## Supporting information for

# New anthracene-thiophene-based copolymers that absorb across the entire UV-vis spectrum for application in organic solar cells

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## Instruments and Reagents.

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker AVANCE 300 spectrometer with tertramethylsilane as an internal reference. For the NMR measurements, chloroform-d ($CDCl_3$) was used as the solvent for monomers and 1,1,2,2,-tetrachloroethane-$d_2$ was used for PAT4. Elemental analysis was performed using EA-1110-FISONS elemental analyzer. UV-vis. spectra were measured by using a Jasco V-530 UV/vis Spectrometer. Thermogravimetric analysis (TGA) measurement was performed under nitrogen atmosphere at a heating rate of 10 °C/min using TA Q500 instrument, and the differential scanning calorimetric (DSC) measurement was made using TA Q100 instrument operated under nitrogen atmosphere. Cyclic voltammetry (CV) measurement was performed on an AUTOLAB/PGSTAT12 at room temperature with a three-electrode cell in a solution of 0.1 M tetrabutylammonium tetrafluoroborate (TBABF4) in anhydrous acetonitrile at room temperature under nitrogen gas with a scan rate of 50mV/s. The working electrode was the oligomer coated platinum, the counter electrode was a platinum wire, and the reference electrode was Ag/$AgNO_3$ (0.10M) which was separated by a diaphragm. The measurements were calibrated using ferrocene as a standard. Synchrotron X-ray diffraction (XRD) analyses of PAT4 films were performed at the 10C1 beam line (wavelength ≈ 1.54 Å) of the Pohang Accelerator Laboratory (PAL). Top contact OTFTs were fabricated on a common gate of highly n-doped silicon with a 300 nm thick thermally grown $SiO_2$ dielectric layer. Substrates were modified with octadecyltrichlorosilane from a toluene solution for 2 h at room temperature. Films of organic semiconductor were spin coated at 2000 rpm from 0.7wt% chlorobenzene solution, with nominal thickness 45 nm. Gold source and drain electrodes were evaporated on the top of semiconductor (100 nm). For all measurements, we used channel lengths (L) of 150 um and channel widths (W) of 1500 um. Electrical characteristics of the TFTs were measured in air using both Keithley 236 source/measure units. The carrier mobility was calculated in the saturation regime from the slope of a plot of the square root of the drain current versus gate voltage ($V_G$) by fitting the data to the following equation: $I_{DS} = (WC_i/2L)\mu(V_G\text{-}V_{th})^2$, where $I_{DS}$ is the drain current, $\mu$ is the carrier mobility and $V_{th}$ is the threshold voltage. PCBM-60 (99%) used in this study was obtained from Aldrich. The PDT2Se2:PCBM-60 blend solutions (weight ratio: 1:1, 1:2, 1:3, 1:4) were prepared in chlorobenzene at a concentration of 20 mg/mL. After cleaning the pre-patterned ITO coated glass, PEDOT–PSS (Baytron P TP AI 4083, Bayer AG) was spin-coated with a thickness of 30–50 nm and annealed at 120°C (for 60 min) in air. Active layer was spin-coated on the PEDOT:PSS layer for 60 seconds with a thickness of 100 nm. Finally, LiF (lithium fluoride) (1 nm)/Al (100 nm) cathodes were thermally deposited. The current density–voltage (J–V) characteristics were measured using Keithley 4200 source/measure units in the dark and under AM 1.5 solar illumination (Oriel 1 kW solar simulator) with respect to the reference cell PVM 132 (calibrated at the National Renewable Energy Laboratory, NREL, at an intensity of 100 mW/cm$^2$). Transmission Electron Microscopy (TEM) was performed on a HITACHI-7600 operating at 100 kV. The incident photon to current conversion efficiency (IPCE) as a function of wavelength was measured with a photomodulation spectroscopic setup. (model Merlin, Oriel)

Chemical reagents were purchased from Aldrich Chemical Co. and were used without further purification.

Solvents with analytical-grade were used during the whole experiments, and all chemicals were used without further purification. 2,6-dibromo-9,10-bis-(triisopropylsilylethynyl)anthracene (TIPSAnt)[1] and 4,4'-didodecyl-5,5'-trimethylstannyl-2,2'-bithiophene (T2)[2] were synthesized according to the reported procedures. Synthesis of 4,4'-didodecyl-5,5'-(5,5'-trimethystannylthiophene-2-yl)-2,2'-bithiophene (T4) will be published elsewhere. [3]

**Synthesis of PAT4**

To an oven-dried 50 mL two neck round-bottom flask equipped with a stir bar under $N_2$ was added TIPSAnt (0.35 g, 0.5 mmol) and T4 (0.5 g, 0.5 mmol). Tris(dibenzylideneacetone)dipalladium (0.01g, 0.01 mmol) and tri-o-tolyphosphine (0.012g, 0.04 mol) was transferred into the mixture in dry box. Subsequently anhydrous chlorobenzene (17mL) was added and purged under nitrogen for 30 min. The reaction mixture was stirred at 140 °C for 3 days and cooled to room temperature. Then, the resulting polymer was precipitated with methanol. The precipitate was collected by filtration, dissolved in chlorobenzene, and precipitated with methanol again. The final collected polymer was subjected to Soxhlet extraction with methanol, acetone, and heptanes. The polymer was extracted with chlorobenzene and collected after precipitation procedure. Finally, the polymer was dried 2 days at vacuum oven at 50 $^{o}$C to give 0.45 g product as black power (74 % yield). $^1$H-NMR (1,1,2,2-tetrachloroethane-$d_2$ at 100$^{o}$C, ppm) δ = 8.95 (s, 2H), 8.72 (d, 2H), 7.96 (d, 2H), 7.57 (br, 2H), 7.28 (br, 2H), 7.15 (s, 2H), 2.93 (t, 4H), 1.84 (br m, 4H), 1.44 (br, 78H), 0.94 (t, 6H). Anal. calcd for $C_{76}H_{106}S_4Si_2$ : C, 75.81 %; H, 8.87 %; S, 10.65 % Found: C, 75.24 %; H, 8.56 %; S, 10.32 %. GPC (in THF) $M_w$ = 10,100 PDI = 1.30.

**Synthesis of PAT2**

To an oven-dried 50 mL two neck round-bottom flask equipped with a stir bar under $N_2$ was added TIPSAnt (0.37 g, 0.53 mmol) and T2 (0.44 g, 0.53 mmol). Tris(dibenzylideneacetone)dipalladium (0.01g, 0.01 mmol) and tri-o-tolyphosphine (0.012g, 0.04 mol) was transferred into the mixture in dry box. Subsequently anhydrous chlorobenzene (17mL) was added and purged under nitrogen for 30 min. The reaction mixture was stirred at 140 °C for 3 days and cooled to room temperature. Then, the resulting crude product was precipitated with methanol. The precipitate was collected and used without further purification. PAT2 was dried 2 days at vacuum oven at 50 $^{o}$C to give 0.32 g product as sticky red liquid (57 % yield). It was hard to assign $^1$H-NMR of PAT2 because of impurity. GPC (in THF) $M_w$ = 3,000 PDI = 1.50.

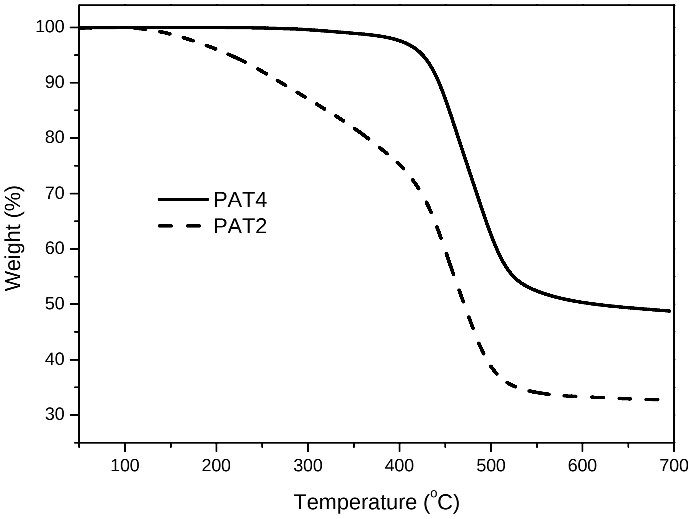

Figure S1. TGA thermograms of PAT2 and PAT4

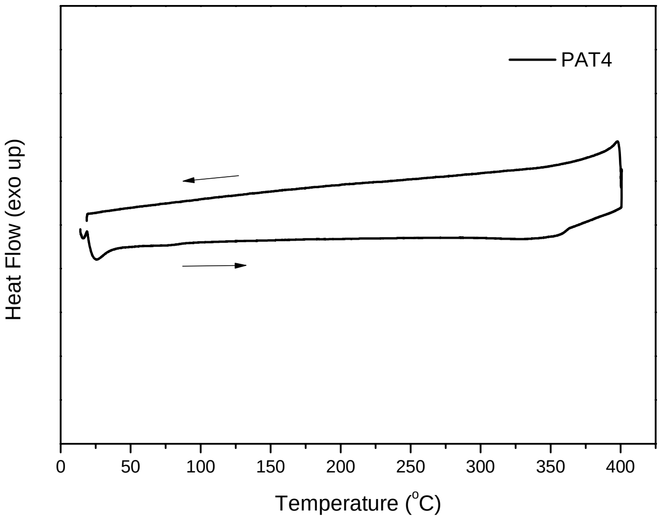

Figure S2. A first DSC scan showing the thermal phase transitions of PAT4

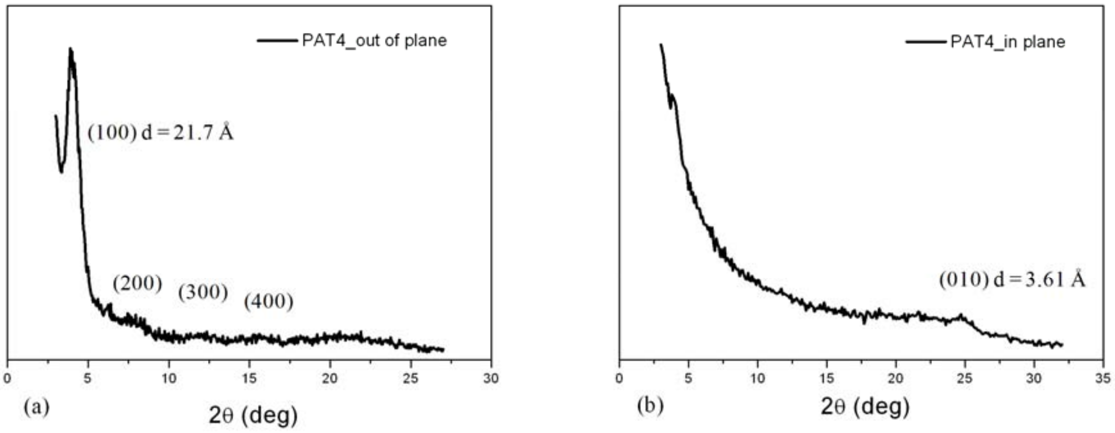

Figure S3. XRD patterns of PAT4 films on octyltrichlorosilane modified silicon oxide. (a) out of plane mode, (b) in plane mode.

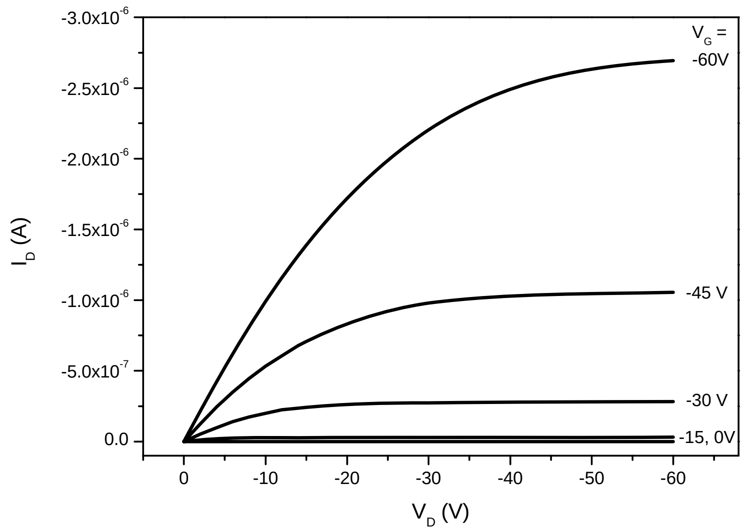

Figure S4. Output characteristics of TFTs based on PAT4 as cast.

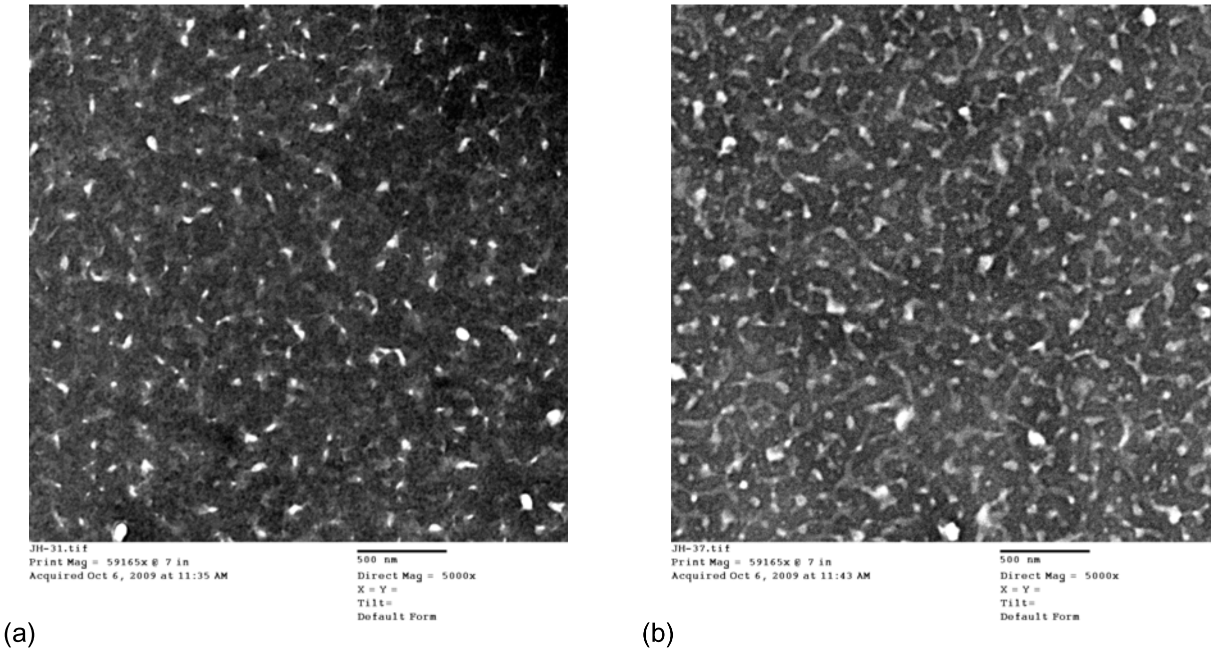

Figure S5. Transmission electron microscopy (TEM) images of PAT4:PCBM blended films. (a) 1:1 ratio, (b) 1:4 ratio.

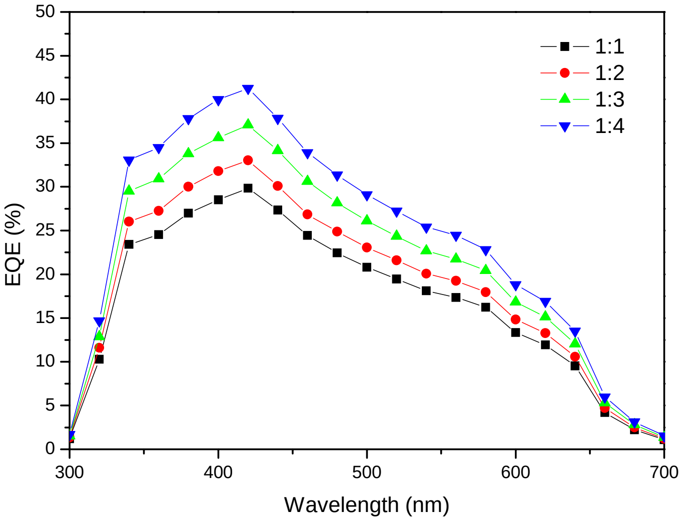

Figure S6. EQE of blends of PAT4/PCBM-60.

## References

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