Tunable charge-transport polarity in thienothiophene–bisoxoindolinylidene-benzodifurandione copolymers for high-performance field-effect transistors

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Contents

1. GPC characterization

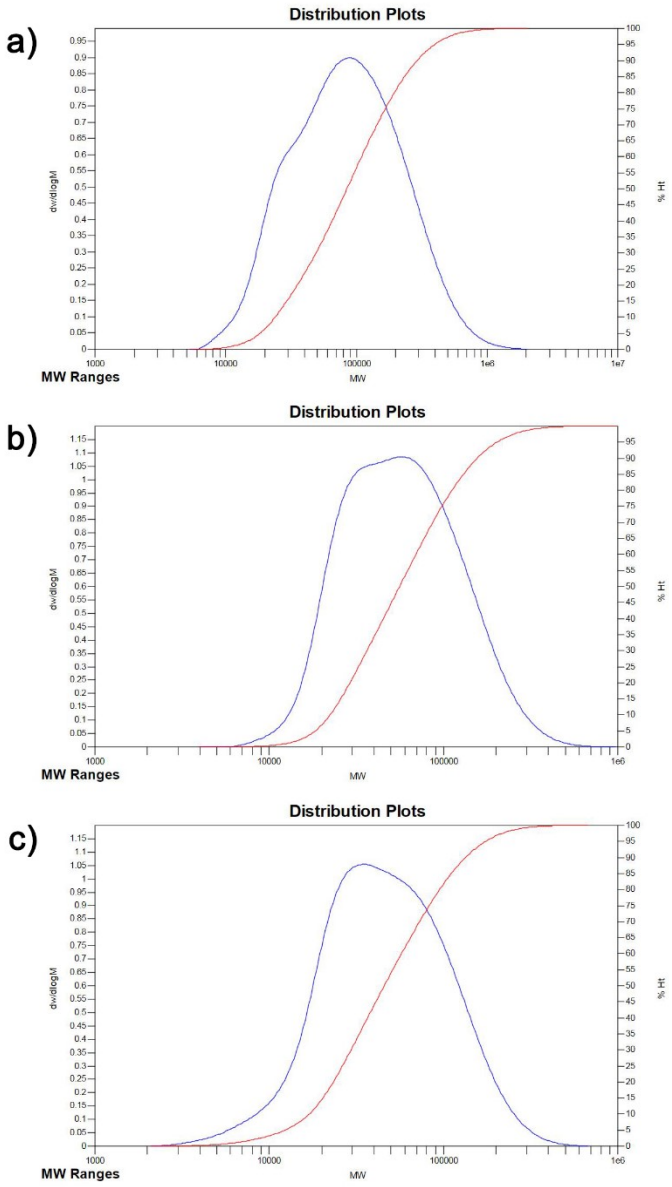


Fig. S1 High temperature GPC plots of **PNBDO-TT**, **PNBDO-DMTT**, and **PNBDO-MOTT**.

Table S1 Molecular weights and distribution data extracted from high temperature GPC plots

polymer	M_p	M_n	M_v	M_w	M_z	M_z+1	$Đ$
PNBDO-TT	88749	54357	113386	128806	277609	491043	2.3696
PNBDO-DMTT	57162	43665	69156	75295	129269	201157	1.7244
PNBDO-MOTT	35061	32462	57315	62940	111681	173678	1.9389

2. Thermogravimetric analysis

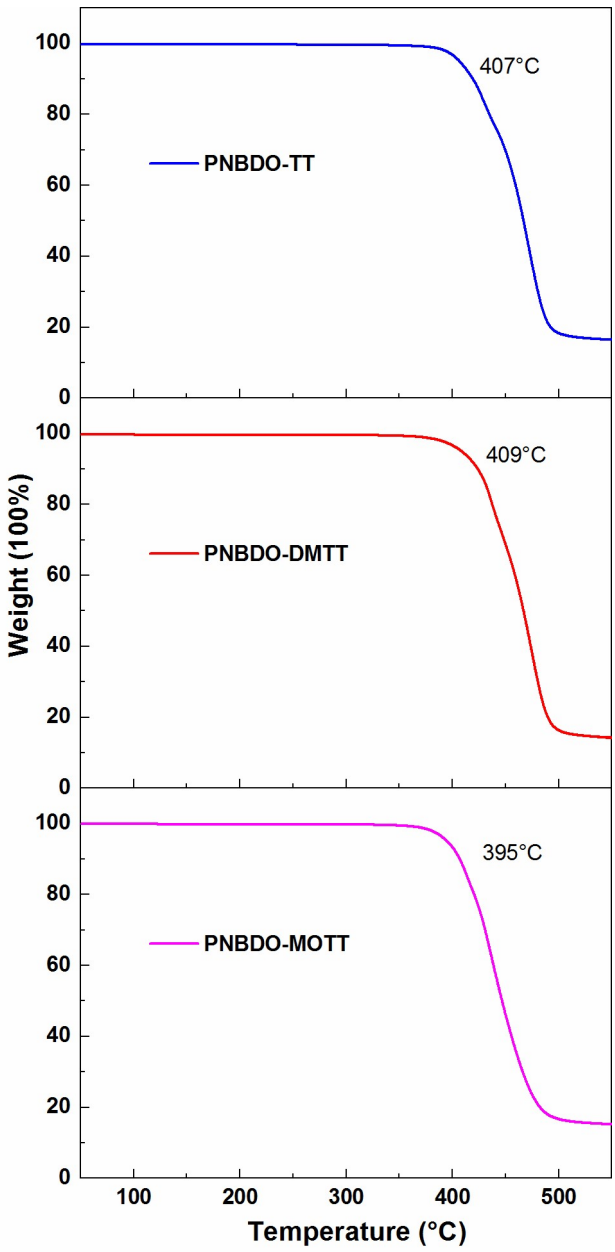


Fig. S2 TGA traces of **PNBDO-TT**, **PNBDO-DMTT**, and **PNBDO-MOTT**. The inset values are their respective T_{dec} of three polymers.

3. UPS measurements

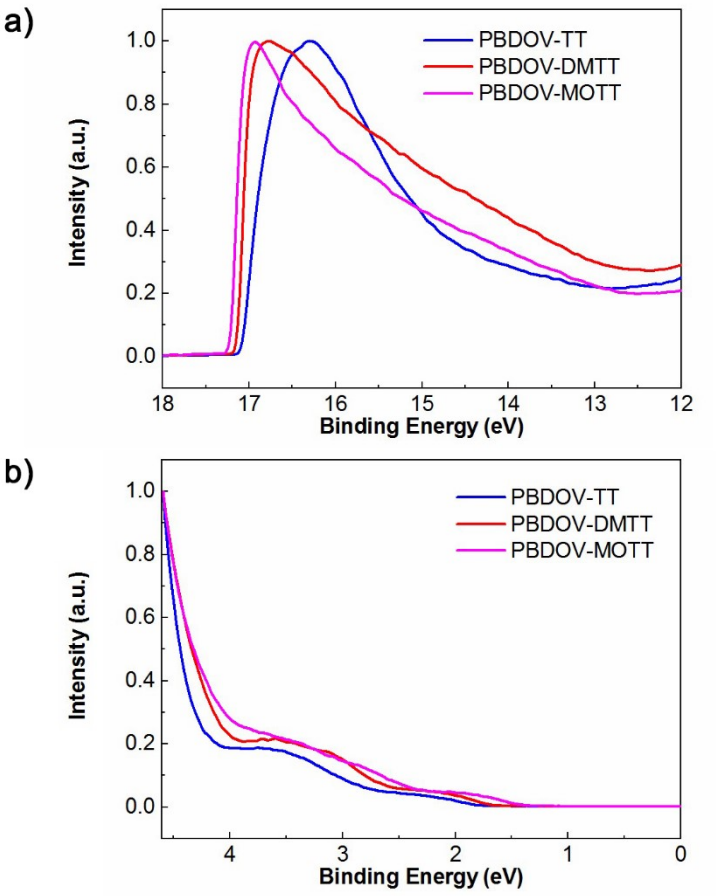


Fig. S3 UPS spectra of **PNBDO-TT**, **PNBDO-DMTT**, and **PNBDO-MOTT** thin films: (a) secondary electron cutoff spectra and (b) valence band spectra.

Table S2 UPS Parameters of **PNBDO-TT**, **PNBDO-DMTT**, and **PNBDO-MOTT**

polymer	E_{cutoff} (eV)	$E_{\text{H, onset}}$ (eV)	IP (eV)	E_{HOMO}^{UPS} (eV)
PNBDO-TT	17.08	1.78	5.92	−5.92
PNBDO-DMTT	17.15	1.65	5.72	−5.72
PNBDO-MOTT	17.22	1.41	5.41	−5.41

4. Cyclic voltammetry

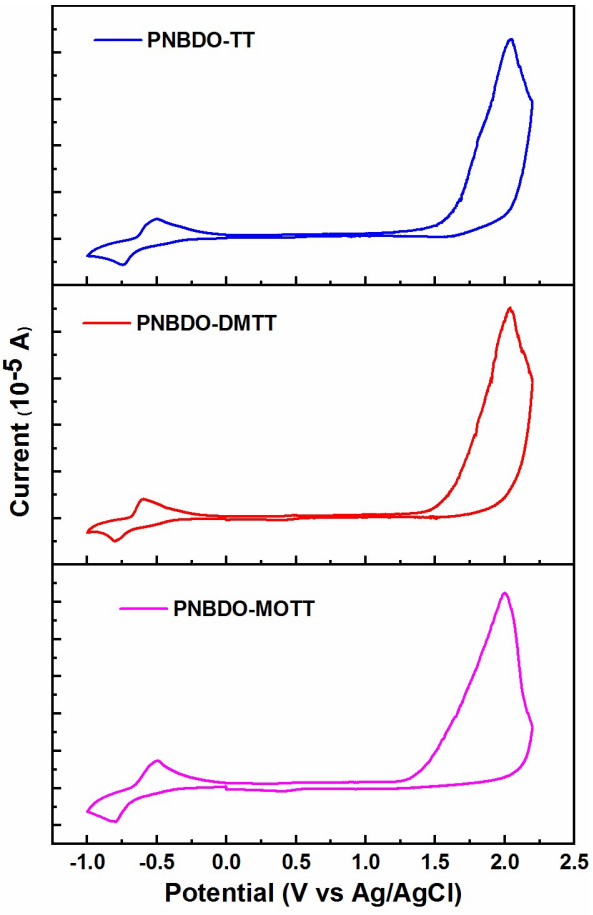


Fig. S4 CV curves of **PNBDO-TT**, **PNBDO-DMTT**, and **PNBDO-MOTT**.

5. Theoretical modeling

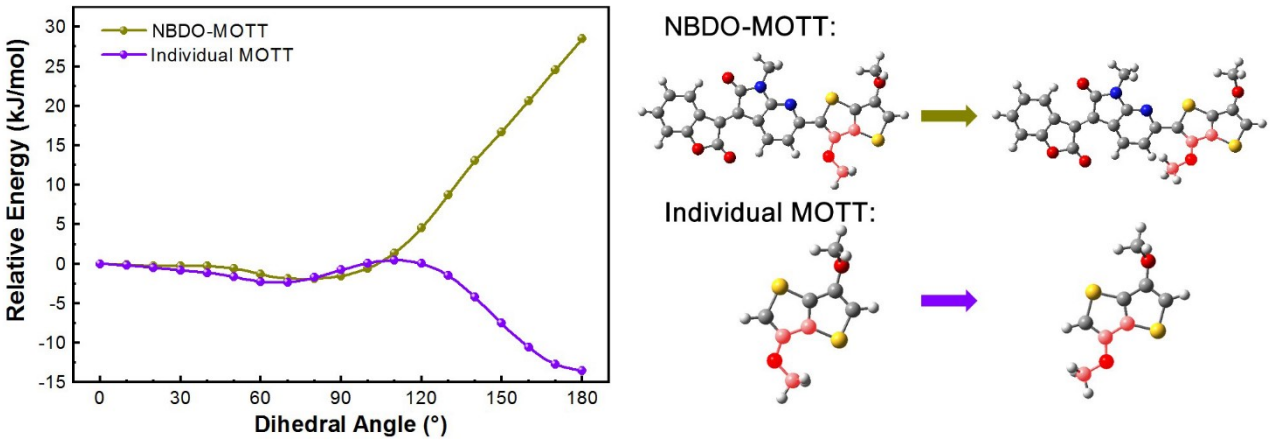


Fig. S5 Potential energy distributions of **MOTT**-based subunit by rotation of the methoxy groups. An individual **MOTT** unit was also studied for comparison. The single point energies were calculated at the MP2/ccpvdz level.

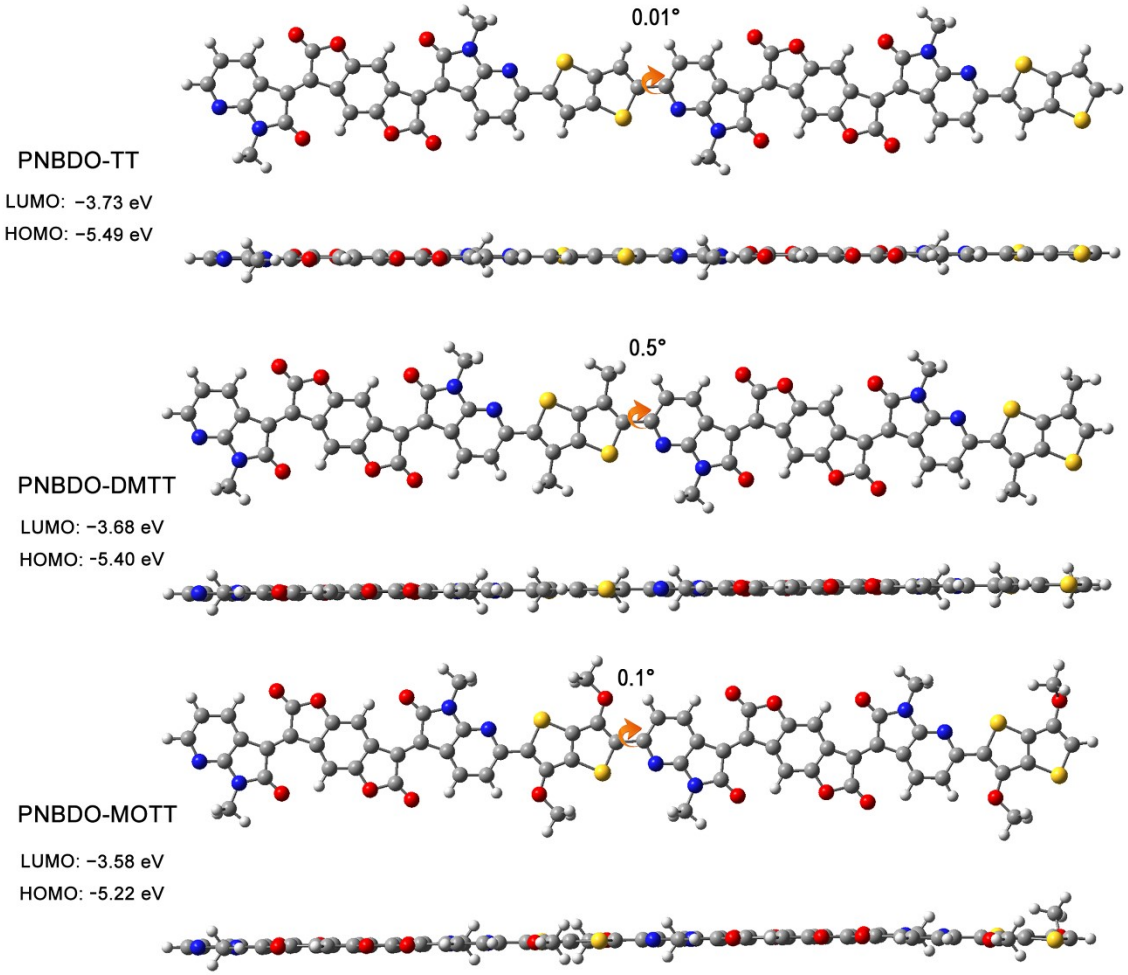


Fig. S6 Optimized molecular geometries of **PNBDO-TT**, **PNBDO-DMTT**, and **PNBDO-MOTT** (dimmers) using the density functional theory at the B3LYP/6-31G(d) level.

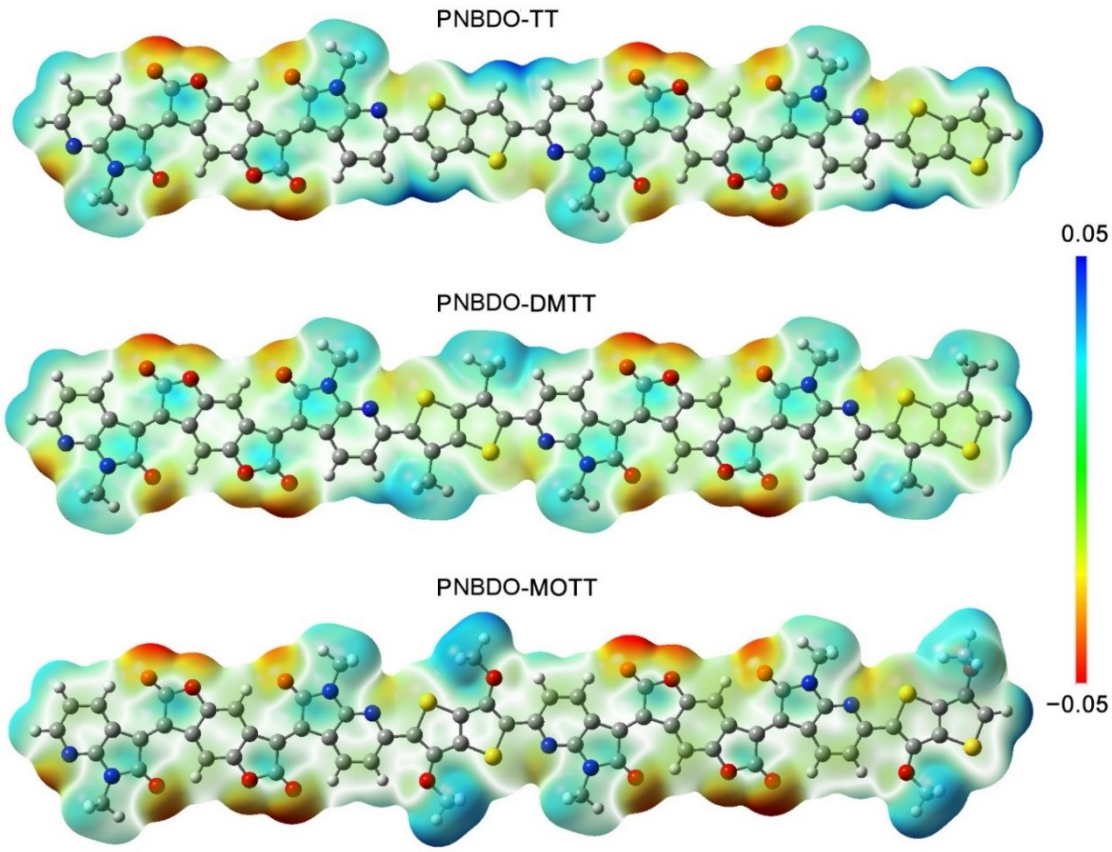


Fig. S7 Electrostatic potential surface plots of **PNBDO-TT**, **PNBDO-DMTT**, and **PNBDO-MOTT** (dimmers) at isovalue = 0.001 au.

Figs. S7−S9 illustrate reduce density gradient versus sign (λ_2)ρ plots of **NBDO-TT**, **NBDO-DMTT**, and **NBDO-MOTT** subunits. The low-gradient, low-density spikes show the noncovalent interactions. Note that the attractions are negative, and their densities are larger than those of the competitive repulsions to stabilize the planar conformations. In all three subunits, considering the strength of attractions, the S···N conformation is the most stable local minimum.

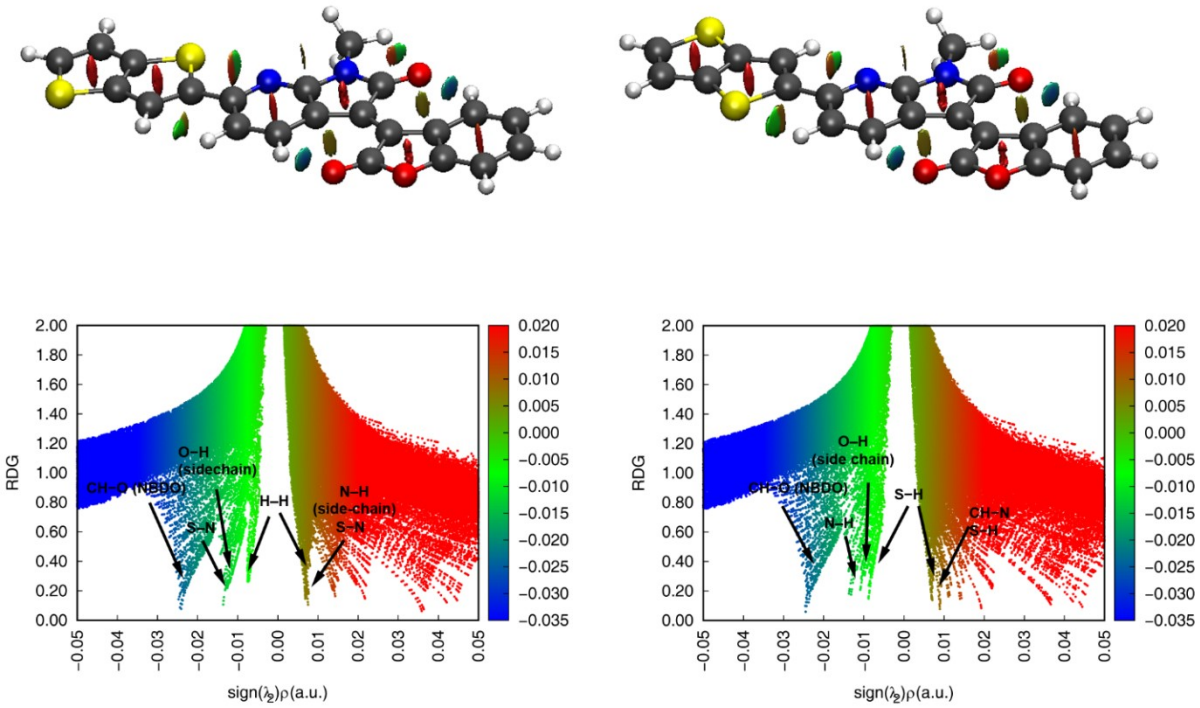


Fig. S8 Reduced density gradient analysis of the **NBDO−TT** subunit.

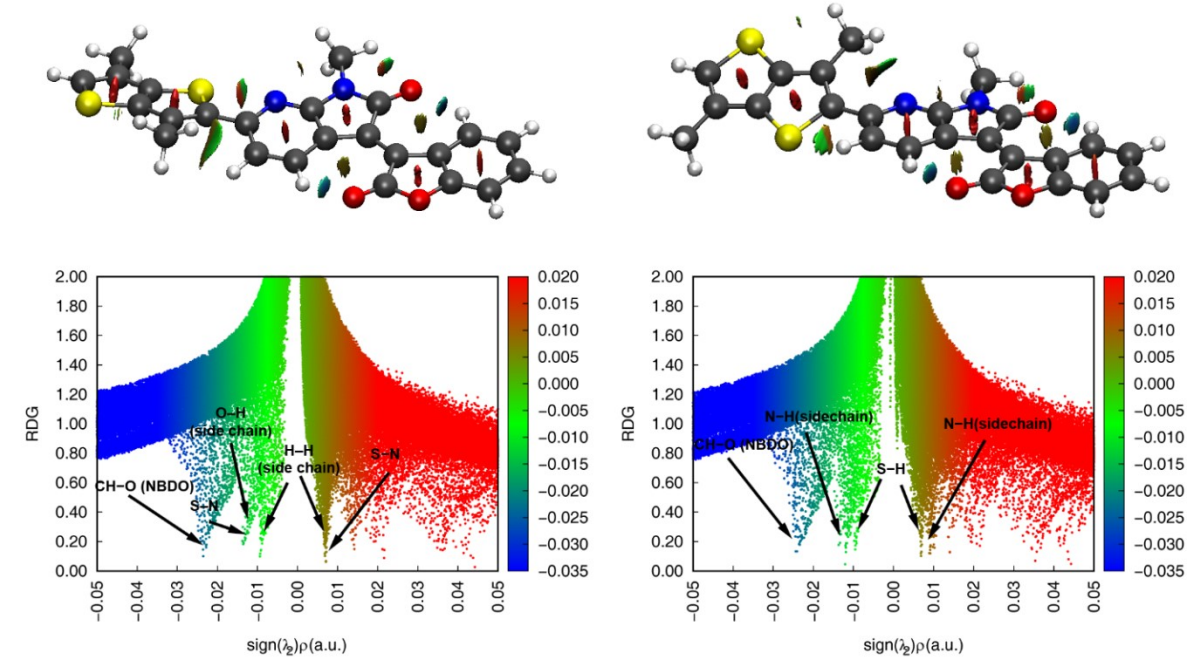


Fig S9 Reduced density gradient analysis of the **NBDO−DMTT** subunit.

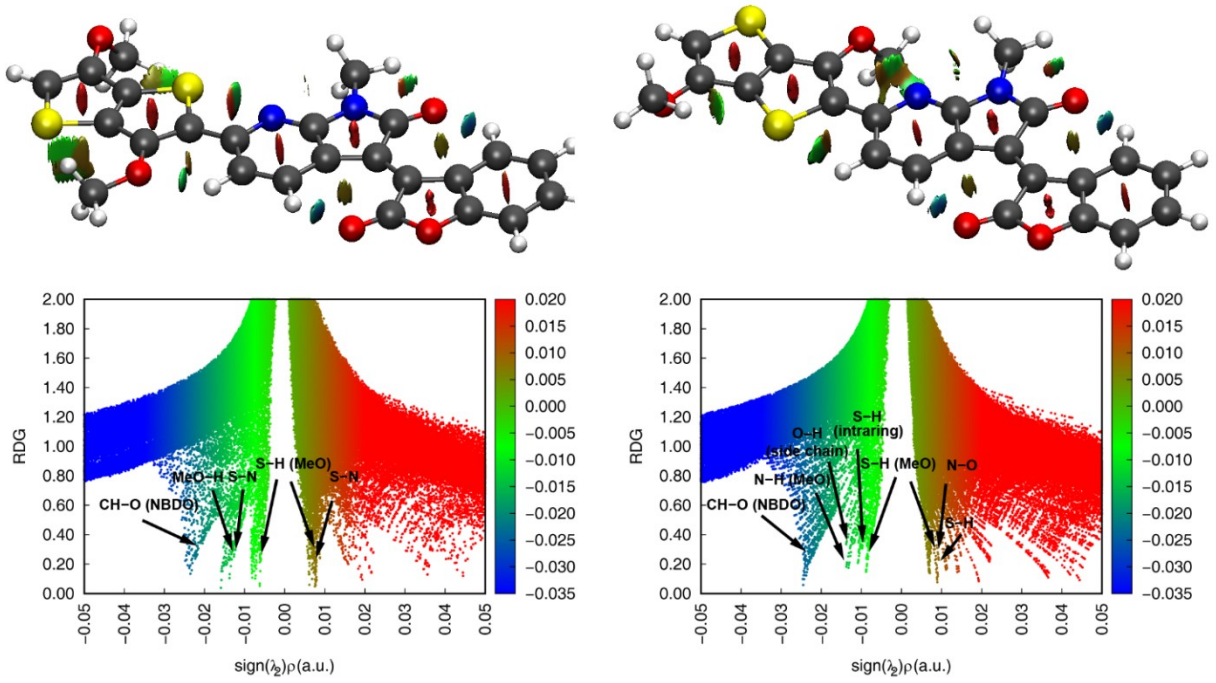


Fig. S10 Reduced density gradient analysis of the **NBDO−MOTT** subunit.

6. Annealing temperature-dependent mobilities of PNBDO-TT

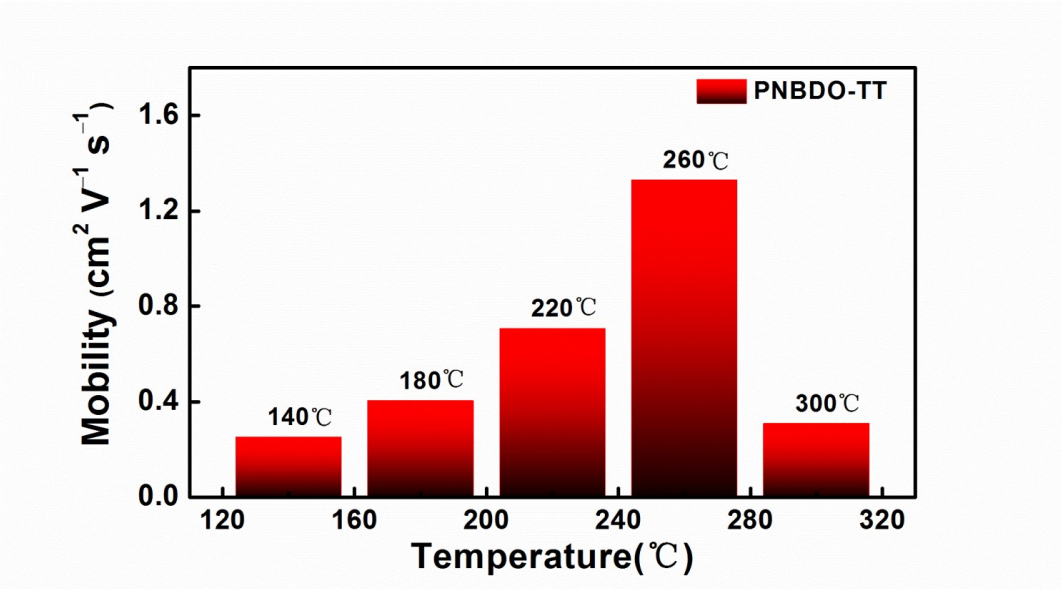


Fig. S11 Annealing temperature-dependent mobilities of **PNBDO-TT**-based FET device.

7. Thin film morphology and aggregation characterizations

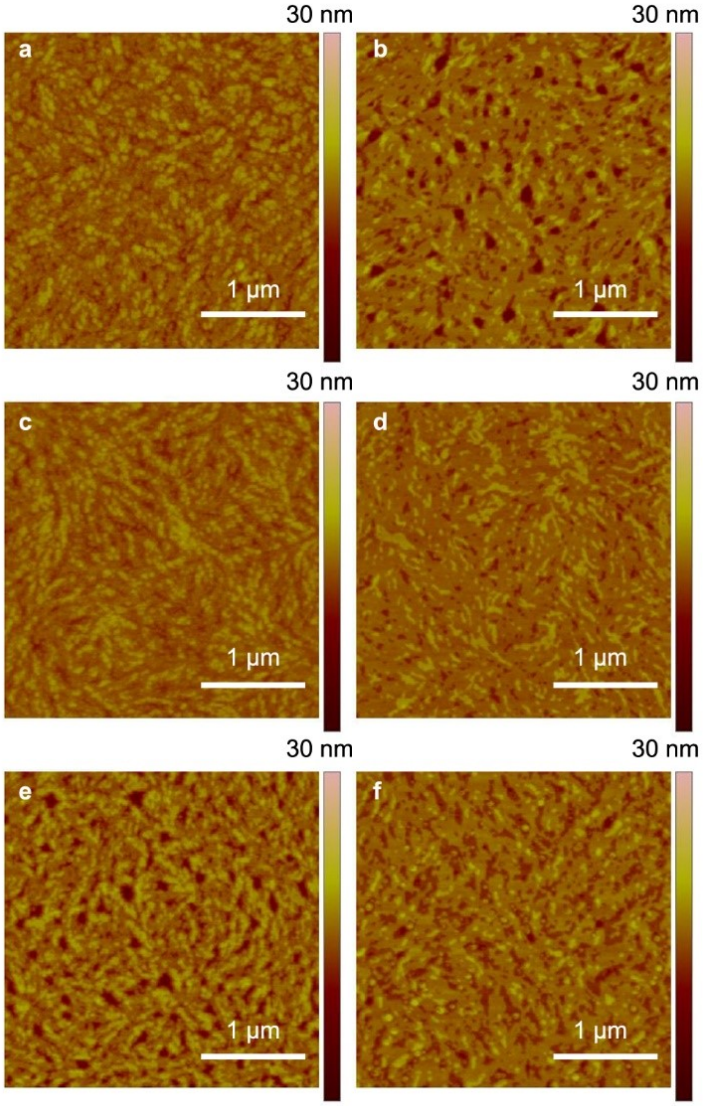


Fig. S12 AFM images of polymer thin films in as-spun (a, c, e) and annealed thin films (b, d, f): (a, b) **PNBDO-TT**, (c, d) **PNBDO-DMTT**, and (e, f) **PNBDO-MOTT**.

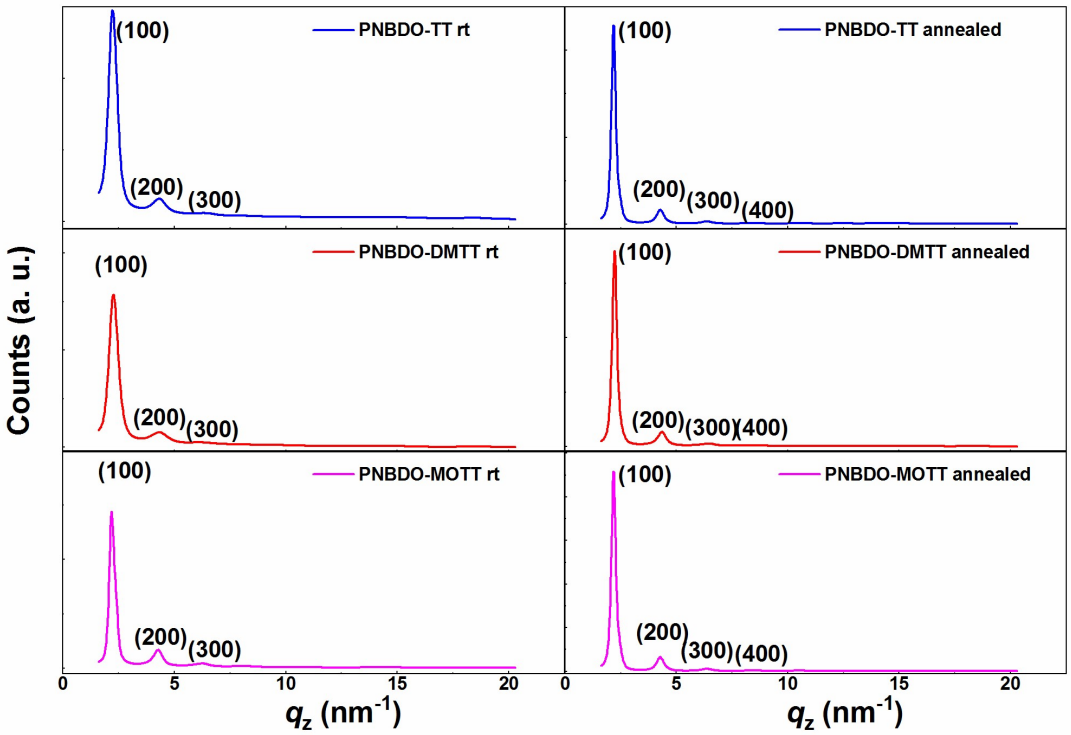


Fig. S13 1D Out-of-plane diffraction patterns of polymer thin films extracted from GIWAXS tests.

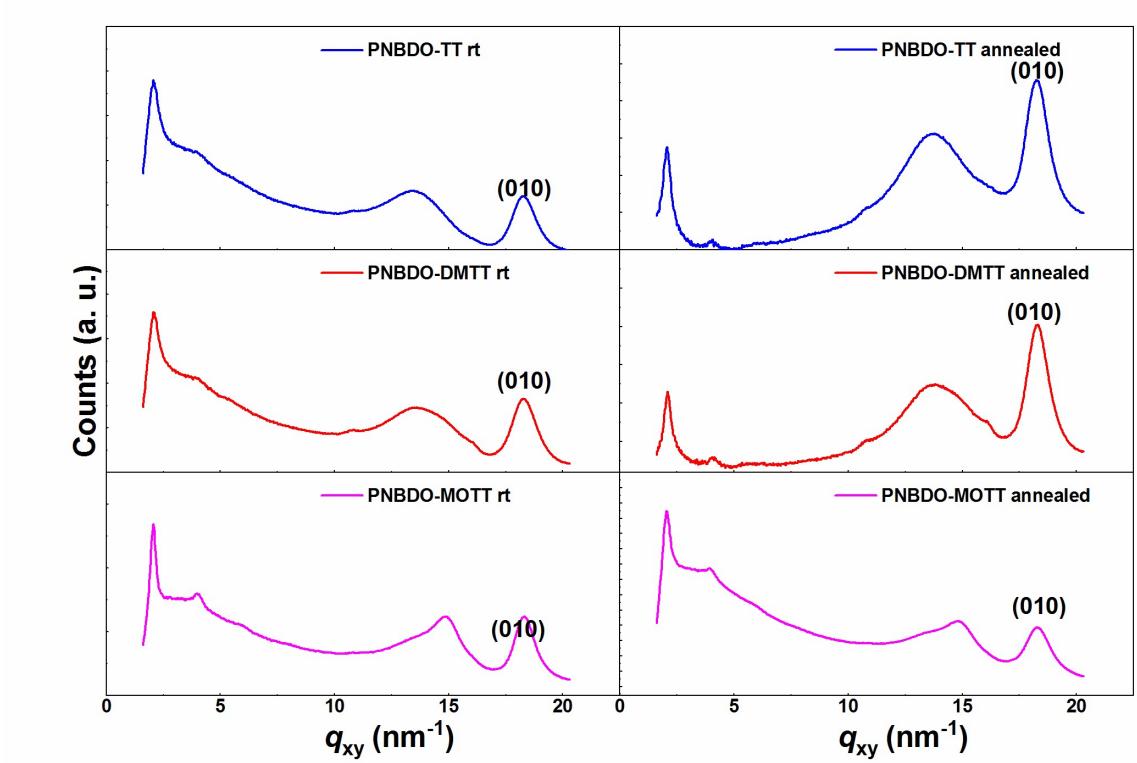
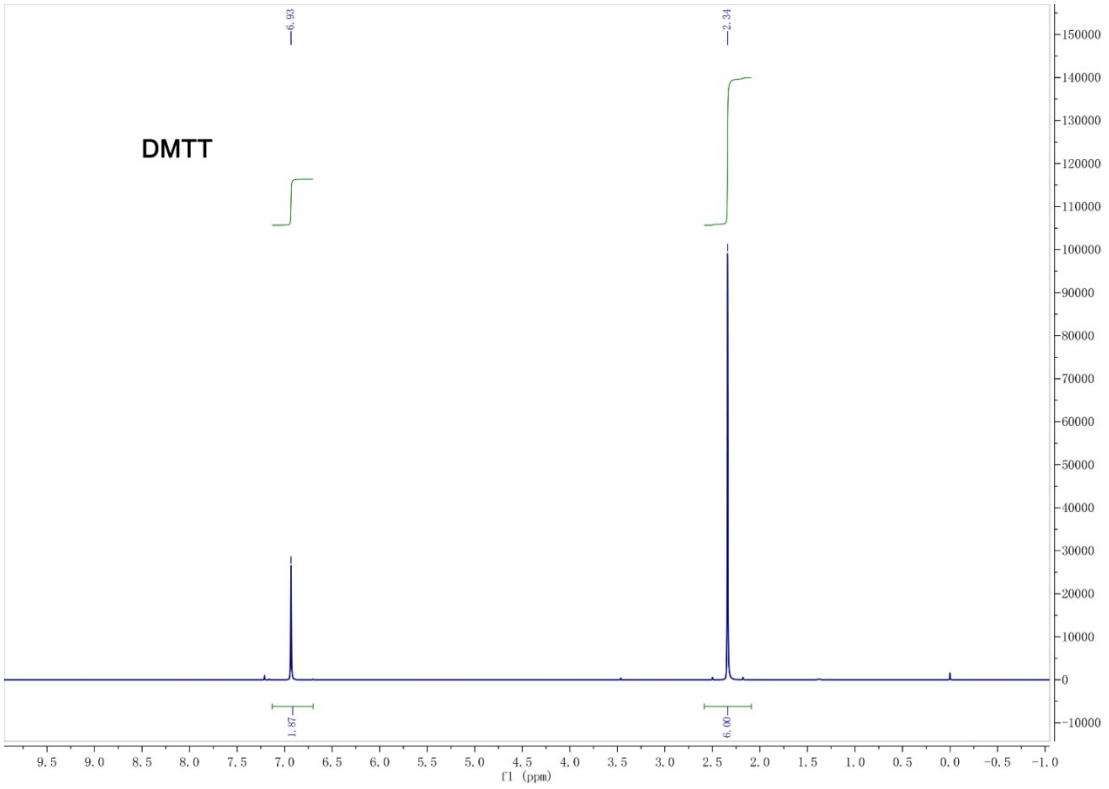
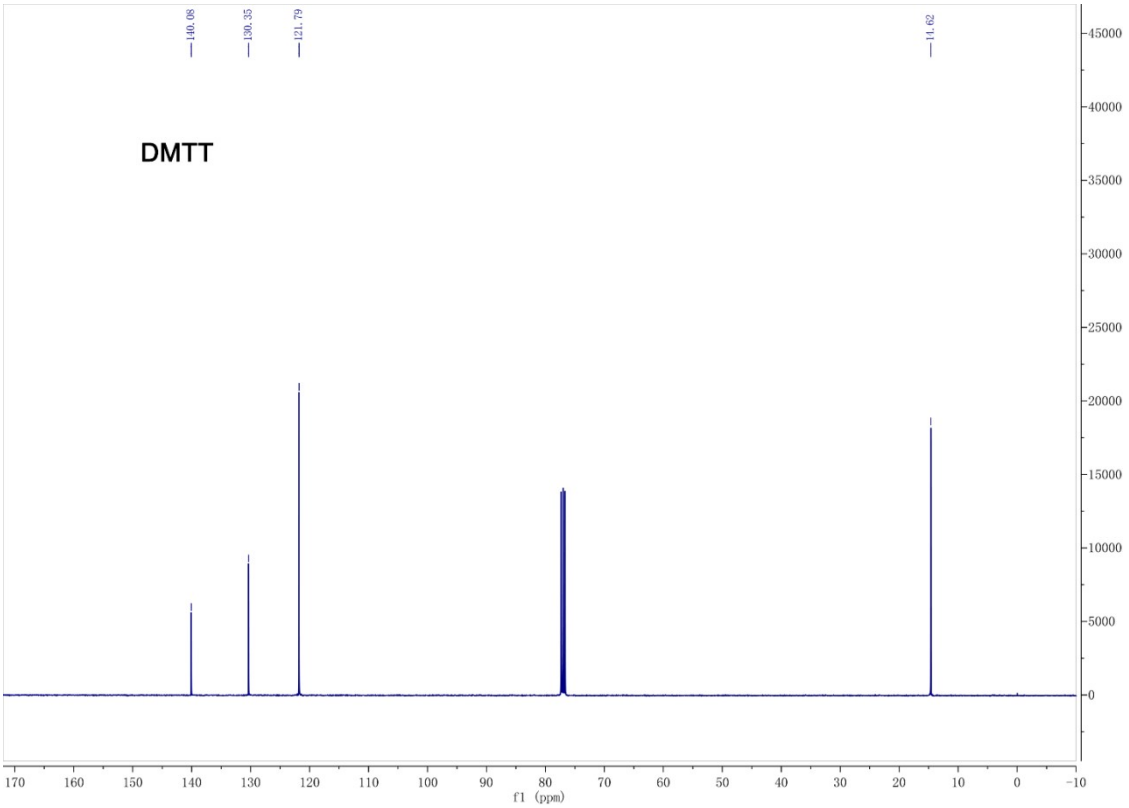
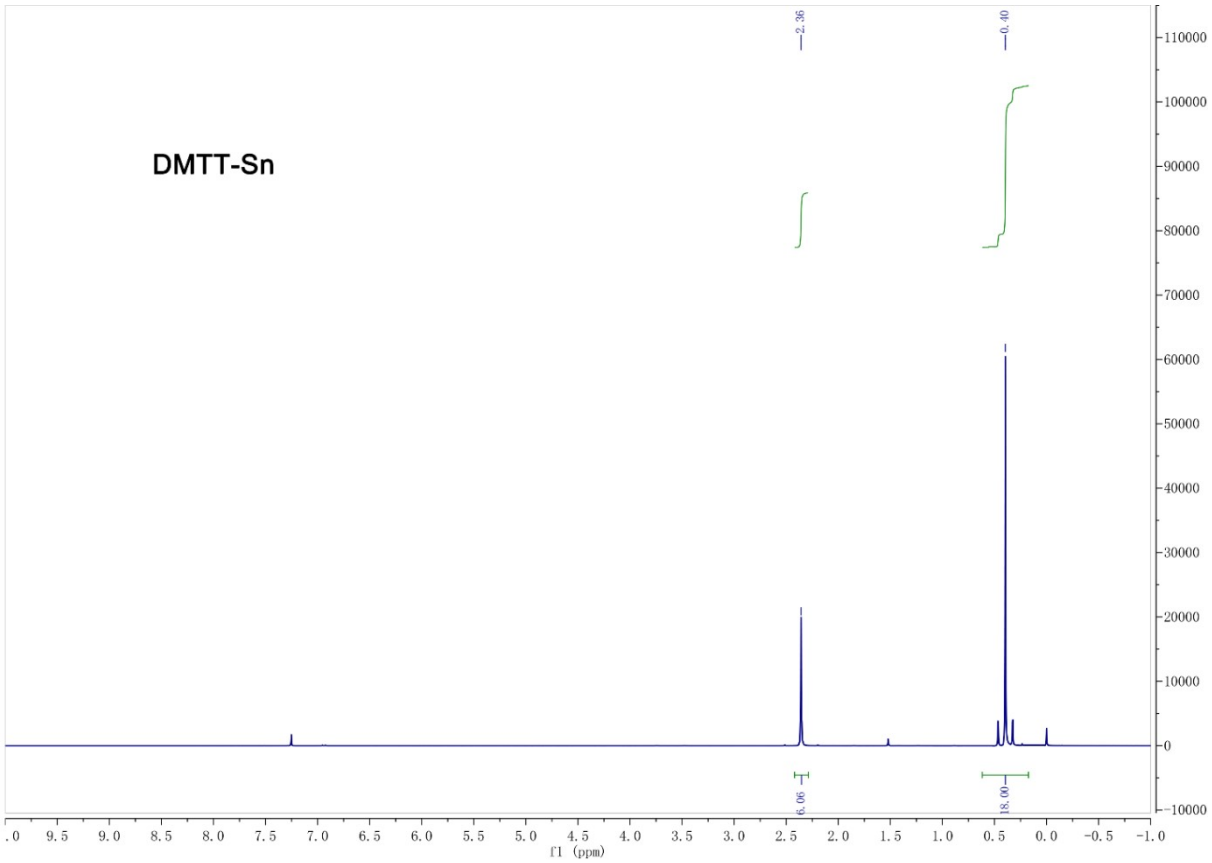


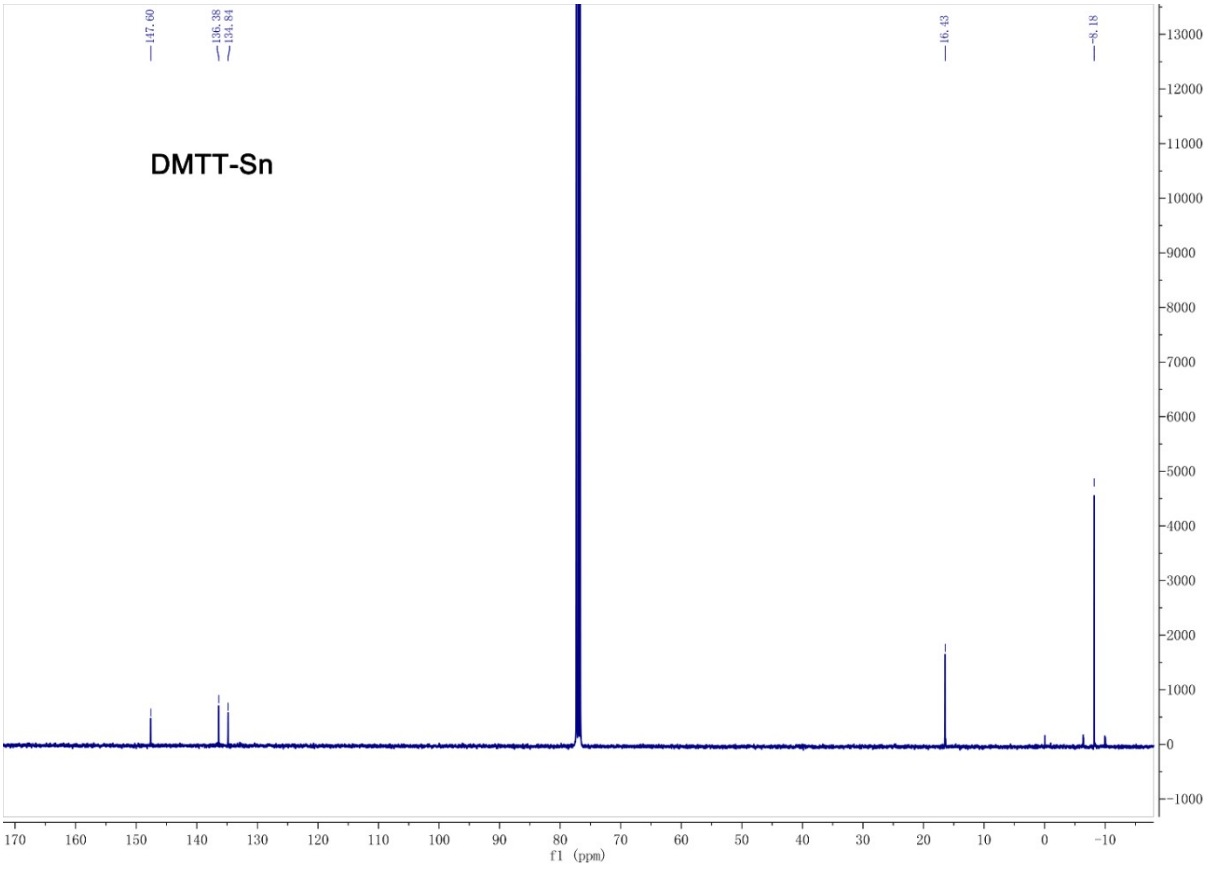
Fig. S14 1D In-plane diffraction patterns of polymer thin films extracted from GIWAXS tests.

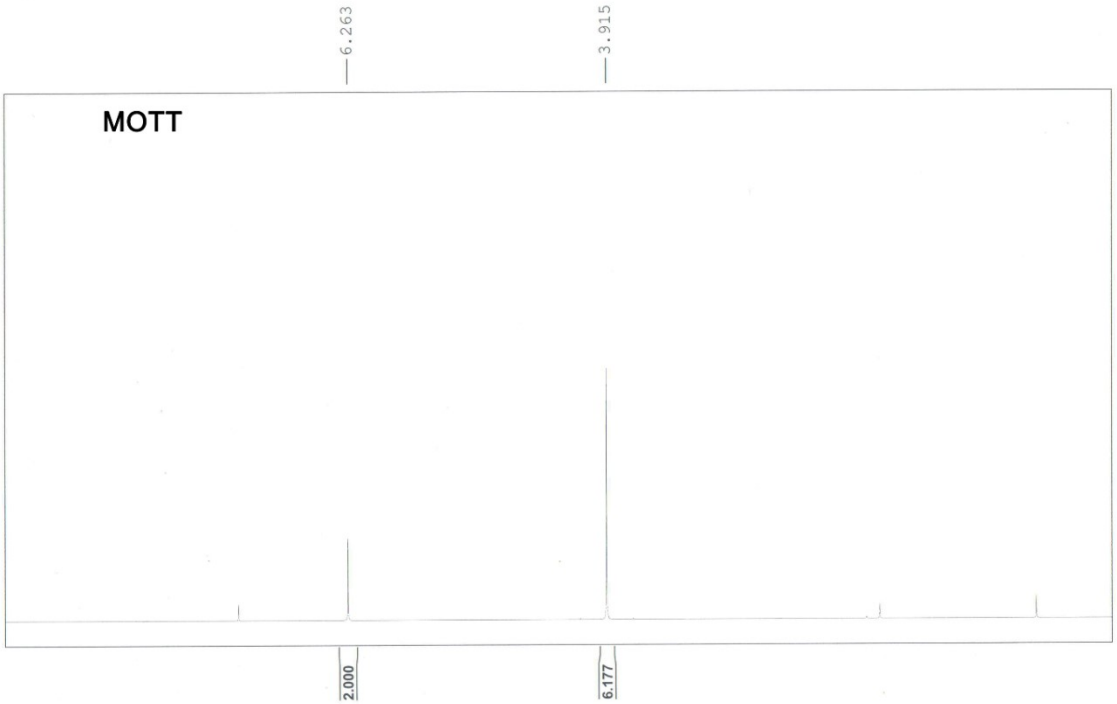
8. NMR spectra of intermediates and polymers

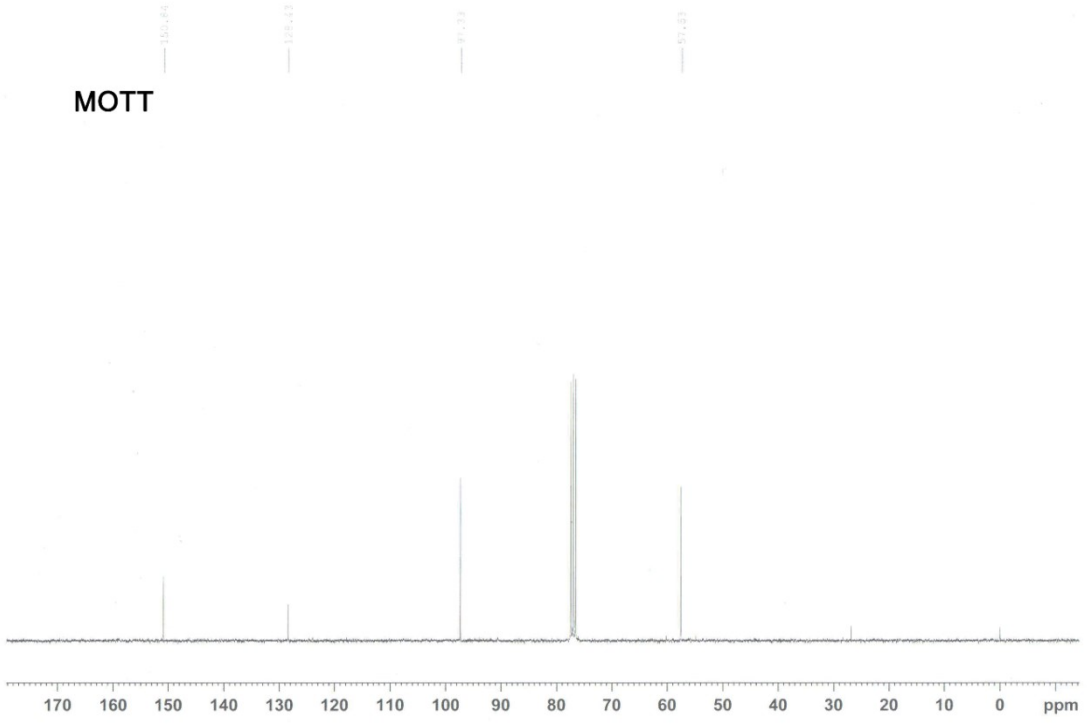


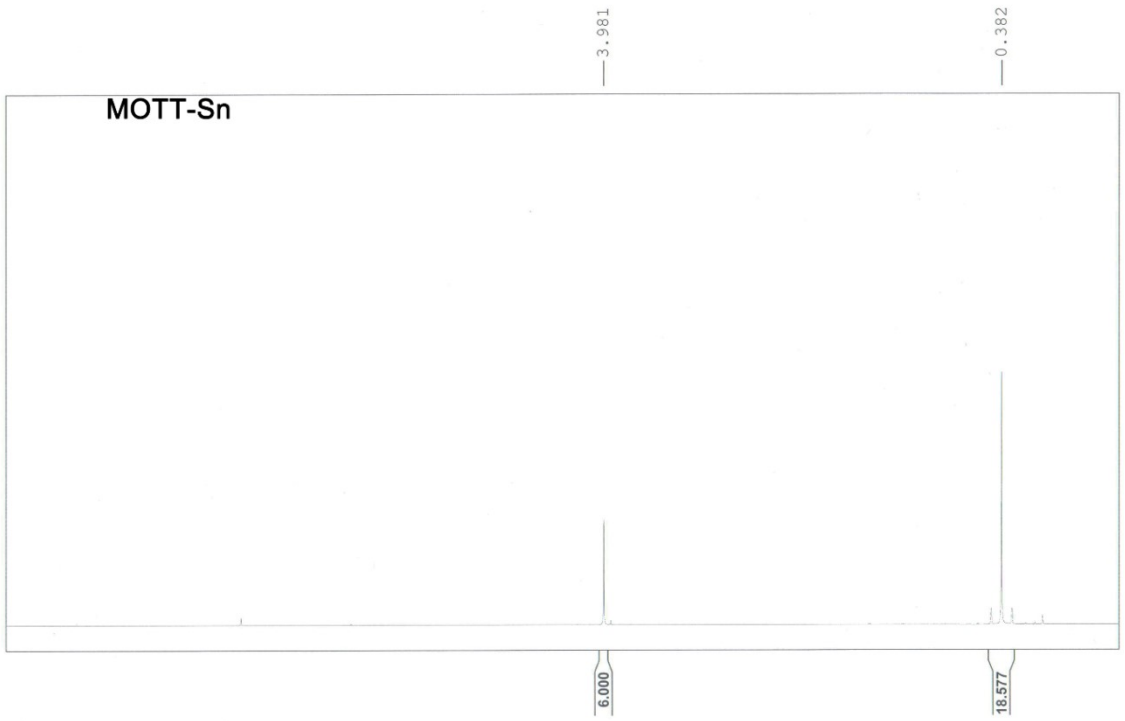


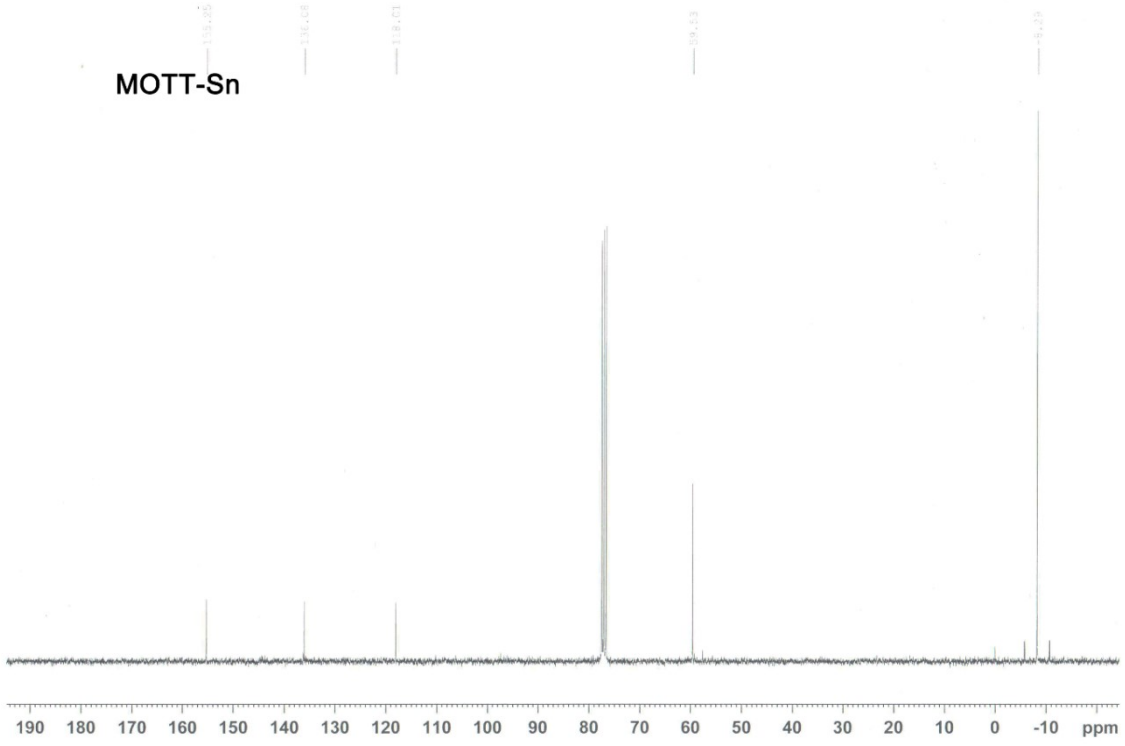

DMTT-Sn
2.36
0.40
6.06
18.00
f1 (ppm)

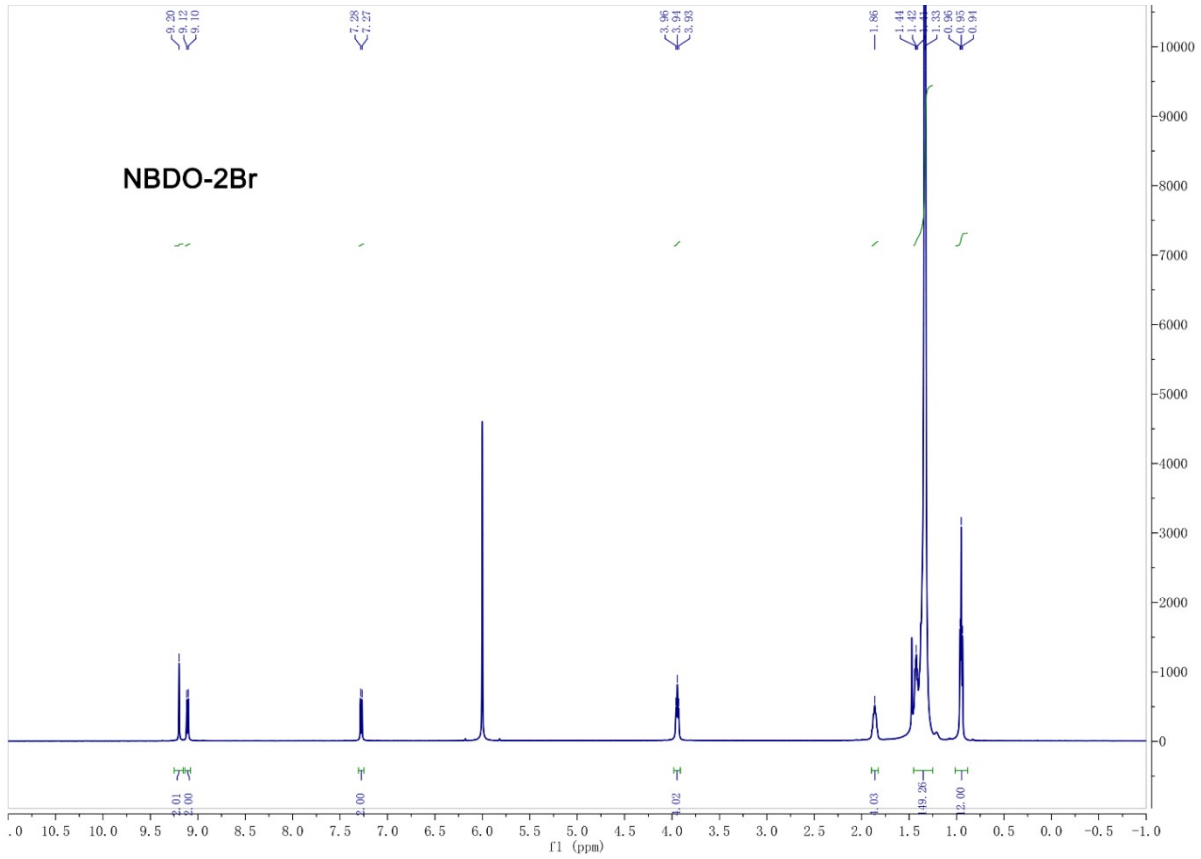

DMTT-Sn
147.60
136.38
134.84
16.43
-8.18
f1 (ppm)

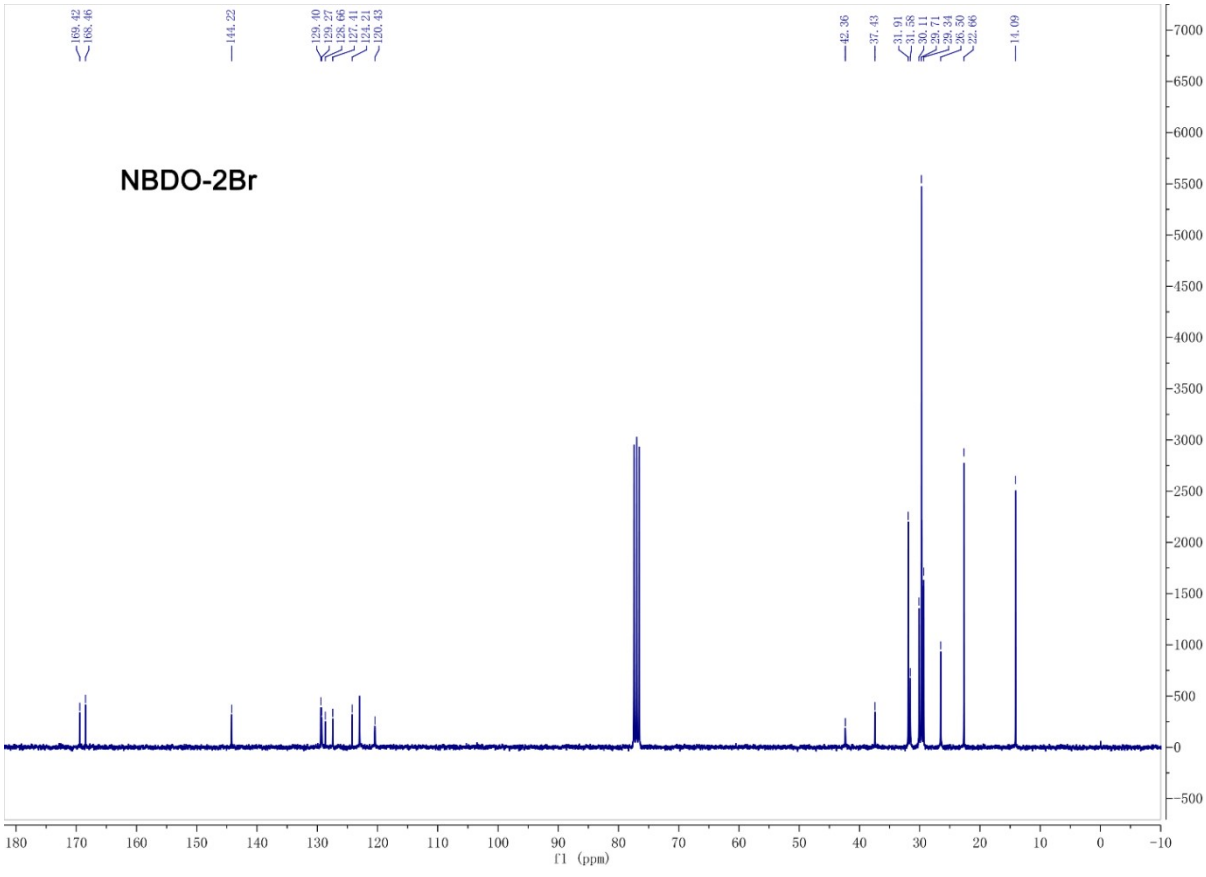

6.263
3.915
MOTT
2.000
6.177

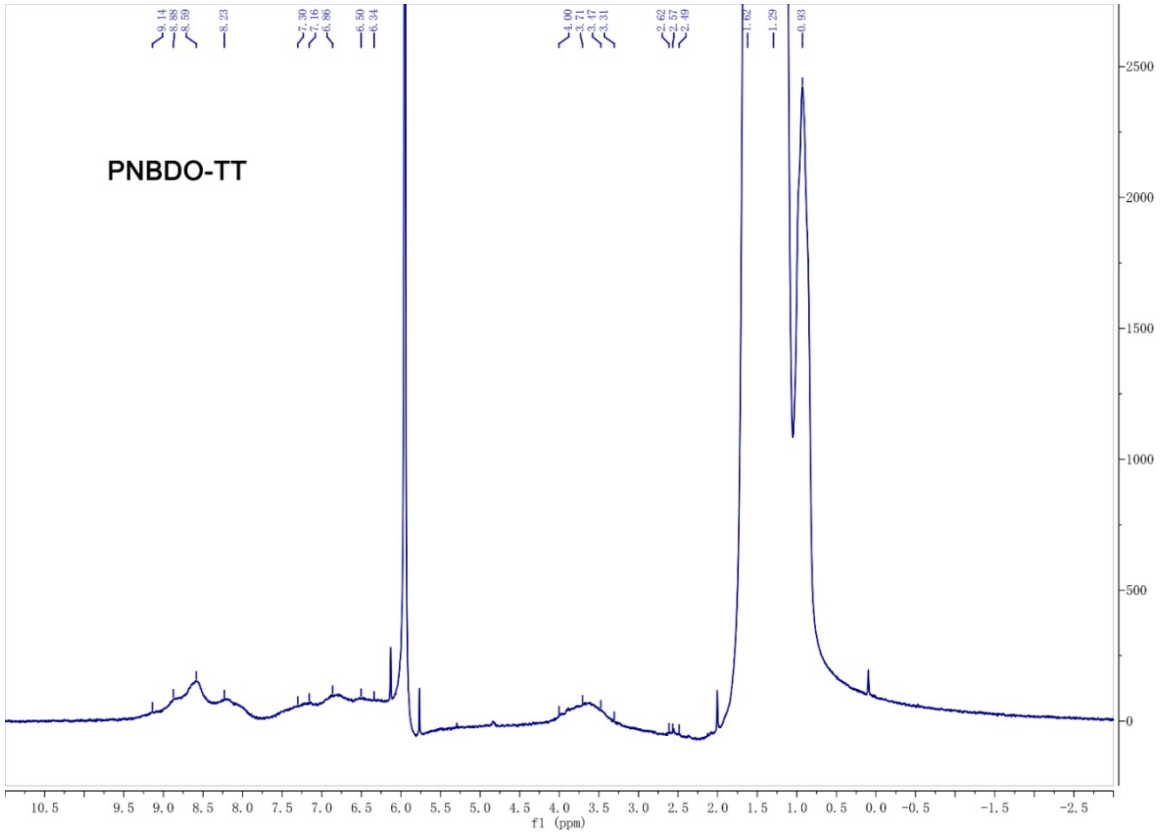

MOTT
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

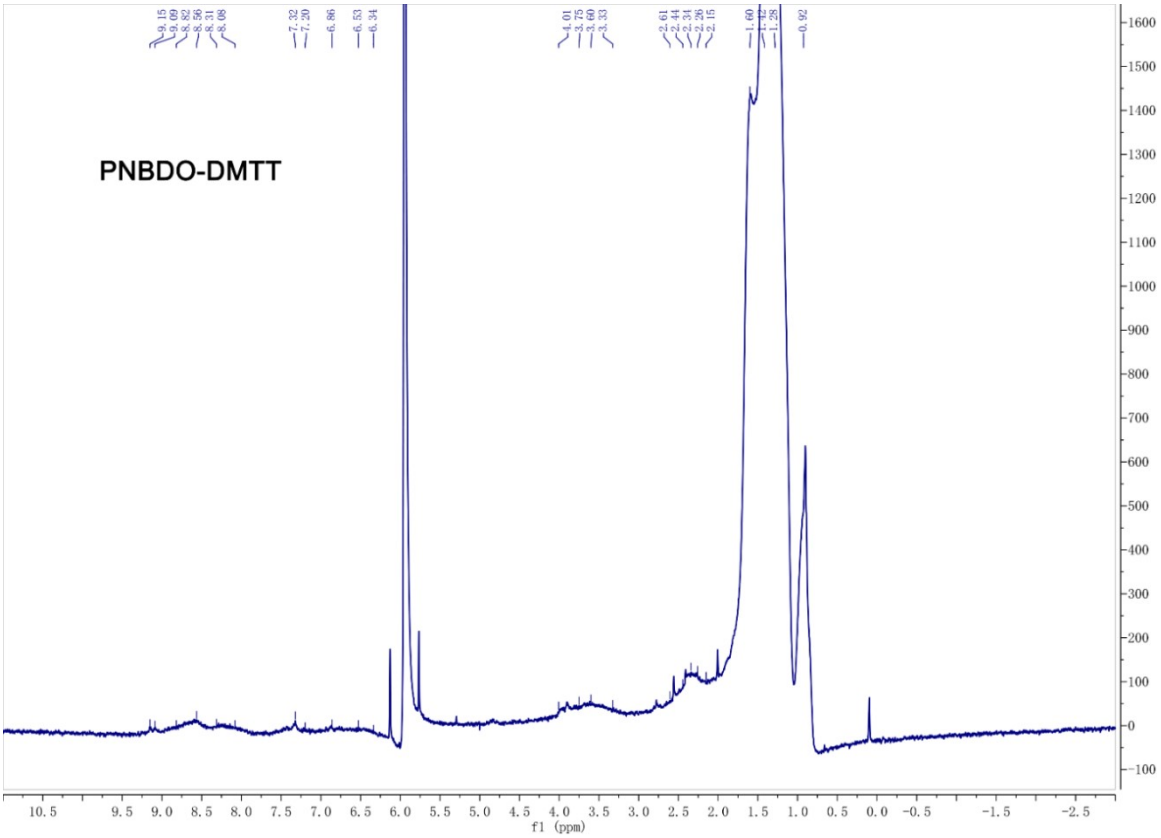

MOTT-Sn
3.981
0.382
6.000
18.577


MOTT-Sn
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


NBDO-2Br
9.20
9.12
9.10
7.28
7.27
3.96
3.94
3.93
1.86
1.44
1.42
1.33
0.96
0.95
0.94
2.01
2.00
2.00
4.02
4.03
149.26
12.00
f1 (ppm)


NBDO-2Br
168.42
168.46
144.22
129.40
129.27
128.66
127.41
124.21
120.43
42.36
37.43
31.91
31.58
30.11
29.71
29.34
26.50
22.06
14.09
f1 (ppm)


PNBDO-TT
9.14
8.88
8.59
8.23
7.39
7.16
6.86
6.59
6.34
4.00
3.71
3.47
3.31
2.62
2.57
2.49
1.62
1.29
0.93
f1 (ppm)


PNBDO-DMTT
9.15
9.09
8.82
8.56
8.31
8.08
7.32
7.29
6.86
6.53
6.34
4.01
3.75
3.60
3.33
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2.44
2.34
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2.15
1.60
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1.28
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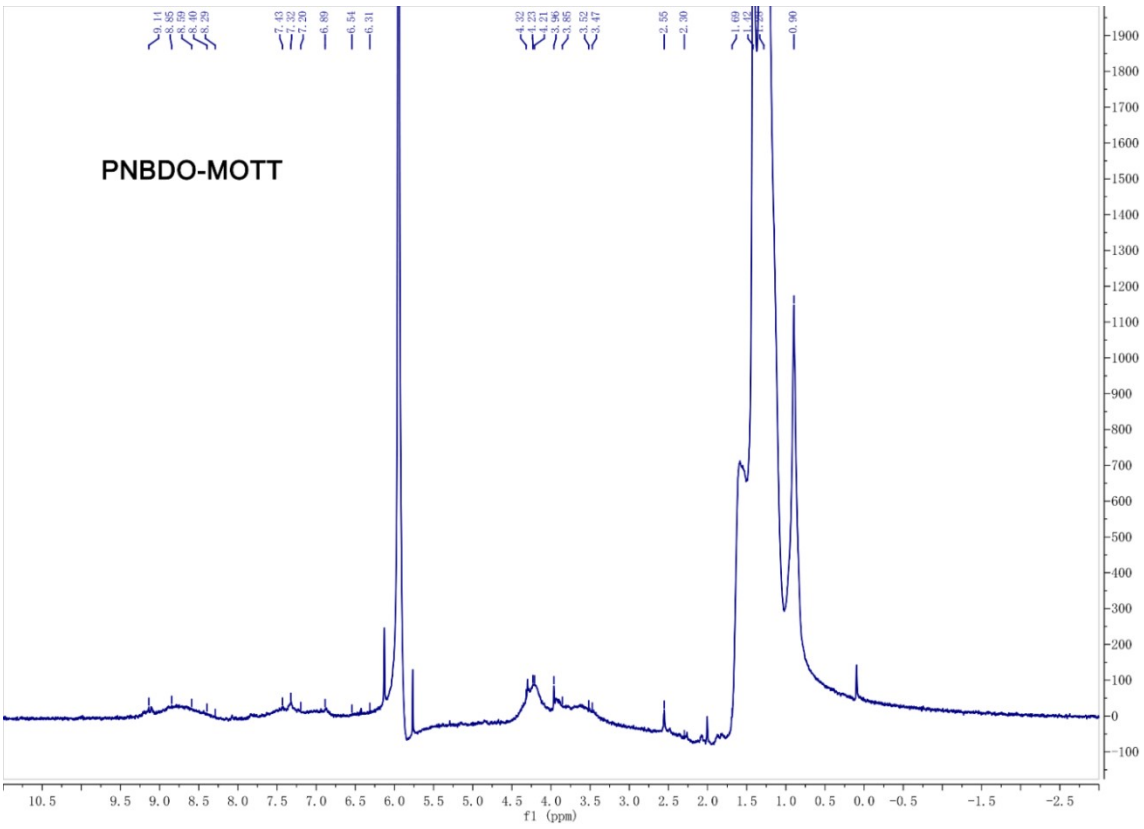
f1 (ppm)


PNBDO-MOTT
9.14
8.95
8.59
8.40
8.29
7.43
7.32
7.20
6.89
6.54
6.31
4.32
4.23
4.21
3.96
3.85
3.52
3.47
2.55
2.30
1.69
0.90
f1 (ppm)