Supplementary Information (SI) for Materials Advances.

Supporting Information

Tri(oxyethylene)-Functionalised Perylene Diimide: A Promising Interlayer Material for Enhanced Organic Photovoltaic Performance

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1. Synthesis of ETL materials (PDIN, PDIA and PDIAO)

All reactions were carried out under a dry, inert nitrogen atmosphere, unless otherwise stated. Solvents used for various reactions were dried using a commercial solvent purification/drying system. Solvents used for extractions and washings, 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 Merck Kieselgel 60 F_{254} silica gel and visualised using UV light (254 and 365 nm). Unless otherwise specified, all ^{1}H and ^{13}C NMR spectra were recorded using Bruker AV400/AV500 spectrometers at 400 MHz/500 MHz and 100.6 MHz/126 MHz, respectively. Chemical shifts (δ) are measured in ppm. For high-resolution mass spectra (HRMS), experiments were run on Thermo Q Exactive ASAP (APCI) and Thermo Exploris GC 240 GC-MS instruments. For PDIN, MS analyses were performed on a Thermo Scientific Q Exactive mass spectrometer fitted with an ASAP ion source (M&M Mass Spec consulting (http://www.asap-ms.com/). The design and method of ionisation have been described previously (*J. Mass Spectrom.*, 2008, **43**, 1565, and *Euro. J. Mass Spectrom*., 2010, **16**, 169). Positive ions were recorded in an appropriate mass range at **140,000** mass resolution. The APCI probe was used without flow of solvent. The nitrogen nebulizing/desolvation gas used for vaporization was heated to 4*50* °C in these experiments. The sheath gas flow rate was set to *25*, the auxiliary gas flow rate to *10* and the sweep gas flow rate to **2** (all arbitrary units). The discharge current was *4* µA and the capillary temperature was *300* °C. For PDIA, positive ion EI mass spectra were run on a Thermo Scientific DFS mass spectrometer using an ionisation energy of 70 eV. Accurate mass measurements were obtained with a resolution of 5000-10000 using PFK (perfluorokerosene) as the reference compound. For PDIAO, mass spectra were obtained with a Thermo Scientific Exploris 240 mass spectrometer using a direct exposure probe. The mass spectrometer used electron ionisation in full scan positive ion mode with an ionisation energy of 70 eV. Resolution was set to 120,000 with a scan range of 450-750 *m*/*z*. The probe was inserted into the mass spectrometer, held for 30 seconds, then ramped at 20 mA/s to 1000 mA where it was held for 3 min. The source was operated at 200 °C and the emission current at 50 µA.

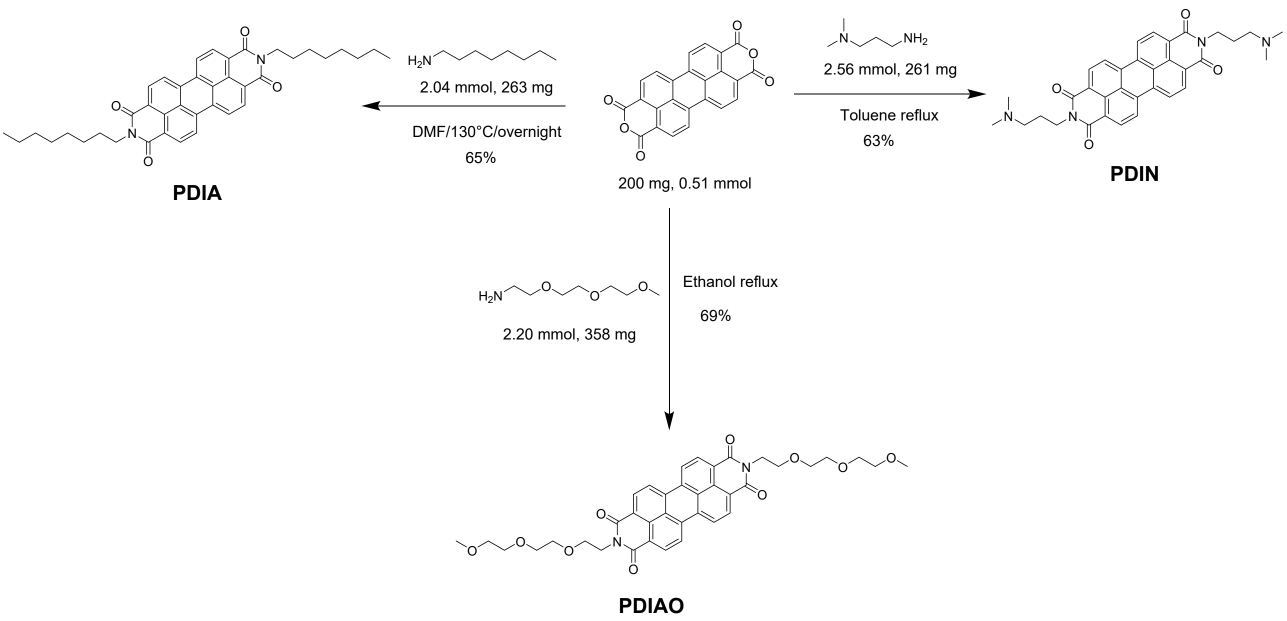


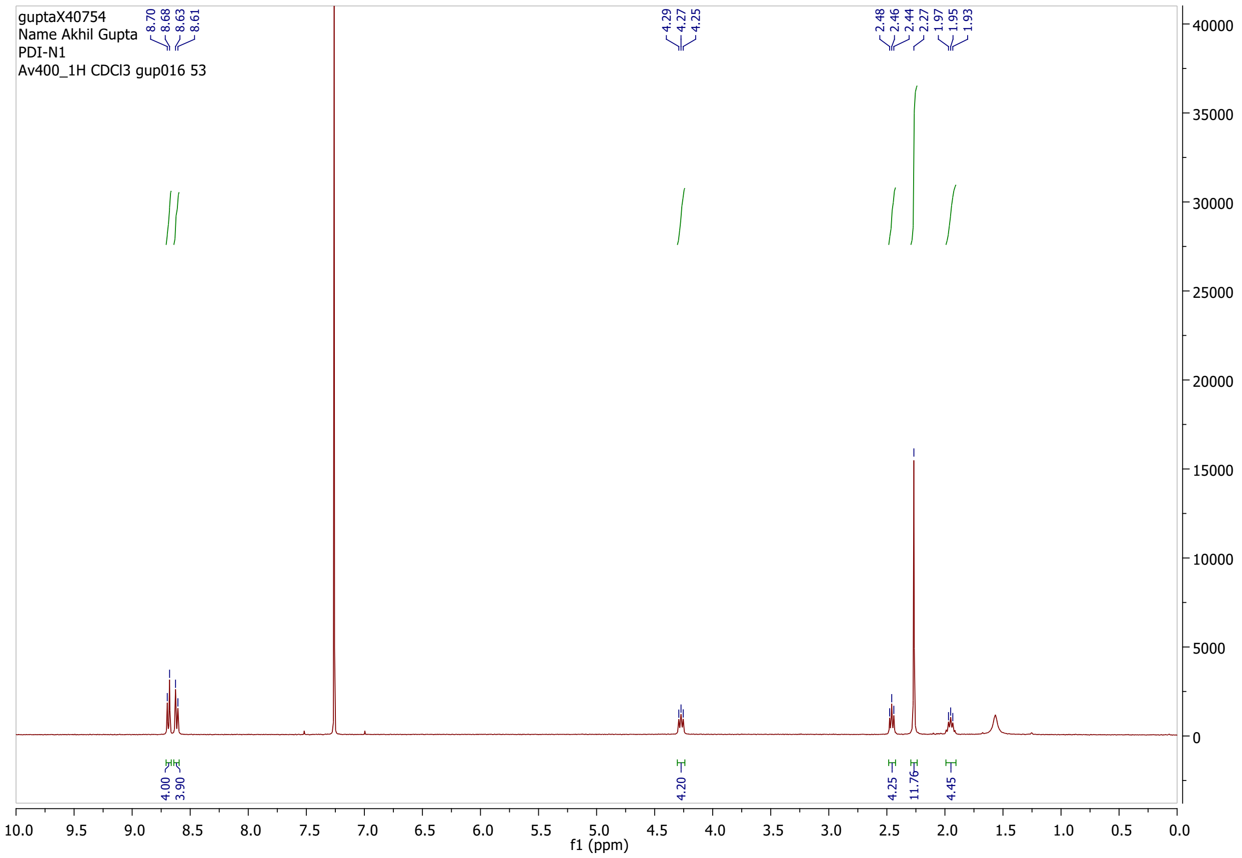
Figure S1. Reaction protocols to generate PDI-based investigated materials.

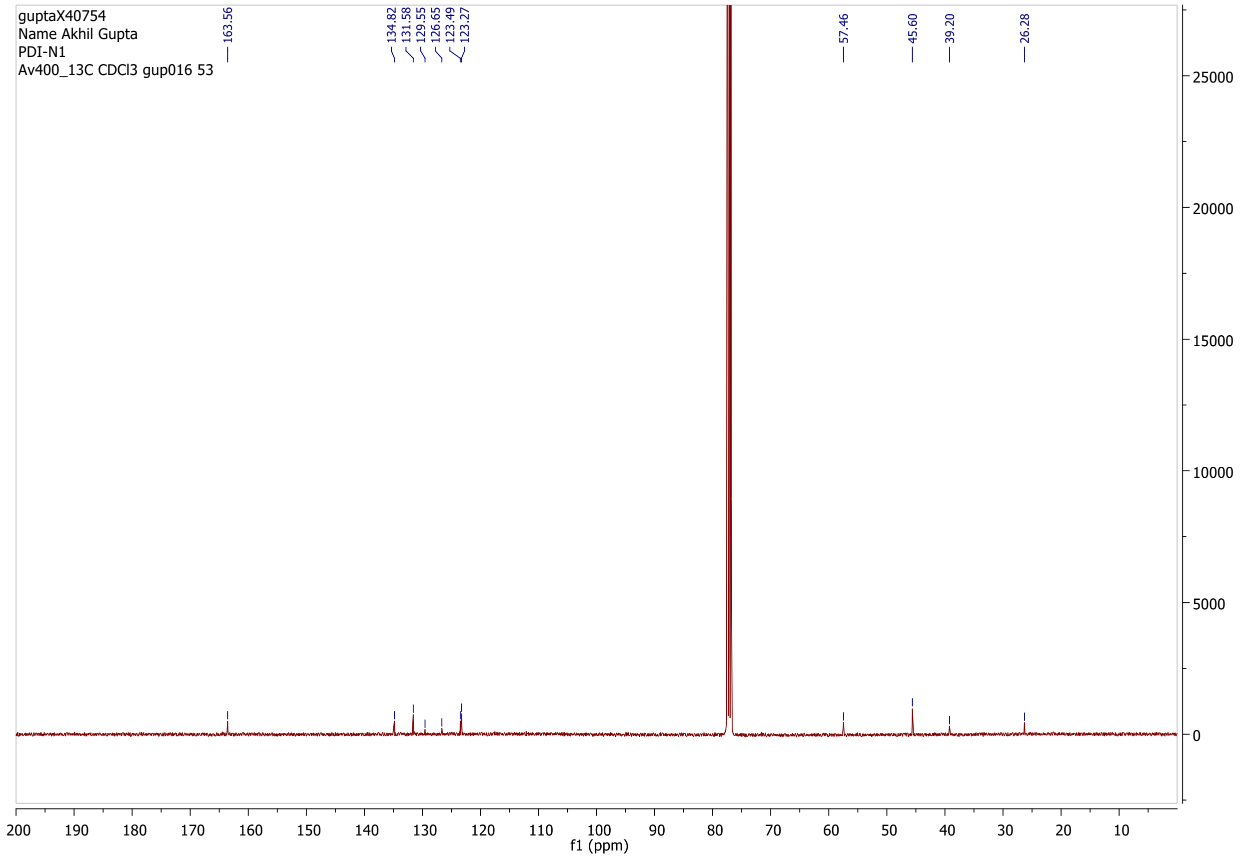
Synthesis of 2,9-bis(3-(dimethylamino)propyl)anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (PDIN): 3,4,9,10-Perylenetetracarboxylic dianhydride (200 mg, 0.51 mmol) and 3-(dimethylamino)-1-propylamine (261 mg, 2.56 mmol) were added to a 100 mL round-bottom flask, followed by dry toluene (30 mL). The resulting slightly reddish reaction mixture was refluxed overnight. The next morning, the clear reaction solution was cooled to room temperature, and the resulting precipitated solid was filtered and washed with toluene and water, followed by methanol, to afford the titled solid as a reddish-brown powder (180 mg, 63%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 – 8.68 (d, *J* = 7.9 Hz, 4H), 8.63 – 8.61 (d, *J* = 8.1 Hz, 4H), 4.29 – 4.25 (m, 4H), 2.48 – 2.44 (t, *J* = 7.2 Hz, 4H), 2.27 (s, 12H), 1.97 – 1.93 (dt, *J* = 14.8, 7.4 Hz, 4H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 163.6, 134.8, 131.6, 129.5, 126.6, 123.5, 123.3, 57.5, 45.6, 39.2, 26.3; HRMS (APCI): [M+H]$^+$ m/z; calculated for $C_{34}H_{33}O_4N_4$ = 561.2496; found = 561.2498; mass accuracy by ppm error = 0.33 ppm (*vs* selection criterion of 5 ppm).

Synthesis of 2,9-dioctylanthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (PDIA): 3,4,9,10-Perylenetetracarboxylic dianhydride (200 mg, 0.51 mmol) and 1-octylamine (263 mg, 2.04 mmol) were added to a 100 mL round-bottom flask, followed by dry DMF (20 mL). The resulting dark reddish reaction mixture was stirred overnight at 120°C. The next morning, the clear reaction solution was cooled to 50°C and added to cold water (10°C), stirring constantly. The resulting precipitated solid was filtered and washed with water, followed by methanol, to afford the titled solid as a crimson red powder (205 mg, 65%); ^{1}H NMR (501 MHz, CDCl$_3$) δ 8.70 – 8.69 (d, *J* = 8.0 Hz, 1H), 8.64 – 8.62 (d, *J* = 8.1 Hz, 1H), 4.22 – 4.19 (m, 1H), 1.80 – 1.74 (dt, *J* = 15.3, 7.6 Hz, 1H), 1.47 – 1.29 (m, 6H), 0.89 – 0.87 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 163.6, 134.8, 131.6, 129.6, 126.7, 123.5, 123.3, 40.9, 31.9, 29.5, 29.4, 28.3, 27.3, 22.8, 14.3; HRMS (EI): [M]$^+$ m/z; calculated for $C_{40}H_{42}O_4N_2$ = 614.3139; found = 614.3141; mass accuracy by ppm error = 0.26 ppm (*vs* selection criterion of 5 ppm).

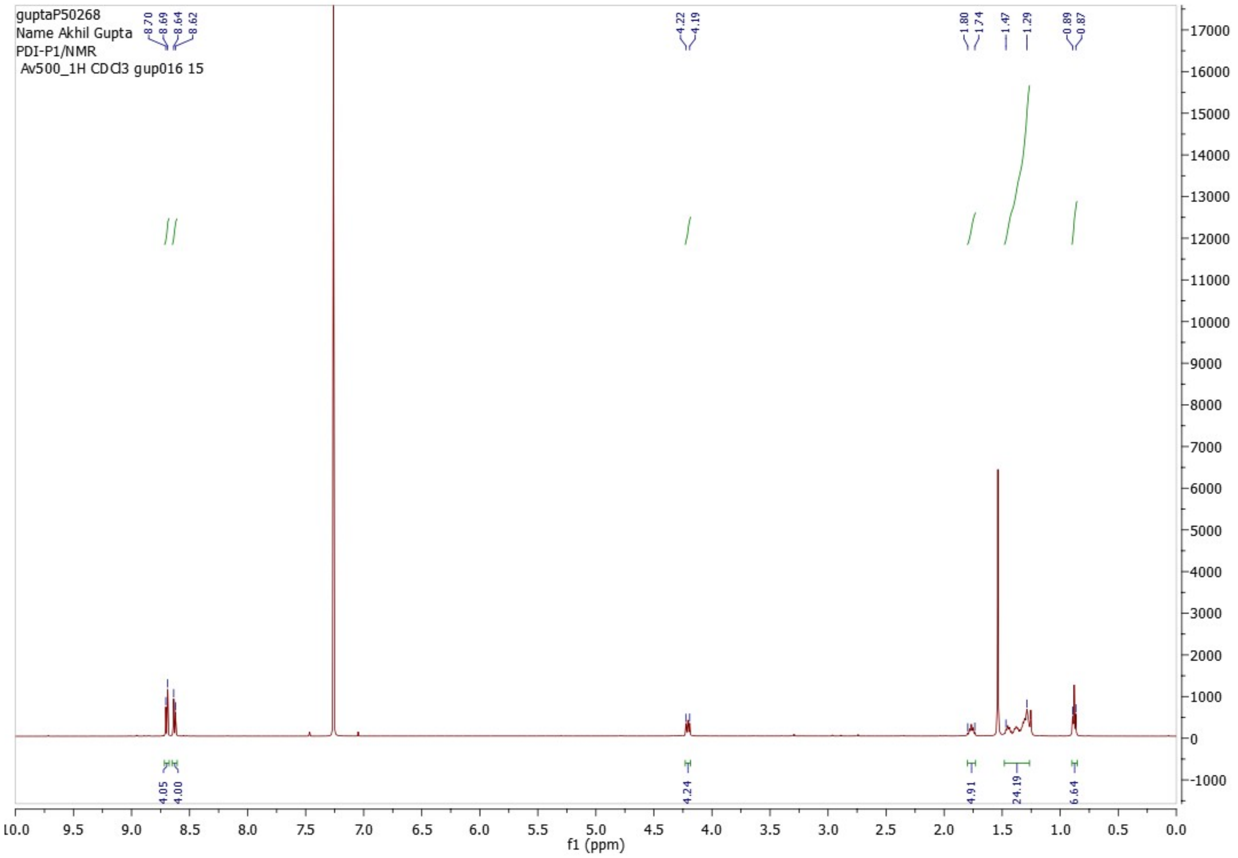
Synthesis of 2,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (PDIAO): 3,4,9,10-Perylenetetracarboxylic dianhydride (200 mg, 0.51 mmol) and 2-(2-(2-methoxyethoxy)ethoxy) ethanamine (358 mg, 2.20 mmol) were added to a 100 mL round-bottom flask, followed by dry ethanol (30 mL). The resulting reddish reaction mixture was refluxed overnight. The next morning, the clear reaction solution was cooled to room temperature, and the resulting precipitated solid was filtered and washed with ethanol and water, followed by methanol, to afford the titled solid as a dark red powder (240 mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 – 8.59 (d, *J* = 7.9 Hz, 4H), 8.51 – 8.48 (d, *J* = 8.1 Hz, 4H), 4.49 – 4.46 (t, *J* = 6.1 Hz, 4H), 3.89 – 3.86 (t, *J* = 6.0 Hz, 4H), 3.76 – 3.73 (dd, *J* = 5.8, 3.7 Hz, 4H), 3.66 – 3.64 (dd, *J* = 5.9, 3.7 Hz, 4H), 3.62 – 3.59 (m, 4H), 3.49 – 3.46 (m, 4H), 3.32 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 134.6, 131.5, 129.4, 126.4, 123.3, 123.2, 72.0, 70.8, 70.7, 70.3, 68.1, 59.2, 39.5; HRMS (GC-MS): $[M]^+$ m/z; calculated for $C_{38}H_{38}O_{10}N_2$ = 682.2521; found = 682.2530; mass accuracy by ppm error = 1.37 ppm (*vs* selection criterion of 5 ppm).

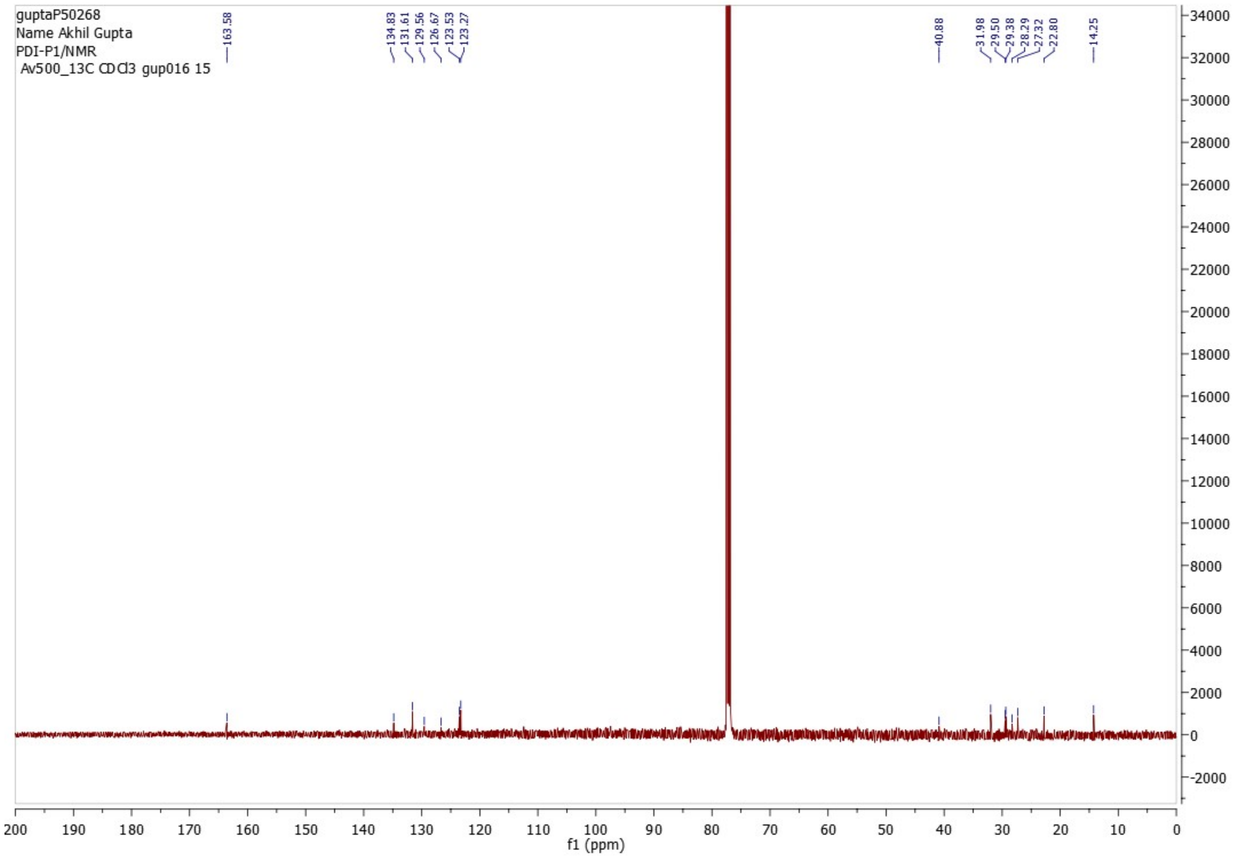
Spectra of PDIN



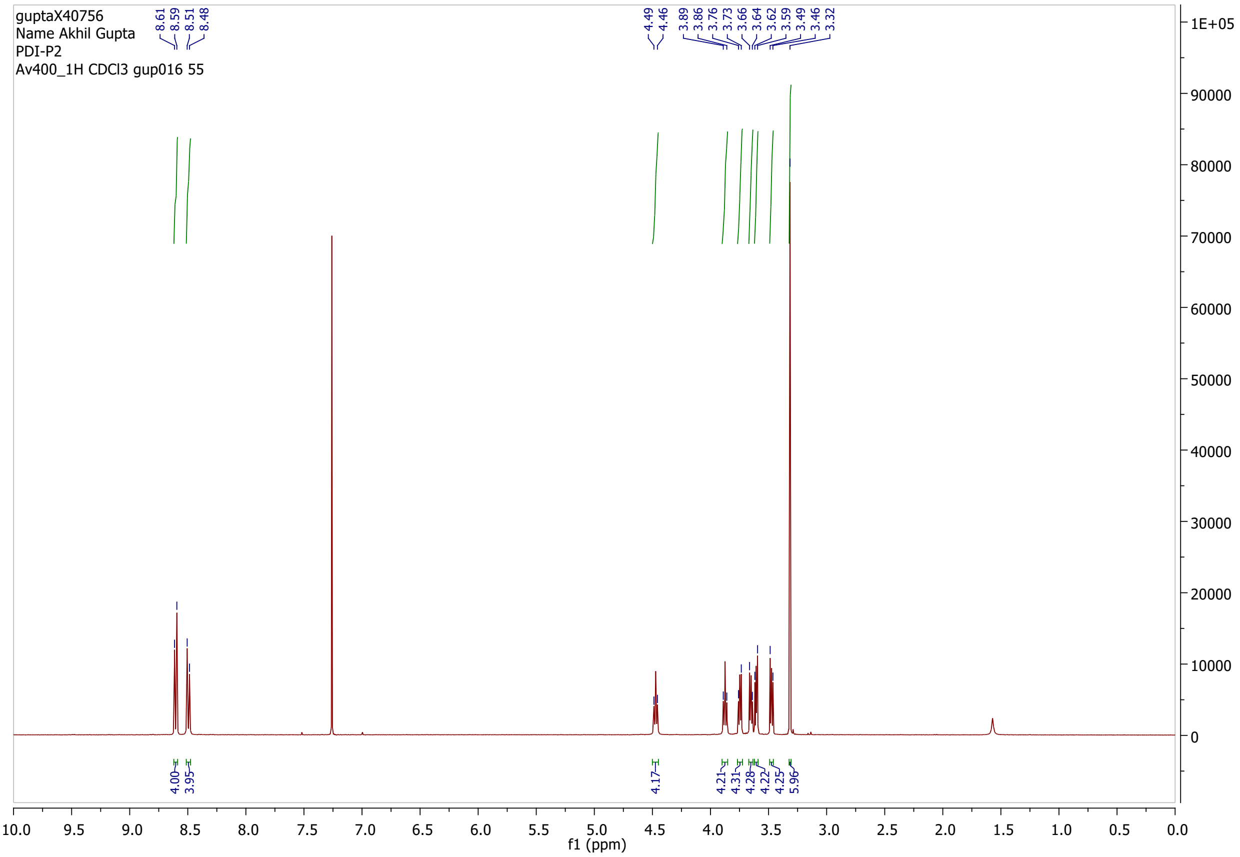


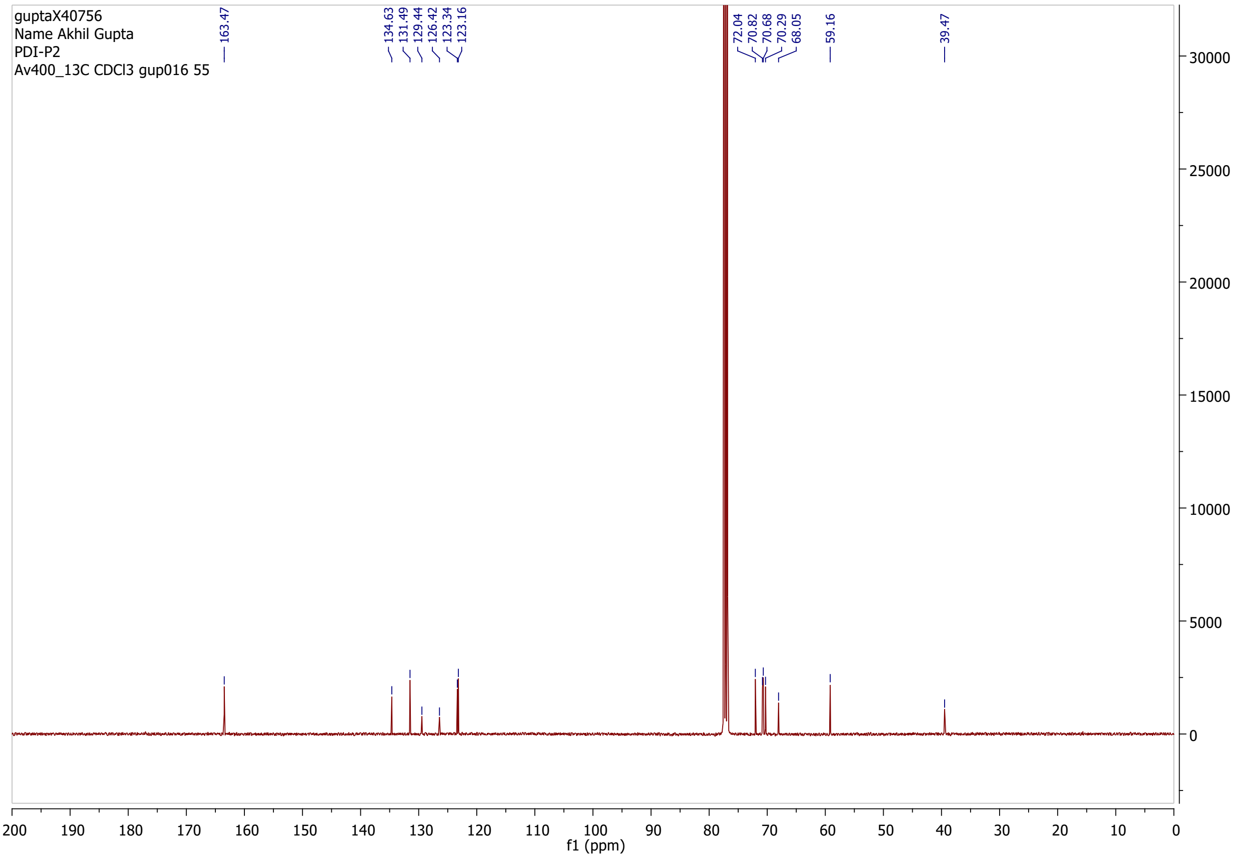
Spectra of PDIA





Spectra of PDIAO





2. Device fabrication and characterisation

Photoactive materials PM6 and acceptor IT-4F and Y6 were purchased from Solarmer Material Inc. The interlayer material PFN-Br was purchased from 1-Material. Organic solar cells were fabricated with the conventional geometry of ITO/PEDOT:PSS (40 nm)/PM6: BTP-eC9 /PFN-Br/Ag. A thin layer of PEDOT: PSS (poly-(3,4-ethylenedioxythiophene):poly(styrene sulfonate)) was spin-cast on pre-cleaned ITO glass from a PEDOT:P SS aqueous solution (Baytron P VP AI 4083 from H. C. Starck) at 6000 rpm and dried subsequently at 150 °C for 10 min in air. Then the device was immediately transferred to a glove box, where the active layer of the blend of the polymer (PM6) and non-fullerene acceptor (BTP-eC9) was spin−coated onto the PEDOT:PSS layer. The active layer was formed by spin-coating chloroform ($CHCl_3$) solution (1 ml) containing PM6 (8 mg): IT-4F (or Y6) (9.6 mg) with 0.5% DIO additives, at 3500 rpm. The active films were annealed at 100 °C for 10 minutes. Then, the trifluoroethanol solution of ETL materials (PDIN/PDIA/PDIAO) and methanol solution of poly9,9-bis6-(*N*,*N*, *N*-trimethylammonium) hexylfluorene-*alt*-*co*-phenylenebromide (PFN-Br) with a concentration of 0.5 mg/mL was spin-coated on the active layer at 4000 rpm for 30s. Finally, the Ag top electrode was deposited in a vacuum at a pressure of ca. 6.0×10^{-7} Pa.

The thickness of the active layer was measured as ~110 nm. The active area of the device was 10 mm^2. The current density-voltage measurements of the devices were carried out using a 1 kW Oriel solar simulator with an AM 1.5G filter as the light source in conjunction with a Keithley 2400 source measurement unit. Solar measurements were carried out under 1000 W/m^2 AM 1.5G illumination conditions. The light intensity was calibrated using a reference silicon solar cell (PV Measurements Inc.) certified by the National Renewable Energy Laboratory for accurate measurement. Device fabrication and characterisations were performed in a glove box without any encapsulation. The active layer thickness of the PSCs was determined by Dektak profilometer. Optical absorption was measured with an Agilent Cary spectrophotometer. Film thickness was determined by Veeco Dektak 150+Surface Profiler. The surface morphology of the blend films was acquired using an Asylum Research Cypher scanning probe microscope operated in tapping mode. Contact angle measurements were performed on a video-based optical contact angle measuring system (OCA20, Data physics Corp.).

UPS data were acquired using a Kratos AXIS Supra X-ray photoelectron spectrometer equipped with a monochromated Al-Kα X-ray source (1486.7 eV) and a concentric hemispherical analyser. Depth profile XPS study was performed by etching the active layer surface by Ar ion beam for about 10 s repeatedly, and XPS spectra were taken after every etching cycle.

3. Optical characterisation

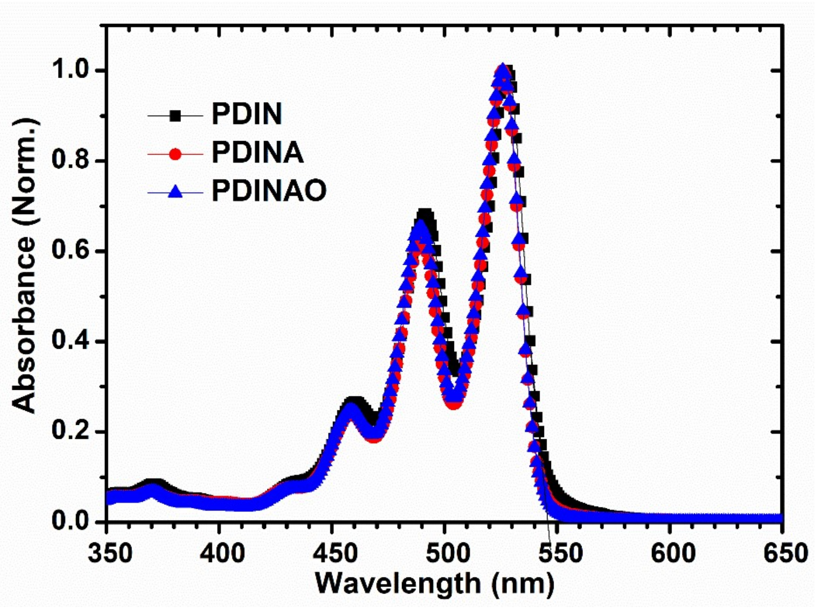


Figure S2. Optical absorption spectra of PDIN, PDIA and PDIAO in solution form.

4. Electrochemical characterisation of ETL materials.

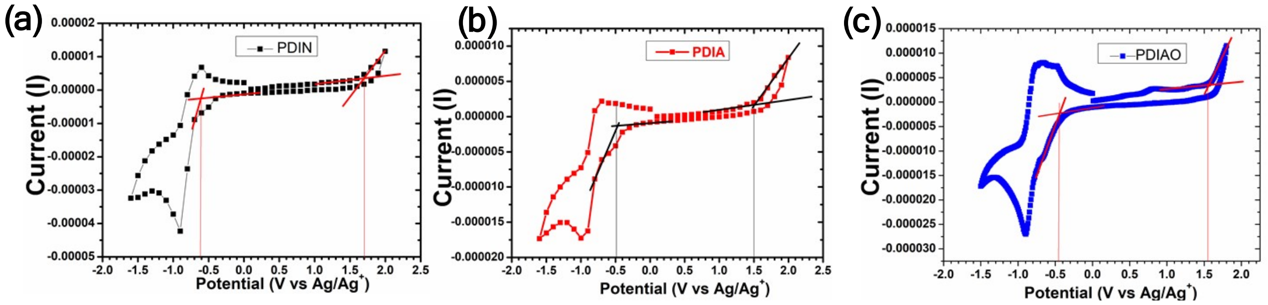


Figure S3. Cyclic voltammograms of ETL materials (a) PDIN, (b) PDIA and (c) PDIAO.

5. Organic photovoltaic devices with PM6:Y6 and conductivity studies of ETL layer

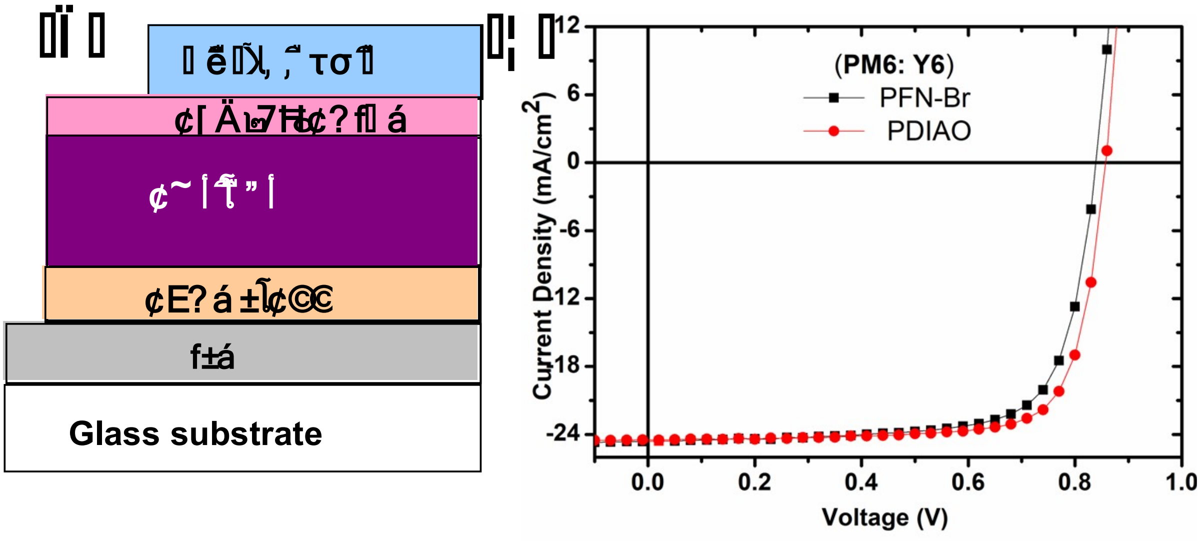


Figure S4. A. Schematic diagram of OPV device and (b) J-V plot of PM6:Y6-based OPV devices with PFN-Br and PDIAO ETL materials.

Table S1. Device performance characteristics of OPV devices with PFN-Br and PDIAO ETL materials.

ETL layer	**J_{sc}(mA/cm^2)**	**V_{oc} (V)**	**FF (%)**	**PCE (%)**
PFN-Br	24.7	0.82	74	15.2
PDIAO	24.6	0.83	78	16.1

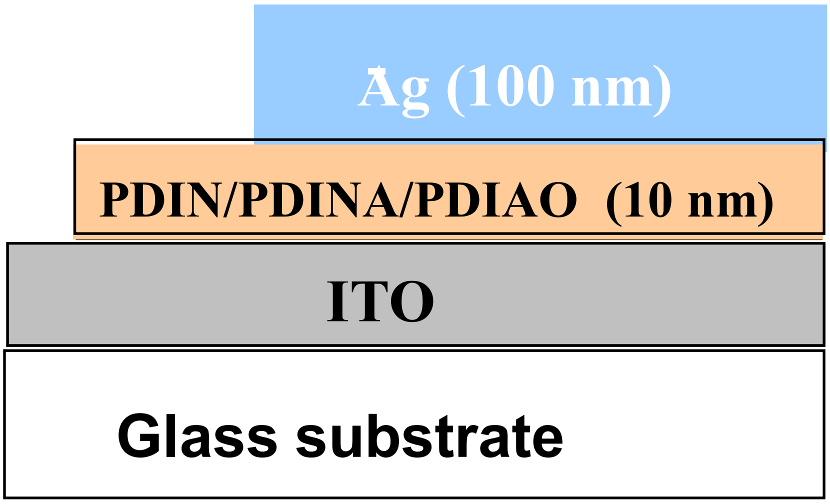


Figure S5. Schematic diagram of a device used for conductivity studies.

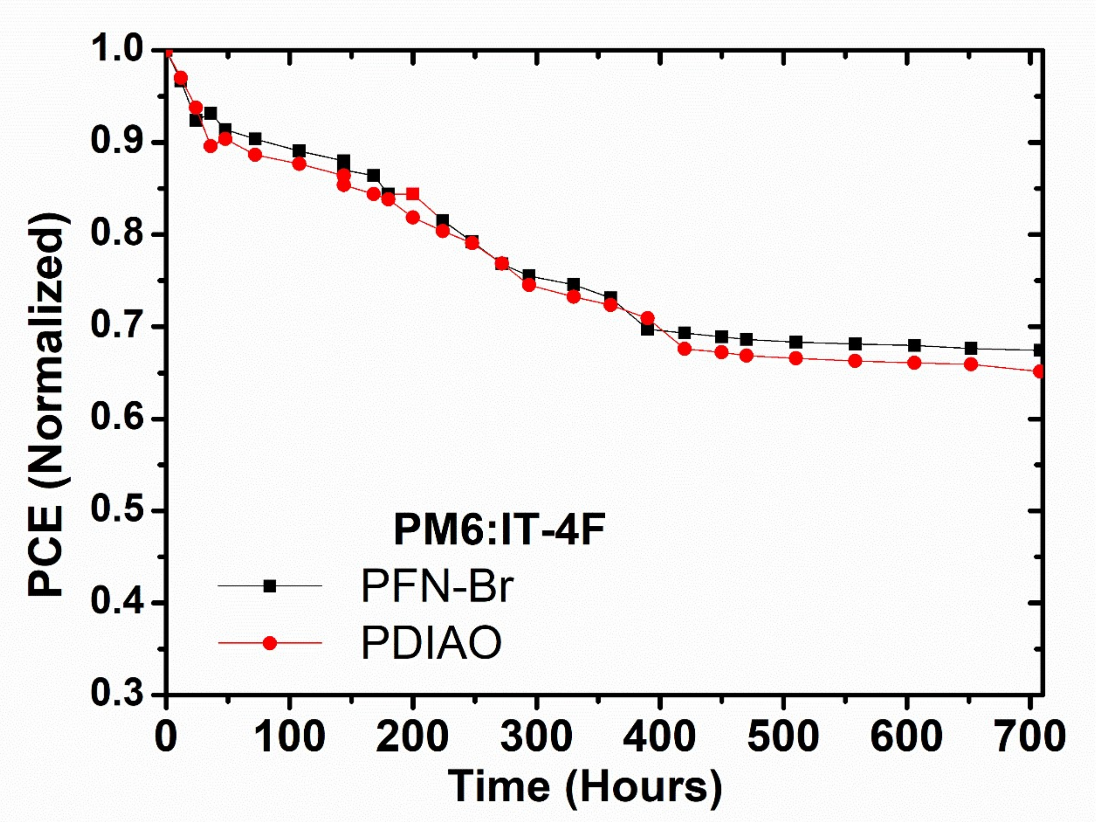


Figure S6. Stability studies of PM6:IT-4F based OPV devices with PFN-br and PDAIO interlayer. All devices are stored in a glove box between the J-V measurements.