Facile synthesis of unsymmetrical and π-extended furan-diketopyrrolopyrrole derivatives through C-H direct (hetero)arylation using a heterogeneous catalyst system

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SUPPORTING INFORMATION
General Methods

Preparations were carried out on a bench top or under a nitrogen atmosphere using Schlenk line techniques and/or a glove box unless otherwise stated. Purification by flash column chromatography was performed using a Biotage® Isolera flash system.

Materials: The heterogeneous catalyst SiliaCat® DPP-Pd was provided by SiliCycle. For details on the catalyst system please see: RSC Adv., 2015, 5, 26097-26106. The homogeneous catalyst Pd(OAc)₂ was purchased from Strem Chemicals Inc. N,N’-dimethylformamide (DMF), 2-cyanofuran and pivalic acid (PivOH) were purchased from TCI America and used without further purification. 2-ethylhexylbromide, 4,4’-dibromobiphenyl, 4-bromotriphenylamine, 9,10-dibromoanthracene and tris(4-bromophenyl)amine were purchased from Sigma-Aldrich and were used without further purification. Anhydrous potassium carbonate (K₂CO₃) was purchased from ACP Chemicals, and after initial usage, was stored in a Gallenkamp Hotbox oven at 100°C. All solvents were purchased from the Dalhousie solvent exchange program and used without further purification, unless otherwise noted.

NMR Characterization: ¹H NMR spectroscopy was used to evaluate conversion to product. ¹H NMR spectra were recorded on Bruker Avance 300 MHz or 500 MHz spectrometer at 300 K. Chemical shifts are referenced to tetramethylsilane, and all experiments performed in CDCl₃. Starting materials 1a, 1b, and 5-bromo-N-(2-ethylpropyl)-phthalimide were synthesized according to their respective literature procedures.¹,²,³

UV-Visible Spectroscopy (UV-vis): UV-vis spectra were recorded using an Agilent Cary 60 spectrophotometer at room temperature. All solution UV-vis experiments were run in CHCl₃ in Teflon® capped 10 mm quartz cuvettes under. Films were prepared by spin-coating solutions from CHCl₃ onto glass substrates cut from corning micro slides at 1000 rpm for 30 seconds. The thin films on glass were annealed at 100 °C for 5 min by direct mounting on a hotplate.

Fluorescence Spectroscopy: The emission profiles were recorded on a Cary Eclipse spectrophotometer. Solution spectra were recorded in CHCl₃.

Cyclic Voltammetry (CV): All experiments were carried out using a BASi cell stand instrument and BASi Epsilon EC software. Measurements were performed in a three-electrode, one compartment configuration equipped with Ag/AgCl electrode, Pt wire and glassy carbon electrode (dia. 3 mm), as the pseudo reference, counter electrode and working electrode respectively, as well as a nitrogen bubbler. Glassy carbon electrodes were polished with alumina. The CV experiments were performed in anhydrous dichloromethane solution with ~0.1 M tetrabutylammoniumhexafluorophosphate (TBAPF₆) as the supporting electrolyte. All solutions were scanned at 100 mV/s, both with and without a ferrocence standard. Solutions were purged with nitrogen for several minutes to agitate the solution and remove oxygen prior to running the voltage scan. Under these conditions, the ferrocence standard was calibrated to be ~0.48 V. Solution CV measurements were carried out with a small molecule concentration of ~1mg/mL in dichloromethane. The ionization energy (IE) and electron affinity (EA) values were obtained by correlating the onsets of oxidation and reduction (Eox, Erd) to the normal hydrogen electrode (NHE), assuming ionization energy (IE) of Fc/Fc⁺ to be 4.8 eV.
Mass Spectrometry: Mass spectrometry measurements were performed courtesy of Xiao Feng in the Dalhousie University Analytical Laboratory. A Bruker-Daltronics Micro TOF Mass Spectrometer was used and run in APCI mode.
Synthetic methods

Direct Arylation reaction (DHA) reaction with furan-DPP (1a)

On the bench top, 3,6-(bis-furan-2-yl)-2,5-bis-(2-ethylhexyl)-2,5-dihydro-pyrrole-1,4-dione (1a, 500 mg, 1.02 mmol), 5-bromo-N-(2-ethylpropyl)-phthalimide (301 mg, 1.02 mmol), potassium carbonate, (K₂CO₃, 352 mg, 2.55 mmol), SiliaCat® DPP-Pd (204 mg, 0.051 mmol Pd) and pivalic acid (PivOH, 21 mg, 0.204 mmol) were added to a 10-20 mL glass vial equipped with a stir bar. N,N'-dimethylformamide (DMF, ~10 mL) was then added as the solvent. The reaction vial was crimped with a Teflon® cap, briefly purged with N₂, and heated in an oil bath at the appropriate temperature (55 °C, optimized temperature) for 24 hours. Analogous reactions carried out in air (i.e. without the N₂ purge) gave similar results. The reaction vial was cooled to room temperature and the vial contents were diluted with dichloromethane (CH₂Cl₂, ~200 mL) and passed through a short SiO₂ plug to remove catalyst and inorganic reagents/by-products. The solvent was removed using a rotary evaporator and the product was loaded on SiO₂ for purification using column chromatography. A pentane to CH₂Cl₂ solvent gradient was used to purify the reaction mixture and 3 fractions were obtained: 1st fraction, orange, ~40 % CH₂Cl₂, ~60 % Pentane (unsubstituted DPP starting material 1a); 2nd fraction, ~95 % CH₂Cl₂, ~5 % pentane (mono-arylated DPP 2a); 3rd fraction, ~95 % CH₂Cl₂, ~5 % ethyl acetate. (bis-arylated DPP 3a). The solvent was removed from each fraction using a rotary evaporator and the products were slurried in water:methanol (9:1) and filtered using a Buchner funnel to isolate the products 2a and 3a.

Changes to Reaction Conditions:

70 °C reaction:

The reported reaction was repeated using the same reaction conditions described above except the temperature was changed to 70 °C.

Yield 1st fraction: 114 mg 23 % (unsubstituted 1a stating material).
Yield 2nd fraction: 297 mg 41 % (mono-arylated 2a).
Yield 3rd fraction: 210 mg 21 % (bis-arylated 3a).

85 °C reaction:
The reported reaction was repeated using the same reaction conditions described above except the temperature was changed to 85 °C.

Yield 1<sup>st</sup> fraction: 106 mg 21 % (unsubstituted 1a stating material).
Yield 2<sup>nd</sup> fraction: 273 mg 38 % (mono-arylated 2a).
Yield 3<sup>rd</sup> fraction: 258 mg 26 % (bis-arylated 3a).

**Toluene, 85 °C reaction:**

The reported reaction was repeated using the same reaction conditions described above except the solvent was changed to toluene and the reaction temperature was changed to 85 °C.

Yield 1<sup>st</sup> fraction: 323 mg 64 % (unsubstituted 1a stating material).
Yield 2<sup>nd</sup> fraction: 131 mg 18 % (mono-arylated 2a).
Yield 3<sup>rd</sup> fraction: 21 mg 2 % (bis-arylated 3a).

**Pd(OAc)<sub>2</sub> reaction:**

The reported reaction was repeated using the same reaction conditions described above except the catalyst was changed to Pd(OAc)<sub>2</sub>.

Yield 1<sup>st</sup> fraction: 46 mg 9 % (unsubstituted 1a stating material).
Yield 2<sup>nd</sup> fraction: 181 mg 25 % (mono-arylated 2a).
Yield 3<sup>rd</sup> fraction: 320 mg 34 % (bis-arylated 3a).

**55 °C Scaled Up Reaction in Air**

The reported reaction was repeated using 1.0g of 1a. A 50 mL round-bottom flask fitted with a reflux condenser was used instead of a sealed Teflon® container. The reaction was heated at 55 °C in an oil bath for 24 hours with the reaction vessel open to the atmosphere to demonstrate the insensitive nature of the heterogeneous catalyst towards atmospheric oxygen and water.

Yield 1<sup>st</sup> fraction: 480 mg 48 % (unsubstituted 1a stating material).
Yield 2<sup>nd</sup> fraction: 472 mg 33 % (mono-arylated 2a).
Yield 3<sup>rd</sup> fraction: 144 mg 8 % (bis-Arylated 3a).
2a: $^1$H NMR (CDCl$_3$, 500 MHz, 298 K): $\delta$ 8.42, (dd, J= 6.0, 3.8 Hz, 2H), 8.16 (s, 1H), 8.09 (d, J= 9.0 Hz, 1H), 7.91 (d, J= 7.8 Hz, 1H), 7.66 (s, 1H), 7.17 (d, J= 3.8 Hz, 1H), 6.74 (dd, J= 3.5, 1.3 Hz, 1H), 4.21 (d, J= 7.8 Hz, 2H), 4.10-4.05 (m, 3H), 2.18-2.13 (m, 2H), 1.92-1.79 (m, 4H), 1.42-1.24 (m, 16H), 0.95-0.81 (m, 18H); $^{13}$C NMR (CDCl$_3$, 125 MHz, 298 K): $\delta$ 168.45, 168.29, 161.20, 154.55, 145.68, 145.46, 144.77, 134.89, 134.73, 133.25, 132.77, 130.93, 129.12, 124.03, 122.14, 118.92, 113.85, 112.06, 108.26, 106.87, 56.09, 46.85, 46.48, 40.15, 39.75, 30.78, 30.58, 28.88, 28.78, 25.49, 24.11, 23.82, 23.31, 23.24, 14.25, 14.17, 11.36, 10.95, 10.79; MS m/z, calcd for C$_{43}$H$_{52}$N$_3$O$_6$ (M+H)$^+$: 708.4; found: 708.4; Melting point 146-148 °C

3a: $^1$H NMR (CDCl$_3$, 500 MHz, 298 K): $\delta$ 8.50 (d, J= 3.8 Hz, 2H), 8.17 (s, 2H), 8.10 (d, J= 7.8 Hz, 2H), 7.91 (d, J= 7.8 Hz, 2H), 7.19 (d, J= 3.8 Hz, 2H), 4.21 (d, J= 7.7 Hz, 4H), 4.10-4.01 (m, 2H), 2.18-2.02 (m, 4H), 1.95-1.83 (m, 6H), 1.46-1.25 (m, 16H), 0.95-0.84 (m, 24H); $^{13}$C NMR (CDCl$_3$, 125 MHz, 298 K): $\delta$ 168.38, 168.23, 161.19, 154.94, 145.54, 134.75, 133.30, 133.27, 131.08, 129.20, 124.08, 122.79, 118.97, 112.17, 108.39, 50.10, 46.94, 39.75, 30.57, 28.76, 25.48, 23.83, 23.30, 14.16, 11.35, 10.77; MS m/z, calcd for C$_{56}$H$_{66}$N$_4$O$_8$ (M+H)$^+$: 923.5; found: 923.5; Elemental analysis: Calcd. C 72.82, H 7.21, N 6.07, Found C 72.46, H 6.93, N 6.02; Melting point 265-266 °C
On the bench top, 3,6-(bis-furan-2-yl)-2,5-bis-(2-ethylhexyl)-2,5-dihydro-pyrrole-1,4-dione (1b, 100 mg, 0.191 mmol), 5-bromo-N-(2-ethylpropyl)-phthalimide (56.4 mg, 0.191 mmol), potassium carbonate (K₂CO₃, 66 mg, 0.48 mmol), SiliaCat® DPP-Pd (38 mg, 0.0096 mmol Pd) and pivalic acid (PivOH, 4 mg, 0.038 mmol) were added to a 2-5 mL glass vial equipped with a stir bar. N,N’-dimethylformamide (DMF, ~4 mL) was then added as a solvent. The reaction vial was crimped with a Teflon® cap, briefly purged with N₂ and heated in an oil bath at 55 °C for 24 hours. The reaction vial was cooled to room temperature and the vial contents were diluted with dichloromethane (CH₂Cl₂, ~200 mL) and passed through a short SiO₂ plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The solvent was removed using a rotary evaporator and the product was loaded on SiO₂ for purification using column chromatography. A pentane to CH₂Cl₂ solvent gradient was used to purify the reaction mixture and 3 fractions were obtained: 1st fraction, orange, ~40 % CH₂Cl₂, ~60 % Pentane (unsubstituted DPP stating material 1b); 2nd fraction, ~95 % CH₂Cl₂, 5 % Pentane (mono-arylated DPP 2b); 3rd fraction, ~95 % CH₂Cl₂, ~5 % ethyl acetate. (bis-Arylated DPP 3b). The solvent was removed from each fraction using a rotary evaporator and the products were slurried in water:methanol (9:1) and filtered using a Buchner funnel to isolate the product mono-adduct (2b) in 42% yield and bis-adduct (3b) in 22% yield.

**2b:** ¹H NMR (CDCl₃, 300 MHz, 298 K): δ 8.95 (dd, J= 3.9, 1.1 Hz, 1H), 8.92 (d, J= 4.1 Hz, 1H), 8.10 (m, 1H), 7.98 (t, J= 1.6 Hz, 1H), 7.86 (d, J= 7.2 Hz, 1H), 7.66 (dd, J= 5.0, 1.1 Hz, 1H), 7.62 (d, J= 4.1 Hz, 1H), 7.29 (t, J= 3.9, Hz, 1H), 4.20-4.01 (m, 5H), 1.85-1.71 (m, 4H), 1.31-1.27 (m, 16H), 0.98-0.84 (m, 18H); ¹³C NMR (CDCl₃, 75 MHz, 298 K): δ 168.26, 161.73, 161.57, 146.36, 141.08, 139.13, 138.90, 136.30, 135.75, 133.09, 130.99, 130.91, 130.84, 129.72, 128.53, 126.39, 123.94, 120.18, 108.99, 108.03, 55.88, 45.98, 39.28, 30.31,30.22, 28.54, 25.28, 23.69, 23.56,
23.05, 14.03, 14.00, 10.55, 10.48; MS m/z, calcd for C\textsubscript{43}H\textsubscript{53}N\textsubscript{3}O\textsubscript{4}S\textsubscript{2} (M+H): 970.4; found: 970.4

3b: H NMR (CDCl\textsubscript{3}, 300 MHz, 298 K): δ 8.98 (d, J= 4.1 Hz, 2H), 8.11 (m, 2H), 8.00 (dd t, J= 1.5 Hz, 2H), 7.88 (d, J= 7.8 Hz, 2H), 7.64 (d, J= 4.2 Hz, 2H), 4.21-4.10 (m, 6H), 2.11 (m, 4H), 1.85-1.71 (m, 6H), 1.44-1.27 (m, 16H), 0.96-0.86 (m, 24H); C NMR (CDCl\textsubscript{3}, 75 MHz, 298 K): δ 168.24, 161.61, 146.88, 139.82, 138.81, 136.77, 133.12, 130.91, 130.76, 126.49, 123.98, 120.25, 109.09, 55.91, 46.11, 39.29, 30.32, 28.55, 25.28, 23.71, 23.06, 14.04, 11.16, 10.56; MS(EI) m/z, calcd for C\textsubscript{56}H\textsubscript{66}N\textsubscript{4}O\textsubscript{6}S\textsubscript{2} (M+H): 955.4; found: 955.5

Synthesis of DPP-1

On the bench top 3-(furan-2-yl)-6-(5-(furan-2-yl)-N-(2-ethylpropyl)-phthalimide)-2,5-bis-(2-ethylhexyl)-2,5-dihydro-pyrrole-1,4-dione (2a, 100 mg, 0.14 mmol), 4-bromotriphenylamine (50 mg, 0.15 mmol), potassium carbonate, (K\textsubscript{2}CO\textsubscript{3} 48 mg, 0.35 mmol), SiliaCat® DPP-Pd (28 mg, 0.007 mmol Pd) and pivalic acid (PivOH, 4 mg, 0.03 mmol) were added to a 2-5 mL glass tube equipped with a stir bar. N,N'- dimethylformamide (DMF, ~3 mL) was then added as a solvent. The reaction vial was crimped with a Teflon® cap, briefly purged with N\textsubscript{2} and heated in an oil bath at 120 °C for 24 hours. Temperatures under 120 °C were found to be insufficient to promote product formation. The reaction vial was then cooled to room temperature and the vial contents were diluted with dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}, ~100 mL) and passed through a short SiO\textsubscript{2} plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The solvent was removed using a rotary evaporator and the product was loaded on SiO\textsubscript{2} for purification using column chromatography. A pentane to CH\textsubscript{2}Cl\textsubscript{2} solvent gradient was used to purify the reaction mixture.
The solvent was removed from the product fraction using a rotary evaporator and the obtained dark blue solid was recrystallized from CH$_2$Cl$_2$/methanol layering with approximately 5 mL of solvent (CH$_2$Cl$_2$) used to dissolve ~100 mg of compound before layering the counter solvent (methanol). After a 24 hour recrystallization period the solids were collected by filtration using a Buchner funnel and washed with methanol to yield the product as a dark blue solid. Yield: 70 mg (52 %)

**DPP-1:** $^1$H NMR (CDCl$_3$, 300 MHz, 298 K): δ 8.55 (d, J= 3.8 Hz, 1H), 8.38 (d, J= 3.8 Hz, 1H), 8.14 (s, 1H), 8.08 (d, J= 9.2 Hz, 1H), 7.89 (d, J= 7.8 Hz, 1H), 7.62 (d, J= 8.8 Hz, 2H), 7.48-7.28 (m, 4H), 7.20-7.08 (m, 6H), 7.10 (d, J= 7.4 Hz, 3H), 6.86 (d, J= 3.9 Hz, 1H), 4.30-4.20 (m, 4H), 4.07 (m, 1H), 2.15-1.77 (m, 4H), 1.46-1.21 (m, 16H), 0.98-0.90 (m, 12H), 0.88-0.80 (m, 6H); $^{13}$C NMR (CDCl$_3$, 125 MHz, 298 K): δ 168.49, 168.33, 161.67, 161.04, 158.10, 154.26, 149.08, 147.20, 145.93, 143.57, 135.00, 134.49, 133.26, 131.56, 130.79, 129.70, 129.01, 125.98, 125.43, 124.89, 124.51, 124.13, 124.07, 122.65, 122.52, 121.54, 118.85, 112.11, 108.70, 108.45, 106.60, 56.08, 46.91, 39.79, 39.61, 30.62, 28.88, 28.82, 25.51, 23.87; MS m/z, calcd for C$_{61}$H$_{66}$N$_4$O$_6$ (M+H)$^+$: 951.5 found: 951.6; Elemental analysis: Calcd. C 77.02, H 6.99, N 5.89, Found C 76.13, H 6.72, N 5.88; Melting point 213-215 °C

**Synthesis of DPP-2**

On the bench top, compound 2a (200 mg, 0.28 mmol), bromo-pentafluorobenzene (100 mg, 0.42 mmol), potassium carbonate (97 mg, 0.7 mmol), pivalic acid (8.6 mg, 0.08 mmol) and SiliaCat® DPP-Pd (56 mg, 0.014 mmol), were added to a 10-20 mL glass vial equipped with a stir bar. N,N’-dimethylformamide (DMF, ~5 mL) was then added as a solvent. The reaction vial was crimped with a Teflon® cap, briefly purged with N$_2$ and heated in an oil bath 85 °C for 24 hours. The reaction was allowed to cool to room temperature and was then diluted with ~100 mL of CH$_2$Cl$_2$ and was filtered through a short SiO$_2$ plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography using a pentane to CH$_2$Cl$_2$ gradient with the product eluting using a CH$_2$Cl$_2$:methanol (99:1) solvent system. The product eluted as a dark blue solution. After fraction collection and solvent removal using a rotary evaporator, the product was slurried in 4:1 methanol:hexane, stirred for one hour, filtered using a Buchner funnel and collected as a dark brown powder. Yield: 167 mg (67%).

**DPP-2:** $^1$H NMR (CDCl$_3$, 500 MHz, 298 K): δ 8.56 (d, J= 3.4 Hz, 1H), 8.48 (d, J= 3.5 Hz, 1H), 8.17 (s, 1H), 8.10 (d, J= 7.9 Hz, 1H), 7.95 (d, J= 7.9 Hz, 1H), 7.19 (d, J= 3.5 Hz, 1H), 7.09 (s, 1H), 4.23 (d, J= 7.7 Hz, 2H), 4.20 (d, J= 7.7 Hz, 2H), 4.15-4.10 (m, 1H), 2.18-2.10 (m, 2H), 1.94-1.82
On the bench top, compound 2a (226 mg, 0.32 mmol), 4,4-dibromobiphenyl (40 mg, 0.12 mmol), potassium carbonate (111 mg, 0.79 mmol), pivalic acid (10 mg, 0.09 mmol) and SiliaCat® DPP-Pd (63 mg, 0.015 mmol) were added to a 10-20 mL glass vial equipped with a stir bar. N,N'-dimethylformamide (DMF, ~5 mL) was then added as a solvent. The reaction vial was crimped with a Teflon® cap, briefly purged with N2 and heated an oil bath at 85 °C for 24 hours. The reaction was allowed to cool to room temperature and was then diluted with ~100 mL of CH2Cl2 and was filtered through a short SiO2 plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography using a pentane to CH2Cl2 gradient with the product eluting using a CH2Cl2:Et3N (98:2) solvent system. The product eluted as a dark blue solution. After fraction collection and solvent removal using a rotary evaporator, the product was slurried in 4:1 methanol:hexane, stirred for one hour, filtered using a Buchner funnel and collected as a dark purple powder. Yield: 167 mg (83%).

DPP-3: 1H NMR (CDCl3, 500 MHz, 298 K): δ 8.57 (d, J= 3.8 Hz, 2H), 8.45 (d, J= 3.8 Hz, 2H), 8.16 (s, 2H), 8.09 (d, J= 7.7 Hz, 2H), 7.90 (d, J= 7.8 Hz, 2H), 7.87 (d, J= 8.3 Hz, 4H), 7.75 (d, J= 8.3 Hz, 4H), 7.18 (d, J= 3.8 Hz, 2H), 7.06 (d, J= 3.8 Hz, 2H), 7.02 (d, J= 3.8 Hz, 2H), 4.22 (t, J= 8.2 Hz, 8H), 4.15-4.05 (m, 2H), 2.12-1.83 (m, 12H), 1.43-1.29 (m, 32H), 0.96-0.84 (m, 36H); MS m/z, calcd for C98H112N6O12 (M+H)+: 1566.8 found: 1566.7; Elemental analysis: Calcd. C 75.16, H 7.21, N 5.37. Found C 74.31, H 6.84, N 5.26; Melting point 324-325 °C. Note: The 13C NMR signal of DPP-3 in aromatic region in CDCl3 was below the detection limit.
On the bench top, compound 2a (200 mg, 0.28 mmol), 9,10-dibromoanthracene (45 mg, 0.13 mmol), potassium carbonate (97 mg, 0.7 mmol), pivalic acid (8 mg, 0.08 mmol) and SiliaCat® DPP-Pd (56 mg, 0.014 mmol) were added to a 10-20 mL glass vial equipped with a stir bar. The reaction vial was crimped with a Teflon® cap, briefly purged with N₂ and heated in an oil bath at 85 °C for 24 hours. N,N’-dimethylformamide (DMF, ~10 mL) was then added as a solvent. The reaction was allowed to cool to room temperature and was then diluted with ~100 mL of CH₂Cl₂ and was filtered through a short SiO₂ plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography using a pentane to CH₂Cl₂ gradient with the product eluting using a CH₂Cl₂:Et₃N (98:2) solvent system. The product eluted as a dark blue solution. After fraction collection and solvent removal using a rotary evaporator, the product was slurried in 4:1 methanol:hexane, stirred for one hour, filtered using a Buchner funnel and collected as a dark blue powder. Yield: 190 mg (89%).

**DPP-4:** ¹H NMR (CDCl₃, 500 MHz, 298 K): δ 8.85 (d, J= 8.8 Hz, 2H), 8.46 (d, J= 3.5 Hz, 2H), 8.17 (s, 2H), 8.11 (d, J= 7.6 Hz, 2H), 8.01-7.95 (m, 4H), 7.91 (d, J= 7.8 Hz, 2H), 7.60-7.50 (m, 4H), 7.18 (d, J= 3.5 Hz, 2H), 7.09 (d, J= 3.3 Hz, 2H), 4.27 (d, J= 6.9 Hz, 4H), 4.12-4.08 (m, 2H), 4.01-3.94 (m, 4H), 2.10-1.79 (m, 12H), 1.47-1.14 (m, 24H), 0.50-0.58 (m, 6H), 0.40-0.45 (m, 6H); ¹³C NMR (CDCl₃, 125 MHz, 298 K): δ 168.46, 168.31, 161.54, 161.35, 161.35, 161.35, 154.67, 154.07, 145.74, 145.46, 134.91, 134.44, 133.30, 132.79, 131.39, 131.01, 129.16, 127.07, 126.37, 124.11, 122.61, 122.31, 118.96, 117.03, 112.15, 108.47, 107.22, 56.12, 46.98, 46.64, 40.02, 39.85, 30.65, 28.85, 28.56, 25.52, 23.87, 23.76, 23.38, 23.04, 14.24, 13.91, 11.38, 10.86; MS m/z, calcd for C₁₀₂H₁₁₂N₆O₁₂ (M+H)+: 1590.8; found: 1590.8; Elemental analysis: Calcd. C 74.72, H 7.17, N 5.93 Found C 72.95, H 6.89, N 5.65; Melting point 174-176 °C.
Synthesis of DPP-5

On the bench top, compound 2a (257 mg, 0.36 mmol), tris(4-bromophenyl)amine (50 mg, 0.1 mmol), potassium carbonate (126 mg, 0.90 mmol), pivalic acid (10 mg, 0.09 mmol) and SiliaCat® DPP-Pd (72 mg, 0.018 mmol) were added to a 10-20 mL glass vial equipped with a stir bar. N,N'-dimethylformamide (DMF, ~10 mL) was then added as a solvent. The reaction vial was crimped with a Teflon® cap, briefly purged with N2 and heated in an oil bath at 85 °C for 24 hours. The reaction was allowed to cool to room temperature and was then diluted with ~100 mL of CH2Cl2 and was filtered through a short SiO2 plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography using a pentane to CH2Cl2 gradient with the product eluting using a CH2Cl2:Et3N (98:2) solvent system. The product eluted as a dark blue solution. After fraction collection and solvent removal using a rotary evaporator, the product was slurried in 4:1 methanol:hexane, stirred for one hour, filtered using a Buchner funnel and collected as a dark blue powder. Yield: 170 mg (69%).

DPP-5: 1H NMR (CDCl3, 500 MHz, 298 K): δ 8.54 (d, J= 3.7 Hz, 3H), 8.43 (d, J= 3.8 Hz, 3H), 8.16 (s, 3H), 8.10 (d, J= 8.7 Hz, 3H), 7.91 (d, J= 7.8 Hz, 3H), 7.75 (d, J= 8.7 Hz, 6H), 7.27 (d, J= 8.6 Hz, 6H), 7.18 (d, J= 3.8 Hz, 3H) 6.96 (d, J= 3.8 Hz, 3H), 4.31-4.21 (m, 12H), 4.15-4.10 (m, 3H), 2.18–2.12 (m, 6H), 1.94-1.83 (m, 12H), 1.44-1.26 (m, 48H), 0.99-0.94 (m, 36H), 0.89-0.84 (m, 18H); 13C NMR (CDCl3, 125 MHz, 298 K); δ 168.45, 168.31, 161.53, 161.23, 161.23, 157.19, 154.48, 147.38, 145.81, 144.05, 134.92, 134.17, 133.27, 132.10, 130.89, 129.07, 126.23, 124.94, 124.84, 124.07, 123.93, 121.91, 118.89, 112.12, 109.23, 108.58, 107.10, 56.09, 46.91, 39.78, 39.62, 30.61, 28.88, 28.81, 25.50, 23.87, 23.37, 23.34, 14.27, 14.19, 11.37, 10.84, 10.78; MS m/z, calcd for C147H168N10O18 (M+H)+: 2363.3 found: 2363.0; Elemental analysis: Calcd. C 75.54, H 7.10, N 5.29 Found C 75.41, H 6.86, N 5.24; Melting point 255-256 °C.
Synthesis of 4a

On the bench top, compound 2a (270 mg, 0.38 mmol), 9,10-dibromoanthracene (384 mg, 1.1 mmol), potassium carbonate (78 mg, 0.57 mmol), pivalic acid (11 mg, 0.1 mmol) and SiliaCat® DPP-Pd (76 mg, 0.019 mmol) were added to a 10-20 mL glass vial equipped with a stir bar. N,N'-dimethylformamide (DMF, ~10 mL) was then added as a solvent. The reaction vial was crimped with a Teflon® cap, briefly purged with N₂ and heated in an oil bath at 85 °C for 24 hours. The reaction was allowed to cool to room temperature and was then diluted with ~100 mL of CH₂Cl₂ and was filtered through a short SiO₂ plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography using a pentane to CH₂Cl₂ gradient. The product eluted as a dark blue solution. After fraction collection and solvent removal using a rotary evaporator, the product was slurried in 4:1 methanol:hexane, stirred for one hour, filtered using a Buchner funnel and collected as a dark blue powder. Yield: 220 mg (61%).

4a: ¹H NMR (CDCl₃, 500 MHz, 298 K): δ 8.82 (d, J= 3.6 Hz, 1H), 8.66 (d, J= 8.8 Hz, 2H), 8.44 (d, J= 3.8 Hz, 1H), 8.16 (s, 1H), 8.11 (d, J= 7.9 Hz, 1H), 7.94-7.85 (m, 3H), 7.69-7.60 (m, 2H), 7.58-7.51 (m, 2H), 7.16 (d, J= 3.7 Hz, 1H), 7.05 (d, J= 3.6 Hz, 1H), 4.26 (d, J= 7.7 Hz, 2H), 4.15-4.08 (m, 1H), 3.98-3.92 (m, 2H), 2.12-1.78 (m, 6H), 1.46-1.27 (m, 12H), 0.96-0.69 (m, 16H), 0.55 (t, J= 7.3 Hz, 3H), 0.42 (t, J= 6.7 Hz, 3H); ¹³C NMR (CDCl₃, 125 MHz, 298 K): δ 168.46, 168.31, 161.53, 161.32, 154.61, 154.08, 145.74, 145.34, 143.91, 134.49, 133.29, 132.99, 132.70, 132.37, 130.97, 130.48, 129.14, 128.51, 127.52, 127.24, 126.59, 126.35, 124.70, 124.10, 122.58, 122.23, 122.15, 118.94, 116.93, 112.13, 108.47, 107.11, 56.11, 46.95, 46.65, 39.99, 39.83, 30.63, 28.84, 28.52, 25.51, 23.84, 23.72, 23.37, 23.00, 14.23, 13.79, 11.38; MS m/z, calcd for C₅₇H₆₀Br₃N₃O₆ (M+H)⁺: 962.4; found: 962.4
Synthesis of DPP-6

On the bench top, compound 1a (30 mg, 0.06 mmol), 4a (128 mg, 0.13 mmol), potassium carbonate (21 mg, 0.15 mmol) pivalic acid (2 mg, 0.02 mmol) and SiliaCat® DPP-Pd (24 mg, 0.013 mmol) were added to a 2-5 mL glass vial equipped with a stir bar. N,N' dimethylformamide (DMF, ~3 mL) was then added as a solvent. The reaction vial was crimped with a Teflon® cap, briefly purged with N₂ and heated in an oil bath at 85 °C for 24 hours. The reaction was allowed to cool to room temperature and was then diluted with ~100 mL of CH₂Cl₂ and was filtered through a short SiO₂ plug to isolate the product from the heterogeneous catalyst SiliaCat® DPP-Pd. The filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography with using a pentane to CH₂Cl₂ gradient with the product eluting using a CH₂Cl₂:Et₃N (98:2) solvent system. The product eluted as a dark blue solution. After fraction collection and solvent removal using a rotary evaporator, the product was slurried in 4:1 methanol:hexane, stirred for one hour, filtered using a Buchner funnel and collected as a dark blue powder. Yield: 113 mg (82%).

**DPP-6:** ¹H NMR (CDCl₃, 500 MHz, 298 K): δ 8.86 (d, J= 3.7 Hz, 2H), 8.81 (d, J= 3.57 Hz, 2H), 8.46 (d, J= 3.8 Hz, 2H), 8.17 (s, 2H), 8.11 (d, J= 8.5 Hz, 2H), 8.05-7.95 (m, 8H), 7.91 (d, J= 7.8 Hz, 2H), 7.58-7.50 (m, 8H), 7.18 (d, J= 3.7 Hz, 2H), 7.10-7.04 (m, 4H), 4.28 (d, J= 7.3 Hz, 4H), 4.18-4.05 (m, 2H), 4.03-3.94 (m, 8H), 2.15-1.79 (m, 14H), 1.45-1.04 (m, 28H), 0.97-0.82 (m, 44H), 0.64-0.46 (m, 24H); MS m/z, calcd for C₁₄₄H₁₅₈N₈O₁₆ (M+H)⁺: 2257.2 found: 2257.2; Elemental analysis: Calcd. C 76.64, H 7.06, N 4.97 Found C 76.03, H 6.78, N 4.97; Melting point 186-188 °C. Note: The ¹³C NMR signal of DPP-6 in aromatic region in CDCl₃ was below the detection limit.
**PL Spectra**

![Photoluminescence spectra of DPP-3, DPP-4, DPP-6, and 4a](image)

**Figure S1.** Photoluminescence spectra of DPP-3, DPP-4, DPP-6, and 4a in (6x10^-6 M CHCl₃), excited at 600 nm.
CV Data

Table S1. Electrochemical properties of 3a and DPP-1 to DPP-6.

<table>
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<th>Entry</th>
<th>E_{ox}</th>
<th>E_{red}</th>
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<tbody>
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<td>3a</td>
<td>0.44_{(onset)}, 0.57, 0.90</td>
<td>-1.22_{(onset)}, -1.38, -1.69, -1.98</td>
</tr>
<tr>
<td>DPP-1</td>
<td>0.18_{(onset)}, 0.33, 0.58</td>
<td>-1.32_{(onset)}, -1.47, -1.73</td>
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<tr>
<td>DPP-2</td>
<td>0.34_{(onset)}, 0.51, 0.81</td>
<td>-1.27_{(onset)}, -1.55, -1.79</td>
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<tr>
<td>DPP-3</td>
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<td>-1.31_{(onset)}, -1.42, -1.71</td>
</tr>
<tr>
<td>DPP-4</td>
<td>0.36_{(onset)}, 0.54, 0.87</td>
<td>-1.24_{(onset)}, -1.34, -1.87</td>
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<tr>
<td>DPP-5</td>
<td>0.19_{(onset)}, 0.32, 0.46, 0.64, 0.81</td>
<td>-1.37_{(onset)}, -1.51, -1.79</td>
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<tr>
<td>DPP-6</td>
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<td>-1.20_{(onset)}, -1.31, -1.42, -1.68</td>
</tr>
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</table>

Figure S2 Cyclic voltammetry plots of compound 3a and DPP-1 in 0.1 M TBAPF₆/CH₂Cl₂ at scan rate 100 mV/s.
**Figure S3** Cyclic voltammetry plots of compound 3a and DPP-2 in 0.1 M TBAPF₆/CH₂Cl₂ at scan rate 100 mV/s.

**Figure S4** Cyclic voltammetry plots of compound 3a and DPP-3 in 0.1 M TBAPF₆/CH₂Cl₂ at scan rate 100 mV/s.
Figure S5 Cyclic voltammetry plots of compound 3a and DPP-4 in 0.1 M TBAPF$_6$/CH$_2$Cl$_2$ at scan rate 100 mV/s.

Figure S6 Cyclic voltammetry plots of compound 3a and DPP-5 in 0.1 M TBAPF$_6$/CH$_2$Cl$_2$ at scan rate 100 mV/s.
Figure S7 Cyclic voltammetry plots of compound 3a and DPP-6 in 0.1 M TBAPF₆/CH₂Cl₂ at scan rate 100 mV/s.
**UV-Vis Data**

![UV-Vis spectrum of compound 3a](image1)

**Figure S8.** UV-Visible spectra of compounds 3a in CHCl₃ solution, thin films were cast at from 1 % wt/volume CHCl₃ solutions onto glass substrates and films annealed at 100 °C for 5 min.

![UV-Vis spectrum of DPP-1](image2)

**Figure S9.** UV-Visible spectra of DPP-1 in CHCl₃ solution, thin films were cast at from 1 % wt/volume CHCl₃ solutions onto glass substrates and films annealed at 100 °C for 5 min.
Figure S10 UV-Visible spectra of DPP-2 in CHCl₃ solution, thin films were cast at from 1 % wt/volume CHCl₃ solutions onto glass substrates and films annealed at 100 ºC for 5 min.

Figure S11. UV-Visible spectra of DPP-3 in CHCl₃ solution, thin films were cast at from 1 % wt/volume CHCl₃ solutions onto glass substrates and films annealed at 100 ºC for 5 min. The as-cast and thermally annealed films give nearly identical absorption spectra.
**Figure S12.** UV-Visible spectra of DPP-4 in CHCl₃ solution, thin films were cast at from 1 % wt/volume CHCl₃ solutions onto glass substrates and films annealed at 100 ºC for 5 min.

**Figure S13.** UV-Visible spectra of DPP-5 in CHCl₃ solution, thin films were cast at from 1 % wt/volume CHCl₃ solutions onto glass substrates and films annealed at 100 ºC for 5 min.
**Figure S14.** UV-Visible spectra of DPP-6 in CHCl₃ solution, thin films were cast at from 1 % wt/volume CHCl₃ solutions onto glass substrates and films annealed at 100 ºC for 5 min.
Figure S15. $^1$H NMR spectra of compound 2a in CDCl$_3$
Figure S16. $^{13}$C NMR spectra of compound 2a in CDCl$_3$
Figure S17. 1H NMR spectra of compound 3a in CDCl3
Figure S18. $^{13}$C NMR spectra of compound 3a in CDCl$_3$
Figure S19. $^1$H NMR spectra of compound 2b in CDCl$_3$. 
Figure S20. $^{13}$C NMR spectra of compound 2b in CDCl₃
Figure S21. $^1$H NMR spectra of compound 3b in CDCl$_3$
Figure S22. $^{13}$C NMR Spectra of compound 3b in CDCl$_3$. 
Figure S23. $^1$H NMR of DPP-1 in CDCl$_3$
Figure S24. $^{13}$C NMR of DPP-1 in CDCl$_3$
Figure S25. $^1$H NMR of DPP-2 in CDCl$_3$
Figure S26. $^{13}$C NMR of DPP-2 in CDCl$_3$
Figure S27. $^{19}$F NMR of DPP-2 in CDCl$_3$
Figure S28. $^1$H NMR spectra of DPP-3 in CDCl$_3$
Figure S29. $^1$H NMR spectra of DPP-4 in CDCl$_3$
Figure S30. $^{13}$C NMR spectra of DPP-4 in CDCl$_3$
Figure S31. $^1$H NMR spectra of DPP-5 in CDCl$_3$
Figure S32. $^{13}$C NMR spectra of DPP-5 in CDCl$_3$. 

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**Figure S32.** $^{13}$C NMR spectra of DPP-5 in CDCl$_3$. 

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Figure S33: $^1$H NMR spectra of compound 4a in CDCl$_3$
Figure S34. $^{13}$C NMR spectra of compound 4a in CDCl$_3$
Figure S35. $^1$H NMR spectra of DPP-6 in CDCl$_3$
REFERENCES

