**Supporting Information**

Non-Fullerene Acceptor Engineering with Three-dimensional Thiophene/Selenophene–annulated Perylene Diimides for High Performance Polymer Solar Cells

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1. General information
All solvents and chemicals used were purchased from Energy Chemical and used without further purification. Tetrakis(4-bromophenyl)ethylene (TPE-Br)$_4^{1,2}$, tetr phenylethylene tetraboronic acid pinacol ester (TPE-Pin)$_4^3$, PDI-S-Br$_4^4$, PDI-Se-Br$_5^5$ and PBDB-T$_1^6$ (Figure S4) were synthesized according to the reported literatures with minor modifications. TLC analyses were carried out by using Sorbent Technologies silica gel (200 mm) sheets. Column chromatography was performed on Sorbent silica gel 60 (40–63 mm). Solution NMR spectra were taken on a Bruker 400 MHz spectrometer in CDCl$_3$ at room temperature, both $^1$H and $^{13}$C NMR spectra were referenced to solvent residue peaks and the spectroscopic solvents were purchased from Cambridge Isotope Laboratories. Mass spectra were measured on a Bruker Maxis UHR-TOF MS spectrometer. UV–vis absorption spectra were performed with a Beijing Purkinje General Instrument Co. Ltd. TU-1901 spectrophotometer. Fluorescence spectra measurements were performed using FLS-920 Edinburgh fluorescence spectrometer. All steady-state measurements were carried out using a quartz cuvette with a path length of 1 cm. Thermogravimetric analysis (TGA) was carried out on a TA Instrument TA Q50 Thermogravimetric Analyzer at a heating rate of 10 °C/min up to 600°C.

2. Solar cell fabrication and characterization
Solar cells were fabricated in a conventional device configuration of ITO/PEDOT: PSS/active layer/ZrAcAc/Al. The ITO substrates were first scrubbed by detergent and then sonicated with deionized water, acetone and isopropanol subsequently, and dried overnight in an oven. The glass substrates were treated by UV-Ozone for 30 min before use. PEDOT: PSS (Heraeus Clevios P VP A 4083) layer was spin-cast onto the ITO substrates at 4000 rmp for 40s, and then dried at 150 °C for 15 min in air. The donor:acceptor blends with 1:1 ratio were dissolved in dichlorobenzene (the concentration of blend solutions are 20 mg/mL for all blend films), and stirred overnight in a nitrogen-filled glove box. The blend solution was spin-cast at 1600 rmp for 40 s on the top of PEDOT: PSS layer followed by annealed at 100 °C for 5 min to remove the residual solvent. A thin ZrAcAc layer (10 nm) and Al layer (100 nm) were
sequentially evaporated through a shadow mask under vacuum of 5×10⁻⁵ Pa. The area of each device was 5.90 mm² defined by a shadow mask. The optimal blend thickness was about 95 nm, measured on a Bruker Dektak XT stylus profilometer. Current density-voltage (J-V) curves were measured in a Keithley 2400 Source Measure Unit. Photocurrent was measured in an Air Mass 1.5 Global (AM 1.5 G) solar simulator (Class AAA solar simulator, Model 94063A, Oriel) with an irradiation intensity of 100 mW cm⁻², which was measured by a calibrated silicon solar cell and a readout meter (Model 91150V, Newport). IPCE spectra were measured by using a QEX10 Solar Cell IPCE measurement system (PV measurements, Inc.).

3. Space charge-limited current (SCLC) device fabrication

The structure of electron-only devices is ITO/ZnO/active layers/ZrAcAc/Al and the structure of hole-only devices is ITO/MoOₓ/active layers/MoOₓ/Al. The fabrication conditions of the active layer films are same with those for the solar cells. The charge mobilities are generally described by the Mott-Gurney equation:

\[ J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{L} \]

where \( J \) is the current density, \( \varepsilon_0 \) is the permittivity of free space (8.85×10⁻¹⁴ F/cm), \( \varepsilon_r \) is the dielectric constant of used materials, \( \mu \) is the charge mobility, \( V \) is the applied voltage and \( L \) is the active layer thickness. The \( \varepsilon_r \) parameter is assumed to be 3, which is a typical value for organic materials. In organic materials, charge mobility is usually field dependent and can be described by the disorder formalism, typically varying with electric field, \( E=V/L \), according to the equation:

\[ \mu = \mu_0 \exp[0.89\gamma \sqrt{\frac{V}{L}}] \]

where \( \mu_0 \) is the charge mobility at zero electric field and \( \gamma \) is a constant. Then, the Mott-Gurney equation can be described by:

\[ J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0 \frac{V^2}{L} \exp[0.89\gamma \sqrt{\frac{V}{L}}] \]
4. Film and Device Characterization
The ultraviolet-visible (UV-Vis) absorption spectra of neat and blend films were obtained using a Shimadzu UV-3101 PC spectrometer. The current-voltage (I-V) curves of all OSCs were measured in a high-purity nitrogen-filled glove box using a Keithley 2400 source meter. AM 1.5G irradiation at 100 mW/cm² provided by An XES-40S2 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, 70×70 mm² photobeam size), which was calibrated by standard silicon solar cells (purchased from Zolix INSTRUMENTS CO. LTD). The external quantum efficiency (EQE) spectra of solar cells were measured in air conditions by a Zolix Solar Cell Scan 100. The morphology of the active layers was investigated by atomic force microscopy (AFM) using a Dimension Icon AFM (Bruker) in a tapping mode.

5. Electrochemical Characterization
Electrochemical measurements were performed under nitrogen in deoxygenated 0.1 M solutions of tetra-n-butylammonium hexafluorophosphate in dry dichloromethane using a CHI 660C electrochemical workstation, a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode. Cyclic voltammograms were recorded at a scan rate of 50 mV s⁻¹. The lowest unoccupied molecular orbital (LUMO) levels were estimated based on the onset reduction potential (E_{red}), and the reduction potential was calibrated using ferrocene (E_{Fe/Fe⁺}) as a reference (E_{red} = [E_{measured} - E_{Fe/Fe⁺} + 4.8] eV). Ferrocene as an internal standard. Under the same condition, the onset oxidation potential of ferrocene was measured to be 0.259 V versus Ag/Ag⁺.

6. AFM Characterization.
AFM measurements were performed by using a Scanning Probe Microscope-Dimension 3100 in tapping mode. All films were coated on ITO glass substrates.

7. Computational Studies
The geometry was optimized by density functional theory (DFT) using the B3LYP hybrid functional with basis set 6-31G(d). Quantum chemical calculation was
performed with the Gaussian 09 package. The long alkyl chains were replaced with an isopropyl group for simplification.

**Figure S1.** The normalized absorption spectra of PBDB-T1:TPE-PDI$_4$-S and PBDB-T1:TPE-PDI$_4$-Se blend films.

**Figure S2.** Cyclic voltammetry of TPE-PDI$_4$-S and TPE-PDI$_4$-Se recorded in dichloromethane.
**Figure S3.** Optimized molecular geometries of TPE-PDI$_4$-S and TPE-PDI$_4$-Se at B3LYP/6-31G(d).

**Figure S4.** The molecular structures of PBDB-T1, TPE-PDI$_4$-S and TPE-PDI$_4$-Se

**Table S1.** The calculated data of TPE-PDI$_4$-S and TPE-PDI$_4$-Se.

<table>
<thead>
<tr>
<th></th>
<th>HOMO</th>
<th>LUMO</th>
<th>$E_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPE-PDI$_4$-S</td>
<td>-6.17</td>
<td>-3.71</td>
<td>2.46</td>
</tr>
<tr>
<td>TPE-PDI$_4$-Se</td>
<td>-6.11</td>
<td>-3.68</td>
<td>2.43</td>
</tr>
</tbody>
</table>

**Table S2.** Hole and electron mobility of TPE-PDI$_4$-S, TPE-PDI$_4$-Se, PBDB-T1: TPE-PDI$_4$-S and PBDB-T1: TPE-PDI$_4$-Se BHJ films.
Table S3. Key photovoltaic parameters calculated from the \( J_{ph-V_{eff}} \) curves of PBDB-T1: TPE-PDI\(_4\)-S and PBDB-T1: TPE-PDI\(_4\)-Se based devices after annealing.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( J_{sat} ) (mA.cm(^{-2}))</th>
<th>( J_{ph}^b ) (mA.cm(^{-2}))</th>
<th>( J_{ph}^c ) (mA.cm(^{-2}))</th>
<th>( J_{ph}^b / J_{sat} ) (%)</th>
<th>( J_{ph}^c / J_{sat} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDB-T1: TPE-PDI(_4)-S</td>
<td>10.508</td>
<td>9.839</td>
<td>7.618</td>
<td>93.6</td>
<td>72.5</td>
</tr>
<tr>
<td>PBDB-T1: TPE-PDI(_4)-S</td>
<td>10.981</td>
<td>10.287</td>
<td>8.563</td>
<td>93.7</td>
<td>78.0</td>
</tr>
</tbody>
</table>

\(^a\)The \( J_{ph} \) under condition of \( V_{eff} \) = 3.0 V; \(^b\)The \( J_{ph} \) under short circuit condition; \(^c\)The \( J_{ph} \) under maximum power output condition.

8. Synthesis and Characterization
Scheme S1. Synthetic routes of TPE-Pin$_4$, PDI-S-Br and PDI-Se-Br.

Tetrakis(4-bromophenyl)ethylene (TPE-Br$_4$).

Bromine (10.05 mL, 196 mmol) was added to a solution of tetraphenylethylene (8.23 g, 25.7 mmol) in 45 mL glacial acetic acid and 35 mL dichloromethane at 0 °C. Then the resulting mixture was stirred at room temperature for 5 h and was monitored using thin-layer chromatography. Then poured into 200 mL ice-water, and extracted with CH$_2$Cl$_2$. The organic phase was dried over Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The crude product was purified by recrystallization with THF:EtOH and obtained a white solid TPE-Br$_4$ (14.9 g, 90%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.26 (d, 8H), 6.84 (d, 8H).

Tetraphenylethylene tetrazaboronic acid-pinacol ester (TPE-Pin$_4$)

In a dried 500 mL two-neck round bottle flask was added anhydrous dioxane (150 mL) and KOAc (7.6 g, 80 mmol), then bubbled with Ar$_2$ for 30 minutes. TPE-Br$_4$ (5 g, 7.7 mmol), bis(pinacolato)diboron (8.82 g, 34 mmol) and Pd(dppf)Cl$_2$ (300 mg, 0.37 mmol)
were added respectively under Ar$_2$ protection. The mixture was heated to 110 °C for 72 h and was monitored using thin-layer chromatography. Then the reaction mixture was cooled to room temperature, removed the dioxane under reduced pressure and poured into ice-cooled water. The solution was stirred for 10 minutes and filtered, washed the residue by water and dried under vacuum. The residue was dissolve in dichloromethane and purified using flash column chromatograph with ethyl acetate/dichloromethane (1/1 v/v) as eluent. Removed the solvents under vacuum to yield TPE-Bpin$_4$ as white product (4.1g, 64%). $^1$H NMR (400MHz, CDCl$_3$, ppm): δ 7.5 (d, 8H), 6.98 (d, 8H), 1.31 (s, 48H).

6-(hydroxyimino)undecane (2)

A solution of 1 (30 g, 176 mmol) in ethanol (530 mL) and pyridine (264 mL) was added hydroxylamine hydrochloride (25.0 g, 360 mmol), then heated to 100 °C for overnight. The resulting mixture was concentrated by rotary evaporation and the residue was extracted between 5% HCl aq (400 mL) and petroleum ether (200 mL × 3). Organic layer was dried with Na$_2$SO$_4$ and after removing the solvent again, yielding compound 2 (32.9 g, 99%) as yellowish viscous liquid. This compound was used directly in the next step without further purification.

1-pentylhexylamine (3)

The oxime 2 (16.4 g, 88.5 mmol) was dissolved in toluene (360 mL, analytical grade), Red Al (70% in toluene, 113 mL) were added over 10 min then the reaction mixture was heated to 140 °C for 4 hours. The resulting mixture was carefully added by 5% HCl aq (200 mL), then concentrated HCl (100 mL) was added and render the mixture acidic (checked with PH paper, PH= 1-2). The solution was extracted by petroleum
ether (300 mL × 3) and washed with 5% NaOH (200 mL), dried with Na$_2$SO$_4$ and after removing the solvent again, yielding compound 3 (16.0 g, 97%) as yellowish viscous liquid. $^1$H NMR (400MHz, CDCl$_3$, ppm): δ 2.48 (m, 1H), 1.00-1.24 (m, 18H), 0.70 (t, 6H).

**N,N'-Bis(1-pentylhexyl)-3,4:9,10-perylene diimides (4)**

![chemical structure of compound 4](image)

A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (3.3g, 7.56 mmol, 90% purity), compound 3 (3.23 g, 18.9 mmol), anhydrous zinc acetate (1.0 g, 5.67 mmol) and imidazole (15.0 g) were added in 100 mL round-bottom flask and stirred at 160 °C for 5 hour. The reaction solution was poured into aqueous solution (500 mL) and the resulting precipitate was collected by filtration and washed with water and methanol, got the crude compound 4 as a red solid (4.75 g, 90%). This compound was used directly in the next step without further purification.

**PDI-NO$_2$**

![chemical structure of PDI-NO$_2$](image)

Compound 4 (9.4 g, 13.4 mmol) and dichloroethane (300 mL) was mixed in 500 mL round-bottom flask and cooled to −5 °C. Then fuming nitric acid (15 mL) was added dropwise to the above mixture (about 20 mins) and stirred for 30 min at −5°C. The
reaction process was monitored using thin-layer chromatography. Then poured methanol (100 mL) to the reaction mixture and stirred for 10 min. Next, CH₂Cl₂ (200 mL) and water (150 mL) were added into the resulting solution, extracted with CH₂Cl₂, washed with saturate brine and dried over Na₂SO₄. The solvent was evaporated and the crude product was purified by chromatography (SiO₂, CH₂Cl₂: petroleum ether) to give compound PDI-NO₂ as a dark-red solid (12.6 g, 91%).

**PDI-S**

![PDI-S](image1)

A mixture of sulfur (1.72 g, 53.78 mmol) and compound PDI-NO₂ (4 g, 5.38 mmol) were heated in N-methylpyrrolidone (NMP, 100 mL) at 190°C under an argon atmosphere for 1 h. Next, the cooled mixture was poured into 2 M HCl (1 L) and stirred for 5 min. the resulting precipitate was filtered, washed with water, dried, and purified by silica gel column chromatography (petroleum ether: CH₂Cl₂, 1:1) to isolate compound PDI-S as a bright yellow solid (3.33 g, 85% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.30-9.26 (d, 2H), 8.91-8.88(m, 4H), 5.30 (m, 2H), 2.37-2.28 (m, 4H), 1.97-1.90 (m, 4H), 1.43-1.25 (m, 24H), 0.85-0.82 (m, 12H).

**PDI-S-Br**

![PDI-S-Br](image2)
In a closed round-bottom flask, bromine (32.8 g, 205 mmol) was added in one portion to a solution of compound PDI-S (3 g, 4.11 mmol) in 50 mL dichloromethane with vigorous stirring for 5 h. Then the excess of bromine was quenched with saturated sodium sulfite solution. The organic layer was separated, dried over MgSO₄, and purified by silica gel column chromatography (petroleum ether : CH₂Cl₂, 4:1) to give PDI-S-Br as an orange solid (3.05 g, 92%). ¹H NMR (400 MHz, CDCl₃): δ 9.81-9.73 (m, 1H), 9.01 (s, 2H), 8.80 (s, 1H), 8.64 (s, 1H), 5.34-5.28 (m, 2H), 2.39-2.35 (m, 4H), 2.00-1.97 (m, 4H), 1.48-1.33 (m, 24H), 0.90-0.87 (m, 12H).

TPE-PDI₄-S

A three-neck flask charged with TPE-Pin₄ (60 mg, 0.072mmol, 1eq), PDI-S-Br (357.6 mg, 0.481 mmol, 6.7eq), Pd(PPh₃)₄ (20 mg, 0.017 mmol), K₂CO₃ (2.07 g, 15 mmol) and degassed dry THF / H₂O (15 mL / 7.5 ml). The reaction mixture was heated at 80 °C for 48 h. After cooled to room temperature, the reaction mixture was extracted by CH₂Cl₂. The crude product was purified by silicon chromatography (petroleum ether / CH₂Cl₂, 1:3, V/V) to get pure product as a red solid (115 mg, 51%) ¹H NMR (400 MHz, CDCl₃): δ 9.39-9.26 (m, 8H), 8.90-8.86 (d, 4H), 8.43-8.41 (d, 4H), 8.29 (s, 4H), 7.85-7.79 (m, 16H), 5.30-4.88 (m, 8H), 2.27 (s, 8H), 2.06 (s, 4H), 1.85 -1.67 (m, 16H), 1.33-1.11 (m, 100 H), 0.80-0.71 (m, 48 H). ¹³C NMR (100 MHz, CDCl₃): δ 165.33, 164.90, 164.14, 163.83, 144.19, 141.97, 141.13, 138.33, 137.68, 134.04, 133.48, 131.76, 130.93, 128.71, 128.35, 127.66, 126.85, 126.17, 125.73,
Selenium (5.10 g, 64.5 mmol) was dissolved in N-methylpyrrolidone (NMP, 260 mL) and heated to 70 °C for 30 min under argon. Then compound PDI-NO₂ (4.8 g, 6.45 mmol) was added and the mixture was heated to 190 °C for 3 h with vigorous stirring until the starting material could not be detected by TLC. Upon cooling to room temperature, the reaction mixture was poured into of HCl (2 M, 1 L), then the precipitate was collected by vacuum filtration, washed with water, dried, and purified by column chromatography on silica gel (petroleum ether / CH₂Cl₂, 1:1 to 1:2, V/V) to give PDI-Se as a yellow-brown solid (4.0 g, 80 %). ¹H NMR (400 MHz, CDCl₃): δ 9.17-9.15 (d, 2 H), 8.76-8.73 (d, 2 H), 8.67-8.65 (d, 2 H), 5.33-5.25 (m, 2H), 2.36-2.29 (m, 4 H), 1.97-1.92 (m, 4H), 1.45-1.27 (m, 24 H), 0.87-0.83 (m, 12 H).

A mixture of PDI-Se (4.0 g, 5.16 mmol) and bromine (74.6 g, 0.46 mol) in
dichloromethane (240 mL, analytical grade) was stirred at room temperature in a closed round-bottom flask for 12 h. The excess of bromine was removed by air bubbling, and the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography with petroleum ether / CH₂Cl₂ (1:1) as an eluent to give PDI-Se-Br as a red solid (3.6 g, 82 % yield).¹H NMR (400 MHz, CDCl₃): δ 9.88-9.86 (d, 1 H), 9.09 (s, 2 H), 8.86 (s, 1 H), 8.65 (s, 1H), 5.32-5.27 (m, 2 H), 2.36-2.31 (m, 4 H), 2.00-1.96 (m, 4 H), 1.47-1.31 (m, 24 H), 0.89-0.86 (m, 12 H).

TPE-PDI₄-Se

A three-neck flask charged with TPE-Pin₄ (80 mg, 0.096 mmol, 1.0 eq), PDI-Se-Br (549.8 mg, 0.643 mmol, 6.7 eq), Pd(PPh₃)₄ (25 mg, 0.022 mmol), K₂CO₃ (2.76 g, 20 mol) and degassed dry THF / H₂O (20 mL / 10 mL). The reaction mixture was heated at 80 °C for 48 h. After cooled to room temperature, the reaction mixture was extracted by CH₂Cl₂. The crude product was purified by silicon chromatography (petroleum ether / CH₂Cl₂, 1:3, V/V) to get pure product as a red solid (180 mg, 55% yield).¹H NMR (400 MHz, CDCl₃): δ 9.39-9.29 (m, 6H), 8.87-8.83 (d, 4H), 8.38-8.28 (m, 6H), 7.78-7.52 (m, 12H), 5.34-4.89 (m, 8H), 2.26-2.07 (m, 12H), 1.83-1.59 (m, 16H), 1.49-1.00 (m, 100 H), 0.85-0.67 (m, 48 H).¹³C NMR (100 MHz, CDCl₃): δ 165.24, 163.83, 144.11, 141.51, 141.42, 141.10, 140.68, 139.95, 134.59, 134.17, 133.51, 131.17, 130.08, 129.27, 128.67, 128.33, 126.45, 126.18, 125.98, 125.81, 122.26, 121.85, 54.93, 37.41, 32.36, 32.11, 31.73, 31.57, 29.72, 26.62, 26.46, 22.52,
22.45, 14.01, 13.94. MAIDI-TOF: C_{210}H_{220}N_{8}O_{16}Se_{4} (M^{+}), calcd, 3429.3383, found 3428.3455.

9. Spectroscopic data

Figure S5. $^1$H NMR spectrum of compound TPE-PDI$_4$-S.
Figure S6. $^{13}$C NMR spectrum of compound TPE-PDI$_4$-S.

Figure S7. $^1$H NMR spectrum of compound TPE-PDI$_4$-Se.
Figure S8. $^{13}$C NMR spectrum of compound TPE-PDI$_4$-Se.

Figure S9. MAIDI-TOF profile of compound TPE-PDI$_4$-S.
Figure S10. MAIDI-TOF profile of TPE-PDI$_4$-Se.

Figure S11. TGA profile of compound TPE-PDI$_4$-S and TPE-PDI$_4$-Se.

10. Reference

2. Xu, Yunfeng; Chang, Dan; Feng, Shi; Zhang, Chong; Jiang, Jia-Xing, New J. Chem., 2016, 40, 9415.

