Electronic Supplementary Information

Panchromatic Co-sensitization for Porphyrin-sensitized Solar Cells to Harvest Near Infrared Light Beyond 900 nm

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Experiments

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 syntheses (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 H₂O was found in the resulting fluid. For electrochemical measurements, THF was distilled over sodium under N₂. Pd(PPh₃)₄ catalyst (Strem, MA, USA) and Pd₂(dba)₃ (Acros Organics, NJ, USA). 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 NCKU), mass spectra (Microflex MALDI-TOF MS, Bruker Daltonics) were recorded with the indicated instruments.

Compound Synthesis and Characterization

The synthesis of LDD1 is depicted in Chart S1.

Compound 1: Di-brominated porphyrin (1420.98 g/mol, 300 mg, 0.281 mmol) was mixed with ester to form the anchoring group (160.17 g/mol., 0.253 mmol., 0.9 eq.) in THF (65 mL) and diethylamine (5 mL). After three cycles of freeze-pump-thaw, Pd(PPh₃)₄ (1156.15 g/mol, 43.9 mg, 15 mol %) and CuI (190.45 g/mol, 7.2 mg, 15 mol %) were added to the solution under an inert atmosphere in a glove box. The reaction was stirred at 40 °C for 20 h. The completion of the reaction was monitored with TLC. Upon completion, the solvent was removed with rotary evaporation. The residue was re-dissolved in CH₂Cl₂ for washes with NH₄Cl_(aq). After drying over Na₂SO₄, the solvent was removed with rotary evaporation. The residue was purified on a column chromatograph (silica gel, eluent THF/n-hexanes = 1/10), followed by crystallization from CH₂Cl₂/MeOH to give 86 mg of compound 1 (dark green solid, 1500.21 g/mol, yield = 22.7 %).

Compound 2: This synthesis is reported.¹

Compound 3: Compound 2 (1485.27 g/mol, 145 mg, 0.098 mmol) was mixed with (triisopropylsilyl)acetylene (182.38 m/mol, 0.22 mL, d = 0.813 g/mL, 0.98 mmol, 10 eq) in THF (65 mL) and triethylamine (5 mL). After three cycles of freeze-pump-thaw, Pd(PPh₃)₂Cl₂ (20 mol %) and CuI were added to the solution under an inert

atmosphere in a glove box. The reaction was stirred at 60 °C for 6 h. The completion of the reaction was monitored with TLC. Upon completion, the solvent was removed with rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for washing with $NH_4Cl_{(aq)}$. After drying over Na_2SO_4 , the solvent was removed with rotary evaporation. The residue was purified on a column chromatograph (silica gel, eluent THF/n-hexanes = 1/10), followed by crystallization from $CH_2Cl_2/MeOH$ to give compound 3 (dark green solid, 1586.74 g/mol, 150 mg, yield = 96.8 %).

Compound 4: Compound 3 (1586.74 g/mol, 90 mg, 0.056 mmol.) was mixed with tetrabutylammonium fluoride (261.46 m/mol, 0.57 mL, 0.06 mmol, 1 eq) in dry and de-gassed THF (20 mL). The reaction was stirred in the dark at 0° C for 1 h. Upon completion, the solvent was removed with rotary evaporation. The residue was redissolved in CH_2Cl_2 for washing with $NH_4Cl_{(aq)}$. After drying over Na_2SO_4 , the solvent was removed with rotary evaporation. The residue on a column chromatograph (silica gel, eluentTHF/n-hexanes = 1/10) to give compound 4 (dark green oil, 1430.40 g/mol, 80 mg, yield = 98.6 %).

Compound 5: Compound 4 (1430.40 g/mol, 80 mg, 0.056 mmol) was mixed with compound 1 (1500.21 g/mol, 75.5 mg, 0.253 mmol, 0.9 eq) in THF (65 mL) and triethylamine (5 mL). After three cycles of freeze-pump-thaw, Pd(PPh₃)₄ (15 mol %) and CuI were added to the solution under an inert atmosphere in a glove box. The reaction was stirred at 40 °C for 40 h. The completion of the reaction was monitored with TLC. Upon completion, the solvent was removed with rotary evaporation. The residue was re-dissolved in CH₂Cl₂ for washing with NH₄Cl_(aq). After drying over Na₂SO₄, the solvent was removed on a rotary evaporator. The residue was purified on a column chromatograph (silica gel, eluent THF/n-hexanes = 1/10), followed by crystallization from CH₂Cl₂/MeOH to give compound 5(dark brown solid, 2849.73 g/mol, 62 mg, yield = 43.2 %).

LDD1: Compound 5 (62 mg, 0.022 mmol.) was dissolved in THF (180 mL) and MeOH (60 mL). After addition of NaOH_(aq), (8.33 M, 30 mL) the solution was stirred at 50 °C for 3 h. The completion of the reaction was monitored with TLC. Upon completion, the solvent was removed with a rotary evaporator. The residue was redissolved in CH₂Cl₂ for washing with NH₄Cl_(aq). After drying over Na₂SO₄, the solvent was removed on a rotary evaporator. The residue was purified on a column chromatograph (silica gel, eluent MeOH/CH₂Cl₂ = 1/9), followed by crystallization from CH₂Cl₂/MeOH to give LDD1 (dark brown solid, 2835.70 g/mol, 55 mg, yield = 89.1 %).

Characterization data

LDD1:¹H-NMR (THF-d₈ at 1.73 ppm and 3.58 ppm): $\delta_{\rm H} = 10.29$ (d, J = 4.2Hz, 2H), 10.26 (d, 4.2Hz, 2H), 9.62 (d, 4.2Hz, 2H), 9.59 (d, 4.2Hz, 2H), 8.92 (d, overlapped,

4.5 Hz, 2H), 8.91 (d, overlapped, 4.7 Hz, 2H), 8.82 (d, 4.2 Hz, 2H), 8.76 (d, 4.3 Hz, 2H), 8.23 (d, 8.2 Hz, 2H), 8.11 (d, 8.2 Hz, 2H), 7.86 (d, 8.5 Hz, 2H), 7.77-7.67 (2t, overlapped, 4H), 7.11 (d, overlapped, 8.6 Hz, 4H), 7.10 (d, overlapped, 8.7 Hz, 4H), 6.91 (d, 8.8 Hz, 2H), 3.93 (t, 6.5 Hz, 16H), 3.10 (s, 6H), 1.20~0.54 (overlapped, 209H). Elemental analysis: calc for $C_{181}H_{243}N_9O_{10}Zn_2 \cdot 2 H_2O C 75.70$ %, H 8.67 %, N 4.39 %; found C 75.58 %, H 8.51 %, N 4.05 %. MALDI-TOF : *m/z* calc for $C_{181}H_{243}N_9O_{10}Zn_2$ 2830.74; found 2830.82.

Chart S1. Synthetic route of LDD1



Cell Fabrication and Photovoltaic Measurements

The PSSC devices were fabricated with a working electrode (titania) and a counter electrode (Pt-coated) in a sandwich-type structure. For the working electrode, octahedral TiO₂ nanocrystals (HD1) were synthesized with hydrothermal methods reported elsewhere;² ethyl cellulose and α -terpinol were added to the ethanol solution of these TiO₂ nanostructures to prepare a viscous paste suitable for screen printing. The TiO₂ paste was coated onto a TiCl₄-treated FTO glass substrate (TEC 7, Hartford, USA) to obtain a film of thickness 15 µm with repetitive screen printing. The film thickness of a scattering layer (ST41A) was 8 µm; the active size of the device was 0.4×0.4 cm². The TiO₂ films were annealed according to 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 annealed films were treated with fresh TiCl₄ aqueous solution (40 mM) at 70 °C for 30 min and sintered at 500 °C for 30 min. The dye uptake of LD14 on these TiO_2 films was performed in a solution (0.15 mM) with an equi-volume mixture of toluene and ethanol at 25 °C for 1-2 h. For the cosensitized system, the two-dye cocktail solution contained LD14 (0.15 mM) and LDD1 (0.015, 0.03 and 0.15 mM) in the presence of CDCA (0.45 mM). The counterelectrode was made on spin-coating the H₂PtCl₆/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 (thickness 40 μ m). The electrolyte injected into the device contained I₂ (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 (volume ratio 85/15).

The current-voltage (J-V) characteristics of the DSSC devices covered with a black mask (aperture area 0.2025 cm²) were determined with a solar simulator (AM 1.5G, XES-40S1, SAN-EI). The spectra of efficiency of conversion of incident photons to current (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). Intensity-modulated photovoltage spectra (IMVS) and charge extraction (CE) were measured with CIMPS instruments (Zahner) reported elsewhere.³

References

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