Supporting Information

Nonplanar perylene diimide-based small molecule and its polymer as electron acceptors

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Equipments

UV spectra measurements were taken by Genesys 10s UV-vis spectrophotometer, Thermoscientific. CV was measured by Chi660e CH instrument. PL spectra was measured by F97 Pro Fluorospectrophotmeter. EQE was measured by QE-R3011 Quantum Efficiency Measurement System, Enlitech. The organic films were spin-casted using Laurell Spin Coater, while as ZnO layer was prepared by EZ4 spin coater. The film thickness was measured by P7 STYLUS PROFILER, KLA Tencor. The HOMO values of A1 and A2 were measured by an Ionization Energy Measurement System Model IPS-4 (Nanjing SunnyTech Ltd., China). Metal electrodes was evaporated using IDF-5227 evaporator.

Synthesis

SDTF-PDI_2

A 100 mL Schlenk bottle was added with SDTF-di$SnMe_3$ (0.135g, 0.15 mmol), PDI-Br (0.275 g, 0.33 mmol), $Pd(PPh_3)_4$ (8.7 mg, 0.0075 mmol), toluene (50 mL), reacted at 110 °C under nitrogen for 24 h. The crude product was extracted by CH_2Cl_2 and purified by gel column chromatography. ^1H NMR (300 MHz, $CDCl_3$, δ): 8.63(s, 3H), 8.58-8.53(dd, 2H), (8.37, 8.34) (d, 2H), (7.70, 7.68) (d, 1H), 7.42-7.30 (2H), (7.17, 7.15) (d,1H), 6.67(s, 1H), 2.24 (s, 4H), 1.84 (s, 4H), (1.43-1.22)(36H), (0.87-0.80)(12H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 152.76, 145.71, 143.97, 142.26, 140.06, 133.00, 132.77, 128.44, 127.96, 127.14, 126.82, 126.41, 124.20, 124.12, 123.99, 123.20, 122.80, 122.66, 122.17, 55.35, 32.76, 32.10, 32.03, 29.52, 27.33, 27.23, 22.89, 22.83, 14.30, 14.25, 1.18. MALDI-TOF-MS (1855.94).

SDTF-FPDI_2

A 50 mL Schlenk bottle added by SDTF-PDI_2(0.256 g, 0.14 mmol), $FeCl_3$ (0.568 g, 3.5 mmol) in dry Toluene (20 mL), CH_3NO_2 (0.7 mL) was added to the reaction system. Reacted at 110 °C for 5 h. Quenched by water and extracted by dicholoromethane (DCM) and the organic phase was collected and evaporated to get the crude product, which was purified by gel column chromatography with hexane:DCM (2:1). The pure dull-red product was collected with a yield of 70%. ^1H NMR (300 MHz, $CDCl_3$, δ): 8.64(s, 3H), 8.58-8.53(dd, 2H), 8.34 (2H), (7.70, 7.68) (d, 1H), 7.42-7.30 (2H), (7.17, 7.15) (d,1H), 6.68(s, 1H), 2.25 (s, 4H), 1.85 (s, 4H), (1.30-1.22) (32H), (0.87-0.80)

(12H), 0.07 (18H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 157.32, 145.66, 143.75, 141.71, 140.63, 134.96, 134.38, 134.30, 133.68, 129.48, 129.36, 128.93, 128.52, 128.25, 127.69, 123.85, 123.42, 122.88, 120.54, 62.94, 54.99, 54.83, 32.58, 32.53, 31.95, 31.90, 29.42, 29.35, 22.78, 22.72, 14.21, 14.17. Calcd for $C_{121}H_{128}N_4O_8S_2$: C, 79.39; H, 7.05; N, 3.06; S, 3.50. Found: C, 79.31; H, 6.79; N, 3.11; S, 2.76. MALDI-TOF-MS (1828.91).

SDTF-FPDI$_2$-diBr

A 25 mL Schlenk bottle added by SDTF-FPDI$_2$ (70 mg, 0.03824 mmol) and $FeCl_3$ (33 mg, 0.317 mmol) in 11 mL $CHCl_3$ (0.003 M), Br_2 (37.5μl, 0.732 mmol) in 3.7 mL $CHCl_3$ was added dropwise at 0°C and returned to RT, and reacted at 70°C for 3 h. The resultant returned to RT, quenched by water and extracted by CH_2Cl_2. The organic phase was evaporated to remove the solvent and the crude product was purified by the gel column chromatography with the solvent of hexane:DCM (2:1) to get pure deep red solid with the yield of 50%. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 9.74 (s, 1H), (9.12-9.19) (dd, 2H), 8.93-9.0 (2H), 8.71 (2H), (7.50-7.53) (dd, 1H), 7.21 (1H), 5.37 (2H), 2.43 (s, 5H), 2.03 (s, 5H), 1.23-1.42 (41H), 0.85-0.91(16H), 0.07 (s, 15H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 150.87, 144.01, 143.75, 142.68, 142.22, 133.05, 132.95, 132.70, 131.44, 128.31, 127.20, 126.89,126.85, 126.16, 126.02, 124.32, 124.00, 123.30, 122.84, 122.76, 122.31, 67.41, 55.39, 32.75, 32.13, 32.01, 29.51, 27.32, 27.23, 22.91, 22.82, 14.30, 14.24, 1.17. Calcd for

$C_{121}H_{126}Br_2N_4O_8S_2$: C, 73.09; H, 6.39; N, 2.82; S, 3.23. Found: C, 73.63; H, 6.19; N, 2.88; S, 2.62. MALDI-TOF-MS (1984.74).

P(SDTF-FPDI$_2$-T)

In 10 mL Schlenk SDTF-FPDI$_2$-diBr (122 mg, 0.06136 mmol), 2,5-bis(trimethylstannyl)thiophene (25.14 mg, 0.06136 mmol), $Pd_2(dba)_3$ (1.68 mg, 0.00184 mmol, 3 mol%) and P(o-Tol)$_3$ (2.989 mg, 0.00982 mmol, 16 mol%) were added, vacuumed and nitrogen purged three times. Dry chlorobenzene (2.35 ml) was added with syringe into the Schlenk. The system reacted at 130 °C under nitrogen for 3 days and returned to RT. And add 250 mL methanol and 15 mL HCl to be stirred overnight. And then filtered and Soxhlet extraction subsequently by methanol, acetone, hexane and chloroform. The number molecular weight M_n is 88,982 and M_w of 104,052, PDI of 1.17. Calcd for $C_{125}H_{128}N_4O_8S_3$: C, 78.6; H, 6.96; N, 2.89; S, 4.96. Found: C, 78.07; H, 6.65; N, 2.79; S, 4.27.

Device fabrication

ITO was successively cleaned by detergent, deionized water, acetone and isopropyl alcohol (IPA). The ITO was dried by nitrogen and then cleaned by UV-O_3 UVO_3 cleaner for 30 min. PEDOT:PSS was deposited on ITO at 6000 rpm for 1 min and annealed at 120 °C for 30 min, with a thickness of 46 nm. The blend solution of PTB7-Th:acceptor dissolved in chlorobenzene was

stirred at 60 °C under nitrogen in the glove box overnight, filtered by poly(tetrafluoroethylene) (PTFE) filter (0.45 μm, 13mm), and deposited as the active layer by spin coating. PDIN (1.5 mg/mL) in methanol with 0.3% acetic acid was prepared at ready and the solution was spin coated on the active layer at 3000 rpm for 30 s without further thermal treatment. LiF and Al were vacuum evaporated on the active layer.

Hole mobility measurement

The hole mobilities were measured using the SCLC method, with the device architecture of ITO/PEDOT:PSS/active layer/MoO_3(2nm)/Al(100nm). The mobilities were obtained by taking current-voltage curves and fitting the curves to a space charge limited form, where the SCLC is described by the equation, $J=(9/8)\varepsilon_r\varepsilon_o\mu(V^2/L^3)$, where ε_o is the permittivity of free space, ε_r is the relative permittivity of the material (assumed to be 3 for organic materials), μ is the hole mobility and L is the film thickness. From the plots of $J^{1/2}$ vs. V, hole mobilities can be deduced.

Electron mobility measurement

The electron mobilities were measured using the SCLC method, employing a device architecture of ITO/ZnO/Active layer/PDIN/Al. The mobilities were obtained by taking current-voltage curves and fitting the curves to a space charge limited form, where the SCLC is described by the equation,

$J=(9/8)\varepsilon_r\varepsilon_o\mu(V^2/L^3)$. By linearly fitting $J^{1/2}$ with V, the mobilities were extracted from the equation of

$$\mu=(8/9)(L^3/\varepsilon_r\varepsilon_o)(J/V^2)= (8/9)(L^3/\varepsilon_r\varepsilon_o)slope^2$$

Absorption coefficient

The absorption coefficient in the solution

SDTF-FPDI$_2$: m=1.7 mg, C=5.29×10^{-6} mol/L, A=0.488, ε=5.22×10^4 L/(mol cm)

SDTF-FPDI$_2$-diBr: m=2 mg, C=1.0×10^{-5} mol/L, A=0.317, ε=3.17×10^4 L/(mol cm)

P(SDTF-FPDI$_2$-T): m=2.8 mg, C=3.15×10^{-7} mol/L, A=0.996, ε=3.2×10^6 L/(mol cm)

The absorption spectra of blend films in Figure S3(b):

SDTF-FPDI$_2$ blend film: d=100 nm, A=0.3217 (λ_{max}=440 nm)

SDTF-FPDI$_2$-diBr blend film: d=108 nm, A=0.2717 (λ_{max}=491 nm)

P(SDTF-FPDI$_2$-T) blend film: d=125 nm, A=0.5249 (λ_{max}=439 nm)

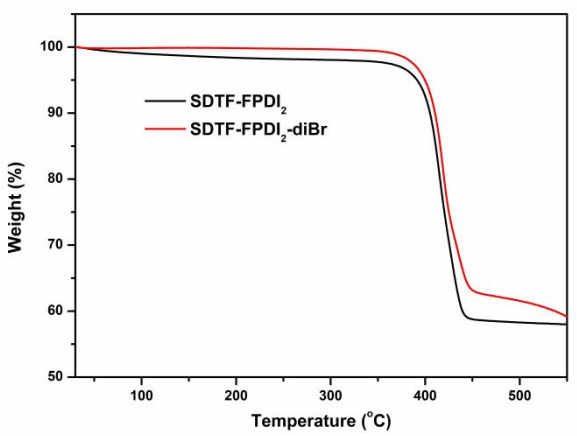


Figure S1. TGA curves of SDTF-FPDI$_2$ and SDTF-FPDI$_2$-diBr

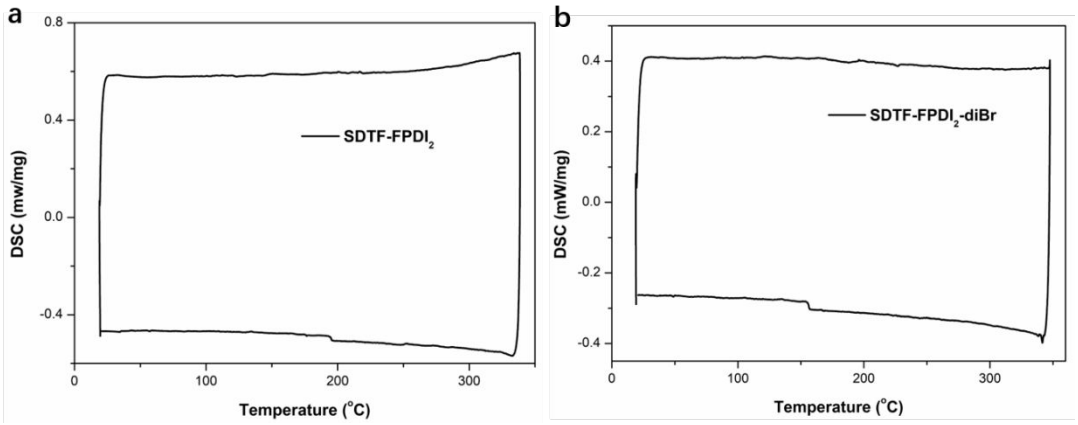


Figure S2. DSC curves of SDTF-FPDI$_2$ and SDTF-FPDI$_2$-diBr

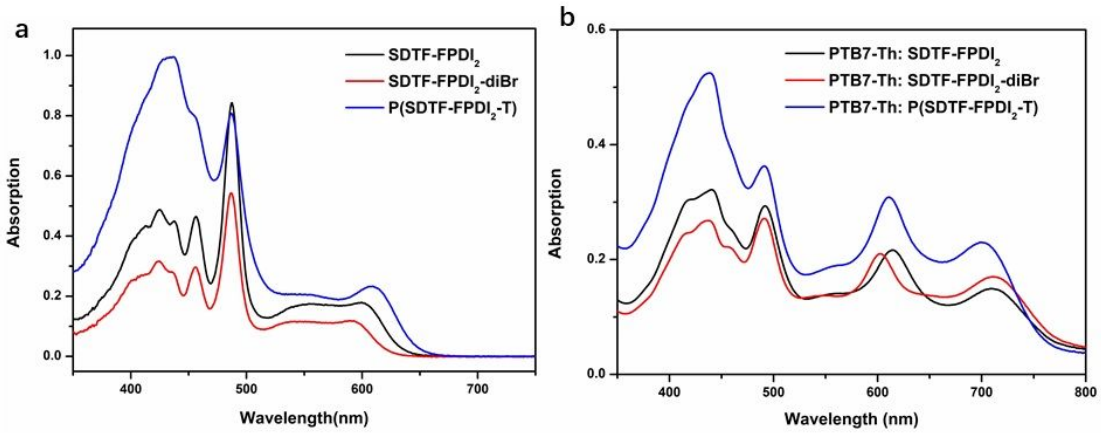


Figure S3. Absorption spectra of three electron acceptors in solution and blend film

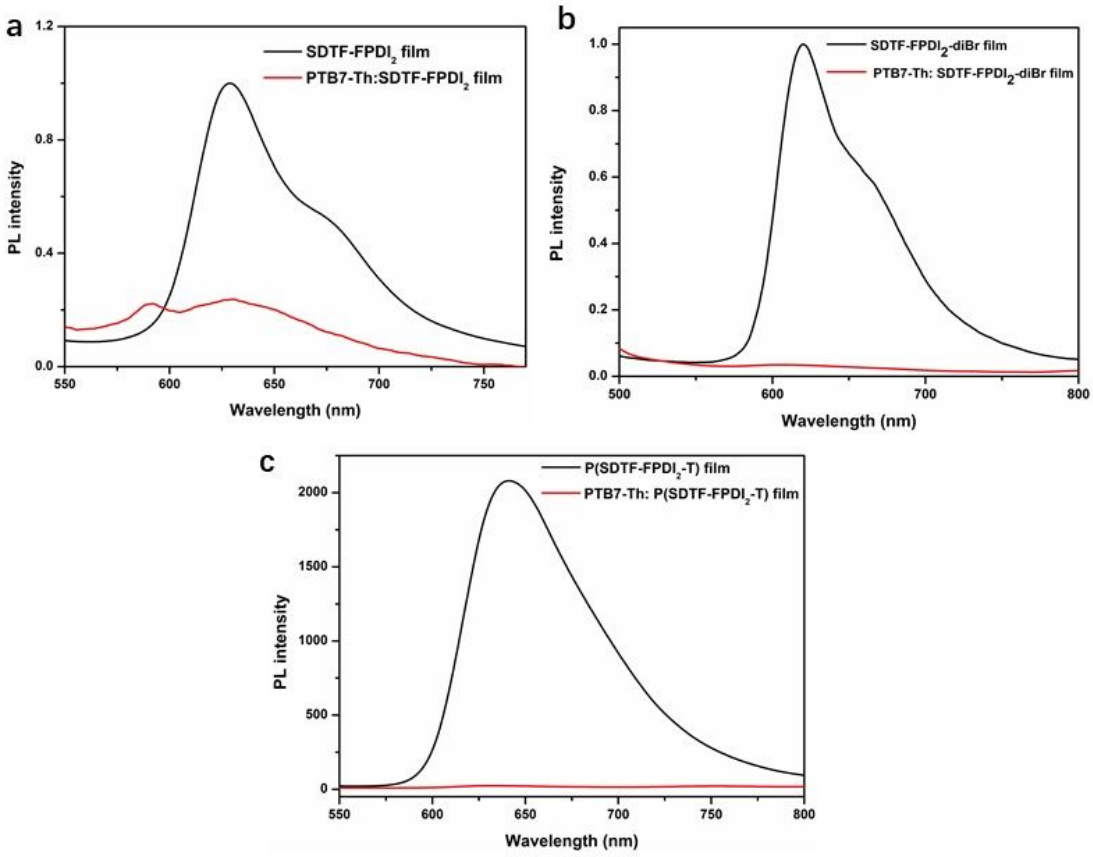


Figure S4. PL spectra of SDTF-FPDI$_2$, SDTF-FPDI$_2$-diBr and P(SDTF-FPDI$_2$-T) films and the blend films with PTB7-Th

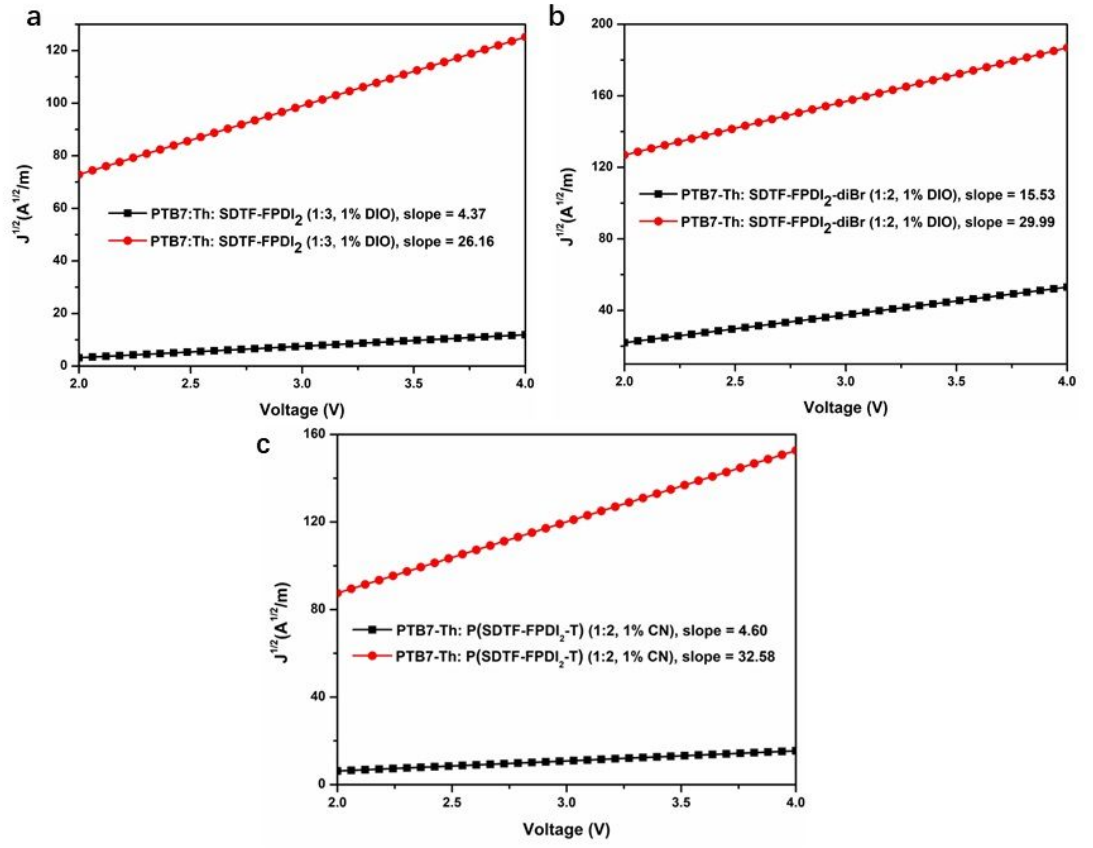


Figure S5. $J^{1/2}$-V curves of electron-only (in dark) and hole-only devices (in red)

Table S1. Photovoltaic performances of devices based on PTB7-Th: SDTF-$FPDI_2$

D:A	Solvent additive	Annealing (°C)	ETL	V_{oc} (V)	*FF* (%)	J_{sc} (mA/cm^2)	PCE (%)
1:1	--	80	LiF	0.74	19.51	1.22	0.17
1:2	--	100	LiF	0.86	25.07	1.32	0.28
1:2	3%CN	100	LiF	0.89	38.91	3.88	1.34
1:2	3%CN	80	PDIN	0.88	42.04	4.33	1.61
1:2	1%CN	--	PDIN	0.85	31.00	3.68	0.97
1:2	1%DIO	80	PDIN	0.87	35.39	7.33	2.26
1:2	3%DIO	80	PDIN	0.8	35.65	5.78	1.76
1:2	1%DPE	100	PDIN	0.90	31.74	6.71	1.91

Table S2. Photovoltaic performances of devices based on PTB7-Th: SDTF-$FPDI_2$-diBr

D:A	Solvent additive	Annealing (°C)	V_{oc} (V)	*FF* (%)	J_{sc} (mA/cm^2)	PCE (%)
1:1	-	80	0.88	11.71	2.73	0.28
1:1	-	100	0.85	11.57	1.72	0.17
1:3	-	100	0.73	12.19	1.42	0.28
1:1	1%DIO	-	0.94	40.64	5.21	1.99
1:1	1%DIO	80	0.74	18.09	3.99	0.53
1:1	1%DIO	100	0.90	22.34	5.28	1.06
1:2	3%DIO	100	0.93	48.54	6.73	3.03
1:2	1%DPE	80	0.90	46.70	8.95	3.75
1:2	3%DPE	100	0.90	41.09	6.54	2.42
1:2	1%CN	80	0.94	22.44	4.83	1.02

Table S3. Photovoltaic performances of devices based on PTB7-Th: P(SDTF-$FPDI_2$-T)

D:A	Solvent additive	Annealing (°C)	ETL	V_{oc} (V)	*FF* (%)	J_{sc} (mA/cm^2)	PCE (%)
2:1	--	--	LiF	0.91	21.97	3.50	0.70
1:1	--	--	LiF	0.94	21.71	7.20	1.47
1:2	--	--	LiF	0.94	21.10	8.58	1.69
1:2	3% CN	80	LiF	0.92	30.53	8.52	2.40
1:4	3% CN	80	LiF	0.94	31.47	7.61	2.25
1:2	3% CN	100	PDIN	0.90	44.42	8.09	3.24

Table S4. The electron and hole mobility of the blend film

D:A	μ_e (cm^2/Vs)	μ_h (cm^2/Vs)
PTB7-Th: SDTF-$FPDI_2$, 1%DIO	$0.64*10^{-5}$	$2.29*10^{-4}$
PTB7-Th: SDTF-$FPDI_2$-diBr, 1%DIO	$1.02*10^{-4}$	$3.79*10^{-4}$
PTB7-Th: P(SDTF-$FPDI_2$-T), 1%CN	$1.38*10^{-5}$	$6.94*10^{-4}$

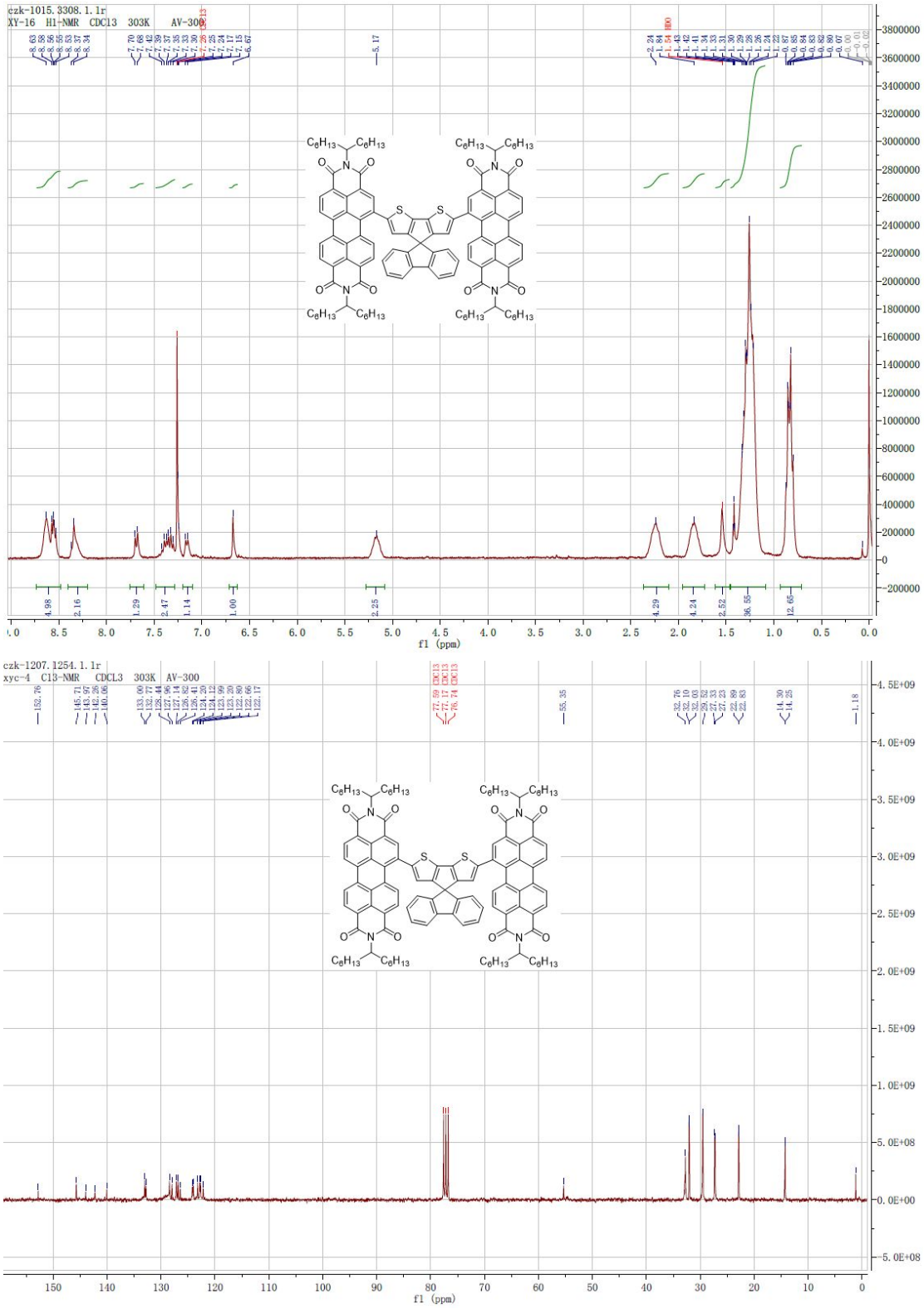


Figure S6. ^{1}HNMR and ^{13}CNMR spectra of SDTF-PDI$_2$

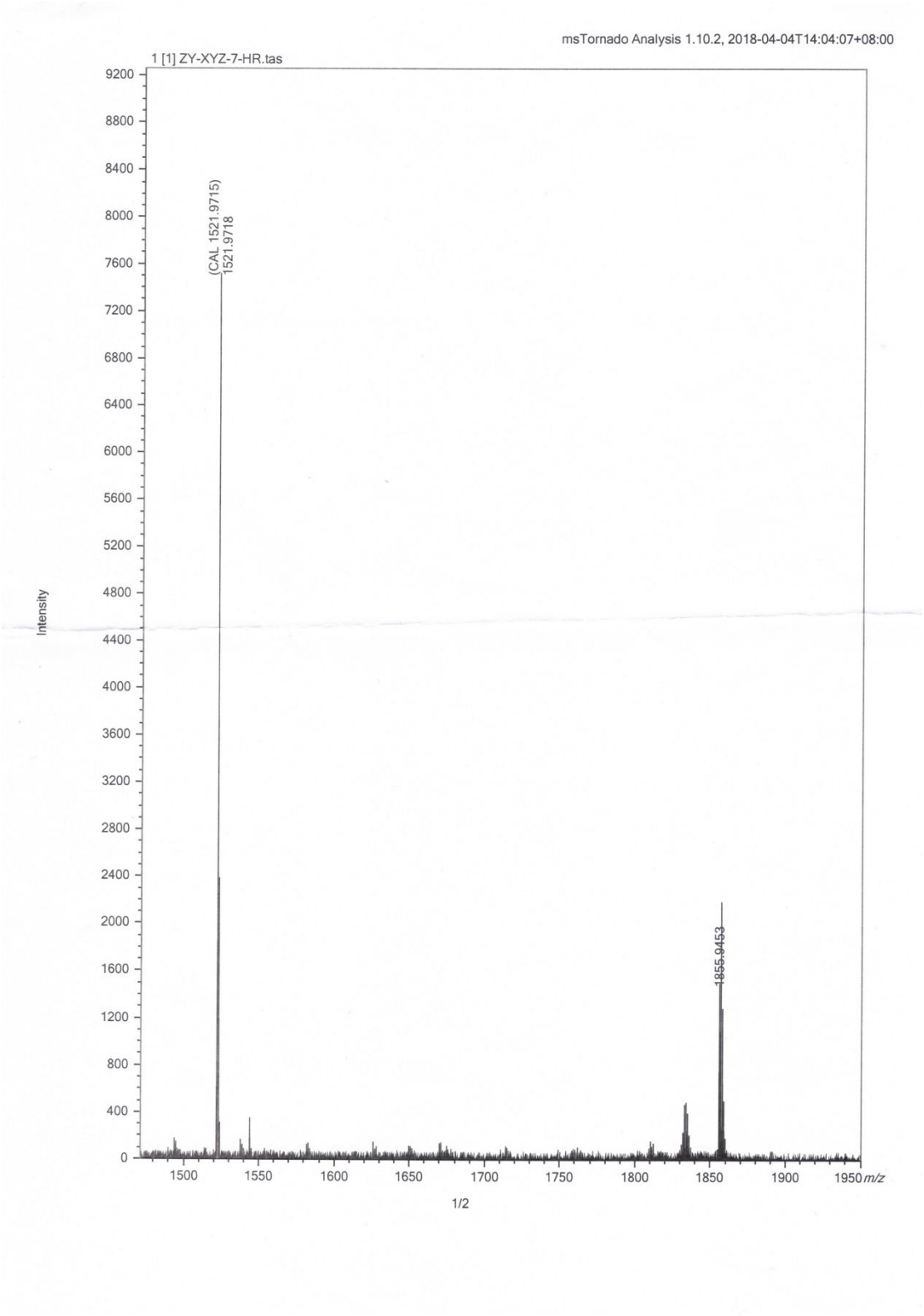


Figure S7. The MALDI-TOF-MS of SDTF-PDI_2

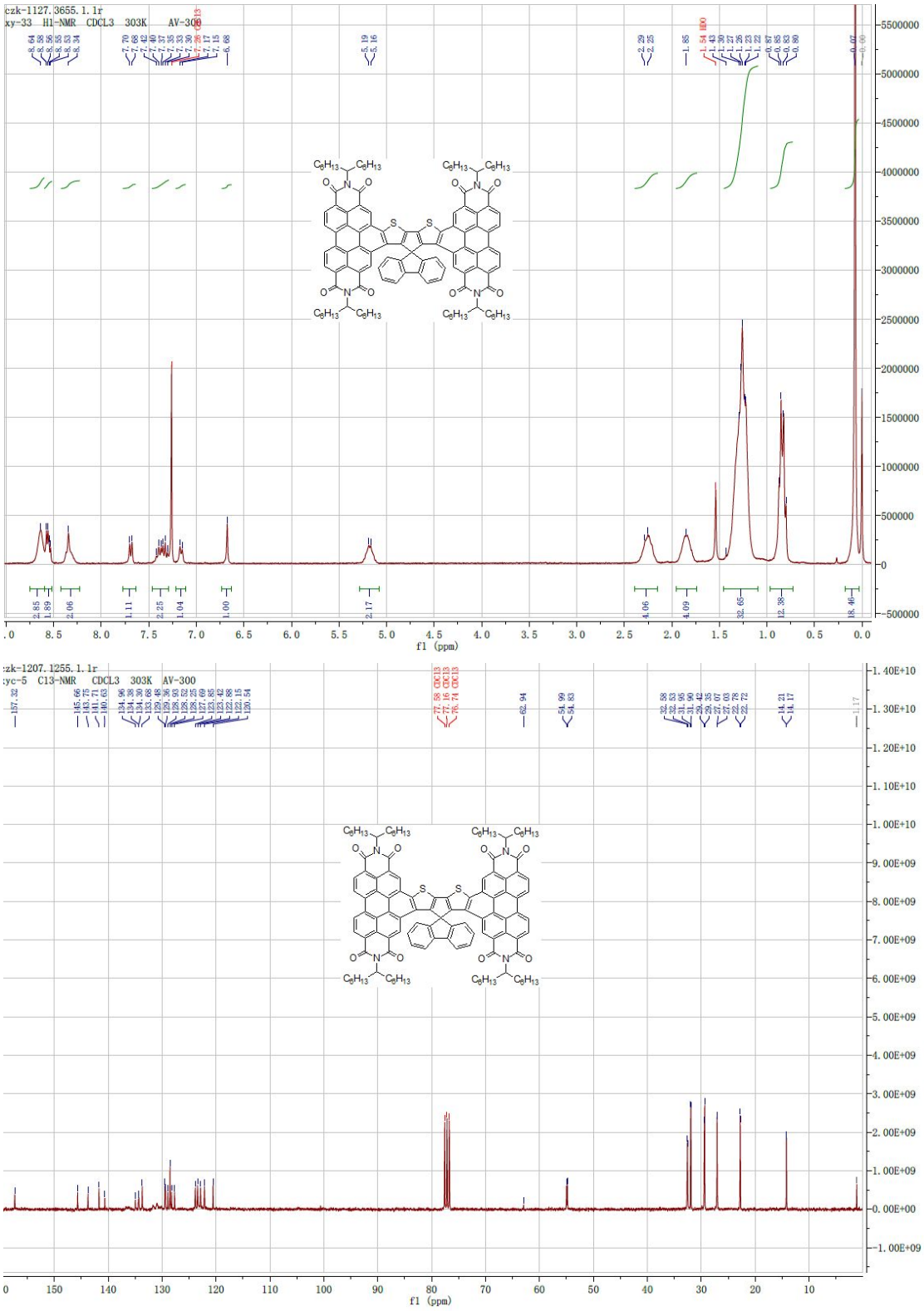
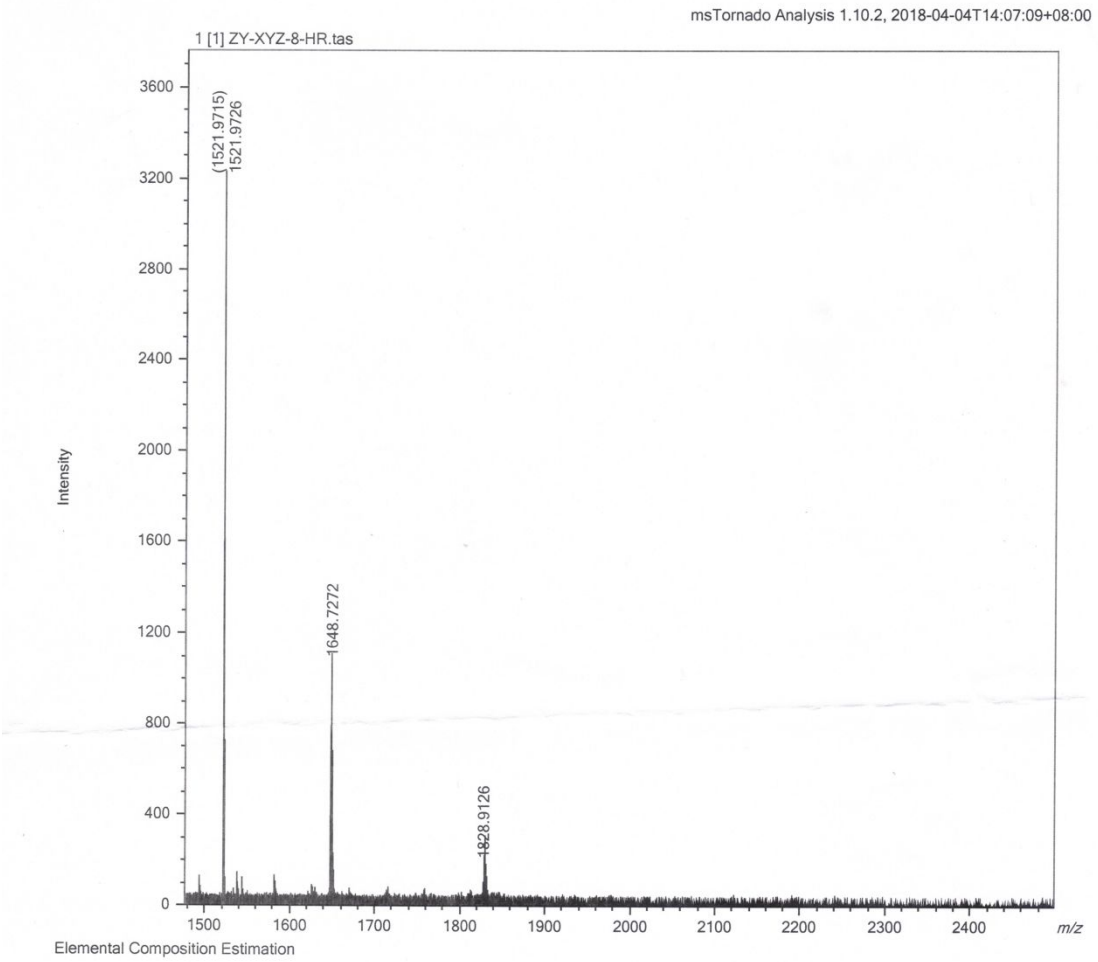


Figure S8. ^{1}HNMR and ^{13}CNMR spectra of SDTF-FPDI$_2$



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
1828.91256 ± 0.00914	5.0 ppm	Odd/Even	+1	-0.5 - 200.0	100

Elements

C 0 - 125 H 0 - 135 N 0 - 4 O 0 - 8 S 0 - 2

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C124 H124 N4 O8 S	1828.91344	65.0	0.00088	-0.00088	-0.48
2	C121 H128 N4 O8 S2	1828.91681	60.0	0.00425	-0.00425	-2.32
3	C125 H126 N3 O6 S2	1828.90826	64.5	0.00430	0.00430	2.35

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Figure S9. The MALDI-TOF-MS of SDTF-FPDI$_2$

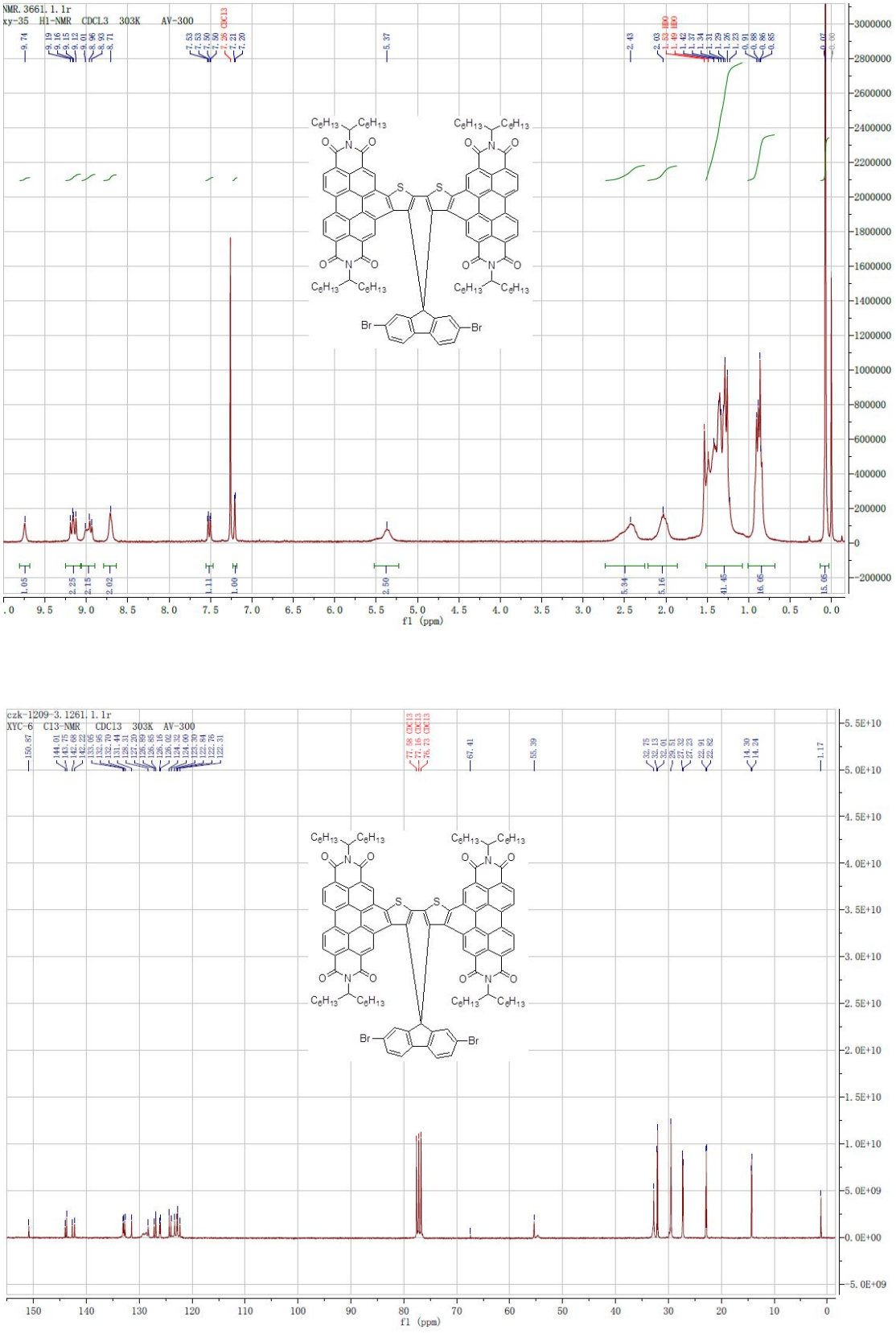
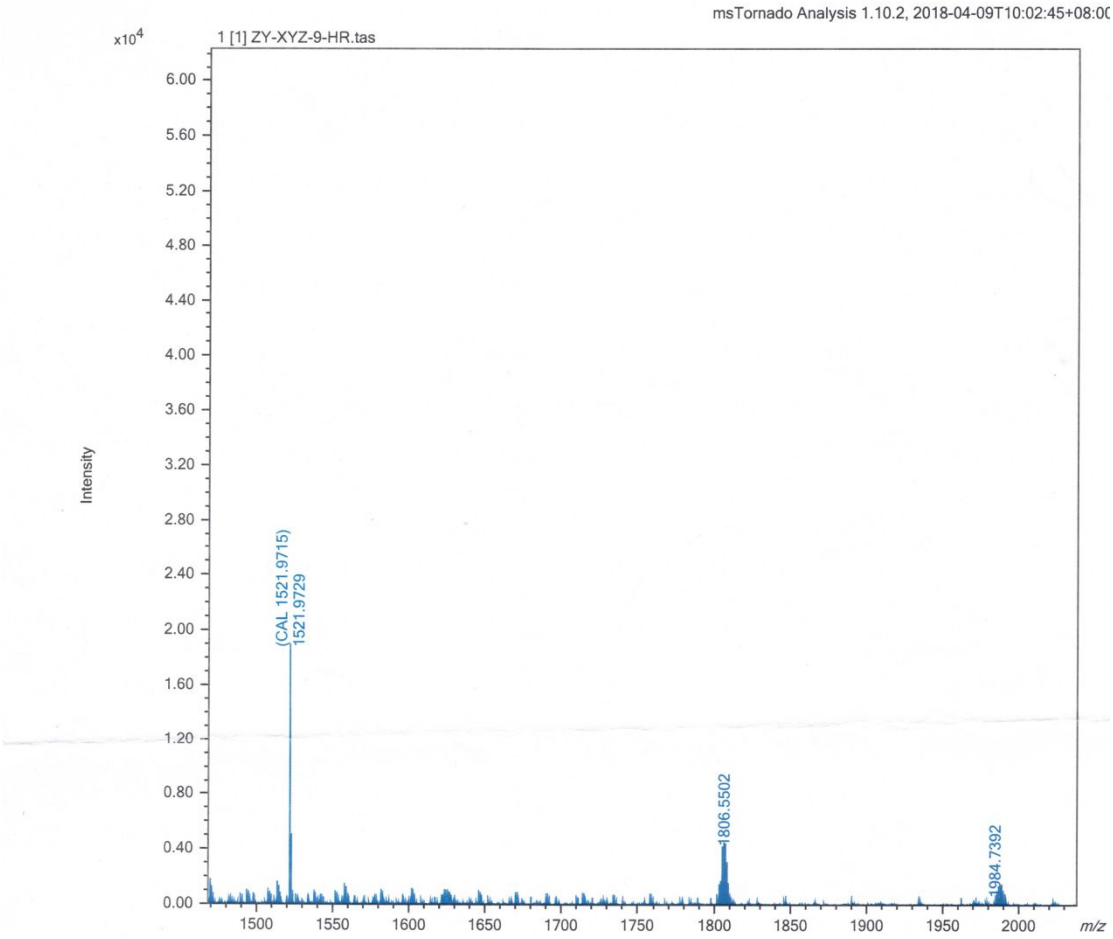


Figure S10. [1]HNMR and [13]CNMR spectra of SDTF-FPDI$_2$-diBr



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
1984.73916 ± 0.00992	5.0 ppm	Odd/Even	+1	-0.5 - 200.0	100

Elements

C 0 - 125 H 0 - 130 N 0 - 5 O 0 - 8 S 0 - 2 Br 0 - 2

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C121 H126 N4 O8 S2 Br2	1984.73784	60.0	0.00133	0.00133	0.67
2	C124 H124 N5 O5 S2 Br2	1984.74052	64.5	0.00135	-0.00135	-0.68
3	C124 H122 N4 O8 S Br2	1984.73446	65.0	0.00470	0.00470	2.37
4	C125 H124 N3 O8 S Br2	1984.74704	64.5	0.00788	-0.00788	-3.97
5	C125 H124 N3 O6 S2 Br2	1984.72928	64.5	0.00988	0.00988	4.98

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Figure S11. The MALDI-TOF-MS of SDTF-FPDI$_2$-diBr

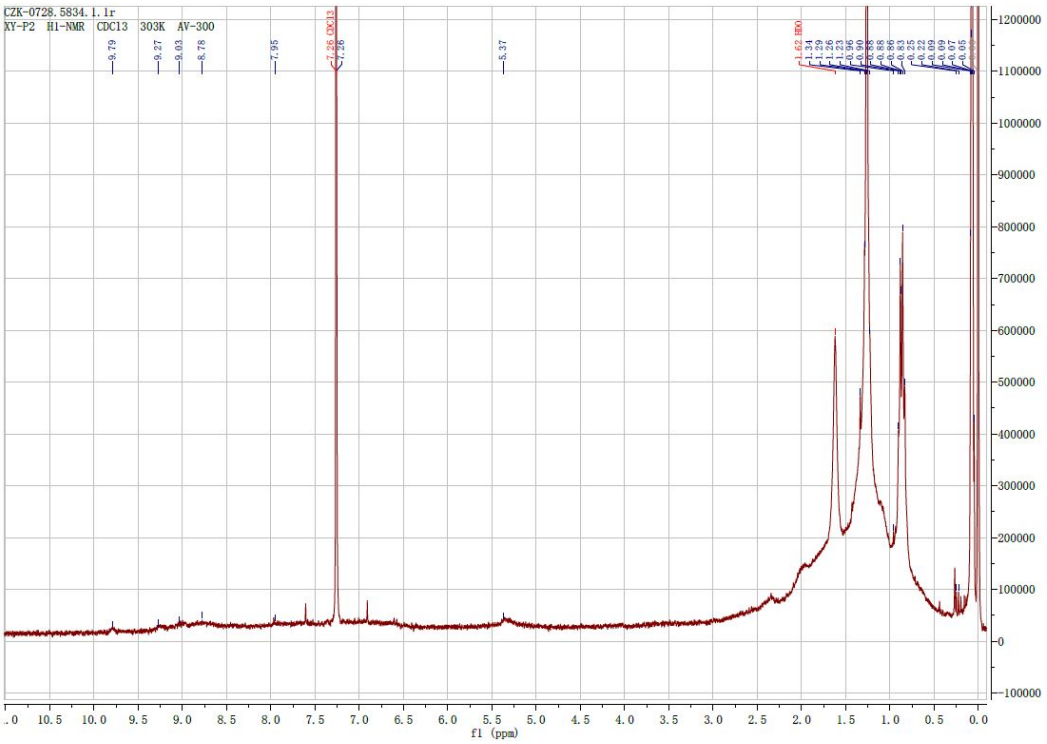


Figure S12. ^{1}HNMR of P(SDTF-FPDI$_2$-T)

Cirrus GPC Sample Injection Report

Generated by: gpc Saturday, June 23, 2018 10:18 AM

Workbook: E:\Cirrus Workbooks\IAM20161212\IAM20161212.plw

Sample Details

Sample Name: XY_2

Acquired: 6/21/2018 6:08:29 PM By Analyst: gpc Batch Name: 20180621

Concentration: 0.10 mg/mlInjection Volume: 200.0 ul K of Sample: 14.1000 Alpha of Sample: 0.7000

Analysis Using Method: 20171213

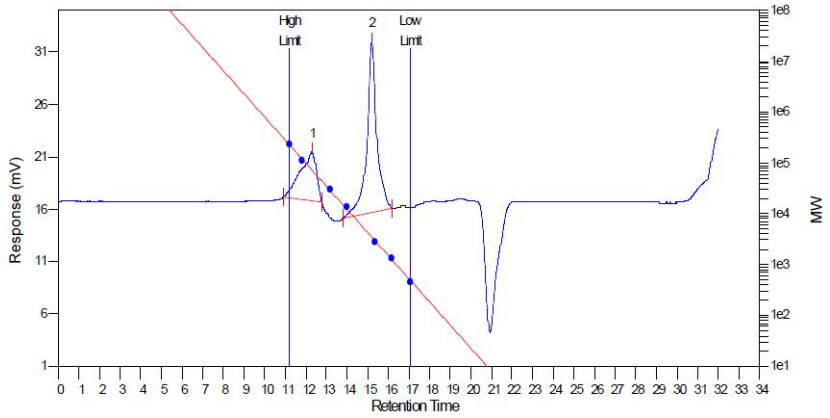
Calibration Used: 1/17/2018 4:36:17 PM

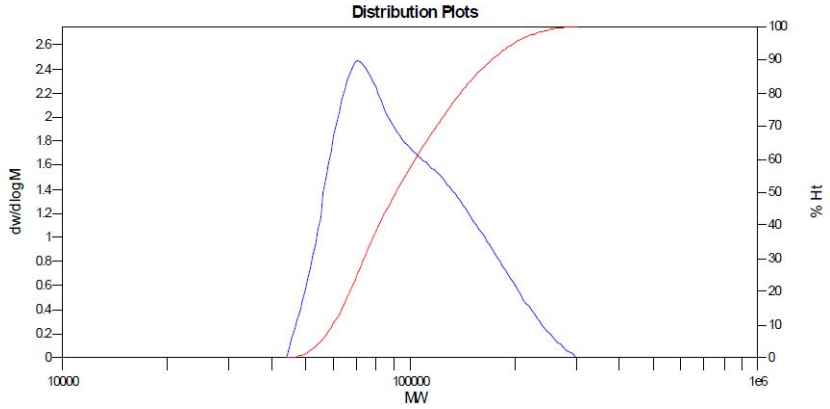
Calibration Type: Narrow Standard Curve Fit Used: 1 K: 14.1000 Alpha: 0.7000

Calibration Curve: y = 10.450770 - 0.454795x^1

High Limit MW RT: 11.22 mins Low Limit MW RT: 17.10 mins

Flow Marker RT: 0.00 mins FRCF: 1.0000 FRM Name:





MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	70665	88982	104052	123726	145966	101430	1.16936
2	3511	3321	3755	4388	5355	3678	1.13068

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.93	12.32	12.77	4.66304	22.2853	249.007	30.8823
2		13.80	15.18	16.17	16.2613	77.7147	557.303	69.1177

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Figure S13. GPC of P(SDTF-FPDI$_2$-T)