A Modular Molecular Framework for Utility in Small-Molecule Solution-Processed Organic Photovoltaic Devices

*Gregory C. Welch[1], Louis A. Perez[1,4], Corey V. Hoven[1], Yuan Zhang[1], Xuan-Dung Dang[1], Alexander Sharenko[1], Michael F. Toney[6], Edward J. Kramer[4,5], Thuc-Quyen Nguyen [1,2,3], and Guillermo C. Bazan[1,2,3,4]**

[1]Center for Energy Efficient Materials
[2]Center for Polymers and Organic Solids
[3]Department of Chemistry & Biochemistry,
[4]Department of Materials,
[5]Department of Chemical Engineering,
University of California, Santa Barbara, California, 93106.

[6]Stanford Synchrotron Radiation Lightsource
Menlo Park, CA 94025, USA

bazan@chem.ucsb.edu

Supporting Information

Table of Contents

Materials and Methods

General Details: Preparations were carried out on a bench top or under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an Vacuum Atmospheres inert atmosphere glove box. Toluene was dried over sodium/benzophenone, distilled under vacuum, and stored over molecular sieves (4 Å). Chloroform was dried over calcium hydride, distilled under vacuum, and stored over molecular sieves (4 Å). Molecular sieves (4 Å) were purchased from Aldrich Chemical Company and dried at 140 ºC under vacuum for 24 hours prior to use. Deuterated solvents were dried over CaH_2 (CD_2Cl_2, $CDCl_3$). All reactants and reagents are commerically available and used as received, unless otherwise noted.

Materials: Compound 5,5'-*Bis*(trimethylstannyl)-3,3'-di-2-ethylhexylsilylene-2,2'-bithiophene {DTS($SnMe_3$)$_2$}[1] and 5'-Hexyl-2,2'-bithiophene-5-trimethylstannane[2] were prepared by methods similar to those reported in the literautre. Compounds 5,5'-dibromo-3,3'-di-2-ethylhexylsilylene-2,2'-bithiophene (DTS-Br_2) and 4,7-dibromo-pyridal[2,1,3]thiadiazole (PTBr_2) were purchased from Luminescence Technology Corp. (Lumtec) and used as received. $PC_{71}BM$ was purchased from Solenne BV and used as recieved. 2-(tributylstannyl)thiophene was purscahsed from Aldrich and used as recived. 2-(tributylstannyl)benzothiophene was purchased from Synthonix and used as recieved. The HIL, Plextronics Plexcore OC AQ-1300 was purchased directly from Plextronics and used as received. The work function of ITO/HIL (-5.35eV) was determined by ultraviolet photoemission (UPS) spectrosocopy.

NMR: ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy spectra were recorded on a Bruker Avance-500 MHz spectrometer at 25°C unless otherwise noted. ^1H and ^{13}C NMR spectra are referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. Chemical shifts are reported in ppm and coupling constants in Hz as absolute values. DEPT, ^1H-^1H, and ^1H-^{13}C correlation experiments were completed for assignment of the carbon atoms. ^1H-^1H NOE experiments were carried out with a mixing time of 0.8 seconds.

UV-vis: UV-visible spectroscopy were recored using wither a Beckman Coulter DU 800 series or Perkin Elmer Lambda 750 spectrophotometer at room temperature unless otherwise noted. All solution UV-vis experiments were run in $CHCl_3$ under an N_2 atmosphere in telfon capped 1mm quartz cuvettes. Films were prepare by spin-coating solutions from $CHCl_3$ onto quartz or ITO/HIL substrates.

CHN: Combustion analyses were performed by the MSI analytical lab at the University of California, Santa Barbara.

DSC: Differential scanning calorimetry (DSC) was determined using a TA Instruments DSC (Model Q-20) with about 5 mg samples at a rate of 10 °C / min in the temperature range of –0 to 300 °C.

Electrochemistry: All electrochemical measurements were performed using CHI instrument model 730B in a standard three-electrode, one compartment configuration equipped with Ag/AgCl electrode, Pt wire and Glassy carbon electrode (dia. 3 mm), as the pseudo reference, counter electrode and working electrode respectively. Glassy carbon electrodes were polished with alumina. The cyclic voltammetry (CV) experiments were performed in anhydrous dichloromethane solution with ~0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte at scan rate 50 mV/s unless otherwise stated. All electrochemical solutions were purged with dry Ar_2 for 5 minutes to deoxygenate the system. Under these conditions, a Fc/Fc^+ standard was calibrated to be ~0.46 V.[3,4] Solution CV measurements were carried out with a small molecule concentration of ~1mg/mL in CH_2Cl_2. The HOMO and LUMO levels were obtained by correlating the onsets ($E_{ox}^{Fc/Fc+}$, $E_{rd}^{Fc/Fc+}$) to the normal hydrogen electrode (NHE), assuming HOMO of Fc/Fc^+ to be 4.88 eV.[3,4]

X-ray Scattering Measurements. Grazing incidence X-ray wide angle scattering (GIWAXS) spectra were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) beamline 11-3 with an X-ray wavelength of 0.9752 Å, at a 40 cm sample to detector distance, with a 2D detector, MAR 2300. The incidence angle, 0.12 and 0.14°, was chosen to be greater than the critical angle of the film but less than the critical angle of the substrate so that the measurement sampled the entire film thickness, but minimized contributions from the substrate. Samples were probed with an exposure time of 20 s while under a helium environment to minimize beam damage and reduce diffuse scattering. The measurements were calibrated using a LaB_6 standard. Samples were prepared by spin-casting a $CHCl_3$ solution of **6** or **6**:$PC_{71}BM$ at 2500 rpm onto a silicon wafer coated with HIL (Plextronics Plexcore OC AQ-1300). The HIL was applied by spin-casting at 3000 rpm followed by annealing at 140 °C for 30 minutes.

Characterization of Film Composition. Dynamic secondary ion mass spectrometry (DSIMS) was performed with a Physical Electronics 6650 dynamic secondary mass ion spectrometer using a 3 keV, 40 nA beam of O_2^+ ions rastered over a 0.09 mm^2 region. Charge neutralization was accomplished using a static, defocused, 1 keV electron beam. Negative ions of H, $^2H(D)$, C, ^{34}S and Si were monitored as a function of time from an electrically gated region in the center of the sputtered crater. This region is less than 15% of the rastered area. Prior to SIMS analysis, a sacrificial layer PS thin film (~100 nm thick) was spun-cast onto a silicon substrate with a thermal oxide grown layer, dipped into a 5% HF solution and then floated off in a distilled water bath, and picked up onto the specimen surface. The samples were then dried for at least 12 hr under high vacuum. This sacrificial layer was used to calibrate the etch rate of the SIMS and also allow for the beam to equilibrate before analyzing the active layer. The sample chamber was cooled with $N_2(l)$. All samples were spun on ITO substrates coated with the HIL that was annealed for 40 min at 140 °C, as suggested by the manufacturer to remove residual solvent, before addition of the active matrix layer. Sample fabrication and film compositions were identical to optimized device conditions.

X-ray Data Collection, Reduction, Solution and Refinement: Single crystals were mounted on a glass fiber and transferred to a Bruker Kappa APEX II CCD diffractometer. The APEX2 software[5] program was used to determine the unite cell parameters and data collection. The data were collected at 100K using Oxford Cryostream Plus system. The raw frame data were processed using APEX2 program. The absorption correction was applied using program

SADABS.[6] Subsequent calculations were carried out using SHELXTL[7] program. All non-H atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors.

Solubility Measurements: The solubility of compound **4** in chloroform was determined as follows: A saturated solution of **4** (~50mg/mL) was stirred for 48 hours at room temperature then allowed to stand still for 12 hours. The slurry was then filtered through a 0.45 μm PTFE filter. The filtrate is assumed to be a saturated solution of **4** in chloroform. A 50 μL aliquot was then diluted to 10mL with chloroform. The UV-vis absorption spectrum was acquired and the concentration determined using a standard calibration curve. The calibration curve was prepared by measuring the absorbance of 3 solutions of **4** in chloroform with a known concentration and plotting λmax vs concentration, in each case a linear relationship was observed. The solubility of **5** and **6** was determined in a similar fashion.

Calculations: All calculations were performed using the Gaussian 03 program.[8] Optimized gas-phase ground state structures were calculated at the density functional theory (DFT) level, using the hybrid B3LYP[9] exchange-correlation functional and the split-valence 6-31G(d,p) basis set, i.e., B3LYP/6-31G(d,p). Frequency calculations were carried out to ensure that the geometries obtained corresponded to minima and not saddle points (i.e. global minima). California NanoSystems Institute at UCSB is acknowledged for computational resources.

Solar Cell Device Fabrication: SM-BHJ photovoltaic devices were fabricated using a standard device architecture of ITO/HIL/**6**:PC$_{71}$BM/Al. Indium tin oxide (ITO) substrates were sonicated in acetone, isoproanol, dried in an oven and then treated by an UV/ozone cleaner. A 50 nm hole injection layer (HIL) (Plextronics Plexcore OC AQ-1300) was filtered through a 0.45 µm pore size Whatman PVDF filter, spin coated on top of the ITO substrate (3000 rpm for 60 seconds), and thermally annealed at 140 °C for 30 minutes. A solution of filtered (1 µm Whatman PTFE filter) **6**:PC$_{71}$BM with varied ratios (30:70, 60:40, 50:50, 40:60, 70:30) in chloroform was spin coated onto the ITO/HIL substrate at varied spin speeds (1500, 2500, 3500 rpm) for different thicknesses. The **6**:PC$_{71}$BM solution concentrations were 2% w/v. The PC$_{71}$BM was 99% pure and used as received from Solenne, and anhydrous chloroform was used as received from Sigma-Aldrich Inc. The **6**:PC$_{71}$BM films thicknesses were determined by profilometry. Devices had a 13 mm^2 area Al cathode evaporated on top of the **6**:PC$_{71}$BM film in a vacuum (~10^{-6} torr) at rate of 1 Å sec^{-1} for the first 10 nm and then 2.5 Å sec^{-1} with a total thickness of approximately 100 nm. All fabrication and testing were carried out inside a nitrogen atmosphere drybox.

Solar Cell Device Testing. Device *J-V* curves were measured with a Keithley 2602 source-measure unit while illuminated with a simulated 100 mWcm^{-2}AM 1.5G light source using a 300W Xe arc lamp with an AM1.5 global filter. Solar-simulator illumination intensity was measured using a standard silicon photovoltaic with a protective KG1 filter calibrated by the National Renewable Energy Laboratory. IPCE spectra measurements were made with a 75W Xe source, monochromater, optical chopper, lock-in amplifier, and a National Institute of Standards and Technology traceable silicon photodiode for monochromatic power-density calibration. Mismatch factors of the integrated IPCE for the devices were calculated to be less than 4%.

Diode Fabrication and Testing: Diode Single-carrier devices were fabricated using the architectures of ITO/HIL/**6**:PC$_{71}$BM/Au for the hole-only and ATPMS (3-aminopropyl-trimethoxysilane)-treated ITO/HIL/**6**:PC$_{71}$BM/Al for the electron-only diodes. Active layers were fabricated based upon the optimized 60:40 **6**:PC$_{71}$BM devices. I-V curves for the devices were obtained using a Keithley 4200 Semiconductor Characterization System under Nitrogen. The μ_{diode} mobilities were extracted by fitting the current density-voltage curves using the Mott-Gurney relationship (space charge limited current). $J=(9/8)\ \varepsilon\varepsilon_0\mu_{SCLC}(V^2/L^3)$. Where, J is the current density, ε_0 the vacuum permittivity, ε_0 the dielectric constant of active layer, μ_{SCLC} the charge carrier mobility, V the potential across the device and L is the thickness of the organic film. Film thicknesses were measured using an AMBIOS Technology XP-100 profilometer.

AFM and pcAFM: Atomic force microscopic characterization of the photoactive layers is performed in a nitrogen flow cell by using an Asylum Research MFP-3D. Experimental details can be found in the previous papers.[10] For tapping mode AFM measurements, silicon probes with spring constants of ~ 3 N/m and resonant frequencies of 75 KHz (Budget Sensors) were used. For both conductive and photoconductive AFM, gold-coated AFM tips (Budget Sensors) were used for this study. The same setup as conductive AFM is photoconductive AFM, but the samples are illuminated from a white light source (300 W Xe lamp). The white light was focused on the sample surface through the inverted optical microscope from the bottom and then the tip was positioned at the center of the light spot using a camera. The voltage is applied to the substrate, and the current is recorded by internal preamplifier (Asylum Research ORCA model, sensitivity 0.2 nA/V).

Synthesis

Synthesis of *7-bromo-4-thienyl[1,2,5]thiadiazolo[3,4-*c*]pyridine* (1): A 20 mL microwave tube was charged with 4,7-dibromo-pyridal[2,1,3]thiadiazole (PTBr$_2$, 750 mg, 2.56 mmol), 2-(tributylstannyl)thiophene (Bu$_3$Sn-Th, 1.0 g, 2.65 mmol), Pd(PPh$_3$)$_4$ (75 mg, 0.06 mmol), toluene (15 mL), and sealed with a teflon cap. The reaction mixture was heated to 120°C for 3 minutes, 140°C for 3 minutes, and 175°C for 60 minutes, using a Biotage microwave reactor. Upon cooling, the residue was passed through a short silica plug eluting with CHCl$_3$ (500 mL). All volatiles were removed *in vacuo* to give the crude product as a orange solid. The solid was slurried in MeOH (300 mL), sonicated for 10 minutes, and filtered. The solid was washed with copious amounts of MeOH and then dried under vacuum for 24 hours. The product was collected as an orange solid. Recovered yield: 645 mg (85%). **^{1}H NMR** (CD$_2$Cl$_2$): δ 8.67 (dd, $^3J_{H\text{-}H}$ = 4 Hz, $^4J_{H\text{-}H}$ = 1 Hz 1H, Th-C*H*), 8.63 (s, 1H, PT-C*H*), 7.64 (dd, $^3J_{H\text{-}H}$ = 4 Hz, $^4J_{H\text{-}H}$ = 1 Hz 1H, Th-C*H*), 7.26 (dd, $^3J_{H\text{-}H}$ = 5 Hz, $^3J_{H\text{-}H}$ = 4 Hz 1H, Th-C*H*), **^{13}C NMR** (CD$_2$Cl$_2$): 156.90, 148.46, 147.96 (s, quaternary), 146.18 (s, *C*H), 141.65 (s, quaternary), 133.09 (s, *C*H), 131.74 (s, *C*H), 129.57 (s, *C*H), 108.91 (s, quaternary). **Anal. Calcd.** for $C_9H_4BrN_3S_2$: C, 36.25; H, 1.35; N, 14.09. Found: C, 36.6; H, 1.35; N, 13.8 %. **HRMS (EI)** *m/z*, calcd for $C_{13}H_7N_3S_3$ (M^+): 298.9; found: 299. **Single Crystal X-Ray Diffraction**: Crystals grown from slow evaporation of dilute CH$_2$Cl$_2$ solution. Monoclinic. P2(1)/c. Cell: a = 4.6471(8) Å, b = 20.920(3) Å, c = 10.6360(18) Å, beta = 92.743(3)°. V=1032.8(3) Å^3. R1 = 0.0703, wR2 = 0.1047.

Synthesis of 4-(benzo[b]thiophen-2-yl)-7-bromo-[1,2,5]thiadiazolo[3,4-c]pyridine (2): ***Suzuki coupling procedure:*** In a N$_2$ filled glove box a 20 mL glass tube was charged with 4,7-dibromo-pyridal[2,1,3]thiadiazole (PTBr$_2$, 510 mg, 1.73 mmol), Na$_2$CO$_3$ (1g), Pd(PPh$_3$)$_4$ (50 mg, 0.04 mmol), anhydrous THF (6 mL), and sealed with a teflon cap. To this mixture was added de-gassed de-ionized water (5mL) under Ar and the mixture stirred for 5 minutes. Benzothiophene-2-boronic acid (340 mg, 1.9 mmol) in anhydrous THF (6 mL) was then added to the reaction mixture which was subsequently purged with Ar for 5 minutes. The reaction mixture was heated to 90°C and vigorously stirred for 16 hours. Upon cooling the reaction mixture was poured into 500 mL of a 1:1 MeOH/H$_2$O solution and stirred for 20 minutes. The precipitate that formed was collect by filtration and washed with 500 mL of a 2:1 MeOH/H$_2$O solution and 100 mL of MeOH (product is slightly soluble in MeOH). The crude product was purified on silica-gel by flash chromatography eluting with a hexaens/CHCl$_3$ gradient. The solid was dried under high vacuum for 48 hours. The product was collected as an orange solid. Recovered yield: 410 mg (68%). ***Stille coupling procedure:*** In a N$_2$ filled glove box a 20 mL glass tube was charged with 4,7-dibromo-pyridal[2,1,3]thiadiazole (PTBr$_2$, 600mg, 2.03 mmol), 2-(tributylstannyl)benzothiophene (Bu$_3$Sn-BzTh, 860 mg, 2.0 mmol), Pd(PPh$_3$)$_4$ (25 mg, 0.02 mmol), toluene (10 mL), and sealed with a teflon cap. The reaction mixture was heated to 120°C for 3 minutes, 140°C for 3 minutes, and 175°C for 60 minutes, using a Biotage microwave reactor. Upon cooling, the residue was passed through a short silica plug eluting with CHCl$_3$ (1% Et$_3$N) (500 mL). All volatiles were removed *in vacuo* to give the crude product as an orange solid. The solid was slurried in MeOH (300 mL), sonicated for 10 minutes, and filtered. The solid was washed with copious amounts of MeOH and then dried under vacuum for 24 hours. The product was collected as an orange solid. Recovered yield: 580 mg (82%). **^{1}H NMR** (CDCl$_3$): δ 8.99 (s, 1H, PT-C*H*), 8.74 (s, 1H, Th-C*H*), 7.94 (d, $^3J_{H\text{-}H}$ = 8 Hz, 1H Bz-C*H*), 7.91

(d, ${}^3J_{H\text{-}H}$ = 8 Hz, 1H Bz-C*H*), 7.74 (t, ${}^3J_{H\text{-}H}$ = 8 Hz, 1H, Bz-C*H*), 7.71 (t, ${}^3J_{H\text{-}H}$ = 8 Hz, 1H, Bz-C*H*). **^{13}C{^{1}H} NMR** ($CDCl_3$): 156.6, 148.4, 147.8 (s, quaternary), 145.7 (s, *C*H), 141.7, 141.1, 140.9 (s, quaternary), 130.3 (s, *C*H), 126.7 (s, *C*H), 125.5 (s, *C*H), 125.1 (s, *C*H), 122.5 (s, *C*H), 109.7 (s, quaternary). **Anal. Calcd.** for $C_{13}H_6BrN_3S_2$: C, 44.84; H, 1.74; N, 12.07. Found: C, 45.0; H, 1.46; N, 11.8 %.

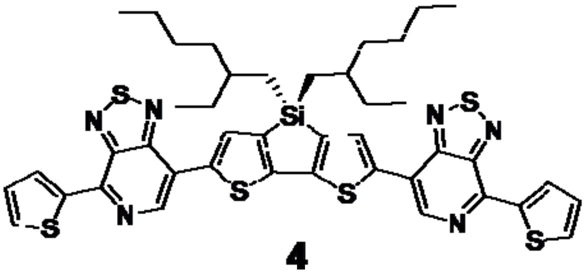
Synthesis of 7-bromo-4-(5-(5-hexylthiophen-2-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine (3): ***Suzuki coupling procedure:*** In a N_2 filled glove box a 20 mL glass tube was charged with 4,7-dibromo-pyridal[2,1,3]thiadiazole ($PTBr_2$, 550mg, 1.86 mmol), Na_2CO_3 (1g), $Pd(PPh_3)_4$ (50 mg, 0.04 mmol), anhydrous THF (10 mL), and sealed with a teflon cap. To this mixture was added de-gassed de-ionized water (5 mL) under Ar and the mixture stirred for 5 minutes. 5'-Hexyl-2,2'-bithiophene-5-boronic acid pinacol ester (725 mg, 1.92 mmol) in anhydrous THF (5 mL) was then added to the reaction mixture which was subsequently purged with Ar for 5 minutes. The reaction mixture was heated to 90°C and vigorously stirred for 16 hours. Upon cooling the reaction mixture was poured into 500 mL of a 1:1 $MeOH/H_2O$ solution and stirred for 20 minutes. The precipitate that formed was collect by filtration and washed with 500 mL of a 2:1 $MeOH/H_2O$ solution and 100 mL of MeOH. The crude product was purified on silica-gel by flash chromatography eluting with a hexanes/$CHCl_3$ gradient. After fraction collection and solvent removal the resulting red solid was dried under high vacuum for 48 hours. The product was collected as red solid. Recovered yield: 555 mg (65%). ***Stille coupling procedure:*** In a N_2 filled glove box a 5 mL glass tube was charged with 4,7-dibromo-pyridal[2,1,3]thiadiazole ($PTBr_2$, 550mg, 1.86 mmol), 5'-Hexyl-2,2'-bithiophene-5-trimethylstannane (770 mg, 1.86 mmol), $Pd(PPh_3)_4$ (25 mg, 0.02 mmol), toluene (4 mL), and sealed with a teflon cap. The reaction mixture was heated to 120°C for 3 minutes, 140°C for 3 minutes, and 175°C for 60 minutes, using a Biotage microwave reactor. Upon cooling, the residue was passed through a short silica plug eluting with $CHCl_3$ (1% Et_3N) (500 mL). All volatiles were removed *in vacuo* to give the crude product as a red solid. The product was slurried in MeOH (200 mL), filtered, washed with MeOH (200 mL), and dried under high vacuum for 24 hours. The product was collected as red solid. Recovered yield: 750 mg (87%). **^{1}H NMR** ($CDCl_3$): δ 8.62 (s, 1H, PT-C*H*), 8.56 (d, 1H, ${}^3J_{\mathrm{H\text{-}H}}$ = 5 Hz, Th-C*H*), 7.21 (m, 1H, Th-C*H*), 7.17 (m, 1H, Th-C*H*), 6.74 (m, 1H, Th-C*H*), 2.83 (d, 2H, ${}^3J_{\mathrm{H\text{-}H}}$ = 8 Hz, Th-$\mathrm{C}H_2$),1.71 (m, 2H, $\mathrm{C}H_2$), 1.41 (m, 2H, $\mathrm{C}H_2$), 1.33 (m, 4H, $\mathrm{C}H_2$), 0.92 (m, 3H, $\mathrm{C}H_3$). **^{13}Ca NMR** ($CDCl_3$): 147.44, 147.26 (s, quaternary), 145.85 (s, *C*H), 143.86, 138.48, 134.32 (s, quaternary), 133.79 (s, *C*H), 128.63 (s, quaternary), 125.00, 124.58 (s, *C*H), 124.07 (s, quaternary), 31.57 (s, $\mathrm{C}H_2$), 31.52 (s, $\mathrm{C}H_2$), 30.30 (s, $\mathrm{C}H_2$), 28.80 (s, $\mathrm{C}H_2$), 22.61 (s, $\mathrm{C}H_2$), 14.12 (s, $\mathrm{C}H_3$). **Anal. Calcd.** for $C_{19}H_{18}BrN_3S_3$: C, 49.13; H, 3.91; N, 9.05. Found: C, 48.8; H, 3.60; N, 9.01 %.

Synthesis of Synthesis of 5,5'-*Bis*{(4-(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine}-3,3'-di-2-ethylhexylsilylene-2,2'-bithiophene (*4*): A 20 mL microwave tube was charged with 5,5'-*Bis*(trimethylstannyl)-3,3'-di-2-ethylhexylsilylene-2,2'-bithiophene {$DTS(SnMe_3)_2$, 961mg, 1.29 mmol}, 7-bromo-4-thienyl[1,2,5]thiadiazolo[3,4-c]pyridine (1, 770 mg, 2.58 mmol), $Pd(PPh_3)_4$ (0.050 g, 0.04 mmol), toluene (15 mL), and sealed with a teflon cap. The reaction mixture was heated to 120°C for 3 minutes, 140°C for 3 minutes, and 175°C for 60 minutes, using a Biotage microwave reactor. Upon cooling, the residue was passed through a short silica plug eluting with $CHCl_3$ (1% Et_3N) (500 mL). All volatiles were removed *in vacuo* to give the crude product as a purple solid. The material was then loaded onto silica-gel and purified by flash chromatography using a hexanes/$CHCl_3$ (1% Et_3N) gradient. After fraction collection and solvent removal a purple solid was obtained. The solid was slurried in MeOH (300 mL), sonicated for 10 minutes, and filtered. The solid was washed with copious amounts of MeOH and then dried under vacuum for 24 hours. The product was collected as purple solid. Recovered yield: 980 mg (88%). **^{1}H NMR** (CD_2Cl_2): δ 8.74 (s, 2H, PT-C*H*), 8.63 (d, $^3J_{H\text{-}H}$ = 4 Hz, 2H Th-C*H*), 8.25 (t, 2H, SDT-C*H*), 7.60 (d, $^3J_{H\text{-}H}$ = 4 Hz, 2H Th-C*H*), 7.27 (dd, $^3J_{H\text{-}H}$ = 5 Hz, $^3J_{H\text{-}H}$ = 4 Hz 2H, Th-C*H*), 1.59 (h, $^3J_{H\text{-}H}$ = 6 Hz, 2H, C*H*), 1.38 (m, 4H, CH_2), 1.32 (m, 4H, CH_2), 1.25 (m, 8H, CH_2), 1.16 (m, 4H, SiCH_2), 0.86 (t, $^3J_{H\text{-}H}$ = 8 Hz, 6H, CH_3), 0.83 (t, $^3J_{H\text{-}H}$ = 8 Hz, 6H, CH_3). **^{13}C{^{1}H} NMR** (CD_2Cl_2): 155.06, 151.01, 148.44, 145.97, 142.57 (s, quaternary), 140.42 (s, *C*H), 139.02, 132.07 (s, C*H*), 131.79 (s, SDT-C*H*), 130.81 (s, C*H*), 129.37 (s, C*H*), 121.39 (s, quaternary), 36.70 (s, C*H*), 36.40 (s, SiCH_2), 29.59 (s, 2xCH_2), 23.62 (s, CH_2), 18.28 (s, CH_2), 14.54 (s, CH_3), 11.24 (s, CH_3). **Anal. Calcd.** for $C_{42}H_{44}N_6S_6Si$: C, 59.12; H, 5.20; N, 9.85. Found: C, 59.0; H, 4.31; N, 9.32 %. **HRMS (EI)** *m/z*, calcd for $C_{42}H_{44}N_6S_6Si$ (M^+): 852; found: 852. **Absorbance**: ($CHCl_3$) λ_{max} = 582 nm, λ_{onset} = 678 nm, ε = 39000 $cm^{-1}M^{-1}$. (As Cast Film) λ_{max} = 604, 652 nm, λ_{onset} = 736 nm. **Single Crystal X-Ray Diffraction**: Crystals grown from slow evaporation of a saturated Beznene/CH_2Cl_2. Monoclinic. P2(1)/n. Cell: a = 18.817(4)Å, b = 7.9805(17) Å, c = 28.301(6) Å, beta = 107.018(3)°. V= 4063.8(15) Å^3. R1 = 0.0841, wR2 = 0.1942.

Synthesis of 5,5'-*Bis*{(4-(benzo[b]thiophen-2-yl))-[1,2,5]thiadiazolo[3,4-c]pyridine}-3,3'-di-2-ethylhexylsilylene-2,2'-bithiophene (*5*): In a N_2 filled glove box a 20 mL microwave tube was charged with 5,5'-*Bis*(trimethylstannyl)-3,3'-di-2-ethylhexylsilylene-2,2'-bithiophene {DTS($SnMe_3$)$_2$, 395 mg, 0.53 mmol}, 4-(benzo[b]thiophen-2-yl)-7-bromo-[1,2,5]thiadiazolo[3,4-c]pyridine (2, 374 mg, 1.07 mmol), Pd(PPh_3)$_4$ (0.025 g, 0.02 mmol), toluene (15 mL), and sealed with a teflon cap. The reaction mixture was heated to 120°C for 3 minutes, 140°C for 3 minutes, and 175°C for 60 minutes, using a Biotage microwave reactor. Upon cooling, the residue was passed through a short silica plug eluting with $CHCl_3$ (1% Et_3N) (500 mL). All volatiles were removed *in vacuo* to give the crude product as a purple solid. The material was then loaded onto silica and purified by flash chromatography using a hexanes/$CHCl_3$ (1% Et_3N) gradient. After fraction collection and solvent removal a purple solid was obtained. The solid was slurried in MeOH (300 mL), sonicated for 10 minutes, and filtered. The solid was washed with copious amounts of MeOH and then dried under vacuum for 24 hours. The product was collected as purple solid. Recovered yield: 350 mg (77%). **^{1}H NMR** ($CDCl_3$): δ 8.77 (s, 2H, PT-C*H*), 8.64 (m, 2H Th-C*H*), 8.27 (t, 2H, SDT-C*H*), 7.88 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H Bz-C*H*), 7.85 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H Bz-C*H*), 7.34 (m, $^3J_{H\text{-}H}$ = 8 Hz, 4H, Bz-C*H*), 1.65 (h, $^3J_{H\text{-}H}$ = 6 Hz, 2H, C*H*), 1.43 (m, 4H, CH_2), 1.38 (m, 4H, CH_2), 1.31 (m, 8H, CH_2), 1.19 (m, 4H, SiCH_2), 0.92 (t, $^3J_{H\text{-}H}$ = 8 Hz, 6H, CH_3), 0.89 (t, $^3J_{H\text{-}H}$ = 8 Hz, 6H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$): 154.17, 150.75, 148.09, 145.50, 145.49, 145.08, 141.74 (s, quaternary), 141.20 (s, *C*H), 139.65 (s, quaternary), 138.60 (s, C*H*), 131.71 (m, SDT-C*H*), 128.82 (s, C*H*), 126.03 (s, quaternary), 125.04 (s, C*H*), 124.59 (s, quaternary), 122.39 (s, C*H*), 121.27 (s, C*H*), 36.13 (s, SiCH_2), 35.89 (s, C*H*), 29.10 (s, 2xCH_2), 23.11 (s, CH_2), 17.81 (s, CH_2), 14.27 (s, CH_3), 10.93 (s, CH_3).**Anal. Calcd.** for $C_{50}H_{48}N_6S_6Si$: C, 62.99; H, 5.07; N, 8.81. Found: C, 62.8; H, 4.59; N, 8.82 %. **HRMS (EI)** *m/z*, calcd for $C_{50}H_{48}N_6S_6Si$ (M^+): 952; found: 952. **Absorbance**: ($CHCl_3$) λ_{max} = 594 nm, λ_{onset} = 696 nm, ε = 40000 $cm^{-1}M^{-1}$. (As Cast Film) λ_{max} = 620, 664 nm, λ_{onset} = 758 nm.

Synthesis of 5,5'-*Bis*{(4-(5-hexylthiophen-2-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine}-3,3'-di-2-ethylhexylsilylene-2,2'-bithiophene (6): In a N_2 filled glove box a 20 mL microwave tube was charged with 5,5’-*Bis*(trimethylstannyl)-3,3’-di-2-ethylhexylsilylene-2,2’-bithiophene {DTS(SnMe$_3$)$_2$, 617 mg, 0.83 mmol}, 7-bromo-4-(5-(5-hexylthiophen-2-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine (3, 770 mg, 1.66 mmol), Pd(PPh$_3$)$_4$ (0.025 g, 0.02 mmol), toluene (15 mL), and sealed with a teflon cap. The reaction mixture was heated to 120°C for 3 minutes, 140°C for 3 minutes, and 175°C for 60 minutes, using a Biotage microwave reactor. Upon cooling, the residue was passed through a short silica plug eluting with CHCl$_3$ (5% Et$_3$N) (500 mL). All volatiles were removed *in vacuo* to give the crude product as a purple solid. The material was then loaded onto silica and purified by flash chromatography using a hexanes/CHCl$_3$ (5% Et$_3$N) gradient. After fraction collection and solvent removal a purple solid was obtained. *Purification by silica-gel column chromatography was carried out twice to ensure purity for OPV device fabrication.* The solid was slurried in MeOH (300 mL), sonicated for 10 minutes, and filtered. The solid was washed with copious amounts of MeOH and then dried under vacuum for 24 hours. The product was collected as purple solid. Recovered yield: 700 mg (71%). **^{1}H NMR** (CDCl$_3$): δ 8.66 (s, 2H, PT-C*H*), 8.45 (d, $^3J_{H-H}$ = 5 Hz, 2H, Th-C*H*), 8.16 (t, 2H, SDT-C*H*), 7.19 (d, $^3J_{H-H}$ = 5 Hz, 2H Th-C*H*), 7.14 (d, $^3J_{H-H}$ = 5 Hz, 2H Th-C*H*), 6.72 (m, 2H, Th-C*H*), 2.84 (t, $^3J_{H-H}$ = 7 Hz, 4H Th-CH_2), 1.74 (h, $^3J_{H-H}$ = 6 Hz, 4H, CH_2), 1.60 (m, 2H, C*H*), 1.43 (m, 4H, CH_2), 1.31 (m, 14H, CH_2), 1.24 (m, 10H, CH_2), 1.13 (m, 4H, SiCH_2), 0.92 (m, 6H, CH_3), 0.85 (m, 12H, CH_3). **^{13}C{^{1}H} NMR** (CDCl$_3$): 154.55, 150.50, 148.03, 146.99, 145.19, 142.82 (s, quaternary), 140.17 (s, *C*H), 139.66, 138.58, 134.62 (s, quaternary), 132.70 (s, *C*H), 130.87 (s, *C*H), 125.22 (s, *C*H), 124.66 (s, *C*H), 124.60 (s, *C*H), 120.47 (s, quaternary), 36.05 (s, C*H*), 35.79 (s, CH_2), 31.57 (s, SiCH_2), 31.54 (s, CH_2), 30.29 (s, ThCH_2), 29.02 (s, CH_2), 28.99 (s, CH_2), 28.78 (s, CH_2), 23.05 (s, CH_2), 22.58 (s, CH_2), 17.75 (s, CH_2), 14.21 (s, CH_3), 14.08 (s, CH_3), 10.87 (s, CH_3). **Anal. Calcd.** for $C_{62}H_{72}N_6S_8Si$: C, 62.79; H, 6.12; N, 7.09. Found: C, 62.5; H, 6.00; N, 7.05 %. **HRMS (EI)** *m/z*, calcd for $C_{62}H_{72}N_6S_8Si$ (M^+): 1184; found: 1184. **Absorbance**: (CHCl$_3$) λ_{max} = 625 nm, λ_{onset} = 725 nm, ε = 35000 cm^{-1}M^{-1}. (As Cast Film) λ_{max} = 655, 720 nm, λ_{onset} = 820 nm.

Solution NMR Spectra



4

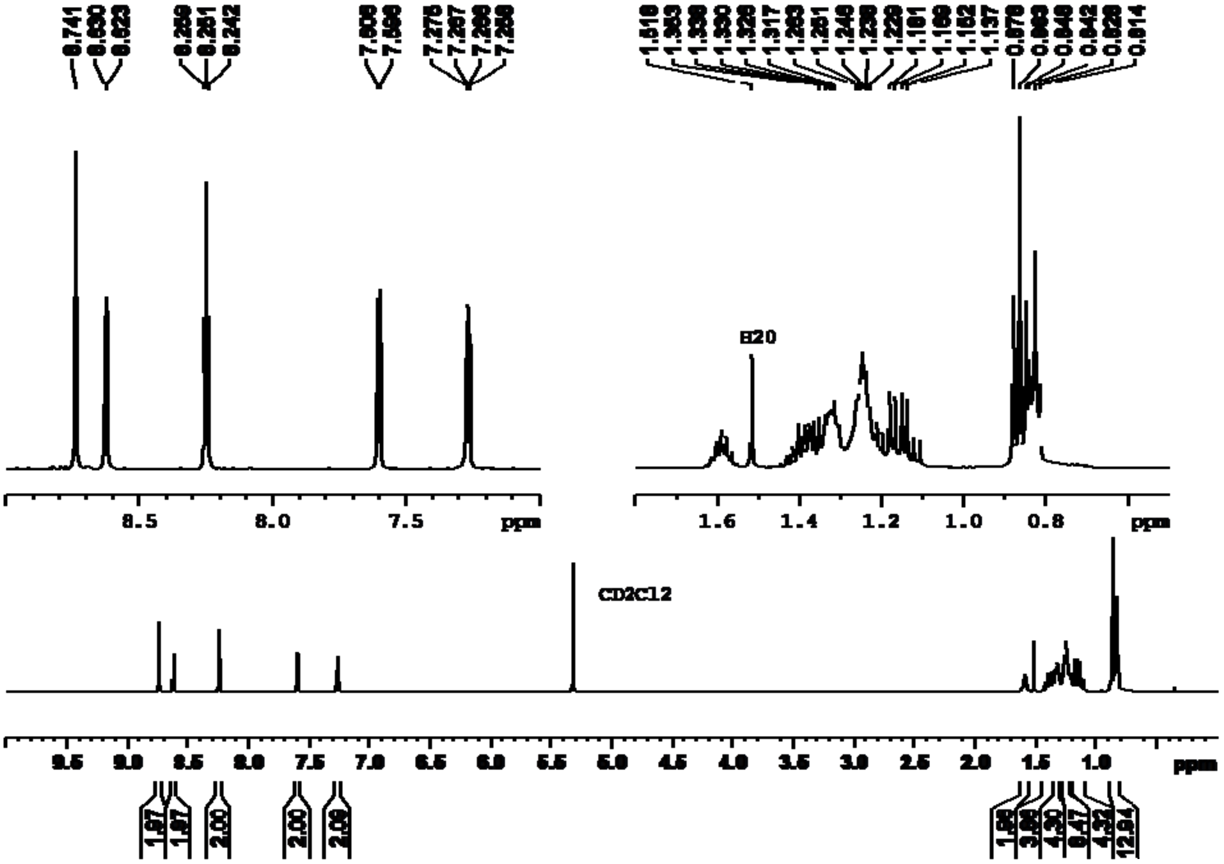


Figure S1. ^{1}H NMR spectrum of compound **4** at 300K in CD_2Cl_2 (δ 5.32 ppm).

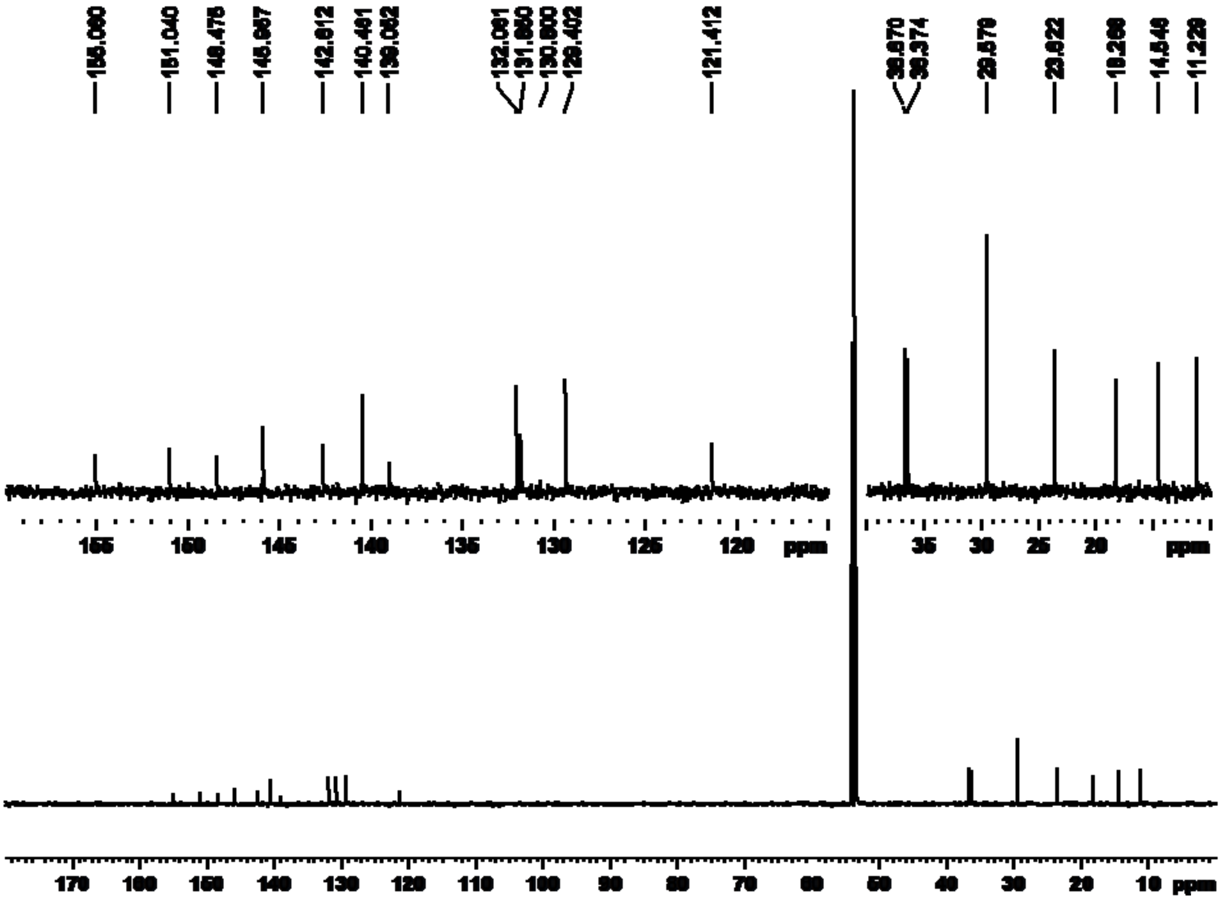
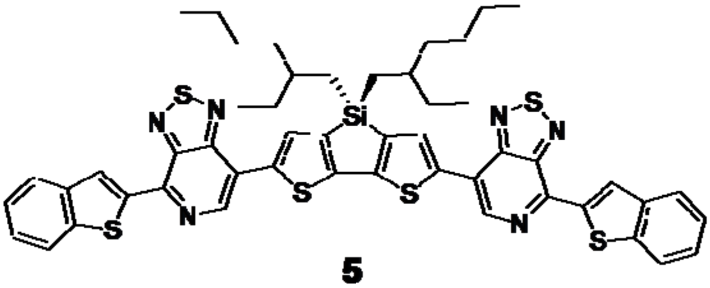


Figure S2. ^{13}C NMR spectrum of compound **4** at 300K in CD_2Cl_2 (δ 54 ppm).



5

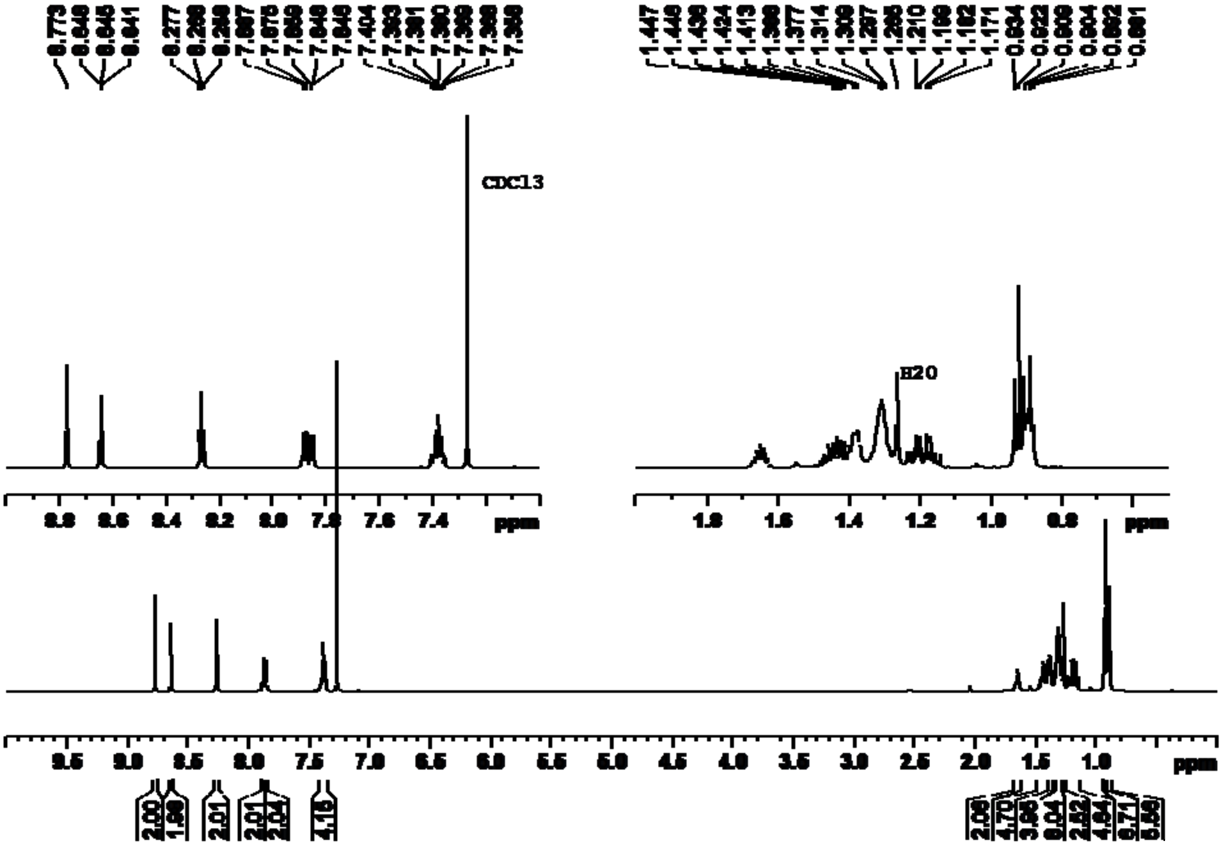


Figure S3. ^{1}H NMR spectrum of compound **5** at 300K in $CDCl_3$ (δ 7.27 ppm).

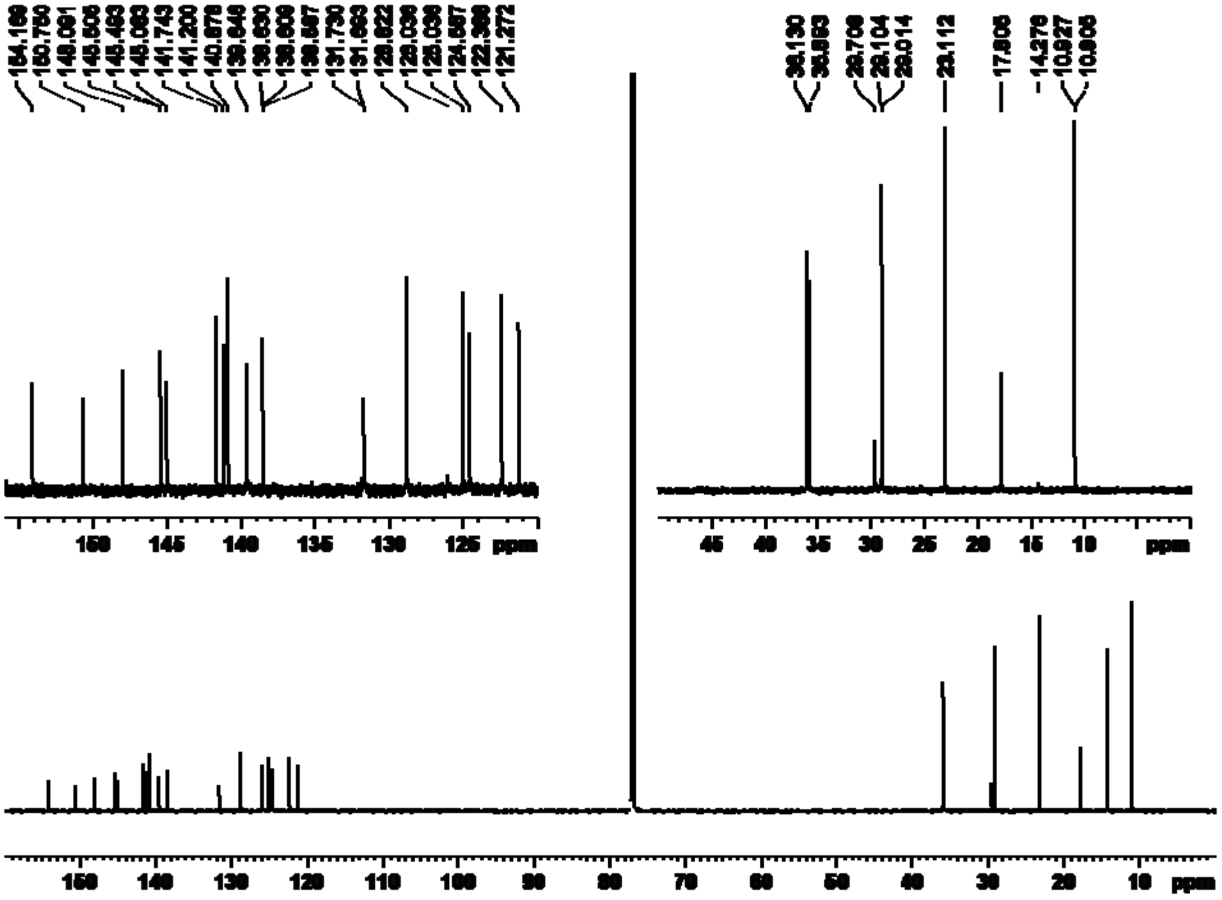
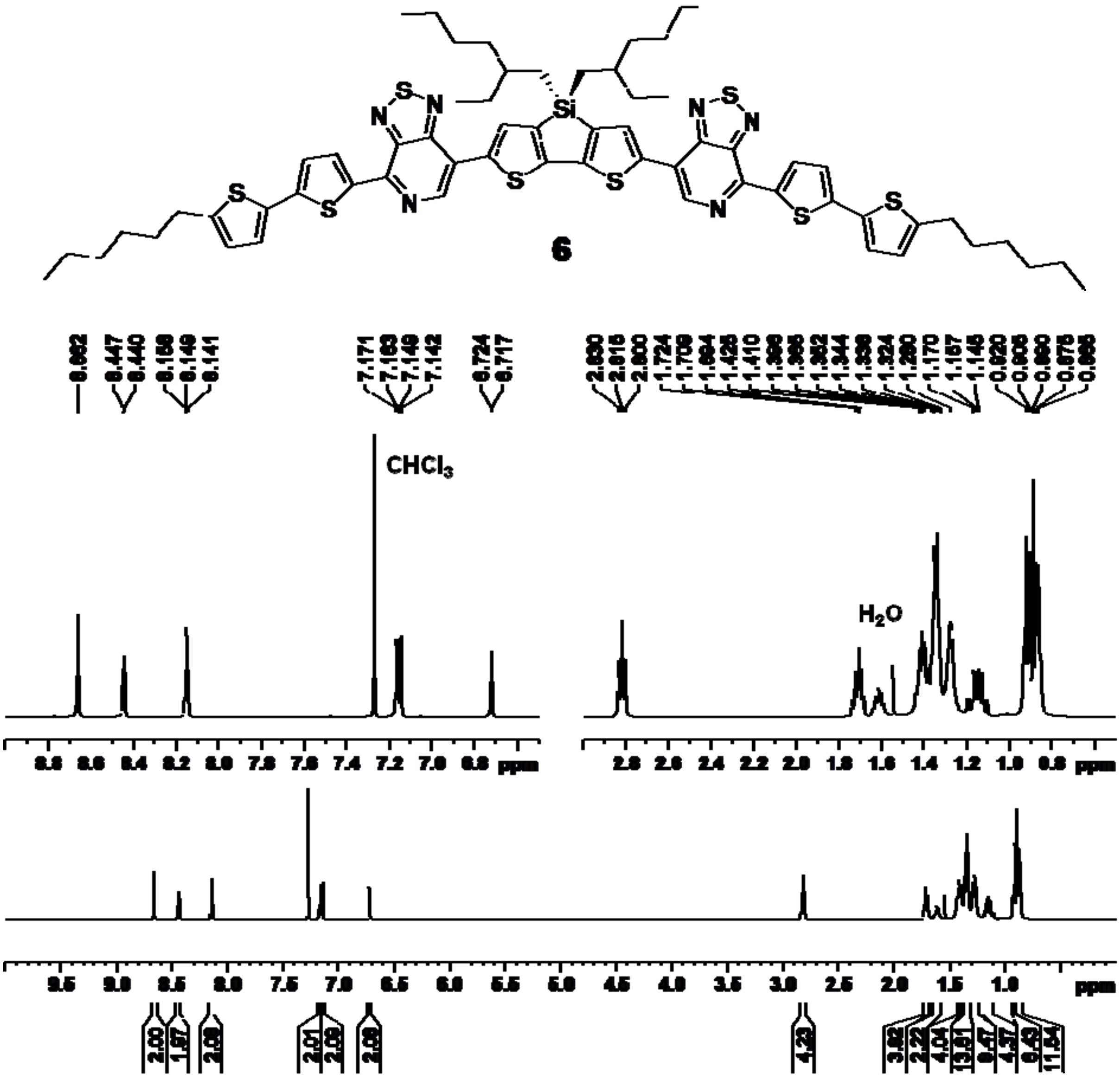


Figure S4. ^{13}C NMR spectrum of compound **5** in $CDCl_3$ (δ 77 ppm).

.



6

Figure S5. ^{1}H NMR spectrum of compound **6** in CDCl$_3$ (δ 7.27 ppm).

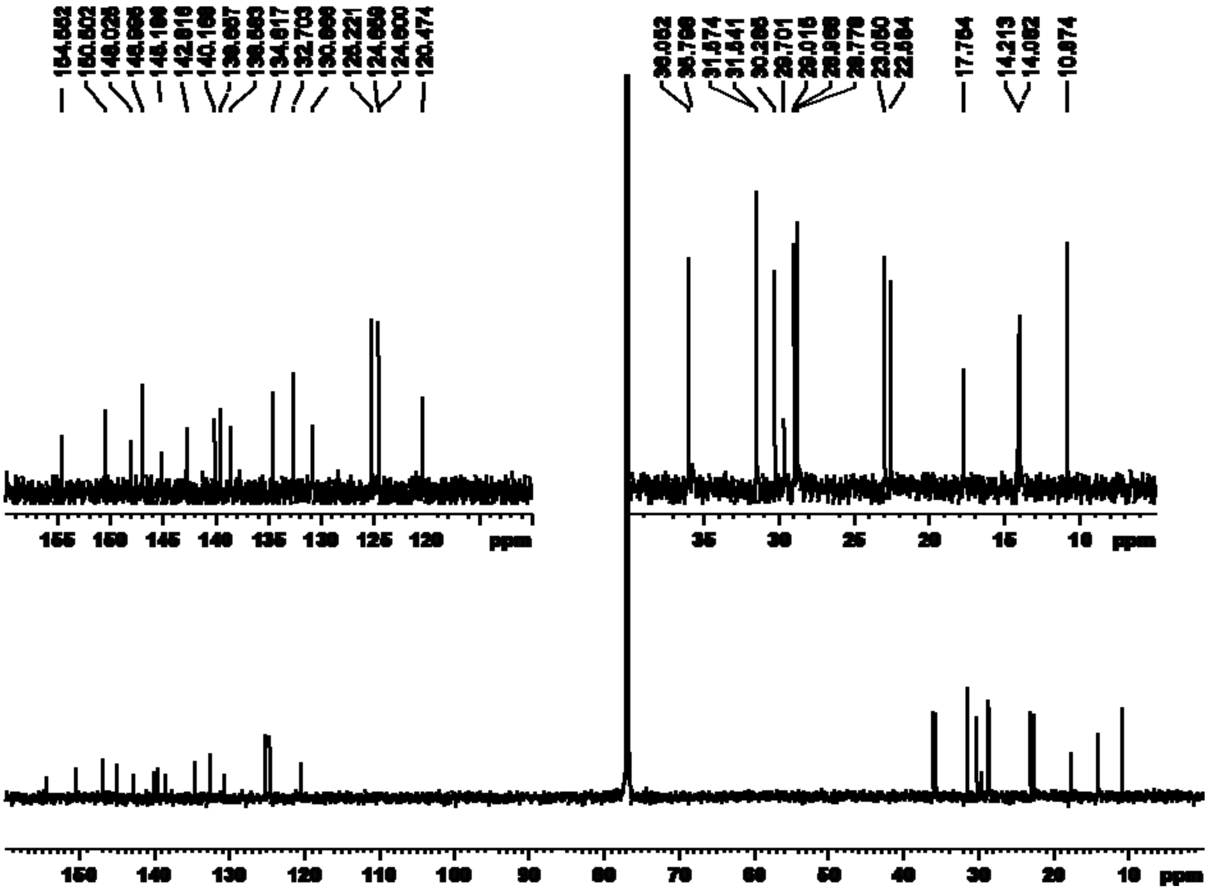


Figure S6. ^{13}C NMR spectrum of compound **6** in $CDCl_3$ (δ 77 ppm).

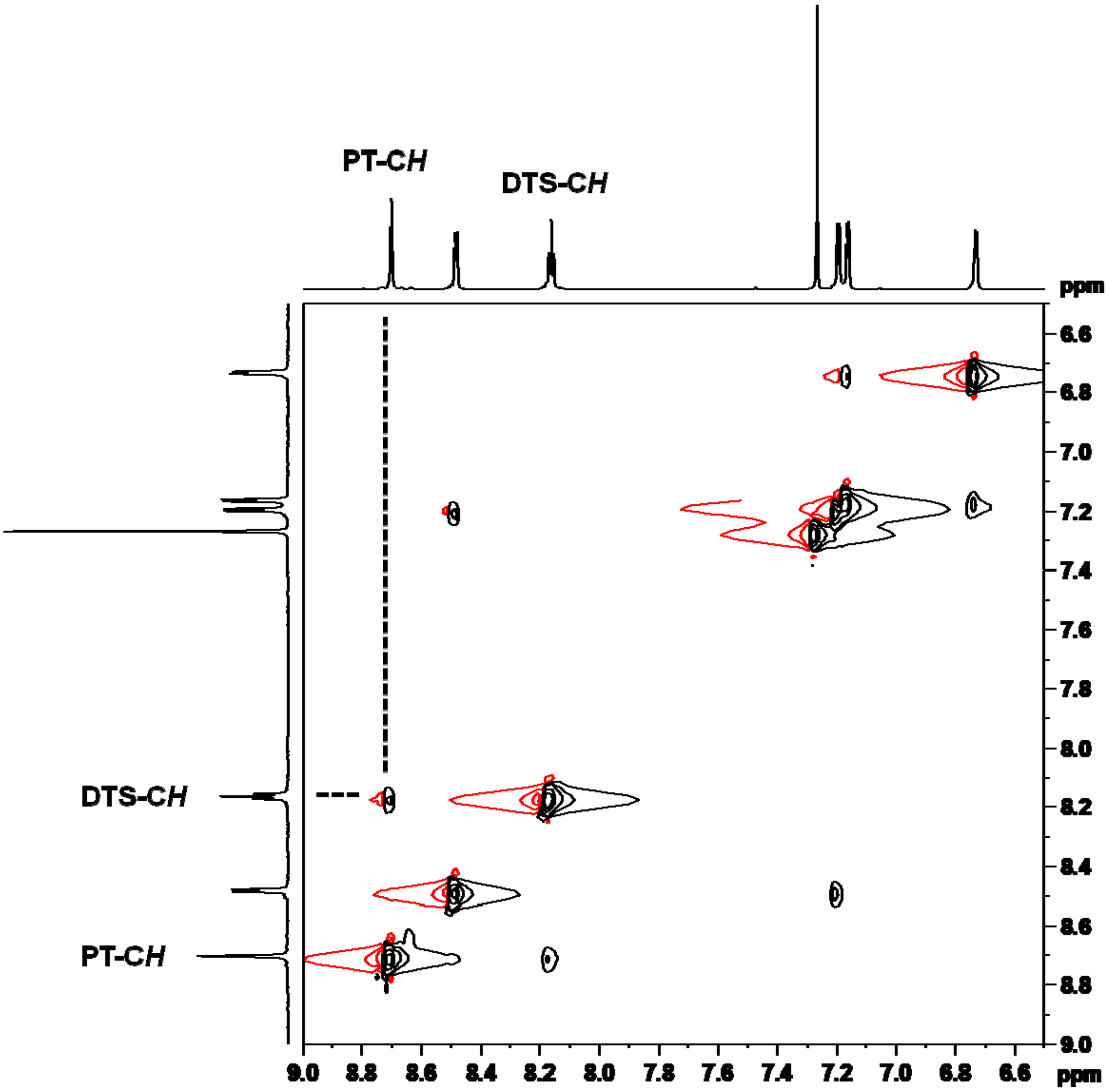


Figure S7. ^{1}H-^{1}H NOE NMR spectrum for **6** ($CDCl_3$). Mixing time = 0.8 sec.

Single Crystal X-Ray Diffraction

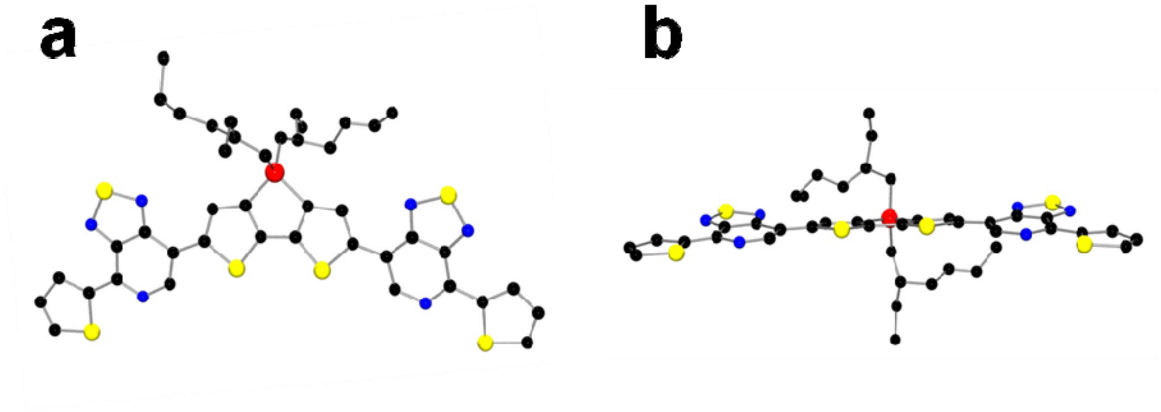


Figure S8. POV-Ray depiction of the single crystal structure of **4**. Carbon) black; Nitrogen) blue; Silicon) red; Sulfur) yellow. Hydrogen atoms omitted for clarity. A) Front view b) Side view. Monoclinic. P2(1)/n. Cell: a = 18.817(4)Å, b = 7.9805(17) Å, c = 28.301(6) Å, beta = 107.018(3)°. V= 4063.8(15) Å^3. R1 = 0.0841, wR2 = 0.1942.

Temperature Dependant UV-Visible Spectra

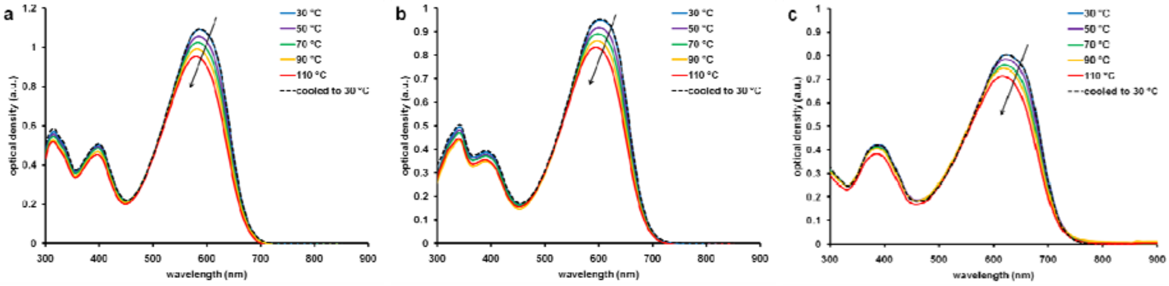


Figure S9. Temperature dependant UV-visible absorption spectroscopy of a) **4** and b) **5** and c) **6** in C_6H_5Cl solution.

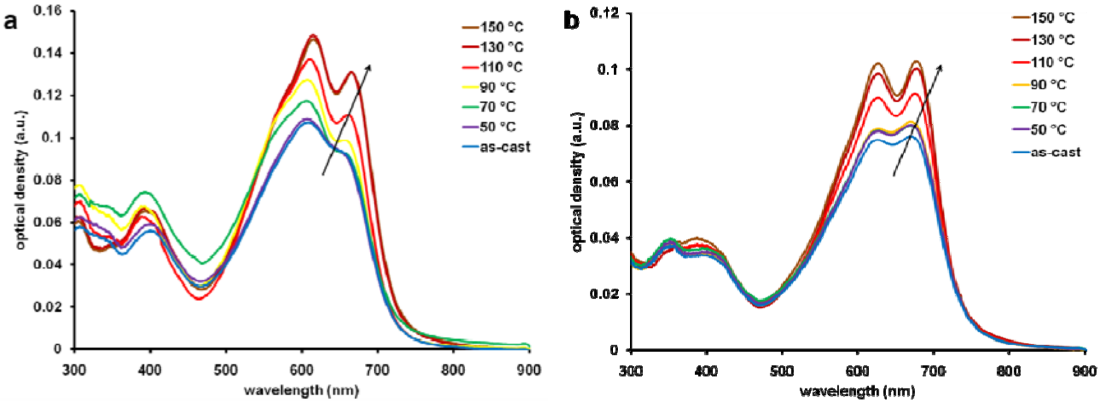


Figure S10. UV-visible absorption spectroscopy of a) **4** and b) **5** as thin films on quartz substrates as a function of annealing temperature. Thin films were sequentially annealed at increasing temperature for 2 minutes.

DFT Calculations

Table S1. HOMO and LUMO energy level determined by DFT calculations.[a]

Compound	HOMO (eV)	LUMO (eV)	E_g (calc)
4	-4.98	-3.03	1.95
5	-5.06	-3.13	1.93
6	-4.76	-2.99	1.77

[a] B3LYP/6-31G(d,p) level of theory

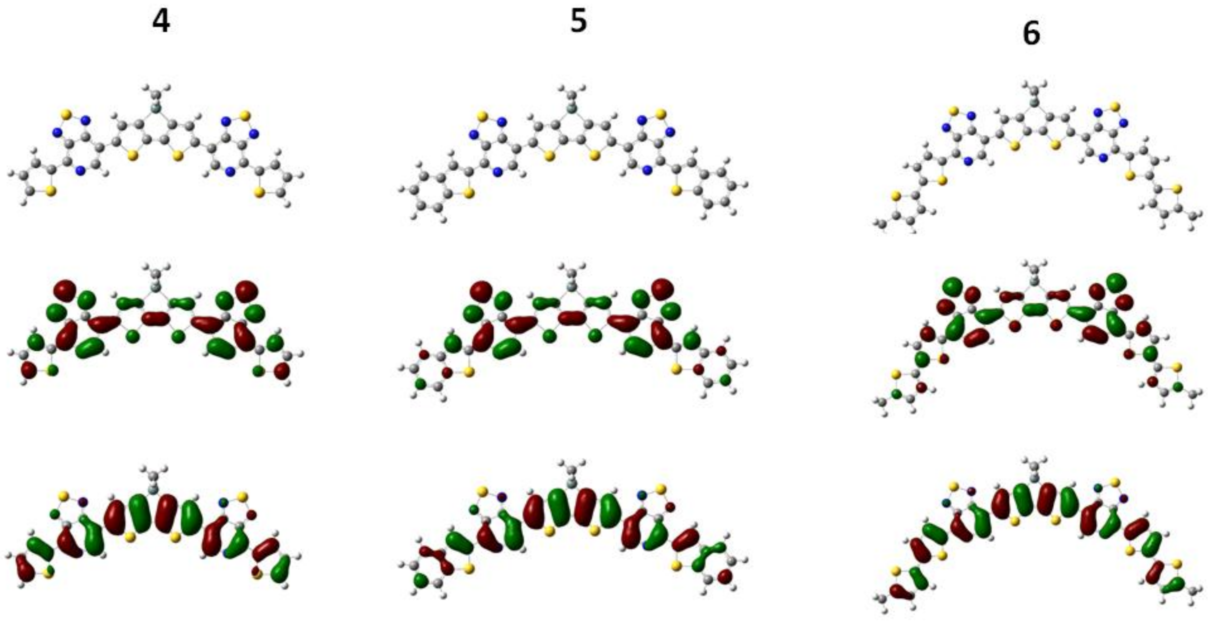


Figure S11. DFT optimized ground state structures of **4**, **5**, and **6**. Me groups were used in replace of hexyl and 2-ehtylhexyl substituents. Calculations were carried out in the gas-phase and do not account for solvent effects or intermolecular interactions. Calculations predict decreasing band gaps from **4** to **6** (Table S4), consistent with the UV-vis spectroscopy and Cyclic Voltammetry. The HOMO and LUMO for all three molecules are delocalized across the π-conjugated backbone, indicating favourable molecular orbital overlap between the donor DTS and acceptor PT moieties.[11] In all cases, the depicted conformation was found to have the lowest energy by a minimum of 5 kJ/mol^{-1}. Each molecule adopts a banana-type structure in the lowest energy configuration.

Thermogravimetric analysis

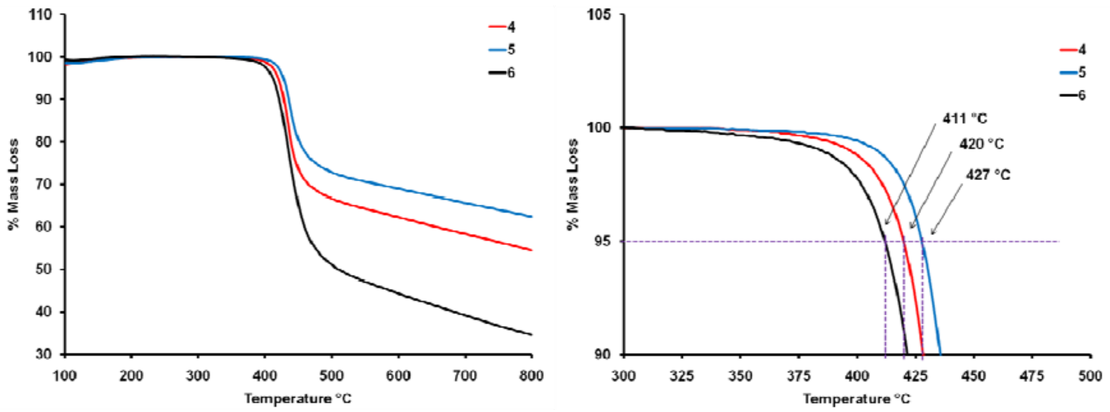


Figure S12. Thermogravimetric analysis (TGA) plots for compounds **4**, **5**, and **6**. Temperature increased from 100 °C to 800 °C at 10 °C/min under N_2.

UV-Visible Spectra of 6:PC$_{71}$BM

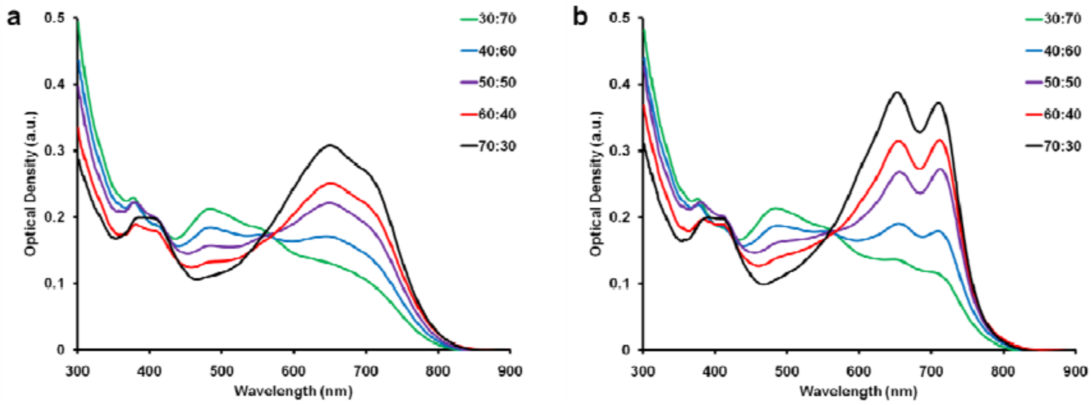


Figure 13. Optical absorption spectra of **6**:PC$_{71}$BM (60:40 w/w)(2% w/v) film spin coated at 2500 rpm atop ITO/HIL. As-cast (a) and after annealing at 110 °C for 2 minutes (b). ITO is indium tin oxide, HIL is a hole injection layer obtained from Plextronics Plexcore OC AQ-1300.

Solar Cell Data

75 nm active layer

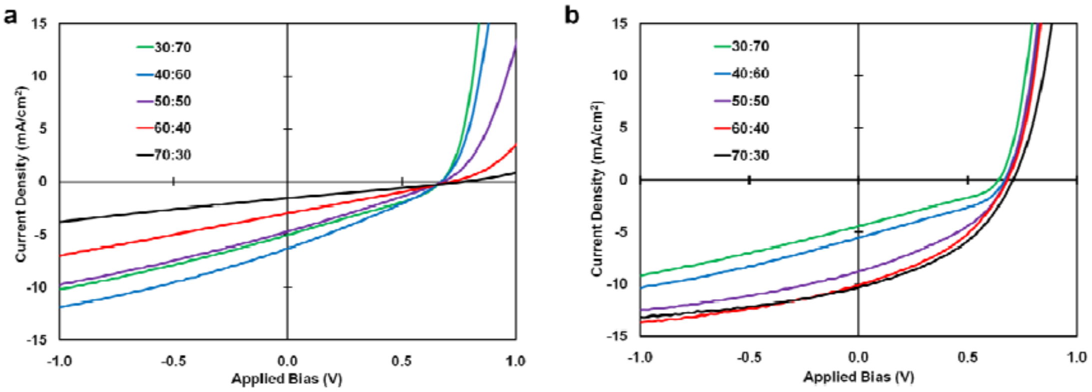


Figure S14. Solar cell device data for a) as-cast b) 110 °C annealed active layer with 75 nm thickness and **6**: PC$_{71}$BM ratio of 30:70 (green), 40:60 (blue), 50:50 (purple), 60:40 (red), 70:30 (black).

Table S2. Solar cell device data for as-cast active layer with 75nm thickness.

6:PC$_{71}$BM Ratio	**30:70**	**40:60**	**50:50**	**60:40**	**70:30**
V_{oc} (V):	0.66	0.68	0.70	0.74	0.80
I_{sc} (mAcm^{-2}):	-7.1	-8.0	-6.2	-3.9	-2.0
FF:	0.31	0.31	0.30	0.27	0.26
PCE:	1.5%	1.7%	1.3%	0.8%	0.4%

Table S3. Solar cell device data for annealed active layer with 75nm thickness.

6:PC$_{71}$BM Ratio	**30:70**	**40:60**	**50:50**	**60:40**	**70:30**
V_{oc} (V):	0.64	0.68	0.68	0.68	0.70
I_{sc} (mAcm^{-2}):	-5.9	-6.2	-7.9	-8.5	-9.3
FF:	0.30	0.37	0.42	0.41	0.42
PCE:	1.1%	1.6%	2.2%	2.4%	2.7%

85 nm active layer

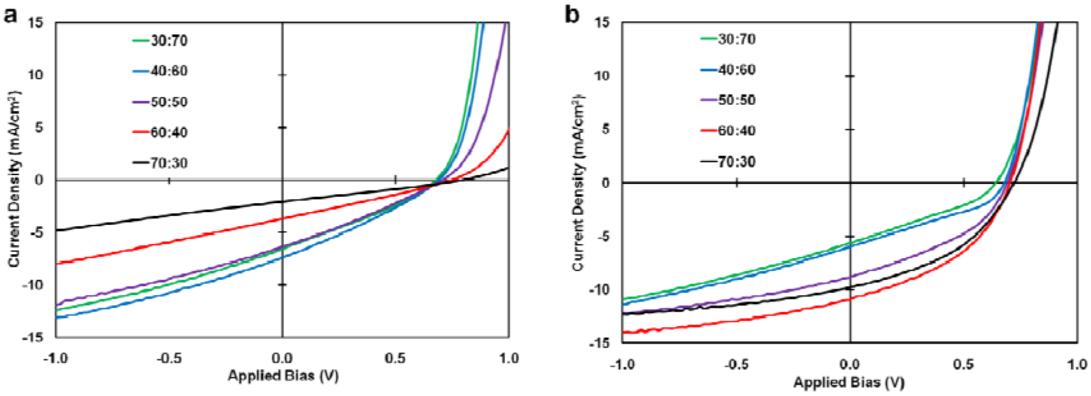


Figure S15. Solar cell device data for a) as-cast b) 110 °C annealed active layer with 85 nm thickness and **6**: $PC_{71}BM$ ratio of 30:70 (green), 40:60 (blue), 50:50 (purple), 60:40 (red), 70:30 (black).

Table S4. Solar cell device data for as-cast active layer with 85nm thickness.

6:PC_{71}BM Ratio	**30:70**	**40:60**	**50:50**	**60:40**	**70:30**
V_{oc} (V):	0.68	0.70	0.70	0.74	0.80
I_{sc} (mAcm^{-2}):	-6.6	-7.4	-6.4	-3.7	-2.1
FF:	0.30	0.29	0.28	0.27	0.27
PCE:	1.3%	1.5%	1.3%	0.7%	0.5%

Table S5. Solar cell device data for annealed active layer with 85nm thickness.

6:PC_{71}BM Ratio	**30:70**	**40:60**	**50:50**	**60:40**	**70:30**
V_{oc} (V):	0.64	0.68	0.70	0.70	0.72
I_{sc} (mAcm^{-2}):	-5.6	-6.0	-8.9	-10.9	-9.7
FF:	0.31	0.33	0.39	0.42	0.42
PCE:	1.1%	1.4%	2.4%	3.2%	2.9%

105 nm active layer

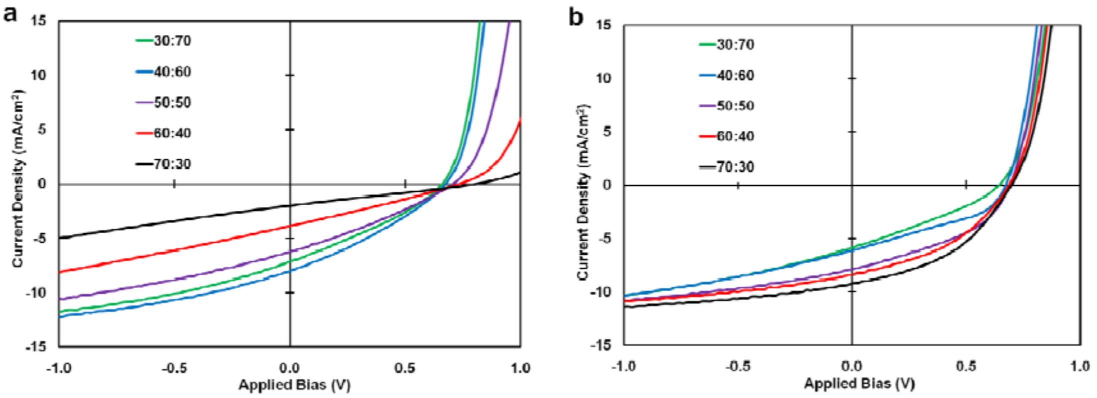


Figure S16. Solar cell device data for a) as-cast b) 110 °C annealed active layer with 105 nm thickness and **6**: PC$_{71}$BM ratio of 30:70 (green), 40:60 (blue), 50:50 (purple), 60:40 (red), 70:30 (black).

Table S6. Solar cell device data for as-cast active layer with 105nm thickness.

6:PC$_{71}$BM Ratio	**30:70**	**40:60**	**50:50**	**60:40**	**70:30**
V_{oc} (V):	0.68	0.68	0.68	0.72	0.78
I_{sc} (mAcm^{-2}):	-5.0	-6.3	-4.7	-3.0	-1.6
FF:	0.30	0.28	0.27	0.26	0.26
PCE:	1.0%	1.2%	0.9%	0.6%	0.3%

Table S7. Solar cell device data for annealed active layer with 105nm thickness.

6:PC$_{71}$BM Ratio	**30:70**	**40:60**	**50:50**	**60:40**	**70:30**
V_{oc} (V):	0.64	0.66	0.68	0.68	0.70
I_{sc} (mAcm^{-2}):	-4.5	-5.5	-8.8	-10.1	-10.3
FF:	0.31	0.36	0.38	0.40	0.41
PCE:	0.9%	1.3%	2.3%	2.7%	3.0%

Mobility and UPS Measurements

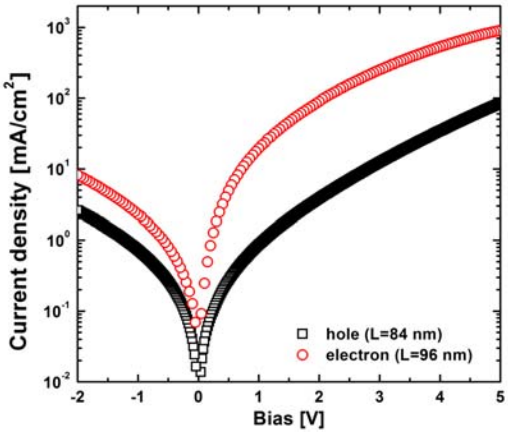


Figure S17. Current versus voltage characteristics of a) hole only and b) electron-only diodes based on 60:40 **6**:PC$_{71}$BM blend films. All films were thermally annealed at 110 °C for 2 min. Hole diode mobility 1.5×10^{-6} cm^2/Vs. Electron diode mobility 5.3×10^{-5} cm^2/Vs.

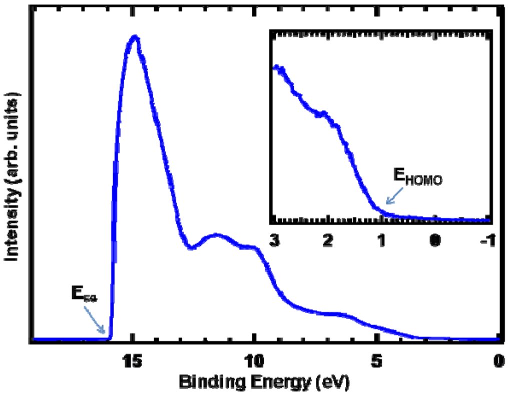


Figure S18. Ultraviolet photoemission spectra (UPS) of Plextronics Plexcore OC AQ-1300 hole injection layer (HIL). Substrate = ITO/HIL. Work Function = hv – E$_{se}$ = 21.2 – 15.85 = 5.35 eV.

References:

---

1 Hou, J. H.; Chen, H. Y.; Zhang, S. Q.; Li, G.; Yang, Y. Journal of the American Chemical Society 2008, 130, 16144-16145.

2 Parab, K.; Venkatasubbaiah, K.; Jakle, F. Journal of the American Chemical Society 2006, 128, 12879-12885.

3 Pavlishchuk, V. V., Addison, W. A. Inorganica Chimica Acta, 2000, 298, 1.

4 Bard, Allen J.; Larry R. Faulkner (2000-12-18). Electrochemical Methods: Fundamentals and Applications (2 ed.). Wiley

5 APEX2 v2011.2-0, Bruker AXS, Inc., Madison, WI 2010

6 Sheldrick, G. M. SADABS, Version 2.05, Bruker AXS, Inc.; Madison, WI 2001.

7 Sheldrick, G. M. SHELXTL, Version 6.12, Bruker AXS, Inc.; Madison, WI 2001.

8 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Gaussian, Inc., Wallingford CT, 2004.

9 a) Becke, A. D. J. Chem. Phys. 1993, 98, 1372. b) Becke, A. D. J. Chem. Phys. 1993, 98, 5648. c) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785.

10 a) Dang, X.-D.; Tamayo, A. B.; Seo, J.; Hoven, C. V.; Walker, B.; Nguyen, T.-Q. Adv. Funct. Mater. 2010, 20, 3314-3321. b) Hoven, C. V.; Dang, X. D.; Coffin, R. C.; Peet, J.; Nguyen, T. Q.; Bazan, G. C. Adv. Mater. 2010, 22, E63-E68.

11 Hung, Y. C.; Jiang, J. C.; Chao, C. Y.; Su, W. F.; Lin, S. T. J. Phys. Chem. B. 2009, 113, 8268-8277