

Electronic Supplementary Information

Enveloping Porphyrins for Efficient Dye-Sensitized Solar Cells

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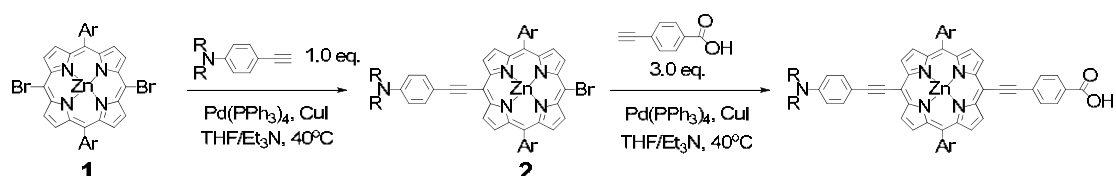
Experimental Section

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 CH_2Cl_2 and 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); H_2O about 50 ppm was found in the resulting THF. For electrochemical measurements, THF was distilled over sodium under 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), electrochemical measurements (CH Instrument Electrochemical Workstation 611A), absorption spectra (Agilent 8453 UV-Visible spectrophotometer) and fluorescence spectra (Varian Cary Eclipse fluorescence spectrometer) were recorded with the indicated instruments.

Compound Synthesis and Characterization. The synthesis of LD13 and LD14 have been previously reported,^{S1,S2} the rest of LD porphyrins were prepared in a similar fashion. As shown in Scheme S1, the typical procedure involves of mixing 200 - 300 mg of suitable di-brominated porphyrin **1**, ~1.0 eq. of 4-ethynyl-*N,N*-dialkylaniline, 70 ml THF and 5 ml triethylamine. The solutions were then degassed by 3 cycles of freeze-pump-thaw technique, followed by the addition of 15 mol. % of $\text{Pd}(\text{PPh}_3)_4$ and CuI under an inert atmosphere in a glovebox. The reaction was stirred at 40 °C for ~24 hours. The completion of the reaction was monitored by TLC. After chromatographic separation on silica gel with suitable eluents (for LD15 and LD16: toluene/ CH_2Cl_2 /n-hexanes = 1/1/6, LD14-C4: THF/n-hexanes = 1/7, LD14-C8: THF/n-hexanes = 1/10) and crystallization (for LD15, LD16 and LD14-C8: CH_2Cl_2 /MeOH, LD14-C4: THF/MeOH), various intermediate porphyrin **2** was collected (yields: for LD15, 26%; for LD16, 24%; for LD14-C4, 26%; and for LD14-C8, 29%). For the second step of cross-coupling reactions, 100 mg of intermediate porphyrin **2** was usually mixed with ~3eq. of 4-Ethynyl benzoic acid, 70 ml THF and 5 ml triethylamine. After 3 cycles of freeze-pump-thaw, 15 mol. % of

Pd(PPh₃)₄ and CuI were added to the solution under N₂ in a glovebox. The reaction was stirred at 40 °C for 20 - 24 hours. The completion of the reaction was monitored by TLC. After chromatographic separation on silica gel (with CH₂Cl₂/MeOH = 9/1) and crystallization (for LD15, LD16 and LD14-C8: CH₂Cl₂/MeOH, for LD14-C4: THF/MeOH), 75%, 75%, 66%, and 62% of LD15, LD16, LD14-C4 and LD14-C8 were collected, respectively.



Scheme S1 General synthetic procedure of LD porphyrins

Characterization data:

LD15: ¹H-NMR (CDCl₃ at 7.26 ppm, 300MHz): δ/ppm, 9.71(d, J = 4.6Hz, 2H), 9.68(d, J = 4.6Hz, 2H), 8.90(d, J = 4.6Hz, 2H), 8.86(d, J = 4.6Hz, 2H), 8.28(d, J = 8.4Hz, 2H), 8.08(d, J = 8.4Hz, 2H), 8.03(d, J = 1.8Hz, 4H), 7.85(d, J = 8.8Hz, 2H), 7.80(t, J = 1.8, 2H), 6.77(d, J = 8.8Hz, 2H), 3.38(t, J = 7.6Hz, 4H), 1.75-1.61(m, 6H), 1.56(s, 36H), 1.43-1.28(m, 20H), 0.92(t, J = 0.67Hz, 6H) Elemental Analysis: C₈₁H₉₃N₅O₂Zn·1.5THF, Calc'd. C 77.89%, H 7.89%, N 5.22%; found: C 77.78%, H 7.49%, N 4.85%. Mass (M⁺) Calc'd. 1231.66, found 1231.58.

LD16: ¹H-NMR (CDCl₃ at 7.26 ppm, 600MHz): δ/ppm, 9.57(d, J = 4.4Hz, 2H), 9.54(d, J = 4.4Hz, 2H), 8.80(d, J = 4.4Hz, 2H), 8.75(d, J = 4.4Hz, 2H), 8.25(d, J = 8.2Hz, 2H), 8.03(d, J = 8.2Hz, 2H), 7.79(d, J = 8.7Hz, 4H), 7.70(t, J = 8.6Hz, 2H), 7.00(d, J = 8.6, 4H), 6.74(d, J = 8.7Hz, 2H), 3.84(t, J = 6.5Hz, 4H), 3.35(t, J = 7.7Hz, 4H), 1.40-1.28(m, 24H), 1.22-1.14(m, 9H), 1.00-0.87(m, 34H), 0.81(t, J = 7.3Hz, 12H), 0.78-0.71(m, 9H), 0.60-0.53(m, 18Hz), 0.44(overlapped, 9H) Elemental Analysis: C₁₁₃H₁₅₇N₅O₆Zn·0.5THF, Calc'd. C 77.47%, H 9.10%, N 3.93%; found: C 77.63%, H 8.70%, N 3.55%. Mass (M⁺) Calc'd. 1744.14, found 1743.69.

LD14-C4: ¹H-NMR (CDCl₃ at 7.26 ppm, 300MHz): δ/ppm, 9.67-9.53(m, 4H), 8.82(d, J = 4.4Hz, 2H), 8.78(d, J = 4.4Hz, 2H), 8.32-8.28(m, 2H), 8.08-8.04(m, 2H), 7.95-7.87(m, 2H), 7.70(t, J = 8.4Hz, 2H), 7.02(d, J = 8.4, 4H), 6.89-6.85(m, 2H), 3.86(t, J = 6.6Hz, 8H), 3.18-1.28(m, 6H), 0.99-0.89(m, 8H), 0.59-0.05 (m, 20H). Elemental Analysis: C₆₇H₆₅N₅O₆Zn·0.5THF·2.5H₂O, Calc'd. C 70.07%, H 6.31%, N 5.92%; found: C 69.86%, H 5.93%, N 5.63%. Mass (M⁺) Calc'd. 1099.42, found 1099.57.

LD14-C8: ¹H-NMR (CDCl₃ at 7.26 ppm, 300MHz): δ/ppm, 9.58(d, J = 4.5Hz, 2H), 9.55(d, J = 4.5Hz, 2H), 8.79(d, J = 4.5Hz, 2H), 8.76(d, J = 4.5Hz, 2H), 8.27(d, J = 8.1Hz, 2H), 8.01(d, J = 8.1Hz, 2H), 7.83(d, J = 8.8Hz, 2H), 7.68(t, J = 8.3Hz, 2H),

7.00(d, $J = 8.3$, 4H), 6.84(d, $J = 8.7$ Hz, 2H), 3.84(t, $J = 6.5$ Hz, 8H), 3.08(s, 6H), 1.26(s, 4H), 0.97-0.85(m, 14H), 0.81-0.66(m, 8H), 0.66-0.50(m, 24H), 0.50-0.24(m, 10H). Elemental Analysis: $C_{33}H_{97}N_5O_6Zn \cdot 1.5THF \cdot H_2O$, Calc'd. C 73.61%, H 7.70%, N 4.82%; found: C 73.66%, H 8.05%, N 4.71%. Mass (M^+) Calc'd. 1323.67, found 1323.56.

Cell Fabrication and Characterization of Performance. The porphyrin-sensitized solar cells devices were fabricated with a working electrode based on TiO_2 nanoparticles (NP) and a Pt-coated counter electrode reported elsewhere.^{S2} For the working electrode, a paste composed of TiO_2 NP (particle size ~ 25 nm) prepared with a sol-gel method^{S3} for the transparent nanocrystalline layer was coated on a $TiCl_4$ -treated FTO glass substrate (TEC 7, Hartford, USA) to obtain the required thickness on repetitive screen printing. To improve the performance of the PSSC, an additional scattering layer (particle size ~ 300 nm) was screen-printed on the transparent active layer. The electrode was then immersed in a dye solution (0.15 mM) with EtOH/Toluene = 1/1 (or THF) at 25 °C for 2 h for dye loading onto the TiO_2 film. The electrolyte solution containing LiI (0.05 M), I_2 (0.05 M), DMPII (1.0 M), 4-tert-butylpyridine (0.5 M) in a mixture of acetonitrile and valeronitrile (volume ratio 85 : 15) was introduced into the space between the two electrodes, so completing the fabrication of these PSSC devices. The performance of a PSSC device was assessed through measurement of an I–V curve with an AM-1.5 G solar simulator (XES-502S, SAN-EI), calibrated with a Si-based reference cell (S1133, Hamamatsu). The incident monochromatic efficiencies for conversion from photons to current (IPCE) spectra of the corresponding devices were measured with a system comprising a Xe lamp (PTi A-1010, 150 W), monochromator (PTi, 1200 $gr\ mm^{-1}$ blazed at 500 nm), and source meter (Keithley 2400, computer controlled). A standard Si photodiode (Hamamatsu S1337-1012BQ) served as a reference to calibrate the power density of the light source at each wavelength.

Molecular Simulation Method. The molecular dynamics (MD) simulations of LD porphyrins were carried out with Consistent-Valence Forcefield (CVFF)^{S4} at 298 K in the Canonical (NVT) statistical ensemble using FORCITE module in the Materials Studio^{S5} software package. To diminish the effect of initial structure on the final geometry of porphyrin, one porphyrin molecule and 400 solvent molecules (400 THF molecules for LD14-C4; 256 EtOH and 144 toluene molecules for LD14-C8, LD14, and LD16) for each case were put into a large unit cell with periodic boundary condition. In this stage, the density of the system is below $0.01\ gcm^{-3}$, which is much lower than that in the solution state. To simplify the MD simulation and exclude axial ligation, these porphyrins were treated as free-base porphyrins. MD simulation was performed until the system reached thermal equilibrium. After that, MD simulation

was carried out for another 10 ps to ensure thermal equilibrium. The lattice constants of the unit cell were reduced to 98% of its original size and MD simulation was then carried out to reach a new thermal equilibrium. The condensation of unit cell was continued until the density of system approach 0.79 g cm^{-3} for LD14-C4 and 0.82 g cm^{-3} for LD14-C8, LD14, and LD16. Then the unit cell was fine tuned to discover the stable structure of the system. After that, another 100 ps thermal annealing was carried out to ensure thermal equilibrium.

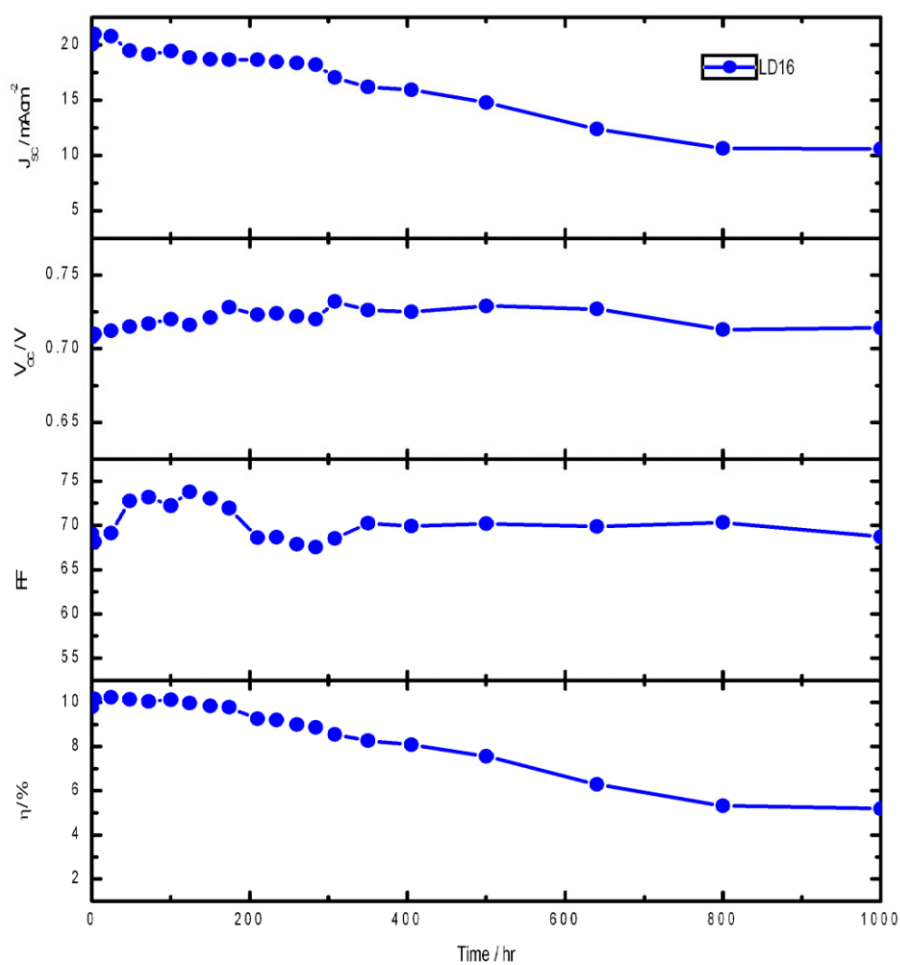


Fig. S1 Photovoltaic parameters of LD 16 under the ambient conditions for 1000 hours.

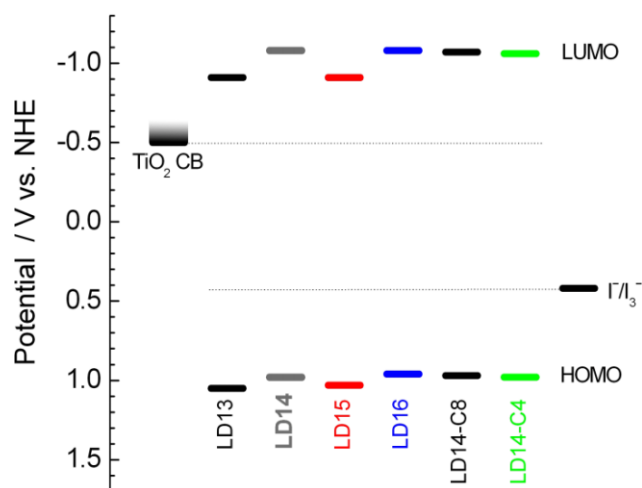
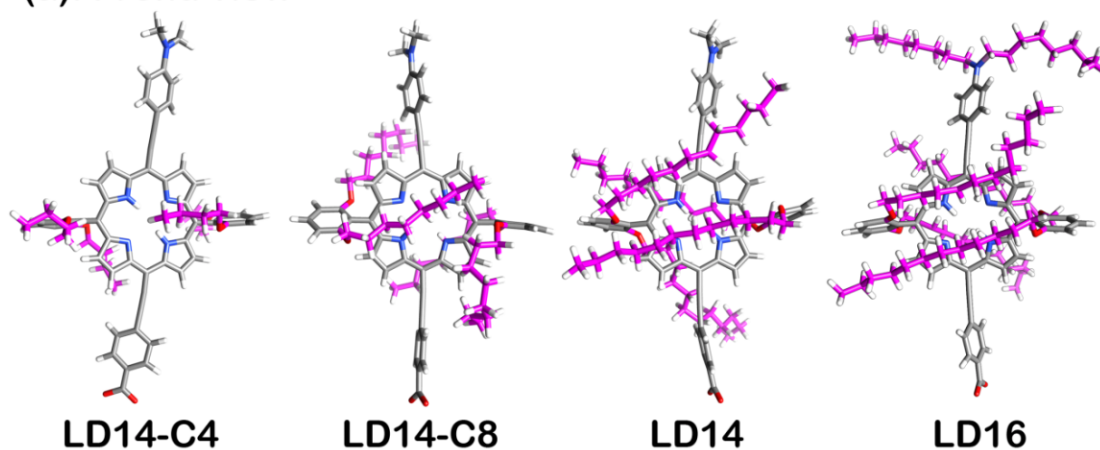


Fig. S2 Energy-level diagram of the LD porphyrins, the electrolyte and TiO₂. The first porphyrin-ring redox potentials were used to estimate the LUMO and HOMO levels.

(a). Front view



(b). Side view

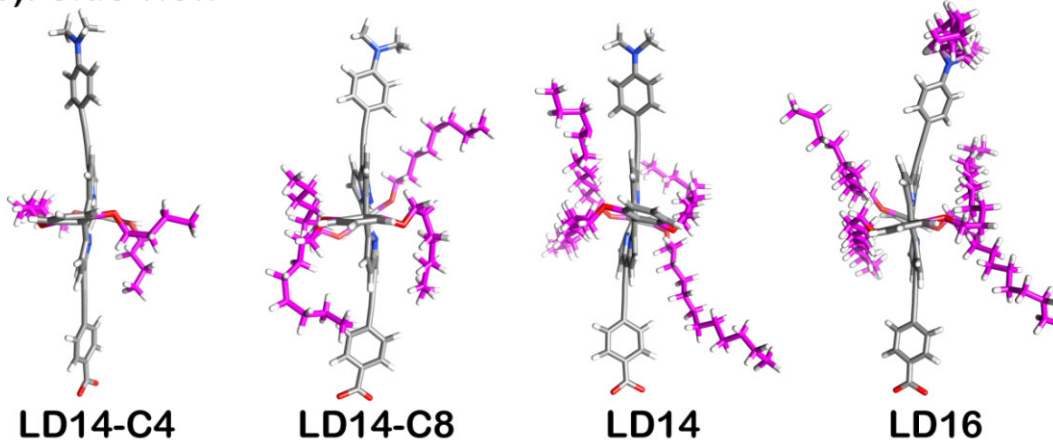


Fig. S3 Simulated structures of (a) LD14-C4 in THF, (b) LD14-C8, (c) LD14, and (d) LD16 in EtOH/toluene = 1/1 (v/v). The alkoxy and alkyl chains are highlighted in purple..

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