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Supplementary Information for

Enhanced Vertical Carrier Mobility in Poly(3-alkylthiophene) Thin Films Sandwiched with Self-assembled Monolayer and Surface-segregated Layer

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Figure S9. Calculation of activation energy.

Synthesis

Allyl-terminated poly(3-butylthiophene) (100 mg, 0.067 mmol), thioacetic acid (2 mL), dry THF (10 mL) and dry diethyl ether (5 mL) were placed in an oven-dried 100 mL two-necked flask equipped with a magnetic stirring bar. The mixture was stirred and degassed with N_2 for 30 min, AIBN (90 mg) was added under N_2, and the mixture was stirred at reflux temperature for 12 h. The polymer was precipitated in MeOH and centrifuged to remove the supernatant. This process was repeated 8 or 9 times until no odor of thioacetic acid was evident. The polymer was dried under vacuum, and diluted in THF. The solution was added drop-wise to a vigorously stirred slurry of $NaBH_4$ (2.0 g) in dry THF (30 mL) at reflux temperature. After 24 h, the solution was washed with distilled water and extracted with $CHCl_3$. The solution was filtered through celite and silica and concentrated in vacuo. Yield: 43%. ^{1}H NMR (500 MHz, CHCl3, δ): 0.92 (t, 3H), 1.20-1.65 (m, 4H), 2.5-2.65(m, -), 2.78-2.83 (m, 2H), 3.35 (d, -), 6.95 (s, 1H) MALDI-TOF-MS charts of P3BT-S (*m*/*z*: 1734.21 [M^+] (calcd: 1732.61 for *n* of 12 with -H/-SH end groups) (Figure S1) GPC: M_n = 2100, M_w = 2300, PDI = 1.06.

Preparation of P3BT-S SAMs

SAMs were prepared by immersing the gold substrates in a dry toluene solution of P3BT-S (5×10^{-7} mol mL^{-1}) at 80 °C and stirring for 24 h under N_2. After the samples were removed from the P3BT-S solution, they were annealed at 160 °C for 6 h under N_2. The samples were rinsed with pure toluene 4-5 times at room temperature and dried under a flow of pure N_2.

The P3BT-S/P3BT/P3BT-F film was prepared by spin-coating (700 rpm for 90 s) a mixture of P3BT-F_{17} and P3BT in $CHCl_3$/chlorobenzene (10:3) with concentrations of 3.0 mg mL^{-1} and 15 mg mL^{-1}, respectively. The films were thermally annealed at 50 °C for 24 h, and then at 150 °C for 2 h.

XPS was performed on an AXIS Ultra DLD spectrometer (Kratos Analytical Ltd.) with Al Kα radiation for all measurements. X-ray diffraction (XRD) and XRR analysis were performed on a Smartlab X-ray diffractometer (Rigaku) using monochromatized CuKα radiation ($\lambda = 0.154$ nm) generated at 45 kV and 200 mA. The thickness fitting was done with GlobalFit (Rigaku). The SE experimental quantities Δ and ψ were measured and fitted by an FE-5000 ellipsometer and FE-ver5 (Photal Otsuka Electronics Co., Ltd.), respectively, in the wavelength range of 300-900 nm. GIXRD was conducted at the SPring-8 on beam line BL19B2 with an X-ray energy of 12.39 keV ($\lambda = 1$ Å). The sample was irradiated at a fixed incident angle of 0.12° through a diffractometer (Huber), and the GIXRD pattern was recorded with a Pilatus 300K 2-D image detector (Dectris). The current density–voltage (*J*-*V*) measurements were conducted on hole-only devices with a structure of ITO/Au (5 nm)/polymer film/MoO_3 (3 nm)/Au (40 nm).

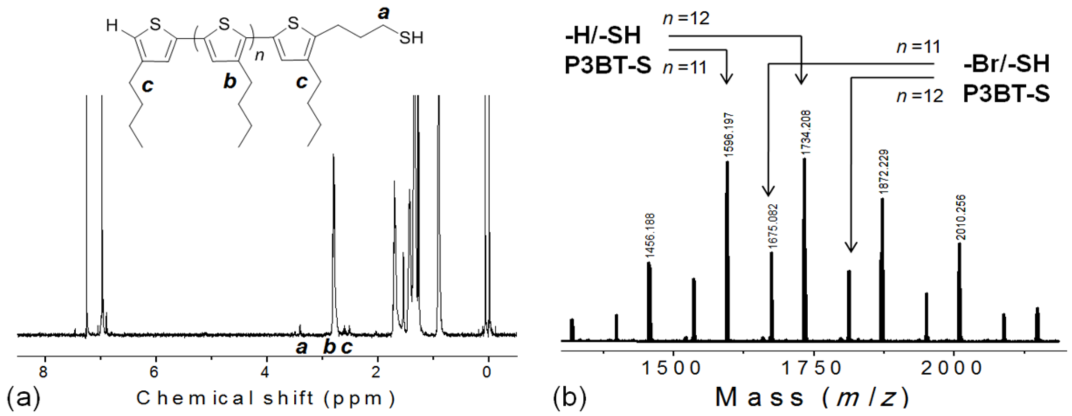


Figure S1. (a) ^{1}H NMR and (b) MALDI-TOF-MS spectrum of P3BT-S.

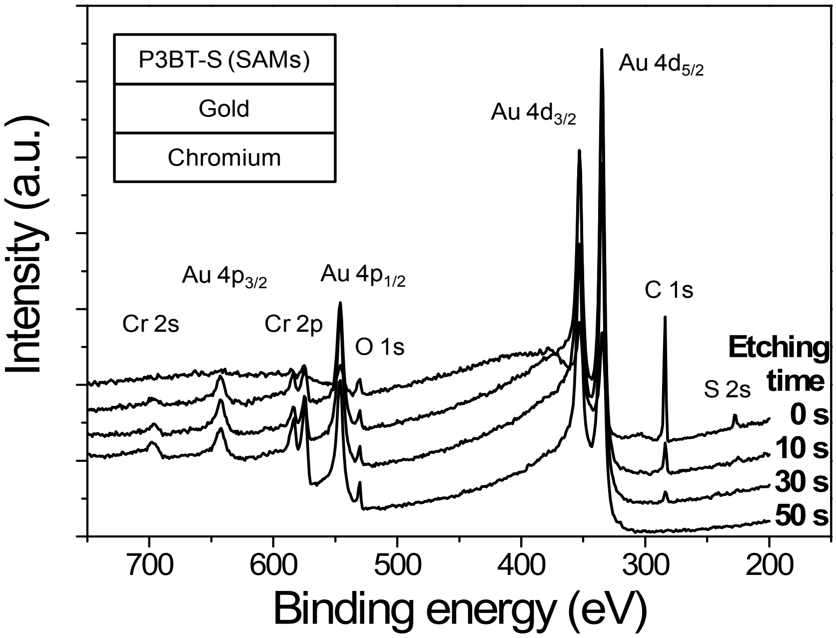
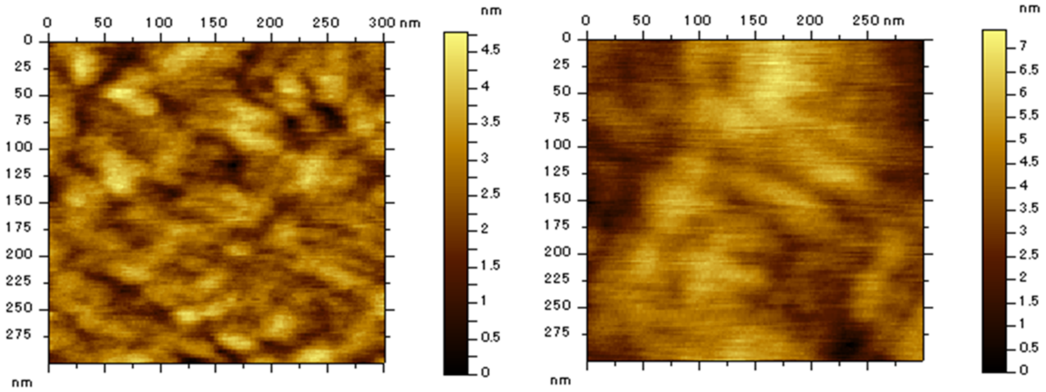


Figure S2. XPS depth profiles of the P3BT-S SAMs on a gold substrate before (0 s) and after etching with Ar$^+$ ions for 10, 30 and 50 s. The etching rate was estimated as ~0.1 nm s^{-1}. The spectra are shifted in the *y* direction for ease of comparison. Chromium was used as an adhesive layer between the gold layer and the silicon substrate



Au
S_q=0.636 nm
S_a=0.509 nm

Au/P3BT-S SAMs
S_q=1.16 nm
S_a=0.953 nm

Figure S3. AFM height images of the Au surface and the P3BT-S SAMs surface.

S_q: root mean square roughness and S_a: arithmetic mean roughness.

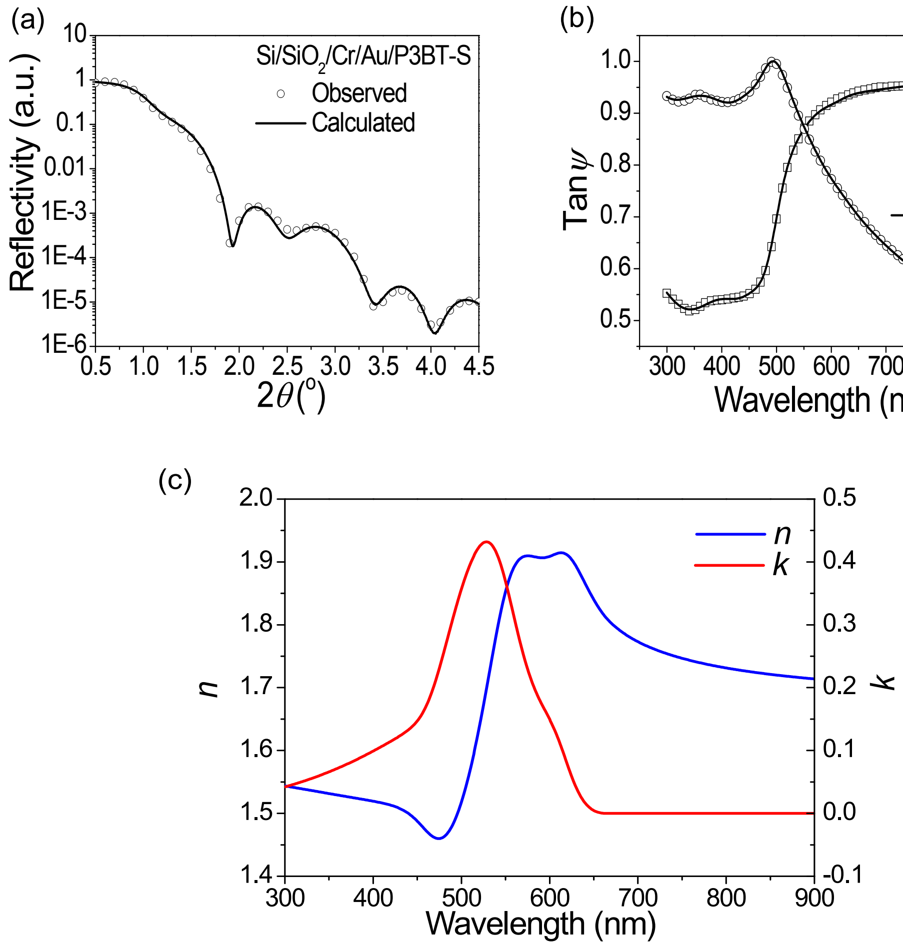


Figure S4. (a) XRR pattern of P3BT-S adsorbed on gold, fitted by using a bilayer model. The thickness and density of the P3BT-S layer extracted from the fitting were 4.45 nm and 0.98 g cm^{-3}, respectively. (b) Experimental data for tan ψ and cos Δ measured by SE and the fitting result with a 4.86-nm-thick P3BT-S layer. (c) Refractive index *n* and extinction coefficient *k* of P3BT-S SAMs for the fitting of the spectral ellipsometry.

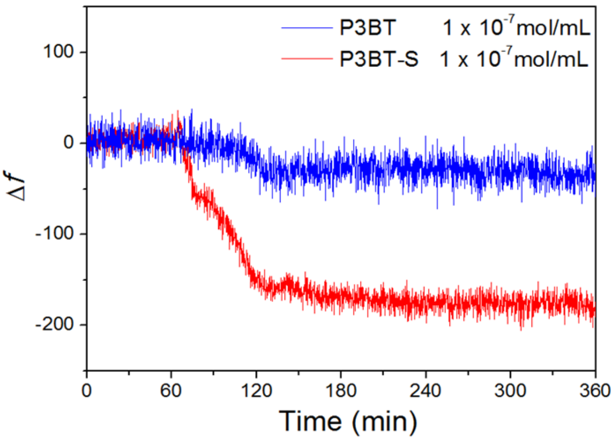


Figure S5. The QCM data for P3BT and P3BT-S absorbed on the Au surface, the weight of P3BT-S growth on Au was calculated by the Sauerbrey Equation:

$$\Delta m = \frac{\sqrt{\rho \cdot \mu}}{2F^2} \cdot (-\Delta f) \qquad \text{5-1}$$

where F is the resonant frequency (9 MHz), ρ is the density of quartz (2.648 g cm^{-3}), and μ is the shear modulus of quartz for AT-cut crystal (2.947×10^{11} g s^{-2} cm^{-2}). Δm for P3BT and P3BT-S solutions were 78 and 460 ng cm^{-2}, respectively. The maximum amount of P3BT-S adsorbed ($m_{\text{end-on}}$) was calculated by assuming that the Au surface was fully covered with a P3BT-S monolayer with an end-on orientation:

$$m_{end-on} = \frac{M}{D_{lamellar} \cdot D_{\pi-\pi} \cdot N_A} \qquad \text{5-2}$$

where M is the number average molecular weight (1734 g/mol by MALDI-TOF-Ms), D_{lamellar} is the lamellar packing distance (13 Å by XRD), $D_{\pi\text{-}\pi}$ is the π-π stacking distance (3.8 Å by XRD), and N_A is Avogadro's constant (6.02×10^{23}). $m_{\text{end-on}}$ was estimated as 582 ng cm^{-2}. Coverage of the Au surface was estimated from $\Delta m/m_{\text{end-on}}$ as 79%.

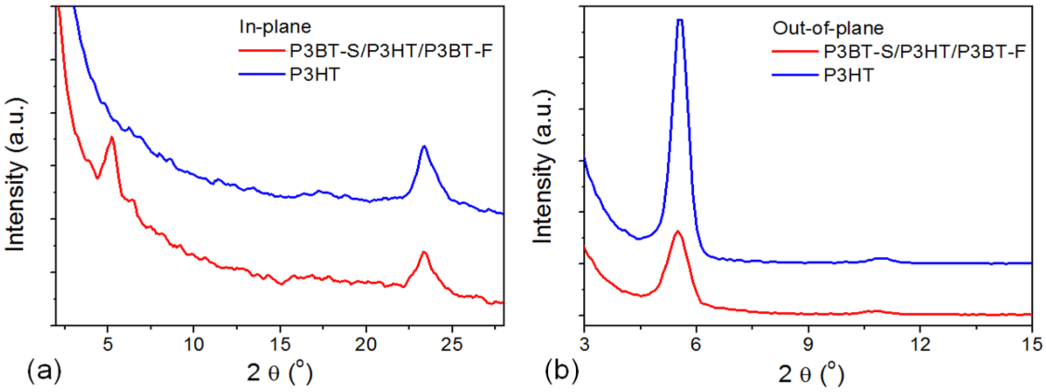


Figure S6. (a) In-plane and (b) out-of-plane GIXRD patterns of the P3HT and P3BT-S/P3HT/P3BT-F films. The out-of-plane and in-plane patterns indicated that in the P3BT-S/P3HT/P3BT-F film (red line) the end-on orientation fraction was larger and the edge-on orientation fraction was smaller compared with the P3HT film (blue line), judging from, respectively. The spectra were shifted in the *y*-direction for ease of comparison.

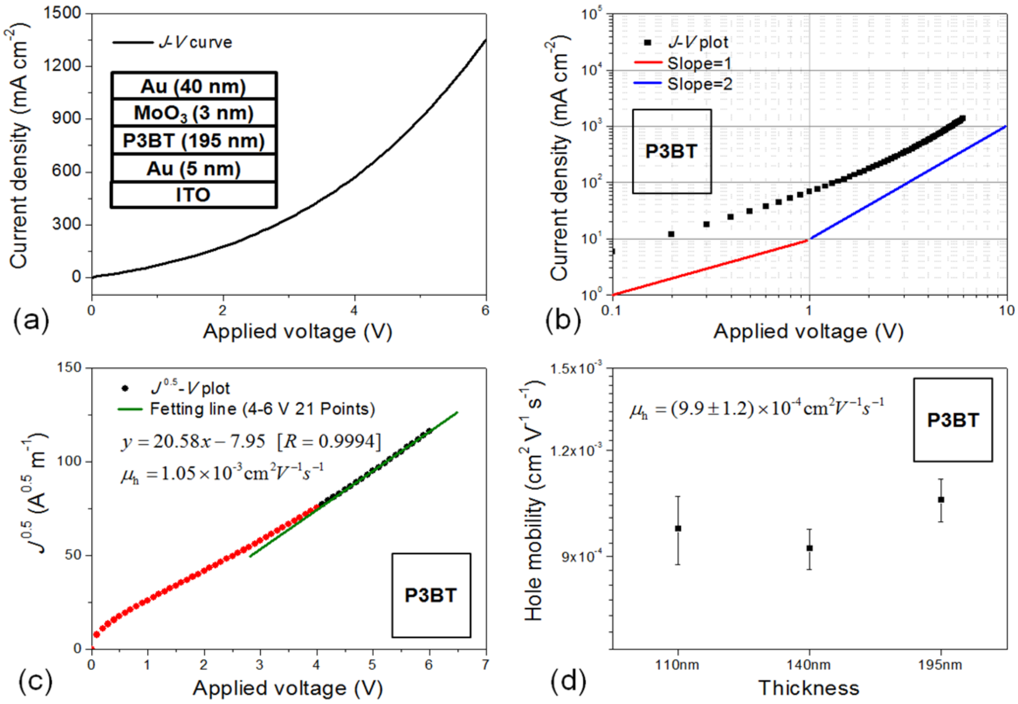


Figure S7. (a), (b), (c), and (d) are row data and mobility calculations for the P3BT film devices. (a) *J*-*V* curve and schematic of corresponding device structure. (b) Double logarithmic *J*-*V* plot. Both the Ohmic region (slope = 1.0) and the SCL region (slope ≈ 2.0) were visible. In the SCL regime, the current was limited by the charge mobility and was consistent with the Mott–Gurney square law,

$$J = \frac{9}{8}\varepsilon_0 \varepsilon_r \mu_{\mathrm{h}} \frac{V^2}{L^3} \tag{8-1}$$

where J is the current density, $\varepsilon_0\varepsilon_r$ is the dielectric constant term, μ_h is the mobility, V is the applied voltage, and L is the active layer thickness. (c) $J^{0.5}$-V plot, we fit 21 points in SCL region to calculate the hole mobility,

$$J^{0.5} = k(V_{app} - V_{bi})\,, k = \frac{\frac{9}{8}\varepsilon_0 \varepsilon_r \mu_{\mathrm{h}}}{L^3} \tag{8-2}$$

where V_{app} is the applied voltage and V_{bi} is the build-in potential. (d) The hole mobility of the P3BT devices with different thicknesses calculated from the SCL

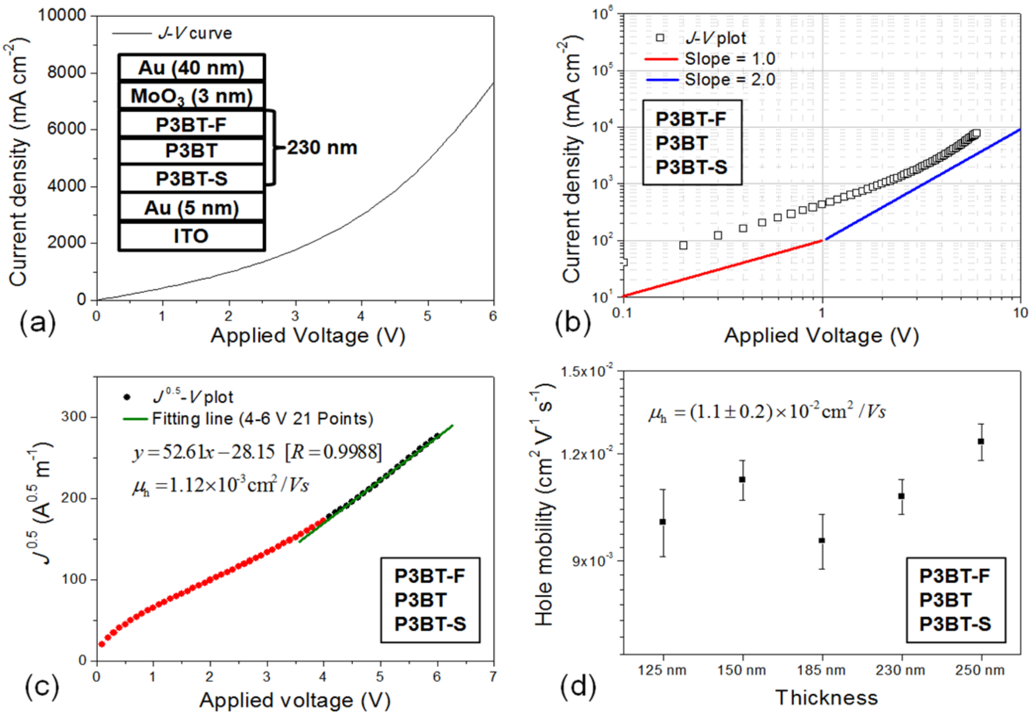


Figure S8. (a), (b), (c), and (d) are row data and mobility calculations for the P3BT-S/P3BT/P3BT-F film devices. (a) *J-V* curve and schematic of corresponding device structure. (b) Double logarithmic *J-V* plot. Both the Ohmic region (slope = 1.0) and SCL region (slope ≈ 2.0) are visible. (c) $J^{0.5}$-V plot. Twenty-one points were fit in SCL region to calculate the hole mobility. (d) The hole mobility of the P3BT-S/P3BT/P3BT-F devices with different thicknesses calculated from the SCL regions.

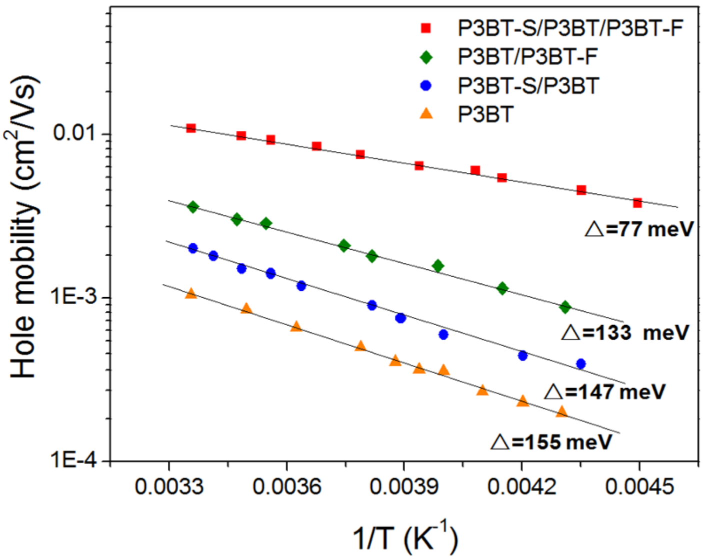


Figure S9. Arrhenius plots of μ_h versus T^{-1} of the different films. The activation energy was calculated from the slope of the lines according to

$$\mu_\mathrm{h} = \mu_0 e^{-\frac{\Delta}{kT}} \tag{9-1}$$

where Δ is the activation energy, μ_0 is the mobility prefactor, k is the Boltzmann constant, and T is the temperature.