

Electronic Supporting Information

Synthetically Facile Organic Solar Cells with > 4% Efficiency using P3HT and a Silicon Phthalocyanine Non-Fullerene Acceptor

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Materials and Methods

P3HT was purchased from Rieke. Alphasexithiophene (α -6T, purified by sublimation) was purchased from TCI and used as received. PC₆₁BM was purchased from Nano-c. Triisopropyl silane was purchased from Gelest. Silicon phthalocyanine dichloride (Cl₂-SiPc) was synthesized according to the literature procedure.¹

Synthesis of bis(tri-n-propylsilyl oxide) silicon phthalocyanine ((3PS)₂-SiPc):

(3PS)₂-SiPc was synthesized following the general procedure described by Gessner et al.² A 100 mL reaction flask was charged with Cl₂-SnPc (1.50 g, 2.45 mmol), sodium hydroxide (0.52 g, 13.05 mmol), tripropylchlorosilane (1.51 g, 7.83 mmol), Aliquat HTA-1 (0.053 g) and chlorobenzene (30 mL). The reaction mixture was stirred under reflux (132 °C) for 1 hour before adding additional tripropylchlorosilane (0.50 g, 2.61 mmol). After a further hour of reflux, sodium hydroxide (0.21 g, 5.25 mmol) and tripropylchlorosilane (0.50 g, 2.61 mmol) were added. The reaction mixture was refluxed for a further 4 hours before being allowed to cool to room temperature. The reaction mixture was filtered, and the filtrate was evaporated to dryness via rotary evaporation. The remaining solids were suspended in methanol, filtered under vacuum, washed with methanol and water, then dried in a vacuum oven (0.79 g, yield = 36 %). The product was purified by train sublimation (200 °C, 100 mtorr, CO₂ carrier gas) before use in devices

(sublimation yield = 91 %, final yield = 33 %). ^1H NMR (400 MHz, CDCl_3) δ : 9.60–9.65 (m, 8 H), 8.28–8.32 (m, 8 H), 0.31–0.34 (m, 18 H), –1.13 to –1.23 (m, 12 H). MS [EI] calculated mass: 886.40; obtained mass: 886.4.

Materials Characterization

Thermogravimetric Analysis (TGA) was performed on a Q500 instrument with a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed on a Discovery 2500 instrument. Ultraviolet-visible (UV-vis) absorption spectra were measured using an Ocean Optics Flame spectrophotometer and a 10 mm path length quartz cuvette. Cyclic voltammetry measurements were performed using a VersaSTAT 3 potentiostat with a standard three electrode setup. The HOMO energy level was estimated using an internal ferrocene reference and the correlation: E_{HOMO} (eV) = $-(E_{\text{ox,onset}} - E_{\text{ox Fc/Fc}^+, \text{onset}}) - 4.80$ eV. AFM experiments were performed using a Bruker Dimension Icon, in ScanAsyst Mode, and equipped with ScanAsyst-Air probes. A scan rate of 0.75 Hz was used.

Fabrication of Photovoltaic Devices

Inverted BHJ OPV devices were fabricated with the structure glass/ITO/ZnO/P3HT:acceptor/MoO_x/Ag. Prepatterned ITO coated slides were cleaned with successive 5 minute washes of soap-water, water, acetone, then methanol in a bath sonicator, before being exposed to air plasma for 15 minutes. A ZnO precursor solution containing zinc acetate dihydrate (0.196 g), ethanol (6 mL), and ethanolamine (0.054 mL) was spin cast at 2000 rpm for 60 seconds onto the plasma treated substrates, then baked in air for 1 h at 180 °C. The active layers were deposited in a nitrogen atmosphere from solutions in 1,2-dichlorobenzene with a P3HT:acceptor mass ratio of 1:1. The P3HT concentration was 20 mg/mL for devices with PC₆₁BM and 15 mg/mL for devices with (3PS)₂-SiPc. P3HT/PC₆₁BM devices were spun at 1000 rpm for 35 seconds, and P3HT/(3PS)₂-SiPc devices were spun at 2000 rpm for 90 seconds. Finally, MoO_x (7 nm) and silver (70 nm) were deposited through a shadow mask to define an area of 0.325 cm² per device.

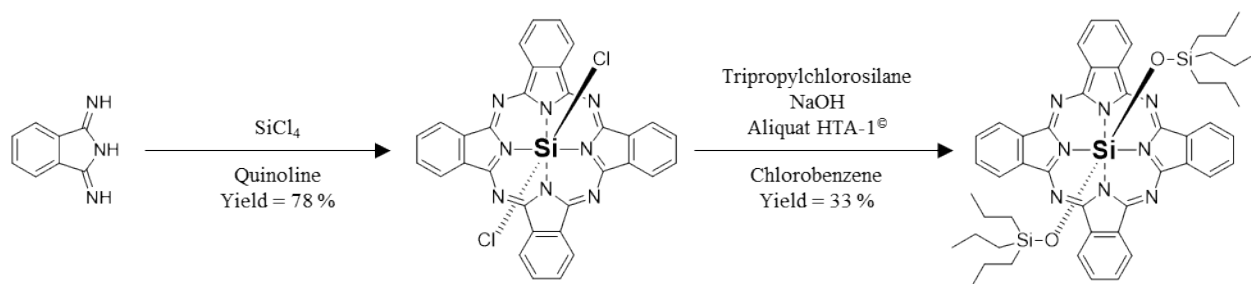
Inverted PHJ OPV devices were fabricated with the structure glass/ITO/ZnO/(3PS)₂-SiPc/ α -6T/MoO_x/Ag. ITO substrates were cleaned and cast with ZnO in the same method as the BHJ devices. (3PS)₂-SiPc (30 nm) and α -6T (40 nm) were deposited sequentially onto the ZnO

films at a rate of 1 Å/s. Thickness of the layers was monitored with a quartz crystal microbalance and were confirmed using stylus profilometry. MoO_x (7 nm) and silver (70 nm) were deposited similarly to the BHJ devices.

Current density vs voltage curves were measured at room temperature in a nitrogen atmosphere with an AM1.5G solar simulator calibrated to 1000 W/m². Devices were encapsulated using an optical adhesive (Norland NOA61) and glass slide for external quantum efficiency measurements in air using a QUANTX-300 instrument.

STXM Measurements

Scanning Transmission X-ray Microscopy (STXM) measurements were performed on HERMES beamline at SOLEIL synchrotron facility. Composition maps of blends were drawn from thickness values obtained from Singular Value Decomposition of energy stacks at the Carbon K-edge using absorption spectra of reference films (P3HT, PC₆₁BM and (3PS)₂-SiPc). These simulations are based on the following parameters: thickness = 1 nm for all 3 reference materials, formula: P3HT = C₁₀H₁₄S, PC₆₁BM = C₇₂H₁₄O₂, (3PS)₂-SiPc = C₅₀H₅₈N₈O₂Si₃, and densities: P3HT = 1.1 g/cc, PC₆₁BM = 1.5 g/cc, (3PS)₂-SiPc = 1.25 g/cc. All processing steps of STXM data are carried out using aXis2000 software (<http://unicorn.chemistry.mcmaster.ca/aXis2000.html>).



Scheme S1. Synthetic pathway of (3PS)₂-SiPc from diiminoisoindoline.

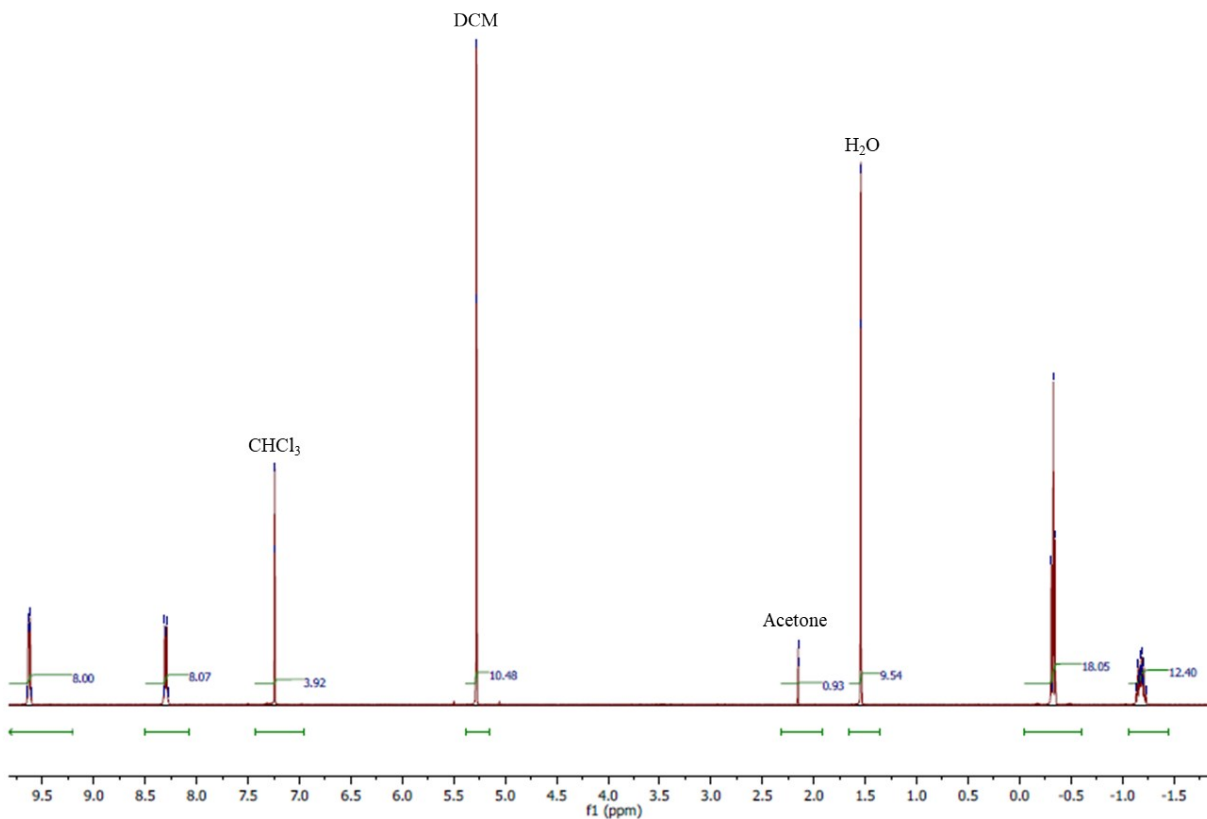


Figure S1. ^1H NMR spectrum of $(3\text{PS})_2\text{-SiPc}$ in CDCl_3

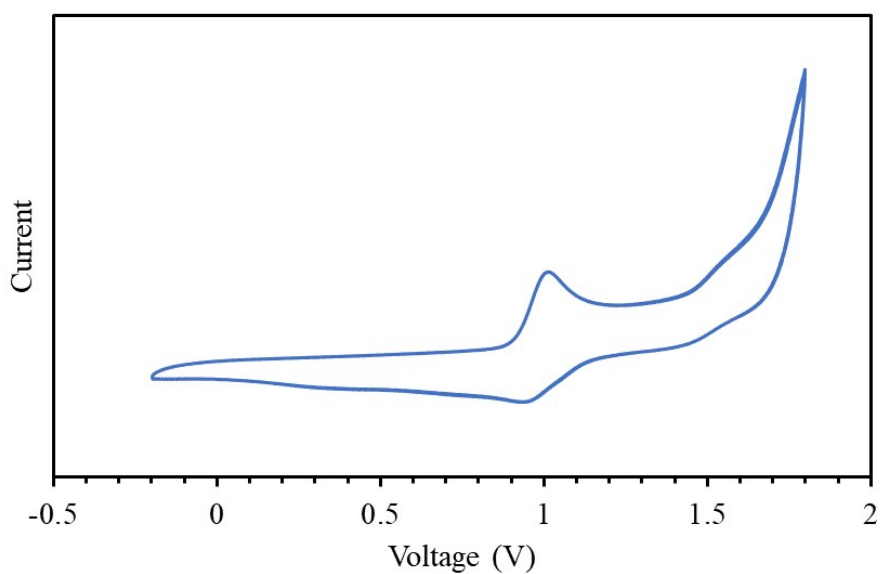


Figure S2. Cyclic voltammogram of $(3\text{PS})_2\text{-SiPc}$ in dichloromethane with tetrabutylammonium perchlorate supporting electrolyte and a scan rate of 0.1 V s^{-1} .

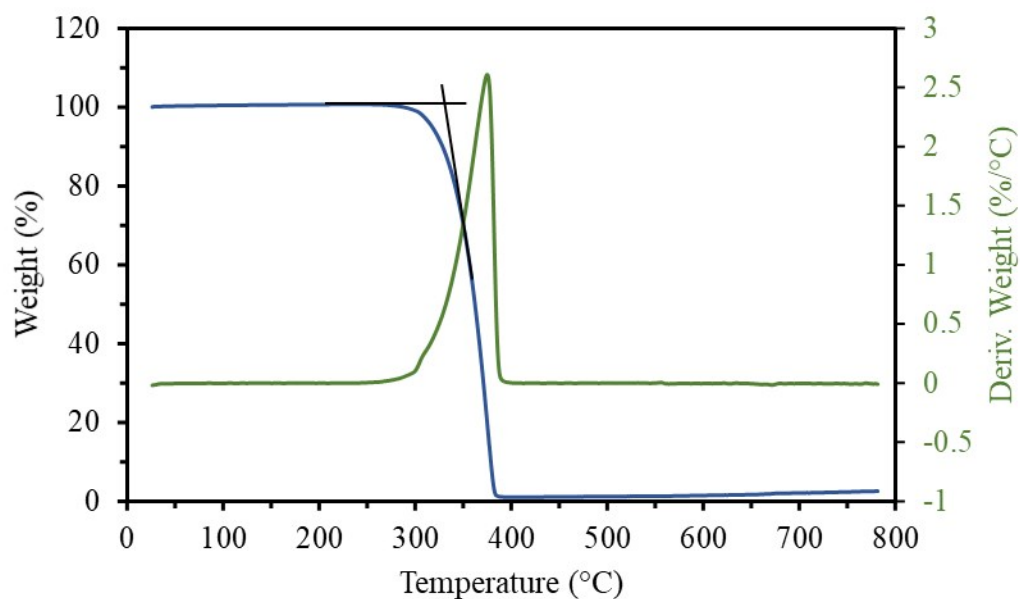


Figure S3. Thermogravimetric analysis (TGA) of (3PS)₂-SiPc measured at a ramp rate of 10 °C min⁻¹.

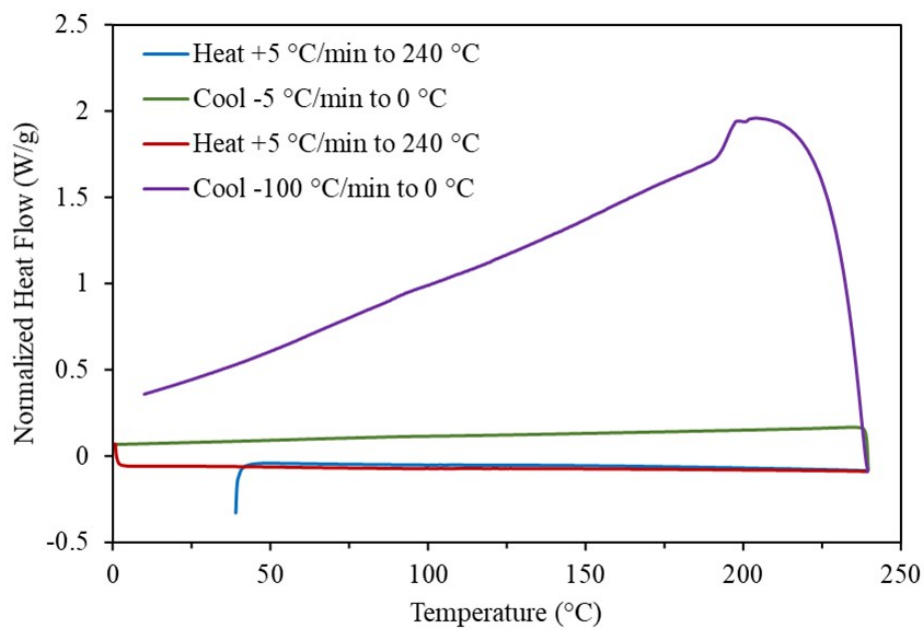


Figure S4: Differential scanning calorimetry (DSC) obtained from (3PS)₂-SiPc powder.

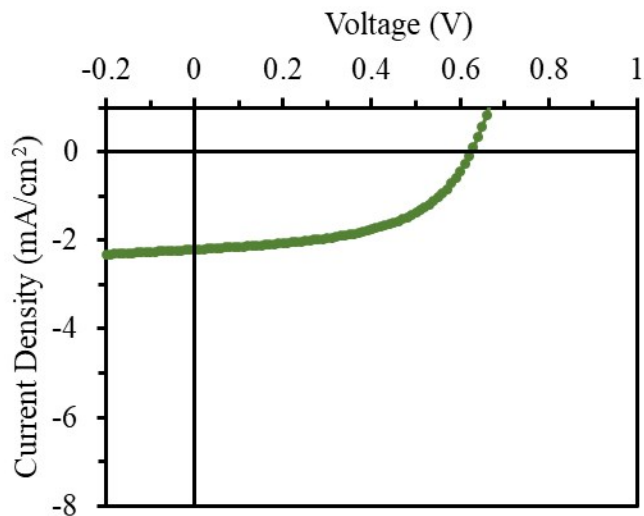


Figure S5: Characteristic current density-voltage (J - V) curve measured under 1000 W/m² AM1.5G irradiation for inverted α -6T (60 nm) / (3PS)₂-SiPc (30 nm) PHJ devices.

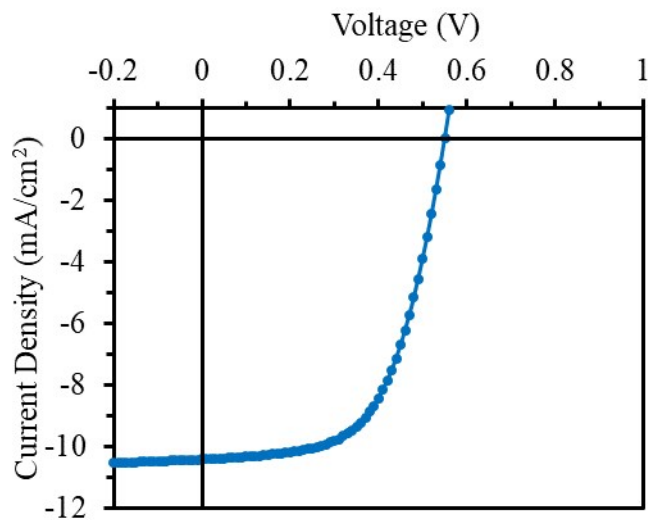


Figure S6: Characteristic current density-voltage (J - V) curve measured under 1000 W/m² AM1.5G irradiation for inverted P3HT/PC₆₁BM/(3PS)₂-SiPc (1:0.8:0.07) BHJ devices.

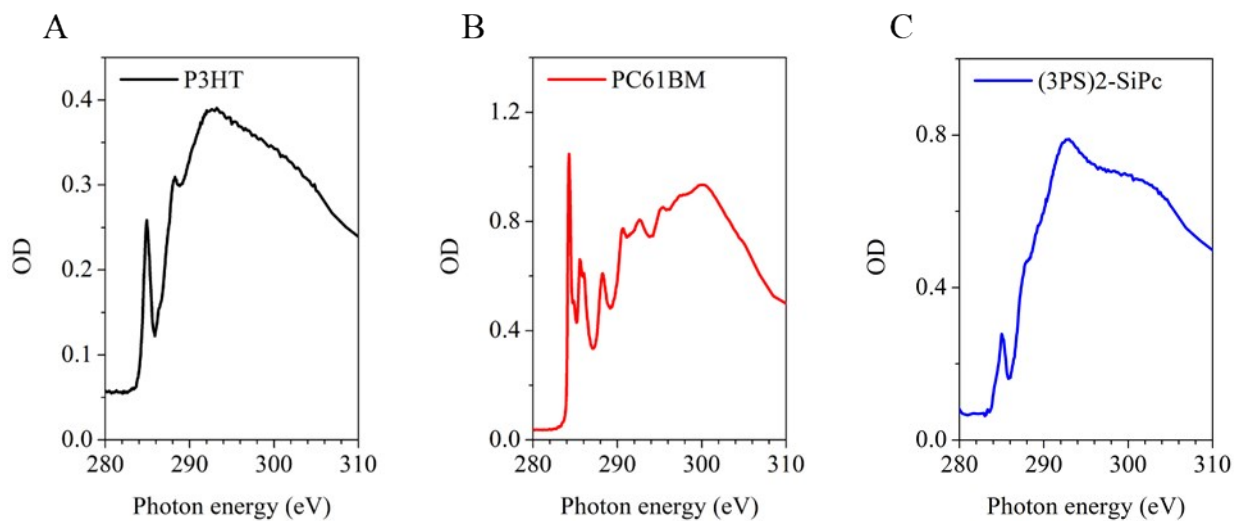


Figure S7: NEXAFS spectra at C K-edge of reference films of (A) P3HT, (B) PC₆₁BM and (C) (3PS)₂-SiPc.

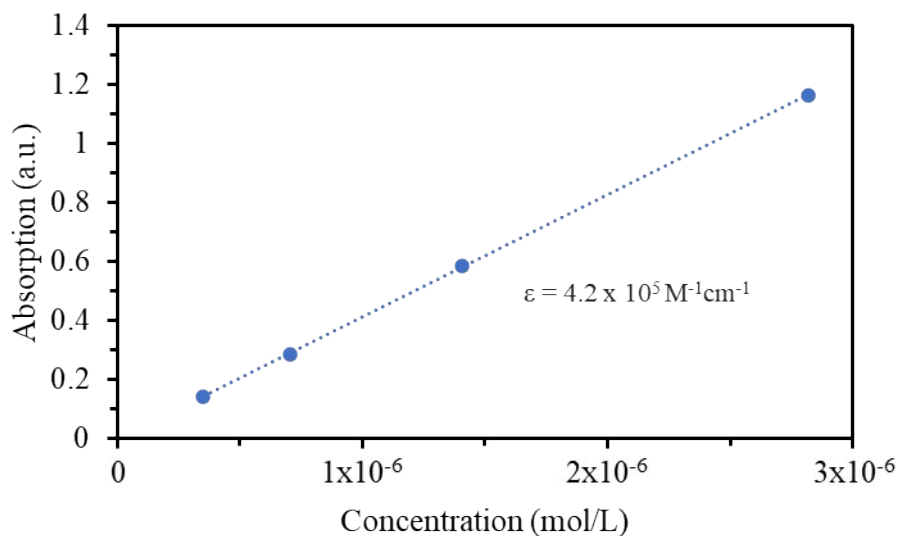


Figure S8. Determination of the molar extinction coefficient of (3PS)₂-SiPc in toluene solution according to the Beer-Lambert law.

- (1) Lowery, M. K.; Starshak, A. J.; Esposito, J. N.; Krueger, P. C.; Kenney, M. E. Dichloro(Phthalocyanino)Silicon. *Inorg. Chem* **1965**, 128.
- (2) Gessner, T.; Sens, R.; Ahlers, W.; Vamvakaris, C. Preparation of Silicon Phthalocyanines and Germanium Phthalocyanines and Related Substances. US 2010/0113767 A1, 2010.