

Supporting Information

Towards High-Performance DPP-based Sensitizers for DSC Applications

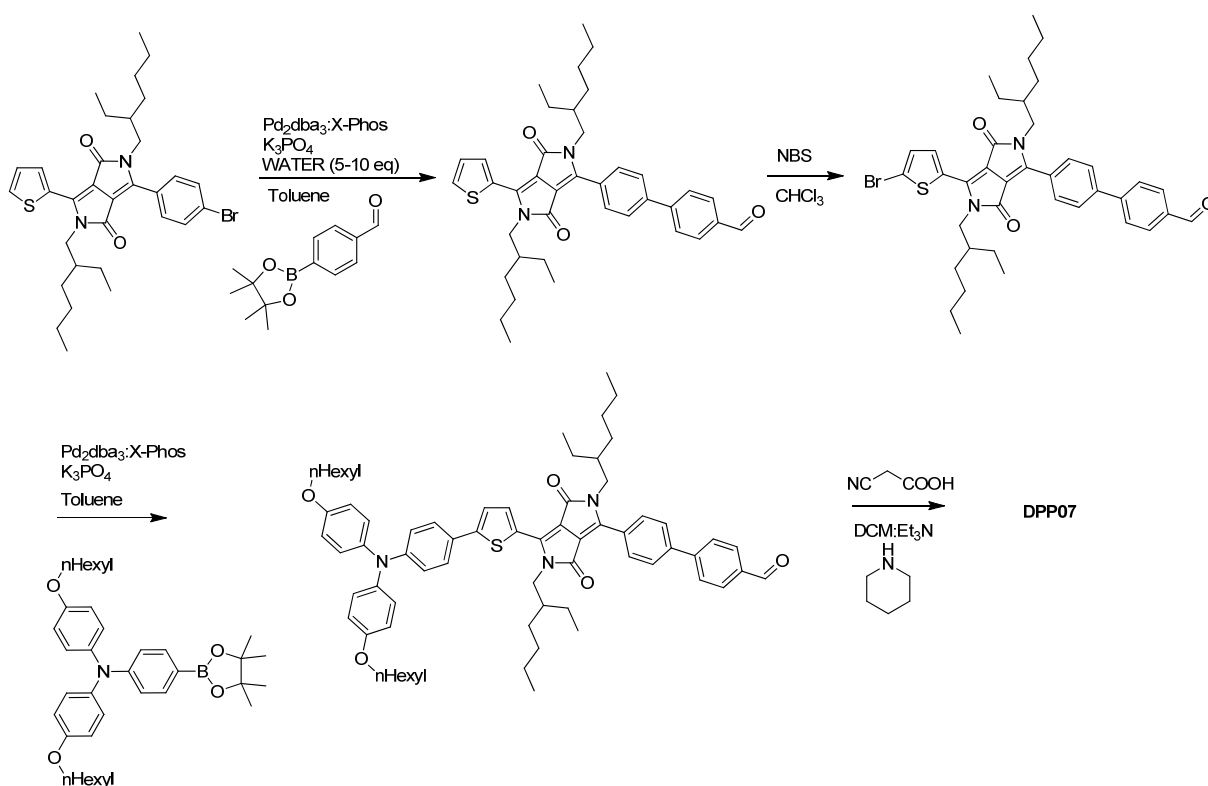
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Methods and Materials: All reagents from commercial sources were used without further purification, unless otherwise noted. All reactions were performed under dry N₂, unless otherwise noted. All dry reactions were performed with glassware that was flamed under high-vacuum and backfilled with N₂. All extracts were dried over powdered MgSO₄ and solvents removed by rotary evaporation under reduced pressure. Flash chromatography was performed using Silicycle UltraPure SilicaFlash P60, 40-63 µm (230-400 mesh). ¹H NMR spectra were recorded on a Bruker Avance-400 (400 MHz), Bruker AvanceIII-400 (400MHz), or Bruker DPX-400 (400 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CD₂Cl₂ at 5.32 ppm).

A general scheme (Scheme S1) for the synthesis of **DPP07**.



3-(4-bromophenyl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione was synthesized in an analogous method to what was reported in PCT Int. Appl. (2011), WO 2011144566 A2 20111124 and PCT Int. Appl. (2010), WO 2010144566 A1 20100506, both by BASF SE.

¹H NMR (400 MHz, Methylene Chloride-d₂) δ 8.90 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.71 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.67 (s, 4H), 7.30 (dd, *J* = 5.1, 3.9 Hz, 1H), 3.99 – 3.86 (m, 2H), 3.86 – 3.70 (m, 2H), 1.85 – 1.75 (m, 1H), 1.49 – 1.40 (m, 1H), 1.40 – 0.99 (m, 16H), 0.89 – 0.68 (m, 12H). ¹³C NMR (100 MHz, Methylene Chloride-d₂) δ 162.03, 161.79, 144.98, 135.49, 131.97, 131.26,

130.15, 129.76, 128.92, 128.28, 128.11, 127.69, 124.85, 45.44, 44.84, 39.06, 38.66, 30.22, 30.13, 30.11, 28.35, 28.23, 23.64, 23.45, 23.02, 22.81, 13.77, 13.70, 10.15

Th-DPP_EthHex-Ph-Benzaldehyde

In a 50 mL single-neck round-bottom flask, 1.1 grams of Th-DPP_EtHex-Ph-Br (1.84 mmol), 0.854 gram of 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-benzaldehyde (3.68 mmol), and 0.976 gram of potassium phosphate tribasic (4.59 mmol) were dissolved in 20 mL of toluene, 0.2 mL tAmylOH, and 0.1 mL water. This solution was degassed for 20 minutes with a stream of N₂, after which time 10 mg of Pd₂dba₃ and 20 mg of X-Phos were added simultaneously, in one batch. The reaction was then brought to 80 °C for 6 hours, and then diluted with DCM and loaded directly onto a large column loaded with 500 mL of silica. A gradient eluent of 40:60 Toluene:DCM to 100% DCM was used to purify the compound. 668 mg (58% yield) of a pure red solid was obtained.

¹H NMR (400 MHz, Methylene Chloride-d₂) δ 10.10 (s, 1H), 8.94 (dd, *J* = 3.9, 1.1 Hz, 1H), 8.07 – 7.98 (m, 2H), 7.98 – 7.92 (m, 2H), 7.92 – 7.83 (m, 4H), 7.74 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.33 (dd, *J* = 5.0, 3.9 Hz, 1H), 4.04 – 3.93 (m, 2H), 3.93 – 3.81 (m, 2H), 1.84 (p, *J* = 6.6 Hz, 1H), 1.55 – 1.48 (m, 1H), 1.44 – 1.04 (m, 16H), 0.96 – 0.85 (m, 6H), 0.85 – 0.69 (m, 6H). ¹³C NMR (100 MHz, Methylene Chloride-d₂) δ 191.63, 162.12, 161.94, 145.70, 142.05, 141.64, 135.76, 135.42, 131.17, 130.17, 129.32, 128.92, 128.27, 128.11, 127.69, 127.56, 125.19, 45.46, 44.94, 39.09, 38.69, 30.25, 30.16, 28.37, 28.24, 23.70, 23.46, 23.03, 22.80, 21.11, 13.77, 13.72, 10.19

BrTh-DPP_EthHex-Ph-Benzaldehyde

In a 50 mL single-neck round-bottom flask, 0.658 gram of Th-DPP_EthHex-Ph-Benzaldehyde (1.06 mmol) was dissolved in 20 mL of chloroform, and 0.198 gram NBS (1.11 mmol) was added in one batch at room temperature. This reaction was stirred for 2 hour at which point the solution was loaded directly onto a short silica column and eluted with 20:80 Tol:DCM. 211 mg (28% yield) of redish/purple solid was obtained.

¹H NMR (400 MHz, Methylene Chloride-d₂) δ 10.07 (s, 1H), 8.66 (d, *J* = 4.2 Hz, 1H), 8.03 – 7.97 (m, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.89 – 7.79 (m, 4H), 7.28 (d, *J* = 4.1 Hz, 1H), 3.95 – 3.78 (m, 4H), 1.80 (p, *J* = 6.6 Hz, 1H), 1.52 – 1.45 (m, 1H), 1.43 – 1.00 (m, 16H), 0.87 (td, *J* = 7.4, 1.9 Hz, 6H), 0.75 (dt, *J* = 17.5, 7.0 Hz, 6H). ¹³C NMR (100 MHz, Methylene Chloride-d₂) δ 191.63, 162.69, 161.86, 145.70, 141.77, 140.60, 135.32, 134.07, 131.41, 130.17, 129.31, 128.62, 127.69, 127.58, 127.69, 127.56, 125.19, 45.54, 44.99, 39.10, 38.67, 30.70, 30.23, 28.32, 28.22, 23.69, 23.47, 23.00, 22.79, 21.11, 13.77, 13.71, 10.18

HexOTPA-Th-DPP_EthHex-Ph-Benzaldehyde

The reaction and purification was performed in the same manner as for Th-DPP_EthHex-Ph-Benzaldehyde.

200 mg (62% yield) of a purple-ish solid was obtained.

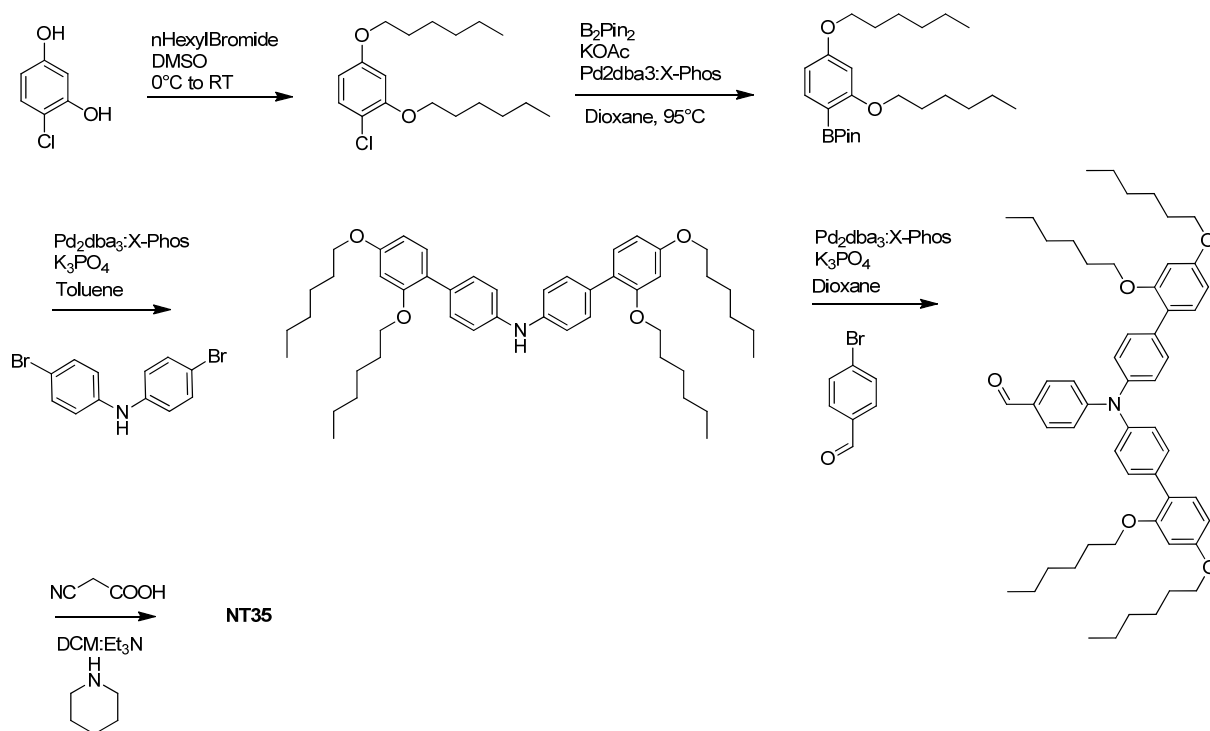
^1H NMR (400 MHz, Methylene Chloride- d_2) δ 10.07 (s, 1H), 9.06 (d, J = 4.1 Hz, 1H), 8.01 – 7.96 (m, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.89 – 7.79 (m, 4H), 7.52 – 7.47 (m, 2H), 7.38 (d, J = 4.2 Hz, 1H), 7.11 – 7.03 (m, 4H), 6.93 – 6.82 (m, 6H), 4.04 – 3.91 (m, 6H), 3.87 (td, J = 6.9, 3.8 Hz, 2H), 1.92 (p, J = 6.6 Hz, 1H), 1.77 (dt, J = 14.6, 6.7 Hz, 4H), 1.53 – 1.42 (m, 4H), 1.42 – 1.04 (m, 22H), 0.99 – 0.82 (m, 12H), 0.82 – 0.69 (m, 6H). ^{13}C NMR (100 MHz, Methylene Chloride- d_2) δ 191.63, 162.32, 161.75, 156.24, 151.41, 149.79, 145.76, 144.21, 142.37, 141.33, 139.63, 137.85, 135.71, 130.16, 129.29, 128.97, 127.66, 127.51, 127.24, 126.89, 126.75, 124.05, 122.66, 119.06, 115.31, 110.23, 107.32, 68.29, 45.53, 44.98, 39.21, 38.71, 31.58, 30.26, 29.26, 28.51, 28.26, 28.25, 25.69, 23.71, 23.58, 23.07, 22.81, 22.61, 13.82, 13.79, 13.73, 10.26, 10.22, 10.21

DPP07, HexOTPA-Th-DPP_EthHex-Ph-PhenylCAA

In a 25 mL single-neck round-bottom flask, 186 mg of HexOTPA-Th-DPP_EthHex-Ph-Benzaldehyde (0.17 mmol) and 120 mg cyanoacetic acid (1.41 mmol) was dissolved in 3 mL DCM, 1.5 mL triethylamine, and 1 drop piperidine. A spatula of MgSO_4 was added to this reaction and then heated to 40 °C overnight. In the morning, the reaction was diluted with DCM and extracted with a water and acetic acid solution, and then pure water. Crude product was rotovapped and then loaded onto a silica column and eluted with 2:3:95 acetic acid:methanol:DCM eluent. 107 mg (55% yield) of purplish/blue solid was obtained.

^1H NMR (400 MHz, Methylene Chloride- d_2) δ 9.06 (d, J = 4.2 Hz, 1H), 8.32 (d, J = 1.7 Hz, 1H), 8.16 – 8.10 (m, 2H), 7.91 (d, J = 8.5 Hz, 2H), 7.88 – 7.79 (m, 4H), 7.53 – 7.47 (m, 2H), 7.39 (d, J = 4.1 Hz, 1H), 7.13 – 7.04 (m, 4H), 6.92 – 6.83 (m, 6H), 4.04 – 3.91 (m, 6H), 3.91 – 3.83 (m, 2H), 1.91 (p, J = 6.6 Hz, 1H), 1.77 (dt, J = 14.6, 6.6 Hz, 4H), 1.46 (p, J = 7.1 Hz, 4H), 1.41 – 1.03 (m, 22H), 0.97 – 0.81 (m, 12H), 0.81 – 0.70 (m, 6H). $\text{C}_{64}\text{H}_{78}\text{N}_4\text{O}_6\text{S}_2[\text{M}^+]$ Exact Mass = 1132.6112, MS (MALDI) = 1132.6071

A general scheme (Scheme S2) for the synthesis of **NT35**.



Bishexyloxy-4-chloro-resorcinol

In a 100 mL single-neck round-bottom flask, 10.00 grams of 4-chlororesorcinol (69.18 mmol) and 9.7 grams of potassium hydroxide (172.87 mmol) were dissolved in 70 mL of DMSO. This solution was cooled to 0°C. 34.26 grams of nHexylbromide (207.55 mmol) was then added via syringe. After stirring for 30 minutes at 0°C, the reaction was removed from the ice-bath and allowed to warm to RT overnight. The reaction was extracted with hexanes and washed with plenty of water. Silica gel chromatography with 100% hexanes was performed until the product started to elute, and then the eluent was increased in polarity to 20:80 DCM:Hexanes until all the product was eluted. 20 grams (93% yield) of a pure clear oil was obtained.

^1H NMR (400 MHz, Methylene Chloride- d_2) δ 7.21 (d, J = 8.7 Hz, 1H), 6.52 (d, J = 2.8 Hz, 1H), 6.42 (dd, J = 8.7, 2.7 Hz, 1H), 3.99 (t, J = 6.6 Hz, 2H), 3.92 (t, J = 6.6 Hz, 2H), 1.90 – 1.69 (m, 4H), 1.51 – 1.42 (m, 4H), 1.41 – 1.28 (m, 8H), 0.99 – 0.86 (m, 6H). ^{13}C NMR (100 MHz, Methylene Chloride- d_2) δ 159.06, 155.20, 129.87, 113.92, 105.76, 101.26, 69.02, 68.32, 31.60, 31.54, 29.21, 29.04, 25.68, 25.62, 22.63, 22.61, 13.82, 13.81

2-(2,4-bis(hexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

In a 100 mL single-neck round-bottom flask, 8.56 grams of bishexyloxy-4-chloro-resorcinol (27.36 mmol), 10.42 grams of Bis(pinacolato)diboron (41.03 mmol), and 8.06 grams potassium acetate (82.12 mmol) were dissolved in 60 mL of dioxane. This solution was degassed for 20 minutes with a stream of N₂, after which time 10 mg of Pd₂dba₃ and 20 mg of X-Phos were added simultaneously, in one batch. The reaction was then brought to 95 °C for 10 hours. The reaction was then cooled to RT, and plugged through a thin pad of MgSO₄ with DCM. The crude product was purified with gradient silica gel chromatography: 100% hexanes to 20:80 Hex:DCM. 6.23 grams (70% yield) of a pure clear oil was obtained.

¹H NMR (400 MHz, Methylene Chloride-d₂) δ 7.54 (d, *J* = 8.2 Hz, 1H), 6.46 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.40 (d, *J* = 2.2 Hz, 1H), 3.96 (dt, *J* = 14.4, 6.4 Hz, 4H), 1.85 – 1.72 (m, 4H), 1.61 – 1.42 (m, 4H), 1.41 – 1.34 (m, 8H), 1.32 (s, 12H), 0.99 – 0.86 (m, 6H). ¹³C NMR (100 MHz, Methylene Chloride-d₂) δ 165.58, 163.11, 137.71, 129.65, 105.10, 99.20, 83.17, 82.81, 68.20, 67.88, 31.66, 31.58, 29.32, 29.20, 25.68, 25.67, 24.83, 24.64, 22.71, 22.60, 13.88, 13.80.

Bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amine

In a 25 mL single-neck round-bottom flask, 1.5 grams of bis(4-bromophenyl)amine (4.59 mmol), 3.99 grams of 2-(2,4-bis(hexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9.86 mmol), and 2.92 grams potassium acetate (13.76 mmol) were dissolved in 10 mL of toluene, 0.2 mL tAmylOH, and 0.1 mL water. This solution was degassed for 20 minutes with a stream of N₂, after which time 10 mg of Pd₂dba₃ and 20 mg of X-Phos were added simultaneously, in one batch. The reaction was then brought to 80 °C for 10 hours. The reaction was then cooled to RT, and plugged through a thin pad of MgSO₄ with DCM. The crude product was purified with silica gel chromatography: 10:90 Et₂O:Hex. 2.26 grams (68% yield) of a pure clear oil, which solidifies in time to a grey wax, was obtained.

¹H NMR (400 MHz, Methylene Chloride-d₂) δ 7.44 (d, *J* = 8.3 Hz, 4H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 4H), 6.54 (d, *J* = 7.5 Hz, 4H), 5.88 (s, 1H), 3.98 (dt, *J* = 9.7, 6.6 Hz, 8H), 1.77 (tt, *J* = 14.7, 6.8 Hz, 8H), 1.47 (qd, *J* = 13.4, 11.7, 6.9 Hz, 8H), 1.35 (dh, *J* = 14.4, 3.7 Hz, 16H), 0.92 (dt, *J* = 10.5, 6.7 Hz, 12H). ¹³C NMR (100 MHz, Methylene Chloride-d₂) δ 159.48, 156.94, 141.53, 131.08, 130.61, 130.26, 123.01, 116.95, 105.33, 100.17, 68.33, 68.12, 31.65, 31.51, 29.33, 29.15, 25.81, 25.76, 22.66, 22.62, 13.85, 13.84

4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)benzaldehyde

In a 25 mL single-neck round-bottom flask, 0.269 gram of 4-bromobenzaldehyde (1.45 mmol), 10.42 grams of Bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amine (1.38 mmol), and 0.587 gram tribasic potassium phosphate (2.76 mmol) were dissolved in 6 mL of dioxane. This solution was degassed for 20 minutes with a stream of N₂, after which time 10 mg of Pd₂dba₃ and 20 mg of X-Phos were added simultaneously, in one batch. The reaction was then brought to 75 °C for 10 hours. The reaction was then cooled to RT, and plugged through a thin pad of MgSO₄ with

DCM. The crude product was purified with gradient silica gel chromatography: a gradient from 100% hexanes to 100% DCM. 1.05 grams (83% yield) of a pure yellow oil was obtained.

^1H NMR (400 MHz, Methylene Chloride- d_2) δ 9.80 (s, 1H), 7.68 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.5 Hz, 4H), 7.24 (dd, J = 15.5, 8.8 Hz, 6H), 7.10 (d, J = 8.7 Hz, 2H), 6.59 – 6.48 (m, 4H), 4.01 (td, J = 6.5, 4.4 Hz, 8H), 1.87 – 1.70 (m, 8H), 1.53 – 1.26 (m, 24H), 1.02 – 0.80 (m, 12). ^{13}C NMR (10 MHz, Methylene Chloride- d_2) δ 190.03, 159.92, 156.97, 153.36, 144.15, 135.47, 131.01, 130.81, 130.57, 128.94, 125.65, 122.24, 119.05, 105.42, 100.10, 68.36, 68.12, 31.59, 31.43, 29.26, 29.05, 25.74, 25.70, 22.62, 22.56, 13.80, 13.78

NT35, 3-(4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)-2-cyanoacrylic acid

In a 50 mL single-neck round-bottom flask, 1 gram of 4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)benzaldehyde (1.21 mmol) and 560 mg cyanoacetic acid (6.58 mmol) was dissolved in 10 mL DCM, 5 mL triethylamine, and 0.1 mL piperidine. Several spatulas of MgSO_4 were added to this reaction and then it was heated to 40 °C overnight. In the morning, the reaction was diluted with DCM and extracted with a water and acetic acid solution, and then pure water. Crude product was rotovapped and then loaded onto a silica column and eluted with 2:3:95 acetic acid:methanol:DCM eluent. 550 mg (51% yield) of red solid was obtained.

^1H NMR (400 MHz, Methylene Chloride- d_2) δ 8.14 (s, 1H), 7.90 (d, J = 9.1 Hz, 2H), 7.56 (d, J = 8.5 Hz, 4H), 7.31 – 7.20 (m, 6H), 7.07 (d, J = 9.0 Hz, 2H), 6.63 – 6.51 (m, 4H), 3.98 (td, J = 6.5, 4.5 Hz, 8H), 1.85 – 1.68 (m, 8H), 1.56 – 1.22 (m, 24H), 1.00 – 0.79 (m, 12H). $\text{C}_{58}\text{H}_{72}\text{N}_2\text{O}_6[\text{M}^+]$ Exact Mass = 892.5390, MS (MALDI) = 892.5385

DSC fabrication and characterization:

DSC fabrication: The nanocrystalline TiO_2 pastes were prepared using a previously reported procedure.¹ The TiO_2 transparent electrodes composed of ~20 nm anatase on fluorine doped thin oxide (FTO, 4 mm thickness, 10 ohms/sq, Nippon Sheet Glass, Japan) conducting glass were controlled to get a desired thickness by the number of screen printing passes. A 4~5 μm scattering layer (400 nm, CCIC, HPW-400) was printed on the top of the transparent layer to increase light path length by scattering. The TiO_2 electrodes were immersed into a 0.025 mM solution of DPP07 with 2.5 mM $3\alpha,7\alpha$ -dihydroxy-5 β -cholic acid (chenodeoxycholic acid) in 4-*tert*-butanol/acetonitrile mixture (1:1 v/v) and kept for 15 h at room temperature. An equivalent concentration of a co-dye i.e. NT35 or D35 is contained in DPP07 solution for co-sensitization. The applied electrolyte consists of 0.6 M 1,3-dimethylimidazolium iodide, 0.03 M I_2 , 0.05 M LiI, 0.05 M guanidinium thiocyanate, and 0.25 M 4-*tert*-butylpyridine in 15/85 (v/v) mixture of valeronitrile and acetonitrile. The dye-adsorbed TiO_2 electrode and platinized counter electrode on FTO (TEC 15 ohms/sq, Pilkington) were assembled into a sealed sandwich type cell with a gap of a hot-melt ionomer film, Surlyn (25 μm , Du-Pont).

DSC characterization: A 450 W xenon light source (Oriel, USA) was used to characterize the solar cells. The spectral output of the lamp was matched in the region of 350–750 nm with the aid of a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) so as to reduce the mismatch between the simulated and true solar spectra to less than 4 %. The current–voltage characteristics of the cell under these conditions were obtained by applying external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). For IPCE measurement, a modulated light intensity data acquisition system was used to control the Incident Photon-to-Current conversion Efficiency (IPCE) measurement. The modulation frequency was about 1 Hz. Light from a 300 W Xenon lamp (ILC Technology, USA) was focused through a computer controlled Gemini-180 double monochromator (Jobin Yvon Ltd., UK) onto the photovoltaic cell under test. A white light bias was used to bring the total light intensity on the device under test closer to operating conditions. The devices were masked to attain an illuminated active area of 0.2 cm². Photovoltage transients were observed by using a pump pulse generated by 4 red light emitting diodes controlled by a fast solid-state switch with a white light bias. The pulse of red light with widths of 50 ms was incident on the photoanode side of the cell, and its intensity was controlled to keep a suitably low level to generate the exponential voltage decay where the charge recombination rate constants are obtained directly from the exponential decay rate.² A white bias light, also incident on the same side of the device, was supplied by white diodes. Small perturbation transient photocurrent measurements were performed in a similar manner to the open-circuit voltage decay measurement.

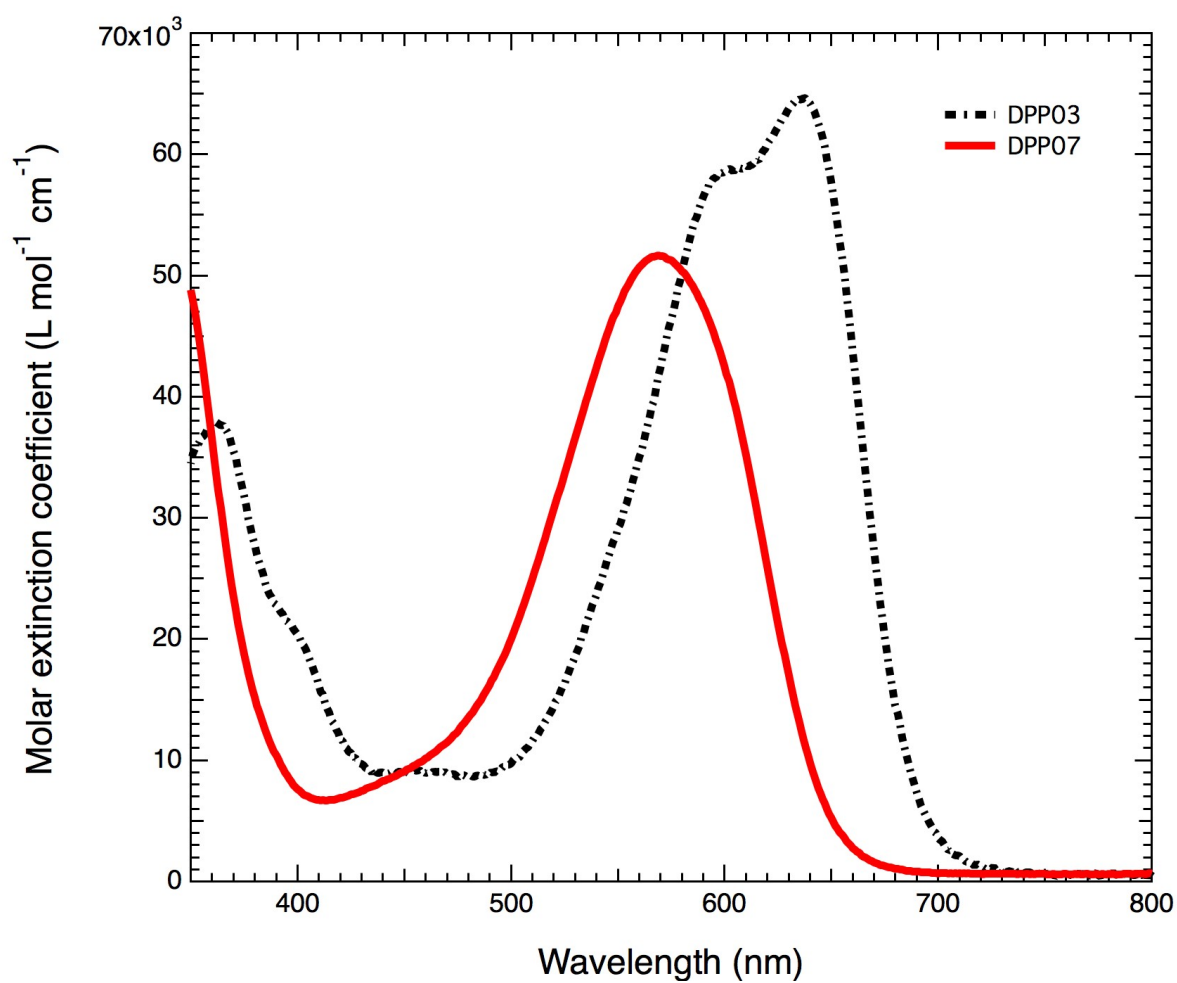


Figure S1. UV-Vis absorption spectra of DPP03 (black dash-dotted line) and DPP07 (red solid line) in THF.

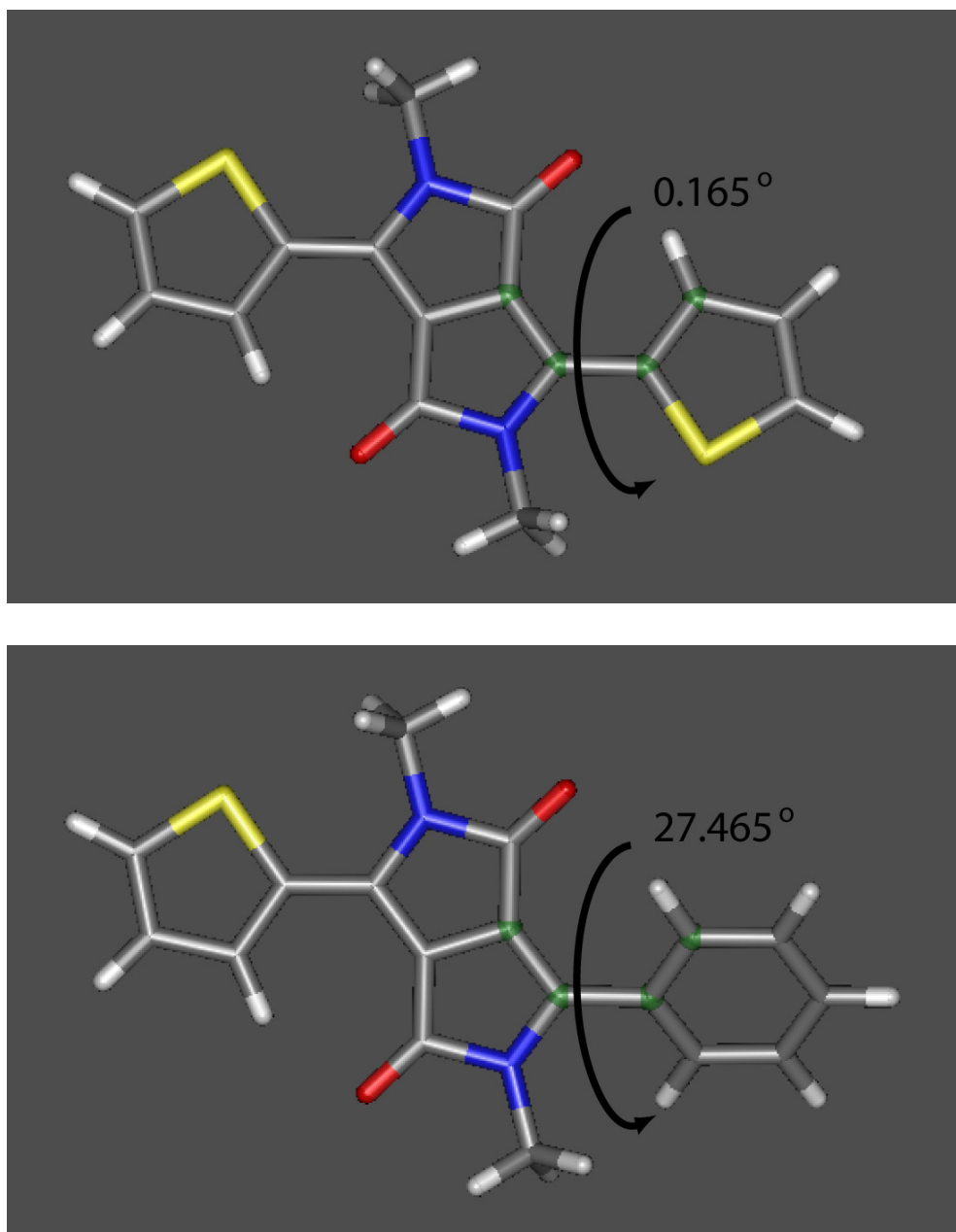


Figure S2. Molecular geometry calculation of thienyl-DPP-thienyl symmetric core (upper) and thienyl-DPP-phenyl asymmetric core (lower) done at the DFT B3LYP/3-21G (d,p) level.

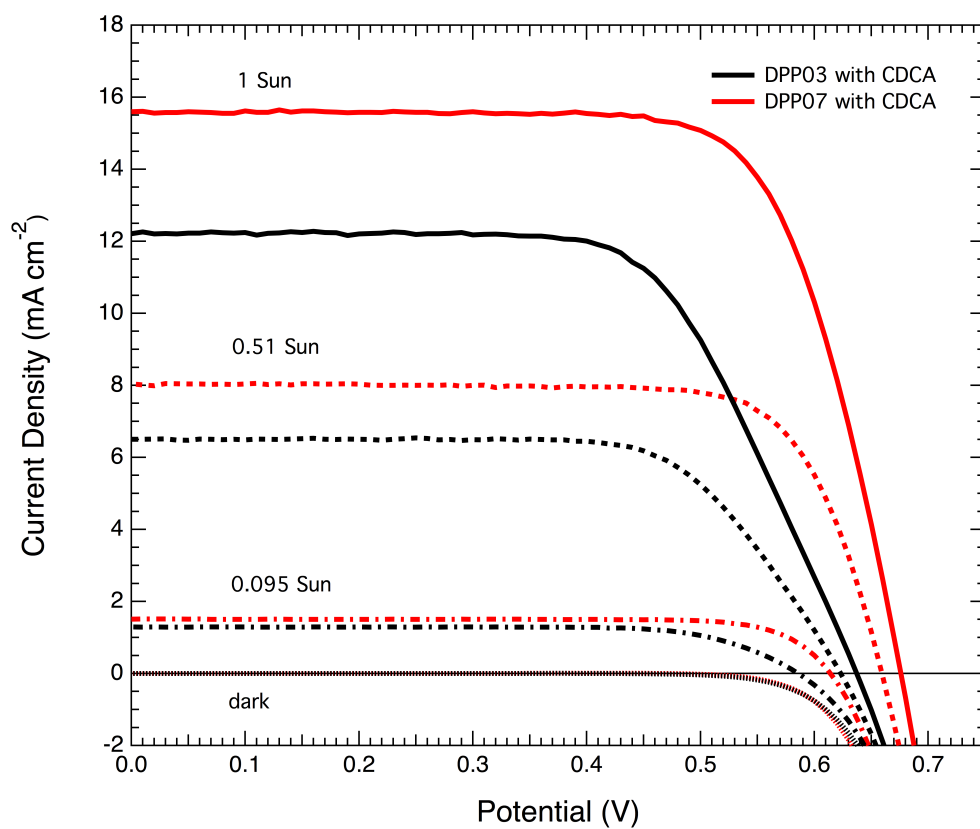


Figure S3. Photovoltaic characteristics of DPP03 (black lines) and DPP07 (red lines) solar cells in presence of CDCA under 9.5%, 51% and 100% sun light intensities.

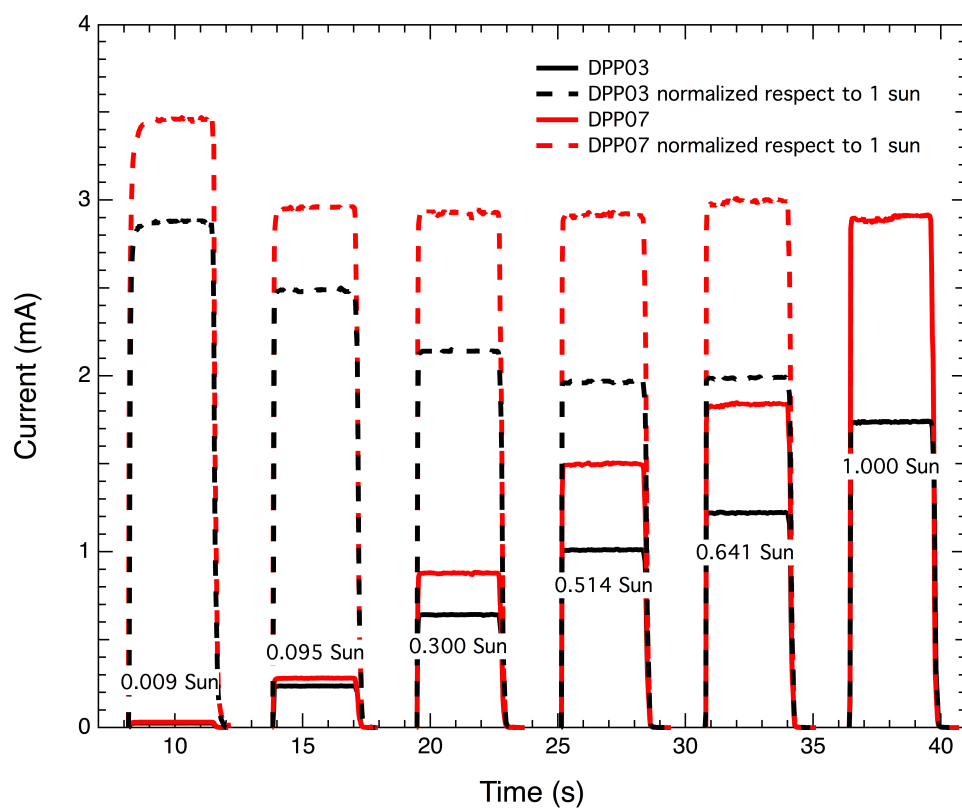


Figure S4. Current dynamics of DPP03 (black lines) and DPP07 (red lines) solar cells without CDCA as function of light intensities: measured currents (solid), and their currents normalized with respect to 1 sun (dashed line).

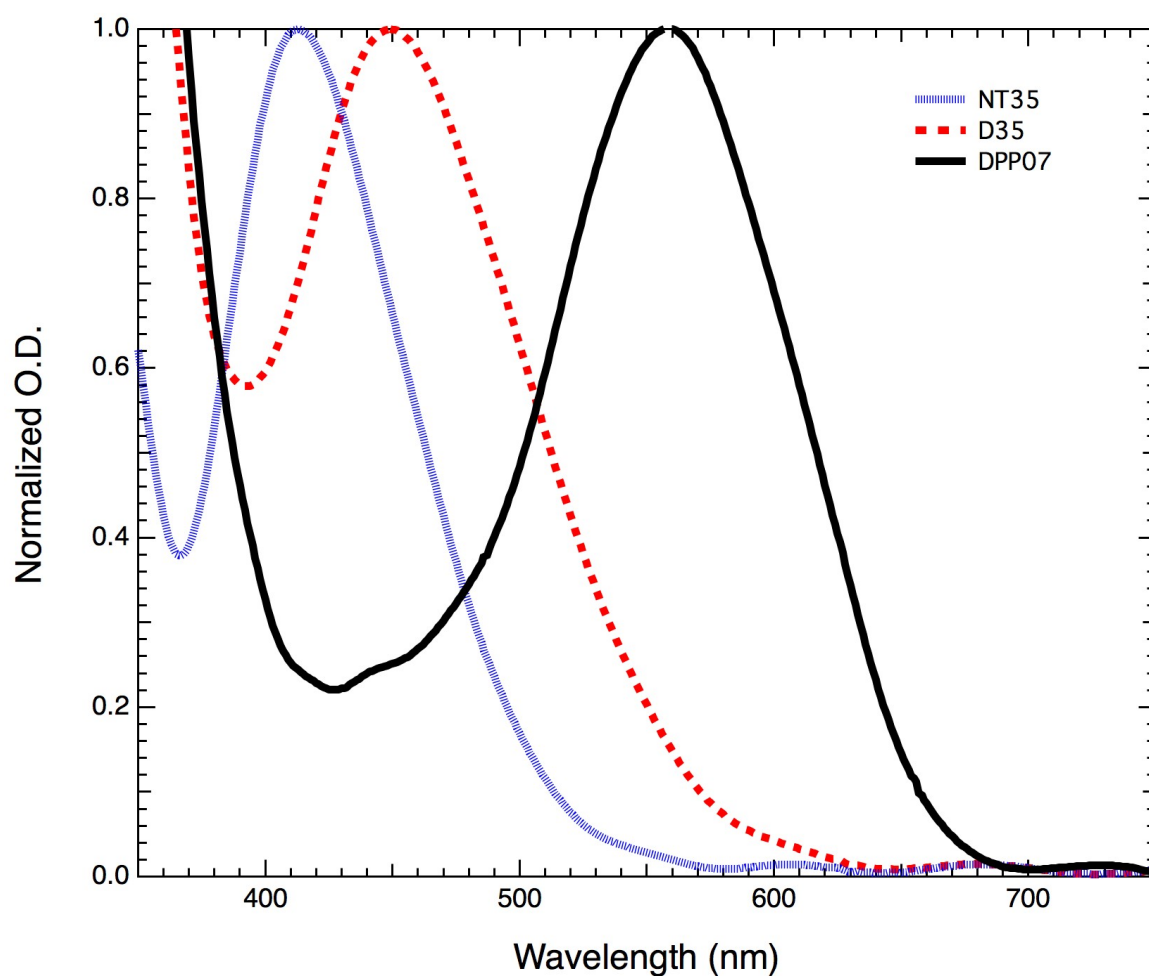


Figure S5. Normalized UV-Vis absorption spectra of NT35 (blue solid line), D35 (red dashed line) and DPP07 (black solid line) on 2 μm thick TiO_2 film.

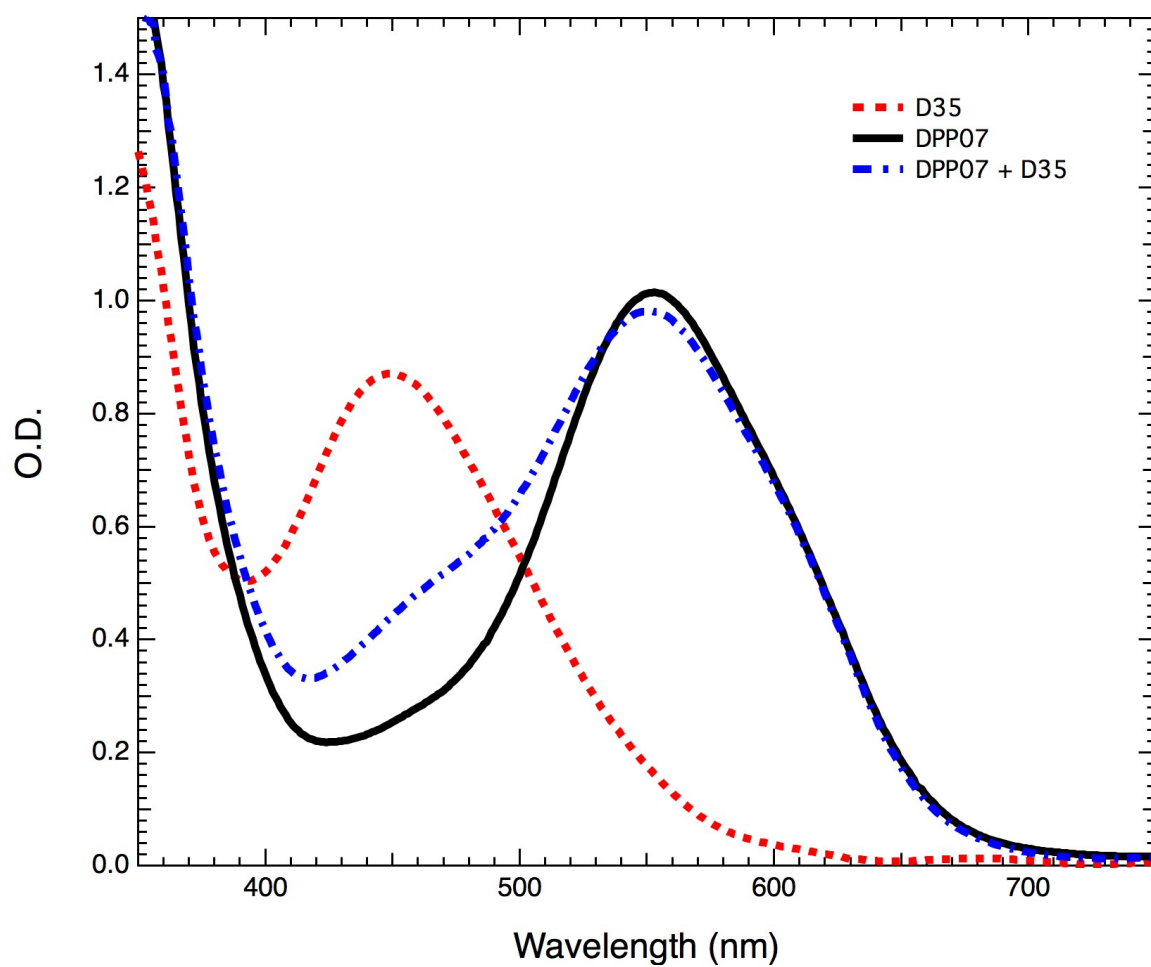


Figure S6. UV-Vis absorption spectra of D35 (red dashed line), DPP07 (black solid line), and DPP07 + D35 (blue dot-dashed line) on 2 μm thick TiO_2 film.

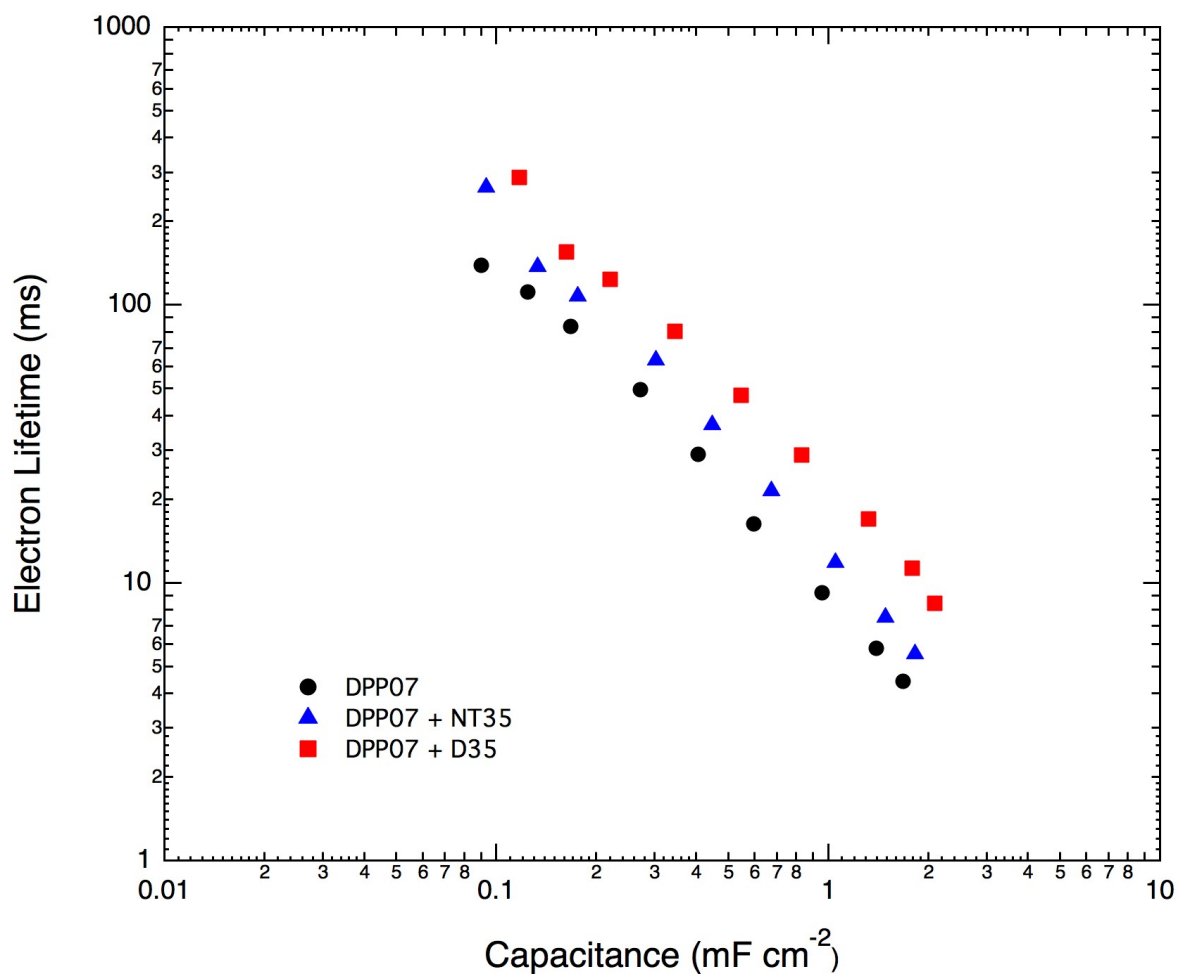


Figure S7. Electron lifetime of DPP07 (black closed circles), DPP07 + NT35 (blue closed triangles), and DPP07 + D35 (red closed squares) solar cells in presence of CDCA.

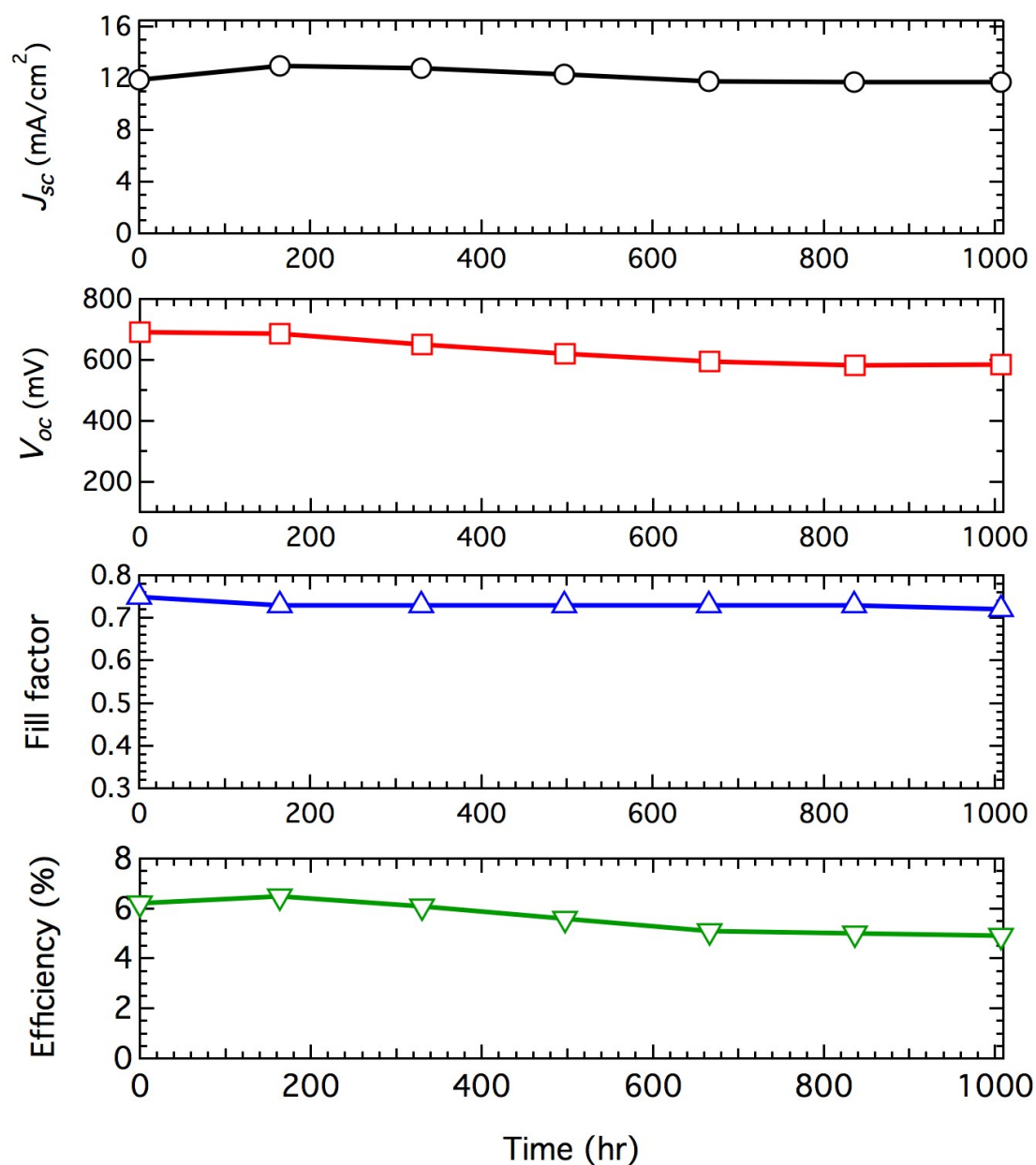


Figure S8. Photovoltaic performance variations with aging time of DPP07 sensitized solar cell with ionic liquid electrolyte (0.2M iodine, 0.5M N-butyl benzimidazole, and 0.1M guanidinium thiocyanate in a mixture of 1-propyl-3-methylimidazolium iodide and 1-ethyl-3-methylimidazolium tetracyanoborate (volume ratio 65:35) during successive 1 sun light soaking at 60 °C.

Computational Results

DFT Computations were performed with GAMESS VERSION = 11 AUG 2011 (R1) after low level optimization with Chem3D Pro 12 (MM2 minimization) and AM1 equilibrium geometry energy minimization with Firefly (PC GAMESS) version 7.1.G, build number 5618.

The following input files were used for the DFT input to GAMESS:

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C 6.000000 2.842038 1.824851 1.162722
S 16.000000 3.871150 2.200092 2.451494
C 6.000000 -5.444425 -0.214468 -0.285575
C 6.000000 -5.150238 -0.001311 1.046347
C 6.000000 -3.777665 0.331060 1.235219
C 6.000000 -3.083913 0.356078 0.029715
S 16.000000 -4.113348 -0.019227 -1.258759
O 8.000000 1.186974 1.092492 -2.088023
O 8.000000 -1.428862 1.088452 3.280315
C 6.000000 1.352793 1.774687 3.793708
C 6.000000 -1.594170 0.403423 -2.601122
H 1.000000 6.185344 2.661084 1.867695
H 1.000000 5.623230 2.253767 -0.676366
H 1.000000 3.087015 1.640218 -1.022016
H 1.000000 -6.427362 -0.480357 -0.674357
H 1.000000 -5.864455 -0.073049 1.869673
H 1.000000 -3.328399 0.540699 2.214545
H 1.000000 0.563490 1.682445 4.589038
```

```
H 1.000000 2.179510 1.041758 4.011438
H 1.000000 1.777073 2.817494 3.818048
H 1.000000 -2.017922 -0.639657 -2.623435
H 1.000000 -2.421241 1.135410 -2.820707
H 1.000000 -0.804638 0.494435 -3.396376
```

\$END

\$SYSTEM MWORDS=200 \$END

\$CONTRL RUNTYP=Optimize \$END

\$STATPT OptTol=0.001 NStep=200 \$END

\$CONTRL SCFTYP=RHF DFTTYP=B3LYP \$END

\$contrl INTTYP=HONDO ICUT=11 ITOL=30 \$end

\$SCF DIRSCF=.T. FDIFF=.FALSE. DIIS=.T. SOSCF=.F. \$END

\$CONTRL ICHARG=0 MULT=1 \$END

\$guess guess=huckel \$end

\$basis gbasis=N21 ngauss=3 ndfunc=1 NPFUNC=1 \$end

\$DATA

Molecule specification

C1

```
C 6.000000 -0.660041 -0.336624 0.075959
C 6.000000 0.659685 0.333379 -0.084621
C 6.000000 1.657913 -0.614208 0.010605
N 7.000000 1.059701 -1.876008 0.222192
C 6.000000 -0.380406 -1.758281 0.262857
C 6.000000 -1.658075 0.611462 -0.017042
N 7.000000 -1.059660 1.873165 -0.229359
C 6.000000 0.380388 1.755046 -0.271220
C 6.000000 3.093555 -0.383351 -0.078803
C 6.000000 -3.093708 0.382058 0.076362
O 8.000000 1.126820 2.723240 -0.453864
O 8.000000 -1.126633 -2.726760 0.444832
C 6.000000 1.723802 -3.137380 0.197075
C 6.000000 -1.722570 3.135088 -0.199461
C 6.000000 -4.017709 1.142279 -0.654897
C 6.000000 -5.381817 0.880726 -0.545439
C 6.000000 -5.837389 -0.139829 0.289431
C 6.000000 -4.922460 -0.911299 1.005401
C 6.000000 -3.556554 -0.659672 0.897209
C 6.000000 4.015827 -1.139282 0.659013
C 6.000000 5.379771 -0.874392 0.555628
C 6.000000 5.836794 0.144874 -0.280036
C 6.000000 4.923515 0.911301 -1.003492
C 6.000000 3.557739 0.656579 -0.901135
H 1.000000 1.007609 -3.920486 -0.174902
H 1.000000 2.620978 -3.097965 -0.476365
H 1.000000 2.054247 -3.424021 1.233185
H 1.000000 -2.616652 3.095719 0.478094
H 1.000000 -1.003942 3.917081 0.170192
H 1.000000 -2.057463 3.423357 -1.233679
H 1.000000 -3.673128 1.934147 -1.337137
```

```
H  1.000000  -6.100118  1.479944  -1.124331
H  1.000000  -6.915586  -0.340287  0.376357
H  1.000000  -5.275570  -1.727863  1.652886
H  1.000000  -2.831357  -1.291683  1.437898
H  1.000000  3.669731  -1.930158  1.341635
H  1.000000  6.096766  -1.469855  1.139991
H  1.000000  6.914827  0.348385  -0.361681
H  1.000000  5.277725  1.726425  -1.652187
H  1.000000  2.833546  1.284950  -1.447351
$END
```

1. S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin and M. Grätzel, *Thin Solid Films*, 2008, **516**, 4613-4619.
2. B. C. O'Regan and F. Lenzmann, *J. Phys. Chem. B*, 2004, **108**, 4342-4350.