Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information

Manipulating Solubility Property of Polymer Donor for High-Performance Layer-by-Layer Processed Organic Solar Cells

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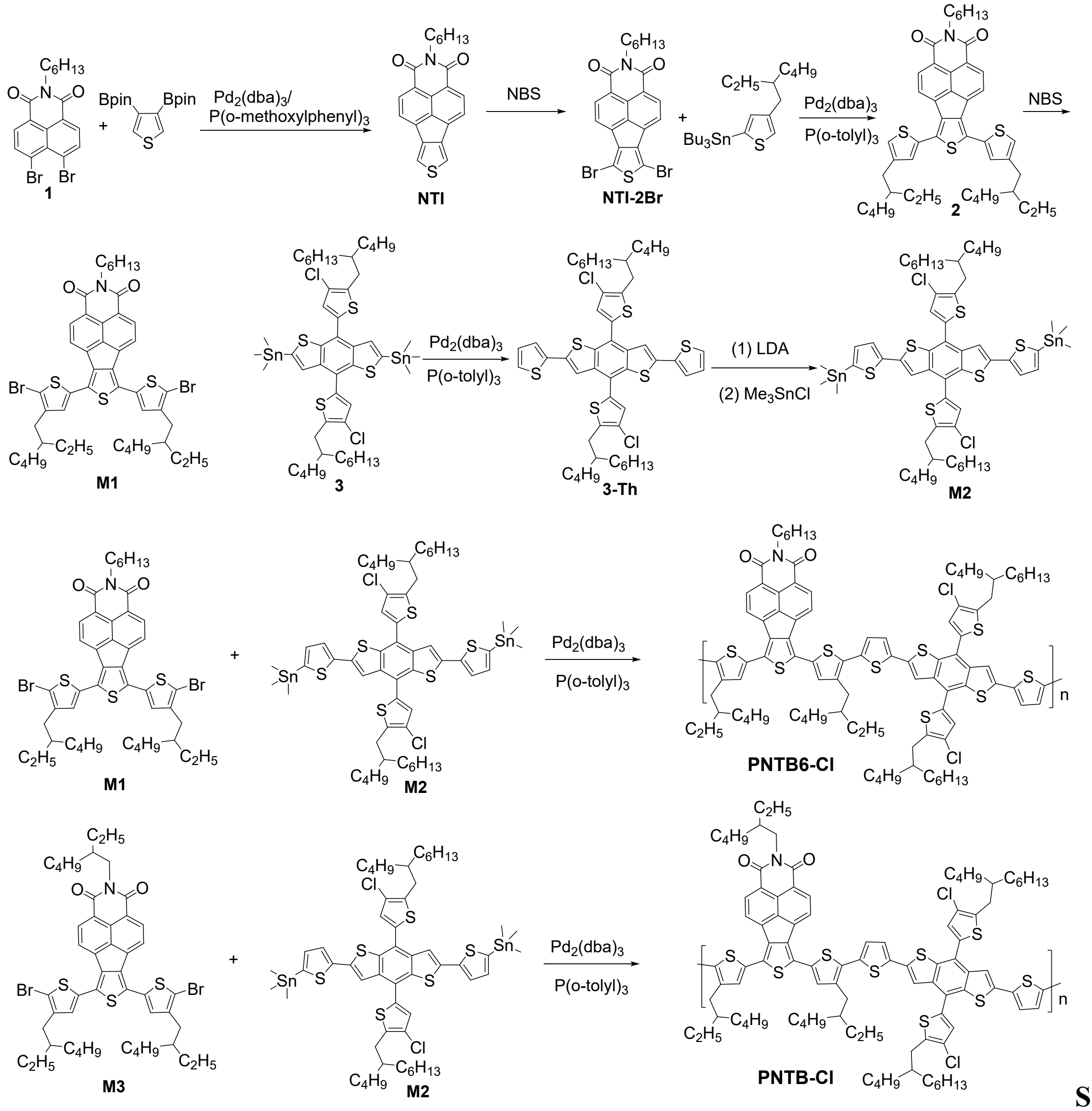
Experimental Procedures

1. The synthesis and characterization



Scheme S1. The synthesis of polymer PNTB-Cl and PNTB6-Cl.

The monomer M3 and compound 1 were synthesized according to the literature. [1]

NTI. THF (15 ml) and 2M K_2CO_3 aqueous solution (4 ml) was added to the mixture of compound **1** (2g), 3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (1.50 g), $Pd_2(dba)_3$ (0.21 g) and $P(MeOPh)_3$ (0.65 g) under nitrogen protection. After refluxing 6 hours, the mixture was poured into ethanol. The precipitate was filtered and purified by column chromatography, using hexane:CH_2Cl_2 = 1:1 as the eluent, 1.24 g **NTI** was obtained in the yield of 75 %. ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 8.33 (d, J = 6.8 Hz, 2H), 7.65 (d, J = 7.2 Hz, 2H), 7.46 (s, 2H), 4.11 (t, J = 8.0 Hz, 2H), 1.70 (br, 2H), 1.34 (br, 6H), 0.89 (t, J = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) (ppm): 163.82, 144.36, 137.93, 132.19, 130.83, 121.17, 119.90, 119.19, 105.13, 40.51, 31.69, 28.43, 26.94, 22.70, 14.19.MS (MALDI-TOF) $C_{22}H_{19}NO_2S$ m/z: 361.11; Found: 361.99 (M+). Anal. Calcd for $C_{22}H_{19}NO_2S$: C, 73.10; H, 5.30; N, 3.88. Found: C, 72.87; H, 5.32; N, 3.94.

NTI-2Br. NBS (1.48 g) were added to the solution of NTI (1.24 g), $CHCl_3$ (28 ml), CF_3COOH (14 ml). After stirring 5 hours, it was purified by column chromatography, using hexane:CH_2Cl_2 = 2:1 as the eluent. 1.43 g **NTI-2Br** (80 %) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 8.41 (d, J = 7.6 Hz, 2H), 7.89 (d, J = 7.6Hz,2H), 4.15 (t, J = 8.0 Hz, 2H), 1.73 (br, 2H), 1.36 (br, 6H), 0.90 (t, J = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) (ppm): 163.42, 143.42, 137.68, 135.71, 131.92, 125.79, 121.57, 119.99, 107.44, 40.60, 31.59, 28.29, 26.88, 22.62, 14.11.MS (MALDI-TOF) $C_{22}H_{17}Br_2NO_2S$ m/z: 516.93; Found: 517.82 (M+). Anal. Calcd for $C_{22}H_{17}Br_2NO_2S$: C, 50.89; H, 3.30; N, 2.70. Found: C, 50.58; H, 3.19; N, 2.68.

Compound 2. Toluene (18 mL) was added to the mixture of compound **NTI-2Br** (1.35 g), compound 2-(tributylstannyl)-4-ethylhexylthiophene (3.77 g), $Pd_2(dba)_3$ (70 mg) and $P(o\text{-}tol)_3$ (180 mg) under nitrogen. After refluxing 4 hours, the solvent was evaporated. The solid was purified by column chromatography, using hexane:CH_2Cl_2 = 3:2 as the eluent. 1.51 g **2** (78 %) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) (ppm): 8.28 (d, J = 7.6 Hz, 2H), 8.08 (d, J = 7.6 Hz, 2H), 7.23 (s, 2H), 7.04 (s, 2H), 4.10 (t, J = 7.6 Hz, 2H), 2.62 (d, J = 7.2 Hz, 4H), 1.61 (br, 2H), 1.34 (br, 22H), 1.15 (br, 15H).^{13}C NMR (101 MHz, $CDCl_3$) (ppm):163.60, 143.17, 138.74, 138.34, 137.32, 133.23, 131.80, 129.17, 126.08, 122.52, 120.81, 120.10, 109.99, 40.41, 40.34, 34.47, 32.53, 31.57, 28.94, 28.24, 26.84, 25.61, 23.07, 22.58, 14.17, 14.06, 10.87.MS (MALDI-TOF) $C_{46}H_{55}NO_2S_3$ m/z: 749.34; Found: 750.20 (M^+). Anal. Calcd for $C_{46}H_{55}NO_2S_3$: C, 73.65; H, 7.39; N, 1.87. Found: C, 73.24; H, 6.99; N, 1.46.

M1. NBS (0.52 g) were added to the solution of **2** (1.10 g), and $CHCl_3$ (22 ml). After stirring 2 hours, the mixture was poured into methanol. The precipitate was filtered and purified by column chromatography, using hexane:CH_2Cl_2 = 1:1 as the eluent. 1.05 g **3** (79 %) was obtained. ^1H NMR (400 MHz, $CDCl_3$) (ppm):8.31 (d, J = 7.6 Hz, 2H), 8.04 (d, J = 7.6 Hz, 2H), 7.07 (s, 2H), 4.09 (t, J = 7.6 Hz, 2H), 2.57 (d, J = 7.2Hz, 4H), 1.69 (br, 2H), 1.35 (br, 22H), 0.95 (br, 15H).^{13}C NMR (101 MHz, $CDCl_3$) (ppm): 163.57, 142.75, 139.34, 136.94, 132.96, 131.95, 130.47, 128.89, 126.22, 125.32, 121.28, 120.39, 111.67, 40.55, 40.13, 33.93, 32.66, 31.69, 28.96, 28.37, 26.97, 25.79, 23.21, 22.72, 14.30, 14.20, 10.95. MS (MALDI-TOF) $C_{46}H_{53}Br_2NO_2S_3$ m/z: 905.16; Found: 905.96 (M+). Anal. Calcd for $C_{46}H_{53}Br_2NO_2S_3$: C,60.85; H, 5.88; N, 1.54. Found: C, 60.61; H, 5.64; N, 1.29.

3-Th. Toluene (20 mL) was added to the mixture of compound **3** (5 g), 2-bromothiophene (4.50 g), $Pd(PPh_3)_4$ (420 mg) under nitrogen. After refluxing 4 hours, the solvent was evaporated. Using hexane as the eluent, the solid was purified by column chromatography and yield 2.50 g **3-Th** (60 %).^1H NMR (400 MHz, $CDCl_3$) (ppm): 7.58 (s, 2H), 7.29 (br, 4H), 7.24 (s, 2H), 7.03 (br, 2H), 2.86 (d, J = 7.2Hz, 4H), 1.81 (br, 2H), 1.30 (br, 32H), 0.91 (br, 12H).^{13}C NMR (101 MHz, $CDCl_3$) (ppm): 163.57, 142.75, 139.34, 136.94, 132.96, 131.95, 130.47, 128.89, 126.22, 125.32, 121.28, 120.39, 111.67, 40.13, 33.93, 32.66, 31.69, 28.96, 28.37, 26.97, 25.79, 23.21, 22.72, 14.30, 10.95.MS (MALDI-TOF) $C_{50}H_{60}Cl_2S_6$ m/z: 922.24; Found: 922.62 (M^+). Anal. Calcd for $C_{50}H_{60}Cl_2S_6$: C, 64.97; H, 6.54. Found: C, 64.68; H, 6.24.

M2. LDA (2.5ml 2M) was added to the solution of compound 3-Th (2.20 g) in 35ml dry THF at -78°C. After stirring for 4 hours at -78°C, Trimethyltin chloride (5ml 1M) was added. It was purified by crystallization in ethanol and yield 2.38 g (81 %) compound 5. ^1H NMR (400 MHz, $CDCl_3$) (ppm): 7.57 (s, 2H), 7.38 (d, J = 3.2 Hz, 2H), 7.23 (s, 2H), 7.11 (d, J = 3.2 Hz, 2H), 2.86 (d, J = 6.4 Hz, 4H), 1.81 (br, 2H), 1.31 (br, 32H), 0.88 (br, 12H), 0.39 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) (ppm): 142.57, 139.75, 138.62, 138.47, 138.37, 137.25, 135.99, 135.66, 127.92, 126.61, 122.75, 122.36, 118.22, 39.37, 33.55, 33.14, 32.57, 31.90, 29.68, 28.84, 26.60, 23.05, 22.70, 14.22, 14.16. MS (MALDI-TOF) $C_{56}H_{76}Cl_2S_6Sn_2$ m/z: 1250.17; Found: 1250.89 (M^+). Anal. Calcd for $C_{56}H_{76}Cl_2S_6Sn_2$: C, 53.81; H, 6.13. Found: C,53.42; H, 5.94.

PNTB-Cl. M3 (96.54 mg), M2 (124.97 mg), P(o-tolyl)$_3$ (4.87 mg), Pd$_2$(dba)$_3$ (1.83 mg) and anhydrous toluene (4.6 mL) was added to 15 ml Schenk tube under nitrogen. After refluxing for 6 hours, the solution was added to methanol with vigorous stirring. The precipitate was filtered and extracted by the Sohxlet with hexane and dichloromethane. After final extraction with chloroform, the concentrated solution was then dropped into 100 mL of methanol with vigorous stirring. The polymer was collected by filtration and dried under reduced pressure to afford the product (140 mg, 82 %). Molecular weight (Mn) = 53.48 kDa; polydispersity (PDI) = 2.62. Anal. Calcd for $C_{98}H_{115}Cl_2NO_2S_9$(per unit): C, 69.30; H, 6.83; N, 0.82. Found: C, 68.84; H, 6.61; N, 0.60.

PNTB6-Cl. 3 (136.19 mg), 5 (187.48 mg), P(o-tolyl)$_3$ (7.30 mg), Pd$_2$(dba)$_3$ (2.75 mg) and anhydrous toluene (6 mL) was added to 35 ml Schenk tube under nitrogen. After refluxing for 4 hours, the reaction solution become gel at 115 °C. Then chlorobenzene (6 ml) was added to the solution and refluxing for another one hour to dissolve the polymer. The solution was added to methanol with vigorous stirring. The precipitate was filtered and extracted by the Sohxlet with hexane and dichloromethane. After final extraction with chlorobenzene, the concentrated solution was then dropped into 100 mL of methanol with vigorous stirring. The polymer was collected by filtration and dried under reduced pressure to afford the product (178 mg, 72 %). Molecular weight (Mn) = 91.52 kDa; polydispersity (PDI) = 2.03. Anal. Calcd for $C_{96}H_{111}Cl_2NO_2S_9$(per unit): C, 69.03; H, 6.70; N, 0.84. Found: C, 68.49; H, 6.59; N, 0.62.

2. Device fabrication

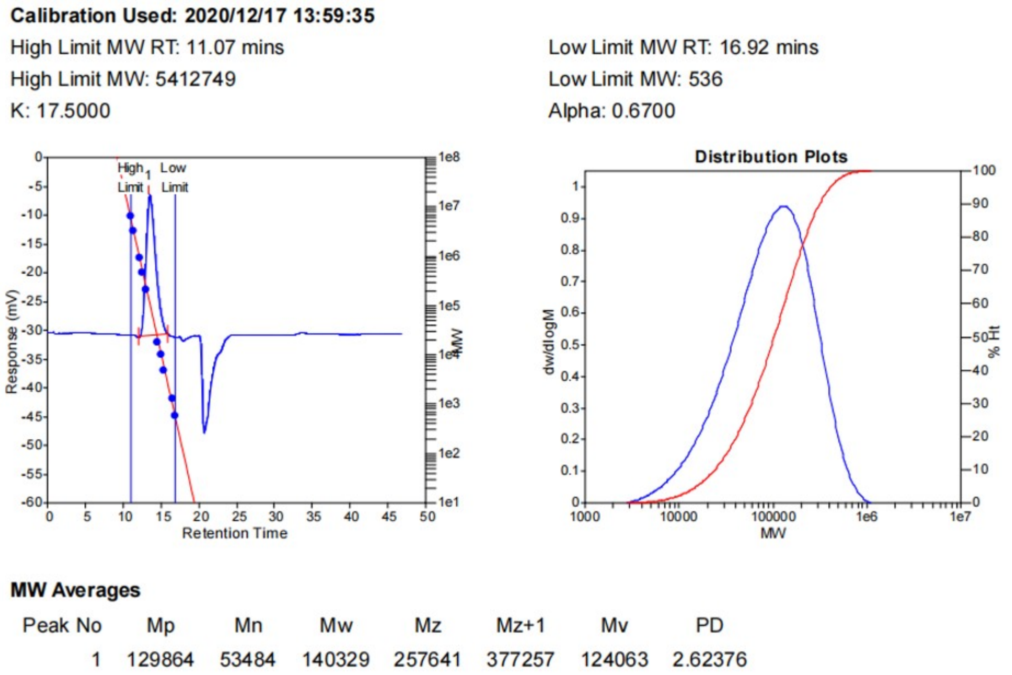
Layer-by-layer solar cell devices were fabricated with the configuration of ITO/PEDOT:PSS/Polymer:Y6/PNDIT-F3N/Ag. The ITO glass was cleaned in ultrasonic bath with dichloromethane and isopropanol for 15min each, followed by UV treatment in ultravioletozone cleaner (SunMonde) for 10 min. PEDOT:PSS (poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate)) (Clevios PVP Al 4083) was deposited on the ITO substrate by spin-coating the solution filtered through a 0.45 mm poly(tetrafluoroethylene) (PTFE) filter at 6,000 rpm for 40 s, followed by baking at 150 ^{o}C for 15 min in the air. The polymer of PNTB6-Cl with molecular weight of 45.27 kDa was dissolved in chlorobenzene with concentration of 10 mg/ml and heated at 110 ℃ for 2 hours. Then, the layer of polymer donor was deposited by spin-coating with rotating speed of 2000 rpm in the N2-filled gloved box. The concentration of 9 mg/ml and 7.5 mg/ml were used for batches of PNTB6-Cl with Mn of 71.42 kDa and 91.53 kDa, respectively. By measuring with Bruker Dektak XT* profilometer, the thickness for PNTB-Cl and PNTB6-Cl were around 65 nm and 70 nm, respectively. On top of polymer donor, the N3 (9.2 mg/ml) solution in chloroform with 0.5 % volume 1,8-diiodooctane (DIO) additive was deposited by spin-coating, resulting in thickness around 105 nm for PNTB-Cl:N3 and around 115 nm for PNTB6-Cl:N3 measured by Bruker Dektak XT* profilometer. An interfacial layer of PNDIT-F3N was deposited by spin-coating solution in methanol (0.5 mg/ml) at 2000rmp for 30s. Finally, Ag (100 nm) was thermally evaporated under a shadow mask at a chamber pressure of $\sim 2 \times 10^{-4}$ torr.

3. Characterization

Steady-state current-voltage (J-V) curves were measured by a Keithley 2400 source-measurement unit under AM 1.5 G spectrum from a solar simulator (Saifan 7ISO503A; FOEN INSTRUMTNTS CO., LTD) calibrated by a NIM-certified monocrystaline silicon reference cell (#238). The J–V characteristics of the OSCs were measured in a nitrogen glove box at room temperature. The voltage step and delay time were 10 mV and 1 ms, respectively. The scan started from - 0.1 to 0.9 V. UV–vis spectra were taken with spectrophotometer (SHIMADZU UV-1780). The Uv-vis spectrometer (AvaSpec-ULS248Cl-EVO) was used to study solubility kinetic of the thin films of PNTB-Cl and PNTB6-Cl (with similar Mn and PDI) in chlorobenzene. Thin films of the polymers were prepared by spin-casting the its chlorobenzene solution onto glasses and peeled off carefully. Cyclic voltammetry measurements were performance on CHI600E (CH Instruments Ins) with platinum working electrode, platinum counter electrode and a silver chloride reference electrode (SCE). Differential scanning calorimeter (DSC) measurement was performed on DSC Q2000 (TA) at a scan rate of 10 ºC min^{-1} under nitrogen. Thermogravimetric analysis (TGA) was conducted on TGA-50 (Japan Shimadzu) in nitrogen with heating ramp of 10 ºC min^{-1}. Active layer morphologies were investigated by using AFM (Bruker, Dimension Icon) in contacting under air condition with a 1×1 mm scan area. The measurement of EQE was performed by a QE-R3011 (Enli Technology Co. Ltd.) with a lock-in amplifier at a chopping frequency of 280 Hz. The monochromatic light for EQE measurement was from a xenon lamp. Photoluminescence (PL) quenching experiments were conducted on Edinburgh FS5 by excited at wavelength of 540 nm for polymer donors and 770 nm for electron acceptor. Grazing-incidence wide-angle X-ray scattering (GIWAXS) was measured at 13A beam line of National Synchrotron Radiation Research Center (NSRRC, Taiwan), and were provided technical support by "Ceshigo Research Service，www.ceshigo.com". All samples for GIWAXS were radiated at 12.13 keV X-ray with an incident angle of 0.10-0.15°. The time-of-flight secondary ion mass spectrometry (TOF-SIMS) was measure on SurfaceSeer-I. The samples were prepared by depositing polymers and N3 on Si substate in the same condition with OSC device fabrication. The hole-only or electron-only devices were tested using the space charge limited current (SCLC) method, adopting the following device architectures: ITO/PEDOT:PSS/active layer /MoO_3/Ag for holes and ITO/ZnO/active layer/PNDIT-F3N/Ag for electrons. The mobilities were obtained by taking current versus voltage plots and fitting the results to a space charge limited form. where the SCLC is defined by

$$J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8L^3}$$

Where ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material (believed to be 3), μ is the hole or electron mobility and L is the thickness of the film. From the fitting curve of J vs V^2, hole and electron mobilities can be calculated.



Calibration Used: 2020/12/17 13:59:35

High Limit MW RT: 11.07 mins

High Limit MW: 5412749

K: 17.5000

Low Limit MW RT: 16.92 mins

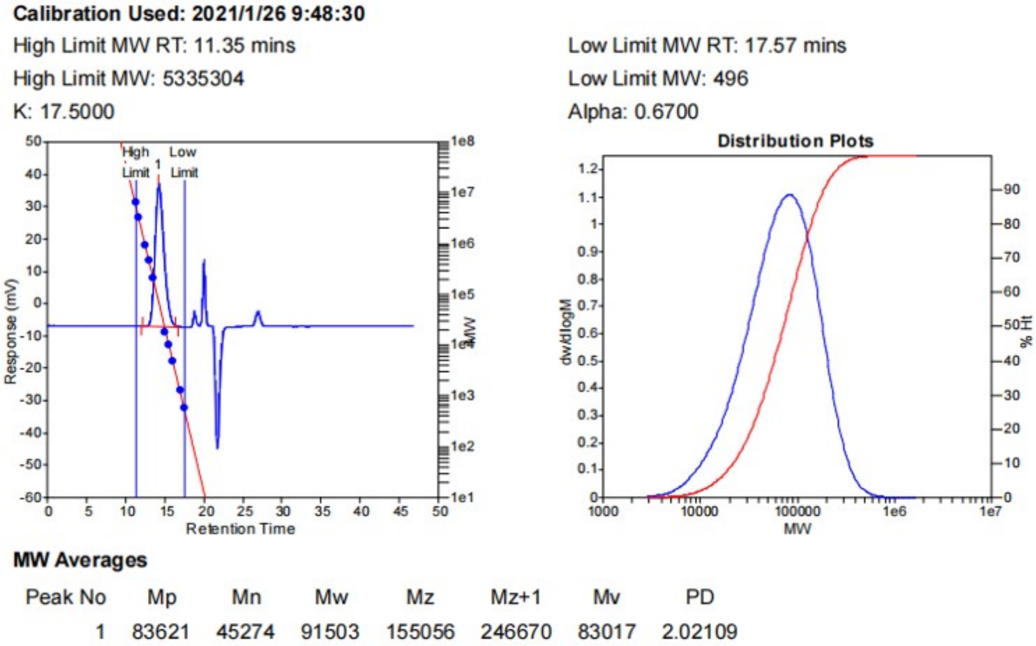
Low Limit MW: 536

Alpha: 0.6700

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	129864	53484	140329	257641	377257	124063	2.62376

Figure S1. The gel permeation chromatography of PNTB-Cl.



Calibration Used: 2021/1/26 9:48:30

High Limit MW RT: 11.35 mins

High Limit MW: 5335304

K: 17.5000

Low Limit MW RT: 17.57 mins

Low Limit MW: 496

Alpha: 0.6700

MW Averages

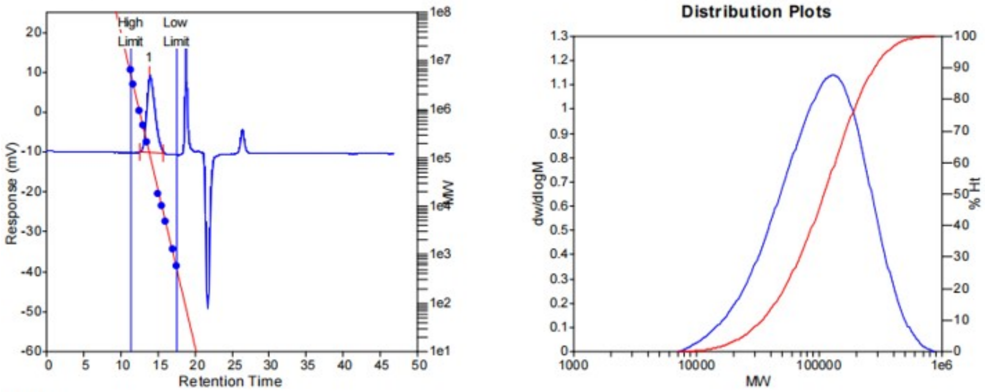
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	83621	45274	91503	155056	246670	83017	2.02109

Figure S2. The gel permeation chromatography of first batch of PNTB6-Cl.

Calibration Used: 2021/1/26 9:48:30

High Limit MW RT: 11.35 mins
High Limit MW: 5335304
K: 17.5000

Low Limit MW RT: 17.57 mins
Low Limit MW: 496
Alpha: 0.6700



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	130873	71420	136093	218587	305529	124312	1.90553

Figure S3. The gel permeation chromatography of second batch of PNTB6-Cl.

Calibration Used: 2021/1/26 9:48:30

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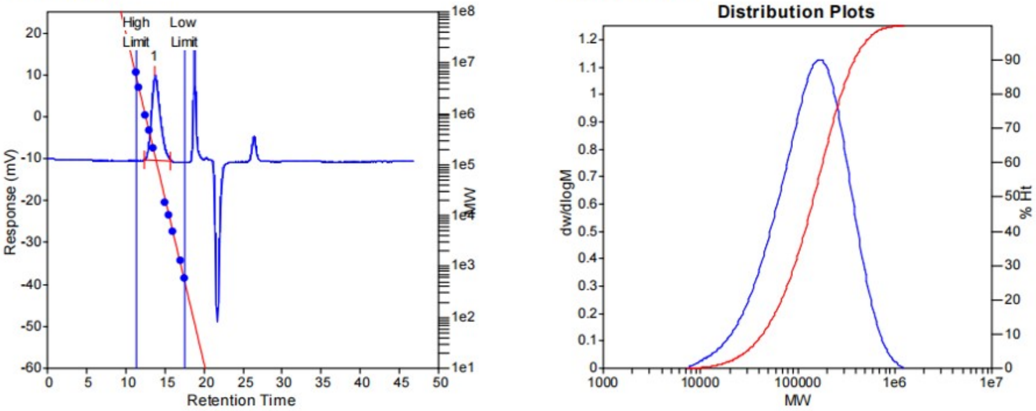
High Limit MW: 5335304
K: 17.5000

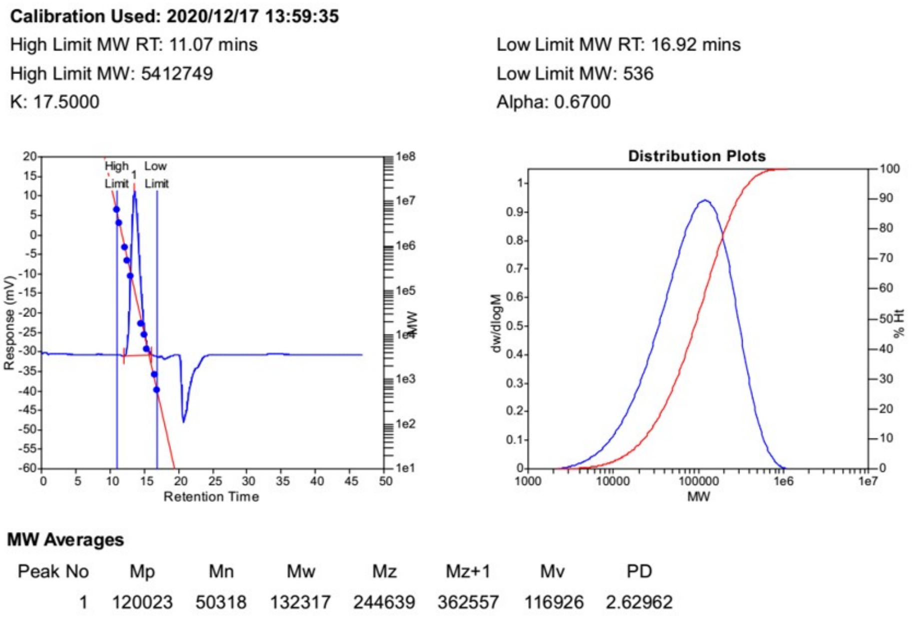
Low Limit MW RT: 17.57 mins
Low Limit MW: 496
Alpha: 0.6700



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	167851	91524	185506	305939	435488	168519	2.02686

Figure S4. The gel permeation chromatography of third batch of PNTB6-Cl.



Calibration Used: 2020/12/17 13:59:35

High Limit MW RT: 11.07 mins

High Limit MW: 5412749

K: 17.5000

Low Limit MW RT: 16.92 mins

Low Limit MW: 536

Alpha: 0.6700

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	120023	50318	132317	244639	362557	116926	2.62962

Figure S5. The gel permeation chromatography of fourth batch of PNTB6-Cl.

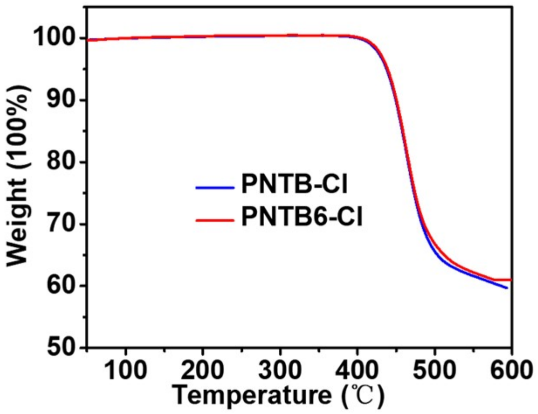


Figure S6. Thermogravimetric analysis (TGA) of polymers PNTB-Cl and PNTB6-Cl in nitrogen with heating ramp of 10 ºC min^{-1}.

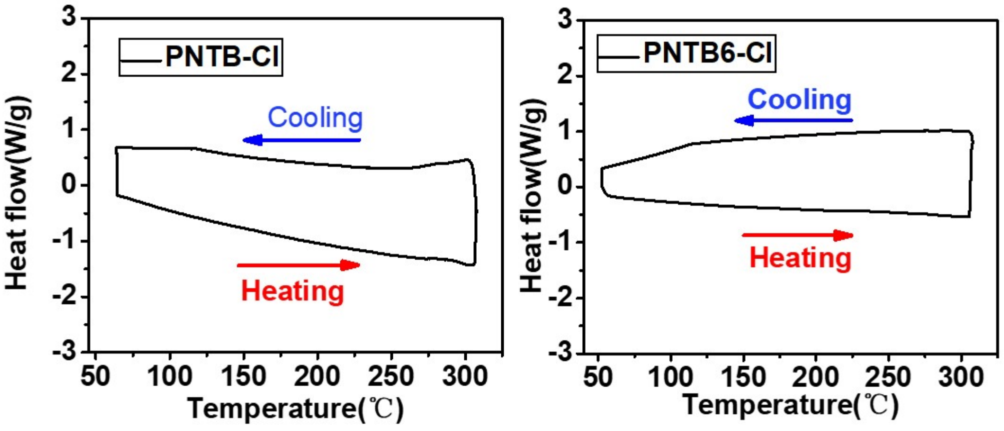


Figure S7. Differential scanning calorimeter (DSC) curves of PNTB-Cl and PNTB6-Cl at a scan rate of 10 ºC min^{-1} under nitrogen.

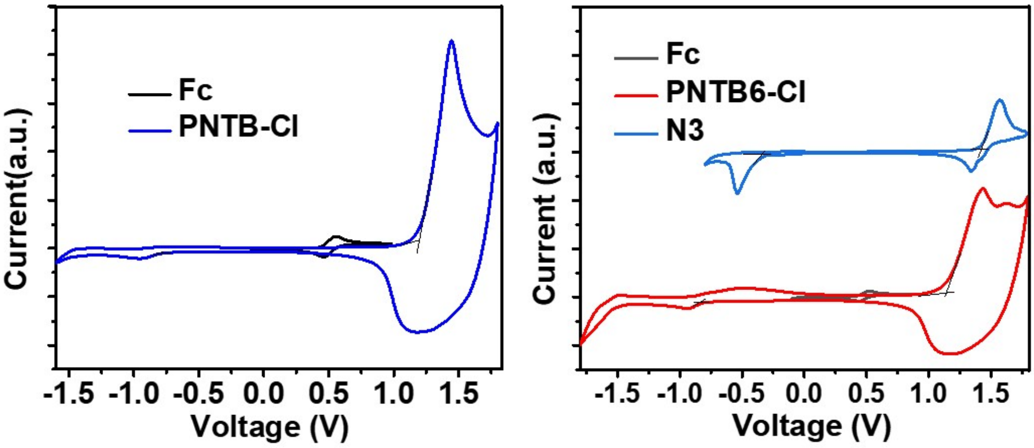


Figure S8. The cyclic voltammograms of the films of PNTB-Cl, PNTB6-Cl and N3 with Fc/Fc+ as the reference.

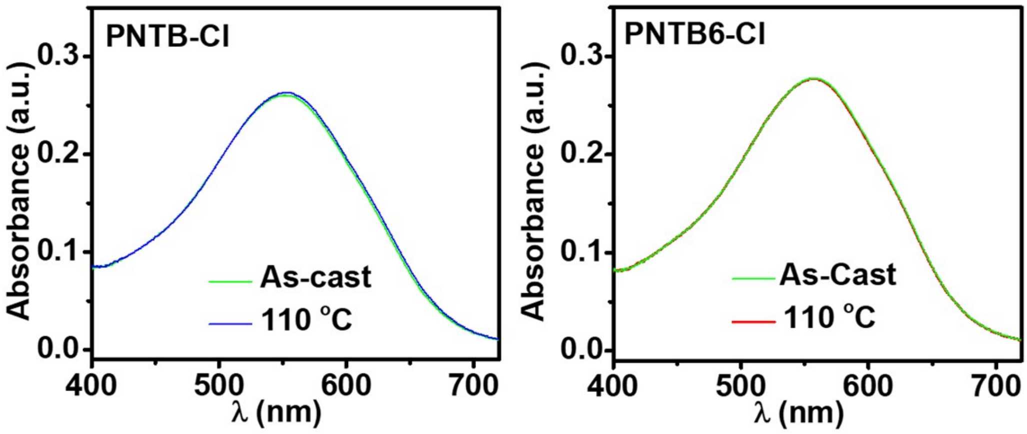


Figure S9. The absorption of as-cast and 110 ºC annealled PNTB-Cl and PNTB6-Cl film.

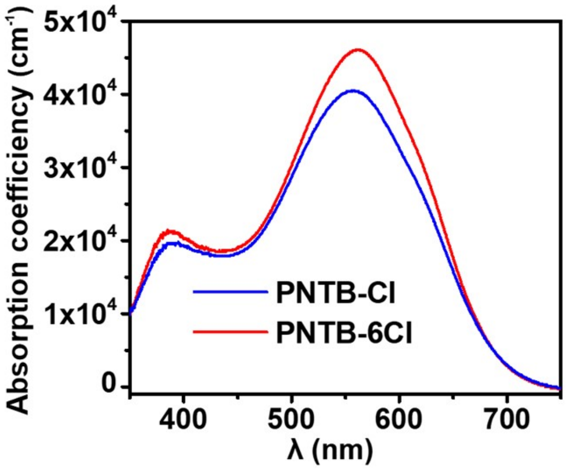


Figure S10. The film absorption coefficiency of PNTB-Cl and PNTB6-Cl.

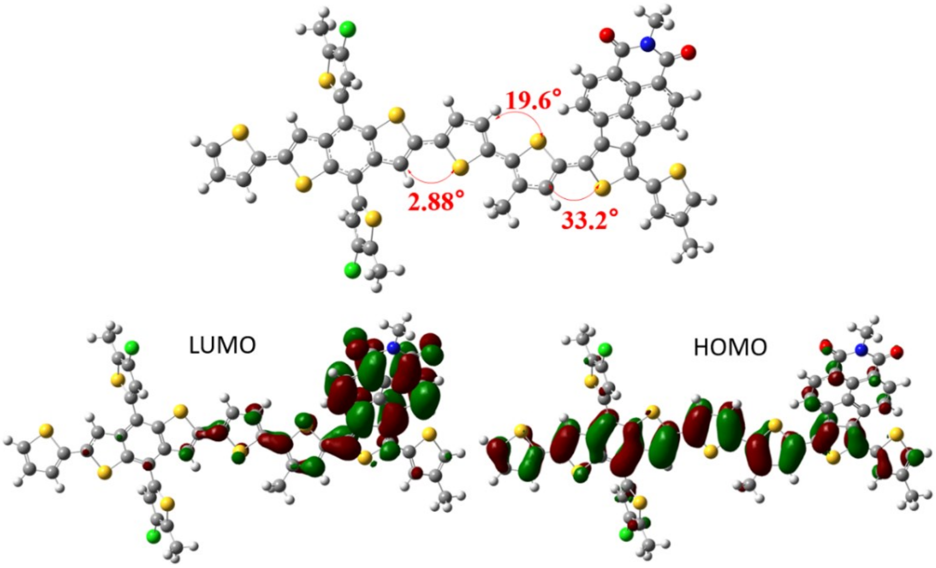


Figure S11. The calculated geometries, LUMO and HOMO orbitals of one repeating unit of polymers by using density functional theory (DFT) at the B3LYP/6-31G* level.

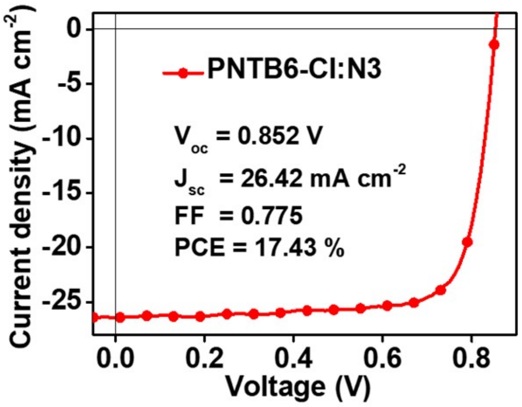


Figure S12. The J-V characteristic of PNTB6-Cl:N3 based device that was fabricated and tested in Prof. Fe'group at Southern University of Science and Technology.

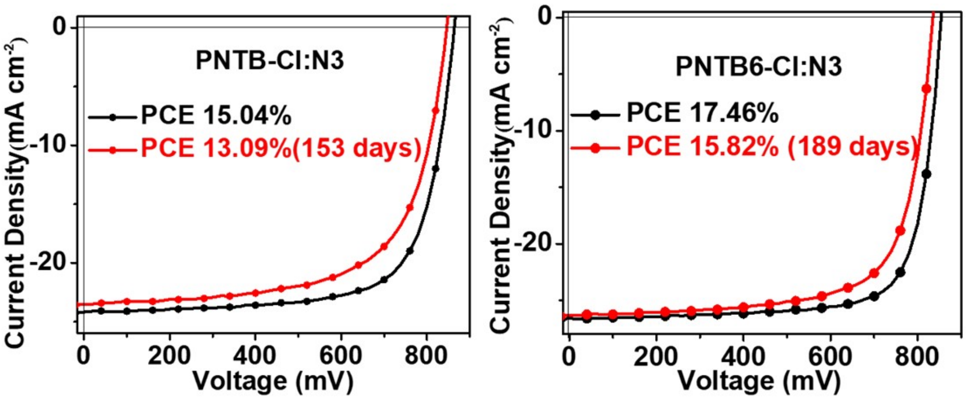


Figure S13. The stability of PNTB-Cl:N3 and PNTB6-Cl:N3 based devices which were stored in nitrogen-filled glovebox under room light.

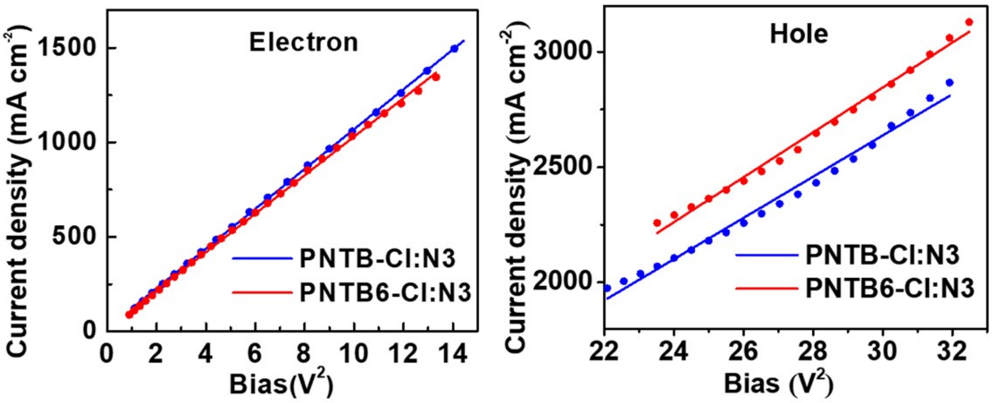


Figure S14. J versus V^2 fitting curves for the electron-only and hole-only devices of PNTB-Cl:N3 and PNTB6-Cl:N3.

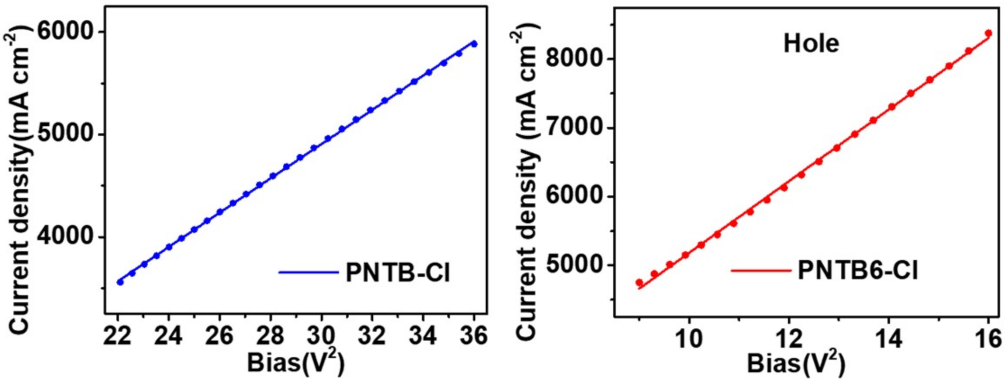


Figure S15. J versus V^2 fitting curves for the hole-only devices of neat PNTB-Cl and PNTB6-Cl film.

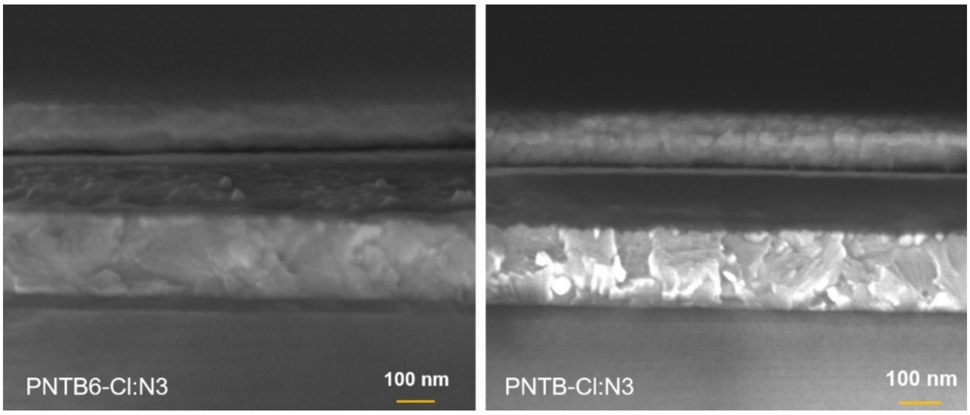


Figure S16. Cross section SEM images of PNTB6-Cl:N3 and PNTB-Cl:N3 based devices.

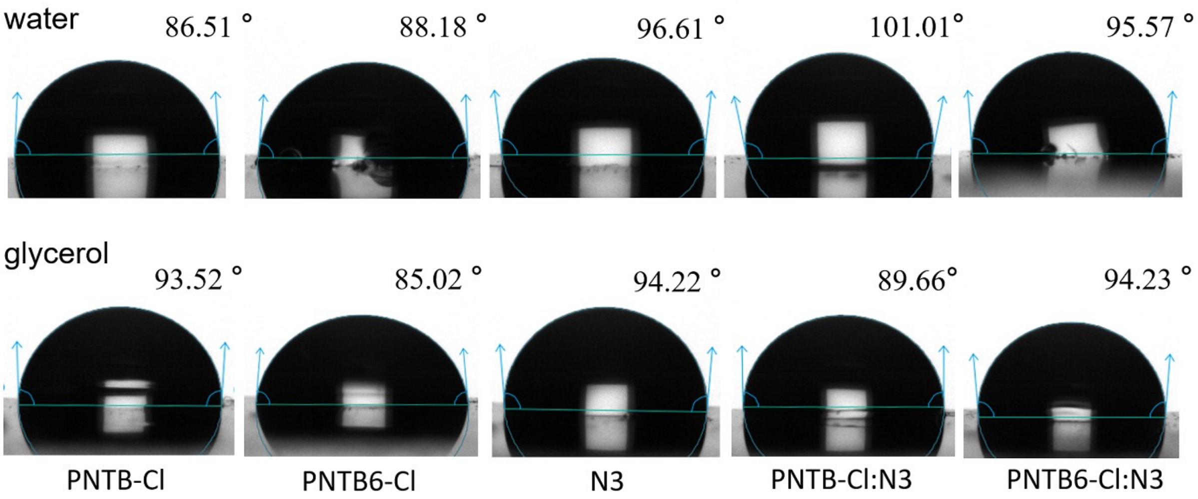


Figure S17. Contact angles of water and glycerol on neat PNTB-Cl, neat PNTB6-Cl, neat N3, PNTB-Cl:N3 and PNTB6-Cl:N3 films.

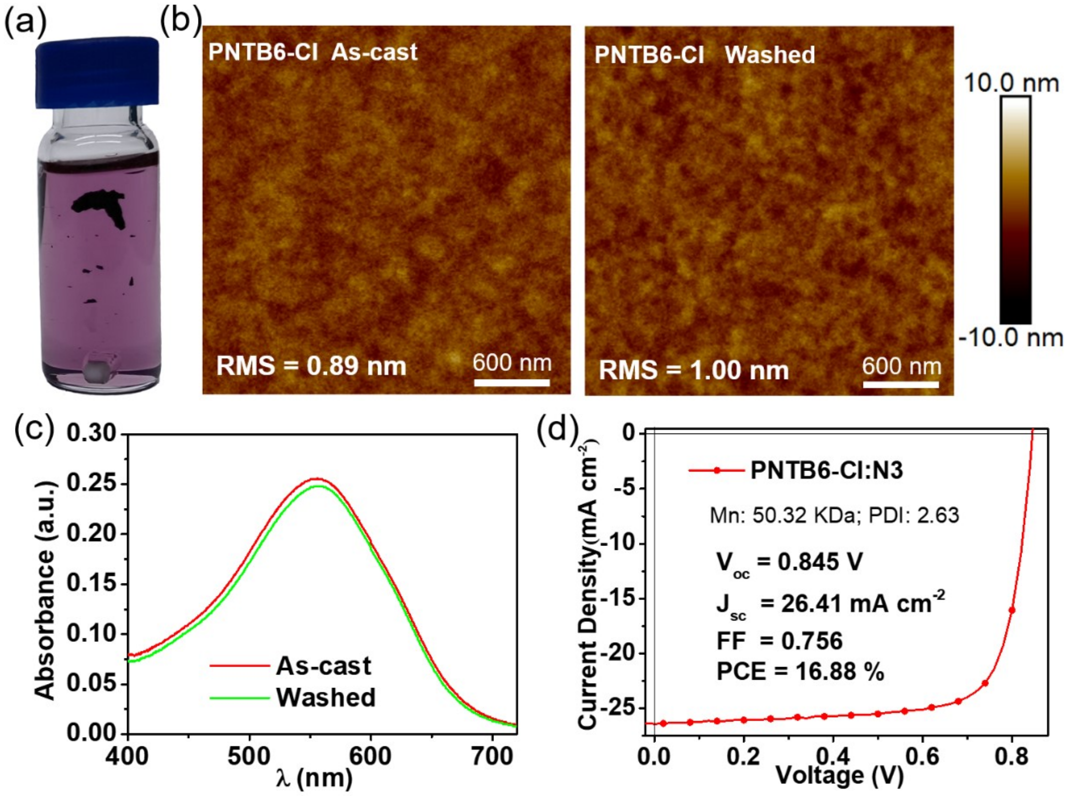


Figure S18. The charaterization of PNTB6-Cl with molecular weight of 50.32 Kda and PDI of 2.63. (a)The solubility of PNTB6-Cl in chloroform after stirring for 8 hours; (b) the tapping-mode AFM height images (3×3 μm) of pristine PNTB6-Cl film and PNTB6-Cl film washed with chloroform; (c) the absorption of pristine PNTB6-Cl film and PNTB6-Cl film washed with chloroform; (d) *J-V* curves of LBL OSCs based on PNTB6-Cl:N3.

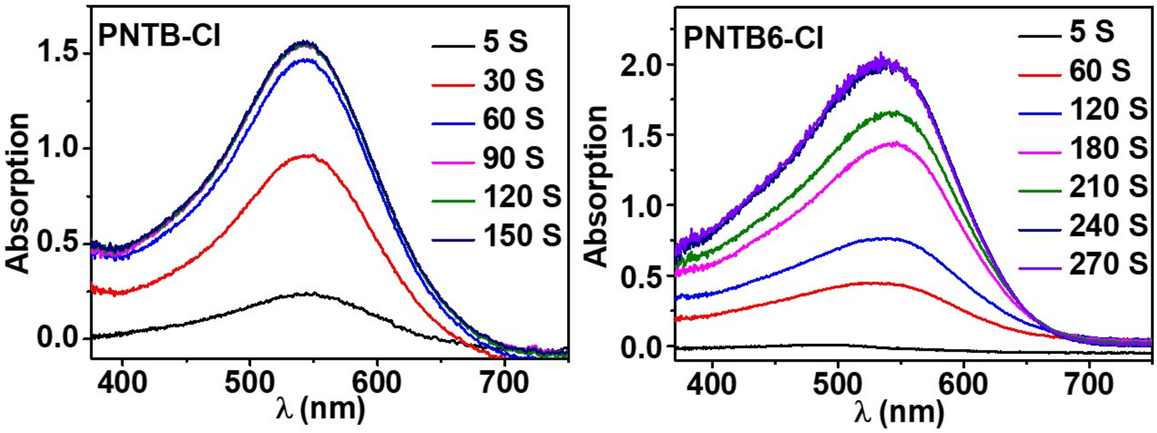


Figure S19. Solubility kinetics of PNTB-Cl films (Mn: 53.48 Kda; PDI: 2.62) in chlorobenzene at 50 ºC and PNTB6-Cl films (Mn: 50.32 Kda; PDI: 2.63) in chlorobenzene at 75 ºC under stiring at 300 r/min.

Table S1. The optical and electronic properties of PNTB-Cl and PNTB6-Cl.

Polymer	LUMO (eV)	HOMO (eV)	E_g (eV)	λ_{max} (nm) Film	λ_{onset} (nm) Film	ε (cm^{-1})
PNTB-Cl	- 3.50	- 5.49	1.99	551	689	4.1×10^4
PNTB6-Cl	- 3.49	- 5.47	1.98	557	686	4.7×10^4

Table S2. J-V characteristics of solar cell devices based on PNTB-Cl:N3 and PNTB6-Cl:N3 without DIO additive.

Active layer	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
PNTB-Cl:N3	0.866	24.35	65.42	13.79 (12.99±0.32)
PNTB6-Cl:N3	0.863	25.60	72.30	15.96 (15.37±0.21)

Table S3. J-V characteristics of BHJ solar cell devices based on PNTB-Cl:N3.

Active layer	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
PNTB-Cl:N3	0.858	24.67	75.55	16.00 (14.80±0.36)

Table S4. J-V characteristics of PNTB6-Cl:N3 based device that was annealed at 80 °C.

Time (h)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
0h	0.846	26.20	77.49	17.17
1h	0.849	26.18	72.01	16.00
2h	0.838	26.26	69.93	15.38
12h	0.784	25.97	63.31	12.90
16h	0.770	26.02	62.07	12.44

Figure S5. J-V characteristics of PNTB-Cl:N3 based device that was annealed at 80 °C.

Time (h)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
0h	0.843	24.51	71.49	14.77
1h	0.840	19.26	59.38	9.61
2h	0.835	17.96	55.37	8.31
8h	0.832	15.78	49.41	6.48
16h	0.815	15.46	48.61	6.13

Table S6. J-V characteristics of solar cell devices based on different batch of PNTB6-Cl.

Active layer	Mn (KDa)	PDI	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
Batch 1	45.27	2.02	0.845	26.60	75.70	17.01 (16.70±0.20)
Batch 2	71.42	1.91	0.854	26.60	76.83	17.45 (17.06±0.14)
Batch 3	91.53	2.03	0.857	26.58	77.26	17.59 (17.31±0.16)

Table S7. Electron and or hole mobility for PNTB6-Cl:N3, PNTB-Cl:N3 LBL film.

Blend Films	Thickness (nm)	Slope-K		μ_e ($cm^2 \cdot V^{-1} \cdot s^{-1}$)	μ_h ($cm^2 \cdot V^{-1} \cdot s^{-1}$)	μ_e/μ_h
		Electron	Hole			
PNTB6-Cl:N3	118	101.8	97.3	5.59×10^{-4}	5.34×10^{-4}	1.05
PNTB-Cl:N3	102	105.6	89.5	3.74×10^{-4}	3.17×10^{-4}	1.18
PNTB6-Cl	69	/	521.1	/	5.73×10^{-4}	/
PNTB-Cl	71	/	167.2	/	2.00×10^{-4}	/

Table S8. The crystal coherence length of neat polymer films of PNTB-Cl and PNTB6-Cl.

Polymer	d-spacing (100) (Å)	d-spacing (010) (Å)	Peak (nm^{-1})	FWHM ($Å^{-1}$)	CCL (Å)
PNTB-Cl	22.59	3.77	16.67	0.25	22.48
PNTB6-Cl	22.19	3.73	16.82	0.24	23.42
N3	22.19	3.50	17.92	0.18	31.40

Table S9. The crystal coherence length of LBL films of PNTB-Cl:N3 and PNTB6-Cl:N3.

Blend film	Peak location ($Å^{-1}$)	FWHM ($Å^{-1}$)	CCL (Å)
PNTB-Cl:N3	1.776	2.39	23.51
PNTB6-Cl:N3	1.759	2.40	23.42

Table S10. The surface energies calculated from the contact angles using Wu model[2-3].

Films	θ_{water} (°)	θ_{GL} (°)	Surface energies (mJ m^{-2})
PNTB-Cl	86.51	93.52	29.22
PNTB6-Cl	88.18	85.02	25.35
N3	96.61	94.22	20.68
PNTB-Cl:N3	101.01	89.66	21.58
PNTB6-Cl:N3	95.57	94.23	21.26

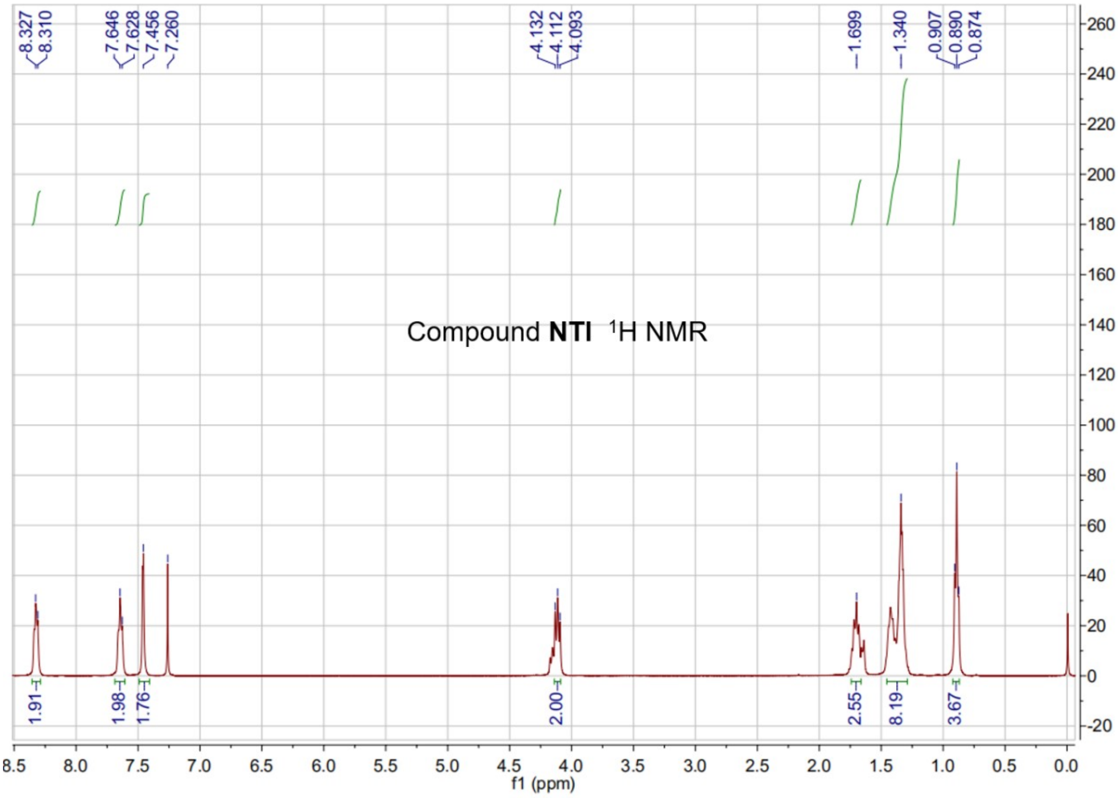


Figure S20. ^{1}H NMR of NTI in $CDCl_3$.

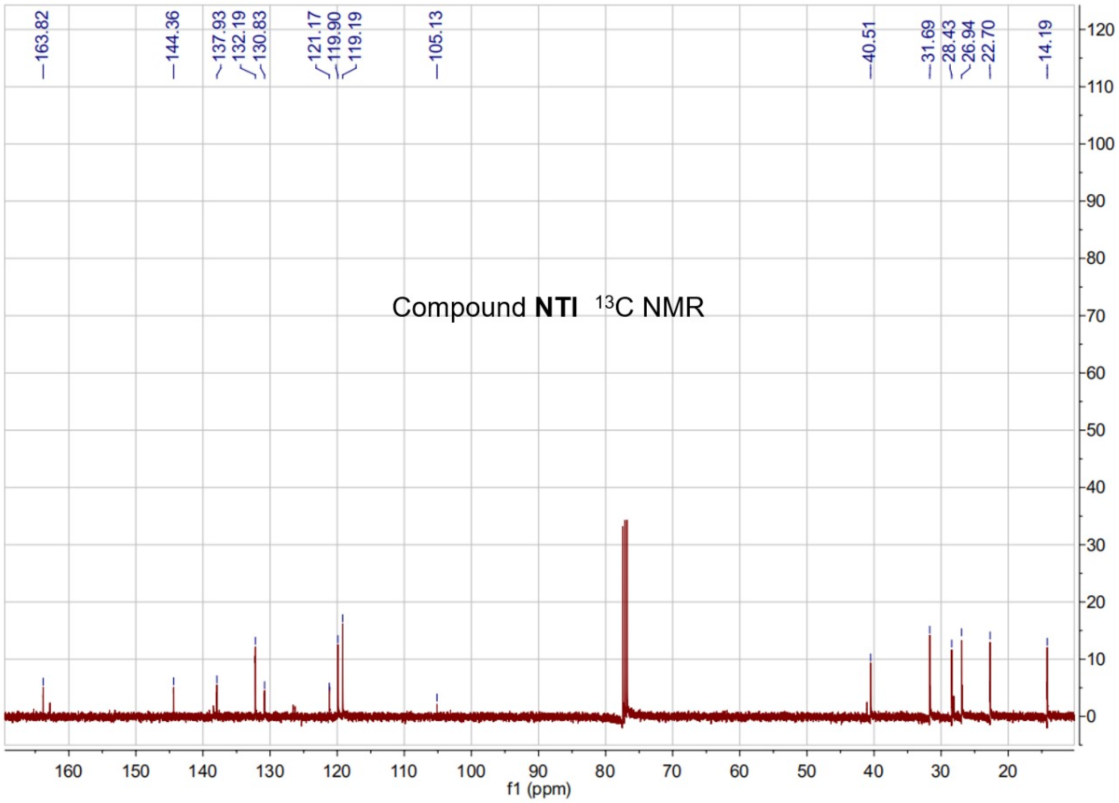


Figure S21. ^{13}C NMR of NTI in $CDCl_3$.

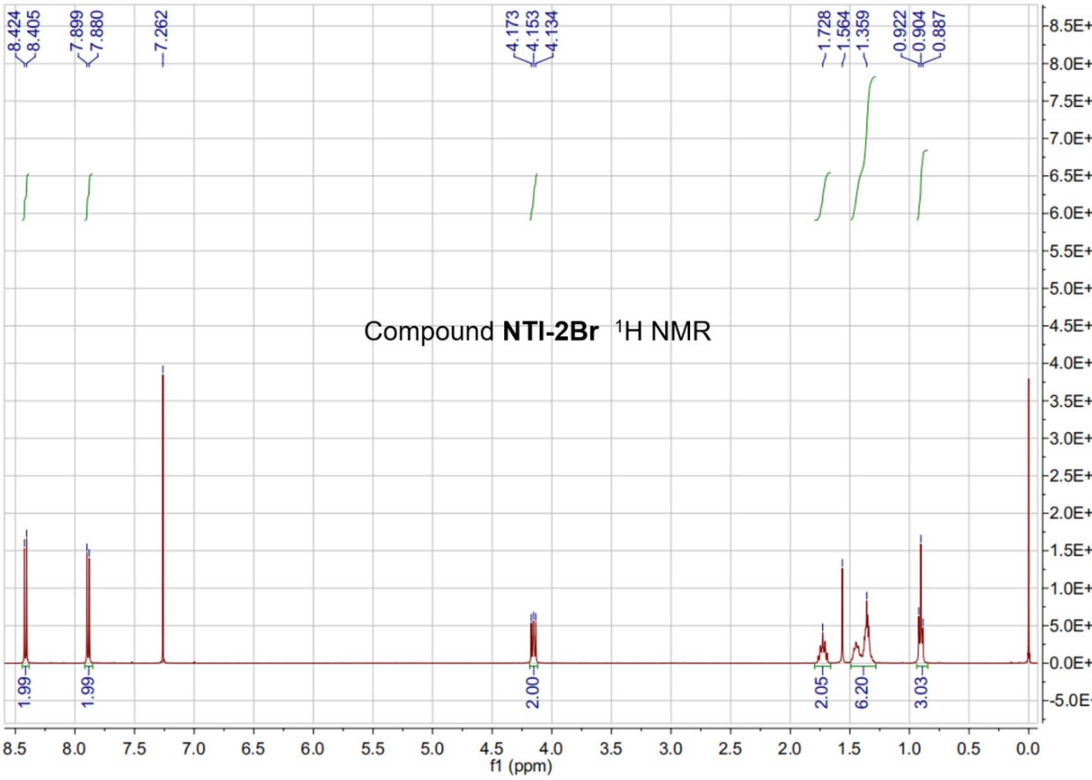


Figure S22. ^{1}H NMR of NTI-2Br in $CDCl_3$.

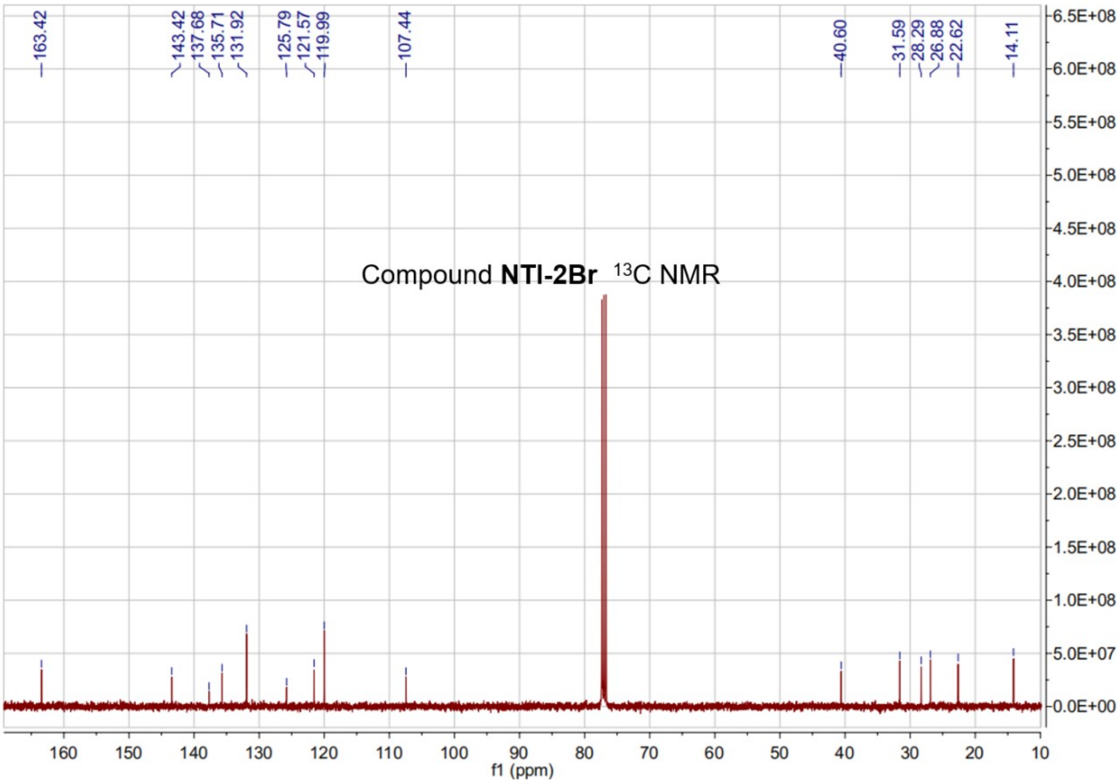


Figure S23. ^{13}C NMR of NTI-2Br in CDCl$_3$.

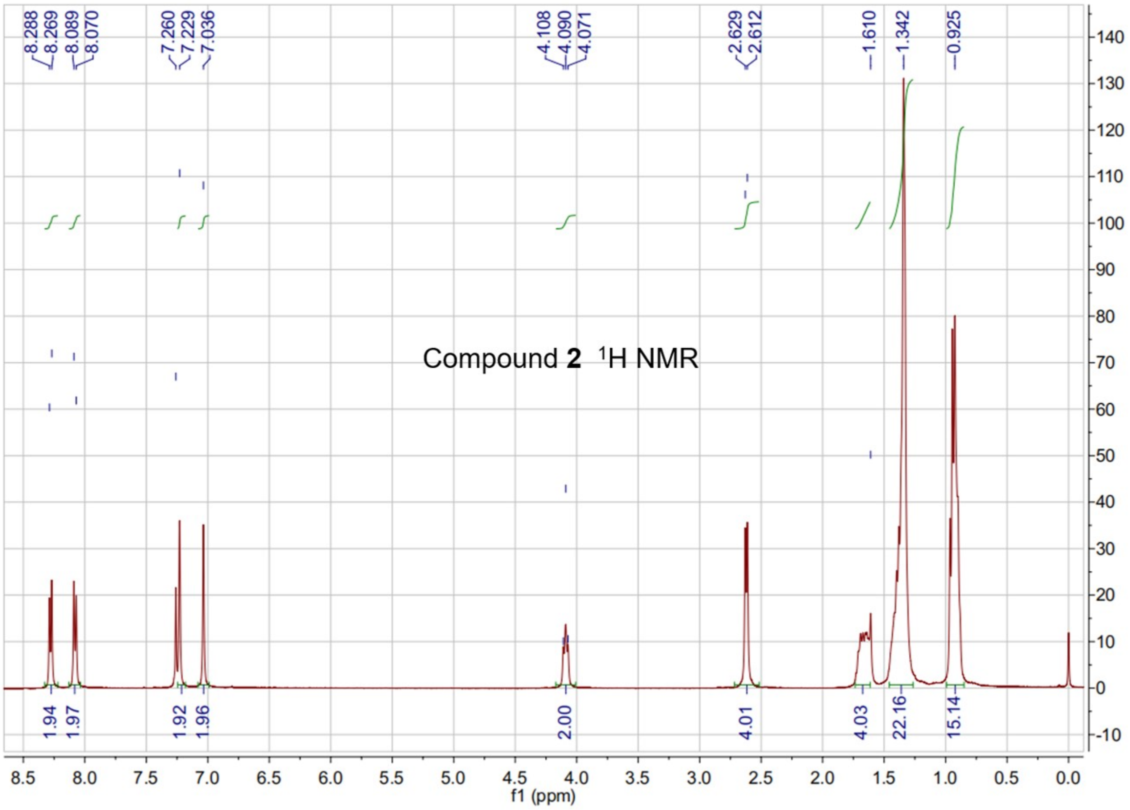


Figure S24. ^{1}H NMR of compound 2 in CDCl$_3$.

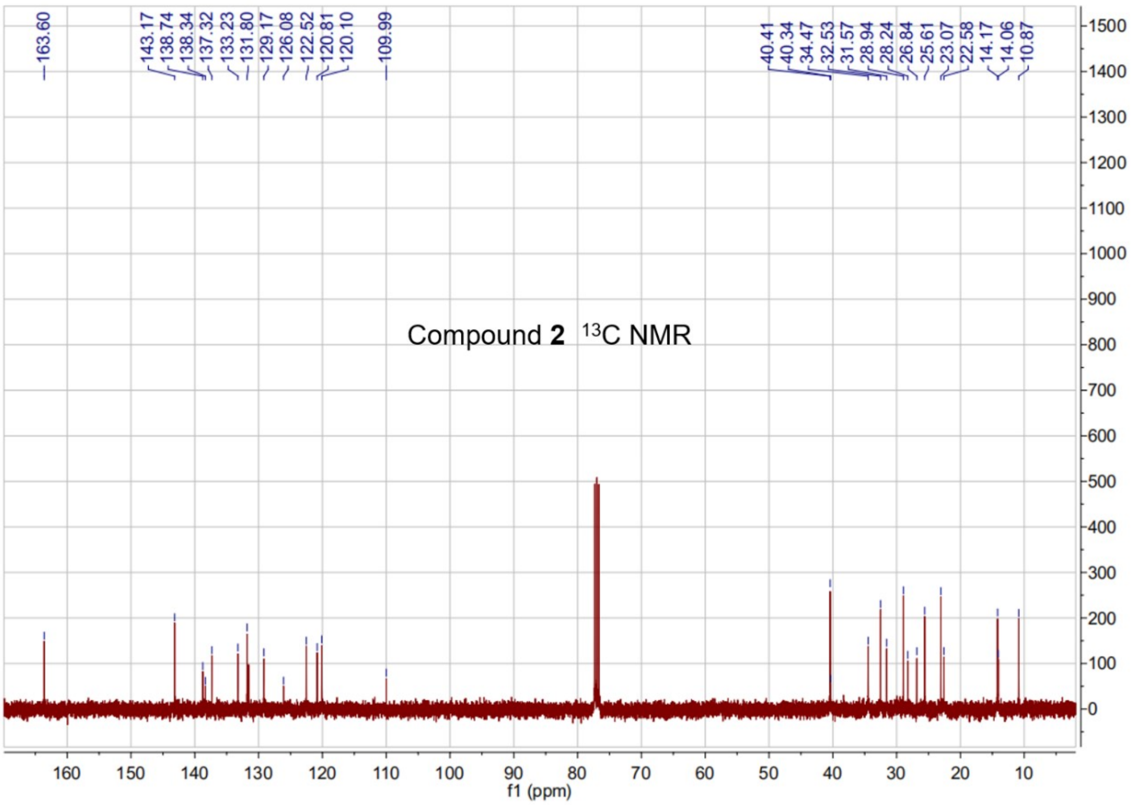


Figure S25. ^{13}C NMR of compound 2 in $CDCl_3$.

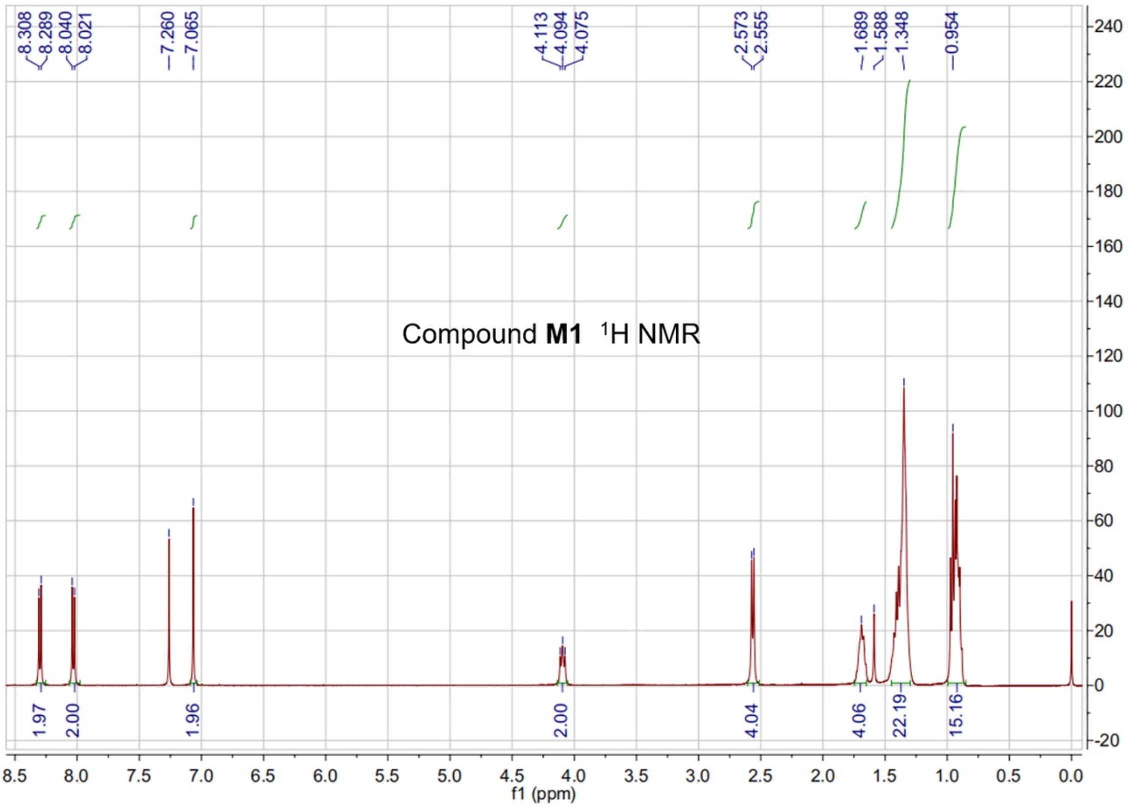


Figure S26. ^{1}H NMR of M1 in $CDCl_3$.

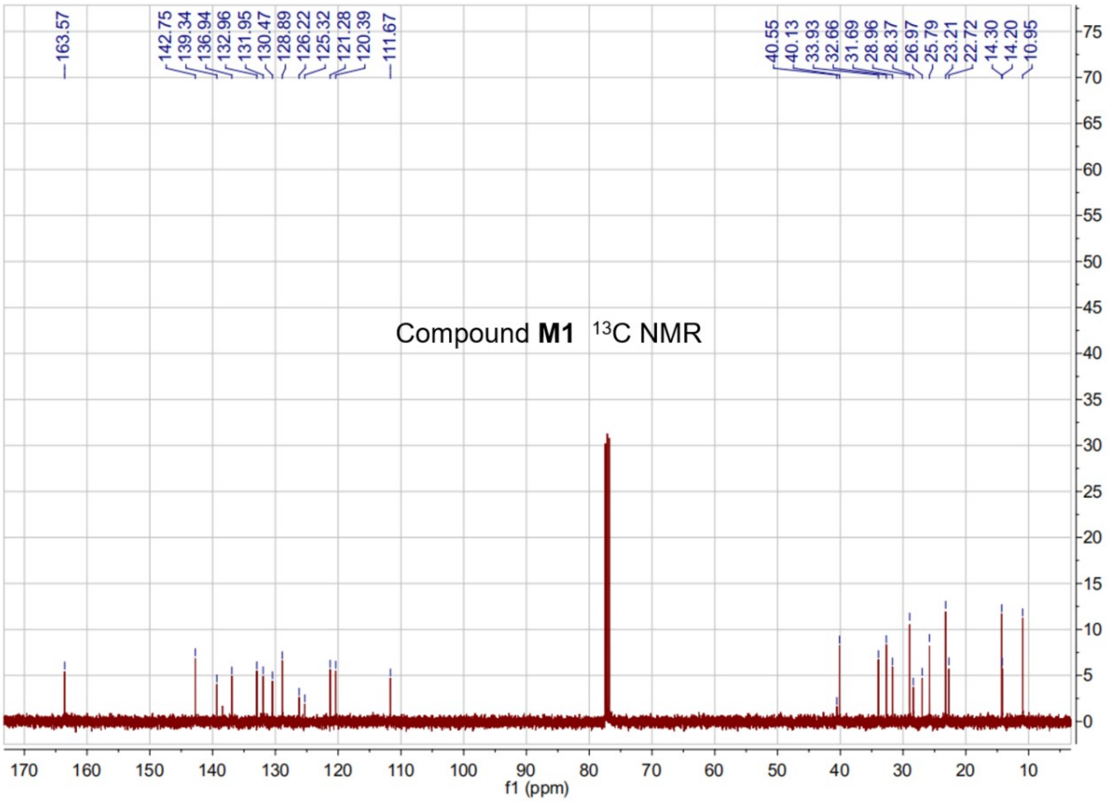


Figure S27. ^{13}C NMR of M1 in $CDCl_3$.

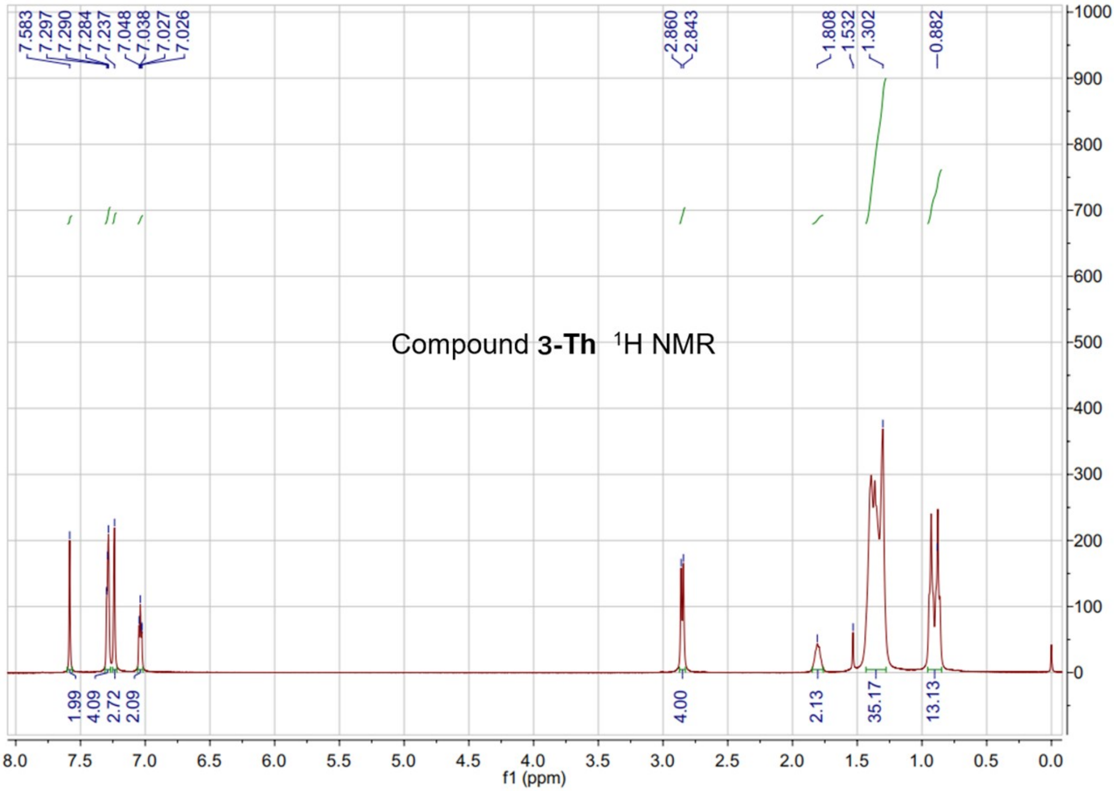


Figure S28. ^{1}H NMR of compound 3-Th in $CDCl_3$.

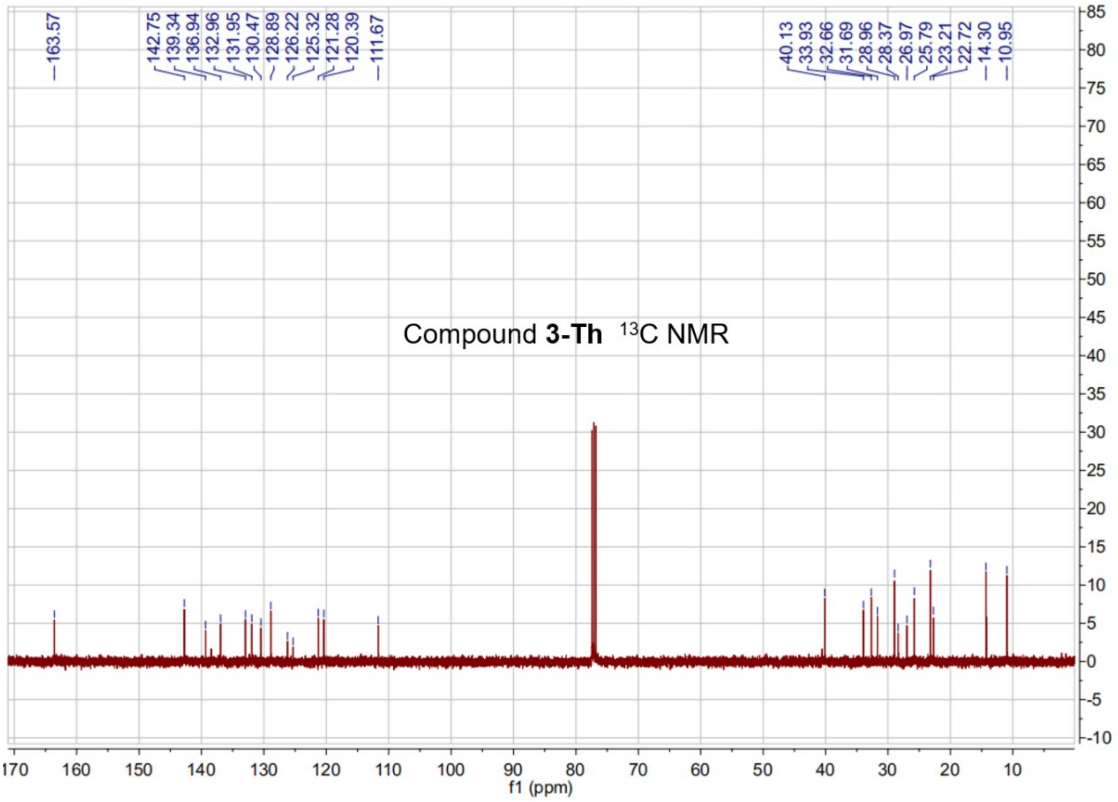


Figure S29. ^{13}C NMR of compound 3-Th in CDCl$_3$.

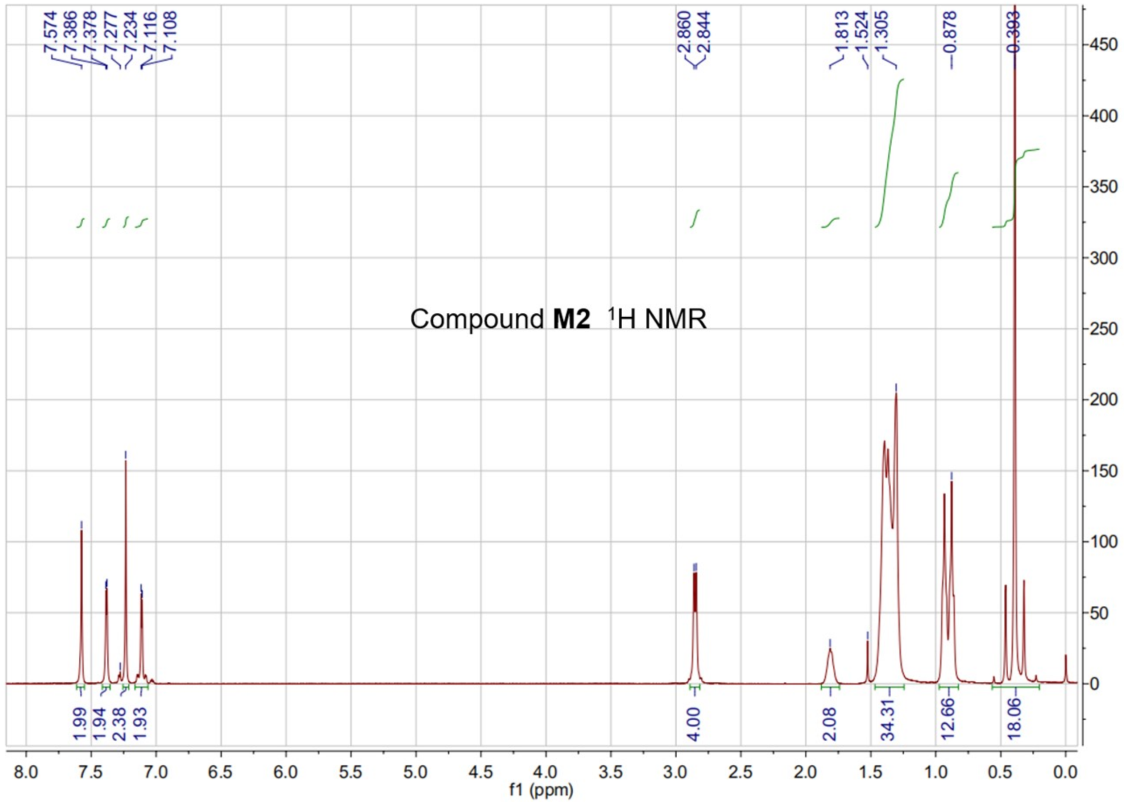


Figure S30. ^{1}H NMR of compound M2 in CDCl$_3$.

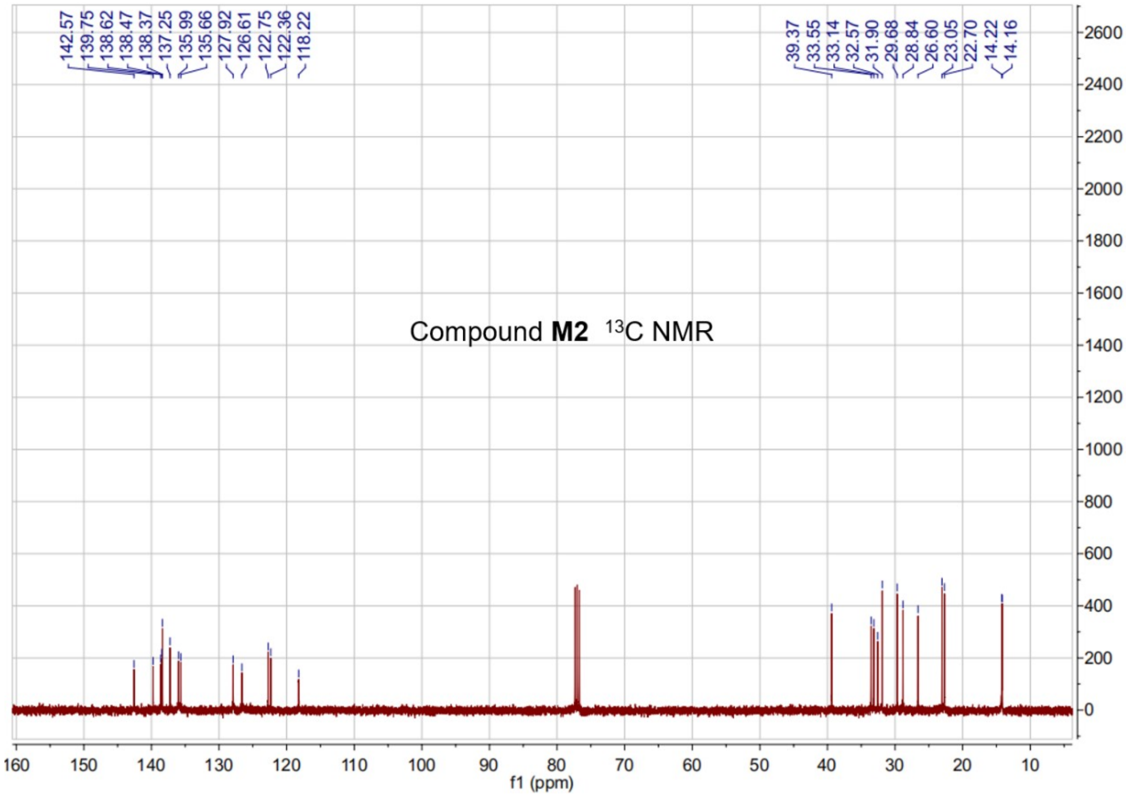


Figure S31. ^{13}C NMR of M2 in $CDCl_3$.

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