Electronic Supplementary Information

Highly efficient porphyrin-sensitized solar cells with enhanced light harvesting ability beyond 800 nm and efficiency exceeding 10 %

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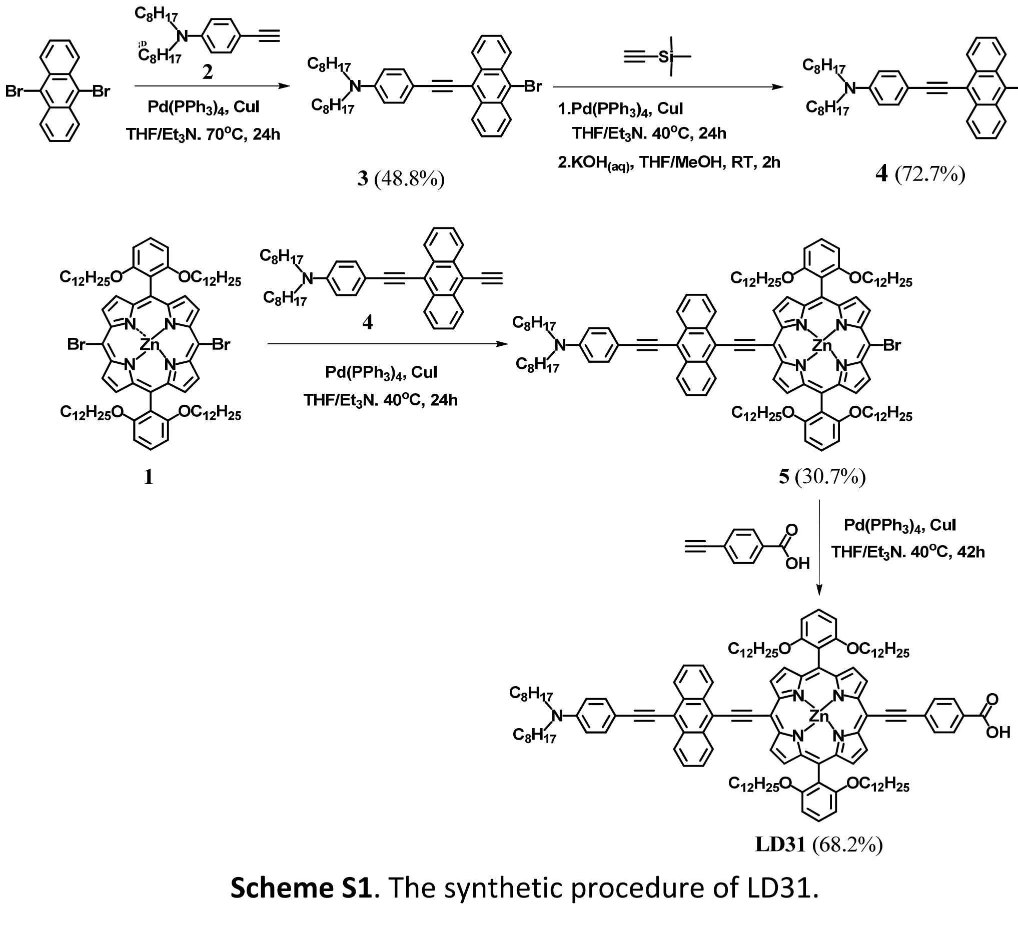
Experimental Section

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); about 50 ppm H_2O was found in the resulting fluid. For electrochemical measurements, THF was distilled over sodium under N_2. $Pd(PPh_3)_4$ catalyst (Strem, MA, USA) and $Pd_2(dba)_3$ (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) were recorded with the indicated instruments.

Compound Synthesis and Characterization.



Scheme S1. The synthetic procedure of LD31.

Compound 1: The synthesis of compound 1 is based on the literature report.[S1]

Compound 2: The synthesis of compound 2 based on the literature report.[S2]

Compound 3: 380 mg of 9,10-dibromo anthracene (M.W. = 336.02, 1.131 mmol.) was mixed with 257.8 mg of compound 2 (M.W. = 341.57, 0.755 mmol.) in 30 ml of THF and 5 ml of triethylamine. After 3 cycles of freeze-pump- thaw, 87.3 mg of $Pd(PPh_3)_4$ (M.W. = 1156,7.55 × 10^{-2} mmol.) and 14.4 mg of CuI (M.W. = 190.45, 7.55 × 10^{-2} mmol.) were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 70^{o}C for 24 hours. The completion of the reaction was monitored by TLC. The solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using CH_2Cl_2/n-hexanes = 1/4 as eluent to give 220 mg of compound 3 (M.W. = 596.68, yield = 48.8 %).

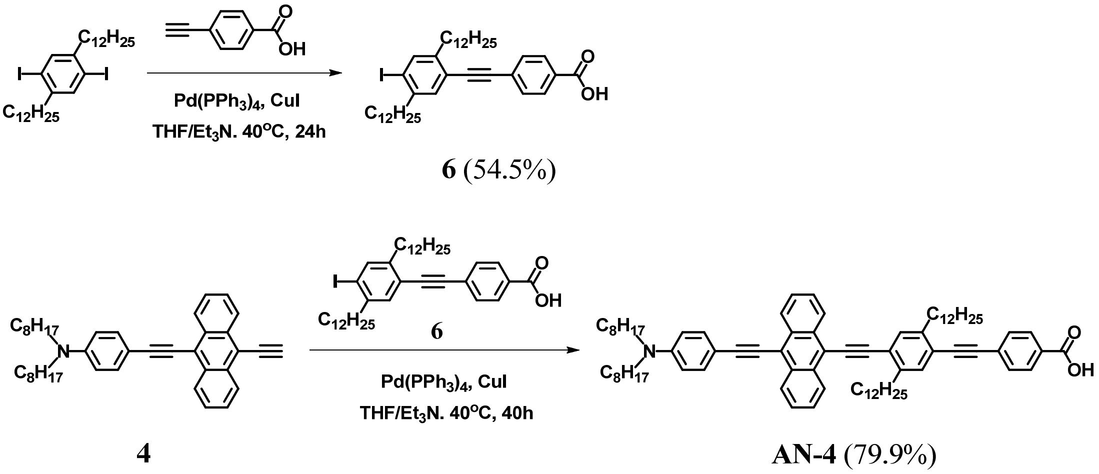
Compound 4: 500 mg of compound 3 (M.W. = 596.68, 0.838 mmol.) was mixed with 2 ml of trimethylsilyl acetylene (M.W. = 98.22, d = 0.69, 3.5 mmol., 16.8 eq.) in 30 ml of THF and 5 ml of triethylamine. After 3 cycles of freeze-pump-thaw, 96.9 mg of $Pd(PPh_3)_4$ (M.W. = 1156, 8.38 × 10^{-2} mmol.) and 16.0 mg of CuI (M.W. = 190.45, 8.38× 10^{-2} mmol.) were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 40^{o}C for 24 hours. The completion of the reaction was monitored by TLC. The solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using CH_2Cl_2/n-hexanes = 1/1 as eluent, 450 mg of brown solids were collected (M.W. = 613.99, yield = 87.5 %)

For the de-protection process, 450 mg of said solids (M.W. = 613.99, 0.733 mmol.) were put in THF/MeOH = 4/1 (v/v) to react with 1ml of 1.0 M KOH(aq) for 2 hours at room temperature. The solvents were then removed under reduced pressure, followed by chromatographic separation on silica gel with CH_2Cl_2/hexanes = 1/1 to afford 330 mg of compound 4 (M.W. = 541.81, yield =83.1%).

Compound 5: 220 mg of compound 1 (M.W. = 1420.98, 0.155 mmol.) was mixed with 92.1 mg of compound 4 (M.W. = 541.81, 0.170 mmol., ~1.1eq.) in 30 ml of THF and 5 ml of triethylamine. After 3 cycles of freeze-pump-thaw, 26.9 mg of $Pd(PPh_3)_4$ (M.W. = 1156, 2.33 × 10^{-2} mmol.) and 4.4 mg of CuI (M.W. = 190.45, 2.33 × 10^{-2} mmol.) were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 40^{o}C for 24 hours. The completion of the reaction was monitored by TLC. The solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using THF/n-hexanes = 1/10 as eluent to give 90.0 mg of compound 5 (M.W. = 1881.88, yield = 30.8 %).

LD31: 78.0 mg of compound 5 (M.W. = 1881.88, 0.041 mmol.) was mixed with 18.1 mg of 4-ethynyl benzoic acid (M.W. = 146.14, 0.124 mmol., ~3.0 eq.) in 30 ml of THF and 5 ml of triethylamine. After 3 cycles of freeze-pump- thaw, 7.2 mg of $Pd(PPh_3)_4$ (M.W. = 1156, 6.2 × 10^{-3} mmol.) and 1.2 mg of CuI (M.W. = 190.45, 6.2 × 10^{-3} mmol.)

were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 40°C for 42 hours. The completion of the reaction was monitored by TLC. The solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using MeOH/CH_2Cl_2 = 1/9 as eluent to give 55.0 mg of LD31 (M.W. = 1947.11, yield = 68.9 %).



6 (54.5%)

4

AN-4 (79.9%)

Scheme S2. The synthetic procedures of AN-4.

Compound 6: 500 mg of 1,4-diiodo-2,5-didodecylbenzene (M.W. = 666.54, 0.750 mmol.) was 120.6 mg of 4-ethynyl benzoic acid (M.W. = 146.14, 0.825 mmol., ~1.1 eq.) in 30 ml of THF and 5 ml of triethylamine. After 3 cycles of freeze-pump-thaw, 43.4 mg of $Pd(PPh_3)_4$ (M.W. = 1156, 3.75×10^{-2} mmol.) and 7.1 mg of CuI (M.W. = 190.45, 3.75×10^{-2} mmol.) were added to the solution 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. The solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using MeOH/CH_2Cl_2 = 1/9 as eluent to give 280 mg of compound 6 (M.W. = 684.77, yield = 54.5 %).

AN-4: 80.0 mg of compound 4 (M.W. = 541.81, 0.148 mmol.) was mixed with 106.2 mg of compound 6 (M.W. = 684.77, 0.155 mmol., ~1.05 eq.) in 30 ml of THF and 5 ml of triethylamine. After 3 cycles of freeze-pump-thaw, 25.7 mg of $Pd(PPh_3)_4$ (M.W. = 1156, 2.22×10^{-2} mmol.) and 4.2 mg of CuI (M.W. = 190.45, , 2.22×10^{-2} mmol.) were added to the solution under an inert atmosphere in a glovebox. The reaction was stirred at 40°C for 40 hours. The completion of the reaction was monitored by TLC. The solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using MeOH/CH_2Cl_2 = 1/9 as eluent to give 130.0 mg of LWO4 (M.W. = 1098.67, yield = 79.9 %).

Characterization data:

LD31: ^{1}H-NMR ($CDCl_3$ at 7.26 ppm, 300MHz, trace amount of d_5-pyridine was added to increase the solubility): δ_H 9.88 (d, J = 4.5 Hz, 2H), 9.59 (d, J = 4.5 Hz, 2H), 9.34 (d, J = 8.4 Hz, 2H), 8.90 (d, J = 4.5 Hz, 2H), 8.84 (d, J = 4.5 Hz, 2H), 8.82 (d, J = 8.4 Hz, 2H), 8.28 (d, J = 8.1 Hz, 2H), 8.04 (d, J = 8.3 Hz, 2H), 7.83-7.60 (m, overlapped, 8H), 7.02 (d, J = 8.4 Hz, 4H), 6.70 (d, J = 8.9 Hz, 2H), 3.88 (t, J = 6.5 Hz, 8H), 3.35 (t, J = 7.6 Hz, 4H), 1.65 (br, 6H), 1.45-1.20 (m, 22H), 1.20-0.62 (m, 72H), 0.62-0.32 (m, 22H). Elemental Analysis: calc'd for $C_{129}H_{165}N_5O_6Zn\cdot 1.5\ H_2O$ C 78.48 %, H 8.58 %, N 3.55 %; found: C 78.21 %, H 8.66 %, N 3.40 %. MALDI-TOF: *m/z* calcd for $C_{129}H_{165}N_5O_6Zn$ 1944.21; found 1944.33$[M]^+$.

AN-4: ^{1}H-NMR ($CDCl_3$ at 7.26 ppm, 300MHz): δ_H 8.75-8.66 (m, overlapped, 4H), 8.11 (d, J = 7.6 Hz, 2H), 7.63-7.60 (overlapped, 9H), 7.48 (s, 1H), 6.67 (d, J = 8.9 Hz, 2H), 3.33 (t, J = 8.1 Hz, 4H), 3.04 (t, J = 7.6 Hz, 2H), 2.89 (t, J = 7.8 Hz, 2H), 1.90-1.70 (m, 6H), 1.70-1.10 (m, 60H), 0.92-0.83 (m, 12H). Elemental Analysis: calc'd for $C_{79}H_{103}NO_2\cdot H_2O$ C 84.97 %, H 9.48 %, N 1.25 %; found: C 84.69 %, H 9.70 %, N 1.12 %. MALDI-TOF: *m/z* calcd for $C_{79}H_{103}NO_2$ 1097.79; found 1097.57 $[M]^+$.

Table S1: UV-visible absorption maxima and wavelengths, fluorescent emission wavelength, first redox potentials, and calculated energy levels of the dyes:

Dye	Absorption, nm (log ε, $M^{-1}cm^{-1}$)	Emission,[a] nm	$E_{1/2}$, V vs. SCE[b]		S^o/S^+,[d] eV	S*, eV
			Ox (1)	Red (1)		
LD14 [e]	459(5.40), 667(4.82)	682	+0.74	-1.32		
LD31	449(5.10), 521(4.92), 691(4.94)	713	+0.86	-1.15	-5.60	-3.84
AN-4	504 (4.72)	597	+0.88[c]	-1.38	-5.62	-3.34

[a] 2.0x10-6 M of compounds in THF, major emissions only. [b] 0.5 mM of the samples in THF/0.1M TBAP/N2.; Pt working and counter electrodes; SCE reference electrode; scan rate = 100 mV/s.
[c] Potential determined by differential pulse voltammetry due to irreversible nature of the oxidation.
[d] The first oxidation potentials were used to estimate the S^o/S^+ levels. Normalized Q-bands and the fluorescence bands were used to estimate the energy differences between the S* and the S^o/S^+ levels.
[e] Taken from ref. 17c.

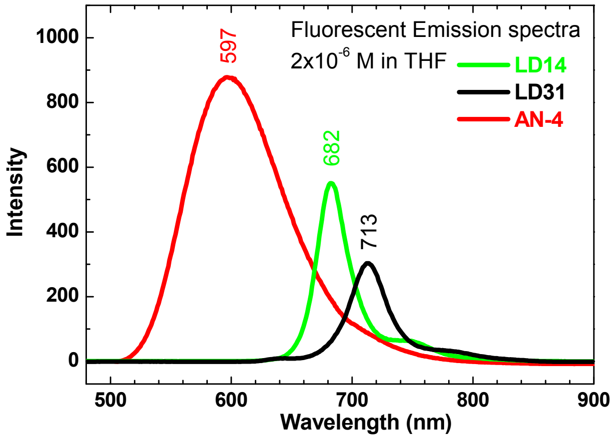


Fig. S1 Fluorescent emission spectra of 2x10^{-6} M of AN-4, LD14 and LD31 in THF.

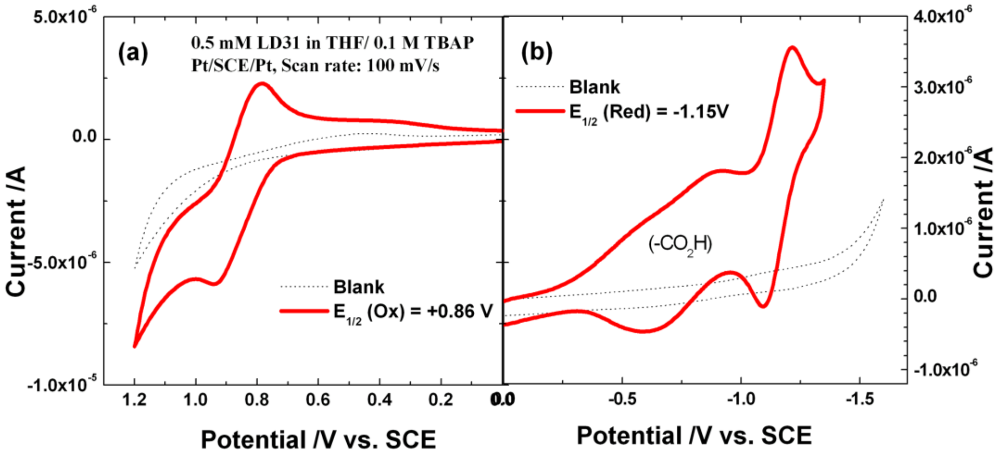


Fig. S2 Cyclic voltammograms of 0.5 mM LD31 in THF/0.1 M TBAP.

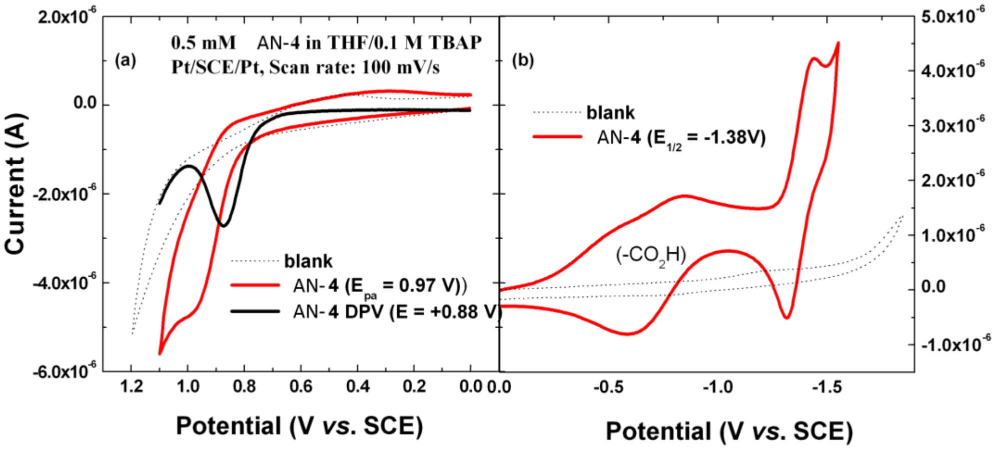


Fig. S3 Cyclic voltammograms of 0.5 mM AN-4 in THF/0.1 M TBAP.

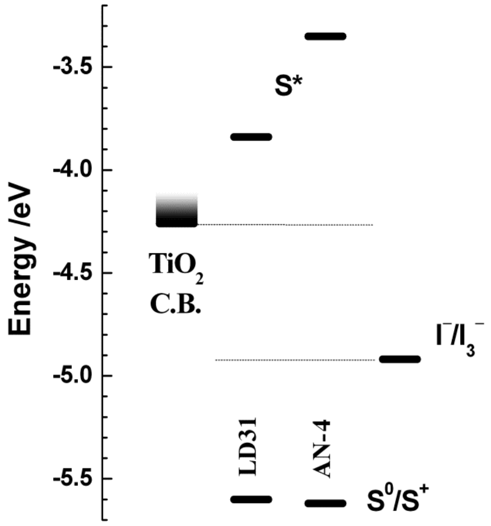


Fig. S4 Comparison of TiO_2, LD31, AN-4, and I^-/I_3^- energy levels.

Cell Fabrication and Photovoltaic Measurements:

The DSSC devices were fabricated with a titania working electrode and a Pt-coated counter electrode in a structure of sandwich type. For the working electrode, varied TiO_2 nanostructures – NP, NR and HD1-HD2 – were synthesized with the hydrothermal methods reported elsewhere; ethyl cellulose and α-terpineol were added to the ethanol solution of these TiO_2 nanostructures to prepare a viscous paste suitable for screen printing. The TiO_2 paste was then coated onto a $TiCl_4$-treated FTO glass substrate (TEC 7, Hartford, USA) to obtain a film of the required thickness (active size 0.4×0.4 cm^2) with repetitive screen printing. The annealing temperature was kept at 125 °C for 6 min for each layer, and the film thickness of a typical screen-printing layer was 3-4 μm. The TiO_2 films, as prepared according to either a ML or a BL configuration to fabricate devices A-D, were annealed according to a programmed procedure. The annealed films were treated with fresh $TiCl_4$ aqueous solution (40 mM) at 70 °C for 30 min and sintered at 500 °C for 30 min. The dye uptake on these TiO_2 films was performed in a solution (LD14, AN-4 and LD31 dyes, 1.5×10^{-4} M) containing chenodeoxycholic acid (CDCA, 7.5×10^{-4} M) in an equi-volume mixture of toluene and ethanol at 25 °C for 2-3 h. For the co-sensitized system, the cocktail solution contained LD31 and AN-4 in a molar ratio of 2/1. The counter electrode was made on spin-coating the H_2PtCl_6/isopropanol solution onto a FTO glass substrate through a typical procedure of thermal decomposition. The two electrodes were assembled into a cell of sandwich type and sealed with a spacer of thickness 40 μm. The electrolyte injected into the device contained I_2 (0.05 M), LiI (0.1 M), PMII (1.0 M), 4-*t*-butylpyridine (0.5 M) in a co-solvent containing acetonitrile and valeronitrile with a volume ratio 85/15.

The current-voltage (*J*–*V*) characteristics of the DSSC devices covered with a black mask (aperture area 0.2025 cm^2) were determined with a solar simulator (AM 1.5G, XES-40S1, SAN-EI). The spectra of incident photon-to-current conversion efficiency (IPCE) of the corresponding devices were measured with a system comprising a Xe lamp (A-1010, PTi, 150 W), monochromator (PTi, 1200 gr mm^{-1} blazed at 500 nm) and source meter (Keithley 2400). The measurements of charge extraction (CE) and transient photovoltage decay (CVD) were reported elsewhere.

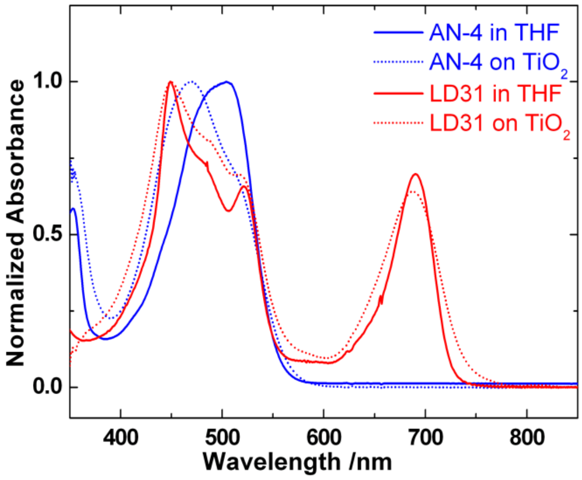


Fig. S5 Absorption spectra of AN-4 (blue curves) and LD31 (red curves) in THF (solid lines) or on TiO2 films (dotted lines).

Table S2. Photovoltaic parameters of DSSCs made of LD14 dye and TiO_2 photoanodes with various film configurations denoted as A - D.[a]

Device	TiO_2 Film Configuration	cell	J_{SC} /mA cm^{-2}	V_{OC} /mV	FF	η /%
A	4NP/3SL	*a*	16.82	716	0.713	8.59
		b	16.87	710	0.713	8.54
		c	16.86	712	0.709	8.51
		average	16.85±0.02	713±2	0.712±0.002	8.55±0.03
B	1NP/3NR/3SL	*a*	17.67	714	0.704	8.88
		b	17.62	714	0.706	8.88
		c	17.56	708	0.709	8.81
		average	17.62±0.04	712±3	0.706±0.003	8.86±0.03
C	1NP/1HD1/1HD3/3SL	*a*	17.81	730	0.709	9.22
		b	17.69	721	0.721	9.20
		c	17.76	721	0.715	9.16
		average	17.75±0.05	724±4	0.715±0.006	9.19±0.02
D	5HD1/3SL	*a*	17.73	738	0.719	9.41
		b	17.39	743	0.723	9.34
		c	17.39	733	0.727	9.27
		average	17.50±0.16	738±4	0.723±0.004	9.34±0.06

[a] All TiO_2 working electrodes (labeled as *a*-*c*) were fabricated under the same experimental conditions; under simulated AM-1.5G illumination (power density 100 mW·cm^{-2}) and active area 0.16 cm^2 with a black mask of area 0.2025 cm^2; the averaged values were obtained from three devices under identical conditions.

Table S3. Photovoltaic parameters of DSSCs made of LD31, AN-4 and the co-sensitized LD31/AN-4 system.[a]

Dye	cell	J_{SC} /mA·cm^{-2}	V_{OC} /mV	FF	η /%
LD31	*a*	19.77	698	0.723	9.98
	b	20.21	701	0.703	9.96
	c	20.09	697	0.708	9.91
	average	20.02±0.23	699±2	0.711±0.01	9.95±0.04
AN-4	*a*	8.86	692	0.726	4.45
	b	8.86	690	0.727	4.44
	c	8.82	693	0.725	4.43
	average	8.85±0.02	692±2	0.726±0.001	4.44±0.01
LD31/AN-4	*a*	20.54	700	0.716	10.30
	b	20.38	699	0.722	10.29
	c	19.90	712	0.715	10.18
	average	20.27±0.33	704±7	0.718±0.004	10.26±0.07

[a] All TiO_2 working electrodes (labeled as *a*-*c*) were fabricated under the same experimental conditions with photoanode configuration D; under simulated AM-1.5G illumination (power density 100 mW·cm^{-2}) and active area 0.16 cm^2 with a black mask of area 0.2025 cm^2; the averaged values were obtained from three devices under identical conditions.

References:

S1. K. E. Splan and J. T. Hupp, *Langmuir*, 2004, **20**, 10560-10566.

S2. J. Zeitouny, C. Aurisicchio, D. Bonifazi, R. D. Zorzi, S. Geremia, M. Bonini, C.-A. Palma, P. Samorı, A. Listorti, A. Belbakra and N. Armaroli, *J. Mater. Chem.*, 2009, **19**, 4715–4724.