SUPPORTING INFORMATION

Diketopyrrolopyrrole and benzothiadiazole based small molecule electron acceptor: Design, synthesis, characterization and photovoltaic properties

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Section 1: Experimental details

1.1. Materials

All the reagents and chemicals used, unless otherwise specified, were purchased from Sigma-Aldrich Co. The solvents used for reactions were obtained from Merck Speciality Chemicals (Sydney, Australia) and were used as such. 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) and 3-(5-bromothien-2-yl)-2,5-bis(2-ethylhexyl)-6-(thien-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione were purchased from Luminescence Technology Corporation, Taiwan and were used as such.

1.2. Instruments and characterization

Unless otherwise specified, all ¹H and ¹³C NMR spectra were recorded using a Bruker AV400 spectrometer at 400 MHz and 100.6 MHz, respectively, or a Bruker AV200 spectrometer at 200 MHz and 50 MHz, respectively. Chemical shifts (δ) are measured in parts per million (ppm). Thin Layer Chromatography (TLC) was performed using 0.25 mm thick plates precoated with Merck Kieselgel 60 F₂₅₄ silica gel, and visualised using ultraviolet (UV) light (254 nm and 365 nm). Melting points were measured using a Gallenkamp MPD350 digital melting point apparatus and are uncorrected. High resolution mass spectra (atmospheric-pressure chemical ionization (APCI)) experiments were carried out on a Thermo Scientific Q-Exactive FTMS, ionizing by APCI from an ASAP probe.^{S1}

All UV-vis absorption spectra were recorded on a Hewlett Packard HP 8453 Diode array UV-visible spectrophotometer. Thin films were spin-coated from *o*-dichlorobenzene (*o*-DCB) at a

spin speed of 3000 rpm for 1 min onto cleaned glass slides. N6 was spin-coated from solutions at a concentration of 17 mg/mL. P3HT: N6 blend solutions were prepared in the same manner as for devices, i.e. P3HT (17 mg) and N6 (17 mg) in a total volume of 1 mL. Films were annealed at 120 °C for 5 min. Fluorescence spectra were recorded using a Perkin-Elmer LS50B fluorimeter. Photoelectron Spectroscopy in Air (PESA) measurements were recorded using a Riken Keiki AC-2 PESA spectrometer with a power setting of 5 nW and a power number of 0.5. Samples for PESA were prepared on glass substrates.

1.3 Device fabrication and characterization of photovoltaic devices, and experimental details for the preparation of thin-film transistors have been reported in our previous work.^{S2}

Section 2: Synthetic Details

N6 was synthesized as per the following procedure:



cheme 1 Synthetic strategy for N6

6,6'-(benzo[c][1,2,5]thiadiazole-4,7-diylbis(thiophene-5,2-diyl))bis(2,5-bis(2-ethylhexyl)-3-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) (**N6**):

2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) (1) (120 mg, 0.31 mmol) was taken in a solvent mixture of doixane:water (3:1) (10.0 mL) in a 100 mL round bottom flask followed by the addition of potassium carbonate (128 mg, 0.93 mmol) and tetrakis(triphenylphosphine)palladium(0) (115 mg, 1 mmol) at room temperature. The resulting solution was stirred for 20 min followed by the addition of 3-(5-bromothien-2-yl)-2,5-bis(2-ethylhexyl)-6-(thien-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**2**) (0.56 mmol, 338 mg) at room temperature. The yellow coloured reaction mixture was heated to 90 °C and stirred overnight. Solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography (hexane:dichloromethane 9:1) to get 258 mg (70.4%) of **N6** as a bluish-black powder. ¹H NMR (400 MHz, CD₂Cl₂): δ 9.10–9.09 (m, 2H), 8.91–8.89 (m, 2H), 8.19–8.18 (m, 2H), 8.03 (s, 2H), 7.66–7.64 (m, 2H), 7.28–7.26 (m, 2H), 4.15-3.98 (m, 8H), 2.03–1.93 (m, 2H), 1.90–1.81 (m, 2H), 1.45–1.21 (m, 32H), 0.96–0.85 (m, 24H); ¹³C NMR (400 MHz, CD₂Cl₂): δ 161.69, 161.60, 152.38, 140.18, 139.88, 136.16, 135.30, 131.95, 130.86, 130.15, 129.10, 128.41, 128.04, 126.01, 125.70, 108.76, 108.39,

46.04, 45.88, 39.68, 39.30, 30.51, 30.31, 28.69, 28.50, 23.37, 23.22, 14.06, 13.95, 10.47, 10.37; HRMS (APCI): M⁺, found 1180.4830. $C_{66}H_{80}N_6O_4{}^{32}S_5$ requires 1180.4839

IH NMR



HRMS/APCI



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All experiments were carried out on a Thermo Scientific Q-Exactive FTMS, employing Atmospheric Pressure Chemical Ionisation (APCI). Page 1 of 3
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[M] [*] m/z	Theo.	Mass	Delta (p	opm)	c	Compo	sition	
1180.4	4830	1180	4830	-0.	04 C	279 H6	6 O4 N	15 S
	1180	4829	0.04	C43	H82	017 N	13 54	
	1180.	4829	0.05	C42	H76	012 N	20 54	
	1180	4830	-0.07	C64	H70	04 N	13 \$3	
	1180	4829	0.07	C58	H78	017 N	45 S2	
	1180	4830	-0.08	C65	H76	O9 N6	3 \$ 3	
	1180.	4829	0.08	C57	H72	O12 N	412 52	
	1180.	4829	0.08	C56	H66	07 N	19 \$2	
	1180.	4831	-0.11	C50	H80	O9 N1	14 85	
	1180	4831	-0.11	C51	H86	014 N	47 \$5	
	1180.	4831	-0.11	C52	H92	O19 5	:5	
	1180.	4828	0.17	C72	H82	N3 S6	5	
	1180.	4827	0.20	C35	H78	O20 N	419 \$3	
	1180	4832	-0.23	C72	H74	O N7	84	
	1180	4827	0.23	C50	H74	O20 N	411 S	
	1180	4832	-0.23	C73	H80	O6 S4	1	
	1180	4827	0.23	C49	H68	015 N	418 S	
	1180.	4833	-0.26	C57	H78	O N1	5 56	
	1180	4833	-0.26	C58	H84	O6 N8	3 \$6	
	1180	4833	-0.27	C59	H90	011 1	4 \$6	
	1180	4826	0.32	C65	H84	08 N	2 85	
	1180.	4826	0.32	C64	H78	O3 N	9.55	
	1180	4834	-0.35	C43	H74	018 N	417 S2	
	1180	4825	0.35	C79	H74	03 N	\$3	
	1180.	4824	0.44	C43	H90	016 N	49 56	
	1180.	4824	0.45	C42	H84	011 1	416 56	
	1180.	4835	-0.47	C64	H62	05 N	175	
	1180	4524	0.47	C58	H86	016 1	154	
	1180.	4835	-0.47	C65	H68	010 1	105	
	1180.	4824	0.47	C57	H80	011 1	48 54	
	1180.	4835	-0.45	066	1174	015 1	43 5	
	1180.	4524	0.48	C56	H/4	06 N	15 54	
	1180	4035	-0.50	030	r1/2	010 1	18 53	
	1180	4024	0.50	072	M/6	0113	14 4 10 10	
	1100.	4635	-0.51	001	r1/6	015 1	1153	
	1160.	4024	0.51	6/1	m/0	06 N	95	

All experiments were carried out on a Thermo Scientific Q-Exactive FTMS, employing Atmospheric Pressure Chemical Ionisation (APCI). 11 October 2013 Page 2 of 3

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180.4836	-0.51 C52 H84 O20 N4 S3
180.4823	0.51 C70 H64 O N14 S2
180.4836	-0.54 C36 H82 O15 N19 S5
180.4836	-0.54 C37 H88 O20 N12 S5
180.4822	0.60 C35 H86 O19 N15 S5
180.4837	-0.63 C72 H66 O2 N11 S2
180.4822	0.63 C50 H82 O19 N7 S3
180.4837	-0.63 C73 H72 O7 N4 S2
180.4822	0.63 C49 H76 O14 N14 S3
180.4837	-0.65 C57 H70 O2 N19 S4
180.4837	-0.66 C58 H76 O7 N12 S4
180.4822	0.66 C64 H72 O14 N6 S
180.4837	-0.66 C59 H82 O12 N5 S4
180.4822	0.66 C63 H66 O9 N13 S
180.4822	0.67 C62 H60 O4 N20 S
180.4838	-0.69 C43 H80 O7 N20 S6
180.4838	-0.69 C44 H86 O12 N13 S6
180.4838	-0.70 C45 H92 O17 N6 S6
180.4820	0.78 C41 H72 O17 N20 S2
180.4839	-0.81 C66 H80 O4 N6 S5
180.4819	0.87 C57 H88 O10 N4 S6
180.4819	0.88 C56 H82 O5 N11 S6
180.4819	0.88 C55 H76 N18 S6
180.4840	-0.90 C51 H70 O16 N15 S
180.4819	0.90 C71 H78 O5 N3 S4
180.4819	0.91 C70 H72 N10 S4
180.4818	0.94 C85 H68 N2 S2
180.4841	-0.97 C74 H84 O S6
180.4817	1.02 C50 H90 O18 N3 S5
180.4817	1.03 C49 H84 O13 N10 S5
180.4817	1.03 C48 H78 O8 N17 S5
180.4842	-1.06 C58 H68 O8 N16 S2
180.4817	1.06 C64 H80 O13 N2 S3
180.4842	-1.06 C59 H74 O13 N9 S2

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13C NMR





Fig. S1 Fluorescence spectra of pristine film of N6 (N6 P) along with its blend with P3HT [as-cast; N6 B), spin-coated from *o*-dichlorobenzene ($\lambda_{exc} = 600$ nm).



Fig. S2 Orbital density distribution for frontier molecular orbitals of N6. Density functional theory calculations were performed using the Gaussian 09 suite of programs and B3LYP/6-311+G(d,p)/B3LYP/6-31G(d) level of theory.



Fig. S3 PESA spectrum of thin film of **N6** from *o*-DCB. The dashed-lines show the fits to extract ionisation potential (-5.06 eV) which corresponds to the HOMO energy level.



Fig. S4 TGA (left) and DSC (right) curves showing thermal stability of N6.



Fig. S5 IPCE spectrum of the best performing device described in Fig. 7.

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