Supporting Information for:

Synthesis, Self-Assembly, and Solution-Processed Nanoribbon Field-Effect Transistor of a Fused-Nine-Ring Thienoacene

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Measurements. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AVANCE 400 MHz spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard. Mass spectra were measured on a Bruker Daltonics BIFLEX III MALDI-TOF Analyzer using MALDI mode. Elemental analyses were carried out using a FLASH EA1112 elemental analyzer. Solution (chloroform) and thin-film (on quartz substrate) UV-vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) in CH_2Cl_2 using a computer-controlled Zahner IM6e electrochemical workstation, a glassy-carbon working electrode, a platinum-wire auxiliary electrode, and an Ag wire anodized with AgCl as a pseudo-reference electrode. Potentials were referenced to the ferrocenium / ferrocene ($FeCp_2^{+/0}$) couple by using ferrocene as an internal standard. Thermogravimetric analysis (TGA) measurements were performed on Shimadzu thermogravimetric analyzer (model DTG-60) under a nitrogen flow at a heating rate of 10 °C/min. DSC measurements were performed using an EXSTAR6000 instrument under N_2 at a heating rate of 10 °C/min. POM images were obtained using an Olympus BH-2 microscope equipped with a Nikon COOLPIX P5100 digital camera. Scanning electron microscopic observations were performed on a scanning electron microscope (JEOL 6700F, Japan). TEM observation and SAED was carried out on JOEL 2011. XRD was performed using a Rigaku D/max-2500 X-ray diffractometer.

FET devices were fabricated with a top-contact configuration. A heavily doped n-type Si wafer with a SiO_2 layer of 500 nm and a capacitance of 7.5 nF/cm^2 was used as the gate. OTS was used as a self-assembled surface modifier for SiO_2. Nanoribbon suspension in ethanol was spin-coated on the OTS treated SiO_2/Si substrate. For spin-coated thin film device, a 100 nm-thick (± 10 nm) semiconductor film was spin-coated on top of the OTS-treated SiO_2 from 10 mg/mL $CHCl_3$ solution of compound **1**. Gold source and drain contacts (50 nm) were deposited on the organic layer through a shadow mask under high vacuum. The channel length and width were 50 μm and 3 mm, respectively. Device annealing was carried out at 80 °C for 1 h in a vacuum oven under a pressure of 0.1 Pa. The current-voltage (I-V) characteristics were measured with the Micromanipulator 6150 probe station in a clean and metallic shielded box at room temperature in air, and recorded with a Keithley 4200 SCS.

Synthesis of I: To a three neck round bottom flask was added 2-*n*-hexyl-5-tri-*n*-butylstannyl-thiophene (12 mmol, 5.5 g) and DTT tetrabromide (1.5 mmol, 0.78 g), and dry toluene (15 mL). The mixture was deoxygenated with nitrogen for 30 min. $Pd(PPh_3)_4$ (0.2 mmol, 200 mg) was added under nitrogen. The mixture was refluxed for two days and then cooled down to room temperature. A solution of KF (10 g) in water (50 mL) was added and stirred at room temperature for 2.5 h to remove the tin impurity. The mixture was extracted with $CHCl_3$ (2 × 100 mL), washed with water (2 × 150 mL), and dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by column chromatography on silica gel using petroleum ether as eluent yielding a yellow solid (0.6 g, 46%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (d, J = 3.4 Hz, 2H), 7.01 (d, J = 3.4 Hz, 2H), 6.75 (d, J = 3.3 Hz, 2H), 6.70 (d, J = 3.3 Hz, 2H), 2.83 (m, 8H), 1.73 (m, 8H), 1.39-1.32 (m, 24H), 0.91 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.80, 146.97, 142.31, 132.55, 132.31, 132.07, 127.66, 127.40, 127.12, 125.29, 124.05, 123.94, 31.34, 31.29, 29.96, 28.57, 28.54, 28.06, 26.56, 22.37, 17.06, 13.88, 13.39. MS (MALDI): *m/z* 860 (M^+). Anal. Calcd for $C_{48}H_{60}S_7$: C, 66.92; H, 7.02. Found: C, 66.90; H, 6.95%.

Synthesis of 1: To a 500 mL round bottom flask was added **I** (0.14 mmol, 120 mg) and 250 mL dry dichloromethane. The solution was deoxygenated with nitrogen for 30 min and cooled to 0 ^{o}C. A solution of anhydrous $FeCl_3$ (1.4 mmol, 228 mg) in dry nitromethane (2.5 mL) was added dropwise at 0 ^{o}C under nitrogen. The dark green mixture was stirred at 0 ^{o}C for 15 min, after which stirred at room temperature for 2.5 h. 50 mL of anhydrous methanol was added to quench the reaction. The mixture was washed by brine, saturated aqueous NH_4Cl, and then dried over $MgSO_4$. After removal of the solvents, the residue was recrystallized from CH_2Cl_2 to give **1** as needle-like crystal (96 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (s, 2H), 6.98 (s, 2H), 2.99 (t, J = 7.5 , 4H), 2.79 (br, 4H), 1.88 (m, 4H), 1.74 (m, 4H), 1.50-1.36 (m, 24H), 0.99-0.92 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.62, 136.35, 132.05, 127.98, 127.34, 123.78, 118.89, 118.56, 31.66, 31.58, 31.03, 30.95, 30.49, 30.41, 28.99, 28.91, 22.62, 22.55, 14.09, 14.04. MS (MALDI): *m/z* 856 (M^+). Anal. Calcd for $C_{48}H_{56}S_7$: C, 67.24; H, 6.58. Found: C, 67.18; H, 6.59%.

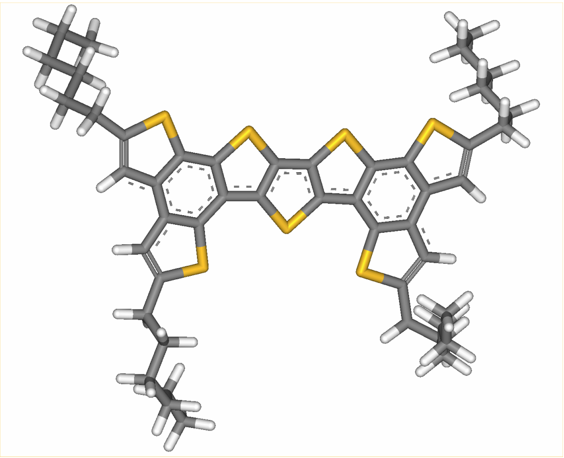

Fig. S1 Optimized configuration of **1** after energy minimization.

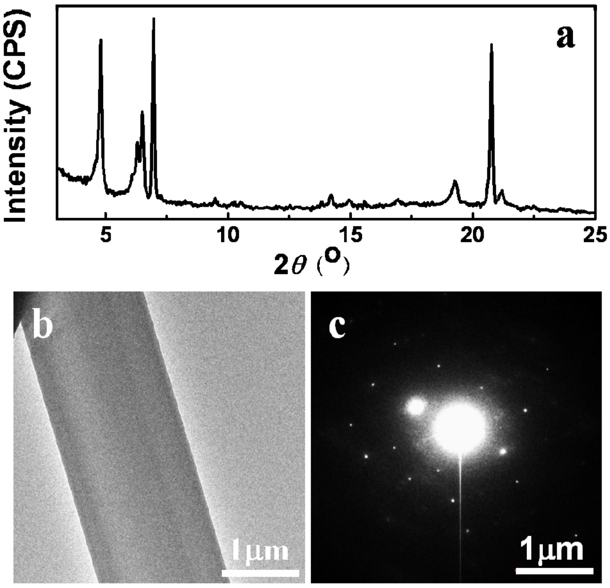

Fig. S2 (a) XRD pattern, (b) TEM image and (c) the corresponding SAED pattern of microribbons of **1**.