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Supporting Information for

Naphtho[2,3-*b*]thiophene Diimide (NTI): a mono-functionalizable Core-extended Naphthalene Diimide for Electron-Deficient Architectures

Wangqiao Chen,[abc] Masahiro Nakano,[a]* Ji-Hoon Kim,[a] Kazuo Takimiya,[a]*, Qichun Zhang[b]

[a]Emergent Molecular Function Research Group, RIKEN Center for Emergent Mater Science (CEMS), 2-1, Hirosawa, Wako, Saitama, 351-0198, Japan
[b]School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[c]Institute for Sports Research, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
*Correspondence - masahiro.nakano@riken.jp

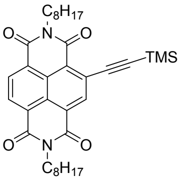
Contents

1. Synthesis

General

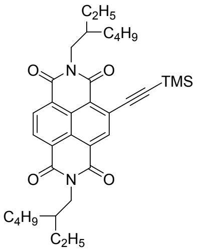
All chemicals and solvents are of reagent grade unless otherwise indicated. Dichloromethane and tetrahydrofuran (THF) were purified with a standard procedure prior to use. *N,N′*-Dioctyl-2-bromo-1,4,5,8-naphthalene tetracarboxylic acid diimide (**6a**)[S1], *N,N′*-bis(2-ethylhexyl)-2-bromo-1,4,5,8-naphthalene tetracarboxylic acid diimide (**6b**)[S2], and *N,N′*-bis(3-decylpentadecyl)-2,7-bis(trimethylstanyl)naphtho[2,3-*b*:6,7-*b*′]dithiophene-4,5,9,10-diimide[4d] were synthesized according to the reported procedures. Melting points were uncorrected. Nuclear magnetic resonance spectra were obtained in deuterated chloroform ($CDCl_3$), tetrachloroethane (TCE-d_4), or *o*-dichlorobenzene (ODB-d_4) with TMS as internal reference; chemical shifts (δ) are reported in parts per million. IR spectra were recorded using a KBr pellet. EI-MS spectra were obtained using an electron impact ionization procedure (70 eV). The molecular ion peaks of the bromine and/or sulfur containing compounds showed a typical isotopic pattern, and all the mass peaks are reported based on ^{32}S, or ^{77}Br, respectively. ESI-MS spectra were obtained using an electrospray ionization method under ambient pressure. HRMS were carried out at Materials Characterization Support Unit, RIKEN Advanced Technology Support Division.

N,N′-Dioctyl-2-[2-(trimethylsilyl)ethynyl)]-1,4,5,8-naphthalene tetracarboxylic acid diimide (7a)



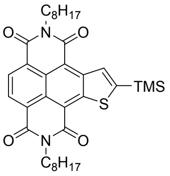
To a stirred solution of *N,N′*-dioctyl-2-bromo-1,4,5,8-naphthalene tetracarboxylic acid diimide (**6a**, 47 mg, 0.083 mmol) in toluene (4 mL), $PdCl_2(PPh_3)_2$ (5.8 mg, 0.008mmol) was added, and the resulting solution was further stirred for 30 min. at room temperature under argon atmosphere. Then, tributyl(trimethylsilyl)ethynyl))tin (96 mg, 0.025 mmol) was added, and the mixture was refluxed for 1 h. After cooling down, the mixture was evaporated under vacuum, and the residue was purified by column chromatography on silica gel eluted with hexane-dichloromethane (v/v = 1:2 to 1:4) to afford a yellow solid (40 mg, 82%). Mp: 145–146 °C; IR (KBr): ν = 1707 cm^{-1}, 1662 cm^{-1} (C=O); ^1H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.72 (d, J = 8.0 Hz, 1H), 8.67 (d, J = 8.0 Hz, 1H), 4.17–4.13 (m, 4H), 1.76–1.67 (m, 4H), 1.44–1.26 (m, 20H), 0.88–0.84 (m, 6H), 0.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 162.19, 162.17, 161.2, 137.4, 131.2, 130.7, 127.1, 127.0, 126.3 (two carbons), 126.2, 125.5, 125.2, 110.4, 103.2, 41.0, 40.9, 31.8, 31.8, 29.2 (two carbons), 29.16, 29.13, 28.0, 27.9, 27.04, 27.01, 22.61, 22.59, 14.1 (two carbons), –0.3. HRMS (ESI) *m/z* calcd for $C_{35}H_{46}N_2O_4Si$: $[M]^+$ 586.3227. Found: 586.3235.

N,N′-Bis(2-ethylhexyl)-2-[2-(trimethylsilyl)ethynyl]-1,4,5,8-naphthalene tetracarboxylic acid diimide (7b)



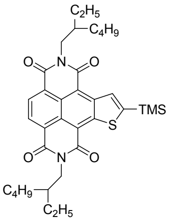
The title compound was synthesized from *N,N′*-bis(2-ethylhexyl)-2-bromo-1,4,5,8-naphthalene tetracarboxylic acid diimide (**6b**) in the same manner as described above (yellow solid, 73% yield). Mp: 129–131 °C; IR (KBr): ν = 1707 cm^{-1}, 1663 cm^{-1} (C=O); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.77 (s, 1H), 8.76 (d, *J* = 8.0 Hz, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 4.19–4.07 (m, 4H), 1.99–1.88 (m, 2H), 1.41–1.29 (m, 16H), 0.95–0.86 (m, 12H), 0.37 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) 163.1, 162.7 (two carbons), 161.6, 137.5, 131.4, 130.8, 127.2, 127.1, 126.41, 126.35, 126.29, 125.7, 125.2, 110.3, 103.3, 44.5, 44.4, 37.9, 37.7, 30.6, 30.5, 28.6, 28.4, 24.0 (two carbons), 23.1 (two carbons), 14.1, 14.1, 10.6 (two carbons), –0.4; HRMS (ESI) *m/z* calcd for $C_{35}H_{46}N_2O_4Si$: [M]$^+$ 586.3227. Found: 586.3226.

N,N′-Dioctyl-2-(trimethylsilyl)naphtho[2,3-*b*]thiophene-4,5,8,9-diimide (8a)



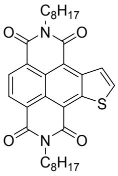
Under argon atmosphere, sodium sulfide hydrate ($Na_2S•9H_2O$, 5.76 g, 24.0 mmol), was added to a stirred suspension of **7a** (2.35 g, 4.0 mmol) in 2-methoxyehtnaol (400 mL) and acetic acid (8.0 mL) at 60 °C. After stirred at the same temperature for 12 h, the mixture was stirred again at room temperature for 3 h under atmospheric condition. Then, the mixture was dropped into stirring water (400 mL) to precipitate a red solid. The precipitate was collected by filtration, and washed successively with water and methanol. The product was further purified by column chromatography on silica gel eluted with hexane: dichloromethane (1:3 v/v) to give an orange solid (1.61g, 65%). Mp: 183–184 °C; IR (KBr): ν = 1698 cm^{-1}, 1655 cm^{-1} (C=O); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.93 (s, 1H), 8.63 (s, 2H), 4.23–4.17 (m, 4H), 1.80–1.72 (m, 4H), 1.47–1.24 (m, 20H), 0.89–0.86 (m, 6H), 0.54 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 163.10, 163.07, 162.53, 162.46, 159.5, 147.9, 143.9, 130.2, 130.1 (two carbons), 126.3, 125.4, 124.5, 123.0, 118.0, 117.6, 41.2, 41.1, 31.8 (two carbons), 29.33, 29.29, 29.2 (two carbons), 28.1, 28.0, 27.19, 27.16, 22.6 (two carbons), 14.1 (two carbons), –0.6; HRMS (ESI) *m/z* calcd for $C_{35}H_{46}N_2O_4SSi$: [M]$^+$ 618.2948. Found: 618.2952.

N,N′-Bis(2-ethylhexyl)-2-(trimethylsilyl)naphtho[2,3-*b*]thiophene-4,5,8,9-diimide (8b)



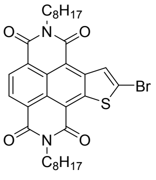
8b was synthesized from **7b** in the same manner (56% yield). Mp: 214–215 °C; IR (KBr): ν = 1697 cm^{-1}, 1655 cm^{-1} (C=O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 8.67 (s, 2H), 4.22–4.10 (m, 4H), 2.04–1.92 (m, 2H), 1.43–1.24 (m, 16H), 0.96–0.86 (m, 12H), 0.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.50, 163.46, 163.03, 162.97, 159.3, 148.1, 144.0, 130.4, 130.2 (two carbons), 126.3, 125.4, 124.7, 123.2, 118.0, 117.7, 44.8, 44.6, 37.8 (two carbons), 30.6(two carbons), 28.6 (two carbons), 24.0, 23.9, 23.1 (two carbons), 14.1 (two carbons), 10.65, 10.57, –0.6; HRMS (ESI) *m/z* calcd for $C_{35}H_{46}N_2O_4SSi$: $[M]^+$ 618.2948. Found: 618.2948.

N,N′-Dioctylnaphtho[2,3-*b*]thiophene-4,5,8,9-diimide (NTI, 1a)



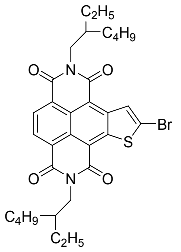
Under argon atmosphere, **8a** (990 mg, 1.6 mmol) was dissolved in THF (120 mL), and acetic acid (1.2 mL), and then, tetra-*n*-butylammmonium fluoride (1.0 M in THF, 16 mL) was added to the solution at 0 °C. After stirred for 3h at room temperature, the solution was diluted with methanol (120 mL). The resulting precipitate was collected by filtration and washed with methanol and purified by column chromatography on silica gel (eluent, hexane: dichloromethane: 1 : 3 v/v) to afford **1a** as an orange solid. (790 mg, 90%). Mp: 224–225 °C; IR (KBr): ν = 1695 cm^{-1}, 1649 cm^{-1} (C=O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (d, *J* = 8.0 Hz, 1H), 8.84 (s, 2H), 8.16 (d, *J* = 8.0 Hz), 4.29–4.24 (m, 4H), 1.82–1.75 (m, 4H), 1.48–1.29 (m, 20H), 0.90–0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.04, 163.00, 162.6, 162.5, 144.69, 142.74, 140.1, 130.3, 130.2, 126.4, 125.46, 124.56, 123.9, 123.3, 118.6, 118.3, 41.1, 41.0, 31.8 (two carbons), 29.32, 29.30, 29.2 (two carbons), 28.07, 28.06, 27.17, 27.15, 22.6 (two carbons), 14.1(two carbons). HRMS (ESI) *m/z* calcd for $C_{32}H_{38}N_2O_4S$: $[M]^+$ 546.2552. Found: 546.2562.

N,N′-Dioctyl-2-bromonaphtho[2,3-*b*]thiophene-4,5,8,9-diimide (9a)



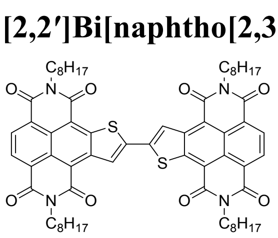
Under argon atmosphere, bromine (960 mg, 6.0 mmol) was added to a stirred suspension of **8a** (248 mg, 0.4 mmol) in dichloromethane (40 mL) at room temperature. After stirring at 40 °C for 15 h, the mixture was quenched with diluted $NaHSO_3$ aqueous solution and extracted with dichloromethane. The combined organic layer was washed with saturated NaCl solution, dried (Na_2SO_4), and then concentrated. The resulting crude product was purified by column chromatography on silica gel (eluent, hexane: dichloromethane = 1: 3 v/v) to give **7a** as an orange solid (190 mg, 76%). Mp: 175–176 °C; IR (KBr): ν = 1697 cm^{-1}, 1647 cm^{-1} (C=O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 2H), 8.58 (s, 1H), 4.15–4.10 (m, 4H), 1.77 –1.69 (m, 4H), 1.46–1.28 (m, 20H), 0.89–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 162.5, 162.1, 162.0, 145.2, 141.6, 132.3, 130.5, 130.5, 126.2, 126.1, 125.2, 124.3, 122.7, 117.1, 116.4, 41.1, 41.0, 31.8 (two carbons), 29.30, 29.26, 29.2 (two carbons), 27.99, 27.96, 27.2, 27.1, 22.6 (two carbons), 14.1 (two carbons); HRMS (ESI) *m/z* calcd for $C_{32}H_{37}BrN_2O_4S$: $[M]^+$ 624.1657. Found: 624.1662.

***N,N′*-Bis(2-ethylhexyl)-2-bromonaphtho[2,3-*b*]thiophene-4,5,8,9-diimide (9b)**



9b was synthesized from **8b** in the same manner (64% yield). Mp: 239–240 °C; IR (KBr): ν = 1697 cm^{-1}, 1647 cm^{-1} (C=O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 1H), 8.78 (s, 2H), 4.22–4.11 (m, 4H), 2.02–1.90 (m, 2H), 1.43–1.31 (m, 16H), 0.97–0.87 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 163.3, 163.0, 162.9, 145.9, 142.3, 132.3, 130.8, 130.7, 126.6, 126.5, 125.6, 124.9, 123.3, 117.7, 117.0, 44.8, 44.6, 37.92, 37.85, 30.7, 30.6, 28.6, 28.5, 24.03, 23.98, 23.1 (two carbons), 14.1 (two carbons), 10.62, 10.58; HRMS (ESI) *m/z* calcd for $C_{32}H_{37}BrN_2O_4S$: $[M]^+$ 624.1657. Found: 624.1647.

[2,2′]Bi[naphtho[2,3-*b*]thienyl]-*N,N′,N′′,N′′′*-tetraoctyl-4,4′,5,5′,8,8′,9,9′-tetraimide (2a)

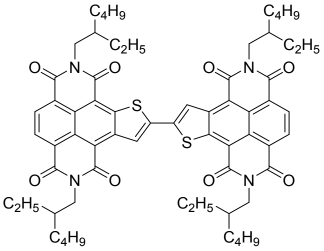


Hexamethylditin (26 mg, 0.08 mmol, 0.017 mL) was added into a solution of **9a** (94 mg, 0.15 mmol), and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$, 0.015 mmol, 18 mg) in 20 mL of toluene under argon atmosphere. The solution was maintained at 95 °C for 3 h and then 105 °C for 10 h. After the solution was cooling down, the resulting precipitate was filtrated to obtain the crude product, which was dissolved in hot *o*-dichlorobenzene (>150 °C), and the hot solution was filtered to remove the insoluble particles. Recrystallization from *o*-DCB twice afforded analytically pure **2a** (60 mg, 73% yield). Mp: > 350 °C; IR (KBr): ν = 1697 cm^{-1}, 1649 cm^{-1} (C=O); ^{1}H NMR (400 MHz, ODB-d_4): δ 9.53 (s, 2H), 8.65 (s, 4H), 4.37 (s, 8H), 1.97–1.94 (m, 8H), 1.57–1.30 (m, 40H), 0.88 (s, 12H);

HRMS (ESI) *m/z* calcd for $C_{64}H_{74}N_4O_8S_2$: $[M]^+$ 1090.4948. Found: 1090.4950.

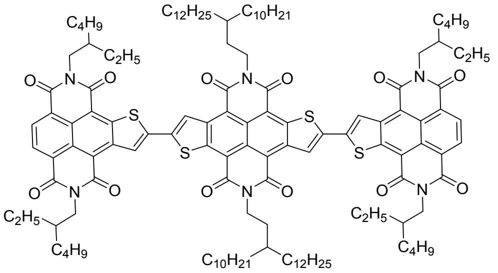
No signal was observed in ^{13}C NMR spectrum even with 20,000 scans, owing to the low solubility of **2a**.

[2,2′]Bi[naphtho[2,3-*b*]thienyl]-*N,N′,N′′,N′′′*-tetrakis(2-ethylhexyl)-4,4′,5,5′,8,8′,9,9′-tetraimide (2b)



2b was synthesized from **9b** in the same manner (74% yield). Mp: > 350 °C; IR (KBr): ν = 1699 cm^{-1}, 1648 cm^{-1} (C=O); ^1H NMR (400 MHz, ODB-*d*$_4$): δ 9.51 (s, 2H), 8.64 (s, 4H), 4.35–4.25 (m, 8H), 2.19–2.12 (m, 4H), 1.54–1.32 (m, 32H), 1.02-0.86 (m, 24H); HRMS (ESI) *m/z* calcd for $C_{64}H_{74}N_4O_8S_2$: $[M]^+$ 1090.4948. Found: 1090.4973. No signal was observed in ^{13}C NMR spectrum even with 20,000 scans, owing to the low solubility of **2b**.

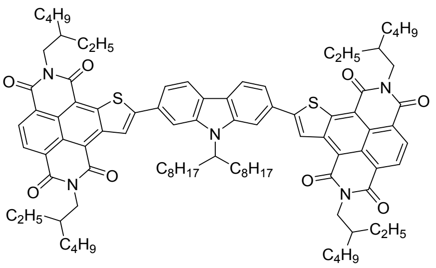
2,7-Bis(*N,N′*-bis-(2-ethylhexyl)naphtho[2,3-*b*]thiophen-2yl-4,5,9,10-tetracarboxylic diimide)-*N,N′*-bis(3-decylpentadecyl)naphtha[2,3-*b*:6,7-*b′*]dithiophene-4,5,9,10-tetracarboxylic imide (3b)



A mixture of *N,N*′-bis(3-decylpentadecyl)-2,7-bis(trimethylstanyl)naphtho[2,3-*b*:6,7-*b*′]dithiophene-4,5,9,10-diimide (56 mg, 0.04 mmol), **9b** (62 mg, 0.1 mmol), Pd(PPh_3)$_4$ (80 mg, 0.07 mmol) and toluene (3 mL) was heated to 100 °C for 12 h under argon atmosphere. After cooling to room temperature, the resulting precipitate was filtrated to obtain the crude product which was dissolved in hot 1,3,5-trichlorobenzene (>160 °C), and the hot solution was filtered to remove the insoluble particles. Recrystallization from 1,3,5-trichlorobenzene twice afforded analytically pure **3b** (45 mg, 52%). MP: > 350 °C; IR (KBr): ν = 1701 cm^{-1}, 1645 cm^{-1} (C=O); ^1H NMR (400 MHz, ODB-*d*$_4$): δ 9.43 (s, 2H), 9.36 (s, 2H), 8.48 (s,4H), 4.63 (t, *J* = 7.2 Hz, 4H), 4.38-4.32 (m, 8H), 2.21 (brs, 4H), 2.11 (brs, 4H), 1.79-1.24 (m, 114H), 1.08-0.79 (m, 36 H); HRMS (ESI) *m/z* calcd for $C_{132}H_{178}N_6O_{12}S_4$: $[M]^+$ 2167.2386. Found: 2167.2384.

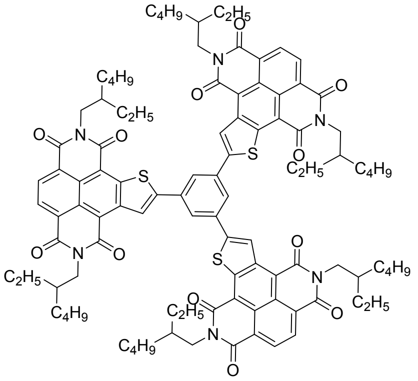
No signal was observed in ^{13}C NMR spectrum even with 20,000 scans, owing to the low solubility of **3b**.

2,7-Bis(naphtho[2,3-*b*]thiophen-2yl)-9-(9-heptadecyl)carbazole-*N*,*N′*,*N′′′*,*N′′′′*-tetrakis(2-ethylhexyl)4,4’,5,5’,8,8’,9,9’-tetraimide (4b)



A mixture of 9-(heptadecyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole (150 mg, 0.22 mmol), **9b** (356 mg, 0.57 mmol), $Pd(PPh_3)_4$ (80 mg, 0.07 mmol), Na_2CO_3 aqueous solution (2 M , 1 mL) and 1,4-dioxane (10 mL) was heated to 80 °C for 48 h under argon atmosphere. After cooling to room temperature, the reaction mixture was poured into 100 mL NaCl aqueous solution and extracted with dichloromethane three times. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the product as deep puple solid (121 mg, 42%). MP: > 350 ^oC; IR (KBr): ν = 1697 cm^{-1}, 1655 cm^{-1} (C=O); ^1H NMR (400 MHz, TCE-d_4): δ 9.42 (s, 2H), 8.89 (d, J = 7.2 Hz, 2H), 8.86 (d, J = 7.2 Hz, 2H), 8.34 (d, J = 8.0 Hz, 2H) 8.20 (s, 2H), 8.04 (d, J = 8.0 Hz, 2H), 4.92 (brs, 1H), 4.36 (m, 8H), 2.55 (brs, 2H), 2.28-2.17 (m, 6H), 1.90-1.55 (m, 32H), 1.47-1.25 (m, 24H), 1.10-0.99 (m, 24H), 0.83 (t, J = 7.6 Hz, 6H); HRMS (ESI) *m/z* calcd for $C_{93}H_{115}N_6O_8S_2$: $[M]^+$ 1493.8187. Found: 1493.8186.
Due to the low solubility, the ^{13}C NMR spectrum of **4b** was unclear even with 20,000 scans.

1,3,5-Tris(naphtho[2,3-*b*]thiophen-2-yl)benzen-*N*,*N′*,*N′′*,*N′′′*,*N′′′′*,*N′′′′′*-hexakis(2-ethylhexyl)-4,4′,4′′,5,5′,5′′,8,8′,8′′,9,9′,9′′-hexaimide (3b)



Under argon atmosphere, aqueous sodium carbonate solution (2 M, 0.75 mL, 1.5 mmol) was added to a solution of **7b** (113 mg, 0.18 mmol), 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (21 mg, 0.045 mmol), and tetrakis(triphenylphosphine)palladium(0) (($Pd(PPh_3)_4$, 0.7 μmol, 8.0 mg) in 10 mL of dioxane, and the resulting mixture was refluxed for 36 h. After cooling, the reaction mixture was added dropwise into 100 mL water to precipitate a red solid, which was collected by filtration, washed successively with water and methanol. The crude product was dissolved into dichloromethane, and the solution was subjected to a short silica gel column firstly eluted with neat dichloromethane to remove less-polar impurities, and then with dichloromethane-methanol (100: 1 v/v) to obtain the target molecule as an orange solid (60 mg, 58% yield). Mp: 330–331 °C; IR (KBr): ν = 1699 cm^{-1}, 1655 cm^{-1} (C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.22 (s, 3H), 8.57 (d, *J* = 8.0 Hz, 3H), 8.53 (d, *J* = 8.0 Hz, 3H), 8.35 (s, 3H), 4.34–4.17 (m, 12H), 2.07–2.19 (m, 6H), 1.48–1.29 (m, 48H), 1.00–0.83 (m, 36H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1 (two carbons), 162.6, 162.5, 154.9, 144.9, 143.5, 135.4, 130.2, 130.0, 127.6, 126.1, 125.1, 124.8, 123.3, 121.0, 118.0, 117.8, 44.8, 44.7, 37.9, 37.78, 30.76, 30.7, 28.61, 28.55, 24.1, 24.0, 23.1 (two carbons), 14.1 (two carbons), 10.8, 10.6. HRMS (ESI) *m/z* calcd for $C_{102}H_{114}N_6O_{12}S_3$: $[M]^+$ 1710.7657. Found: 1710.7656.

2. Single crystal X-ray analysis of 1a

Single crystals of **1a** suitable for single crystal X-ray analysis were obtained by recrystallization from chloroform. The X-ray crystal structure analyses was made on a Rigaku R-AXIS RAPID (Cu Kα radiation, $\lambda = 1.54187$ Å, graphite monochromator, $T = 100$ K. The structure was solved by the direct methods. Non-hydrogen atoms were refined anisotropically using SHELXL-2014 program,[S3] and hydrogen atoms were included in the calculations but not refined.

Crystallographic data for **1a**: $C_{32}H_{38}N_2O_4S$ (546.70), red plate, 0.60 × 0.10 × 0.01 mm^3, *monoclinic*, space group, $P2_1$/n (#14), $a = 21.7114(4)$, $b = 4.9659$ (1), $c = 26.7513(5)$ Å, β = 90.2752 (9), $V = 2884.2(1)$ Å^3, $Z = 4$, $R(F) = 0.0618$ for 4060 observed reflections ($I > 2\sigma(I)$) and 363 variable parameters, $wR(F^2) = 0.2025$ for all data.

3. Theoretical calculations

Geometry optimizations and normal mode calculations of isolated molecules were performed at the B3LYP/6-31G(d) level using the Gaussian 09 program package.[S4]

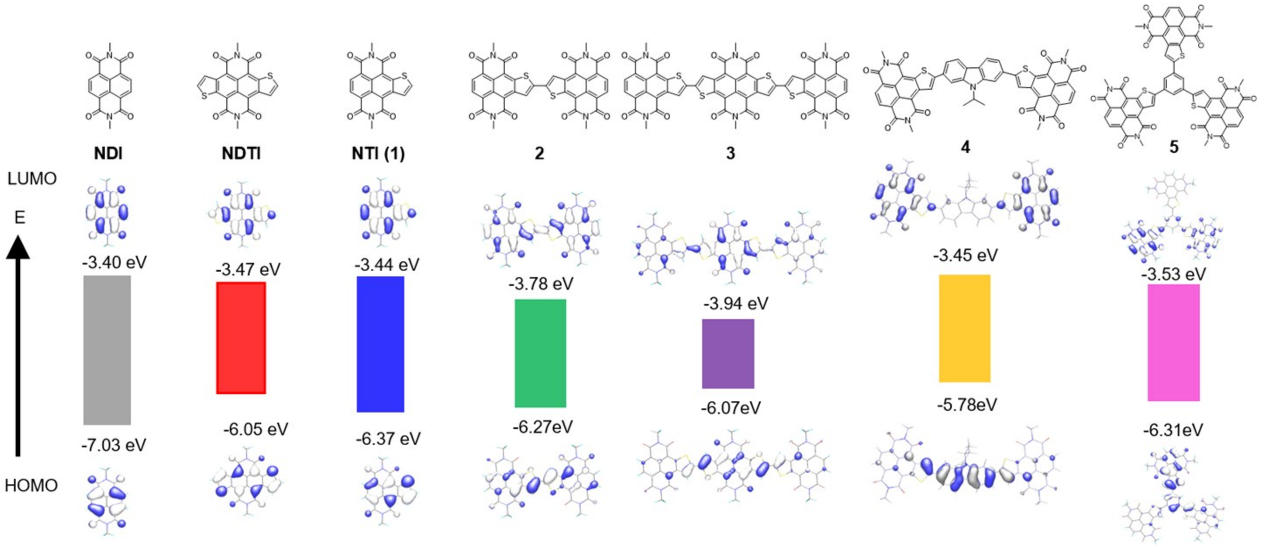


Figure S1. Calculated HOMO and LUMO of NDI, NDTI, NTI (**1**), NTI dimer (**2**), triads (**3**)(**4**), and NTI trimer (**5**). Note that all the alkyl groups are substituted with methyl group.

4. Differential pulse voltammetry of NTI derivatives

Differential pulse voltammetry (DPV) of **5b** was carried out on an ALS Electrochemical Analyzer Model 612D in benzonitrile containing tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) as supporting electrolyte. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl. All the potentials were calibrated with the standard ferrocene/ferrocenium redox couple (Fc/Fc$^+$: $E_{1/2}$ = +0.44 V measured under identical conditions).

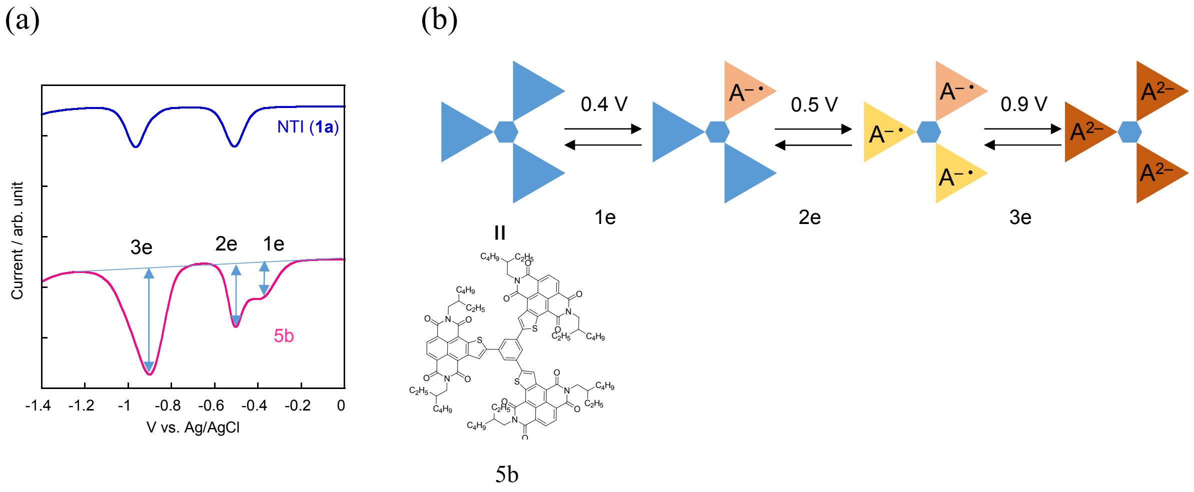


Figure S2. DPV of **5b** (a) and schematic representation of the redox processes (b).

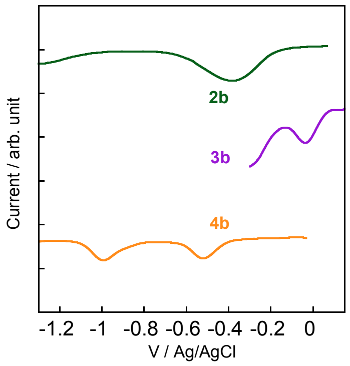


Figure S3. DPV of **2b**, **3b**, and **4b.**

5. Fabrication and evaluation of FET and OPV devices

Fabrication and characteristics of OFET devices

OFET devices based on **2a**, **2b**, and, **3b** were fabricated in a top-contact-bottom-gate (TCBG) configuration on a heavily doped n^+-Si (100) wafer with a 200 nm thermally grown SiO_2 (C_i = 17.3 nF cm^{-2}). The substrate was treated with octadecyltrichlorosilane (ODTS) as reported previously.[S5] The **2a**- and **2b**- thin film was vacuum-deposited on the Si/SiO_2 substrates maintained various temperatures (T_{sub}) at a rate of 1 Å s^{-1} under a pressure of ~10^{-3} Pa. The thin films of 3b were fabricated by the spin-coating method (6000 rpm, 30 sec) using hot 1,3,5-trichlorobenzene solution (4 g/L) and following thermal anneal (150 ^{o}C or 200 ^{o}C, 30 min). On the top of the organic thin film, gold films (80 nm) as drain and source electrodes were deposited through a shadow mask. For a typical device, the drain-source channel length (L) and width (W) are 40 μm and 1.5 mm, respectively. The device characteristics were measured at room temperature under ambient conditions with a Keithley 4200 semiconducting parameter analyzer. Field-effect mobility (μ_{FET}) was calculated in the saturation regime using the following equation,

$$I_d = C_i \, \mu_{FET} \, (W/2L) \, (V_g - V_{th})^2$$

where C_i is the capacitance of the SiO_2 insulator, and V_g and V_{th} are the gate and threshold voltages, respectively. Current on/off ratio (I_{on}/I_{off}) was determined from the I_d at V_g = -10 ~ 0 V (I_{off}) and V_g = 40 V. The μ_{FET} data reported are typical values from more than nine different devices.

Table S1. Transistor characteristics of **2a** and **2b** based OFETs fabricated on Si/SiO_2 substrates modified with ODTS-SAM.

compound	*method*	T_{sub} / ^{o}C	μ^{max} / $cm^2V^{-1}s^{-1}$	$\mu^{average}$ / $cm^2V^{-1}s^{-1}$	I_{on}/I_{off}	V_{th} / V
2a	*Vacuum Deposition*	*150*	*0.17*	*0.15*	~10^8	*19.3*
		175	*0.23*	*0.17*	~10^7	*20.7*
2b		*100*	*0.28*	*0.16*	~10^8	*-3.2*
		150	*0.43*	*0.25*	~10^8	*-4.5*
		200	*0.25*	*0.18*	~10^7	*-8.6*
3b	*Spin-coating*	*150*	*0.031*	*0.016*	~10^7	*2.1*
		200	*0.10*	*0.073*	~10^4	*-11.4*

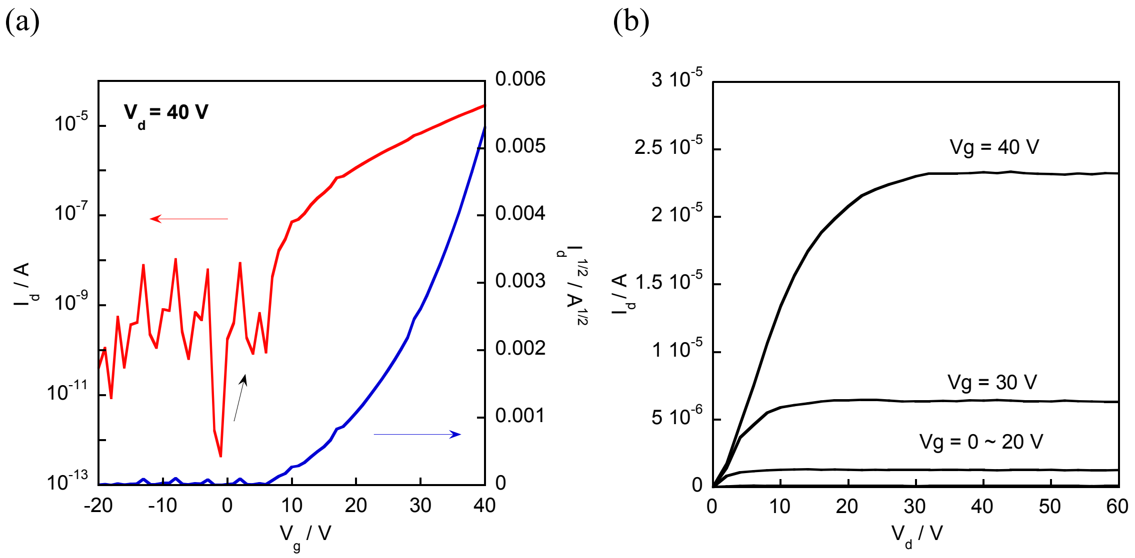


Figure S4. Transfer (a) and output characteristic (b) of the OFET device based on **2a** (T_{sub} = 175 °C).

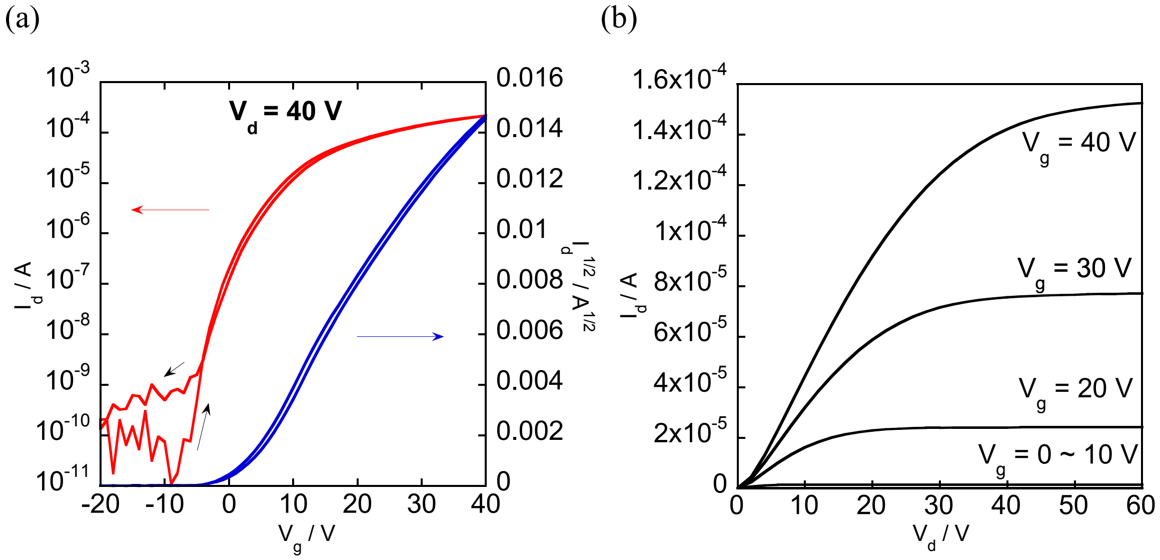


Figure S5. Transfer (a) and output characteristic (b) of the OFET device based on **2b** (T_{sub} = 150 °C).

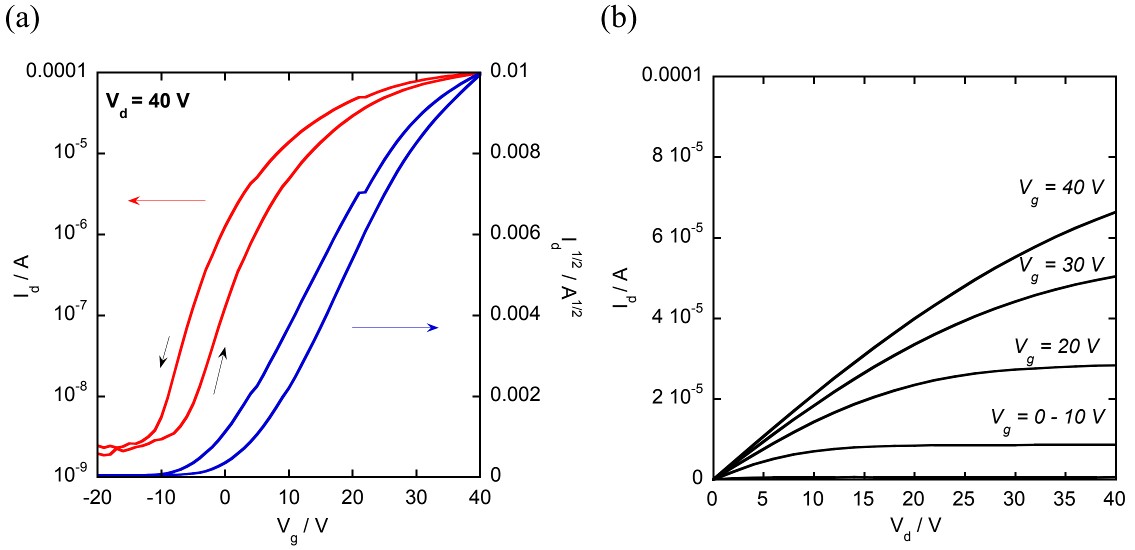


Figure S6. Transfer (a) and output characteristic (b) of the OFET device based on **3b** (T_{sub} = 200 °C).

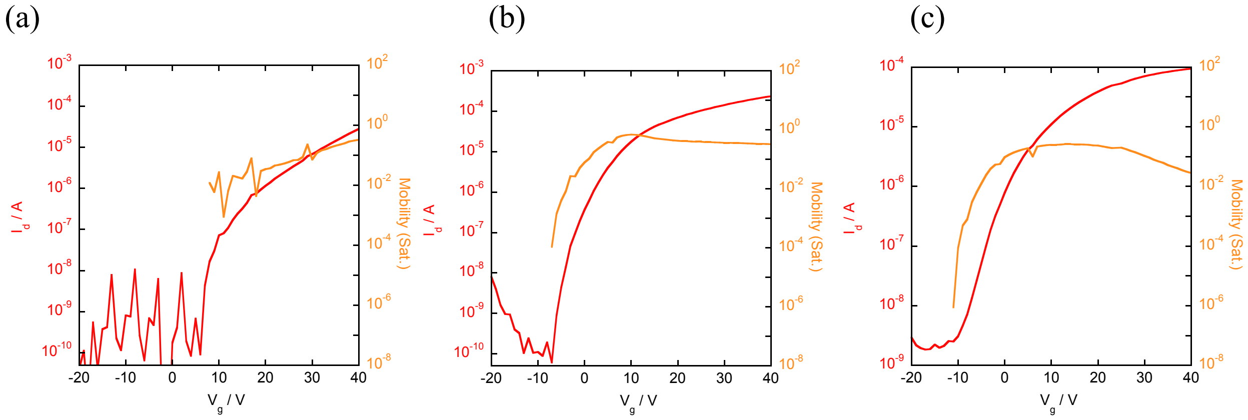


Figure S7. Transfer curve and gate-voltage dependence of mobility of the OFET devices based on **2a** (a, T_{sub} = 175 °C), **2b** (b, T_{sub} = 150 °C), and **3b** (c, T_{sub} = 200 °C).

Fabrication and characterization of OPV devices

Patterned ITO substrates (purchased from Atsugi Micro) were first pre-cleaned sequentially by sonicating in a detergent bath, de-ionized water, acetone, and isopropanol at room temperature, and in boiled isopropanol each for 10 min, and then baked at 120 °C for 10 minutes in air. The substrates were then subjected to a UV/ozone treatment at rt for 20 min. ZnO layer was prepared by spin-coating (at 5000 rpm, 30 sec) a precursor solution prepared from zinc acetate dehydrate (0.27 g) and ethanolamine (0.07 mL) in 2.5 mL of 2-methoxyethanol. Then, the substrates were annealed at 170 °C on a hot plate in air for 30 minutes and rinsed with aceton, isopropanol, and boiled isopropanol for 10 minutes. The glass/ITO/ZnO substrate was transferred into a nitrogen-filled glove box (KOREA KIYON, KK-011AS-EXTRA). Active layer (PTB7-Th and acceptor molecule) solution in chlorobenzene was spin-coated at 1500 or 4000 rpm for 30 s. Then, MoO_x (7.5 nm) and Ag anode (100 nm) were thermally deposited in vacuum to complete the solar cell devices. The active area of the cells was 0.16 cm^2. *J*–*V* characteristics of the cells were measured using a Keithley 2400 source-measure unit in nitrogen atmosphere under the 1 sun (AM1.5G) condition using a solar simulator (SAN-EI Electric, XES-40S1). The light intensity was calibrated with a reference PV cell (KONICA MINOLTA AK-100 certified at National Institute of Advanced Industrial Science and Technology, Japan). EQE spectra were measured with a Spectral Response Measuring System (SOMA OPTICS, S-9241). More than 8 different devices were made and measured to collect the photovoltaic properties.

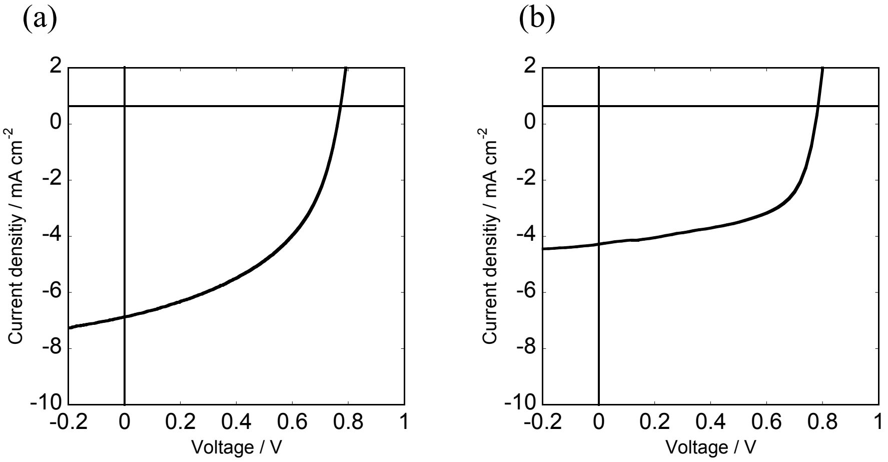


Figure S8. The *J-V* curve of photovoltaic cell consisting of PTB7-Th and **5b** (a) or **4b** (b).

Table S2. Characteristics of OPV devices based on **4b** and **PTB-7-Th**.

solvent	p/n [a]	DIO / vol% [b]	spin-rate /rpm	J_{sc} / mAcm^{-2} [c]	V_{oc} / V [c]	*FF* [c]	*PCE* / % [c]
CB[d]	1:1	3	1500	2.95 (3.20)	0.83 (0.84)	0.44 (0.45)	1.07 (1.22)
	1:1.5	3	1500	4.01 (4.27)	0.76 (0.77)	0.57 (0.58)	1.73 (1.90)
	1:2	3	1500	2.89 (2.91)	0.74 (0.75)	0.54 (0.55)	1.15 (1.20)

[a]ratio of PTB7-Th (p) and **4b** (n), [b]1,8-diiodooctane (DIO), [c]averaged values (maximum values were in brackets), [d]chlorobenzene.

Table S3. Characteristics of OPV devices based on **5b** and **PTB-7-Th**.

solvent	p/n[a]	DIO / vol%[b]	spin-rate / rpm	J_{sc} / mAcm^{-2} [c]	V_{oc} / V [c]	*FF* [c]	*PCE* / % [c]
CB[d]	1:1	-	1500	6.21 (6.55)	0.73 (0.78)	0.38 (0.40)	1.70 (1.96)
		1	1500	6.11 (6.29)	0.74 (0.75)	0.40 (0.41)	1.80 (1.96)
		3	1500	4.93 (5.17)	0.71 (0.74)	0.36 (0.37)	1.26 (1.40)
		-	4000	5.48 (5.68)	0.78 (0.79)	0.41 (0.41)	1.75 (1.85)
		1	4000	6.76 (6.93)	0.74 (0.76)	0.46 (0.47)	2.32 (2.46)
	1:2	-	1500	4.63 (4.81)	0.74 (0.77)	0.33 (0.34)	1.14 (1.22)
		1	1500	5.10 (5.28)	0.75 (0.76)	0.36 (0.36)	1.36 (1.44)
CF[e]	1:1	-	1500	0.92 (1.41)	0.37 (0.41)	0.29 (0.29)	0.15 (0.16)
		1	1500	2.48 (3.36)	0.30 (0.39)	0.32 (0.35)	0.25 (0.39)
		-	4000	1.72 (2.03)	0.31 (0.38)	0.30 (0.32)	0.16 (0.25)
		1	4000	2.64 (2.75)	0.36 (0.42)	0.33 (0.36)	0.31 (0.31)

[a]ratio of PTB7-Th (p) and **5b** (n), [b]1,8-diiodooctane (DIO), [c]averaged values (maximum values were in brackets), [d]chlorobenzene, [e]chloroform.

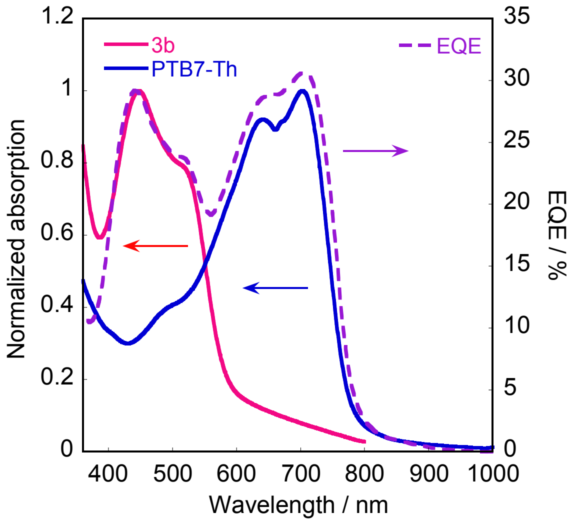


Figure S9. Comparison of absorption spectra of **5b-**, PTB7-Th- thin films, and EQE spectra of **5b-**PTB7-Th-based OPV devices.

6. XRD patterns and AFM images.

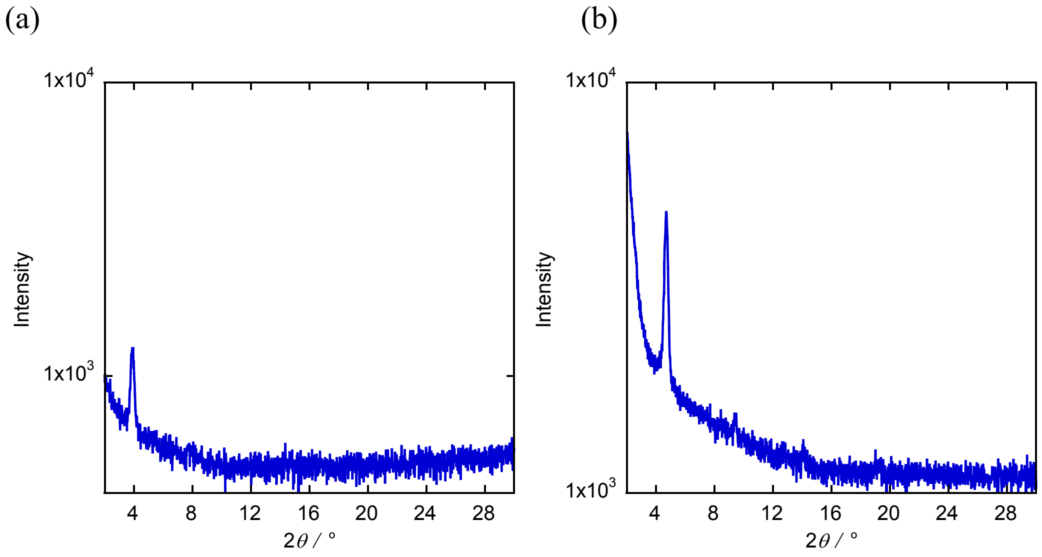


Figure S10. Out-of-plane XRD patterns of thin-film of **2a** (a) and **2b** (b) on ODTS-treated Si/SiO_2 substrate.

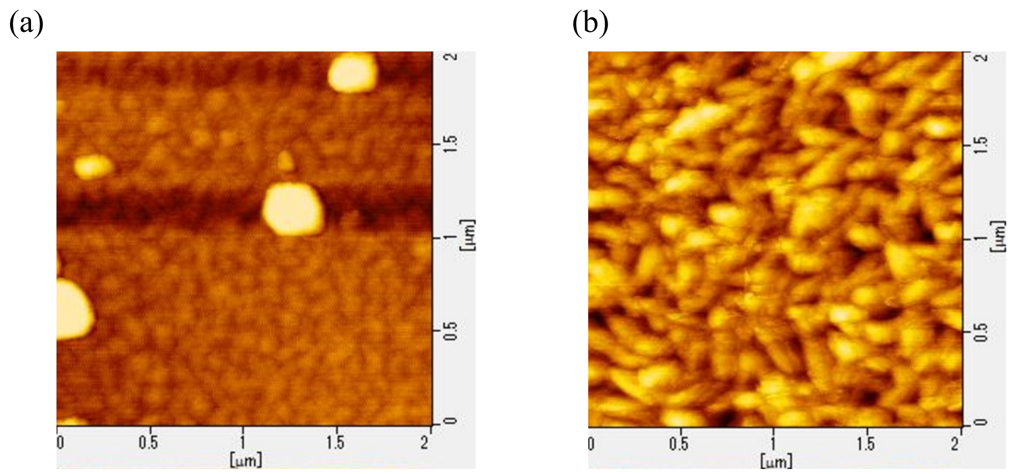


Figure S11. AFM images of thin-film of **2a** (a) and **2b** (b) on ODTS-treated Si/SiO_2 substrate.

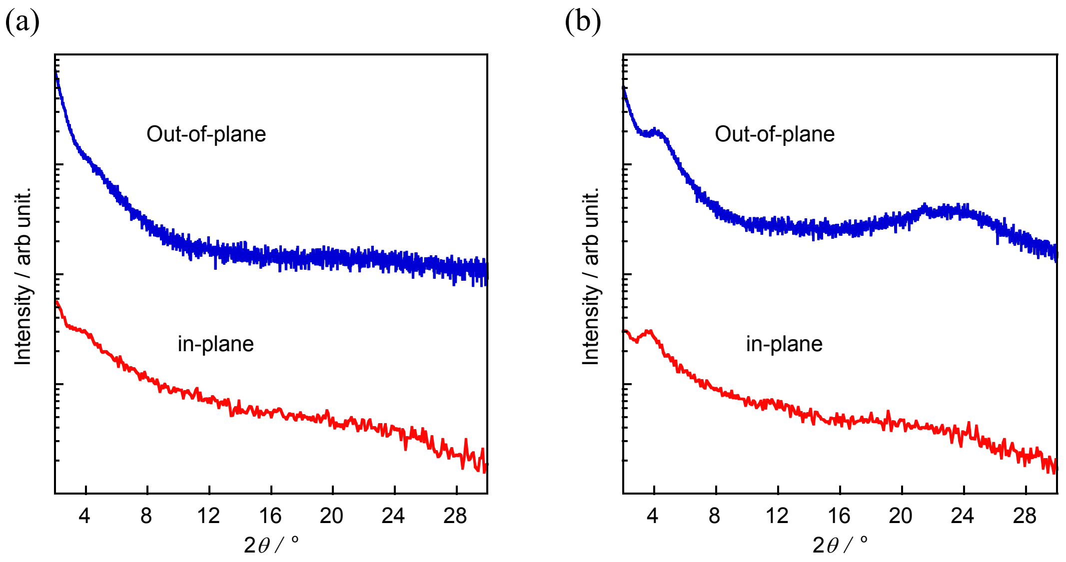


Figure S12. Out-of-plane and in-plane XRD patterns of thin-film of **3b** (a) and the blend film of **3b** and PTB7-Th (b, ratio: 1:1, wt%) on ZnO-coated Si/SiO_2 substrate.

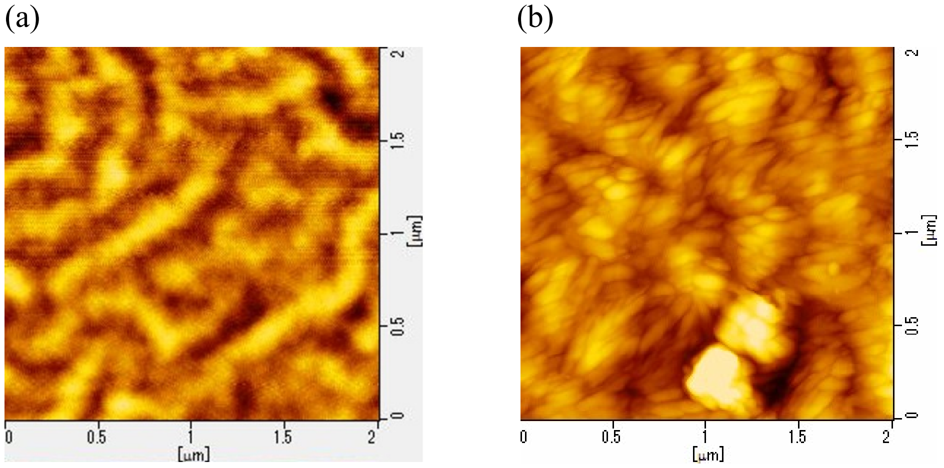
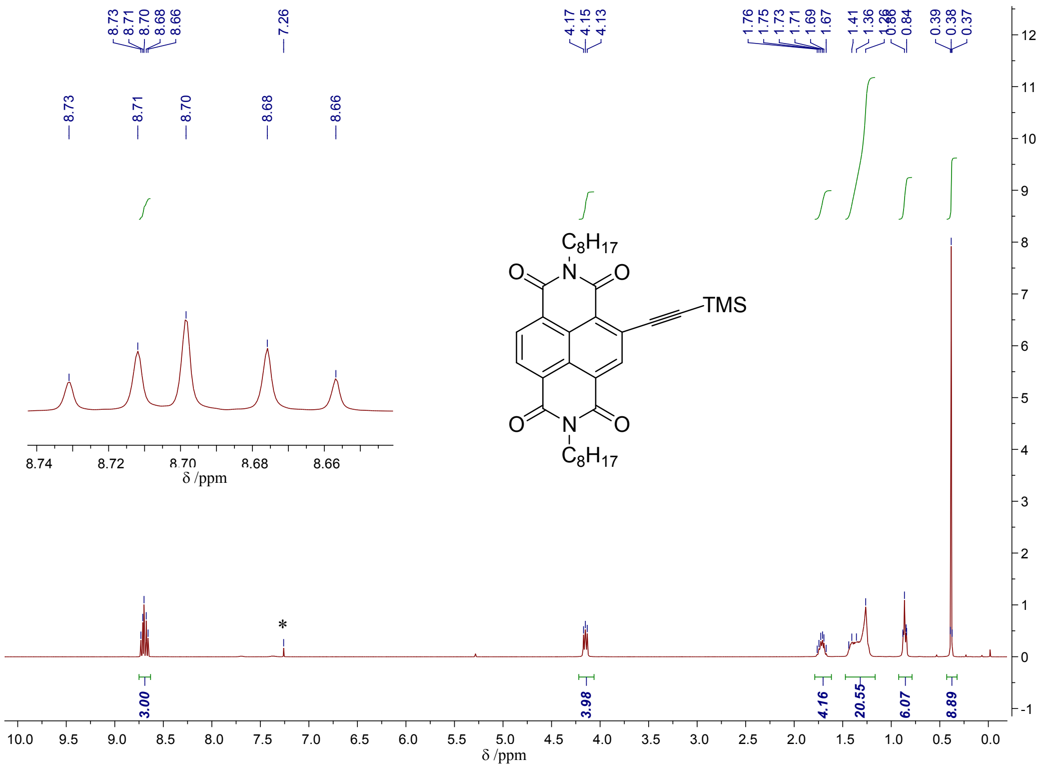
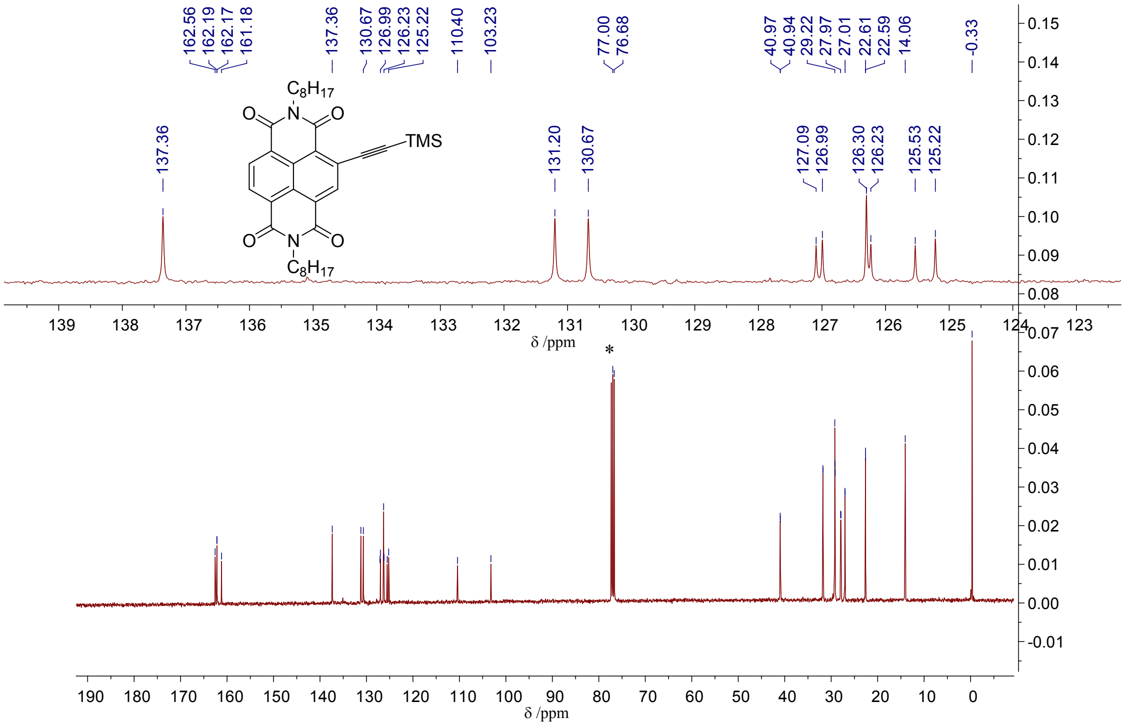


Figure S13. AFM image of the blend thin-film of **5b**/PTB7-Th (a) and **4b**/PTB7-Th (b) on ZnO-coated ITO substrate.

6. NMR spectra.

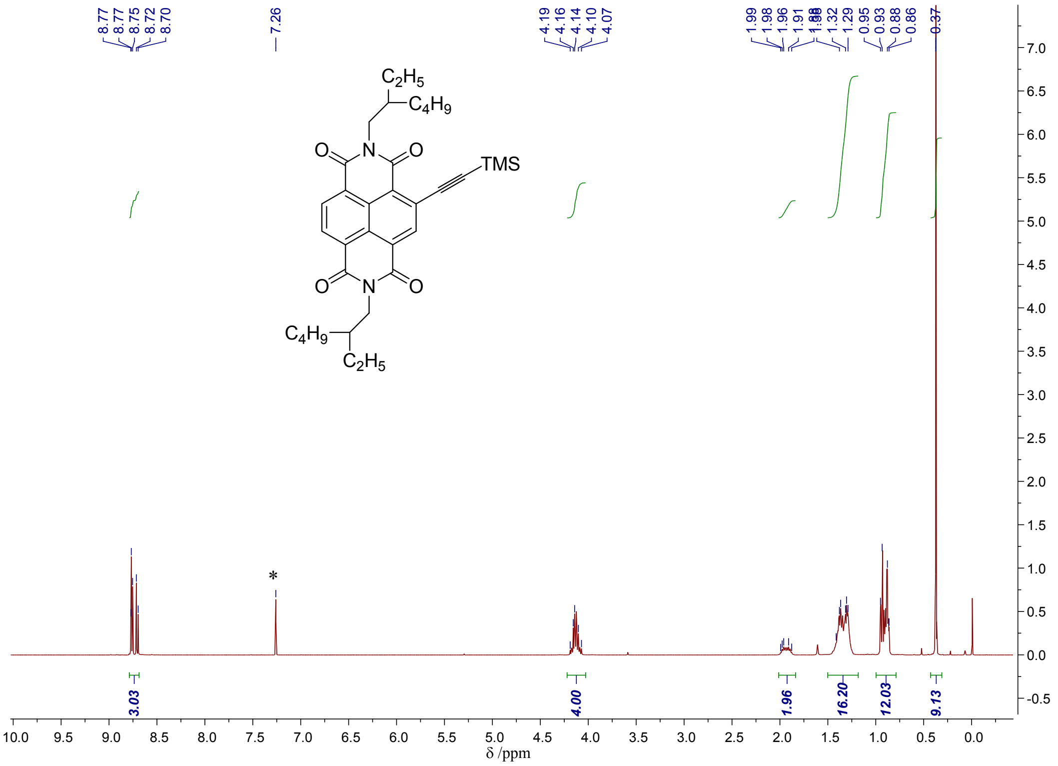
***N,N′*-dioctyl-2-[2-(trimethylsilyl)ethynyl)]-1,4,5,8-naphthalene tetracarboxylic acid diimide (5a)**

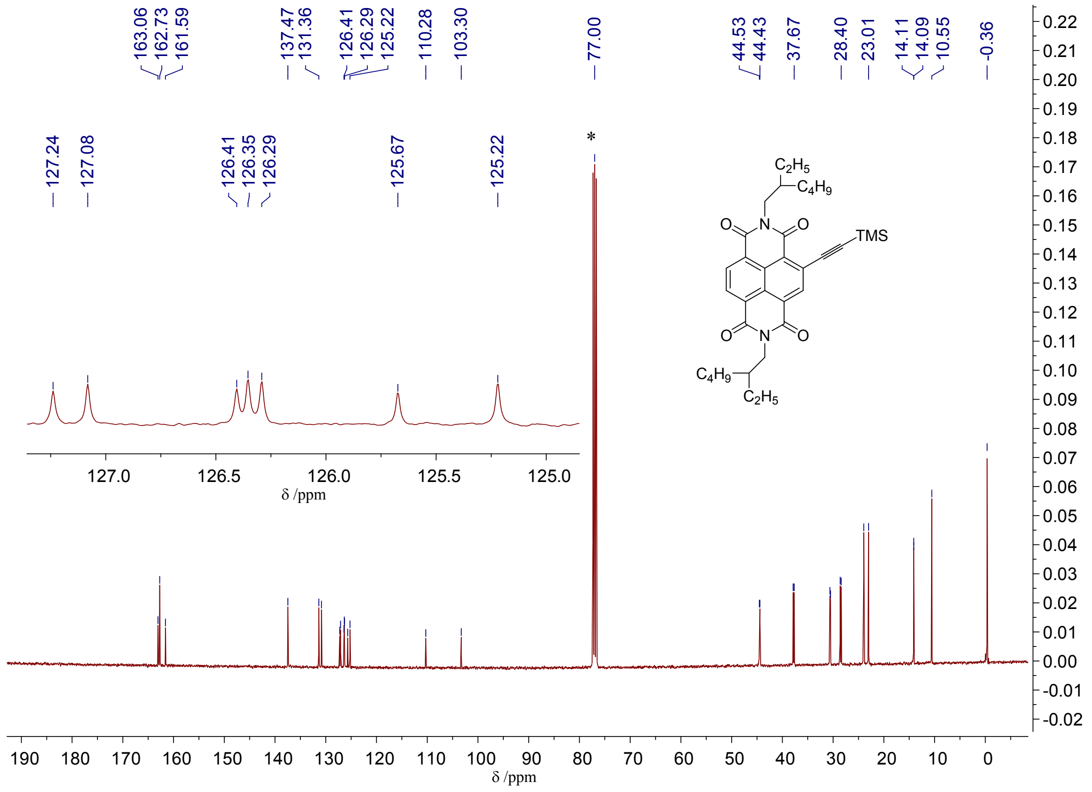




*from $CDCl_3$

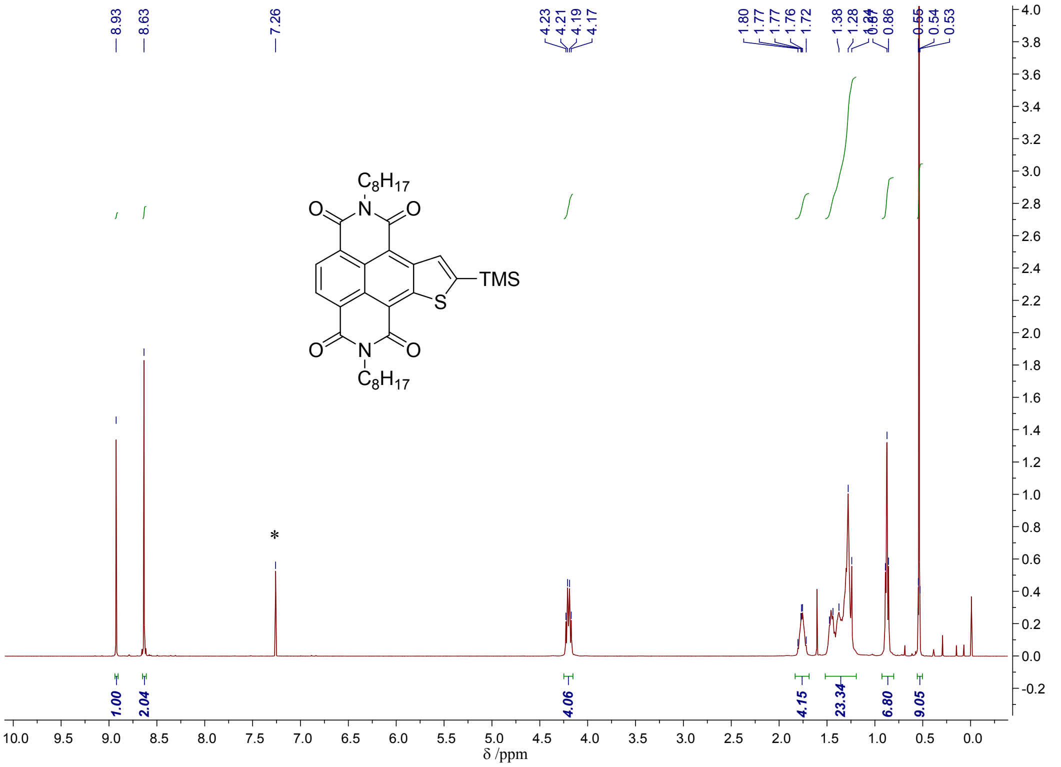
N,N'-Bis(2-ethylhexyl)-2-[2-(trimethylsilyl)ethynyl]-1,4,5,8-naphthalene tetracarboxylic acid diimide (5b)

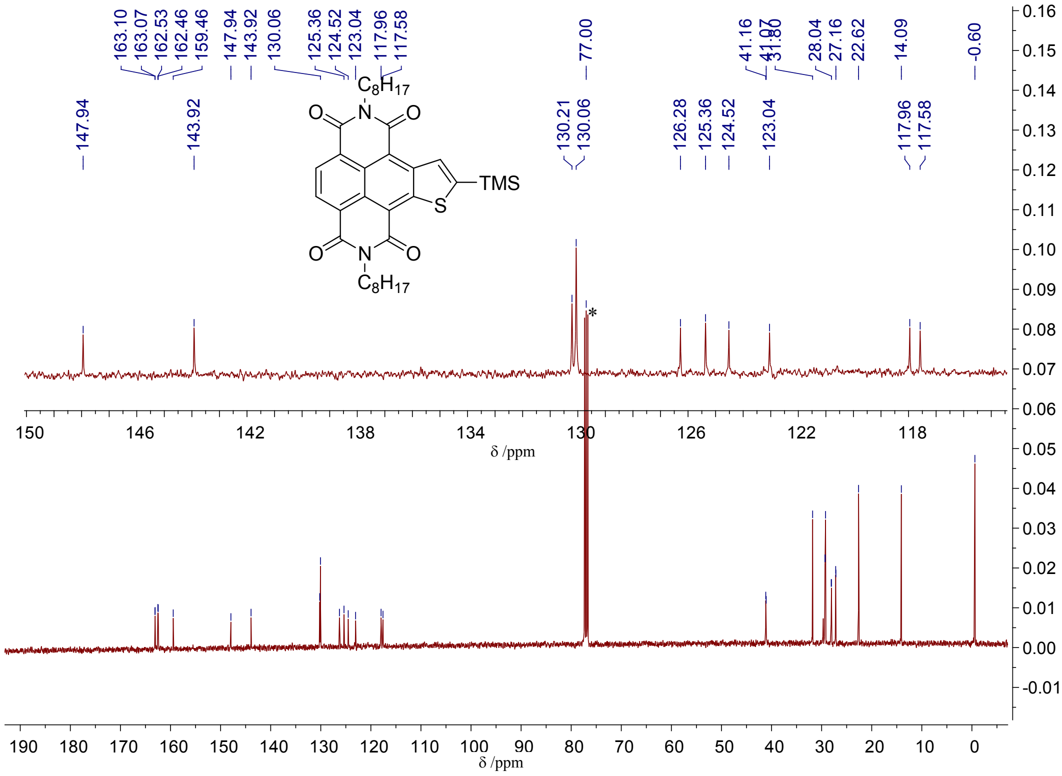




*from $CDCl_3$

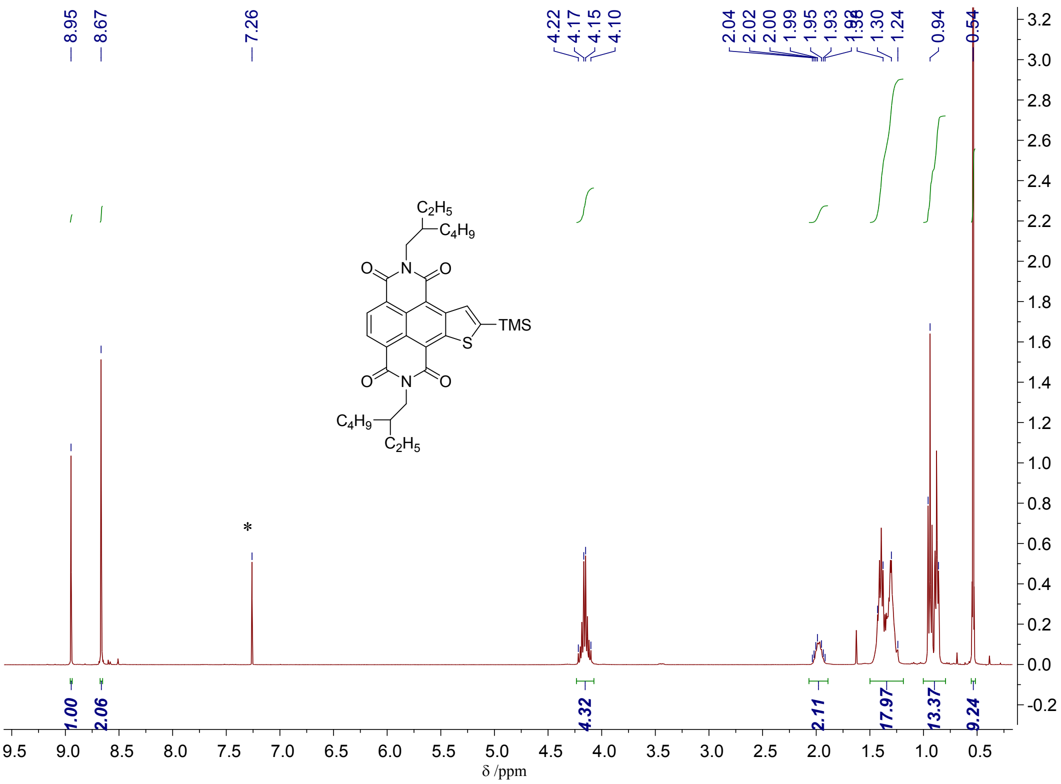
N,N′-Dioctyl-2-(trimethylsilyl)naphtho[2,3-*b*]thiophene-4,5,8,9-diimide (6a)

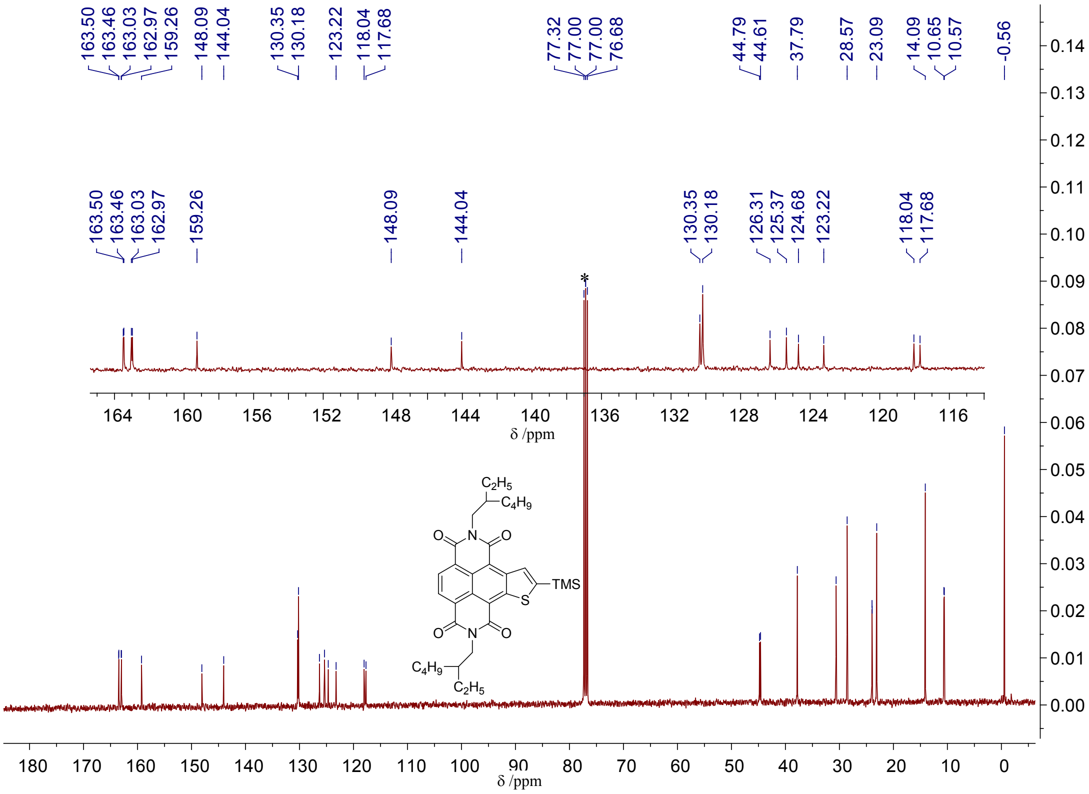




*from $CDCl_3$

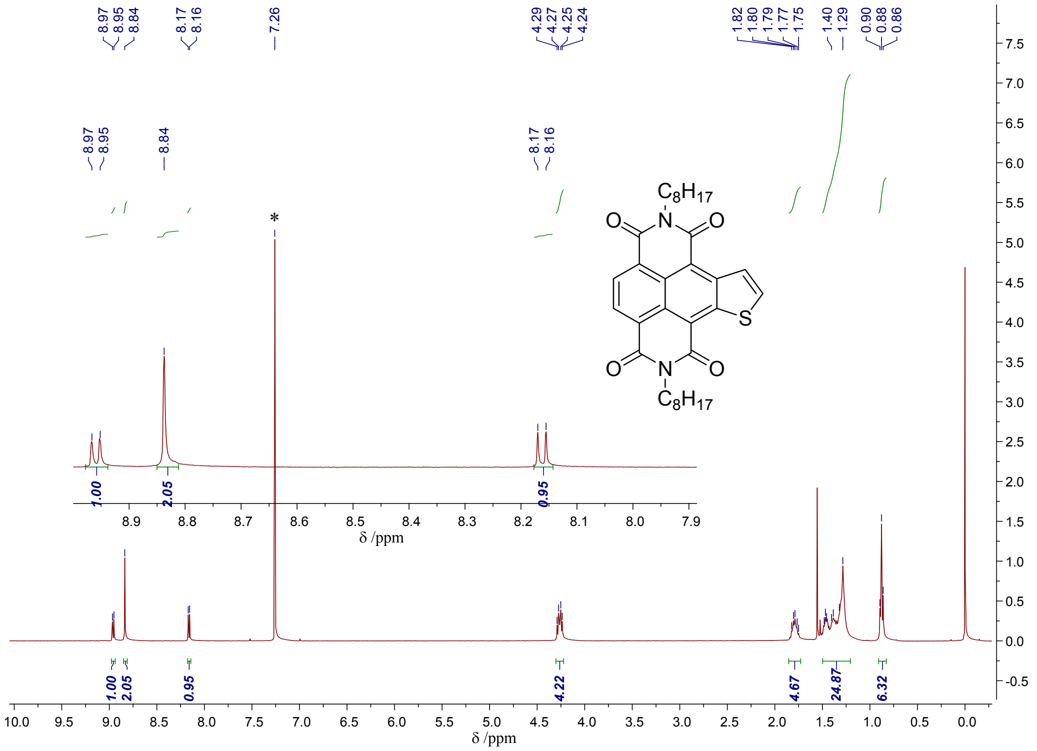
N,N′-Bis(2-ethylhexyl)-2-(trimethylsilyl)naphtho[2,3-*b*]thiophene-4,5,8,9-diimide (6b)

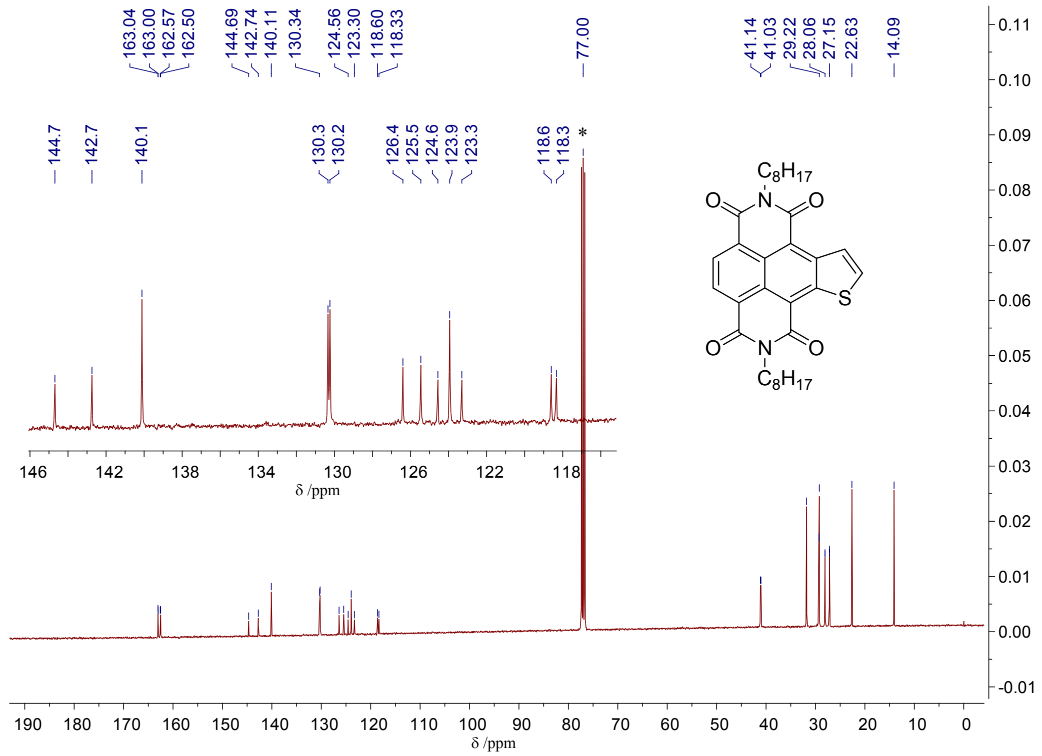




*from CDCl$_3$

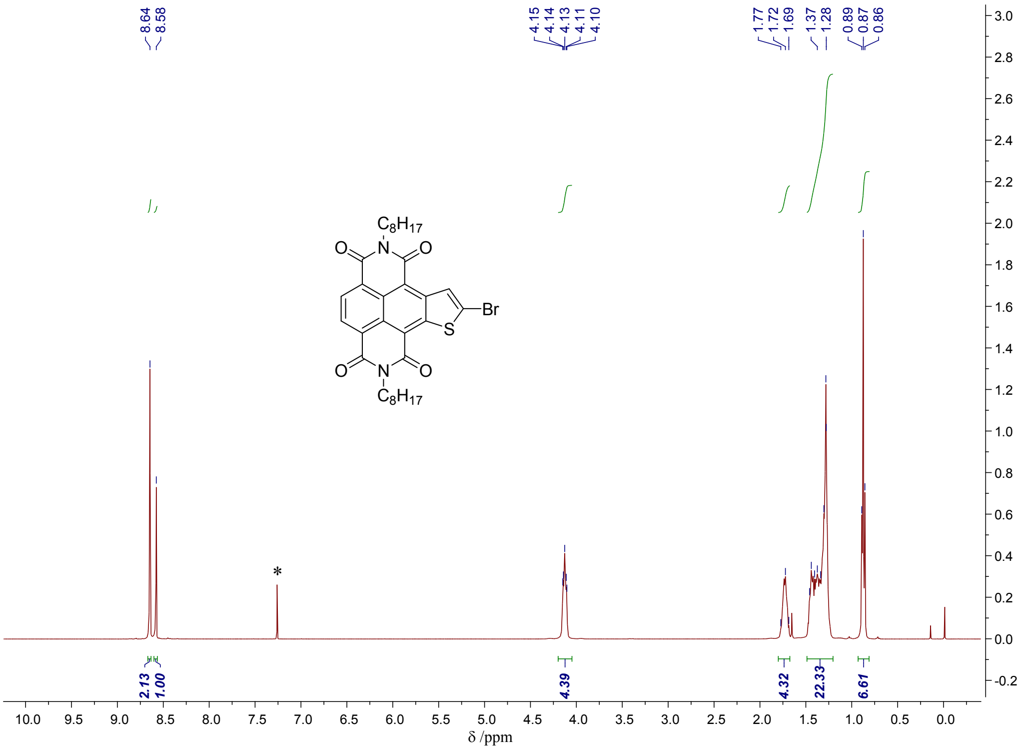
N,N′-Dioctylnaphtho[2,3-*b*]thiophene-4,5,8,9-diimide (NTI, 1a)

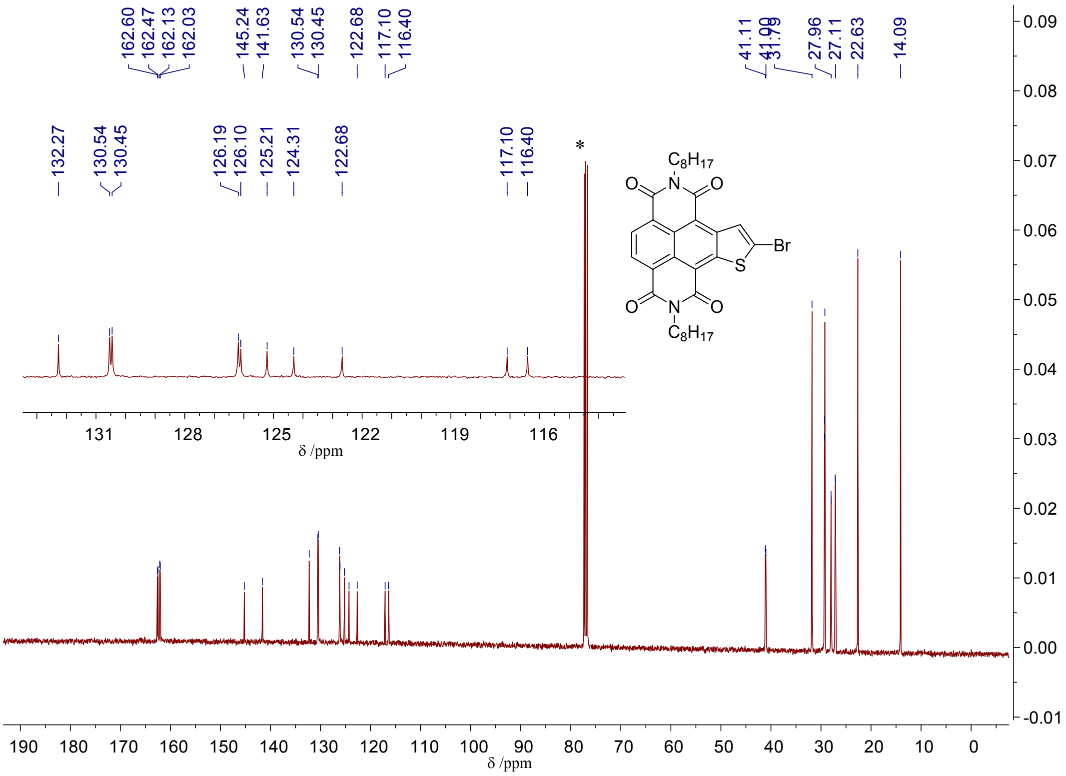




*from $CDCl_3$

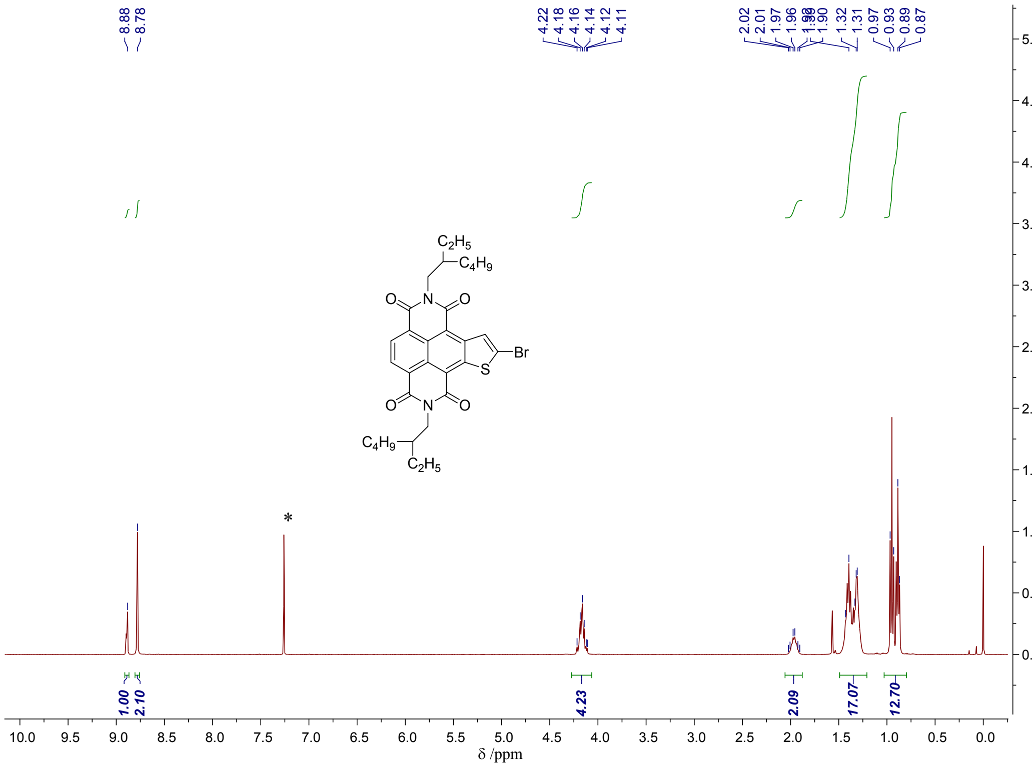
N,N′-Dioctyl-2-bromonaphtho[2,3-*b*]thiophene-4,5,8,9-diimide (7a)

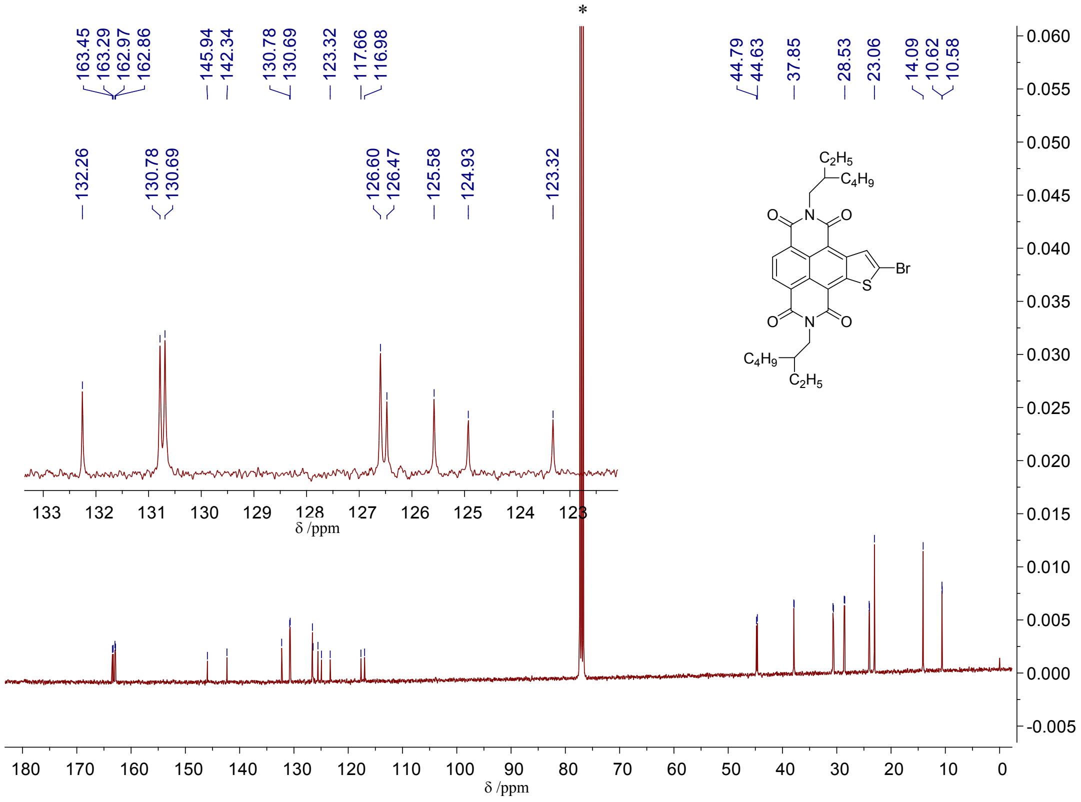




*from $CDCl_3$

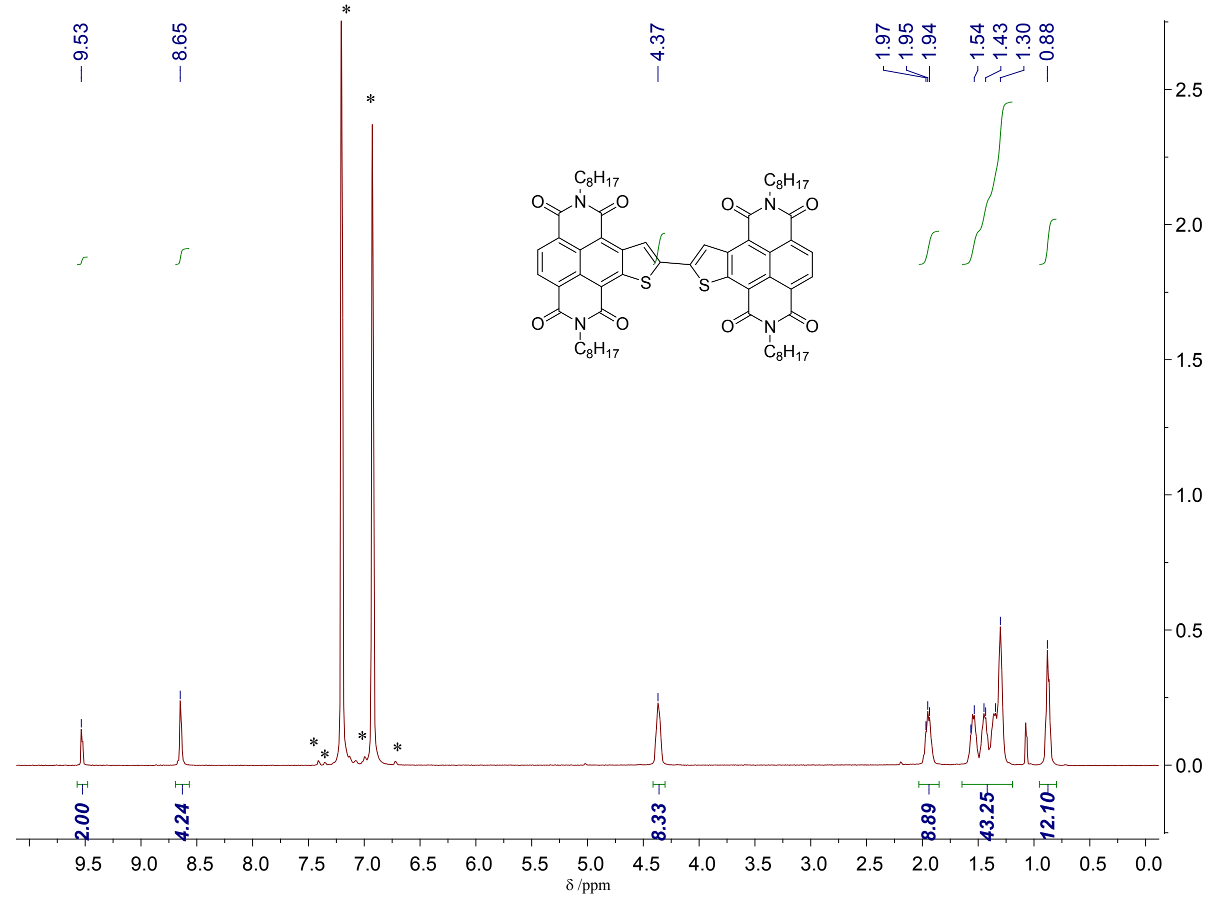
N,N′-Bis(2-ethylhexyl)-2-bromonaphtho[2,3-*b*]thiophene-4,5,8,9-diimide (7b)





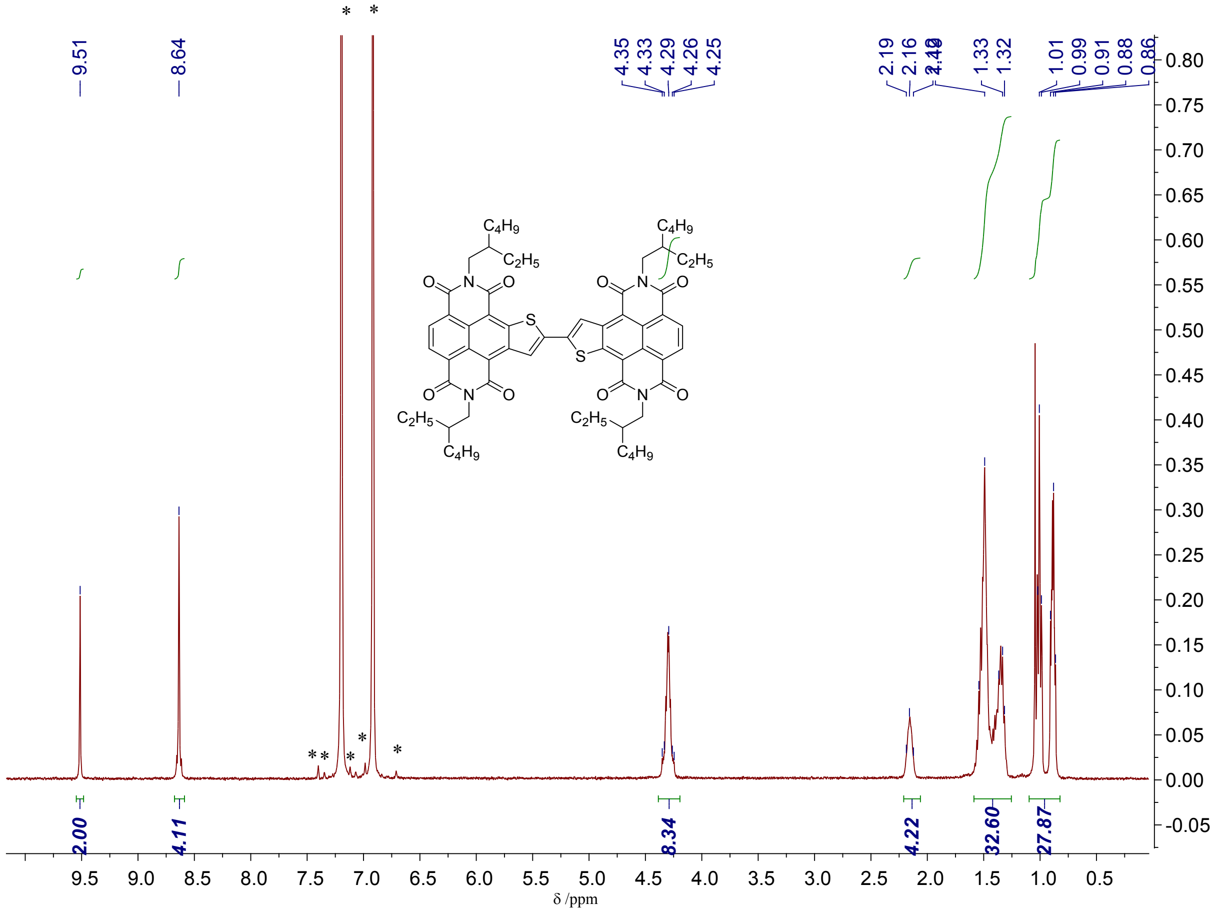
*from $CDCl_3$

[2,2′]Bi[naphtho[2,3-*b*]thienyl]-*N*,*N*′,*N*″,*N*‴-tetraoctyl-4,4′,5,5′,8,8′,9,9′-tetraimide (2a)



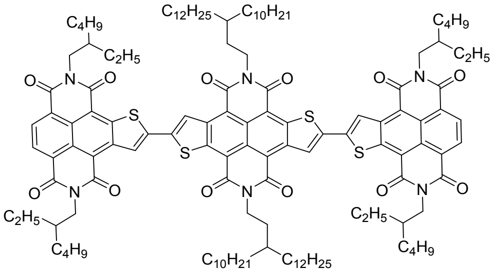
*From ODB-d_4

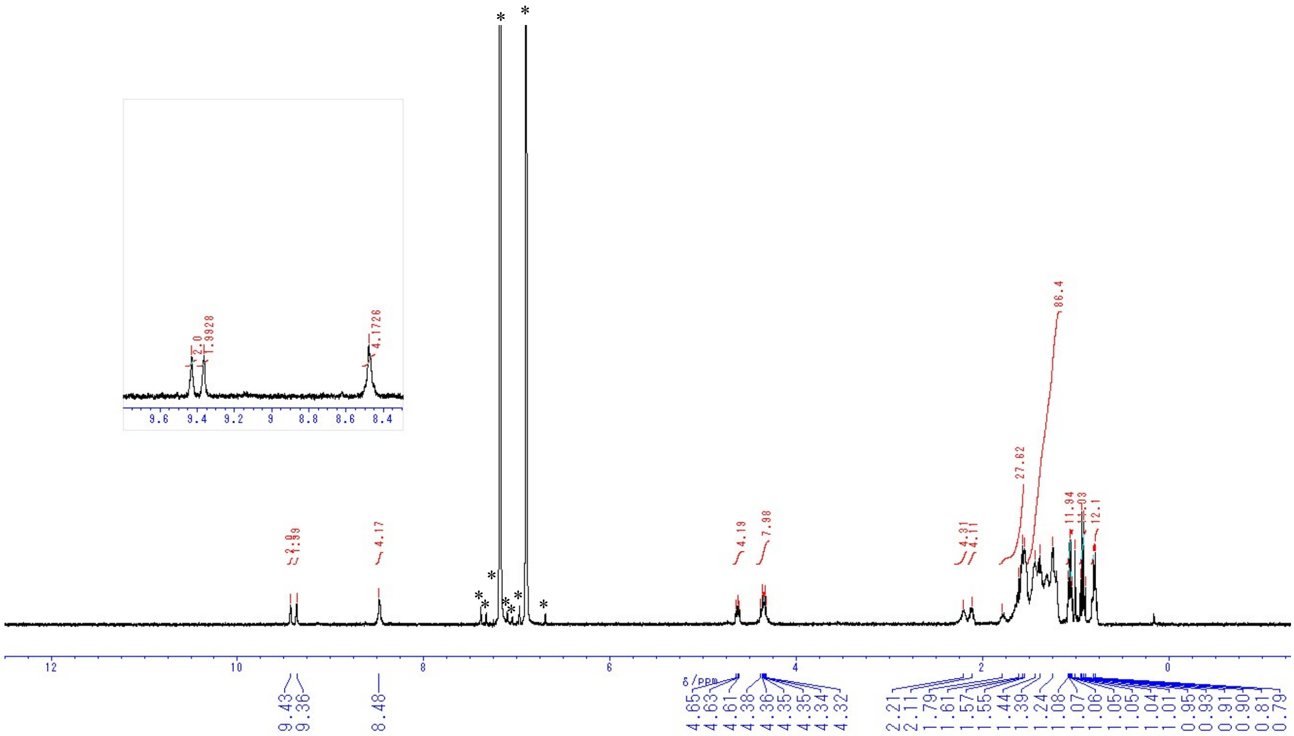
[2,2′]Bi[naphtho[2,3-*b*]thienyl]-*N*,*N*′,*N*′′,*N*′′′-tetrakis(2-ethylhexyl)-4,4′,5,5′,8,8′,9,9′-tetraimide (2b)



*From ODB-d_4

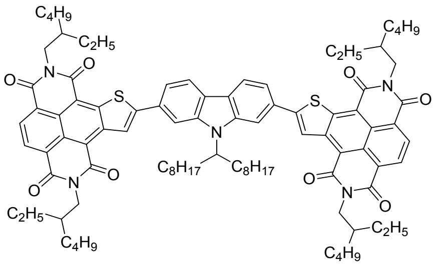
2,7-Bis(*N*,*N′*-bis-(2-ethylhexyl)naphtho[2,3-*b*]thiophen-2yl-4,5,9,10-tetracarboxylic diimide)-*N*,*N′*-bis(3-decylpentadecyl)naphtha[2,3-*b*:6,7-*b′*]dithiophene-4,5,9,10-tetracarboxylic imide (3b)

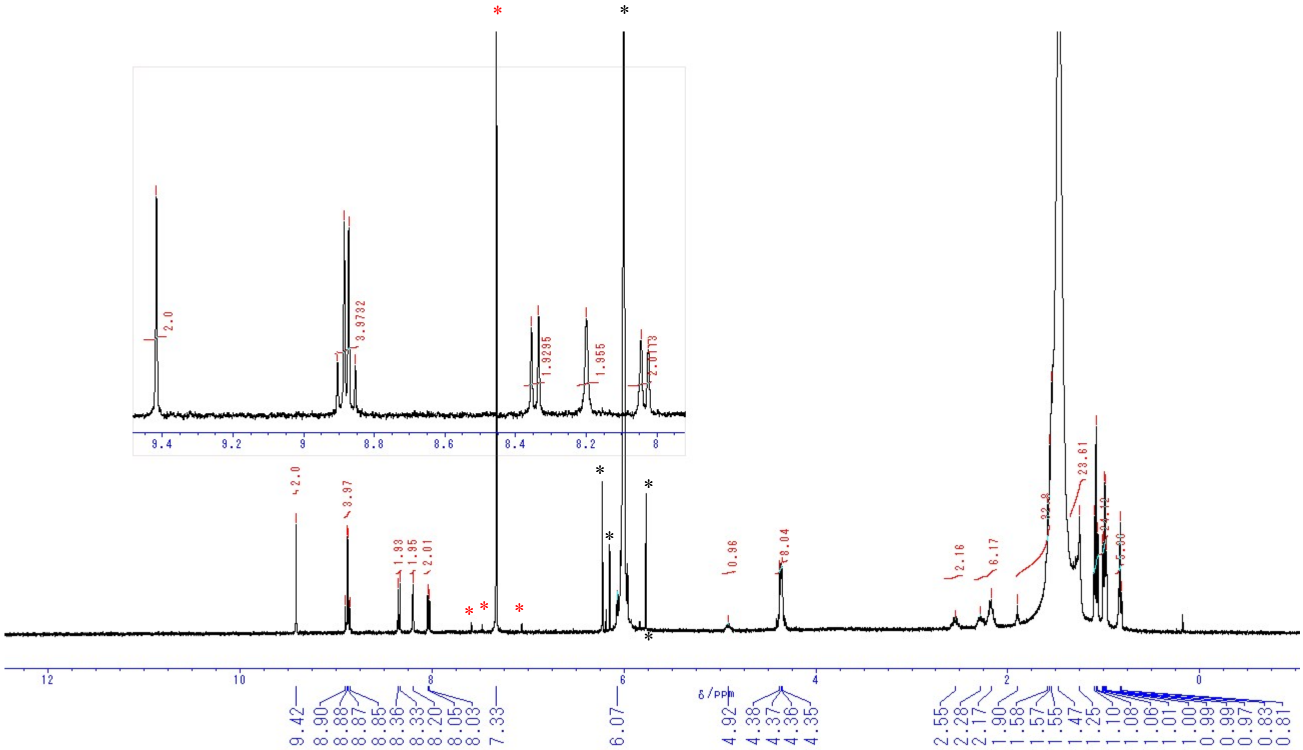




*From ODB-d_4

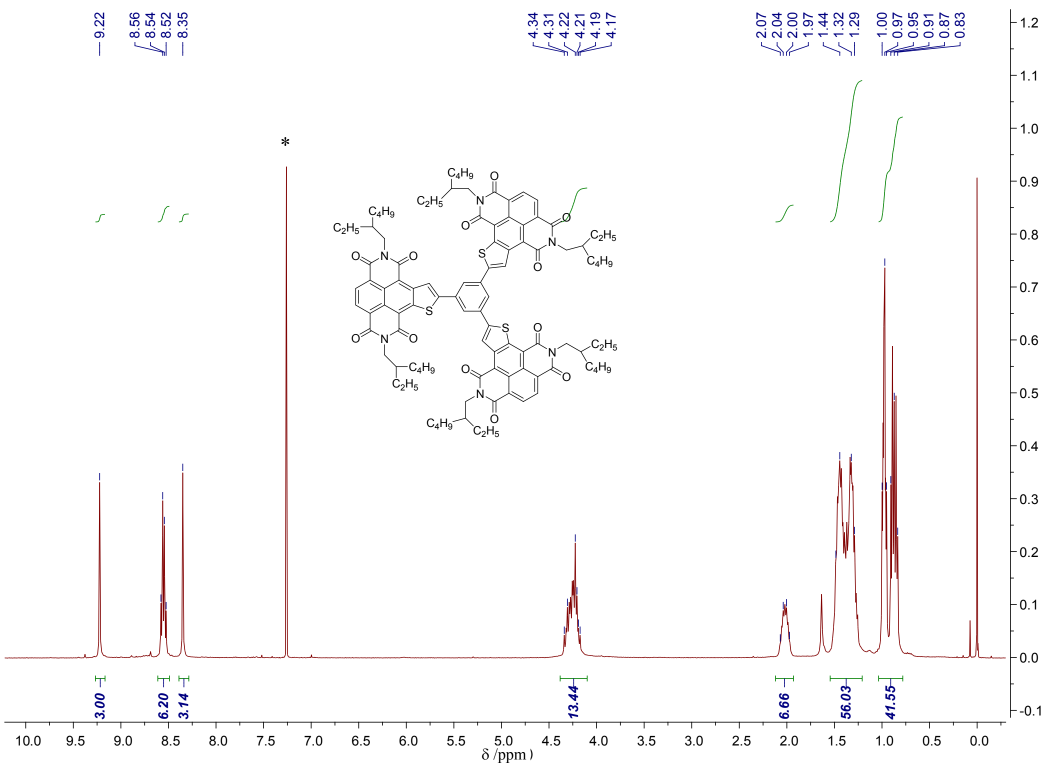
2,7-Bis(naphtho[2,3-*b*]thiophen-2yl)-9-(9-heptadecyl)carbazole-*N*,*N′*,*N′′′*,*N′′′′*-tetrakis(2-ethylhexyl)4,4’,5,5’,8,8’,9,9’-tetraimide (4b)

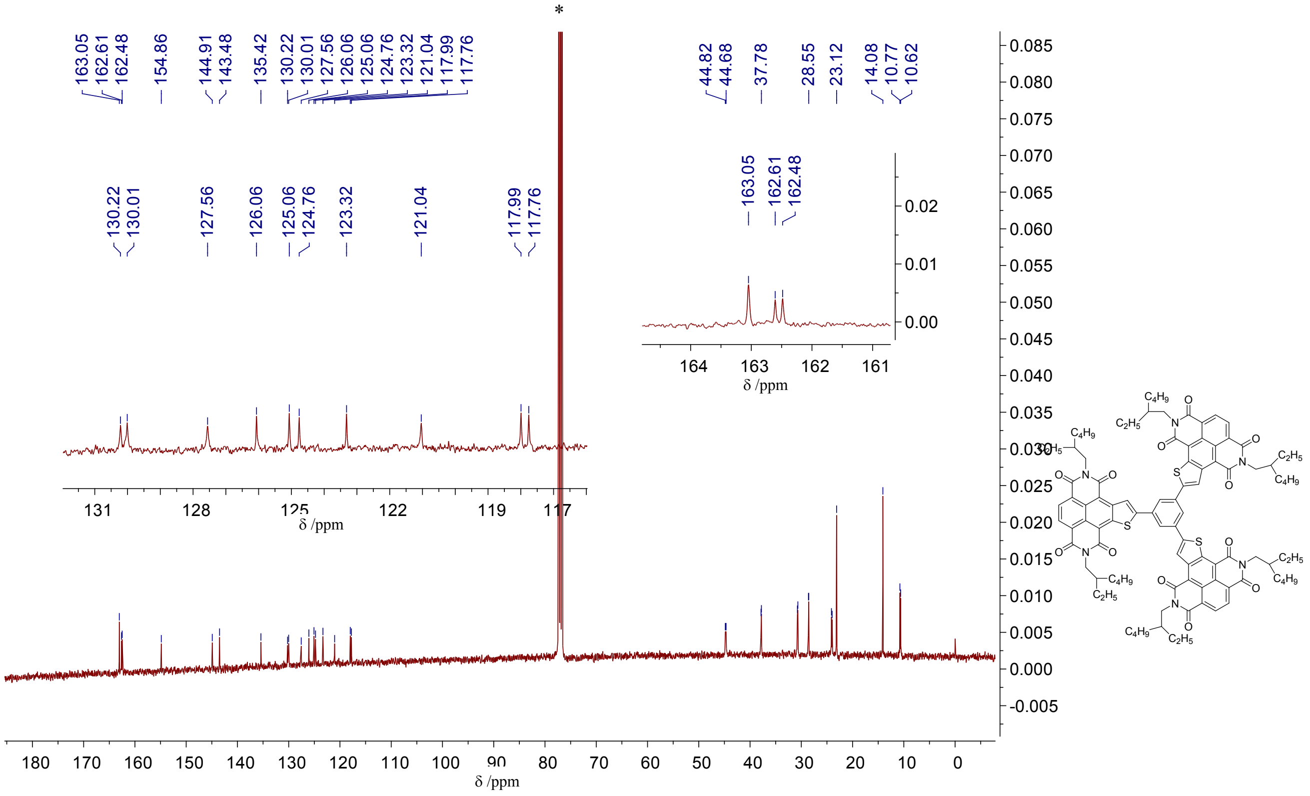




*From TCE-d_2 *From solvent residue ($CHCl_3$)

1,3,5-Tris(naphtho[2,3-*b*]thiophen-2-yl)benzen-*N*,*N′*,*N″*,*N‴*,*N⁗*,*N′⁗*-hexakis(2-ethylhexyl)-4,4′,4″,5,5′,5″,8,8′,8″,9,9′,9″-hexaimide (5b)





*from $CDCl_3$

7. References.

S1. Jones, B. A.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Chem. Mater.* **2007**, *19*, 2703–2705.

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