

Supporting information

Novel porphyrins-preparation, characterization, and application in solar energy conversion system

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Experimental:

Chemicals: All solvents and reagents, unless other stated, were of analytical grade quality and used as received. Standard Schlenk technique was utilized to manipulate oxygen- and moisture-sensitive chemicals. Tetrahydrofuran (THF) was dried with sodium sand with benzophenones indicator; dichloromethane (DCM), ether, triethylamine (TEA) were dried out with calcium hydride before using. The starting compound methyl 4-bromobenzoate and 4,7-dibromobenzo[c][1,2,5]thiadiazole were purchased from Aldrich, methyl 4-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)benzoate (compound **2**) was synthesized according to the literature,¹ 5-bromo-15-(4-N,N-dimethylamino-phenyl)ethynyl-10,20-bis[2,6-di(dodecyloxy)phenyl]porphyrin zinc(II) (coded as **Por-1**) were synthesized as we previously reported.² All reactions were carried out under a dry nitrogen atmosphere. For comparison purpose, the LD14 sensitizer was also synthesized according to the literature.³ ¹H NMR and ¹³C NMR spectra were recorded on a spectrometer operating at 400 MHz. Deuterated trichloromethane (CDCl₃), deuterated pyridine and dimethyl sulfoxide (DMSO-d₆) served as solvents.

Synthesis of LW24 porphyrin

The LW24 porphyrin was achieved with a convergent synthesis route (Scheme 2), which has been designed according to the Sonogashira coupling reactions.

Synthesis of methyl 4-(7-((trimethylsilyl)ethynyl)benzo[c][1,2,5]thiadiazol-4-yl)benzoate (**3**): Compound **3** was prepared with a modified condition according to the literature procedure.⁴ A two neck round bottom flask equipped with a reflux condenser was charged with CuI (7.6 mg, 0.04 mmol), Pd(OAc)₂ (9 mg, 0.04 mmol) and freshly recrystallized PPh₃ (29 mg, 0.11 mmol), methyl 4-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)benzoate (261 mg, 0.75 mmol), freshly distilled TEA (10 mL) and THF (10 mL), the mixture solution was stirred at 0 °C for 30 min. Then, trimethylsilylacetylene (0.32 mL, 2.25 mmol) was dropped in and stirred for another 30 min in an ice bath before being warmed to room temperature. After reacting for 30 min at room temperature, the mixture was kept at 45 °C for 18 h. The solution was then allowed to cool down at room temperature and the solvent mixture was evaporated in vacuum. The residue was purified by column chromatography on silica gel with a solvent combination of DCM/hexane (1:1) as eluent to provide compound **3** as yellow solid (191 mg, 70%). ¹H NMR (CDCl₃) 8.23 (d,

$J = 8.7$ Hz, 2H), 8.00 (m, 3H), 7.67 (d, $J = 8.2$ Hz, 1H), 3.99 (s, 3H), 0.30 (s, 9H). MS (MALDI-TOF) m/z : calcd for 366.086 u; found 366.199 u.

Synthesis of methyl 4-(7-ethynylbenzo[c][1,2,5]thiadiazol-4-yl) benzoate (**4**): Compound **4** was prepared with a modified condition as we previously reported.⁵ A two neck round bottom flask was charged with compound **3** (366 g, 1 mmol), K_2CO_3 (234 mg, 3 mmol) and MeOH (6 mL) under nitrogen. The reaction was stirred at room temperature for 6 h, then the solvent was removed under vacuum. The solid was re-dissolved in DCM and washed with aqueous $NaHCO_3$ three times. The organic layer was dried over with Na_2SO_4 and evaporated under vacuum, affording product **4** (286 mg, 98%). 1H NMR ($CDCl_3$) 8.22 (d, $J = 8.7$ Hz, 2H), 8.01 (d, $J = 8.7$ Hz, 2H), 7.99 (d, $J = 8.2$ Hz, 1H), 7.65 (d, $J = 8.2$ Hz, 1H), 3.81 (s, 1H). MS (MALDI-TOF) m/z : calcd for 294.046 u; found 293.979 u.

Synthesis of 5-methyl 4-(7-ethynylbenzo[c][1,2,5]thiadiazol-4-yl)benzoate-15-(4-*N,N*-dimethylamino-phenyl)ethynyl-10,20-is[2,6-di(dodecyloxy)phenyl] porphyrin zinc(II) (**Por-2**) and LW24: Compound **Por-2** was prepared with a modified condition according to previous reported.^{4,6} A two neck round bottom flask equipped with a reflux condenser was charged with **Por-1** (149 mg, 0.1 mM), **4** (87 mg, 0.3 mM), distilled THF (70.0 mL) and anhydrous TEA (6 mL) under N_2 . The reaction was stirred at 45 °C for 20 h. The progress of the reaction was monitored with TLC. After the reaction was over, the solvent was removed under vacuum. The residue was purified on silica chromatograph using hexane/THF=1/10 as eluent. The product was re-crystallized from DCM/MeOH to give green solid of compound **Por-2** (127 mg, 75%). A two neck round bottom flask was charged with compound **Por-2** (170 mg, 0.1 mmol), THF (30 mL), MeOH (20 mL) and a solution of NaOH (20% w/w in H_2O , 6 mL). The mixture was heated to 40 °C for 2 h and monitored with TLC. After the reaction was over, the mixture was diluted in ether and washed with water (30 mL), HCl (1 M, 30 mL), water (30 mL) twice. Then, the organic layer was dried over Na_2SO_4 and evaporated under vacuum. The residue was purified on silica chromatograph twice using DCM/MeOH=30/1 as eluent. The LW24 was recrystallized with $CHCl_3$ /MeOH as a brown-green solid (89 mg, 53%). 1H NMR ($CDCl_3$ /pyridine- d_5) δ H 9.87 (d, $J = 4.5$ Hz, 2H), 9.55 (d, $J = 4.5$ Hz, 2H), 8.84 (d, $J = 4.2$ Hz, 2H), 8.74 (d, $J = 4.2$ Hz, 2H), 8.32 (d, $J = 4.2$ Hz, 2H), 8.14 (m, 3H), 7.87 (d, $J = 8.6$ Hz, 2H), 7.79 (d, $J = 8.6$ Hz, 2H), 7.65 (t, $J = 8.8$ Hz, 2H), 6.98 (d, $J = 15.8$ Hz, 4H), 7.81 (d, $J = 8.7$ Hz, 2H), 3.84 (t, $J = 6.9$ Hz, 8H), 3.00 (s, 6H), 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}C NMR ($\text{CDCl}_3/\text{pyridine-d}_5$) δ C 158.7, 151.3, 150.5, 150.2, 143.5, 137.7, 132.5, 132.1, 131.6, 131.1, 130.6, 129.9, 129.4, 125.7, 125.1, 124.3, 121.4, 114.7, 112.0, 105.2, 102.3, 100.5, 97.1, 96.7, 91.8, 87.6, 68.5, 40.1, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 28.8, 25.4, 22.6, 14.1. IR (KBr, cm^{-1}): 3453, 2919, 2858, 2362, 2339, 2180, 1689, 1607, 1590, 1545, 1508, 1452, 1423, 1351, 1295, 1269, 1245, 1203, 1150, 1098, 1080, 993, 937, 821, 792, 698, 635, 585. MS (MALDI-TOF) m/z : calcd for 1681.917 u; found $[\text{M}+\text{H}^+]$ 1683.765 u. Element analysis (%) calcd for $\text{C}_{105}\text{H}_{131}\text{N}_7\text{O}_6\text{S}_4\text{Zn}$, C, 74.86; H, 7.84; N, 5.82; found C, 74.78, H 75.90; N, 5.89.

Device fabrication and Characterizations

FTO glass plate (3 mm thickness, 15 Ω /square, Nippon Sheet Glass) was cleaned in detergent solution using the ultrasonic bath for 20 min and then rinsed with deionized water, ethanol, and acetone for 20 min, respectively. A 7.5 μm thick transparent layer of 20 nm TiO_2 particles was first printed on the FTO conducting glass electrode and then coated with a 5- μm thick second layer of 400 nm light scattering anatase particles (WER2-O, Dyesol). The thickness of film was measured using a profilometer (DEKTAK, VECCO, Bruker). After treated with 40 mM aqueous TiCl_4 at 70 $^\circ\text{C}$ for 30 min, the TiO_2 film was first sintered at 500 $^\circ\text{C}$ for 30 min and then cooled to about 80 $^\circ\text{C}$ in air. The details for the preparation of the 20 nm TiO_2 particles and TiO_2 films have been described elsewhere.² The fresh TiO_2 film electrodes were dipped into a 200 μM dye solution in a mixture of toluene and ethanol (volume ratio, 1:1) at room temperature for 5 h. After being washed with ethanol and dried by air flow, the sensitized titania electrodes were assembled with thermally platinized conductive glass electrodes. The working and counter electrodes were separated by a 45 μm thick hot melt ring (Surlyn, DuPont) and sealed by heating. The internal space was filled with liquid electrolytes using a vacuum back filling system. The electrolyte (coded W08) for devices was 0.1 M LiI, 0.05 M I_2 , 0.6 M PMII, and 0.5 M 4-tertbutylpyridine in a mixture of valeronitrile and acetonitrile (volume ratio, 15: 85).

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. The current-voltage (J - V) curve of the cell was 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 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 cm^2 were tested with a metal mask of 0.09 cm^2 . The photovoltaic parameters were obtained by measuring five independently samples.

The time-resolved photoluminescence was carried out with Edinburgh instruments (FLSP920 spectrometers) as previously reported.^{2,7} The method of transient photovoltage decay (TPD) and charge extraction measurements, cyclic voltammograms were similar with our previous reports.² The UV-visible absorption spectra were observed with a PE950 spectrophotometer and Fluorescent emission spectra were obtained with a Jasco FP-6500 spectrophotometer at $25 \text{ }^\circ\text{C}$. FT-IR spectra were recorded on a Bruker VERTEX 70.

The pump lamp was a tunable Nd:YAG laser system (EKSPLA, NT 342/1/UV); the pump pulses at 450 nm are attenuated with neutral density filters before excitation of the sample with a fluence less than $40 \text{ } \mu\text{J}/\text{cm}^2$. The sample was probed with continuous light from a CW laser (CNI, MIL-III-1342-200mW); the probe light was focused on the sample; after passing the sample, the light was sent through a band-pass filter and focused on the detector (Thorlabs, DET20C); the induced transient voltage signal was recorded with an oscilloscope (Lecory, HDO4034); the device was triggered with a small fraction of the pumping beam driven into a detector (Thorlabs, DET210); a typical transient trace was averaged over 2000 laser shots.

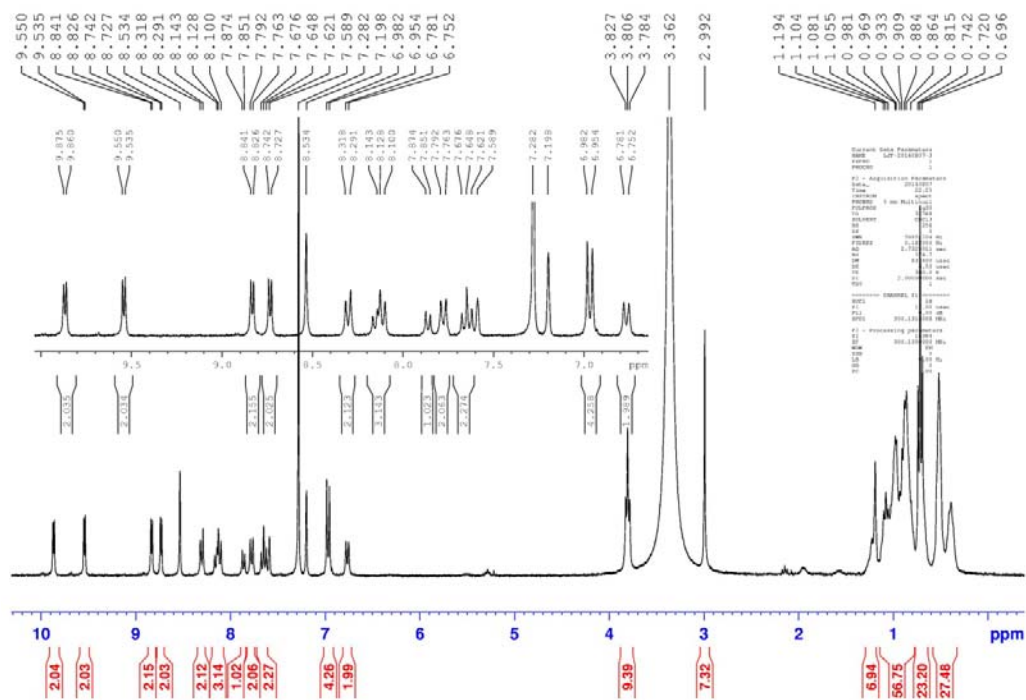


Figure S1. ^1H NMR spectrum of LW24 (400 MHz, $\text{CDCl}_3/\text{pyridine-d}_5$, 298 K).

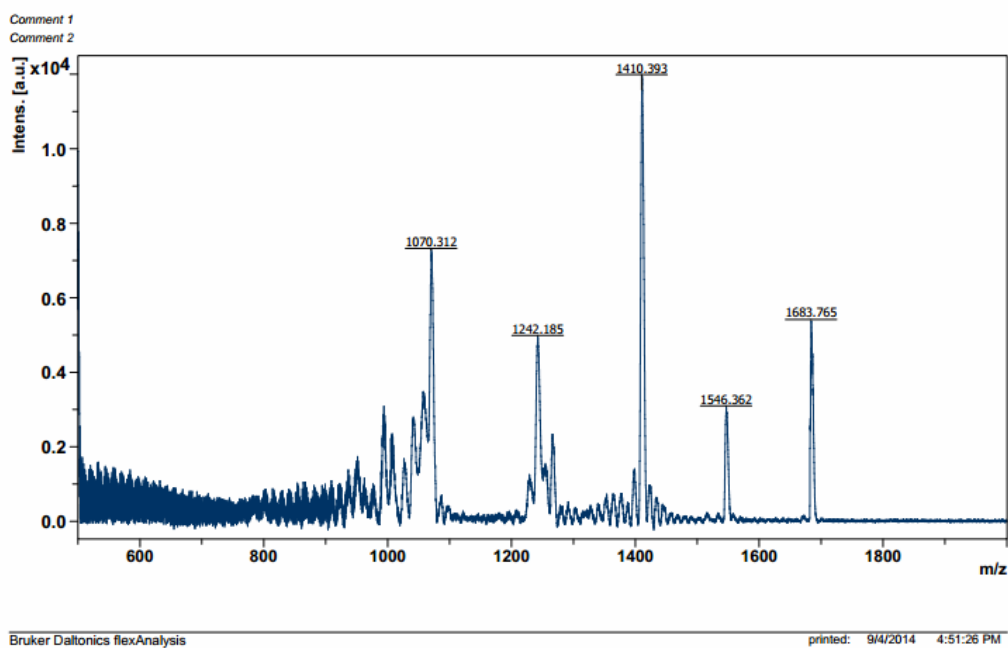


Figure S2. MS (MALDI-TOF) of LW24 m/z: calcd for 1681.917 u; found $[\text{M}+\text{H}^+]$ 1683.765 u

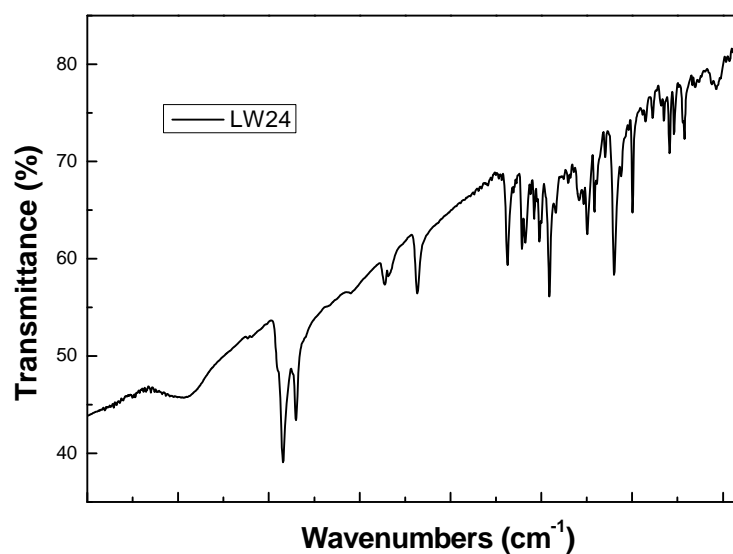


Figure S3. FT-IR spectra of LW24.

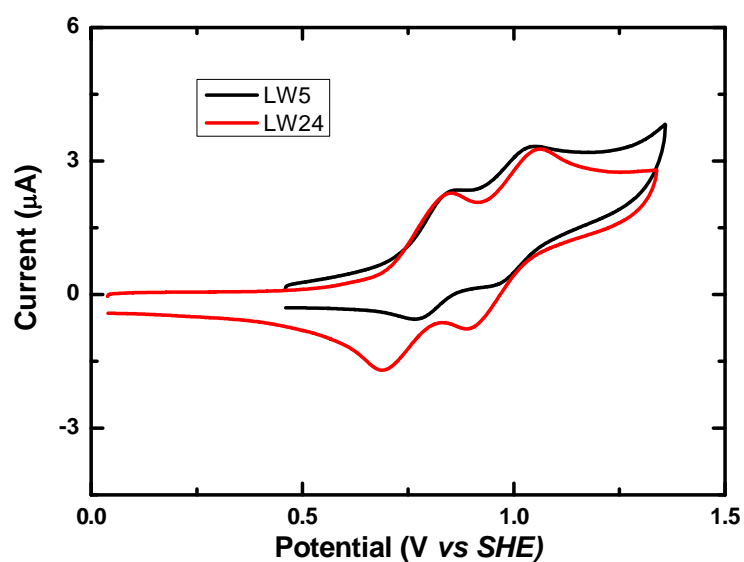


Figure S4. Cyclic voltammograms of Zn(II)-porphyrin dyes in THF were performed at 25 °C with each porphyrin (0.5 mM) in THF/0.1 M TBAP/N₂, GC working and Pt counter electrodes, Ag/AgCl reference electrode, scan rate=50 mV s⁻¹.

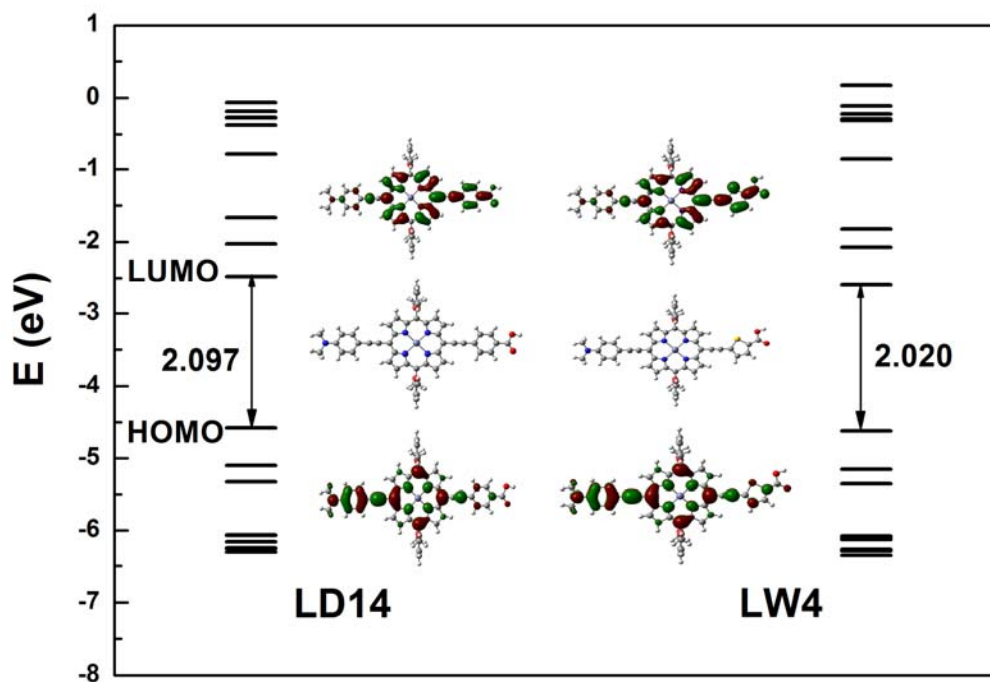


Figure S5. Energy-level diagram and frontier molecular orbital profiles of the LD14 and LW4 porphyrins by density-functional theory (DFT).

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