

SUPPLEMENTARY INFORMATION

Diketopyrrolopyrrole-based Sensitizers for Dye-sensitized Solar cell Applications: Anchor Engineering

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Synthetic 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 and ¹³C NMR spectra were recorded on a Bruker Avance-400 (400 MHz), Bruker AvanceIII-400 (400MHz), Bruker DPX-400 (400 MHz), or Bruker DRX-600 spectrometer and are reported in ppm using solvent as an internal standard: Methylene Chloride-d₂ at 5.32 ppm and 54.00 ppm for ¹H and ¹³C, respectively; THF-d₈ at 3.58 ppm and 67.57 ppm for ¹H and ¹³C, respectively.

Synthetic Procedures:

3-(4-bromophenyl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (Th-DPP_EtHex-Ph-Br) and **DPP07** were synthesized previously, in reference [9].

3-(5-bromopyridin-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (Th-DPP_EtHex-Py-Br) was synthesized as in reference [9].

¹H NMR (400 MHz, Methylene Chloride-d₂) δ 9.05 (d, *J* = 3.7 Hz, 1H), 8.86 (d, *J* = 8.6 Hz, 1H), 8.74 (d, *J* = 2.3 Hz, 1H), 8.01 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.74 (d, *J* = 4.8 Hz, 1H), 7.34 – 7.29 (m, 1H), 4.36 – 4.22 (m, 2H), 4.06 – 3.91 (m, 2H), 1.90 – 1.78 (m, 1H), 1.60 – 1.51 (m, 1H), 1.42 – 1.11 (m, 16H), 0.92 – 0.79 (m, 12H). ¹³C NMR (100 MHz, Methylene Chloride-d₂) δ 162.77, 162.25, 150.50, 147.10, 143.18, 142.62, 140.02, 136.89, 132.34, 130.19, 129.02, 128.46, 122.28, 111.38, 109.17, 46.33, 46.32, 46.26, 40.36, 39.68, 39.67, 32.51, 31.11, 31.09, 30.74, 30.72, 30.49, 30.28, 30.24, 29.94, 29.19, 28.93, 28.92, 24.44, 24.05, 23.63, 23.61, 14.46, 14.40, 14.36, 11.08, 10.77.

Th-DPP_EtHex-Py-Benzaldehyde

In a 50 mL single-neck round-bottom flask, 1.00 grams of Th-DPP_EtHex-Py-Br (1.67 mmol), 0.58 grams of 4-formylphenylboronic acid, pinacol ester (2.50 mmol), and 1.06 grams of potassium phosphate tribasic (5.00 mmol) were dissolved in 15 mL of toluene, 1 mL tAmylOH, and 0.5 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 plugged through a thin pad of MgSO₄ with DCM. Volatile organics were removed and the crude compound loaded onto a medium column loaded with 200 mL of silica. A gradient eluent of 40:60 Toluene:DCM to 100% DCM was used to purify the compound. 0.84 grams (81% yield) of a pure red solid was obtained.

¹H NMR (400 MHz, Methylene Chloride-d₂) δ 10.05 (s, 1H), 9.07 (d, *J* = 4.0 Hz, 1H), 9.04 (d, *J* = 8.3 Hz, 1H), 8.97 (d, *J* = 2.4 Hz, 1H), 8.12 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.03 – 7.97 (m, 2H), 7.85

(d, $J = 8.1$ Hz, 2H), 7.73 (d, $J = 4.8$ Hz, 1H), 7.34 – 7.28 (m, 1H), 4.45 – 4.30 (m, 2H), 4.07 – 3.91 (m, 2H), 1.89 – 1.79 (m, 1H), 1.66 – 1.57 (m, 1H), 1.45 – 1.14 (m, 16H), 0.95 – 0.77 (m, 12H). ^{13}C NMR (100 MHz, Methylene Chloride- d_2) δ 191.98, 162.73, 162.30, 148.30, 147.86, 143.32, 143.11, 142.93, 136.86, 136.69, 135.70, 135.52, 132.25, 130.85, 130.20, 128.99, 128.17, 127.33, 111.44, 109.27, 46.35, 46.29, 40.35, 39.69, 39.68, 31.12, 31.10, 30.73, 30.71, 29.19, 28.92, 28.91, 24.47, 24.04, 23.63, 23.61, 14.43, 14.37, 11.12, 10.77.

Br-Th-DPP EtHex-Py-Benzaldehyde

In a 50 mL single-neck round-bottom flask, 0.84 gram of Th-DPP_EthHex-Py-Benzaldehyde (1.35 mmol) was dissolved in 20 mL of chloroform, and 0.25 gram NBS (1.40 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. 0.47 grams (50% yield) of red/purple solid was obtained.

^1H NMR (400 MHz, Methylene Chloride- d_2) δ 10.07 (s, 1H), 9.03 (d, $J = 8.4$ Hz, 1H), 8.98 (d, $J = 2.3$ Hz, 1H), 8.81 (d, $J = 4.3$ Hz, 1H), 8.13 (dd, $J = 8.4, 2.4$ Hz, 1H), 8.01 (d, $J = 8.2$ Hz, 2H), 7.86 (d, $J = 8.1$ Hz, 2H), 7.27 (d, $J = 4.2$ Hz, 1H), 4.43 – 4.28 (m, 2H), 3.91 (p, $J = 7.4$ Hz, 2H), 1.89 – 1.78 (m, 1H), 1.67 – 1.56 (m, 1H), 1.44 – 1.13 (m, 16H), 0.94 – 0.78 (m, 12H). ^{13}C NMR (100 MHz, Methylene Chloride- d_2) δ 192.02, 162.50, 162.25, 148.23, 147.94, 143.62, 143.31, 141.50, 136.74, 135.89, 135.57, 132.14, 131.71, 130.89, 128.23, 127.43, 120.24, 111.34, 109.53, 46.44, 46.41, 40.35, 39.71, 31.12, 31.10, 30.69, 30.67, 29.20, 28.89, 28.88, 24.46, 24.06, 23.61, 14.42, 14.37, 11.11, 10.76.

HexOTPA-Th-DPP EtHex-Py-Benzaldehyde

The reaction and purification were performed in the same manner as for the synthesis of Th-DPP_EthHex-Py-Benzaldehyde, with the coupling partner *N,N*-bis[4-(hexyloxy)phenyl]-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzamine. 125 mg (55% yield) of purple-ish/blue solid was obtained.

^1H NMR (400 MHz, Methylene Chloride- d_2) δ 10.05 (s, 1H), 9.22 (d, $J = 4.2$ Hz, 1H), 9.05 (d, $J = 8.4$ Hz, 1H), 8.96 (d, $J = 2.3$ Hz, 1H), 8.10 (dd, $J = 8.5, 2.5$ Hz, 1H), 8.03 – 7.96 (m, 2H), 7.88 – 7.81 (m, 2H), 7.51 – 7.45 (m, 2H), 7.37 (d, $J = 4.2$ Hz, 1H), 7.12 – 7.04 (m, 4H), 6.92 – 6.83 (m, 6H), 4.46 – 4.31 (m, 2H), 4.08 – 3.99 (m, 2H), 3.95 (t, $J = 6.5$ Hz, 4H), 2.00 – 1.90 (m, 1H), 1.78 (dt, $J = 14.7, 6.7$ Hz, 4H), 1.70 – 1.60 (m, 1H), 1.52 – 1.45 (m, 4H), 1.41 – 1.33 (m, 12H), 1.33 – 1.16 (m, 12H), 0.95 – 0.82 (m, 18H). ^{13}C NMR (100 MHz, Methylene Chloride- d_2) δ 191.99, 162.97, 162.11, 156.89, 152.64, 150.47, 148.57, 147.78, 143.46, 143.39, 143.22, 141.53, 140.18, 139.45, 136.64, 135.42, 135.31, 130.98, 130.88, 129.50, 128.90, 128.14, 127.88, 127.39, 127.28, 127.17, 126.06, 124.54, 123.40, 119.56, 115.94, 111.82, 108.75, 68.89, 46.47, 40.43, 39.86, 32.20, 31.18, 30.87, 29.88, 29.26, 29.09, 27.51, 26.32, 24.51, 24.19, 23.70, 23.66, 23.22, 14.47, 14.44, 14.42, 11.18, 10.90.

DPP10, HexOTPA-Th-DPP_EtHex-Py-PhenylCAA

In a 25 mL single-neck round-bottom flask, 100 mg of HexOTPA-Th-DPP_EthHex-Py-Benzaldehyde (0.09 mmol) and 65 mg cyanoacetic acid (0.76 mmol) was dissolved in 3 mL DCM, 1.5 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. 48 mg (45% yield) of blue solid was obtained.

¹H NMR (600 MHz, THF-d₈) δ 9.44 (d, *J* = 4.1 Hz, 1H), 9.31 (d, *J* = 8.5 Hz, 1H), 9.15 (d, *J* = 2.0 Hz, 1H), 8.36 (d, *J* = 7.3 Hz, 2H), 8.37 (s, 1H), 8.27 (d, *J* = 8.1 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 4.4 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 4H), 6.94 (d, *J* = 8.7 Hz, 3H), 6.92 (d, *J* = 9.0 Hz, 4H), 4.20 – 4.09 (m, 2H), 4.57 – 4.47 (m, 2H), 3.99 (t, *J* = 6.4 Hz, 4H), 2.12 – 1.99 (m, 1H), 1.81 (dd, *J* = 8.4, 6.2 Hz, 4H), 1.75 – 1.70 (m, 1H) [under THF solvent peak], 1.56 – 1.50 (m, 4H), 1.50 – 1.23 (m, 24H), 0.97 (h, *J* = 4.4, 3.6 Hz, 8H), 0.95 – 0.84 (m, 10H). ¹³C NMR (150 MHz, THF-d₈) δ 163.81, 163.15, 162.29, 157.55, 153.91, 153.00, 151.12, 149.09, 148.19, 143.23, 142.28, 141.92, 140.87, 140.17, 135.78, 133.20, 132.71, 128.55, 128.19, 127.82, 127.79, 125.35, 124.01, 120.33, 116.42, 116.28, 112.23, 109.27, 105.22, 68.94, 68.07, 46.74, 46.52, 40.99, 40.46, 32.77, 31.65, 31.25, 30.82, 30.47, 29.66, 29.47, 26.93, 25.96, 24.87, 24.51, 24.15, 23.73, 14.60, 14.57, 11.29, 10.94. C₇₁H₈₃N₅O₆S[M⁺] Exact Mass = 1133.6064, MS (MALDI) = 1133.6086

Th-DPP_EthHex-Ph-FluoroBenzaldehyde

In a 50 mL single-neck round-bottom flask, 0.8 grams of Th-DPP_EtHex-Ph-Br (1.34 mmol), 0.4 grams of 3-Fluoro-4-formylphenylboronic acid, pinacol ester (1.61 mmol), and 0.85 gram of potassium phosphate tribasic (4.00 mmol) were dissolved in 13 mL of toluene, 1 mL tAmylOH, and 0.5 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 plugged through a thin pad of MgSO₄ with DCM. Volatile organics were removed and the crude compound loaded onto a medium column loaded with 200 mL of silica. A gradient eluent of 40:60 Toluene:DCM to 100% DCM was used to purify the compound. 700 mg (82% yield) of a pure red solid was obtained.

¹H NMR (400 MHz, Methylene Chloride-d₂) δ 10.38 (s, 1H), 8.91 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.72 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.62 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.51 (dd, *J* = 11.6, 1.6 Hz, 1H), 7.31 (dd, *J* = 5.0, 3.9 Hz, 1H), 4.03 – 3.91 (m, 2H), 3.91 – 3.77 (m, 2H), 1.86 – 1.73 (m, 1H), 1.55 – 1.45 (m, 1H), 1.40 – 1.00 (m, 16H), 0.91 – 0.82 (m, 6H), 0.75 (dt, *J* = 17.7, 6.9 Hz, 6H). ¹³C NMR (100 MHz, Methylene Chloride-d₂) δ 186.90, 186.84, 166.59, 164.03, 162.62, 162.32, 148.60, 148.51,

145.87, 142.72, 140.68, 140.67, 136.23, 131.85, 130.34, 130.03, 129.89, 129.81, 129.78, 128.86, 127.91, 123.82, 123.78, 123.75, 115.35, 115.13, 110.66, 108.40, 46.03, 45.46, 39.66, 39.65, 39.24, 32.50, 31.80, 30.85, 30.83, 30.75, 30.73, 30.50, 30.27, 30.23, 30.22, 29.93, 28.95, 28.93, 28.82, 25.42, 24.30, 24.09, 24.08, 23.63, 23.38, 23.27, 14.49, 14.39, 14.38, 14.33, 10.80, 10.78.

Br-Th-DPP EthHex-Ph-FluoroBenzaldehyde

The reaction and purification were performed in the same manner as for the synthesis of Br-Th-DPP_EtHex-Py-Benzaldehyde. 200 mg (26% yield) of a red/purple solid. This product was used semi-crude, because complete purification was not possible – separation of a completely pure material was achieved on the following step.

HexOTPA-Th-DPP EthHex-Ph-FluoroBenzaldehyde

The reaction and purification were performed in the same manner as for the synthesis of HexOTPA-Th-DPP_EtHex-Py-Benzaldehyde. 100 mg (33% yield) of a purple-ish solid.

^1H NMR (400 MHz, Methylene Chloride- d_2) δ 10.40 (s, 1H), 9.08 (d, $J = 4.2$ Hz, 1H), 8.02 – 7.93 (m, 1H), 7.94 (d, $J = 8.3$ Hz, 2H), 7.82 (d, $J = 8.4$ Hz, 2H), 7.63 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.55 – 7.49 (m, 3H), 7.40 (d, $J = 4.2$ Hz, 1H), 7.14 – 7.07 (m, 4H), 6.94 – 6.87 (m, 6H), 4.08 – 3.83 (m, 8H), 1.93 – 1.89 (m, 1H), 1.80 (dt, $J = 14.6, 6.7$ Hz, 4H), 1.55 – 1.45 (m, 5H), 1.44 – 1.06 (m, 24H), 0.99 – 0.85 (m, 12H), 0.83 – 0.72 (m, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 187.14, 187.09, 166.69, 164.12, 162.92, 162.30, 156.87, 152.16, 150.43, 148.76, 144.45, 143.16, 140.61, 140.24, 138.57, 130.99, 130.19, 129.98, 129.89, 129.87, 129.51, 128.90, 128.00, 127.85, 127.46, 127.37, 125.19, 124.65, 123.90, 123.87, 123.85, 123.76, 123.28, 119.67, 115.94, 115.60, 115.47, 115.26, 111.00, 107.90, 68.90, 46.17, 45.60, 39.83, 39.34, 32.19, 30.88, 30.28, 29.87, 29.12, 28.87, 26.30, 24.32, 24.20, 23.67, 23.41, 23.21, 14.42, 14.39, 14.33, 10.88, 10.82.

DPP12, HexOTPA-Th-DPP EthHex-Ph-FluorophenylCAA

The reaction and purification were performed in the same manner as for the synthesis of **DPP10**. 45 mg (42% yield) of a purple solid.

^1H NMR (600 MHz, THF- d_8) δ 9.28 (s, 1H), 8.65 – 8.45 (m, 2H), 8.11 (d, $J = 8.5$ Hz, 2H), 8.00 (d, $J = 8.5$ Hz, 2H), 7.87 (d, $J = 8.2$ Hz, 1H), 7.81 (d, $J = 11.2$ Hz, 1H), 7.58 (d, $J = 8.2$ Hz, 2H), 7.54 (d, $J = 4.3$ Hz, 1H), 7.11 (d, $J = 8.7$ Hz, 4H), 7.01 – 6.81 (m, 6H), 4.41 – 3.91 (m, 8H), 2.29 – 2.21 (m, 1H), 2.10 – 1.98 (m, 4H), 1.70 – 1.45 (m, 5H), 1.51 – 1.26 (m, 24H), 0.94 – 0.78 (m, 12H), 0.77 – 0.73 (m, 6H). ^{13}C NMR (150 MHz, THF- d_8) δ 162.35, 161.62, 161.33, 156.35, 151.18, 149.85, 146.65, 143.61, 141.84, 139.78, 139.60, 138.12, 129.66, 129.42, 129.26, 127.06, 126.99, 126.83, 126.59, 124.32, 123.17, 122.68, 119.38, 119.26, 115.11, 114.98, 114.00, 110.21, 107.31, 105.60, 67.77, 45.09, 44.56, 39.32, 38.70, 31.61, 30.27, 29.67, 29.31, 28.35, 28.16, 25.77, 23.60, 23.39, 22.99, 22.76, 22.57, 13.42, 13.35, 9.78. $\text{C}_{72}\text{H}_{83}\text{FN}_4\text{O}_6\text{S}[\text{M}^+]$ Exact Mass = 1150.6017, MS (MALDI) = 1150.6003

Computational discussion:

Concerning the electron affinity of pyridine, and the relevance of this affinity to the visible light absorption spectrum, **Figure S1** compares **DPP10** and **DPP03** (a symmetric DPP dye reported in our previous study¹¹). It is clear that the thiophene provides a lower bandgap; the electron affinity of pyridine is not likely the greatest factor in causing the red-shift for **DPP10** compared to **DPP03**.

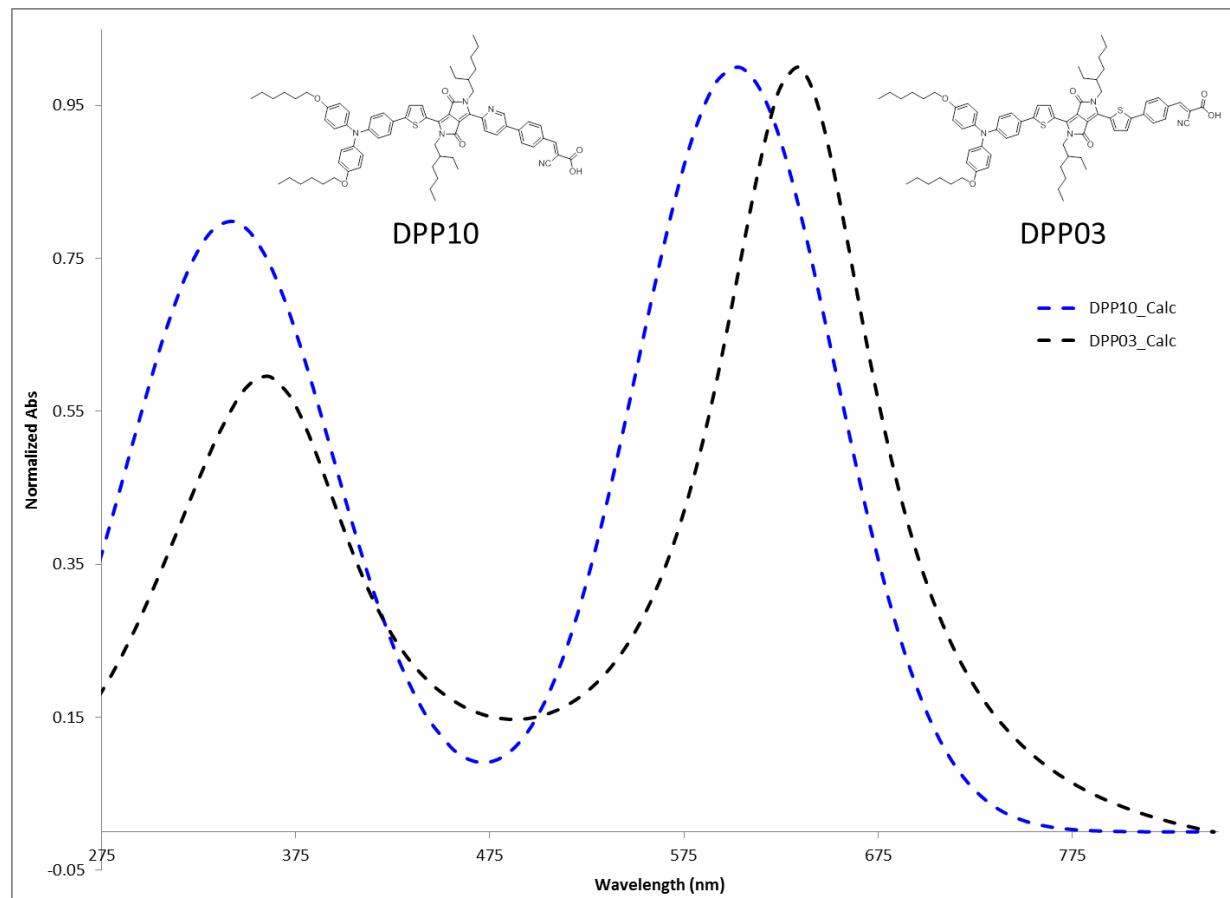


Figure S1. The effect of pyridine compared to thiophene substitution on the DPP chromophore. The calculation was performed as described in the main text.

Table S1. Averaged photovoltaic characteristics of DPP dyes, corresponding to Table 2 in the main text.

Dye	Electrolyte	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF (%)	η (%)
DPP07	I ₃ ⁻ /I ⁻	15.8 ± 0.08	667 ± 1	69.2 ± 0.4	7.29 ± 0.01
	Co[(bpy)] ^{3+/2+}	15.0 ± 0.08	776 ± 3	67.0 ± 1.5	7.79 ± 0.25
DPP10	I ₃ ⁻ /I ⁻	11.8 ± 0.01	665 ± 1	69.2 ± 0.1	5.44 ± 0.02
	Co[(bpy)] ^{3+/2+}	11.9 ± 0.09	730 ± 1	70.5 ± 0.3	6.13 ± 0.07
DPP12	I ₃ ⁻ /I ⁻	15.6 ± 0.12	698 ± 3	66.8 ± 0.2	7.28 ± 0.02
	Co[(bpy)] ^{3+/2+}	13.2 ± 0.04	746 ± 3	68.3 ± 0.5	6.99 ± 0.01

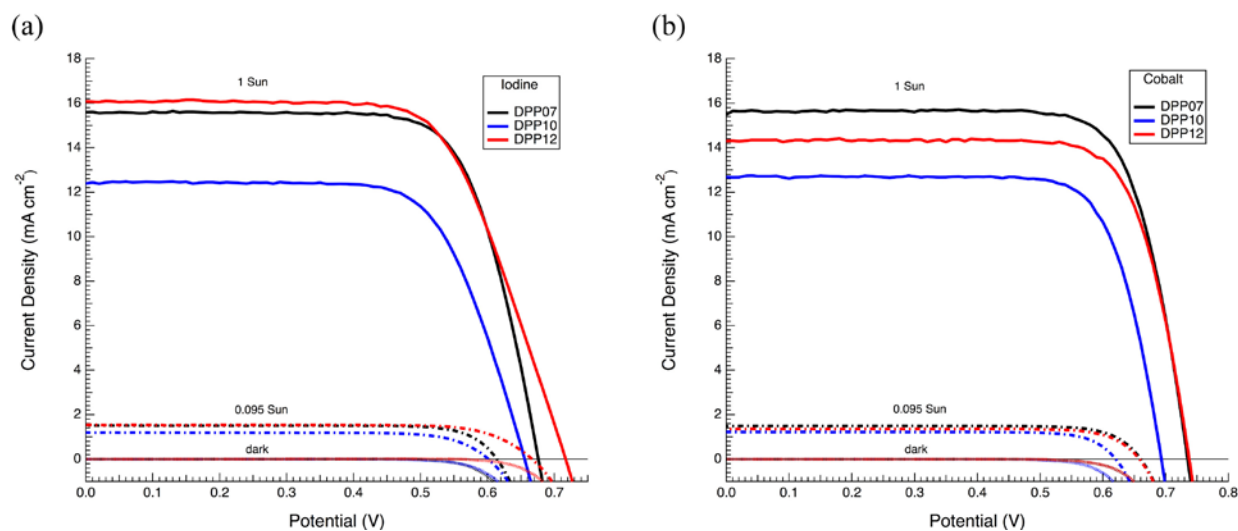


Figure S2. *JVs* of the best photovoltaic performance of DPP dyes. DSCs sensitized with **DPP07** (black lines), **DPP10** (blue lines), and **DPP12** (red lines) with (a) I₃⁻/I⁻ electrolyte and (b) Co[(bpy)]^{3+/2+} electrolyte.

References

1. T. W. Holcombe, J.-H. Yum, J. Yoon, P. Gao, M. Marszalek, D. D. Censo, K. Rakstys, M. K. Nazeeruddin and M. Graetzel, *Chem. Commun.*, 2012, **48**, 10724-10726.