

Naphthodithiophene Diimide (NDTI)-Based Semiconducting Copolymers: From Ambipolar to Unipolar n-Type Polymers

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1. Polymerization method of PNDTI-BTz and -NTz

Attempted synthesis of PNDTI-BTz and –NTz by Suzuki Polymerization

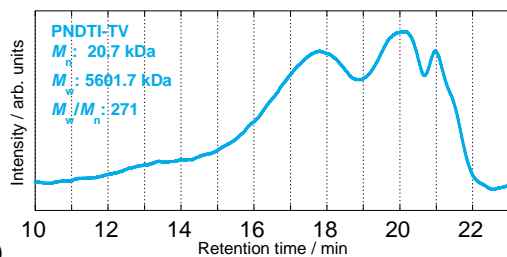
To a 0.5–2.0 mL microwave pressurized vial equipped with a stirring bar, 2,7-dibromo-NDTI (**1**, 0.05 mmol), 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-BTz or 5,10-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-NTz (0.05 mmol), tetrakis(triphenylphosphine)palladium (1.2 mg, 1.0 μ mol), potassium carbonate (167 mg, 1.2 mmol), water (0.5 mL), toluene (1.3 mL), and Aliquat 336 (13 mg) were added. The tube was sealed, refilled with argon, put into microwave reactor, and then heated to 140 °C for 3 h. After cooling, the reaction mixture was poured into methanol (50 mL), the resulting precipitate was collected by filtration and was subjected to sequential Soxhlet extraction with methanol, hexane to remove low molecular weight fractions. The residue was extracted with chloroform, and then the concentrated fraction was reprecipitated in 50 mL of methanol to yield PNDTI -BTz or -NTz in 42% or 37% yield, respectively.

Attempted synthesis of PNDTI-BTz and -NTz by Stille polymerization

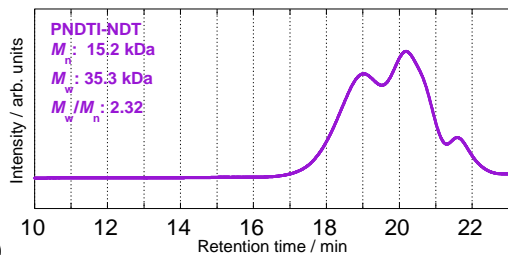
To a 0.5–2.0 mL microwave pressurized vial equipped with a stirring bar, *N,N'*-bis(2-decyltetradecyl)-2,7-bis(trimethylstannyl)-NDTI (**2**, 0.05 mmol), brominated 4,7-dibromo-BTz or 5,10-dibromo-NTz (0.05 mmol), tris(dibenzylideneacetone)dipalladium (0.8 mg, 0.9 μ mol), tri(*o*-tolyl)phosphine (1.1 mg, 3.5 μ mol) and toluene (1.8 mL) were added. The tube was sealed, refilled with argon, put into microwave reactor, and then heated to 180 °C for 60 min. After cooling to room temperature, the reaction mixture was poured into methanol (25 mL) containing hydrochloric acid (1 M, 0.5 mL) and stirred for 6 h. The resulting precipitate was collected by filtration and was subjected to sequential Soxhlet extraction with methanol, hexane, and dichloromethane to remove low molecular weight fractions. The residue was extracted with chloroform, and then the concentrated fraction was reprecipitated into 20 mL of methanol to yield PNDTI-BTz or –NTz in 97% or 91% yield, respectively.

2. GPC charts of PNDTI-Xs

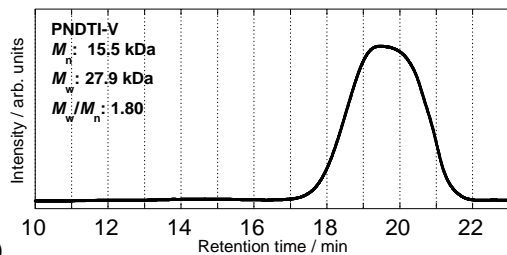
(a)



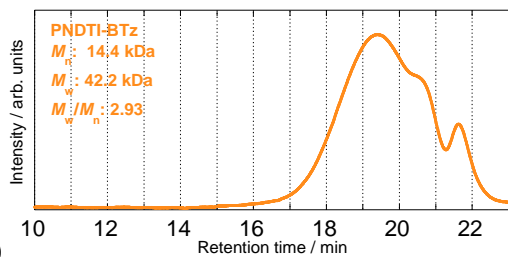
(b)



(c)



(d)



(e)

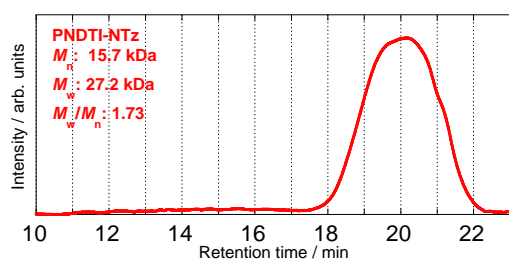


Figure S1. GPC charts of PNDTI-TV (a), -NDT (b), -V (c), -BTz (d), and -NTz (e) in *o*-dichlorobenzene at 140 °C (their polymerization degree were estimated against the polystyrene standards).

3. AFM images of thin films of PNDTI-Xs on Si/SiO₂ substrate

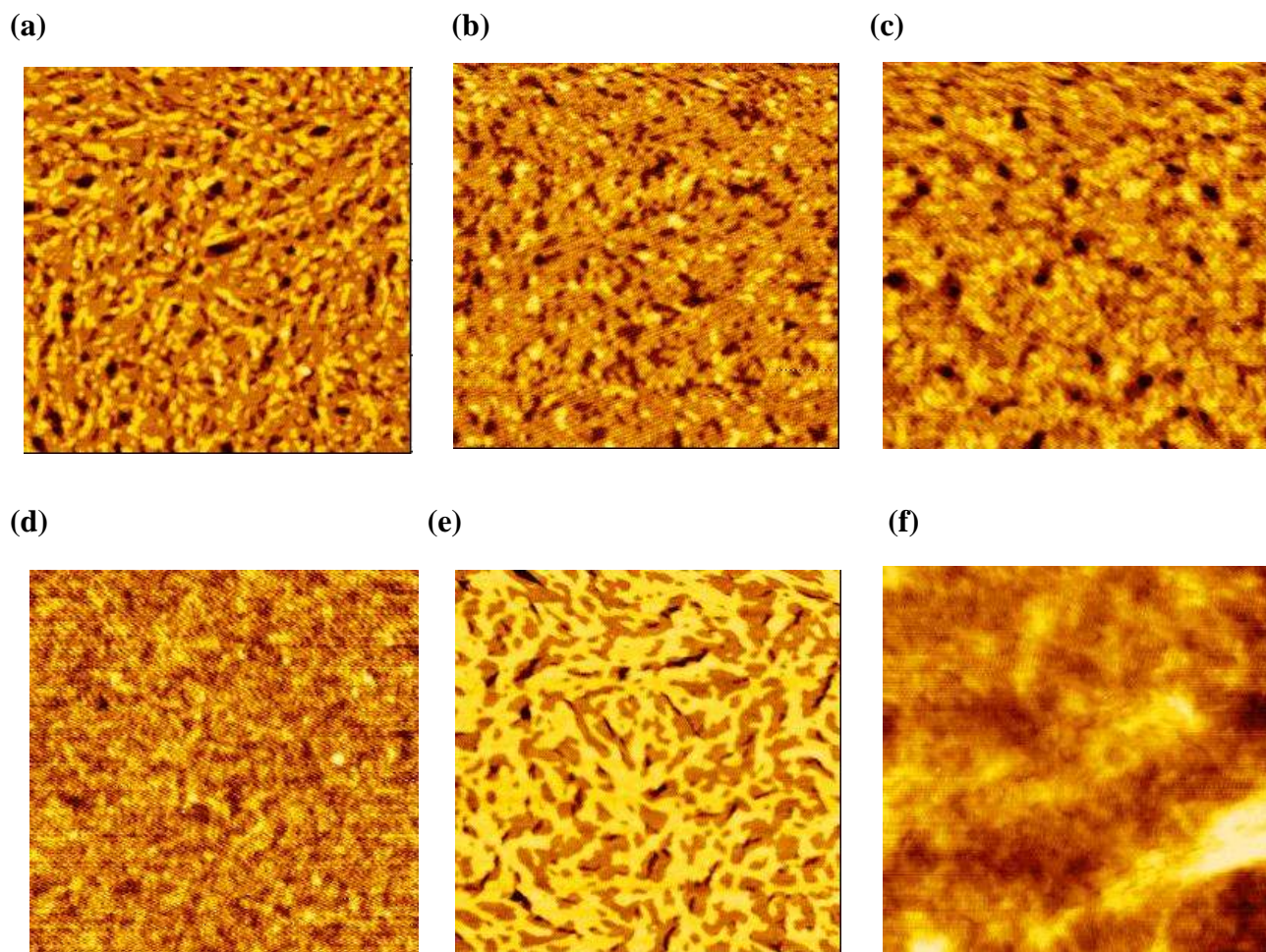


Figure S2. AFM images ($2 \times 2 \mu\text{m}$) of the thin films of PNDTI-BT (a), -TV (b), -NDT (c), -V (d), -BTz (e), and -NTz (f) on Si/SiO₂ substrate.

4. Cyclic voltammogram of PNDTI-BT

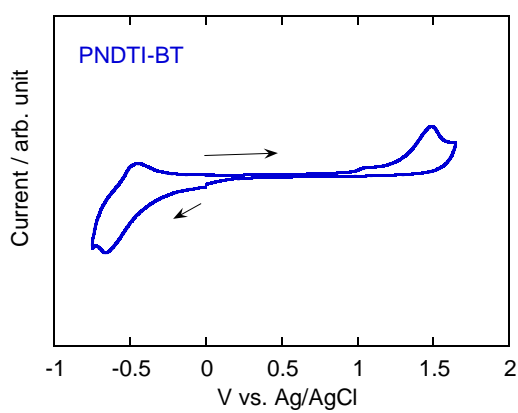
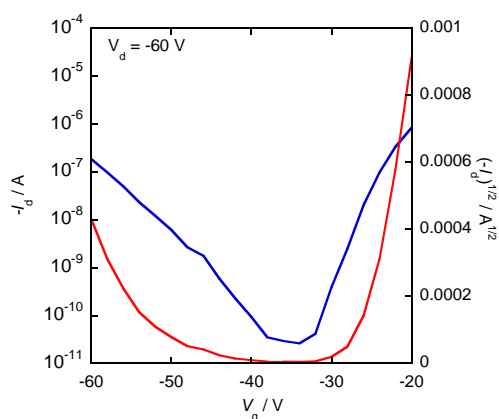


Figure S3. Cyclic voltammogram of PNDTI-BT.

5. Transfer and output curves of PNDTI-BTz based transistors under negative bias conditions

(a)



(b)

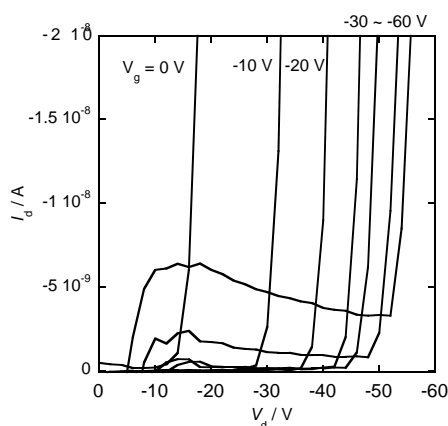


Figure S4. Transfer (a) and output (b) curves of PNDTI-BTz based transistors under negative bias conditions.

6. Schematic illustration of steric congestion of branched alkyl groups of model compound for PNDTI-V

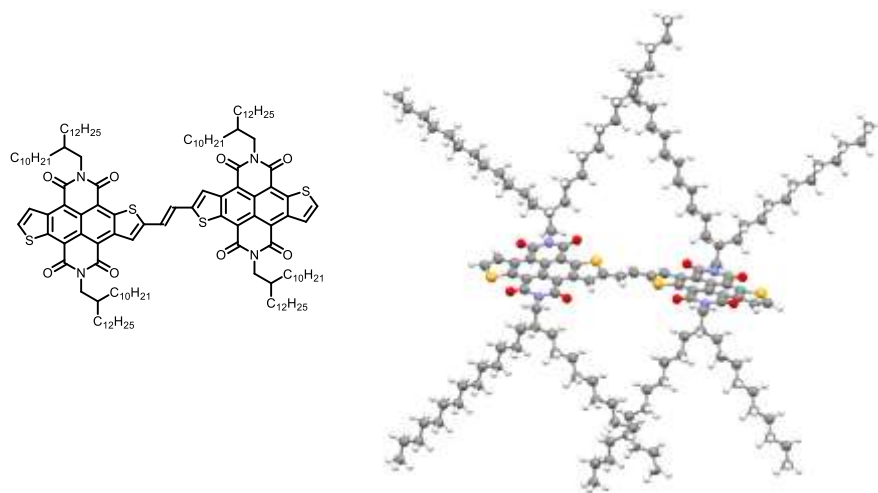


Figure S5. Schematic illustration of steric congestion of branched alkyl groups of PNDTI-V simulated by the MM2 module in Chem-3D Ultra 6.0 (CambridgeSoft, Cambridge, MA).

7. DSC profiles of PNDTI-Xs

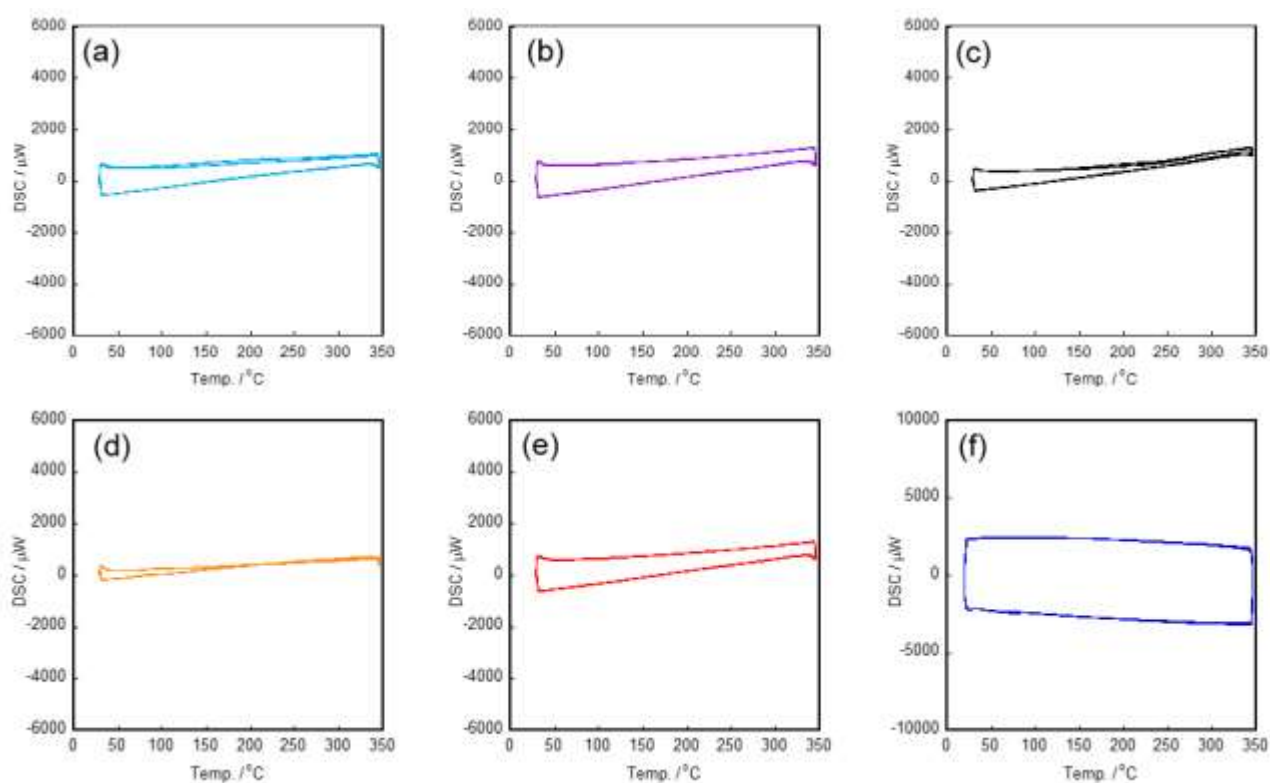


Figure S6. Differential scanning calorimetry (DSC) profiles of PNDTI-TV (a), -NDT (b), -V (c), -BTz (d), -NTz (e), and -BT (f).

8. XRD patterns of the thin film of PNDTI-BT annealed at different temperatures

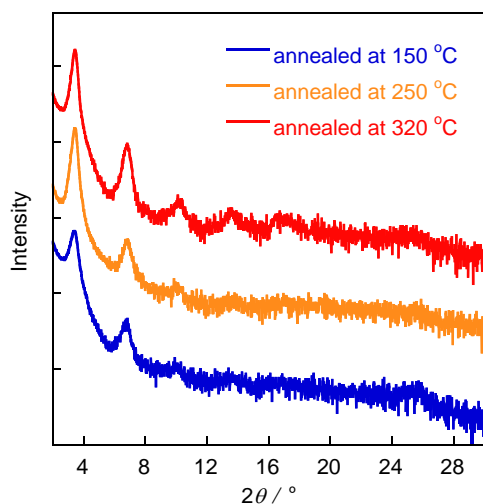


Figure S7. Out-of-plane XRD patterns of the drop-casted thin film of PNDTI-BT on the Si/SiO₂ substrate annealed at different temperatures.

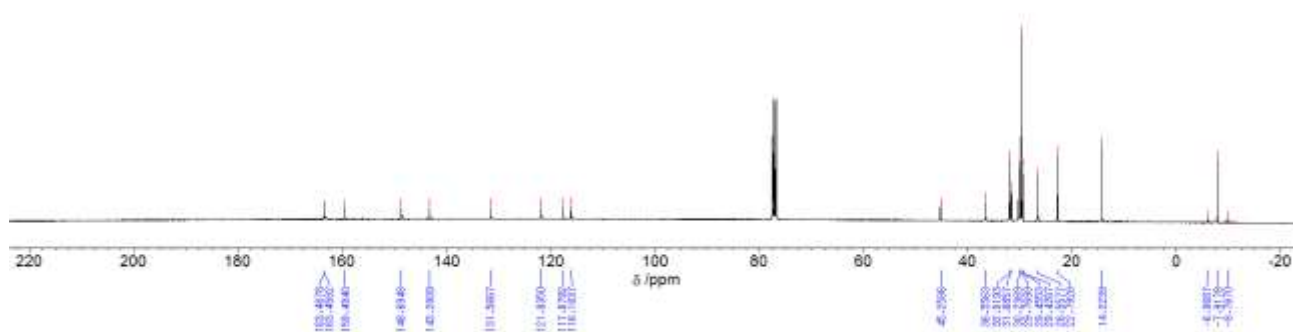
9. FET characteristics of PNDTI-Xs-based OFETs

Table S1. FET characteristics of PNDTI-Xs-based OFETs.

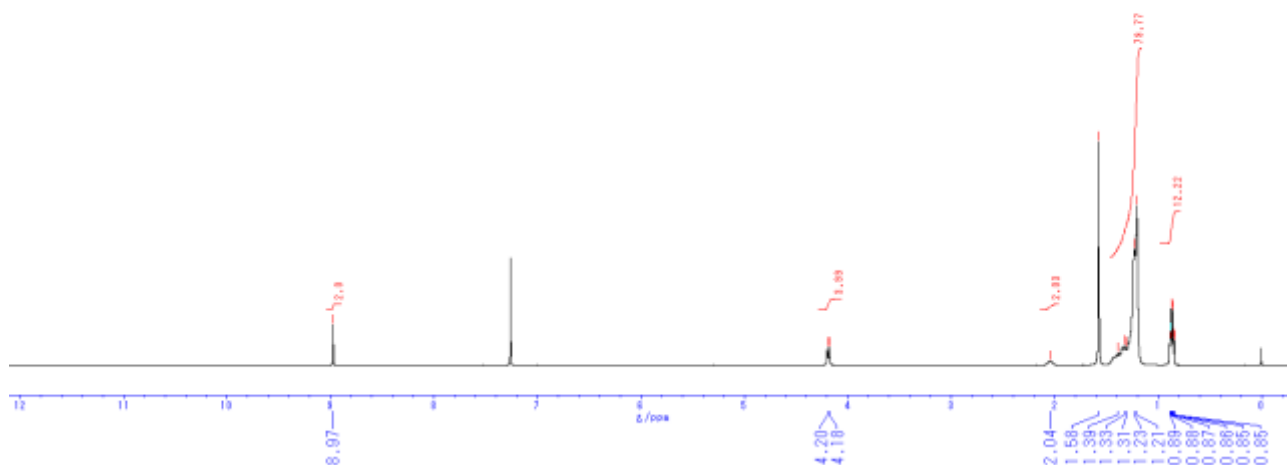
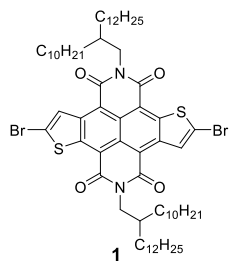
PNDTI-X	anneal / °C	p-channel operation			n-channel operation		
		μ_h /cm ² V ⁻¹ s ⁻¹ ^a	I_{on}/I_{off}	V_{th} / V	μ_e /cm ² V ⁻¹ s ⁻¹ ^a	I_{on}/I_{off}	V_{th} / V
BT	150	5.5×10^{-2}	2×10^5	-15	9.6×10^{-2}	3×10^3	13
	250	2.4×10^{-2}	9×10^4	-25	0.10	2×10^3	20
	320	0.13	9×10^3	-28.3	0.27	5×10^2	15
NDT	150	2.7×10^{-2}	7×10^5	-11.8	1.7×10^{-2}	2×10^3	19
	320	8.2×10^{-2}	6×10^4	-24.6	2.9×10^{-2}	5×10^3	30
V	150	-	-	-	2.8×10^{-4}	1×10^4	15
	320	-	-	-	9.5×10^{-4}	5×10^4	26
BTz	150	-	-	-	2.4×10^{-2}	3×10^7	13
	320	-	-	-	0.10	1×10^4	20
NTz	150	-	-	-	2.3×10^{-2}	2×10^3	13
	250	-	-	-	0.10	2×10^3	10
	320	-	-	-	0.21	1×10^4	15

^a Extracted from the saturation regime

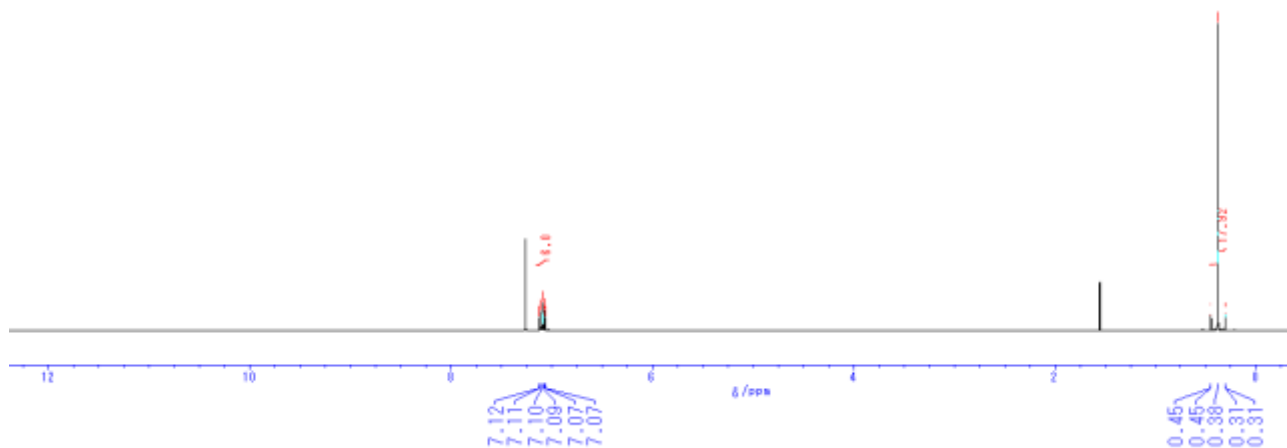
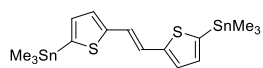
***N,N'*-Bis(2-decyltetradecyl)-2,7-bis(trimethylstanyl)naphtho[2,3-*b*:6,7-*b'*]dithiophene-4,5,9,10-diimide (2)**



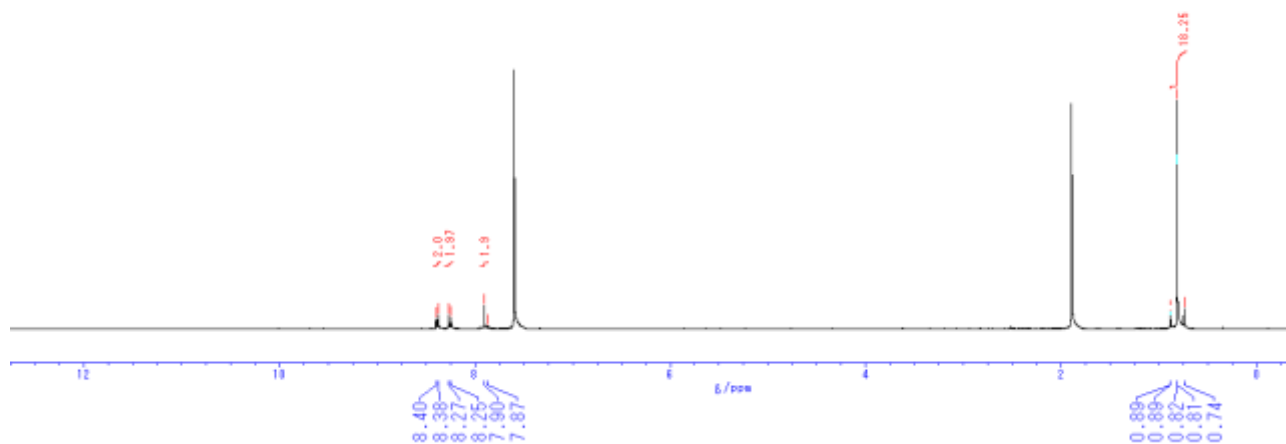
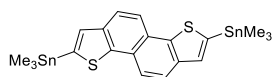
***N,N'*-Bis(2-decyltetradecyl)-2,7-dibromonaphtho[2,3-*b*:6,7-*b'*]dithiophene-4,5,9,10-diimide (1)**



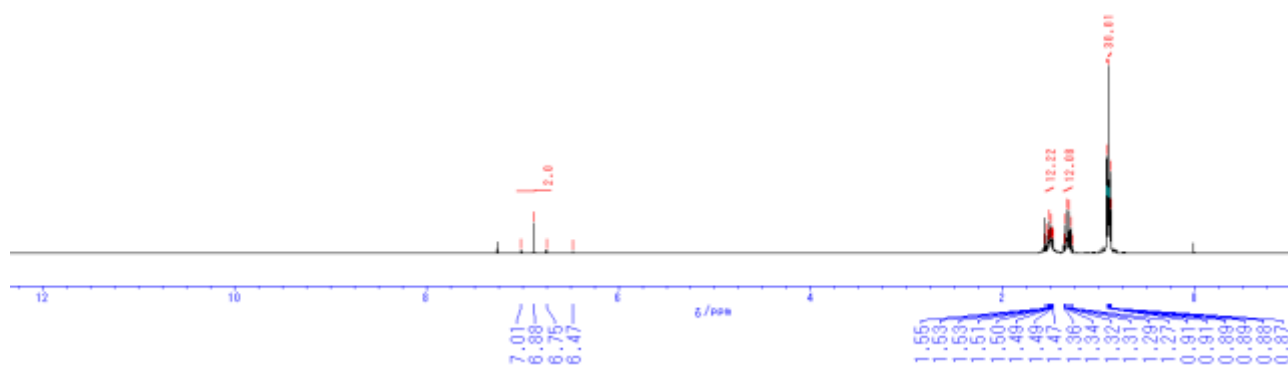
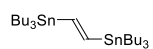
(*E*)-1,2-Bis[5-(trimethylstannyl)thiophen-2-yl]ethene (TV-Sn)



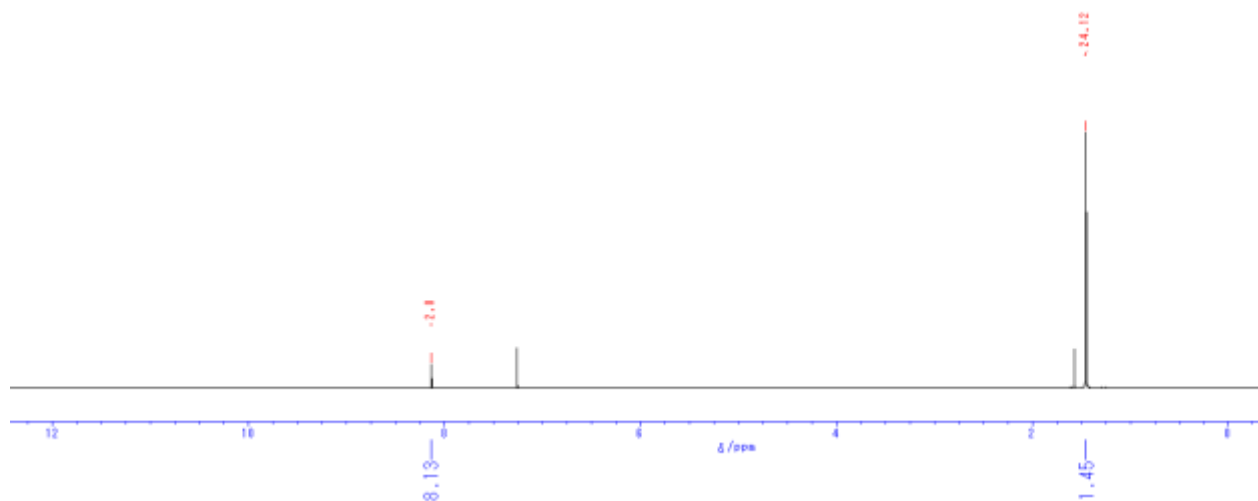
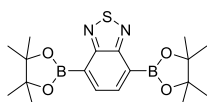
2,7-Bis(trimethylstannyl)naphtho[1,2-*b*:5,6-*b'*]dithiophene (NDT-Sn)



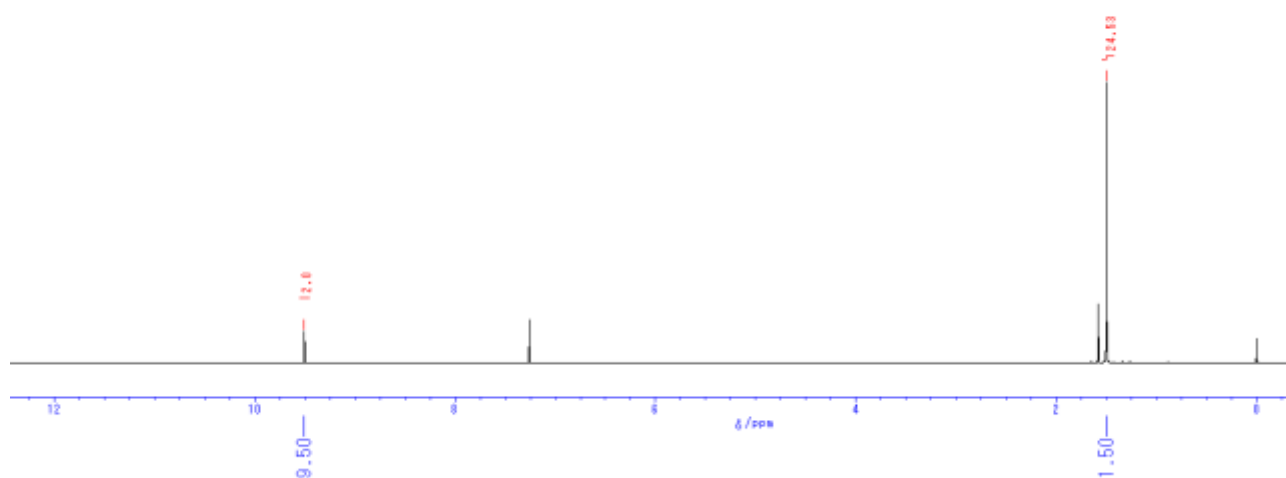
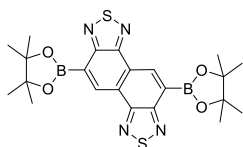
trans-1,2-Bis(tributylstannyl)ethylene (V-Sn)



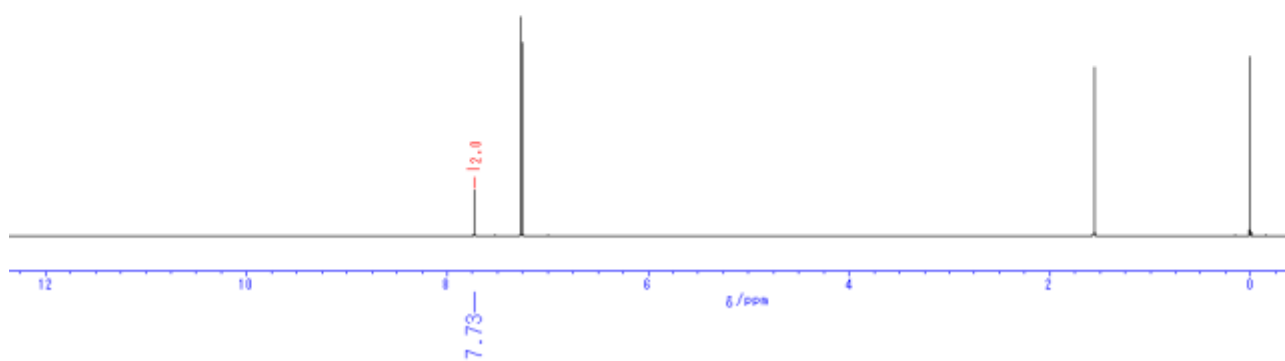
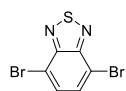
4,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole (BTz-BPin)



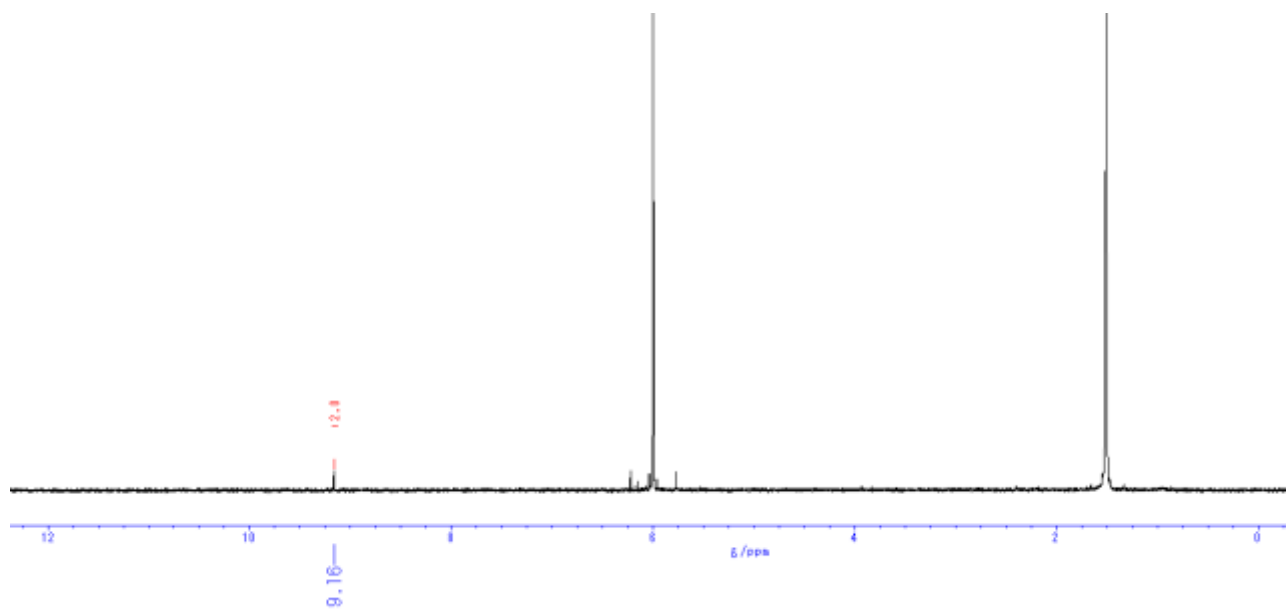
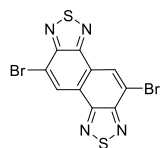
5,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-naphtho[1,2-c:5,6-c']bis[1,2,5]thiadiazole (NTz-BPin)



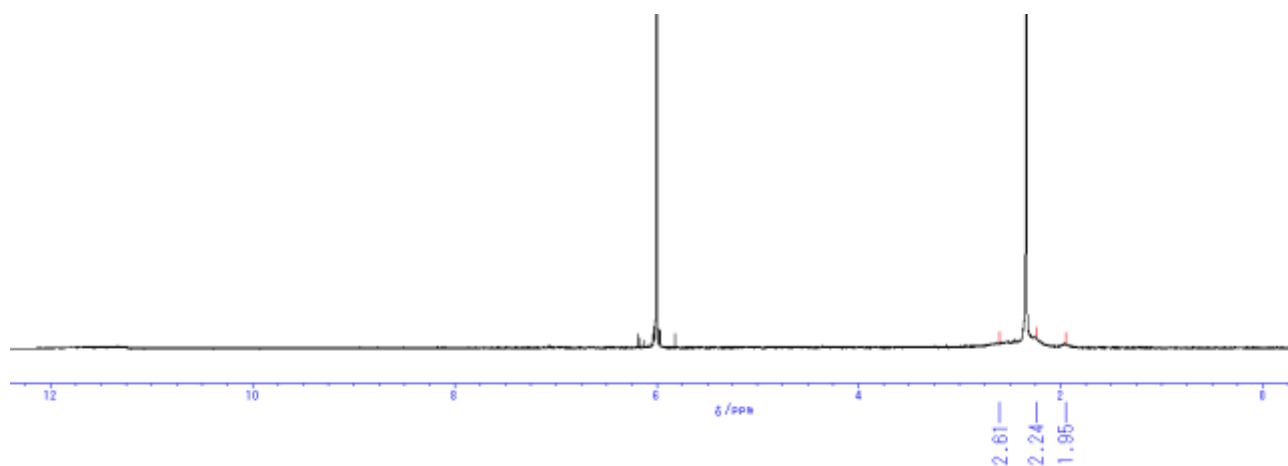
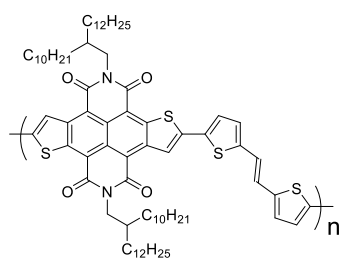
4,7-Dibromo-2,1,3-benzothiadiazole (BTz-Br)



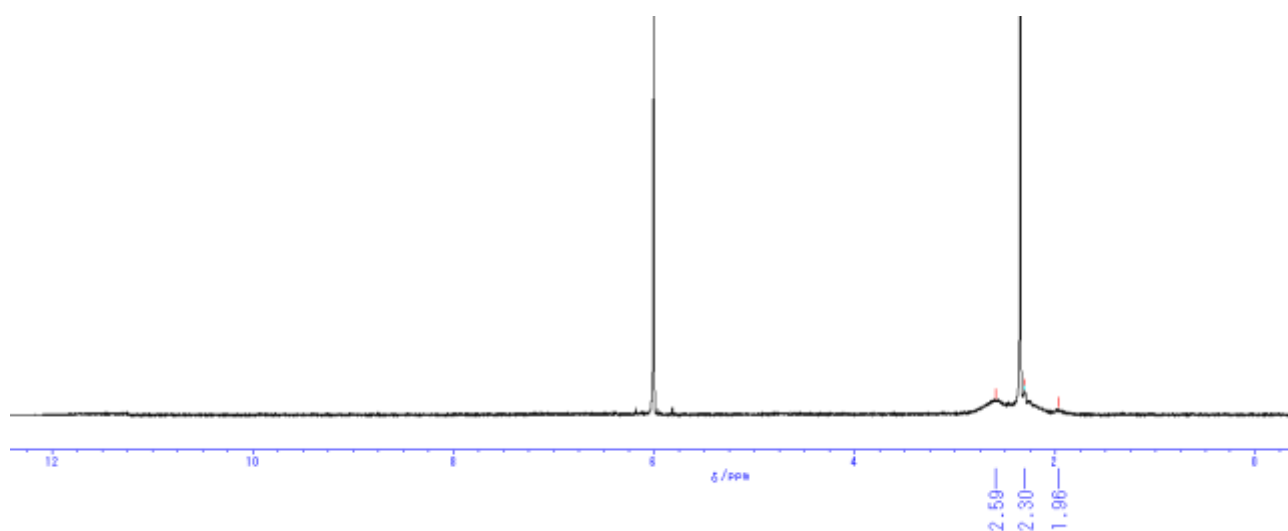
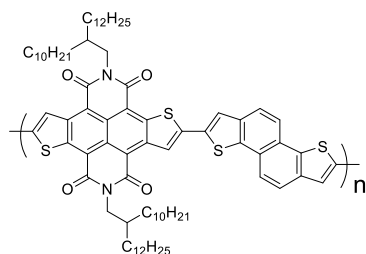
5,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-naphtho[1,2-*c*:5,6-*c'*]bis[1,2,5]thiadiazole (NTz-Br)



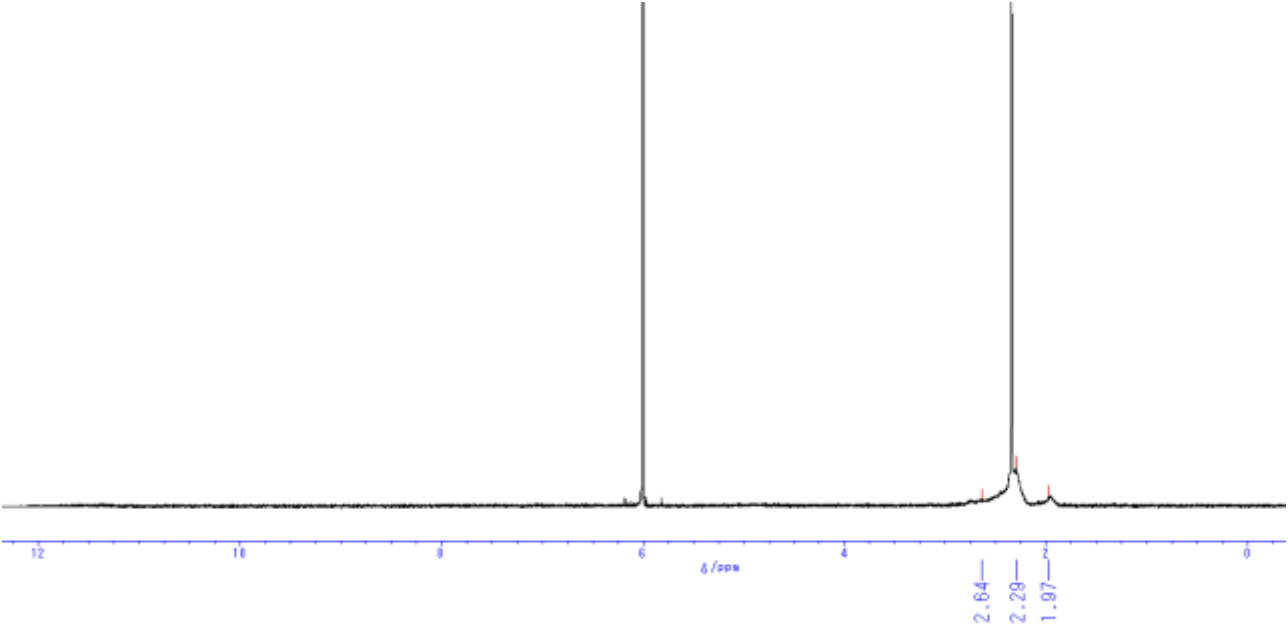
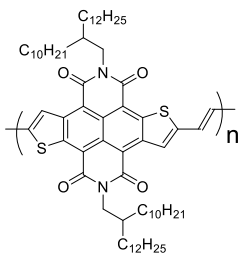
PNDTI-TV



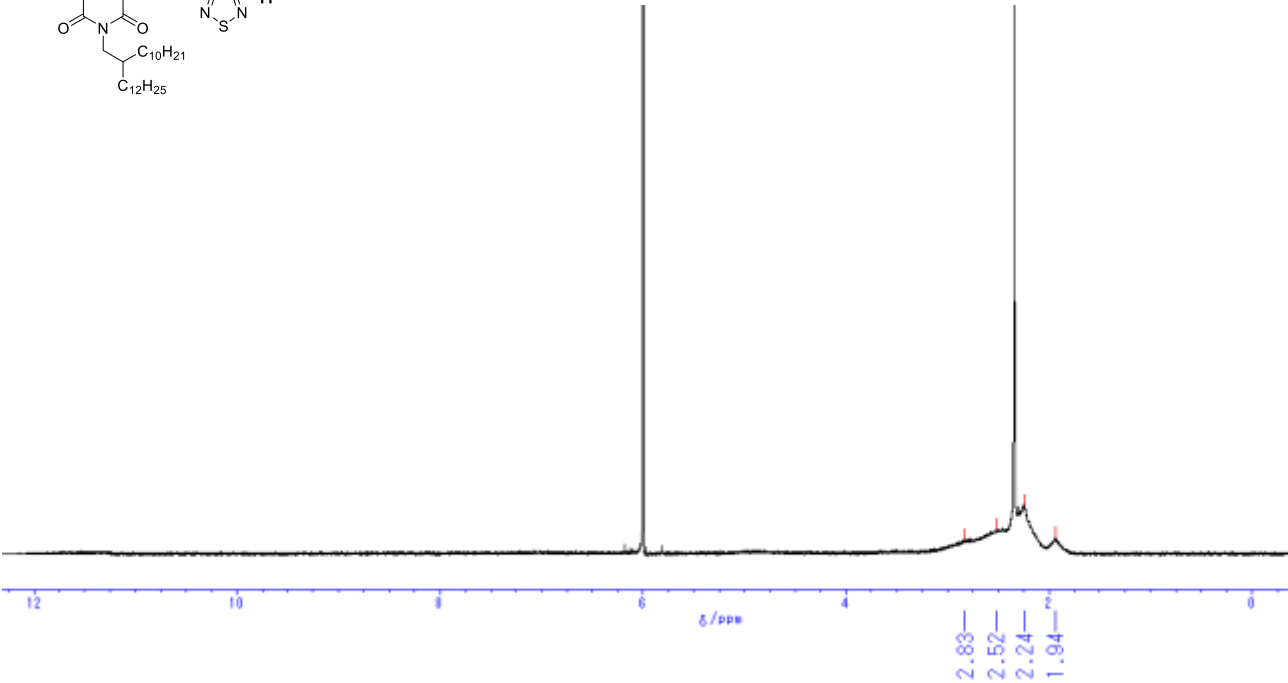
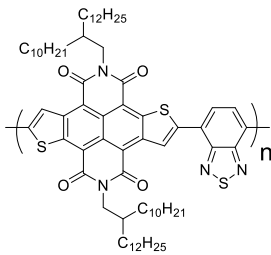
PNDTI-NDT



PNDTI-V



PNDTI-BTz



PNDTI-NTz

