Supporting Information for

Effects of substituents on intermolecular interaction, morphology, and charge transport of novel bis-lactam-based molecules†

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† Electronic Supplementary Information (ESI) available: *Supporting data (Fig. S1-S10 and Tables S1-S8) and NMR Spectra.*

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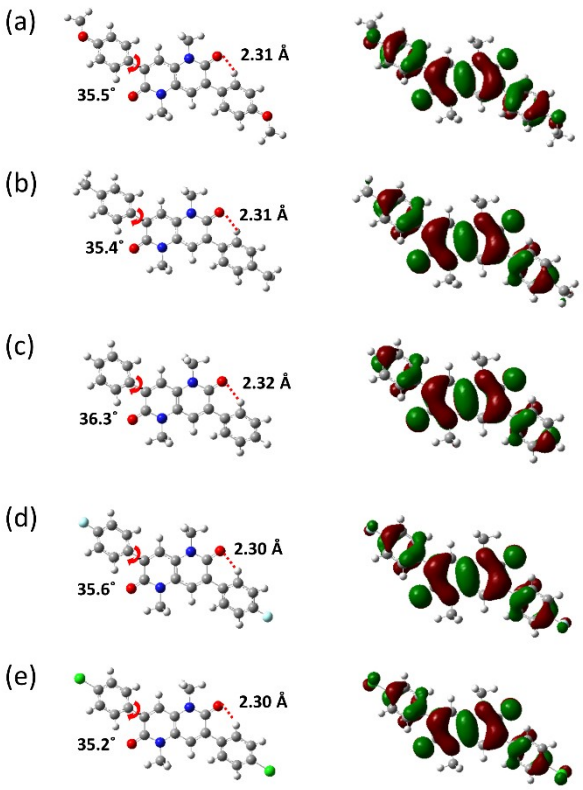


Fig. S1 The optimized molecular geometries (left) and the corresponding HOMO diagrams (right) of (a) **NTDP-OMe**, (b) **NTDP-Me**, (c) **NTDP**, (d) **NTDP-F**, and (e) **NTDP-Cl**, respectively, calculated by DFT method using B3LYP/6-31G(d,p). The red dotted lines represent the intramolecular distance between C–H···O.

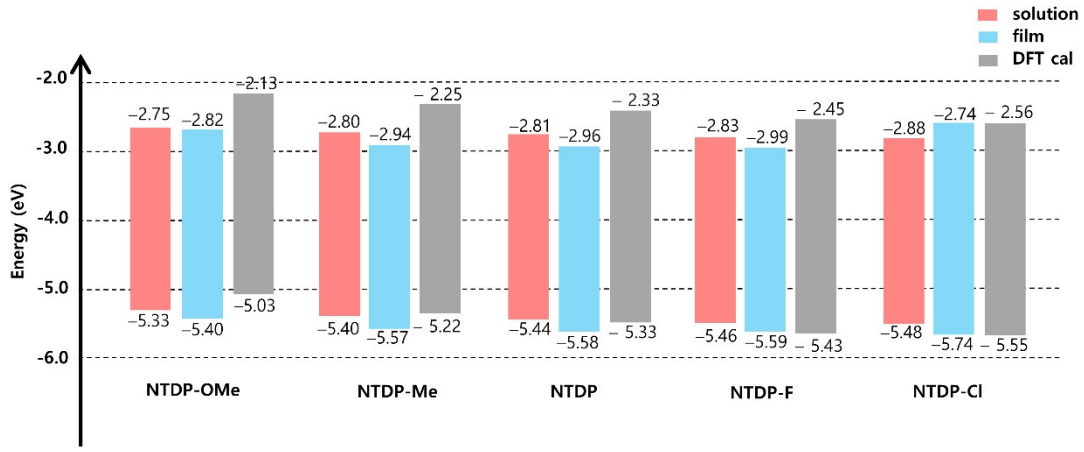


Fig. S2 The energy levels diagrams determined from cyclic voltammetry of **NTDP-OMe**, **NTDP-Me**, **NTDP**, **NTDP-F**, and **NTDP-Cl** in the solution states (red bar) and in the thin-film states (blue bar), and calculated by the DFT calculation (gray bar).

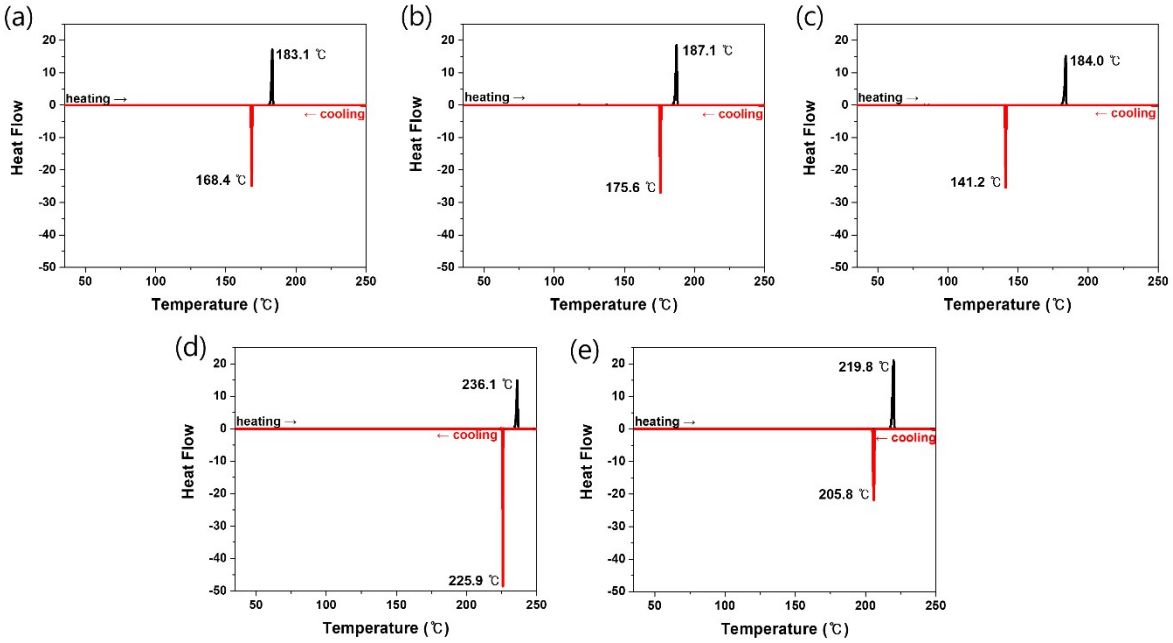


Fig. S3 The DSC thermograms of (a) **NTDP-OMe**, (b) **NTDP-Me**, (c) **NTDP**, (d) **NTDP-F**, and (e) **NTDP-Cl**. The black and red lines demonstrate the heating process and cooling process, respectively.

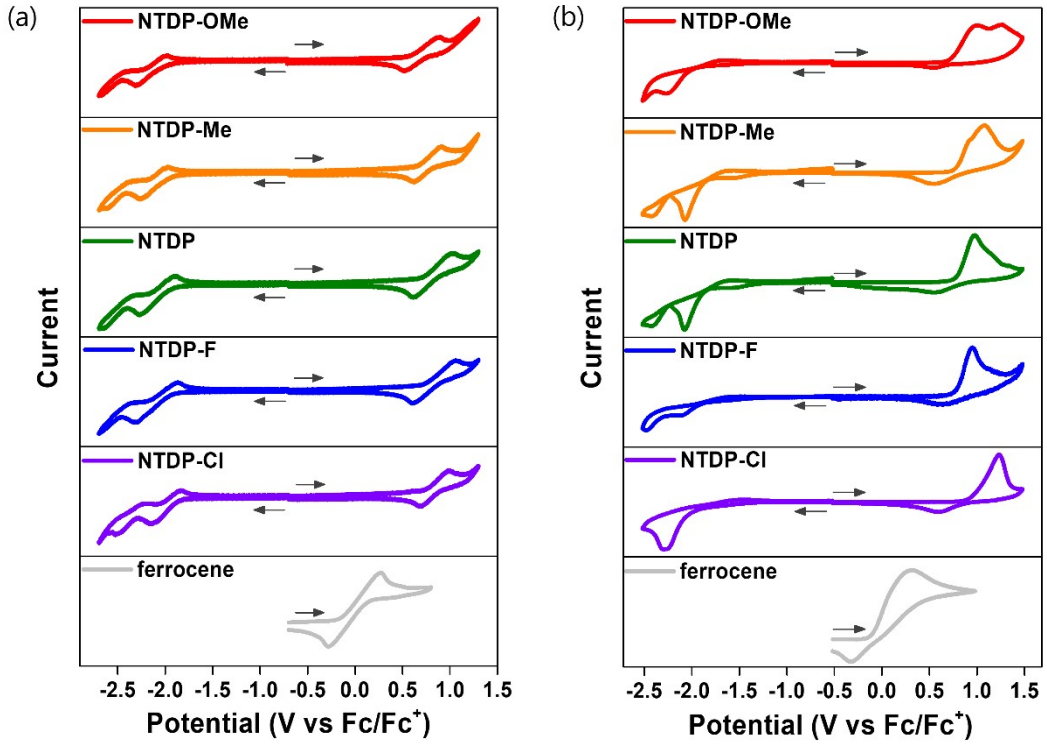


Fig. S4 The CV curves of the NTDP derivatives (a) in CH_2Cl_2/TBAHFP (0.1 M), (b) in thin-film states.

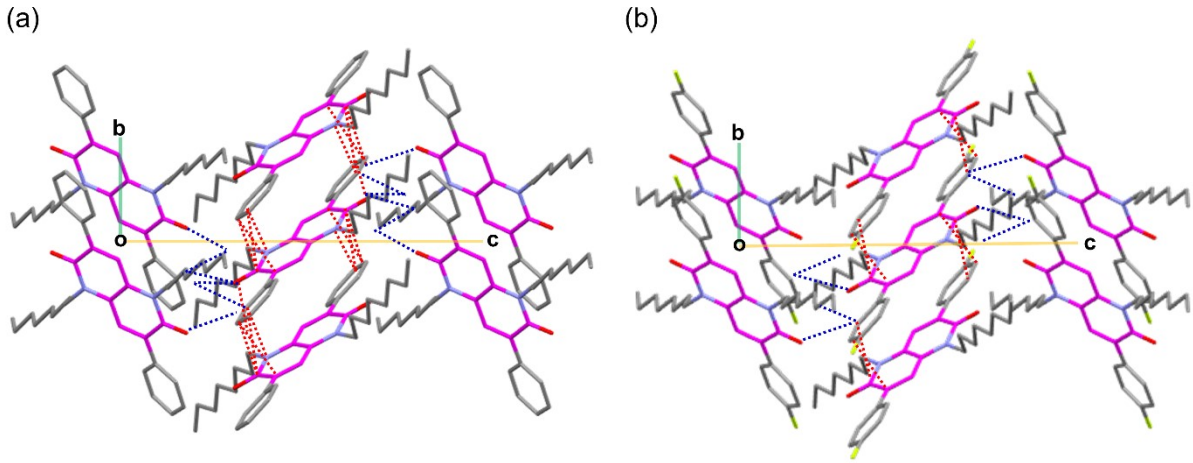


Fig. S5 The intermolecular short contacts of (a) **NTDP** and (b) **NTDP-F**, respectively. The red and blue dotted lines demonstrated intermolecular short contacts in the [010] and [001] directions, respectively.

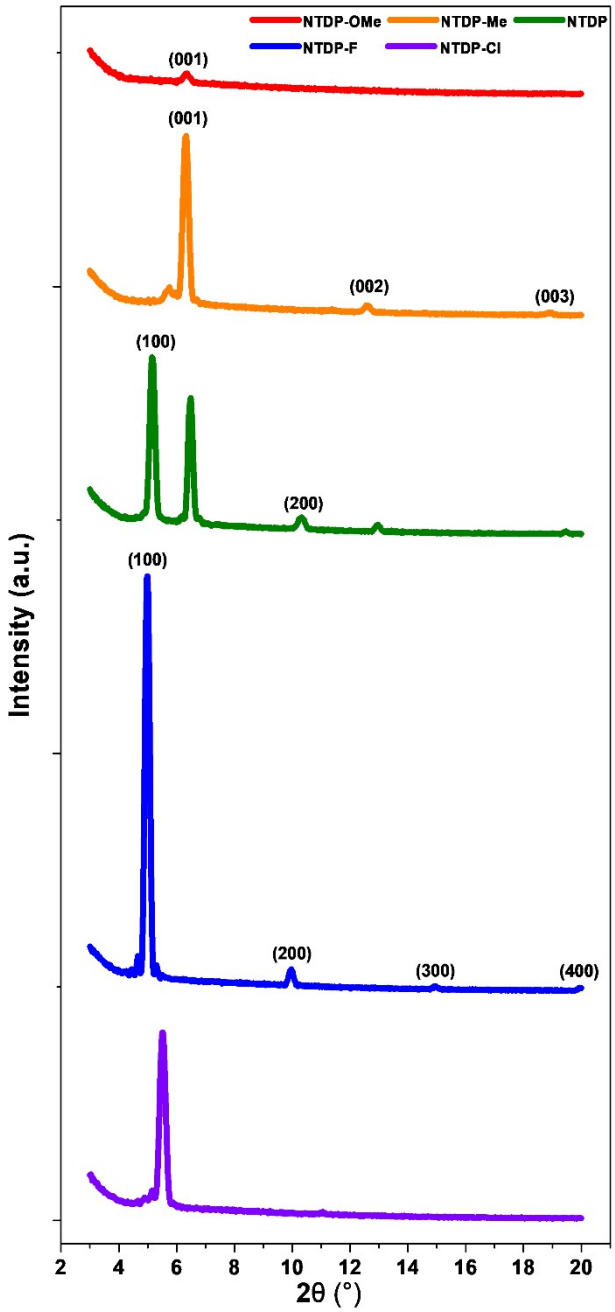


Fig. S6 The out of plane XRD profiles for the vacuum-deposited NTDP thin films.

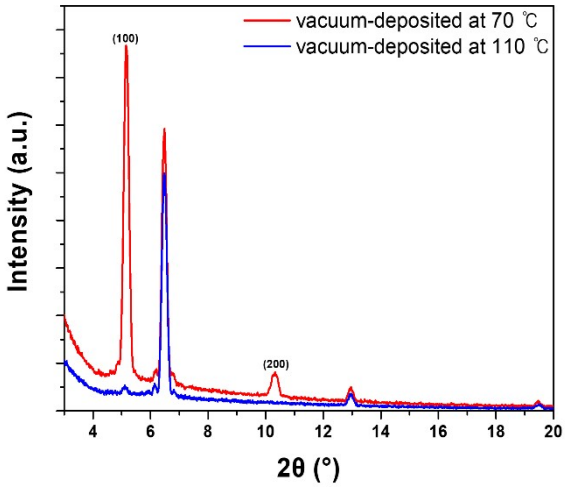


Fig. S7 The out of plane XRD profile for the **NTDP** thin-film at 70°C (optimized tempertature) and 110 °C.

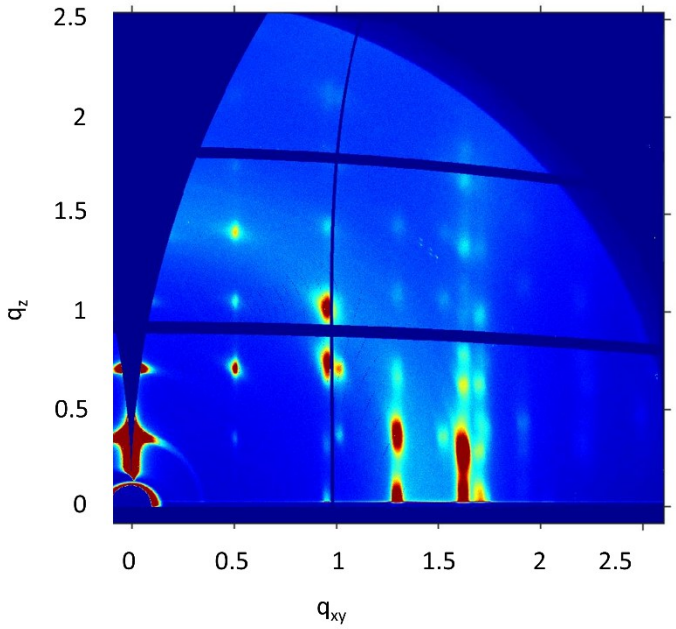


Fig. S8 The GIXD image of the **NTDP-F** spin-coated thin-film.

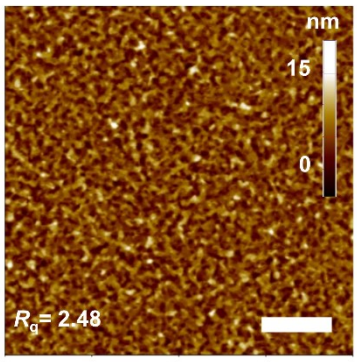


Fig. S9 The AFM image of the spin-coated **NTDP-F** thin film. (Scale bar 20 μm)

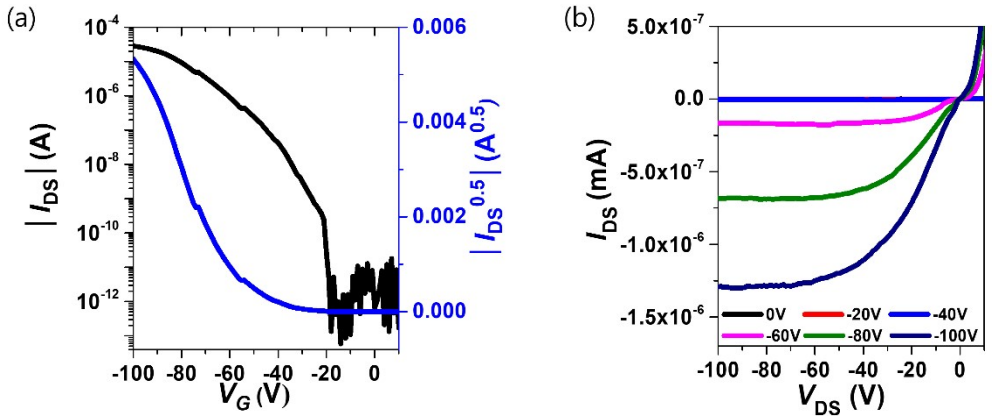


Fig. S10 The transfer and output curve for the spin-coated OFET of **NTDP-F**.

Table S1. The calculated vibronic energies (ω_{abs}, $E_{0\text{-}1}$–$E_{0\text{-}0}$ (eV)) of the NTDP derivatives in the vacuum-deposited thin-films.

	$E_{0\text{-}1}$ (eV)	$E_{0\text{-}0}$ (eV)	$E_{0\text{-}1}$–$E_{0\text{-}0}$ (eV)
NTDP-OMe	2.768	2.594	0.174
NTDP-Me	2.774	2.594	0.180
NTDP	2.713	2.536	0.177
NTDP-F	2.805	2.600	0.205
NTDP-Cl	2.761	2.583	0.178

Table S2. Crystallographic data of the **NTDP-OMe** single crystal.

Identification code	NTDP-OMe	
Empirical formula	C38 H50 N2 O4	
Formula weight	598.80	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.8379(7) Å	α = 107.121(5)°.
	b = 13.0844(10) Å	β = 99.386(5)°.
	c = 15.0165(11) Å	γ = 107.685(5)°.
Volume	1691.0(2) $Å^3$	
Z	2	
Density (calculated)	1.176 Mg/m^3	
Absorption coefficient	0.075 mm^{-1}	
F(000)	648	
Crystal size	0.334 x 0.243 x 0.152 mm^3	
Theta range for data collection	1.477 to 28.431°.	
Index ranges	-13<=h<=13, -17<=k<=17, -19<=l<=20	
Reflections collected	25703	
Independent reflections	8352 [R(int) = 0.0701]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.5430	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8352 / 0 / 397	
Goodness-of-fit on F^2	0.992	
Final R indices [I>2sigma(I)]	R1 = 0.0747, wR2 = 0.2026	
R indices (all data)	R1 = 0.1607, wR2 = 0.2575	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.558 and -0.284 $e.Å^{-3}$	

Table S3. Crystallographic data of the **NTDP-Me** single crystal.

Identification code	Me	
Empirical formula	C38 H50 N2 O2	
Formula weight	566.80	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9421(5) Å	α = 107.482(3)°.
	b = 12.3885(6) Å	β = 99.832(3)°.
	c = 15.1226(7) Å	γ = 104.852(3)°.
Volume	1654.05(14) $Å^3$	
Z	2	
Density (calculated)	1.138 Mg/m^3	
Absorption coefficient	0.069 mm^{-1}	
F(000)	616	
Crystal size	0.513 x 0.322 x 0.021 mm^3	
Theta range for data collection	1.466 to 28.295°.	
Index ranges	-13<=h<=10, -16<=k<=16, -20<=l<=20	
Reflections collected	31183	
Independent reflections	8191 [R(int) = 0.0564]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.4930	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8191 / 0 / 380	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0724, wR2 = 0.1980	
R indices (all data)	R1 = 0.1234, wR2 = 0.2303	
Extinction coefficient	0.0050(15)	
Largest diff. peak and hole	0.445 and -0.238 $e.Å^{-3}$	

Table S4. Crystallographic data of the **NTDP** single crystal.

Identification code	NTDP	
Empirical formula	C36 H46 N2 O2	
Formula weight	538.75	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.7449(3) Å	α = 90°.
	b = 5.12040(10) Å	β = 106.5180(10)°.
	c = 17.2448(3) Å	γ = 90°.
Volume	1502.21(5) $Å^3$	
Z	2	
Density (calculated)	1.191 Mg/m^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	584	
Crystal size	0.712 x 0.177 x 0.153 mm^3	
Theta range for data collection	2.394 to 28.337°.	
Index ranges	-23<=h<=23, -6<=k<=6, -22<=l<=22	
Reflections collected	25950	
Independent reflections	3728 [R(int) = 0.0291]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.7019	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3728 / 0 / 181	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0435, wR2 = 0.1116	
R indices (all data)	R1 = 0.0519, wR2 = 0.1177	
Extinction coefficient	Multi-scan SADABS	
Largest diff. peak and hole	0.350 and -0.212 e.$Å^{-3}$	

Table S5. Crystallographic data of the **NTDP-F** single crystal.

Identification code	ntdp-f	
Empirical formula	C36 H44 F2 N2 O2	
Formula weight	574.73	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.8570(4) Å	α = 90°.
	b = 5.13060(10) Å	β = 105.4039(14)°.
	c = 17.2716(4) Å	γ = 90°.
Volume	1525.53(6) $Å^3$	
Z	2	
Density (calculated)	1.251 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	616	
Crystal size	0.596 x 0.114 x 0.087 mm^3	
Theta range for data collection	2.366 to 28.279°.	
Index ranges	-23<=h<=23, -6<=k<=6, -19<=l<=22	
Reflections collected	13597	
Independent reflections	3712 [R(int) = 0.0711]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	(SADABS; Sheldrick, 2014)	
Max. and min. transmission	0.7457 and 0.5962	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3712 / 0 / 190	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0925, wR2 = 0.2545	
R indices (all data)	R1 = 0.1224, wR2 = 0.2719	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.404 and -0.435 $e.Å^{-3}$	

Table S6. Crystallographic data of the **NTDP-Cl** single crystal.

Identification code	NTDP-Cl	
Empirical formula	C36 H44 Cl2 N2 O2	
Formula weight	607.63	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.58810(10) Å	α = 108.5410(10)°.
	b = 12.12040(10) Å	β = 99.8950(10)°.
	c = 15.3508(2) Å	γ = 101.3960(10)°.
Volume	1604.28(3) $Å^3$	
Z	2	
Density (calculated)	1.258 Mg/m^3	
Absorption coefficient	0.237 mm^{-1}	
F(000)	648	
Crystal size	0.638 x 0.117 x 0.020 mm^3	
Theta range for data collection	1.446 to 27.488°.	
Index ranges	-12<=h<=12, -15<=k<=15, -19<=l<=19	
Reflections collected	43280	
Independent reflections	7346 [R(int) = 0.0386]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6897	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7346 / 0 / 379	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.1193	
R indices (all data)	R1 = 0.0613, wR2 = 0.1300	
Extinction coefficient	Multi-scan SABADS	
Largest diff. peak and hole	0.589 and -0.318 e.$Å^{-3}$	

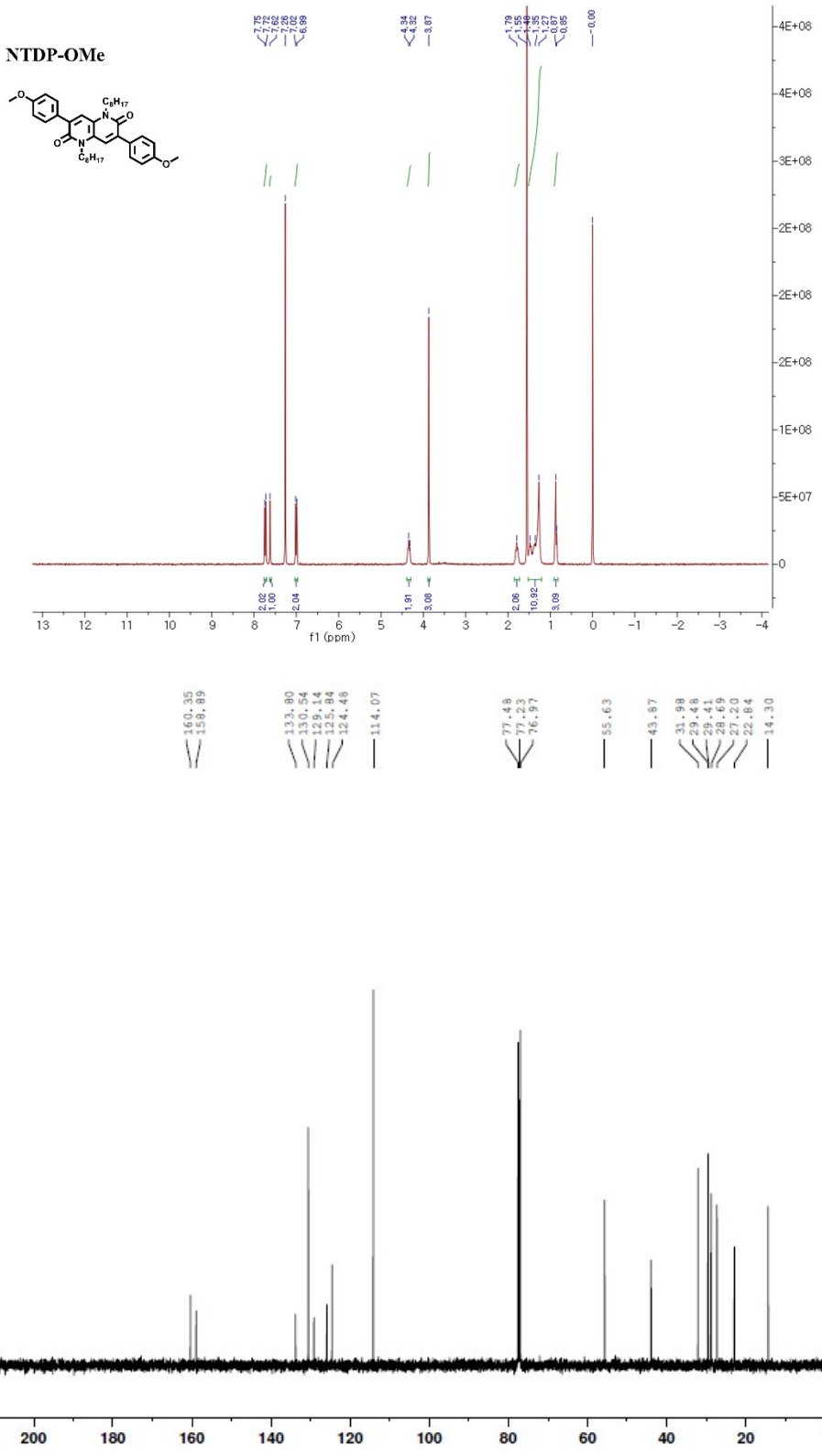
Table S7. [hk] planes deduced from the reflection columns along the q_{xy}-direction in the vacuum deposited thin-film.

	q_{xy} (Å^{-1})	hk
NTDP-OMe	0.51	[01]
	0.67	[10]
	0.71	[1–1]
	0.95	[11]
	1.01	[02]
	1.03	[1–2]
	1.27	[2–1]
	1.33	[20]
NTDP-Me	0.52	[01]
	0.65	[10]
	0.72	[1–1]
	0.94	[11]
	1.05	[02]
	1.07	[1–2]
	1.26	[2–1]
	1.30	[20]
NTDP	0.73	[02]
	1.23	[10]
	1.28	[11]
	1.41	[12]
	1.45	[04]
	1.62	[13]
NTDP-F	0.52	[01]
	0.97	[11]
	1.03	[02]
	1.32	[12]
	1.65	[20]
	1.72	[21]
	1.76	[13]
	1.95	[22]

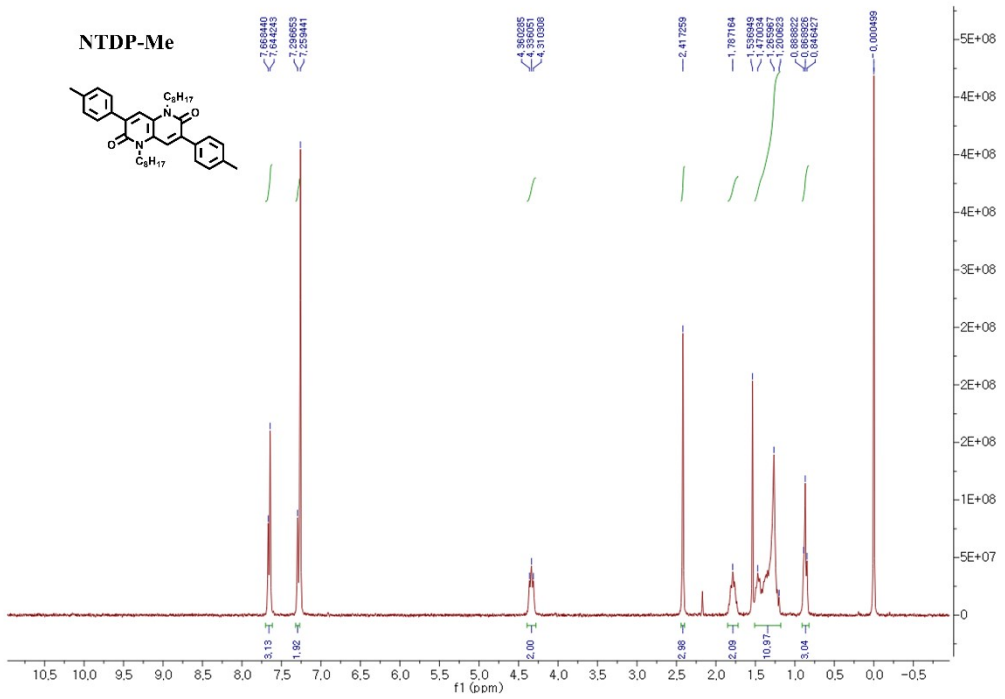
]

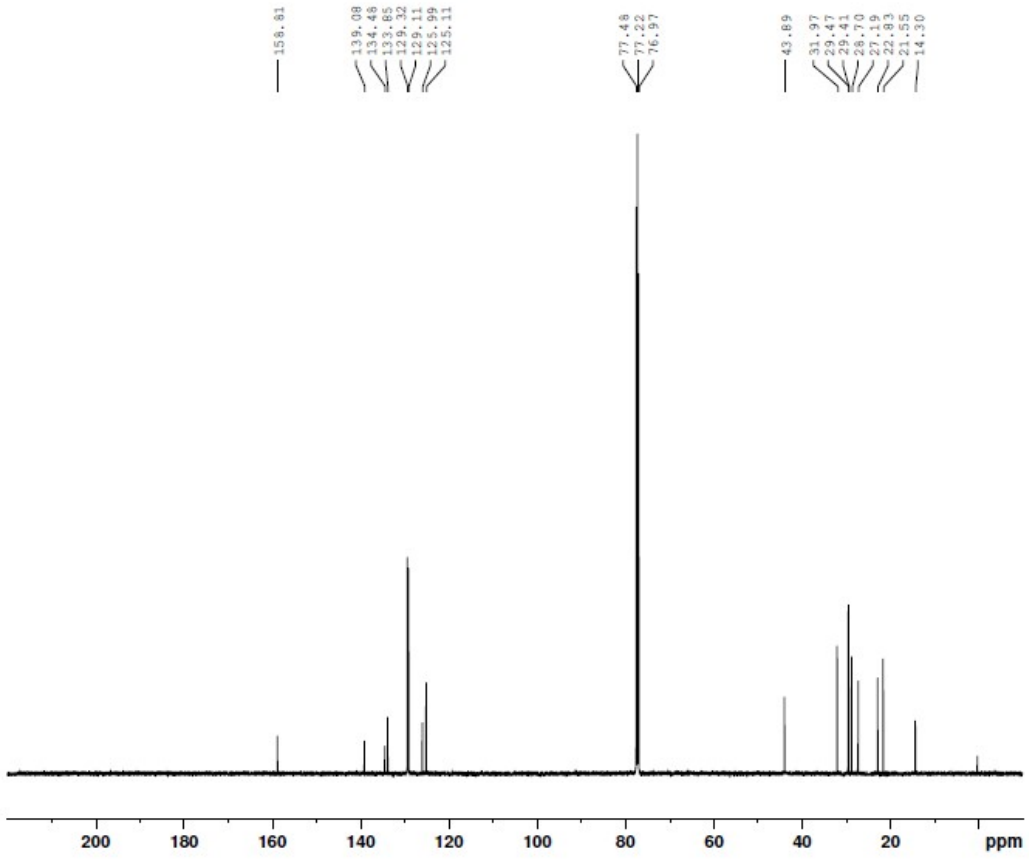
Table S8. [hk] planes deduced from the reflection columns along the q_{xy}-direction of the **NTDP-F** spin-coated film. The extracted lattice parameters were b = 7.67 Å, c = 12.35 Å, and α = 90.2°.

q_{xy} (Å^{-1})	hk
0.51	[01]
0.97	[11]
1.02	[02]
1.30	[12]
1.53	[03]
1.64	[20]
1.70	[21]
1.71	[13]
1.94	[22]

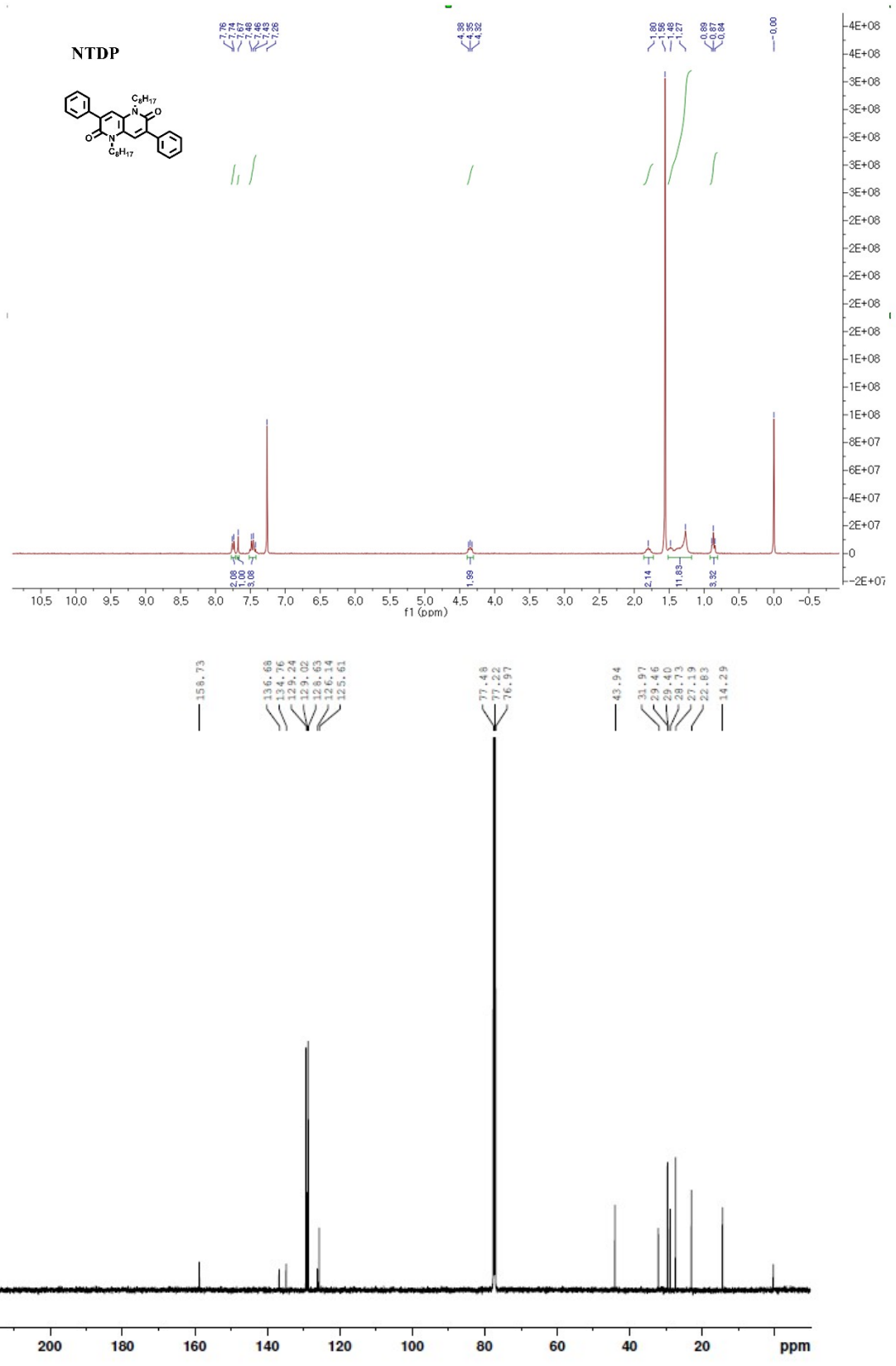


^{1}H-NMR and ^{13}C-NMR Spectra of **NTDP-OMe**.

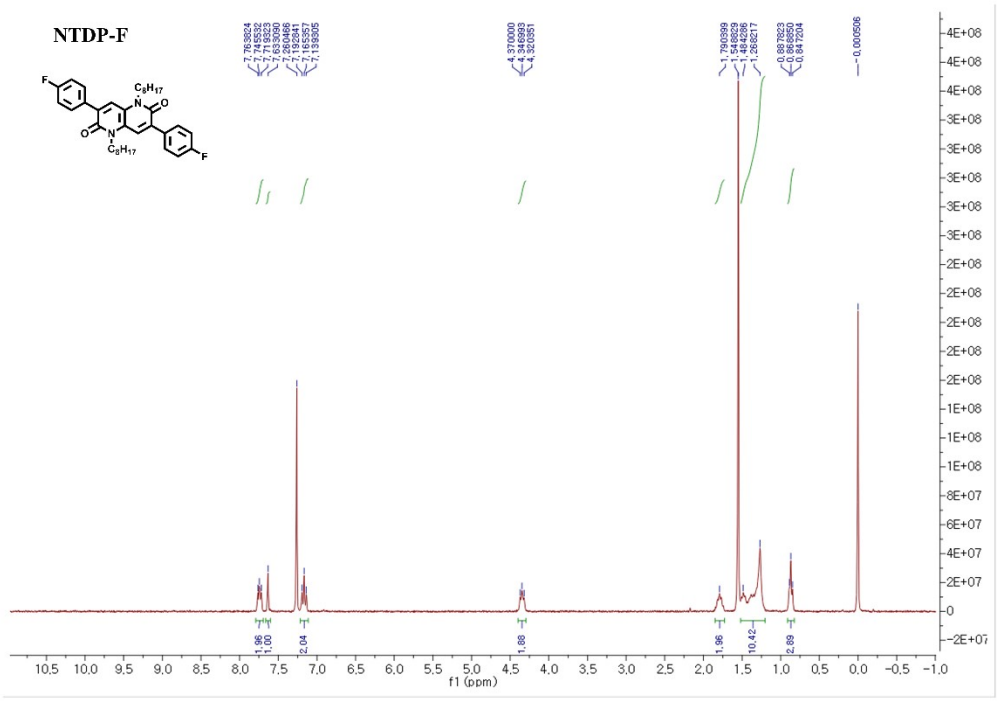


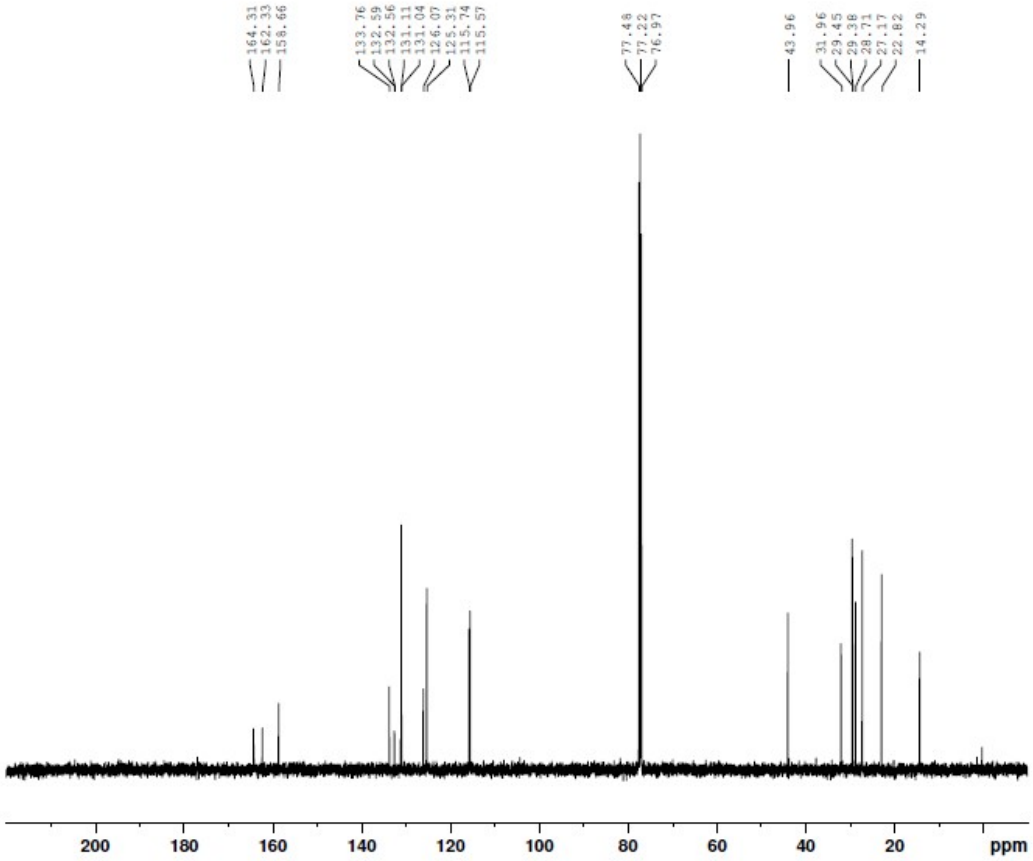


^{1}H-NMR and ^{13}C-NMR Spectra of **NTDP-Me**.

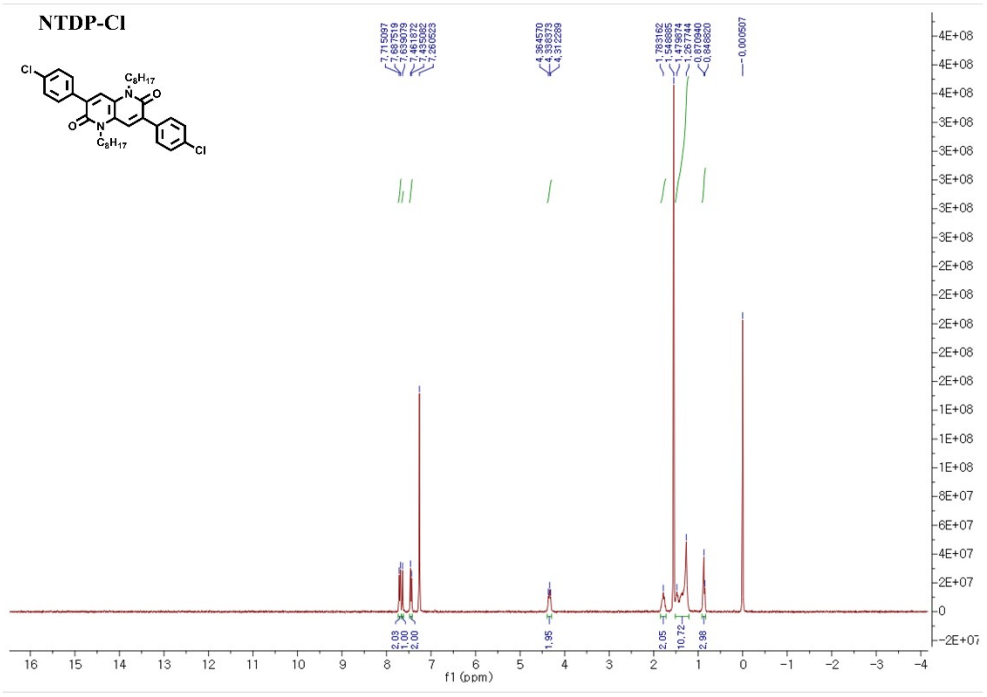


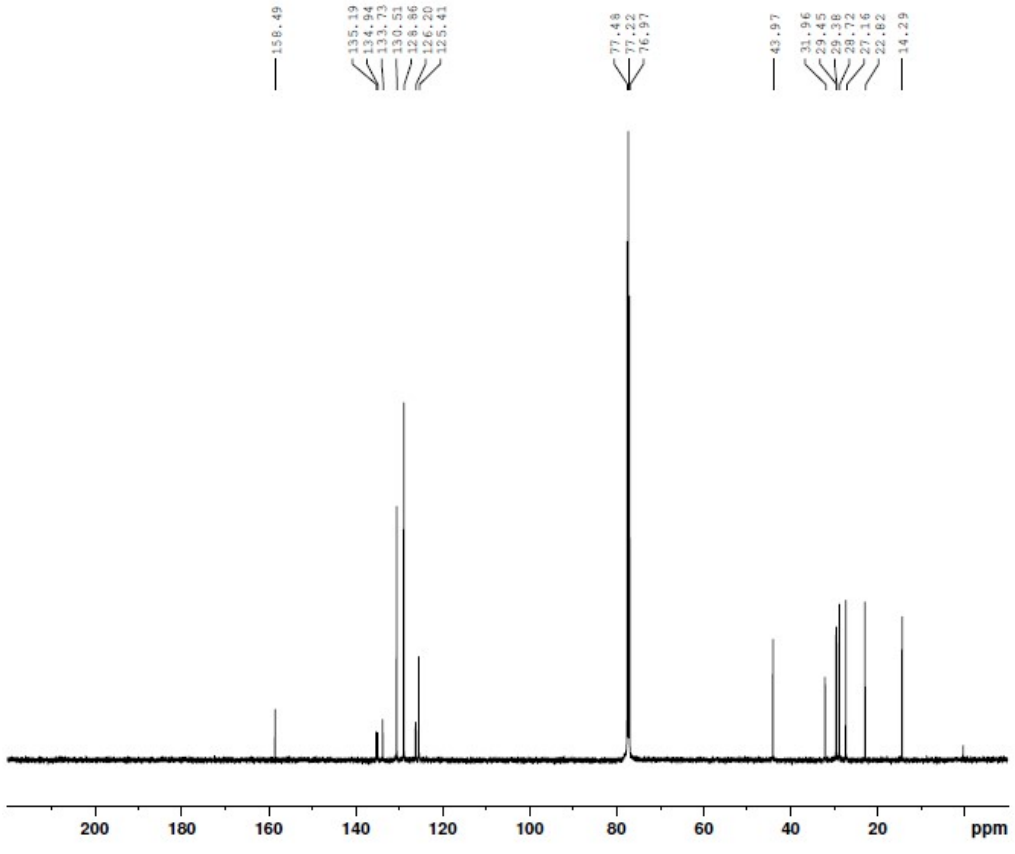
^{1}H-NMR and ^{13}C-NMR Spectra of **NTDP**.





^{1}H-NMR and ^{13}C-NMR Spectra of **NTDP-F**.





^{1}H-NMR and ^{13}C-NMR Spectra of **NTDP-Cl**