Supporting Information

Visible-Near-Infrared Absorbing A-π₂-D-π₁-D-π₂-A Type Dimeric Porphyrin Donor for High Performance Organic Solar Cells

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Experimental Procedures

Characterization

$^1$H NMR spectra were recorded using a Bruker Ultrashield 400 Plus NMR spectrometer. High-resolution matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained with a Bruker Autoflex MALDI-TOF mass spectrometer. UV-Vis spectra of dilute solutions ($1 \times 10^{-5} \text{ M}$) of samples in dichloromethane (DCM) were recorded at room temperature (ca. 25°C) using a Shimadzu UV-3600 spectrophotometer. Solid films for UV-Vis spectroscopic analysis were obtained by spin-coating the molecule solutions onto a quartz substrate. Cyclic voltammetry (CV) of the molecule solution was performed using a Versastat II electrochemical workstation in a standard three-electrode configuration equipped with a silver wire pseudo-reference, platinum wire counter electrode and glassy carbon working electrode. The cyclic voltammetry experiments were performed in an anhydrous solution of dichloromethane (CH$_2$Cl$_2$) with ~0.1 M tetrabutylammoniumhexafluorophosphate (TBAPF$_6$) supporting electrolyte. The potentials were measured against an Ag/Ag$^+$ (0.01 M AgNO$_3$) reference electrode; the ferrocene/ferrocenium ion (Fc/Fc$^+$) pair was used as the external standard. Samples were scanned at a rate of 50 mV/s following a dry N$_2$ purge to deoxygenate the solution. The onset potentials were determined from the intersection of two tangents drawn at the rising and background currents of the cyclic voltammograms. Estimations of the energy levels were obtained by correlating the onset ($E_{\text{ox}}$ Fc/Fc$^+$, $E_{\text{red}}$ Fc/Fc$^+$) to the normal hydrogen electrode (NHE), assuming a IP energy of 4.80 eV for Fc/Fc$^+$. Optical band gap estimated from the formula of $\frac{1240}{\lambda_{\text{onset}}}$, $\lambda_{\text{onset}}$ is the absorption onset of the film spectrum. The IP and EA values were calculated by the the oxidation and reduction potentials in solution: $E_{\text{IP}} = E_{\text{ox}} + 4.8 \text{ (eV)}$, $E_{\text{EA}} = E_{\text{red}} + 4.8 \text{ (eV)}$. And HOMO and LUMO energies can be also given by the following equation: $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8) \text{ (eV)}$, $E_{\text{LUMO}} = -(E_{\text{red}} + 4.8) \text{ (eV)}$. 

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Device Fabrication

Solution-processed bulk-heterojunction solar cells were fabricated as follows: Indium tin oxide (ITO) coated glass substrates were cleaned prior to device fabrication by sonication in acetone, detergent, distilled water, and isopropyl alcohol. After treated with an oxygen plasma for 5 min, 40 nm thick poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) (Bayer Baytron 4083) layer was spin-coated on the ITO-coated glass substrates at 2500 rpm for 30s, the substrates were subsequently dried at 150°C for 10 min in air and then transferred to a N₂-glovebox. The active layers were spun from solution of donor material:PC₇₁BM at weight ratio of 4:5 (or other ratio) with an overall concentration of 20 mg/mL. The thicknesses of active layers were measured by a profilometer. Finally, Al (~80 nm) was evaporated with a shadow mask as the top electrode. The effective area was measured to be 16 mm². Hole mobilities of the blends were measured by the space charge limited current (SCLC) method using ITO/PEDOT:PSS/CS-DP:PC₇₁BM/MoO₃/Al device structure.

Device Characterization and Measurement

The values of power conversion efficiency were determined from J-V characteristics measured by a Keithley 2400 source-measurement unit under AM 1.5G spectrum from a solar simulator (Oriel model 91192). Masks made from laser beam cutting technology with a well-defined area of 16 mm² were attached to define the effective area for accurate measurement. Solar simulator illumination intensity was determined using a monocrystal silicon reference cell (Hamamatsu S1133, with KG-5 visible color filter) calibrated by the National Renewable Energy Laboratory (NREL). The active layer was spin coated from blend chloroform or chlorobenzene solutions with a weight ratio of donor materials and PC₇₁BM at 1:1 (or other ratios) and then was placed in a glass petri dish containing 0.3 mL THF for 15s for solvent vapor annealing. The atomic force microscopy (AFM) measurements of the surface morphology of blend films were conducted on a NanoScope NS3A system (Digital Instrument). External quantum efficiency (EQE) values of the encapsulated devices were measured by using an integrated system (Enlitech, Taiwan, China) and a lock-in amplifier with
a current preamplifier under short-circuit conditions. The devices were illuminated by monochromatic light from a 100 W xenon lamp. The light intensity was determined by using a calibrated silicon photodiode.

**Morphology Characterization**

Grazing-incidence wide-angle X-ray scattering (GIWAXS) was done at either beamline 7.3.3 Lawrence Berkeley National Lab (LBNL). The sample was put inside a helium chamber, and Pilatus 2M detector was used to collect the signal. GIWAXS results were analyzed using Nika software package and peak information was accessed by gaussian fitting. RSoXS was performed at beamline 11.0.1.2 Lawrence Berkeley National Lab. Thin films was flowed and transferred S\textsubscript{16} onto Si\textsubscript{3}N\textsubscript{4} substrate and experiment was done in transition mode. AFM was performed on a Digital Instruments Dimension 3100, operating in tapping mode.

**Device Optimization**

Devices were optimized in the 1) donor:acceptor ratio; 2) solvent vapour annealing time.
Figure S1. (a) Current density-voltage ($J-V$) curves of difference rate of CS-DP:PC$_{71}$BM devices; (b) Current density-voltage ($J-V$) curves of CS-DP:PC$_{71}$BM (4:5) with SVA devices.

Table S1. Photovoltaic performance of the solar cells based on CS-DP/PC$_{71}$BM with different mixture rate under illumination of AM 1.5 G, 100 mW cm$^{-2}$.

<table>
<thead>
<tr>
<th>Rate</th>
<th>Additive</th>
<th>Annealing °C</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE (best) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0:1.0</td>
<td>3% Pyridine</td>
<td>90</td>
<td>8.30</td>
<td>0.828</td>
<td>39.8</td>
<td>2.73±0.15(2.89)</td>
</tr>
<tr>
<td>1.0:1.25</td>
<td>3% Pyridine</td>
<td>90</td>
<td>9.50</td>
<td>0.837</td>
<td>42.2</td>
<td>3.36±0.23(3.58)</td>
</tr>
<tr>
<td>1.0:1.5</td>
<td>3% Pyridine</td>
<td>90</td>
<td>8.89</td>
<td>0.840</td>
<td>43.3</td>
<td>3.22±0.1(3.32)</td>
</tr>
</tbody>
</table>

The average values are calculated from 16 devices with standard deviation.
Table S2. Photovoltaic performance of the solar cells based on CS-DP/PC$_7$1BM with different THF vapor annealing time under illumination of AM 1.5 G, 100 mW cm$^{-2}$.

<table>
<thead>
<tr>
<th>Treatment time (s)</th>
<th>Additive</th>
<th>Annealing °C</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE (best) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3% Pyridine</td>
<td>110</td>
<td>12.72</td>
<td>0.784</td>
<td>64.0</td>
<td>6.38±0.12(6.50)</td>
</tr>
<tr>
<td>20</td>
<td>3% Pyridine</td>
<td>110</td>
<td>15.14</td>
<td>0.781</td>
<td>69.8</td>
<td>8.23±0.06(8.29)</td>
</tr>
<tr>
<td>30</td>
<td>3% Pyridine</td>
<td>110</td>
<td>13.30</td>
<td>0.780</td>
<td>63.1</td>
<td>6.55±0.32(6.87)</td>
</tr>
</tbody>
</table>

The average values are calculated from 16 devices with standard deviation.

Synthetic Route

Synthesis of compound 1

PZnBr$_2$ (1 g, 1.055 mmol) was mixed 4-ethynyl-2,5-bis(hexyloxy)benzaldehyde (313.3 mg, 0.950 mmol, ~0.9 eq) in 50 ml of THF and 20 ml of triethylamine. After degassed with N$_2$ for 20 min, Pd(PPh$_3$)$_4$ (60 mg, 0.053 mmol) and CuI (10 mg, 0.053 mmol) were added to the solution under an N$_2$ atmosphere. 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 using CH$_2$Cl$_2$/n-hexanes = 1/2 as eluent to give compound 1 (403 mg, 32%). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 0.68–0.78 (m, 12H), 0.85–1.06 (m, 30H), 1.16–1.38 (m, 12H), 1.39–1.59 (m, 16H), 1.82 (m, 2H), 1.96 (m, 2H), 2.34 (m, 2H), 2.73 (m, 4H), 2.93 (m, 4H), 4.23 (m, 2H), 4.34 (m, 2H), 7.48 (s, 2H), 9.59–9.71 (m, 6H), 9.87 (m, 2H), 10.46 (s, 1H).

Synthesis of compound 2

Compound 1 (200 mg, 0.166 mmol), Pd(PPh$_3$)$_4$ (22 mg, 0.019 mmol), CuI (4 mg, 0.021 mmol) were mixed in THF (20 mL) and triethylamine (5 mL) to yield a green solution under nitrogen atmosphere. A solution of (triisopropylsilyl)acetylene (75 mg, 0.412 mmol) in triethylamine (5 mL) was slowly added to the reaction mixture at room temperature. The reaction mixture was then stirred at 40°C for overnight to give
deep green suspension. The completion of the reaction was verified by spot TLC. The solvent was then removed under reduced pressure, and the residue was chromatographed on silica gel using n-hexane as eluent to give compound 2 (156 mg, 72%). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 0.67–0.75 (m, 12H), 0.85–1.32 (m, 47H), 1.39–1.61 (m, 32H), 1.84 (m, 2H), 1.96 (m, 2H), 2.35 (m, 2H), 2.68 (m, 4H), 2.91 (m, 4H), 4.28 (t, $J$ = 6.4 Hz, 2H), 4.38 (t, $J$ = 6.4 Hz, 2H), 7.52 (s, 1H), 7.55 (s, 1H), 9.61 (t, $J$ = 4.4 Hz, 2H), 9.69 (d, $J$ = 4.8 Hz, 2H), 9.75 (dd, $J_1$ = 4.8 Hz, $J_2$ = 6.8 Hz, 2H), 9.92 (t, $J$ = 4.8 Hz, 2H), 10.53 (s, 1H).

**Synthesis of compound 3**

To a solution of compound 2 (150 mg, 0.115 mmol) was added TBAF (0.15 mL of 1.0 M solution in THF, 0.15 mmol) in THF (5 mL). The solution was stirred under N$_2$ for 30 min to obtain intermediate, and then added mixture of compound 1 (150 mg, 0.124 mmol) in dry THF (10 mL) and triethylamine (5 mL). The solution was degassed with dinitrogen for 20 min; then Pd(PPh$_3$)$_4$ (11 mg, 0.01 mmol) and CuI (2 mg, 0.01 mmol) were added to the mixture. The reaction mixture was then stirred at 50°C for overnight under nitrogen. The solvent was removed in vacuo, and the residue was purified on a column chromatograph (silica gel) using CHCl$_3$ as eluent. Recrystallization from CHCl$_3$/CH$_3$OH gave compound 3 (165 mg, 63%). Compound 3 does not show satisfied NMR spectra due to its expanded π structure. (MALDI-TOF, m/z) calculated for C$_{144}$H$_{198}$N$_8$O$_6$Zn$_2$: 2267.4032; found: 2267.3987.

**Synthesis of CS-DP**

Compound 3 (150 mg, 0.066 mmol) was dissolved in a solution of dry CHCl$_3$, two drops of piperidine and then 3-ethylrhodanine (106 mg, 0.66 mmol) were added, and the resulting solution was refluxed and stirred for 12h under argon. The reaction was quenched into water (30 mL). The aqueous layers were extracted with CHCl$_3$ (3 × 20 mL). The organic layer was dried over NaSO$_4$. After removal of solvent, it was purified by chromatography on a silica gel column using CHCl$_3$ as eluant and was purified by preparative thin layer chromatography using a CHCl$_3$ as eluents. Then the crude solid was recrystallized from CHCl$_3$ and CH$_3$OH mixture to afford CS-DP as a
gray green solid (102 mg, 60%). CS-DP does not show satisfied NMR spectra due to its expanded π structure. (MALDI-TOF, m/z) calculated for C_{154}H_{208}N_{10}O_{6}S_{4}Zn_{2}: 2553.2846; found: 2553.3750.

**Figure S2.** Thermogravimetric analysis of MP and CS-DP.

**Figure S3.** Absorption spectra of CS-DP/PC_{71}BM films under different processing conditions.
**Figure S4.** Cyclic voltammogram of MP and CS-DP measured in 0.1 mol L$^{-1}$ TBAPF$_6$ CH$_2$Cl$_2$ solutions.

**Figure S5.** The space charge limited current (SCLC) curves of CS-DP with additive. The sample without and with TA treatment exhibit a high hole mobilities of $7.75 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $1.40 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively.
Figure S6. Plots of key parameters dependent on the device processing conditions.

Figure S7. The $^1$H NMR (400 MHz) spectrum of compound 1 in CDCl$_3$. 
Figure S8. The $^1$H NMR spectrum of compound 2 in CDCl$_3$.

Figure S9. The $^1$H NMR spectrum of 3 in CDCl$_3$. 
Figure S10. The $^1$H NMR spectrum of CS-DP in CDCl$_3$.

Figure S11. The MALDI-TOF mass spectrum of compound 3.
Figure S12. The MALDI-TOF mass spectrum of CS-DP.