A Structure-Property-Performance Investigation of Perylenediimides as Electron Accepting Materials in Organic Solar Cells

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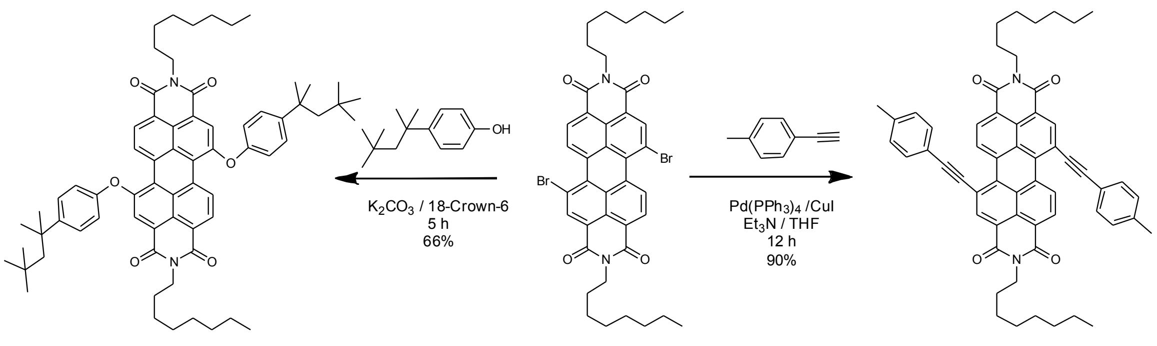
Supplementary Information

***N,N'*-Dioctyl-1,7-di(4'-*tert*-octylphenoxy)-3:4,9:10-perylenetetracarboxydiimide (PDI 2):** A mixture of 4-*tert*-octylphenol (320 mg, 1.55 mmol), K_2CO_3 (307 mg, 2.22 mmol) and 18-crown-6 (1.64 g, 6.33 mmol), in dry toluene (100 ml), was stirred for 20 min under argon and subsequently *N,N'*-dioctyl-1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (300 mg, 0.39 mmol) was added. The reaction mixture was stirred for 5 h at 90 ºC under argon atmosphere. After being cooled to room temperature, the solution was filtered, washed with several portions of water, and dried. The crude product was dissolved in chloroform and purified by flash chromatography (SiO_2, chloroform) to afford the regioisomeric mixture 1,7:1,6 (88:12:) of **PDI 2** (262 mg, 66%) as a brown solid. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 9.57 (d, 2H, *J*=8.4 Hz, 2x*H*-PDI), 8.58 (d, 2H, *J*=8.4 Hz, 2x*H*-PDI), 8.32 (s, 2H, 2x*H*-PDI), 7.46 (d, 4H, *J*=8.9 Hz, 4x*H*-Ar), 7.08 (d, 4H, *J*=8.8 Hz, 4x*H*-Ar), 4.14 (t, 4H, *J*= 7.6 Hz, 2xN-CH_2-$(\mathrm{CH}_2)_6$-CH_3), 1.79 (s, 4H, 2xPh-C$(\mathrm{CH}_3)_2$-CH_2-C$(\mathrm{CH}_3)_3$), 1.73 (m, 4H, 2xN-CH_2-CH_2-$(\mathrm{CH}_2)_5$-CH_3), 1.39-1.27 (m, 20H, 2xN-CH_2-CH_2-(CH_2)$_5$-CH_3), 0.88 (t, 6H, *J*=6.9 Hz, 2xN-CH_2-CH_2-$(\mathrm{CH}_2)_5$-CH_3), 0.81 (s, 30H, 2xPh-C(CH_3)$_2$-CH_2-C(CH_3)$_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.2, 162.7, 155.3, 152.3, 147.4, 133.1, 129.9, 128.9, 128.6, 128.2, 124.7, 123.6, 123.4, 123.4, 121.9, 118.9, 57.1, 40.6, 38.5, 32.4, 31.8, 31.8, 31.5, 29.3, 29.2, 28.0, 27.1, 22.6, 14.1 ppm;. IR (KBr) ν: 2921, 2852, 1699 (C=O imide), 1646 (C=O imide), 1597,1458, 1343, 1270, 1074, 812 cm-1; UV/Vis (chloroform), λ_{max} (log ε): 406 (3.98), 512 (4.51), 548 nm (4.67); HR-MS (MALDI-TOF): m/z: calculated for $C_{68}H_{82}N_2O_6$: 1022.617 $[M]^-$; found: m/z: 1022.637 $[M]^-$.

***N,N'*-Dioctyl-1,7-di(*p*-tolylethynyl)-3:4,9:10-perylenetetracarboxydiimide (PDI 4):** 300 mg (0.40 mmol) of *N,N'*-dioctyl-1,7-dibromo-3:4,9:10-perylenetetracarboxydiimide, 0.24 mL (1.55 mmol) of 4-ethynyltoluene, 10 mg (0.05 mmol) of copper(I) iodide and 50 mg (0.04 mmol) of $Pd(PPh_3)_4$ were added to 300 mL of THF/Et_3N 1:1 v/v. The reaction mixture was intensively stirred under argon at 90 °C for 12 h. The solution was washed with a 300 mL of 6 M HCl and dried with anhydrous sodium sulfate and evaporated in vacuum The crude product was purified by column chromatography (SiO_2, dichloromethane) to afford the regioisomeric 1,7 and 1,6 mixture of **PDI 4** (295 mg, 90%). Pure 1,7-regioisomer of **PDI 4** was obtained after recrystallization from dichloromethane (143 mg, 44%). ^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ = 9.7 (d, 2H, H_{PDI}, *J*= 8.3 Hz), 8.4 (s, 2H, H_{PDI}), 8.3 (d, 2H, H_{PDI}, *J*= 8.3 Hz), 7.4 (d, 4H, H_{Ar}, *J*=8.0 Hz), 7.2 (d, 4H, H_{Ar}, *J*=8.1 Hz), 4.1 (t, 4H, $H_{N\text{-}PDI}$, *J*=7.4 Hz), 2.4 (s, 6H, $H_{CH3\text{-}Ar}$), 1.8-1.7

(m, 4H, H_{CH2}), 1.5-1.3 (m, 20H, H_{CH2}), 0.9-0.8 ppm (m, 6H, H_{CH3}); ^{13}C-NMR (75 MHz, $CDCl_3$): δ= 162.8, 162.4, 140.1, 137.1, 133.5, 132.7, 131.7, 129.7, 129.5, 126.9, 126.8, 126.7, 122.5, 121.6, 120.0, 119.0, 99.7, 90.4, 40.6, 31.9, 29.4, 29.3, 28.0, 27.2, 22.7, 21.7, 14.1 ppm; IR (KBr) ν: 2910, 2841, 2189 (alkyne), 1692 (C=O imide), 1655 (C=O imide), 1500, 1407, 1321, 1231, 1166, 1097, 804 cm^{-1}; UV/Vis (chloroform), l_{max} (log ε): 436 (4.1), 542 (4.4), 580 nm (4.6); HR-MS (MALDI-TOF): m/z: calculated for $C_{58}H_{54}N_2O_4$: 842.4081 [M]$^-$; found: m/z: 842.4006 [M]$^-$.

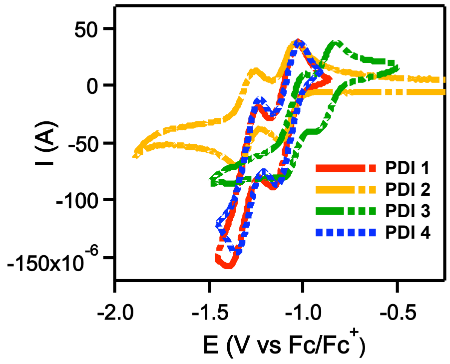


PDI 2

PDI 4

Scheme SI 1. Synthesis of PDI 2 and PDI 4.

a



b

Acceptor	HOMO (eV)	LUMO (eV)
PDI 1	–6.0	–3.8
PDI 2	–5.9	–3.7
PDI 3	–5.4	–3.5
PDI 4	–6.0	–3.8

Figure SI 2. (a) Cyclic voltammagrams of PDIs measured against ferrocene/ferrocinium and (b) Table of HOMO and LUMO values calculated from the CV data and the optical bandgap.

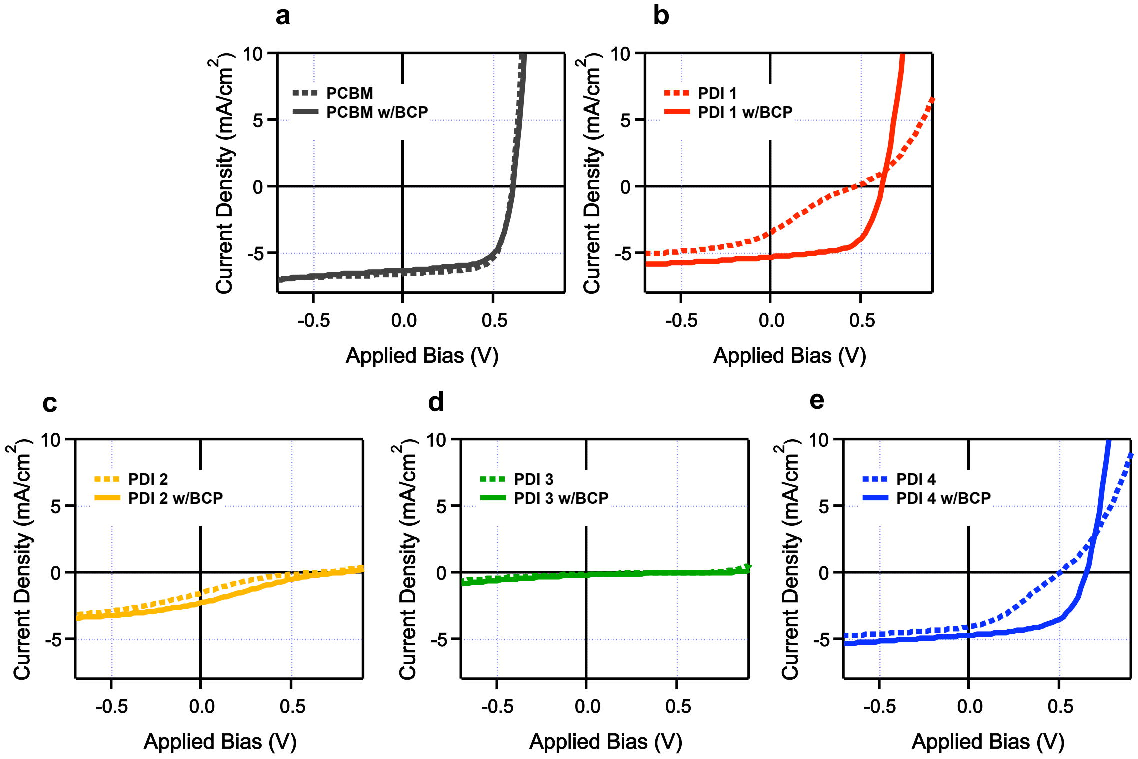


Figure SI 3. **Bilayer OPV device current-voltage (*J-V*) curves under AM1.5 G simulated illumination. Devices with and without an interfacial bathocuproine (BCP) layer are shown. The device architecture used is ITO/PEDOT:PSS/BP/acceptor/with or without BCP/Al.**

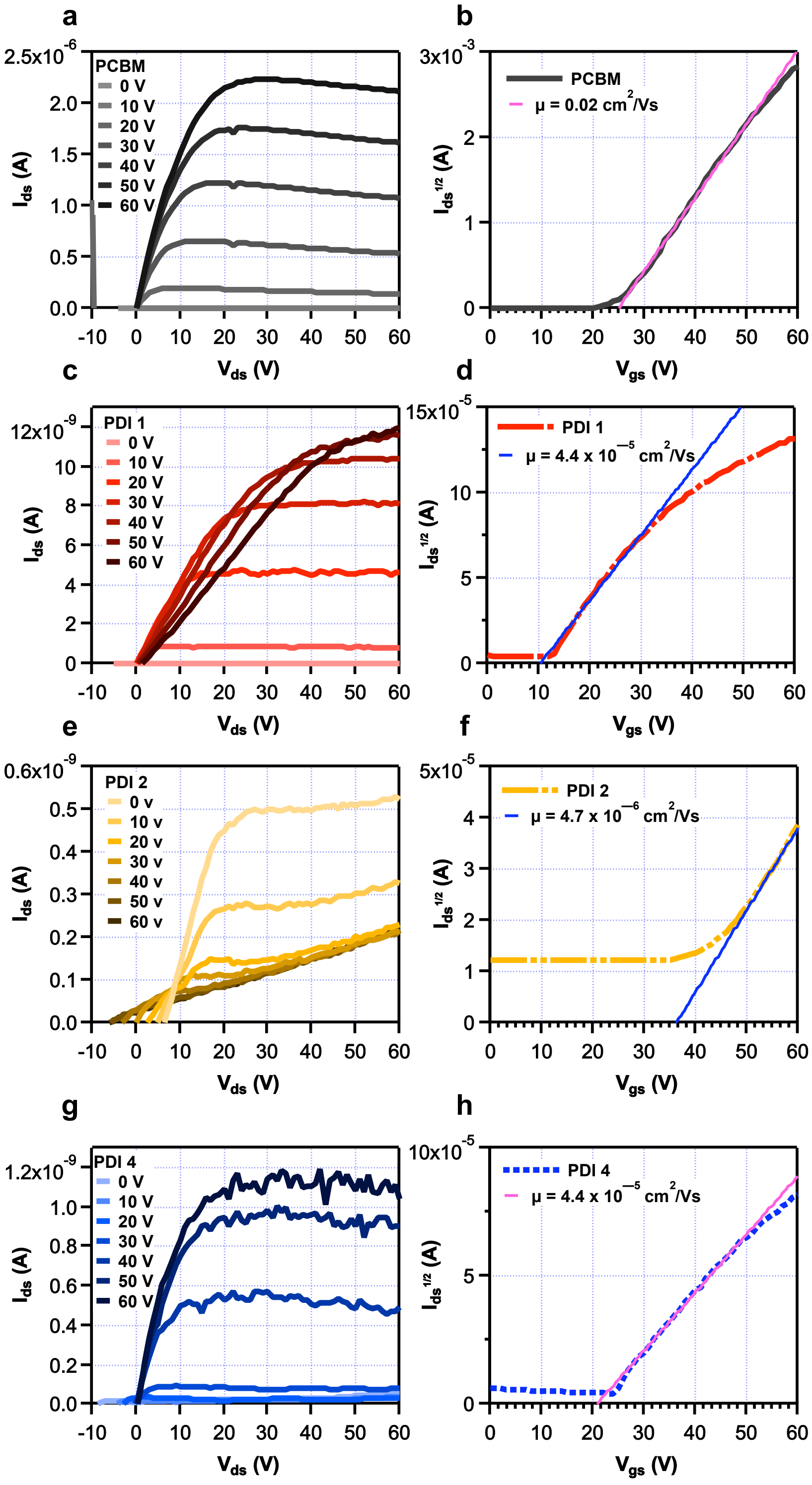


Figure SI 4. FET measurements of PDIs. Output characteristics (a, c, e, g) and transfer characteristics in the saturation regime (b, d, f, h) are shown.

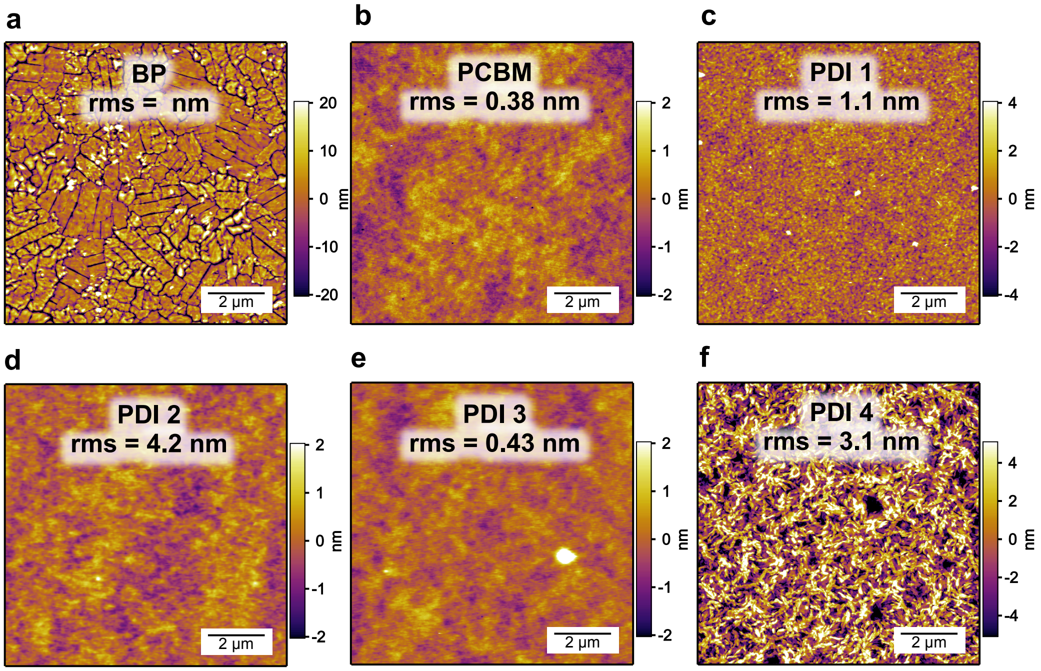


Figure SI 5. Tapping mode AFM height images of neat films of the materials used in this study on ITO/PEDOT:PSS substrates. Root mean square (RMS) values are shown below the material name. Images are 10 × 10 µm.