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Supporting information

Design and Synthesis of Amino-Functionalized Non-Fullerene Acceptor as Cathode Interfacial Layer for Polymer Solar Cells

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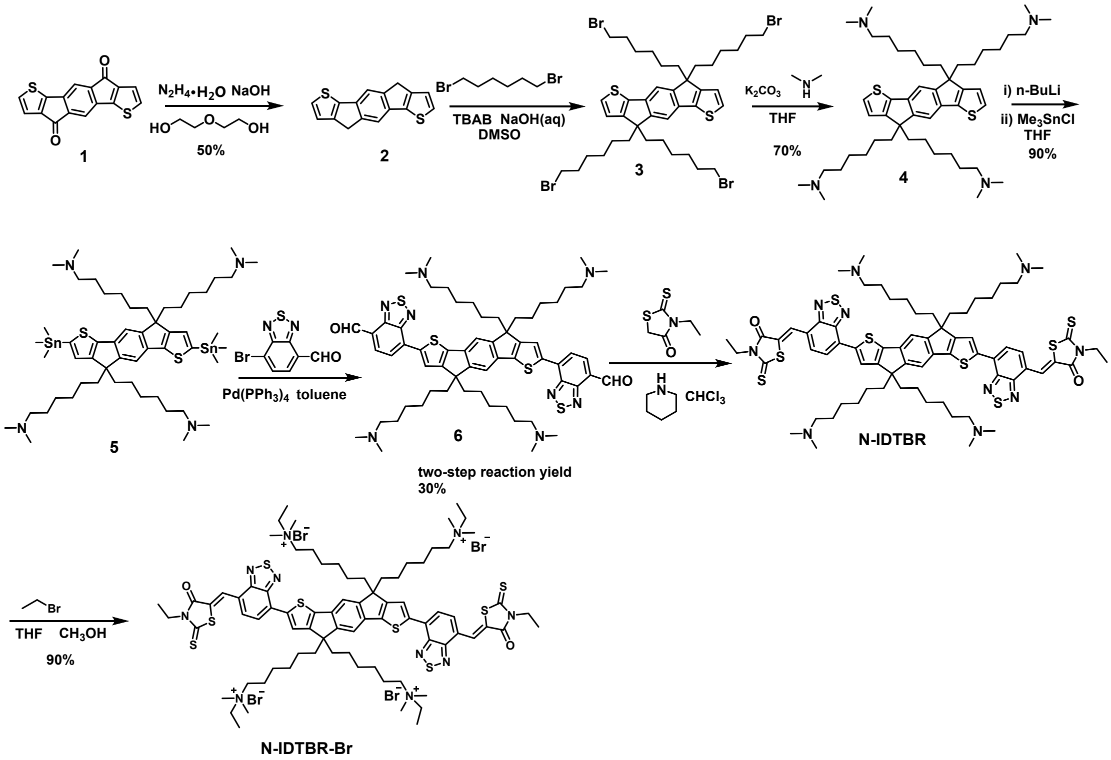
Materials

The number average molecular weight of poly(3-hexylthiophene) is about 30 kDa with a polydspersity index of 1.8. All reagents and solvents were commercial available and were used as received.



Scheme S1 Synthetic route for N-IDTBR and N-IDTBR-Br

Synthesis of N-IDTBR and N-IDTBR-Br

4,9-Dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (**2**). In a round-bottom flask equipped with a condenser, a mixture of **1** (3 g, 10.2 mmol), hydrazine monohydrate (10.2 g, 204.0 mmol) and potassium hydroxide (11.4 g, 204.0 mmol) in diethylene glycol (150 mL) was heated at 110 °C for 1 h. The condenser was then removed and the reaction mixture was heated at 180 °C for 4 h. After being cooled to room temperature, the reaction mixture was poured into hydrochloric acid (150 mL, 2.0 M) and stirred overnight under room temperature. The mixture was filtered and the filter cake was suspended in acetone. The suspension was sonicated for 30 min and anhydrous magnesium sulfate was added. The mixture was filtered and the solvent was removed. The residue was roughly purified by column chromatograph on silica, eluting with hexanes/dichloromethane (1:1), to afford the crude product. The crude product was recrystallized in acetone in a freezer and then purified by column chromatography on silica, eluting with hexanes/dichloromethane (10:1), to afford a nearly white solid in 50% yield. ^{1}H NMR (400 MHz, CDCl3) δ: 7.58 (s, 2H), 7.26 (d, 2H), 7.09 (d, 2H), 3.70 (s, 4H). ^{13}C NMR (125 MHz, CDCl3) δ: 147.0, 145.4, 143.5, 136.1, 126.3, 122.8, 115.8, 33.9.

4,4,9,9-Tetrakis(6-bromohexyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (**3**). In a round-bottom flask, a suspension of **2** (1.26 g, 4.73 mmol) in anhydrous dimethyl sulfoxide (40 mL) was slightly heated until the dissolution of the solid, followed by the addition of tetrabutylammonium bromide (200 mg) and 50% aqueous NaOH (4 ml). After the addition of 1, 6-dibromohexane (10.3 g, 42.6 mmol) dropwise, the reaction mixture was heat to 50 °C for 16 h. After being cooled to room temperature, the reaction mixture was poured into brine and extracted with hexanes. The organic phase was collected and dried over anhydrous magnesium sulfate. The mixture was filtered and the solvent was removed. The liquid residue purified by column chromatography on silica, eluting with petroleum ether. Further recrystallization of the solid in petroleum ether twice at room temperature afforded a light yellow solid in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (m, 4H), 6.96 (d, 2H), 3.29 (t, 8H), 2.02-1.81 (m, 8H), 1.75-1.62 (m, 8H), 1.31-1.20 (m, 8H), 1.18-1.07 (m, 8H), 0.94-0.73 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 154.77, 152.99, 141.65, 135.65, 126.54, 121.56, 113.12, 53.55, 39.01, 33.98, 32.65, 29.04, 27.86, 23.95.

6,6',6'',6'''-(4,9-Dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-4,4,9,9-tetrayl)tetrakis(N,N-dimethylhexan-1-amine (**4**). Compound **3** (2.7 g, 2.94 mmol), K_2CO_3 (1.48 g, 10.7 mmol) and dimethylamine (4M, 42 mL in THF solution) were added in a flask containing 20 ml THF under nitrogen atmosphere. Then it was sealed and the mixture was refluxed overnight. After cooling to room temperature, it was extracted with DCM for three times, washed with water and the organic phase was dried over anhydrous $MgSO_4$. Then the solvent was removed under reduced pressure, and the crude product was purified using column chromatography of silica gel to afford a nearly white solid in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (s, 2H), 7.25 (d, 2H), 2.16 (m, 32H), 2.03-1.78 (m, 8H), 1.37-1.25 (m, 8H), 1.20-1.05 (m, 8H), 0.95-0.75 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 154.97, 153.17, 141.60, 135.51, 126.19, 121.70, 113.12, 59.82, 53.57, 45.46, 39.03, 29.94, 27.63, 27.19, 24.17.

6,6',6'',6'''-(2,7-Bis(trimethylstannyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-4,4,9,9-tetrayl)tetrakis(N,N-dimethylhexan-1-amine) (**5**). A solution of

4 (1.61 g, 2.07 mmol) in anhydrous tetrahydrofuran (150 ml) was stirred at -78℃ for 30 min. *n*-BuLi (4.2 ml, 8.3 mmol, 2 M in hexanes) was added dropwise and the solution was stirred at -78℃ for 30 min followed by -10℃ for 30 min. After cooling again to -78℃, trimethyltin chloride was added (12.5 ml, 12.5 mmol, 1 M in hexanes) and the solution was allowed to return to room temperature overnight. The reaction was then poured into water and extracted with hexane, washed successively with acetonitrile to remove excess trimethyltin chloride and dried over $MgSO_4$ to yield **5** as a yellow oil in 90% yield. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.25 (s, 2H), 6.96 (s, 2H), 2.24-2.06 (m, 32H), 2.02-1.73 (m, 8H), 1.35-1.25 (m, 8H), 1.17-1.07 (m, 8H), 0.93-0.78 (m, 16H), 0.52-0.31 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.99, 153.41, 147.66, 139.33, 135.23, 129.33, 113.39, 59.86, 52.97, 45.50, 39.09, 30.02, 27.71, 27.22, 24.22.

7,7'-(4,4,9,9-Tetrakis(6-(dimethylamino)hexyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(benzo[c][1,2,5]thiadiazole-4-carbaldehyde) (**6**). A solution of 5 (1.35 g, 1.23 mmol) and 7-bromo-2,1,3-benzothiadiazole-4-carboxaldehyde (0.74 g, 3.06 mmol) in anhydrous toluene (50 ml) was degassed for 15 min before $Pd(PPh_3)_4$ (81 mg, 0.07 mmol) was added and this solution was heated at 100℃ overnight. The reaction was then poured into water and extracted with hexane. The organic phase was collected and dried over anhydrous magnesium sulfate. The mixture was filtered and solvent was removed. The compound was unstable on silica, so the crude was used in next step without further purification.

(5Z,5'Z)-5,5'-(((4,4,9,9-Tetrakis(6-(dimethylamino)hexyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(benzo[c][1,2,5]thiadiazole-7,4-diyl))bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one) (N-IDTBR). The crude **6** (1 g) and 3-ethylrhodanine (806 mg, 5 mmol) were dissolved in $CHCl_3$ (50 ml). Two drops of piperidine were added and the solution was left to stir at 85℃ overnight. The product was extracted with $CHCl_3$ and dried over $MgSO_4$. The crude product was purified by flash column chromatography on silica and precipitated from methanol. The precipitate was collected and dried by vacuum filtration to afford N-IDTBR a dark blue solid. The yield of two steps is about 30%. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.53 (s, 2H), 8.21 (s, 2H), 8.03 (d, 2H), 7.74 (d, 2H), 7.42 (s, 2H), 4.26 (m, 4H), 2.34-1.81 (m, 40H), 1.50-1.08 (m, 32H), 1.07-0.78 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 192.01, 166.54, 155.85, 153.57, 153.09, 150.72, 144.95, 140.08, 135.30, 130.35, 129.43, 126.24, 123.53, 123.29, 123.01, 122.91, 112.93, 58.55, 53.25, 44.13, 38.91, 38.03, 28.88, 26.27, 26.10, 23.29, 11.31.

6,6',6'',6'''-(2,7-Bis(7-((Z)-(3-ethyl-4-oxo-2-thioxothiazolidin-5-ylidene)methyl) benzo[c][1,2,5]thiadiazol-4-yl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-4,4,9,9-tetrayl)tetrakis(N-ethyl-N,N-dimethylhexan-1-aminium) bromide (N-IDTBR-Br). A 100 mL flask with a magnetic stirring bar was charged with N-IDTBR (100 mg) dissolved in 20 mL THF solution. Excess bromoethane and 10 mL of methanol were added to this solution. The solution was stirred at 50℃ for 3 days in darkness. Most solvent were evaporated. The crude was then precipitated in about 100 mL of ethyl acetate, collected by centrifugation, washed with chloroform and tetrahydrofuran, and dried overnight in a vacuum at 40°C (112 mg, yield: 90%). ^{1}H NMR (400 MHz, DMSO) δ: 8.47-8.32 (m, 6H), 8.02-7.96 (m, 2H), 7.86-7.81 (m, 2H), 4.18-4.06 (m, 4H), 3.28-2.62 (m, 40H), 2.25-1.93 (m, 8H), 1.6-1.4 (m, 8H) 1.3-0.82 (m, 42H).

Measurements and Characterization

^{1}H NMR and ^{13}C NMR spectra were characterized on a Bruker AV-500 in d-chloroform solvent with tetramethylsilane (TMS) as an internal reference at room temperature. Thermogravimetric analyses (TGA) were performed on NETZSCH TG 209 at a heating rate of 10°C min^{-1} under a nitrogen flow rate of 20 mL min^{-1}. Differential scanning calorimetry (DSC) were conducted on a NETZSCH(DSC200F3) apparatus at a heating or cooling rate of 10°C min^{-1} with a nitrogen atmosphere. UV-vis absorption spectra were recorded on a Shimadzu UV3600 spectrophotometer. The electrochemical cyclic voltammetry (CV) experiments were carried out on a CHI600D electrochemical workstation at a scan rate of 100 mV s^{-1} with Bu_4NPF_6 (0.1 M) in acetonitrile as the electrolyte, and glassy-carbon, platinum wire, and saturated calomel electrode as the working, counter, and reference electrode, respectively. Potentials were calibrated using ferrocene as an external standard. The current density-voltage measurements were carried out on a computer-controlled Keithley 2400 source-meter under 1 sun, AM 1.5G solar simulator (Taiwan, Enlitech SS-F5). Before measurement, we have calibrated the light intensity at each wavelength by a standard Si solar cell (certified by the NREL). The calibrated light intensity is 100 mW cm^{-2} during the *J-V* measurements. The EQE spectra were recorded on a Enlitech commercial measurement system (Enlitech, QE-R). The $J^{1/2}$-V characteristics of single carrier deivces (including hole-only and electron-only devices) were recorded with a Keithley 236 source-meter in the dark. Scanning Kelvin probe microscopy was implemented on a KP Technology SKP5050. The transient photocurrent of devices was measured by applying 580 nm laser pulses with a pulse width of 120 fs and a low pulse energy to the short circuited devices in dark. The laser pulses were generated from optical parametric amplifier (TOPAS-Prime) pumped by a mode-locked Ti:sapphire oscillator seeded regenerative amplifier with a pulse energy of 1.3 mJ at 800 nm and a repetition rate of 1 kHz (SpectraPhysics Spitfire Ace).

Fabrication PSCs

The polymer solar cells were fabricated with a conventional configuration of indium tin oxide (ITO)/poly (3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/active layer/CIL/Ag, where PEDOT:PSS and N-IDTBR were used as anode and cathode interlayer, respectively. The ITO-coated glass substrates were cleaned sequentially under sonication with detergent, deionized water, acetone, and isopropyl alcohol and then dried at 80 °C in a baking oven overnight, followed by a 2 min oxygen plasma treatment. PEDOT:PSS was spin-coated onto the above ITO glass substrates and annealed at 150 °C on a hot plate for 10 min in air. Afterwards, the substrates were transferred into a nitrogen protected glove box. The active layer solutions (D:A=1:1, *wt:wt*) with the donor concentration of about 15 mg mL^{-1} in *o*-

xylene and 2-methylanisole/1-methylnaphthalene (*o*-MA/1-MN) solvents were spin-coated onto the PEDOT:PSS layer at ~1800 rpm to yield ~100 nm active layers. All the resulting blend films were annealed at 100 ^{o}C for 10 min. Then, different thickness of N-IDTBR was coated onto the active layers from its in MeOH:EtOH solution (0.5, 1, 2 and 5 mg mL^{-1}). Subsequently, ~100 nm Ag was thermally deposited atop in a vacuum chamber with base pressure of 7×10^{-7} torr, through a shadow mask with effective area of 0.0516 cm^{2}.

Fabrication of Electron-only Devices

Electron-only devices were fabricated with the device structure of ITO/ZnO/active layer/N-IDTBR (various thickness)/Ag. The SCLC mobility was determined by fitting the dark current in the quadratic region.

Fabrication of Photoconductive Devices

Photoconductive devices were fabricated with the device structure of ITO/N-IDTBR (100nm)/Ag (100 nm). The photoconductivity of N-IDTBR was recorded under AM 1.5G irradiation with an intensity of 100 mW cm^{-2}.

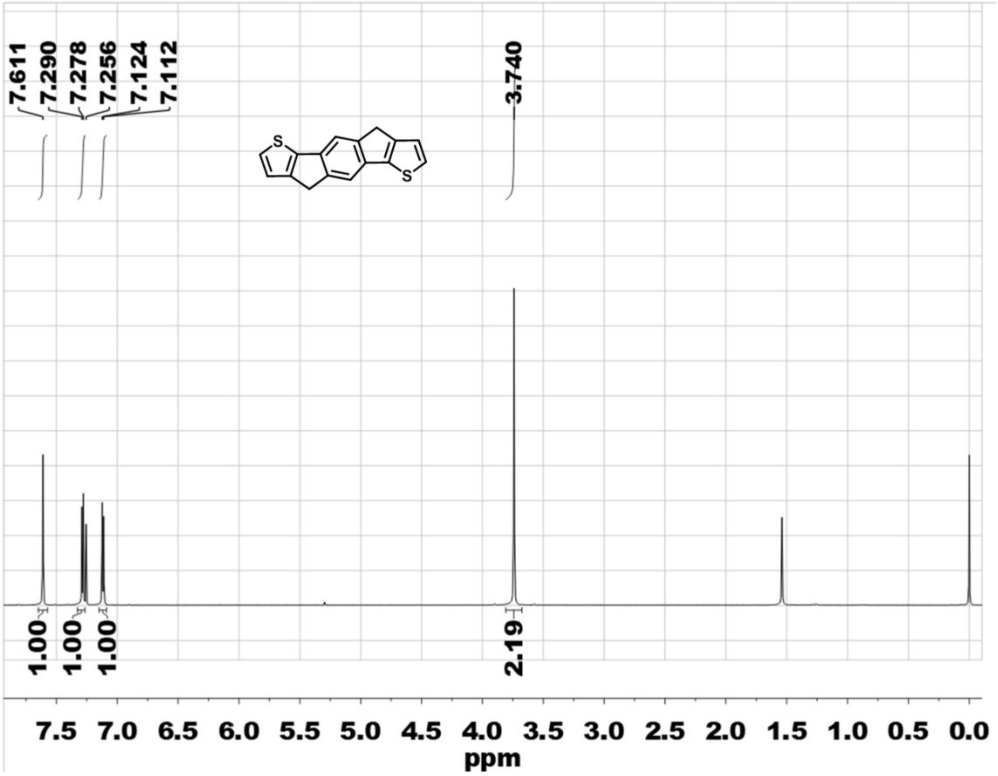


Fig. S1 ^{1}H-NMR spectrum of **2** in $CDCl_3$.

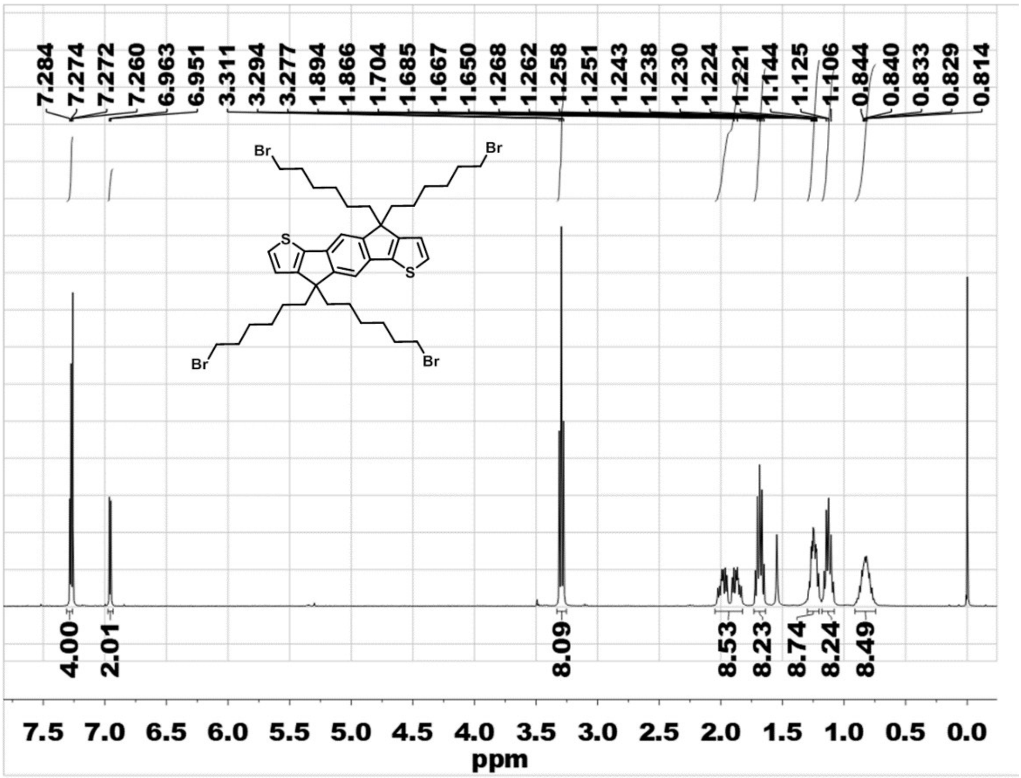


Fig. S2 ^{1}H-NMR spectrum of **3** in $CDCl_3$.

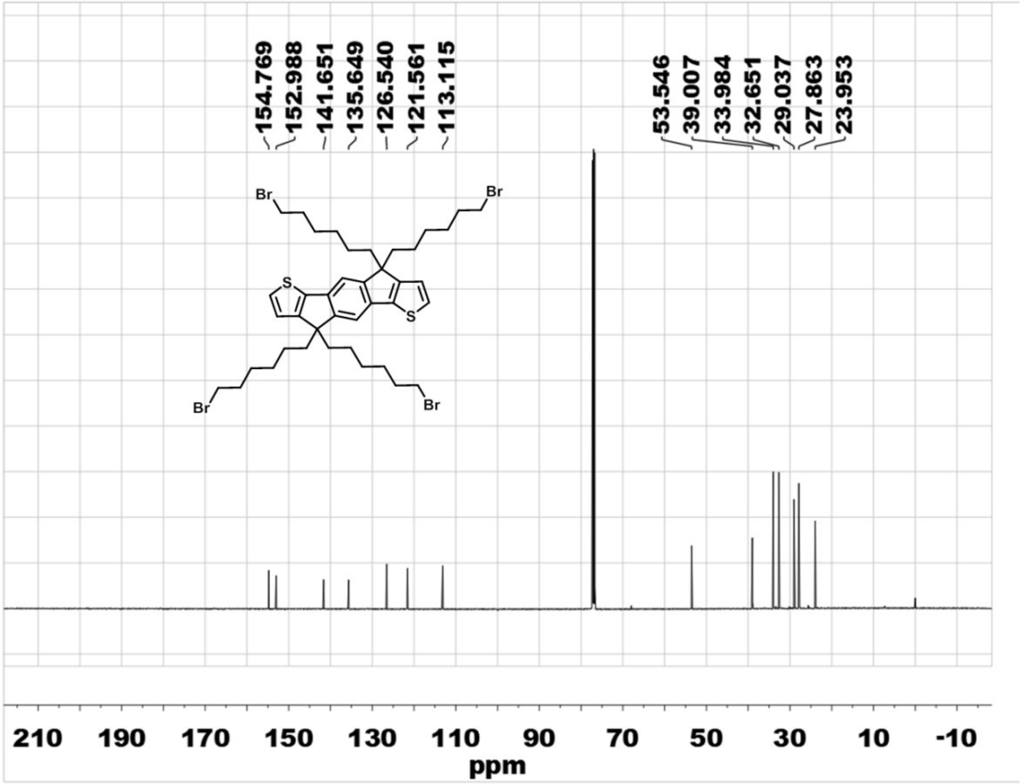


Fig. S3 ^{13}C-NMR spectrum of **3** in $CDCl_3$

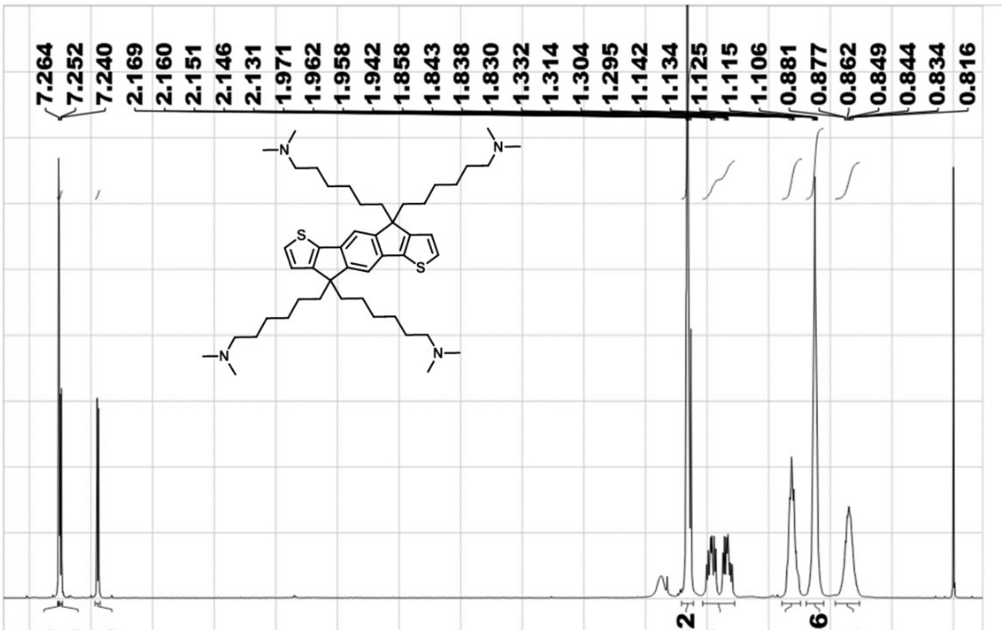


Fig. S4 ^{1}H-NMR spectrum of **4** in $CDCl_3$.

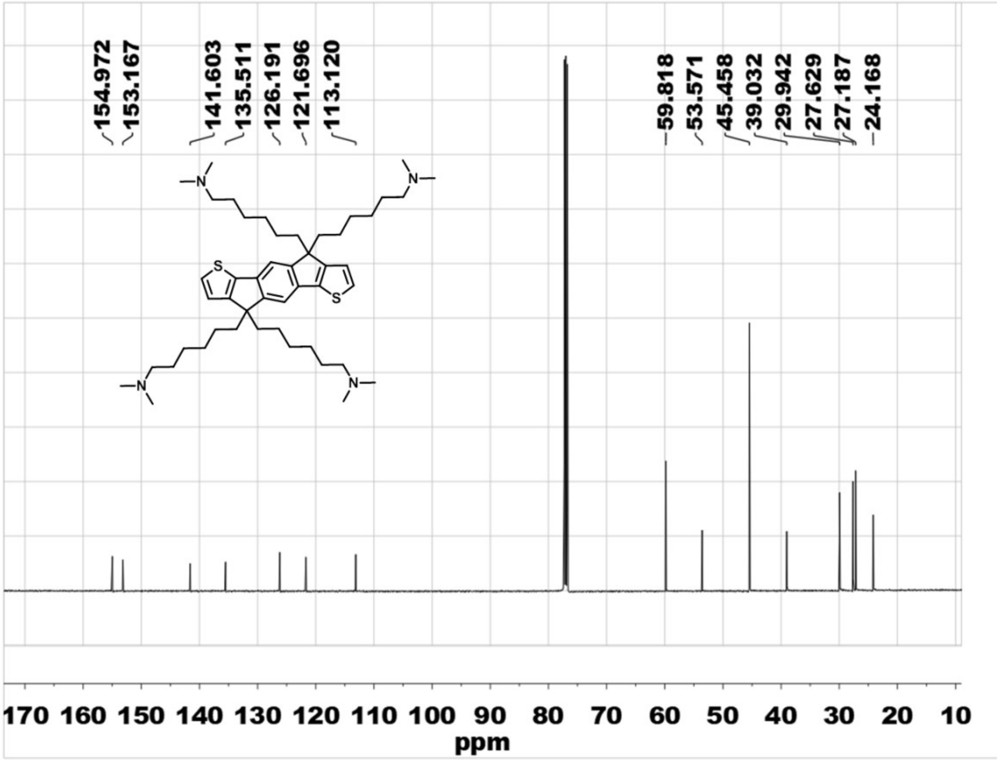


Fig. S5 ^{13}C-NMR spectrum of **4** in $CDCl_3$

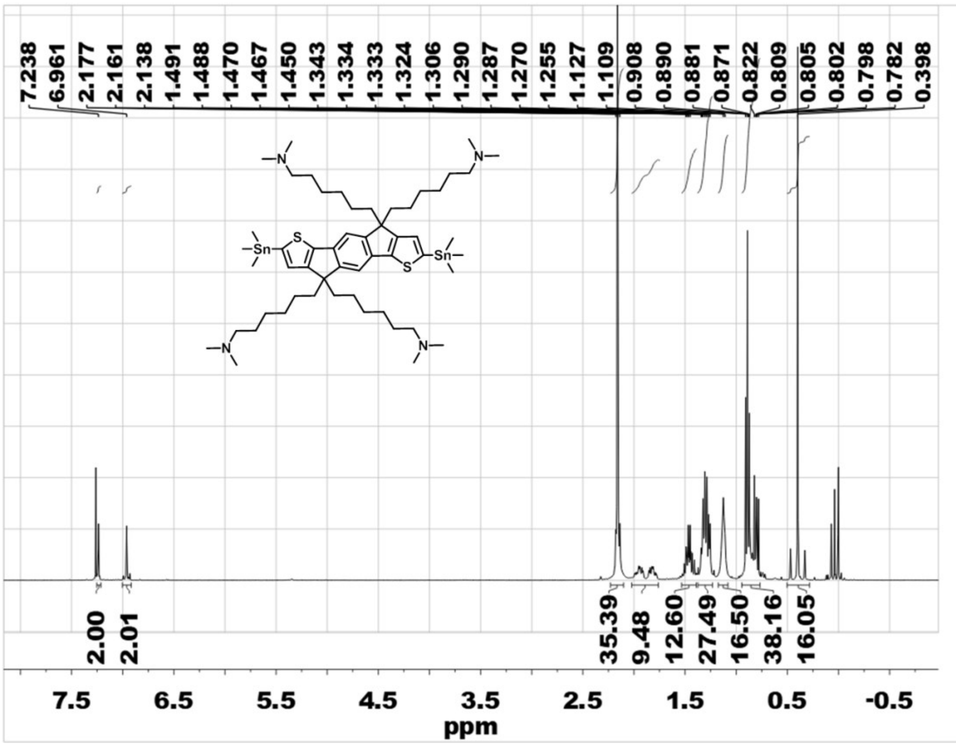


Fig. S6 ^{1}H-NMR spectrum of **5** in $CDCl_3$.

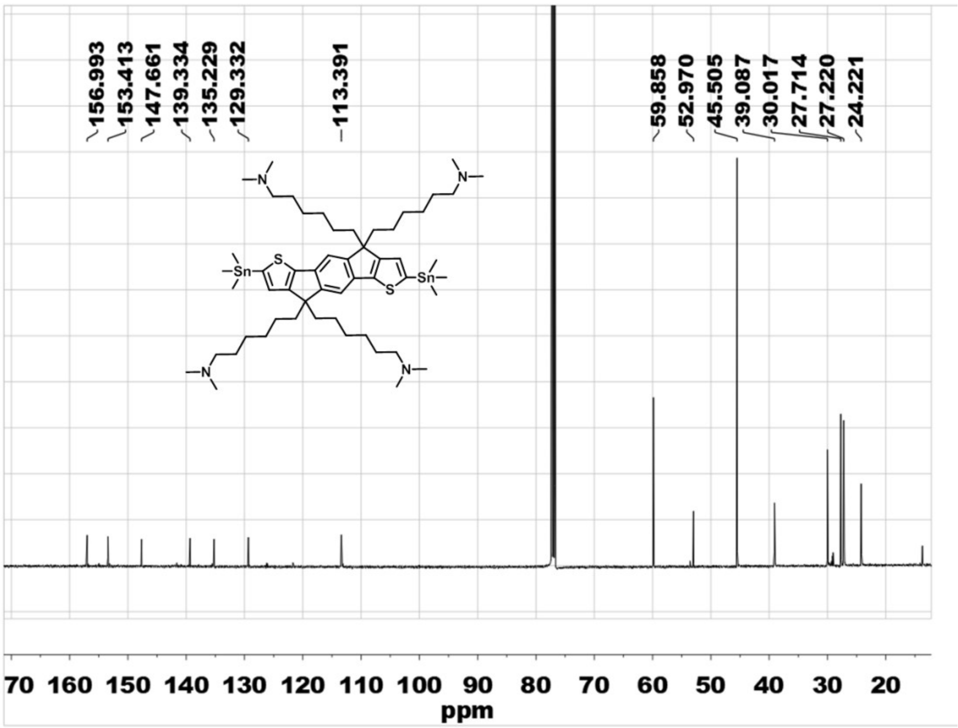


Fig. S7 ^{13}C-NMR spectrum of **5** in CDCl$_3$

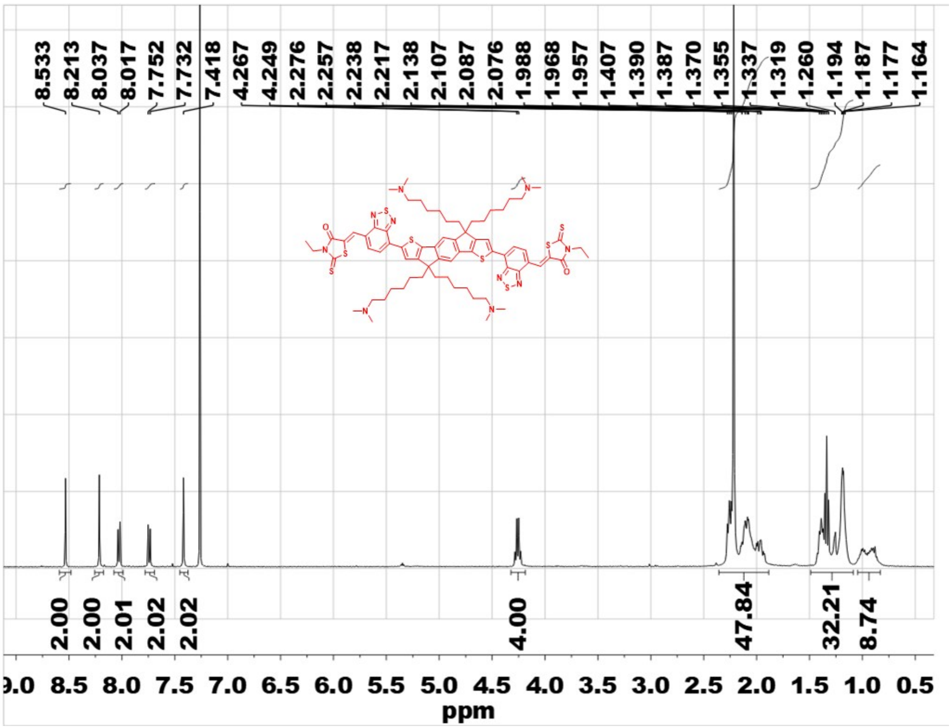


Fig. S8 ^{1}H-NMR spectrum of **N-IDTBR** in CDCl$_3$.

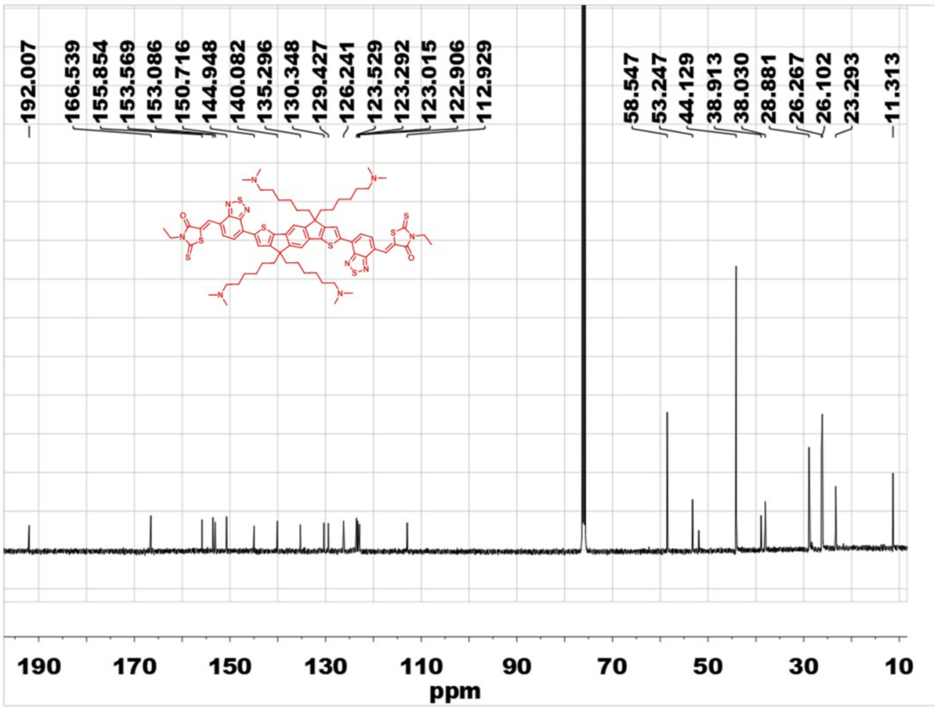


Fig. S9 ^{13}C-NMR spectrum of **N-IDTBR** in $CDCl_3$

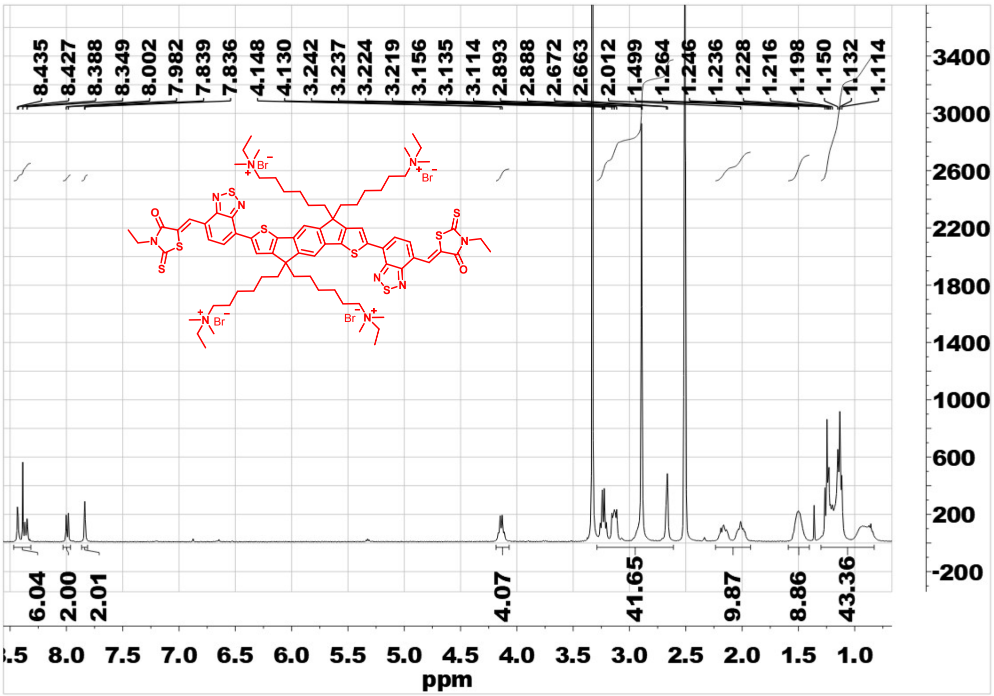


Fig. S10 ^{1}H NMR spectrum of N-IDTBR-Br in $CDCl_3$.

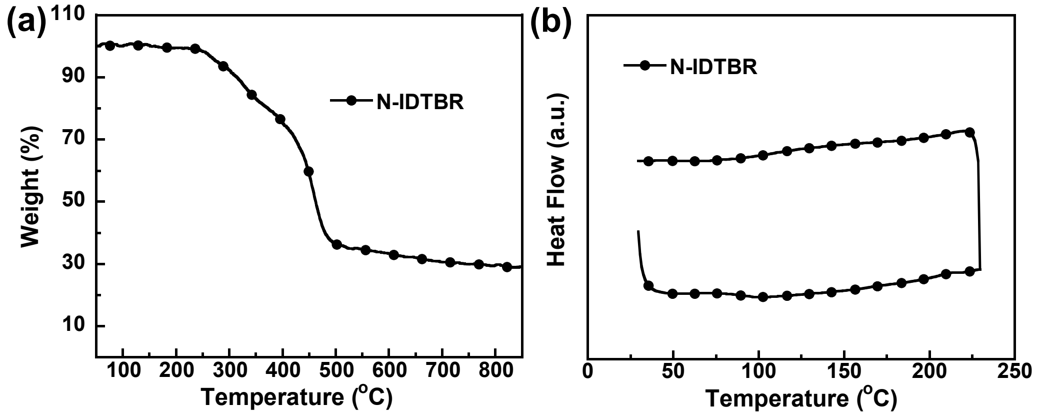


Fig. S11 (a) Thermal gravimetric analysis of N-IDTBR in nitrogen atmosphere; (b) Differential scanning chromatography of N-IDTBR in nitrogen atmosphere.

Table S2 Photovoltaic parameters of devices based on N-IDTBR-Br as the CIL[a]

CIL	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
N-IDTBR-Br	0.73	11.31	65.14	5.35

[a] Devices structure: ITO/PEDOT:PSS/P3HT:O-IDTBR/N-IDTBR-Br/Ag

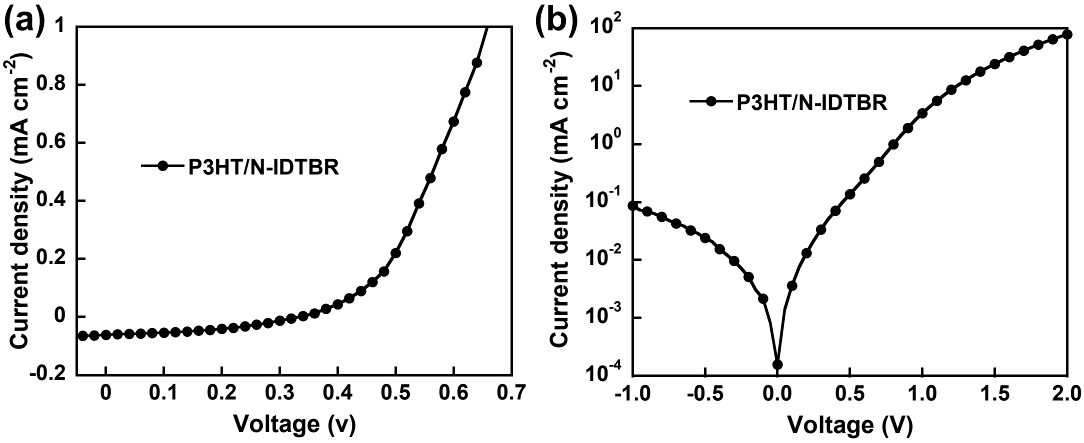


Fig. S12 *J-V* characteristics of pristine polymer P3HT and its bilayers with N-IDTBR devices under illumination (a) and in dark (b).

Table S1 Photovoltaic parameters of devices based on P3HT/N-IDTBR bilayer structure

Bilayer	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	Rs (Ω cm^2)	Rsh (Ω cm^2)
P3HT/N-IDTBR	0.33	0.06	40.07	0.0081	7.56	1.4×10^5

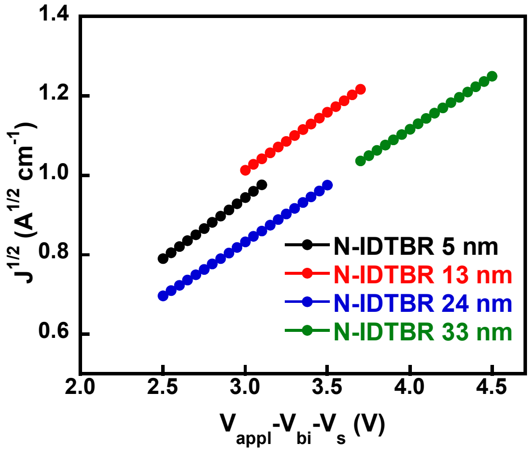


Fig. S13 $J^{1/2}$-V characteristic for electron-only devices measured in the dark. Device structure: ITO/ZnO/BHJ/N-IDTBR/Ag. The electron-mobility was calculated to be 2.8±0.4 cm^{-2} V^{-1} s^{-1}.