Supporting Information for

Mixed-Orbital Charge Transport in N-Shaped Benzene- and Pyrazine-Fused Organic Semiconductors

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1. Materials and General Characterization Methods

Reagents and solvents were purchased from Tokyo Chemical Industry Co., Ltd, Sigma Aldrich, Wako Chemicals, and Kanto Chemicals. Anhydrous solvents were purified by the solvent purification system prior to use. All reactions were carried out under an atmosphere of argon. Analytical thin-layer chromatography (TLC) was performed on glass plates with silica gel containing fluorescent indicator (Merck TLC Silica gel 60 F254, 1 mm). Column chromatography was performed on Kanto silica gel 60. All NMR spectra were recorded on JEOL ECS400 spectrometer. Chemical shifts were reported in parts per million (ppm, δ scale) from residual protons in the deuterated solvent for $^1$H NMR (5.93 ppm for 1,1,2,2-tetrachloroethane-d$_2$ (TCE-d$_2$) and 7.26 ppm for chloroform-d (CDCl$_3$)) and $^{13}$C NMR (73.78 ppm for 1,1,2,2-tetrachloroethane-d$_2$ (TCE-d$_2$) and 77.16 ppm for chloroform-d (CDCl$_3$)). The data were presented in the following format: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of a doublet, m = multiplet), coupling constant in Hertz (Hz), signal area integration in natural numbers. Time-of-flight high-resolution mass (TOF-MS) spectrometry measurements were measured on a BRUKER compact-TKP2 mass spectrometer with the atmospheric pressure chemical ionization (APCI) method. Elemental analysis measurements were carried out on a JScience Lab JM10 CHN analyzer at the Comprehensive Analysis Center, the Institute of Scientific and Industrial Research, Osaka University.

2. Theoretical Calculations

The initial molecular structures were constructed in the GaussView 5.0 Software and optimized at the B3LYP/6-311G(d) level of theory. Kohn-Sham energy levels of the compounds in this work were calculated at the same level with the Gaussian09 package. Based on the packing structure, transfer integral ($t$) values of the HOMOs between neighboring molecules were estimated by the dimer method with Density Functional Theory, and the electronic band structure using the periodic boundary were both calculated at the PBEPBE/6-31G(d) level of theory. Effective mass of holes were calculated as $m^* = \hbar^2 \left( \frac{\partial^2 E(x)}{\partial x^2} \right)^{-1}$ along respective directions.
Figure S1. Effective masses and band structures of C_{10}–DNBDT–NW from plane-wave and tight-binding approximations (colored shades illustrate the band widths).

3. Synthetic Procedures

2,5-bis(3-bromo-6-decynaphthalen-2-yl)pyrazine (2a)

To a three-neck round bottom flask was added 3-bromo-6-decyl-2-iodonaphthalene (5.87 g, 12.4 mmol, 1.00 equiv.) and anhydrous THF (50.0 mL). After the solution was cooled to -78 °C, 1.0 M of iPrMg in THF (13.0 mL, 13.00 mmol, 1.05 equiv.) was added dropwise via a syringe, and the mixture was stirred at the same temperature for 15 min before 1.0 M of ZnCl$_2$ in THF (13.0 mL, 13.0 mmol, 1.05 equiv.) was added. The mixture was slowly raised to room temperature and 0.5 M of LiCl in THF (26.0 mL, 13.0 mmol, 1.05 equiv.) was added dropwise via a syringe, followed by additions of 2,5-dibromopyrazine (1.33 g, 5.58 mmol, 0.45 equiv.), Pd(dba)$_2$ (213 mg, 0.370 mmol, 3 mol%), and P(2-furyl)$_3$ (172 mg, 0.740 mmol, 6 mol%) under argon. The mixture was stirred at room temperature for 19 h before the reaction was quenched by saturated aqueous NH$_4$Cl, and the crude was extracted by CHCl$_3$, dried over MgSO$_4$, and concentrated in vacuo. The crude was purified by column chromatography using hexanes/CHCl$_3$ (1:1, v/v) as eluents to afford the target compound as a white solid (3.30 g, 77% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 9.12 (s, 2H), 8.19 (s, 2H), 8.12 (s, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.59 (s, 2H), 7.42 (dd, J = 1.6 Hz, 6.8 Hz, 1.6 Hz, 2H), 2.81 (t, J = 7.6 Hz, 7.6 Hz, 4H), 1.73 (quint, J = 7.6 Hz, 6.8 Hz, 7.6 Hz, 8.0 Hz, 4H), 1.36-1.27 (m, 28H), 0.89 (t, J = 7.2 Hz, 6.8 Hz, 6H). $^{13}$C NMR (100.6 MHz, CDCl$_3$): δ 152.2, 144.8, 143.1, 134.8, 134.4, 132.0, 131.4, 130.8, 128.9, 128.3, 125.3, 118.9, 36.3, 32.0, 31.3, 29.7 (apparent t), 22.8, 14.3. HRMS (APCI$^+$-TOF): Calcd for C$_{44}$H$_{54}$Br$_2$N$_2$ [M+H] 769.2732. Found, 769.2666.
2,5-bis(3-bromo-6-(trimethylsilyl)naphthalen-2-yl)pyrazine (2b)

To a flame-dried three-neck round bottom flask was added (7-bromo-6-iodonaphthalen-2-yl)trimethylsilane (25.1 g, 61.9 mmol, 1.00 equiv.) and anhydrous THF (65.0 mL). After the solution was cooled to -78 °C, 1.0 M of iPrMg in THF (65.0 mL, 65.0 mmol, 1.05 equiv.) was added dropwise via cannula transfer, and the mixture was stirred at the same temperature for 15 min before 1.0 M of ZnCl₂ in THF (65.0 mL, 65.0 mmol, 1.05 equiv.) was added. The mixture was slowly raised to room temperature and 0.5 M of LiCl in THF (130 mL, 65.0 mmol, 1.05 equiv.) was added dropwise via cannula transfer, followed by additions of 2,5-dibromopyrazine (6.64 g, 27.9 mmol, 0.45 equiv.), Pd(dba)₂ (1.07 g, 1.86 mmol, 3 mol%), and P(2-furyl)₃ (861 mg, 3.71 mmol, 6 mol%) under argon. The mixture was stirred at room temperature for 19 h before the reaction was quenched by saturated aqueous NH₄Cl, and the crude was extracted by CHCl₃, dried over MgSO₄, and concentrated in vacuo. The crude was purified by column chromatography using hexanes/CHCl₃ (3:2, v/v) as eluents to afford the target compound as a white solid (11.8 g, 67% yield).

1H NMR (400 MHz, CDCl₃): δ 9.14 (s, 2H), 8.27 (s, 2H), 8.15 (s, 2H), 7.99 (s, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.69 (dd, J = 0.8 Hz, 6.8 Hz, 1.2 Hz, 2H), 0.38 (s, 18H). 13C NMR (100.6 MHz, CDCl₃): δ 152.2, 144.9, 141.1, 135.5, 134.0, 132.6 (apparent t), 131.5, 131.2, 127.4, 118.7, -1.0. HRMS (APCI⁺-TOF): Calcd for C₃₀H₃₀Br₂N₂Si₂ [M+H]⁺ 633.0393. Found, 633.0338.

2,5-dibromo-3,6-bis(3-bromo-6-decynaphthalen-2-yl)pyrazine (3a)

Preparation of tBuZn(TMP)Li: To a flame-dried three-neck round bottom flask was added anhydrous THF (80.0 mL) and TMPH (13.1 mL, 77.0 mmol, 6.00 equiv.) under argon, and the solution was cooled to -78 °C before 1.54 M of n-BuLi in hexanes (50.0 mL, 77.0 mmol, 6.00 equiv.) was added dropwise via cannula transfer. In a separate flame-dried three-neck round bottom flask was added 1.0 M of ZnCl₂ in THF (77.0 mL, 77.0 mmol, 6.0equiv.) under argon, and the solution was cooled to 0 °C before 1.77 M of t-BuLi in pentane (87.0 mL, 154 mmol, 12.0 equiv.) was added via cannula transfer. The gray suspension was then added to the first organometallic solution via cannula transfer.

To a flame-dried Schlenk tube was added compound 2b (8.12 g, 12.8 mmol, 1.00 equiv.) and anhydrous THF (75.0 mL) under argon and the mixture was cooled to -78 °C. Then, as prepared tBuZn(TMP)Li solution was added to the Schlenk tube containing compound 2b via cannula transfer, and the mixture was stirred at 0 °C for 2 h. Subsequently, BrCCl₃CCl₂Br (83.7 g, 257
mmol, 20.0 equiv.) was added portionwise to the dark brown mixture under argon at 0 °C, and the mixture was stirred at room temperature for 20 h. The reaction was quenched by saturated aqueous NH₄Cl, extracted with CHCl₃, dried over MgSO₄, and the solvent was removed in vacuo. The crude was purified by column chromatography using hexanes/CHCl₃ (7:3, v/v) as eluents to give the target compound as a white solid (3.44 g, 34% yield). ¹H NMR (400 MHz, TCE-d₂): δ 9.01 (s, 2H), 8.25 (s, 2H), 8.03 (d, J = 8.8 Hz, 2H), 7.71 (s, 2H), 7.43 (d, J = 8.8 Hz, 2H), 2.85 (t, J = 7.6 Hz, 7.6 Hz, 4H), 1.78 (quint, J = 6.8 Hz, 8.0 Hz, 7.2 Hz, 7.2 Hz, 4H), 1.38-1.29 (m, 28H), 0.88 (t, J = 6.8 Hz, 6.8 Hz, 6H).

2,5-dibromo-3,6-bis(3-bromo-6-(trimethylsilyl)naphthalen-2-yl)pyrazine (3b)

Preparation of tBuZn(TMP)Li: To a flame-dried three-neck round bottom flask was added anhydrous THF (35.0 mL) and TMPH (4.21 mL, 24.8 mmol, 6.00 equiv.) under argon, and the solution was cooled to -78 °C before 1.54 M of n-BuLi in hexane (16.1 mL, 24.8 mmol, 6.00 equiv.) was added dropwise via cannula transfer. In a separate flame-dried three-neck round bottom flask was added 1.0 M of ZnCl₂ in THF (24.8 mL, 24.8 mmol, 6.0 equiv.) under argon, and the solution was cooled to 0 °C before 1.77 M of t-BuLi in pentane (30.0 mL, 49.5 mmol, 12.0 equiv.) was added via cannula transfer. The gray suspension was then added to the first organometallic solution via cannula transfer.

To a flame-dried Schlenk tube was added compound 2b (3.18 g, 4.13 mmol, 1.00 equiv.) and anhydrous THF (25.0 mL) under argon and the mixture was cooled to -78 °C. Then, as prepared tBuZn(TMP)Li solution was added to the Schlenk tube containing compound 2b via cannula transfer, and the mixture was stirred at 0 °C for 2 h. Subsequently, BrCCl₂CCl₂Br (26.9 g, 82.5 mmol, 20.0 equiv.) was added portionwise to the dark brown mixture under argon at 0 °C, and the mixture was stirred at room temperature for 20 h. The reaction was quenched by saturated aqueous NH₄Cl, extracted with CHCl₃, dried over MgSO₄, and the solvent was removed in vacuo. The crude was purified by column chromatography using hexanes/CHCl₃ (7:3, v/v) as eluents to give the target compound as a white solid (437 mg, 11% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.24 (s, 2H), 7.99 (d, J = 6.0 Hz, 4H), 7.88 (d, J = 8.4 Hz, 2H), 7.71 (dd, J = 0.8 Hz, 7.2 Hz, 1.2 Hz, 2H), 0.38 (s, 18H). ¹³C NMR (100.6 MHz, CDCl₃): δ 157.7, 144.7, 141.7, 138.3,
To a flame-dried Schlenk tube was added compound 2a (344 mg, 0.370 mmol, 1.00 equiv.), and anhydrous Et₂O (15.0 mL) under argon. The solution was cooled to -78 °C and 1.54 M of n-BuLi in hexane (1.00 mL, 1.54 mmol, 4.20 equiv.) was added via a syringe, and the mixture was slowly brought to 0 °C. In a separate flame-dried Schlenk tube was added benzenesulfonic thioanhydride (267 mg, 0.850 mmol, 2.30 equiv.) and anhydrous THF (10.0 mL), and the solution was added to the reaction vessel containing compound 2a via cannula transfer at -78°C. The reaction mixture was stirred at -78 °C for 2 h, and it was slowly raised to room temperature and further stirred overnight. The mixture was then poured into MeOH, and the precipitates were dissolved in oDCB at 100 °C and filtered through a short pad of silica gel column. The crude was then recrystallized from toluene to give the target compound as a bright yellow solid (130 mg, 52% yield). ¹H NMR (400 MHz, TCE-d₂, 100 °C): δ 9.01 (s, 2H), 8.25 (s, 2H), 8.03 (d, J = 8.4 Hz, 2H), 7.71 (s, 2H), 7.43 (d, J = 8.4 Hz, 2H), 2.85 (t, J = 7.6 Hz, 7.6 Hz, 4H), 1.78 (quint, J = 6.8 Hz, 8.0 Hz, 7.2 Hz, 7.2 Hz, 4H), 1.38-1.29 (m, 28H), 0.88 (t, J = 6.8 Hz, 6.8 Hz, 6H). ¹³C NMR could not be obtained due to insufficient solubility. HRMS (APCI^+-TOF): Calcd for C₃₀HBrN₂S₂[M+H] 788.8603. Found, 788.8671.

3,11-didecylbis(naphtho[2',3':4,5]thieno)[2,3-b:2',3'-e]pyrazine (C₁₀–BNTP)

To a flame-dried Schlenk tube was added compound 2b (500 mg, 0.635 mmol, 1.00 equiv.), and anhydrous Et₂O (25.0 mL) under argon. The solution was cooled to -78 °C and 1.54 M of n-BuLi in hexane (1.73 mL, 2.67 mmol, 4.20 equiv.) was added via a syringe, and the mixture was slowly brought to 0 °C. In a separate flame-dried Schlenk tube was added benzenesulfonic thioanhydride (459 mg, 1.46 mmol, 2.30 equiv.) and anhydrous THF (17.0 mL), and the solution was added to the reaction vessel containing compound 2a via cannula transfer at -78°C. The reaction mixture was stirred at -78 °C for 2 h, and it was slowly raised to room temperature and further stirred overnight. The mixture was then poured into MeOH, and the precipitates were dissolved in oDCB at 100 °C and filtered through a short pad of silica gel column. The crude was then recrystallized from toluene to give the target compound as a yellow solid (194 mg, 57% yield). ¹H NMR (400 MHz, TCE-d₂, 100 °C): δ 9.04 (s, 2H), 8.35 (s, 2H), 8.10 (t, J
= 4.4 Hz, 8.4 Hz, 4H), 7.69 (d, J = 8.4 Hz, 2H), 0.40 (s, 18H). $^{13}$C NMR could not be obtained due to insufficient solubility. HRMS (APCI$^+$-TOF): Calcd for C$_{30}$H$_{28}$N$_2$S$_2$Si$_2$ [M+H] 537.1311. Found, 537.1301. Elemental Analysis. Calcd for C$_{30}$H$_{28}$N$_2$S$_2$Si$_2$: C, 67.12; H, 5.26; N, 5.22. Found: C, 66.88; H, 5.36; N, 5.06.

3,11-diiodobis(naphtho[2',3':4,5]thieno)[2,3-b:2',3'-e]pyrazine (I–BNTP)

To a flame-dried Schlenk tube was added TMS-BNTP (500 mg, 0.931 mmol, 1.00 equiv.), and oDCB (10 mL) and 1.00 M of ICl in CH$_2$Cl$_2$ (2.50 mL, 2.50 mmol, 2.69 equiv.) at -78 °C. After stirring at -78 °C for 0.5 h, the deep red mixture was slowly warmed to room temperature and heated at 80 °C for 1 h. The reaction mixture was cooled to room temperature and quenched with saturated aqueous solution of sodium hydrosulfite. The precipitates were collected, washed with MeOH, dissolved in hot oDCB and filtered through a short pad of silica gel column to give the target compound as an orange solid (486 mg, 81% yield). $^1$H NMR (400 MHz, TCE-d$_2$, 100 °C): $\delta$ 9.03 (s, 2H), 8.38 (s, 2H), 8.22 (s, 2H), 7.83 (q, J = 8.4 Hz, 5.6 Hz, 8.8 Hz, 4H). $^{13}$C NMR could not be obtained due to insufficient solubility. HRMS (APCI$^+$-TOF): Calcd for C$_{24}$H$_{10}$I$_2$N$_2$S$_2$ [M+H] 644.8453. Found, 644.8439. Elemental Analysis. Calcd for C$_{24}$H$_{10}$I$_2$N$_2$S$_2$: C, 44.74; H, 1.56; N, 4.35. Found: C, 44.96; H, 1.83; N, 4.20.

3,11-diphenylbis(naphtho[2',3':4,5]thieno)[2,3-b:2',3'-e]pyrazine (Ph–BNTP)

To a flame-dried Schlenk tube was added anhydrous toluene (6.30 mL), 0.85 M of phenylmagnesium bromide in THF (0.46 mL, 0.389 mmol, 3.00 equiv.), 1.0 M of Zn$_2$Cl in THF (0.390 mL, 0.390 mL, 3.00 equiv.), and 0.5 M of LiCl in THF (0.830 mL, 0.415 mmol, 3.20 equiv.) at 0 °C under argon. The solution was stirred at 0 °C for 15 min before I–BNTP (83.5 mg, 0.130 mmol, 1.00 equiv.) and Pd(dppf)Cl$_2$.CH$_2$Cl$_2$ (4.23 mg, 0.00518 mmol, 4 mol%) were added under argon. The mixture was then heated at 110 °C for 12 h, and it was poured into MeOH after cooling to room temperature. The precipitates were collected, dissolved in hot oDCB and filtered through a short pad of silica gel column. The collected product was further recrystallized from oDCB to give the target compound as an orange solid (59.1 mg, 70% yield). $^1$H NMR (400 MHz, TCE-d$_2$, 100 °C): $\delta$ 9.10 (s, 2H), 8.40 (s, 2H), 8.18 (t, J = 8.8 Hz, 13.2 Hz, 4H), 7.86 (dd, J = 2.0 Hz, 6.80 Hz, 2.0 Hz, 2H), 7.77 (d, J = 7.2 Hz, 4H), 7.51 (t, J = 8.0 Hz, 7.6 Hz, 4H), 7.42-7.32 (m, 2H). $^{13}$C NMR could not be obtained due to insufficient solubility. HRMS (APCI$^+$-TOF): Calcd for C$_{36}$H$_{20}$N$_2$S$_2$ [M+H] 545.1146. Found, 545.1137.
Elemental Analysis. Calcd for C₃₆H₂₀N₂S₂: C, 79.38; H, 3.70; N, 5.14. Found: C, 78.79; H, 3.86; N, 5.21.

3,11-bis(4-decylphenyl)bis(naphtho[2′,3′:4,5]thieno)[2,3-b:2′,3′-c]pyrazine (C₁₀Ph–BNTP)

To a flame-dried Schlenk tube was added 1-bromo-4-decylbenzene (0.340 mL, 1.24 mmol, 4.00 equiv.), anhydrous THF (4.00 mL), and 1.6 M of n-BuLi in hexane (0.780 mL, 1.24 mmol, 4.00 equiv.) at -78 °C under argon, and the mixture was stirred for 1 h at the same temperature. Then, 2.0 M of ZnCl₂ in THF (0.621, 1.24 mmol, 4.00 equiv.) was added via a syringe at -78 °C and the mixture was further stirred for 10 min before warming to room temperature. Subsequently, I–BNTP (200 mg, 0.310 mmol, 1.00 equiv.), Pd(dppf)Cl₂·CH₂Cl₂ (10.0 mg, 0.0124 mmol, 4 mol%), and anhydrous toluene (4.00 mL) were added under argon, and the mixture was heated at 110 °C for 24 h. After pouring the mixture into MeOH, the precipitates were collected, dissolved in hot oDCB and filtered through a short pad of silica gel column. The collected product was further recrystallized from oDCB to give the target compound as an orange solid (215 mg, 84% yield). ¹H NMR (400 MHz, TCE-d₂, 100 °C): δ 9.07 (s, 2H), 8.37 (s, 2H), 8.16 (t, J = 8.8 Hz, 10.8 Hz, 4H), 7.85 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 8.4 Hz, 4H), 7.32 (d, J = 8.4 Hz, 4H), 2.69 (t, J = 7.6 Hz, 7.2 Hz, 4H), 1.70 (quint, J = 6.4 Hz, 6.0 Hz, 8.4 Hz, 6.8 Hz, 4H), 1.45-1.27 (m, 28H), 0.89 (t, J = 6.2 Hz, 6.8 Hz, 6H). ¹³C NMR could not be obtained due to insufficient solubility. HRMS (APCl⁻-TOF): Calcd for C₅₆H₆₀N₂S₂ [M+H] 825.4276. Found, 825.4272. Elemental Analysis. Calcd for C₅₆H₆₀N₂S₂: C, 81.51; H, 7.33; N, 3.39. Found: C, 81.29; H, 7.28; N, 3.41.
4. NMR Spectra

Figure S2. $^1$H NMR of compound 1a in CDCl$_3$.

Figure S3. $^{13}$C NMR of compound 1a in CDCl$_3$. 
Figure S4. $^1$H NMR of compound 1b in CDCl$_3$.

Figure S5. $^{13}$C NMR of compound 1b in CDCl$_3$.
Figure S6. $^1$H NMR of compound 2a in TCE-$d_2$.

Figure S7. $^{13}$C NMR of compound 2a in CDC$_3$. 
Figure S8. $^1$H NMR of compound 2b in CDCl₃.

Figure S9. $^{13}$C NMR of compound 2b in CDCl₃.
Figure S10. $^1$H NMR of compound C$_{10}$–BNTP in TCE-$d_2$ at 100 °C.

Figure S11. $^1$H NMR of compound TMS–BNTP in TCE-$d_2$ at 100 °C.
Figure S12. $^1$H NMR of compound I–BNTP in TCE-$d_2$ at 100 °C.

Figure S13. $^1$H NMR of compound Ph–BNTP in TCE-$d_2$ at 100 °C.
Figure S14. $^1$H NMR of compound C$_{10}$Ph–BNTP in TCE-$d_2$ at 100 °C.
5. Fundamental Properties

Photoelectron Yield Spectroscopy

Photoelectron yield spectroscopy (PYS) was performed on a Sumitomo Heavy Industries Advanced Machinery PYS-202. Thin film (ca. 100 nm) of R–BNTP derivatives were thermally evaporated on an ITO-coated quartz substrate and the measurement were performed in vacuum.

Figure S15. Photoelectron yield spectroscopy of 100 nm-thick C_{10}–BNTP vacuum-deposited film.
Figure S16. Photoelectron yield spectroscopy of 100 nm-thick Ph–BNTP vacuum-deposited film.
Figure S17. Photoelectron yield spectroscopy of 100 nm-thick C\textsubscript{10}Ph–BNTP vacuum-deposited film.
Thin-Film UV-vis Spectroscopy

The UV-vis absorption spectra were recorded with a Jasco V-670 spectrometer. Thin film (ca. 100 nm) of C₁₀–BNTP was thermally evaporated on a synthetic quartz substrate.

Figure S18. UV-vis absorbance of 100 nm-thick C₁₀–BNTP vacuum-deposited film.
Figure S19. UV-vis absorbance of 100 nm-thick Ph–BNTP vacuum-deposited film (the step around 330 nm corresponds to the change of light source).
Figure S20. UV-vis absorbance of 100 nm-thick C_{10}Ph–BNTP vacuum-deposited film.
Thermal Properties

Thermogravimetric analysis (TGA) was performed on a Rigaku Thermo Plus EVO II TG 8121 at a heating rate of 1 K min$^{-1}$ under a nitrogen flow of 100 mL min$^{-1}$. The differential scanning calorimetry measurements were performed with a Rigaku Thermo Plus EVO II DSC 8270 at a heating rate of 5 K min$^{-1}$ under a nitrogen flow of 50 mL min$^{-1}$.

Figure S21. TGA curve of C$_{10}$–BNTP.
Figure S22. TGA curve of Ph–BNTP.

Figure S23. TGA curve of C_{10}Ph–BNTP.
Figure S24. DSC of C₁₀–BNTP.

Figure S25. DSC of Ph–BNTP.
Figure S26. DSC of C_{10}Ph–BNTP.
Solubility

To a weighed sample of around 1 mg was added 50 µL of oDCB, repeatedly. The resulting suspension was shaken and sonicated at 60 °C. The total amount of solvent (mL) was converted into solubility in wt%.

Table S1. Solubility of C_{10}\text{DNBDT–NW}, C_{10}\text{BNTP}, Ph–BNTP, C_{10}\text{Ph–BNTP}.

| Compound         | Solubility (wt%) |
|------------------|------------------|
| C_{10}\text{DNBDT–NW} | 0.043^{3}       |
| C_{10}\text{BNTP}   | 0.095            |
| Ph–BNTP           | < 0.001          |
| C_{10}\text{Ph–BNTP} | 0.052          |
6. X-Ray Crystallography

Single-crystal X-ray diffraction data were collected on a Rigaku R-AXIS RAPID II imaging plate diffractometer with CuKα radiation ($\lambda = 1.54187$ Å) at room temperature. The structures were solved by direct methods [SHELXT (2015)] and refined by full-matrix least-squares procedures on F2 for all reflections [SHELXL (Ver. 2017/1)]. While positions of all hydrogen atoms were calculated geometrically, and refined by applying riding model, all other atoms were refined anisotropically.

Table S2. Single-crystal data of R–BNTP.

| Material          | $C_{10}$–BNTP | Ph–BNTP–1$D$ | Ph–BNTP–2$D$ | $C_{10}$Ph–BNTP |
|-------------------|----------------|--------------|--------------|-----------------|
| Formula           | $C_{44}H_{52}N_{2}S_{2}$ | $C_{36}H_{20}N_{2}S_{2}$ | $C_{36}H_{20}N_{2}S_{2}$ | $C_{56}H_{60}N_{2}S_{2}$ |
| Formula weight    | 673.03         | 544.69       | 544.69       | 825.23          |
| Crystal system    | monoclinic     | monoclinic   | monoclinic   | monoclinic     |
| Space group       | $C2/c$         | $P2_1/n$     | $P2_1/c$     | $P2_1/c$       |
| $a$ / Å           | 42.937(2)      | 17.9201(11)  | 26.1972(5)   | 47.8955(19)    |
| $b$ / Å           | 4.7395(2)      | 3.8805(3)    | 7.37277(13)  | 7.7465(3)      |
| $c$ / Å           | 18.0902(8)     | 19.5452(13)  | 6.51159(12)  | 6.1364(2)      |
| $a$ / °           | 90             | 90           | 90           | 90              |
| $\beta$ / °       | 97.201(7)      | 113.554(8)   | 91.805(7)    | 90.107(6)      |
| $\gamma$ / °      | 90             | 90           | 90           | 90              |
| $V$ / Å$^3$        | 3652.3(3)      | 1245.91(16)  | 1257.06(4)   | 2276.74(15)    |
| $Z$               | 4              | 2            | 2            | 2               |
| $T$ / K           | 243            | 296          | 296          | 296             |
| $R_1$[$I > 2\sigma(I)$] | 0.0422         | 0.0495       | 0.0444       | 0.0689          |
| $wR_2$ [all data] | 0.1273         | 0.1132       | 0.1051       | 0.1845          |
| GOF               | 1.061          | 1.007        | 1.023        | 0.846           |
Figure S27. The distribution of HOMO, SHOMO, and THOMO of a) C$_{10}$–BNTP, b) Ph–BNTP, and c) C$_{10}$Ph–BNTP calculated at the B3LYP/6-311G(d) level of theory using the single-crystal structures. Alkyl chains are omitted for clarity.
Single-Crystalline Thin-Film X-Ray Diffractions

Figure S28. Out-of-plane X-ray diffractions of edge-casted C_{10}–BNTP single-crystalline thin film.

Figure S29. In-plane X-ray diffractions of PVT-grown Ph–BNTP single-crystal.
Figure S30. X-ray diffractions of edge-casted C\textsubscript{10}Ph–BNTP single-crystalline thin film in the a) out-of-plane, and b) in-plane directions.
7. Charge Transport Calculations

Figure S31. Band structures and effective masses of a) C_{10}-BNTP, and b) Ph-BNTP.
Table S3. Transfer integrals in six charge-transport directions of the herringbone assembly in units of meV involving HOMO, SHOMO, and THOMO of C_{10}–DNBDT–NW, Ph–BNTP-2D, and C_{10}Ph–BNTP calculated at the PBEPBE/6-31G(d) level of theory.

| Compound   |   |   |   |   |   |   |
|------------|---|---|---|---|---|---|
|            | $t_1$ | $t_2$ | $t_3$ | $t_4$ | $t_5$ | $t_6$ |
| **Ph–BNTP-2D** |   |   |   |   |   |   |
| HOMO→HOMO  |  +6.90  |  +47.9  |  +47.9  |  +6.90  |  +47.9  |  +47.9  |
| HOMO→SHOMO |  +0.131  |  −17.4  |  +30.9  |  −0.131  |  +17.4  |  −30.9  |
| SHOMO→SHOMO |  −2.61  |  −49.4  |  −49.4  |  −2.62  |  −49.4  |  −49.4  |
| HOMO→THOMO |  −8.93  |  −42.9  |  −42.3  |  −8.93  |  −42.9  |  −42.3  |
| THOMO→THOMO |  +12.8  |  +6.80  |  +6.80  |  +12.8  |  +6.80  |  +6.80  |
| **C_{10}Ph–BNTP** |   |   |   |   |   |   |
| HOMO→HOMO  |  +16.6  |  −28.8  |  −28.8  |  +16.6  |  −28.8  |  −28.8  |
| HOMO→SHOMO |  +1.48  |  +16.3  |  −31.0  |  −1.48  |  −16.3  |  +31.0  |
| SHOMO→SHOMO |  −1.35  |  −17.8  |  −17.8  |  −1.35  |  −17.8  |  −17.8  |
| HOMO→THOMO |  −14.9  |  −46.3  |  −49.0  |  −14.9  |  −46.3  |  −49.0  |
| THOMO→THOMO |  +25.7  |  +22.8  |  +22.8  |  +25.7  |  +22.8  |  +22.8  |
| **C_{10}–DNBDT–NW** |   |   |   |   |   |   |
| HOMO→HOMO  |  +50.0  |  +49.9  |  +49.9  |  +50.0  |  +49.9  |  +49.9  |
| HOMO→SHOMO |  −2.64  |  +29.0  |  −6.44  |  +2.64  |  −29.0  |  +6.43  |
| SHOMO→SHOMO |  +10.9  |  −37.6  |  −37.6  |  +10.9  |  −37.6  |  −37.6  |
| HOMO→THOMO |  −23.8  |  −38.5  |  −36.0  |  −23.8  |  −38.5  |  −36.0  |
| THOMO→THOMO |  +26.8  |  −11.6  |  −11.6  |  +26.8  |  −11.6  |  −11.6  |
Table S4. Experimental $\mu$, bandwidths, and $m^*$ calculated from plane-wave and tight-binding approximations of Ph–BNTP–2D, C$_{10}$Ph–BNTP, and C$_{10}$–DNBDT–NW.

|                      | Ph–BNTP–2D | C$_{10}$Ph–BNTP | C$_{10}$–DNBDT–NW |
|----------------------|------------|-----------------|-------------------|
| $\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$) | 0.8        | 9.6             | 16                |
| Plane-Wave ($\Gamma$–Z) |            |                 |                   |
| Bandwidth (eV)       | 0.32       | 0.33            | 0.47              |
| $m^*$ (column direction) | 1.54     | 1.43            | 1.13              |
| Tight-Binding (HOMO only) |          |                 |                   |
| Bandwidth (eV)       | 0.22       | 0.18            | 0.40              |
| $m^*$ (column direction) | 2.94     | 3.26            | 1.36              |
| Tight-Binding (mixed-orbital) |        |                 |                   |
| Bandwidth (eV)       | 0.24       | 0.24            | 0.43              |
| $m^*$ (column direction) | 2.42     | 2.03            | 1.13              |
8. OFET Performances

Two-probe OFETs were fabricated using the edge-casting method\(^4\) for C\(_{10}^-\) and C\(_{10}\)Ph–BNTP. The surfaces of a heavily-doped silicon wafers with thermally-oxidized SiO\(_2\) were pretreated with the parylene diX-SR (thickness of 28 nm) insulating layer and \(\beta\)-phenylethyl trimethoxysilane (\(\beta\)-PTS) self-assembled monolayer (SAM), where the SiO\(_2\) thicknesses were 100 and 200 nm for diX-SR and \(\beta\)-PTS, respectively. A droplet of solution of C\(_{10}^-\) and C\(_{10}\)Ph–BNTP, dissolved in 1,3-dimethoxybenzene (0.03 wt%) and \(o\)-dichlorobenzene (0.01–0.02 wt%) were placed near the sustaining glass blade and the single-crystalline thin films were grown at 100 and 60 °C, respectively. Then, F\(_4\)–TCNQ (2–3 nm) and Au electrodes (40 nm) were thermally deposited through a shadow mask to construct the bottom-gate/top-contact OFET architecture. Channels were created by the conventional Nd:YAG laser-etching technique. The devices were thermally annealed at 100 °C for 1–12 h prior to electrical evaluations. The gate capacitance per unit area (\(C\_i\)) for the parylene diX-SR- and \(\beta\)-PTS containing gate dielectrics was measured to be 25 and 17 nF cm\(^{-2}\), respectively, by a Keithley 4200-SCS.

The lamination method was used to fabricate devices with Ph–BNTP-2D single crystals grown by physical vapor transport. The surfaces of a heavily-doped silicon wafers with thermally-oxidized SiO\(_2\) (500 nm) were pretreated with the heptadecafluorodecyl triethoxysilane (F-DTS) self-assembled monolayer (SAM). Yellow platelet Ph–BNTP crystals were gently laminated on the F-DTS SAM. Au electrodes (40 nm) were thermally deposited through a shadow mask to construct the bottom-gate/top-contact OFET architecture.

Electrical evaluations of OFETs were conducted on a Keithley 4200-SCS semiconductor parameter analyzer in air. Electron mobility and threshold voltage were extracted from the transfer characteristics by using the conventional equation for the saturation regime:

\[
\sqrt{|I_D|} = \frac{W\mu C_i}{2L} (V_G - V_{th}),
\]

where \(I_D\) is the drain current, \(W\) the channel width, \(\mu\) the mobility in the saturation regime, \(C_i\) the gate capacitance per unit area, \(L\) the channel length, \(V_G\) the gate voltage, and \(V_{th}\) the threshold voltage.
Figure S32. Optical microscopic images of the OFET channels of a) C$_{10}$–BNTP and b) Ph–BNTP. Transfer, output characteristics, and gate voltage dependent mobility of c) C$_{10}$–BNTP, and d) Ph–BNTP single-crystalline thin-film OFETs.

Figure S33. Histogram distribution of $\mu$ of 17 single-crystalline thin-film devices of C$_{10}$Ph–BNTP.
Figure S3. a) Polarized optical microscopic image of the channel, b) transfer characteristic, c) output characteristic, and d) gate voltage-dependent $\mu$ of single-crystalline thin-film OFET fabricated with C$_{10}$Ph–BNTP on the $\beta$–PTS dielectric layer (SiO$_2$ thickness = 200 nm, $C_i = 17$ nF cm$^{-2}$).
Figure S35. Bias-stress of the single-crystalline OFETs based on C_{10}Ph–BNTP. The plot shows the output characteristic of single-crystalline C_{10}Ph–BNTP OFET measured before the transfer curve measurement.
8. Summary of Fundamental and Electrical Properties

Table S5. Summary of fundamental properties and OFET performances of C\textsubscript{10}–DNBDT–NW and R–BNTP derivatives.

| Compound          | $T_{95}$ (°C) | $\lambda_{\text{max}}$ (nm) | IP (eV) | Solubility (wt%) | $\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$) |
|-------------------|---------------|-----------------------------|---------|-----------------|----------------------------------|
| C\textsubscript{10}–DNBDT–NW | 426           | 445                         | 5.24    | 0.042           | 16                               |
| C\textsubscript{10}–BNTP     | 377           | 478                         | 5.81    | 0.095           | N/A                              |
| Ph–BNTP            | 469           | 488                         | 5.55    | < 0.001         | 0.8                              |
| C\textsubscript{10}Ph–BNTP  | 440           | 504                         | 5.52    | 0.052           | 9.6                              |

\textsuperscript{a}The data are taken in our previous report.\textsuperscript{3}
9. References

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