

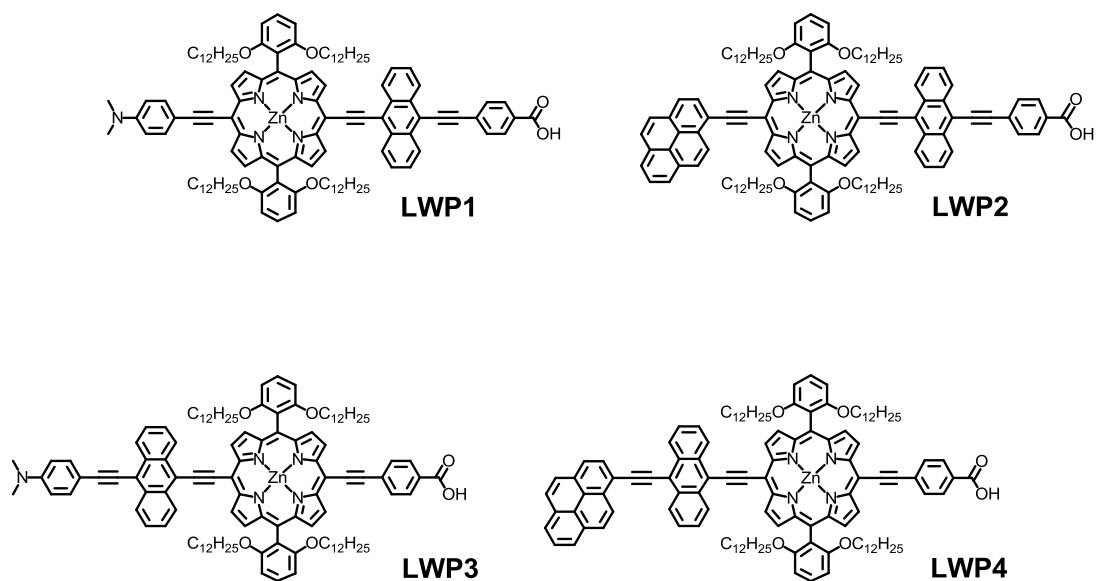
# Electronic Supplementary Information

## Porphyrins for Efficient Dye-Sensitized Solar Cells Covering Near-IR Region

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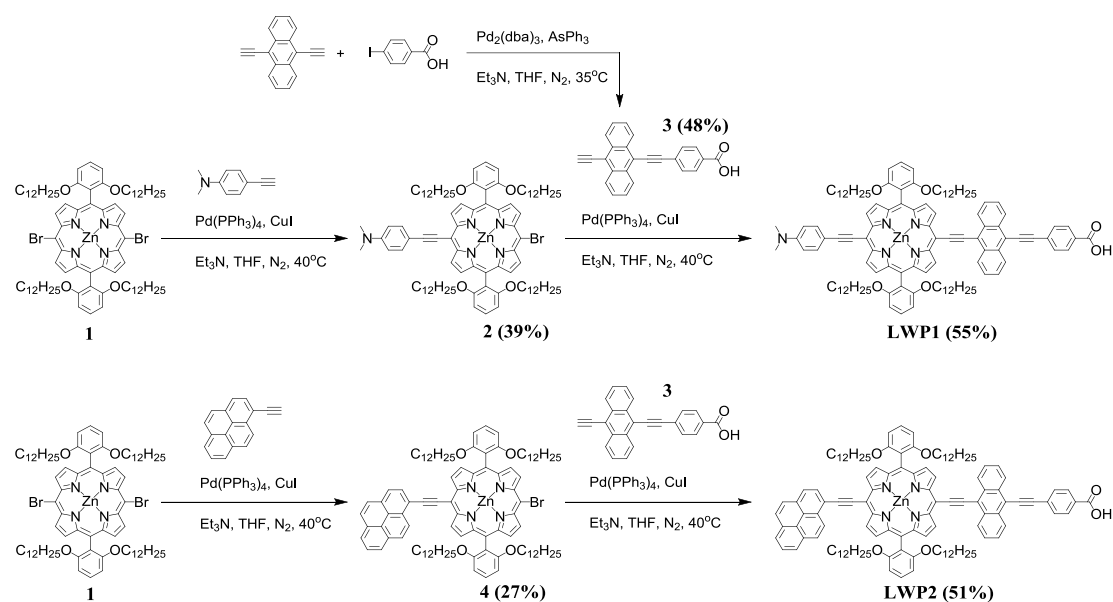
**Chart S1.** Structures of the LWP porphyrins.

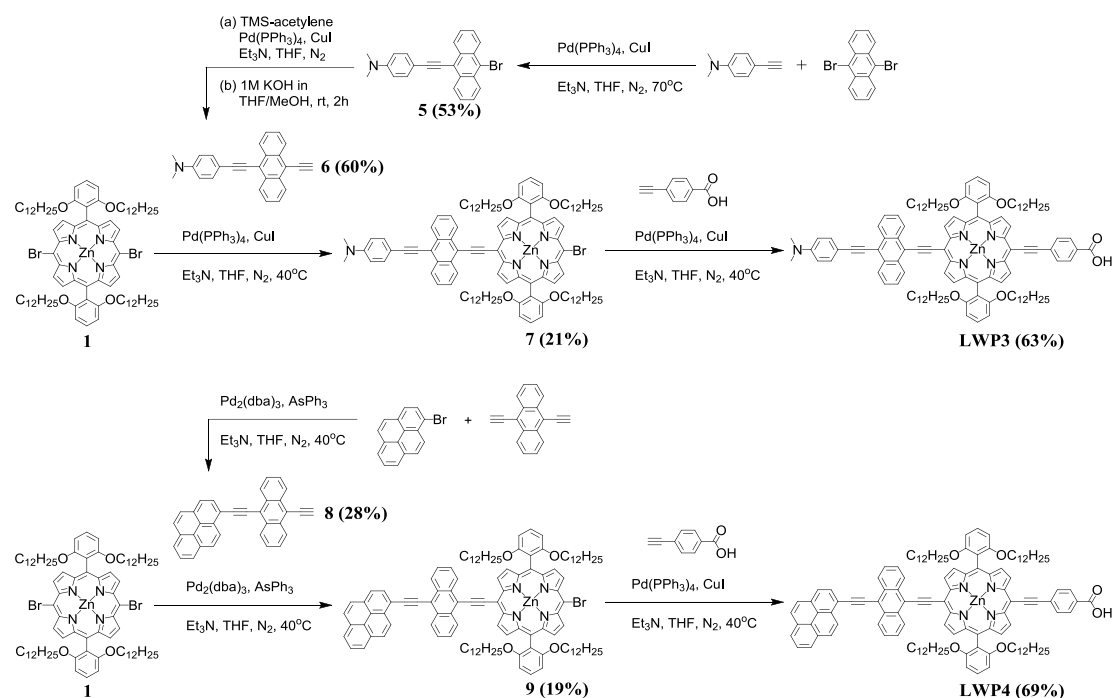
## Experimental Section

**Materials.** Air-sensitive solids were handled in a glove box (MBraun Uni-lab). A vacuum line and standard Schlenk techniques were employed to process air-sensitive solutions. Solvents for the synthesis (ACS Grade) were  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  (Mallinckrodt Baker, KE USA), hexanes (Haltermann, Hamburg Germany) and THF (Merck, Darmstadt Germany). These solvents were used as received unless otherwise stated. Other chemicals were obtained commercially (Acros Organics, NJ, USA). THF for cross-coupling reactions was purified and dried with a solvent purification system (Asiawong SD-500, Taipei, Taiwan); about 50 ppm  $\text{H}_2\text{O}$  was found in the resulting fluid. For electrochemical measurements, THF was distilled over sodium under  $\text{N}_2$ .  $\text{Pd}(\text{PPh}_3)_4$  catalyst (Strem, MA, USA) and  $\text{Pd}_2(\text{dba})_3$  (Acros Organics, NJ, USA) were used as received. For chromatographic purification, we used silica gel 60 (230-400 mesh, Merck, Germany).

**Instruments.** NMR spectra (Bruker Avance II 300 MHz NMR Spectrometer at National Chi Nan University or Varian Inova 600 NMR Spectrometer at NSC Instrumentation Center in National Chung Hsing University), elemental analyses (Elementar Vario EL III at NSC Instrumentation Center in N. C. H. Univ.), mass spectra (Microflex MALDI-TOF MS, Bruker Daltonics) were recorded with the indicated instruments.

**Compound Synthesis and Characterization.** The syntheses of the LWP porphyrins are based on the Sonogashira and Lindsey's copper-free cross-coupling methods.<sup>1,2</sup> The preparation procedures (shown below) are similar to our past publication.<sup>3-5</sup>





**Scheme S1.** The synthetic procedures of the LWP porphyrins.

**Compound 1:** The synthesis of compound 1 is based on the literature report.<sup>6</sup>

**Compound 2:** The synthesis of compound 2 has been previously reported.<sup>5</sup>

**Compound 3:** 9,10-Bis(ethynyl)anthracene (100 mg, M.W. = 226.272, 0.442 mmol, 1.0 eq.) and 4-Iodobenzoic acid (87.7 mg, M.W. = 248.02, 0.354 mmol, 0.8 eq.), and 5 ml of triethylamine were mixed in 70 ml of THF. The solutions were then degassed by 3 cycles of freeze-pump-thaw technique, followed by adding Pd<sub>2</sub>(dba)<sub>3</sub> (24.3 mg, M.W. = 915.73, 0.027 mmol) and AsPh<sub>3</sub> (65 mg, M.W. = 305.92, 0.212 mmol) under an inert atmosphere in a glovebox. The reaction was stirred at 35°C for 16 hours. The completion of the reaction was monitored by TLC. After removing the solvents under reduced pressure, chromatographic separation on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 9/1, and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexanes, 80 mg of brownish yellow solids were collected (M.W. = 346.38, yield = 48 %).

**LWP1:** Compound 2 (100mg, M.W. = 1485.27, 0.068 mmol, 1.0 eq.), compound 3 (46.6 mg, M.W. = 346.38, 0.134 mmol, 2.0 eq.), and 5 ml of triethylamine were mixed in 70 ml of THF. The solutions were then degassed by 3 cycles of freeze-pump-thaw technique, followed by adding Pd(PPh<sub>3</sub>)<sub>4</sub> (20 mg, M.W. = 1155.56, 0.016 mmol) and CuI (3.0 mg, M.W. = 190.45, 0.016 mmol) in a glovebox. The reaction was stirred at 40°C for 48 hours, monitored by TLC. After removing the solvents under reduced pressure, chromatographic separation on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 9/1, and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 66 mg of green solids were collected (M.W. = 1750.74, yield = 55 %).

**Compound 4:** Compound 1 (100mg, M.W. = 1420.98, 0.07 mmol, 1.0 eq.), pyrene-ethyne (31.9 mg, M.W. = 226.27, 0.127 mmol, 1.00eq.), <sup>4a</sup> and 5 ml of triethylamine were mixed in 70 ml of THF. The solutions were then degassed by 3 cycles of freeze-pump-thaw technique, followed by adding Pd(PPh<sub>3</sub>)<sub>4</sub> (40.7 mg, M.W. = 1155.56, 0.035 mmol) and CuI (6.6 mg, M.W. = 190.45, 0.035 mmol) in a glovebox. The reaction was stirred at 40°C for 24 hours, monitored by TLC. After removing the solvents under reduced pressure, chromatographic separation on silica gel with THF/hexanes = 1/9, and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 60 mg of green solids were collected (M.W. = 1566.34, yield = 27 %).

**LWP2:** Compound 4 (158 mg, M.W. = 1566.34, 0.101 mmol, 1.0 eq.), compound 3 (70 mg, M.W. = 346.38, 0.202 mmol, 2.0 eq.), and 5 ml of triethylamine were mixed in 70 ml of THF. The solutions were then degassed by 3 cycles of freeze-pump-thaw technique, followed by adding Pd(PPh<sub>3</sub>)<sub>4</sub> (29.2 mg, M.W. = 1155.56, 0.025 mmol) and CuI (4.8 mg, M.W. = 190.45, 0.025 mmol) in a glovebox. The reaction was stirred at 40°C for 48 hours, monitored by TLC. After removing the solvents under reduced pressure, chromatographic separation on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 9/1, and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 93.6 mg of green solids were collected (M.W. = 1750.74, yield = 51 %).

**Compound 5:** 9,10-Dibromoanthracene (300mg, M.W. = 336.02, 0.89 mmol, 1.5 eq.), 4-ethynyl-*N,N*-dimethylaniline (86mg, M.W. = 145.20, 0.59 mmol, 1.0 eq.), and 5 ml of triethylamine were mixed in 70 ml of THF. The solutions were then degassed by 3 cycles of freeze-pump-thaw technique, followed by adding Pd(PPh<sub>3</sub>)<sub>4</sub> (134 mg, M.W. = 1155.56, 0.118 mmol) and CuI (22 mg, M.W. = 190.45, 0.118 mmol) in a glovebox. The reaction was stirred at 70°C for 24 hours, monitored by TLC. After removing the solvents under reduced pressure, chromatographic separation on silica gel with THF/hexanes = 1/2, and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 125 mg of orange solids were collected (M.W. = 400.31, yield = 53 %).

**Compound 6:** Compound 5 (100 mg, M.W. = 400.31, 0.25 mmol, 1.0 eq.), trimethylsilylacetylene (1.0 ml, M.W. = 98.22, d = 0.69, 7.0 mmol, 28 eq.), and 35 ml of triethylamine were mixed in 35 ml of THF. The solutions were then degassed by 3 cycles of freeze-pump-thaw technique, followed by adding Pd(PPh<sub>3</sub>)<sub>4</sub> (57 mg, M.W. = 1155.56, 0.049 mmol) and CuI (9 mg, M.W. = 190.45, 0.047 mmol) in a glovebox. The reaction was stirred at 50°C for 40 hours, monitored by TLC. After removing the solvents under reduced pressure, and chromatographic separation on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/hexanes = 1/3, 171 mg of light brown solids were collected (M.W. = 417.62, yield = 82 %). For the de-protection process, 100mg of said solids (M.W. = 417.62, 0.24 mmol) were put in THF/MeOH = 4/1 (v/v) to react with 1ml of 1.0 M KOH<sub>(aq)</sub> for 2 hours at room temperature. The solvents were then removed under reduced

pressure, followed by chromatographic separation on silica gel with THF/hexanes = 1/5 to afford 60 mg of yellow solids (M.W. = 345.44, yield = 73 %).

**Compound 7:** Compound 1 (247 mg, M.W. = 1420.98, 0.17 mmol, 1.2 eq.), compound 6 (50 mg, M.W. = 345.44, 0.145 mmol, 1.0 eq.), and 5 ml of triethylamine were mixed in 70 ml of THF. The solutions were then degassed by 3 cycles of freeze-pump-thaw technique, followed by adding Pd<sub>2</sub>(dba)<sub>3</sub> (40 mg, M.W. = 915.73, 0.043 mmol) and AsPh<sub>3</sub> (106 mg, M.W. = 305.92, 0.347 mmol) in a glovebox. The reaction was stirred at 40°C for 24 hours, monitored by TLC. After removing the solvents under reduced pressure, chromatographic separation on silica gel with THF/hexanes = 1/5, and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 52 mg of drak green solids were collected (M.W. = 1681.88, yield = 21 %).

**LWP3:** Compound 7 (130 mg, M.W. = 1681.88, 0.077 mmol, 1.0 eq.), 4-ethynyl-benzoic acid (56 mg, M.W. = 146.14, 0.383 mmol, 5.0 eq.), and 5 ml of triethylamine were mixed in 70 ml of THF. The solutions were then degassed by 3 cycles of freeze-pump-thaw technique, followed by adding Pd(PPh<sub>3</sub>)<sub>4</sub> (18 mg, M.W. = 1155.56, 0.016 mmol) and CuI (3 mg, M.W. = 190.45, 0.016 mmol) in a glovebox. The reaction was stirred at 40°C for 40 hours, monitored by TLC. After removing the solvents under reduced pressure, chromatographic separation on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 9/1, and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 85 mg of drak green solids were collected (M.W. = 2119.37, yield = 63 %).

**Compound 8:** 1-bromopyrene (100 mg, M.W. = 281.16, 0.356 mmol, 1.0 eq.), 9,10-Bis(ethynyl)anthracene (160 mg, M.W. = 226.27, 0.71 mmol, 2.0 eq.), and 5 ml of triethylamine were mixed in 70 ml of THF. The solutions were then degassed by 3 cycles of freeze-pump-thaw technique, followed by adding Pd<sub>2</sub>(dba)<sub>3</sub> (98 mg, M.W. = 915.73, 0.106 mmol) and AsPh<sub>3</sub> (261 mg, M.W. = 305.92, 0.853 mmol) in a glovebox. The reaction was stirred at 40°C for 24 hours, monitored by TLC. After removing the solvents under reduced pressure, chromatographic separation on silica gel with THF/hexanes = 1/5, and precipitating from MeOH, 42 mg of drak green solids were collected (M.W. = 428.25, yield = 28 %).

**Compound 9:** Compound 1 (399 mg, M.W. = 1420.98, 0.28 mmol, 1.2 eq.), compound 8 (100 mg, M.W. = 426.51, 0.23 mmol, 1.0 eq.), and 5 ml of triethylamine were mixed in 70 ml of THF. The solutions were then degassed by 3 cycles of freeze-pump-thaw technique, followed by adding Pd<sub>2</sub>(dba)<sub>3</sub> (68 mg, M.W. = 915.73, 0.073 mmol) and AsPh<sub>3</sub> (173 mg, M.W. = 305.92, 0.566 mmol) in a glovebox. The reaction was stirred at 40°C for 24 hours, monitored by TLC. After removing the solvents under reduced pressure, chromatographic separation on silica gel with THF/hexanes = 1/5, and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 80 mg of drak green solids were collected (M.W. = 1762.86, yield = 19 %).

**LWP4:** Compound 9 (80 mg, M.W. = 1762.86, 0.045 mmol, 1.0 eq.), 4-ethynyl-benzoic acid (30 mg, M.W. = 146.14, 0.21mmole, 4.5 eq.), and 5 ml of triethylamine were mixed in 70 ml of THF. The solutions were then degassed by 3 cycles of freeze-pump-thaw technique, followed by adding Pd(PPh<sub>3</sub>)<sub>4</sub> (18 mg, M.W. = 1155.56, 0.016 mmol) and CuI (3 mg, M.W. = 190.45, 0.016 mmol) in a glovebox. The reaction was stirred at 40°C for 40 hours, monitored by TLC. After removing the solvents under reduced pressure, chromatographic separation on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 9/1, and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 57 mg of drak green solids were collected (M.W. = 1828.98, yield = 69 %).

#### Characterization data:

LWP1: <sup>1</sup>H NMR (CDCl<sub>3</sub> at 7.26 ppm, 300MHz, trace amount of d<sub>5</sub>-pyridine was added to increase the solubility): porphyrin, δ/ppm, 9.84 (d, *J* = 4.5 Hz, 2H), 9.59 (d, *J* = 4.5 Hz, 2H), 8.89 (d, *J* = 4.5 Hz, 2H), 8.78 (d, *J* = 4.5 Hz, 2H), 7.69 (t, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 4H), 3.86 (t, *J* = 6.5 Hz, 8H), 1.26 (s, 4H), 1.19-1.09 (m, 8H), 1.03-0.81 (m, 40H), 0.8-0.69 (t, *J* = 7.2 Hz, 16H), 0.62-0.51 (m, 16H), 0.51-0.54 (m, 8H); anthracene: δ 9.39 (d, *J* = 8.0 Hz, 2H), 8.80 (d, overlapped, 2H), 7.78 (t, *J* = 8.0 Hz, 4H); dimethylaniline group : δ 7.84 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 3.07 (s, 6H); benzoic acid: δ 8.22 (d, *J* = 6.6 Hz, 2H), 7.89 (d, *J* = 6.6 Hz, 2H). Elemental Analysis for C<sub>115</sub>H<sub>137</sub>N<sub>5</sub>O<sub>6</sub>Zn·THF·H<sub>2</sub>O: calc'd C 77.64%, H 8.05%, N 3.80%; found C 77.49%, H 7.80%, N 3.60%. MS (MH<sup>+</sup>): calc'd 1747.99, found 1748.98.

LWP2: <sup>1</sup>H NMR (CDCl<sub>3</sub> at 7.26 ppm, 300MHz, trace amt of d<sub>5</sub>-pyridine): porphyrin, δ/ppm, 9.88 (d, *J* = 4.5 Hz, 2H), 9.84 (d, *J* = 4.5 Hz, 2H), 8.94 (d, *J* = 4.5 Hz, 2H), 8.91 (d, *J* = 4.5 Hz, 2H), 7.69 (t, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 4H), 3.90 (t, *J* = 6.3 Hz, 8H), 1.07-0.76 (m, 48H), 0.73-0.63 (t, *J* = 7.1 Hz, 20H), 0.62-0.40 (m, 24H); anthracene: δ 9.39 (d, *J* = 8.7 Hz, 2H), 8.81 (d, *J* = 8.7 Hz, 2H), 7.79 (t, overlapped, 4H); pyrene: δ 9.30 (d, *J* = 9.0 Hz, 1H), 8.67 (d, *J* = 7.8 Hz, 1H), 8.36 (d, *J* = 9.0 Hz, 1H), 8.30 (m, overlapped, 2H), 8.23 (d, overlapped, 1H), 8.15 (s, 2H), 8.07 (t, d, *J* = 7.7 Hz, 1H); benzoic acid: δ 8.21 (d, overlapped, 2H), 7.87 (d, *J* = 7.2 Hz, 2H). Elemental Analysis for C<sub>123</sub>H<sub>136</sub>N<sub>4</sub>O<sub>6</sub>Zn, calc'd C 80.65%, H 7.48%, N 3.06%; found C 81.05%, H 7.64%, N 2.93%. MS (MH<sup>+</sup>): calc'd 1828.98, found 1829.98.

LWP3: <sup>1</sup>H NMR (CDCl<sub>3</sub> at 7.26 ppm, 600MHz, trace amt of d<sub>5</sub>-pyridine): porphyrin, δ/ppm, 9.88 (d, *J* = 4.4 Hz, 2H), 9.59 (d, *J* = 4.4 Hz, 2H), 8.90 (d, *J* = 4.4 Hz, 2H), 8.84 (d, *J* = 4.4 Hz, 2H), 7.71 (t, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 4H), 3.88 (t, *J* = 6.4 Hz, 8H), 1.02-0.92 (m, 26H), 0.91-0.81 (m, 20H), 0.78-0.73 (m, 14H), 0.72-0.68 (m, 8H), 0.58-0.52 (m, 16H), 0.47-0.43 (m, 8H); anthracene: δ 9.35 (d, *J* = 8.5 Hz, 2H), 8.82 (d, *J* = 8.5 Hz, 2H), 7.78 (t, *J* = 8.5 Hz, 2H), 7.71 (t, overlapped, 2H); dimethylaniline: δ 7.71 (d, overlapped, 2H), 6.74 (d, *J* = 7.6 Hz, 2H), 3.01 (s, 6H);

benzoic acid:  $\delta$  8.28 (d, br, 2H), 8.04 (d, br, 2H). Elemental Analysis for  $C_{115}H_{137}N_5O_6Zn \cdot H_2O$ , calc'd C 78.09%, H 7.92%, N 3.96%; found C 77.90%, H 7.90%, N 3.88%. MS ( $M^+$ ): calc'd 1747.99, found 1747.98.

LWP4:  $^1H$  NMR ( $CDCl_3$  at 7.26 ppm, 600MHz, trace amt of  $d_5$ -pyridine): porphyrin,  $\delta$ /ppm, 9.91 (d,  $J = 4.5$  Hz, 2H), 9.61 (d,  $J = 4.5$  Hz, 2H), 8.93 (d,  $J = 4.5$  Hz, 2H), 8.85 (d,  $J = 4.5$  Hz, 2H), 7.70 (t,  $J = 8.2$  Hz, 2H), 7.03 (d,  $J = 8.3$  Hz, 4H), 3.88 (t,  $J = 6.3$  Hz, 8H), 1.39-0.32 (m, 92H); anthracene:  $\delta$  9.43 (d, br, 2H), 9.03 (d, overlapped, 2H), 7.84 (t, br, 4H); pyrene:  $\delta$  9.03 (d, overlapped, 1H), 8.53 (d,  $J = 7.9$  Hz, 1H), 8.31 (m, overlapped, 4H), 8.07 (m, overlapped, 3H); benzoic acid:  $\delta$  8.31 (d, overlapped, 2H), 8.07 (d, overlapped, 2H). Elemental Analysis for  $C_{123}H_{136}N_4O_6Zn \cdot 2H_2O$ , calc'd C 79.09%, H 7.55%, N 3.00%; found C 78.98%, H 7.47%, N 2.93%. MS ( $M^+$ ): calc'd 1828.98, found 1828.82.



### Dye soaking conditions vs. photovoltaic characteristics:

During the synthesis, we noticed that solubility of the LWP porphyrins are lower than that of LD14. Among the LWP dyes, LWP1 and LWP3 have better solubility in organic solvents than LWP2 and LWP4. The poor solubility of LWP2 and LWP4 is likely due to their very planar chemical structures. The poorer the solubility is, the easier molecular aggregation would occur during dye soaking procedures. Since dye aggregation has been suggested to considerably affect photovoltaic performance of DSSCs,<sup>7</sup> we carried out the following experiments to explore this possibility. In these tests, we changed dye soaking conditions of the anodes then observed photovoltaic properties of the DSSCs. The results are collected in **Table S1** and **Figure S1 - S6**. Four dye soaking conditions were examined. The first three conditions (a - c) involve soaking the TiO<sub>2</sub> anodes in dye solutions with different concentrations at room temperature in one session. The fourth condition (d) involves two or three cycles of soaking at room temperature followed by washing at 50°C in order to remove loosely attached dyes from the surface of TiO<sub>2</sub>. Detailed procedure is described in the experimental section of the main text.

**Table S1.** Soaking conditions and DSSC parameters of the LWP, LD14 and N719 cells:<sup>a</sup>

	Adsorption condition	Jsc mA/cm <sup>2</sup>	Voc V	FF	η %	Dye-load nmol/cm <sup>2</sup>	2 <sup>nd</sup> EIS semicircles
LWP1	(a) 2x10 <sup>-4</sup> M, 6hrs	15.29	0.71	0.73	7.93	256	large
	(b) 1x10 <sup>-4</sup> M, 3hrs	17.43	0.73	0.63	8.02	200	large
	(c) 5x10 <sup>-5</sup> M, 9hrs	17.03	0.70	0.61	7.27	160	large
	(d) 5x10 <sup>-5</sup> M, HW2	17.82	0.73	0.75	9.76	165	small
LWP2	(a) 2x10 <sup>-4</sup> M, 6hrs	13.97	0.69	0.72	6.94	254	large
	(b) 1x10 <sup>-4</sup> M, 3hrs	13.22	0.68	0.72	6.47	176	large
	(c) 5x10 <sup>-5</sup> M, 9hrs	15.31	0.68	0.66	6.87	162	large
	(d) 5x10 <sup>-5</sup> M, HW2	14.29	0.68	0.73	7.09	161	large
LWP3	(a) 2x10 <sup>-4</sup> M, 6hrs	16.72	0.71	0.73	8.67	197	large
	(b) 1x10 <sup>-4</sup> M, 3hrs	16.36	0.69	0.69	7.79	149	large
	(c) 5x10 <sup>-5</sup> M, 9hrs	17.13	0.70	0.67	8.03	154	large
	(d) 5x10 <sup>-5</sup> M, HW2	17.83	0.72	0.75	9.63	120	small
LWP4	(a) 2x10 <sup>-4</sup> M, 6hrs	13.43	0.68	0.67	6.12	156	large
	(b) 1x10 <sup>-4</sup> M, 3hrs	14.15	0.68	0.63	6.06	139	large
	(c) 5x10 <sup>-5</sup> M, 9hrs	14.40	0.68	0.68	6.66	134	large
	(d) 5x10 <sup>-5</sup> M, HW2	14.24	0.68	0.70	6.78	114	large
LD14	(a) 2x10 <sup>-4</sup> M, 6hrs	18.90	0.72	0.74	10.07	156	small
	(b) 1x10 <sup>-4</sup> M, 3hrs	18.54	0.73	0.73	9.88	149	small
	(c) 5x10 <sup>-5</sup> M, 9hrs	18.71	0.71	0.73	9.70	156	small
N719	(c) 5x10 <sup>-4</sup> M, 12hrs	16.80	0.73	0.74	9.08	---	small

<sup>a</sup> data obtained from the I-V, IPCE, and EIS measurements shown in **Fig. S1-S6**. The colored texts in the table correspond to the colored curves and dots in **Fig. S1-S6**.

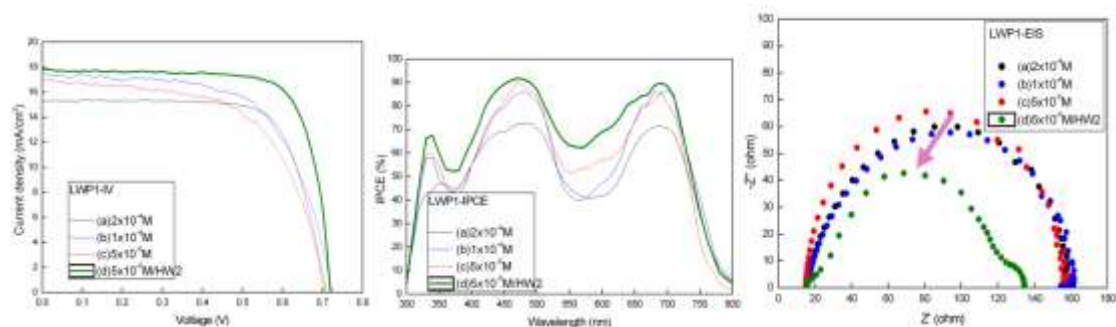


Fig. S1 I-V, IPCE, and EIS of LWP1-DSSCs prepared by different soaking conditions.

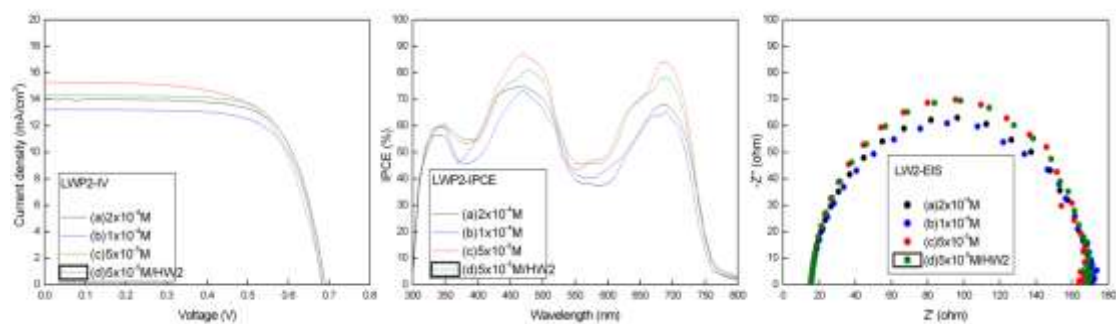


Fig. S2 I-V, IPCE, and EIS of LWP2-DSSCs prepared by different soaking conditions.

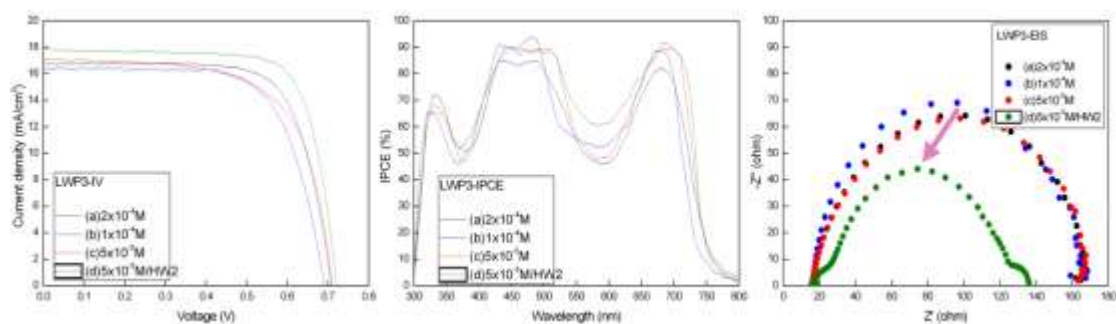


Fig. S3 I-V, IPCE, and EIS of LWP3-DSSCs prepared by different soaking conditions.

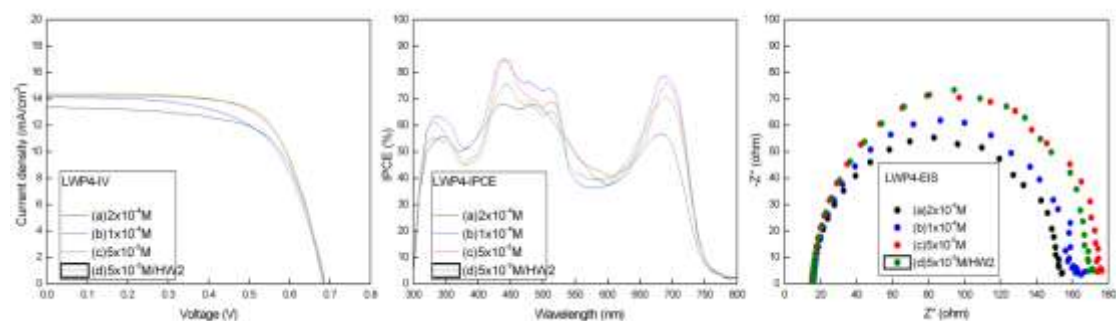
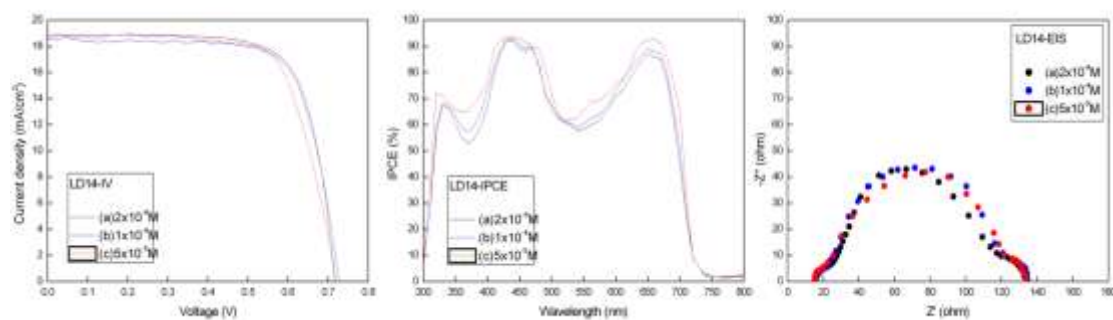
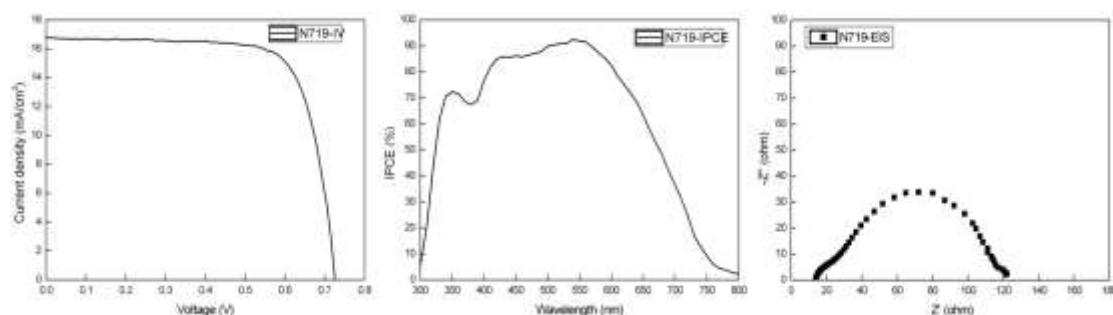


Fig. S4 I-V, IPCE, and EIS of LWP4-DSSCs prepared by different soaking conditions.



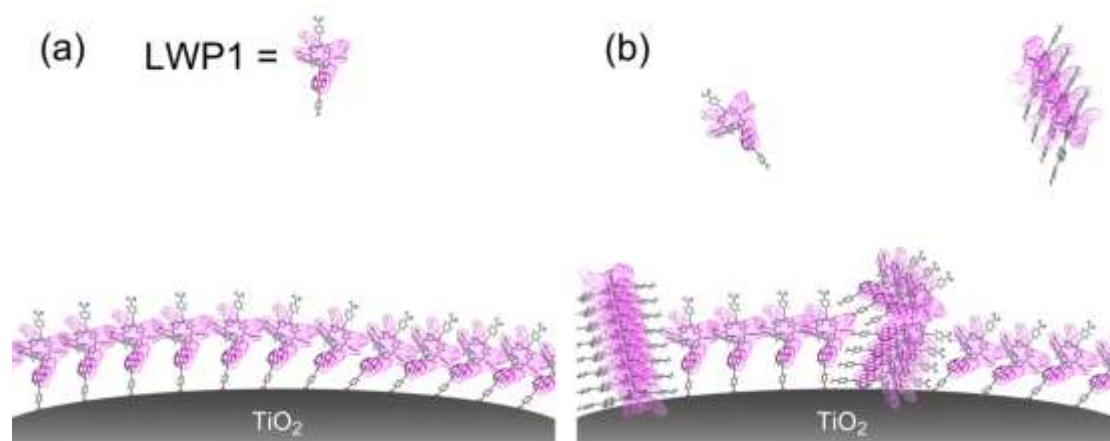
**Fig. S5** I-V, IPCE, and EIS of LD14-DSSCs prepared by different soaking conditions.



**Fig. S6** I-V, IPCE, and EIS of N719-DSSC.

As compared in the table and figures, the superior solubility of N719 and LD14 effectively lessened dye aggregation and we observed high DSSC performance and small second EIS semicircles even at higher dye concentrations. For the LWP porphyrins, we decreased the concentrations of dye solutions from  $2 \times 10^{-4} \text{ M}$  to  $5 \times 10^{-5} \text{ M}$  from conditions (a) to (c) in an attempt to lessen dye aggregation in the soaking solutions. However, the results showed that merely lowering concentration of the dye soaking solutions did not seem to improve photovoltaic performance of the DSSCs nor to largely affect the widths of second semicircles in the EIS. This suggested that a more drastic measure ought to be taken. With vigorous washes at  $50^\circ \text{C}$  multiple times to remove loosely attached dyes from  $\text{TiO}_2$  surfaces, condition (d) largely improved the photovoltaic properties of the LWP1 and LWP3 cells and notably reduced the widths of the second EIS semicircles. Unfortunately for LWP2 and LWP4, procedure (d) did not significantly improve the photovoltaic performance of the DSSCs, and the second EIS semicircles remained very large. This is likely due to the much planar chemical structures and thus the much poorer solubility in organic solutions of LWP2 and LWP4. Considering the photovoltaic parameters, the dye-loadings, and the widths of middle semicircles observed in the EIS for all four dye soaking conditions, we were then convinced that dye aggregation may very well

contribute to (i) the poor performance of the DSSCs and to (ii) the larger second semicircles in the EIS. To visualize this suggestion, we have prepared a cartoon (**Fig. S7**). In this cartoon, we show (a) ideal and (b) no ideal dye adsorption on TiO<sub>2</sub>.



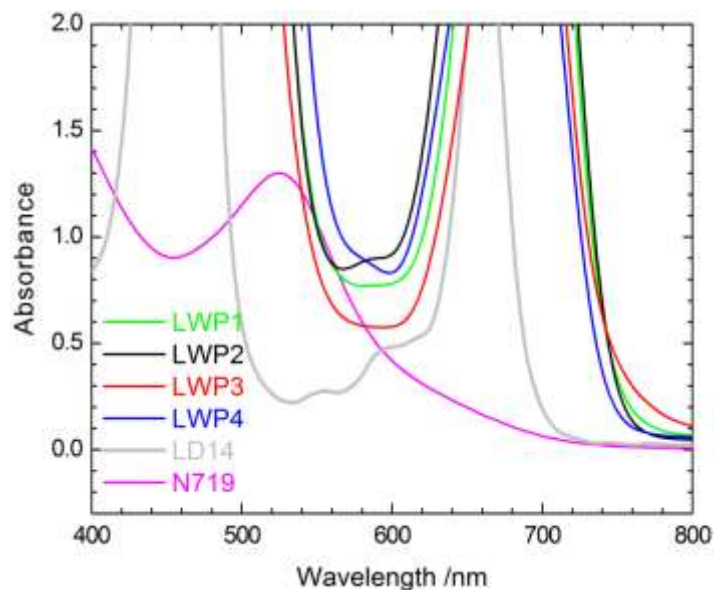
**Fig. S7** A cartoon suggesting (a) ideal and (b) not ideal dye adsorption on the surface of a TiO<sub>2</sub> nano-particle.

Therefore, we chose condition (d) for the LWP dyes to finalize the photovoltaic measurements and the raw data are put in **Table S2**. In addition, **Fig. S8** collects the typical UV-visible absorption spectra of the anodes used in this work. As shown in the figure, intensities of the absorption bands of the dyes exceed 1.0 absorbance, suggesting sufficient photon absorption of the dyes on the anodes.

**Table S2:** Photovoltaic parameters of LWP-sensitized solar cells.<sup>a</sup>

	N719			LD14			LWP1			LWP2			LWP3		LWP4			
J <sub>sc</sub> (mA/cm <sup>2</sup> )	16.80	16.73	16.69	18.85	18.82	18.79	17.82	17.77	17.71	14.29	14.12	14.11	17.83	17.8	17.66	14.24	14.22	14.15
V <sub>oc</sub> (V)	0.73	0.73	0.73	0.72	0.73	0.72	0.73	0.73	0.73	0.68	0.69	0.68	0.72	0.72	0.72	0.68	0.68	0.69
FF	0.74	0.73	0.73	0.74	0.73	0.74	0.75	0.75	0.75	0.73	0.71	0.72	0.75	0.74	0.74	0.70	0.69	0.68
Eff (%)	9.08	8.92	8.89	10.04	10.03	10.01	9.76	9.73	9.70	7.09	6.92	6.91	9.63	9.48	9.41	6.78	6.67	6.64

<sup>a</sup> under AM1.5 illumination (power 100 mW cm<sup>-2</sup>) with an active area of 0.096 cm<sup>2</sup>, three independent cells were measured to obtain these values. Dye soaking conditions are described in the main text.



**Fig. S8** Typical UV-visible absorption spectra of the anodes in this work.

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