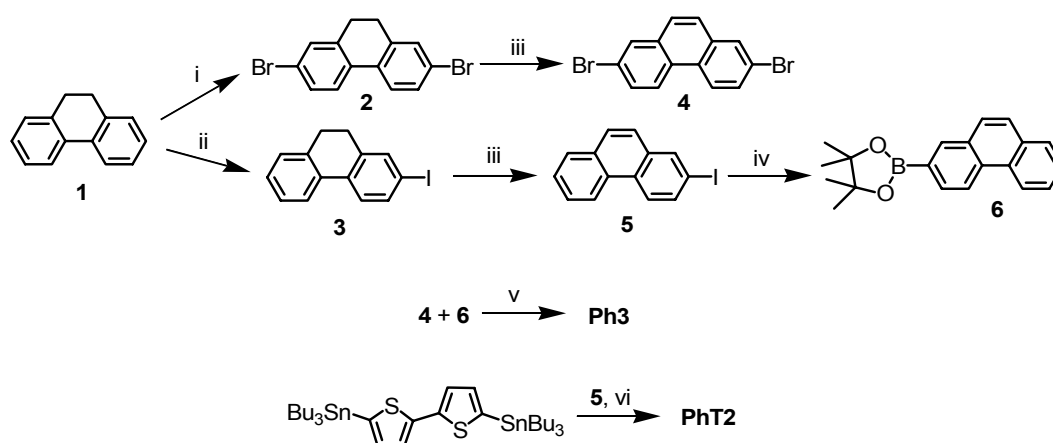


General. Elemental analysis was obtained on an Eager 300 elemental analyzer. Nuclear magnetic resonance spectra were taken on a Bruker 300- and 400-M Hz spectrometer. Chemical shifts of phenanthrene-based oligomers were reported as δ values (ppm) relative to $C_2D_2Cl_4$ at 5.94 ppm. Chemical shifts of other compounds were reported relative to internal tetramethylsilane. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA7 thermogravimetric analyzer at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ at a nitrogen flow. Differential scanning calorimetry (DSC) was run on a Perkin-Elmer DSC7 at a heating /cooling rate of $10/-10\text{ }^\circ\text{C min}^{-1}$ at a nitrogen flow. UV-vis and fluorescence spectra were obtained on a Perkin-Elmer Lambda 35 and Perkin-Elmer LS50B.



i) Br_2 , FeCl_3 , CHCl_3 , room temperature. ii) I_2 , H_5IO_6 , H_2O , H_2SO_4 , CH_3COOH , $80\text{ }^\circ\text{C}$. iii) (1) NBS, BPO, CCl_4 ; (2) CH_3COOK , CH_3COOH , CCl_4 , reflux. iv) (1) $n\text{-BuLi}$, $-78\text{ }^\circ\text{C}$, THF; (2) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, $-78\text{ }^\circ\text{C}$ to room temperature. v) $\text{Pd}(\text{PPh}_3)_4$, $\text{Na}_2\text{CO}_3(2\text{M})$, toluene, $90\text{ }^\circ\text{C}$. vi) $\text{Pd}(\text{PPh}_3)_4$, DMF, $90\text{ }^\circ\text{C}$.

Materials. All chemical reagents and solvents were used as received from commercial sources without further purification except tetrahydrofuran (THF) and toluene that had been distilled over sodium/benzophenone. N, N-dimethyl formamide (DMF) was dried with CaH_2 and distilled under reduces pressure. 9,10-dihydrophenanthrene (**1**)^[1], 2,7-dibromophenanthrene (**4**)^[2], 2-iodophenanthrene (**5**)^[2] and 5,5'-bis(tri-n-butylstannyl)- 2,2'-bithiophene^[3] were synthesized according to the reported methods.

2,7-Dibromo-9, 10-dihydrophenanthrene (2)

The procedure for the synthesis of **2** was similar to the bromination of fluorene^[4] to afford the product as a white needle-like crystal after recrystallization with CHCl₃ in a yield of 85%. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.55 (d, *J*=8.4 Hz, 2 H), 7.42 (dd, *J*=2.0 Hz, 8.2 Hz, 2 H), 7.38 (d, *J*=2.0 Hz), 2.83 (s, 4 H).

2-Iodo-9,10-dihydrophenanthrene (3)

A mixture of 9,10-dihydrophenanthrene (3.0 g 16.64 mmol), glacial HOAc (17 ml), concd. H₂SO₄ (0.25 ml) and water (3.3 ml) was heated to 80 °C. Periodic acid dehydrate (H₅IO₆, 0.76 g, 3.33 mmol) and pulverized I₂ (1.70 g, 6.70 mmol) were added. The mixture was stirred for 12 hrs under 80 °C. Upon dilution with aqueous NaHSO₃, the mixture changed from purple to yellow. The mixture was extracted with methylene chloride. The organic layer was washed with brine before dried over MgSO₄. Upon evaporation off the solvent, the residue was purified with column chromatography on silica gel with petroleum ether as the eluent to afford **3** (3.77g, 74%) as a yellow oil that was sufficiently pure to be used without further purification though containing unreacted 9,10-dihydrophenanthrene. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.74 (d, *J*=7.44 Hz, 1 H), 7.67-7.62 (m, 2 H), 7.48 (dd, *J*= 4.62 Hz, 7.92 Hz, 1 H), 7.36-7.26 (m, 3 H), 2.87 (m, 4 H).

2,7-Dibromophenanthrene (4)

The compound **4** was synthesized according to the known method^[2] from **2** as a white crystal after recrystallization with CHCl₃ in a 98% yield. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 8.43 (d, *J*=9.0 Hz, 2 H), 8.01 (d, *J*=2.4 Hz, 2 H), 7.71 (dd, *J*=1.8 Hz, 9.0 Hz, 2 H), 7.64 (s, 2 H).

2-Iodophenanthrene (5)

The compound **5** was synthesized according to the known method^[2] from **3** as a white solid after recrystallization with ethanol in a 95% yield. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 8.63 (d, *J*=7.83 Hz, 1H), 8.40 (d, *J*=8.76 Hz, 1 H), 8.26 (d, *J*=1.8 Hz, 1 H), 7.9 (dd, *J*=2.1 Hz, 8.70Hz, 1 H), 7.73 (d, *J*=8.60 Hz, 1 H), 7.67-7.60 (m, 4 H).

Phenanthren-2-yl-4,4,5,5-tetramethyl-[1,3,2] dioxaborolane (6)

Into a solution of **5** (3.12 g, 10.3 mmol) in anhydrous THF (130 ml) was added *n*-BuLi (2.86 M in hexane, 4.30 ml, 12.3 mmol) at -78 °C. The reaction mixture was stirred for 1h before adding 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (2.50 ml, g, 12.31 mmol). The mixture was warmed to room temperature, stirred overnight and poured into a large amount of water for extraction with chloroform. The organic extracts were washed with brine and dried over MgSO₄. Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum ether:methylene chloride (1:1) as the eluent to afford **6** (2.4 g, 77%) as a white solid. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 8.72 (d, *J*=7.77 Hz, 1 H), 8.68 (d, *J*=8.34 Hz, 1 H), 8.39 (s, 1 H), 8.04 (dd, *J*=1.14 Hz, 8.28 Hz, 1 H), 7.89 (dd, *J*=1.77 Hz, 7.68 Hz, 1 H), 7.78 (d, *J*=8.90 Hz, 1H), 7.72 (d, *J*=8.90 Hz, 1H), 7.68-7.58 (m, 2 H), 1.41 (s, 12 H).

2,2';7',2''-Terphenanthrenyl (Ph3)

Into a mixture of **4** (1.0 g, 3.0 mmol), **6** (2.0 g, 6.57 mmol) and Pd(PPh₃)₄ (173 mg, 0.15 mmol) in a 100 ml Schlenk tube was added toluene (40 ml) and 2.0 M Na₂CO₃ solution (27 ml). The reaction mixture was stirred at 90 °C for 2 days. After the mixture was cooled to room temperature, the precipitation was collected by filtration and washed successively with water and acetone to give a white solid. The product was further purified by vacuum sublimation before characterizations to provide a white crystal (0.86 g, 54%). M.p. 434 °C (determined by DSC). Anal. Calcd for C₄₂H₂₆: C, 95.06; H, 4.94. Found: C, 94.75; H, 5.03.

5,5'-Bis(phenanthren-2-yl)-2,2'-bithiophene (PhT2)

Into a mixture of **5** (2.85 g, 9.37 mmol), 5, 5'-bis(tri-*n*-butylstannyl)-2,2'-bithiophene (3.48 g, 4.67 mmol) and Pd(PPh₃)₄ (135 mg, 0.12 mmol) in a 100 ml Schlenk tube was added DMF (45 ml). The reaction mixture was stirred at 90 °C for 2 days. After the mixture was cooled to room temperature, the precipitation was collected by filtration and washed successively with water and acetone. The product was further purified by vacuum sublimation before characterizations to provide a yellow crystal (1.20 g, 50%). M.p. 393 °C (determined by DSC). ¹H NMR (400 MHz, C₂D₂Cl₄, 100 °C): δ (ppm)

8.69-8.64 (m, 4 H), 8.09 (s, 2 H), 7.92-7.88 (m, 4 H), 7.76 (s, 4 H), 7.66 (d, $J=7.2$ Hz, 2 H), 7.58 (t, $J=7.2$ Hz, 2 H), 7.43 (m, 2 H), 7.29 (m, 2 H). Anal. Calcd for $C_{36}H_{22}S_2$: C, 83.36; H, 4.28; S, 12.36 Found: C, 83.03; H, 4.09; S, 12.26

Cyclic voltammetry (CV) measurements. CV measurements were performed on a CHI660a electrochemical analyzer with a three-electrode cell in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in acetonitrile at a scan rate of 80 mV/s. The thin films of **Ph3** and **PhT2** for CV measurements were prepared by vacuum depositing the oligomers onto a platinum electrode (0.6 cm^2). A Pt wire was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. Its potential was calibrated by the ferrocene/ferrocenium (0.42 V vs Ag/AgCl in acetonitrile). HOMO energies was estimated by the empirical equation $HOMO = -(4.44 + E_{oxd}^{onset})$.^[6]

X-ray Diffraction Studies. X-ray diffraction (XRD) measurements were carried out with a D\Max 2500V X-ray diffractometer system using Cu $K\alpha$ radiation ($\lambda = 1.54056\text{ \AA}$) at 50 KV and 250 mA with a graphite monochromator.

AFM Studies. AFM measurements were carried out in air using SPI3800N in non-contact mode.

OFETs Device Fabrication. OFETs were constructed on heavily doped n-type silicon wafers with resistivities of 0.01– 0.015 ($\Omega\cdot\text{cm}$) covered with 3000 \AA -thick thermally grown silicon dioxide (SiO_2) with a capacitance of 10 (nF/cm^2) for **Ph3**, and with 1500 \AA -thick thermally grown silicon dioxide (SiO_2) with a capacitance of 23 (nF/cm^2) for **PhT2**. The SiO_2 acts as a gate dielectric layer, and the silicon wafer serves as gate electrode. The SiO_2 was also pretreated with OTS for the device fabrication of **PhT2**. The **Ph3** and **PhT2** were deposited on the SiO_2 by vacuum evaporation at a rate 0.1-10 $\text{\AA}/\text{s}$ under pressure of $4.2\text{--}6.8 \times 10^{-4}\text{ Pa}$. The thickness of the semiconductor layer was 30 nm monitored by a quartz oscillator. During the evaporation, the temperature of the substrate was maintained by heating a copper block on which the substrate was mounted. Gold (40 nm) was used as source and drain electrodes and deposited on the organic semiconductor layer through a showed mask with a channel width (W) of 1300

μm and a channel length (L) of $200\ \mu\text{m}$. The electrical measurements were performed with two Keithley 236 source/measure units at room temperature in air ambient. Photo-stability of the devices was tested with UV irradiation ($0.32\ \text{mW}$) at a wavelength of $365\ \text{nm}$ under a laboratory UV lamp.

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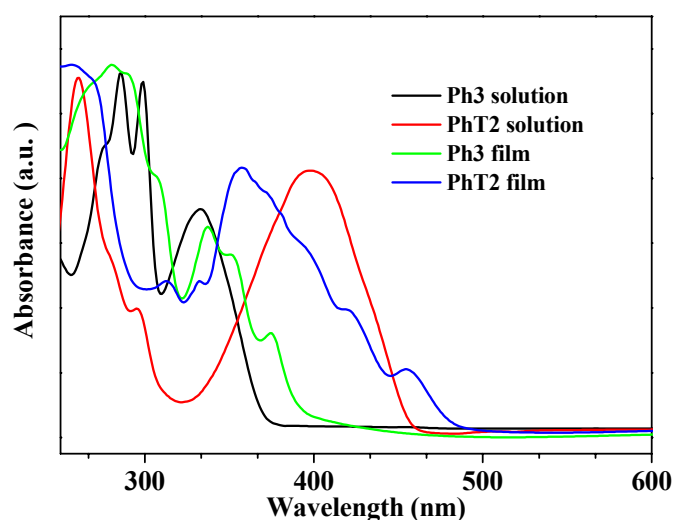


Figure S1. UV-vis spectra of **Ph3** and **PhT2** solution ($10^{-5}\ \text{M}$ in chloroform) and films.

Table S1. OFETs performance of **Ph3** and **PhT2**

compound	T _S (°C)	μ _{FET} (cm ² /V·s)	I _{on} /I _{off}	V _T (V)
Ph3	100	5.9 × 10 ⁻⁴	3 × 10 ²	-50
	150	1.1 × 10 ⁻²	2 × 10 ⁵	-46
	200	4.4 × 10 ⁻³	1 × 10 ⁴	-56
PhT2	50	1.9 × 10 ⁻²	5 × 10 ⁴	-18
	100	(4.2 ± 0.2) × 10 ⁻² ^b	(1-2) × 10 ⁵ ^b	-12 ± 3 ^b
	150	2.5 × 10 ⁻²	4 × 10 ⁴	-14
	100 ^a	0.105 ± 0.05 ^b	(1-3) × 10 ⁵	-27 ± 3 ^b

^a The substrate was modified with OTS. ^b The average of three individual devices.