

Supporting Information

Electrochemical Stability and Ambipolar Charge Transport in Diketopyrrolopyrrole-Based Organic Materials

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1. Materials and Methods

All solvents were dried by standard methods. Chemicals were purchased from Aldrich, Acros Organics, S.D. fine chemicals, and Spectrochem and used without further purification. All reactions were performed in round bottomed flask equipped with reflux condenser and argon bladder. Column chromatography was performed on silica gel (100-200 mesh). The ¹H and ¹³C NMR spectra were taken in CDCl₃ with TMS as an internal reference in Bruker Advance NMR spectrometer at 400 MHz frequency. The chemical shifts were reported as δ values (ppm) relative to TMS. The optical absorption spectra of the molecules in solution were recorded with Perkin-Elmer (Lambda-35) spectrometer at room temperature. Ultraviolet photoelectron spectroscopy (UPS) of the samples spin coated on Si-wafers were performed inside ultrahigh vacuum (UHV) chamber (ESCALAB 250Xi) using a double differentially pumped He gas discharge lamp emitting He I radiation (hν =

21.22 eV) with a pass energy of 5 eV/h. MALDI-MS was performed in Microtof Focus II instruments. Cyclic voltammetric (CV) measurements were carried out in anhydrous CH₂Cl₂ solution containing 0.1 M Bu₄NPF₆ as supporting electrolyte under nitrogen atmosphere at room temperature. Ag/AgCl was used as the reference electrode where platinum (Pt) was employed as both working and counter electrode and ferrocene/ferrocenium (Fc/Fc⁺) couple as standard. The LUMO energy levels were calculated using the equation; LUMO = -(E_{red} + 4.52) eV.

Theory

Structures were optimized in D2 symmetry at the B3P86/6-31G* level with 30% of exact exchange in the hybrid functional.^{1,2} Vertical absorption spectra were obtained with time-dependent density functional theory (TDDFT) with same functional and basis set. Charges of ground and excited states were determined with natural population analysis (NPA).³ All calculations were done with Gaussian 09,⁴ plots were prepared with GaussView 5 and GabEdit.⁵

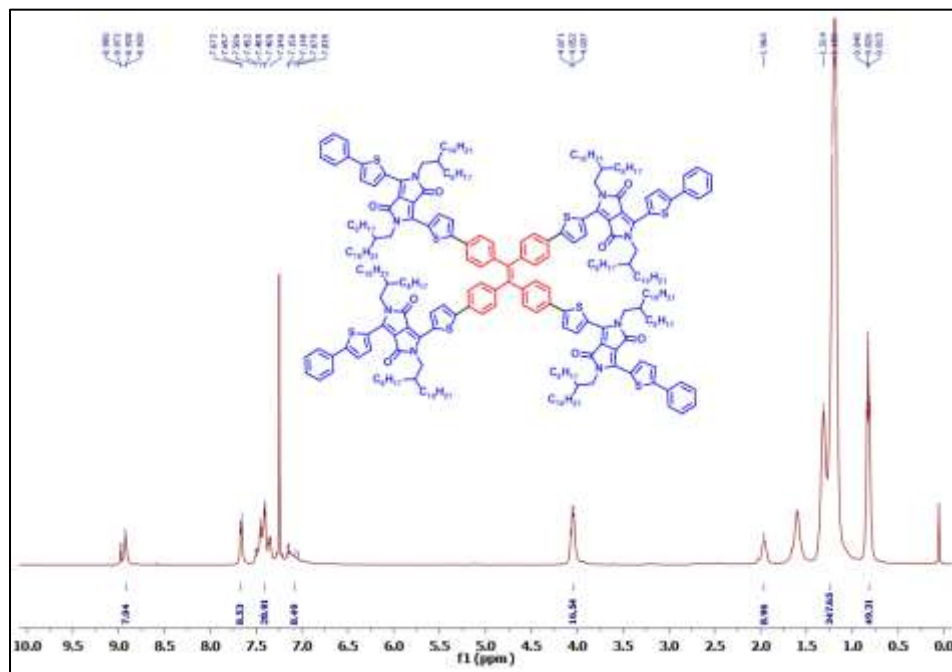
2. Synthesis and Spectroscopic characterization of TPE-TDPP and TPE-SeDPP

Synthesis and Spectroscopic characterization of TPE-TDPP (3a): In a 50 mL Schlenk flask equipped with Ar bladder, 3-(5-Bromo-thiophen-2-yl)-2,5-bis-(2-octyl-dodecyl)-6-(5-phenylthiophen-2-yl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (**1a**) (6.0 eqv), tetrakis(phenylethyl)boronic ester (**2**) (1 eqv), K₃PO₄ (8 eqv in 5 mL deionized water) and Pd₂(dba)₃ (0.05 eqv) in 30 mL anhydrous degassed toluene were refluxed at 110 °C for 72 hours. The resulting mixture was washed thoroughly three times with saturated solution of Na₂EDTA and then with 2N HCl solution. It was then extracted with dichloromethane (DCM) (3 × 100 mL), and the extracts were combined, washed with brine, and dried over Na₂SO₄. After evaporation of solvent, the residue was purified by Soxhlet extraction using methanol and acetone to afford a greenish blue solid in 45% isolated yield. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ: 8.98-8.92 (8H, m), 7.67-7.66 (8H, m), 7.51-7.34 (28H, m), 7.16-7.04 (8H, m), 4.07-4.04 (16H, m), 1.96 (8H, br s), 1.31-1.19 (256H, br m), 0.83 (12H, t, J = 5.6 Hz); ¹³C NMR (100 MHz, CDCl₃, Me₄Si) δ: 161.8, 149.8, 149.0, 140.0, 139.8, 136.9, 136.8, 133.4, 133.3, 132.3, 132.0, 129.2, 128.9, 126.2, 125.7, 124.5, 108.4, 108.3, 46.4, 38.0, 32.0, 31.4, 30.1, 29.8, 29.7, 29.6, 29.4, 26.4, 22.8, 22.7; MS (MALDI): m/z found for C₂₆₆H₃₈₀N₈O₈S: 4073.496.

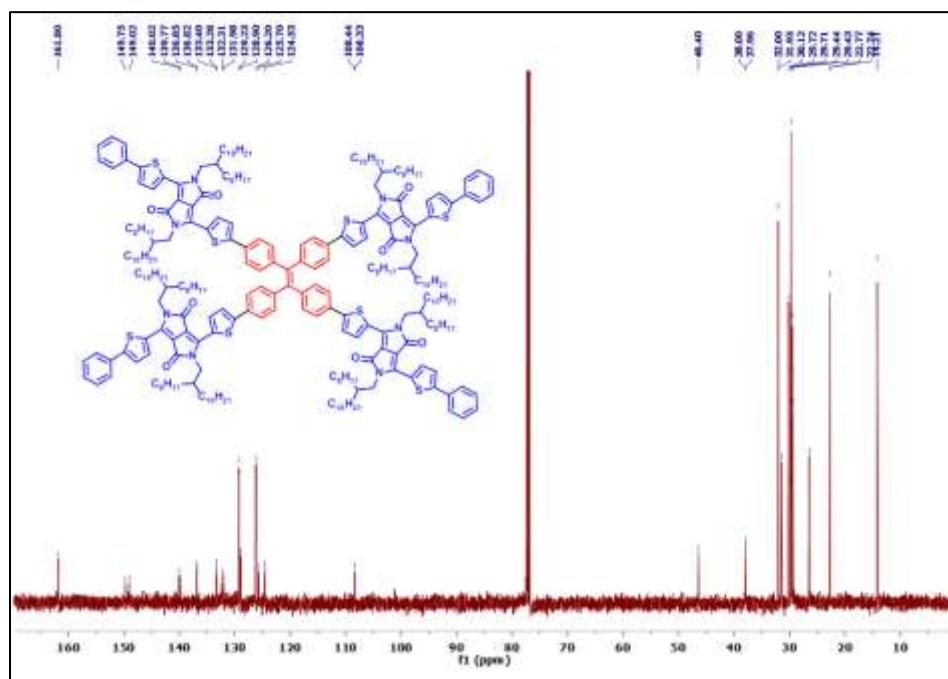
Synthesis and Spectroscopic characterization of TPE-SeDPP (3b): Compound **3b** was prepared in 41% yields from 3-(5-Bromo-selenophene-2-yl)-2,5-bis-(2-octyl-dodecyl)-6-(5-phenylselenophene-2-yl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (**1b**) following the procedure as described for the synthesis of **3a**. ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ: 8.85 (6H, br s), 8.71 (2H, br s), 7.65-7.61 (14H, m), 7.56-7.38 (22H, m), 7.17-7.15 (8H, m), 4.01 (16H, br s), 1.99 (8H, br s), 1.34-1.23 (256H, br m), 0.86 (48H, t, J = 3.6 Hz); ¹³C NMR (100 MHz, CDCl₃, Me₄Si) δ: 161.8, 157.1, 156.3, 143.9, 141.7, 141.5, 140.8, 137.9, 135.5, 134.1, 132.9, 132.3, 129.3, 128.8, 126.5, 126.1, 108.3, 46.4, 37.8, 37.7, 32.0, 31.3, 30.1, 29.7, 29.6, 29.5, 29.4, 25.8, 22.8, 14.0; MS (MALDI): m/z found for C₂₆₆H₃₈₀N₈O₈Se₈: 4446.029.

3. ^1H NMR and ^{13}C NMR spectra for 3a-3b

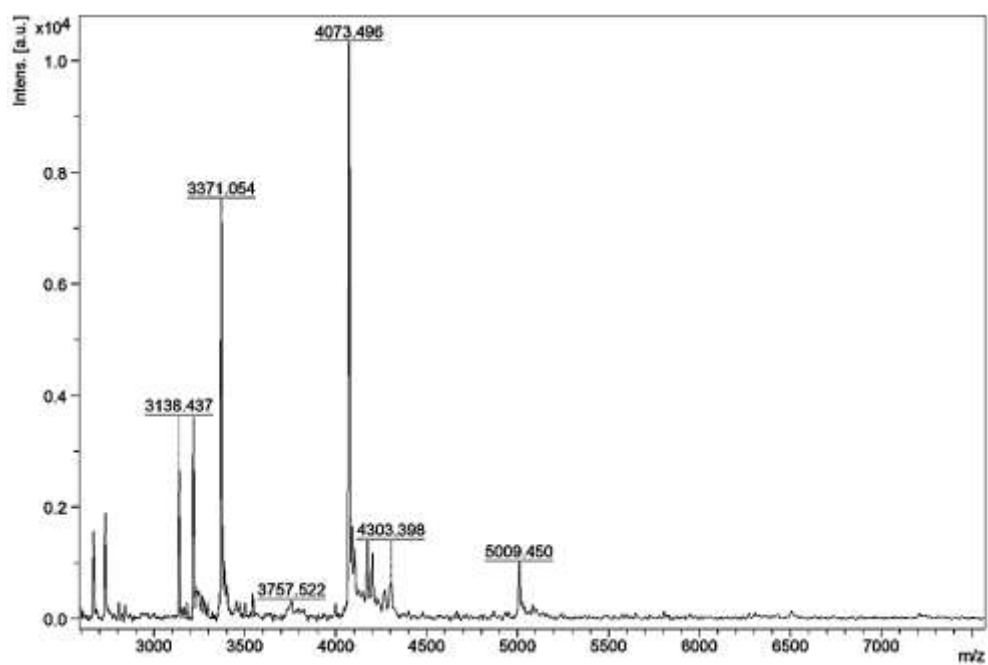
^1H NMR spectrum of TPE-TDPP



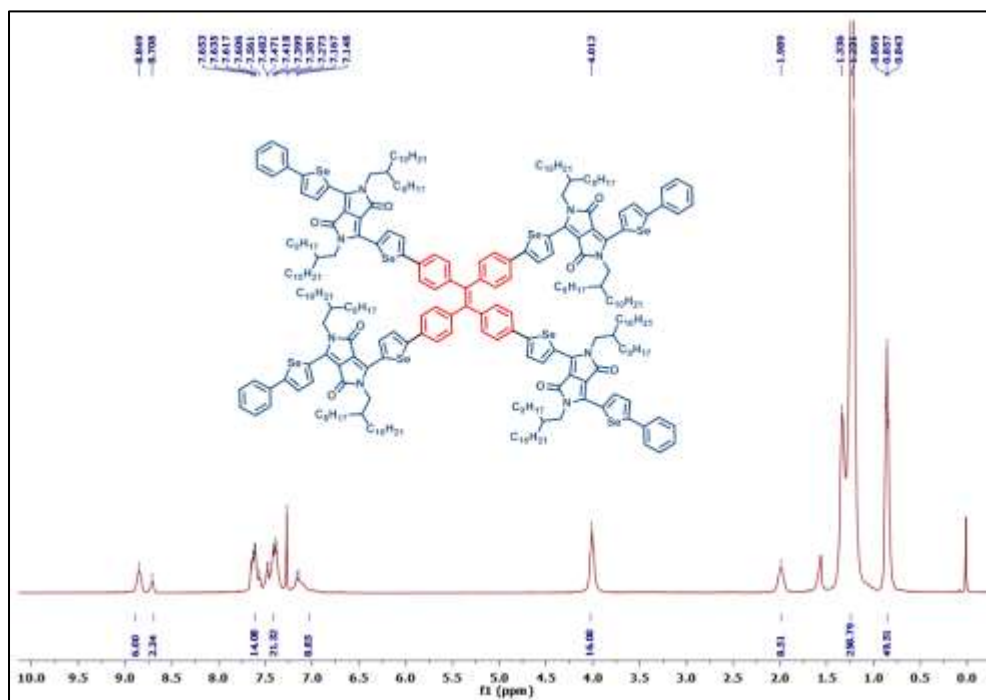
^{13}C NMR spectrum of TPE-TDPP



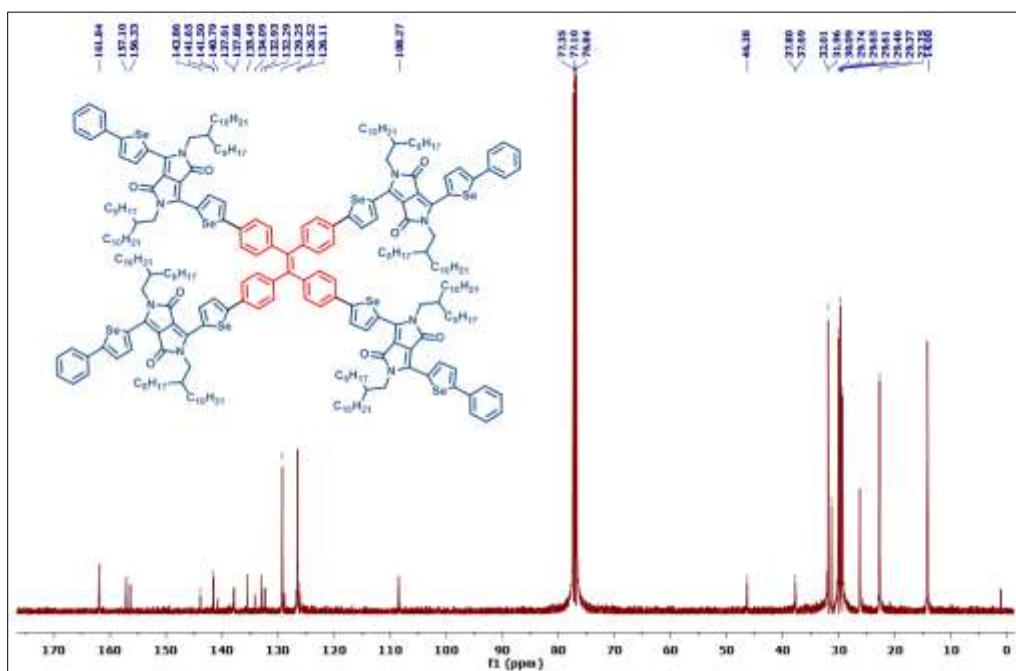
MALDI-MS spectrum of TPE-TDPP



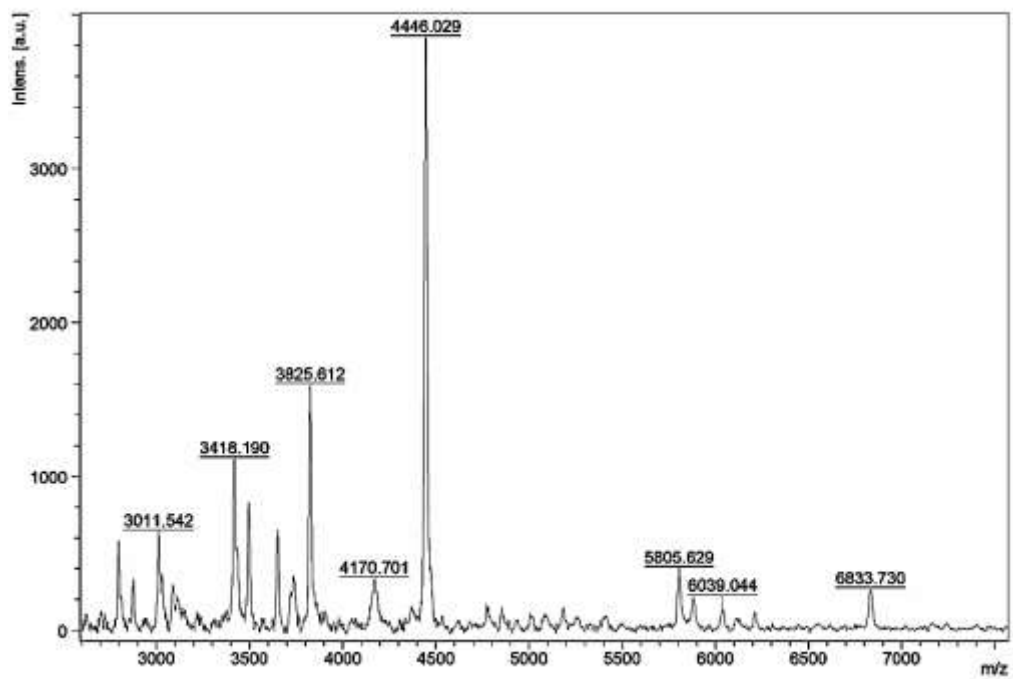
^1H NMR spectrum of TPE-SeDPP



^{13}C NMR spectra um of TPE-TDPP



MALDI-MS spectrum of TPE-SeDPP



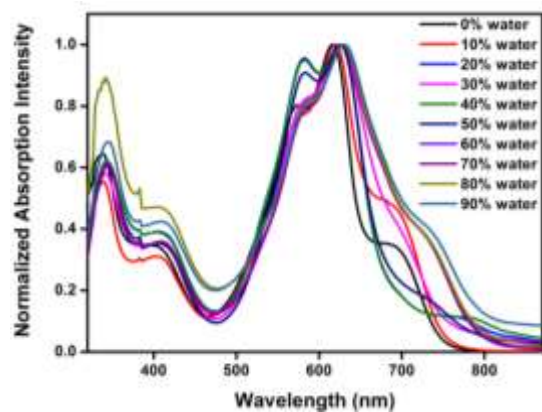


Figure S1. Uv-visible spectra of TPE-TDPP in different ratios of THF-water mixture.

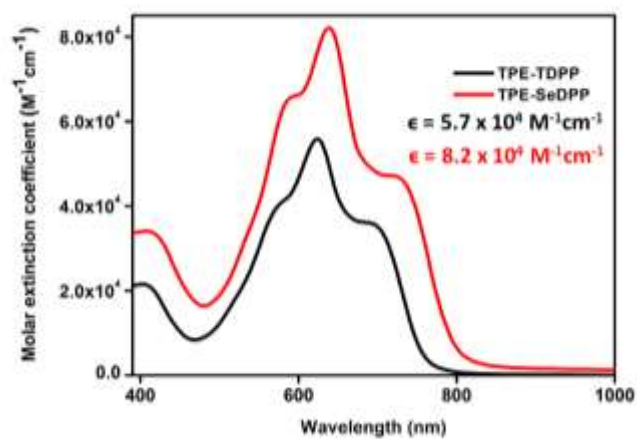


Figure S2. Molar extinction coefficients of TPE-TDPP and TPE-SeDPP.

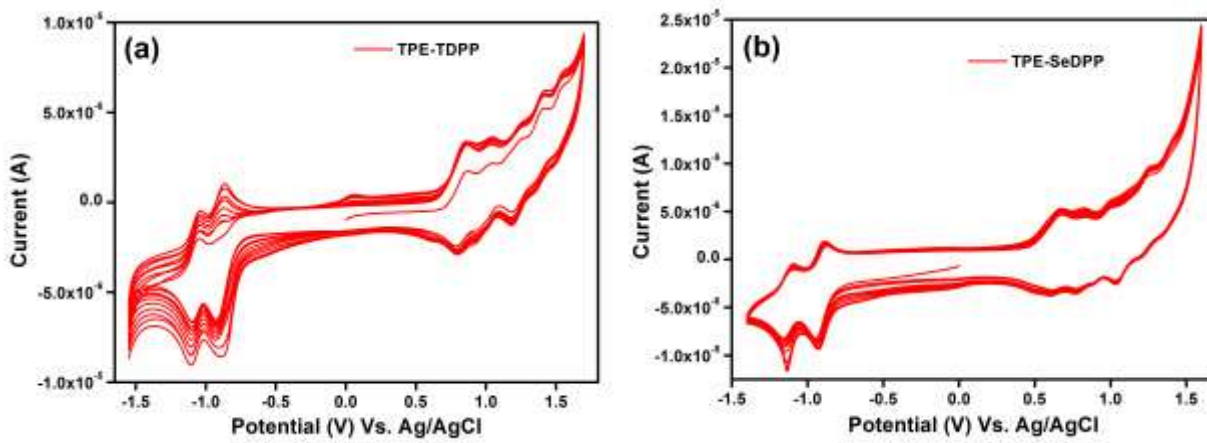


Figure S3. Multiple segments cyclic voltammograms of TPE-TDPP and TPE-SeDPP.

Device Fabrication

Bottom-contact top-gate architecture transistors were fabricated on a glass substrate to evaluate the charge carrier mobility of the **TPE-TDPP** and **TPE-SeDPP** materials. Source and drain electrodes were thermally evaporated through shadow mask in high vacuum (10^{-6} mbar); to extract hole mobility 40 nm of Au were used, where for the electron mobility a bilayer of 20/20 nm Au/Al. A self-assembled monolayer (SAM) was used to adjust the workfunction of Au electrodes. Au source-drain were immersed for 45 minutes in a pentafluorothiophenol (PFBT) solution in isopropanol. The organic semiconductor materials were spin-coated from a 5 mg ml⁻¹ chlorobenzene:chloroform (1:1) solution at 2000 rpm for 30 seconds. The semiconducting films were then annealed at 50 °C and 100°C for 15 minutes. 900 nm of CYTOP were used as dielectric layer. Finally, 40 nm of Al were evaporated to form the gate electrode through shadow masks. Solution preparation, transistor fabrication and electrical measurements were performed in a nitrogen atmosphere with an Agilent B2902A semiconductor parameter analyzer.

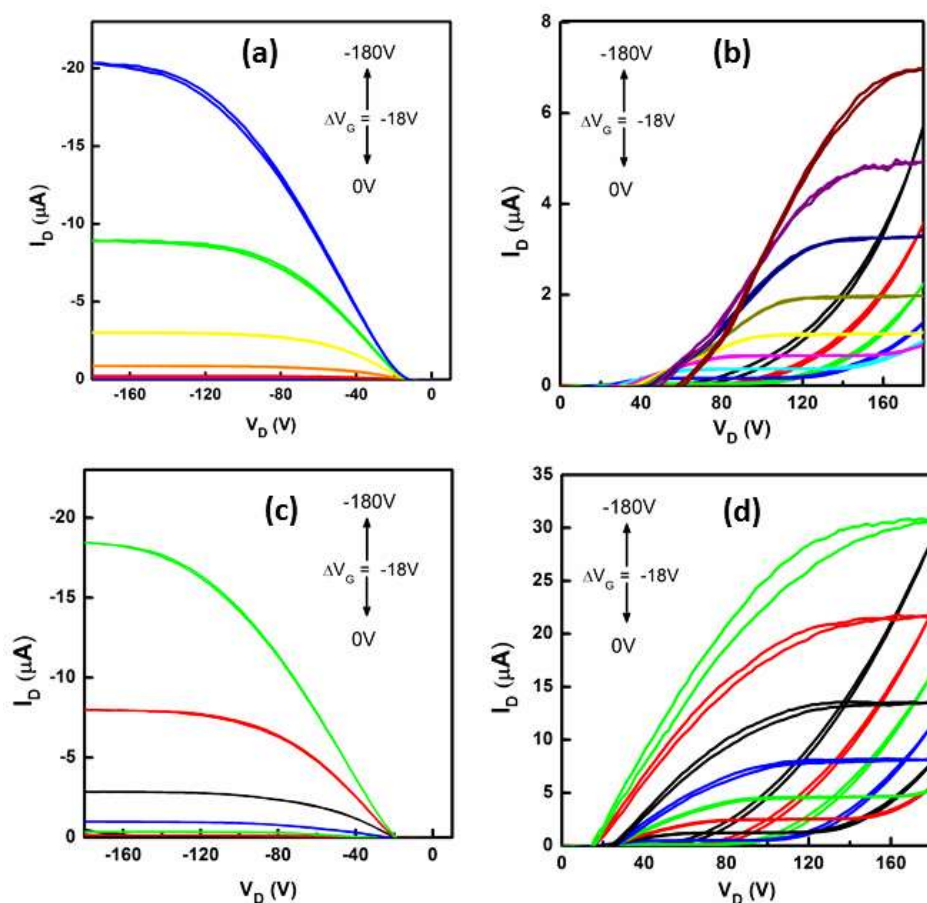


Figure S4: Output characteristics for **TPE-TDPP** oligomer when annealed at 50°C (a & b) and at 100°C (c & d). BC-TG TFTs with au source-drain electrodes were used for holes (a and c), where a bilayer of Au/Al for electron charge carriers (b and d)

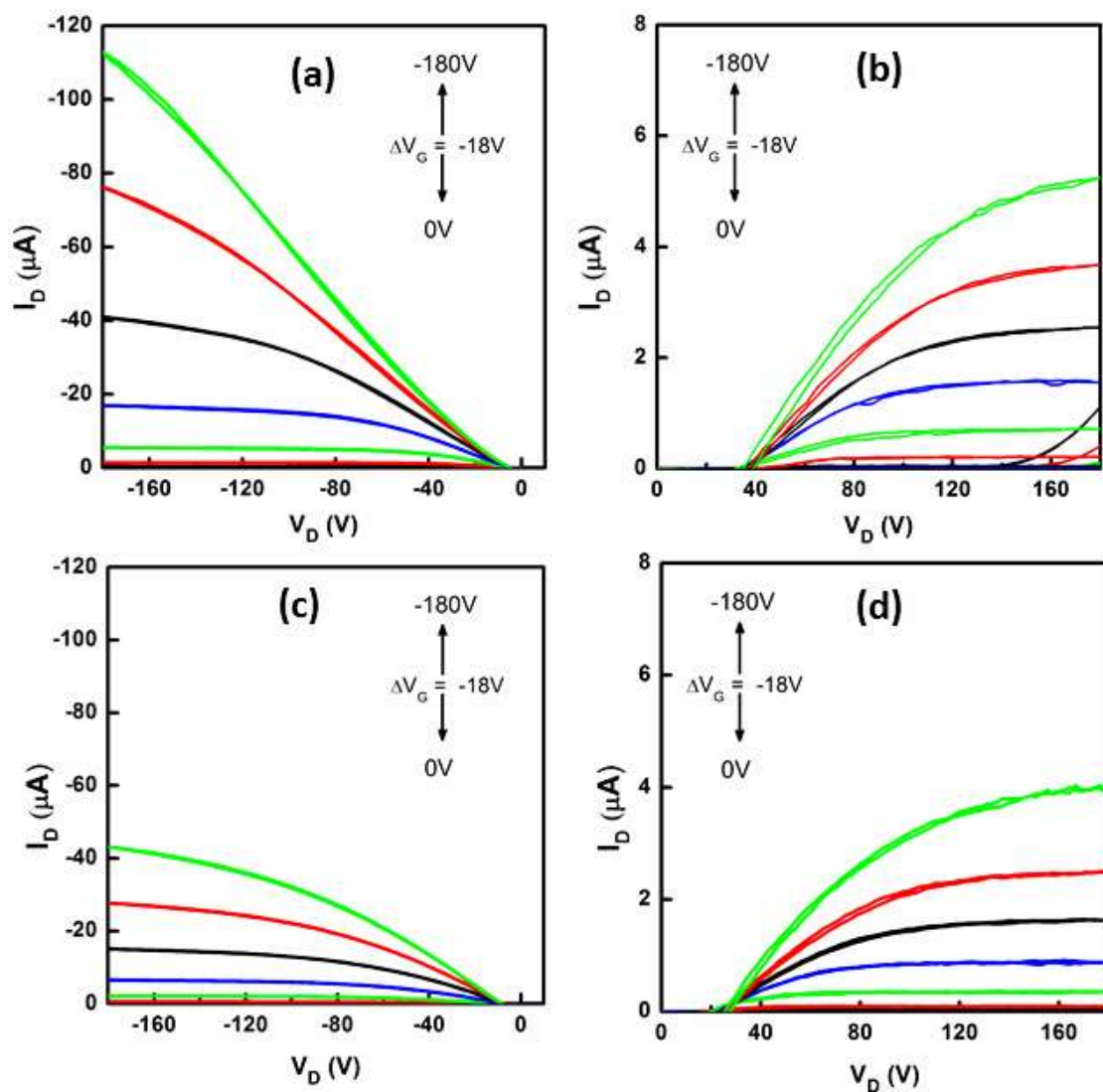


Figure S5: Output characteristics for **TPE-SeDPP** oligomer when annealed at 50°C (a & b) and at 100°C (c & d). BC-TG TFTs with au source-drain electrodes were used for holes (a and c), where a bilayer of Au/Al for electron charge carriers (b and d)

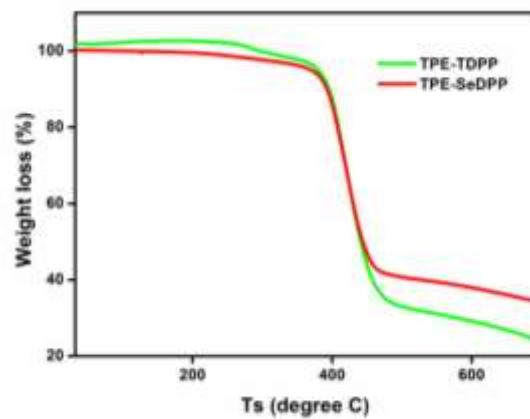


Figure S6. TGA of TPE-TDPP and TPE-SeDPP under N₂ atmosphere.

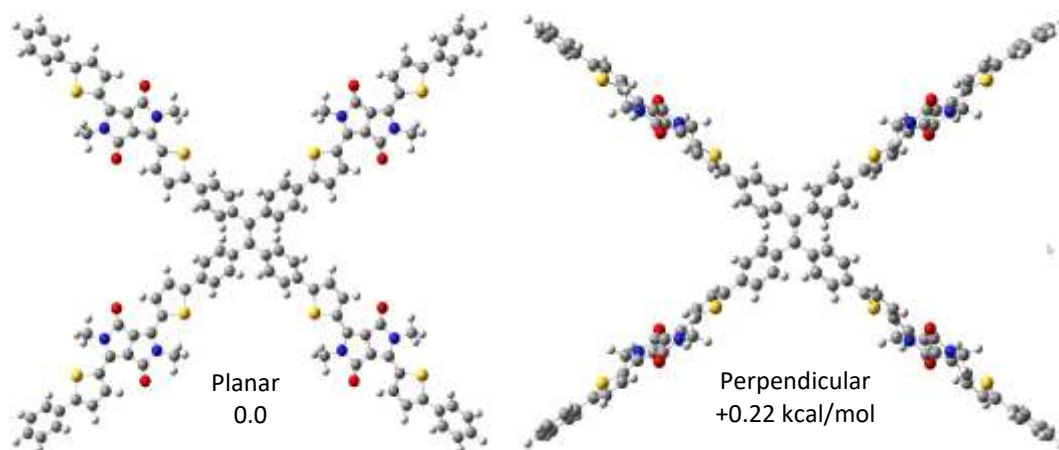


Figure S7. Calculated structures with different almost planar and almost perpendicular arrangements of the arms with respect to the ethylene double bond of TPE.

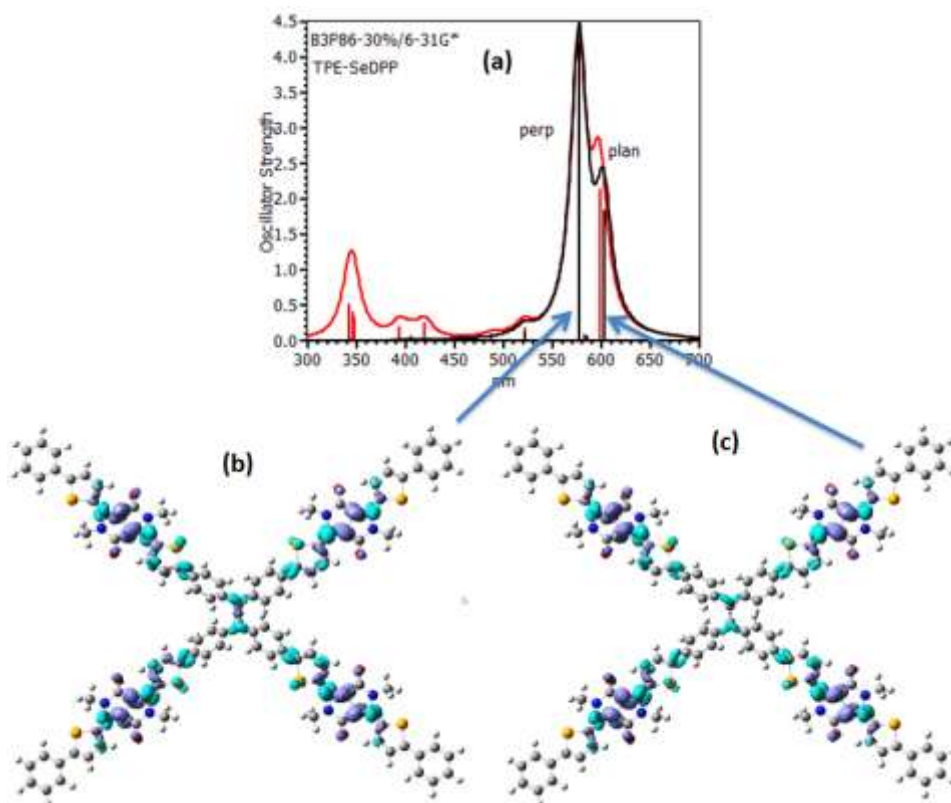


Figure S8. (a) TPE-SeDPP with almost planar (red) and almost perpendicular (black) conformations; (b) density differences between ground and first excited state; (c) density differences between ground and second excited state of TPE-SeDPP.

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