

# Electronic Supplementary Information

## **A Strategy to Design Highly Efficient Porphyrin Sensitizers for Dye-sensitized Solar Cells**

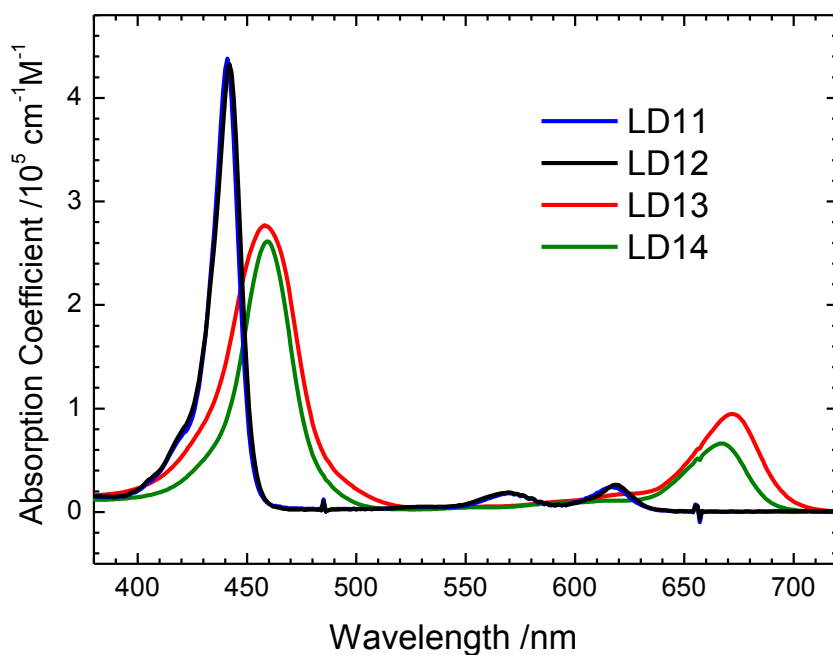
Yu-Cheng Chang,<sup>1</sup> Chin-Li Wang,<sup>2</sup> Tsung-Yu Pan,<sup>1</sup> Shang-Hao Hong,<sup>2</sup> Chih-Ming  
Lan,<sup>1</sup> Hshin-Hui Kuo,<sup>2</sup> Chen-Fu Lo,<sup>2</sup> Hung-Yu Hsu,<sup>1</sup> Ching-Yao Lin,<sup>2,\*</sup> Eric  
Wei-Guang Diao<sup>1,\*</sup>

<sup>1</sup>*Department of Applied Chemistry and Institute of Molecular Science, National Chiao  
Tung University, Hsinchu 30050, Taiwan*

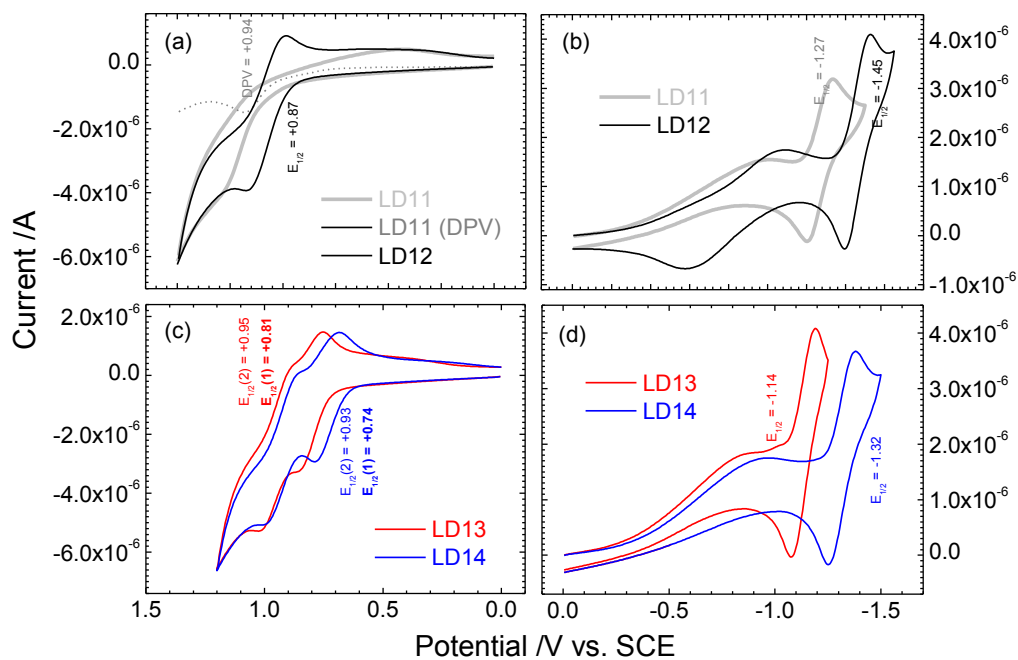
<sup>2</sup>*Department of Applied Chemistry, National Chi Nan University, Puli, Nantou Hsien  
54561, Taiwan.*

---

\* Corresponding authors. E-mail: [cyl@ncnu.edu.tw](mailto:cyl@ncnu.edu.tw); [diao@mail.nctu.edu.tw](mailto:diao@mail.nctu.edu.tw).



**Figure S1.** UV-visible absorption spectra of the LD11-LD14 porphyrins in THF.



**Figure S2.** Cyclic voltammograms of four porphyrins (0.5 mM) in THF/0.1M TBAP/N<sub>2</sub> with potential scans toward oxidation (a and c) and reduction (b and d) directions. As the LD11 oxidation reaction was irreversible, differential pulse voltammetry (DPV) was employed to estimate the oxidation potential.

**Table S1.** Spectral and electrochemical data of porphyrins LD11-LD14.<sup>a</sup>

Dyes	Absorption	Emission <sup>b</sup>	$E_{0-0}$ <sup>c</sup>	$E_{1/2}$ /V vs. SCE	
	$\lambda_{\max}/\text{nm}$ ( $\log \epsilon/M^{-1} \text{cm}^{-1}$ )	$\lambda_{\max}/\text{nm}$	/eV	Ox(1) <sup>d</sup>	Red(1) <sup>d</sup>
LD11	441 (5.64), 569 (4.26), 616 (4.38)	624, 676	2.00	+0.94 <sup>e</sup>	-1.27
LD12	442 (5.64), 569 (4.28), 619 (4.42)	624, 679	2.00	+0.87	-1.45
LD13	458 (5.44), 672 (4.98)	684, 747	1.84	+0.81	-1.14
LD14	459 (5.40), 667 (4.82)	682, 748	1.83	+0.74	-1.32

<sup>a</sup> Absorption and emission data were measured in THF at 25 °C. Electrochemical measurements were performed at 25 °C with each porphyrin (0.5 mM) in THF/0.1M TBAP/N<sub>2</sub>, Pt working and counter electrodes, SCE reference electrode, scan rate = 100 mV s<sup>-1</sup>.

<sup>b</sup> Excitation wavelength/nm: LD11, 441; LD12, 442; LD13, 458; LD14, 459.

<sup>c</sup> Estimated from the intersection wavelengths of the normalized UV-vis absorption and the fluorescence spectra.

<sup>d</sup> first porphyrin ring oxidation and reduction.

<sup>e</sup> potential estimated by differential pulse voltammetry as the oxidation reaction is irreversible.

**Table S2.** Summary of transient photocurrent and photovoltage data for LD11.

$I_0$ /mWcm <sup>-2</sup>	$J_{\text{SC}}$ /mAcm <sup>-2</sup>	$V_{\text{OC}}$ /mV	$\tau_{\text{C}}$ /ms	$\tau_{\text{R}}$ /ms	$\Delta V$ /mV	$\Delta Q$ /μCcm <sup>-2</sup>	$C_{\mu}$ /mFcm <sup>-2</sup>
11	0.47	645	3.21	82.3	2.77	6.5	2.35
16	0.69	658	2.77	56.7	3.50	10.7	3.05
20	0.87	666	2.50	47.8	2.78	10.7	3.85
25	1.14	675	2.20	37.3	3.57	17.2	4.81
35	1.56	684	1.85	28.4	2.68	17.4	6.47
43	1.92	690	1.67	23.3	2.16	17.6	8.15
64	2.86	701	1.29	17.5	2.20	26.9	12.21

**Table S3.** Summary of transient photocurrent and photovoltage data for LD12.

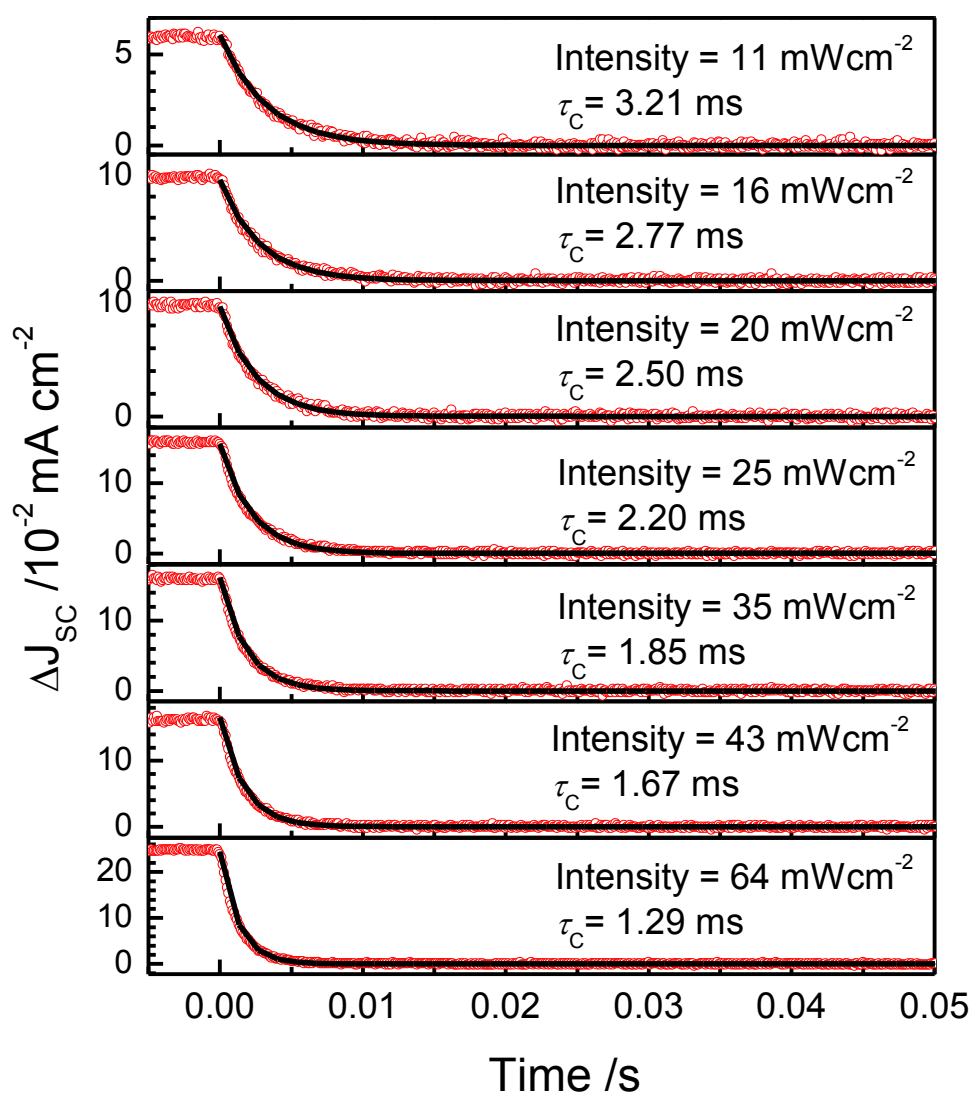
$I_0$ /mWcm <sup>-2</sup>	$J_{\text{SC}}$ /mAcm <sup>-2</sup>	$V_{\text{OC}}$ /mV	$\tau_{\text{C}}$ /ms	$\tau_{\text{R}}$ /ms	$\Delta V$ /mV	$\Delta Q$ /μCcm <sup>-2</sup>	$C_{\mu}$ /mFcm <sup>-2</sup>
11	0.84	707	3.12	63.1	4.25	16.7	3.93
16	1.23	720	2.40	44.2	3.11	16.7	5.37
20	1.55	726	2.19	35.1	2.52	16.7	6.63
25	2.03	734	1.86	28.8	3.22	27.9	8.65
35	2.78	742	1.63	22.1	2.32	27.9	12.02
43	3.43	747	1.45	18.0	2.99	44.1	14.74
64	5.10	757	1.14	13.2	2.89	67.5	23.32

**Table S4.** Summary of transient photocurrent and photovoltage data for LD13.

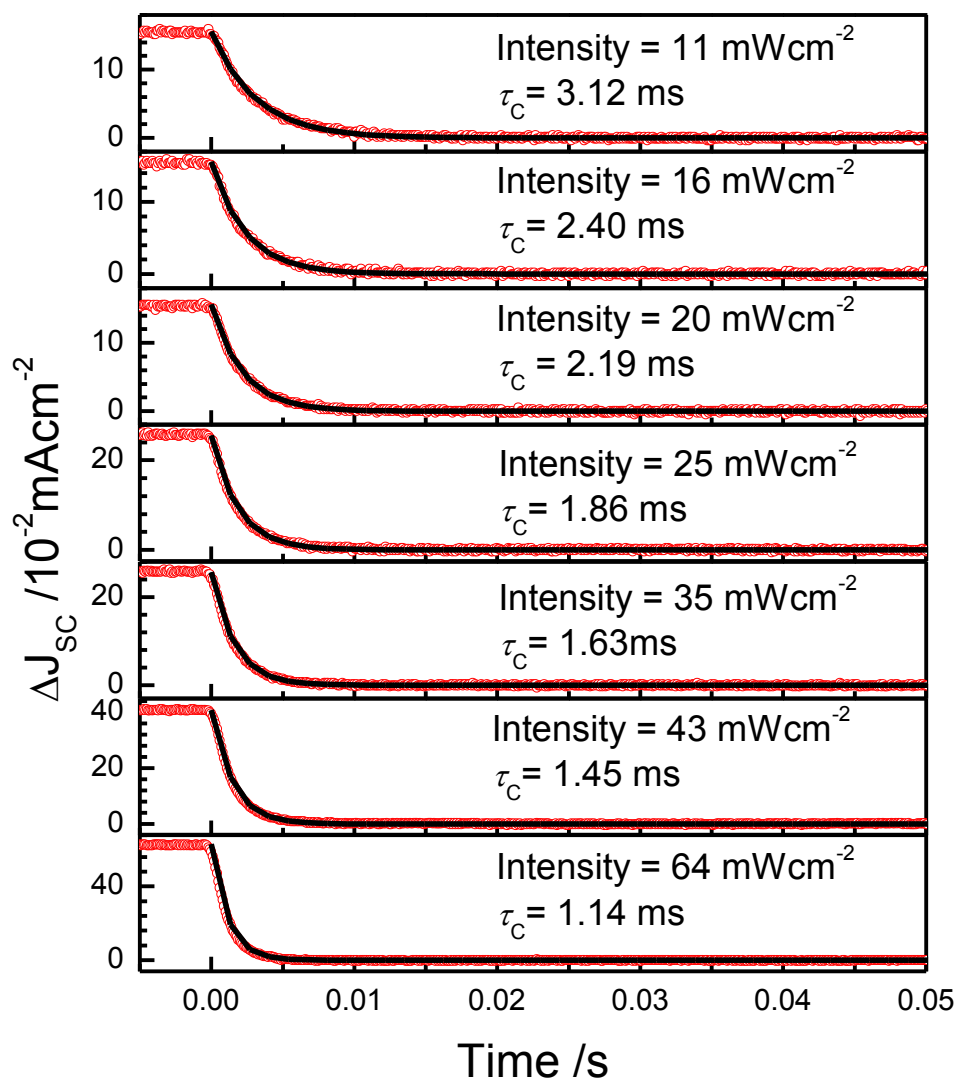
$I_0$ /mWcm <sup>-2</sup>	$J_{sc}$ /mAcm <sup>-2</sup>	$V_{oc}$ /mV	$\tau_C$ /ms	$\tau_R$ /ms	$\Delta V$ /mV	$\Delta Q$ /μCcm <sup>-2</sup>	$C_\mu$ /mFcm <sup>-2</sup>
12	0.64	662	1.28	5.26	3.22	4.1	1.13
17	0.94	675	1.02	3.69	4.77	9.1	1.61
21	1.16	682	0.95	3.35	3.99	9.1	2.06
28	1.52	690	0.87	2.72	3.61	11.3	2.79
38	2.08	700	0.75	2.14	4.10	17.8	3.78
47	2.55	706	0.69	1.82	5.30	28.6	4.74
70	3.78	717	0.59	1.34	5.11	43.2	6.96

**Table S5.** Summary of transient photocurrent and photovoltage data for LD14.

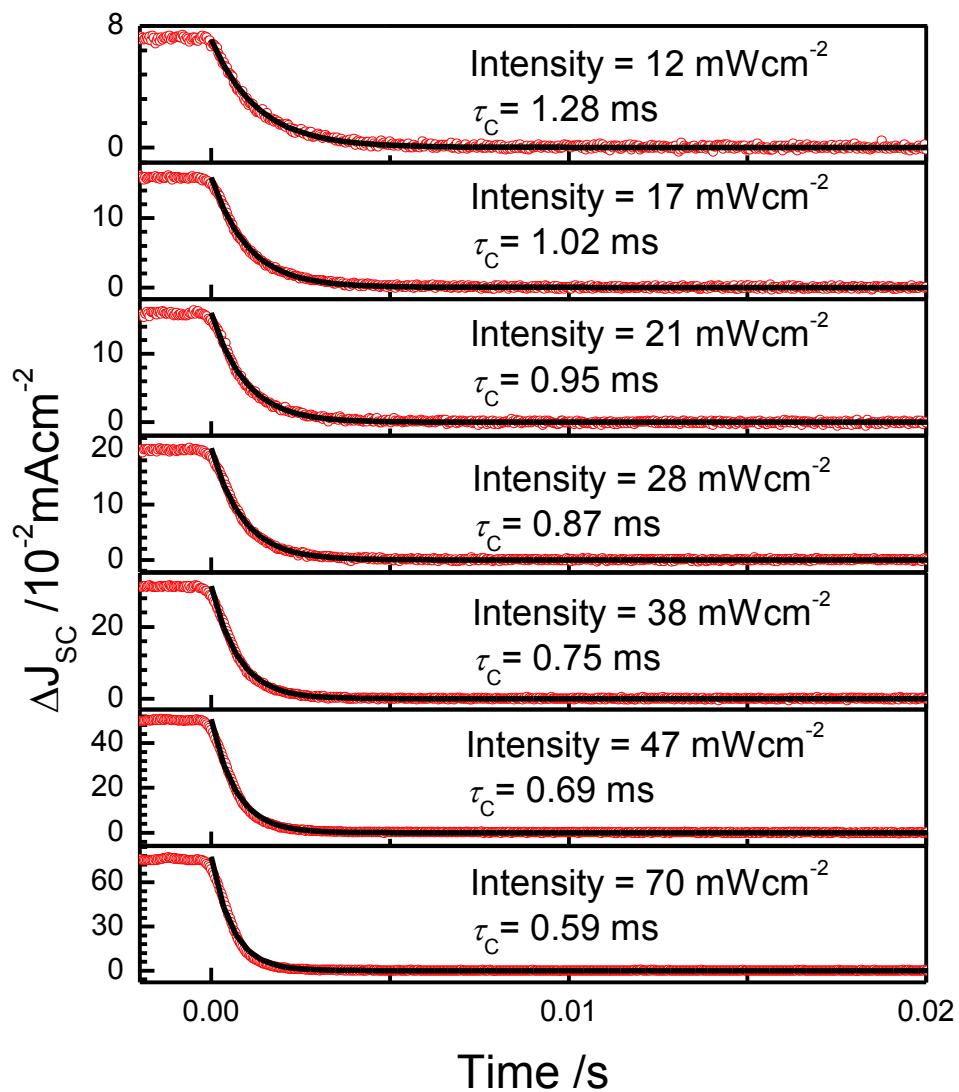
$I_0$ /mWcm <sup>-2</sup>	$J_{sc}$ /mAcm <sup>-2</sup>	$V_{oc}$ /mV	$\tau_C$ /ms	$\tau_R$ /ms	$\Delta V$ /mV	$\Delta Q$ /μCcm <sup>-2</sup>	$C_\mu$ /mFcm <sup>-2</sup>
12	0.69	699	1.37	13.02	3.43	4.3	1.24
17	1.00	711	1.14	9.12	5.05	10.1	2.00
21	1.25	718	1.06	7.51	3.98	10.1	2.52
28	1.62	726	0.91	6.34	5.76	20.1	3.49
38	2.21	735	0.80	5.01	4.11	19.9	4.86
47	2.72	740	0.73	4.27	5.17	33.1	6.40
70	4.02	749	0.65	3.04	3.42	32.8	9.61



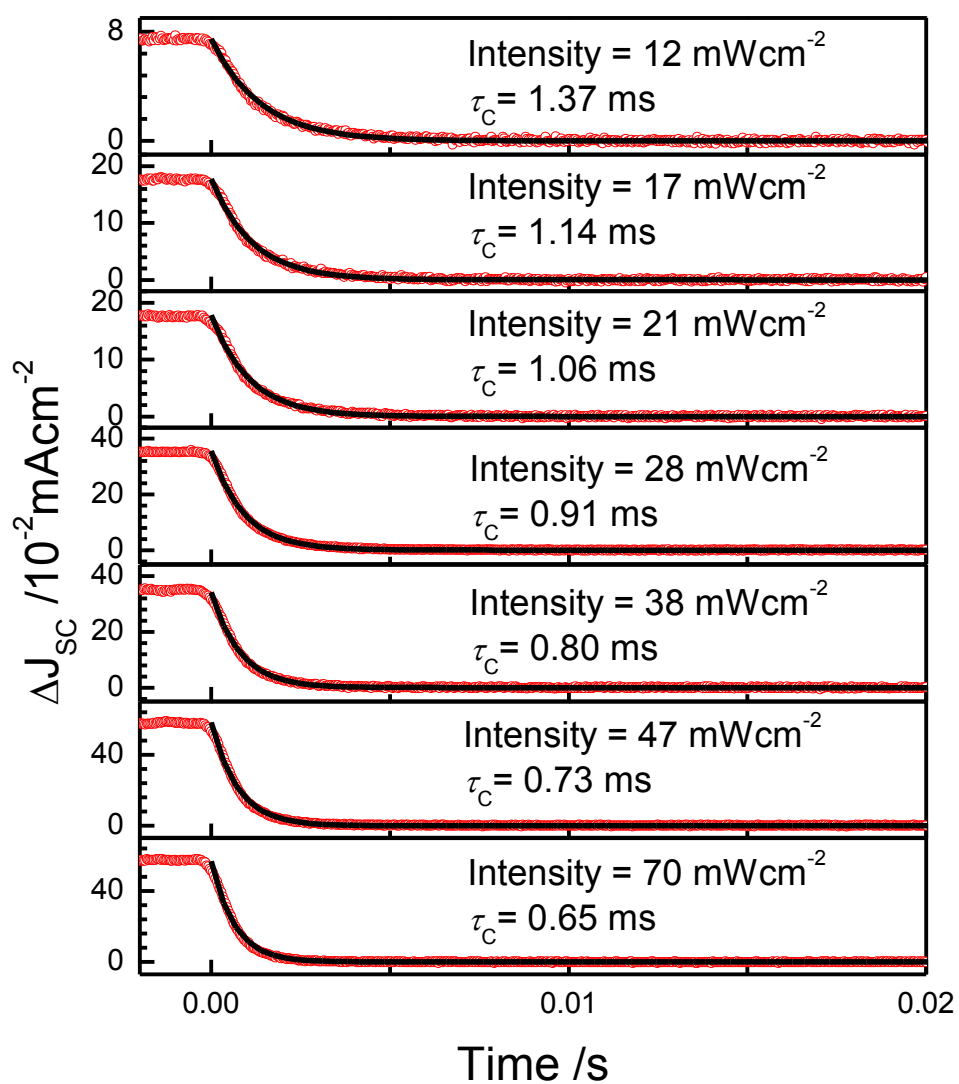
**Figure S3.** Light-induced photocurrent transients of LD11 device ( $\text{TiO}_2$  film of thickness  $\sim 2.5 \mu\text{m}$ ) obtained at a short-circuit condition with pulsed probe at 655 nm under steady-state white-light bias illumination of seven intensities as indicated. The transient data (red circles) were fitted according to a single exponential decay with the fitted curves (black traces) as indicated.



**Figure S4.** Light-induced photocurrent transients of LD12 device ( $\text{TiO}_2$  film of thickness  $\sim 2.5 \mu\text{m}$ ) obtained at a short-circuit condition with pulsed probe at 655 nm under steady-state white-light bias illumination of seven intensities as indicated. The transient data (red circles) were fitted according to a single exponential decay with the fitted curves (black traces) as indicated.

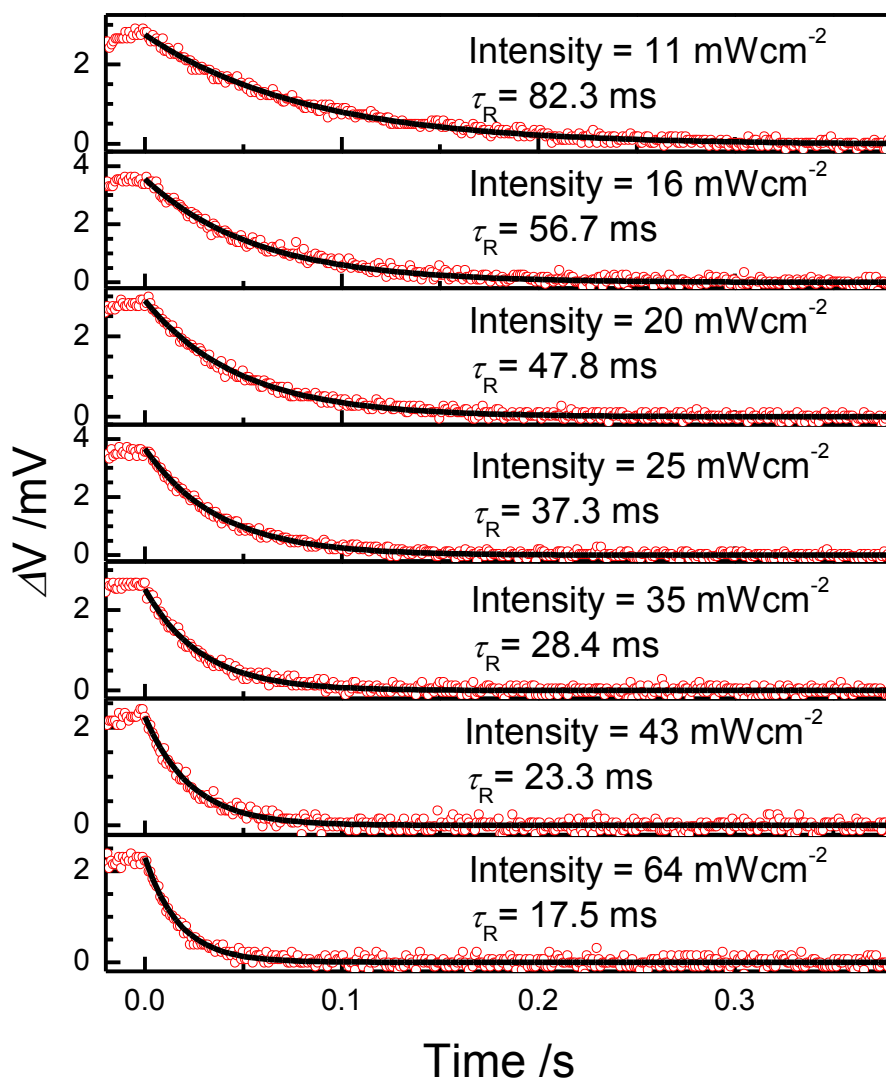


**Figure S5.** Light-induced photocurrent transients of LD13 device ( $\text{TiO}_2$  film of thickness  $\sim 1.5 \mu\text{m}$ ) obtained at a short-circuit condition with pulsed probe at 655 nm under steady-state white-light bias illumination of seven intensities as indicated. The transient data (red circles) were fitted according to a single exponential decay with the fitted curves (black traces) as indicated.

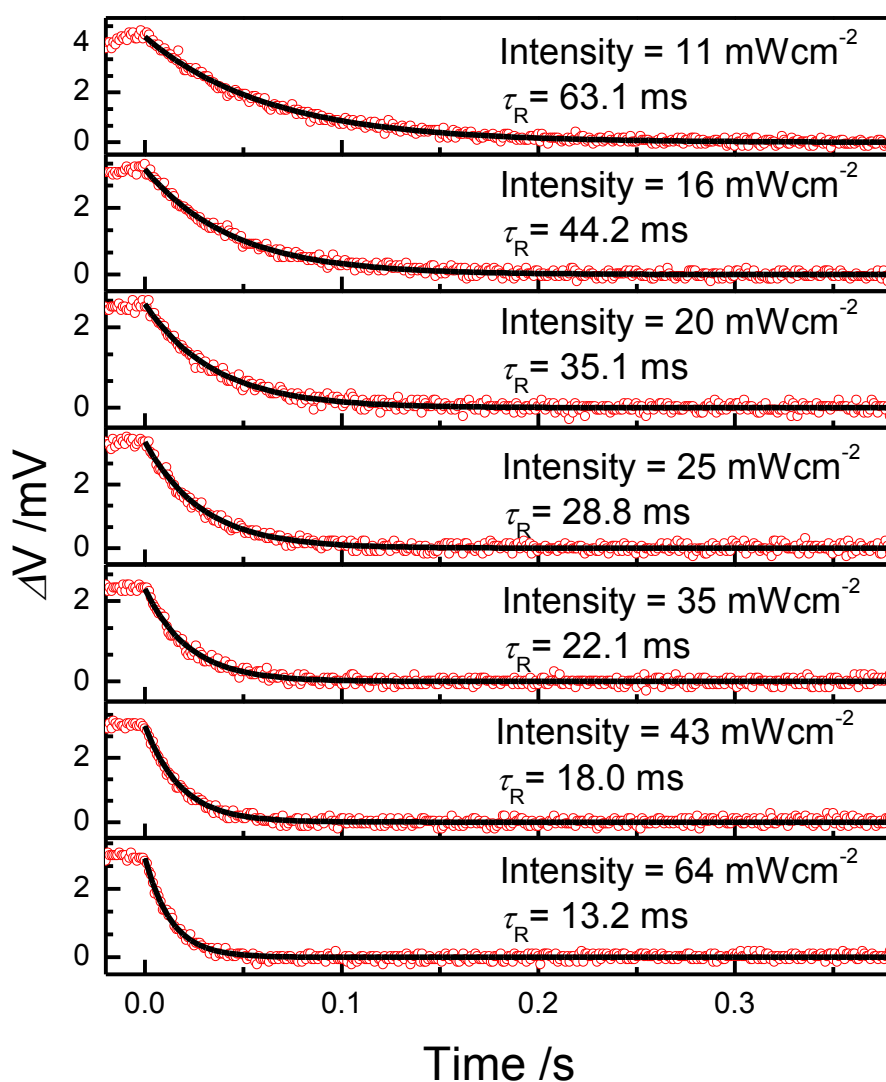


**Figure S6.** Light-induced photocurrent transients of LD14 device ( $\text{TiO}_2$  film of thickness  $\sim 1.5 \mu\text{m}$ ) obtained at a short-circuit condition with pulsed probe at 655 nm under steady-state white-light bias illumination of seven intensities as indicated. The transient data (red circles) were fitted according to a single exponential decay with the fitted curves (black traces) as indicated.

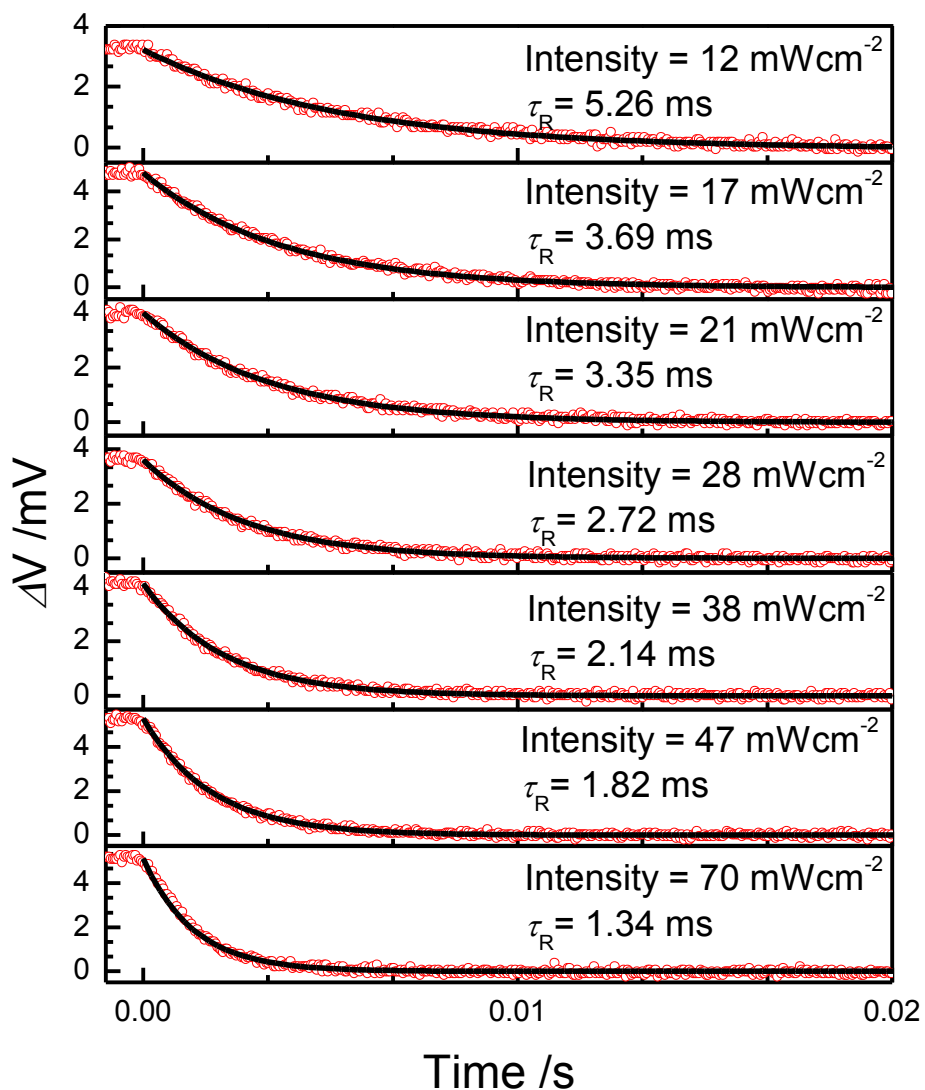




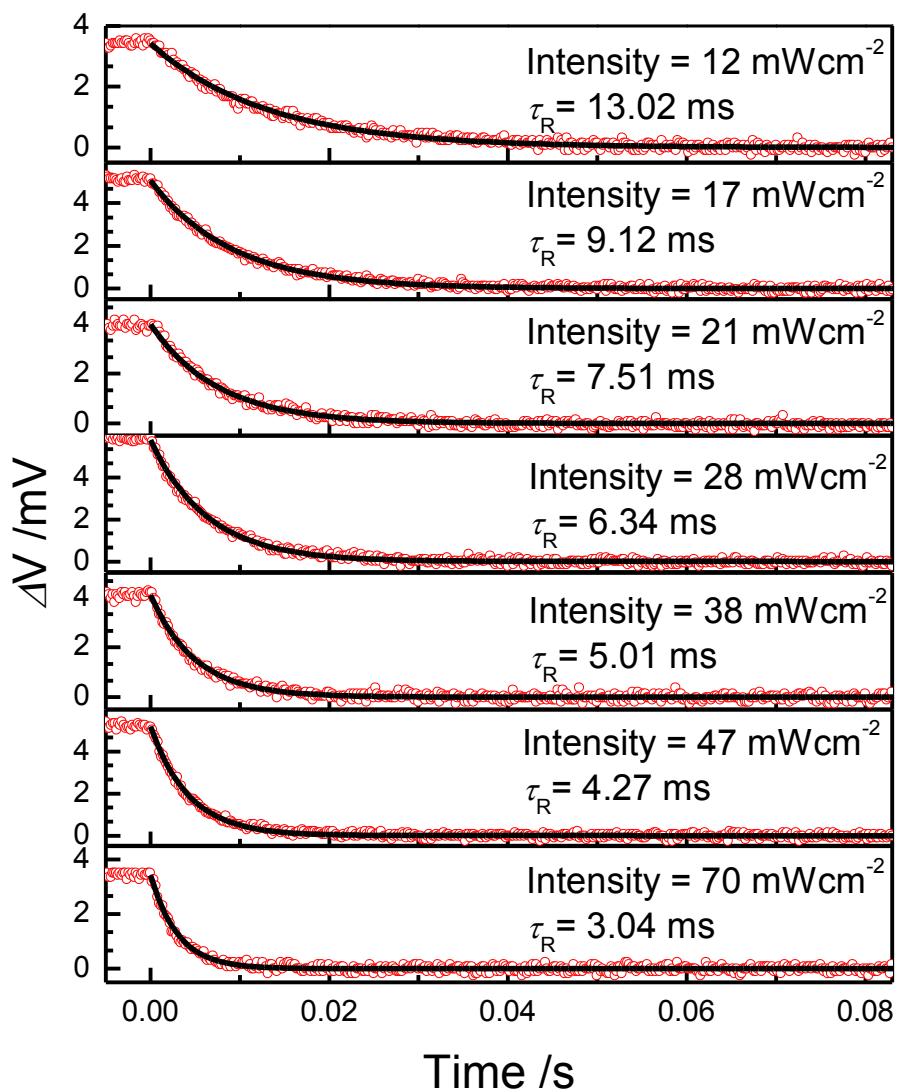
**Figure S7.** Light-induced photovoltage transients of LD11 device ( $\text{TiO}_2$  film of thickness  $\sim 2.5 \mu\text{m}$ ) obtained at an open-circuit condition with pulsed probe at 655 nm under steady-state white-light bias illumination of seven intensities as indicated. The transient data (red circles) were fitted according to a single exponential decay with the fitted curves (black traces) as indicated.



**Figure S8.** Light-induced photovoltage transients of LD12 device ( $\text{TiO}_2$  film of thickness  $\sim 2.5 \mu\text{m}$ ) obtained at an open-circuit condition with pulsed probe at 655 nm under steady-state white-light bias illumination of seven intensities as indicated. The transient data (red circles) were fitted according to a single exponential decay with the fitted curves (black traces) as indicated.



**Figure S9.** Light-induced photovoltage transients of LD13 device ( $\text{TiO}_2$  film of thickness  $\sim 1.5 \mu\text{m}$ ) obtained at an open-circuit condition with pulsed probe at 655 nm under steady-state white-light bias illumination of seven intensities as indicated. The transient data (red circles) were fitted according to a single exponential decay with the fitted curves (black traces) as indicated.



**Figure S10.** Light-induced photovoltage transients of LD14 device ( $\text{TiO}_2$  film of thickness  $\sim 1.5 \mu\text{m}$ ) obtained at an open-circuit condition with pulsed probe at 655 nm under steady-state white-light bias illumination of seven intensities as indicated. The transient data (red circles) were fitted according to a single exponential decay with the fitted curves (black traces) as indicated.

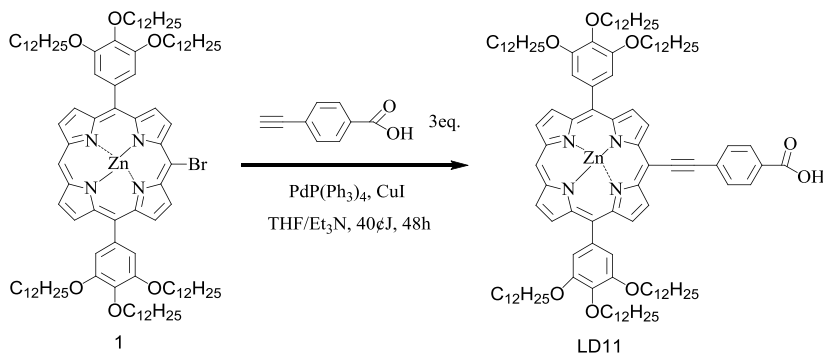
## Synthesis and characterization of compounds

**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 National Chung Hsing University), elemental analyses (Elementar Vario EL III, NSC Instrumentation Center at National Chung Hsing University), mass spectra (Microflex MALDI-TOF MS, Bruker Daltonics), electrochemical measurements (CHI Electrochemical Workstation 611A), absorption spectra (Agilent 8453 UV-Visible spectrophotometer) and fluorescence spectra (Varian Cary Eclipse fluorescence spectrometer) were recorded with the indicated instruments.

## 5-(4-carboxyphenyl)ethynyl-10,20-bis[3,4,5-tri(dodecyloxy)phenyl]porphinato

### zinc(II) – LD11

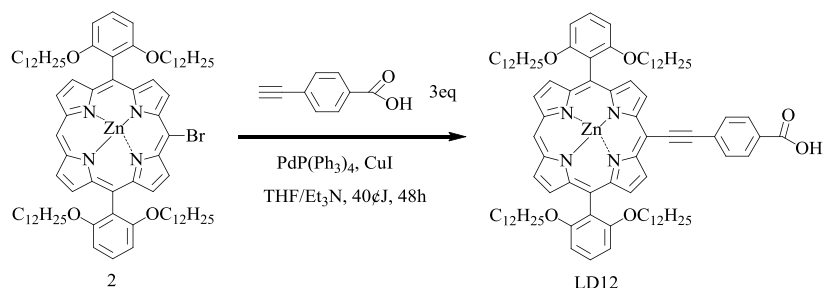


LD11 was prepared under modified conditions of a literature procedure.<sup>S1,S2</sup> Compound 1 (molecular mass = 1710.72 u, 200 mg, 0.117 mmol) was mixed with 4-ethynyl benzoic acid (molecular mass = 146.14 u, 51.26 mg, 0.351 mmol., ~3eq.) in THF (70 mL) and triethylamine (5 mL). After three cycles of freeze-pump-thaw, Pd(PPh<sub>3</sub>)<sub>4</sub> (molecular mass = 1156 u, 20.3 mg, 1.76×10<sup>-2</sup> mmol) and CuI (molecular mass = 190.45 u, 3.3 mg, 1.76×10<sup>-2</sup> mmol) were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 40 °C for 48 h. The progress of the reaction was monitored with TLC. The solvent was removed under diminished pressure. The residue was purified on a column chromatograph (silica gel) using CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 12/1 as eluent. The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to yield LD11 (molecular mass = 1775.96 u, 169.9 mg, yield = 81.8 %).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300MHz) δ<sub>H</sub> 10.10 (s, 1H), 9.81(d, J = 4.5 Hz, 2H), 9.26(d, J = 4.5 Hz, 2H), 9.09(d, J = 4.5 Hz, 2H), 9.04(d, J = 4.5 Hz, 2H), 8.32(d, J = 8.3 Hz, 2H), 8.10(d, J = 8.3 Hz, 2H), 7.41(s, 4H), 4.31(t, J = 6.4 Hz, 4H), 4.11(t, J = 6.4 Hz, 8H), 2.50-1.80(m, 44H), 1.72-1.63(m, 5H), 1.55-1.22(m, 97H), 0.94-0.78(m, 17H).  
Elemental Analysis: calcd for C<sub>113</sub>H<sub>168</sub>N<sub>4</sub>O<sub>8</sub>Zn·H<sub>2</sub>O C 75.65%, H 9.55%, N 3.12%;  
found: C 75.83%, H 9.74%, N 3.09%. MALDI-TOF: *m/z* calcd for C<sub>113</sub>H<sub>168</sub>N<sub>4</sub>O<sub>8</sub>Zn

1773.22; found 1773.01 [M]<sup>+</sup>.

**5-(4-carboxy-phenyl)ethynyl-10,20-bis[2,6-di(dodecyloxy)phenyl]porphinato  
zinc(II) – LD12**



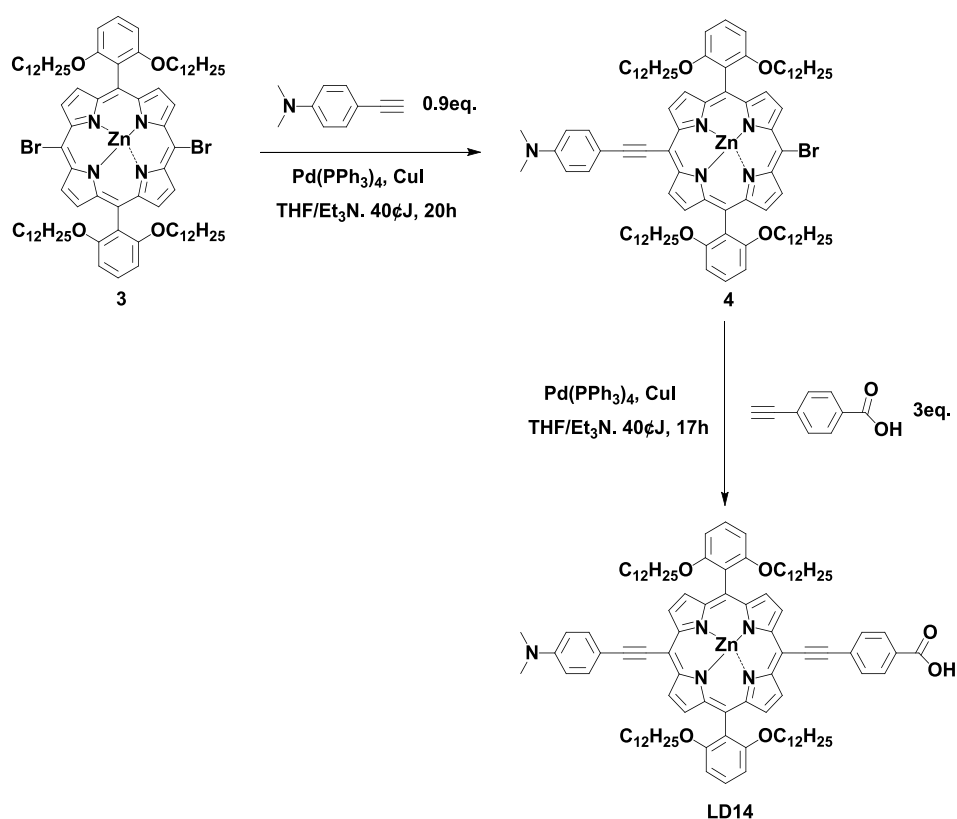
LD12 was prepared under modified conditions of a literature procedure.<sup>S1,S2</sup> Compound 2 (molecular mass = 1342.09 u, 80 mg, 0.0596 mmol.) was mixed with 4-ethynyl benzoic acid (molecular mass = 146.14 u, 26.13 mg, 0.1788 mmol., ~3eq.) in THF (30 mL) and triethylamine (5 mL). After three cycles of freeze-pump-thaw, Pd(PPh<sub>3</sub>)<sub>4</sub> (molecular mass = 1156 u, 10.3 mg, 8.94 x 10<sup>-3</sup> mmol) and CuI (molecular mass = 190.45 u, 1.70 mg, 8.94 x 10<sup>-3</sup> mmol) were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 40°C for 48 h. The progress of the reaction was monitored with TLC. The solvent was removed under diminished pressure. The residue was purified on a column chromatograph (silica gel) using CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 9/1 as eluent. The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to yield LD12 (molecular mass = 1407.32, 45 mg, yield = 53.6 %).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300MHz) δ<sub>H</sub> 10.06(s, 1H), 9.76(d, J = 4.5Hz, 2H), 9.23(d, J = 4.5Hz, 2H), 9.00(d, J = 4.5Hz, 2H), 8.95(d, J = 4.5Hz, 2H), 8.19(d, J = 7.5Hz, 2H), 8.07(d, J = 7.5Hz, 2H), 7.71(t, J = 8.4Hz, 2H), 7.02(d, J = 8.4Hz, 4H), 3.85(t, J = 6.4Hz, 8H), 1.26-1.00(m, 26H), 0.99-0.87(m, 16H), 0.82(t, overlapped, J = 6.4Hz, 12H),

0.87-0.74(m, 8H), 0.68-0.55(m, 8H), 0.50-0.301(m, 23H).

Elemental Analysis: calcd for  $C_{89}H_{120}N_4O_6Zn$  C 75.96%, H 8.59%, N 3.98%; found C 76.03%, H 8.68%, N 3.95%. MALDI-TOF:  $m/z$  calcd for  $C_{89}H_{120}N_4O_6Zn$  1404.85; found 1405.65  $[MH]^+$ .

**5-(4-carboxy-phenyl)ethynyl-15-(4-N,N-dimethylamino-phenyl)ethynyl-10,20-bis[2,6-di(dodecyloxy)phenyl]porphinato zinc(II) – LD14**



LD14 was prepared under modified conditions of a literature procedure.<sup>S1,S2</sup> Compound 3 (molecular mass = 1420.98 u, 200 mg, 0.141 mmol) and 4-ethynyl-N,N-dimethylaniline (molecular mass = 145.2 u, 18.4 mg, 0.127 mmol, ~0.9eq.), THF (70 mL) and triethylamine (5 mL) were degassed with three cycles of freeze-pump-thaw technique, followed by addition of  $Pd(PPh_3)_4$  (molecular mass = 1156 u, 24.4 mg,  $2.11 \times 10^{-2}$  mmol) and  $CuI$  (molecular mass = 190.45 u, 4 mg,  $2.11 \times 10^{-2}$  mmol) under an



inert atmosphere in a glovebox. The reaction was stirred at 40 °C for 20 h. The progress of the reaction was monitored with TLC. The solvent was removed under diminished pressure. The residue was purified on a column chromatograph (silica gel) using THF/*n*-hexanes = 1/10 as eluent. The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to yield compound 4 (molecular mass = 1485.27 u, 45 mg, yield = 39.23%).

Compound 4 (molecular mass = 1485.27 u, 160 mg, 0.108 mmol) was mixed with 4-ethynyl benzoic acid (molecular mass = 146.14 u, 47.23 mg, 0.323 mmol, ~3eq) in THF (70 mL) and triethylamine (5 mL). After three cycles of freeze-pump-thaw, Pd(PPh<sub>3</sub>)<sub>4</sub> (molecular mass = 1156 u, 18.7 mg, 1.62x10<sup>-2</sup> mmol) and CuI (molecular mass = 190.45 u, 3.1 mg, 1.62x10<sup>-2</sup> mmol) were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 40 °C for 17 h. The progress of the reaction was monitored with TLC. The solvent was removed under diminished pressure. The residue was purified on a column chromatograph (silica gel) using CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 9/1 as eluent. The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to yield LD14 (molecular mass = 1550.5 u, 107 mg, yield = 64.07 %).

<sup>1</sup>H-NMR (CDCl<sub>3</sub> 600MHz) δ<sub>H</sub> 9.58(d, J = 4.5Hz, 2H), 9.55(d, J = 4.5Hz, 2H), 8.80(d, J = 4.5Hz, 2H), 8.76(d, J = 4.5Hz, 2H), 8.25(d, J = 8.4Hz, 2H), 8.02(d, J = 8.4Hz, 2H), 7.83(d, J = 8.7Hz, 2H), 7.69(t, J = 8.5Hz, 2H), 7.00(d, J = 8.5Hz, 4H), 6.82(d, J = 8.7Hz, 2H), 3.84(t, J = 6.3Hz, 8H), 3.05(s, 6H), 1.21-1.15(m, 8H), 1.11-1.04(m, 18H), 0.98-0.88(m, 28H), 0.81(t, J = 7.3Hz, 12H), 0.78-0.71(br, 8H), 0.61-0.53(br, 18H), 0.47-0.40(br, 8H). Elemental Analysis: calcd for C<sub>99</sub>H<sub>129</sub>N<sub>5</sub>O<sub>6</sub>Zn·1.5H<sub>2</sub>O C 75.37%, H 8.43%, N 4.44%; found C 75.50%, H 8.39%, N 4.55%. MALDI-TOF: *m/z* calcd for C<sub>99</sub>H<sub>129</sub>N<sub>5</sub>O<sub>6</sub>Zn 1547.92; found 1547.80 [M]<sup>+</sup>.

## Device fabrication and characterization

The porphyrin-sensitized solar cells (PSSC) devices were fabricated with a working electrode based on TiO<sub>2</sub> nanoparticles (NP) and a Pt-coated counter electrode reported elsewhere.<sup>S3</sup> For the working electrode, a paste composed of TiO<sub>2</sub> NP (particle size ~25 nm) prepared with a sol-gel method<sup>S4</sup> for the transparent nanocrystalline layer was coated on a TiCl<sub>4</sub>-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. Crystallization of TiO<sub>2</sub> films was performed with a programmed procedure: (1) heating at 80 °C for 15 min; (2) heating at 135 °C for 10 min; (3) heating at 325 °C for 30 min; (4) heating at 375 °C for 5 min; (5) heating at 450 °C for 15 min, and (6) heating at 500 °C for 15 min. The resulting layer had a transparent layer (thickness ~ 17 μm) and a scattering layer (thickness ~ 5 μm), which were treated again with TiCl<sub>4</sub> at 70 °C for 30 min and sintered at 500 °C for 30 min. The electrode was then immersed in a dye solution (0.2 mM) with EtOH/Toluene = 1/1 at 25 °C for 2 h for dye loading onto the TiO<sub>2</sub> film. The Pt counter electrodes were prepared on spin-coating drops of H<sub>2</sub>PtCl<sub>6</sub> solution onto FTO glass and heating at 385 °C for 15 min. To prevent a short circuit, the two electrodes were assembled into a cell of sandwich type and sealed with a hot-melt film (SX1170, Solaronix, thickness 30 μm). The electrolyte solution containing LiI (0.1 M), I<sub>2</sub> (0.05 M), PMII (0.6 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<sup>-1</sup> 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.

### **Transient photocurrent and photovoltage measurements**

The photocurrent and photovoltage decays were measured with an instrumental setup similar to that reported elsewhere.<sup>S5</sup> In these experiments, varied steady-state light intensities were obtained as bias irradiations from a portable solar simulator (XES-151S, SAN-EI, with optical fiber) on tuning the driving voltage and a ND filter. A solid-state CW laser (655nm) controlled with a quick shutter (SH05, THORLABS) was used to generate a perturbation pulse of duration 50-100 ms.<sup>S6</sup> Both the pulsed red light and the steady-state white light were shone on the photoanode side of the cell. The pulsed-probe irradiations were controlled with a ND filter to maintain the modulated photovoltage less than 5 mV in each measurement. The probe beams generated carriers causing a small photocurrent increase ( $\Delta J_{SC}$ ) near  $J_{SC}$  of the cell at the short-circuit condition, or a small photovoltage increase ( $\Delta V_{OC}$ ) near  $V_{OC}$  of the cell at the open-circuit condition, subjected to the white bias light and the current and voltage decay processes were thereby measured, respectively. The resulting photocurrent and photovoltage transients were recorded on a digital oscilloscope (TDS1012B, Tektronix); the signals passed a current preamplifier (SR570, SRC) at a short-circuit condition and a voltage preamplifier (SR560, SRC) at an open-circuit condition. The chemical capacitance of the TiO<sub>2</sub>/electrolyte interface at each  $V_{OC}$  is calculated as  $C_{\mu} = \Delta Q/\Delta V$ :  $\Delta V$  is the

maximum photovoltage transient and  $\Delta Q$  is the number of electrons injected during the red-light flash.

## References

- S1. (a) C.-F. Lo, L. Luo, E. W.-G. Diao, I.-J. Chang and C.-Y. Lin, *Chem. Commun.*, 2006, 1430; (b) C.-F. Lo, S.-J. Hsu, C.-L. Wang, Y.-H. Cheng, H.-P. Lu, E. W.-G. Diao and C.-Y. Lin, *J. Phys. Chem. C*, 2010, **114**, 12018.
- S2. (a) K. E. Splan and J. T. Hupp, *Langmuir*, 2004, **20**, 10560; (b) X. Huang, C. Zhu, S. Zhang, W. Li, Y. Guo, X. Zhan, Y. Liu and Z. Bo, *Macromolecules*, 2008, **41**, 6895.
- S3. C.-L. Wang, Y.-C. Chang, C.-M. Lan, C.-F. Lo, E. W.-G. Diao and C.-Y. Lin, *Energy Environ. Sci.*, 2011, **4**, 1788.
- S4. (a) S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Péchy and M. Grätzel, *Prog. Photovolt: Res. Appl.*, 2007, **15**, 603; (b) S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin and M. Grätzel, *Thin Solid Films*, 2008, **516**, 4613.
- S5. L. Luo, C.-J. Lin, C.-S. Hung, C.-F. Lo, C.-Y. Lin and E. W.-G. Diao, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12973.
- S6. L. Alibabaei, M. Wang, R. Giovannetti, J. Teuscher, D. Di Censo, J.-E. Moser, P. Comte, F. Pucciarelli, S. M. Zakeeruddin and M. Grätzel, *Energy Environ. Sci.*, 2010, **3**, 956.