Supporting Information

A Structural Study of DPP-based Sensitizers for DSC Applications

Thomas W. Holcombe,‡a* Jun-Ho Yum,‡a Junghyun Yoon,b Peng Gao,a Davide Di Censo,a Kasparas Rakstys,a Md. K. Nazeeruddin,a* and Michael Graetzel,a

a Laboratory for Photonics and Interfaces, Institution of Chemical Sciences and Engineering, School of Basic Sciences, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland. E-mail: tom.holcombe@gmail.com, junho.yum@epfl.ch

b R & D Center DSC Team, Dongjin Semichem Co., LTD. 445-935 Hwasung, South Korea.
**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), Bruker DRX-600 (600 Mhz), or Bruker DPX-400 (400 MHz) spectrometer and are reported in ppm using solvent as an internal standard.

A general scheme for the synthesis of DPP01. A similar route was followed for all sensitizers.

Monobromo-EthylHexyl-ThDPP was synthesized as reported in *J. Am. Chem. Soc.*, 2011, 133 (21), pp 8142–8145.

**ThDPP EtHex-Benzaldehyde**

In a 50 mL single-neck round-bottom flask, 1 gram of Monobromo-EtHex-ThDPP (1.65 mmol), 0.576 gram of 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-benzaldehyde (2.47 mmol), and 0.703 gram of potassium phosphate tribasic (3.30 mmol) were dissolved in 20 mL of toluene and 0.2 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 10:90 Hex:DCM to 100% DCM was used to purify the compound. 845 mg (81% yield) of a pure purple solid was obtained.

\(^1\)H NMR (400 MHz, Methylene Chloride-d2) \(\delta\) 10.02 (s, 1H), 8.94 (d, \(J = 4.2\) Hz, 1H), 8.90 (dd, \(J = 3.8, 1.2\) Hz, 1H), 7.94 (d, \(J = 8.4\) Hz, 2H), 7.87 (d, \(J = 8.3\) Hz, 2H), 7.70 (dd, \(J = 5.1, 1.2\) Hz, 1H), 7.65 (d, \(J = 4.1\) Hz, 1H), 7.30 (dd, \(J = 5.0, 3.9\) Hz, 1H), 4.15 – 3.94 (m, 4H), 1.90-1.80 (m, 2H), 1.47 – 1.14 (m, 16H), 0.98 – 0.74 (m, 12H).

**Br-ThDPP_EtHex-Benzaldehyde**

In a 25 mL single-neck round-bottom flask, 0.418 gram of ThDPP_EtHex-Benzaldehyde (0.66 mmol) was dissolved in 9 mL of chloroform, and 0.130 gram NBS (0.73 mmol) was added in one batch at room temperature. This reaction was stirred for 1 hour at which point the solution was loaded directly onto a short silica column and eluted with pure DCM to remove a minor impurity light blue in color, and then the product was completely eluted with a 99:1 DCM:EtOAc eluent. 420 mg (89% yield) of purple solid was obtained.

\(^1\)H NMR (400 MHz, Methylene Chloride-d2) \(\delta\) 10.02 (s, 1H), 8.95 (d, \(J = 4.1\) Hz, 1H), 8.65 (d, \(J = 4.1\) Hz, 1H), 7.94 (d, \(J = 8.3\) Hz, 2H), 7.87 (d, \(J = 8.3\) Hz, 2H), 7.65 (d, \(J = 4.1\) Hz, 1H), 7.27 (d, \(J = 4.2\) Hz, 1H), 4.13 – 3.86 (m, 4H), 1.90-1.80 (m, 2H), 1.5 – 1.15 (m, 16H), 0.97 – 0.78 (m, 12H).

**ThDPP_EtHex-ThienylAldehyde**

The reaction and purification was performed in the same manner as for ThDPP_EtHex-Benzaldehyde. 290 mg (67% yield) of a purple/blue solid was obtained.

\(^1\)H NMR (400 MHz, Methylene Chloride-d2) \(\delta\) 9.89 (s, 1H), 8.90 (dd, \(J = 4.0, 1.2\) Hz, 1H), 8.88 (d, \(J = 4.1\) Hz, 1H), 7.75 (d, \(J = 4.0\) Hz, 1H), 7.71 (dd, \(J = 5.0, 1.2\) Hz, 1H), 7.53 (d, \(J = 4.1\) Hz, 1H), 7.42 (d, \(J = 3.9\) Hz, 1H), 7.30 (dd, \(J = 5.0, 3.9\) Hz, 1H), 4.10 – 3.95 (m, 4H), 1.90-1.80 (d, \(J = 25.3\) Hz, 2H), 1.5-1.15 (m, 16H), 0.97 – 0.78 (m, 12H).

**Br-ThDPP_EtHex-ThienylAldehyde**

The reaction and purification was performed in the same manner as for Br-ThDPP_EtHex-Benzaldehyde. 129 mg (40% yield) of a purple/blue solid was obtained.

\(^1\)H NMR (400 MHz, Methylene Chloride-d2) \(\delta\) 9.89 (s, 1H), 8.90 (d, \(J = 4.1\) Hz, 1H), 8.66 (d, \(J = 4.2\) Hz, 1H), 7.74 (d, \(J = 4.0\) Hz, 1H), 7.52 (d, \(J = 4.2\) Hz, 1H), 7.42 (d, \(J = 4.0\) Hz, 1H), 7.27 (d, \(J = 4.1\) Hz, 1H), 3.98 (dt, \(J = 29.4, 7.0\) Hz, 4H), 1.87-1.80 (m, 2H), 1.42 – 1.16 (m, 16H), 0.94-0.80 (m, \(J = 6.9\) Hz, 12H).
HexOTPA-ThDPP_EtHex-Benzaldehyde

The reaction and purification was performed in the same manner as for ThDPP_EtHex-Benzaldehyde.
256 mg (59% yield) of a bluish/green solid was obtained.

$^1$H NMR (400 MHz, Methylene Chloride-d2) δ 10.02 (s, 1H), 9.05 (d, $J = 4.2$ Hz, 1H), 8.89 (d, $J = 4.2$ Hz, 1H), 7.94 (d, $J = 8.3$ Hz, 2H), 7.87 (d, $J = 8.3$ Hz, 2H), 7.64 (d, $J = 4.2$ Hz, 1H), 7.49 (d, $J = 8.8$ Hz, 2H), 7.38 (d, $J = 4.2$ Hz, 1H), 7.13 – 7.05 (m, 4H), 6.92 – 6.83 (m, 6H), 4.15 – 3.99 (m, 4H), 3.95 (t, $J = 6.6$ Hz, 4H), 1.90 – 1.80 (m, 2H), 1.77 (dt, $J = 14.6, 6.6$ Hz, 4H), 1.50 – 1.18 (m, 28H), 0.98 – 0.78 (m, 18H).

HexOTPA-ThDPP_EtHex-ThienylAldehyde

The reaction and purification was performed in the same manner as for ThDPP_EtHex-Benzaldehyde.
110 mg (65% yield) of a blue solid was obtained.

$^1$H NMR (400 MHz, Methylene Chloride-d2) δ 9.89 (s, 1H), 9.06 (d, $J = 4.2$ Hz, 1H), 8.84 (d, $J = 4.2$ Hz, 1H), 7.74 (d, $J = 4.0$ Hz, 1H), 7.55 – 7.46 (m, 3H), 7.40 (dd, $J = 12.1, 4.1$ Hz, 2H), 7.08 (d, $J = 8.9$ Hz, 4H), 6.91 – 6.84 (m, 6H), 4.12 – 3.99 (m, 4H), 3.95 (t, $J = 6.6$ Hz, 4H), 1.91-1.80 (m, 2H), 1.77 (dt, $J = 14.7, 6.7$ Hz, 4H), 1.51 – 1.12 (m, 28H), 0.99 – 0.77 (m, 18H).

HexODPA-ThDPP_EtHex-Benzaldehyde

In a 10 mL 2-neck round-bottom flask, 200 mg of Br-ThDPP_EtHex-Benzaldehyde (0.28 mmol), 120 mg bis(4-hexyloxy)diphenylamine (0.32 mmol), and 90 mg K$_3$PO$_4$ (0.42 mmol) were dissolved in 5 mL dimethoxyethane and degassed for 20 minutes with N$_2$. After the addition of 12 mg Pd$_2$dba$_3$ and 24 mg X-Phos, the reaction was heated to 70 °C for 12 hours. The reaction was then diluted with DCM and flashed through a plug of MgSO$_4$ to remove inorganic salts and metallic palladium. This crude residue was purified by flash chromatography with pure DCM. 160 mg (57% yield) of bluish/green-solid was obtained.

$^1$H NMR (400 MHz, Methylene Chloride-d2) δ 10.00 (s, 1H), 9.12 (d, $J = 4.6$ Hz, 1H), 8.71 (d, $J = 4.1$ Hz, 1H), 7.91 (d, $J = 8.4$ Hz, 2H), 7.84 (d, $J = 8.1$ Hz, 2H), 7.60 (d, $J = 4.1$ Hz, 1H), 7.26 (d, $J = 8.9$ Hz, 4H), 6.91 (d, $J = 8.9$ Hz, 4H), 6.39 (d, $J = 4.6$ Hz, 1H), 4.06 (q, $J = 6.9$ Hz, 2H), 3.96 (t, $J = 6.5$ Hz, 4H), 3.90 – 3.71 (m, 2H), 1.94 – 1.70 (m, 6H), 1.51 – 1.08 (m, 28H), 1.01 – 0.74 (m, 18H).

HexODPA-ThDPP_EtHex-ThienylAldehyde

The reaction and purification was performed in the same manner as for HexODPA-ThDPP_EtHex-Benzaldehyde.
91 mg (50% yield) of a bluish solid was obtained.

$^1$H NMR (400 MHz, Methylene Chloride-d2) δ 9.87 (s, 1H), 9.14 (d, $J = 4.6$ Hz, 1H), 8.66 (d, $J = 4.2$ Hz, 1H), 7.72 (d, $J = 4.0$ Hz, 1H), 7.47 (d, $J = 4.1$ Hz, 1H), 7.37 (d, $J = 4.0$ Hz, 1H), 7.26
DPP01, HexODPA-PhenylCAA

In a 25 mL single-neck round-bottom flask, 80 mg of HexODPA-ThDPP_EtHex-Benzaldehyde (0.080 mmol) and 160 mg cyanoacetic acid (1.89 mmol) was dissolved in 4 mL DCM, 1 mL triethylamine, and 1 drop piperidine. A spatula of MgSO₄ 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. 20 mg (24% yield) of greenish solid was obtained.

^1^H NMR (400 MHz, DMSO-d6) δ 9.11 (d, J = 4.5 Hz, 1H), 8.62 (d, J = 4.2 Hz, 1H), 8.11 (s, 1H), 7.92 (d, J = 1.7 Hz, 2H), 7.91 (d, J = 2.7 Hz, 1H), 7.37 (d, J = 8.9 Hz, 4H), 7.01 (d, J = 9.0 Hz, 4H), 6.35 (d, J = 4.5 Hz, 1H), 4.03–3.70 (m, 8H), 1.74–1.70 (m, 4H), 1.44–1.40 (m, 2H), 1.37–1.03 (m, 28H), 0.92–0.71 (m, 18H).

^1^H NMR (400 MHz, THF-d8) δ 9.31 (d, J = 4.5 Hz, 1H), 8.94 (d, J = 4.2 Hz, 1H), 8.12 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 4.2 Hz, 1H), 7.29 (d, J = 8.9 Hz, 4H), 6.94 (d, J = 9.0 Hz, 4H), 6.39 (d, J = 4.6 Hz, 1H), 4.20–4.04 (m, 2H), 3.98 (t, J = 6.4 Hz, 4H), 3.94–3.78 (m, 2H), (THF solvent signal obscures 2 protons), 1.55–1.44 (m, 4H), 1.44–1.11 (m, 28H), 0.96–0.80 (m, 18H).

^13^C NMR (150 MHz, THF-d8) δ 164.81, 162.75, 161.47, 158.89, 153.21, 146.08, 143.12, 140.84, 140.22, 138.55, 135.71, 135.11, 132.78, 132.73, 132.63, 128.00, 127.09, 126.90, 116.77, 116.41, 116.25, 111.52, 110.32, 106.28, 104.94, 69.05, 46.35, 46.16, 40.69, 40.59, 40.57, 32.75, 31.31, 31.27, 30.39, 29.57, 29.32, 29.30, 26.89, 24.53, 24.34, 24.20, 24.17, 23.72, 14.63, 14.59, 14.57, 11.00, 10.98.

C₆₄H₇₈N₄O₆S₂[M⁺] Exact Mass = 1062.5363, MS (ESI-TOF) = 1062.5439

DPP02, HexODPA-ThienylCAA

The reaction and purification were performed in the same manner as for DPP01. 26 mg (30% yield) of a greenish solid was obtained.

^1^H NMR (400 MHz, DMSO-d6) δ 9.14 (d, J = 4.6 Hz, 1H), 8.56 (d, J = 4.2 Hz, 1H), 8.38 (s, 1H), 7.94 (d, J = 3.3 Hz, 1H), 7.77 (d, J = 4.2 Hz, 1H), 7.67 (d, J = 4.0 Hz, 1H), 7.37 (d, J = 8.9 Hz, 4H), 7.01 (d, J = 9.0 Hz, 4H), 6.36 (d, J = 4.6 Hz, 1H), 4.04–3.90 (m, 6H), 3.72 (ddd, J = 45.9, 14.2, 6.7 Hz, 2H), 1.82–1.62 (m, 4H), 1.43–1.40 (m, 2H), 1.38–1.01 (m, 28H), 0.97–0.65 (m, 18H).
$^1$H NMR (400 MHz, THF-d$_8$) $\delta$ 9.33 (d, $J = 4.5$ Hz, 1H), 8.89 (d, $J = 4.2$ Hz, 1H), 8.35 (s, 1H), 7.84 (d, $J = 4.1$ Hz, 1H), 7.64 (d, $J = 4.2$ Hz, 1H), 7.50 (d, $J = 4.0$ Hz, 1H), 7.29 (d, $J = 8.8$ Hz, 4H), 6.95 (d, $J = 8.9$ Hz, 4H), 6.40 (d, $J = 4.5$ Hz, 1H), 4.15 – 4.01 (m, 2H), 3.98 (t, $J = 6.4$ Hz, 4H), 3.94 – 3.78 (m, 2H), 1.50 (t, $J = 7.6$ Hz, 4H), 1.43 – 1.09 (m, 28H), 1.01 – 0.76 (m, 18H).

$^{13}$C NMR (150 MHz, THF-d$_8$) $\delta$ 165.17, 164.09, 162.77, 161.39, 158.95, 146.21, 143.38, 141.18, 140.22, 140.14, 138.99, 136.67, 135.32, 134.37, 132.90, 128.10, 128.04, 126.22, 116.75, 116.42, 116.00, 110.79, 106.33, 100.48, 69.05, 46.31, 46.18, 40.68, 40.65, 40.63, 32.75, 31.35, 31.30, 31.25, 30.82, 30.39, 29.50, 29.28, 29.27, 26.89, 24.54, 24.52, 24.35, 24.20, 24.14, 23.72, 14.61, 14.58, 14.57, 11.02, 10.99, 1.55.

$C_{60}H_{76}N_4O_6S_3[M^+]$ Exact Mass = 1068.4927, MS (ESI-TOF) = 1068.4907

DPP03, HexOTPA-PhenylCAA

The reaction and purification were performed in the same manner as for DPP01. 27 mg (38% yield) of a green solid was obtained.

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 8.91 (d, $J = 4.2$ Hz, 1H), 8.84 (d, $J = 4.1$ Hz, 1H), 7.98 (d, $J = 8.7$ Hz, 2H), 7.95 (d, $J = 4.2$ Hz, 1H), 7.91 (d, $J = 8.4$ Hz, 2H), 7.88 (s, 1H), 7.66 (d, $J = 4.2$ Hz, 1H), 7.61 (d, $J = 8.6$ Hz, 2H), 7.10 (d, $J = 8.9$ Hz, 4H), 6.95 (d, $J = 9.0$ Hz, 4H), 6.79 (d, $J = 8.5$ Hz, 2H), 4.07 – 4.00 (m, 4H), 3.96 (t, $J = 6.4$ Hz, 4H), 1.76 – 1.67 (m, 4H), 1.43 – 1.40 (s, 2H), 1.39 – 1.14 (m, 28H), 0.95 – 0.76 (m, 18H).

$^1$H NMR (400 MHz, THF-d$_8$) $\delta$ 9.23 (d, $J = 4.2$ Hz, 1H), 9.10 (d, $J = 4.2$ Hz, 1H), 8.27 (s, 1H), 8.15 (d, $J = 8.4$ Hz, 2H), 7.94 (d, $J = 8.4$ Hz, 2H), 7.80 (d, $J = 4.2$ Hz, 1H), 7.54 (d, $J = 8.8$ Hz, 2H), 7.49 (d, $J = 4.2$ Hz, 1H), 7.07 (d, $J = 8.9$ Hz, 4H), 6.88 (t, $J = 8.6$ Hz, 6H), 4.12 (ddd, $J = 11.6, 7.8, 4.8$ Hz, 4H), 3.95 (t, $J = 6.4$ Hz, 4H), 2.05 – 1.92 (m, 2H), 1.49 (dd, $J = 10.4, 4.8$ Hz, 4H), 1.45 – 1.20 (m, 28H), 0.98 – 0.79 (m, 18H).

$^{13}$C NMR (150 MHz, THF-d$_8$) $\delta$ 163.91, 162.37, 161.95, 157.50, 153.54, 152.08, 150.97, 147.78, 141.45, 140.93, 139.10, 138.63, 138.36, 137.27, 133.04, 132.81, 131.96, 128.15, 128.12, 127.72, 127.28, 127.15, 125.50, 123.90, 120.42, 116.54, 116.27, 110.03, 108.56, 104.71, 68.93, 46.48, 40.53, 40.47, 32.77, 31.29, 31.26, 30.82, 30.47, 29.55, 29.47, 26.93, 24.52, 24.15, 23.73, 14.62, 14.60, 14.57, 10.97, 10.95, 10.94.

$C_{70}H_{82}N_4O_6S_2[M^+]$ Exact Mass = 1138.5676, MS (MALDI) = 1138.5769
DPP04, HexOTPA-ThienylCAA

The reaction and purification were performed in the same manner as for DPP01. 25 mg (28% yield) of a green solid was obtained.

$^1$H NMR (400 MHz, DMSO-d6) $\delta$ 8.96 (d, $J = 4.1$ Hz, 1H), 8.76 (d, $J = 4.3$ Hz, 1H), 8.50 (s, 1H), 8.03 (d, $J = 4.1$ Hz, 1H), 7.85 (d, $J = 4.4$ Hz, 1H), 7.75 (d, $J = 4.2$ Hz, 1H), 7.64 (d, $J = 4.4$ Hz, 1H), 7.58 (d, $J = 8.3$ Hz, 2H), 7.08 (d, $J = 8.3$ Hz, 4H), 6.94 (d, $J = 8.4$ Hz, 4H), 6.77 (d, $J = 8.3$ Hz, 2H), 4.05-3.90 (m, 8H), 1.75 – 1.68 (m, 4H), 1.43 – 1.40 (m, 2H), 1.38 – 1.09 (m, 28H), 0.95 – 0.76 (m, 18H).

$^1$H NMR (400 MHz, THF-d8) $\delta$ 9.27 (d, $J = 4.2$ Hz, 1H), 9.07 (d, $J = 4.2$ Hz, 1H), 8.38 (s, 1H), 7.88 (d, $J = 4.1$ Hz, 1H), 7.71 (d, $J = 4.2$ Hz, 1H), 7.60 – 7.52 (m, 3H), 7.50 (d, $J = 4.2$ Hz, 1H), 7.09 (d, $J = 8.9$ Hz, 4H), 6.90 (dd, $J = 8.8, 6.5$ Hz, 6H), 4.19 – 4.03 (m, 4H), 3.97 (t, $J = 6.4$ Hz, 4H), 1.99 (dt, $J = 20.1, 6.5$ Hz, 2H), 1.52 (dd, $J = 9.1, 3.5$ Hz, 4H), 1.46 – 1.19 (m, 28H), 0.92 (dt, $J = 22.3, 7.2$ Hz, 18H).

$^{13}$C NMR (150 MHz, THF-d8) $\delta$ 164.00, 162.35, 161.87, 157.51, 152.30, 151.00, 146.23, 145.70, 141.67, 140.90, 140.71, 140.19, 139.31, 138.00, 137.16, 136.94, 132.10, 129.30, 128.17, 128.06, 127.74, 126.72, 125.45, 123.93, 120.37, 116.69, 116.27, 110.42, 108.60, 100.86, 68.93, 46.53, 46.42, 40.59, 40.46, 40.45, 34.43, 33.05, 32.77, 31.34, 31.31, 31.27, 31.24, 30.82, 30.78, 30.53, 30.47, 30.32, 29.48, 29.44, 26.93, 24.52, 24.14, 23.73, 14.61, 14.57, 10.99, 10.97, 10.95, 1.55.

$C_{68}H_{80}N_4O_6S_3[M^+]$ Exact Mass = 1144.5240, MS (MALDI) = 1144.5274
DSC fabrication and characterization:

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, 6~8 µm, by twice repeated screen printing. A ~4 µm scattering layer (400 nm, CCIC, HPW-400) was printed on the top of the transparent layer to increase light path length by light scattering. The TiO$_2$ electrodes were immersed into a 0.025 mM solution of dyes without or with 2.5 mM 3α,7α-dihydroxy-5β-cholic acid (chenodeoxycholic acid) in 4-tert-butanol/acetonitrile mixture (1:1 v/v) and kept for ~5 h at room temperature. The applied electrolyte consists of 0.6 M 1,3-dimethylimidazolium iodide (DMII), 0.03 M I$_2$, 0.05 M LiI, 0.05 M guanidinium thiocyanate (GuSCN), and 0.25 M 4-tert-butylpyridine (TBP) 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). A self-adhesive, anti-reflecting, UV cut-off film (λ < 380 nm, ARKTOP, ASAHI Glass) was attached to the top of the best performing cell to make further improvement by decreasing light reflection loss. 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 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 IPCE measurement. The modulation frequency was about 1~2 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 cells under test. A white light bias was used to bring the total light intensity on the cell under test closer to operating conditions. The cells have an active area of 0.28 cm$^2$ and were masked to attain an illuminated area of 0.2 cm$^2$. 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. 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. The electron lifetimes are plotted as function of the charge density in order to compare them at the fixed Fermi level of the TiO$_2$. 

Electronic Supplementary Material (ESI) for Chemical Communications
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Table S1. Output characteristics of DSC devices fabricated with DPP sensitizers as various light intensities.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Light intensity (Sun)</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF</th>
<th>PCE [%]</th>
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<td>DPP01</td>
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<tr>
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</tbody>
</table>

Devices fabricated with TiO$_2$ thickness of 6 + 4 (20 nm and 400 nm particles) microns, with electrolyte composition 0.6M DMII, 0.05M LiI, 0.03M I$_2$, 0.25M TBP, 0.05M GuSCN in Acetonitrile:Valeronitrile (85:15).

Table S2. Output characteristics of DSC devices fabricated with DPP03 as various CDCA concentration.

<table>
<thead>
<tr>
<th>Dye</th>
<th>CDCA (mM)</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPP03</td>
<td>1.25</td>
<td>9.80</td>
<td>0.62</td>
<td>0.63</td>
<td>3.84</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>9.60</td>
<td>0.61</td>
<td>0.66</td>
<td>3.90</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>9.36</td>
<td>0.62</td>
<td>0.67</td>
<td>3.90</td>
</tr>
</tbody>
</table>

Devices fabricated with TiO$_2$ thickness of 8 + 5 (20 nm and 400 nm particles) microns, 15 hour dye loading, with electrolyte composition 0.6M DMII, 0.05M LiI, 0.03M I$_2$, 0.25M TBP, 0.05M GuSCN in Acetonitrile:Valeronitrile (85:15).
Figure S1. UV-Vis spectra of all dyes with (solid lines) and without (dashed lines) CDCA on 2 microns thick TiO$_2$ film. CDCA is known to adsorb competitively with dyes on the surface and thus reduces dye loading.$^{1,2}$ Normalized spectra are depicted in a lower figure.
Figure S2. Electron lifetime of DPP03 (green circles) and DPP04 (black squares) sensitized solar cells as function of charge density. Open symbols indicate electron lifetimes of the corresponding sensitizer without CDCA.

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