Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information:

Peripherally Diketopyrrolopyrrole-Functionalized Dendritic Oligothiophenes – Synthesis, Molecular Structure, Properties and Applications

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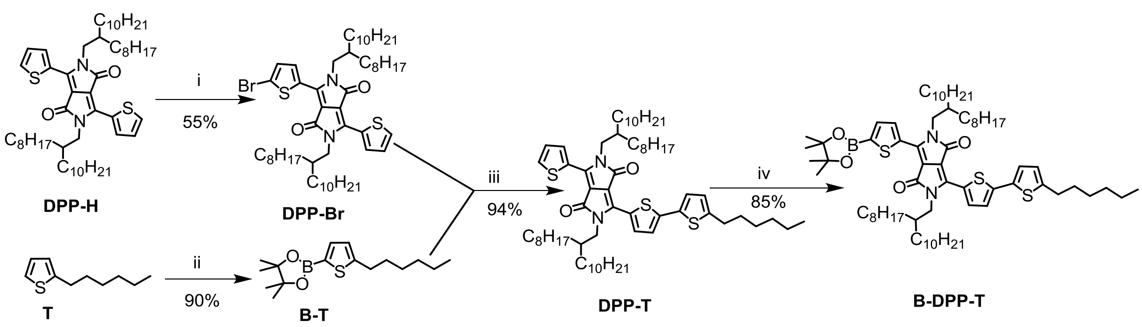
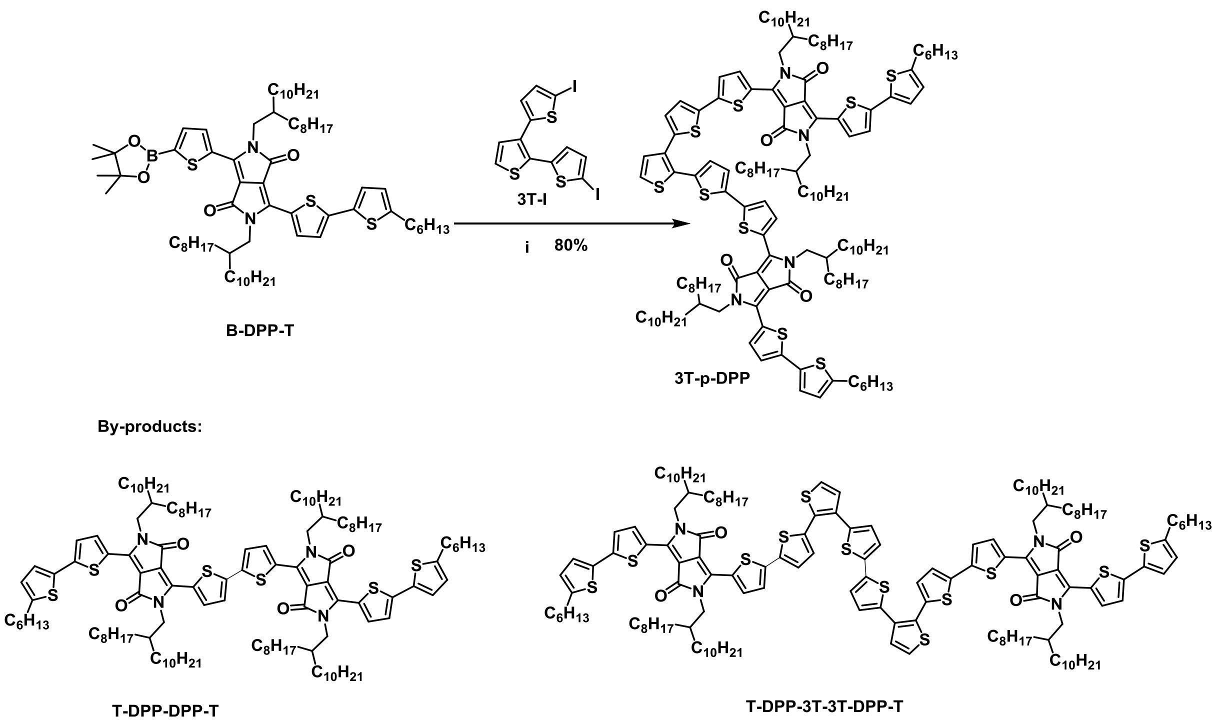


Scheme S1. Synthetic route to the key precursor **B-DPP-T**.

Reagents and conditions: i) NBS (1.1 eq), $CHCl_3$; ii) *1.* *n*-BuLi/THF, *2.* 2-isopropyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; iii) $[Pd_2(dba)_3]$ $CHCl_3$, $HP(tBu)_3BF_4$, K_2CO_3, THF; iv) $[Ir(OMe)(COD)]_2$, dtbpy, HBpin, THF. (dba= dibenzylideneacetone; COD = 1,5-cyclooctadiene; dtbpy = 4,4'-di-tert-butyl-2,2'-bipyridine).



Scheme S2. Synthesis of first-generation dendrons **3T-p-DPP.**

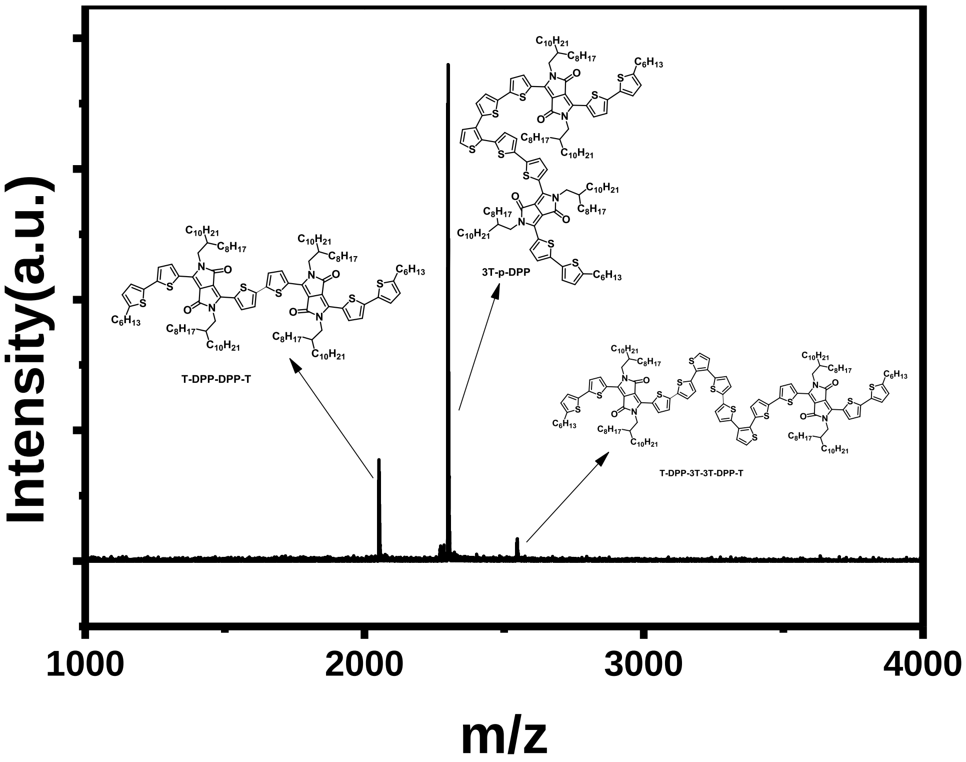
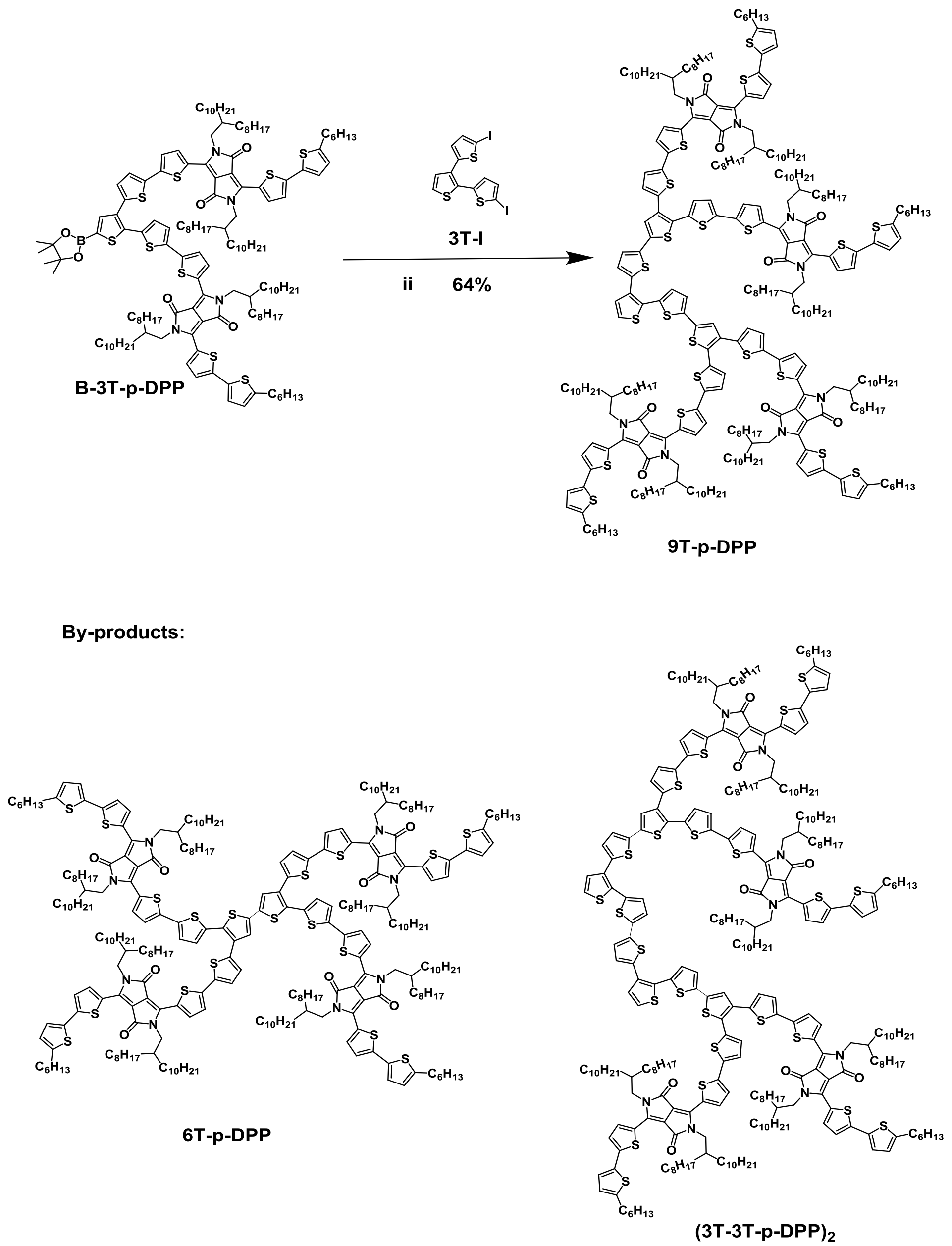


Figure S1. MALDI-TOF Mass-spectrometric characterization of **3T-p-DPP** and corresponding by-products (T-DPP-DPP-T and T-DPP-3T-3T-DPP-T).



Scheme S3. Synthesis of second-generation dendrons **9T-p-DPP** by using **B-3T-p-DPP** and **3T-I.**

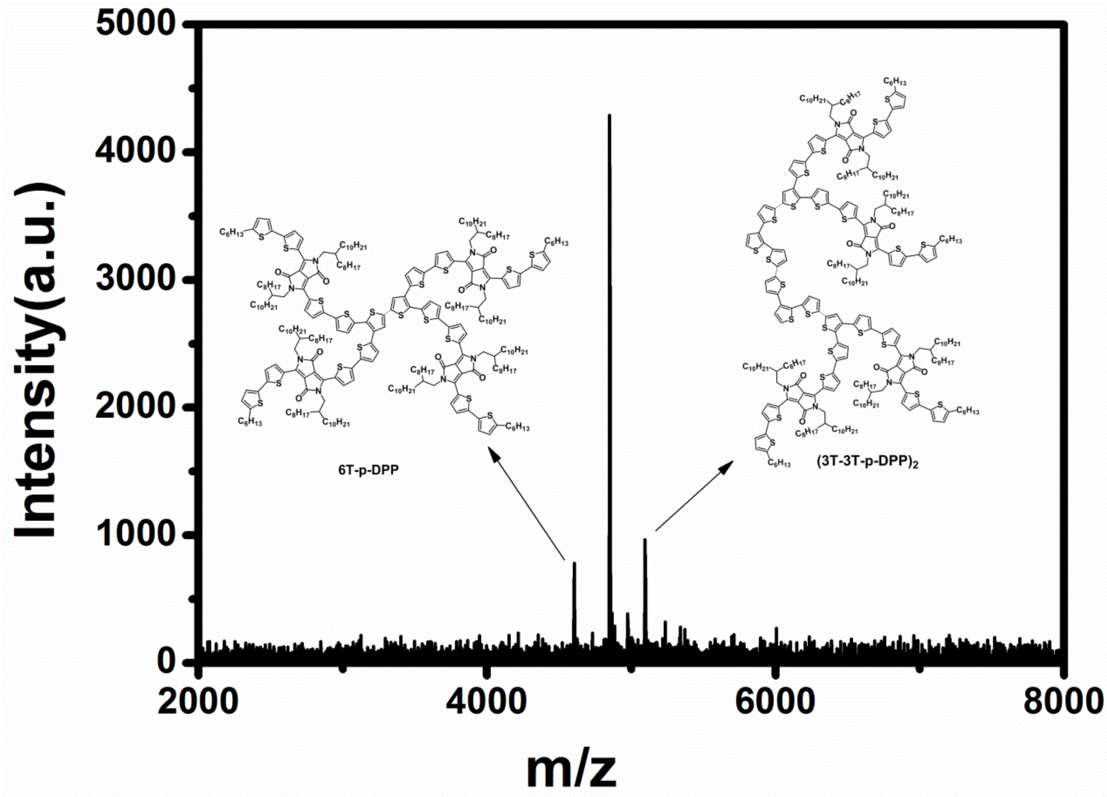
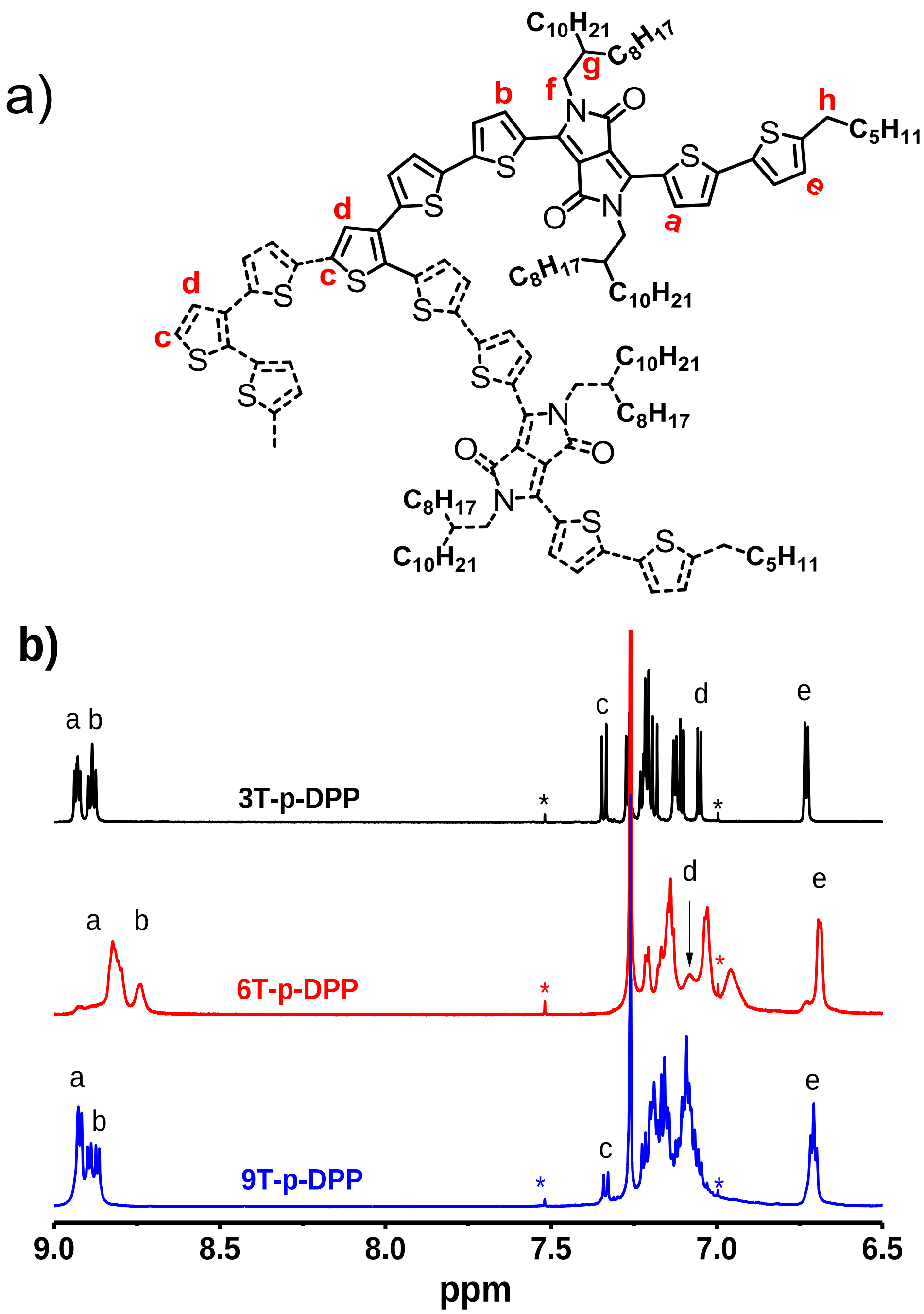


Figure S2. MALDI-TOF Mass-spectrometric characterization of **9T-p-DPP** and corresponding by-products (**6T-p-DPP** and (**3T-3T-p-DPP**)$_2$).



a)
C10H21
C8H17
f
g
b
h
C5H11
e
a
d
c
N
O
S
b)
a b
c
d
e
3T-p-DPP
6T-p-DPP
9T-p-DPP
9.0
8.5
8.0
7.5
7.0
6.5
ppm

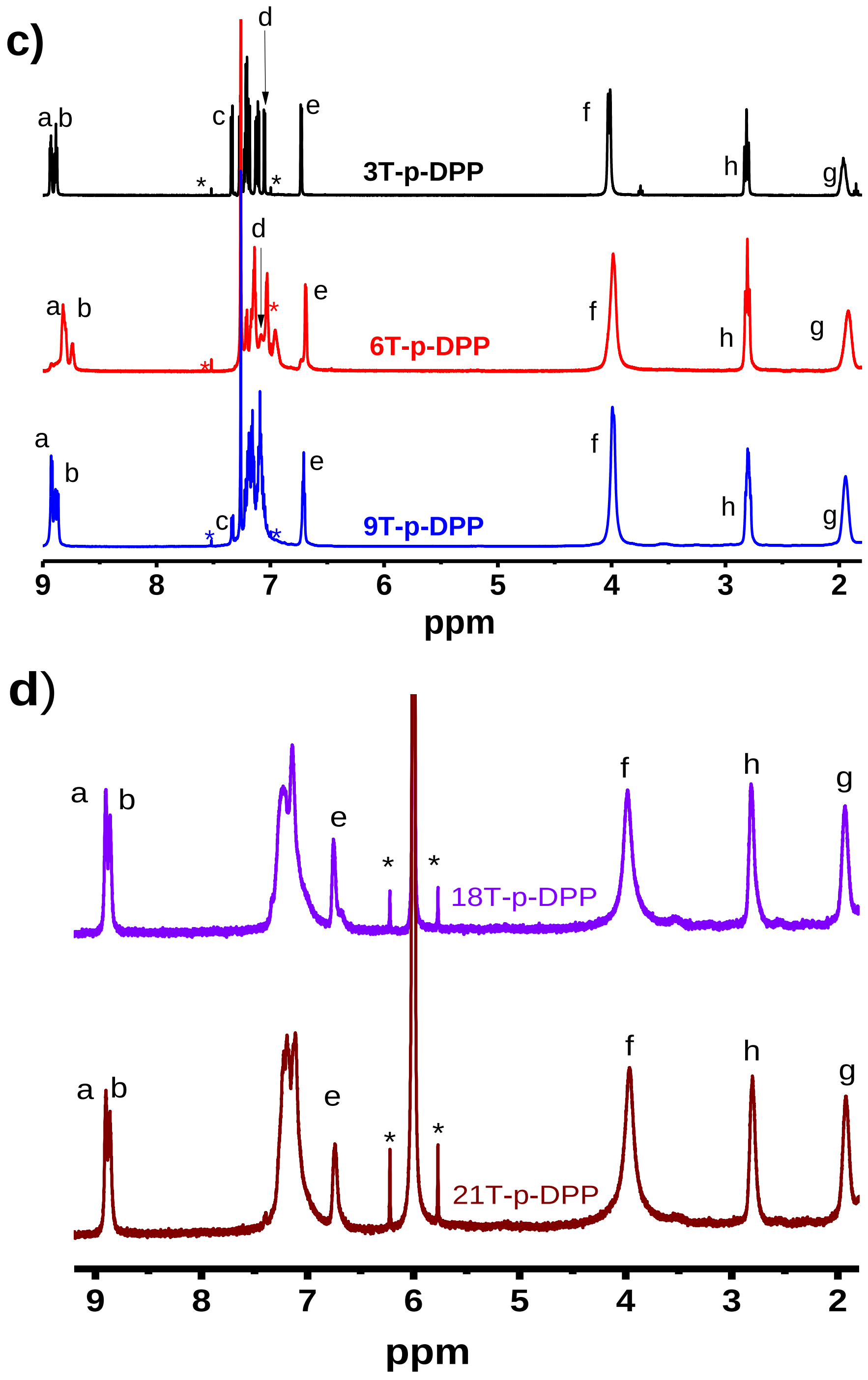
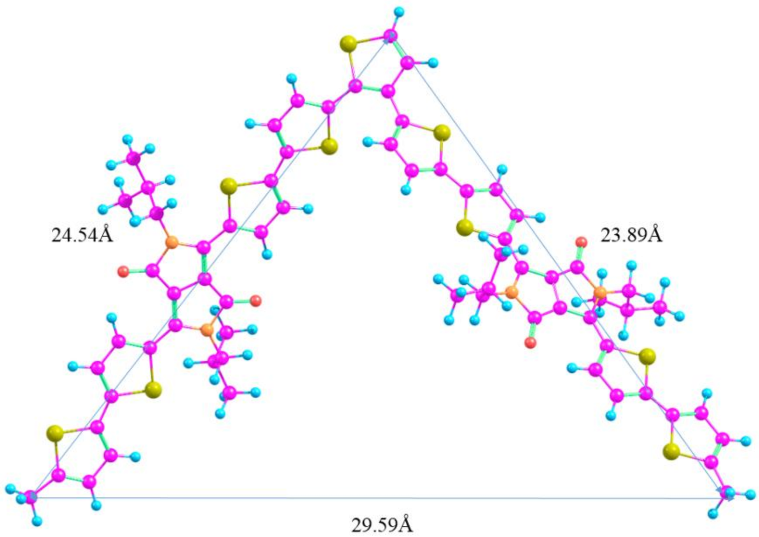
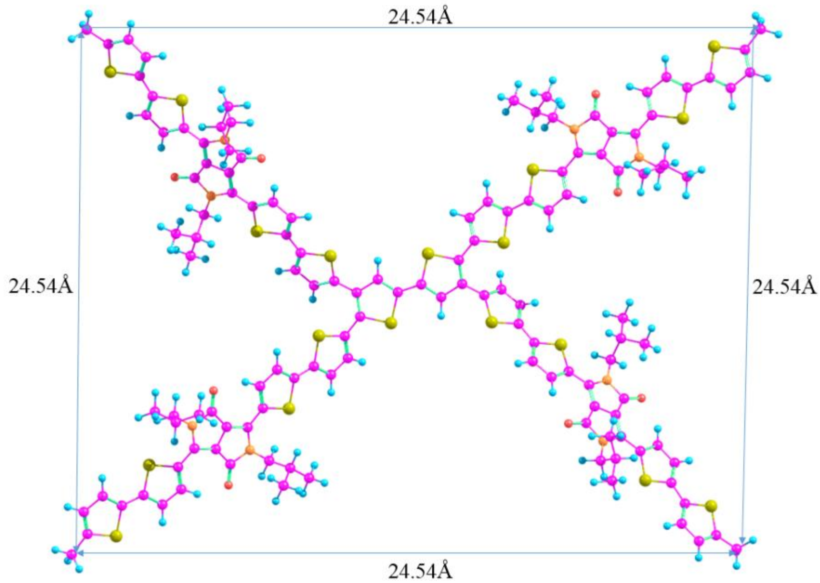


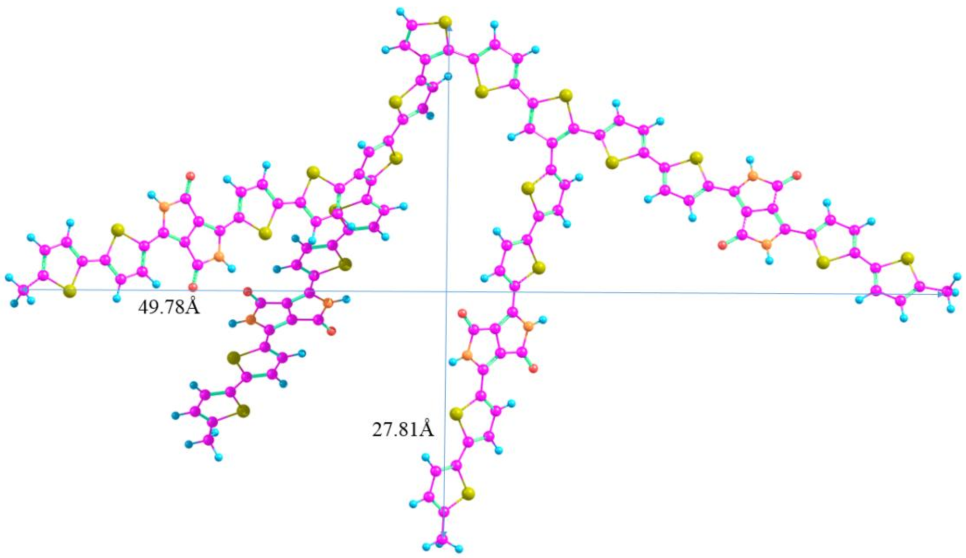
Figure S3. a) Chemical structure representation of DOT-p-DPPs; b) ^{1}H NMR spectra of **3T-p-DPP**, **6T-p-DPP**, **9T-p-DPP** in the aromatic range; c)1H NMR spectra of **3T-p-DPP**, **6T-p-DPP** and **9T-p-DPP** in $CDCl_3$; c) 1H NMR spectra of **18T-p-DPP** and **21T-p-DPP** in $C_2D_2Cl_4$ (two single peaks marked with * are the C-H coupling peak of the $CDCl_3$ or $C_2D_2Cl_4$).



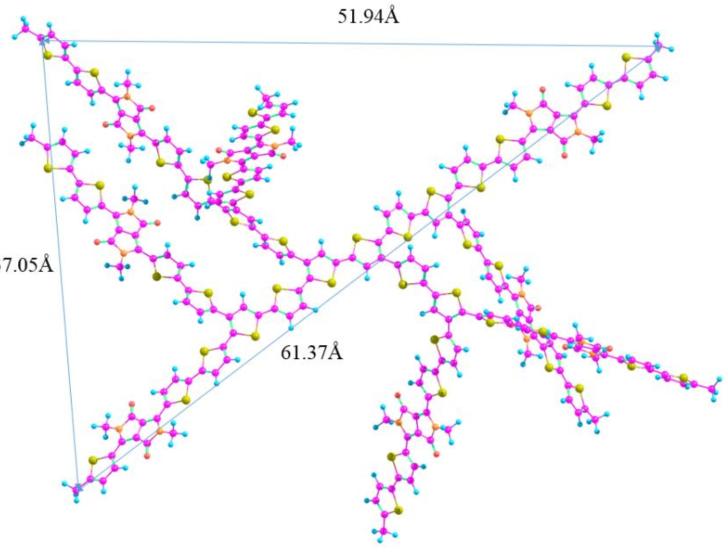
3T-p-DPP



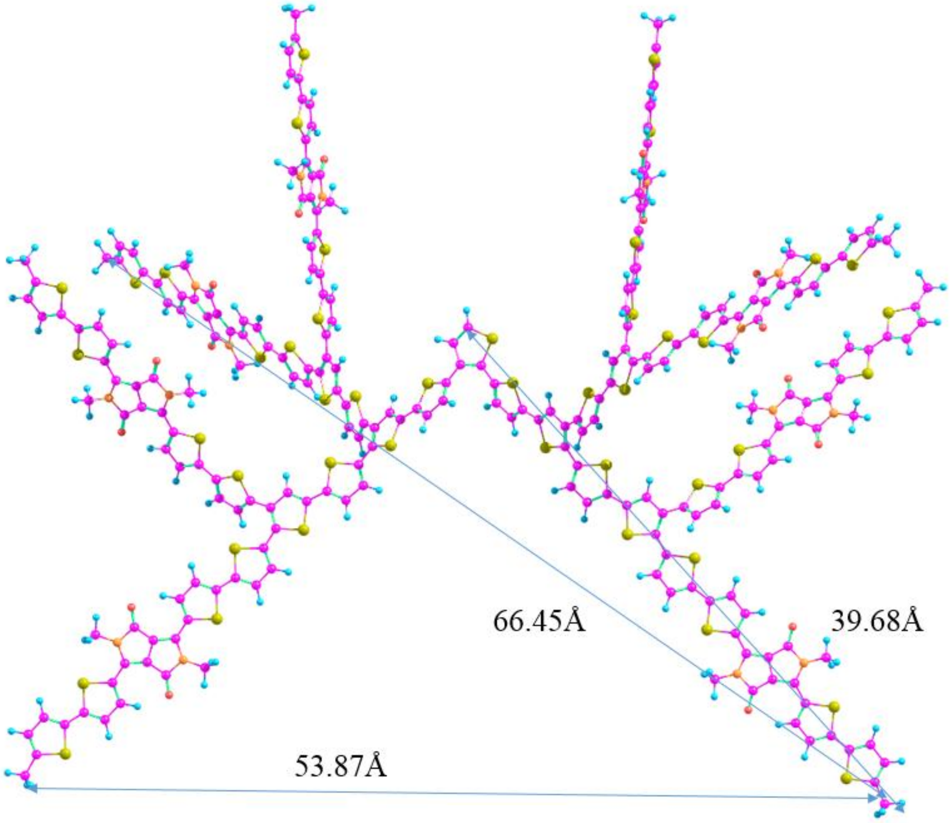
6T-p-DPP



9T-p-DPP



18T-p-DPP



21T-p-DPP

Figure S4. Molecular size of DOT-p-DPPs by molecular simulation.

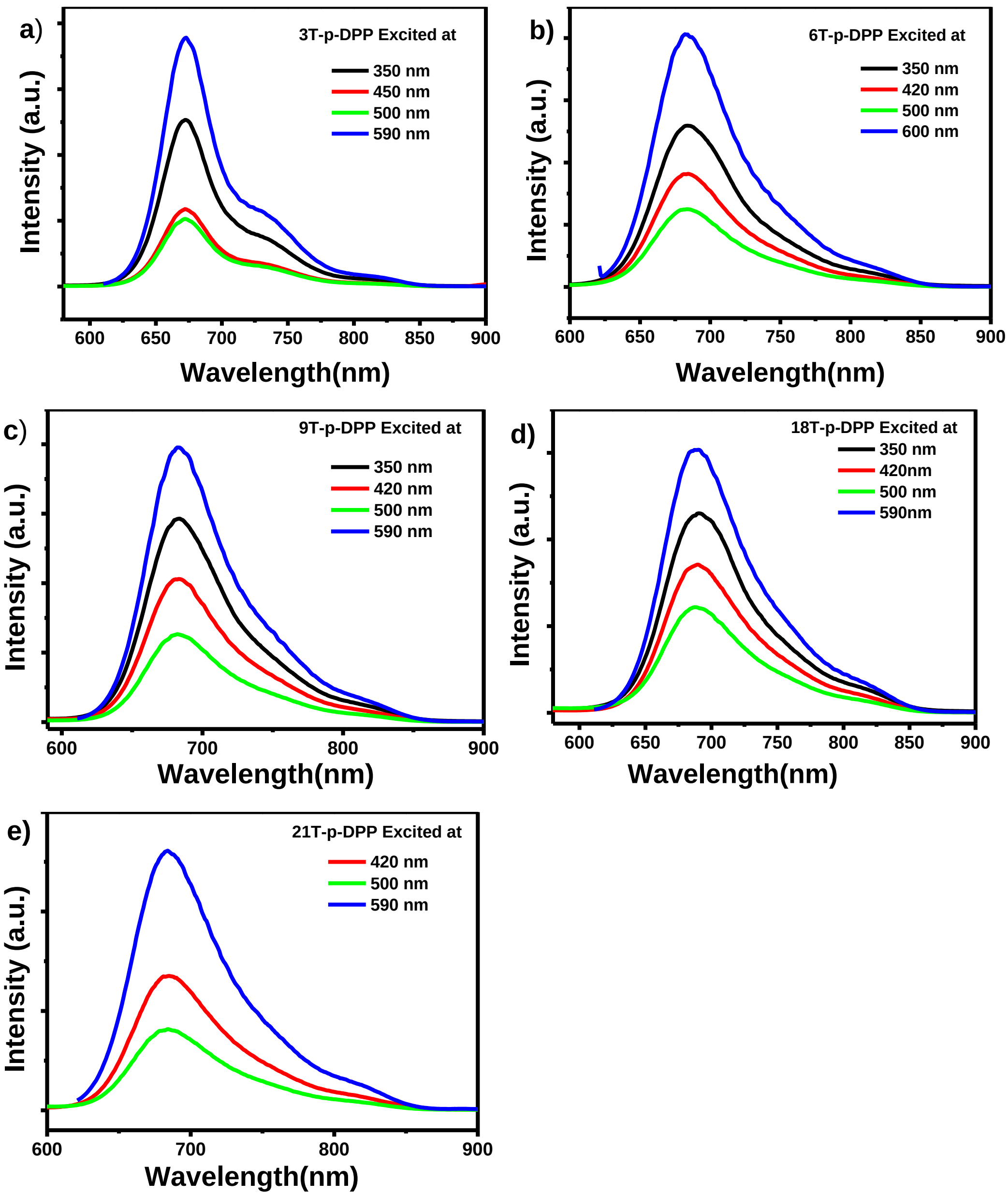


Figure S5. Emission spectra of DOT-p-DPPs measured at different excitation wavelengths.

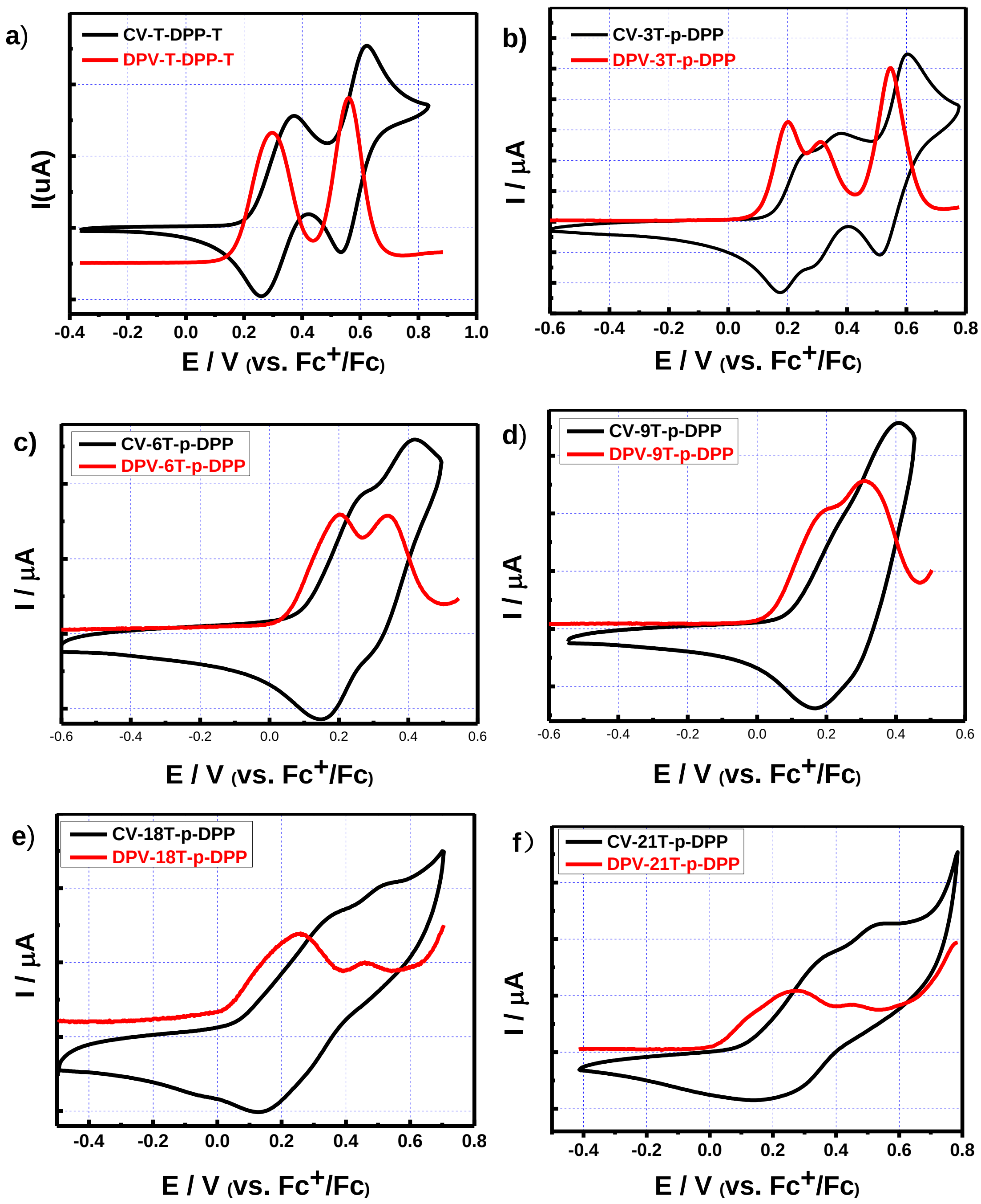


Figure S6. a, b, c, d) CV and DPV of T-DPP-T, 3T-p-DPP, 6T-p-DPP, 9T-p-DPP at 1 $\times 10^{-3}$ mol • L^{-1} in CH_2Cl_2 $TBAPF_6$(0.1 M), room temperature, V = 100 mV s^{-1}; e) 18T-p-DPP at 5×10^{-4} mol • L^{-1} in CH_2Cl_2, room temperature, $TBAPF_6$(0.1 M), V = 100 mV s^{-1}; f) 21T-p-DPP at 2.5×10^{-4} mol • L^{-1} in CH_2Cl_2, room temperature, $TBAPF_6$(0.1 M), V = 100 mV s^{-1}

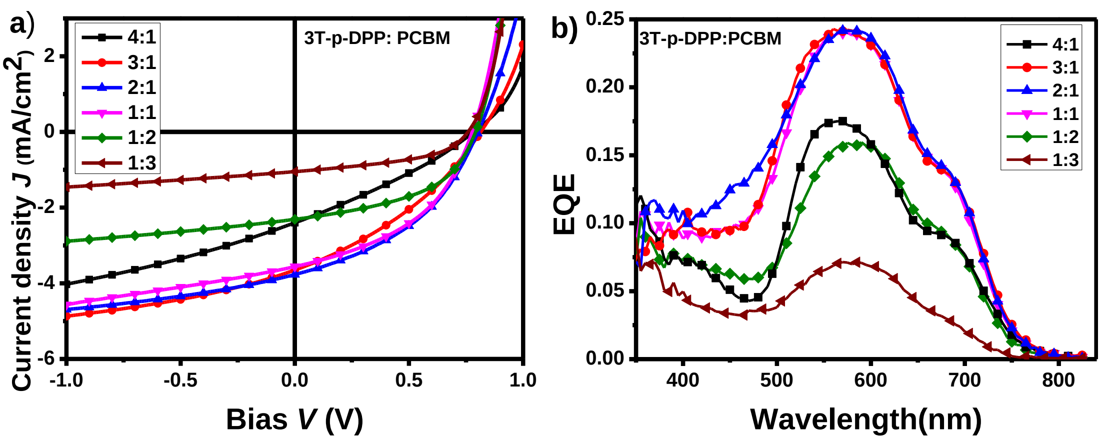


Figure S7. a) J–V curves for BHJ solar cells with varying ratios of 3T-p-DPP and $PC_{61}BM$ under illumination (nominal AM1.5G, 100 mW cm^{-2}) and b) EQE spectra of the corresponding devices.

Table S1. Summary of device performance for BHJ solar cells with varying ratios of 3T-p-DPP and $PC_{61}BM$

D:A (solvent)	Thickness (nm)	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	Mpp
4:1	180	2.40	0.78	0.30	0.56
3:1	142	3.65	0.81	0.34	1.01
2:1	106	3.77	0.80	0.41	1.24
1:1	110	3.56	0.78	0.44	1.22
1:2	103	2.31	0.79	0.48	0.88
1:3	230	1.05	0.76	0.47	0.38

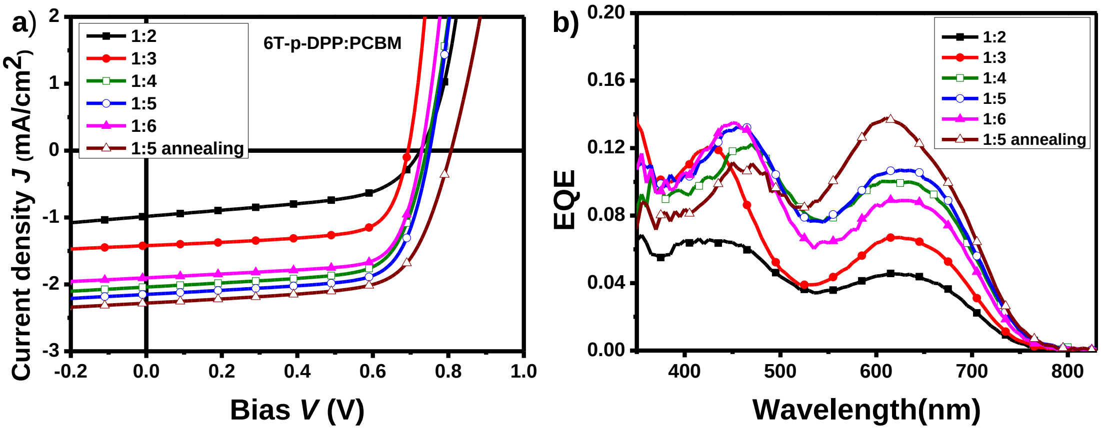


Figure S8. a) J–V curves for BHJ solar cells with varying ratios of 6T-p-DPP and $PC_{61}BM$ under illumination (nominal AM1.5G, 100 mW cm^{-2}) and b) EQE spectra of the corresponding devices.

Table S2. Summary of device performance for BHJ solar cells with varying ratios of 6T-p-DPP and $PC_{61}BM$

D:A (solvent)	Thickness (nm)	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	Mpp
1:2	80	0.98	0.73	0.53	0.38
1:3	94	1.42	0.69	0.69	0.68
1:4	84	2.04	0.74	0.69	1.04
1:5	90	2.15	0.75	0.70	1.13
1:6	83	1.9	0.73	0.71	0.98
1:5(annealing)	90	2.28	0.81	0.67	1.24

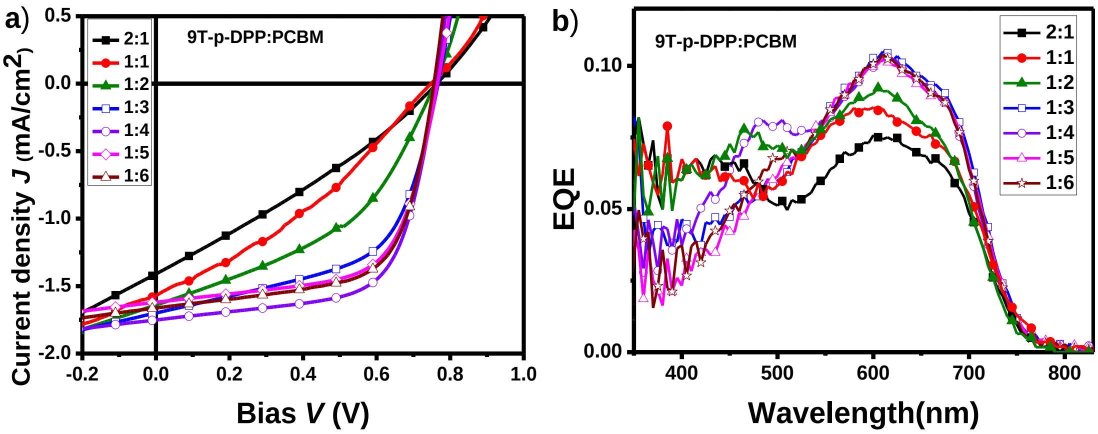


Figure S9. a) J–V curves for BHJ solar cells with varying ratios of 9T-p-DPP and $PC_{61}BM$ under illumination (nominal AM1.5G, 100 mW cm^{-2}) and b) EQE spectra of the corresponding devices.

Table S3. Summary of device performance for BHJ solar cells with varying ratios of 9T-p-DPP and $PC_{61}BM$

D:A (solvent)	Thickness (nm)	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	Mpp
2:1	129	1.41	0.77	0.31	0.34
1:1	153	1.57	0.75	0.33	0.39
1:2	80	1.64	0.76	0.43	0.54
1:3	94	1.7	0.77	0.56	0.73
1:4	84	1.75	0.76	0.65	0.86
1:5	90	1.62	0.77	0.64	0.80
1:6	83	1.66	0.76	0.65	0.82

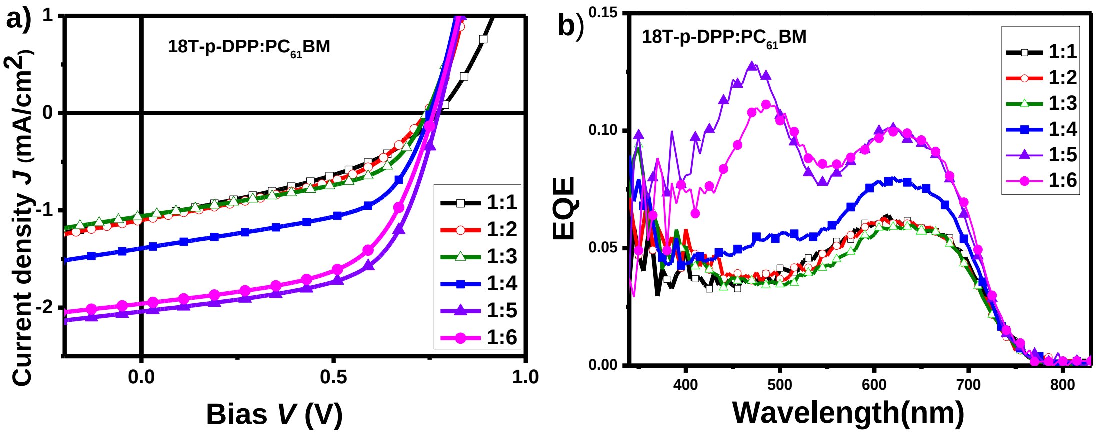


Figure S10. a) J–V curves for BHJ solar cells with varying ratios of 18T-p-DPP and $PC_{61}BM$ under illumination (nominal AM1.5G, 100 mW cm^{-2}) and b) EQE spectra of the corresponding devices.

Table S4. Summary of device performance for BHJ solar cells with varying ratios of 18T-p-DPP and $PC_{61}BM$

D:A (solvent)	Thickness (nm)	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	Mpp
1:1	112	1.08	0.77	0.38	0.32
1:2	104	1.10	0.74	0.43	0.35
1:3	104	1.06	0.74	0.49	0.38
1:4	95	1.39	0.75	0.54	0.56
1:5	84	2.04	0.77	0.59	0.93
1:6	90	1.96	0.76	0.56	0.83

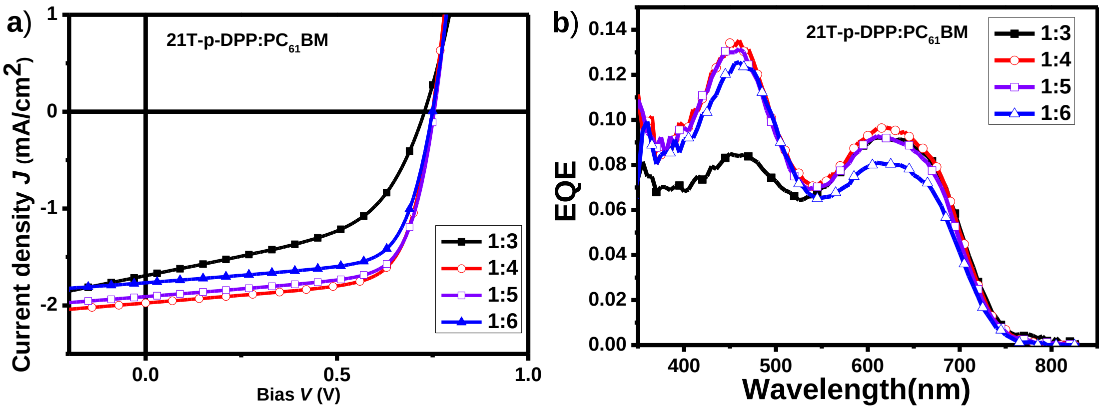


Figure S11. a) J–V curves for BHJ solar cells with varying ratios of 21T-p-DPP and $PC_{61}BM$ under illumination (nominal AM1.5G,100 mW cm^{-2}) and b) EQE spectra of the corresponding devices.

Table S5. Summary of device performance for BHJ solar cells with varying ratios of 21T-p-DPP and $PC_{61}BM$

D:A (solvent)	Thickness (nm)	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	Mpp
1:3	86	1.69	0.73	0.51	0.63
1:4	81	1.97	0.75	0.69	1.02
1:5	74	1.91	0.75	0.69	0.99
1:6	79	1.76	0.74	0.70	0.91

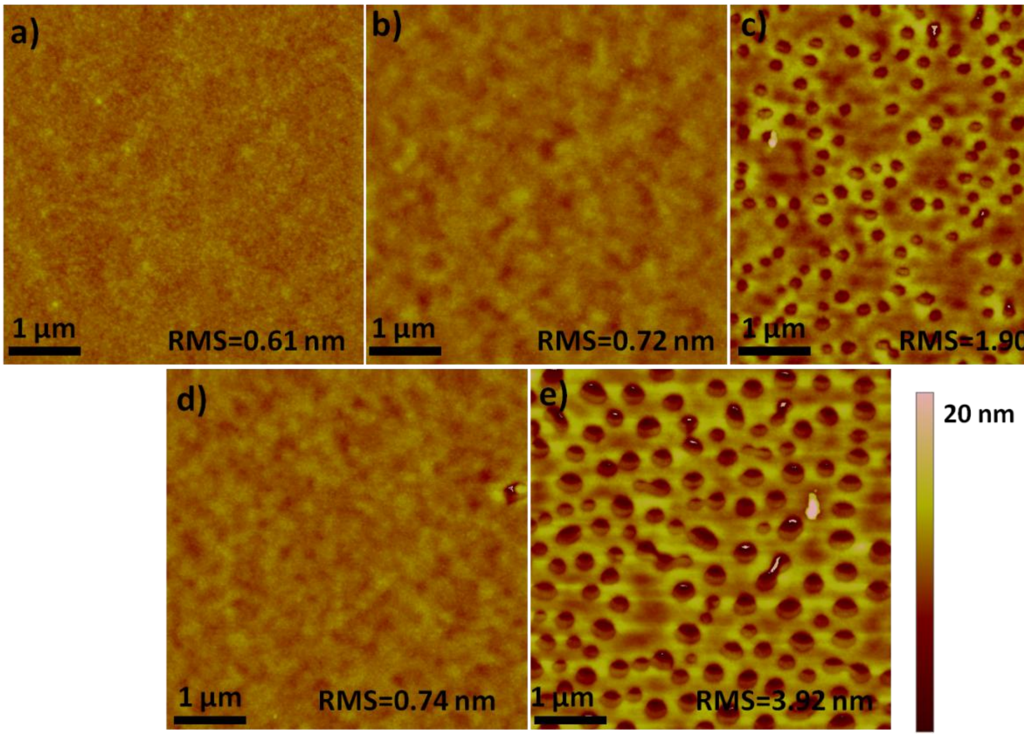


Figure S12. AFM height images of DOT-p-DPP:$PC_{61}BM$ blend film. a)3T-p-DPP; b) 6T-p-DPP; c) 9T-p-DPP; d) 18T-p-DPP; e) 21T-p-DPP. The scan area of all images was 5 × 5 µm.

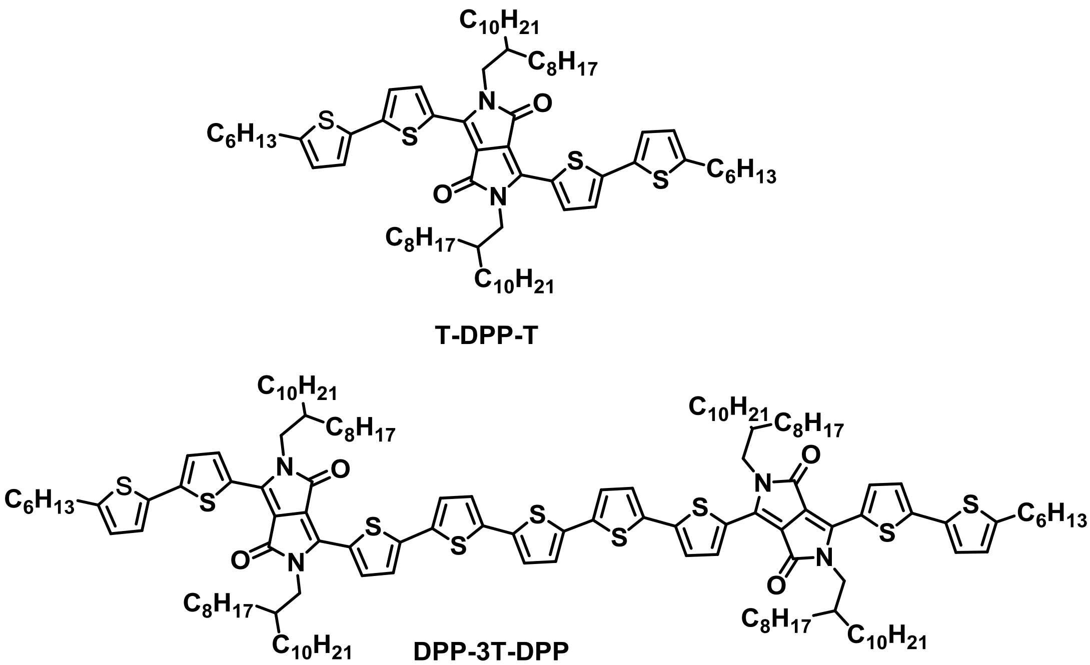
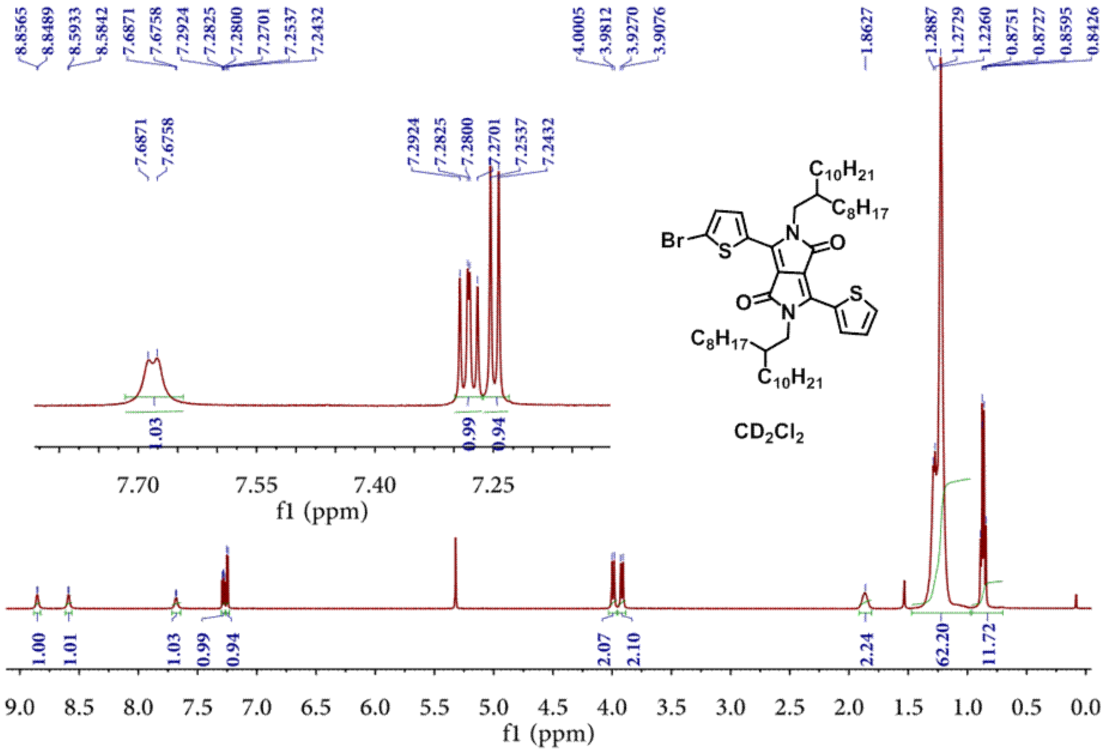
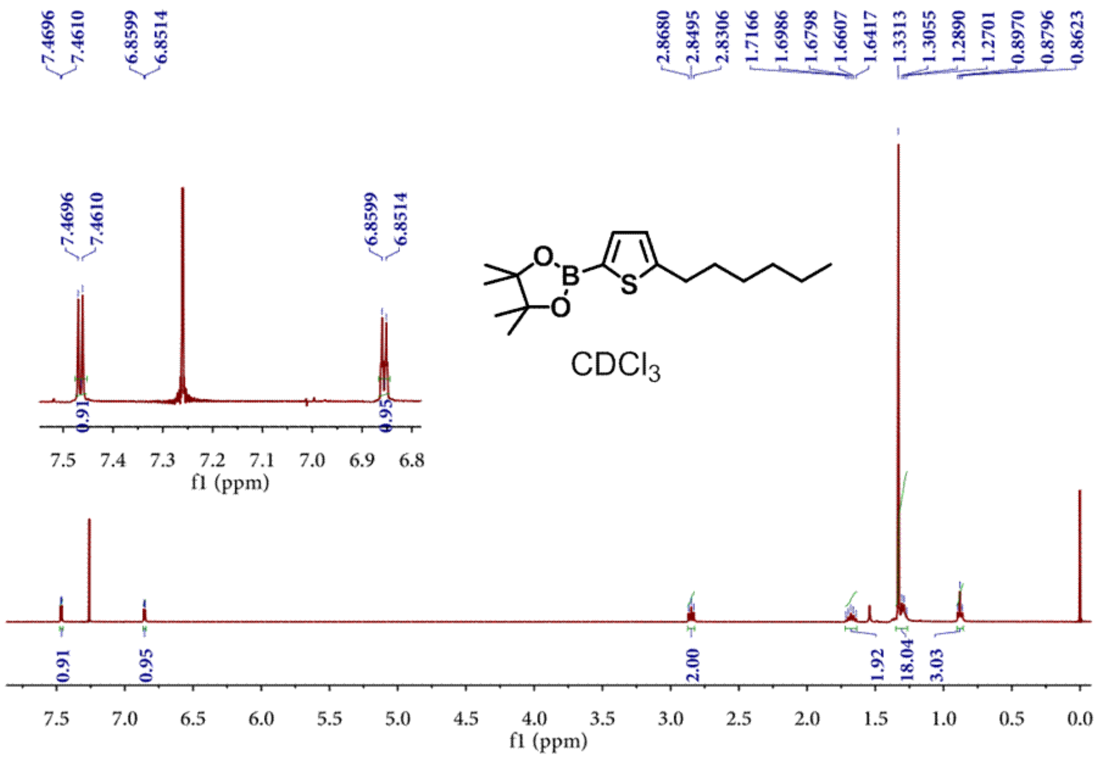


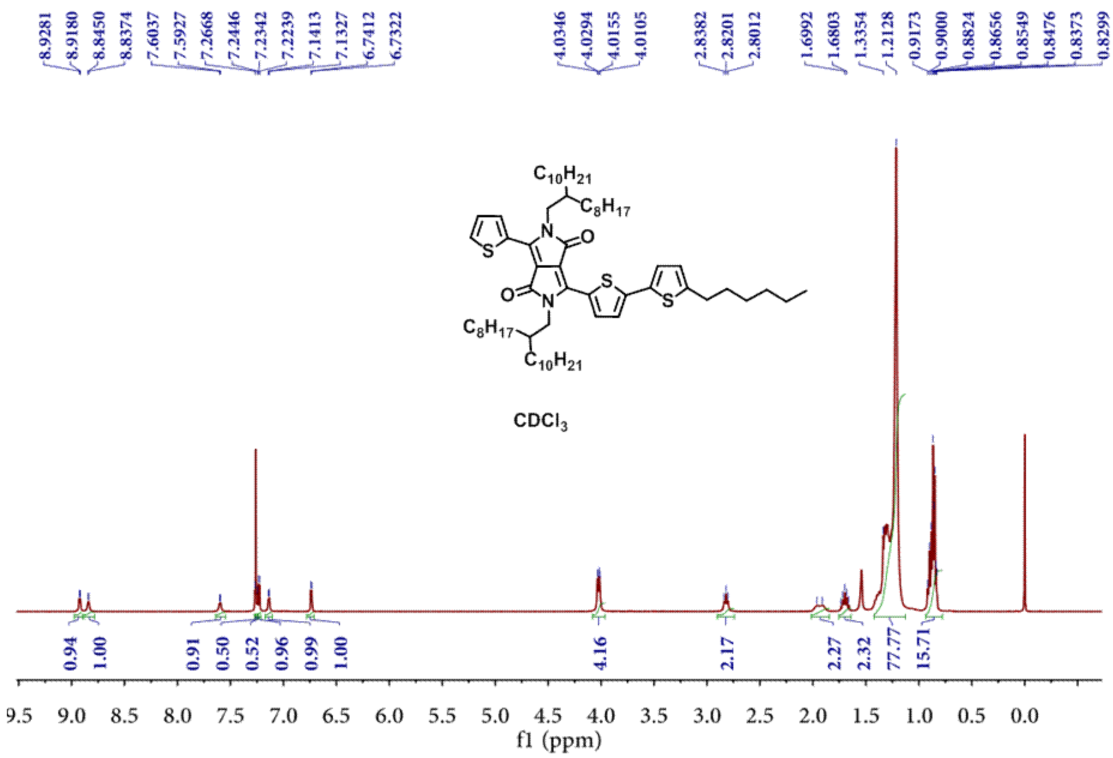
Figure S13. Chemical structure representation of T-DPP-T,DPP-3T-DPP.



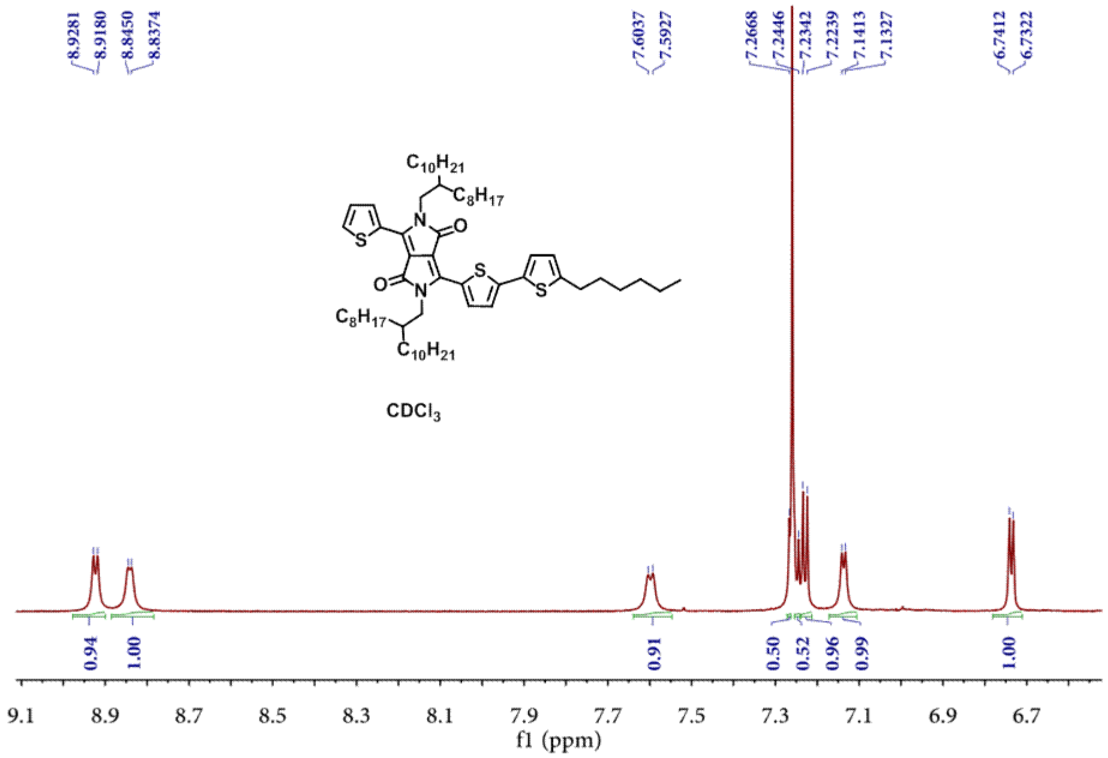
^{1}H NMR of **DPP-Br**



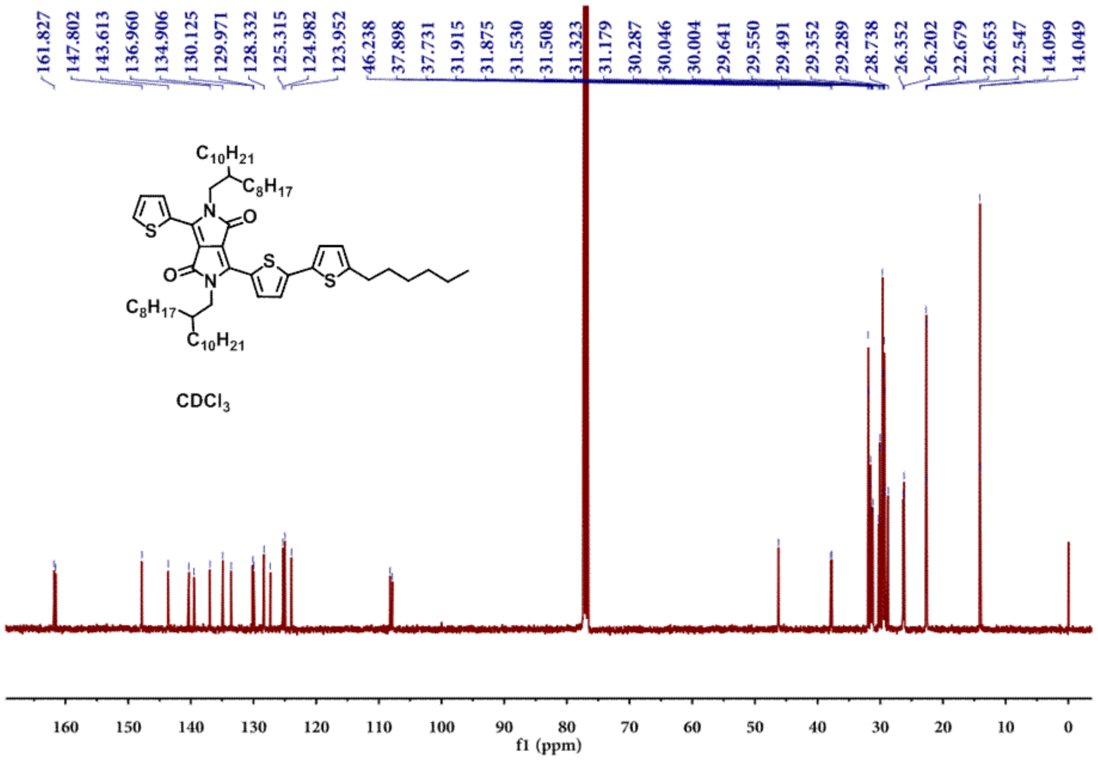
^{1}H NMR of **B-T**



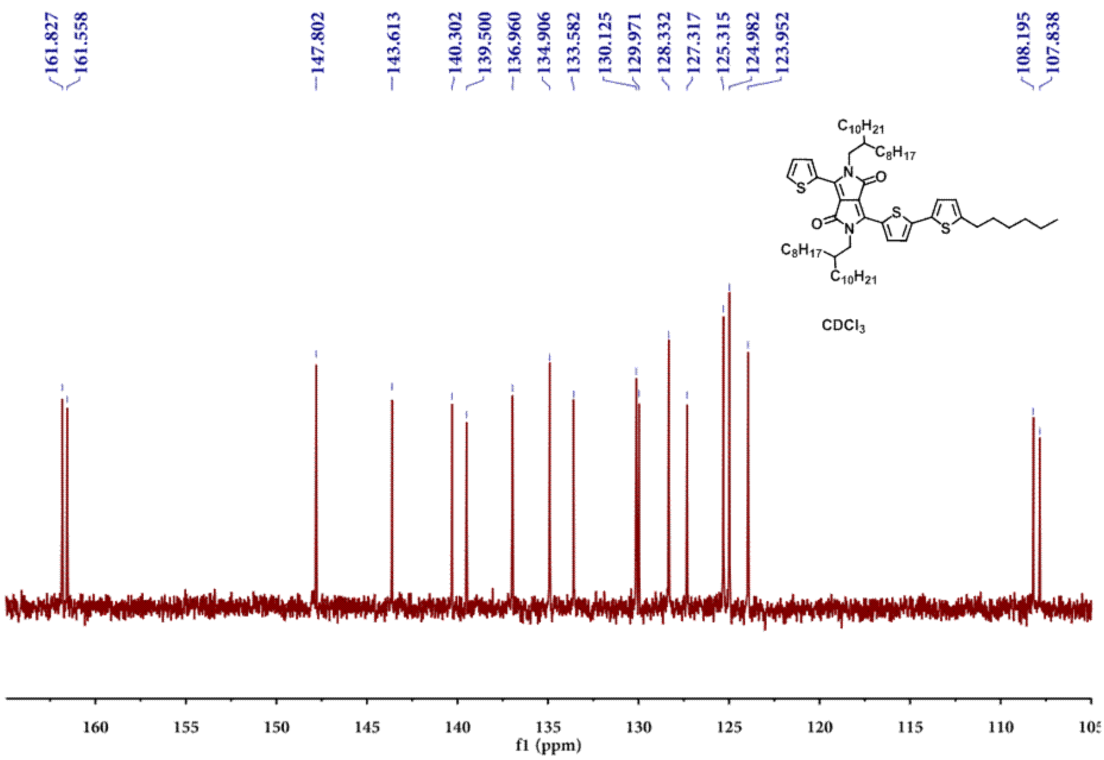
[1]H NMR of **DPP-T**



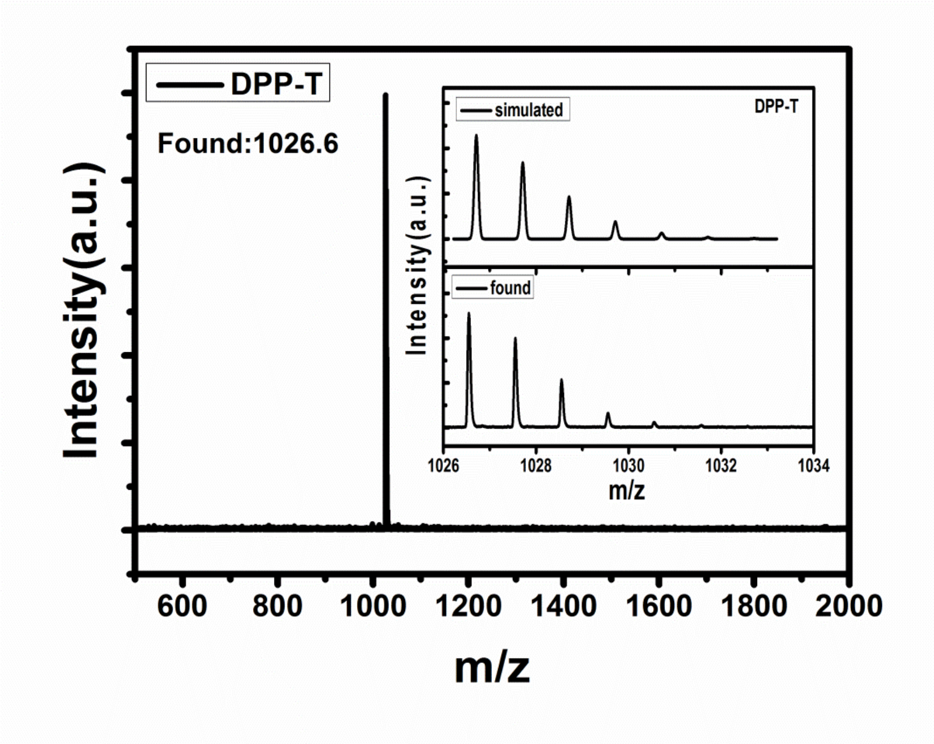
[1]H NMR of **DPP-T** (Zoom)



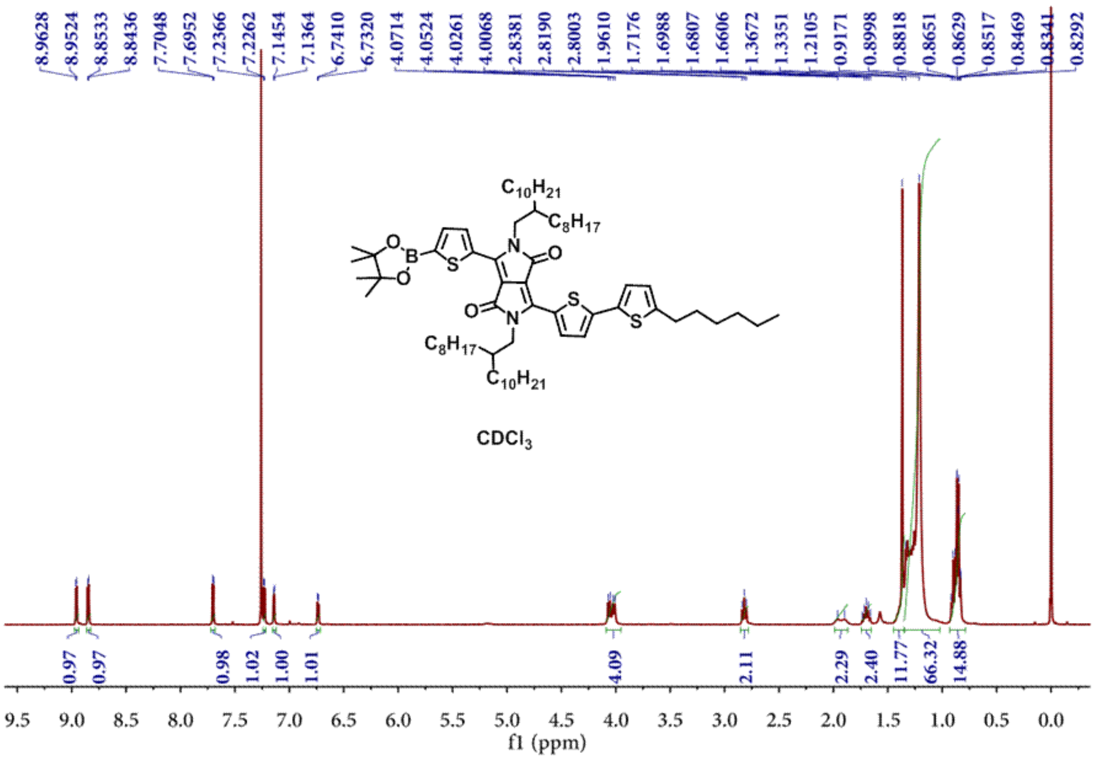
^{13}C NMR of **DPP-T**



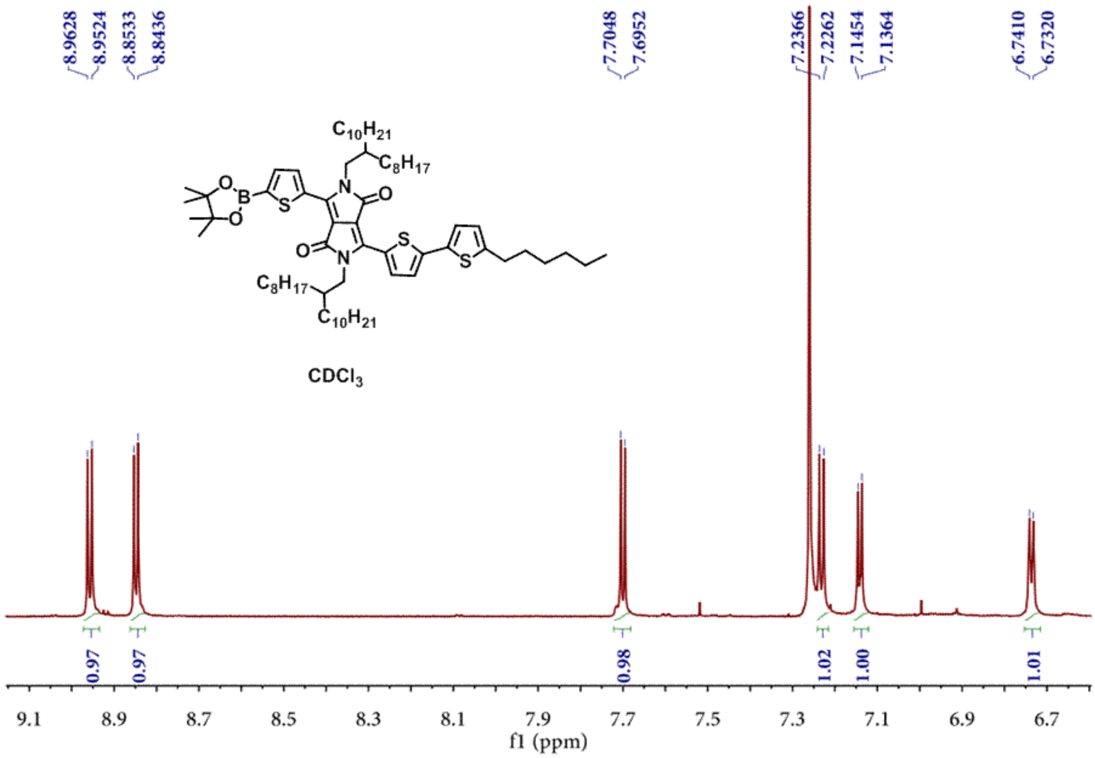
^{13}C NMR of **DPP-T** (Zoom)



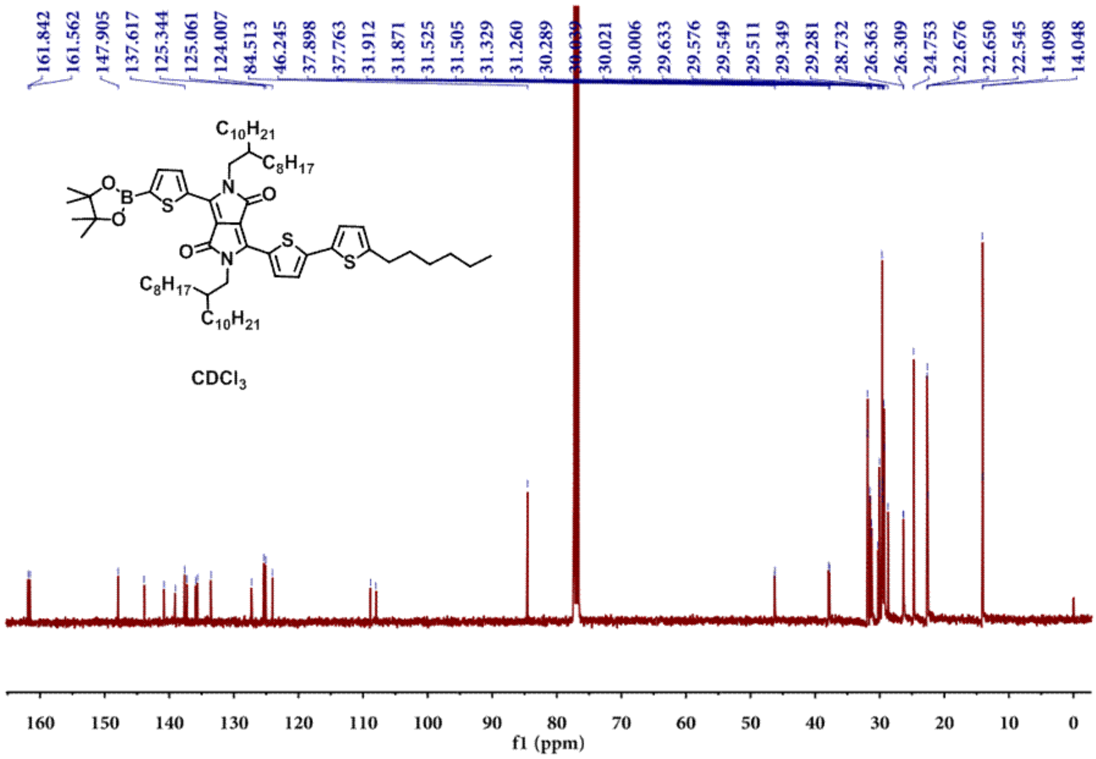
MALDI-TOF MS of **DPP-T**



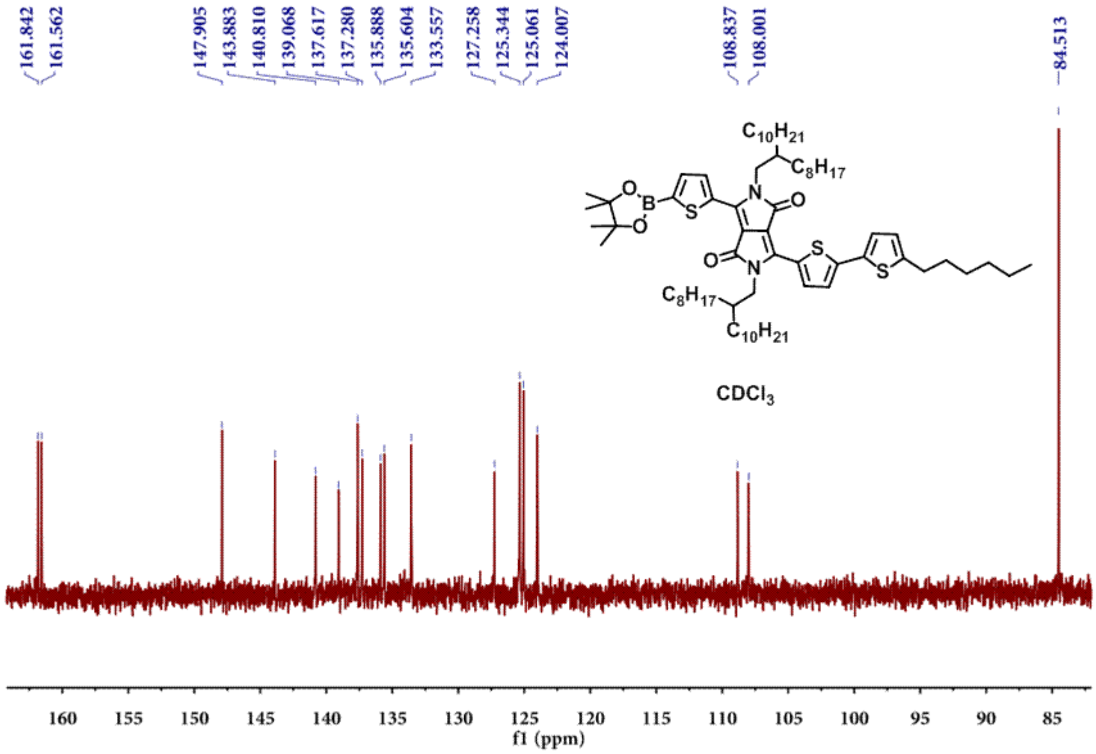
^{1}H NMR of **B-DPP-T**



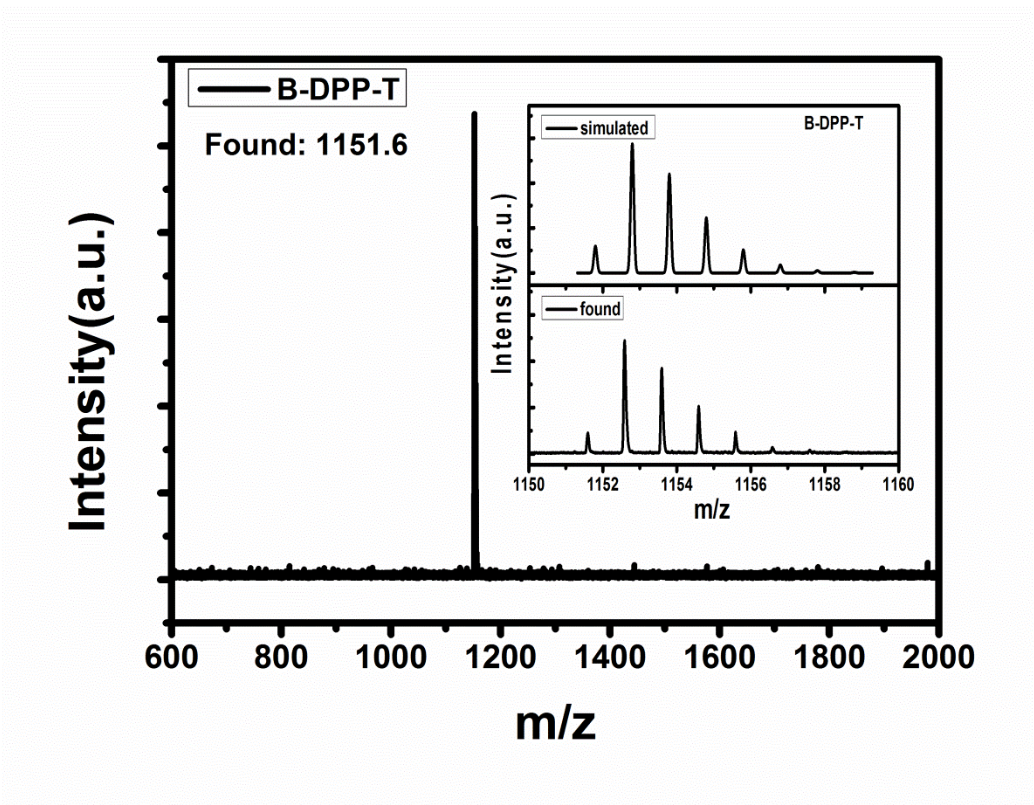
^{1}H NMR of **B-DPP-T** (zoom)



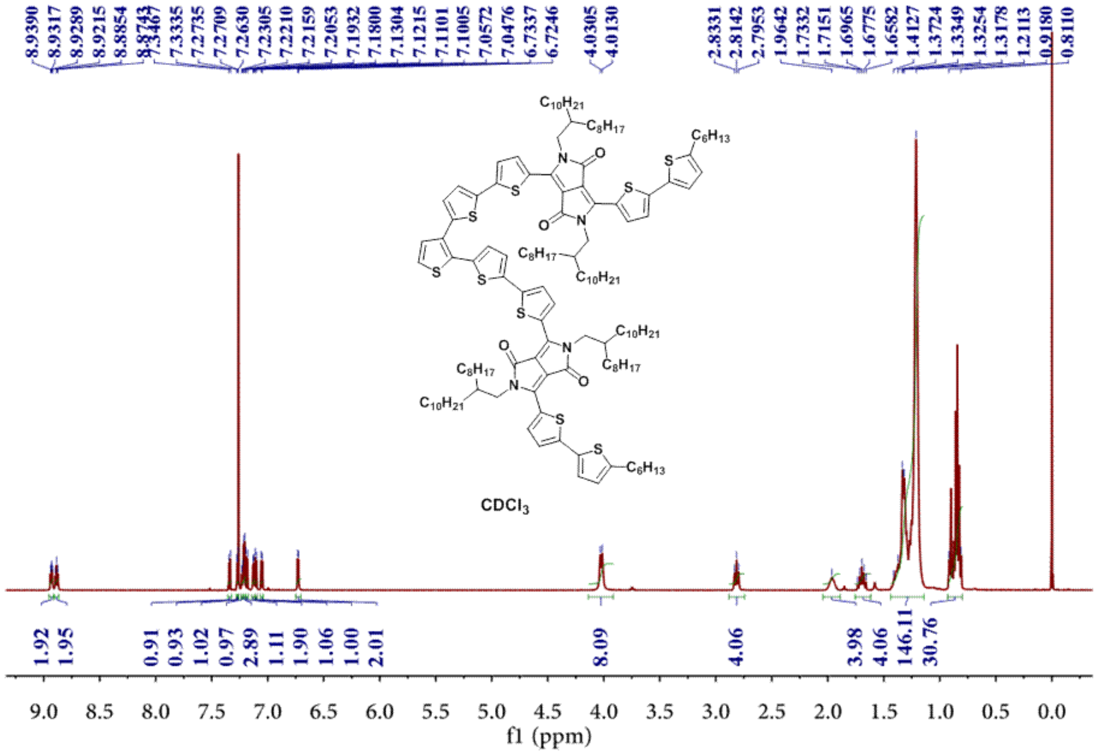
^{13}C NMR of **B-DPP-T**



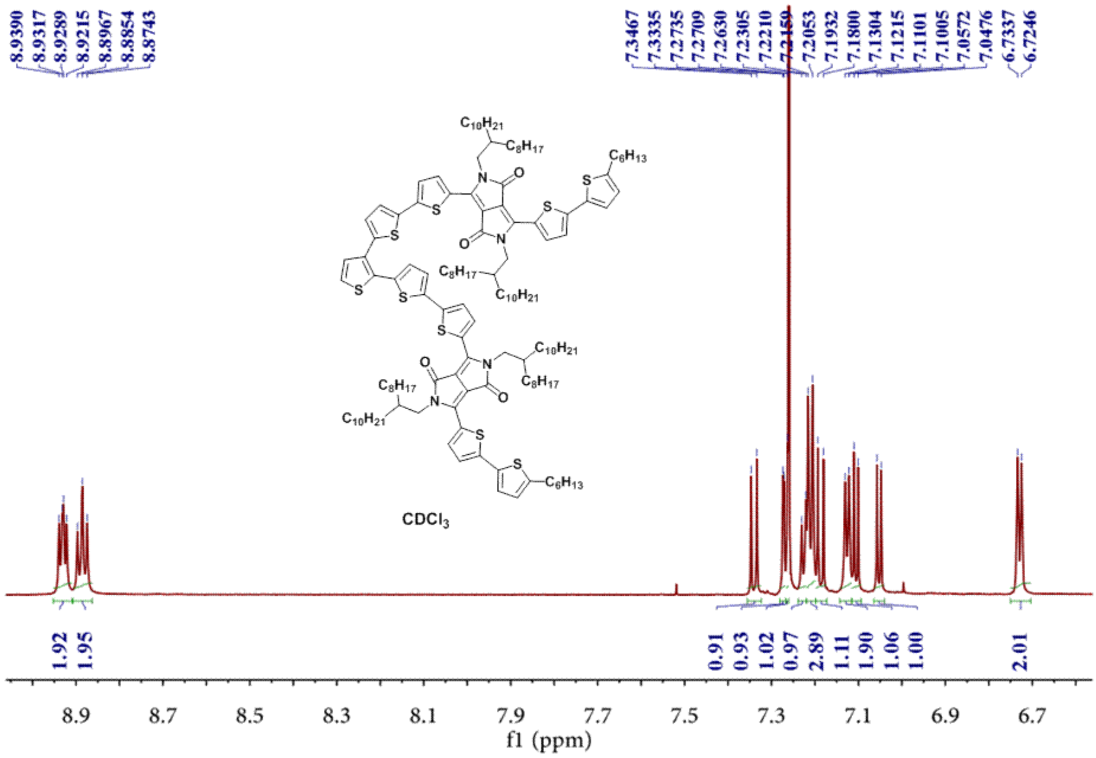
^{13}C NMR of **B-DPP-T** (Zoom)



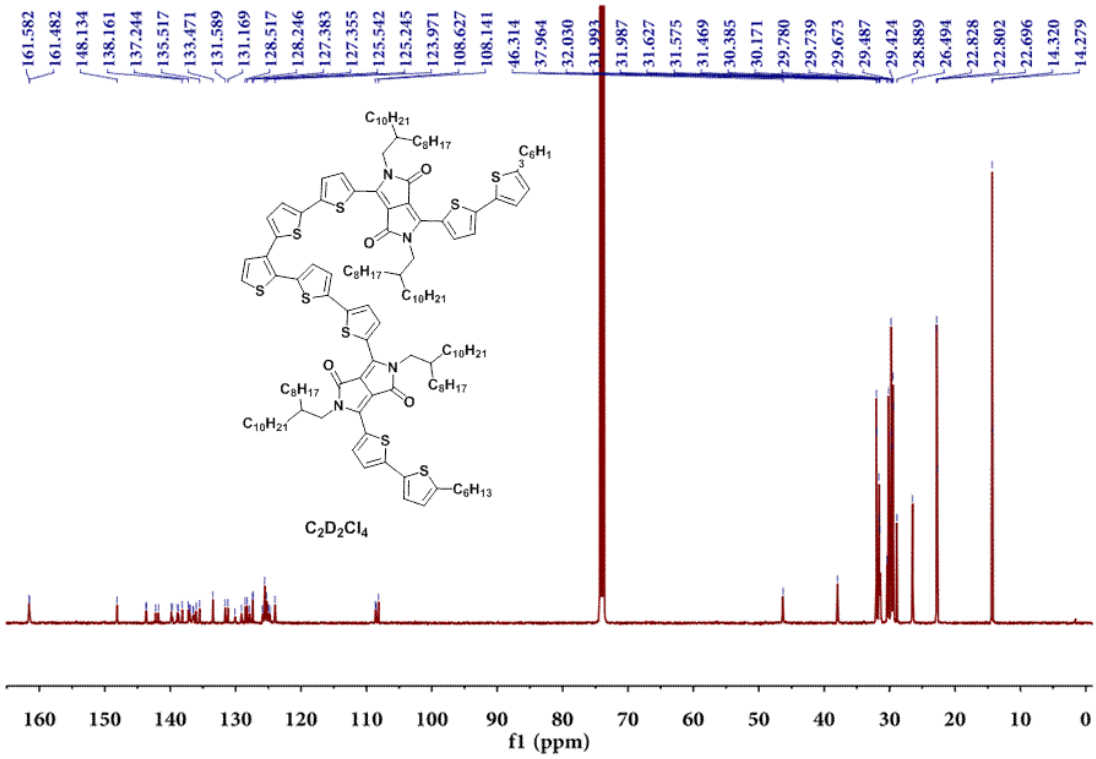
MALDI-TOF MS of **B-DPP-T**



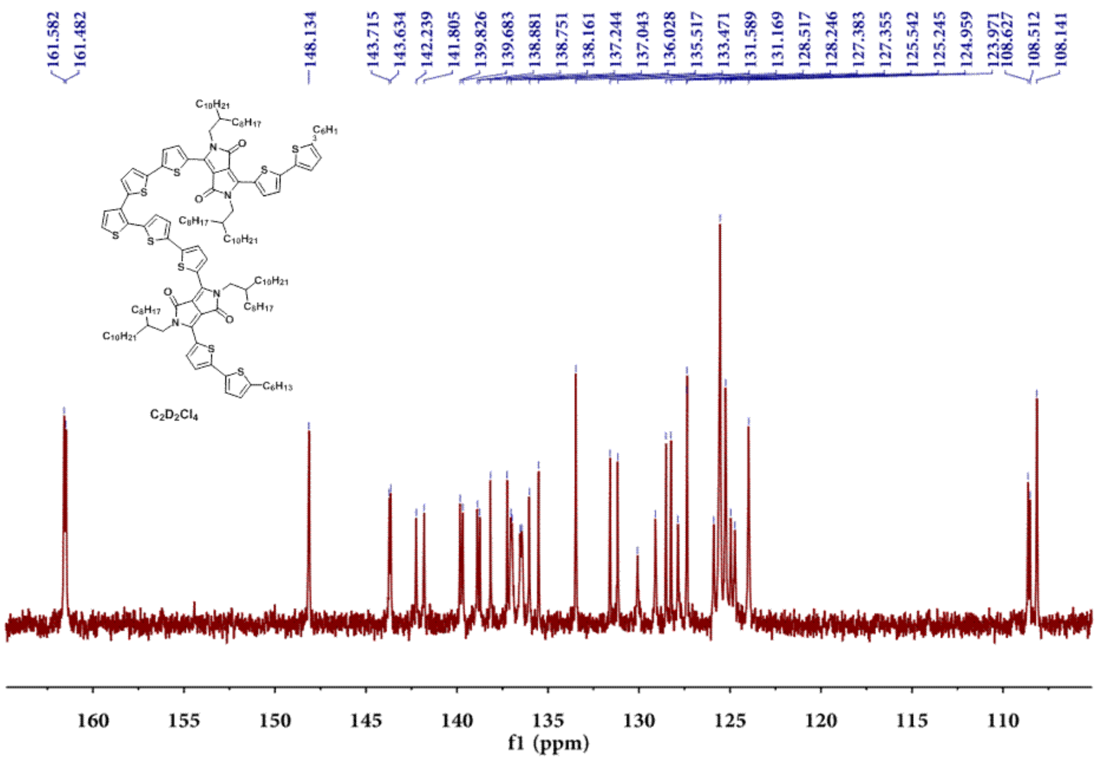
[1]H NMR of **3T-p-DPP**



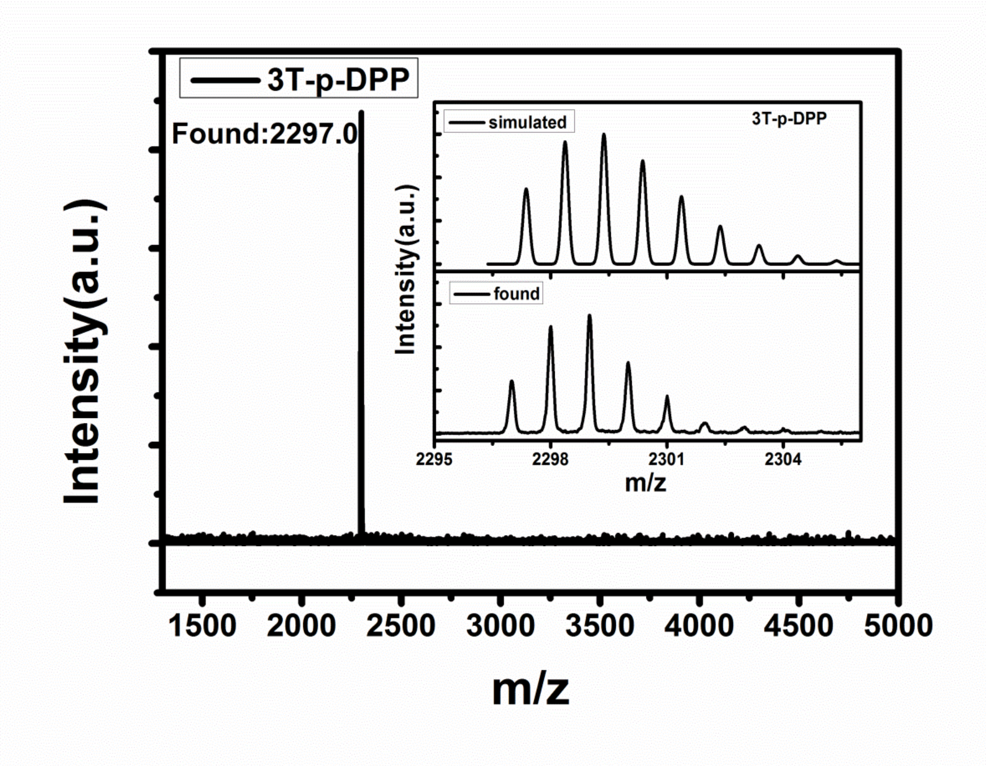
[1]H NMR of **3T-p-DPP** (zoom)



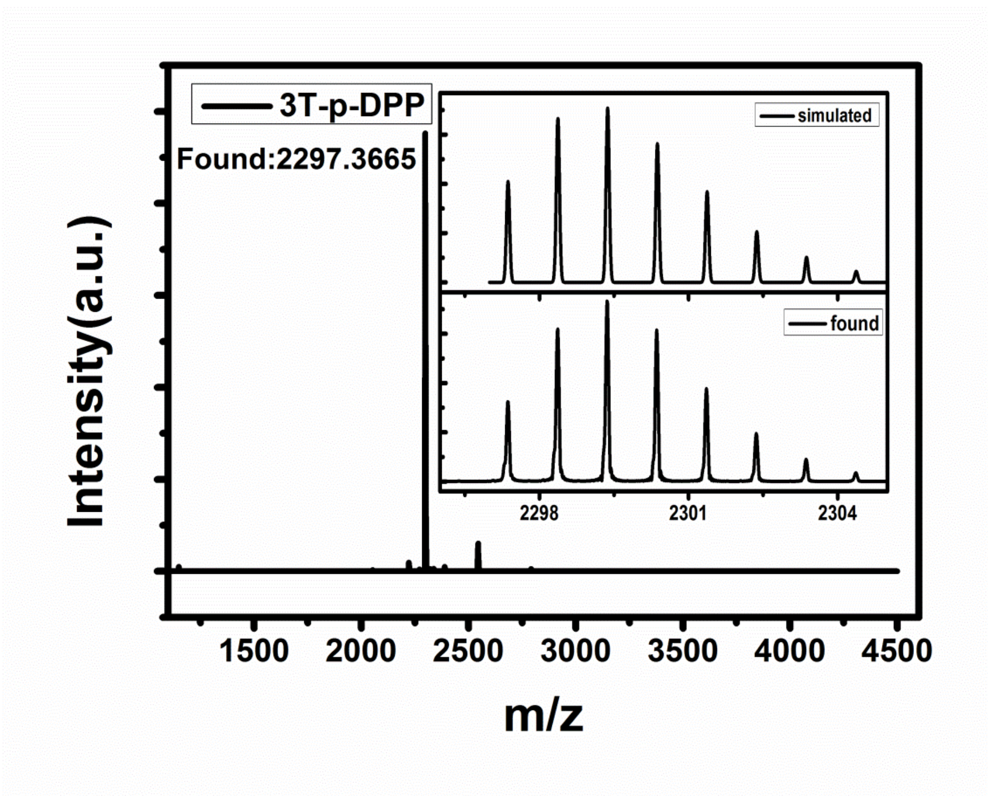
^{13}C NMR of **3T-p-DPP**



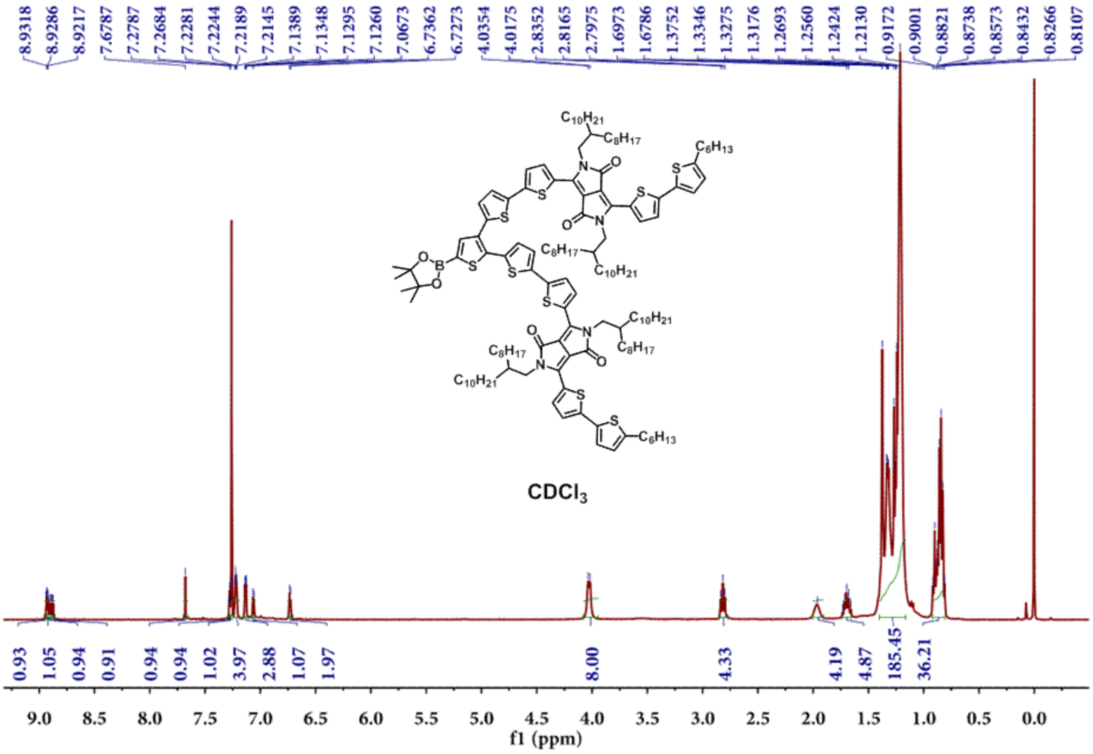
^{13}C NMR of **3T-p-DPP** (zoom)



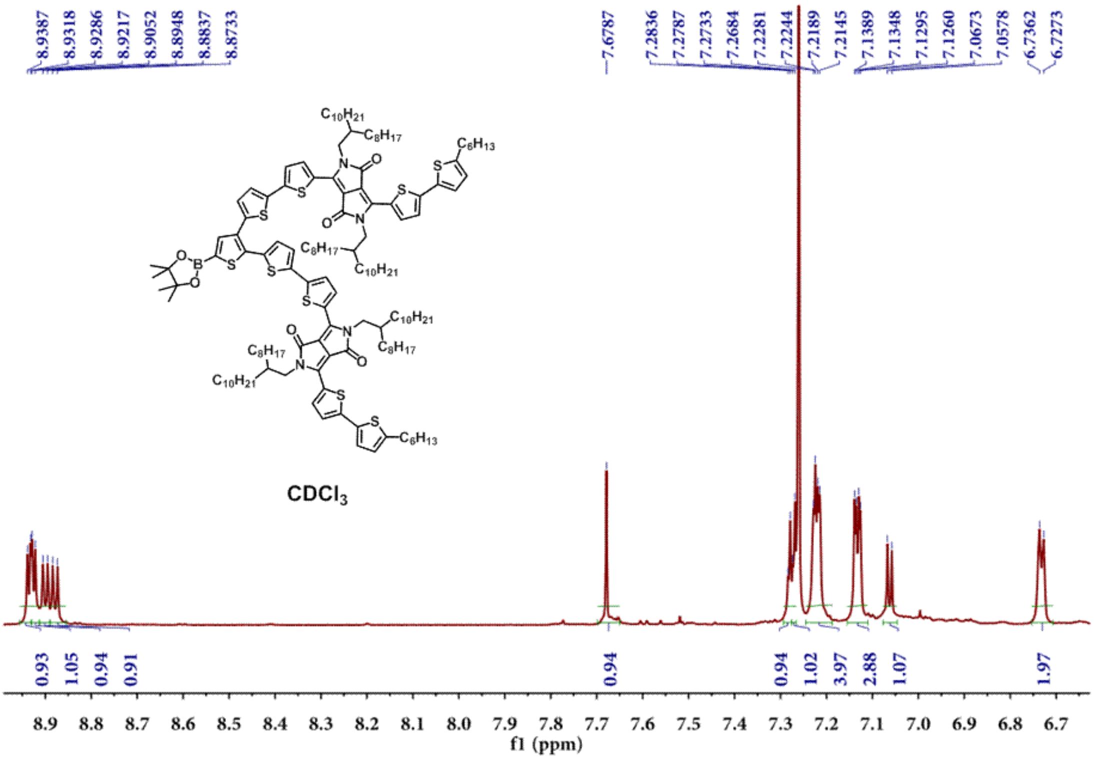
MALDI-TOF MS of **3T-p-DPP**



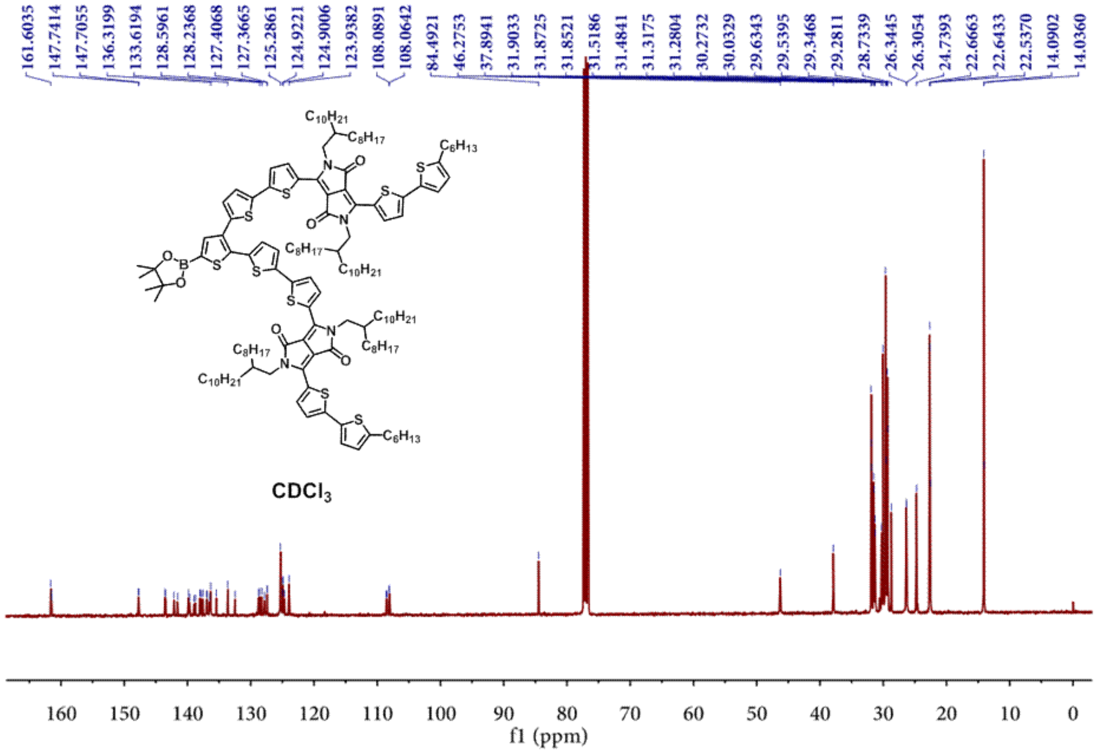
HR MS of **3T-p-DPP**



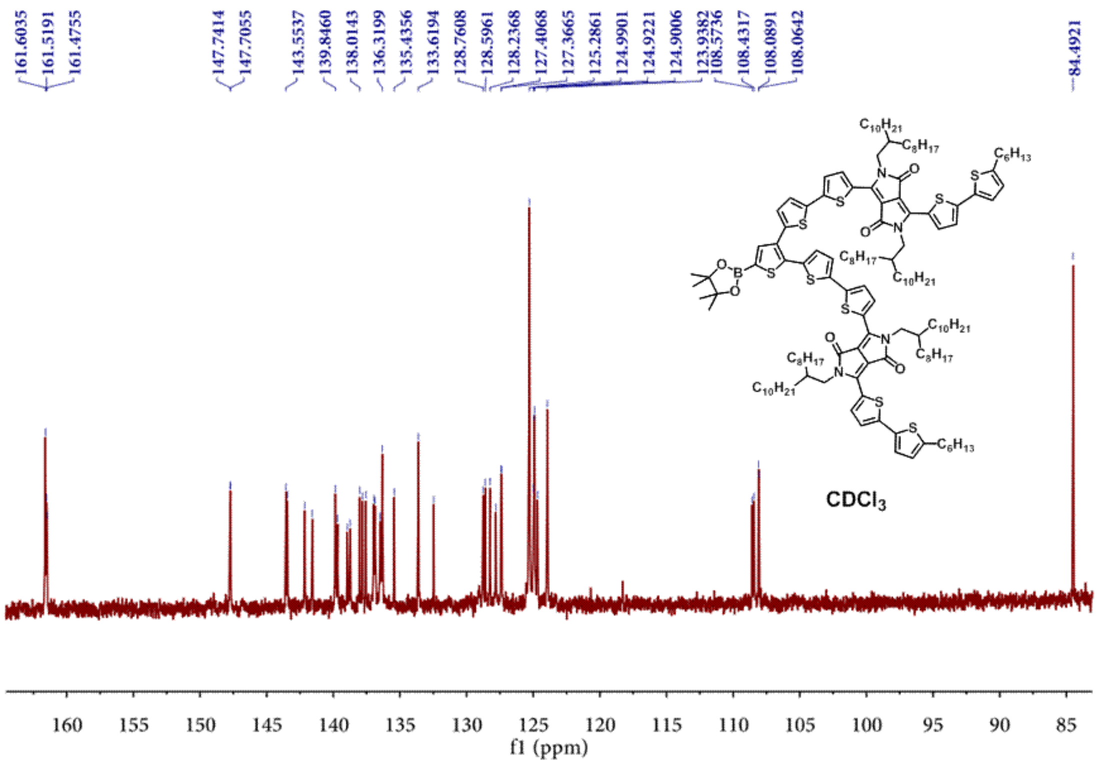
[1]H NMR of **B-3T-p-DPP**



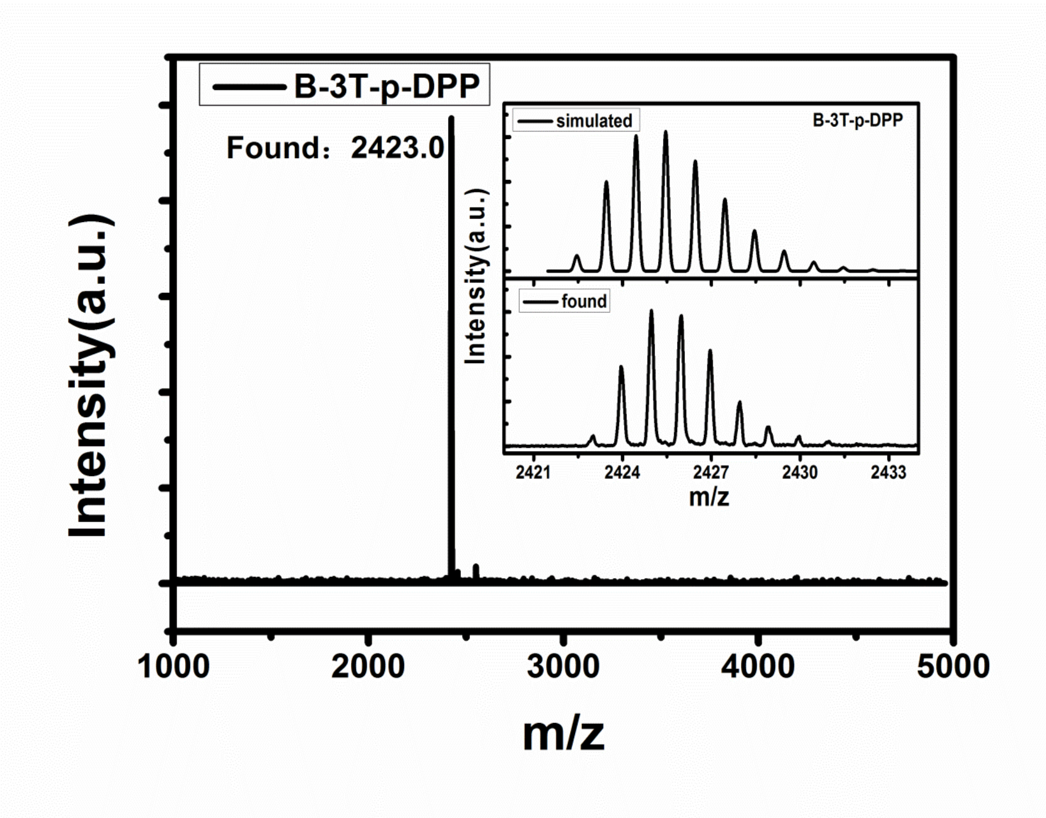
[1]H NMR of **B-3T-p-DPP** (zoom)



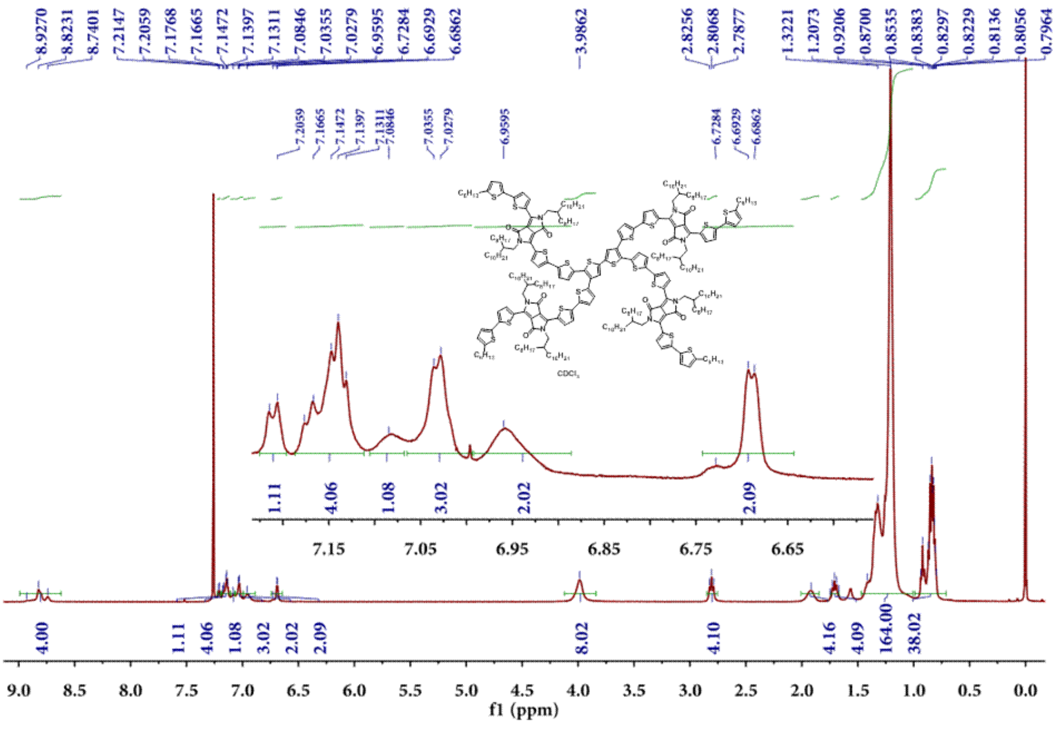
^{13}C NMR of **B-3T-p-DPP**



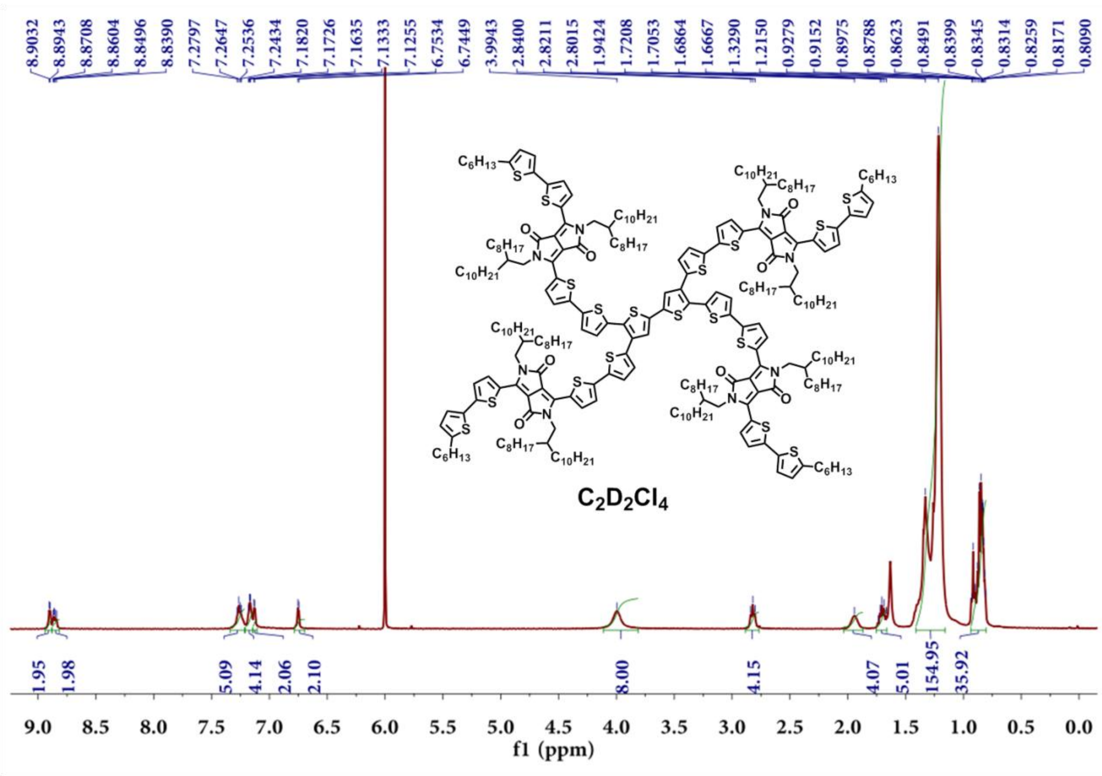
^{13}C NMR of **B-3T-p-DPP** (zoom)



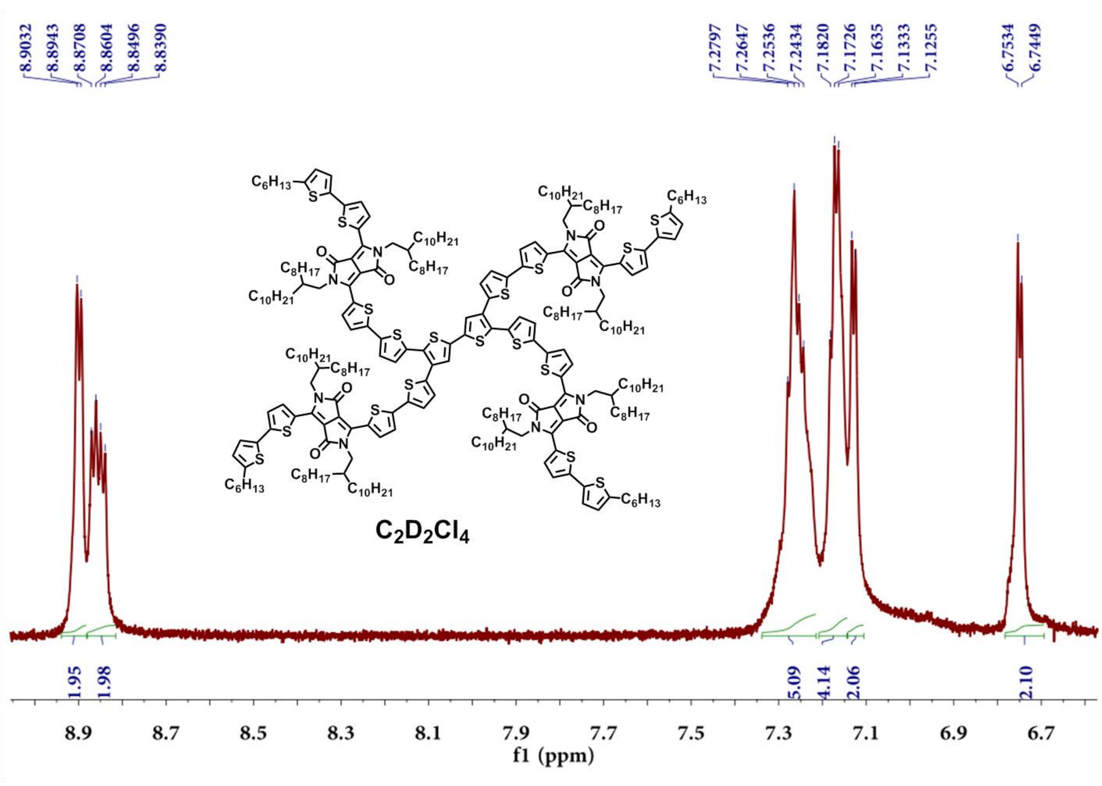
MALDI-TOF MS of **B-3T-p-DPP**



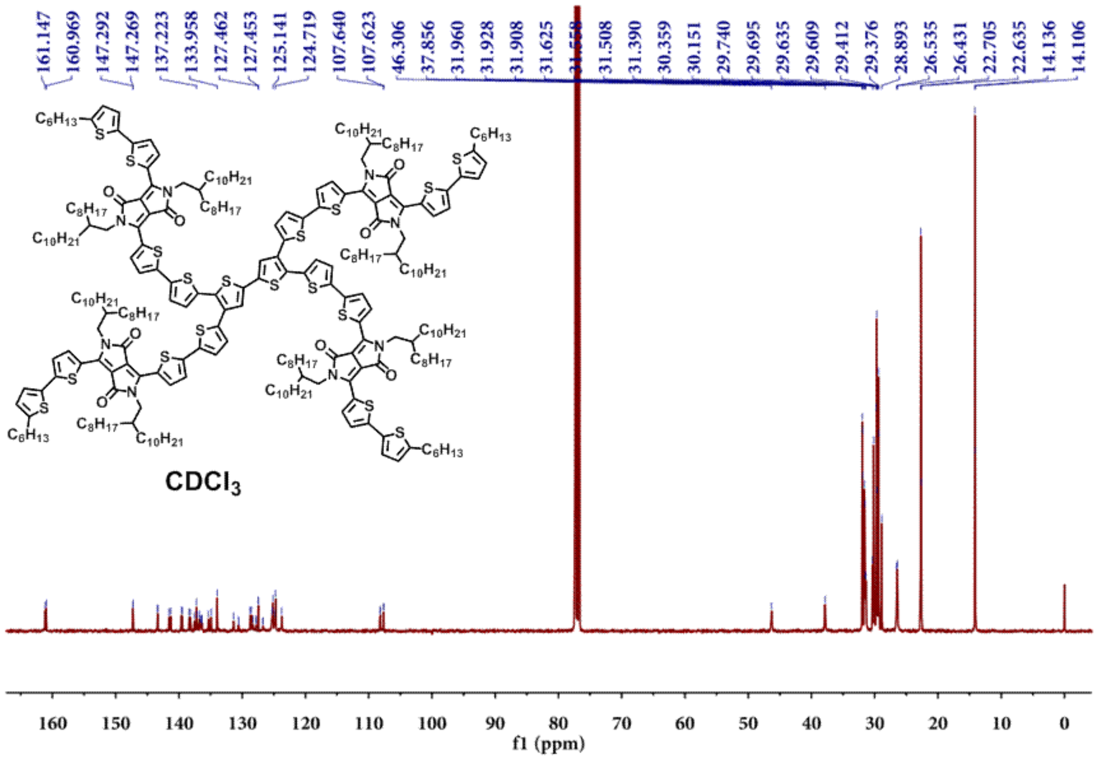
[1]H NMR of **6T-p-DPP** (in $CDCl_3$)



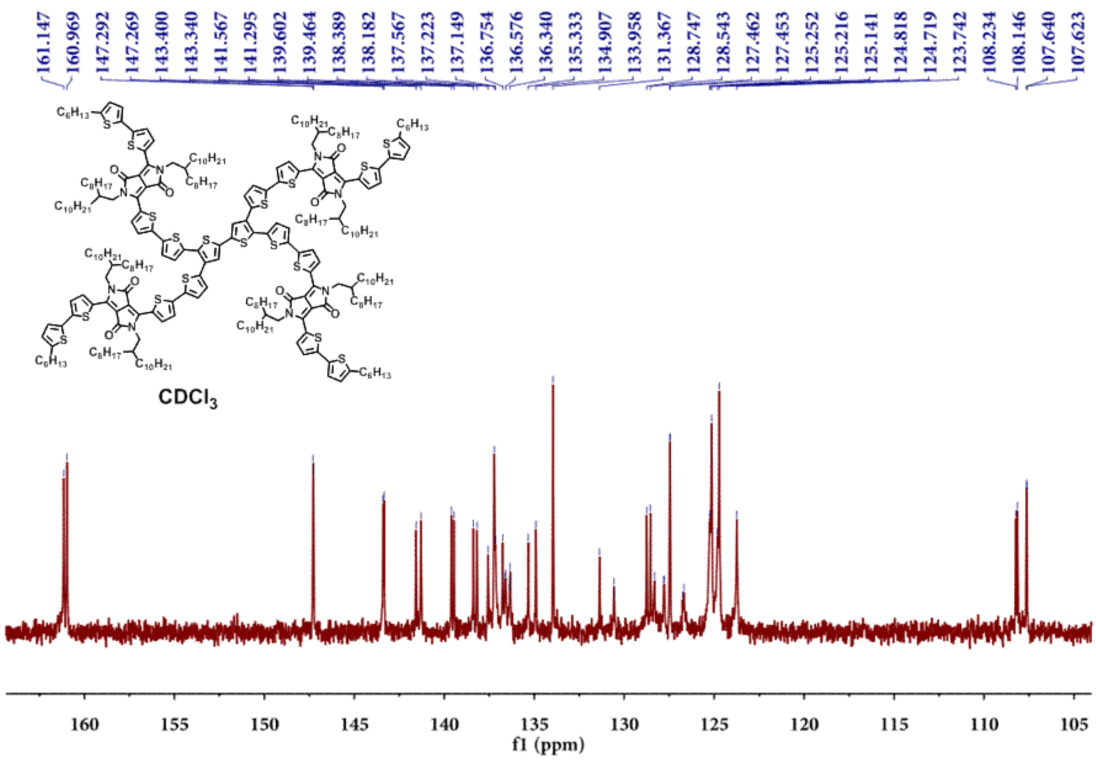
[1]H NMR of **6T-p-DPP**



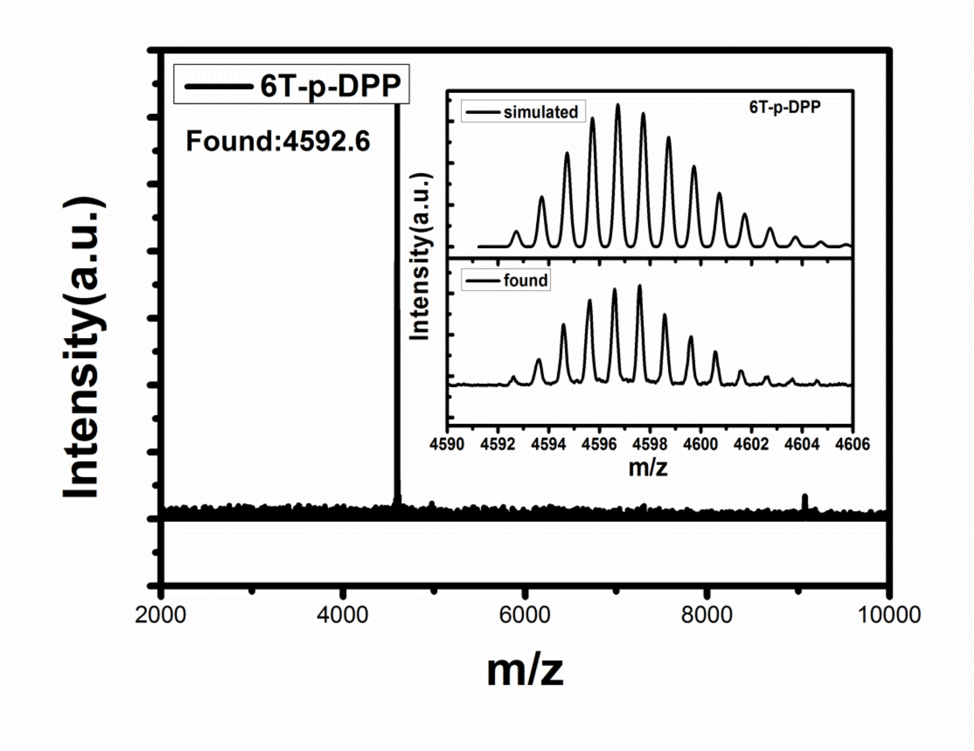
[1]H NMR of **6T-p-DPP** (zoom)



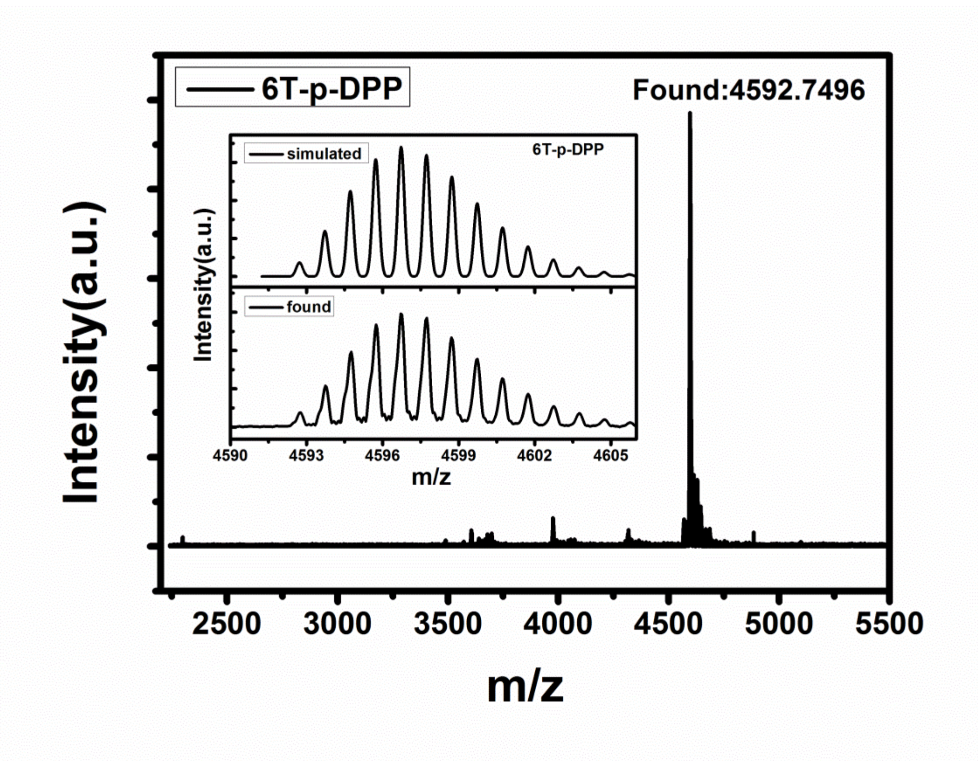
^{13}C NMR of **6T-p-DPP**



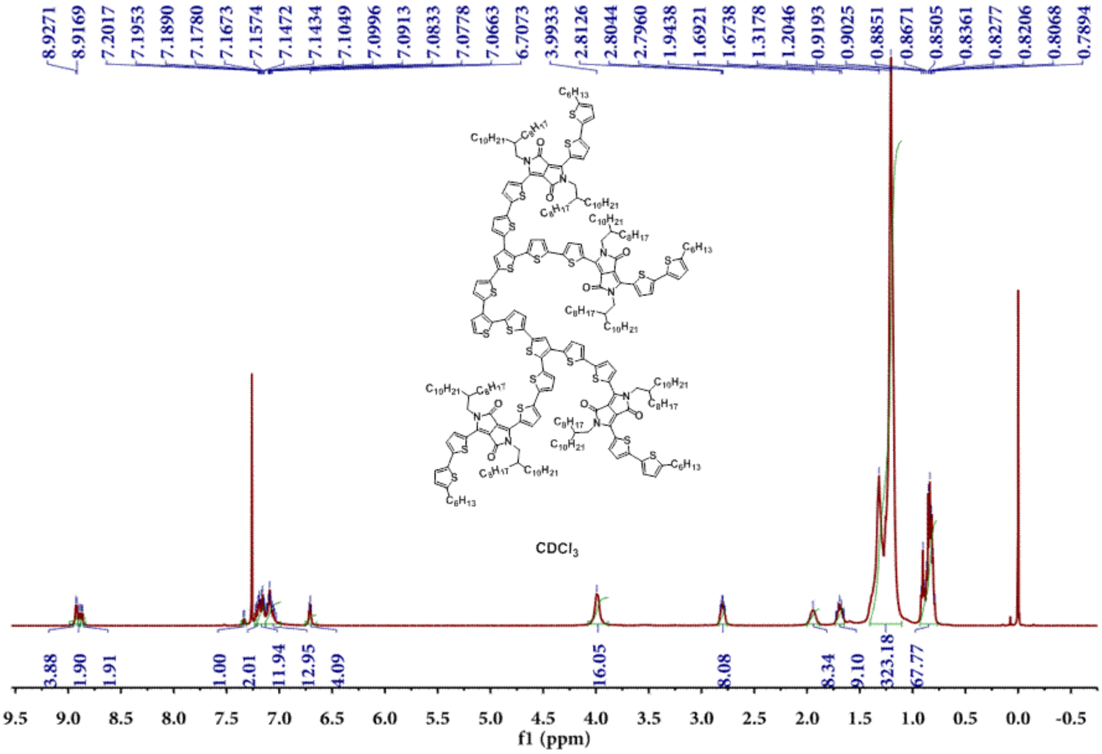
^{13}C NMR of **6T-p-DPP** (zoom)



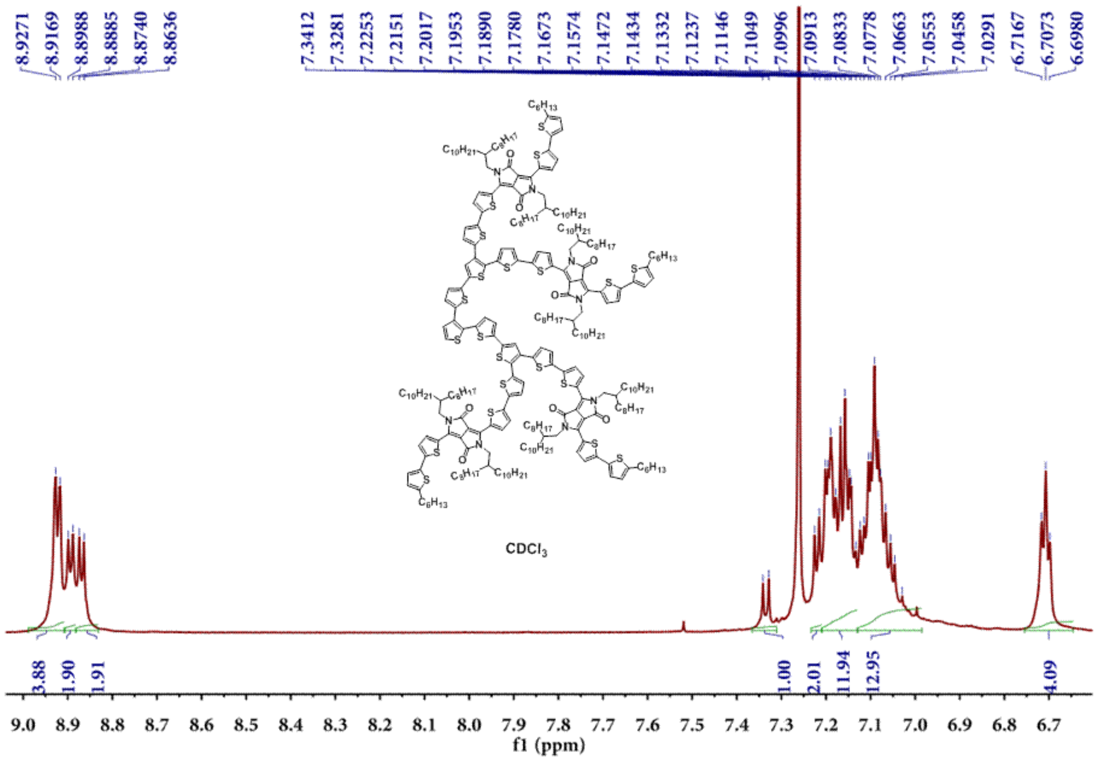
MALDI-TOF MS of **6T-p-DPP**



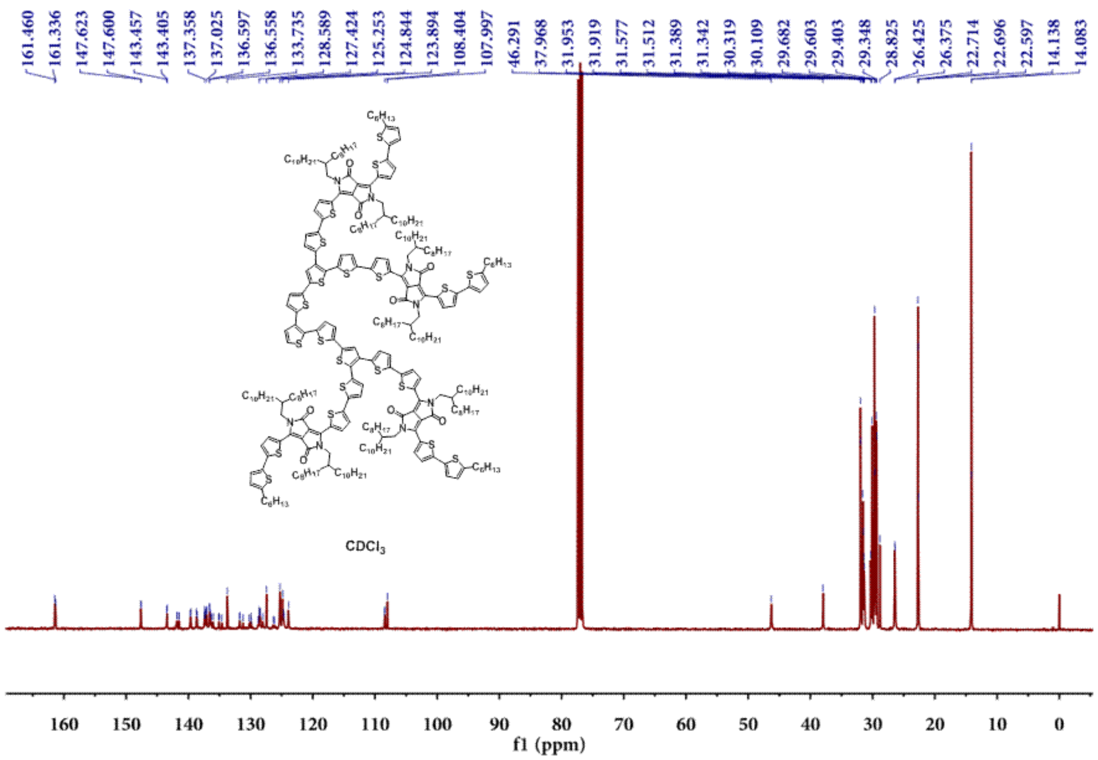
HR MS of **6T-p-DPP**



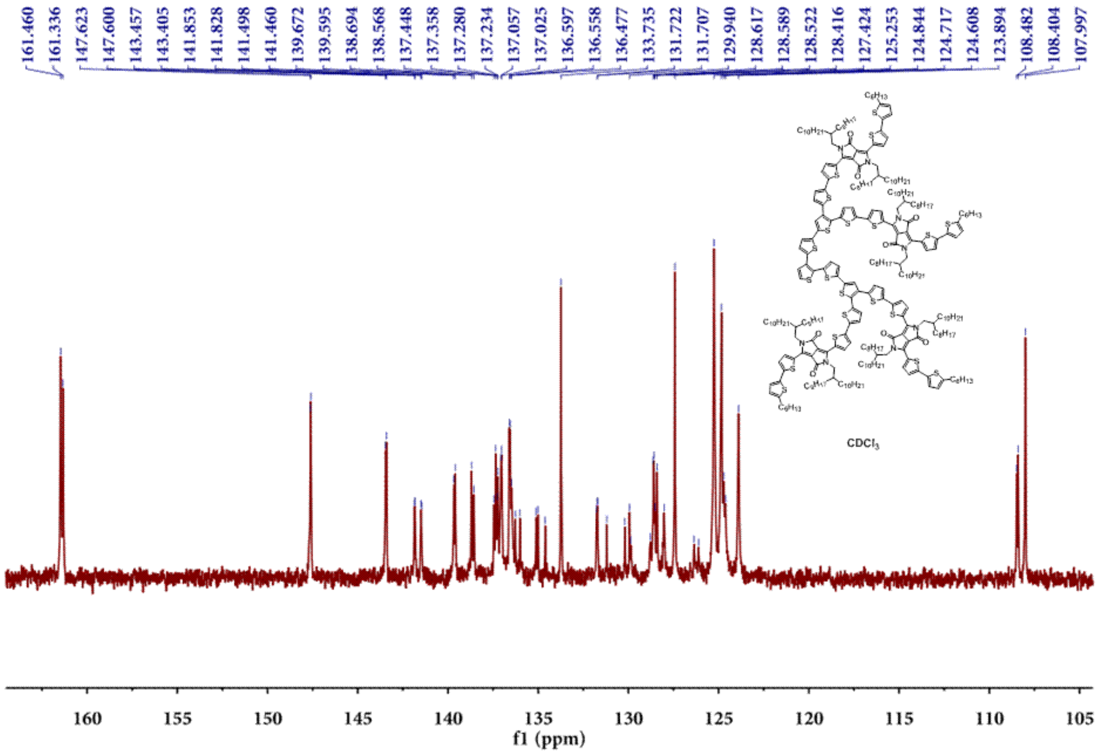
[1]H NMR of **9T-p-DPP**



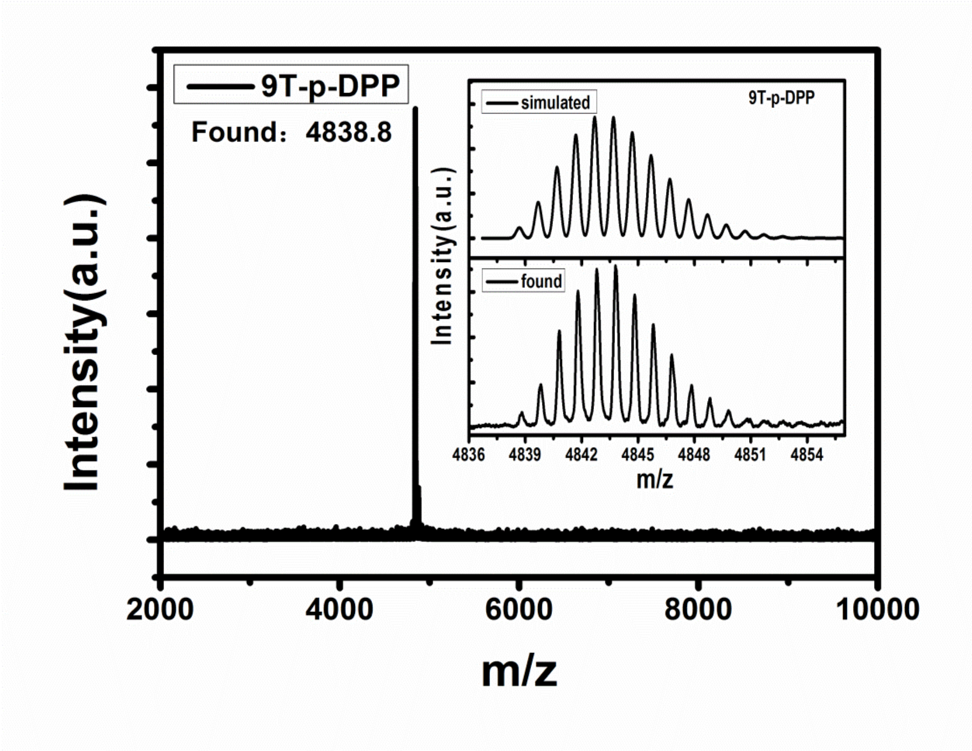
[1]H NMR of **9T-p-DPP** (zoom)



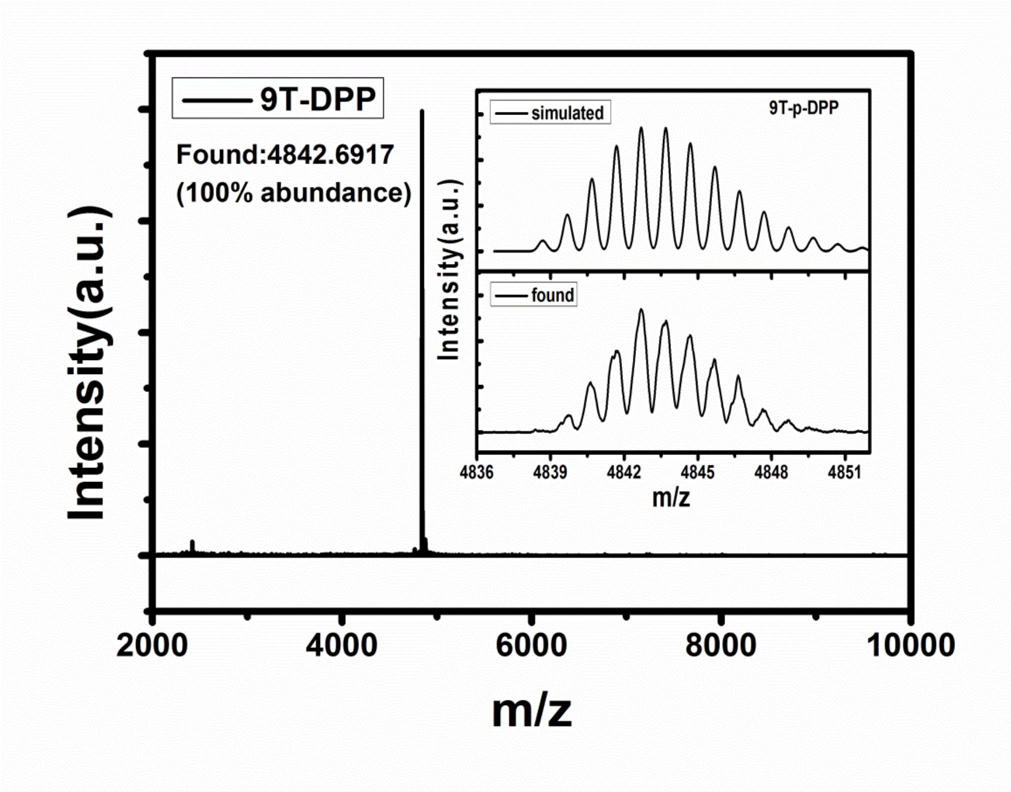
^{13}C NMR of **9T-p-DPP**



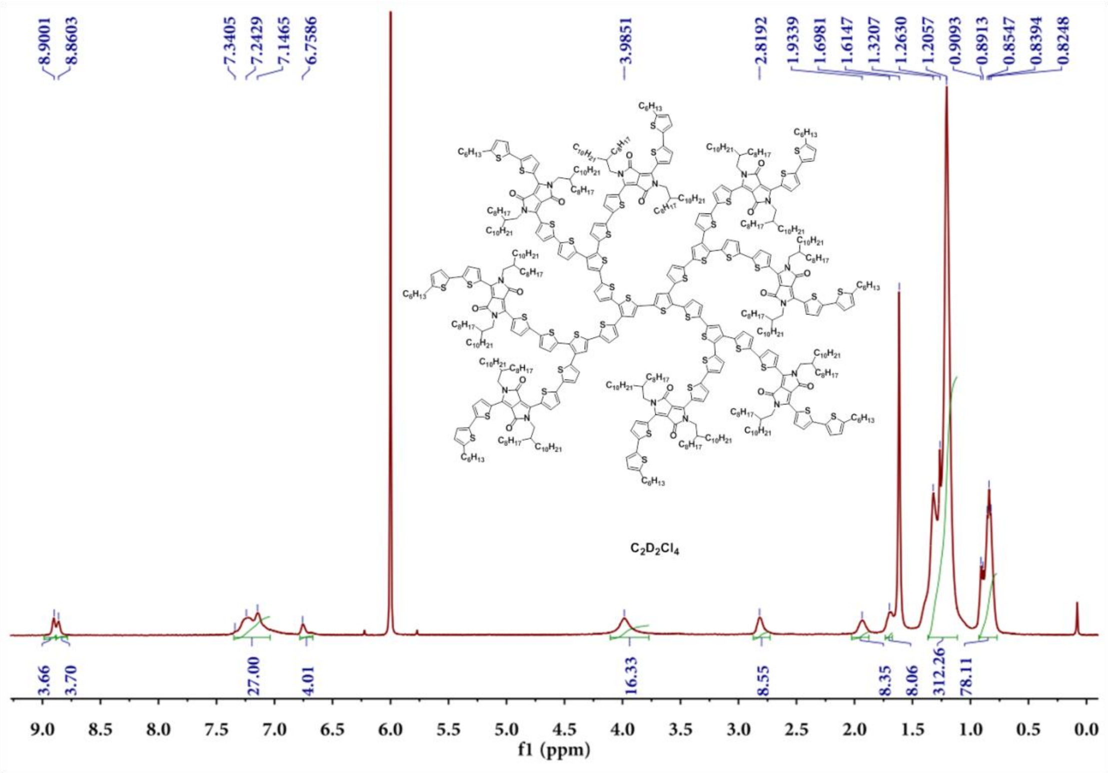
^{13}C NMR of **9T-p-DPP** (zoom)



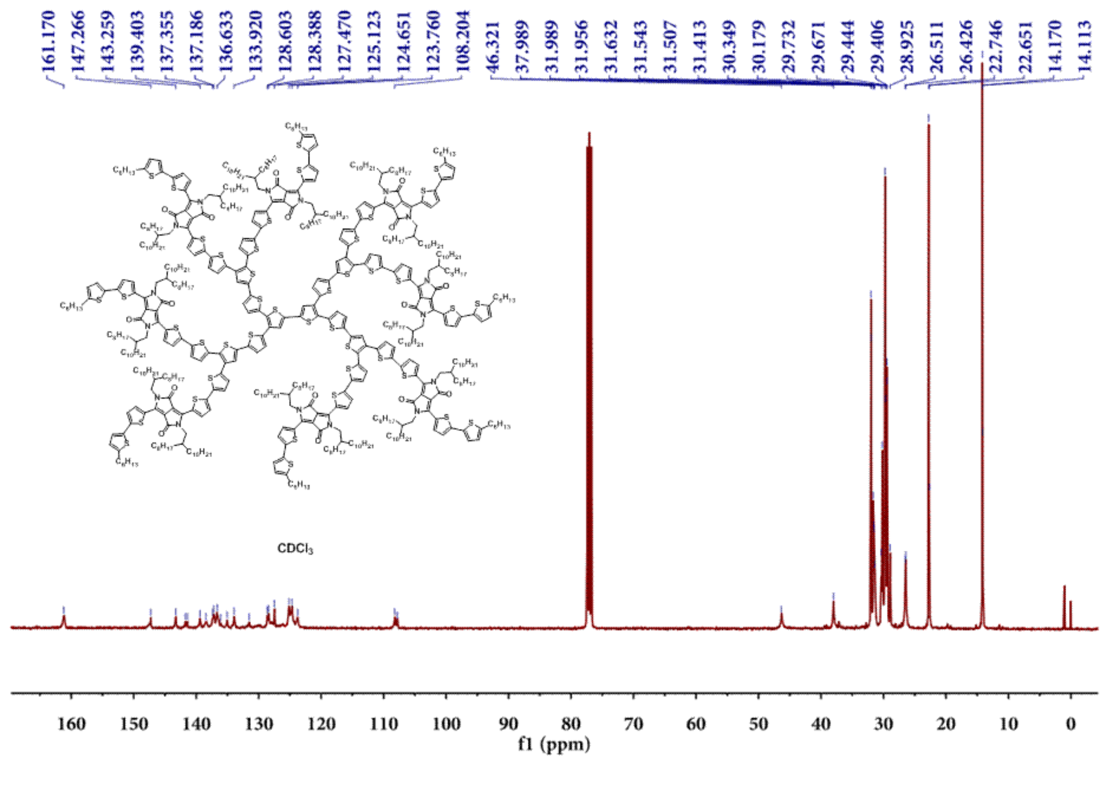
MALDI-TOF MS of **9T-p-DPP**



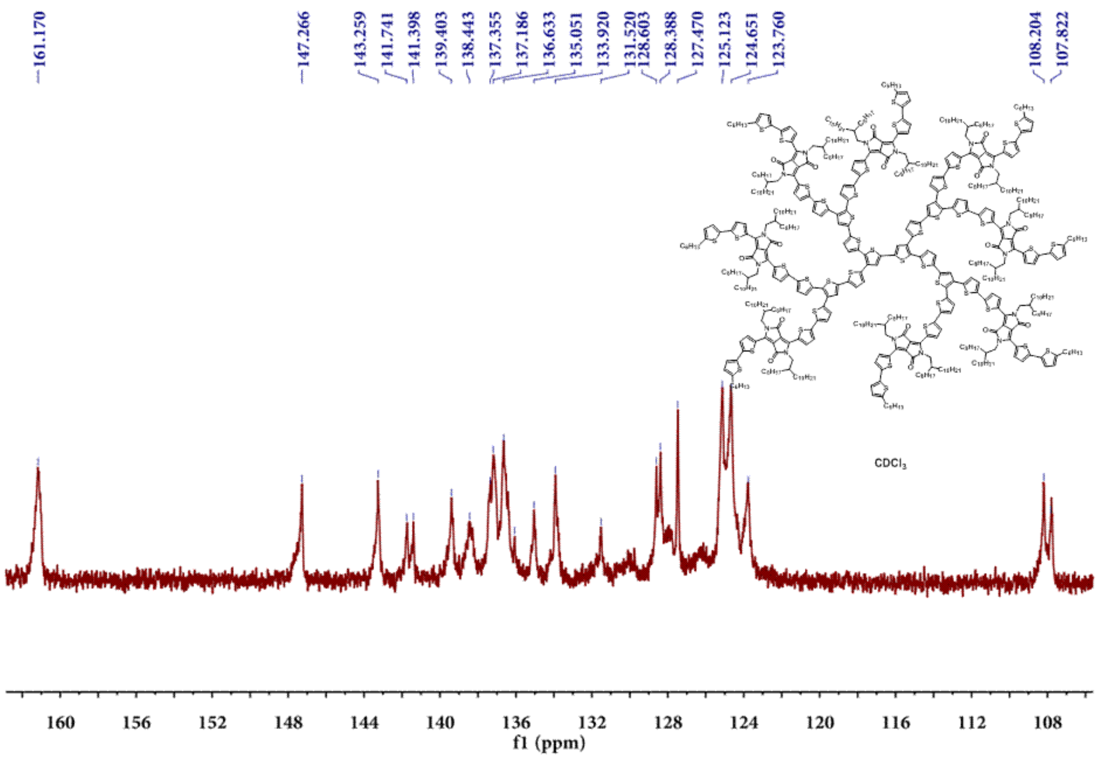
HR MS of **9T-p-DPP**



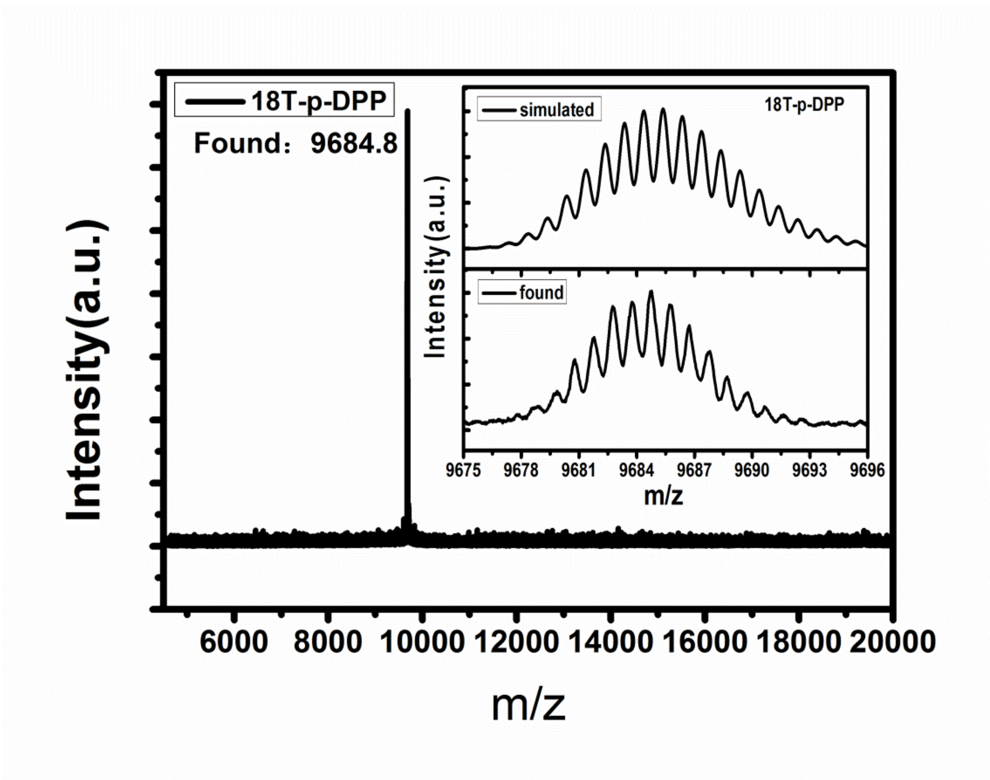
[1]H NMR of **18T-p-DPP**



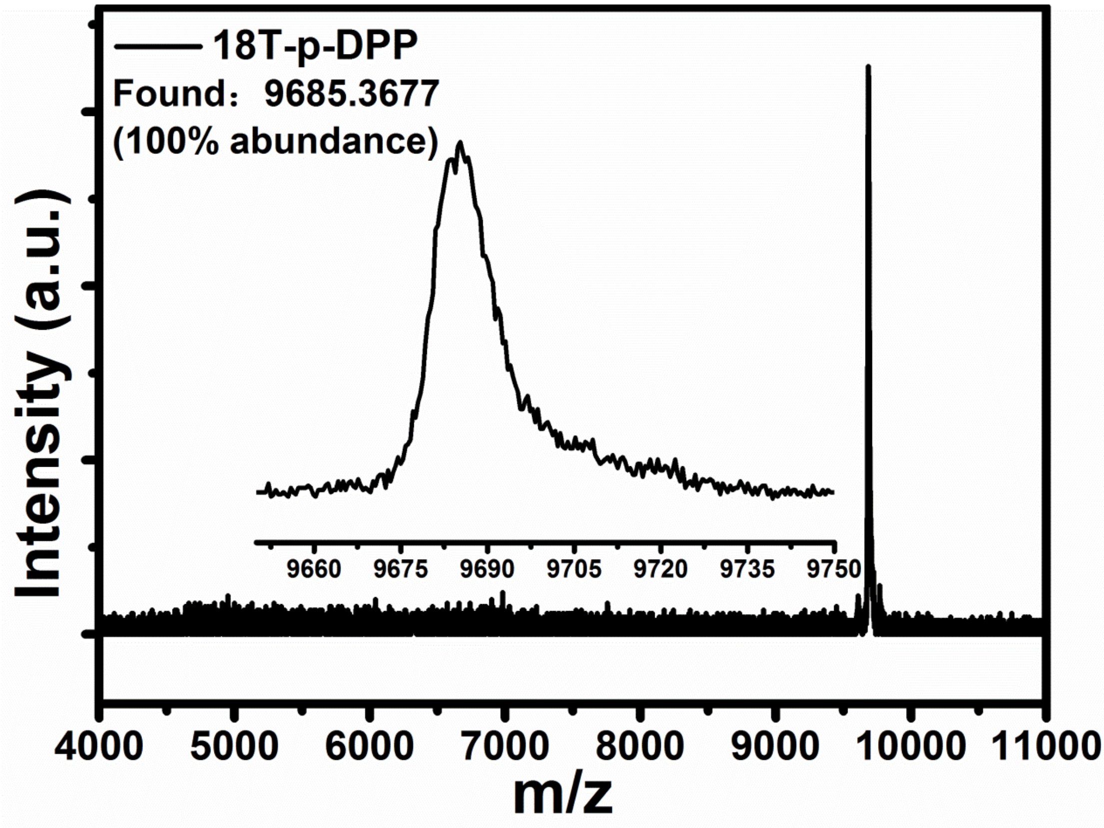
[13]C NMR of **18T-p-DPP**



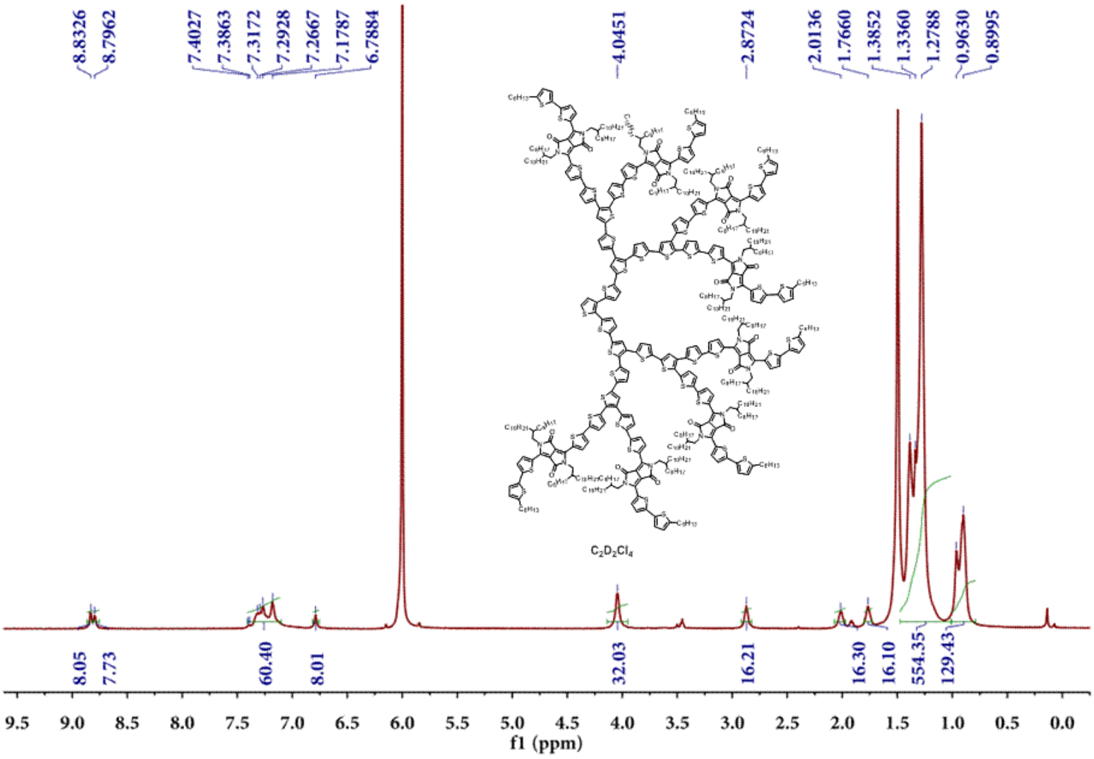
^{13}C NMR of **18T-p-DPP** (zoom)



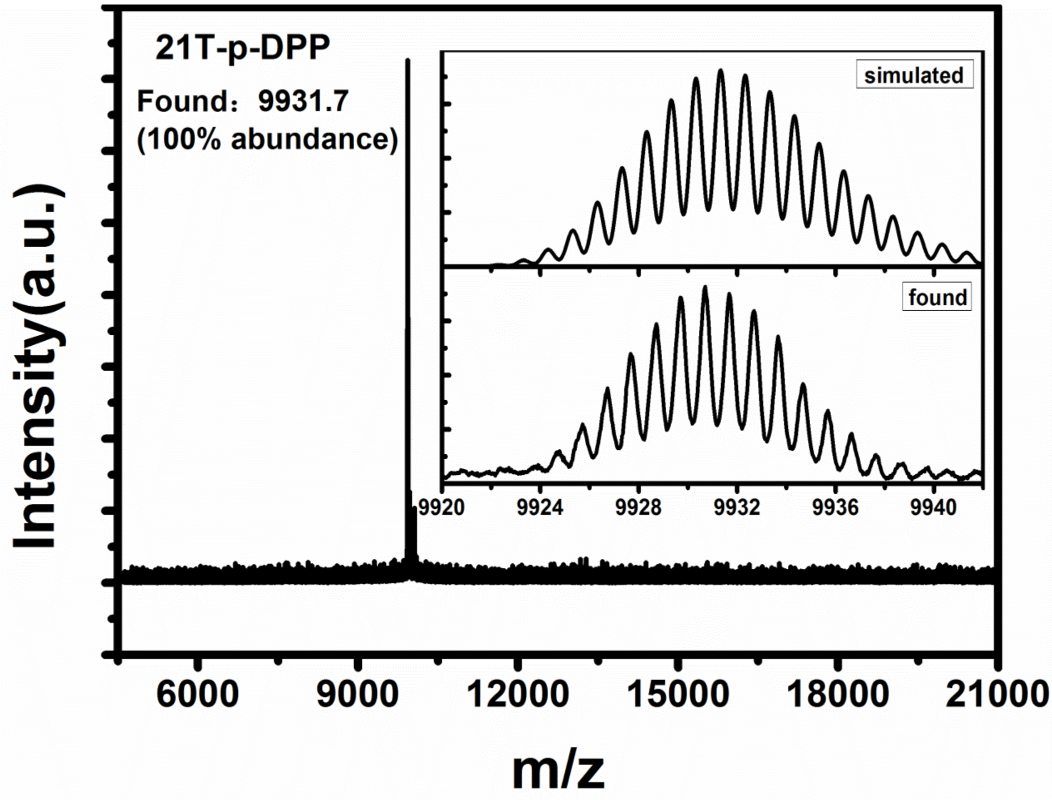
MALDI-TOF MS of **18T-p-DPP**



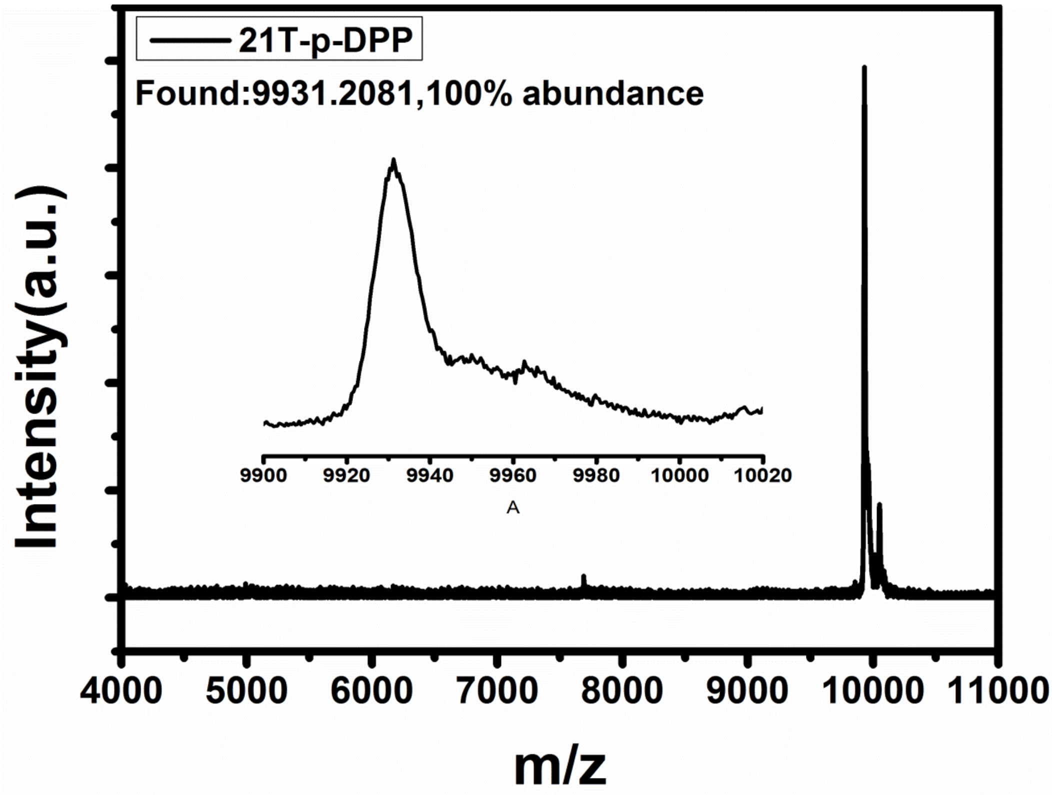
HR MS of **18T-p-DPP**



[1]H NMR of **21T-p-DPP**



MALDI-TOF MS of **21T-p-DPP**



HR MS of **21T-p-DPP**