

Supplementary information

**Fusion of Perylene Bisimides and Hexaazatriphenylene
into Star-Shaped Ladder Conjugated N-Type
Semiconductor**

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1 Material and methods

Building block molecule (**1**)^{S1} and **PBI**^{S2} were synthesized according by a literature method. All other reactants were purchased from commercial sources. ¹H- and ¹³C-NMR in CDCl₃ and 1,2-dichlorobenzene-d₄ was recorded at 400 MHz using Bruker AV-400 and Bruker AV-500 spectrometers with TMS as internal reference. Chemical shifts are reported in parts per million (δ), and the signals have been designated as follows: s (singlet), d (doublet), t (triplet), m (multiplet) and b (broad). Matrix-assisted laser desorption ionization (MALDI) mass spectra were measured on 4800 MALDI TOF/TOF analyzer from Applied Biosystems.

Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV) was performed with a BSA100B/W electrochemical analyzer system in a three electrode single-component cell under argon. The measurements were carried out at 25 °C in an anhydrous and nitrogen-saturated 5 × 10⁻⁴ M solution with ferrocene as internal standard for the calibration of potential. Working electrode: glassy carbon; reference electrode: Ag/AgCl; auxiliary electrode: Pt wire. Samples were measured in 0.05 M solution of Bu₄NPF₆ in THF with a scan rate of 100 mV/s. The LUMO energy levels were determined from the reduction peak taking into account the SCE level at - 5.08 eV.^{S3} Film thicknesses were determined on an Alphastep 500 surface profilometer.

UV-vis spectra of solutions in chlorobenzene with a concentration of 10⁻⁵ mol L⁻¹ and thin films spincoated on quartz glass were recorded on a HP-8453 UV-Vis spectrophotometer. Fluorescence spectra were measured on a JASCO FP-6500 fluorescence and The fluorescence quantum yields were determined with Rhodamine 6G in ethanol as the reference.^{S4} Thermogravimetric analysis (TGA) was performed on TA Instruments TGA Q1000 Series using dynamic scans under nitrogen. DSC measurements were performed on a TA Q1000 under nitrogen with a heating and cooling rate of 10 K min⁻¹. The quantum chemical calculations were performed with the Gaussian03 package.^{S5}

SCLC devices: SCLC electron-only devices were fabricated using the following structure: glass/ITO/ZnO/Active layer/LiF/Al. Commercial ITO-coated glass substrates with a sheet resistance of 13 Ohms per sq (Lumtec) were cleaned using the following sequence in an ultrasonic bath: water, acetone, and 2-propanol. Each ITO substrate was patterned using photolithography techniques. After ozone treatment of the substrates for 5 min, ZnO (25nm) was spin-coated onto the ITO surface and dried at 120 °C for 30 min. After cooling the substrate, the active layer was spin-coated from chloroform solutions. The substrates were then put in a thermal evaporation chamber to evaporate the top electrode (1.5 nm LiF/100 nm Al) under high vacuum (1 × 10⁻⁶ mbar) through a shadow mask (active area 12 mm²). The current–voltage characteristics of the devices were measured using a Keithley 2400 (I-V) Digital SourceMeter at 25 °C.

The active area amounts to 1.2 × 10⁻⁵ m². I – V characteristics of the devices were recorded at up to 10 V at room temperature in air. At high voltages the current is space-charge-limited only, assuming ohmic contacts to the injecting electrode. It should be noted that for current densities larger than 0.1 A cm⁻², the applied voltage should be adjust for voltage drop from the indium tin oxide (ITO) series resistance V_{Rs}, which typically amounts to 30–35 Ω in our substrates.

References:

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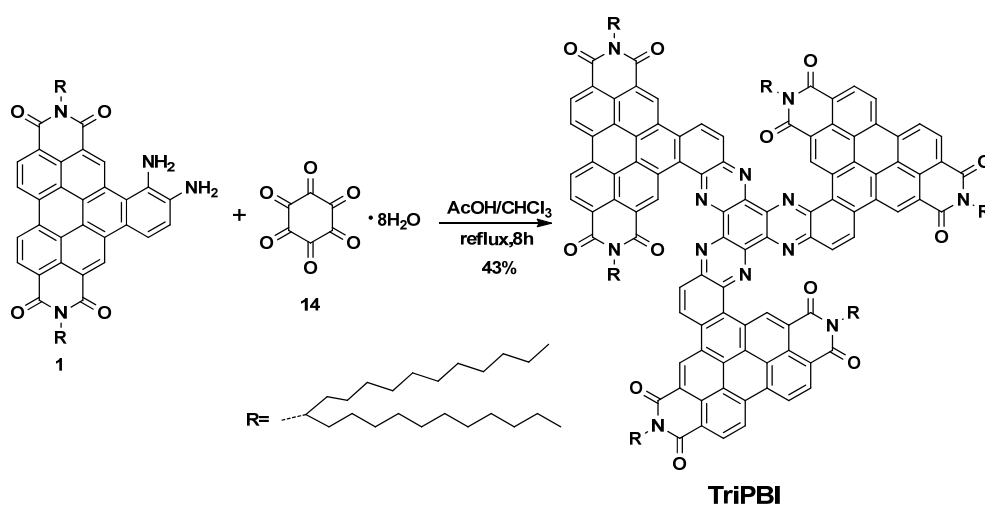
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2 Synthesis of target compound



Synthesis of compound TriPBI.

A mixture of Compound **1** (340 mg, 0.297 mmol), Compound **14** (18.5 mg, 0.059 mmol), 10 mL CHCl₃, 30 mL AcOH were stirred reflux for 8 h. Then, the crude product was purified through silica gel column chromatography with mixture of CH₂Cl₂ and hexane 1:1 as eluent. **TriPBI** was obtained as dark red solid (89 mg, 43%). MALDI-TOF-MS: Calcd for C₂₃₄H₃₀₆N₁₂O₁₂ 3476.3703, found: 3476.4043. ¹H NMR (400 MHz, CDCl₃) δ 12.65 (s, 1H), 10.72 (s, 1H), 10.24 (s, 1H), 9.96 (s, 1H), 9.44 (s, 1H), 9.27 (s, 1H), 8.52 (s, 1H), 8.04 (s, 1H), 5.54 (m, 2H), 3.65 – 2.63 (m, 4H), 2.34 (d, *J* = 85.2 Hz, 8H), 1.85 – 1.22 (m, 48H), 0.70 (d, m, 32H).; ¹³C NMR (10 MHz, CDCl₃) δ 165.63, 164.58, 164.21, 163.90, 163.84, 163.12, 145.58, 145.43, 142.08, 140.88, 133.61, 133.08, 131.77, 130.71, 128.52, 128.33, 128.12, 127.19, 126.46, 125.67, 125.47, 124.86, 123.24, 123.01, 122.52, 56.09, 55.76, 32.11, 31.86, 30.24, 29.70, 29.55, 27.61, 22.86, 22.58, 14.26, 14.01.

3 Differential pulse voltammetry (DPV) of TriPBI and PBI

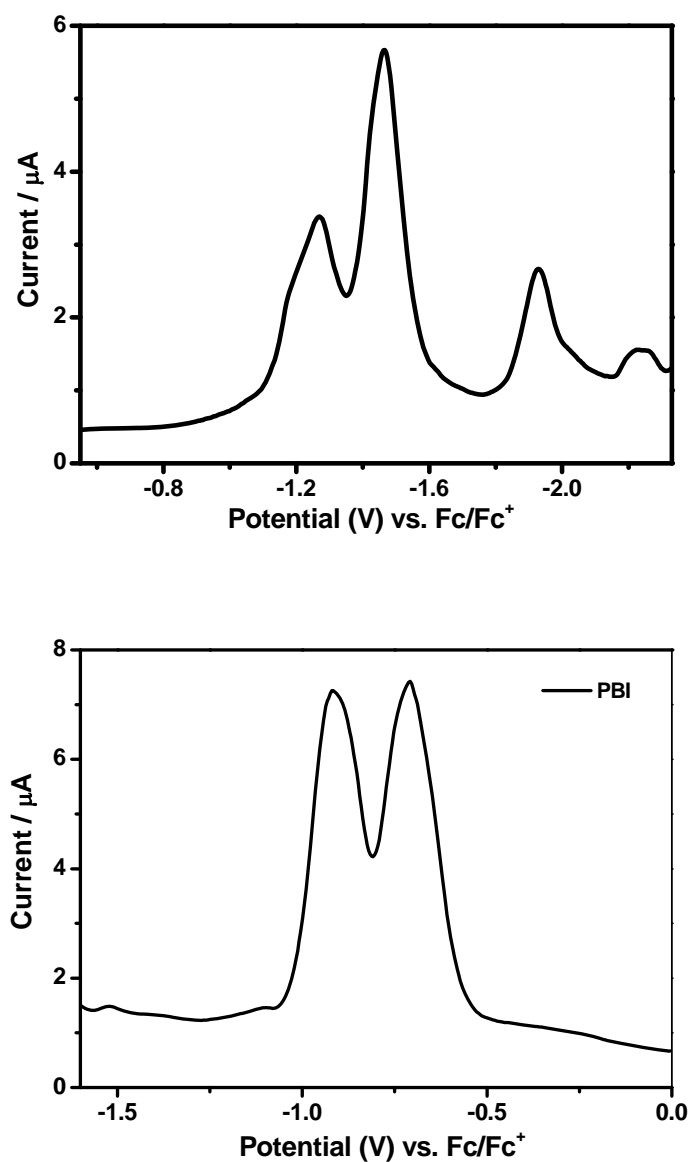


Fig. S1 Differential pulse voltammogram (DPV) of **TriPBI** and **PBI** in dichloromethane -TBAPF₆ (0.1 M), scan speed 10 mV/s.

4 TGA of TriPBI

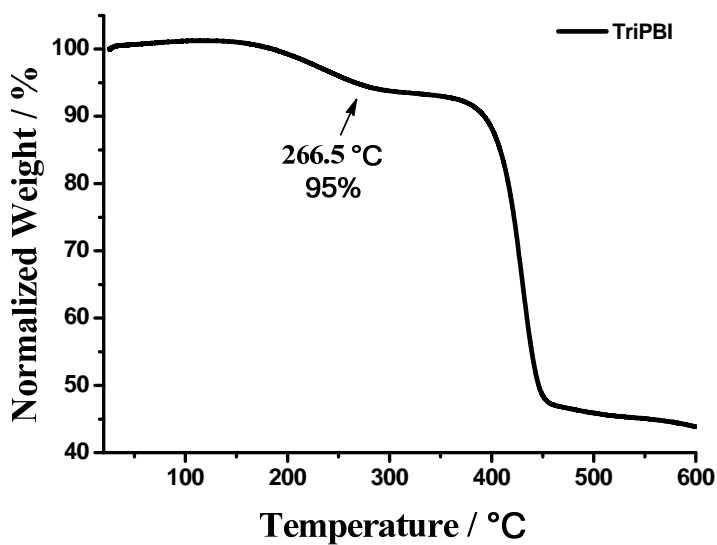


Fig. S2 TGA curves of compounds **TriPBI**

5 Optimized structures of TriPBI and PBI monomer

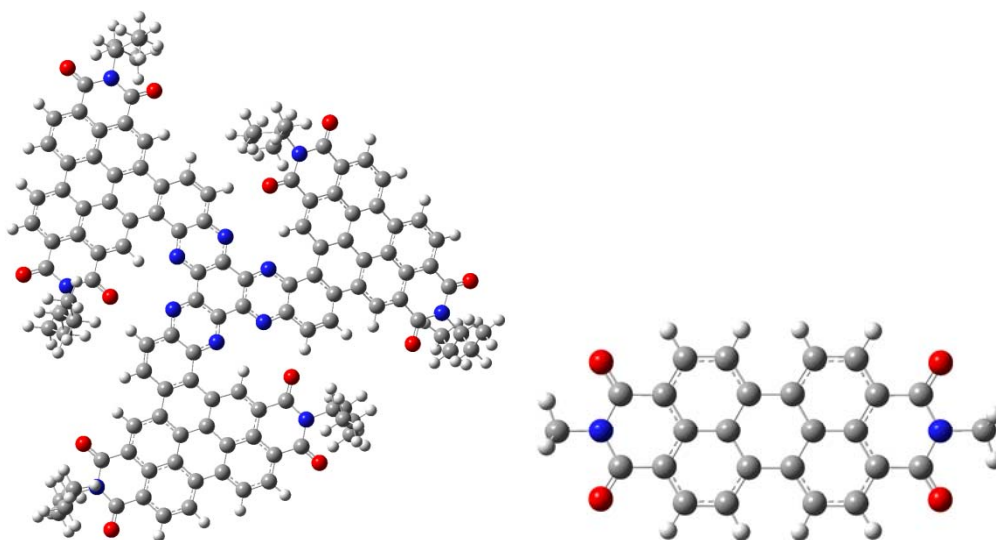


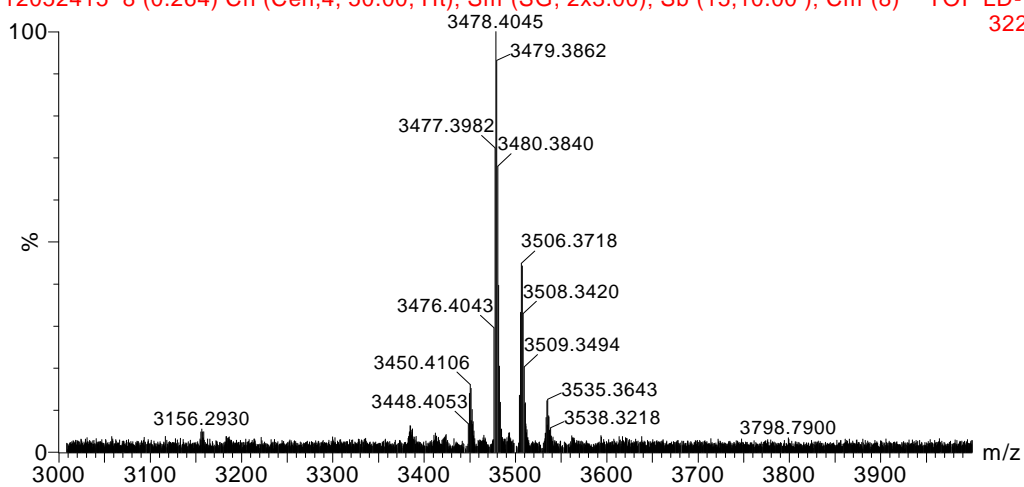
Fig. S3 Optimized structures of **TriPBI** (left) and **PBI** monomer (right)

To well explain different optical properties between **TriPBI** and **PBI** monomer, aromatic core structures of **TriPBI** and **PBI** monomer were calculated by the Gaussian 03 program, DFT-B3LYP/6-31G method. The dihedral angle between HAT core and PBI “arms” is 8.52°.

6 Mass spectrum of TriPBI

ZZB(S)

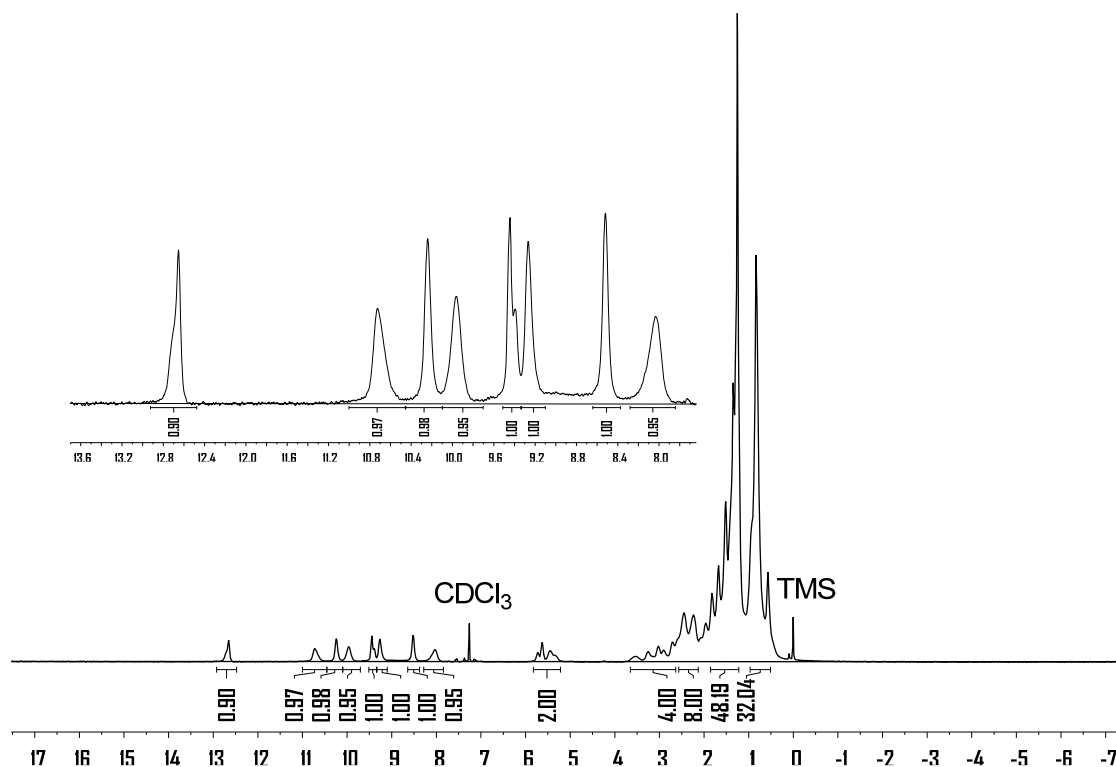
12052415 8 (0.264) Cn (Cen,4, 50.00, Ht); Sm (SG, 2x3.00); Sb (15,10.00); Cm (8) TOF LD-322



7 Copy of NMR spectrum

^1H and ^{13}C NMR spectrum of TriPBI

^1H NMR (400 MHz) spectrum of TriPBI in CDCl_3 and its enlarged low-field section (inserted figure)



^{13}C NMR (100 MHz) spectrum of TriPBI in CDCl_3 and its enlarged low-field section (inserted figure)

