## **Electronic Supplementary Information**

# An efficient non-fullerene acceptor based on central and peripheral naphthalene diimides

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### **Experimental section**

#### Materials and methods

All the reactions were carried out under nitrogen atmosphere, unless otherwise stated. Solvents used for various reactions were dried using a commercial solvent purification/drying system. Solvents used for extractions and column chromatography, and all other reagents were used as supplied by commercial vendors without further purifications or drying. 4,9-bis(5-bromothiophen-2-yl)-2,7-dioctylbenzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone and 2-octyl-7-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

yl)phenyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone were prepared according to the reported literature.<sup>S1,S2</sup> Thin layer chromatography (TLC) was performed using 0.25 mm thick plates pre-coated with Merck Kieselgel 60 F<sub>254</sub> silica gel, and visualized using UV light (254 and 365 nm). Petroleum spirits with a boiling point range of 40–60 °C was used wherever indicated. Column chromatography was performed on either 40-60 or 20-40 µm silica gel. 1H NMR spectra were recorded at 300, 400 or 500 MHz, as indicated. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, and dt = doublet of triplets. 13C NMR spectra were recorded at 75 or 101 MHz, as indicated. 1H and 13C chemical shifts were calibrated using residual non-deuterated solvent as an internal reference and are reported in parts per million ( $\delta$ ) relative to tetramethylsilane ( $\delta = 0$ ). TGA experiments were carried out using Q-500 TGA instrument with nitrogen as a purging gas. Samples were heated to 800 °C at a rate of 10 °C per minute under nitrogen atmosphere. Details of spectroscopic measurements, and device fabrication and characterization of photovoltaic devices were reported previously.<sup>S3</sup> Atomic force microscopy topographic maps were directly performed on the active layers of P3HT: N10 blends using an Asylum Research MFP-3D-SA instrument. The AFM was run in intermittent contact mode (tapping mode) using MicroMasch NSC18 tips (typical resonant frequency ~100 kHz, typical probe radius ~10 nm and typical aspect ratio 3: 1). TEM samples were prepared by solvent evaporation on a holey carbon grid and micrographs were produced using a JOEL 1010 100 Kv TEM.

#### Synthetic details

## 7,7'-(((2,7-Dioctyl-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydrobenzo[*lmn*][3,8]phenanthroline-4,9-diyl)bis(thiophene-5,2-diyl))bis(4,1-phenylene))bis(2-

octylbenzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone) (N10): Compounds 1 (200 mg, 0.24 mmol), 2 (314 mg, 0.54 mmol) and cesium fluoride (56 mg, 0.36 mmol) were taken in a 3: 1 ( $\nu/\nu$ ) solvent mixture of 1,4-dioxane: water (10 mL), and the reaction mixture was degassed for 1 h before adding [1,1'-bis(diphenylphospino)ferrocene]dichloropalladium(II) (10 mg, 5 mol%) complex. The reaction mixture was heated to 100 °C and stirred under  $N_2$ atmosphere for 24 h. The reaction progress was monitored by thin layer chromatography. After completion, the reaction mixture was cooled down and the solvent was evaporated under reduced pressure. The crude residue was dissolved in dichloromethane and washed with water followed by brine. The organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated. The crude product was purified by column chromatography on silica (petroleum spirit: ethyl acetate 7: 3) to afford N10 as a bluish-black solid (203 mg, 53%). FT-TR (in KBr, cm<sup>-1</sup>): 2922.91, 2852.43, 1707.11, 1664.53, 1577.56, 1451.80, 1372.14, 1343.05, 1248.28, 1186.89, 1090.89, 1090.32, 796.16, 767.33; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.95–8.88 (m, 10H), 7.89 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.4 Hz, 4H), 7.50 (d, J = 3.7 Hz, 1H), 7.47 (d, J = 8.4 Hz, 4H), 7.41 (t, J= 5.9 Hz, 2H), 4.28–4.19 (m, 8H), 1.82–1.74 (m, 8H), 1.49–1.27 (m, 40H), 0.90–0.85 (m, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.29, 163.72, 141.93, 133.23, 132.57, 132.02, 129.01, 128.81, 127.51, 127.12, 127.03, 126.81, 126.38, 41.88, 31.77, 29.21, 27.96, 27.01, 22.61, 13.95; MALDI-TOF: calculated for  $C_{94}H_{91}N_6O_{12}S_2$  [M+H] <sup>+</sup>(m/z) 1559.6130; found = 1559.609. Elemental analysis calculated for C<sub>94</sub>H<sub>90</sub>N<sub>6</sub>O<sub>12</sub>S<sub>2</sub> (%): C 72.38, H 5.82, N 5.39; found C 72.35, H 5.79, N 5.37.



Fig. S1 Orbital density distribution for the frontier molecular orbitals of N10. DFT calculations were performed using the Gaussian 09 suite of programs and the B3LYP/6-311+G(d,p)/B3LYP/6-31G(d) level of theory.

Excited State	1: Singlet-AU	1.8758 eV	660.95 nm	f=0.6234	<s**2>=0.000</s**2>
Excited State	2: Singlet-AG	1.8815 eV	658.98 nm	f=0.0000	<s**2>=0.000</s**2>
Excited State	3: Singlet-AU	1.8815 eV	658.98 nm	f=0.0013	<s**2>=0.000</s**2>
Excited State	4: Singlet-AG	2.1648 eV	572.73 nm	f=0.0000	<s**2>=0.000</s**2>
Excited State	5: Singlet-AU	2.2440 eV	552.51 nm	f=0.0001	<s**2>=0.000</s**2>
Excited State	6: Singlet-AG	2.2440 eV	552.51 nm	f=0.0000	<s**2>=0.000</s**2>
Excited State	7: Singlet-AG	2.9901 eV	414.65 nm	f=0.0000	<s**2>=0.000</s**2>
Excited State	8: Singlet-AU	3.0238 eV	410.03 nm	f=0.0747	<s**2>=0.000</s**2>
Excited State	9: Singlet-AU	3.1273 eV	396.46 nm	f=0.0603	<s**2>=0.000</s**2>
Excited State	10: Singlet-AG	3.1278 eV	396.39 nm	f=0.0000	<s**2>=0.000</s**2>



Fig. S2 Theoretical optical absorption transitions and spectrum of N10.



**Fig. S3** PESA spectrum of pristine film of **N10**. The dashed-lines show the fits to extract ionisation potential (-5.70 eV) which corresponds to the HOMO energy level.



Fig. S4 TGA (upper) and DSC (lower) curves showing thermal stability of N10.

Acceptor	Donor	Testing	V <sub>oc</sub>	$J_{\rm sc}$	FF	Best	Average PCE
		conditions	conditions (V)	(m <b>A</b> /om <sup>2</sup> )		PCE	(%)
		(D: A) <sup>a</sup>		(mA/cm <sup>-</sup> )		(%)	(± std dev) <sup>c</sup>
N10	P3HT	1: 1.2	0.99	12.08	0.64	7.65	7.60 (± 0.10)
		(annealed)					
N10	P3HT	1: 1.2	0.89	9.01	0.59	4.78	4.73 (± 0.08)
		(no annealing)					
PC <sub>61</sub> BM	РЗНТ	1: 1.2 <sup>b</sup>	0.57	8.28	0.64	3.03	2.99 (± 0.06)

<sup>a</sup> BHJ devices with specified weight ratio. Device structure was ITO/PEDOT: PSS (38 nm)/active layer/Ca (20 nm)/Al (100 nm) with an active layer thickness of ~70 nm

 $^{\rm b}$  A standard P3HT:  $PC_{61}BM$  device afforded 3.03% efficiency when tested under alike annealing conditions

<sup>c</sup> A total of ten devices were made for each combination



**Fig. S5** Histogram of the photovoltaic performance parameters of the P3HT: **N10** (1: 1.2) solar cell.



Fig. S6 IPCE curve of the best performing device described in Fig. 3.

#### **Experimental Spectra**



#### Fig. S7 FT-IR of compound N10.



Fig. S8 <sup>1</sup>H NMR of compound N10.



Fig. S9 <sup>13</sup>C NMR of compound N10.

## References:

- S1 D. Srivani, et al., Dyes Pigm., 2017, 143, 1
- S2 Y. Zhao, et al., Tetrahedron, 2012, 68, 1547.
- S3 P. Srinivasa Rao, et al., Dyes Pigm., 2017, 146, 502.