# **Electronic Supplementary Information**

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# **Experimental details**

#### Materials and methods

**Materials:** 2-Methoxyethyl cyanoacetate was purchased from Sigma-Aldrich Co., Bengaluru, Karnataka, India. Pyridine was purchased from Avra Synthesis Pvt Ltd. Acetonitrile was purchased from S. D. Fine Chemicals Limited (SDFCL), India. Dichloromethane and methanol (both AR grade) were purchased from Finar chemicals, India and were used without further purification. Syntheses of 5,5'-(2,7-dioctyl-1,3,6,8-tetraoxo-1,2,3,6,7,8hexahydrobenzo[*lmn*][3,8]phenanthroline-4,9-diyl)bis(thiophene-2-carbaldehyde) and cyanopyridone were reported previously.<sup>S1,S2</sup>

General details: All the reactions were performed under an inert atmosphere of anhydrous nitrogen gas unless otherwise stated. Solvents used for various reactions were dried using a commercial solvent purification system. Solvents used in reaction extractions and chromatography, and all other reagents were used as supplied by commercial vendors without further purifications or drying. Thin layer chromatography (TLC) was performed using 0.25 mm thick plates pre-coated with silica gel (40-60 µm, F<sub>254</sub>) 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. <sup>1</sup>H 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.  $^{13}$ C NMR spectra were recorded at 75, 101 or 125 MHz as indicated. <sup>1</sup>H and <sup>13</sup>C chemical shifts were calibrated using residual non-deuterated solvent as an internal reference and are reported in parts per million ( $\delta$ ) relative to tetramethylsilane ( $\delta = 0$ ). IR-Spectra were recorded on Thermo Nicolet Nexus 670 spectrometer in the form of non-hygroscopic KBr pellets. MALDI spectra were taken from Shimadzu Biotech Axima Performance instrument. For high-resolution mass spectra (HRMS), atmospheric-pressure chemical ionization (APCI) experiments were carried out on FTMS, ionizing by APCI from an atmospheric solids analysis probe (ASAP). DSC experiments were carried out by using Q-100 DSC instrument with nitrogen as a purging gas. Samples were heated to 350 °C at a heating rate of 10 °C/minute. 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/minute under nitrogen atmosphere. UV-Vis absorption spectra were recorded using a Hewlett Packard HP 8453 diode array spectrometer. 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 cleaned glass substrates. Electrochemical measurements were carried out using a PowerLab ML160 potentiostat interfaced via a PowerLab 4/20 controller to a PC running E-Chem for Windows version 1.5.2. The measurements were run in argon-purged dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. The cyclic voltammograms were recorded using a standard three electrode configuration with a glassy carbon (2 mm diameter) working electrode, a platinum wire counter electrode and a silver wire pseudo reference electrode. The silver wire was cleaned in concentrated nitric acid followed by concentrated hydrochloric acid and then washed with deionised water. Cyclic voltammograms were recorded with a sweep rate of 50 mV sec<sup>-1</sup>. All the potentials were referred to the  $E_{1/2}$  of ferrocene/ferrocenium redox couple.

Details of device fabrication and characterization of photovoltaic devices were reported previously.<sup>S2,S3</sup> Atomic force microscopy (AFM) topographic maps were directly performed on the active layers of the P3HT: **N5/N6** 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). A Bruker AXS D8 Discover instrument with a general area detector diffraction system (GADDS) using Cu K $\alpha$  source was utilized to obtain XRD patterns.

# Synthetic details

Synthesis of compound N5:



Scheme S1 Synthetic pathway for N5

(2Z,2'Z)-bis(2-methoxyethyl)-3,3'-(5,5'-(2,7-dioctyl-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahy drobenzo[*lmn*][3,8]phenanthroline-4,9-diyl)bis(thiophene-5,2-diyl))bis(2-cyano acrylate) (N5): Triethylamine (1.40 mL, 10.0 mmol) was added dropwise to the reaction mixture of 5,5'-(2,7-dioctyl-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydrobenzo[*lmn*][3,8]phenanthroline-4,9diyl)bis(thiophene-2-carbaldehyde), 1, (150 mg, 0.21 mmol) and 2-methoxy ethyl cyanoacetate (150 mg, 1.05 mmol) in degassed solvent mixture [DCM: CH<sub>3</sub>CN 1: 1; 30 mL) at room temperature over the period of 30 minutes. The reaction vessel was sealed using a septum under the nitrogen atmosphere, and the reaction mixture was stirred at room temperature for 15 h. The progress of reaction was monitored by TLC. After the completion of reaction, the mixture was poured into precooled water containing hydrochloric acid and was subsequently extracted with dichloromethane. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using dichloromethane: methanol (9:1, v/v) solvent mixture so as to afford titled product N5 as an orange coloured solid (132 mg, 65%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm) δ: 8.73 (s, 2H), 8.41 (s, 2H), 7.89–7.90 (d, 2H, J = 3.8 Hz), 7.33–7.34 (d, 2H, J = 3.8 Hz), 4.48–4.49 (t, 4H, J = 9.4Hz), 4.07-4.11 (t, 4H), 3.71-3.73 (t, 4H, J = 9.4 Hz), 3.44-3.47 (s, 6H), 1.66-1.69 (m, 4H), 1.24–1.38 (m, 20H), 0.84–0.87 (t, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, Deuterated TFA, 125 MHz)  $\delta$ : 163.17, 162.26, 161.75, 151.72, 148.57, 139.21, 138.98, 137.53, 136.12, 129.42, 127.72,

125.72, 124.31, 114.74, 97.88, 70.22, 65.02, 59.02, 41.08, 31.70, 29.13, 29.09, 27.83, 26.94, 22.55, 13.95; FT-IR (KBr, cm<sup>-1</sup>) v: 3422, 2924, 2852, 2215, 1708.41, 1660, 1588, 1506, 1438, 1378, 1315, 1239, 1203, 1132, 1085, 1022, 821, 793, 760, 586, 537, 466; MALDI-TOF: [M + Na]<sup>+</sup> 983.58; HRMS (APCI): Calculated for (M)<sup>+</sup>:  $C_{52}H_{56}N_4O_{10}S_2 = 960.3432$ ; found = 960.3432.

#### Synthesis of compound N6



Scheme S2 Synthetic pathway for N6

Synthesis of (5*Z*,5'*Z*)-5,5'-((5,5'-(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(methanylylidene))bis(4-methyl-1-octyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3carbonitrile) (N6): Pyridine (0.37 mL, 4.60 mmol) was added to the reaction mixture of compound 1 (150 mg, 0.21 mmol) and cyanopyridone (128 mg, 0.585 mmol) in 30.0 mL degassed dichloromethane and the resulting reaction mixture was stirred at room temperature for 2 hours. For full consumption of 1, subsequent quantities of cyanopyridone (20.0 mg, 0.09 mmol) and pyridine (40  $\mu$ L, 0.47 mmol) together with CuI (123 mg, 0.65 mmol) were added. The resulting reaction mixture was refluxed for 48 h. The reaction mixture was cooled down and poured into precooled water containing hydrochloric acid and was extracted with dichloromethane. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using dichloromethane: pet spirits (8: 2,  $\nu/\nu$ ) solvent mixture as an eluent to afford **N6** as a black solid (160 mg, 63%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, Deuterated TFA, 400 MHz, ppm)  $\delta$ : 8.80 (s, 2H), 8.18 (d, 2H), 7.97–7.98 (s, 2H, J = 4 Hz), 7.47–7.48 (d, 2H, J = 4 Hz), 4.08–4.11 (t, 4H), 3.96–4.00 (t, 4H), 2.73 (s, 6H), 1.54–1.65 (m, 8H), 1.18–1.39 (m, 40H), 0.85–0.87 (m, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, Deuterated TFA, ppm)  $\delta$ : 162.84, 162.39, 161.94, 161.20, 158.60, 146.87, 139.53, 139.39, 139.26, 135.99, 129.50, 127.68, 125.59, 124.25, 117.26, 114.01, 103.26, 41.89, 41.21, 31.94, 31.72, 29.71, 29.38, 29.15, 29.09, 28.96, 27.85, 27.60, 26.95, 26.85, 22.69, 22.55, 19.09, 14.05, 13.93; FT-IR (KBr, cm<sup>-1</sup>) v: 3448, 2921, 2852, 2219, 1641, 1579, 1543, 1424, 1376, 1315, 1244, 1168, 1084, 783, 722, 669, 586, 539, 450; MALDI-TOF [M+H]<sup>+</sup> 1199.97, [M+Na]<sup>+</sup> 1221.97; HRMS (APCI): Calculated for (M)<sup>+</sup>: C<sub>70</sub>H<sub>82</sub>N<sub>6</sub>O<sub>8</sub>S<sub>2</sub> = 1198.5630; found = 1198.5639.



Fig. S1 UV–Vis absorption spectra of N5 and N6 in chloroform solutions (N5S: solid black curve; N6S: solid red curve) and molar absorptivity for N5 and N6 is also represented (N5 MA: dotted black curve; N6 MA: dotted red curve).

# **Detailed DFT calculations**<sup>S4,S5,S6</sup>

In order to obtain information about the theoretical density distributions of **N5** and **N6**, the Gaussian 09 abinito/DFT quantum chemical stimulation package was employed. To further investigate the geometry optimization of **N5** and **N6**, density functional theory (DFT) calculations at the B3LYP/6-31G(d) level of theory were performed. To simplify, the octyl chains were replaced by methyl group. To confirm the optimized geometries to be real, the frequency analyses were carried out. The time-dependent density functional theory (TD-DFT) calculations were used to investigate the absorption properties of the optimized geometries of **N5** and **N6**, obtained by Becke 3-parameter exchanges and the Lee-Yang-Parr correlation B3LYP and vibrational frequency calculations with a 6-31g(d) basis set. The obtained results are tabulated in Table S1. The TD-DFT calculations showed absorption bands at 324 nm, 337 nm and 411 nm for **N5**, and 337 nm, 363 nm and 432 nm for **N6**. The frontier molecular orbitals (FMOs) shown in Fig. S2 were calculated at the CAM-B3LYP/6-31G(d) level of theory and were generated using Avogadro.

 Table S1 DFT calculations

	Excitation	Excitation	Oscillator	
Molecules	Energy (eV)	Wavelength (nm)	Strength (f)	Excitations
N5	3.0196	411	0.5242	$191 \rightarrow 199 (\text{H-}7 \rightarrow \text{L})$
				$197 \rightarrow 200 \text{ (H-1} \rightarrow \text{L+1)}$
				$198 \rightarrow 199 (H \rightarrow L)$
	3.6814	337	0.4234	$191 \rightarrow 199 \text{ (H-7} \rightarrow \text{L)}$
				$196 \rightarrow 199 \text{ (H-2} \rightarrow \text{L)}$
	3.8228	324	1.1608	$185 \rightarrow 199 \text{ (H-13} \rightarrow \text{L)}$
				$186 \rightarrow 199 \text{ (H-12} \rightarrow \text{L)}$
				$187 \rightarrow 199 \text{ (H-11} \rightarrow \text{L)}$
				$188 \rightarrow 199 \text{ (H-10} \rightarrow \text{L)}$
				$191 \rightarrow 199 \text{ (H-7} \rightarrow \text{L)}$
				$193 \rightarrow 199 \text{ (H-5} \rightarrow \text{L)}$
				$197 \rightarrow 200 \text{ (H-1} \rightarrow \text{L+1)}$
				$198 \rightarrow 201 \text{ (H} \rightarrow \text{L+2)}$
N6	2.8708	432	1.4131	$199 \rightarrow 209 \text{ (H-9} \rightarrow \text{L)}$
				$206 \rightarrow 209 \text{ (H-2} \rightarrow \text{L)}$
				$207 \rightarrow 210 \text{ (H-1} \rightarrow \text{L+1)}$
				$208 \rightarrow 209 \ (\text{H} \rightarrow \text{L})$
				$208 \rightarrow 211 \text{ (H} \rightarrow \text{L+2)}$
	3.4134	363	1.7814	$206 \rightarrow 209 \text{ (H-2} \rightarrow \text{L)}$
				$207 \rightarrow 210 \text{ (H-1} \rightarrow \text{L+1)}$
				$208 \rightarrow 209 \text{ (H} \rightarrow \text{L)}$
				$208 \rightarrow 211 \text{ (H} \rightarrow \text{L+2)}$
	3.6836	337	0.2107	$199 \rightarrow 209 \text{ (H-9} \rightarrow \text{L)}$
				$201 \rightarrow 209 \text{ (H-7} \rightarrow \text{L)}$
				$204 \rightarrow 209 \text{ (H-4} \rightarrow \text{L)}$
				$206 \rightarrow 209 \text{ (H-2} \rightarrow \text{L)}$

N5		eV	
201	L+2	-1.538	
200	L+1	-1.56412	
199	L	-2.74674	
198	Н	-7.68537	

197	H-1	-7.82334	
196	Н-2	-8.6571	
193	Н-5	-8.87724	
191	H-7	-9.31181	

188	H-10	-9.55046	
187	H-11	-9.551	
186	H-12	-9.55046	
185	Н-13	-9.60733	
N6			

211	L+2	-2.20659	
210	L+1	-2.26047	
209	L	-3.05341	
208	Н	-7.67258	
207	H-1	-7.76401	

206	Н-2	-8.87071	
204	H-4	-9.03126	
201	H-7	-9.20759	
199	Н-9	-9.37548	

Fig. S2 Frontier molecular orbitals of N5 and N6 with energy levels shown in eV.



Fig. S3 The computed optical absorption spectrum of N5.



Fig. S4 The computed optical absorption spectrum of N6.

**NOTE**: The above shown computed spectra indicated the red-shifted transition peaks for **N6** when compared with the transition peaks of **N5**, a result that is persistent with our experimental finding of optical absorption.



**Fig. S5** A pair of NTOs produced by means of subsequent analysis of the transition density matrix via natural transition orbitals with a very similar character as the corresponding hole/electron pair

Table S2	Percentage	contributions	for	transitions*
	0			

Molecules	Excitation Wavelength (nm)	Oscillator Strength (f)	Excitations	Percentage contribution for transition
N5	411	0.5242	$H \rightarrow L$	85%
			$H-7 \rightarrow L$	3%
			$H-1 \rightarrow L+1$	4%
N6	432	1.4131	$H \rightarrow L$	75%
			$H-1 \rightarrow L+1$	10%
			$H-9 \rightarrow L$	4%
			$H-2 \rightarrow L$	2%
			$H \rightarrow L+2$	3%

\*major contribution is from transition involving HOMO to LUMO



Fig. S6 The energy level diagram showing alignments of various components of a BHJ device based on N5 and N6 acceptors.



Fig. S7 PESA curve of N5.



Fig. S8 PESA curve of N6.

## Cyclic voltammetery data:

Cyclic voltammetry experiments indicated that N5 and N6 undergo reversible reduction processes providing overall bandgaps of 2.61 eV and 2.40 eV (Table S3), respectively, a finding consistent with the PESA study.



Fig. S9 Cyclic voltammograms of N5 and N6.

Table S3 Electrochemical data of N5 and N6 obtained from CV ex	periment
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S. No	Molecule	Reduction potential w.r.t. F <sub>c</sub> /F <sub>c</sub> +	E <sub>LUMO</sub> (eV)	E <sub>HOMO</sub> (eV)	Band gap (solution) (eV)
1	N5	-1.07	-3.73	-6.34	2.61
2	N6	-0.82	-3.98	-6.38	2.40



Fig. S10 TGA curve of N5 heated up to 800 °C at the rate of 10 °C/minute.



Fig. S11 TGA curve of N6 heated up to 800 °C at the rate of 10 °C/minute.



Fig. S12 DSC curve of N5 heated up to 350 °C at 10 °C /minute.



Fig. S13 DSC curve of N6 heated up to 350 °C at 10 °C /minute.

Material	Testing conditions (donor: acceptor) <sup>a</sup>	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	Best PCE (%)	Average PCE (± std dev) <sup>c</sup> (%)
N5	1: 1.2	0.97	7.03	0.59	4.03	3.91 (± 0.09)
N6	1:1.2	0.90	10.78	0.63	6.11	5.98 (± 0.08)
N5	1:2	0.88	5.54	0.36	1.77	$1.64 (\pm 0.09)$
N6	1:2	0.77	7.65	0.49	2.86	$2.76 (\pm 0.07)$
PC <sub>61</sub> BM	1: 1.2 <sup>b</sup>	0.58	8.28	0.64	3.02	2.95 (± 0.10)

 Table S4
 Photovoltaic cell parameters for P3HT: N5/N6 blends under different conditions

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

<sup>b</sup> A standard P3HT: PC<sub>61</sub>BM device afforded 3.02% efficiency

<sup>c</sup> A total of ten devices were made for each combination; cell area =  $0.2 \text{ cm}^2$ 



Fig. S14 IPCE spectra for P3HT: N5 and P3HT: N6.



**Fig. S15** AFM images for the unannealed blends of P3HT: **N5** (above) and P3HT: **N6** (below) with the weight ratios of 1: 1.2 (donor: acceptor). RMS roughnesses of 3.4 nm and 1.3 nm were observed for the unannealed blend surfaces, **N5** and **N6**, respectively.



Fig. S16 XRD spectra of neat and blend films of N5 and N6 indicating the surfaces to be featureless.



Fig. S17 <sup>1</sup>H NMR spectrum of N5 in CDCl<sub>3</sub>.



Fig. S18 <sup>13</sup>C NMR spectrum of N5 in CDCl<sub>3</sub> and deuterated TFA.



### Fig. S19 IR spectrum of N5.

#### D.SRIVANI,SVB-S4-P3

Data: SVB-S4-P30001.1G3[c] 13 Jan 2017 20:04 Cal: TOF MIX-130117 13 Jan 2017 19:24 Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron\_HiRes, Power: 85, Blanked, P.Ext. @ 2300 (bin 99) %Int. 764 mV[sum= 16808 mV] Profiles 1-22 Smooth Gauss 5



Fig. S20 MALDI-TOF spectrum of N5.



Fig. S21 <sup>1</sup>H NMR spectrum of N6 in CDCl<sub>3</sub> and deuterated TFA.



Fig. S22 <sup>13</sup>C NMR spectrum of N6 in CDCl<sub>3</sub> and deuterated TFA.



Fig. S23 IR spectrum of N6.

#### D. Srivani, SVB-S4-P4

Data: SVB-S4-P40001.4F3[c] 22 Nov 2016 17:55 Cal: REF-22-11-2016 22 Nov 2016 17:37 Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron\_HiRes, Power: 95, Blanked, P.Ext. @ 2300 (bin 99) %Int. 307 mV[sum= 4916 mV] Profiles 1-16 Smooth Gauss 5



Fig. S24 MALDI-TOF spectrum of N6.

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