

Electronic Supplementary Information (ESI):

**Light-emitting organic field-effect transistors based on highly
luminescent single crystals of thiophene/phenylene co-oligomers**

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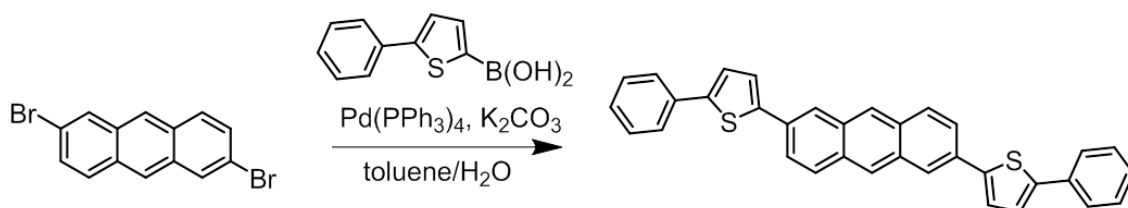
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General. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on a Bruker Daltonics Autoflex III spectrometer using dithranol as the matrix. Elemental analyses were carried out with a Yanaco MT-5 CHN coder. The photoluminescence (PL) spectra were measured with a HORIBA scientific FluoroMax-4 spectrophotometer. The photoluminescence quantum yields (Φ_{PL}) were measured with a Hamamatsu Photonics Quantaaurus-QY absolute PLQY spectrometer. The PL lifetimes (τ_{flu}) were measured with a Hamamatsu Photonics C4334 streak camera. The ASE spectra were recorded with a Hamamatsu Photonics PMA-11 multi-channel photodiode. An excitation source was an USHO optical system Ken-X2020 nitrogen gas laser (excitation wavelength of 337 nm, pulse width of ~800 ps, and repetition rate of 20 Hz). The HOMO energy levels of thin films were determined using a Riken-Keiki AC-3 photoelectron spectrometer. The optical microscopic images were taken using a Nikon LV150 optical microscope. X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV diffractometer with $\text{CuK}\alpha$ radiation. The density-functional theory (DFT) computations were performed on the Gaussian 09 program package, using the B3LYP functional with the 6-311G (d,p) basis set.

Materials and Syntheses. All reagent and solvent were purchased from, Sigma-Aldrich, Tokyo Chemical Industry (TCI), or Wako Pure Chemical Industries, and used as received unless otherwise noted. The synthetic route to obtain BPTA, BPTN, and BPTB are outlined in Scheme S1-S3. All reactions were performed under an N_2 atmosphere in dry solvents.

Scheme S1. Preparation of 2,6-bis(5-phenylthiophene-2-yl)anthracene (BPTA)



To a solution of 2,6-dibromoanthracene (1.00 g, 2.97 mmol) and 5-phenylthiophene-2-boronic acid (1.47 g, 7.20 mmol) in toluene (80 mL) were added $\text{Pd}(\text{PPh}_3)_4$ (0.17 g, 0.15 mmol) and aqueous K_2CO_3 (2.0 M, 30 mL; N_2 bubbled before use). The mixture was stirred for 24 h at 80 °C. After cooling to room temperature, the reaction mixture was poured into water. The formed precipitate was collected by filtration, and washed with water and methanol in that order. The product was obtained as a yellow solid (yield: 1.22 g, 83 %). The compound was further purified by temperature-gradient sublimation under a reduced pressure.

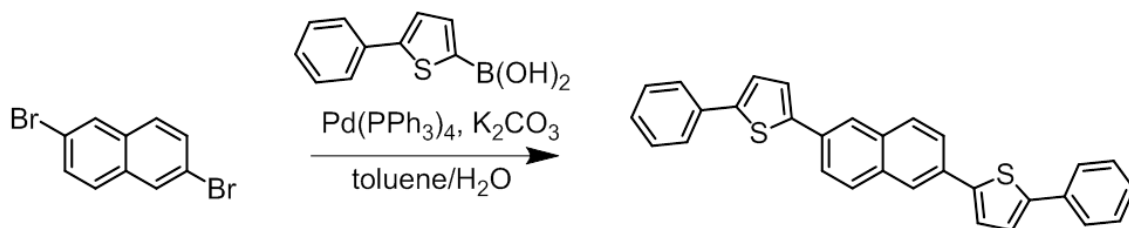
[MS]

MALDI-TOF m/z [M]⁺: 494.12; found: 494.16.

[Elemental analysis]

Calcd (%) for $\text{C}_{34}\text{H}_{22}\text{S}_2$: C, 82.55; H, 4.48; found: C, 82.43; H, 4.32.

Scheme S2. Preparation of 2,6-bis(5-phenylthiophen-2-yl)naphthalene (BPTN)



This compound was synthesized from 2,6-dibromonaphthalene (0.85 g, 2.97 mmol), 5-phenylthiophene-2-boronic acid (1.47 g, 7.20 mmol), and Pd(PPh₃)₄ (0.17 g, 0.15 mmol) by adopting the procedure used for BPTA. The product was obtained as a light green solid (yield: 0.98 g, 74 %). The compound was further purified by temperature-gradient sublimation under a reduced pressure.

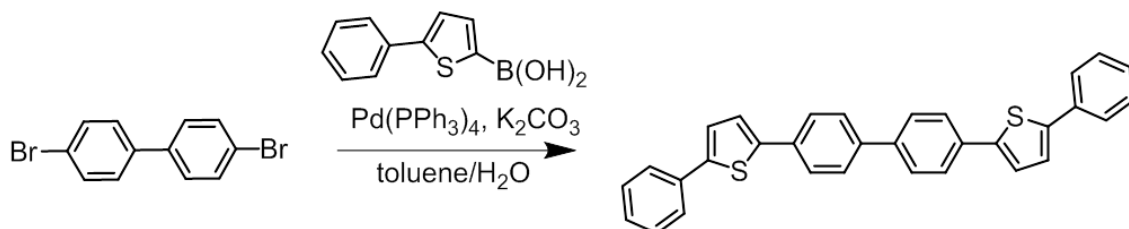
[MS]

MALDI-TOF m/z [M]⁺: 444.10; found: 444.13.

[Elemental analysis]

Calcd (%) for C₃₀H₂₀S₂: C, 81.04; H, 4.53; found: C, 80.97; H, 4.49.

Scheme S3. Preparation of 4,4'-bis(5-phenylthiophen-2-yl)-1,1'-biphenyl (BPTB)



This compound was synthesized from 4,4'-dibromobiphenyl (0.92 g, 2.99 mmol), 5-phenylthiophene-2-boronic acid (1.47 g, 7.20 mmol), and Pd(PPh₃)₄ (0.17 g, 0.15 mmol) by adopting the procedure used for BPTA. The product was obtained as a light green solid (yield: 0.89 g, 63 %). The compound was further purified by temperature-gradient sublimation under a reduced pressure.

[MS]

MALDI-TOF m/z [M]⁺: 470.12; found: 470.17.

[Elemental analysis]

Calcd (%) for C₃₂H₂₂S₂: C, 81.66; H, 4.71; found: C, 81.59; H, 4.68.

No NMR signals could be obtained for BPTA, BPTN, and BPTB because the solubility in solvents (CDCl₃ and DMSO-*d*₆) is not sufficient for the measurements even at elevated temperatures.

Calculation of transition dipole moments.

Table S1: Transition dipole moment characterization for BPTA, BPTN, and BPTB calculated using time-dependent density functional theory (TD-DFT) at the B3LYP/6-311G level of theory.

Compound	μ (D)	θ (deg)
BPTA	8.51	11.5
BPTN	26.8	1.5
BPTB	24.3	0.1

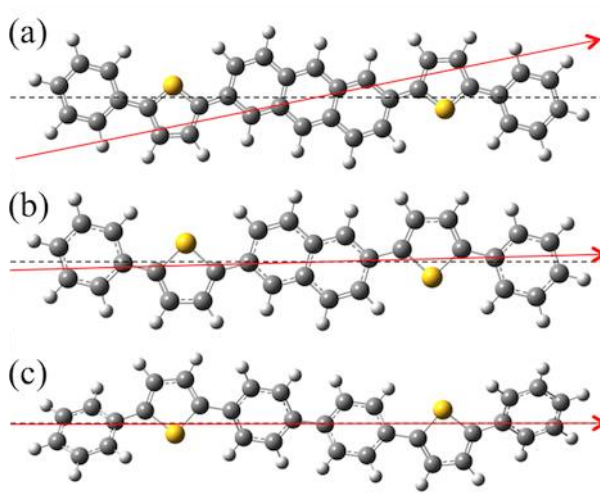


Fig. S1: The transition dipole moment for (a) BPTA, (b) BPTN, and (c) BPTB. Dashed lines denote the molecular long axes, and the red arrows indicate the transition dipole moments.

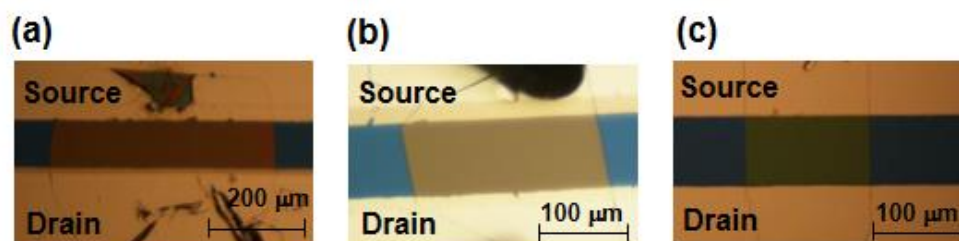


Fig. S2: Optical photomicrographs of single-crystal OFETs based on (a) BPTA, (b) BPTN, and (c) BPTB.

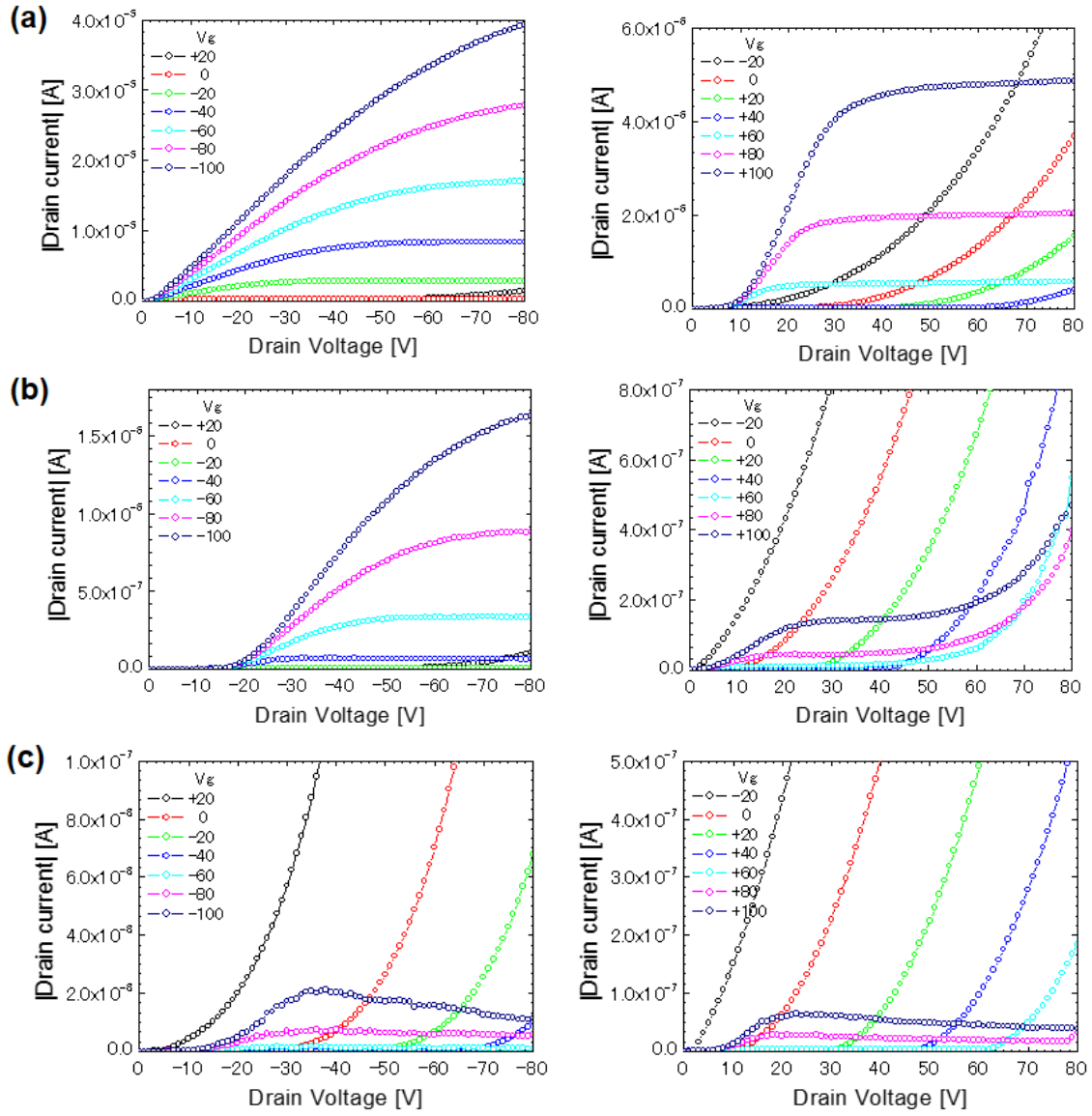


Fig. S3: Output characteristics of OFET devices based on (a) BPTA, (b) BPTN, and (c) BPTB single crystals for *p*-channel (left panels) and *n*-channel (right panel) operations.