M.; Hagfeldt, A.; Sun, L. C. *J. Phys. Chem. C* **2010**, *114*, 9101-9110.
- (4) Lee, S. J.; Mulfort, K. L.; Zuo, X.; Goshe, A. J.; Wesson, P. J.; Nguyen, S. T.; Hupp, J. T.; Tiede, D. M. *J. Am. Chem. Soc.* **2008**, *130*, 836-838.
- (5) Lee, C. Y.; She, C. X.; Jeong, N. C.; Hupp, J. T. *Chem. Commun.* **2010**, 46, 6090-6092.
- (6) Jeong, N. C.; Farha, O. K.; Hupp, J. T. *Langmuir* **2011**, *27*, 1996-1999.
- (7) Lee, G. W.; Kim, D.; Ko, M. J.; Kim, K.; Park, N. G. *Solar Energy* **2010**, *84*, 418-425.
- (8) Ito, S.; Nazeeruddin, M. K.; Liska, P.; Comte, P.; Charvet, R.; Pechy, P.; Jirousek, M.; Kay, A.; Zakeeruddin, S. M.; Gratzel, M. *Progress in Photovoltaics* **2006**, *14*, 589-601.