Supporting Information

Benzo[1,2-*b*:4,5-*b*']diselenophene-fused nonfullerene acceptors with alternative aromatic ring-based and monochlorinated end group: new synergistic strategy to simultaneously achieve highly efficient organic solar cells with energy loss of 0.49 eV

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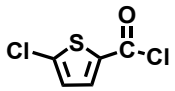
Experimental Section

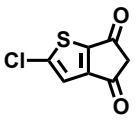
Materials and Characterization: All air and water-sensitive reactions were carried out under N_2. Toluene and THF were dried by Na and then freshly distilled before to use. The other precursors were used as the common commercial level. ^{1}H and ^{13}C NMR spectra were carried out on a Bruker Ascend-400 and 700 NMR spectrometer. All chemical shifts were reported in ppm. Chemical shifts in ^{1}H NMR were referenced to TMS and in ^{13}C NMR were referenced to $CDCl_3$. MALDI-TOF-MS was recorded on a Bruker BIFLEX III mass spectrometer. Thermogravimetric analysis (TGA) was performed using a TA Instrument Q600 analyzer under nitrogen gas flow with a heating rate of 10 ºC min^{-1}. Elemental analyses were performed using a German Vario EL III elemental analyzer. UV-vis absorption spectra were taken on an Hitachi UH5300 UV-vis spectrometer. The electrochemical cyclic voltammetry was carried out on CHI electrochemical workstation with glass carbon disk, Ag/Ag$^+$ electrode, and Pt wire, as working electrode, reference electrode, and counter electrode, respectively, in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. During CV measurements, the films were drop-cast on the glass carbon working electrode from THF solution. Atomic force microscopy (AFM) measurements were taken on a Bruker Inova atomic microscope in tapping mode. Transmission electron microscope (TEM) measurements were performed using a ZEISS LIBRA 200 FE instrument at 200 kV accelerating voltage. Grazing incidence X-ray scattering (GIXD) data were performed at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF).

BHJ-OSC Fabrication and Characterization: The device structure was Glass/ITO/ZnO/active layer/MoO_3/Ag. The hole-only devices structure was Glass/ITO/PEDOT:PSS/active layer/MoO_3/Au and the electron-only device structure was Glass/Al/active layer/Al. A glass substrate with a pre-patterned ITO (sheet resistance = 15 Ω sq^{-1}) was ultrasonicated subsequently in detergent, deionized water, acetone, and isopropanol. After the plates were dried by high-pressure air flow, the substrates were cleaned by UV-ozone treatment for 30 min. ZnO precursor (2M diethylzinc solution in toluene, diluted with THF) was spin-coated on the substrates at 5000 rpm for 30 s in dry air, which were then baked on a

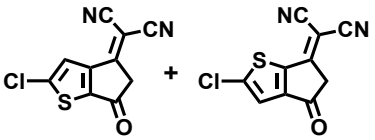
hot plate at 180 °C for about 30 min. After cooled to room temperature, the substrates were sent to an argon filled glove box. A blend film of PM7: NF-SMAs (**BDSeThCl** or **BDSePhCl)** (1:1, w/w) was prepared by spin-coating its hot solution (80 °C) of chlorobenzene/1,8-diiodoctane (99.5:0.5, total concentration: 18 mg mL^{-1}) at 3000 rpm for 30 s. The substrates were then thermal annealed at 100 °C for 10 min. A thin layer (10 nm) of MoO_3 and Ag cathode (100 nm) were deposited by thermal evaporation in a high vacuum chamber (~10^{-6} mbar). The optimal thickness of the active layer was typical 100 nm, which was measured using a Dektak 6 M surface profilometer. The device area was exactly fixed at 4.0 mm^2. The *J-V* characterization of the devices was carried out on a computer-controlled Keithley 2400 Source Measurement system with a solar simulator (XES-70S1, SAN EI Co., Ltd.) was used as the light source. The light intensity was monitored by using a standard Si solar cell (KONICA MINOLTA, INC.). The EQE values were tested with a Newport Model 77890 (Newport Co., Ltd.) during illumination with monochromatic light from a xenon lamp.



5-chlorothiophene-2-carbonyl chloride (compound 2): In a 100 mL round-bottom flask, 5-chlorothiophene-2-carboxylic acid（3.0 g, 16.6 mmol）was evacuated and backfilled with N_2 three times, and freshly distilled toluene (50 mL) and 0.5 mL of dry DMF was added. Then, thionyl chloride (13.4 mL, 166 mmol) was added to the solution. The reaction mixture was stirred at 85 °C for 3 h. The excess thionyl chloride was removed by under reduced pressure, and the compound 2 was used for next step without further purification.

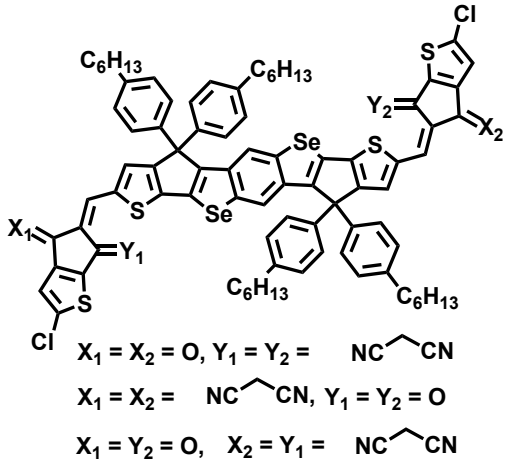


2-chloro-4H-cyclopenta[b]thiophene-4,6(5H)-dione (compound 3): In a 100 mL two-neck round-bottom flask, $AlCl_3$ (14.7 g, 110 mmol), malonyl dichloride (12.1 mL, 74.5 mmol) was added. The reaction mixture was evacuated and backfilled with N_2 three times, and then freshly distilled dichloromethane (50 mL) was added into the reaction mixture at 0 °C. A solution of compound **2** (3 g, 16.5 mmol) in dichloromethane (40 mL) was added into the reaction mixture and the reaction mixture was refluxed for 8 h. After being cooled to room temperature, the mixture was poured into oxalic acid aqueous solution slowly. Afterwards, the pH of the solution was tuned close to 7 by using $NaHCO_3$ aqueous solution. The crude product was purified by silica gel column chromatography, eluting with dichloromethane to obtain the product as yellow solid (1.24 g, 41%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.26 (s, 1H, Th-H), 3.35 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 189.2, 187.5, 156.5, 152.9, 147.4, 120.1, 47.3.

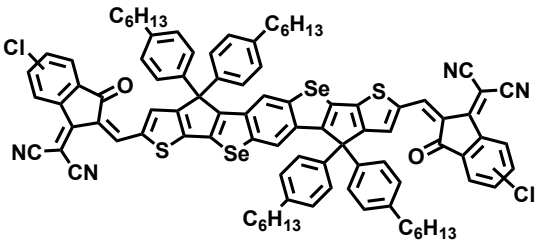


ThCl: In a 100 mL round-bottom flask, sodium acetate (0.72 g, 8.7 mmol) was added to a solution of malononitrile (0.72 g, 11.0 mmol) and compound **3** (1.24 g, 6.6 mmol) in anhydrous EtOH (40 mL). The reaction mixture was stirred at room temperature for 2 h. Then 10 mL of water was added into the reaction mixture and acidified by HCl (pH 1-2) and the precipitate was filtered and washed with water and petroleum ether. The crude product was purified by

flash column chromatography (silica gel), eluting with petroleum ether/dichloromethane (1:1) to afford the product as brown yellow solid (1.55 g, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.79 (s, 2H, Th-H), 7.32 (s, 1H, Th-H), 3.82 (s, 6H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 186.7, 184.9, 160.8, 160.5, 153.9, 152.6, 152.2, 148.7, 148.1, 121.7, 120.7, 120.6, 112.1, 111.6, 111.2, 111.1, 44.8, 44.7, 44.6. HR-ESI-MS (m/z): calcd for $C_{10}H_3ClN_2OS$: 233.9655 (100%). Found: 233.9652



BDSeThCl: In a 100 mL two-neck round-bottom flask, compound **BDSeT-CHO**[1] (0.26 g, 0.22 mmol), **ThCl** (0.37 g, 1.21 mmol) was added. The reaction mixture was evacuated and backfilled with N_2 three times, and then freshly degassed chloroform (50 mL) and pyridine (0.8 mL) were added into the reaction mixture. The reaction mixture was stirred at 85 °C for 12 h. Then the solution was poured into methanol and the precipitate was filtered off and washed with methanol. The crude product was purified by silica gel column chromatography, eluting with petroleum ether/dichloromethane (1:1) to give the product as purple solid (0.26 g, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.58 (s, 1.26H, CH), 8.56 (s, 0.72H, Th-H), 8.09 (s, 0.56H, Th-H), 7.99 (s, 2H, Th-H), 7.84 (s, 1.36H, Th-H), 7.60 (s, 2H, Ph-H), 7.13-7.15 (d, J = 8.0 Hz, 8H, Ph-H), 7.08-7.10 (d, J = 8.0 Hz, 8H, Ph-H), 2.55 (t, J = 8.0 Hz, 8H, CH_2), 1.54-1.60 (m, 8H, CH_2), 1.26-1.34 (m, 24H, CH_2), 0.84-0.88 (m, 12H, CH_3). ^{13}C NMR ($CDCl_3$, 175 MHz, ppm): δ 181.9, 180.3, 162.2, 158.3, 158.2, 157.1, 157.0, 156.8, 155.9, 150.2, 149.1, 148.2, 145.2, 145.1, 144.9, 144.2, 142.5, 139.3, 139.1, 138.1, 137.2, 136.9, 136.4, 136.3, 133.2, 128.8, 128.1, 122.8, 122.7, 122.0, 121.6, 120.5, 114.4, 114.0, 113.6, 113.4, 69.3, 67.0, 63.7, 35.5, 31.7, 31.2, 29.1, 22.6, 14.1. MALDI-TOF MS (m/z): calcd for $C_{90}H_{76}Cl_2N_4O_2S_4Se_2$: 1602.2 (100%) Found: 1602.4. Elemental Analysis: calcd for $C_{90}H_{76}Cl_2N_4O_2S_4Se_2$: C, 67.45; H, 4.78; N, 3.50. Found: C, 67.24; H, 4.74; N, 3.48.



BDSePhCl: In a 100 mL two-neck round-bottom flask, compound **BDSeT-CHO** (0.11 g, 0.10 mmol), **PhCl**[2] (0.12 g, 0.60 mmol) was added. The reaction mixture was evacuated and backfilled with N_2 three times, and then freshly degassed chloroform (40 mL) and pyridine (0.8 mL) were added into the reaction mixture. The reaction mixture was stirred at room temperature for 12 h. Then the solution was poured into methanol and the precipitate was filtered off and washed with methanol. The crude product was purified by silica gel column chromatography,

eluting with petroleum ether/dichloromethane (1:1) to give the product as purple solid (0.13 g, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.86 (s, 2H, CH), 8.64 (s, 1.2H, Ph-H), 8.59-8.61 (d, J = 8.0 Hz, 0.8H, Ph-H), 8.02 (s, 2H, Th-H), 7.81-7.83 (d, J = 8.0 Hz, 2H, Ph-H), 7.67-7.69 (d, s, J = 8.0 Hz, 4H, Ph-H), 7.14-7.16 (d, J = 8.0 Hz, 8H, Ph-H), 7.09-7.11 (d, J = 8.0 Hz, 8H, Ph-H), 2.56 (t, J = 8.0 Hz, 8H, CH_2), 1.54-1.60 (m, 8H, CH_2), 1.26-1.34 (m, 24H, CH_2), 0.84-0.88 (m, 12H, CH_3). ^{13}C NMR ($CDCl_3$, 175 MHz, ppm): δ 187.2, 187.0, 162.7, 159.4, 159.3, 159.2, 159.1, 158.7, 144.6, 144.5, 142.6, 141.6, 141.1, 140.6, 138.6, 138.5, 138.2, 138.1, 137.9, 136.7, 134.9, 134.7, 134.3, 133.3, 128.9, 128.1, 126.3, 125.3, 124.5, 123.7, 120.9, 120.8, 114.6, 114.5, 114.4, 114.3, 69.2, 68.6, 63.7, 63.6, 35.5, 31.6, 31.2, 29.1, 22.5, 14.1. MALDI-TOF MS (m/z): calcd for $C_{94}H_{80}Cl_2N_4O_2S_2Se_2$: 1591.3 (100%). Found: 1591.1. Elemental Analysis: calcd for $C_{94}H_{80}Cl_2N_4O_2S_2Se_2$: C, 70.98; H, 5.07; N, 3.52. Found: C, 70.44; H, 5.14; N, 3.42.

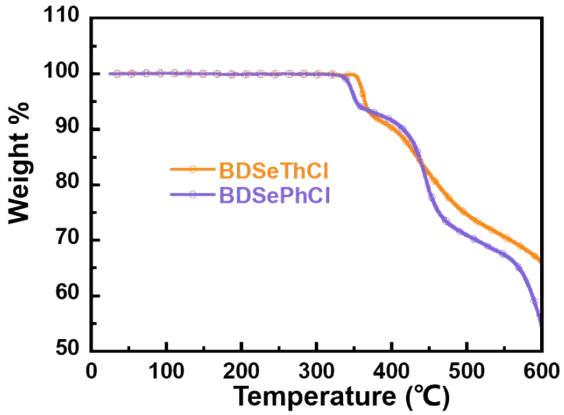
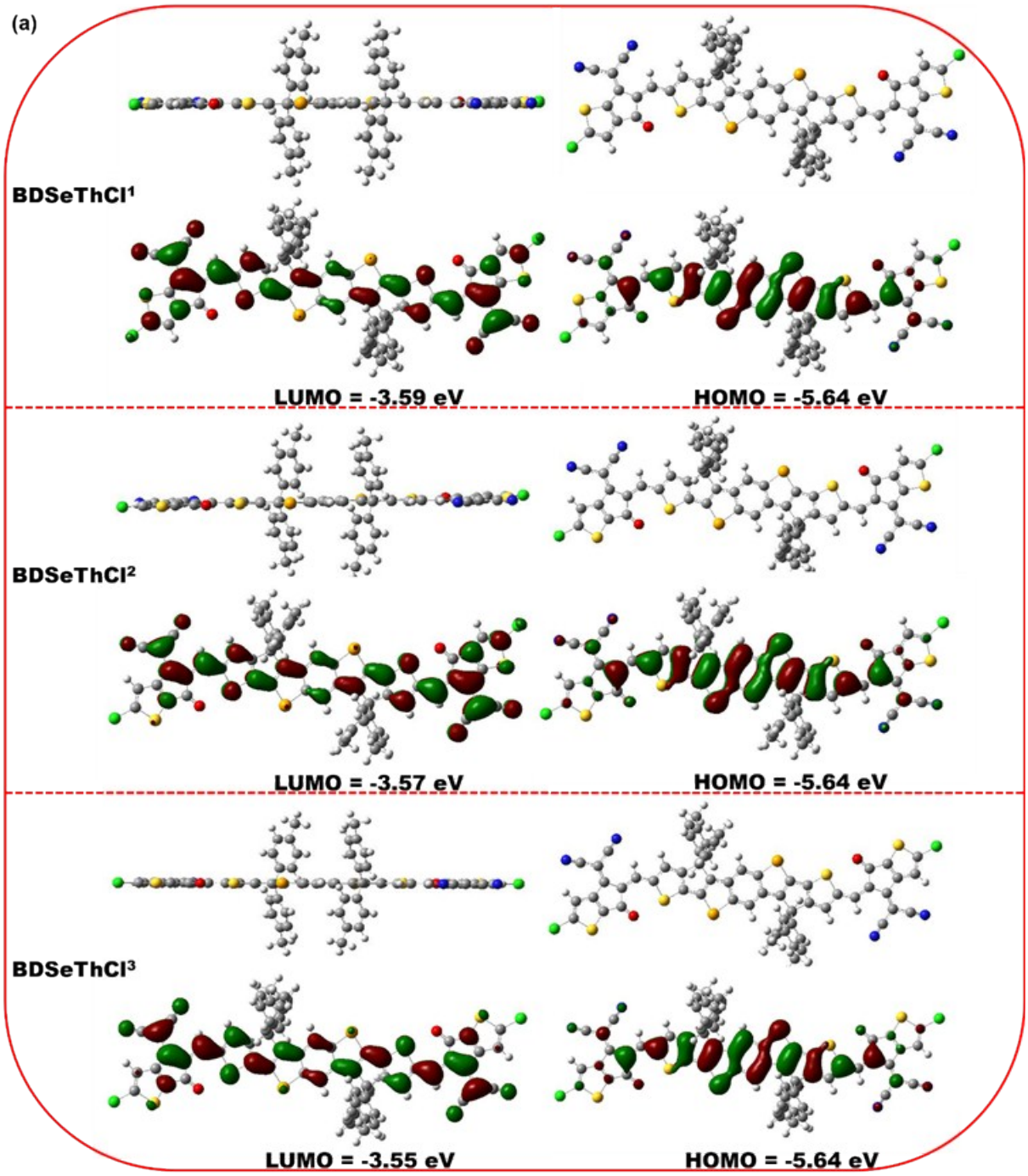


Figure S1. Thermal gravity analyse (TGA) of **BDSeThCl** and **BDSePhCl** with a heating rate of 10 ^{o}C/min under N_2 atmosphere.


(a)
BDSeThCl¹
LUMO = -3.59 eV
HOMO = -5.64 eV
BDSeThCl²
LUMO = -3.57 eV
HOMO = -5.64 eV
BDSeThCl³
LUMO = -3.55 eV
HOMO = -5.64 eV

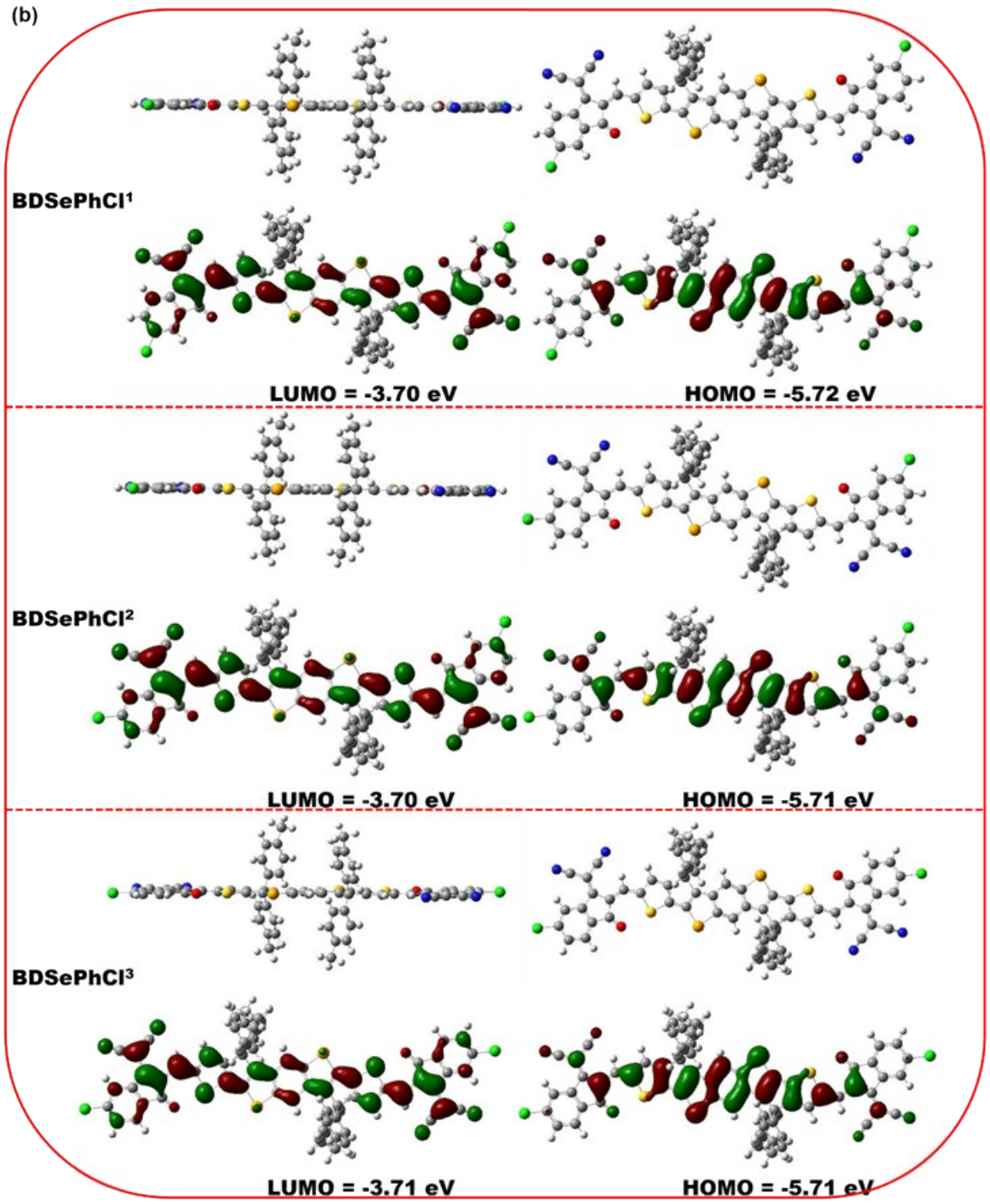


Figure S2. (a) Molecular geometry and energy levels for the **BDSeThCl** with three isomers. (b) Molecular geometry and energy levels for the **BDSePhCl** with three isomers.

Table S1. LUMO and HOMO energy levels of **BDSeThCl** (three isomers) and **BDSePhCl** (three isomers) calculated by DFT/B3LYP/6-31G, with methyl groups replacing alkyl substituents to simplify the calculations.

NF-SMA	$LUMO_{cal}$ [eV]	$HOMO_{cal}$ [eV]	E_{gcal} [eV]
BDSeThCl¹	-3.59	-5.64	2.05
BDSeThCl²	-3.57	-5.64	2.07

BDSeThCl[3]	-3.55	-5.64	2.09
BDSePhCl[1]	-3.70	-5.72	2.02
BDSePhCl[2]	-3.70	-5.71	2.01
BDSePhCl[3]	-3.71	-5.71	2.00

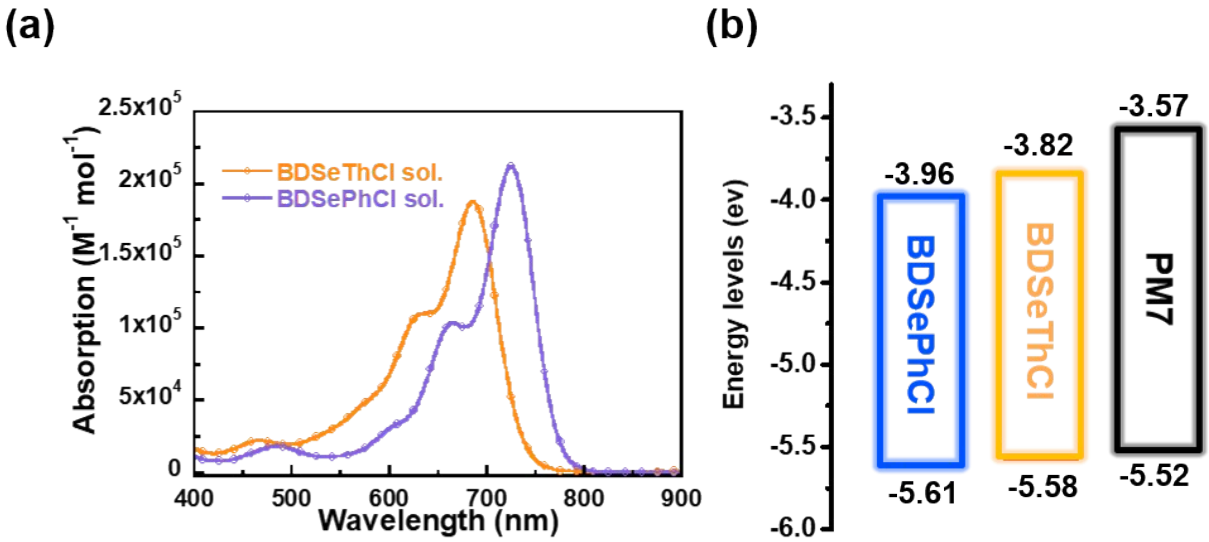


Figure S3. (a) Absorption spectrum of **BDSeThCl** and **BDSePhCl** in chloroform solutions (2.0×10^{-5} M). (b) The energy levels alignment of **BDSeThCl** and **BDSePhCl**.

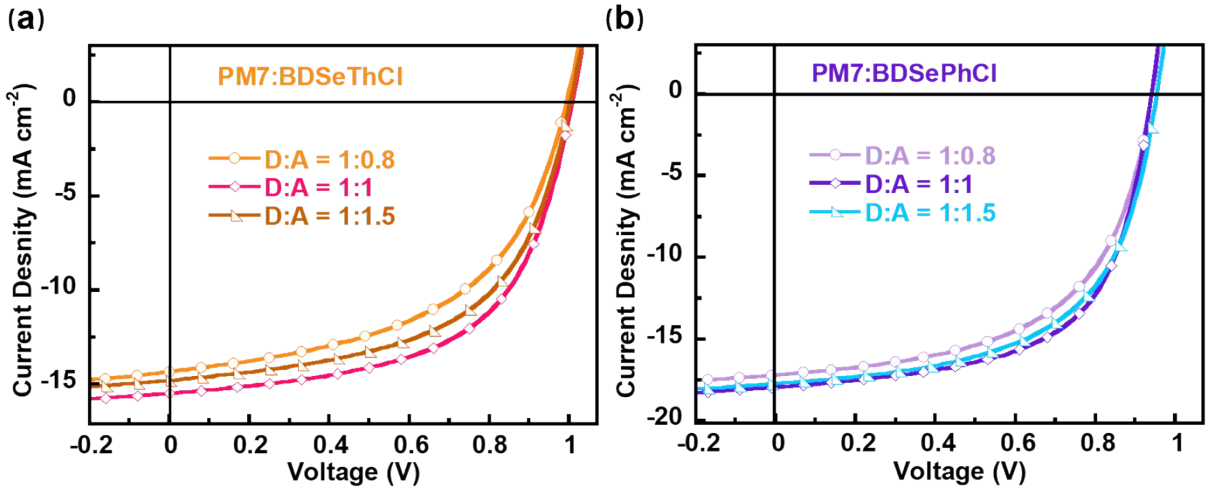


Figure S4. Characteristic *J*–*V* curves of (a) **PM7:BDSeThCl**, (b)**PM7:BDSePhCl** with different D/A ratios, under the irradiation of AM 1.5G, 100 mW cm^{-2}.

Table S2. The device performance parameters for the OPVs based on **PM7**:**BDSeThCl/BDSePhCl** with different D/A ratios, under the irradiation of AM 1.5G, 100 mW cm^{-2}.

Active layer (D/A)	D:A	V_{oc}[V]	J_{sc}[mA cm^{-2}]	FF[%]	PCE[%]
PM7/BDSeThCl	1:0.8	0.99	14.36	52.0	7.39
PM7/BDSeThCl	1:1	1.00	15.52	58.2	9.03
PM7/BDSeThCl	1:1.5	0.99	14.82	56.6	8.30

PM7/BDSePhCl	1:0.8	0.94	17.21	56.4	9.12
PM7/BDSePhCl	1:1	0.94	17.95	60.7	10.23
PM7/BDSePhCl	1:1.5	0.95	17.73	58.3	9.82

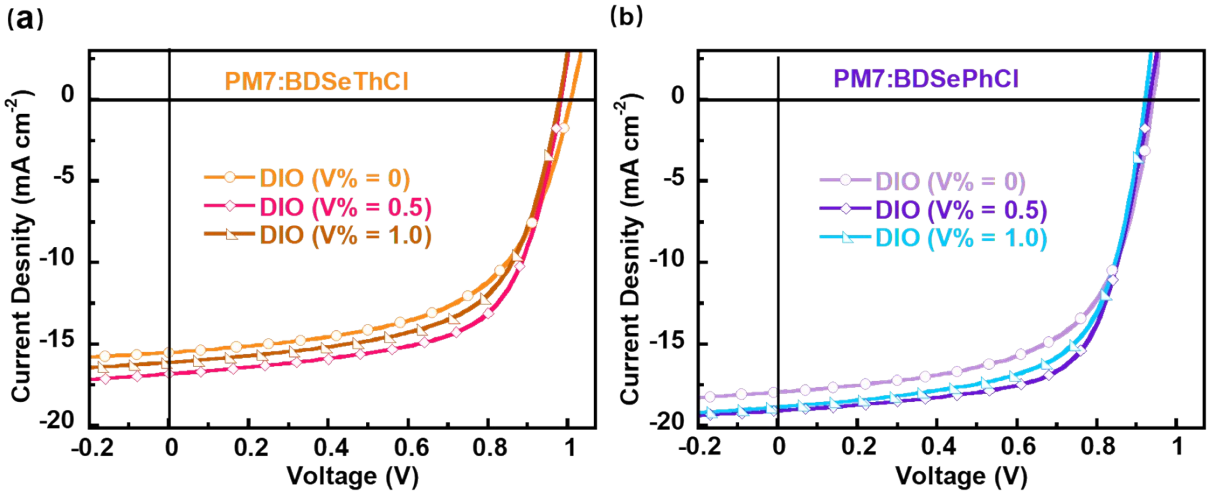


Figure S5. Characteristic *J*–*V* curves of (a) **PM7:BDSeThCl**, (b)**PM7:BDSePhCl** with different DIO additive, under the irradiation of AM 1.5G, 100 mW cm^{-2}.

Table S3. The device performance parameters for the OPVs based on **PM7**:**BDSeThCl/BDSePhCl** at 1:1 weight ratio with DIO additive, under the irradiation of AM 1.5G, 100 mW cm^{-2}.

Active layer (D/A)	DIO(V%)	V_{oc}[V]	J_{sc}[mA cm^{-2}]	FF[%]	PCE[%]
PM7/BDSeThCl	0	1.0	15.52	58.2	9.03
PM7/BDSeThCl	0.5	0.98	16.83	63.8	10.52
PM7/BDSeThCl	1.0	0.97	16.13	61.8	9.67
PM7/BDSePhCl	0	0.94	17.95	60.7	10.23
PM7/BDSePhCl	0.5	0.93	19.11	66.3	11.78
PM7/BDSePhCl	1.0	0.92	18.87	64.1	11.13

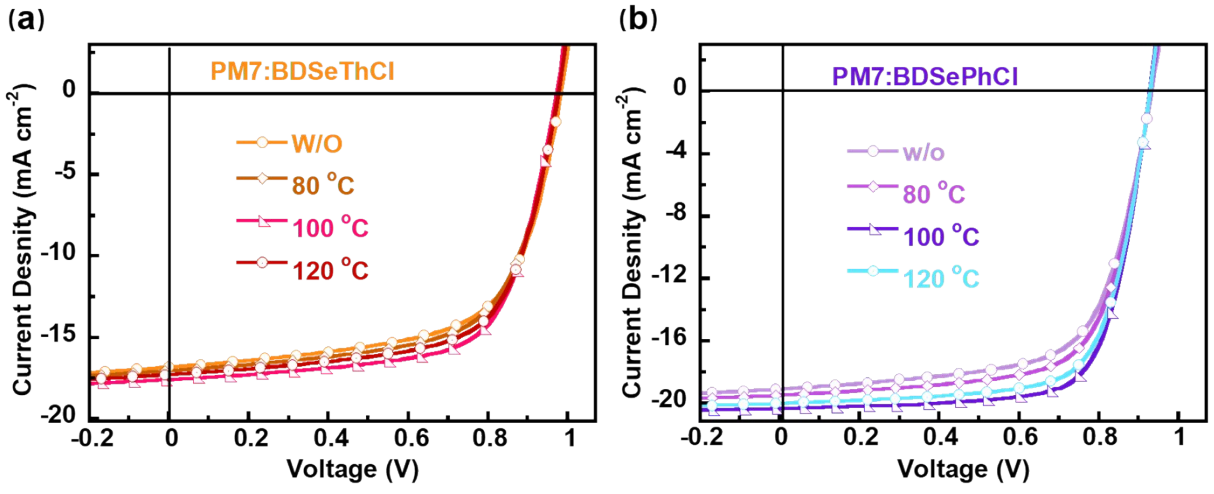


Figure S6. Characteristic *J–V* curves of (a) **PM7:BDSeThCl**, (b)**PM7:BDSePhCl** at 1:1 weight ratio with different thermal annealing temperature for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm^{-2}.

Table S4. The device performance parameters for the OPVs based on **PM7**:**BDSeThCl/BDSePhCl** at 1:1 weight ratio with 0.5% DIO and different thermal annealing temperature for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm^{-2}.

Active layer (D/A)	Treatment(°C)	V_{oc}[V]	J_{sc}[mA cm^{-2}]	FF[%]	PCE[%]
PM7/BDSeThCl	As-cast	0.98	16.83	63.8	10.52
PM7/BDSeThCl	80	0.97	17.06	65.3	10.80
PM7/BDSeThCl	100	0.97	17.61	67.1	11.46
PM7/BDSeThCl	120	0.97	17.30	66.0	11.08
PM7/BDSePhCl	As-cast	0.93	19.11	66.3	11.78
PM7/BDSePhCl	80	0.93	19.51	68.2	12.37
PM7/BDSePhCl	100	0.92	20.35	73.1	13.68
PM7/BDSePhCl	120	0.92	20.03	71.5	13.17

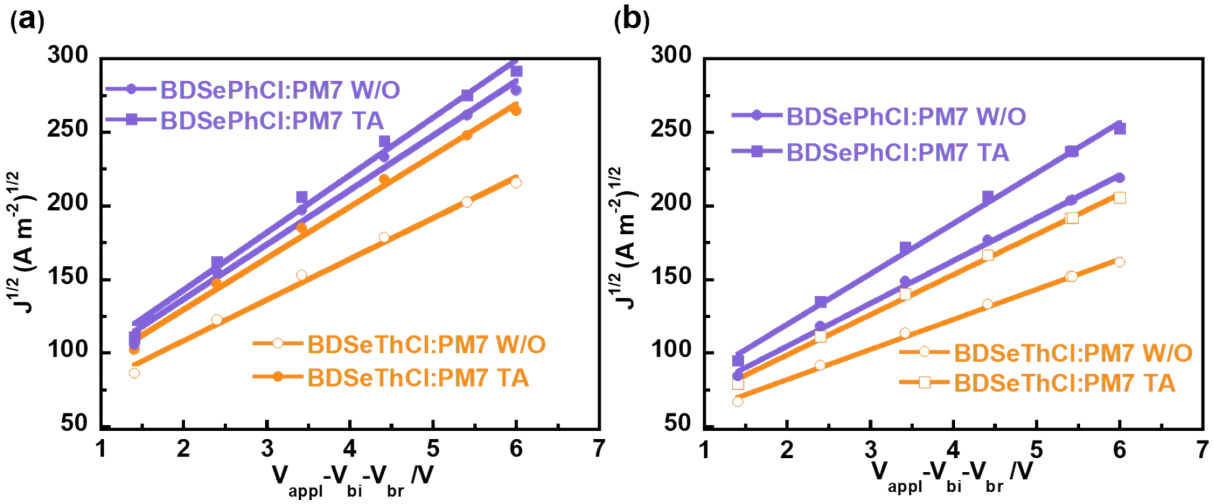


Figure S7. (a) The dark *J-V* plots of electron-only devices based on as-cast/optimal **BDSeThCl**:**PM7** and as-cast/optimal **BDSePhCl**:**PM7** blend films, respectively. (b) The dark *J-V* plots of hole-only devices based on as-cast/optimal **BDSeThCl**:**PM7** and as-cast/optimal **BDSePhCl**:**PM7** blend films, respectively.

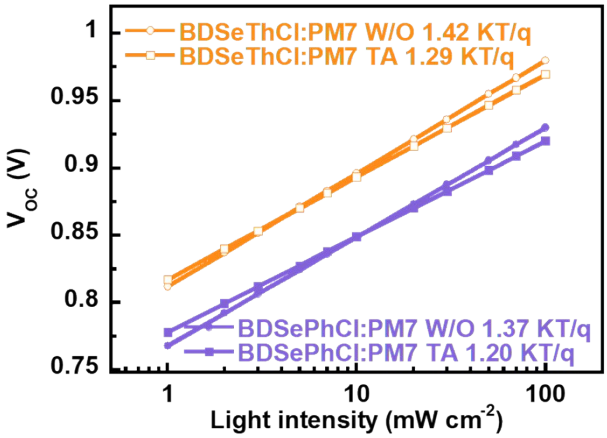


Figure S8. The V_{oc}-P_{light} plots of the as-cast/optimal **BDSeThCl**:**PM7**-based and the as-cast/optimal **BDSePhCl**:**PM7**-based devices.

Table S5. The key parameters of PSCs based on A-D-A type NF-SMAs/polymer donor based binary organic solar cells in comparison with our two NF-SMAs/**PM7** based devices.

Active layer (D/A)	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE$_{max}$ [a)] [%]	E_{loss} [b)] [eV]	EQE$_{max}$ [c)] [%]	Ref.
PM6/BDSeIC	0.97	14.0	52	7.1(6.8)	0.54	—	[S1]
PM6/BDSeIC2Br	0.89	20.3	69	12.5(12.3)	0.52	—	[S1]
PM6/BDSeIC4Br	0.85	16.4	69	9.6(9.4)	0.54	—	[S1]
PTPDBDT/Br-ITIC	0.93	15.4	66	9.4(9.1)	0.60	51	[S2]
PTPDBDT/F-ITIC	0.94	14.1	66	8.8(8.3)	0.62	64	[S2]
PTPDBDT/Cl-ITIC	0.94	15.6	65	9.5(9.0)	0.62	66	[S2]
PTPDBDT/I-ITIC	0.95	14.5	65	8.9(8.3)	0.60	65	[S2]
PTPDBDT/H-ITIC	1.04	10.6	58	6.4(6.1)	0.55	59	[S2]
PBT1-C/TPTT-IC	0.96	15.5	69	10.5(10.3)	0.67	77	[S3]
PBT1-C/ITIC	0.97	15.0	69	10.2(10.0)	0.63	78	[S3]
PTB7-Th/6TBA	0.98	15.2	68	10.1(9.7)	0.54	71	[S4]
PTB7-Th/4TIC	0.77	18.7	71	10.3(9.9)	0.62	71	[S4]
J51/IDTIDSe-IC	0.91	15.1	58	8.0(7.8)	0.61	63	[S5]
PTB7-Th/A1	0.89	12.5	52	5.8(5.4)	0.51	78	[S6]
PTB7-Th/A2	0.71	20.8	62	9.1(8.8)	0.65	—	[S6]
PBDB-T/ITC6-IC	0.97	16.4	73	11.6	0.63	80	[S7]
PBDB-T/IDTCN	0.85	12.1	63	6.4(6.3)	0.80	60	[S8]
PBDB-T/ITCPTC	0.84	17.5	73	10.7(10.5)	0.74	80	[S8]
PBDB-T/IDT6CN	0.83	15.1	73	9.3(9.2)	0.80	76	[S8]

PBDB-T/IDT6CN-Th	0.81	16.8	77	10.4(10.3)	0.80	78	[S8]
PBDB-T/IDT6CN-M	0.91	16.0	77	11.2(11.1)	0.74	80	[S8]
J61/BT-IC	0.87	16.3	67	9.5(9.3)	0.56	—	[S9]
J71/BT-IC	0.90	17.7	65	10.4(10.3)	0.53	67	[S9]
J71/BDT-IC	0.92	17.3	65	10.9(10.5)	0.61	72	[S10]
J71/IT-IC	0.96	14.8	64	9.3(9.0)	0.63	66	[S10]
PBDB-T/CDTDI	0.86	7.8	30	2.75(2.54)	0.50	35	[S11]
PBDB-T/ITDI	0.94	13.9	59	8.0(7.8)	0.59	62	[S11]
PCE-10/BT-CIC	0.70	22.5	71	11.6(11.2)	0.63	74	[S12]
PCE-10/BT-IC	0.81	17.5	59	8.5(8.3)	0.62	71	[S12]
PTB7-Th/ITIC-2F	0.75	16.2	70	8.7(8.5)	0.81	75	[S13]
PTB7-Th/IOTIC-2F	0.82	21.9	65	12.1(11.6)	0.50	78	[S13]
PTB7-Th/ITOTIC-2F	0.78	7.0	61	3.7(3.3)	0.54	28	[S13]
PBDB-T/IXIC	0.82	20.9	65	11.3	0.53	72	[S14]
PBDB-T/IXIC-2Cl	0.73	23.6	70	12.2	0.57	76	[S14]
PBDB-T/IXIC-4Cl	0.69	22.9	71	11.2	0.56	70	[S14]
PBDB-T/DTNIC6	0.96	7.7	45	3.3(3.2)	0.74	42	[S15]
PBDB-T/DTNIC8	0.96	12.9	72	9.0(8.9)	0.77	76	[S15]
PBDB-T/IDTT2F	0.81	18.5	59	8.8(8.7)	0.65	68	[S15]
PBDB-T/IDTOT2F	0.85	20.8	72	12.7(12.5)	0.59	76	[S16]
PBDB-T/IDTO-T-4	0.86	20.1	72	12.6	0.59	70	[S17]
PBDB-T/IDTO-Se-4	0.83	18.5	69	10.6	0.57	66	[S17]
PBDB-T/IDTO-TT-4	0.85	17.2	69	10.2	0.52	58	[S17]
P1/IT-4F	0.89	20.5	64	11.5(11.0)	0.60	—	[S18]
P2/IT-4F	0.90	20.7	76	14.2(14.0)	0.59	81	[S18]
P3/IT-4F	0.90	20.3	61	11.2(10.8)	0.59	—	[S18]
PTQ10/TPTC	0.95	4.8	42	1.97	0.57	24	[S19]
PTQ10/TPTIC	0.90	17.1	67	10.4	0.59	68	[S19]
PTB7-Th/DTNR	1.08	15.7	56	9.5(9.2)	0.64	72	[S20]

PBDB-T/4TIC-4F	0.65	21.5	57	7.9(7.5)	0.66	75	[S21]
PBDB-T/6TIC-4F	0.72	23.0	67	11.1(10.6)	0.52	73	[S21]
PBDB-T/F-Br	0.87	18.2	76	12.0(11.8)	0.69	79	[S22]
PBDB-T/F-Cl	0.87	17.6	75	11.5(11.3)	0.71	80	[S22]
PBDB-T/F-F	0.88	17.4	71	10.9(10.7)	0.71	78	[S22]
PBDB-T/F-H	0.94	15.0	67	9.6(9.4)	0.69	73	[S22]
PTB7-Th/DTPC-IC	0.86	8.5	42	3.1(2.8)	0.42	—	[S23]
PTB7-Th/DFIC	0.76	21.9	61	10.2(10.0)	0.45	68	[S23]
PBDB-T/NFBDT-Me	0.91	17.3	70	11.0(10.8)	0.67	73	[S24]
PBDB-T/NFBDT-F	0.79	19.3	69	10.6(10.5)	0.71	75	[S24]
FTAZ/F5IC	0.70	14.4	52	5.6(5.3)	0.94	68	[S25]
FTAZ/F7IC	0.74	18.4	59	8.2(7.8)	0.82	77	[S25]
FTAZ/F9IC	0.85	20.2	66	11.7(11.4)	0.64	78	[S25]
J71/IDTT-BH	0.90	17.8	69	11.0(10.8)	0.64	—	[S26]
J71/IDTT-OBH	0.92	14.7	61	8.0(7.9)	0.65	—	[S26]
PDCBT/IDTT-BH	0.88	17.1	68	10.4(10.1)	0.66	70	[S26]
PDCBT/IDTT-OBH	0.91	14.0	65	8.2(8.1)	0.66	—	[S26]
PBDB-T/IDTT-BH	0.85	16.9	69	9.9(9.8)	0.69	—	[S26]
PBDB-T/IDTT-OBH	0.87	17.5	72	10.9(10.8)	0.70	66	[S26]
PBTIBDTT/ITIC-F	0.92	16.4	74	11.2(10.9)	0.64	69	[S27]
PBDB-T/NITI	0.86	20.5	71	12.7	0.63	81	[S28]
PBDB-T/IT-OM-1	1.01	12.3	51	6.3(6.0)	0.66	—	[S29]
PBDB-T/ IT-OM-2	0.93	17.5	73	11.9(11.5)	0.66	—	[S29]
PBDB-T/ IT-OM-3	0.97	16.4	68	10.8(10.5)	0.67	—	[S29]
PBDB-T/ IT-OM-4	0.96	14.7	56	7.9(7.5)	0.67	—	[S29]
PTB7-Th/IHIC	0.75	19.0	68	9.8(9.4)	0.63	73	[S30]
PTB7-Th/FOIC	0.74	23.5	67	12.0(11.6)	0.58	81	[S31]
PTB7-Th/ITIC3	0.76	17.0	62	8.1(8.0)	0.79	—	[S31]
PTB7-Th/DICTF	0.85	16.3	55	7.9(7.6)	1.04	67	[S32]
PTB7-Th/COi7IC	0.82	13.1	58	6.3(6.2)	0.78	66	[S33]

PTB7-Th/COi7DFIC	0.67	17.3	71	8.3(8.0)	0.88	71	[S33]
PBDB-T/NNBDT	0.88	18.6	71	11.7(11.5)	0.55	69	[S34]
PBDB-T/FDNCTF	0.91	16.0	74	10.8(10.6)	0.69	76	[S34]
PBDB-T/DCF-2HT	1.02	11.3	50	5.7(5.5)	0.91	68	[S35]
PTB7-Th/DCF-2HT	0.96	12.4	40	4.8(4.6)	0.87	—	[S35]
PBDB-T/NTIC	0.94	13.6	68	8.6(8.5)	0.74	71	[S36]
PBDB-T/NTIC-Me	0.96	13.0	66	8.3(8.1)	0.78	69	[S36]
PBDB-T/NTIC-OMe	0.97	13.5	66	8.6(8.5)	0.74	68	[S36]
PBDB-T/NTIC-F	0.81	15.0	66	8.1(7.9)	0.85	74	[S36]
PBDB-T/F-M	0.98	14.6	71	10.3(10.1)	0.67	—	[S37]
PTB7-Th/NOBDT	0.77	19.2	70	10.6(10.3)	0.62	—	[S37]
PBDB-T/DICTF	0.93	10.3	60	5.9(5.7)	0.97	58	[S38]
PBDB-T/FDICTF	0.94	15.8	66	10.1(9.8)	0.69	75	[S38]
FTAZ/IDIC	0.84	20.8	72	12.5(12.1)	0.76	79	[S39]
FTAZ/IDIC1	0.90	13.6	59	7.1(7.0)	0.77	77	[S40]
FTAZ/IHIC1	0.95	14.3	68	9.2(8.9)	0.74	—	[S40]
FTAZ/ITIC-Th	0.92	15.8	61	8.9(8.7)	0.69	—	[S41]
FTAZ/ITIC-Th1	0.85	19.3	74	12.1(11.9)	0.70	80	[S41]
FTAZ/ITIC-Th2	0.75	17.2	70	9.1(8.9)	0.79	—	[S41]
FTAZ/ITIC-Th3	0.96	16.3	68	10.7(10.6)	0.67	—	[S41]
PTB7-Th/IUIC	0.80	21.7	0.65	11.2(11.0)	0.61	80	[S42]
PBDB-T/DICTiF	0.98	11.2	65	7.1(6.9)	0.77	—	[S43]
PBDB-T-2F/IT-2Cl	0.92	19.1	75	13.2(13.0)	0.63	—	[S44]
PBDB-T-2F/IT-4Cl	0.79	22.7	75	13.5(13.2)	0.69	80	[S44]
FTAZ/IHIC2	0.78	15.7	61	7.5(7.3)	0.89	—	[S45]
FTAZ/IOIC2	0.90	19.7	69	12.3(12.1)	0.65	83	[S45]
PTB7-Th/F6IC	0.61	18.5	64	7.1(6.8)	0.61	80	[S46]
PTB7-Th/F8IC	0.64	25.1	68	10.9(10.5)	0.53	—	[S46]
PTB7-Th/F10IC	0.73	20.8	67	10.2(10.0)	0.52	—	[S46]
PTB7-Th/IDT-FBTR	1.02	15.2	58	9.1(8.9)	0.65	74	[S47]
FTAZ/INIC	0.96	13.5	58	7.7(7.5)	0.61	—	[S48]

FTAZ/INIC1	0.93	16.6	64	10.1(9.9)	0.63	—	[S48]
FTAZ/INIC2	0.90	17.6	67	10.8(10.6)	0.62	—	[S48]
FTAZ/INIC3	0.86	19.4	67	11.5(11.2)	0.62	77	[S48]
PBTA-TF/ITCC	1.00	15.5	67	10.4(10.1)	0.67	—	[S49]
PBTA-TF/IT-M	0.97	17.8	71	12.2(11.9)	0.76	—	[S49]
PBTA-TF/IT-4F	0.73	20.2	72	10.6(10.1)	0.62	—	[S49]
PBDB-T/FDNCTF	0.93	16.3	73	11.2(10.9)	0.67	—	[S50]
PTB7-Th/IOIC2	0.83	17.2	66	9.3(9.1)	0.71	78	[S51]
PTB7-Th/IOIC3	0.76	22.9	75	13.1(12.8)	0.69	86	[S51]
PBQ-0F/ITIC	0.69	16.1	60	6.7	0.92	—	[S52]
PBQ-QF/ITIC	0.83	17.1	62	8.9	0.78	—	[S52]
PBQ-4F/ITIC	0.95	17.9	67	11.3	0.66	—	[S52]
J71/ITVIC	0.89	14.5	58	7.3(7.1)	0.51	—	[S53]
J71/ITVfIC	0.84	19.7	59	9.7(9.5)	0.53	—	[S53]
J71/ITVffIC	0.81	20.6	63	10.5(10.2)	0.54	81	[S53]
PTQ10/m-ITIC-2F	0.96	18.9	69	12.5(12.0)	0.61	—	[S54]
PTQ10/m-ITIC-4F	0.90	19.8	70	12.5(12.0)	0.63	83	[S54]
PCE-10/BT-CIC	0.70	22.5	71	11.6(11.2)	0.63	—	[S55]
PBDB-T/TTIC	0.77	22.3	62	10.6(10.3)	0.63	63	[S56]
PBDB-T/TTIC-M	0.80	20.5	70	11.5(11.4)	0.64	68	[S55]
PBDB-T/IDT-BC6	0.91	5.6	44	2.3(2.2)	0.83	36	[S57]
PBDB-T/IDT-BOC6	1.01	17.5	54	9.6(9.4)	0.62	80	[S57]
J71/ITCPTC	0.89	17.7	74	11.6(11.3)	0.68	—	[S58]
J71/MeIC	0.92	18.5	74	12.5(12.1)	0.66	74	[S58]
PBDB-T/BTCN-O	0.95	5.0	34	1.62(1.61)	0.67	—	[S59]
PBDB-T/BTCN-M	0.98	12.0	50	5.9(5.7)	0.65	—	[S59]
PBDB-T/ZITI	0.89	19.8	74	13.0(12.9)	0.64	80	[S60]
J71/ZITI	0.93	20.4	69	13.2(13.0)	0.60	79	[S60]
PBDB-T/IDTC	0.92	16.6	61	9.3(9.0)	0.59	70	[S61]
PBDB-T/IDTO	0.94	16.3	65	10.0(9.7)	0.57	65	[S61]
PBDB-T/IDT-2B	0.89	13.3	54	6.4(6.3)	0.84	—	[S62]

PBDB-T/IDT-OB	0.88	16.1	71	10.1(9.9)	0.78	—	[S62]
PBDB-T/IDT-2O	0.86	15.6	72	9.7(9.6)	0.78	75	[S62]
PBDB-TF/HFO-PCIC	0.93	12.6	71	8.36	0.55	—	[S63]
PBDB-TF/OF-PCIC	0.91	13.8	73	9.1	0.68	—	[S63]
PBDB-TF/HF-PCIC	0.91	17.8	71	11.5	0.59	75	[S63]
PBDB-T/IT-IC	0.90	16.8	74	11.2(10.7)	0.67	—	[S64]
PBDB-T/IT-M	0.94	17.4	74	12.1(11.5)	0.66	77	[S64]
PBDB-T/IT-DM	0.97	16.5	71	11.3(10.8)	0.66	75	[S64]
J52/IEICO-4Cl	0.70	23.8	61	10.1	0.53	—	[S65]
PBDB-T/IEICO-4Cl	0.74	20.8	63	9.7	0.56	—	[S65]
PTB7-Th/IEICO-4Cl	0.73	22.8	62	10.3	0.57	—	[S65]
PBDB-T/NCBDT	0.84	20.3	71	12.1(11.6)	0.61	74	[S66]
PBDB-T/TTIC	0.80	20.6	66	10.9(10.7)	0.58	68	[S67]
PBDB-T/TTIC-F	0.71	21.3	63	9.5(9.4)	0.64	65	[S67]
PTB7-TH/ITIC	0.81	14.2	59	6.8(6.6)	0.78	73	[S68]
PTB7-Th/IDT-IC	0.83	9.5	40	3.2(3.1)	0.89	50	[S69]
PTB7-Th/IDTIDT-IC	0.94	14.5	48	6.5(6.3)	0.59	63	[S69]
PEDTTT-E-T/IEIC	0.90	11.7	47	4.9(4.7)	0.60	50	[S70]
PEDTTT-E-T/IEICO	0.82	17.7	58	8.4(8.3)	0.52	66	[S70]
PBDB-T-SF/IT-4F	0.88	20.9	71	13.1(13.0)	0.61	83	[S71]
PDCBT-2F/IT-M	1.13	10.4	56	6.6	0.46	50	[S72]
PBDB-T/INPIC	0.96	8.5	53	4.3(4.2)	0.50	—	[S73]
PBDB-T/INPIC-4F	0.85	21.6	72	13.1(13.0)	0.54	—	[S73]
PBDB-T/ITIC-C6	0.87	15.6	65	9.2(8.8)	0.72	—	[S74]
PBDB-TF/ITIC-C6	0.98	14.4	64	9.3(9.1)	0.61	—	[S74]
PBDB-T/ITIC-C9	0.87	15.1	69	9.5(9.0)	0.72	75	[S74]
PBDB-TF/ITIC-C9	0.99	14.5	67	10.2(9.5)	0.60	—	[S74]
FTAZ/ITIC-Th	0.92	15.8	61	8.9(8.7)	0.69	80	[S75]
FTAZ/ITIC-Th1	0.85	19.3	74	12.1(11.9)	0.71	—	[S75]

PDBT-T1/IC-C6IDT-IC	0.89	15.1	65	8.7(8.5)	0.73	76	[S76]
J61/ITIC	0.90	17.9	65	10.5(10.3)	0.69	78	[S77]
J61/m-ITIC	0.91	18.3	70	11.8(11.5)	0.69	80	[S77]
PTB7-Th/ITIC-Th	0.80	15.9	68	8.7(8.5)	0.80	80	[S78]
PDBT-T1/ITIC-Th	0.88	16.1	67	9.6(9.3)	0.72	—	[S78]
PBDTTT-EFT/IEICO-4F	0.74	22.8	59	10.0(9.7)	0.50	72	[S79]
J52/IEICO-4F	0.73	21.9	58	9.4(9.3)	0.51	74	[S79]
PM6/ITIC	1.04	16	58	9.7(9.5)	0.51	71	[S80]
PBDB-TF/IDTI	0.99	13.0	57	7.4(6.9)	0.73	—	[S81]
PBDB-TF/IDTN	0.95	16.8	78	12.2(12.0)	0.64	74	[S81]
PTB7-Th/6TIC	0.83	20.1	66	11.1(10.7)	0.54	—	[S82]
PTB7-TH/IEIC	0.97	13.6	48	6.3(6.1)	0.60	57	[S83]
PTB7-Th/Th-4TIC	0.77	18.8	72	10.4(9.9)	0.63	69	[S84]
PBDB-T/Th-ITIC	0.92	16.1	71	10.6	0.49	69	[S84]
PM6/IT-4F	0.84	22.2	73	13.5(13.2)	0.65	87	[S85]
PBDB-T1/ITIC	0.87	15.4	64	8.6(8.3)	0.68	—	[S86]
PBDB-T1/ITTIC	0.92	15.9	62	9.1(8.9)	0.54	—	[S86]
FTAZ/ITIC1	0.92	15.8	56	8.1(8.0)	0.63	—	[S87]
FTAZ/ITIC2	0.93	18.9	63	11.0(10.6)	0.61	78	[S87]
PBDTTT-C-T/DC-IDT2T	0.90	8.3	52	3.9(3.7)	0.65	41	[S88]
PBDB-T/ITCPTC-Th	0.86	17.1	73	10.6(10.3)	0.74	81	[S89]
PBDB-T/ITCPTC-Se	0.87	15.2	68	9.0(8.8)	0.72	—	[S89]
PBDB-T/BDTIT-M	0.90	17.6	71	11.3(11.0)	0.65	78	[S90]
PBDB-T/BDThIT-M	0.94	18.0	71	12.1(11.9)	0.59	78	[S90]
PM6/IDIC	0.97	17.8	69	11.9(11.7)	0.59	80	[S91]
PTB7-Th/FNIC1	0.77	19.9	66	10.2(10.0)	0.71	79	[S92]
PTB7-Th/FNIC2	0.73	23.9	73	13.0(12.7)	0.64	80	[S92]
PBDB-T-SF/NCBDT-4Cl	0.85	22.3	74	14.1	0.55	—	[S93]

PBDB-T2Cl/IDIC-4H	0.98	10.3	45	4.5	0.71	59	[S94]
PBDB-T2Cl/IDIC-4F	0.88	13.0	61	7.1	0.78	66	[S94]
PBDB-T2Cl/IDIC-4Cl	0.83	16.2	68	9.2	0.75	73	[S94]
PM6/SeTIC	0.95	15.5	51	7.4	0.63	—	[S95]
PM6/SeTIC-4Cl	0.78	22.9	75	13.3	0.66	83	[S95]
PBDB-T/AT-NC	0.91	17.1	69	10.9	0.71	77	[S96]
PBDB-T/AT-4Cl	0.90	19.5	75	13.3	0.70	83	[S96]
FTAZ/IDCIC	0.87	21.9	71	13.5	0.58	81	[S97]
PBDB-TF/IDIC-C4Ph (TA)	0.94	19.1	78	14.0	0.68	83	[S98]
PBDB-TF/IDIC-C4Ph (as-cast)	0.95	18.1	76	13.2	0.67	80	[S98]
PBDB-TF/IDIC-C4Ph (TA+DIO)	0.93	18.9	77	13.5	0.69	—	[S98]
PTB7-Th/COi8DFIC	0.69	27.3	71	13.8	0.57	—	[S99]
PTB7-Th/COi8DFIC	0.69	26.2	71	13.2	0.57	—	[S99]
PM7/BDSeThCl	**0.97**	**17.8**	**69**	**11.9**	**0.58**	**80**	**This work**
PM7/BDSePhCl	**0.92**	**20.3**	**73**	**13.7**	**0.49**	**80**	**This work**

[a]The values in parentheses are the average PCE values.[b] $E_{loss} = E_g - eV_{oc}$, where E_g is the lowest energy bandgap of the donor and acceptor components.[c] "—" don't involve the maximum data in the literature.

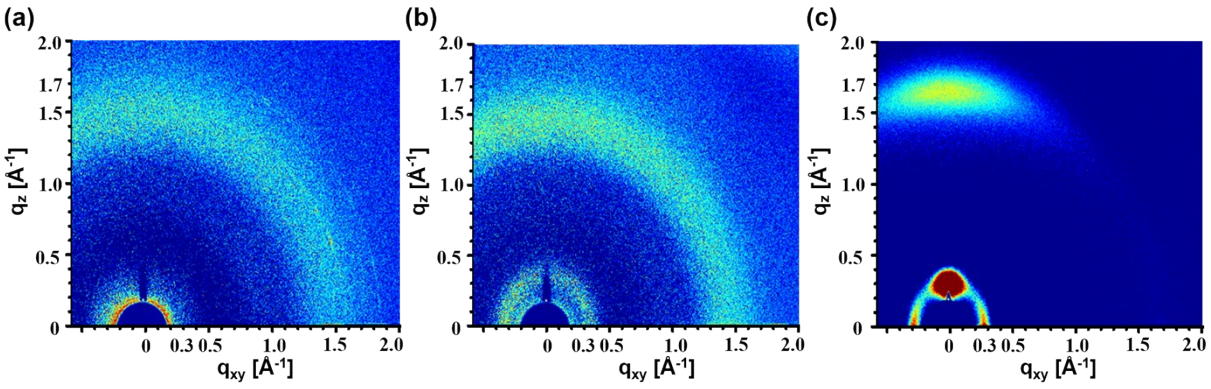


Figure S9. GIXD patterns for pure **BDSeThCl**, **BDSePhCl**, and **PM7** neat films.

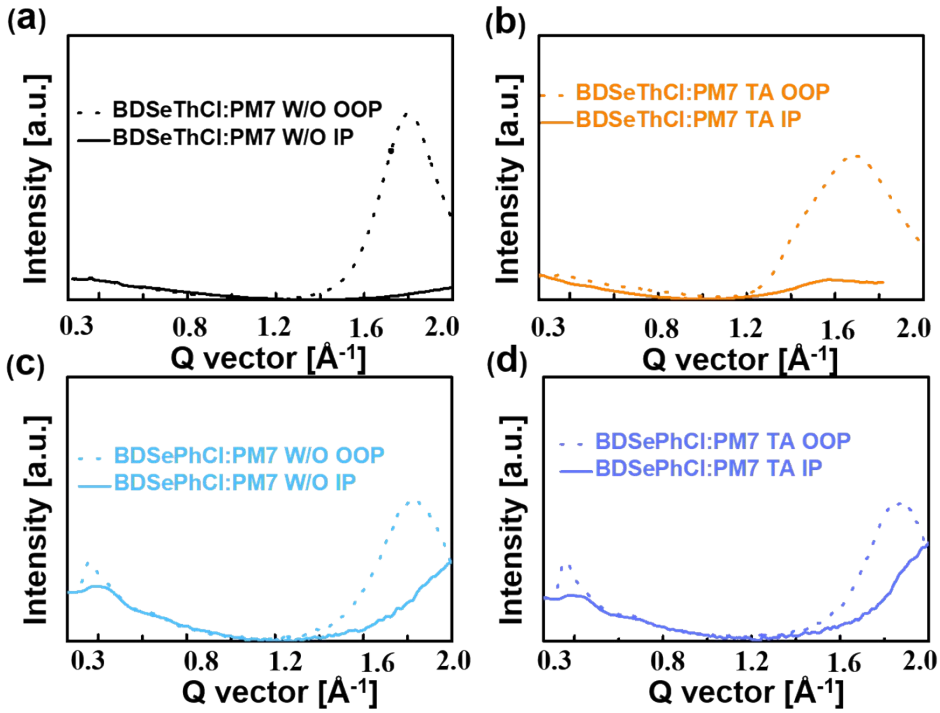


Figure S10. The out-of plane (dotted line) and in-plane (solid line) line-cuts in GIXD for the **PM7**:**BDSeThCl** or **PM7**:**BDSePhCl** blend films.

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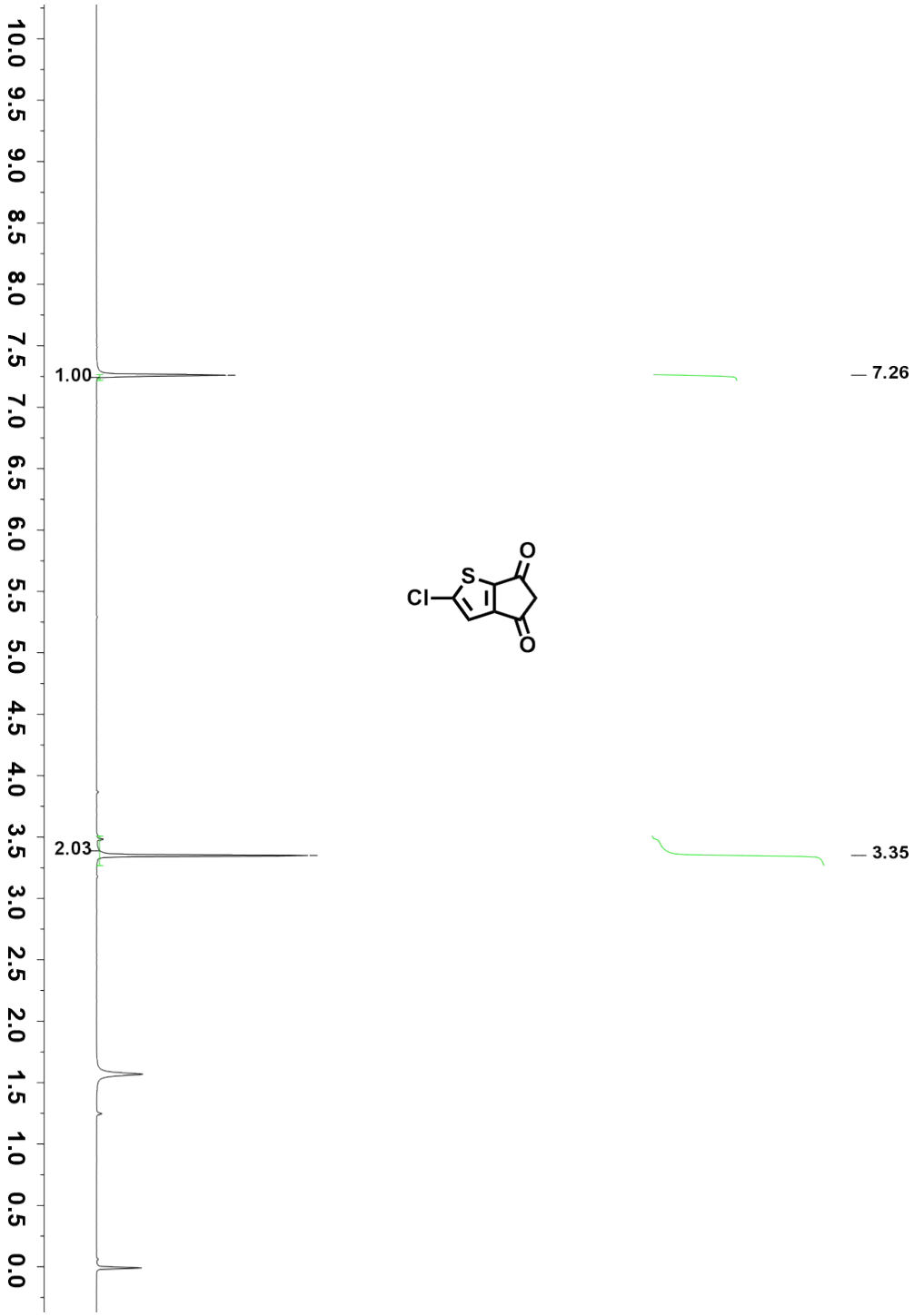
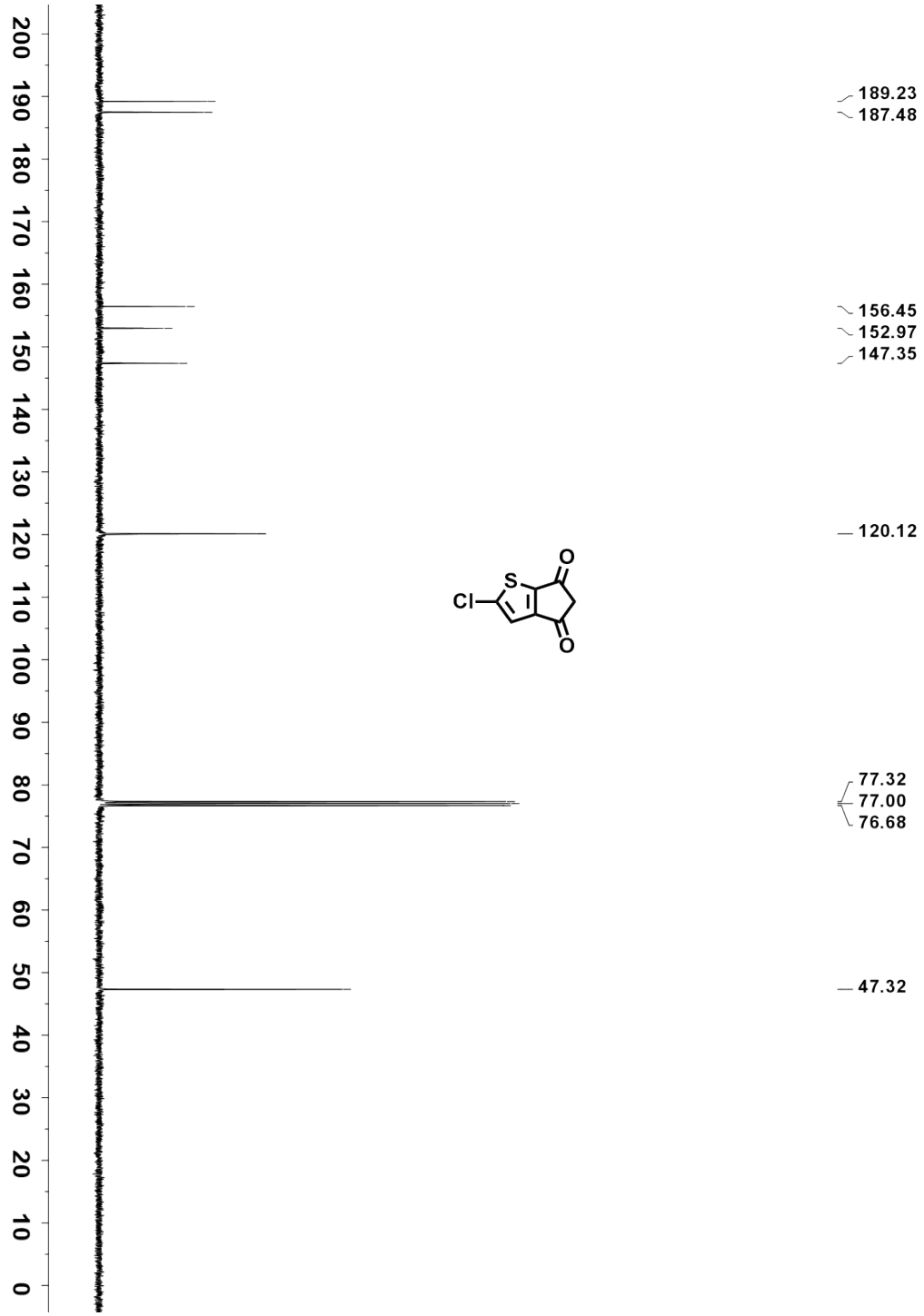
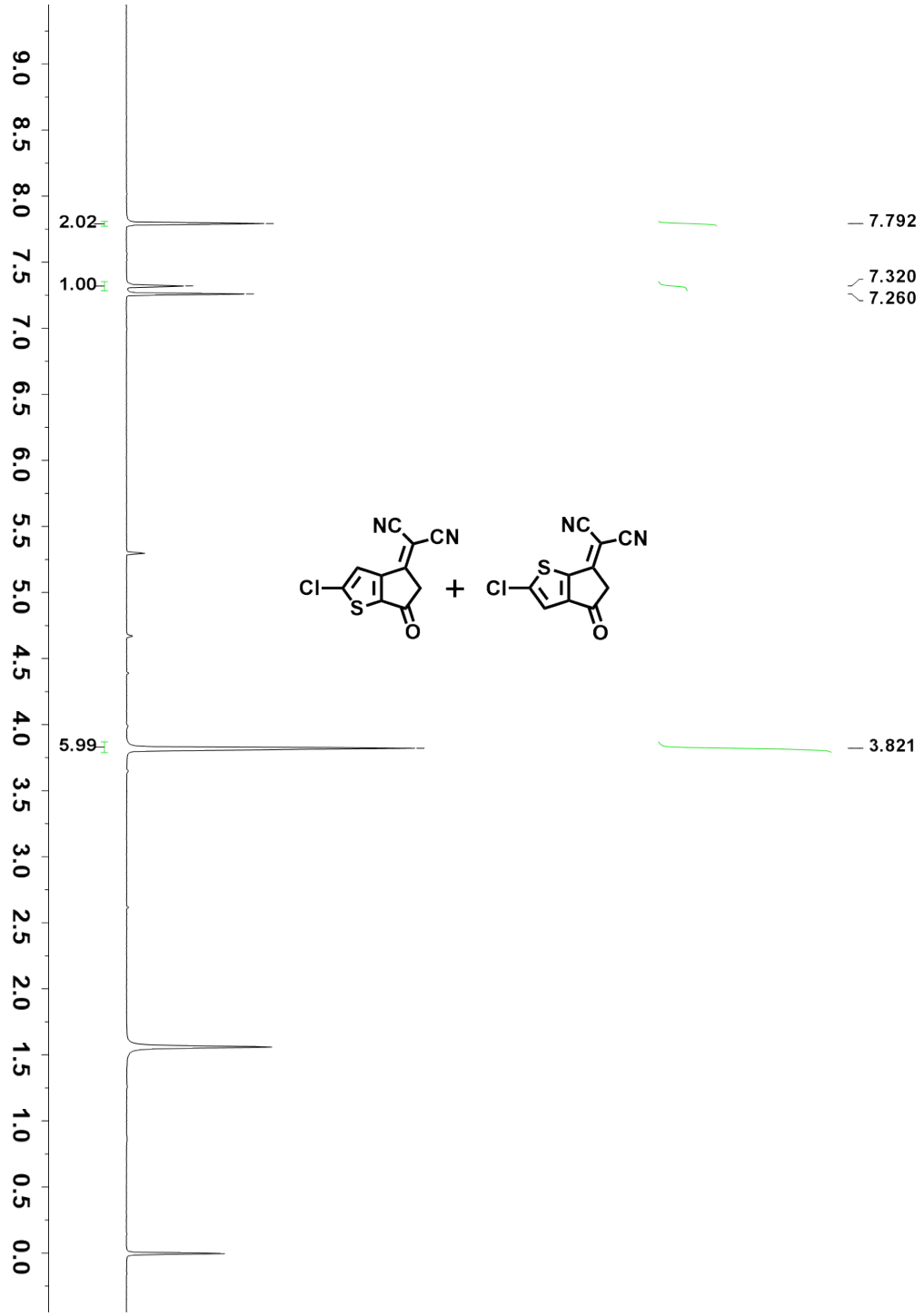


^{1}H NMR spectrum for **compound 3**



^{13}C NMR spectrum for **compound 3**



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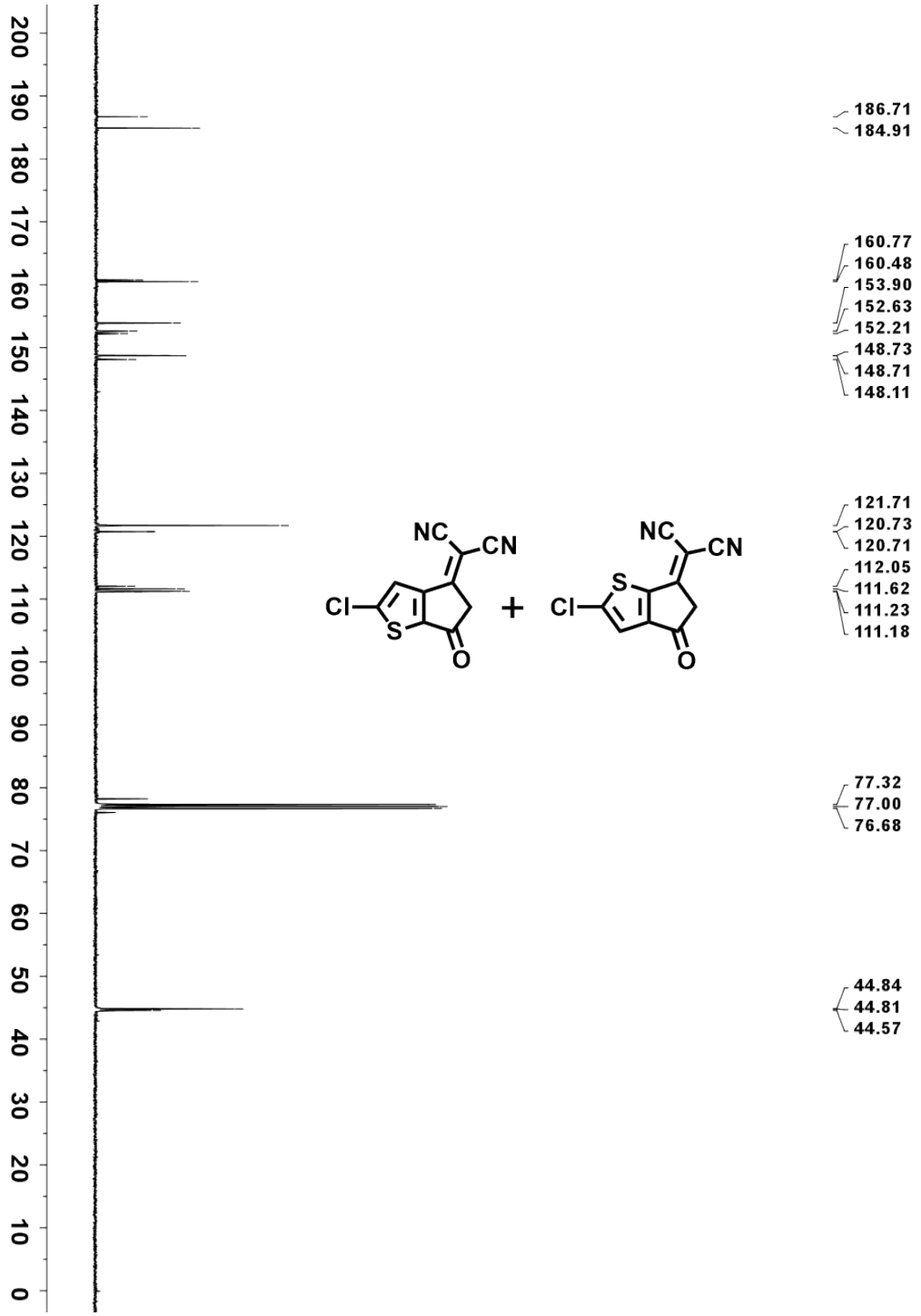

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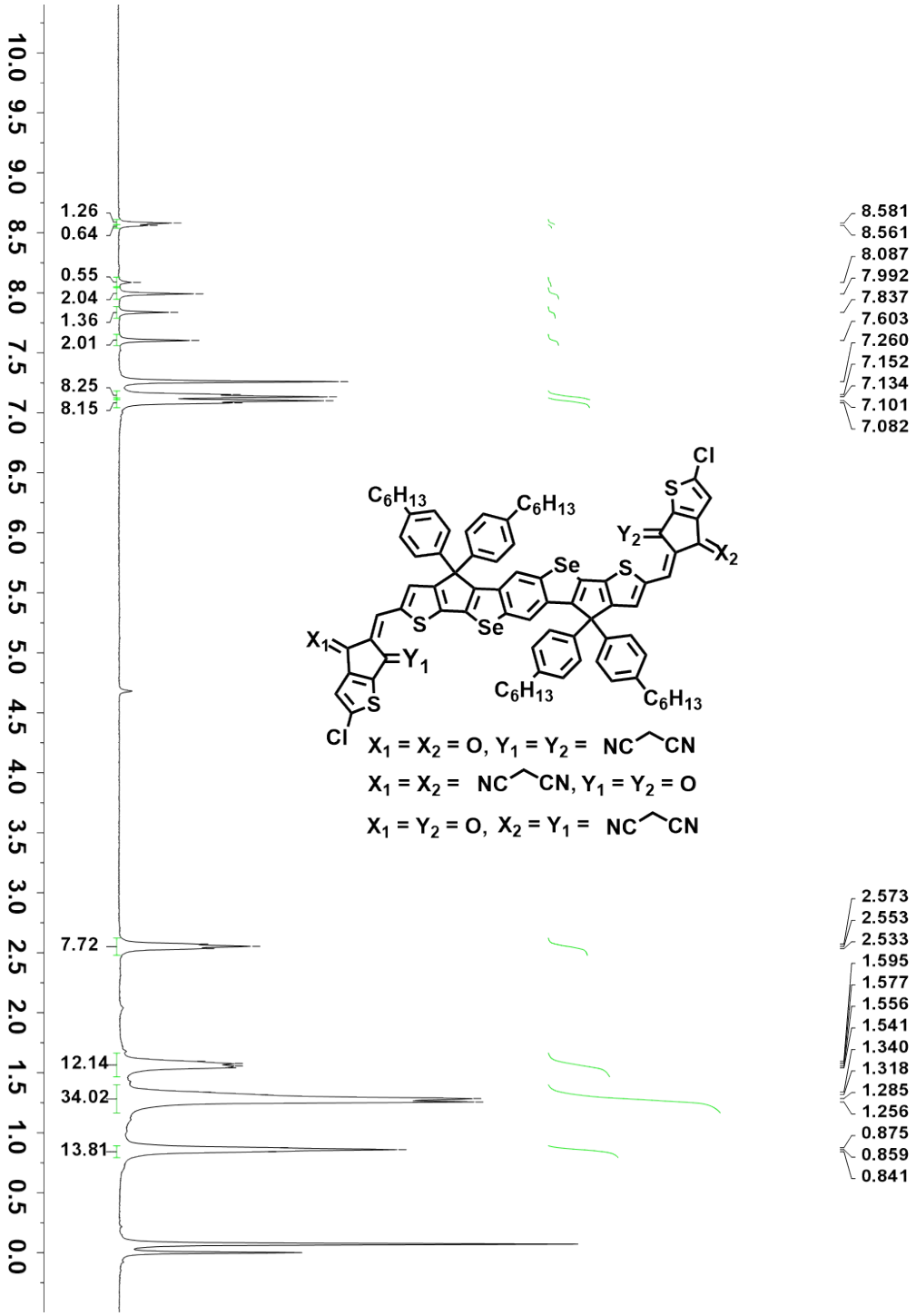

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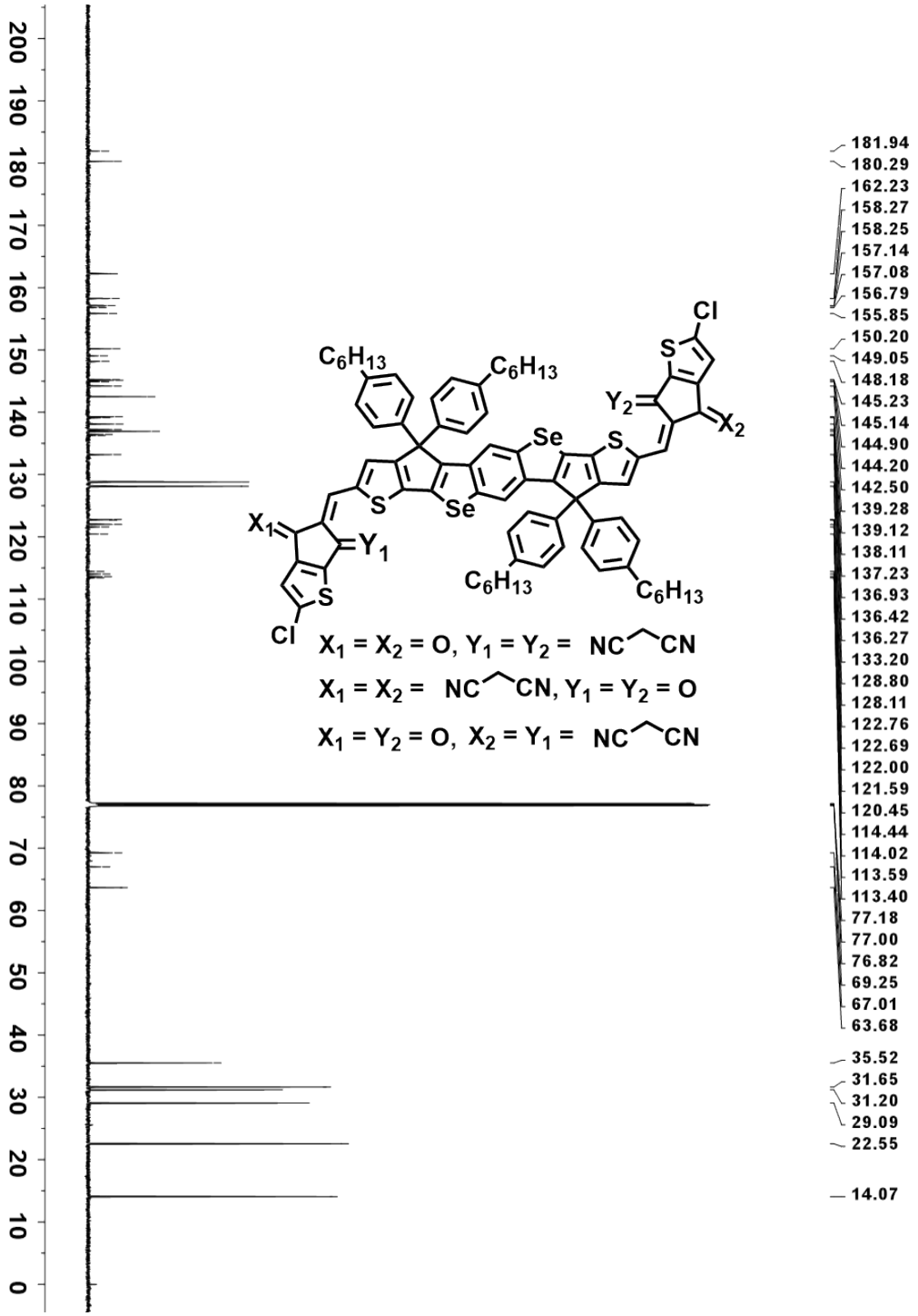

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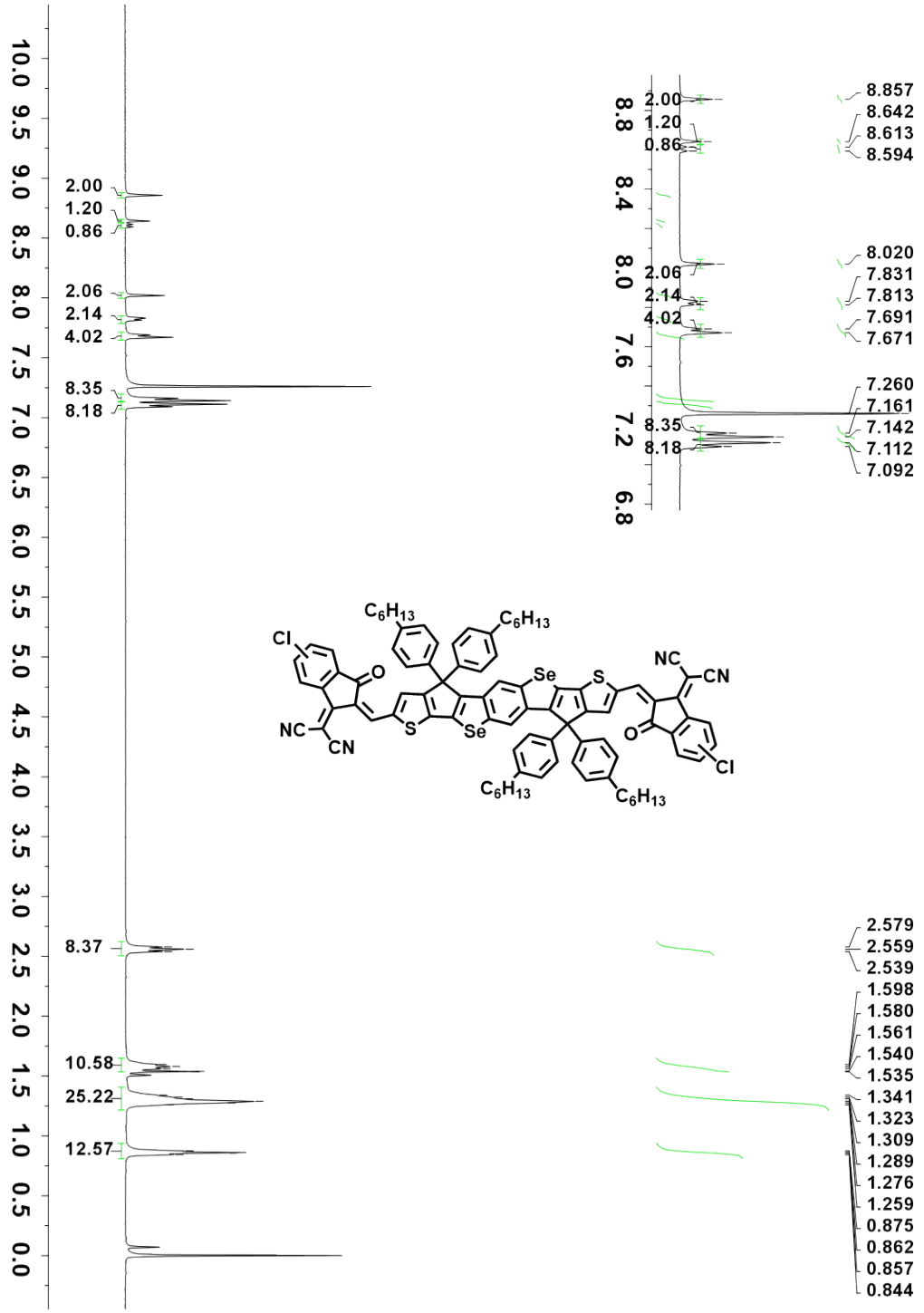

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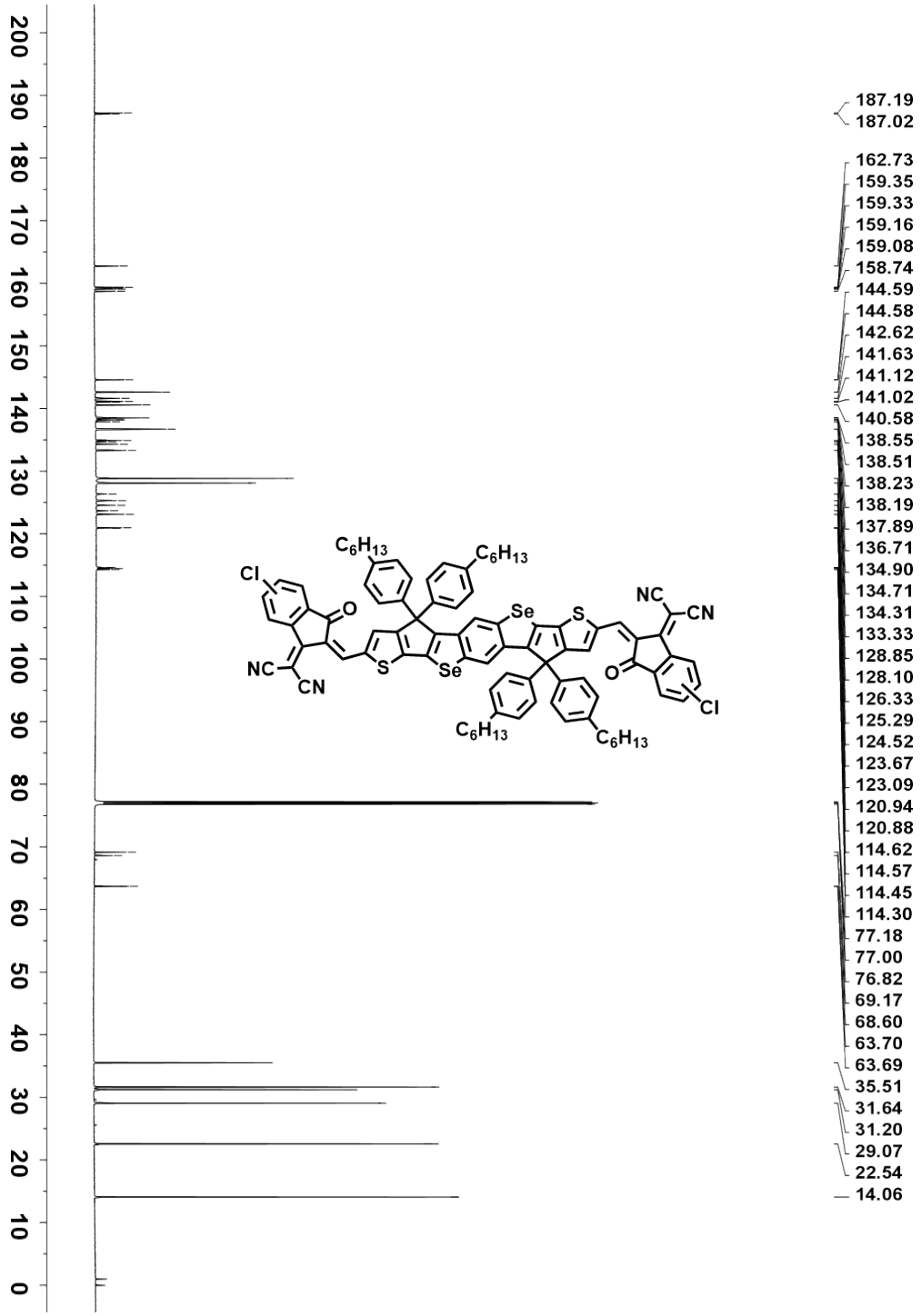

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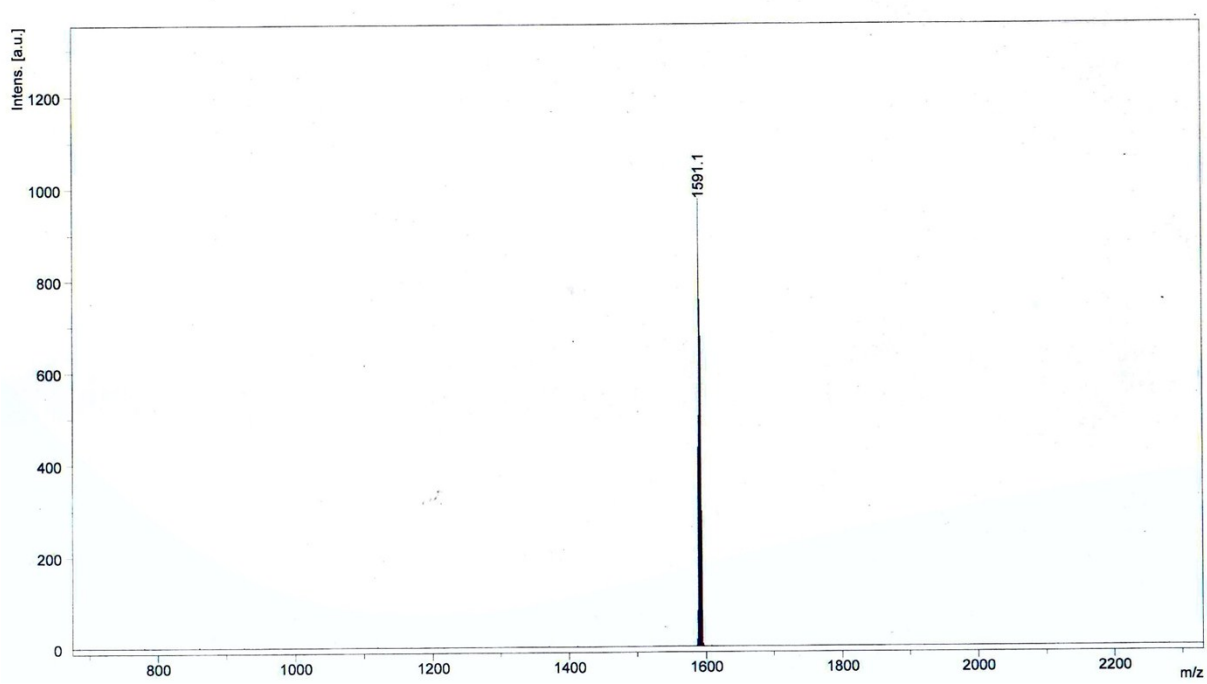
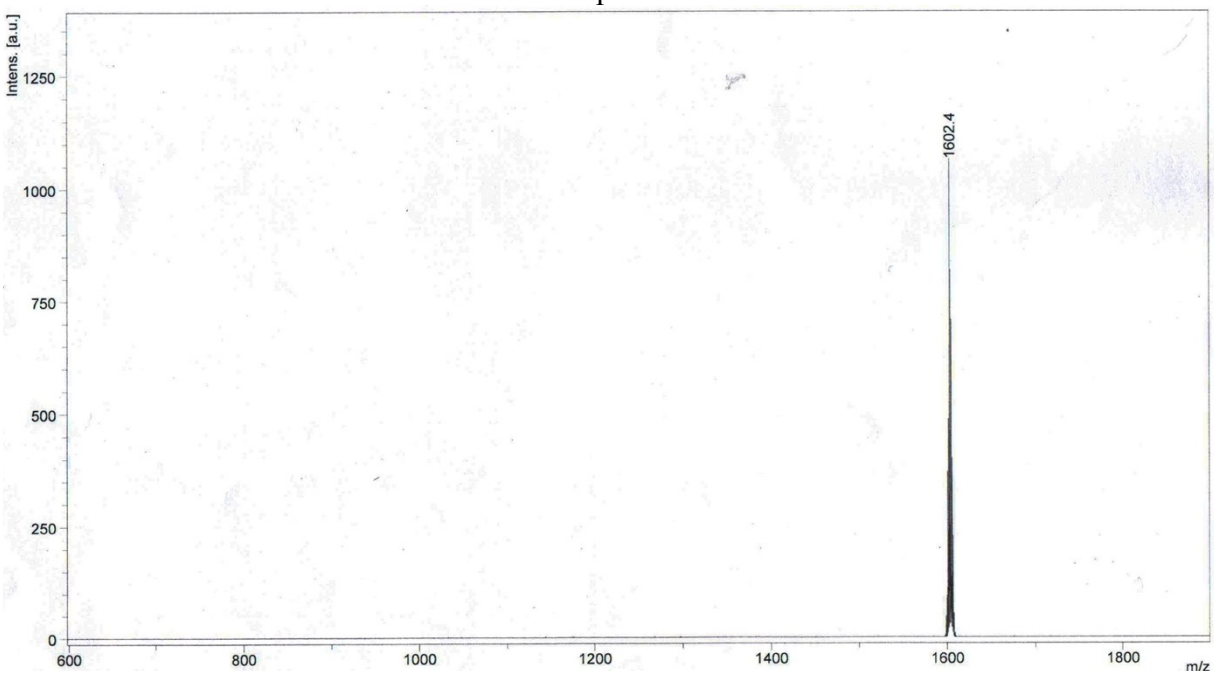


MALDI-TOF mass spectrum of **BDSePhCl**



MALDI-TOF mass spectrum of **BDSeThCl**