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Electronic Supporting Information

A NIR Absorbing *Ortho*-π-extended Perylene Bisimide as Promising Material for Bulk Heterojunction Organic Solar Cell

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7. Photovoltaic parameters of the devices based on various ratios of donor and acceptor (Table S1)

1. General Information:

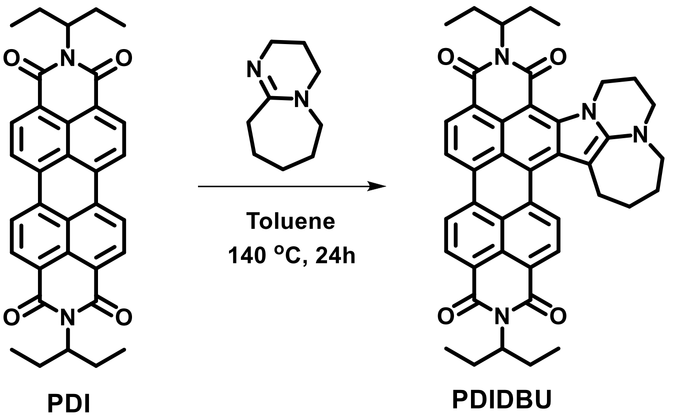
All reactions were carried out under argon atmosphere. Spectroscopic grade solvents were used for measuring electrochemical and optical properties. Samples synthesized were purified by alumina column chromatography followed by recrystallisation. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 500 MHz spectrometers in $CDCl_3$ with trimethylsilane (TMS) as internal reference. High-resolution mass spectrum (HRMS) measurements were done on a microTOF-QII high resolution mass spectrometer from Bruker Daltonics coupled to a Waters Acquity UPLC system. Steady-state absorption measurements were done on Cary 5000 UV/vis/NIR spectrophotometer. Quartz cell with optical path length of 10 mm was used for all measurements. Cyclic voltammetric measurements were carried out using CH potentiostat from CHI Instruments. CV experiments were done under continuous argon flow and a conventional three-electrode electrochemical cell was used. A glassy carbon working, a platinum wire counter and SCE reference electrodes were used. All the measurements were done in dry dichloromethane solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) as supporting electrolyte. The voltammogram was recorded at a scan rate of 100 mV/s. The DFT calculations were performed using Gaussian 09 software suite.

2. Device fabrication and characterization:

The convention device structure i.e. ITO/PEDOT(poly(3,4-ethylenedioxythiophene)):PSS (poly(styrenesulfonate))/PDIDBU:PC71BM/PFN (poly[9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene])/Al is fabricated. First of all the ITO coated substrates were cleaned sequentially in the ultrasonic bath using detergent (deionized water), acetone and isopropanol for 10 min each and dried in the vacuum oven at 50° C. PEDOT:PSS solution was filtered and spin coated onto the pre-cleaned ITO substrates at 3500 rpm for 30 s and then annealed at 110 ° C for 10 minutes and cooled down to room temperature before the active layer was deposited. The blends of PDIDBU and $PC_{71}BM$ (different weight ratios of donor and acceptor, total concentration 14 mg/mL) were dissolved in chloroform (CF). The solutions were spin coated on top of the PEDOT:PSS layer at 2000 rpm for 60 s and the samples were dried in a vacuum oven at 40° C. For solvent vapor annealing the active layer was placed petri disc containing THF for 40 s. A thin layer of PFN was spin coated on the top of active layer, which was dissolved in methanol and mixed with acetic acid with a concentration of 0.5 mg/ml and then spin coated at rpm of 2000 to get a thin film of about 10 nm. Finally, the aluminium (Al) electrode was deposited on top of the active layer by thermal evaporation under a vacuum of 10^{-5} Torr. The current-voltage characteristics of the devices were measured using a computer-controlled Keithley 2400 source meter under stimulated AM1.5 G at an intensity of 100 mW/cm^2 provided by a solar simulator. The incident photon to current efficiency (IPCE) of the devices was measured using a PVE300 EQE system (Bentham Make).

The hole and electron only devices having the structure ITO/PEDOT:PSS/ active layer/ Au and ITO/Al/active layer/ Al, respectively were fabricated to measure the hole and electron mobilities in the active layers.

3. Synthesis and characterization:



Scheme S1: Synthetic Scheme of **PDIDBU** derivative**.**

Synthesis of PDIDBU: The starting precursor PDI was synthesized as per the reported procedures.[1] In a sealed tube, mixture of PDI (100 mg, 0.1887 mmol) and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) (281 µL, 1.887 mmol) in dry toluene (10 mL) was stirred at 140 °C for 24 hours. After stirring for 24 h, the reaction mixture was washed with water and dichloromethane twice. The organic layer was collected over anhydrous sodium sulphate and dried under reduced pressure. The obtained crude mixture was then subjected to column chromatography for further purification. The brown fraction was purified using alumina column chromatography with dichloromethane/ethyl acetate solvent mixture. The obtained solid was further recrystallised using methanol and a shiny brown solid was obtained in 32% (41 mg) yield. ^{1}H NMR (500 MHz, $CDCl_3$, 243K) δ (ppm): 8.52 (merged multiplets, 5H), 7.57 (d, *J* = 5.6 Hz, 1H), 5.19 – 4.81 (broad, 2H), 4.51 (broad, 1H), 3.95 (t, *J* = 12.2 Hz, 1H), 3.75 (d, *J* = 11.1 Hz, 1H), 3.53 (broad, 2H), 3.43 (d, *J* = 12.3 Hz, 1H), 2.81 (broad, 1H), 2.27 (broad, 5H), 2.07 (broad, 1H), 1.89 (merged, 8H), 1.60 (broad, 1H), 1.01 – 0.75 (broad, 12H). ^{13}C NMR (126 MHz, $CDCl_3$, 298K) δ (ppm): 164.74, 164.69, 163.89, 163.42, 163.34, 153.85, 135.07, 133.10, 130.24, 129.65, 129.37, 128.77, 128.39, 126.09, 125.58, 124.69, 123.87, 122.10, 120.00, 119.79, 119.47, 93.52, 56.24, 55.92, 52.57, 51.36, 45.98, 45.73, 26.38, 25.97, 24.01, 23.75, 23.35, 22.41, 10.60, 10.29. HR-MS (APCI) m/z: $[M+H]^+$ calc. for $C_{43}H_{43}N_4O_4$ 679.3279; found 679.3266.

4. Absorption spectra of PDIDBU:

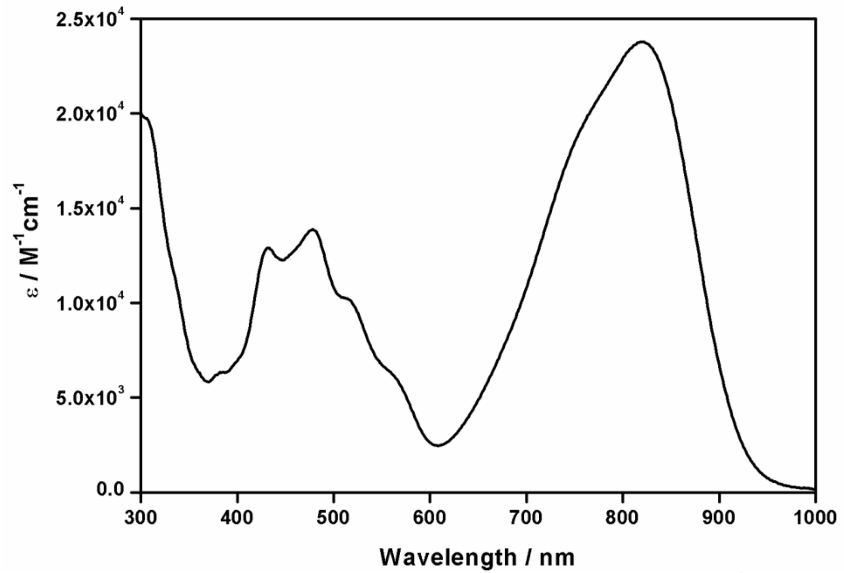


Figure S1. Absorption spectra of **PDIDBU** in chloroform (10^{-6} M) solution.

5. Cyclic voltammogram of PDIDBU:

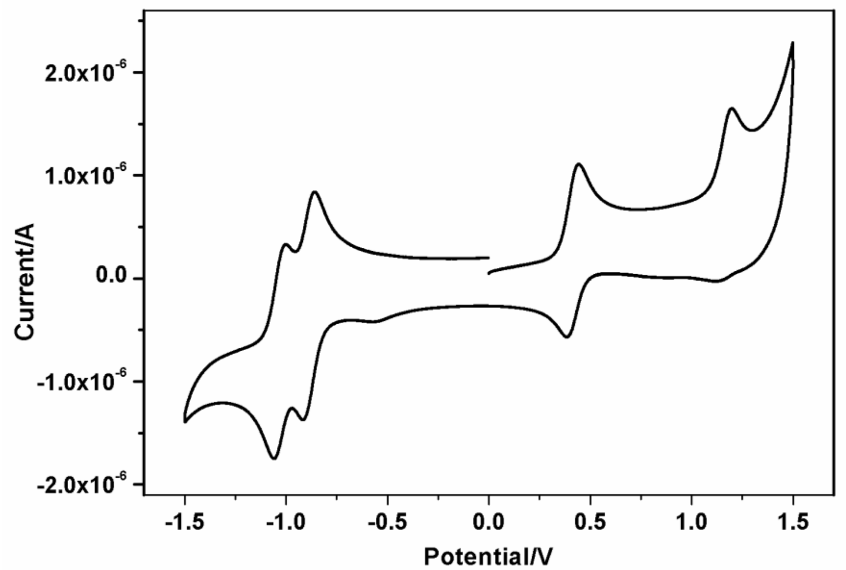


Figure S2. Cyclic voltammogram of **PDIDBU** in dichloromethane solution.

The HOMO and LUMO energy levels were estimated from the formula described below

HOMO= -(E_{oxd} +4.51) eV and LUMO = -(E_{red}+4.51) eV.

6. ^{1}H, ^{13}C NMR and HR-Mass spectra:

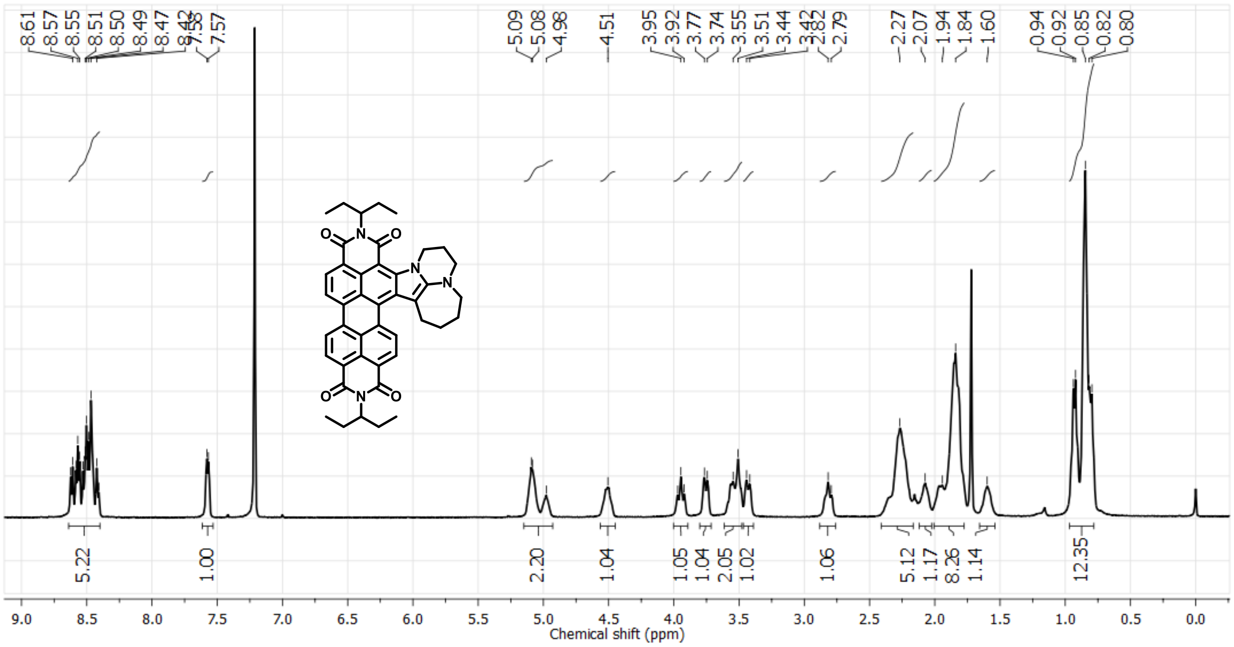


Figure S3: ^{1}H NMR spectrum of **PDIDBU** in $CDCl_3$ (500 MHz).

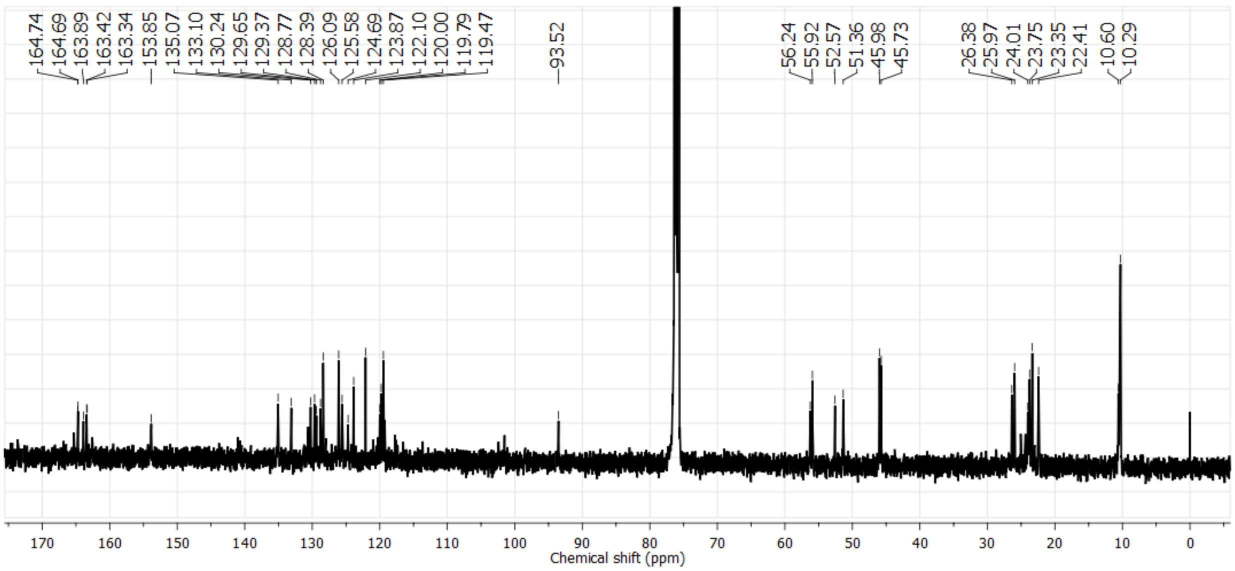


Figure S4: ^{13}C NMR spectrum of **PDIDBU** in $CDCl_3$ (500 MHz).

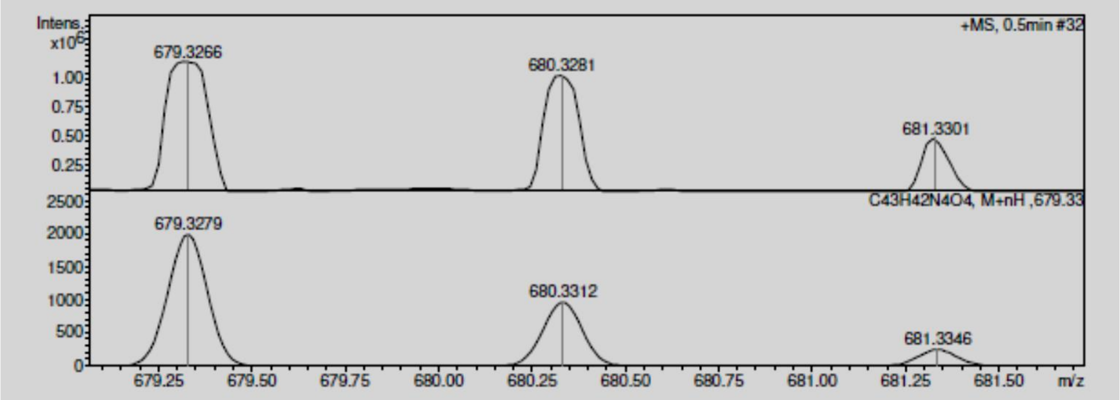


Figure S5: APCI-HR mass spectrum of **PDIDBU**.

Table S1 Photovoltaic parameters of the OSCs based on different weight ratio of PDIDBU and $PC_{71}BM$

PDIDBU:$PC_{71}BM$ weight ratios	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
1:0.5	7.98	0.80	0.365	2.33
1:1	9.13	0.78	0.392	2.79
1:1.5	10.18	0.79	0.41	3.28
1:2	9.61	0.77	0.396	2.93

References

1. (a) H. Langhals, O. Krötz, K. Polborn and P. Mayer, *Angew. Chem., Int. Ed.*, 2005, ***44***, 2427; (b) R. Regar, A. R. Sekhar, R. Mishra and J. Sankar, *Indian J. Chem. Sec*. B 2018, ***57B***, 308.