An unsymmetrical non-fullerene acceptor: synthesis via direct heteroarylation, self-assembly, and utility as a low energy absorber in organic photovoltaic cells.

Abby-Jo Payne^a, Shi Li^b, Sergey V. Dayneko,^a Chad Risko^{b*} and Gregory C. Welch^{a*}

^aDepartment of Chemistry, University of Calgary 2500 University Drive NW Calgary, AB, Canada T2N 1N4

^bDepartment of Chemistry & Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky, 40506, USA.

* Corresponding Authors Email: gregory.welch@ucalgary.ca, chad.risko@uky.edu

SUPPORTING INFORMATION

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Materials and Methods

Materials: Diketopyrrolopyrrole was purchased from Brilliant Matters and 6-bromo-2oxindole was acquired from Ontario Chemicals Inc. Silia*Cat*® DPP-Pd was received from SiliCycle. All remaining reagents were purchased from Sigma-Aldrich. All solvents and materials purchased were used without further purification. Purification by flash column chromatography was performed using a Biotage® Isolera flash system.

Nuclear Magnetic Resonance (NMR): ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance-500 MHz spectrometer at 300 K. Chemical shifts are reported in parts per million (ppm). Multiplicities are reported as: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), multiplet (m), quintet (quin), overlapping (ov), and broad (br).

High-resolution Mass Spectrometry (HRMS): High-resolution MALDI mass spectrometry measurements were performed courtesy of Jian Jun (Johnson) Li in the Chemical Instrumentation Facility at the University of Calgary. A Bruker Autoflex III Smartbeam MALDI-TOF (Na:YAG laser, 355nm), setting in positive reflective mode, was used to acquire spectra. Operation settings were all typical, e.g. laser offset 62-69; laser frequency 200Hz; and number of shots 300. The target used was Bruker MTP 384 ground steel plate target. Sample solution (~ 1 μ g/mL in dichloromethane) was mixed with matrix trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) solution (~ 5mg/mL in methanol). Pipetted 1 μ l solution above to target spot and dried in the fume hood.

Cyclic Voltammetry (CV): All electrochemical measurements were performed using a Model 1200B Series Handheld Potentiostat by CH Instruments Inc. equipped with Ag wire, Pt wire, and glassy carbon electrode, as the pseudo reference, counter electrode, and working electrode, respectively. Glassy carbon electrodes were polished with alumina. The cyclic voltammetry experiments were performed in anhydrous dichloromethane solution with ~0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at scan rate 100 mV/s. All electrochemical solutions were purged with dry N₂ for 5 minutes to deoxygenate the system. Solution CV measurements were carried out with a small molecule concentration of ~0.5 mg/mL in dichloromethane. The ionization potentials (IP) and electron affinities (EA) were estimated by correlating the onsets $(E_{ox}Fc/Fc+, E_{red}Fc/Fc+)$ to the normal hydrogen electrode (NHE), assuming the IP of Fc/Fc+ to be 4.80 eV.¹

UV-Visible Spectroscopy (UV-Vis): All absorption measurements were recorded using Agilent Technologies Cary 60 UV-Vis spectrometer at room temperature. All solution UV-Vis spectroscopy experiments were run in CHCl₃ using 10 mm quartz cuvettes. Neat films were prepared by spin-coating ~0.2 mL from a 1 % wt/v solution (CHCl₃) onto clean onto Corning glass micro slides. Prior to use, glass slides were cleaned with soap and water, acetone and isopropanol, and followed by UV/ozone treatment using a Novascan UV/ozone cleaning system.

Photoluminescence (PL): All emission measurements were recorded using an Agilent Technologies Cary Eclipse fluorescence spectrophotometer at room temperature. Thinfilms were prepared by spin-coating 1 wt/v% solutions from CHCl₃ on Corning glass micro slides. Prior to use, glass slides were cleaned with soap and water, and acetone and isopropanol, and followed by UV/ozone treatment using a Novascan UV/ozone cleaning system.

X-ray Diffraction (XRD): Thin film XRD analysis of PDI-DPP-IQ (1% w/v CHCl₃ 2500 RPM, 10,000 RPM/s², 30 s spun cast on quartz substrates) were performed on a PROTO AXRD benchtop powder diffractometer with Cu K α radiation operating at a power level of 30 kV and 20 mA. Samples were scanned in plane (θ -2 θ scans) from 4°-8° 2 θ using a $\Delta 2\theta^{\circ}$ of 0.01963, a dwell time of 40 s, and a 0.5 mm divergence slit.

Atomic Force Microscopy (AFM): AFM measurements were performed by using a TT2-AFM (AFM Workshop) in tapping mode and WSxM software with an 0.01-0.025 Ohm/cm Sb (n) doped Si probe with a reflective back side aluminum coating. Samples for AFM measurement were the same ones that were used to collect the respective device parameters and EQE profiles.

Power Conversion Efficiency (PCE) and External Quantum Efficiency (EQE): The current density-voltage (J-V) curves were measured by a Keithley 2420 source measure unit. The photocurrent was measured under AM 1.5 illumination at 100mW/cm² under a Solar Simulator (Newport 92251A-1000). The standard silicon solar cell (Newport 91150V) was used to calibrate light intensity. EQE was measured in a QEX7 Solar Cell Spectral Response/QE/IPCE Measurement System (PV Measurement, Model QEX7, USA) with an optical lens to focus the light into an area about 0.04cm², smaller than the dot cell. The silicon photodiode was used to calibration of the EQE measurement system in the wavelength range from 300 to 1100 nm.

Experimental

Final compounds synthesized:



The diketopyrrolopyrrole dye was alkylated using our modified literature procedure.² The N-annulated perylene diimide and indoloquinoxaline building blocks were synthesized according to our previously reported literature procedures.^{3–5}



Synthesis of PDI-DPP(octyl)

In a 100 mL pressure flask, 2,5-bis(octyl)-3,6-di(thiophen-2-yl)diketopyrrolopyrrole (750 mg, 1.06 mmol, 1 eq.), 11-bromo-5-hexyl-2,8-bis(1-ethylpropyl)perylene diimide (675 mg, 0.96 mmol, 0.9 eq.), Silia*Cat*® DPP-Pd (5 mol % Pd), pivalic acid (30 mol %) and potassium carbonate (1.5 eq.) were added with a stir bar followed by the addition of anhydrous N,N'-dimethylacetamide (40 mL). The reaction mixture was sealed with a Teflon® cap under N_2 and heated at 80 °C in a LabArmor® bead bath for 24 hours until the PDI was gone by TLC. After 24 hours, the reaction mixture was poured into MeOH and allowed to stir overnight. The precipitated product was collected by filtration and the filtrate was discarded. The solid product was subsequently washed with dichloromethane to solubilize the product and isolate it from the insoluble silica-supported catalyst. The filtrate was concentrated by rotary evaporation and prepared for purification by flash column chromatography. Using a hexane to dichloromethane gradient, residual DPP starting material can be removed at 50-60 % dichloromethane. The product, PDI-DPP, elutes from 80-100% dichloromethane and the bis-substituted product, PDI-DPP-PDI, is subsequently pulled off with ethyl acetate. Solvent was removed from the resulting mono and bis substituted fractions and they were subsequently slurried in MeOH and filtered washing with MeOH to yield both PDI-DPP (500 mg, 0.43 mmol, 45 % yield) and PDI-DPP-PDI (250 mg, 0.14 mmol, 15 % yield) as shiny green iridescent flakes.

¹**H NMR** (500 MHz, CDCl₃, ppm): δ 9.31 (d, *J*= 3.9 Hz, 1H), 9.10 (s, br, 1H) 9.03 (s, br, 1H), 8.94 (d, *J*= 3.0 Hz, 1H), 8.87 (s, br, 1H), 8.57 (s, br, 1H) 8.30 (d, *J* = 8.4 Hz, 1H), 7.68 (dd, *J*= 5.1 Hz, 1.1 Hz, 1H) 7.65 (d, *J*= 3.9Hz, 1H), 7.31 (dd, *J*= 5.0 Hz, 3.9 Hz, 1H), 5.24 (m, 1H) 5.17 (m, 1H), 4.92 (t, 2H), 4.06 (t, 2H), 3.95 (t, br, 2H), 2.41-2.25 (m, ov, 4H) 2.23 (quin, 2H), 2.05-1.95 (m, ov, 4H), 1.75 (sept, 4H), 1.51-1.45 (m, ov, 2H), 1.45-1.37 (m, ov 4H), 1.37-1.20 (m, ov, 14H) 1.17-1.06 (m, ov, 6H), 0.99 (t, 6H) 0.95 (t, 6H), 0.90-0.86 (m, ov, 6H), 0.68 (t, 3H).

¹³C NMR (500 MHz, CDCl₃, ppm): δ 160.70, 160.52, 146.78, 139.71, 138.44, 136.17,135.06, 134.39, 132.13, 132.02, 131.34, 131.31, 130.39, 129.05, 128.42, 128.12, 127.41, 124.34, 124.23, 122.43, 122.38, 119.23, 119.10, 107.76, 107.06, 57.32, 57.18,

46.40, 41.75, 41.65, 31.22, 31.04, 30.98, 30.81, 29.53, 29.36, 28.64, 28.63, 28.51, 28.50, 26.34, 26.32, 26.26, 24.61, 22.07, 21.92, 21.91, 13.55, 13.40, 13.38, 10.86.

Tabulated Aromatic Peaks: 25 Tabulated Aliphatic Peaks: 26

¹H NMR spectrum for PDI-DPP-PDI corresponds to that previously reported.^{6,7}

Synthesis of PDI-DPP(EH)



In a 20 mL pressure vial 2,5-bis(2- ethylhexyl)-3,6-di(thiophen-2-yl)diketopyrrolopyrrole (425 mg, 0.81 mmol, 1 eq.), 11-bromo-5-hexyl-2,8-bis(1-ethylpropyl)perylene diimide (500 mg, 0.71 mmol, 0.9 eq.), Silia*Cat*® DPP-Pd (5 mol % Pd), pivalic acid (30 mol %) and potassium carbonate (1.5 eq.) were added with a stir bar followed by the addition of anhydrous N,N'-dimethylacetamide (17 mL). The reaction mixture was sealed with a Teflon® cap under N₂ and heated at 80 °C in a LabArmor® bead bath for 24 hours until the PDI was gone by TLC. After 24 hours, the reaction mixture was poured into MeOH and allowed to stir for an hour. The precipitated product was collected by filtration and the filtrate was discarded. The solid product was subsequently washed with dichloromethane to solubilize the product and isolate it from the insoluble silica-supported catalyst. The filtrate was concentrated by rotary evaporation and prepared for purification by flash column chromatography. Using a hexane to dichloromethane gradient, residual DPP starting material can be removed at 50 % dichloromethane. The mono substituted product elutes at 75 % dichloromethane and the bis-substituted product at 100 % dichloromethane. Solvent was removed from the resulting mono and bis substituted fractions and they were subsequently slurried in MeOH and filtered washing with MeOH to yield both PDI-DPPEH (380 mg, 0.33 mmol, 47 % yield) and PDI-DPPEH-PDI (266 mg, 0.15 mmol, 21 % yield) as shiny green iridescent flakes.

¹**H NMR** (500 MHz, CDCl₃, ppm): δ 9.30 (d, *J*= 3.8 Hz, 1H), 9.10 (s, br, 1H), 9.01 (s, br, 1H), 8.89 (s, br, 1H), 8.87 (s, br, 1H), 8.54 (s, br 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.66 (m, *J*= 5.1 Hz, 1.0 Hz, 1H) 7.65 (d, *J*= 3.9Hz, 1.1H), 7.29 (dd, *J*= 3.9 Hz, *J*= 1.1 Hz, 1H), 5.24 (m, 1H) 5.16 (m, 1H), 4.91 (t, 2H), 4.00 (m, 2H), 3.87 (m, 2H), 2.41-2.28 (m, ov, 4H) 2.23 (quin, 2H), 2.05-1.95 (m, ov, 5H), 1.43-1.13 (m, ov 23H), 0.99 (t, 6H) 0.95 (t, 6H), 0.90-0.85 (m, ov, 12H), 0.68 (t, br, 3H).

¹³**C NMR** (500 MHz, CDCl₃, ppm): δ 161.06, 160.86, 146.69, 138.81, 136.26, 135.09, 134.39, 134.37, 132.09, 132.07, 131.38, 131.32, 130.23, 129.08, 128.26, 127.92, 127.44, 124.32, 124.21, 122.42, 122.35, 119.23, 119.07, 107.94, 107.24, 57.31, 57.18, 46.40, 45.45, 45.22, 38.62, 38.46, 30.98, 30.81, 29.62, 29.59, 27.79, 27.68, 24.63, 24.62, 24.60, 22.94, 22.51, 22.43, 22.42, 21.92, 13.50, 13.40, 13.30, 10.85, 9.90, 9.89.

Tabulated Aromatic Peaks: 25 Tabulated Aliphatic Peaks: 27

¹H NMR for PDI-DPP(EH)-PDI corresponds to that previously reported by our group.⁶

Synthesis of PDI-DPP-IQ (1)



In a 20 mL pressure vial, PDI-DPP (300 mg, 0.26 mmol, 1eq), IQ (133 mg, 0.32 mmol, 1.2 eq), Silia*Cat*® DPP-Pd (5 mol % Pd), pivalic acid (30 mol %), and potassium carbonate (1.5 eq.) were added with a stir bar followed by the addition of anhydrous N,N'-dimethylacetamide (15 mL). The reaction mixture was sealed with a Teflon® cap under N₂ and heated at 90 °C in a LabArmor® bead bath for 24 hours. After 24 hours, the reaction mixture was poured into acetone (100 mL) and allowed to stir for two hours. The precipitated product was collected by filtration and the filtrate was discarded. The solid product was subsequently dissolved in dichloromethane and sent through a short silica plug to remove the silica-supported catalyst and any remaining inorganics. Upon removal of solvent, the resulting material was stirred and heated in acetone (50 mL) for 2 hours to remove any remaining unreacted starting material (PDI-DPP or IQ). The product was filtered washing with acetone and isolated as a dark purple powder (330 mg, 0.22 mmol, 85 % yield).

¹**H NMR** (500 MHz, CDCl₃, ppm): δ 9.34 (d, *J*= 3.9 Hz, 1H), 9.10 (s, br, 1H), 9.04 (m, ov, 2H), 8.87 (s, br, 1H), 8.58 (s, br, 1H), 8.49 (d, *J*=8.4 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.29 (dd, *J*=7.3 Hz, *J*=1.1 Hz, 1H), 8.14 (dd, *J*= 7.4 Hz, *J*= 1.0 Hz, 1H), 7.77 (m, 1H), 7.72-7.68 (m, ov, 4H), 7.65 (d, *J*= 3.9Hz, 1H), 5.25 (m, 1H) 5.18 (m, 1H), 4.90 (t, 2H), 4.54 (t, 2H), 4.11 (t, 4H), 2.40-2.28 (m, ov, 4H) 2.22 (quin, 2H), 2.05-1.96 (m, ov, 6H), 1.82 (sept, 4H), 1.51-1.23 (m, ov, 30H), 1.19-1.07 (m, ov, 6H), 1.00 (t, 6H) 0.96 (t, 6H), 0.89-0.84 (m, ov, 9H), 0.69 (t, 3H).

¹³**C NMR** (500 MHz, CDCl₃, ppm): δ 160.76, 160.53, 149.32, 146.91, 145.65, 144.19, 140.20, 139.17, 139.03, 138.70, 138.43, 136.43, 136.26, 134.88, 134.39, 132.11, 132.00, 131.32, 129.08, 128.76, 128.44, 127.42, 127.35, 125.66, 125.23, 124.34, 124.25, 122.80, 122.44, 122.38, 119.25, 119.10, 118.66, 108.02, 107.70, 106.02, 57.34, 57.19, 46.38, 41.86, 41.76, 40.95, 31.26, 31.25, 31.05, 30.97, 30.79, 29.57, 29.49, 28.72, 28.69, 28.64, 28.53, 27.96, 26.52, 26.42, 26.33, 26.30, 24.61, 22.09, 22.06, 21.92, 13.55, 13.52, 13.89, 10.86.

Tabulated Aromatic Peaks: 36 Tabulated Aliphatic Peaks: 30

MS (MALDI-TOF): *m*/*z* 1478.73. calcd. 1478.74.

Synthesis of PDI-DPP(EH)-IQ(octyl) (4) and PDI-DPP(octyl)-IQ(ethyl) (5)



PDI-DPP(EH)-IQ(octyl) (4)

PDI-DPP(octyl)-IQ(ethyl) (5)

Side chain derivatives of PDI-DPP-IQ were prepared in a similar fashion to **1**, however by substituting octyl DPP for ethyl hexyl DPP to form PDI-DPP(EH)-IQ(octyl) (**4**) and using ethyl IQ instead of octyl IQ to access PDI-DPP(octyl)-IQ(ethyl) (**5**).

PDI-DPP(EH)-IQ(octyl)

¹**H NMR** (500 MHz, CDCl₃, ppm): δ 9.32 (d, *J*= 3.6 Hz, 1H), 9.11 (s, br, 1H), 9.07 (s, br, 1H), 9.05 (s, br, 1H), 8.87 (s, br, 1H), 8.57 (s, br 1H), 8.53 (d, J=8.5 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 2H), 8.16 (dd, *J*= 7.4 Hz, *J*= 1.0 Hz, 1H), 7.79 (m, 1H), 7.74-7.69 (m, ov, 4H), 7.64 (s, br, 1H), 5.25 (m, 1H) 5.18 (m, 1H), 4.92 (t, br, 2H), 4.58 (t, 2H), 4.07 (m, 4H), 2.42-2.28 (m, ov, 4H) 2.23 (quin, 2H), 2.2 (m, ov, 8H), 1.50-1.27 (m, ov, 32H), 1.00-0.85 (m, ov, 29H), 0.71 (t, br, 3H).

¹³C NMR (500 MHz, CDCl₃, ppm): δ 161.21, 160.92, 149.17, 146.84, 145.73, 144.26, 140.22, 139.05, 138.87, 138.77, 136.64, 136.33, 134.96, 134.43, 132.12, 132.04, 131.43, 131.35 129.08, 128.77, 128.44, 127.48, 127.36, 125.69, 125.08, 124.36, 124.26, 122.87, 122.47, 122.41, 119.26, 119.14, 118.60, 108.28, 107.92, 106.03, 57.30, 57.14, 46.40, 45.59, 45.44, 31.25, 30.97, 30.80, 29.84, 29.66, 28.73, 28.64, 28.64, 28.02, 27.98, 27.72,

26.54, 26.33, 24.62, 23.18, 22.99, 22.60, 22.46, 22.45, 22.06, 21.92, 13.58, 13.52, 13.39, 13.33, 10.86, 10.83, 10.08, 10.07, 9.96.

Tabulated Aromatic Peaks: 36 Tabulated Aliphatic Peaks: 35

MS (MALDI-TOF): *m*/*z* 1478.73. calcd. 1478.74.

PDI-DPP(octyl)-IQ(ethyl)

¹**H** NMR (500 MHz, CDCl₃, ppm): δ 9.34 (d, *J*= 3.9 Hz, 1H), 9.10 (s, br, 1H), 9.04 (m, ov, 2H), 8.87 (s, br, 1H), 8.58 (s, br, 1H), 8.49 (d, *J*=8.4 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.29 (dd, *J*=7.3 Hz, *J*=1.1 Hz, 1H), 8.14 (dd, *J*= 7.4 Hz, *J*= 1.0 Hz, 1H), 7.77 (m, 1H), 7.72-7.68 (m, ov, 4H), 7.65 (d, *J*= 3.9Hz, 1H), 5.25 (m, 1H) 5.18 (m, 1H), 4.90 (t, br, 2H), 4.63 (q, *J*= 7.1 Hz, 2H), 4.11 (t, br, 4H), 2.40-2.28 (m, ov, 4H) 2.22 (quin, 2H), 2.05-1.96 (m, ov, 4H), 1.82 (sept, 4H), 1.60 (t, 3H), 1.51-1.23 (m, ov, 20H), 1.19-1.07 (m, ov, 6H), 1.00 (t, 6H) 0.96 (t, 6H), 0.89-0.84 (m, ov, 9H), 0.69 (t, 3H).

¹³C NMR (500 MHz, CDCl₃, ppm): δ 160.77, 160.53, 149.26, 146.92, 145.26, 143.81, 140.13, 139.17, 139.04, 138.87, 138.45, 136.37, 136.26, 134.94, 134.40, 132.12, 131.98, 131.32, 129.10, 128.80, 128.44, 127.42, 127.27, 125.71, 125.25, 124.35, 124.25, 122.89, 122.45, 122.39, 119.34, 119.23, 118.71, 108.03, 107.71, 105.82, 57.40, 57.19, 46.39, 41.86, 41.76, 35.75, 31.25, 31.05, 30.99, 30.80, 29.51, 28.69, 28.54, 28.53, 26.42, 26.33, 26.30, 24.61, 22.09, 21.92, 13.55, 13.39, 13.23, 10.86.

Tabulated Aromatic Peaks: 36 Tabulated Aliphatic Peaks: 24

MS (MALDI-TOF): *m/z* 1394.64. calcd. 1394.64

Synthesis of PDI-DPP-TPA (2)



In a 5 mL pressure vial, PDI-DPP (148 mg, 0.13 mmol, 1eq), TPA (59 mg, 0.18 mmol, 1.4 eq), Silia*Cat*® DPP-Pd (5 mol % Pd), pivalic acid (30 mol %), and potassium carbonate (2.0 eq.) were added with a stir bar followed by the addition of anhydrous N,N'-dimethylacetamide (3 mL). The reaction mixture was sealed with a Teflon® cap under N₂ and heated at 100 °C in a LabArmor® bead bath for four hours. The reaction mixture was

poured into methanol (75 mL) and allowed to stir for one hour. The precipitated product was collected by filtration and the filtrate was discarded. The solid product was subsequently dissolved in dichloromethane and sent through a short silica plug to remove the silica-supported catalyst and any remaining inorganics. Upon removal of solvent, the resulting material was slurried in a minimum amount of cold hexanes and filtered to yield PDI-DPP-TPA as a dark purple powder (150 mg, 0.11 mmol, 85 % yield).

¹**H NMR** (500 MHz, CDCl₃, ppm): δ 9.31 (d, *J*= 3.8 Hz, 1H), 9.10 (s, br, 1H) 9.00 (s, br, 1H), 8.95 (s, br, 1H), 8.88 (s, br, 1H), 8.55 (s, br, 1H) 8.30 (d, *J* = 8.4 Hz, 1H), 7.71 (s, br, 1H), 7.56 (d, *J*=8.7 Hz, 2H), 7.39 (d, *J*=4.1 Hz, 1H), 7.32 (m, 4H), 7.18 (m, 4H). 7.12 (m, 4H), 5.25 (m, 1H) 5.16 (m, 1H), 4.85 (t, 2H), 4.06 (t, 2H), 3.78 (m, br, 2H), 2.43-2.29 (m, ov, 4H) 2.21 (quin, 2H), 2.05-1.95 (m, ov, 4H), 1.75-1.68 (m, 4H), 1.50-1.20 (m, ov, 20H) 1.17-1.06 (m, ov, 6H), 1.00 (t, 6H) 0.96 (t, 6H), 0.90-0.86 (m, ov, 6H), 0.69 (t, 3H).

¹³C NMR (500 MHz, CDCl₃, ppm): δ 160.68, 160.19, 150.07, 148.25 146.45, 146.34, 139.58, 137.34, 137.11, 135.94, 134.38, 134.35, 132.20, 132.08, 131.49, 131.34, 128.94, 128.61, 127.38, 126.65, 126.43, 125.66, 124.56, 124.31, 124.21, 123.28, 122.99, 122.42, 122.36, 122.04, 119.25, 119.10, 107.96, 106.67, 57.30, 57.22, 46.36, 41.73, 41.47, 31.24, 31.05, 30.97, 30.80, 29.54, 29.32, 28.63, 28.61, 28.52, 28.50, 26.34, 26.28, 26.27, 24.64, 22.07, 21.94, 21.91, 13.55, 13.41, 13.39, 10.90, 10.87.

Tabulated Aromatic Peaks: 34 Tabulated Aliphatic Peaks: 27

MS (MALDI-TOF): m/z 1392.65. calcd. 1392.65



Synthesis of PDI-DPP-BA (3)

In a 5 mL pressure vial, PDI-DPP (120 mg, 0.10 mmol, 1eq), BA (23 mg, 0.12 mmol, 1.2 eq), Silia*Cat*® DPP-Pd (5 mol % Pd), pivalic acid (30 mol %), and potassium carbonate (2.0 eq.) were added with a stir bar followed by the addition of anhydrous N,N'-dimethylacetamide (3 mL). The reaction mixture was sealed with a Teflon® cap under N₂ and heated at 80 °C in a LabArmor® bead bath for 20 hours. The reaction mixture was poured into methanol (50 mL) and allowed to stir for three hours. The precipitated product was subsequently dissolved in dichloromethane and sent through a short silica plug to remove

the silica-supported catalyst and any remaining inorganics. Upon removal of solvent, the resulting material was slurried in 1:1 methanol:hexanes and filtered to yield PDI-DPP-BA as a dark purple powder (104 mg, 0.08 mmol, 82 % yield).

¹**H NMR** (500 MHz, CDCl₃, ppm): δ 10.06 (s, 1H), 9.35 (d, *J*= 3.9 Hz, 1H), 9.12 (s, br, 1H) 9.06 (s, br, 1H), 9.01 (d, *J*= 4.1 Hz, 1H), 8.87 (s, br, 1H), 8.58 (s, br, 1H) 8.30 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J*= 8.45 Hz, 2H) 7.88 (d, *J*= 8.3 Hz, 2H), 7.65 (d, *J*= 4.2 Hz, 1H), 7.63 (d, *J*= 3.9 Hz, 1H), 5.24 (m, 1H) 5.17 (m, 1H), 4.92 (t, 2H), 4.06 (t, 2H), 3.95 (t, br, 2H), 2.41-2.25 (m, ov, 4H) 2.23 (quin, 2H), 2.05-1.95 (m, ov, 4H), 1.75 (sept, 4H), 1.51-1.20 (m, ov, 20H) 1.17-1.06 (m, ov, 6H), 0.99 (t, 6H) 0.95 (t, 6H), 0.90-0.86 (m, ov, 6H), 0.68 (t, 3H).

¹³**C NMR** (500 MHz, CDCl₃, ppm): δ 190.65, 160.66, 160.54, 147.19 147.08, 138.87, 138.75, 138.02, 136.52, 136.11, 135.45, 134.42, 132.10, 131.92, 131.33, 131.22, 130.04, 129.87, 128.50, 127.40, 125.87, 125.81, 124.38, 124.25, 122.45, 122.40, 119.24, 119.11, 108.01, 107.95, 57.34, 57.19, 46.40, 41.86, 41.72, 31.24, 31.04, 30.97, 30.79, 29.54, 29.44, 28.64, 28.63, 28.52, 28.50, 26.34, 26.33, 26.27, 24.61, 22.07, 21.92, 21.91, 13.56, 13.40, 13.38, 10.85.

Tabulated Aromatic Peaks: 30 Tabulated Aliphatic Peaks: 26

MS (**MALDI-TOF**): *m*/*z* 1253.57. calcd. 1253.57.

NMR Spectra



Figure S1. ¹H NMR spectrum of PDI-DPP(octyl) in CDCl₃.



Figure S2. ¹³C NMR spectrum of PDI-DPP(octyl) in CDCl₃



Figure S3. ¹H NMR spectrum of PDI-DPP(EH) in CDCl₃.



Figure S4. ¹³C NMR spectrum of PDI-DPP(EH) in CDCl₃.



Figure S5. ¹H NMR spectrum of PDI-DPP-IQ (1) in CDCl₃.



Figure S6. ¹H NMR spectrum of PDI-DPP-IQ (1) in CDCl₃ aromatic region.



Figure S7. ¹³C NMR spectrum of PDI-DPP-IQ (1) in CDCl₃



Figure S8. 2D ¹H–¹H COSY NMR spectrum of PDI-DPP-IQ (1) in CDCl₃



Figure S9. 2D $^{1}H^{-1}H$ COSY NMR spectrum of **PDI-DPP-IQ** (1) in CDCl₃ aromatic region.



Figure S10. ¹H NMR spectra stack plot of IQ(octyl), PDI-DPP-IQ (1), and PDI-DPP(octyl) in CDCl₃ aromatic region.



Figure S11. ¹H NMR peak assignment of **PDI-DPP-IQ** (1) by dye building block, **PDI** (red), **DPP** (blue), and **IQ** (orange).



Figure S12. ¹H NMR spectrum of PDI-DPP(EH)-IQ(octyl) (4) in CDCl₃.



Figure S13. ¹³C NMR spectrum of PDI-DPP(EH)-IQ(octyl) (4) in CDCl₃.



Figure S14. ¹H NMR spectrum of PDI-DPP(octyl)-IQ(ethyl) (5) in CDCl₃.



Figure S15. ¹³C NMR spectrum of PDI-DPP(octyl)-IQ(ethyl) (5) in CDCl₃.



Figure S16. ¹H NMR spectrum of PDI-DPP-BA (2) in CDCl₃.



Figure S17. ¹³C NMR spectrum of PDI-DPP-BA (2) in CDCl₃



Figure S18. ¹H NMR spectrum of PDI-DPP-TPA (3) in CDCl₃.



Figure S19. ¹³C NMR spectrum of PDI-DPP-TPA (3) in CDCl₃

Mass Spectra (MALDI-TOF)



Figure S20. MALDI-TOF mass spectrum of PDI-DPP-IQ (1).



Figure S21. MALDI-TOF mass spectrum of PDI-DPP(EH)-IQ(octyl) (4).



Figure S22. MALDI-TOF mass spectrum of PDI-DPP(octyl)-IQ(ethyl) (5).



Figure S23. MALDI-TOF mass spectrum of PDI-DPP-BA (2).



Figure S24. MALDI-TOF mass spectrum of PDI-DPP-TPA (3).



Figure S25. A) Structure of **PDI-DPP-IQ** (1) with individual components highlighted. B) Individual thin film UV-Vis spectra (CHCl₃) of IQ, PDI, and DPP. C) Oxidation and reduction waves of IQ, PDI and DPP. D) Estimated energy levels from cyclic voltammetry.



Figure S26. Cyclic voltammogram of **PDI-DPP-IQ** (1) (black solid trace) and each individual component: **IQ** (orange dotted trace), **PDI** (red dotted trace), and **DPP** (blue dotted trace).

 Table S1. Optical and electrochemical data for compound 1.

		Sol	ution Data		Thin Film Data			ilm Data Electrochemical Data				
	λ_{max}^{1} (nm)	λ_{on}^{1} (nm)	Eg _(opt) ¹ (eV)	$\begin{array}{c} \epsilon^{1}(\lambda_{max}) \\ (M^{-1}cm^{-1}) \end{array}$	λ_{max}^2 (nm)	λ_{on}^2 (nm)	Eg _(opt) ² (eV)	Ox _{onset} (V) ^a	Red _{onset} (V) ^a	Oxidations E _{1/2} (V) ^a	Reductions E _{1/2} (V) ^a	
1	533	720	1.70	99672	536	780	1.59	0.375	-1.15	0.47, 0.76	-1.27, -1.49, -1.70, -1.90	
1 SVA	-	-	-	-	702	792	1.57	-	-	-	_	



Figure S27. Differential scanning calorimeter thermogram of **1** at a ramp rate of 10 °C/min under a flow of N_2 . Melting is observed at 206 °C.



Figure S28. Thermal gravimetric analysis thermogram of 1 at a ramp rate of 10 °C/min under a flow of N_2 (100 mL/min). 5% mass loss at 400 °C.



Figure S29. Thin film UV-Vis (CHCl₃) of symmetrical derivative **PDI-DPP-PDI** (pink) versus unsymmetrical **PDI-DPP-IQ** (1) (purple). Both display maximum absorbance at 536 nm characteristic of perylene diimide, while **PDI-DPP-IQ** (1) exhibits a more prominent low energy shoulder extending out to 800 nm in addition to an absorption band centered at 410 nm as a result of the IQ unit.



Figure S30. Thin film UV-Vis of **PDI-DPP-IQ** (1) as-cast and upon thermal annealing for five minutes at each temperature. Left) as-cast to 200 °C, Middle) 200 °C – 240 °C (note that compound 1 melts ~206°C), Right) Photo of film after heating to 240 °C. Significant de-wetting of the film is observed.



Figure S31. Optical microscope images (5x magnification) of a thin film of 1 during heating of the film on a thermal stage past the compound's melting point (~206 °C) and subsequently cooled back to room temperature. Live images show a uniform thin film which progressively de-wets with temperatures approaching and surpassing the compound's melting point.



Figure S32. Compound **1** cast from *o*-xylene (left) and CHCl₃ (right) solvent vapor annealed from *o*-xylene. Films were spun from 1% W/V solutions at 1000 RPM, 10000 RPM/s, 60 s for *o*-xylene and 2500 RPM, 10000 RPM/s, 30 s for CHCl₃.



Figure S33. Optical absorption spectra of thin films of **PDI-DPP-IQ** (1) and various other **PDI-DPP** based derivatives, as-cast and SVA using *o*-xylene. All compounds where spun from 10 mg/mL CHCl₃ solutions at 2500 RPM, 10000 RPM/s, 30 s and were annealed from *o*-xylene for 15 minutes (note, compounds that did not respond to SVA from *o*-xylene up

to 15 minutes were treated with solvent vapour up to 1 hour to confirm no response). THF and CHCl₃ were also screened as SVA solvents for the compounds that did not respond to *o*-xylene with no changes observable by UV-Vis spectroscopy.



Figure S34. SVA of **PDI-DPP-IQ** (1) (left) and **PDI-DPP-IQE** (right) from *o*-xylene. Films were spun from 10 mg/mL CHCl₃ solutions at 2500 RPM, 10000 RPM/s, 30 s.

Organic Solar Cells

Devices were fabricated using ITO-coated glass substrates cleaned by sequentially ultra-sonicating detergent and de-ionized water, and acetone and isopropanol, followed by exposure to UV/zone for 30 minutes. ZnO was subsequently deposited as a sol-gel precursor solution in air following the method of Sun *et al.*⁸ The room temperature solution was filtered and spin-cast at a speed of 4000 RPM and then annealed at 200 °C in air for 15 min.

Active layer solutions of **P3HT** and **PDI-DPP-IQ** (1) were prepared in air with a total concentration of 7 mg/mL in CHCl₃. Solutions were stirred overnight at room temperature prior to filtration through a PTFE filter. Active layer materials were combined in a 1:3 weight ratio and cast at room temperature in air at a speed of 1500 rpm for 60 seconds. An acceptor heavy ratio of 1:3 was chosen in order to observe photocurrent generation from **PDI-DPP-IQ** (1), and it was found that 7 mg/mL total solids concentration in CHCl₃ resulted in uniform thin films when spin cast (1500 RPM).

Post-deposition solvent vapour annealing was carried out by containing a raised ascast substrate within a screw cap glass jar with 0.5 mL of *o*-xylene as a solvent in the bottom of the jar. Substrates were left exposed to the solvent vapour for pre-determined durations. A solvent exposure time of five minutes was found to be optimal for 1:3 blends of **P3HT:1** in terms of overall device performance (Table S3, Figure S31).

The substrates were then kept in an N₂ atmosphere glovebox overnight before evaporating MoO₃ and Ag. The evaporation of 10 nm of MoO₃ followed by 100 nm of Ag were thermally deposited under vacuum ($1x10^{-6}$ Torr). The active areas of resulting devices were 0.09 cm². Completed devices were then tested in air using a Newport 92251A-1000 AM 1.5 solar simulator which had been calibrated using a standard silicon solar cell (Newport 91150V) to obtain an irradiance level of 1000 W/m².

A P3HT:PC₆₁BM control solar cell was fabricated following literature conditions (40 mg/mL *o*-DCB 1:1 ratio, spun at 1500 RPM, 60 s followed by thermal annealing at 130 °C for 20 minutes).⁹ P3HT:PC₆₁BM devices were also prepared according to the optimized P3HT:1 devices for direct comparison. Statistics listed below for each device were tabulated from two substrates containing two devices each for a total of four devices.

Materials	Ratio	Parameters	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)	R _s	$R_{sh} \left(\Omega \ cm^2\right)$
			Avg.	Avg. (best)	Avg.	Avg.	$(\Omega \text{ cm}^2)$	
			(best)		(best)	(best)		
P3HT:11	1:3	As-cast	0.76 (0.83)	0.59 (0.63)	25.7 (25.1)	0.11 (0.13)	1087	1336
P3HT:11	1:3	SVA 5 min	0.75 (0.75)	2.51 (2.47)	41.8 (43.4)	0.78 (0.81)	85	908
P3HT:PC61BM1	1:3	As-cast	0.66	3.25	42.0	0.89	53	458
P3HT:PC61BM1	1:3	SVA 5 min	0.42	5.04	50.5	1.06	18	403
P3HT:PC ₆₁ BM	1:1	130 °C 20						
		min	0.58	10.1	61.6	3.6	7.8	717

 Table S2. Optimized organic solar cell data.

Materials	Ratio	SVA Time	$V_{oc}\left(V ight)$	J _{sc} (mA/cm ²)	FF (%)	PCE (%)	$R_s (\Omega \ cm^2)$	$R_{sh}(\Omega~cm^2)$
P3HT:1	1:3	0 min	0.83	0.63	25.1	0.13	1082	1340
P3HT:1	1:3	2 min	0.79	1.60	34.8	0.44	203.1	900
P3HT:1	1:3	5 min	0.75	2.47	43.4	0.81	70.3	781
P3HT:1	1:3	10 min	0.76	1.92	47.3	0.68	52.8	1314

Table S3. Organic solar cell data as function of SVA time.



Figure S35. UV-Vis spectra, JV-Curves, and EQE profiles of P3HT:1 blends as a function of SVA time.



Figure S36. AFM Images of P3HT:1 organic solar cell devices. Left) As-cast. Right) solvent vapour annealed for 5 minutes from *o*-xylene.

Density Functional Theory (DFT) Calculations

All density functional theory (DFT) and time-dependent DFT (TDDFT) calculations were carried out at the OT- ω B97X-D/6-31g(d,p) level of theory, with the tuned ω parameter reported in Table S4; the optimized ω parameter for **PDI-DPP-IQ(1)** was used for all subsequent calculations, including the (optimized) rotational scans and dimer configurations. All optimized, unconstrained geometries were confirmed as minima on the potential energy surface through normal mode analyses. Note that all alkyl groups were truncated to methyl groups to reduce the computational cost. The Gaussian09 (Revision E.01)¹⁰ software suite was used for the DFT and TDDFT calculations. Absorption spectra were simulated through convolution of the vertical transition energies and oscillator strengths with Gaussian functions characterized by a full width at half-maximum (fwhm) of 0.33 eV.

Table S4. Select DFT and TDDFT data for **PDI-DPP-IQ** (1) and three rotational isomers as determined at the $OT-\omega B97X-D/6-31g(d,p)$ level of theory.

Materials	Tuned ω	Relative Energy (kcal/mol)	IP ^a (eV)	EA ^b (eV)	S ₀ →S ₁ (eV [nm])	f	Electronic Configuration of the $S_0 \rightarrow S_1$ Transition
1	0.123	0.00	6.00	2.21	2.37 [523]	1.27	$HOMO \rightarrow LUMO + 1 (85\%)$ $HOMO \rightarrow LUMO (9\%)$
rotational isomers							
1a	0.123	2.25	6.03	2.20	2.39 [518]	1.30	$HOMO \rightarrow LUMO + 1 (92\%)$
1b	0.125	13.44	6.04	2.16	2.48 [500]	1.06	$HOMO \rightarrow LUMO + 1 (94\%)$
1c	0.125	12.33	6.07	2.16	2.47 [503]	0.96	$HOMO \rightarrow LUMO + 1 (90\%)$

^aIP = ionization potential. ^{b}EA = electron affinity.

Optimized Structure (i.e. twisted)



Figure S37. Pictorial representations of select frontier molecular orbitals of **PDI-DPP-IQ** (1) as determined at the OT- ω B97X-D/6-31g(d,p) level of theory.

Table S5. First ten excited states of the optimized **PDI-DPP-IQ** (1) structure as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory.

Excited State	Energy [λ] (eV [nm])	f
1	2.37 [523]	1.27
2	2.63 [471]	0.16
3	2.75 [450]	0.57
4	3.08 [403]	0.11
5	3.32 [373]	0.02
6	3.43 [361]	0.00
7	3.50 [354]	0.66
8	3.69 [335]	0.31
9	3.72 [333]	0.00
10	3.76 [330]	0.00



Figure S38. Pictorial representations of the natural transition orbitals (NTO) for the $S_0 \rightarrow S_1$ of **PDI-DPP-IQ** (1) as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory. λ is the fraction of the hole–particle contribution to the excitation.



Figure S39. Pictorial representations of the natural transition orbitals (NTO) for the $S_0 \rightarrow S_2$ of **PDI-DPP-IQ** (1) as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory. λ is the fraction of the hole–particle contribution to the excitation.



Figure S40. Pictorial representations of the natural transition orbitals (NTO) for the $S_0 \rightarrow S_3$ of **PDI-DPP-IQ** (1) as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory. λ is the fraction of the hole–particle contribution to the excitation.



Figure S41. Pictorial representations of the natural transition orbitals (NTO) for the $S_0 \rightarrow S_4$ of **PDI-DPP-IQ** (1) as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory. λ is the fraction of the hole–particle contribution to the excitation.



Figure S42. Pictorial representations of the natural transition orbitals (NTO) for the $S_0 \rightarrow S_7$ of **PDI-DPP-IQ** (1) as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory. λ is the fraction of the hole–particle contribution to the excitation.



Figure S43. Potential energy surface for twisting the **PDI** moiety in **PDI-DPP-IQ** (1) as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory. For each **PDI** twist, the dihedral angle highlighted in red was frozen at the associated angle and the remainder of the molecule was allowed to minimize through a DFT optimization; no normal mode analyses were carried out on these constrained geometries. These geometries were then used in the follow-up TDDFT calculations reported in Figure S40.



Figure S44. Simulated absorption spectra of **PDI-DPP-IQ** (1) as a function of the orientation of the **PDI** group as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory. Absorption spectra were simulated through convolution of the vertical transition energies and oscillator strengths with Gaussian functions characterized by a full width at half-maximum (fwhm) of 0.33 eV.

Table S6. First ten excited states of the "optimized" dimer of **PDI-DPP-IQ** (1) as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory. For this calculation, the dimer was set with a distance of 3.5 Å between the DPP units.

Excited State	Energy (eV [nm])	f
1	2.31 [537]	1.47
2	2.33 [532]	0.58
3	2.53 [489]	0.11
4	2.55 [486]	0.09
5	2.74 [453]	0.55
6	2.74 [452]	0.71
7	2.81 [441]	0.08
8	2.92 [424]	0.01
9	3.07 [403]	0.18
10	3.08 [403]	0.14



Figure S45. Pictorial representations of the natural transition orbitals (NTO) for the $S_0 \rightarrow S_1$ of the "optimized" dimer of **PDI-DPP-IQ** (1) as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory. Both top and side views are presented. λ is the fraction of the hole–particle contribution to the excitation. Here, the optimized geometric structure of 1 is maintained, and a dimer is formed by stacking two molecules in a head-to-tail fashion with a separation of 3.5 Å.



Figure S46. Pictorial representations of the natural transition orbitals (NTO) for the $S_0 \rightarrow S_2$ of the "optimized" dimer of **PDI-DPP-IQ** (1) as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory. Both top and side views are presented. λ is the fraction of the hole–particle contribution to the excitation. Here, the optimized geometric structure of 1 is maintained, and a dimer is formed by stacking two molecules in a head-to-tail fashion with a separation of 3.5 Å.

Constrained Structure (i.e. planar)



Figure S47. Pictorial representations of select frontier molecular orbitals of planar **PDI-DPP-IQ** (1) as determined at the OT- ω B97X-D/6-31g(d,p) level of theory. For this planar configuration, all dihedral angles among the aromatic moieties are set to 0°. Note that while the LUMO and LUMO+1 energies are essentially the same as that for the fully optimized 1, the HOMO is energetically destabilized by 0.1 eV.

Excited State	Energy [λ] (eV [nm])	f
1	2.13 [582]	1.58
2	2.62 [473]	0.39
3	2.86 [434]	0.25
4	3.09 [401]	0.16
5	3.30 [376]	0.02
6	3.37 [368]	0.00
7	3.40 [364]	0.34
8	3.55 [349]	0.67
9	3.63 [342]	0.25
10	3.77 [329]	0.03

Table S7. First ten excited states of the planar **PDI-DPP-IQ** (1) structure as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory.



Figure S48. Pictorial representations of the natural transition orbitals (NTO) for the $S_0 \rightarrow S_1$ of **PDI-DPP-IQ** (1) in the planar configuration as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory. λ is the fraction of the hole–particle contribution to the excitation. For this planar configuration, all dihedral angles among the aromatic moieties are set to 0°.



Figure S49. Potential energy surface (PES) for the stacking of two, planar configurations of **PDI-DPP-IQ** (1) as determined at the OT- ω B97X-D/6-31g(d,p) level of theory. The planar molecules were oriented in a head-to-tail arrangement.



Figure S50. Potential energy surface (PES) for the sliding of two, planar **PDI-DPP-IQ** (1) as determined at the OT- ω B97X-D/6-31g(d,p) level of theory. The intermolecular distance was set to 3.4 Å, based on Figure S41.

Table S8. First ten excited states of a "planar" dimer of **PDI-DPP-IQ** (1) as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory. The geometry of the planar dimer for this calculation was based on the PES shown in Figures S41 and S42.

Excited State	Energy [λ] (eV [nm])	f
1	1.93 [641]	0.00
2	2.08 [596]	0.93
3	2.19 [566]	0.00
4	2.23 [555]	1.78
5	2.52 [492]	0.29
6	2.55 [486]	0.00
7	2.63 [471]	0.44
8	2.65 [468]	0.00
9	2.82 [440]	0.29
10	2.82 [440]	0.00



Figure S51. Pictorial representations of the natural transition orbitals (NTO) for the $S_0 \rightarrow S_2$ of the planar dimer of **PDI-DPP-IQ** (1) as determined at the TD-OT- ω B97X-D/6-31g(d,p) level of theory. Both top and side views are presented. λ is the fraction of the hole–particle contribution to the excitation.

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