Supporting Information for:

Small Molecule BODIPY Dyes as Acceptors in

Bulk Heterojunction Organic Photovoltaics

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Materials

All reagents were purchased from commercial sources and used as received, unless otherwise mentioned. Tetrahydrofuran was distilled over sodium and benzophenone. 8-(thiomethyl)-4,4,difluoro-3,5-diethyl-4-bora-3a,4a-diaza-*s*-indacene¹, 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene², 4,4-Bis(2-ethylhexyl)-2,6-bis(trimethylstannanyl)-4H-cyclopenta-[2,1-b:3,4-b]dithiophene³, N-(2-ethylhexyl)-2,6-bis(trimethylstannyl)-dithieno[3,2-*b*:2',3'-*d*]pyrrole⁴ were synthesized according to previously reported procedures.

Instrumentation

¹H NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer and recorded in ppm using the residual solvent peak as the internal standard (CDCl₃ at 7.26 ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. ¹³C NMR spectra were proton decoupled and recorded on a 100 MHz Bruker NMR spectrometer using the carbon signal of the deuterated solvent as the internal standard (CDCl₃ at 77.16 ppm).

UV-vis absorption spectra were recorded on a Cary 100 scan UV-vis spectrophotometer. Electrochemical measurements were performed on a BASi Epsilon potentiostat in anhydrous dichloromethane using a Pt disc electrode as a working electrode and a Pt wire as the auxiliary electrode. The potentials were measured against a Ag/Ag^+ reference at a scan rate of 50 mV s⁻¹.

The surface morphology of the bulk heterojunction films ($10 \ \mu m \ x \ 10 \ \mu m$) was observed using a Digital Instruments Dimension 3100 atomic force microscope (AFM) operating in tapping mode.



8-(2-bromo-3-hexylthien-5-yl)-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene

In a dry 250 mL three neck round bottom flask, diisopropylamine (1.7 mL, 12 mmol) was dissolved in tetrahydrofuran. The solution was cooled to -78°C using a dry ice/acetone bath. Butyllithium (4.4 mL, 2.5M in hexane) was added dropwise and the mixture was stirred for 30 minutes at -78°C. A solution of 2-bromo-3-hexylthiophene (2 mL, 10 mmol) in THF (5 mL) was added dropwise over 30 min and the reaction was stirred at -78°C for 1 hour. Triisopropylborate (5.8 mL, 25 mmol) was added at once and the reaction was allowed to reach room temperature and stirred overnight. 10% aq. HCl was added and the reaction was stirred for 1 hour. The crude product was extracted with ethyl acetate. The combined organics were washed with water and dried over sodium sulfate. The solvent was removed *in vacuo* to give the crude product to be used without further purification. 1H NMR confirmed a 1:0.6 ratio of starting material to product.

8-(thiomethyl)-4,4,difluoro-3,5-diethyl-4-bora-3a,4a-diaza-*s*-indacene (0.355 g, 1.5 mmol) and the crude (5-bromo-4-hexylthiophen-2-yl) boronic acid (1.30 g, 4.5 mmol) were dissolved in tetrahydrofuran under argon. The mixture was purged with argon for 10 minutes. Copper (I) thiophene-2-carboxylate (0.852 g, 4.5 mmol), Pd_2dba_3 (34 mg, 2.5 mol%) and tris(2-furyl)phosphine (26 mg, 7.5 mol%) were added as a solid mixture. The reaction was placed into a preheated oil bath and stirred at 55°C for 15 hr. The solvent was removed *in vacuo* and the crude product was purified by silica gel column chromatography using hexanes and ethyl acetate as eluents. The solvents were removed *in vacuo* to give a red solid (0.523 g, 80%). ¹H-NMR (400

MHz, CDCl₃): δ 7.92 (s, 2H), 7.27 (s, 2H), 7.26 (s, 1H), 6.58 (d, J = 3.2 Hz, 2H), 2.66 (t, J = 7.7 Hz, 2H), 1.65 (m, 2H), 1.41-1.33 (m, 6H), 0.91 (t, J = 6.9 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ 144.1, 138.6, 134.0, 131.2, 118.7, 116.6, 31.6, 29.7, 29.7, 29.0, 22.7, 14.2. FAB/MS Calculated m/z = 438.06, Found m/z = 438.05



BDP-BDT

2,6-bis(trimethylstannyl)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-

b]dithiophene (108 mg, 0.12 mmol) and 8-(2-bromo-3-hexylthien-5-yl)-4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene (120 mg, 0.275 mmol) were dissolved in degassed toluene, followed by the addition of Pd₂dba₃ (8 mg, 2.5 mol%) and tri(*o*-tolyl)phosphine (8 mg, 7.5 mol%). The reaction was heated to reflux and stirred for 24 hr. The solvents were removed *in vacuo* and the crude was purified by silica gel column chromatography using hexanes and ethyl acetate as eluents. The solvents were removed *in vacuo* to give the product as a purple solid (123 mg, 80%). ¹**H-NMR** (400 MHz, CDCl₃): δ 7.93 (s, 4H), 7.81 (s, 2H), 7.46 (s, 2H), 7.37 (m, 6H), 6.95 (d, *J* = 3.5 Hz, 2H), 6.60 (m, 4H), 2.92 (m, 8H), 1.75-1.69 (m, 6H), 1.47-1.39 (m, 12H), 1.34 (m, 16H), 0.96 (t, *J* = 7.4 Hz, 6H), 0.90 (m, 12H). ¹³**C-NMR** (100 MHz, CDCl₃): δ 146.5, 143.7, 142.4, 139.6, 139.0, 138.2, 137.2, 136.6, 136.5, 136.2, 134.1, 133.7, 131.2, 131.2, 128.1, 125.8, 124.1, 123.2, 122.9, 118.6, 118.5, 41.6, 34.4, 32.6, 31.7, 30.7, 29.7, 29.4, 29.0, 25.8, 23.18, 22.7, 14.3, 14.2, 11.0. MALDI/MS Calculated *m/z* = 1290.5, Found *m/z* = 1291.3.



BDP-CPDT

4,4-Bis(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4*H*-cyclopenta-[2,1-*b*:3,4-*b*']dithiophene (73 mg, 0.10 mmol) and 8-(2-bromo-3-hexylthien-5-yl)-4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*indacene (100 mg, 0.23 mmol) were dissolved in degassed toluene, followed by the addition of Pd₂dba₃ (3 mg, 2.5 mol%) and tri(o-tolyl)phosphine (3 mg, 7.5 mol%). The reaction was heated to 100°C and stirred for 24 hr. The solvents were removed *in vacuo* and the crude product was purified by silica gel column chromatography using hexanes and ethyl acetate as eluents. The solvents were removed *in vacuo* to give the product as a purple solid (86 mg, 77%). ¹**H-NMR** (400 MHz, CDCl₃): δ 7.92 (s, 4H), 7.48 (s, 2H), 7.40 (d, *J* = 4.1 Hz, 4H), 7.18 (s, 2H), 6.62-6.60 (m, 4H), 4.16-4.12 (m, 2H), 2.95 (t, *J* = 7.9 Hz, 4H), 2.06-1.96 (m, 2H), 1.82-1.73 (m, 4H), 1.50-1.29 (m, 20H), 0.98-0.88 (m, 12H). ¹³**C-NMR** (100 MHz, CDCl₃): δ 158.8, 143.2, 140.6, 139.7, 139.2, 138.7, 137.0, 135.2, 134.0, 134.0, 132.1, 131.0, 131.0, 130.9, 122.3, 118.4, 118.3, 118.3, 54.5, 43.3, 35.4, 34.4, 31.8, 30.6, 29.8, 29.4, 28.8, 27.6, 23.0, 22.8, 14.2, 14.2, 10.9, 10.9. FAB/MS Calculated *m/z* = 1114.5, Found *m/z* = 1114.5



BDP-DTP

N-(2-ethylhexyl)-2,6-bis(trimethylstannyl)-dithieno[3,2-*b*:2',3'-*d*]pyrrole (140 mg, 0.23 mmol) and 8-(2-bromo-3-hexylthien-5-yl)-4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene (200 mg, 0.46 mmol) were dissolved in degassed toluene, followed by the addition of Pd₂dba₃ (5 mg, 2.5 mol%) and tri(o-tolyl)phosphine (5 mg, 7.5 mol%). The reaction was heated to 100°C and stirred for 24 hr. The solvents were removed *in vacuo* and the crude product was purified by silica gel column chromatography using hexanes and ethyl acetate as eluents. The solvents were removed *in vacuo* to give the product as a purple solid (217 mg, 94%). ¹**H-NMR** (400 MHz, CDCl₃): δ 0.99-0.88 (m, 12H), 1.49-1.34 (m, 20H), 1.79-1.74 (m, 4H), 2.04-1.98 (m, 2H), 2.95 (t, *J* = 7.9 Hz, 4H), 4.14 (dd, *J* = 7.0, 5.6 Hz, 2H), 6.61 (dd, *J* = 4.1, 1.7 Hz, 4H), 7.18 (s, 2H), 7.40 (d, *J* = 4.1 Hz, 4H), 7.48 (s, 2H), 7.92 (s, 4H). ¹³C-**NMR** (100 MHz, CDCl₃): δ 145.7, 143.2, 140.9, 140.1, 139.2, 137.1, 134.0, 133.2, 132.4, 131.0, 118.4, 116.5, 110.7, 51.5, 40.6, 31.8, 30.9, 30.7, 29.8, 29.5, 28.6, 24.3, 23.2, 22.8, 14.2, 10.8. ESI-HR Calculated *m/z* = 1003.4, Found *m/z* = 1003.4



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Fig. S1. Cyclic voltammograms in 0.1M TBAPF₆/CH₂Cl₂ measured against Ag/Ag+ reference cell, corrected with respect to Fc/Fc⁺ redox couple of a) **BDP-BDT**, b) **BDP-CPDT**, c) **BDP-DTP**

OFET fabrication

Organic field effect transistor (OFET) devices were fabricated using pre-patterned n-doped silicon substrates. Gold electrodes were deposited on the gate layer to yield the bottom contact OFETs. The channel width of all transistors was 10 mm. The channel length was 2.5, 5, 10 or 20 μ m. The capacitance of the insulator is 14.9 nF cm⁻² for 230 nm of SiO₂. The OFET substrates were rinsed with acetone to remove the protective layer before film deposition. Organic thin films were deposited on the surface by spin coating a 10 mg mL⁻¹ chlorobenzene solution at 1000 RPM for 60 s. The devices were allowed to dry at room temperature for 1 hour. The devices were measured directly after drying. All measurements were performed under a controlled atmosphere in a glove box using an Agilent 4165C precision semiconductor parameter analyzer.

Table S1. Field effect charge carrier mobilities.						
	$\mu_{ m e}^{ m avg}$	$\mu_{ m e}^{ m best}$	$I_{ m on/off}$	V_{T}		
	$[x10^{-5} cm^2 V^{-1} s^{-1}]$	$[x10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}]$		[V]		
BDP-BDT	$3.20 \pm .06$	3.30	10^{1}	7.3		
BDP-CPDT	$5.29 \pm .28$	5.77	10^{2}	17.7		
BDP-DTP	$4.59 \pm .37$	5.39	10^{2}	27.3		

Electron mobility calculated from the saturated regime of the transfer characteristics. Active material was spun cast from chlorobenzene solutions (10 mg mL^{-1}) at 1000 RPM for 60 s.



Fig. S2. Output (left) and transfer (right) characteristics of OFET devices fabricated using a) BDP-BDT,b) BDP-CPDT, c) BDP-DTP (*W/L* = 2000)

Solar cell fabrication

ITO coated glass sheets (20 ohm/sq., TFD) were successively washed in acetone, ethanol and isopropanol in an ultrasonic bath and exposed to UV-ozone for 15 min. A zinc acetate precursor solution was prepared by dissolving zinc acetate dihydrate Fisher, crystalline, 196 mg) and ethanolamine (Aldrich, 54 μ L) in 6 ml absolute ethanol and stirring for 2 hr at 45°C. The precursor solution was spin cast onto the cleaned substrates at 1800 rpm for 60 s, after which the layer was baked on a hot plate at 180°C for 60 min. The coated substrates were transferred to a glove box with a controlled atmosphere (O₂, H₂O < 0.1 ppm).

Active layer solutions were prepared from stock solutions in o-dichlorobenzene of P3HT (30 mg mL⁻¹), the synthesized acceptor (15 mg mL⁻¹) and additional solvent. They were heated to 80°C for 1 hr followed by heating at 50°C overnight. The active layer was formed by spin coating the prepared solutions at 1500 rpm for 45 s. After spin coating, the samples were annealed at 150°C for 2 min and then placed into the thermal evaporator to deposit a 7 nm thick MoO_3 layer (0.14 nm s⁻¹), followed by 100 nm thick Ag layer (1.25 nm s⁻¹) under a secondary vacuum (10⁻⁶ mbar) through a shadow mask to define an 6 mm² active area. The devices were characterized using a K.H.S SolarCelltest-575 solar simulator with AM1.5G filters set at 100 mW cm⁻¹.



Fig. S3. J-V curves (left) and IPCE plots (right) of P3HT:BDP-BDT devices with various ratios

Table 2. Photo	voltaic cell performance (ITO	/ZnO/P3	HT:BDP-BD	T/Mo	O ₃ /Ag)
Acceptor	P3HT:acceptor ratio	V _{OC}	J _{SC}	FF	PCE
			$[mA cm^{-2}]$		[%]
BDP-BDT	1:1	.62	2.16	.57	.76
	1:1.5	.65	3.09	.60	1.21
	1:2	.61	2.08	.60	.75



Fig. S4. J-V curves (left) and IPCE plots (right) of P3HT:BDP-CPDT devices with various ratios

Table 3. Photovoltaic cell performance (ITO/ZnO/P3HT:BDP-CPDT/MoO ₃ /Ag)						
Acceptor	P3HT:acceptor ratio	V _{OC}	J_{SC}	FF	PCE	
DDD CDDT	1.1			(1	[/0] 02	
BDP-CPD1	1.1	.03	2.10	.01	.83	
	1:1.5	.01	2.78	.30	1.02	
	1:2	.58	1.51	.62	.54	



Fig. S5. J-V curves (left) and IPCE plots (right) of P3HT:BDP-DTP devices with various ratios

Table 4. Photo	ovoltaic cell performance (ITC	D/ZnO/P3	HT:BDP-DT	P/Mo	O ₃ /Ag)
Acceptor	P3HT:acceptor ratio	V _{oc}	J _{SC} [mA cm ⁻²]	FF	PCE [%]
BDP-DTP	1:1	.51	1.83 2.18	.52	.49 .84
	1:2	.52	1.72	.38	.34



Fig. S6. J-V curves (left) and IPCE plots (right) of P3HT: BDP-BDT devices with various amounts of CN



Fig. S7. J-V curves (left) and IPCE plots (right) of P3HT:BDP-CPDT devices with various amounts of CN



Fig. S8. J-V curves (left) and IPCE plots (right) of P3HT:BDP-DTP devices with various amounts of CN



Fig. S9. Height (left) and phase (right) AFM images of P3HT:BDP-CPDT films with a) 0%, b) 1%, c)

3%, or d) 5% CN added

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