

## Electronic Supplementary Information

# Fluorene-Modified Porphyrin for Efficient Dye-Sensitized Solar Cell

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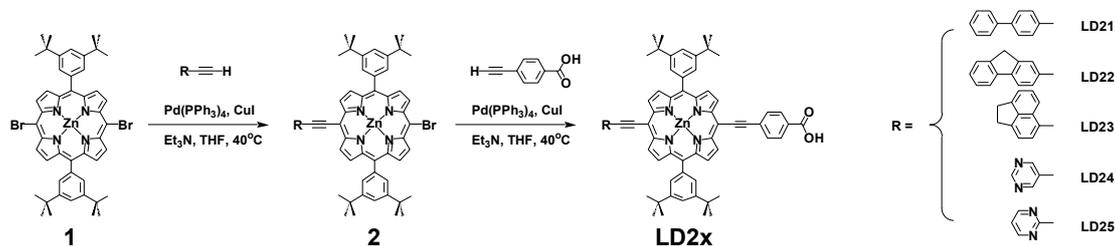
## Experimental Section

**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  $\text{CH}_2\text{Cl}_2$  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);  $\text{H}_2\text{O}$  about 50 ppm was found in the resulting THF. 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 NCHU), 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.** As shown in Scheme S1, the LD2x dyes were readily prepared in two steps based on the Sonogashira cross-coupling method.<sup>S1,S2</sup> The typical procedure involves of mixing 100 mg of di-brominated porphyrin **1**, ~1.0 eq. of a suitable 4-ethynyl polyaromatic or heterocyclic substituent, 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  $\text{CuI}$  under an inert atmosphere 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 suitable eluents (THF/Hex = 1/9 for LD21 – LD23, THF/Hex = 1/5 for LD24, and THF/Hex = 1/2 for LD25) and crystallization (THF/Hex), intermediate porphyrin **2**'s were collected (yields: for LD21, 30%; for LD22, 23%; for LD23, 33%; for LD24, 20%; and for LD25, 17%). For the second step of cross-coupling reactions, 40 mg of intermediate porphyrin **2** were 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  $\text{Pd}(\text{PPh}_3)_4$  and  $\text{CuI}$  were added to the solution under  $\text{N}_2$  in a glovebox. The reaction was stirred at 40 °C for 60 – 72 hours. The completion of the reaction was monitored by TLC. After

chromatographic separation on silica gel (MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1/9) and crystallization (THF/Hex), 74%, 78%, 78%, 85%, and 60% of LD21, LD22, LD23, LD24 and LD25 were collected, respectively.



Scheme S1 General synthetic procedure of LD porphyrins

### Characterization data:

LD21: <sup>1</sup>H NMR (300 MHz, THF-d<sub>8</sub> at 1.73 ppm, 3.58 ppm): δ/ppm, porphyrin, 9.80 (two overlapped doublets,  $J = 4.5$  Hz, 4H), 8.94 (two overlapped doublets,  $J = 4.5$  Hz, 4H), 8.14 (d,  $J = 1.5$  Hz, 4H), 7.91 (t,  $J = 1.5$  Hz, 2H), 1.60 (s, 36H); biphenylethynyl: 8.17 (d, overlapped, 2H), 7.90 (d, overlapped, 2H), 7.80 (d,  $J = 7.8$  Hz, 2H), 7.50 (t,  $J = 7.6$  Hz, 2H), 7.38 (t,  $J = 7.4$  Hz, 1H); benzoic acid: 8.25 (d,  $J = 8.2$  Hz, 2H), 8.17 (d, overlapped, 2H). Elemental Analysis: C<sub>71</sub>H<sub>64</sub>N<sub>4</sub>O<sub>2</sub>Zn·THF·0.5H<sub>2</sub>O, calc'd C 78.21%, H 6.39%, N 4.86%; found: C 78.56%, H 6.10%, N 4.53%. MS (M<sup>+</sup>): calc'd 1068.43, found 1068.60.

LD22: <sup>1</sup>H NMR (300 MHz, THF-d<sub>8</sub> at 1.73 ppm, 3.58 ppm): δ/ppm, porphyrin, 9.82 (d,  $J = 4.6$  Hz, 2H), 9.78 (d,  $J = 4.6$  Hz, 2H), 8.94 (d,  $J = 4.6$  Hz, 2H), 8.93 (d,  $J = 4.6$  Hz, 2H), 8.15 (d,  $J = 1.5$  Hz, 4H), 7.93 (t,  $J = 1.5$  Hz, 2H), 1.60 (s, 36H); fluorenylethynyl: 8.29 (s, 1H), 8.10 (d, overlapped, 1H), 8.05 (d,  $J = 7.9$  Hz, 1H), 7.95 (d, overlapped, 1H), 7.63 (d,  $J = 7.5$  Hz, 1H), 7.42 (t,  $J = 7.3$  Hz, 1H), 7.35 (t,  $J = 7.3$  Hz, 1H), 4.10 (s, 2H); benzoic acid: 8.25 (d,  $J = 8.1$  Hz, 2H), 8.18 (d, overlapped, 2H). Elemental Analysis: C<sub>72</sub>H<sub>64</sub>N<sub>4</sub>O<sub>2</sub>Zn·0.5H<sub>2</sub>O, calc'd C 79.21%, H 6.00%, N 5.13%; found: C 79.06%, H 5.73%, N 4.79%. MS (M<sup>+</sup>): calc'd 1080.43, found 1080.57.

LD23: <sup>1</sup>H NMR (300 MHz, THF-d<sub>8</sub> at 1.73 ppm, 3.58 ppm): δ/ppm, porphyrin, 9.90 (d,  $J = 4.6$  Hz, 2H), 9.78 (d,  $J = 4.6$  Hz, 2H), 8.94 (two overlapped doublets, 4H), 8.14 (d,  $J = 1.5$  Hz, 4H), 7.93 (t,  $J = 1.5$  Hz, 2H), 1.60 (s, 36H); acenaphthenylethyuyyl: 8.58 (d,  $J = 8.2$  Hz, 1H), 8.25 (d, overlapped, 1H), 7.75 (t,  $J = 7.5$  Hz, 1H), 7.50 (d,  $J = 7.2$  Hz, 1H), 7.45 (d,  $J = 6.9$  Hz, 1H), 3.52 (s, 4H); benzoic acid: 8.25 (d, overlapped, 2H), 8.15 (d, overlapped, 2H). Elemental Analysis: C<sub>71</sub>H<sub>64</sub>N<sub>4</sub>O<sub>2</sub>Zn·H<sub>2</sub>O, calc'd C 78.33%, H 6.11%, N 5.15%; found: C 78.55%, H 5.73%, N 4.79%. MS (M<sup>+</sup>) calc'd 1068.43, found 1068.95.

LD24:  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$  at 2.50 ppm):  $\delta$ /ppm, porphyrin, 9.85 (d,  $J = 4.6$  Hz, 2H), 9.80 (d,  $J = 4.5$  Hz, 2H), 8.87 (two overlapped doublets, 4H), 8.06 (d,  $J = 1.5$  Hz, 4H), 7.89 (t,  $J = 1.5$  Hz, 2H), 1.56 (s, 36H); 5-pyrimidylethyuyyl: 9.61 (s, 2H), 9.33 (s, 1H); benzoic acid:  $\delta$  8.26 (d,  $J = 8.2$  Hz, 2H), 8.17 (d,  $J = 8.2$  Hz, 2H). Elemental Analysis:  $\text{C}_{63}\text{H}_{58}\text{N}_6\text{O}_2\text{Zn}\cdot 1.5\text{THF}\cdot 1.5\text{H}_2\text{O}$ , calc'd C 73.23%, H 6.50%, N 7.43%; found: C 73.29%, H 6.66%, N 7.54%. MS ( $\text{M}^+$ ) calc'd 994.39, found 994.04.

LD25:  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$  at 2.50 ppm):  $\delta$ /ppm, porphyrin, 9.82 (d,  $J = 4.6$  Hz, 2H), 9.71 (d,  $J = 4.5$  Hz, 2H), 8.92 (d,  $J = 4.5$  Hz, 2H), 8.87 (d,  $J = 4.6$  Hz, 2H), 8.06 (d,  $J = 1.5$  Hz, 4H), 7.89 (t,  $J = 1.5$  Hz, 2H), 1.56 (s, 36H); 2-pyrimidylethyuyyl: 9.07 (d,  $J = 4.9$  Hz, 2H), 7.66 (t,  $J = 5.0$  Hz, 1H); benzoic acid: 8.27 (d,  $J = 8.0$  Hz, 2H), 8.17 (d,  $J = 8.1$  Hz, 2H). Elemental Analysis:  $\text{C}_{63}\text{H}_{58}\text{N}_6\text{O}_2\text{Zn}\cdot 0.5\text{THF}\cdot 0.5\text{H}_2\text{O}$ , calc'd C 74.95%, H 6.10%, N 8.07%; found: C 75.09%, H 5.98%, N 8.07%. MS ( $\text{M}^+$ ) calc'd 994.39, found 994.19.

**Cell Fabrication and Characterization of Performance.** The porphyrin-sensitized solar cells devices were fabricated with a working electrode based on  $\text{TiO}_2$  nanoparticles (NP) and a Pt-coated counter electrode reported elsewhere.<sup>S3</sup> For the working electrode, a paste composed of  $\text{TiO}_2$  NP (particle size  $\sim 25$  nm) prepared with a sol-gel method<sup>S4</sup> for the transparent nanocrystalline layer was coated on a  $\text{TiCl}_4$ -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  $\sim 300$  nm) was screen-printed on the transparent active layer. The electrode was then immersed in a dye solution (0.15 mM in THF) at 25 °C for 1.5 h for dye loading onto the  $\text{TiO}_2$  film. The electrolyte solution containing LiI (0.05 M),  $\text{I}_2$  (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  $\text{mm}^{-1}$  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.

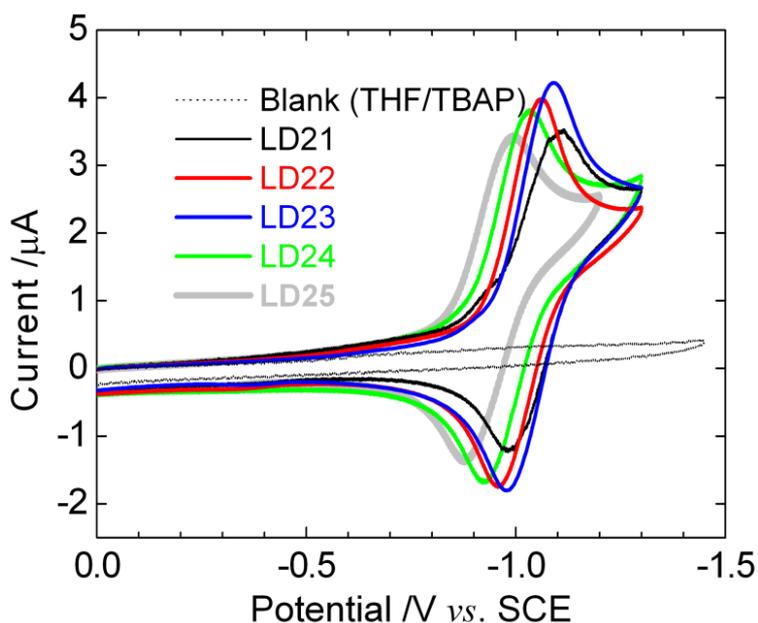


Fig. S1 Cyclic voltammograms of LD2x porphyrins in THF/TBAP. Experimental conditions: 0.5 mM of LD2x porphyrins in THF/0.1M TBAP/N<sub>2</sub>; Pt working and counter electrodes; SCE; scan rate = 100 mV/s.

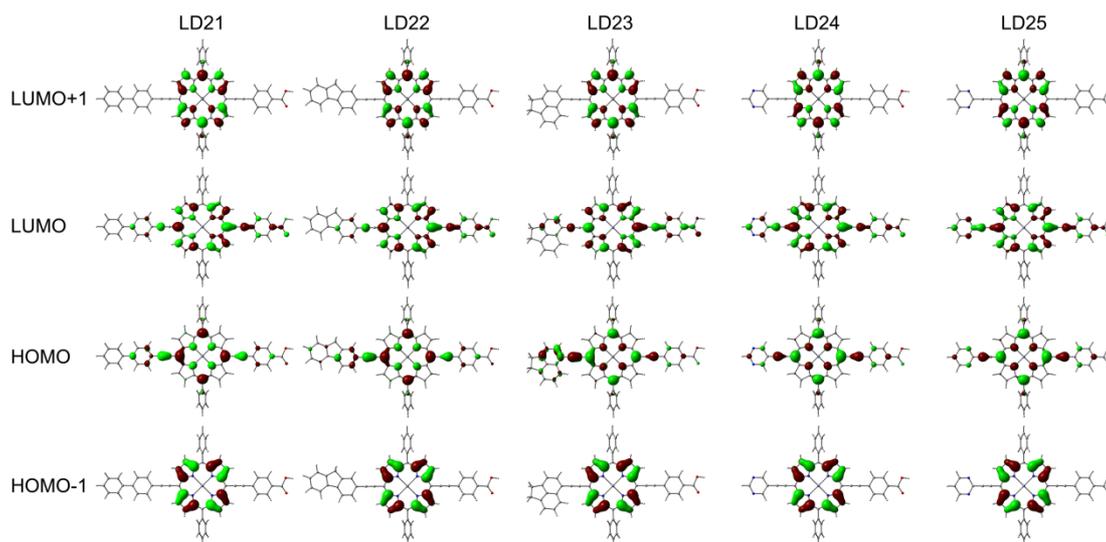


Fig. S2 MO patterns of LD2x porphyrins (DFT, B3LYP/LanL2DZ). LD22 and LD23 show more MO pattern localization at the HOMO and LUMO levels, suggesting that the push-pull effects may occur upon dye excitation.

## References:

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