Supplementary Information

Instrumentation: NMR spectra were recorded on a Varian 400 MHz spectrometer in $C_2D_2Cl_4$. AFM images were obtained in air using MultiMode microscopewith a Nanoscope controller IIIa (Veeco). X-ray diffraction (XRD) measurements were carried out on a Panalytical X'Pert Pro (PW 3040) with a Cu *Kα* source (λ = 1.5405 Å) in air. The thin films were deposited on SiO_2/Si substrates as a 30 nm thickness.

Material Syntheses: All chemicals are reagent grade unless otherwise indicated. Tetrakis(triphenylphosphine)palladium, 5'-hexyl-2,2'-bithiophene-5-boronic acid pinacol ester, selenophene, and other chemicals were purchased from Strem and Aldrich and used without further purification.

2,2-Biselenophene (1). Into a stirred solution of selenophene (5g, 38.16 mmol) in dry ether (50 mL) at 0 °C under Ar atmosphere was added a 1 equivalent of 1.6 M n-BuLi in pentane, and the reaction mixture was stirred for 1 hour at room temperature. After copper (II) chloride (6.81g, 50.18 mmol) was added portionwise to the reaction at – 78°C, the mixture was stirred for 24 hours at room temperature. The reaction mixture was diluted by ether (50 mL) and filtered. The solid was successively washed 1 N hydrochloric acid, 5 % sodium hydrogen carbonate aquous solution, and finally water. After dried, the residue was purified with recrystallization in methanol and column chromatography. The product, yellow solid was 1.02g (42%). ^{1}H NMR ($CDCl_3$), 200 MHz): δ (ppm) 7.20 (dd, 2H), 7.25 (d, 2H), 7.84 (d, 2H). ^{13}C NMR ($CDCl_3$, 200MHz): δ (ppm) 126.5, 129.4, 130.3. Anal. Calcd for $C_8H_6Se_2$: C, 36.95; H, 2.33. Found: C, 35.43; H, 2.09.

5,5-Dibromo-2,2-biselenophene (2). Into a stirred solution of biselenophene (1) (1.0g, 3.84 mmol) in chloroform-acetic acid (1:1 v/v 25 mL), N-bromosuccinimide (NBS) (1.4g, 3.84 mmol) was added portionwise in dark and the reaction was stirred overnight at room temperature. The mixture was poured into water, and extracted with dichloromethane and brine. After removing solvent, the residue was purified with column chromatography and reprecipitation in methanol. The yellow product was obtained (1.3g, 83%). ^{1}H NMR ($CDCl_3$), 200 MHz): δ (ppm) 6.84 (dd, 2H), 7.13 (d, 2H). ^{13}C NMR ($CDCl_3$, 200MHz): δ (ppm) 115.4, 132.9. Anal. Calcd for $C_8H_4Br_2Se_2$: C, 23.00; H, 0.96. Found: C, 23.34; H, 1.06.

5-hexyl-2-thiopheneboronic acid pinacol ester (3). Into a stirred solution of 2-bromothiphene (5g, 29.7 mmol) in THF (100 mL), 1.7 M n-BuLi in pentane (19.21 mL, 32.67 mmol) was added into reaction mixture slowly at 0°C. After the reaction mixture was stirred for 30 minutes and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10.93g, 59.40 mmol) was added and stirred for 24 hours. The mixture was poured into water (100 mL), and extracted with ether. After removing solvents, the residue was dried over under vacuum and purifed with the triethylamine-treated column chromatography. The slightly yellow liquid was obtained, 7.2g (82.4%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 7.48 (d, 1H), 6.85 (d, 1H), 2.83 (t, 2H), 1.72 (m, 2H), 1.33 (m, 18H), 0.88 (m, 3H). ^{13}C NMR ($CDCl_3$, 200MHz): δ (ppm) 139.9, 138.1, 126.5, 125.12, 84.6, 32.4, 32.3, 30.8, 29.4, 25.4,23.3, 14.8 Anal. Calcd for $C_{16}H_{27}BO_2S$: C, 65.31; H, 9.25. Found: C, 65.02; H, 9.31.

The reaction of **Se2Th1** and **Se2Th2**. Into a 50 mL two-necked flask were added 0.5g (1.15 mmol) of 5,5-Dibromo-2,2-biselenophene (2) and 0.75g (2.55mmol) of 5-hexyl-2-thiopheneboronic acid pinacol ester or 0.96g (2.55 mmol) 5'-hexyl-2,2'-bithiophene-5-boronic acid pinacol ester, tetrakis(triphenylphosphine)palladium (3 mol%) in 10 mL anhydrous toluene were transferred into the mixture. Subsequently, 2 M aqueous sodium carbonate (15 mL) deaerated for 30 minutes and the phase transfer catalyst, Aliquat 336, in toluene purged under argon for 1 hour was transferred via cannula. The reaction mixture was stirred at 80°C for 24 hours. The mixture was cooled to room temperature and then poured into methanol and the solid precipitation was collected. The crude product was heated up to 100°C in the 20 mL of chlorobenzene, cooled down to room temperature, the precipitate was collected by filtration, and then dried in vacuo giving as orange and brown solids (0.64g, 93% and 0.68g, 78%). **Se2Th1** ^{1}H NMR ($C_2D_2Cl_2$, 400 MHz, 120 °C): δ (ppm) 7.12 (dd, 4H), 6.91 (d, 2H), 6.63 (d, 2H). Anal. Calcd for $C_{28}H_{34}S_2Se_2$: C, 56.75; H, 5.78. Found: C, 55.68; H, 6.09. **Se2Th2** ^{1}H NMR ($C_2D_2Cl_2$, 400 MHz, 120°C): δ (ppm) 7.18 (m, 4H), 6.96 (m, 6H), 6.64 (d, 2H). Anal. Calcd for $C_{36}H_{38}S_4Se_2$: C, 57.13; H, 5.06. Found: C, 55.97; H, 5.19.

UV-Vis. Spectroscopy: The absorption spectra were collected diluted in tetrahydrofuran as below. **Se2Th1** and **Se2Th2** have 425 and 419 nm as an absorption maximum respectively. Because **Se2Th2** has a large shoulder absorption around 500 nm and wide absorption width, it appears dark brown in color.

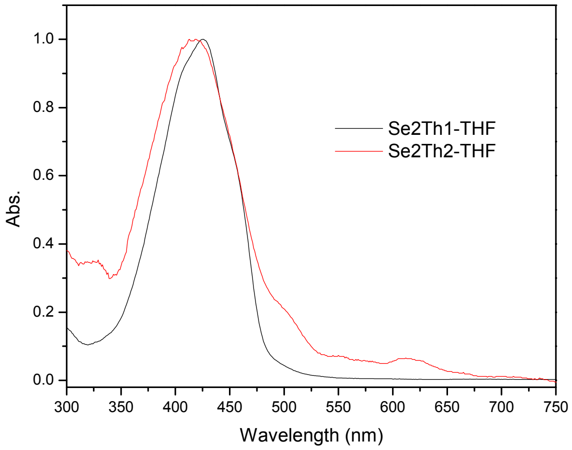

Fig. 1. UV-Visible Spectroscopy

OFET Device Fabrication and Additional Information: All OFETs were fabricated on heavily doped n-type silicon (Si) wafers each covered with a thermally grown silicon dioxide (SiO_2) layer with thickness of 200 nm. The doped Si wafer functions as the gate electrode, and the SiO_2 layer functions as the gate insulator. The active layer was deposited by thermal evaporation under the pressure of $3\text{x}10^{-7}$ torr. The thickness of the deposited films was about 50 nm. Source and drain electrodes using Au were deposited by thermal evaporation using a shadow mask. The thickness of source and drain electrodes was 50 nm. Channel length (L) and channel width (W) were 50 µm and 1.5 mm, respectively. All OFET devices were made in the top contact geometry as shown in Figure 2. Electrical characterization was performed using a Keithley semiconductor parametric analyzer (Keithley 4200) under N_2 atmosphere. The electron mobility (μ) was determined using the following equation in the saturation regime;

$$I_{ds}=(WC_i/2L)\times\mu\times(V_{gs}-V_T)^2,$$

where C_i is the capacitance per unit area of the SiO_2 dielectric (C_i=15 nF/cm^2), V_T is the threshold voltage.

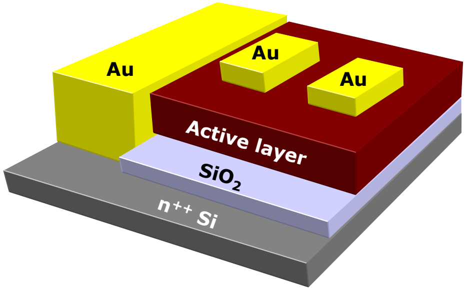

Figure 2. Schematic view of a **Se2Th1** and **Se2Th2** OFET device