

## Supporting information

### Pyrene-conjugated Porphyrins for Efficient Mesoscopic Solar Cells: the role of spacer

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## 1.1 Chemicals:

All solvents and reagents, unless otherwise stated, were of analytical grade quality and used as received. Standard Schlenk techniques were employed to manipulate oxygen- and moisture-sensitive chemicals. 1-ethynylpyrene was purchased from Aldrich and used as received. 15-dibromo-10,20-bis[2,6-di(dodecyloxy)phenyl]porphyrin zinc(II) (coded as **ZnPBr<sub>2</sub>**) was synthesized according to the literature.<sup>1</sup> 4-ethynylbenzoic acid, 5-ethynylthiophene-2-carboxylic acid, 4-(5-ethynylthiophen-2-yl)benzoic acid were synthesized according to the literature.<sup>2-4</sup> Tetrahydrofuran (THF) was dried with sodium sand, and benzophenone indicator, dichloromethane (DCM), ether, triethylamine (TEA) were dried out with calcium hydride before using. Reactions were carried out under a dry nitrogen atmosphere. <sup>1</sup>H NMR and <sup>13</sup>CNMR spectra were measured on a Bruker-AF301 AT 400MHz spectrometer. High resolution mass spectra (HRMS) were measured with a Bruker micro TOF mass spectrometer.

## 1.2 Synthesis of LW17-LW19

**Synthesis of 5-bromo-15-(1-pyrene)ethynyl-10,20-bis[2,6-di(dodecyloxy) phenyl]porphinato zinc(II) (Por-1).** Compound **Por-1** was prepared under modified conditions of literature procedure.<sup>1</sup> Pd(PPh<sub>3</sub>)<sub>4</sub> (11.6 mg, 0.01 mmol) and CuI (1.9 mg, 0.01 mmol) was added into a solution of **ZnPBr<sub>2</sub>** (149 mg, 0.1 mmol) and 1-ethynylpyrene (20 mg, 0.09 mmol) in fresh distilled THF (70.0 mL) and anhydrous TEA (6 mL) under N<sub>2</sub>. The reaction was stirred at 45 °C for 18 h. The progress of the reaction was monitored with TLC. The solvent was removed under vacuum. The residue was purified on silica chromatograph using THF/hexane = 1/20 as eluent. The product was re-crystallized from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to give green solid of **Por-1** (62 mg, 35%). <sup>1</sup>H NMR (CDCl<sub>3</sub>/pyridine-d<sub>5</sub>) δ 9.96 (d, J = 4.87 Hz, 1H), 9.65 (d, J = 4.87 Hz, 2H), 9.33 (d, J = 9.13 Hz, 1H), 9.02 (d, J = 5.2 Hz, 2H), 8.91 (d, J = 4.87 Hz, 2H), 8.73 (d, J = 1.3 Hz, 2H), 8.05 (t, J = 20.6 Hz, 2H), 7.75 (t, J = 8.85 Hz, 2H), 7.04 (t, J = 9.0 Hz, 4H), 3.84 (t, J = 13.2 Hz, 8H), 1.21-1.04(m, 26H), 0.98-0.88(m, 22H), 0.81(t, J=7.3Hz, 12H), 0.78-0.71(br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40(br, 8H). MS (APCI) m/z: calcd for 1566.33; found 1566.1.

**Synthesis of compound LW17 porphyrins.** **LW17** was prepared under modified conditions of literature procedure.<sup>1</sup> Pd(PPh<sub>3</sub>)<sub>4</sub> (11.6 mg, 0.01 mmol) and CuI (1.9 mg, 0.01 mmol) was added into a solution of **Por-1** (157 mg, 0.1 mmol) and 4-ethynylbenzoic acid (45 mg, 0.3 mmol) in fresh distilled THF (70.0 mL) and anhydrous TEA (6 mL) under N<sub>2</sub>. The reaction was stirred at 50 °C for 12 h. The progress of the reaction was monitored with TLC. The solvent was removed under vacuum. The residue was purified on silica chromatograph using DCM/MeOH= 20/1 as eluent. The product was re-crystallized from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to give green solid of **LW17** (127 mg, 78%). <sup>1</sup>H NMR (CDCl<sub>3</sub>/pyridine-d<sub>5</sub>) δ 9.84 (d, J = 3.89 Hz, 2H), 9.61 (d, J = 4.87 Hz, 2H), 9.31 (d, J = 9.13 Hz, 1H),

9.02 (d, J = 5.2 Hz, 2H), 8.91 (d, J = 4.38 Hz, 2H), 8.86 (d, J = 1.3 Hz, 2H), 8.67 (d, J = 8.7 Hz, 2H), 8.35 (t, J = 8.6 Hz, 1H), 8.30 (m, 4H), 8.25 (t, J = 7.3 Hz, 1H), 7.70 (t, J = 9.2 Hz, 2H), 7.04 (d, J = 8.7 Hz, 4H), 3.88 (t, J = 13.2 Hz, 8H), 1.21-1.04(m, 26H), 0.98-0.88(m, 22H), 0.81(t, J = 7.3 Hz, 12H), 0.78-0.71(br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40(br, 8H).  $^{13}\text{HNMR}$  ( $\text{CDCl}_3/\text{pyridine-d}_5$ ) 160.0, 151.6, 151.5, 150.6, 149.7, 135.8, 132.0, 131.7, 131.4, 131.3, 130.9, 130.4, 130.2, 130.0, 129.7, 129.6, 128.4, 127.9, 127.4, 126.2, 125.5, 125.4, 124.9, 124.6, 123.4, 121.3, 119.7, 115.3, 105.1, 100.2, 98.8, 97.0, 94.8, 68.6, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 28.7, 25.3, 22.6, 14.1. MS (APCI) m/z: calcd for 1628.9125; found 1628.9161. Elemental analysis calcd (%) for  $\text{C}_{107}\text{H}_{128}\text{N}_4\text{O}_6\text{Zn}$ : C 78.77, H 7.91, N 3.43; found C 78.57, H 7.96, N 3.45.

**Synthesis of LW18 porphyrins.** The product was re-crystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  to give green solid of **LW18** (83%).  $^1\text{H NMR}$  ( $\text{CDCl}_3/\text{pyridine-d}_5$ )  $\delta$  9.84 (d, J = 3.89 Hz, 2H), 9.51 (d, J = 4.87 Hz, 2H), 9.30 (d, J = 8.13 Hz, 1H), 8.91 (d, J = 5.2 Hz, 2H), 8.84 (d, J = 4.38 Hz, 2H), 8.67 (d, J = 7.5 Hz, 1H), 8.35 (t, J = 8.6 Hz, 1H), 8.30 (t, J = 7.3 Hz, 2H), 8.24 (d, J = 7.5 Hz, 1H), 8.14 (s, 2H), 8.07 (d, J = 14.0 Hz, 1H), 7.71 (t, J = 9.2 Hz, 2H), 7.65 (s, 1H), 7.57 (s, 1H), 7.04 (d, J = 8.7 Hz, 4H), 3.89 (t, J = 13.2 Hz, 8H), 1.21-1.04(m, 26H), 0.98-0.88(m, 22H), 0.81(t, J = 7.3 Hz, 12H), 0.78-0.71(br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40(br, 8H).  $^{13}\text{HNMR}$  ( $\text{CDCl}_3/\text{pyridine-d}_5$ ) 160.0, 151.5, 151.4, 150.6, 150.7, 149.7, 135.7, 132.1, 131.9, 131.7, 131.5, 131.3, 131.0, 130.4, 130.1, 129.7, 129.6, 128.4, 127.9, 127.4, 126.2, 125.5, 125.4, 125.0, 124.8, 124.6, 123.5, 121.3, 119.6, 115.4, 105.1, 100.2, 68.6, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 28.7, 25.3, 22.6, 14.1. MS (APCI) m/z: calcd for 1634.8690; found 1634.8670. elemental analysis calcd (%) for  $\text{C}_{105}\text{H}_{126}\text{N}_4\text{O}_6\text{SZn}$ : C 77.01, H 7.76, N 3.42; found C 76.97, H 7.77, N 3.42.

**Synthesis of LW19 porphyrins.** The product was re-crystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  to give brown-green solid of **LW19** (85%).  $\delta$  9.83 (d, J = 3.89 Hz, 2H), 9.54 (d, J = 4.87 Hz, 2H), 9.31 (d, J = 9.13 Hz, 1H), 8.91 (d, J = 4.38 Hz, 2H), 8.83 (d, J = 1.3 Hz, 2H), 8.66 (d, J = 8.7 Hz, 2H), 8.35 (d, J = 7.7 Hz, 1H), 8.30 (t, J = 15.0 Hz, 2H), 8.24 (d, J = 7.3 Hz, 1H), 8.20 (d, J = 7.3 Hz, 2H), 8.05 (t, J = 7.3 Hz, 2H), 7.80 (t, J = 9.2 Hz, 2H), 7.72 (t, J = 9.2 Hz, 2H), 7.6 (s, 1H), 7.5 (s, 1H), 7.04 (d, J = 8.7 Hz, 4H), 3.89 (t, J = 13.2 Hz, 8H), 1.21-1.04(m, 26H), 0.98-0.88(m, 22H), 0.81(t, J = 7.3 Hz, 12H), 0.78-0.71(br, 8H), 0.61-0.53 (br, 16H), 0.47-0.40(br, 8H).  $^{13}\text{HNMR}$  ( $\text{CDCl}_3/\text{pyridine-d}_5$ ) 160.0, 149.8, 135.7, 132.1, 131.7, 131.6, 131.5, 131.3, 131.0, 130.4, 130.1, 129.7, 129.6, 128.4, 127.9, 127.4, 126.2, 125.5, 125.4, 125.0, 124.8, 124.6, 123.5, 121.3, 119.6, 115.4, 105.1, 100.2, 68.6, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 28.7, 25.3, 22.6, 14.1. MS (APCI) m/z: calcd for 1710.9003; found 1710.8832. elemental analysis calcd (%) for  $\text{C}_{111}\text{H}_{130}\text{N}_4\text{O}_6\text{SZn}$ : C 77.80, H 7.65, N 3.27; found C 77.67, H 7.66, N, 3.26.

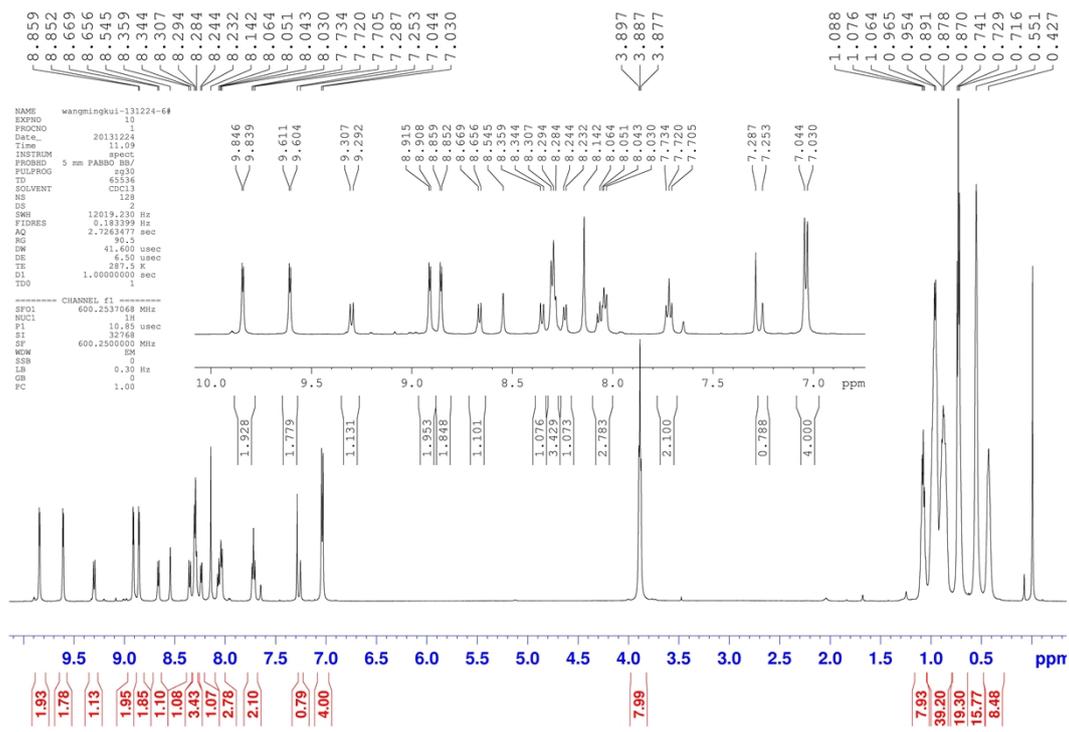


Fig. S1. <sup>1</sup>H NMR spectrum of LW17 porphyrin (400 MHz, CDCl<sub>3</sub>/pyridine-d<sub>5</sub>, 298 K).

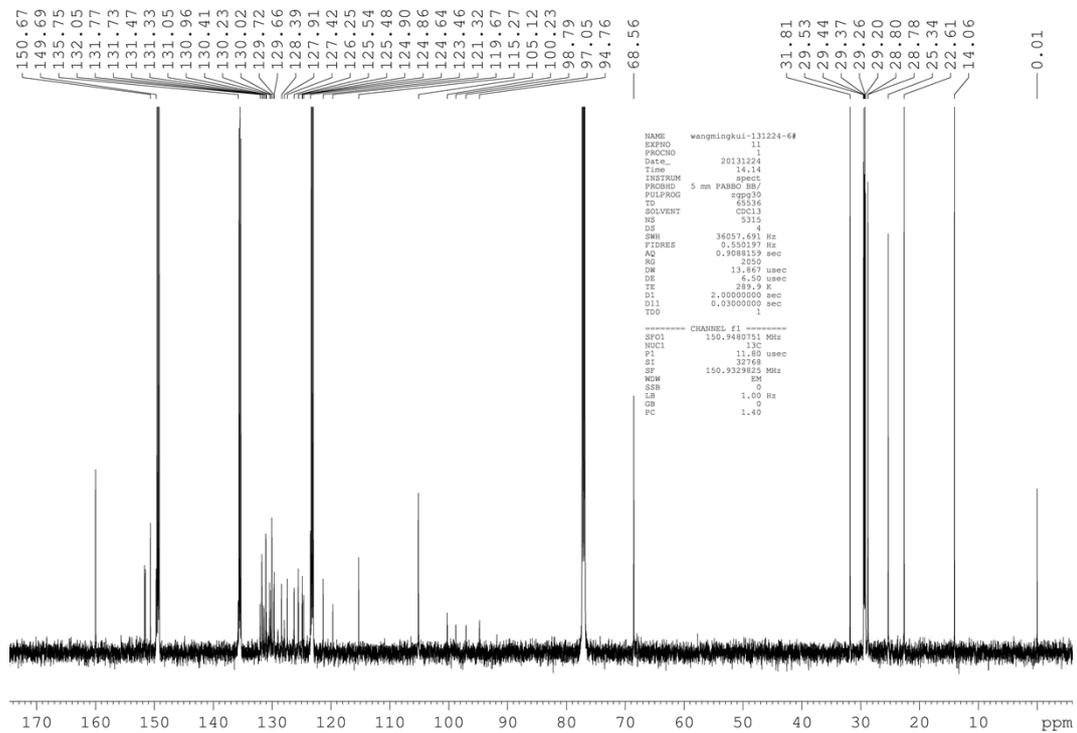


Fig. S2. <sup>13</sup>C NMR spectrum of LW17 porphyrin (400 MHz, CDCl<sub>3</sub>/pyridine-d<sub>5</sub>, 298 K).

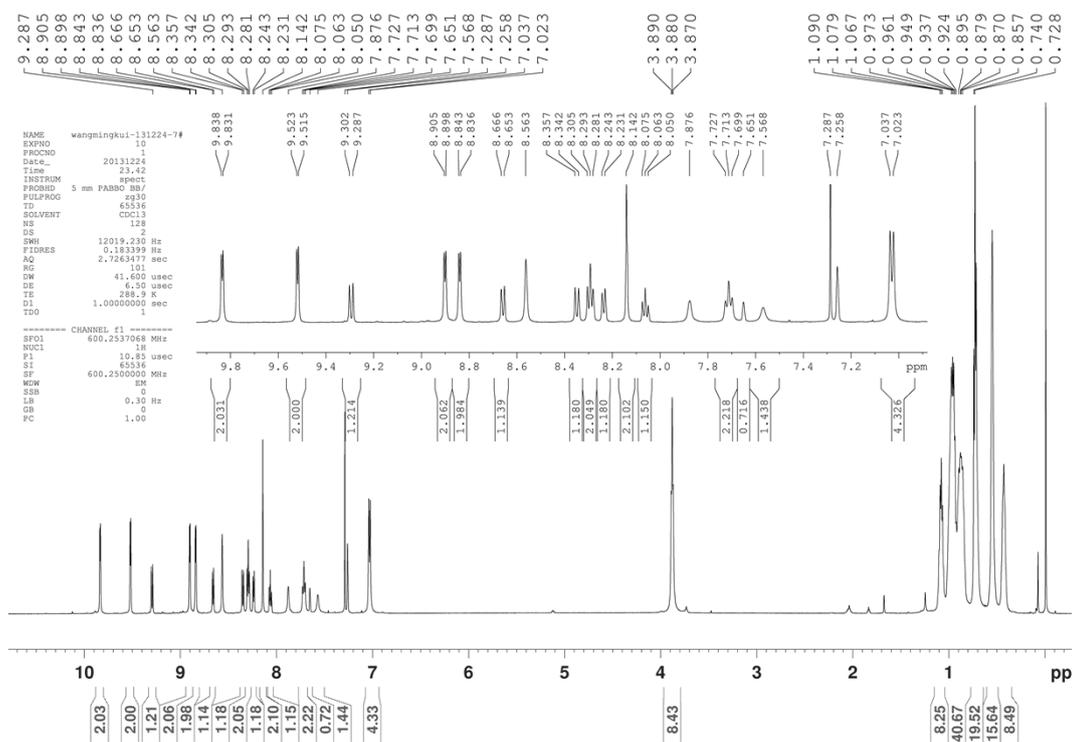


Fig. S3.  $^1\text{H}$  NMR spectrum of LW18 porphyrin (400 MHz,  $\text{CDCl}_3/\text{pyridine-d}_5$ , 298 K).

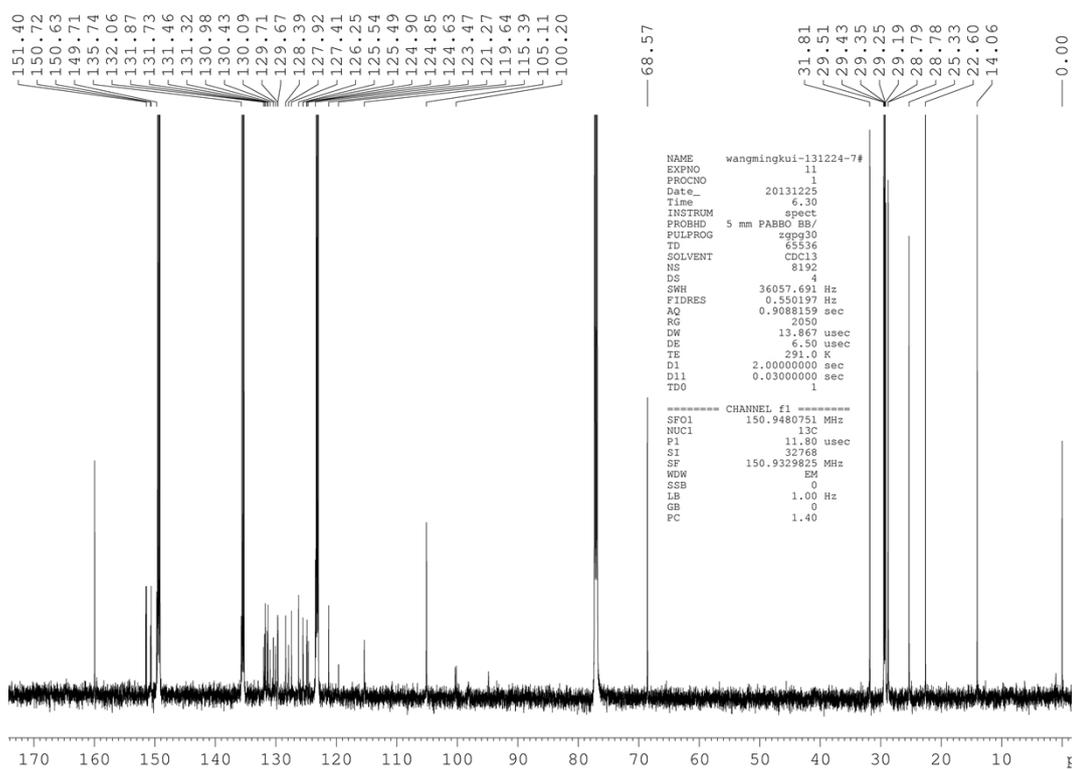


Fig. S4.  $^{13}\text{C}$  NMR spectrum of LW18 porphyrin (400 MHz,  $\text{CDCl}_3/\text{pyridine-d}_5$ , 298 K).

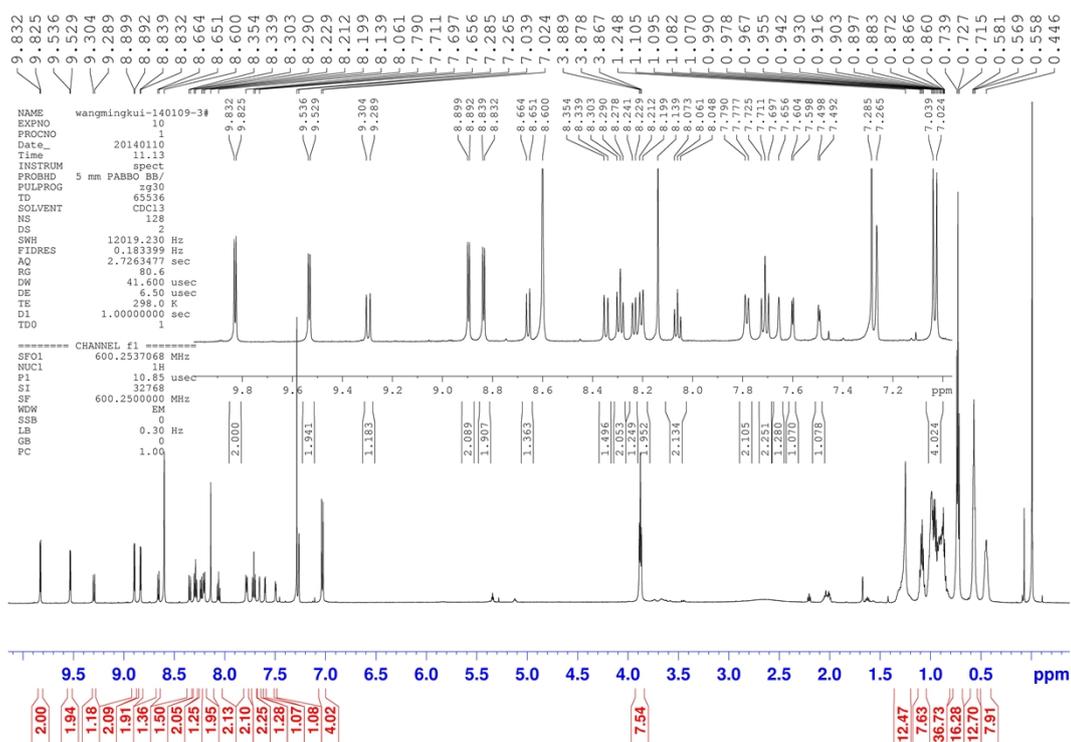


Fig. S5.  $^{13}\text{C}$  NMR spectrum of LW19 porphyrin (400 MHz,  $\text{CDCl}_3/\text{pyridine-d}_5$ , 298 K).

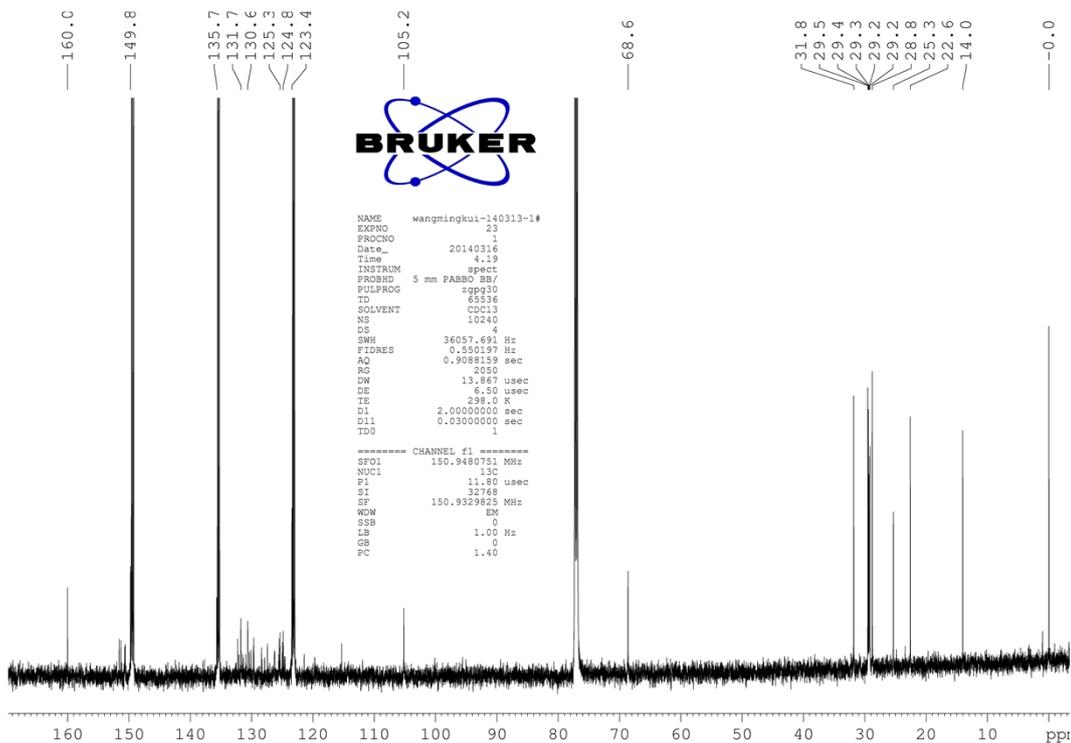
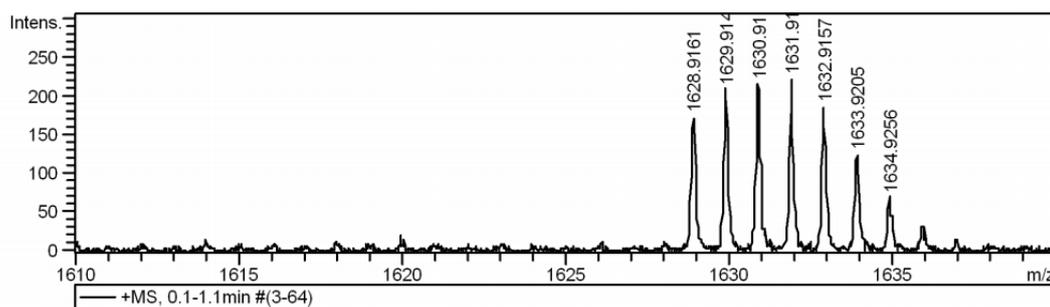


Fig. S6.  $^{13}\text{C}$  NMR spectrum of LW19 porphyrin (400 MHz,  $\text{CDCl}_3/\text{pyridine-d}_5$ , 298 K).



#	m/z	Res.	S/N	I	FWHM
1	1628.9161	11133	29.5	172	0.1463
2	1629.9143	11358	36.2	208	0.1435
3	1630.9138	10031	37.6	215	0.1626
4	1631.9197	14869	38.4	220	0.1098
5	1632.9157	10800	32.2	184	0.1512
6	1633.9205	12098	21.3	122	0.1351
7	1634.9256	11823	12.0	68	0.1383

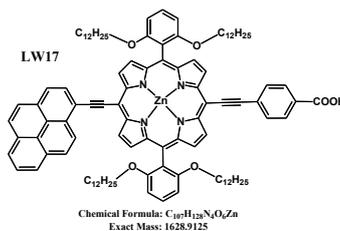
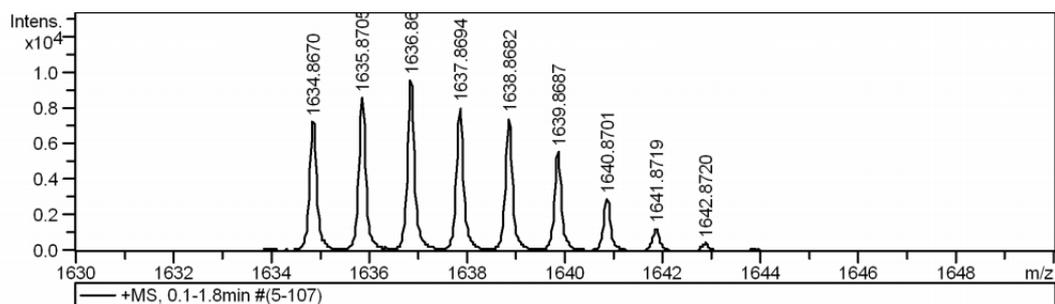


Fig. S7. HRMS of LW17 porphyrin.



#	m/z	Res.	S/N	I	FWHM
1	701.3809	7851	161.7	7661	0.0893
2	745.4037	7585	146.5	8009	0.0983
3	1634.8670	10657	409.1	7216	0.1534
4	1635.8705	10825	485.6	8573	0.1511
5	1636.8686	10835	542.4	9591	0.1511
6	1637.8694	11006	455.1	8046	0.1488
7	1638.8682	10936	420.1	7431	0.1499
8	1639.8687	11346	311.5	5516	0.1445
9	1640.8701	11139	165.2	2926	0.1473
10	1641.8719	10538	71.7	1271	0.1558
11	1642.8720	9905	25.9	460	0.1659
12	1747.9750	10846	379.9	6665	0.1612
13	1974.1981	10348	52.4	460	0.1908

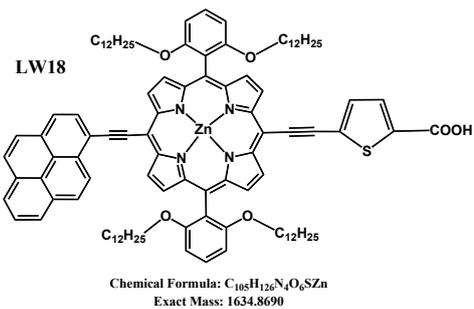


Fig. S8. HRMS of LW18 porphyrin.



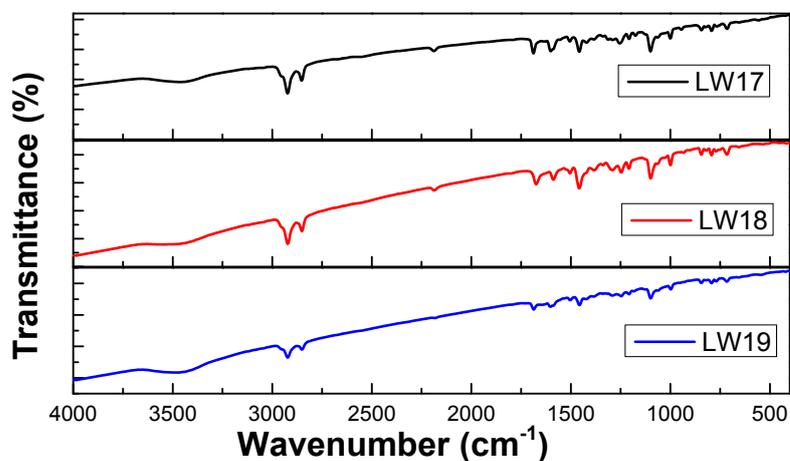
A 450 W xenon light source solar simulator (Oriel, model 9119) with AM 1.5G filter (Oriel, model 91192) was used to give various irradiance at the surface of the solar cell. The current-voltage characteristics of the cell under these conditions were obtained by applying external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). Incident photon-to-electron conversion efficiency (IPCE) spectra were recorded with a Keithley 2400 source meter as a function of wavelength under a constant white light bias of approximately  $1 \text{ mW cm}^{-2}$  supplied by a white LED array (IQE-LIGHT-BIAS, Newport). The excitation beam comes from a 300 W xenon lamp (Oriel Co.) in combination with a Corstner 260 monochromator (Newport) and is chopped at approximately 10 Hz. The devices with the photoanode area of  $0.16 \text{ cm}^2$  were tested with a metal mask of  $0.09 \text{ cm}^2$ . The photovoltaic parameters were obtained by measuring a number of independently samples individuals.

#### **4. Transient photovoltage decay (TPD) measurements**

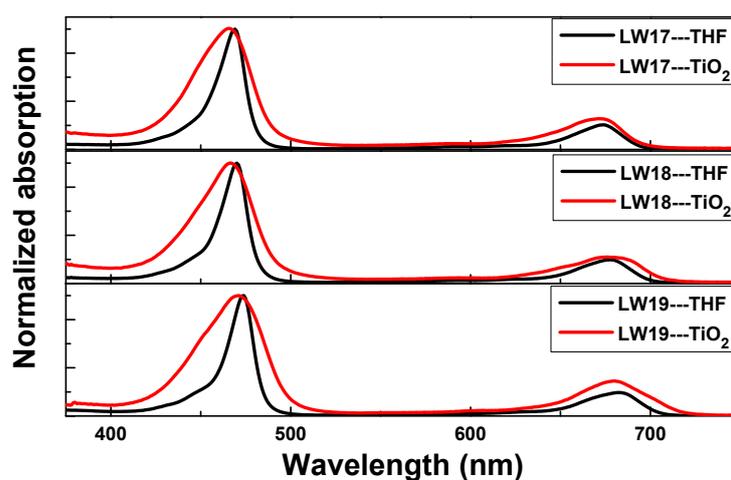
The determination of the interfacial charge recombination lifetime was performed by the TPD measurement and charge extraction experiments. For the transient decay measurements, a white-light bias was generated from an array of diodes. Blue light pulse diodes (0.05 s square pulse-width, 100 ns rise and fall time) that were controlled by a fast solid-state switch were used as the perturbation source. The voltage dynamics were recorded on a PC-interfaced Keithley 2602A source meter with a 500 ms response time. The perturbation light source was set to a suitably low level for the voltage-decay kinetics to be mono-exponential. By varying the intensity of white-light bias, the recombination lifetime could be estimated over a range of open-circuit voltages. The chemical capacitance of the  $\text{TiO}_2$ /electrolyte interface at  $V_{oc}$  was calculated according to  $C_{\mu} = \Delta Q / \Delta V$ , where  $\Delta V$  is the peak of the photovoltage transient and  $\Delta Q$  is the number of electrons injected during the red-light flash. The latter parameter was obtained by integrating a short circuit transient photocurrent that was generated from an identical red-light pulse. Before the LEDs switched to the next light intensity, a charge-extraction routine was executed to measure the electron density in the film. In the charge-extraction techniques, the LED illumination source was turned off within  $<1 \mu\text{s}$ , whilst, simultaneously, the cell was switched from open circuit to short circuit. The resulting current, as the cell returned to  $V=0$  and  $J=0$ , was integrated to give a direct measurement of the excess charge in the film at that  $V_{oc}$  value.

## 5. Spectrum and electrochemical characterization of LW17-LW19

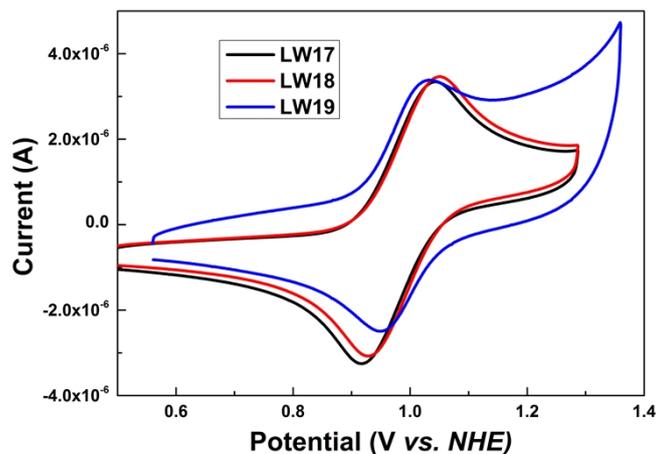
The UV-visible absorption spectra were observed with a PE950 spectrophotometer and Fluorescent emission spectra were obtained with a Jasco FP-6500 spectrophotometer. The TRPL decays were recorded with Edinburgh instruments (FLSP920 spectrometers). The excitation light source was a picosecond pulsed light-emitting diodes centered at 445 nm, operated at a frequency of 10 MHz. The TiO<sub>2</sub> nanoparticles were screen-printed on quartz substrates. The substrates coated with nanoparticles were immersed 200  $\mu$ M dye solution, followed by rinsing and drying to remove the excess dye. FT-IR spectra were recorded on a Bruker VERTEX 70. Square-wave voltammograms of various dyes were measured on a CHI660C electrochemical workstation. Glassy carbon electrode was used as the working electrode a platinum wire as the counter electrode, and Ag/AgCl (2 M LiCl in EtOH) as the reference electrode.



**Figure S10.** FT-IR spectra of LW17, LW18, and LW19.

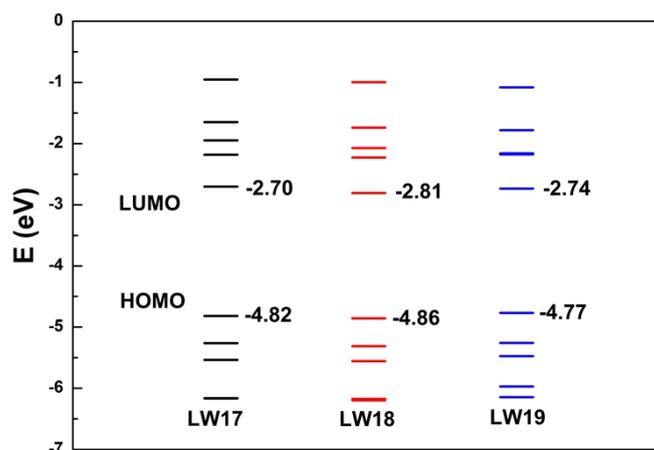


**Figure S11.** Normalized UV-visible spectra of LW17, LW18, and LW19 in THF (black curve) and on TiO<sub>2</sub> films (transparent layers 2.3  $\mu$ m thick of 20 nm TiO<sub>2</sub> particles) in air (red curve).



**Figure S12.** Cyclic voltammograms of Zn(II)-porphyrin dyes in THF at a scan rate of 50 mV/s at room temperature with 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte.

## 6. The calculated energy-level diagram



**Figure S13.** Energy-level diagram of the LW17-LW19 porphyrins by density-functional theory (DFT).

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