

Supporting Information

Energy Level Tuning of Non-Fullerene Acceptors in Organic Solar Cells

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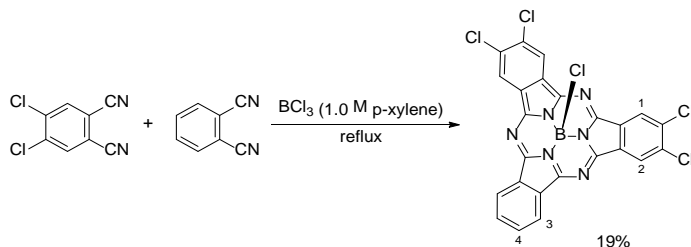
Synthesis

All chemicals were purchased from Sigma-Aldrich Co., TCI Europe N.V. and Alfa Aesar and used without further purification. Solvents were purchased from Carlo Erba Reagents and Scharlab. Dry dimethylformamide was prepared using molecular sieves (irradiated with microwaves and dried under vacuum). 4-iodophthalonitrile^{1,2} and 4,5-dichlorophthalonitrile³ were prepared using a described procedure. Column chromatography was carried out on silica gel Merck-60 and TLC was carried out on aluminium sheets percolated with silica gel 60 F254 (Merck). ¹H NMR and ¹³C NMR spectra were obtained using a Bruker Avance 300 spectrometer or a Bruker DRX-500 spectrometer. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) MS and high-resolution mass spectrometry (HRMS) spectra were recorded with a Bruker Reflex III spectrometer. UV/Vis spectra were recorded with a Jasco V-660 instrument. Electrochemical measurements were performed with an Autolab PGStat 30 system using a three electrode configuration system. The measurements were carried out using THF solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆). A glassy carbon electrode (3 mm diameter) was used as the working electrode, and a platinum wire and an Ag/AgNO₃ (in CH₃CN) electrode were employed as the counter and the reference electrodes, respectively. Ferrocene (Fc) was added as an internal reference and all the potentials were given relative to the Fc/Fc⁺ couple. The scan rate was 100 mV/s.

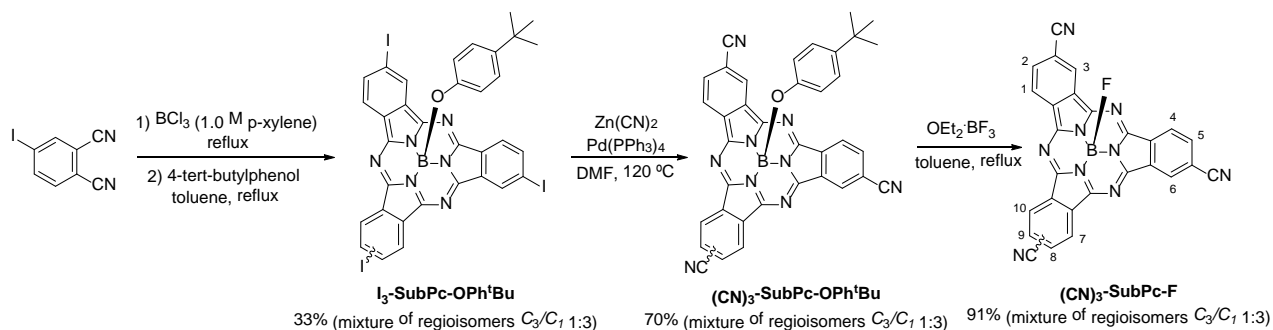
Cl₆-SubPc-Cl: this compound was synthesized according to the procedure previously described.⁴

F₁₂-SubPc-Cl: this compound was synthesized according to the procedure previously described.⁵

Cl₄-SubPc-Cl:



In a 25 mL two-necked round-bottomed flask, equipped with a condenser, magnetic stirrer and rubber seal, BCl₃ (5 mL, 1 M solution in p-xylene) was added to 4,5-dichlorophthalonitrile (788 mg, 4.0 mmol) and phthalonitrile (256 mg, 2.0 mmol) under argon atmosphere. The reaction mixture was stirred under vigorous reflux for 2 h. The purple solution was allowed to cool to room temperature and flushed with argon. The solvent was removed by vacuum distillation and the resulting dark solid was subjected to column chromatography on silica gel using toluene/heptane (3:1) as an eluent. By washing with heptane, **Cl₄-SubPc-Cl** was further purified, obtaining a purple solid (216 mg, 19%). mp > 250 °C; ¹H NMR (300 MHz, CDCl₃, δ): 8.98 (s, 2H; H-2), 8.94 (s, 2H; H-1), 8.92-8.83 (dd, 2H; H-3), 8.05-7.96 (dd, 2H; H-4); UV-vis (CHCl₃): λ_{max} (log ε) = 573 (4.5), 539 (sh), 520 (sh), 315 nm (4.2), 274 (4.2); MALDI-TOF MS m/z (%): 568.0 (100) [M⁺]; HRMS (MALDI-TOF) m/z : [M]⁺ calcd for C₂₄H₈BCl₅N₆, 567.9317; found, 567.9345.

(CN)₃-SubPc-F:

Compound **I₃-SubPc-OPh^tBu** was synthesized according to the procedure previously described.^{6,7}

Then, in a 25 mL two-necked round-bottomed flask, equipped with a condenser, magnetic stirrer and rubber seal, a solution of **I₃-SubPc-OPh^tBu** (mixture of regioisomers C₃/C₁ 1:3) (460 mg, 0.50 mmol) in dry DMF (10 mL), Zn(CN)₂ (94 mg, 0.80 mmol) and tetrakis(triphenylphosphine)palladium(0) (87 mg, 0.075 mmol) were added under argon atmosphere. The reaction mixture was heat at 120 °C for 1.5 h. Water (30 mL) was added and the product was extracted with dichloromethane (3×25 mL). The combined organic extracts were dried over MgSO₄ and the solvent was removed by rotary evaporation. The solid residue was purified by column chromatography on silica gel using toluene/THF (150:1) as an eluent, yielding product **(CN)₃-SubPc-OPh^tBu** as a purple solid (mixture of regioisomers C₃/C₁ 1:3) (218 mg, 70%).

(CN)₃-SubPc-F was synthesized by adapting the method of M. V. Fulford *et al.*^{8,9} In a 25 mL two-necked round-bottomed flask, equipped with a condenser, magnetic stirrer and rubber seal, **(CN)₃-SubPc-OPh^tBu** (mixture of regioisomers C₃/C₁ 1:3) (218 mg, 0.35 mmol) is dissolved in dry toluene (4 mL) under argon atmosphere. Boron trifluoride diethyl etherate (Et₂O·BF₃, 1.1 mL, 25 molar equiv) was added dropwise. The reaction mixture was stirred under reflux for 5 h. The purple solution was allowed to cool to room temperature and pyridine was added dropwise

until the color of the reaction to a characteristic SubPc pink color. The flask was placed in an ice bath for one hour, and the precipitate subsequently isolated by vacuum filtration. The filter cake was rinsed with methanol followed by ether to give a purple solid (156 mg, 91%). mp > 250 °C; ^1H NMR (300 MHz, THF- d_8 , δ): 9.30 (s, 3H; H-3, H-6, H-7/H-10), 9.01 (d, $J = 8.3$ Hz, 3H; H-1, H-4, H-7/H-10), 8.36-8.27 (m, 3H; H-2, H-5, H-8/H-9); ^{19}F NMR (300 MHz, THF- d_8 , δ): -159.52 (q, $J = 27.8$ Hz); UV-vis (THF): λ_{max} ($\log \epsilon$) = 572 (4.7), 554 (sh), 537 (sh), 521 (sh), 314 nm (4.3); MALDI-TOF MS m/z (%): 489.2 (100) [M^+]; HRMS (MALDI-TOF) m/z : [M] $^+$ calcd for $\text{C}_{27}\text{H}_9\text{BFN}_9$, 489.1057; found, 489.1052.

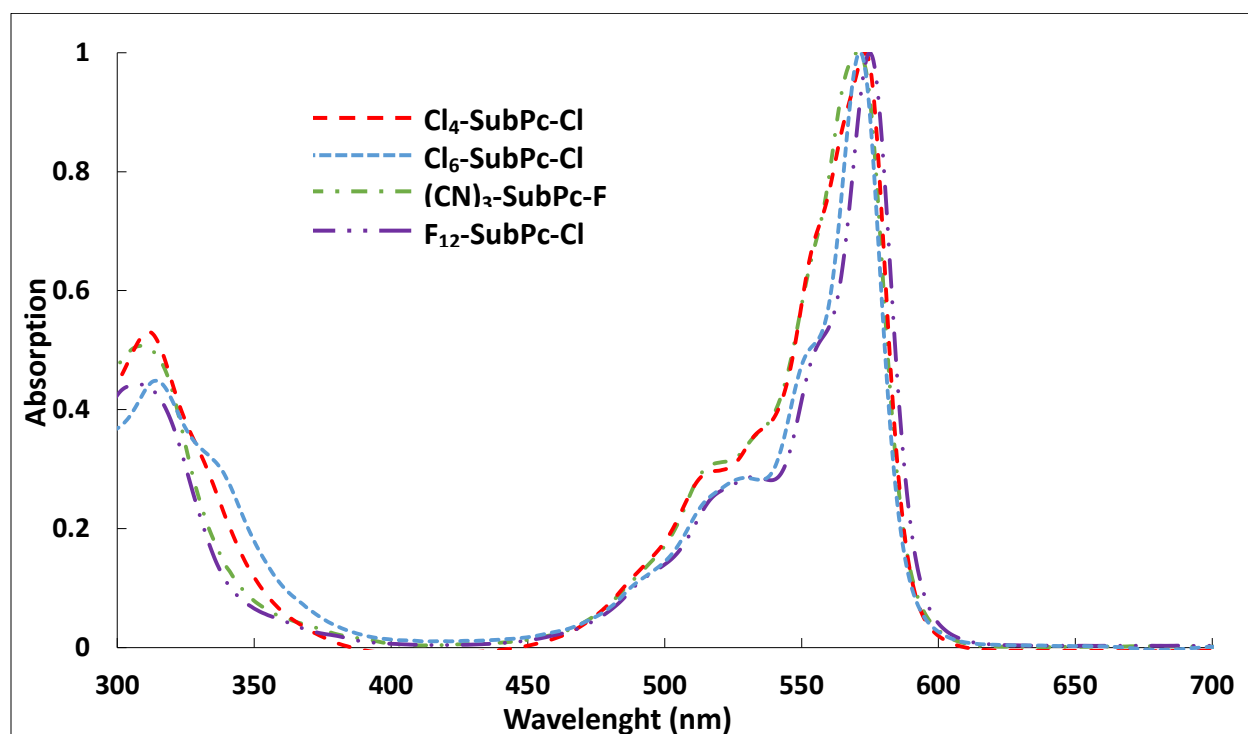


Figure S1. Normalized UV-Vis absorption spectra of compounds $\text{Cl}_6\text{-SubPc-Cl}$, $\text{F}_{12}\text{-SubPc-Cl}$, $\text{Cl}_4\text{-SubPc-Cl}$ and $(\text{CN})_3\text{-SubPc-F}$ in chloroform.

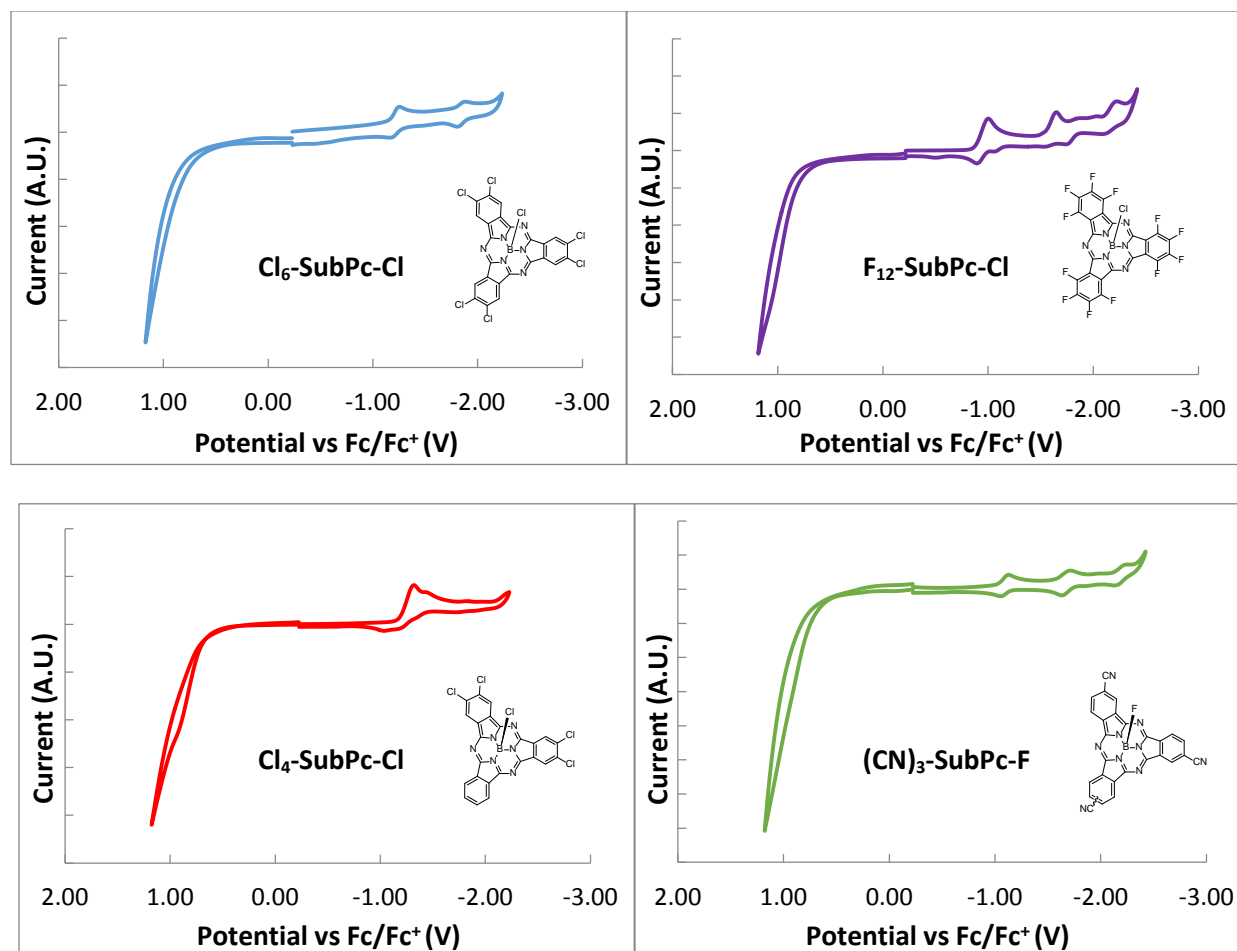


Figure S2. Cyclic voltammograms of compounds Cl₆-SubPc-Cl, F₁₂-SubPc-Cl, Cl₄-SubPc-Cl and (CN)₃-SubPc-F (referred to Fc/Fc⁺) in THF.

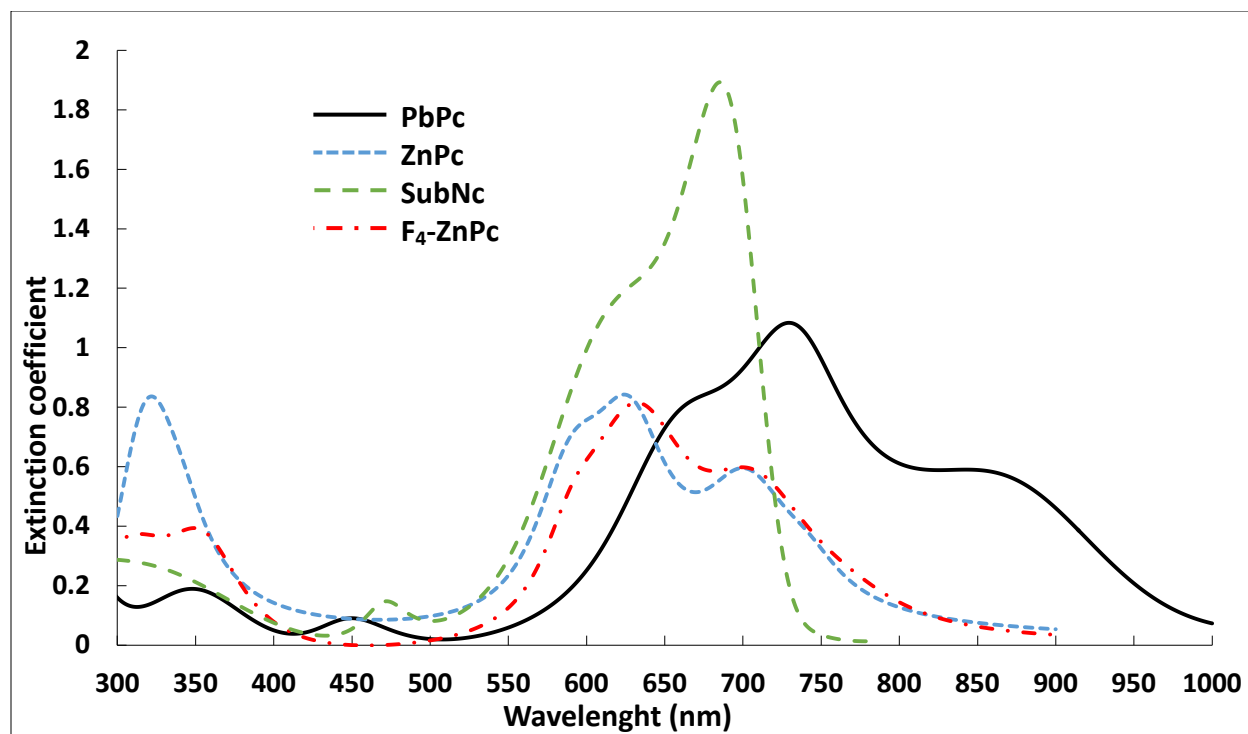


Figure S3. Extinction coefficients of the donor materials, determined by spectroscopic ellipsometry on thin films on Si/SiO₂ substrates.

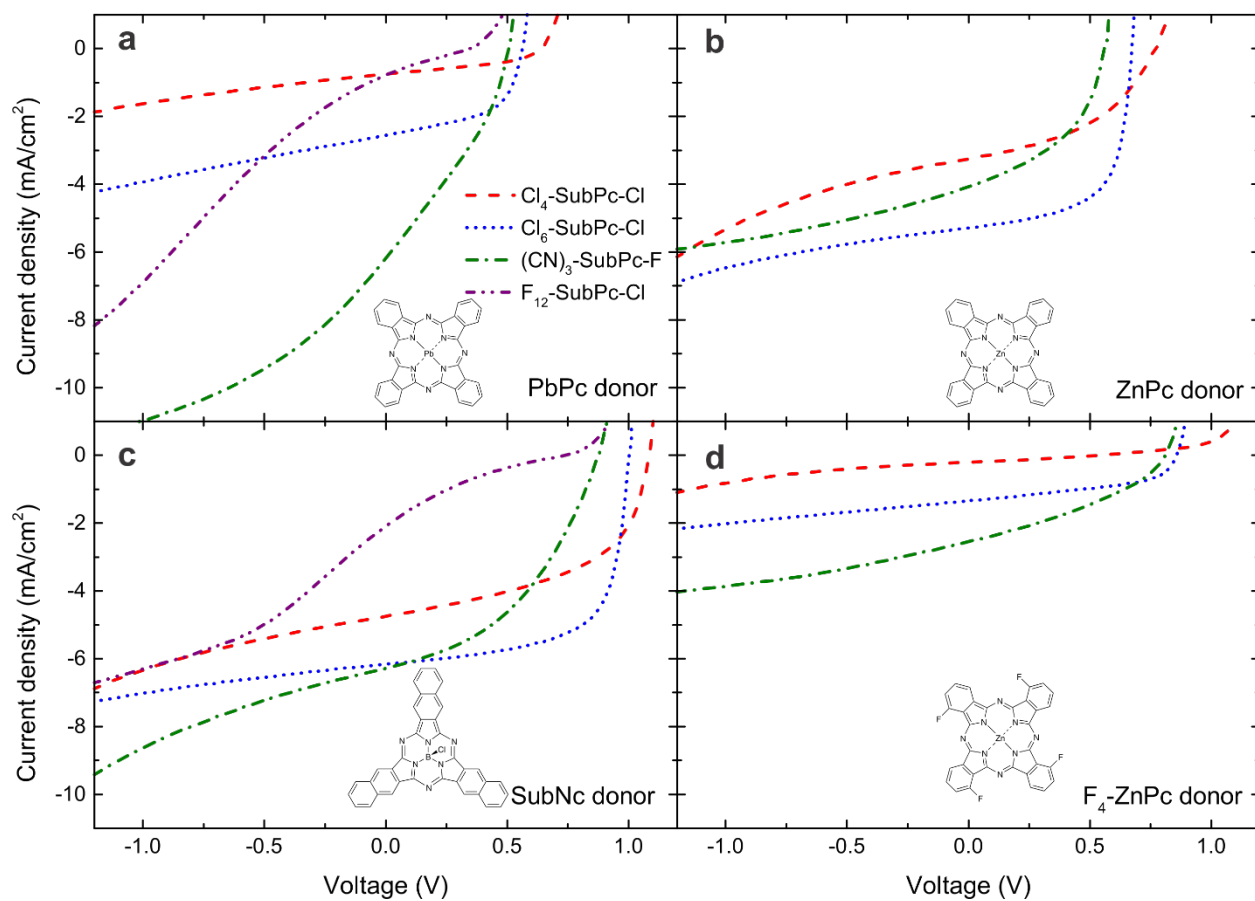


Figure S4. Current density-voltage measurements under simulated solar illumination of all heterojunction devices tested in this work. In each panel several SubPc derivative acceptors are combined with a small-bandgap donor material: (a) PbPc, (b) ZnPc, (c) SubNc, and (d) F₄-ZnPc.

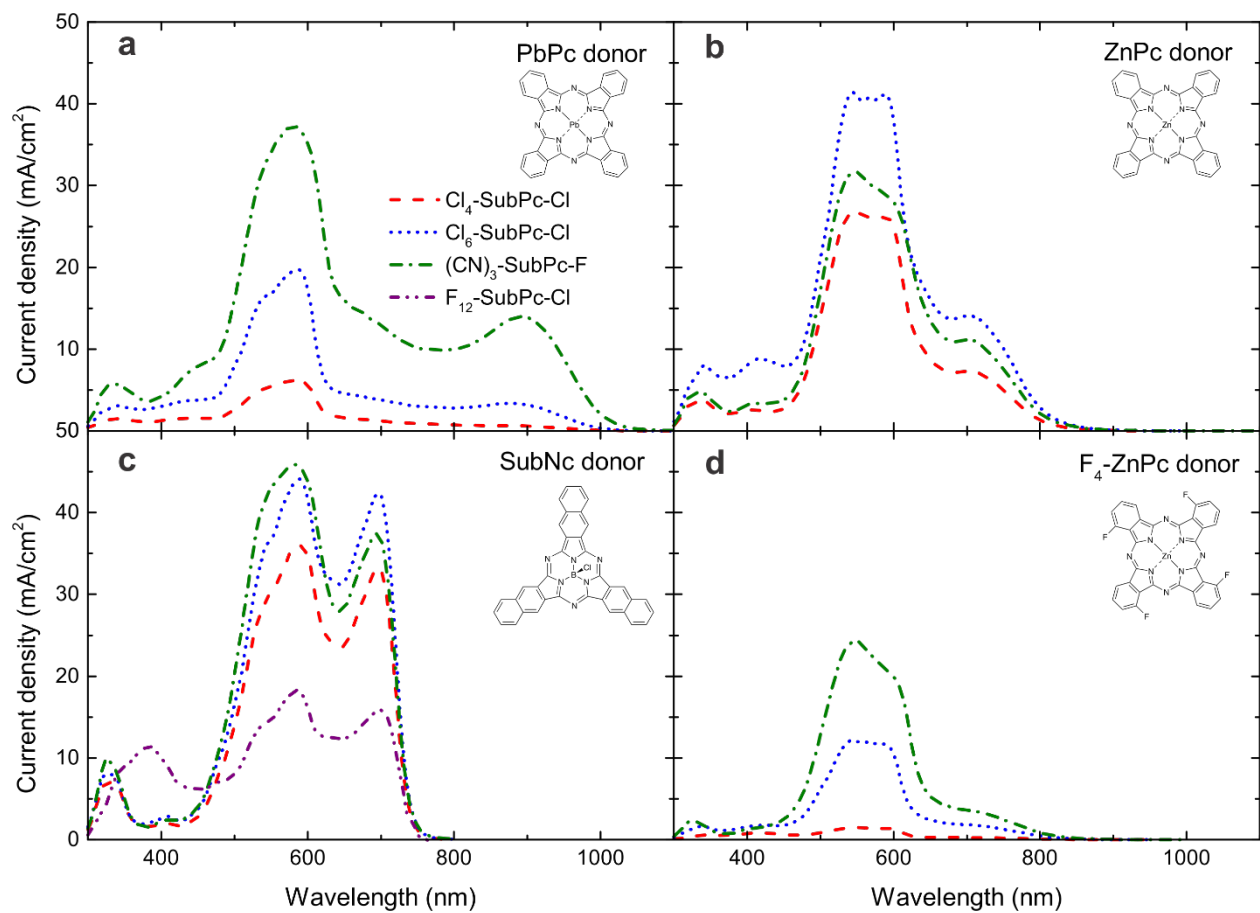


Figure S5: External quantum efficiency of all heterojunction devices tested in this work. In each panel several SubPc derivative acceptors are combined with a small-bandgap donor material: (a) PbPc, (b) ZnPc, (c) SubNc, and (d) F₄-ZnPc.

Table S1. Interface energy gap (E_{DA}) and J - V characteristics for each heterojunction device studied in this work. Average values (and standard deviations) of V_{OC} , J_{SC} , FF, and PCE are calculated for at least 3 devices on a single substrate.

| Donor | Acceptor | E_{DA} (eV) | V_{OC} (V) | J_{SC} (mA/cm ²) | FF (%) | PCE (%) |
|---------------------------|---------------------------------|------------------|------------------|-----------------------------------|-----------------|------------------|
| PbPc | F₁₂-SubPc-Cl | 1.15 | 0.33 (± 0.01) | 0.88 (± 0.07) | 23.4 (± 0.2) | 0.07 (± 0.01) |
| | (CN)₃-SubPc-F | 1.29 | 0.50 (± 0.01) | 6.00 (± 0.1) | 32.5 (± 0.4) | 0.97 (± 0.02) |
| | Cl₆-SubPc-Cl | 1.39 | 0.57 (± 0.01) | 2.51 (± 0.03) | 53.9 (± 0.5) | 0.76 (± 0.01) |
| | Cl₄-SubPc-Cl | 1.46 | 0.64 (± 0.01) | 0.76 (± 0.01) | 40.1 (± 1.4) | 0.19 (± 0.01) |
| ZnPc | (CN)₃-SubPc-F | 1.40 | 0.56 (± 0.01) | 4.07 (± 0.04) | 43.5 (± 0.7) | 0.97 (± 0.02) |
| | Cl₆-SubPc-Cl | 1.50 | 0.67 (± 0.01) | 5.28 (± 0.01) | 62.6 (± 1.2) | 2.23 (± 0.03) |
| | Cl₄-SubPc-Cl | 1.57 | 0.77 (± 0.01) | 3.25 (± 0.01) | 43.9 (± 1.0) | 1.10 (± 0.02) |
| SubNc | F₁₂-SubPc-Cl | 1.52 | 0.75 (± 0.01) | 2.4 (± 0.2) | 17.2 (± 0.3) | 0.30 (± 0.03) |
| | (CN)₃-SubPc-F | 1.66 | 0.89 (± 0.01) | 6.18 (± 0.08) | 43.2 (± 0.6) | 2.36 (± 0.03) |
| | Cl₆-SubPc-Cl | 1.76 | 1.00 (± 0.01) | 6.12 (± 0.04) | 65.3 (± 0.4) | 3.89 (± 0.04) |
| | Cl₄-SubPc-Cl | 1.83 | 1.08 (± 0.01) | 4.83 (± 0.07) | 48.2 (± 3.0) | 2.44 (± 0.14) |
| F₄-ZnPc | (CN)₃-SubPc-F | 1.75 | 0.81 (± 0.01) | 2.52 (± 0.04) | 34.8 (± 0.4) | 0.70 (± 0.01) |
| | Cl₆-SubPc-Cl | 1.85 | 0.87 (± 0.01) | 1.34 (± 0.01) | 47.4 (± 0.5) | 0.53 (± 0.01) |
| | Cl₄-SubPc-Cl | 1.92 | 0.66 (± 0.1) | 0.21 (± 0.02) | 26.3 (± 1.1) | 0.04 (± 0.01) |

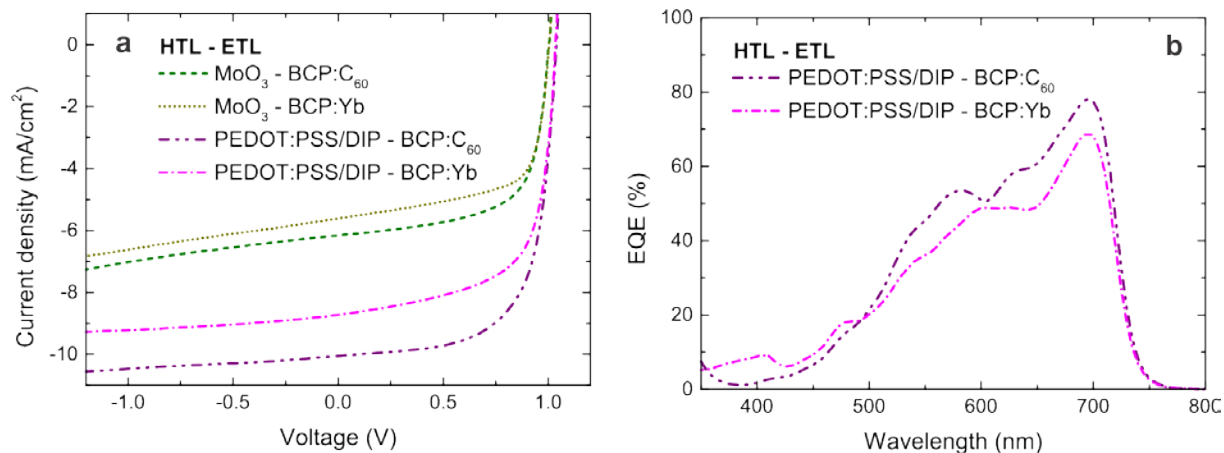


Figure S6: (a) Current density-voltage curves, measured under simulated solar illumination, and (b) EQE curves for SubNc/Cl₆-SubPc-Cl heterojunction devices with different hole and electron transport layers.

Table S2: Solar cell performance parameters for SubNc/Cl₆-SubPc-Cl heterojunction devices with different hole and electron transport layers

| HTL - ETL | V_{OC} (V) | J_{SC} (mA/cm ²) | FF (%) | PCE (%) |
|--|-----------------|-----------------------------------|-----------|------------|
| MoO ₃ - BCP:C ₆₀ | 1.00 | 6.17 | 65.9 | 3.96 |
| MoO ₃ - BCP:Yb | 1.00 | 5.62 | 66.4 | 3.62 |
| PEDOT:PSS/ DIP - BCP:C ₆₀ | 1.04 | 10.1 | 66.6 | 6.86 |
| PEDOT:PSS/ DIP - BCP:Yb | 1.04 | 8.69 | 64.9 | 5.99 |

SUPPLEMENTARY REFERENCES

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