Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Influence of fluorination in π-extended backbone polydiketopyrrolopyrroles on charge carrier mobility and depth-dependent molecular alignment

Christian J. Mueller,[a] *Eliot Gann,*[b,c] *Christopher R. McNeill*[c] *and Mukundan Thelakkat*[a*]

[a.] Applied Functional Polymers, Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany. *E-Mail: mukundan.thelakkat@uni-bayreuth.de

[b.] Australian Synchrotron, 800 Blackburn Road, Clayton, VIC, 3168, Australia.

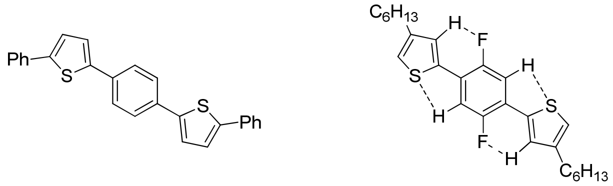
[c.] Department of Materials Engineering, Monash University, Wellington Road, Clayton VIC, 3800, Australia.

[*] Corresponding author: mukundan.thelakkat@uni-bayreuth.de

Table of Contents

1 Literature Analysis on Single Crystal Structures

Single crystal structures were evaluated from previous publications[1-5] on fluorinated oligoaromatic systems which reported single crystal X-ray data that was deposited at the library of the Cambridge Crystallographic Data Centre (CCDC). We analyzed all structures in the database with the relevant thiophene-*n*-fluorophenylene-thiophene motif, where $n = 0, 2, 4$. The most crystal structures describe oligomers that are either slightly larger (i.e. with terminal groups attached) or with solubilizing sidechains, mostly a hexyl-group on the thiophene ring. The relevant dihedral angles between a thiophene ring and an adjacent *n*-fluorinated phenyl ring are therefore printed bold in Table S1. The exact structures of all molecules with the measured dihedral angles as bold bonds and their respective values given in red is shown in Figure S1 and Figure S2.



Contained Motif: **TPT**
CCDC DOI: 10.5517/ccpxk48
Literature DOI: 10.1143/JJAP.46.7478
CCDC # 653050
Refcode # **WOPPIB**

Contained Motif: **TPF$_2$T**
CCDC DOI: 10.5517/ccn9wxq
Literature DOI: 10.1021/cm051563i
CCDC # 605334
Refcode # **LEGHOV**

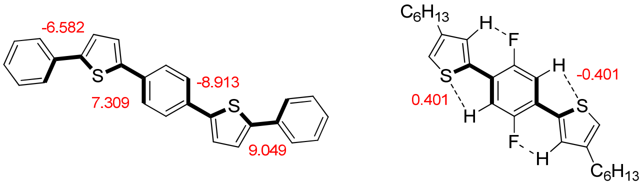
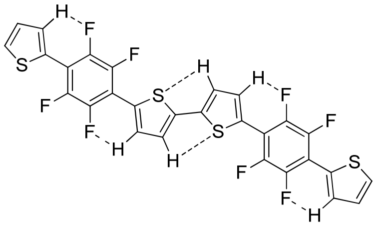
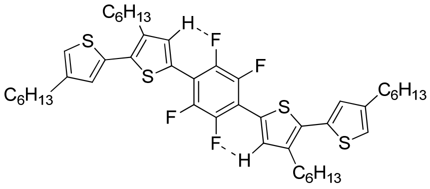


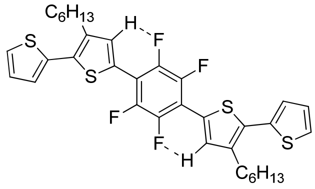
Figure S1. Structures with CCDC database details and the measured dihedral angles for the TPT motif (left) and the TPF$_2$T motif (right).



Contained Motif: **TPF$_4$T**
CCDC DOI: 10.5517/cc6yt75
Literature DOI: 10.1002/anie.200351253
Literature DOI: 10.1021/ja060016a
CCDC # 207397
Refcode # **UKUPEV**



Contained Motif: **TPF$_4$T**
CCDC DOI: 10.5517/cc873yj
Literature DOI: 10.1039/b417642a
CCDC # 245177
Refcode # **XAKDUJ**



Contained Motif: **TPF$_4$T**
CCDC DOI: 10.5517/cc873zk
Literature DOI: 10.1039/b417642a
CCDC # 245178
Refcode # **XAKFAR**

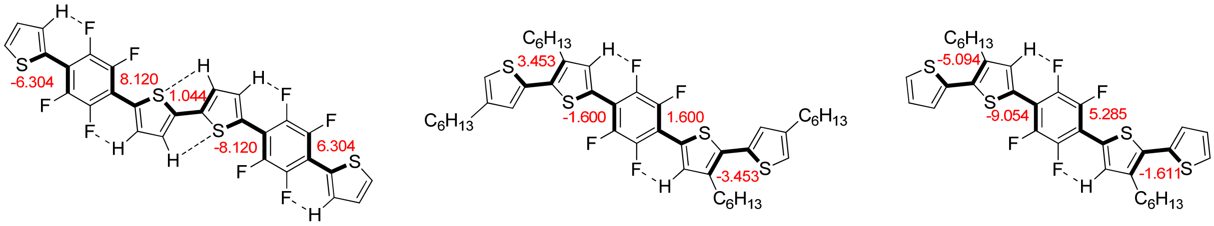


Figure S2. Structures with CCDC database details and the measured dihedral angles for the TPF$_4$T motif (right).

Table S1. Dihedral angles between aromatic units determined by single crystal X-ray crystallography. Bold entries describe the relevant angle between a thiophene ring and a *n*-fluorinated phenyl ring.

CCDC Refcode	structural motif contained	*n*	dihedral angle 1	dihedral angle 2	dihedral angle 3	dihedral angle 4	dihedral angle 5
WOPPIB[5]	TPT	0	-6.582	**7.309**	**-8.913**	9.049	
LEGHOV[4]	TPF$_2$T	2	**0.401**	**-0.401**			
UKUPEV[2-3]	TPF$_4$T	4	**-6.304**	**8.120**	1.044	**-8.120**	**6.304**
XAKDUJ[1]	TPF$_4$T	4	3.453	**-1.600**	**1.600**	-3.453	
XAKFAR[1]	TPF$_4$T	4	-5.094	**9.054**	**5.285**	-1.611	

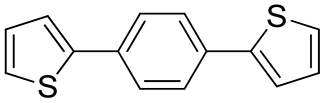
It is noteworthy that the dihedral angles decrease from roughly 8° in the unsubstituted TPT[28] to 0.4° in the difluorinated[13] TPF$_2$T and increase again upon tetrafluorination[14, 29, 30] in TPF$_4$T. This might be ascribed to the unfavourable interactions of fluorine- and sulphur-lone pairs.

2 Monomer Syntheses

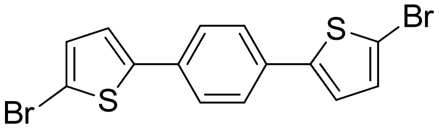
2.1 Materials and methods

All reagents were used without further purification unless otherwise noted. Syntheses were conducted under argon using a double manifold schlenk line. Glasware was severely dried under high vacuum. Solvents were degassed by three freeze-pump-thaw cycles. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AC 300 spectrometer and calibrated according to the respective solvent resonance signal. ^{19}F-NMR spectra were measured on the same spectrometer using either internal or external hexafluorobenzene as calibrant. ^{119}Sn NMR were recorded on a Varian INOVA 400 spectrometer. EIMS measurements were performed on a Finnigan MAT8500 using an ionization energy of 70 eV.

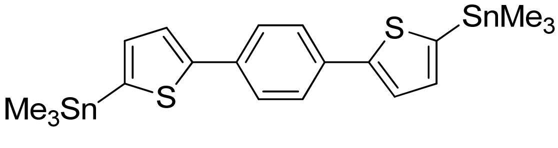
2.2 TPT monomer



1,4-di(thiophene-2-yl)benzene **(2a)**. In a dry 250 two neck flask 2-tributyltinthiophene (8.28 mL, 26.1 mmol) and 1,4-dibromobenzene (**1a**) (3.00 g, 12.7 mmol) were dissolved in 100 mL anhydrous toluene. The mixture was purged with argon for 15 min before tetrakis(triphenylphosphine)palladium(0) (735 mg, 636 µmol) was added and purging with argon was continued for another 15 min. The mixture was then refluxed at 115 °C for 21 h. The Solution was cooled to 40 °C and the solvent was removed into a liquid nitrogen trap under high vacuum to remove all volatile tin compounds. The oily residue was redissolved in 200 mL toluene and washed with water (3 x 150 mL). Finally the organic phase was washed with brine and dried over magnesium sulfate. After filtration the solvent was removed under reduced pressure. The crude yellow product was recrystallized from a mixture of hexane/ethanol/toluene (4:1.5:1). Vacuum filtration and washing with ethanol yielded 2.405 g 1,4-di(thiophene-2-yl)benzene (9.92 mmol, 78%) (**2a**) as pale yellow crystals. ^{1}H-NMR (300 MHz, $CHCl_3$): δ (ppm) 7.62 (s, 4 H, Ph-H), 7.34 (dd, 2 H, J = 3.6 Hz J = 1.1 Hz), 7.29 (dd, 2 H, J = 5.1 Hz, J = 1.1 Hz), 7.10 (dd, 2 H, J = 5.1 Hz, J = 3.6 Hz). EIMS (70 eV) *m/z*: M^+ 242 (100), 197 (20), 165 (5), 152 (5), 139 (5), 121(5).

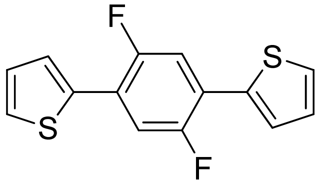


1,4-bis(5-bromothiophen-2-yl)benzene (3a). A mixture of 1,4-di(thiophene-2-yl)benzene (**2a**) (2.00 g, 8.25 mmol) and *N*-bromosuccinimide (3.67 g, 20.6 mmol) was dissolved in 183 mL anhydrous DMF. The resulting solution was stirred at 80 °C for 20 h. After addition of 600 mL water the precipitate was filtered off. The precipitate was washed with water. Recrystallization from a mixture of toluene/ethanol/chloroform (5:2:0.3) gave 2.258 g 1,4-bis(5-bromothiophen-2-yl)benzene (5.64 mmol, 68%) (**3a**) as silvery flakes. ^{1}H-NMR (300 MHz, $CHCl_3$): δ (ppm) 7.51 (s, 4 H, Ph-H), 7.07 (m, 2 H), 7.04 (m, 2 H). EIMS (70 eV) *m/z*: M^+ 400 (100), 320 (15), 277 (20), 240 (20), 195 (10), 139 (10).

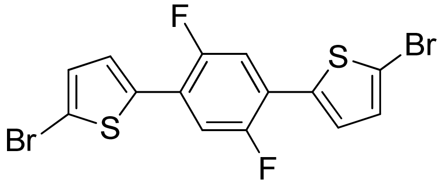


1,4-bis(5-(trimethylstannyl)thiophene-2-yl)benzene (4a). 1,4-bis(5-bromothiophen-2-yl)benzene (**3a**) (1.80 g, 4.51 mmol) was treated with 250 mL anhydrous THF in an ultrasoundbath for 1 h to afford a fine suspension of the starting material. After cooling to -78 °C *n*BuLi (2.5 M in hexane) (3.78 mL, 9.46 mmol) was added slowly. The resulting bright green suspension was stirred at -78 °C for 60 min and subsequently allowed to warm to room temperature over the course of 60 min. After cooling to -78 °C again, trimethyltin chloride (1.89 g, 9.46 mmol) in 9.5 mL anhydrous THF was added via cannula. After complete addition the suspension was allowed to warm to room temperature within 1 h. Water (500 mL) and ethanol (250 mL) were added to precipitate the product. The precipitate was filtered off, washed with water and dried under vacuum. Recrystallization from a mixture of ethanol/toluene (10:1) gave 1.426 g 1,4-bis(5-(trimethylstannyl)thiophene-2-yl)benzene (2.51 mmol, 56%) (**4a**) as yellow-green needles. ^{1}H-NMR (300 MHz, $CHCl_3$): δ (ppm) 7.61 (s, 4 H, Ph-H), 7.44 (d, 2 H, J = 3.4 Hz), 7.17 (d, 2 H, J = 3.4 Hz). EIMS (70 eV) *m/z*: M^+ 468 (25), $[M-CH_3]^+$ 453 (100), 423 (20), 393 (10), 219 (15), 165 (15).

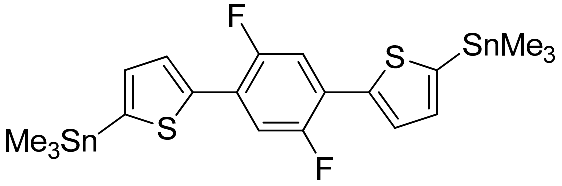
2.3 TPF$_2$T monomer



2,2’-(2,5-difluoro-1,4-phenylene)dithiophene (2b). In a dry 250 mL two-necked flask 100 mL anhydrous toluene, 2-tributyltinthiophene (4.79 ml, 15.1 mmol) and 1,4-dibromo-2,5-difluorobenzene (**1b**) (2.00 g, 7.36 mmol) were added. The mixture was purged with argon for 15 min, tetrakis(triphenylphosphine)palladium(0) (425 mg, 368 µmol) was added and purging with argon was continued for another 15 min. The mixture was then refluxed at 125 °C for 96 h. Water (100 mL) was added. The organic phase was separated and the aqueous phase was extracted with diethyl ether (3 x 80 mL). The combined organic phases were washed with brine and dried over magnesium sulfate. Solvents were removed under reduced pressure to obtain a fluorescent yellow solid, which was recrystallized from hexane/EtOH (1:1) to afford 1.66 g 2,2’-(2,5-difluoro-1,4-phenylene)dithiophene (5.96 mmol, 81%) (**2b**) as bright yellow crystals. ^{1}H-NMR (300 MHz, $CHCl_3$): δ (ppm) 7.52 (d, 2 H, J = 3.7 Hz), 7.45-7.39 (m, 4 H), 7.14 (dd, 2 H, J = 5.1 Hz, J = 3.8 Hz); ^{19}F-NMR (282.4 MHz, $CHCl_3$): δ (ppm) -122.39; ^{13}C-NMR (75.5 MHz, $CHCl_3$): δ (ppm) 156.62 (d, J = 3.3 Hz), 155.07 (d, J = 5.4 Hz), 153.34 (d, J = 3.3 Hz), 135.91, 128.04, 126.97 (t, J = 3.2 Hz), 126.69 (t, J = 1.9 Hz), 122.15, 122.00, 121.83, 115.69, 115.52, 115.44, 115.27. EIMS (70 eV) *m/z*: M^+ 278 (100), 246 (10), 233 (50), 220 (15), 201 (10), 188 (10), 175 (10), 139 (10).

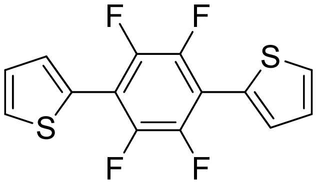


5,5'-(2,5-difluoro-1,4-phenylene)bis(2-bromothiophene) (3b). A mixture of 2,2’-(2,5-difluoro-1,4-phenylene)dithiophene (**2b**) (1.60 g, 5.75 mmol) and *N*-bromosuccinimide (2.56 g, 14.4 mmol) was dissolved in 100 mL anhydrous DMF. The resulting solution was stirred at 80 °C for 24 h. Toluene (200 mL) and water (200 mL) were added to the mixture. The organic layer was isolated and the aqueous layer was extracted with toluene (2 x 100 mL). The combined organic phases were washed with brine and dried over magnesium sulfate before the solvent was removed under reduced pressure. Recrystallization of the crude yellow solid from hexane/toluene (10:1) afforded 2.36 g 5,5'-(2,5-difluoro-1,4-phenylene)bis(2-bromothiophene) (5.41 mmol, 94%) (**3b**) as yellow needles. ^{1}H-NMR (300 MHz, $CHCl_3$): δ (ppm) 7.33 (dd, 2 H, J = 9.2 Hz, J = 8.8 Hz), 7.24 (d, 2 H, J = 4.0 Hz), 7.09 (d, 2 H, J = 4.0 Hz); ^{19}F-NMR (282.4 MHz, $CHCl_3$): δ (ppm) -121.89.

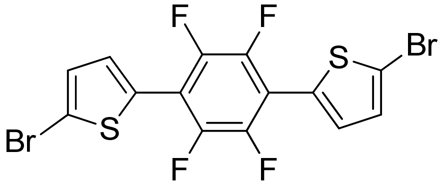


(5,5'-(2,5-difluoro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) (4b). To a solution of 5,5'-(2,5-difluoro-1,4-phenylene)bis(2-bromothiophene) (**3b**) (2.14 g, 4.90 mmol) in 200 mL anhydrous THF was added *n*BuLi (2.5 M in hexane) (4.11 mL, 10.3 mmol) at -78 °C. The resulting bright green suspension was stirred at -78 °C for 30 min and subsequently allowed to warm to room temperature over the course of 60 min. After cooling to -78 °C again a stock solution of trimethyl tin chloride (2.24 g, 11.26 mmol) in 11.2 mL anhydrous THF was added dropwise. After complete addition the solution was stirred for 60 min at -78 °C before it was allowed to warm to room temperature and stirred for additional 2 h. Water (270 mL) was added and the mixture was extracted with diethyl ether (4 x 100 mL). The combined organic layers were then washed with brine and dried over magnesium sulfate. Solvents were removed under reduced pressure to obtain 2.921 g (5,5'-(2,5-difluoro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) (4.84 mmol, 99%) (**4b**) as a bright yellow crystalline solid. Samples were recrystallized from toluene before the monomer was used in polymerizations. ^{1}H-NMR (300 MHz, $CHCl_3$): δ (ppm) 7.61 (d, 2 H, J = 3.4 Hz), 7.41 (t, 2 H, J = 9.0 Hz), 7.21 (d, 2 H, J = 3.4 Hz), 0.41 (m, 18 H, J($^{117/119}$Sn-H) = 55.3 / 57.8 Hz, -$SnMe_3$); ^{19}F-NMR (282.4 MHz, $CHCl_3$): δ (ppm) -122.39; ^{13}C-NMR (75.5 MHz, $CHCl_3$): δ (ppm) 156.39 (d, J = 3.1 Hz), 153.12 (d, J = 3.1 Hz), 141.63, 139.89, 136.11, 127.92 (t, J = 3.3 Hz), 121.84 (dd, J = 13.4 Hz, J = 11.7 Hz), 115.44 (dd, J = 18.3 Hz, J = 12.9 Hz), -8.04; ^{119}Sn-NMR (186.5 MHz, $CDCl_3$): δ (ppm) -25.46 (m, J(^{119}Sn-CH_3) = 374.3 Hz, J(^{119}Sn-C^1) = 483.6 Hz). EIMS (70 eV) *m/z*: M^+ 604 (70), $[M-CH_3]^+$ 589 (100), 559 (35), 529 (10), 409 (10), 287 (30), 257 (15).

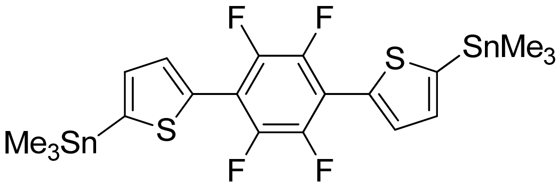
2.4 TPF$_4$T monomer



2,2'-(perfluoro-1,4-phenylene)dithiophene (2c). In a dry 250 mL two-necked flask 100 mL anhydrous toluene, 2-tributyltinthiophene (4.23 ml, 13.3 mmol) and 1,4-dibromo-2,3,5,6-tetrafluorobenzene (**1c**) (2.00 g, 6.50 mmol) were added. The mixture was purged with argon for 15 min, tetrakis(triphenylphosphine)palladium(0) (375 mg, 325 μmol) was added and purging with argon was continued for another 15 min. The mixture was then refluxed at 130 °C for 48 h. Water (100 mL) was added. The organic phase was separated and the aqueous phase was extracted with diethyl ether (3 x 80 mL). The combined organic phases were washed with brine and dried over magnesium sulfate. Solvents were removed under reduced pressure to obtain a fluorescent yellow solid, which was recrystallized from hexane/EtOH (1:1) to afford 1.36 g 2,2'-(perfluoro-1,4-phenylene)dithiophene (4.33 mmol, 67%) (**2c**) as bright yellow crystals. ^{1}H-NMR (300 MHz, $CHCl_3$): δ (ppm) 7.68 (d, 1 H, J = 3.8 Hz), 7.57 (dd, 1 H, J = 5.2 Hz, J = 1.1 Hz), 7.21 (t, 1 H, J = 4.9 Hz); ^{19}F-NMR (282.4 MHz, $CHCl_3$): δ (ppm) -144.00; ^{13}C-NMR (75.5 MHz, $CHCl_3$): δ (ppm) 130.36 (t, J = 3.0 Hz), 128.46 (m), 127.97 (m), 127.49. EIMS (70 eV) *m/z*: M$^+$ 314 (100), 269 (30), 256 (10), 211 (5), 157 (5), 46 (5).



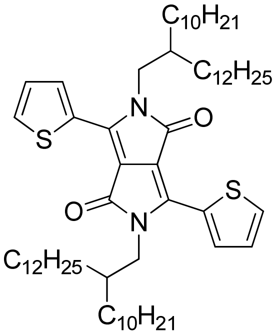
5,5'-(perfluoro-1,4-phenylene)bis(2-bromothiophene) (3c). A mixture of 2,2'-(perfluoro-1,4-phenylene)dithiophene (**2c**) (1.20 g, 3.82 mmol) and *N*-bromosuccinimide (1.70 g, 9.54 mmol) was dissolved in 60 mL anhydrous DMF. The resulting solution was stirred at 80 °C for 72 h. Toluene (150 mL) and water (150 mL) were added to the mixture. The organic layer was isolated and the aqueous layer was extracted with toluene (2 x 100 mL). The combined organic phases were washed with brine and dried over magnesium sulfate before the solvent was removed under reduced pressure. Recrystallization of the crude yellow solid from hexane afforded 1.48 g 5,5'-(perfluoro-1,4-phenylene)bis(2-bromothiophene) (3.13 mmol, 82%) (**3c**) as yellow needles. ^{1}H-NMR (300 MHz, $CHCl_3$): δ (ppm) 7.43 (d, 1 H, J = 4.1 Hz), 7.16 (d, 1 H, J = 4.1 Hz); ^{19}F-NMR (282.4 MHz, $CHCl_3$): δ (ppm) -143.60.



(5,5'-(perfluoro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) (4c). To a solution of 5,5'-(perfluoro-1,4-phenylene)bis(2-bromothiophene) (**3c**) (1.00 g, 2.11 mmol) in 260 mL anhydrous THF was added *n*BuLi (2.5 M in hexane) (1.78 mL, 4.44 mmol) at -78 °C. The resulting dark green suspension was stirred at -78 °C for 30 min and subsequently allowed to warm to room temperature over the course of 60 min. After cooling to -78 °C again a stock solution of trimethyl tin chloride (0.97 g, 4.86 mmol) in 5 mL anhydrous THF was added dropwise. After complete addition the solution was stirred for 60 min at -78 °C before it was allowed to warm to room temperature and stirred for additional 2 h. Water (270 mL) was added and the mixture was extracted with diethyl ether (4 x 100 mL). The combined organic layers were then washed with brine and dried over magnesium sulfate. Solvents were removed under reduced pressure to obtain 1.31 g (5,5'-(perfluoro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) (2.05 mmol, 97%) (**4c**) as a yellow crystalline solid. Samples were recrystallized from toluene before the monomer was used in polymerizations. ^{1}H-NMR (300 MHz, $CHCl_3$): δ (ppm) 7.61 (d, 1 H, J = 3.4 Hz), 7.41 (m, 1 H, J = 9.0 Hz, J = 3.4 Hz), 0.41 (m, 18 H, J($^{117/119}$Sn-H) = 55.3 / 57.9 Hz, -$SnMe_3$); ^{19}F-NMR (282.4 MHz, $CHCl_3$): δ (ppm) -144.10; ^{13}C-NMR (75.5 MHz, $CHCl_3$): δ (ppm) 141.98, 135.38, 133.50, 131.12, 131.09, 131.05, 131.02, -8.00; ^{119}Sn-NMR (186.5 MHz, $CDCl_3$): δ (ppm) -24.43 (m, J(^{119}Sn-CH_3) = 374.8 Hz). EIMS (70 eV) *m/z*: M^+ 640 (55), $[M-CH_3]^+$ 625 (100), 595 (25), 565 (10), 305 (20), 275 (10), 177 (10).

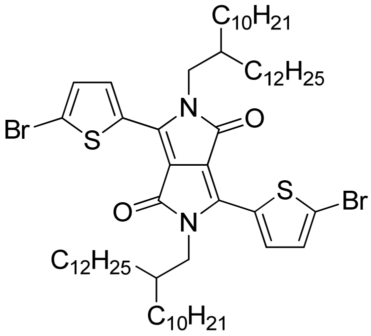
2.5 DPP monomer

DPP[T]$_2$ was synthesized following a previously reported procedure.[6]



DPP[T]$_2${2DTd}$_2$. In a 500 mL three necked flask DPP[T]$_2$ (10.0 g, 33.3 mmol), potassium carbonate (18.4 g, 133 mmol) and 18-crown-6 (616 mg, 2.33 mmol) were suspended in 110 mL anhydrous DMF. The solution was stirred at 130 °C for 1 h before 1-bromo-2-dodecyl-tetradecane (41.7 g, 100 mmol) was added dropwise within 5 min. The reaction mixture was then stirred for 42 h at 100 °C. After cooling to room temperature and addition of 100 mL water the solution was stirred for 30 min. Solvents were removed completely under reduced pressure, the remains redissolved in chloroform washed with water. The aqueous phase was extracted with chloroform (2 x 100 mL). The combined organic phases were dried over magnesium sulfate. Solvents were removed under reduced pressure and the crude product was redissolved in 350 mL 1,4-dioxane. 1.4 mL concentrated hydrochloric was added and the mixture was stirred at 130 °C for 2 h. After cooling to room temperature the mixture was filtrated over a short aluminium oxide plug and the solvent was removed under reduced pressure. Flash chromatography (silica gel) using hexane:chloroform 1:1 as eluent and subsequent recrystallization of the product from ethanol afforded 21.58 g DPP[T]$_2${2HD}$_2$ (22.16 mmol, 67%) as a red tacky solid. ^{1}H-NMR (300 MHz,

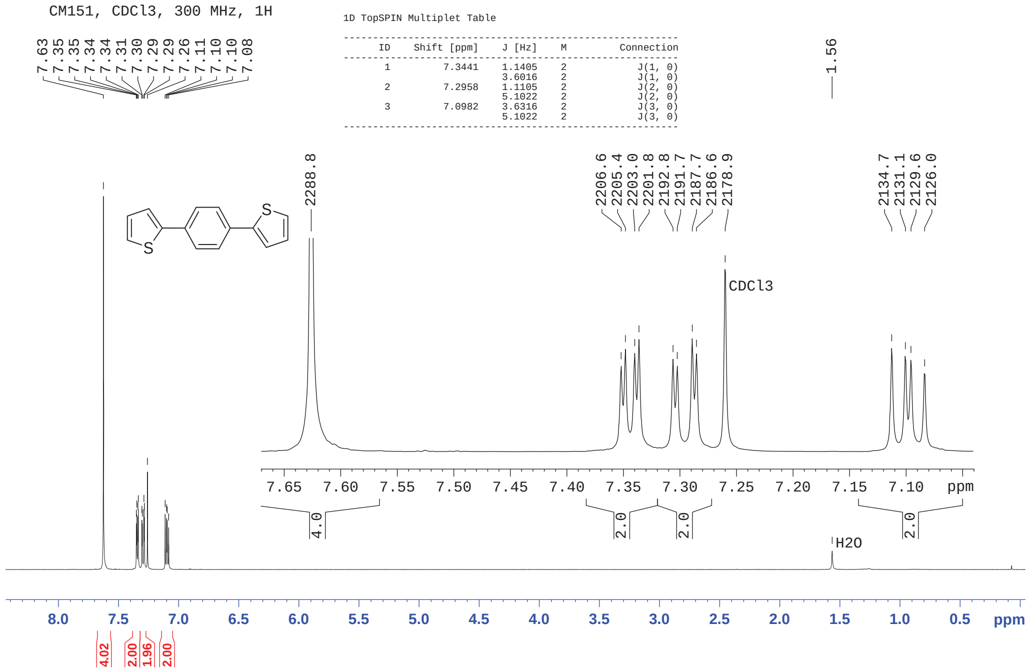
$CHCl_3$): δ (ppm) 8.88 (d, 2H, J = 3.0 Hz), 7.62 (d, 2H, J = 4.2 Hz), 7.26 (m, 2H), 4.01 (d, 4H, J = 7.7 Hz), 1.90 (s, 2H), 1.25-1.20 (m, calc: 80H, observed: 122H), 0.87 (m, calc: 12H, observed: 17H) (Note: Alkyl-Protons in DPPs are prone to overestimation).



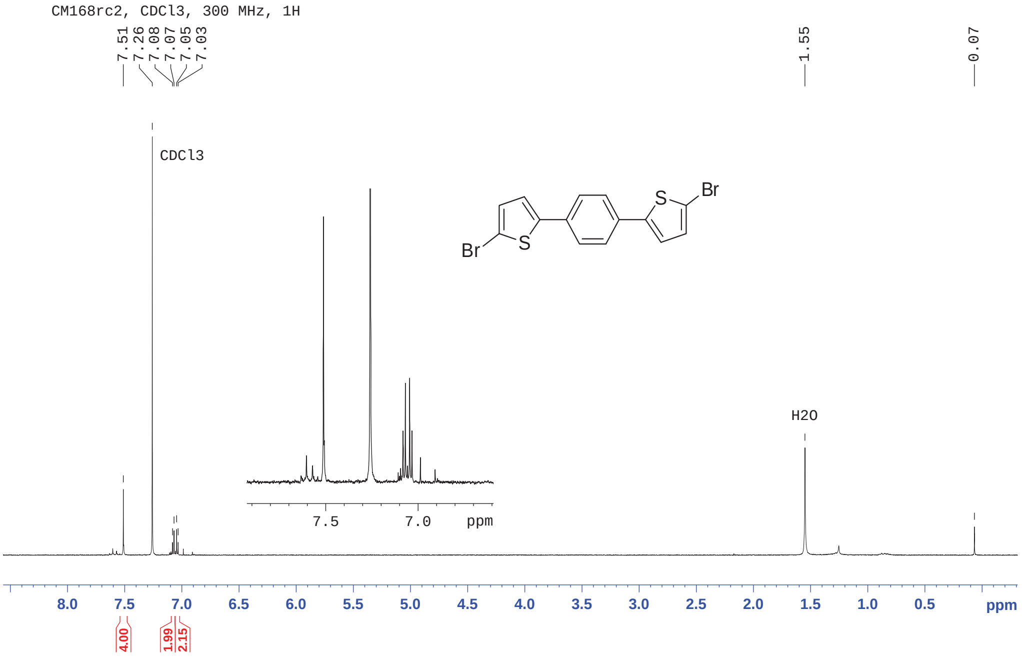
DPP[T]$_2${2DTd}$_2$Br$_2$. DPP[T]$_2${2DTd}$_2$ (10.0 g, 10.3 mmol) and *N*-bromosuccinimide (4.02 g, 22.6 mmol) were dissolved in 100 mL chloroform. The solution was purged with argon for 5 minutes and protected from light. After stirring at room temperature for 48 h the solution was concentrated to ca. 50 mL under reduced pressure and poured into 400 mL methanol. After waiting for 15 min without stirring the precipitate was filtered. Recrystallisation from ethanol the product still contained impurities and was subjected to flash chromatography (silica gel) using hexane/dichloromethane 3:1 as eluent. The product fractions were dried under reduced pressure and recrystallized from ethanol to yield 2.43 g DPP[T]$_2${2DTd}$_2$Br$_2$ (2.15 mmol, 21%) as a red waxy solid. ^{1}H-NMR (300 MHz, $CHCl_3$): δ (ppm) 8.63 (d, 2H, J = 4.2 Hz), 7.21 (d, 2H, J = 4.2 Hz), 3.92 (d, 4H, J = 7.6 Hz), 1.87 (s, 2H), 1.21 (m, calc: 80H, observed: 87H), 0.87 (m, calc: 12H, observed: 13H) (Note: Alkyl-Protons in DPPs are prone to overestimation).

3 Monomer Characterization

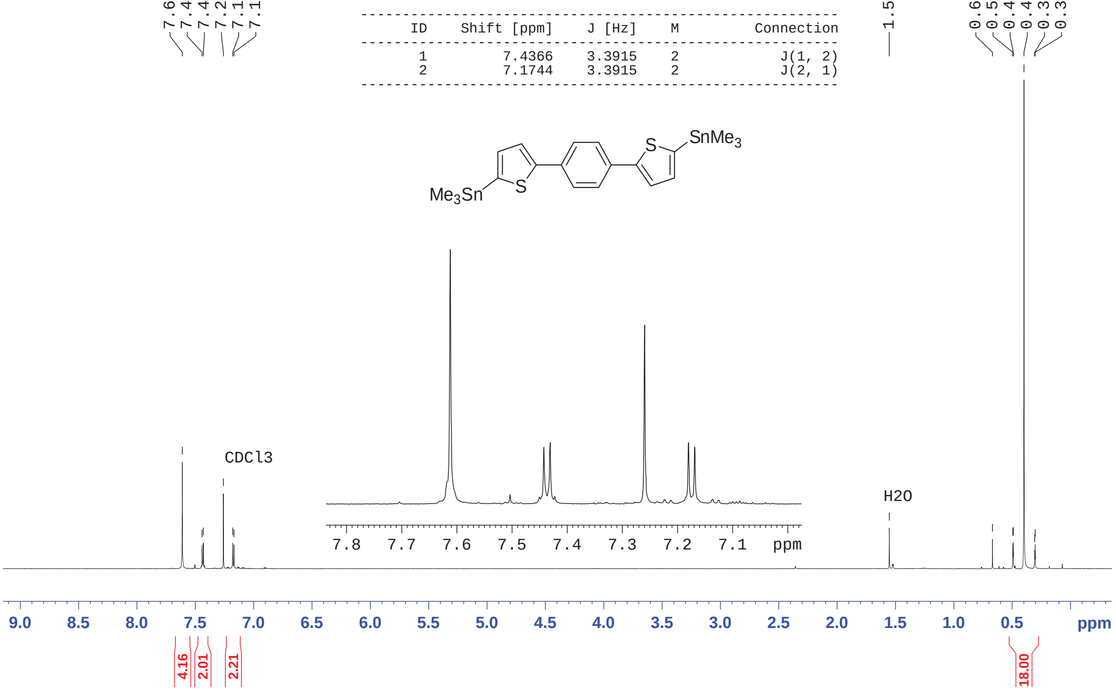
3.1 NMR spectra of the monomers



```
1D TopSPIN Multiplet Table

-----------------------------------------------------------
    ID    Shift [ppm]     J [Hz]     M          Connection
-----------------------------------------------------------
     1         7.3441     1.1405     2             J(1, 0)
                          3.6016     2             J(1, 0)
     2         7.2958     1.1105     2             J(2, 0)
                          5.1022     2             J(2, 0)
     3         7.0982     3.6316     2             J(3, 0)
                          5.1022     2             J(3, 0)
-----------------------------------------------------------
```

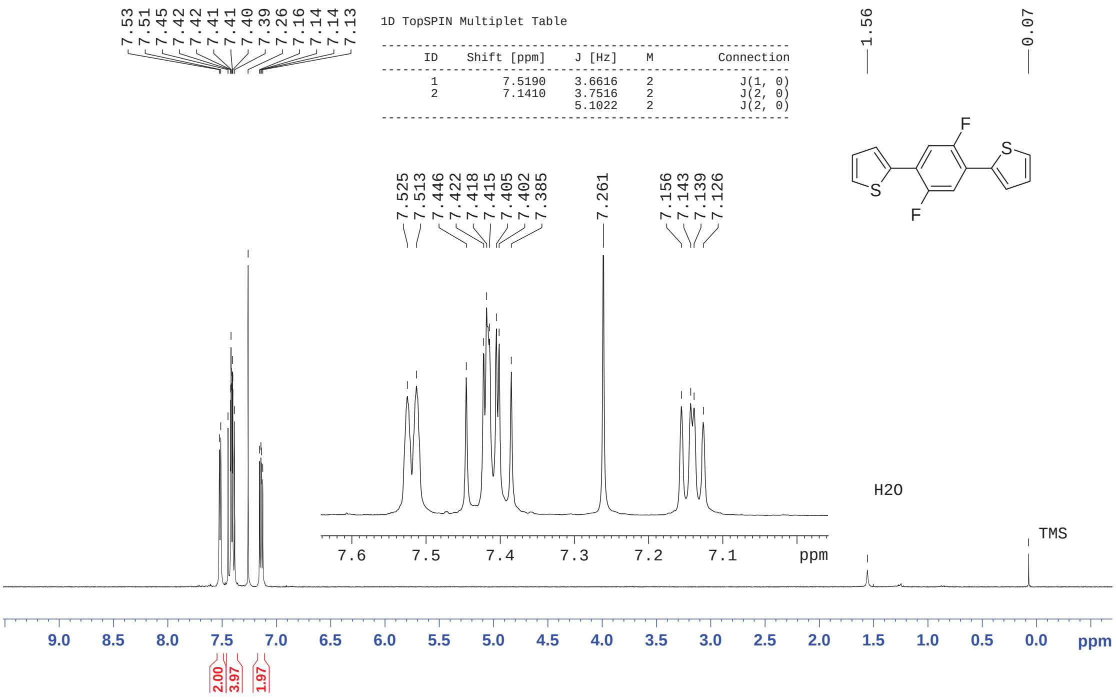


CM169, CDCl3, 300 MHz, 1H

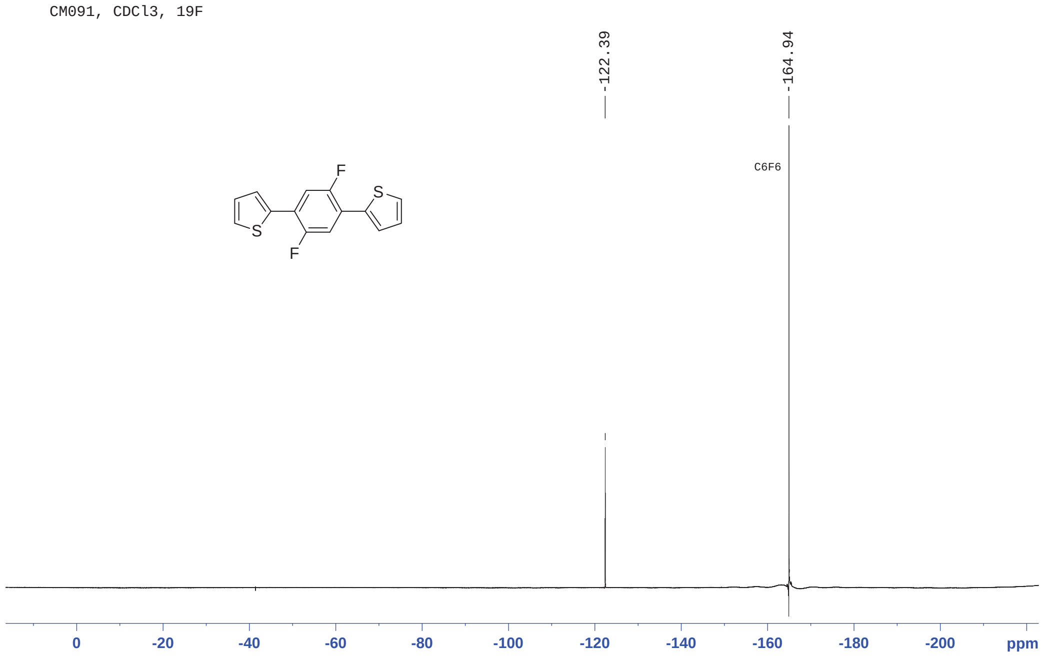


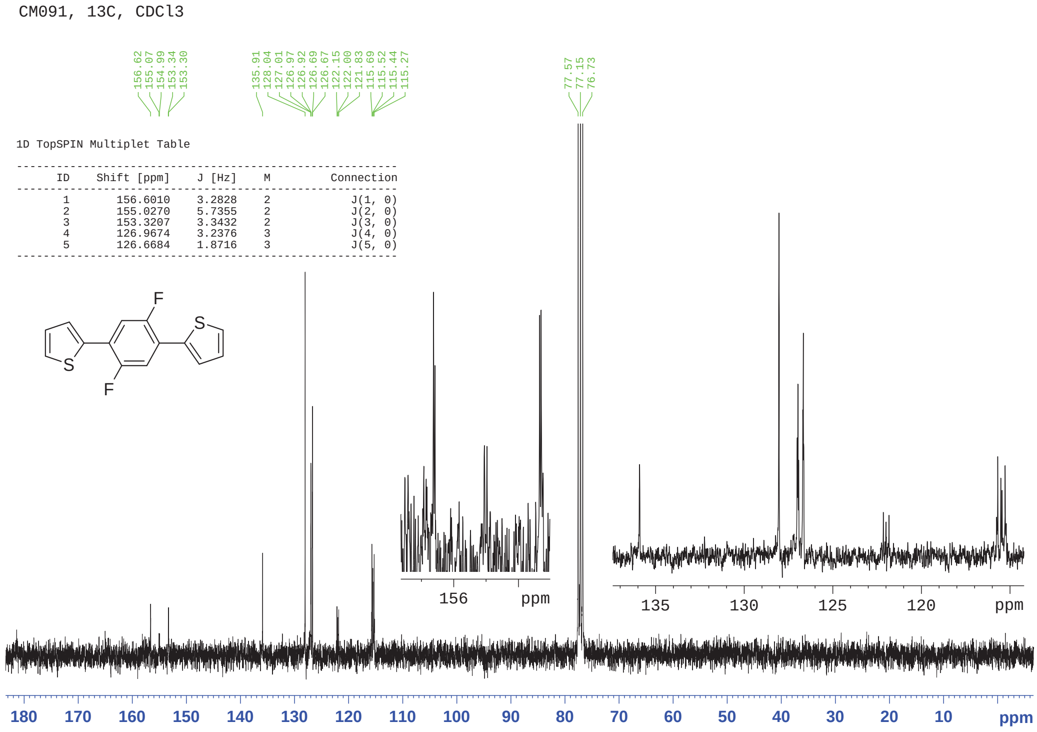
```
1D TopSPIN Multiplet Table

-----------------------------------------------------------------
   ID     Shift [ppm]     J [Hz]      M             Connection
-----------------------------------------------------------------
    1          7.4366     3.3915      2               J(1, 2)
    2          7.1744     3.3915      2               J(2, 1)
-----------------------------------------------------------------
```

CM091, CDCl3, 1H

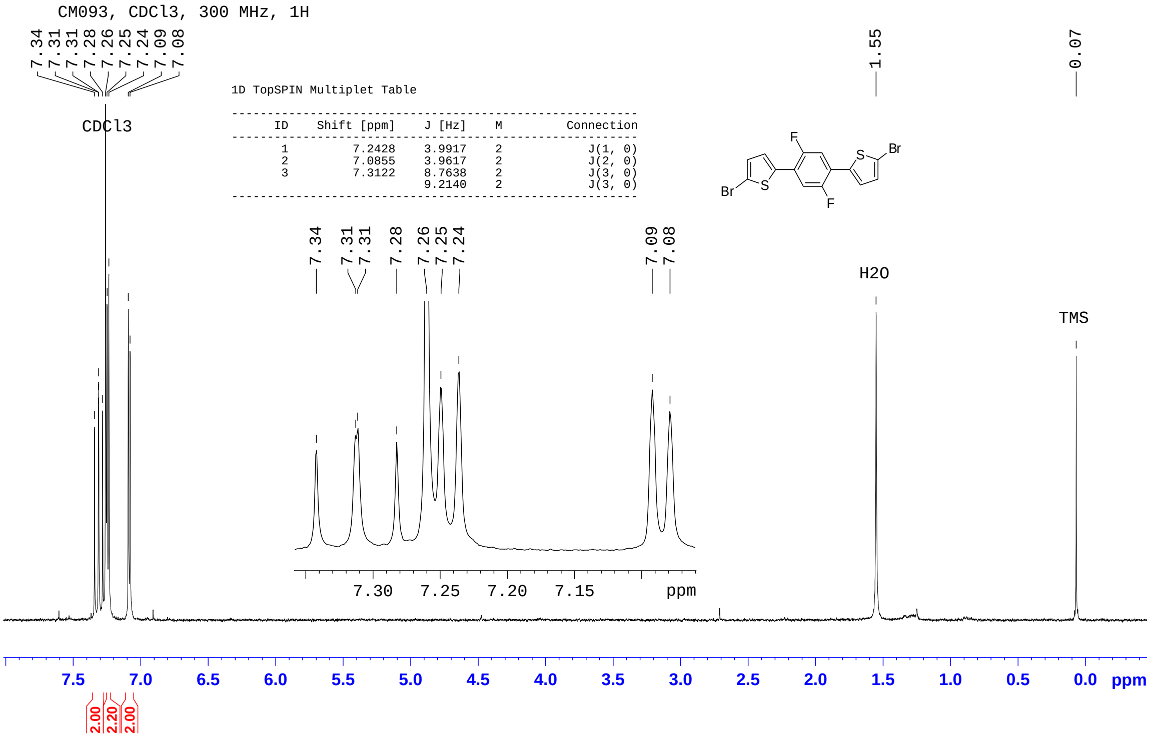


```
1D TopSPIN Multiplet Table

-----------------------------------------------------------------
   ID     Shift [ppm]     J [Hz]      M             Connection
-----------------------------------------------------------------
    1          7.5190     3.6616      2               J(1, 0)
    2          7.1410     3.7516      2               J(2, 0)
                          5.1022      2               J(2, 0)
-----------------------------------------------------------------
```



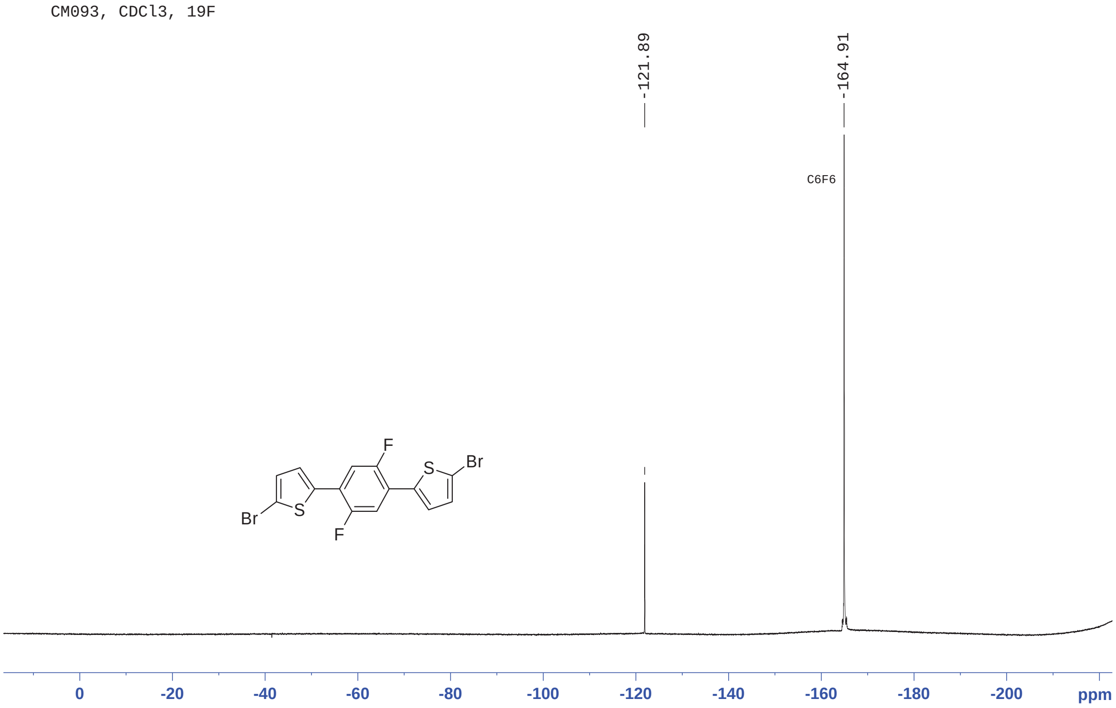


```
1D TopSPIN Multiplet Table

-----------------------------------------------------------
    ID    Shift [ppm]     J [Hz]     M            Connection
-----------------------------------------------------------
     1       156.6010     3.2828     2               J(1, 0)
     2       155.0270     5.7355     2               J(2, 0)
     3       153.3207     3.3432     2               J(3, 0)
     4       126.9674     3.2376     3               J(4, 0)
     5       126.6684     1.8716     3               J(5, 0)
-----------------------------------------------------------
```

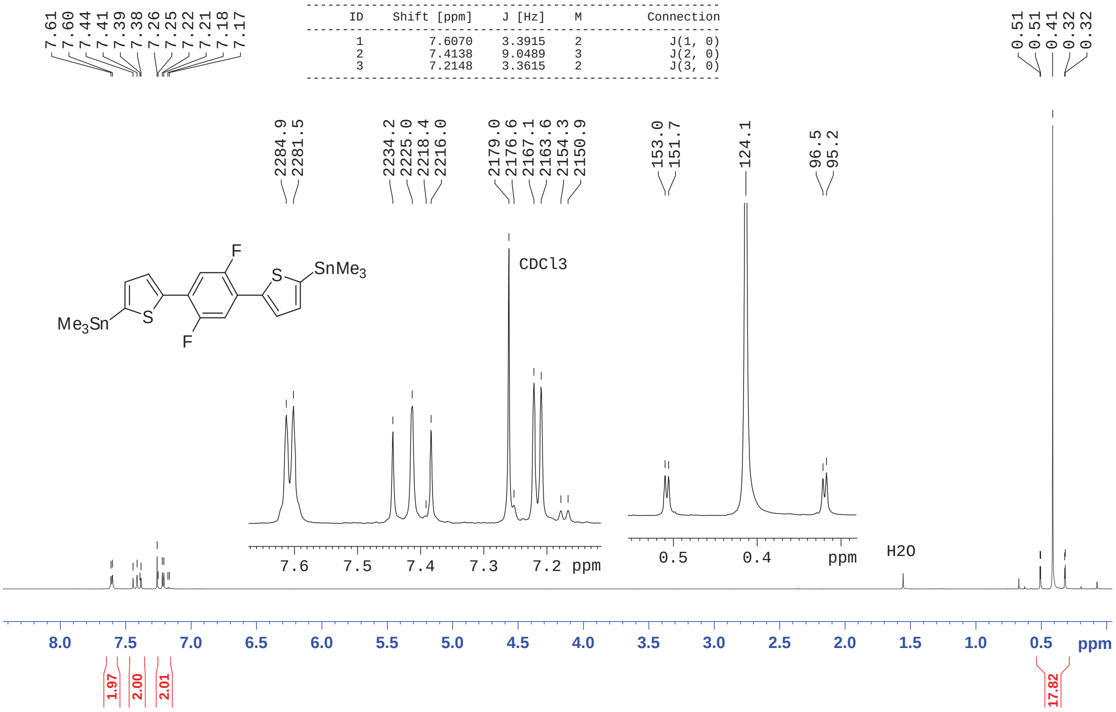


1D TopSPIN Multiplet Table

ID	Shift [ppm]	J [Hz]	M	Connection
1	7.2428	3.9917	2	J(1, 0)
2	7.0855	3.9617	2	J(2, 0)
3	7.3122	8.7638	2	J(3, 0)
		9.2140	2	J(3, 0)

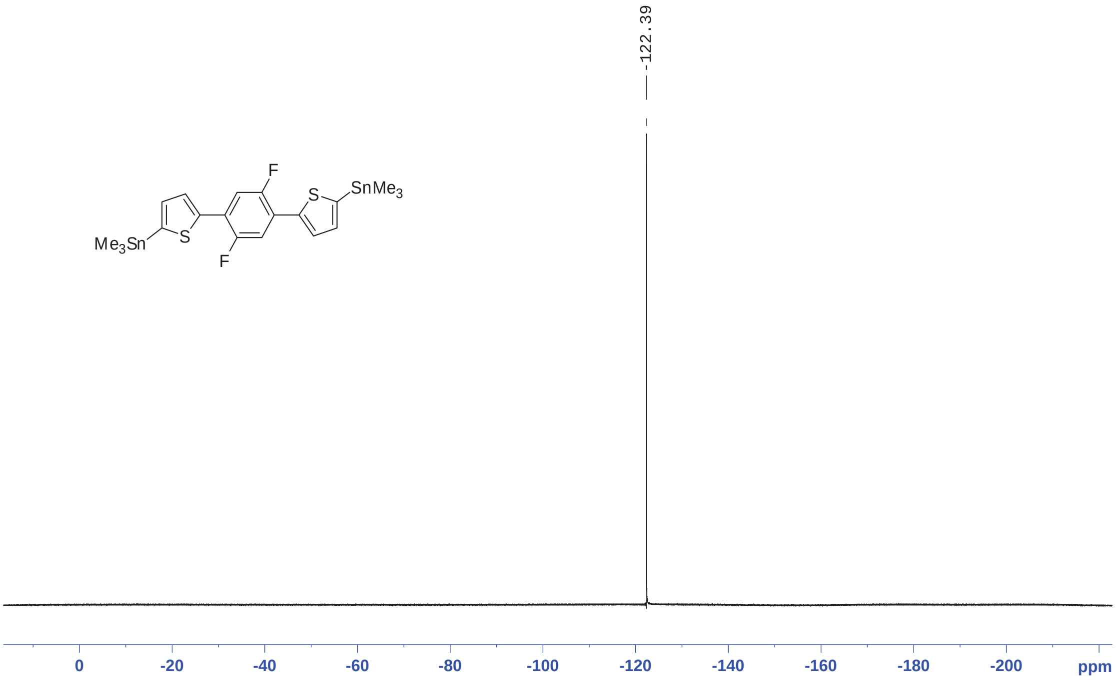


CM145, CDCl3, 300 MHz, 1H

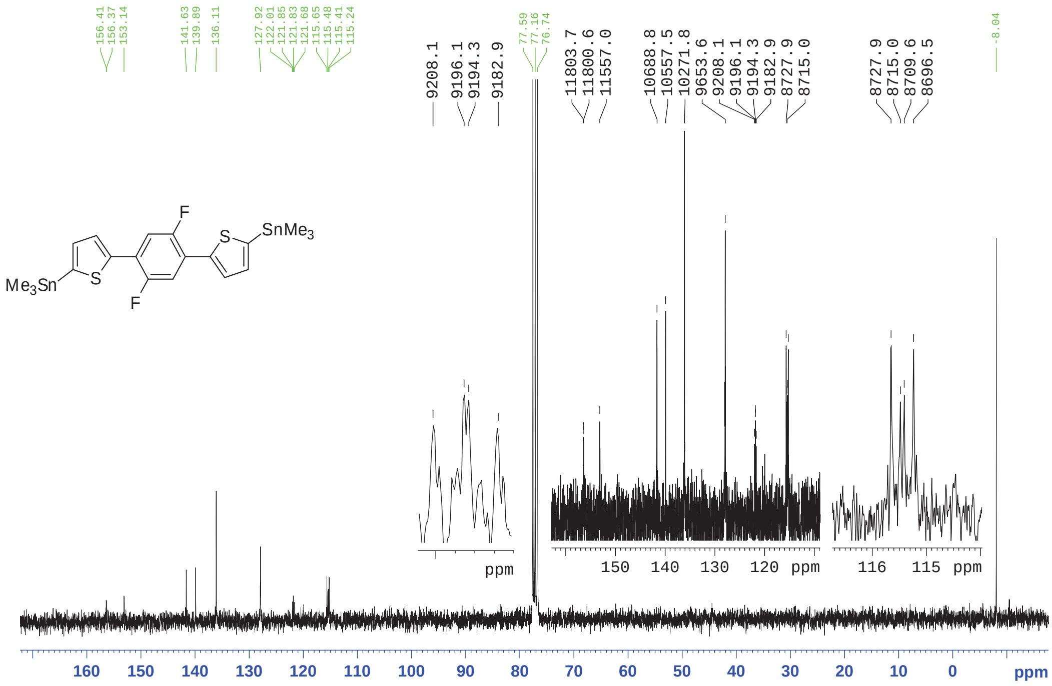


```
1D TopSPIN Multiplet Table
-----------------------------------------------------------------
  ID      Shift [ppm]      J [Hz]      M            Connection
-----------------------------------------------------------------
   1          7.6070      3.3915       2              J(1, 0)
   2          7.4138      9.0489       3              J(2, 0)
   3          7.2148      3.3615       2              J(3, 0)
-----------------------------------------------------------------
```

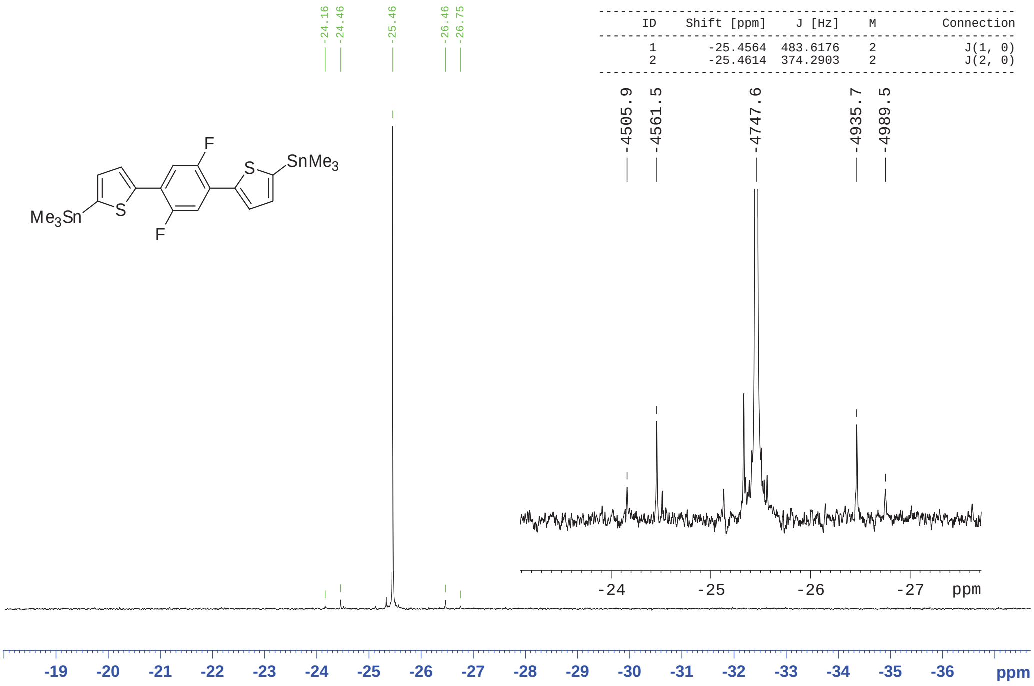
CM145, CDCl3, 19F



CM145, 13C, CDCl3

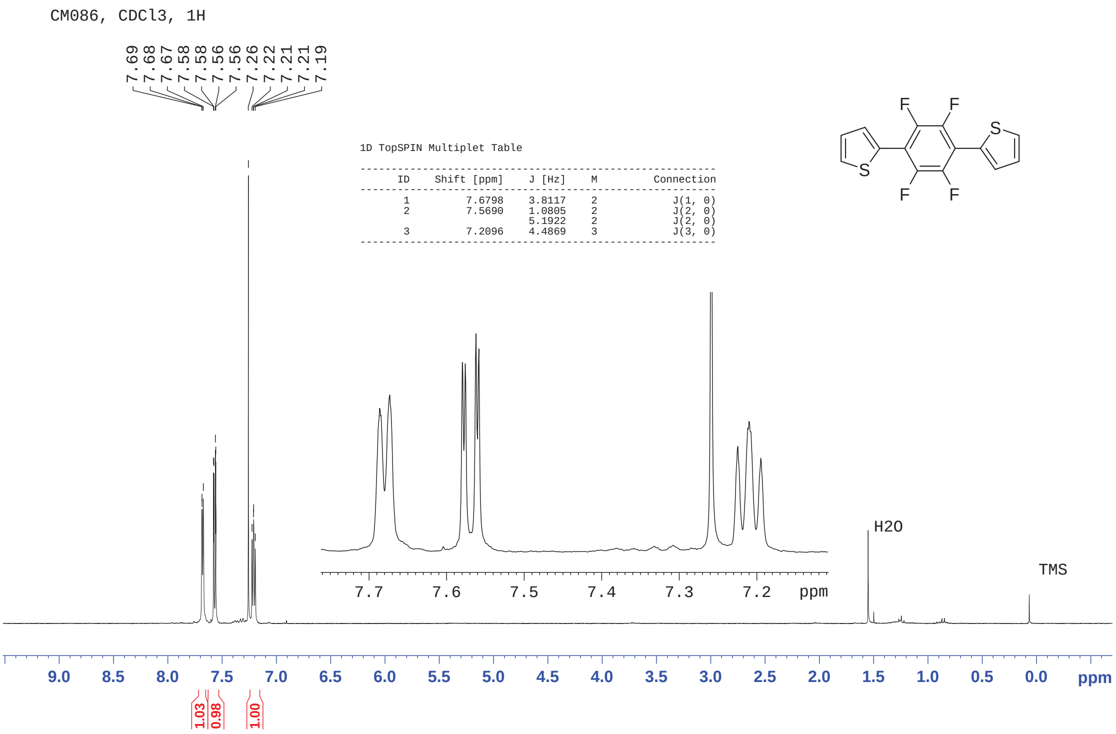


CM145, 119Sn, CDCl3, INEPTRD, 186 MHz

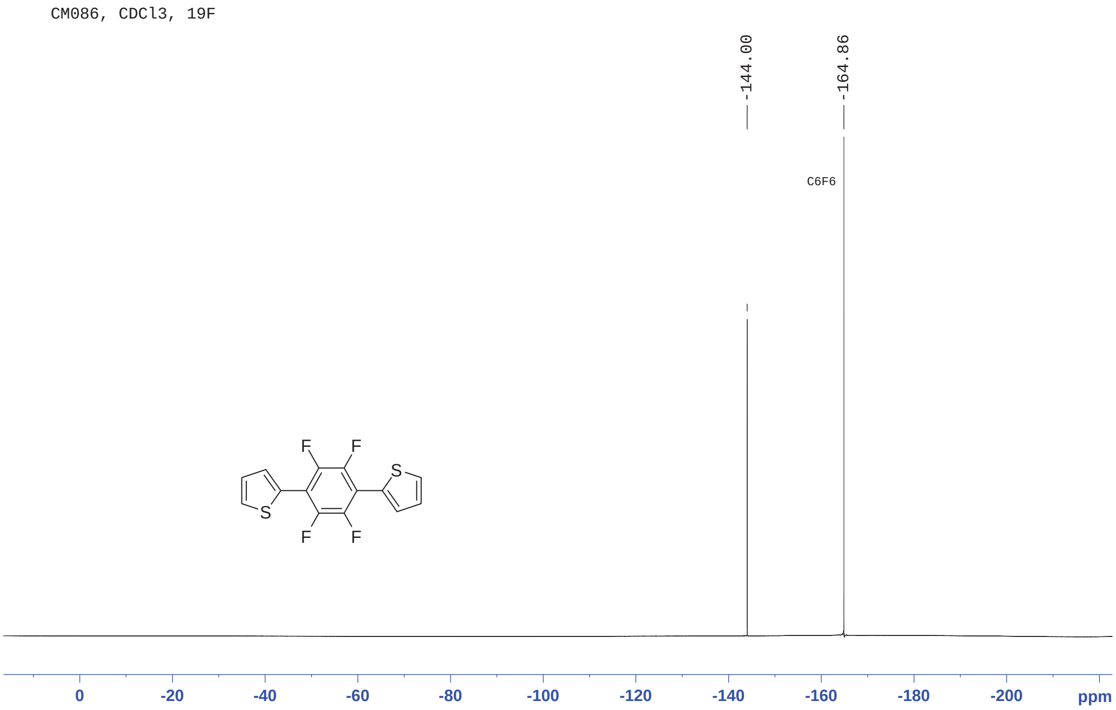


1D TopSPIN Multiplet Table

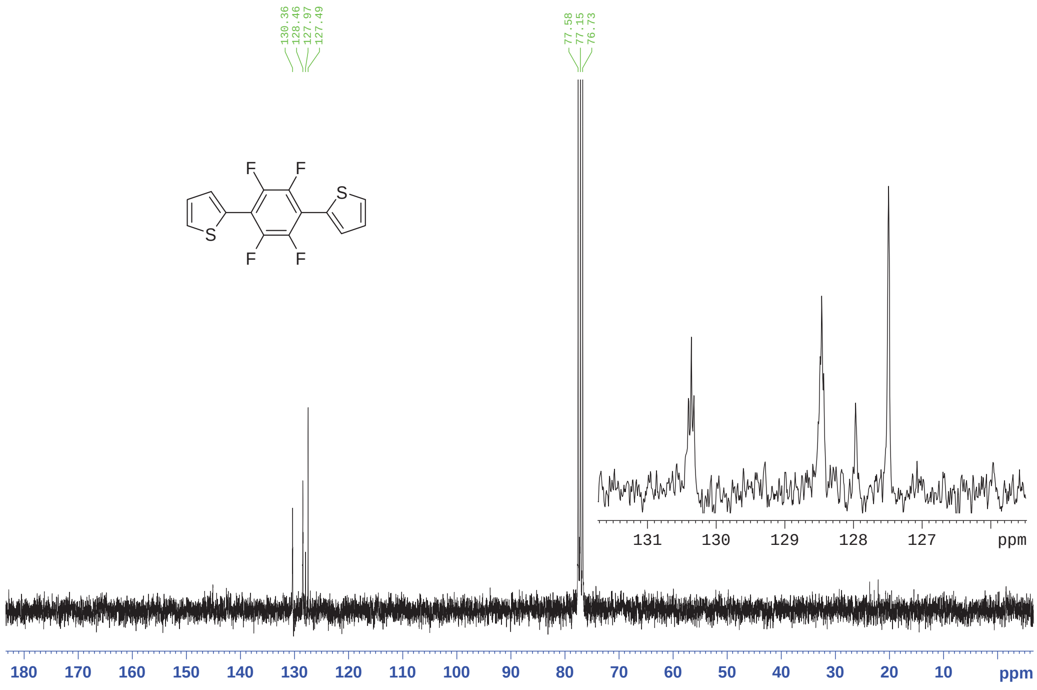
ID	Shift [ppm]	J [Hz]	M	Connection
1	-25.4564	483.6176	2	J(1, 0)
2	-25.4614	374.2903	2	J(2, 0)



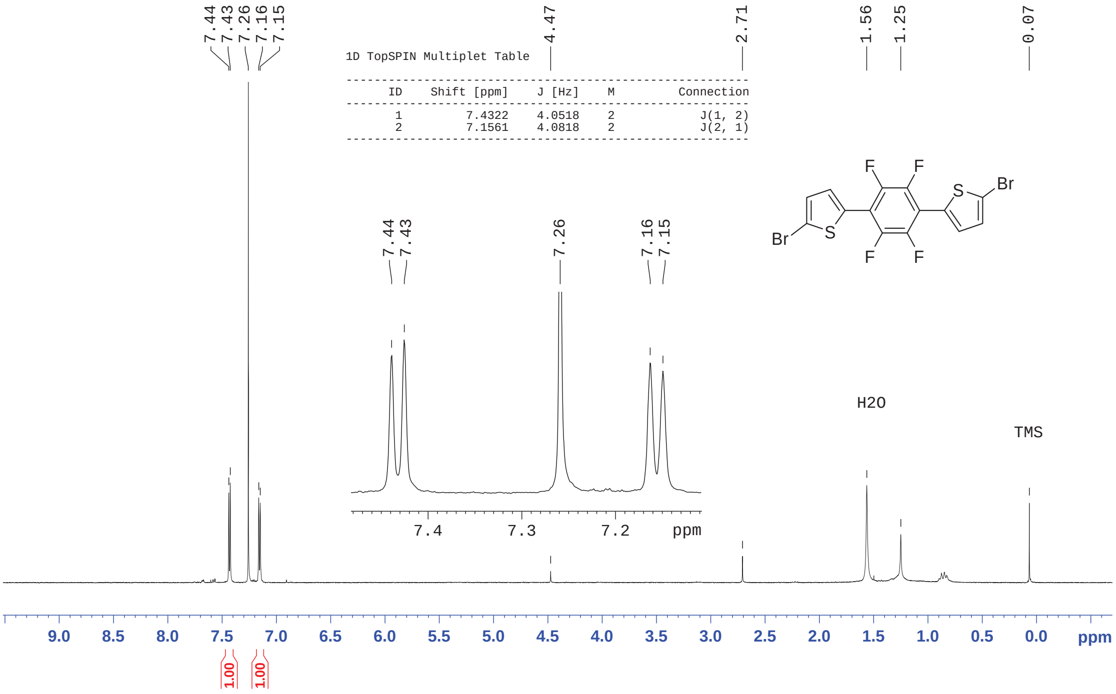
```
1D TopSPIN Multiplet Table

--------------------------------------------------------------------
     ID    Shift [ppm]     J [Hz]      M             Connection
--------------------------------------------------------------------
      1         7.6798     3.8117      2               J(1, 0)
      2         7.5690     1.0805      2               J(2, 0)
                           5.1922      2               J(2, 0)
      3         7.2096     4.4869      3               J(3, 0)
--------------------------------------------------------------------
```



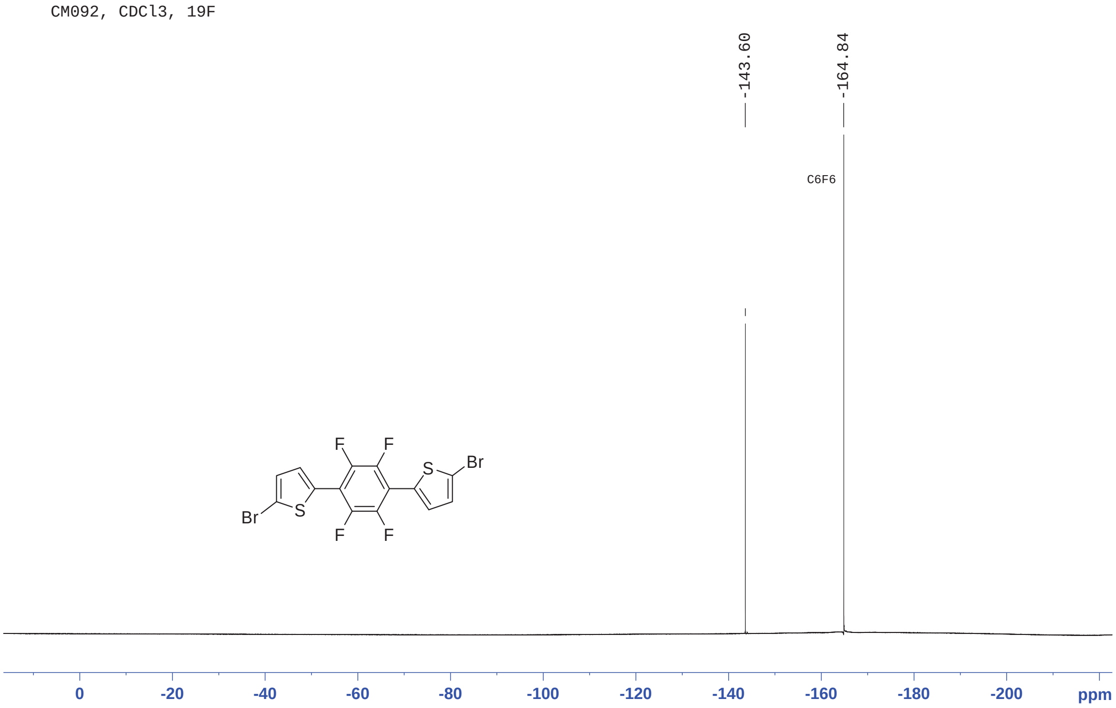
CM086, 13C, CDCl3

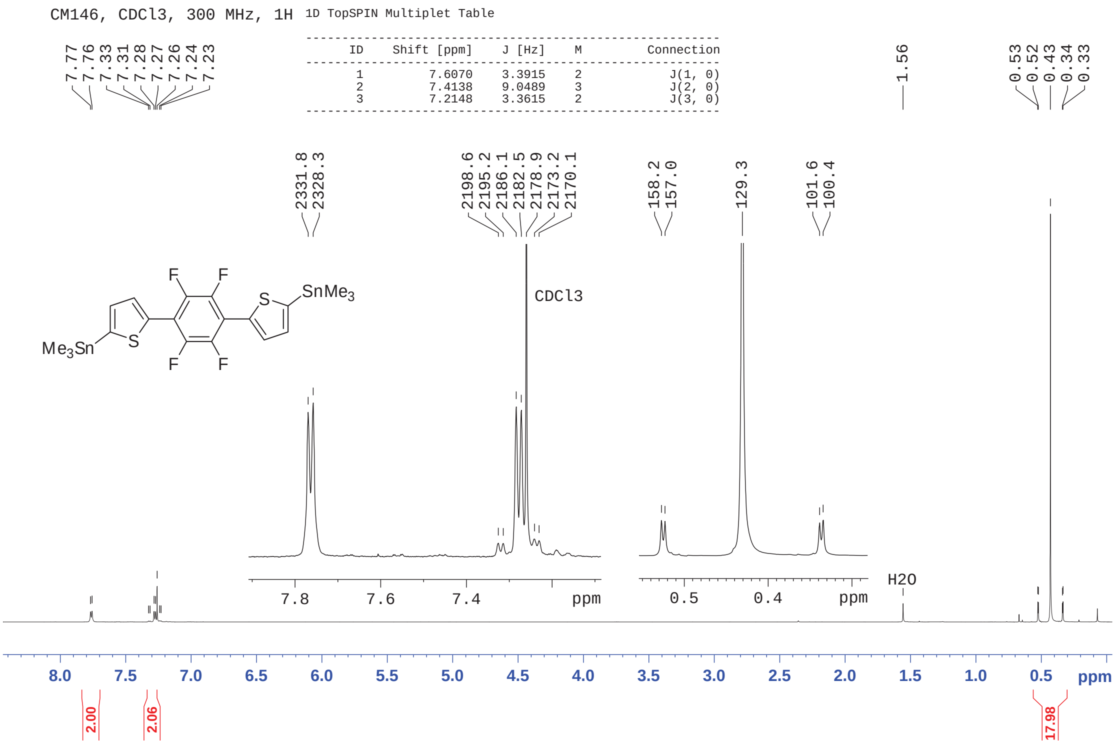


CM092, CDCl3, 1H



```
1D TopSPIN Multiplet Table
-----------------------------------------------------------------------
     ID     Shift [ppm]     J [Hz]      M              Connection
-----------------------------------------------------------------------
      1          7.4322     4.0518      2                J(1, 2)
      2          7.1561     4.0818      2                J(2, 1)
-----------------------------------------------------------------------
```

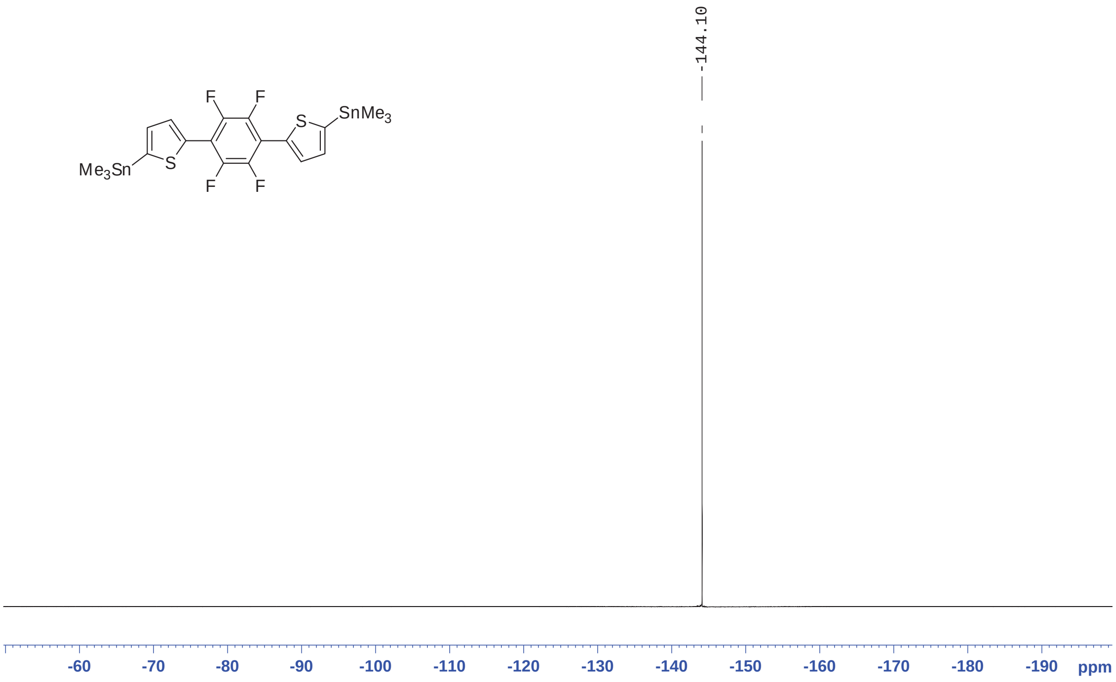




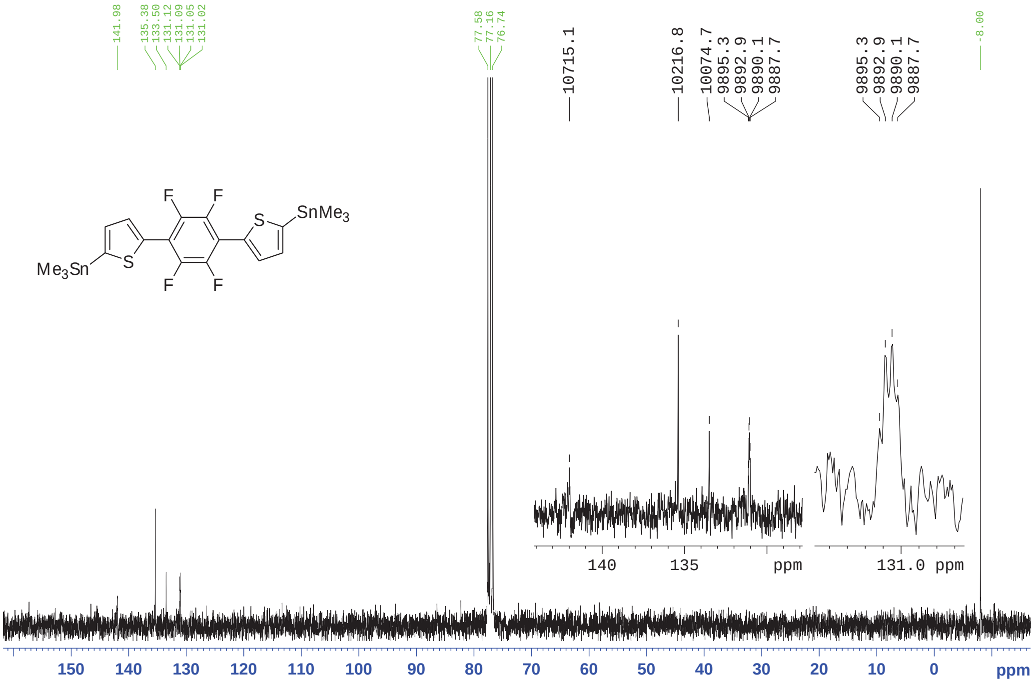
1D TopSPIN Multiplet Table

```
----------------------------------------------------------------
  ID     Shift [ppm]     J [Hz]     M            Connection
----------------------------------------------------------------
   1          7.6070     3.3915     2              J(1, 0)
   2          7.4138     9.0489     3              J(2, 0)
   3          7.2148     3.3615     2              J(3, 0)
----------------------------------------------------------------
```

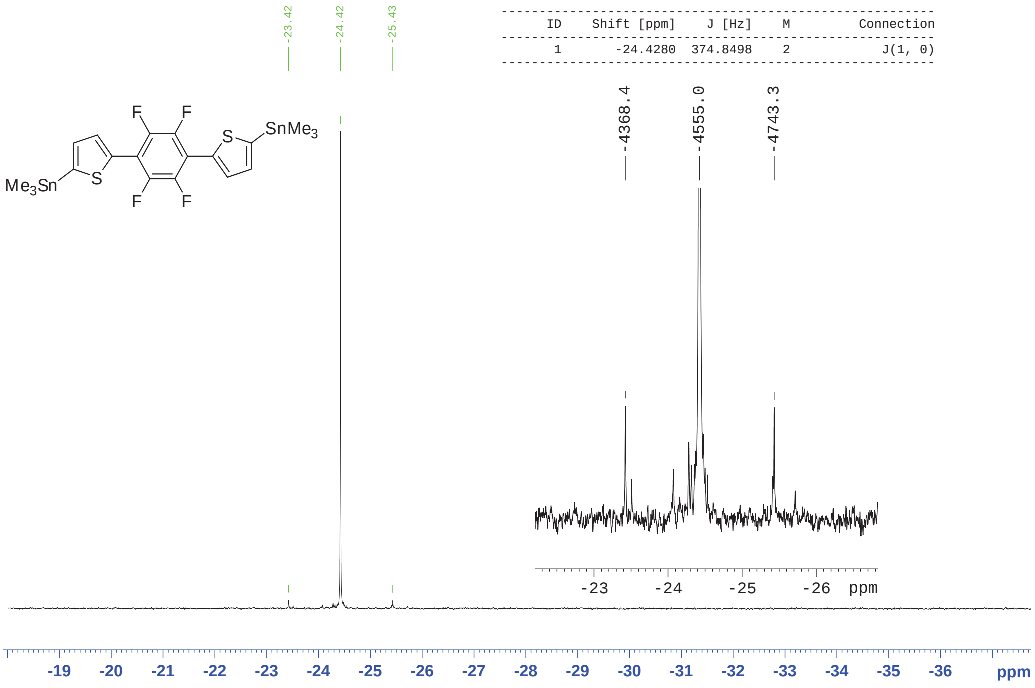
CM146, CDCl3, 19F



CM146, 13C, CDCl3



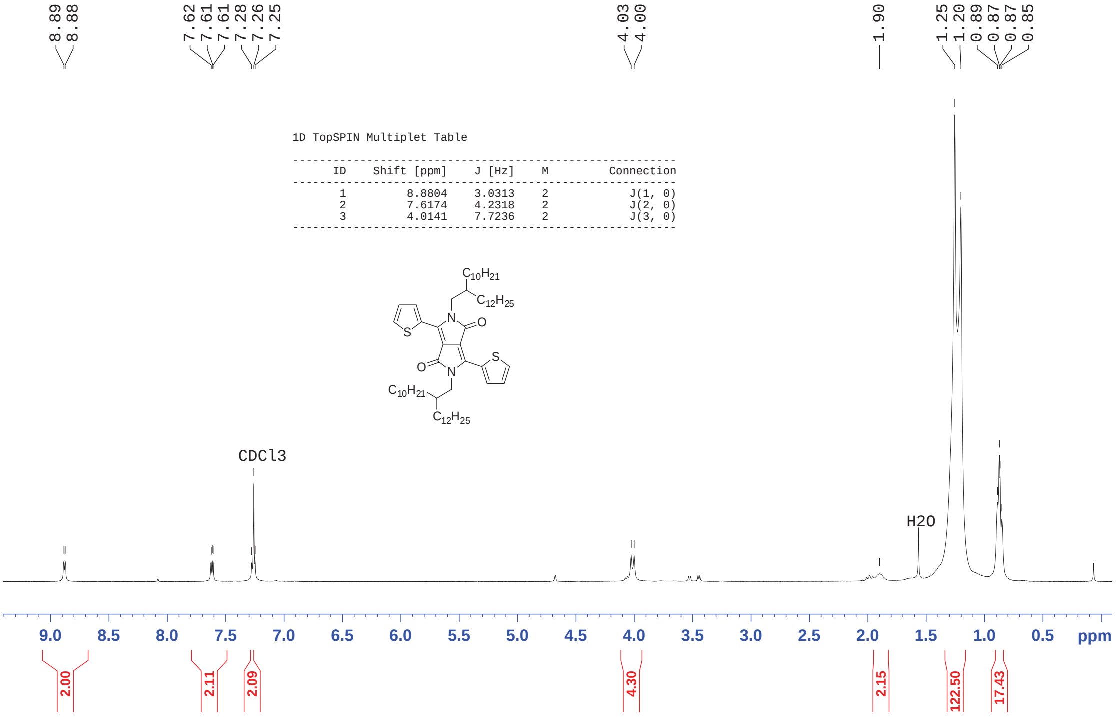
CM146, 119Sn, CDCl3, INEPTRD, 186 MHz



1D TopSPIN Multiplet Table

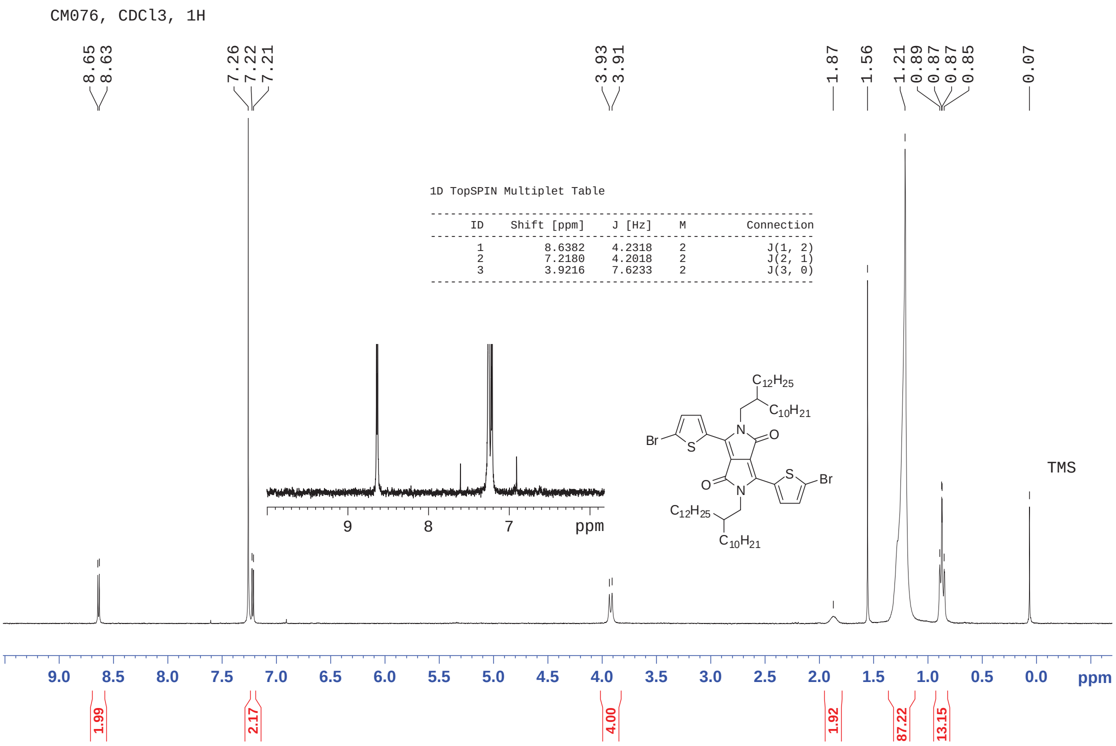
ID	Shift [ppm]	J [Hz]	M	Connection
1	-24.4280	374.8498	2	J(1, 0)

MF029rc, CDCl3, 300 MHz, 1H



1D TopSPIN Multiplet Table

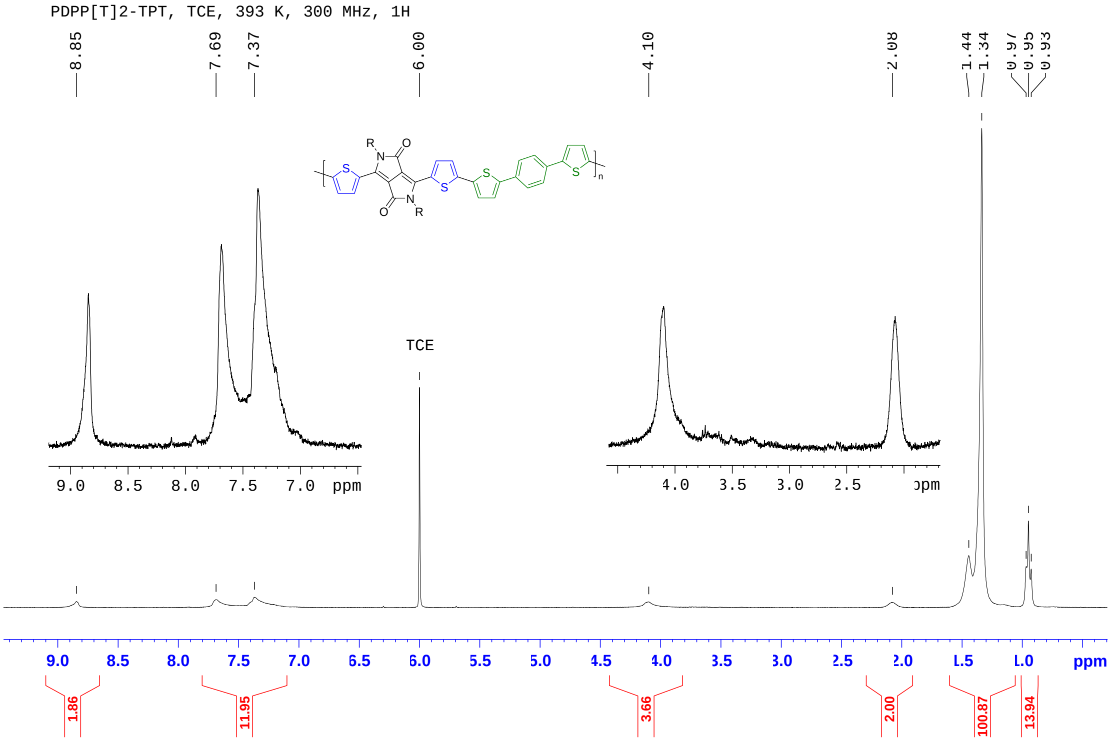
ID	Shift [ppm]	J [Hz]	M	Connection
1	8.8804	3.0313	2	J(1, 0)
2	7.6174	4.2318	2	J(2, 0)
3	4.0141	7.7236	2	J(3, 0)

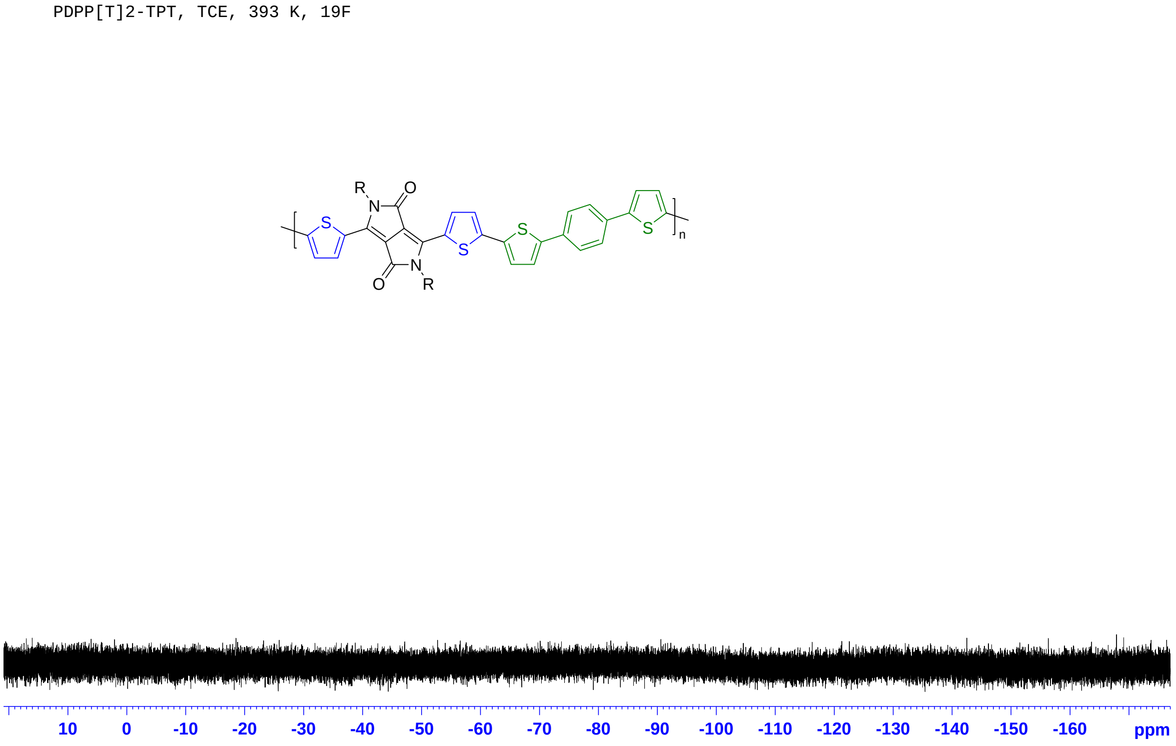


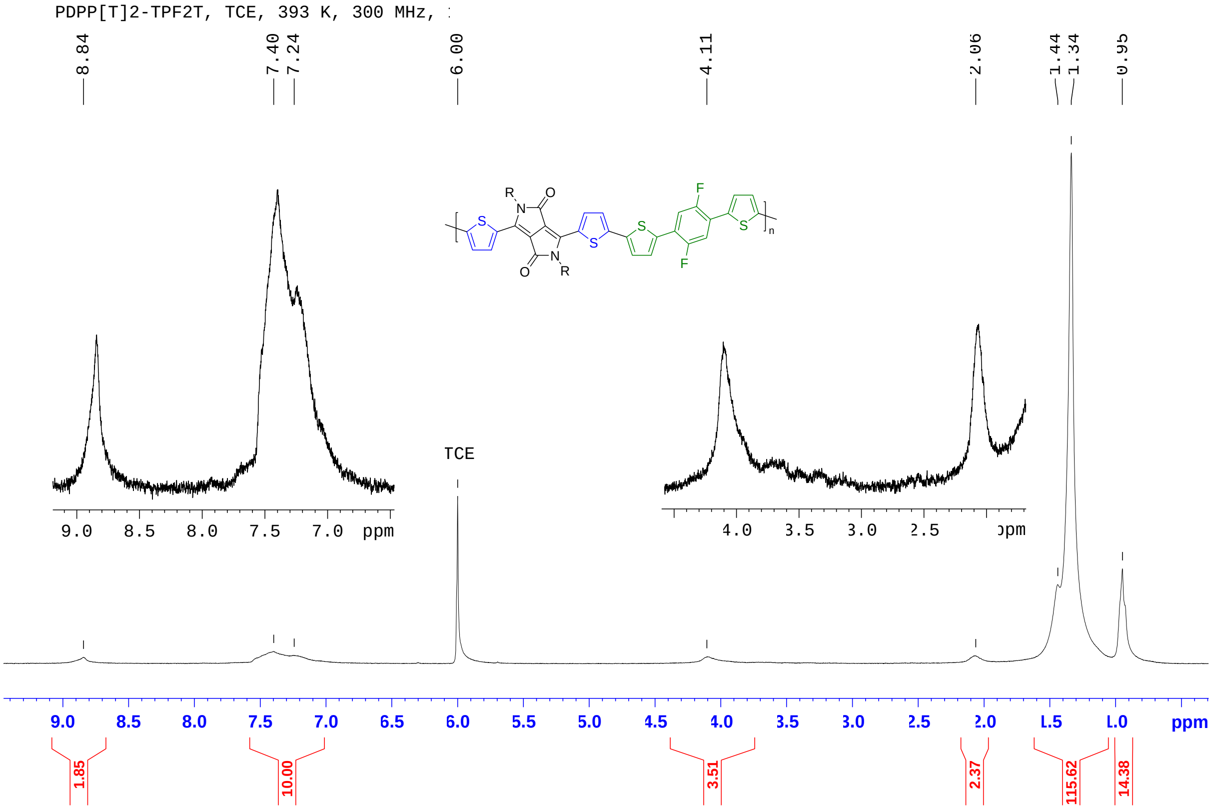
```
1D TopSPIN Multiplet Table

--------------------------------------------------------------
        ID     Shift [ppm]     J [Hz]      M          Connection
--------------------------------------------------------------
         1          8.6382     4.2318      2             J(1, 2)
         2          7.2180     4.2018      2             J(2, 1)
         3          3.9216     7.6233      2             J(3, 0)
--------------------------------------------------------------
```

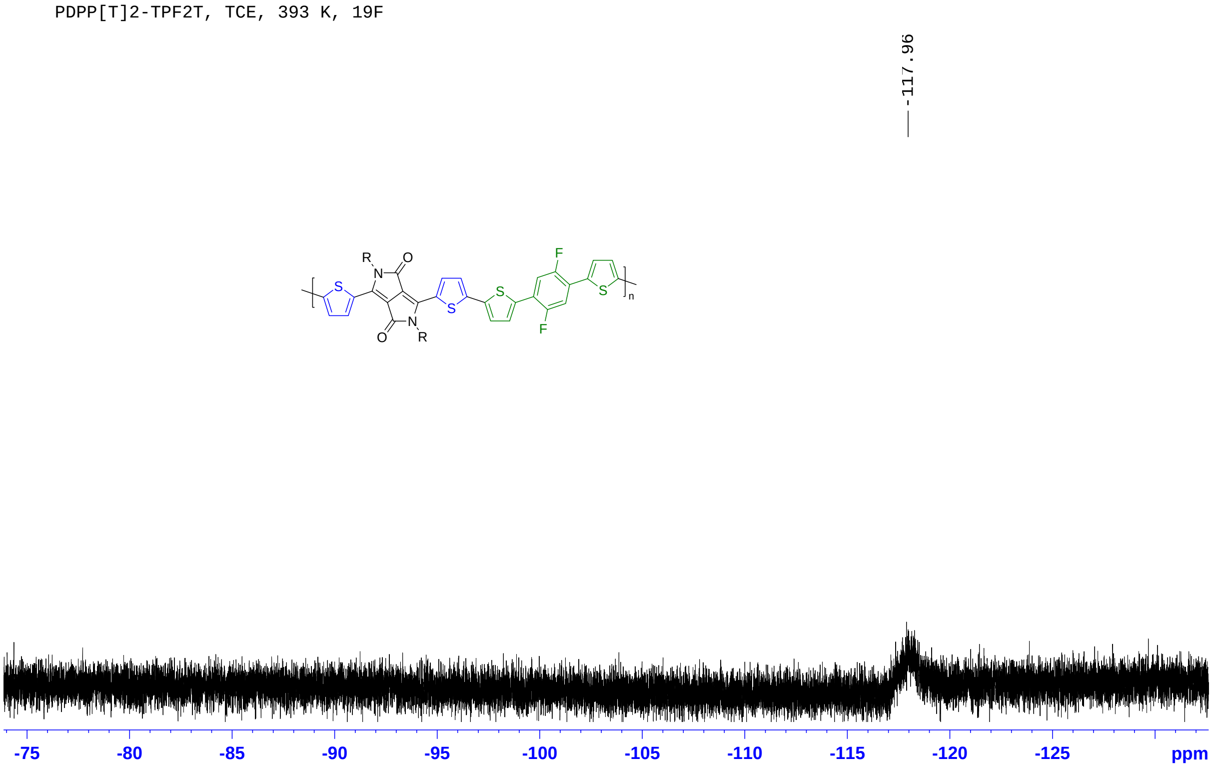
4 Polymer Characterization

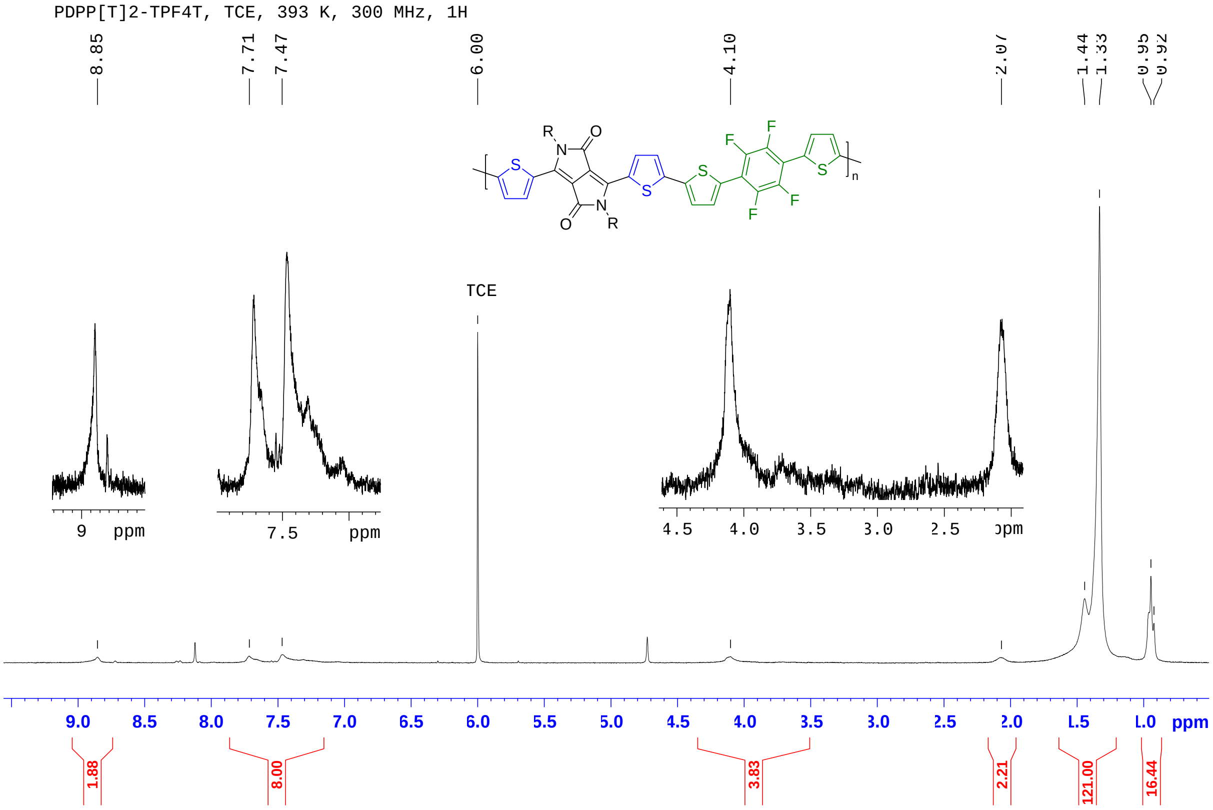
4.1 Polymer NMR

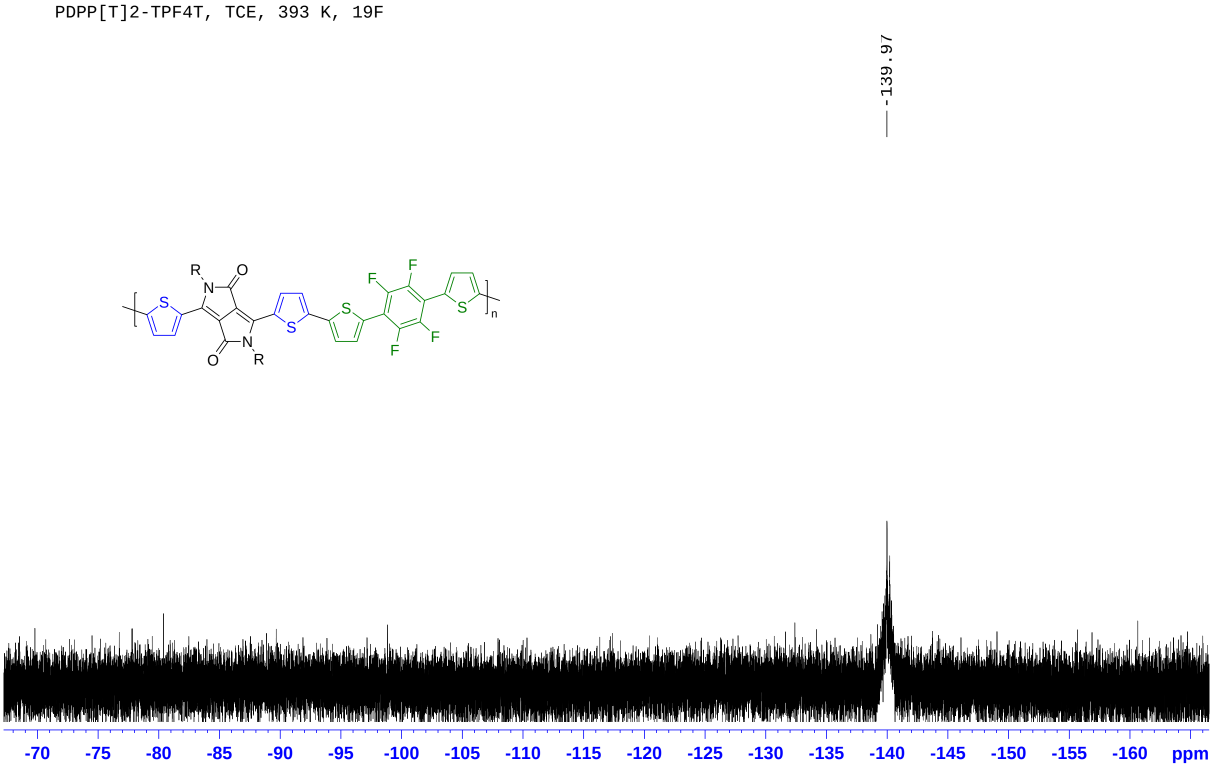




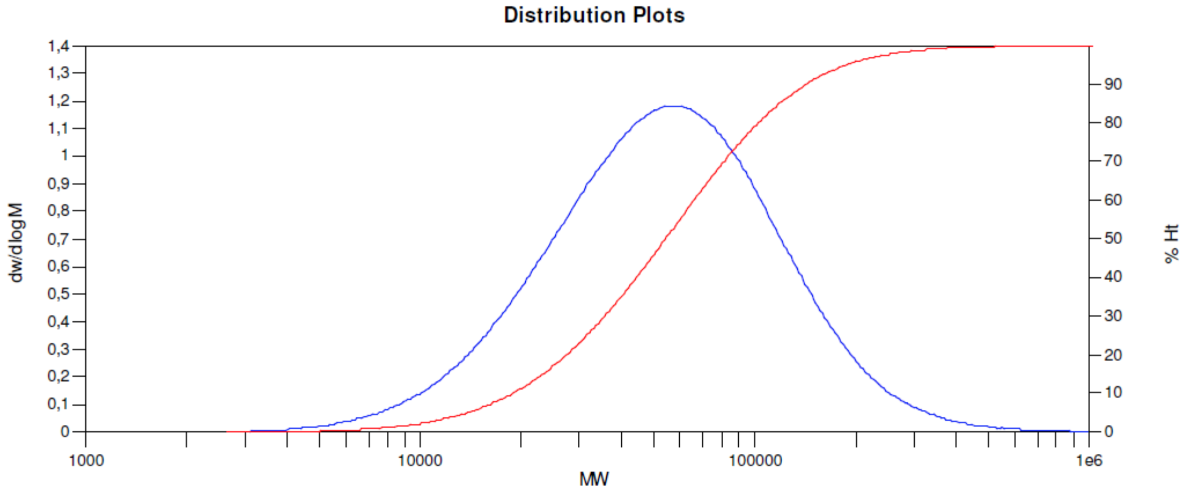

PDPP[T]2-TPF2T, TCE, 393 K, 300 MHz, :
8.84
7.40
7.24
6.00
4.11
2.06
1.44
1.34
0.95
TCE
R
N
O
S
F
n
9.0 8.5 8.0 7.5 7.0 ppm
4.0 3.5 3.0 2.5 ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.85
10.00
3.51
2.37
115.62
14.38


PDPP[T]2-TPF2T, TCE, 393 K, 19F
-117.96
R
N
O
S
F
n
-75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 ppm


PDPP[T]2-TPF4T, TCE, 393 K, 300 MHz, 1H
8.85
7.71
7.47
6.00
4.10
2.07
1.44
1.33
0.95
0.92
R
N
O
S
F
n
TCE
9 ppm
7.5 ppm
4.5 4.0 3.5 3.0 2.5 ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.88
8.00
3.83
2.21
121.00
16.44


PDPP[T]2-TPF4T, TCE, 393 K, 19F
-139.97
R
N
O
S
F
n
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 ppm

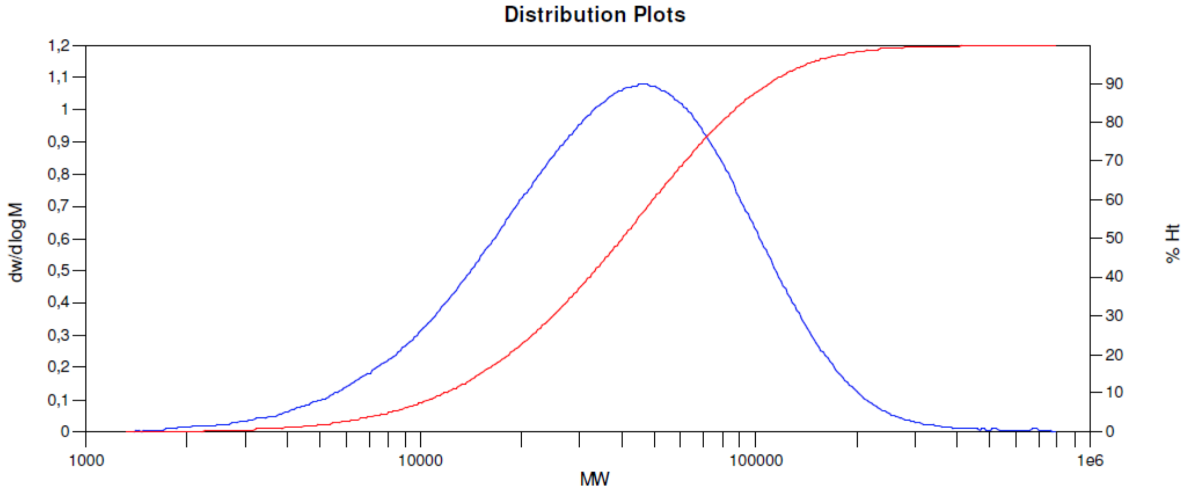
4.2 Gel Permeation Chromatography (GPC)



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	56256	38058	71357	129835	232475	65316	1.87495

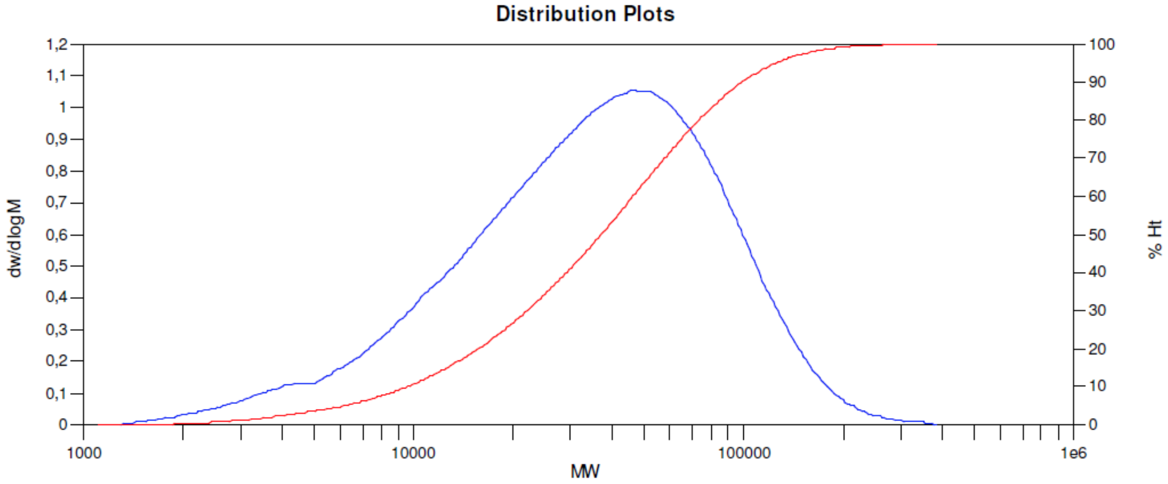
Figure S3: GPC trace of PDPP[T]$_2$-TPT.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	44968	24498	53062	100577	189620	48105	2.16597

Figure S4: GPC trace of PDPP[T]$_2$-TPF$_2$T.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	46372	20386	47232	80624	117322	43022	2.31688

Figure S5: GPC trace of PDPP[T]$_2$-TPF$_4$T.

4.3 Thermogravimetric Analysis (TGA)

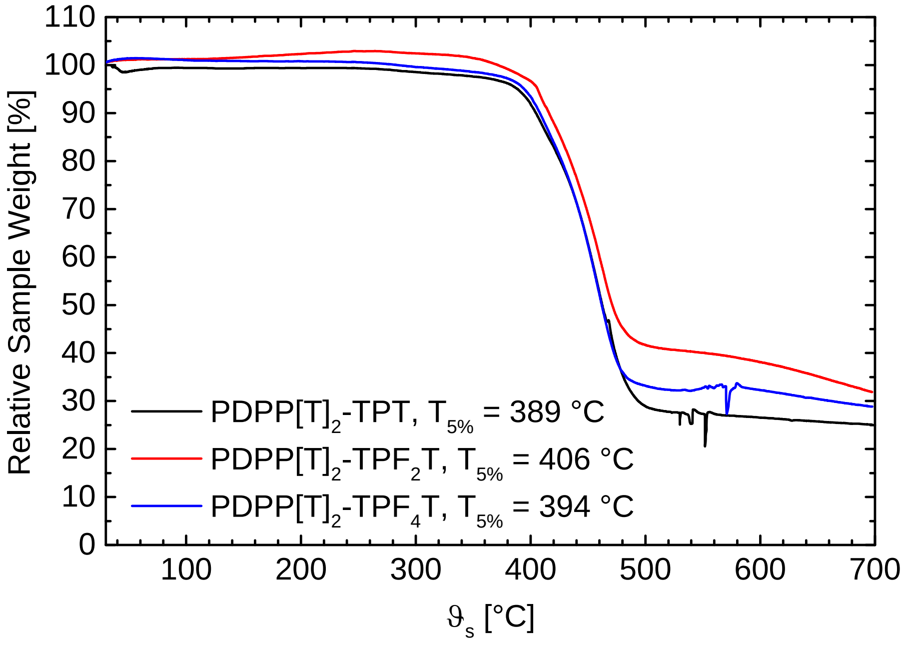
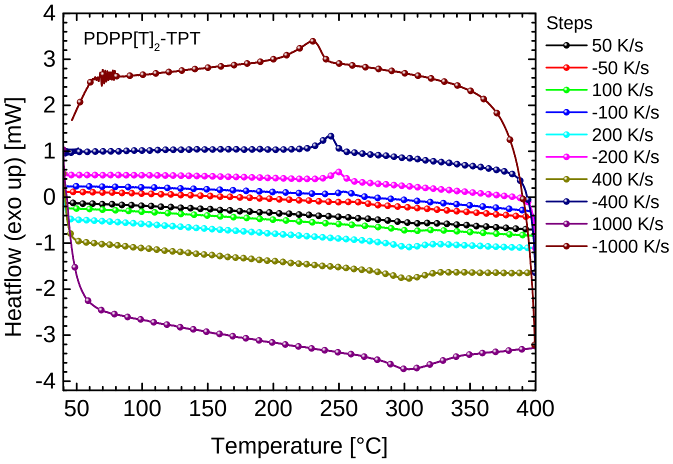
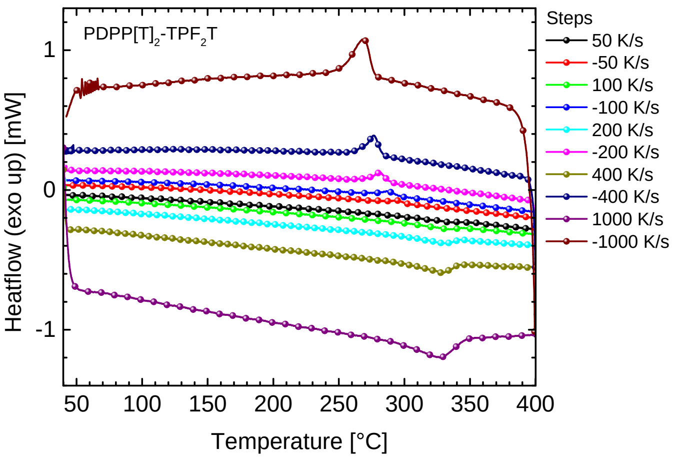


Figure S6. Thermogravimetric analysis of the PDPPs with the decomposition onset ($T_{5\%}$).

4.4 Flash-DSC





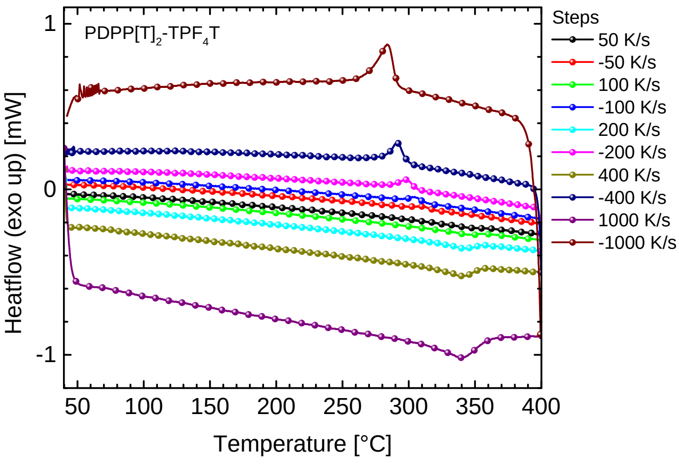


Figure S7. Flash-DSC curves for all three copolymers at different scan rates.

4.5 Cyclic Voltammetry

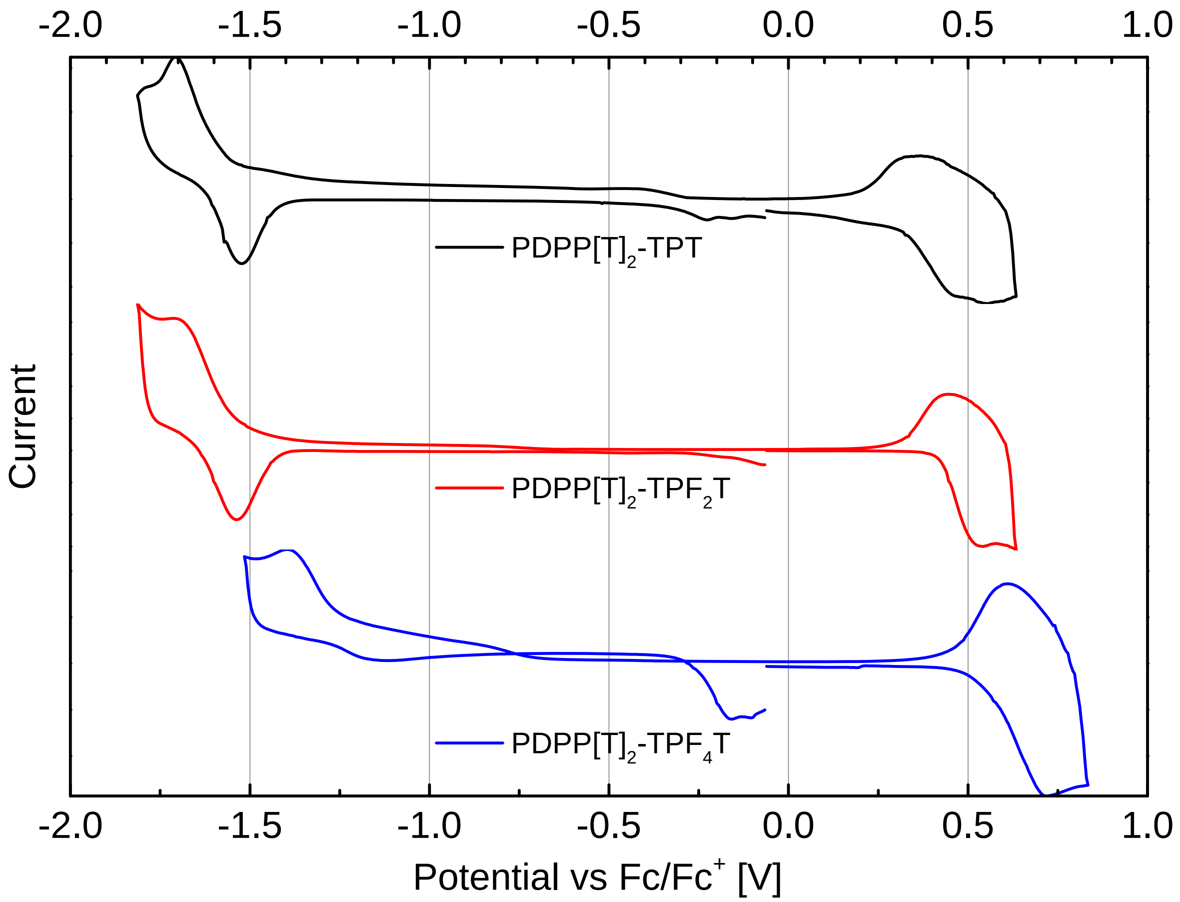


Figure S8: Solid state cyclic voltammograms for the DPP copolymers with a varying degree of fluorination.

5 GIWAXS analysis and S-Parameter calculation

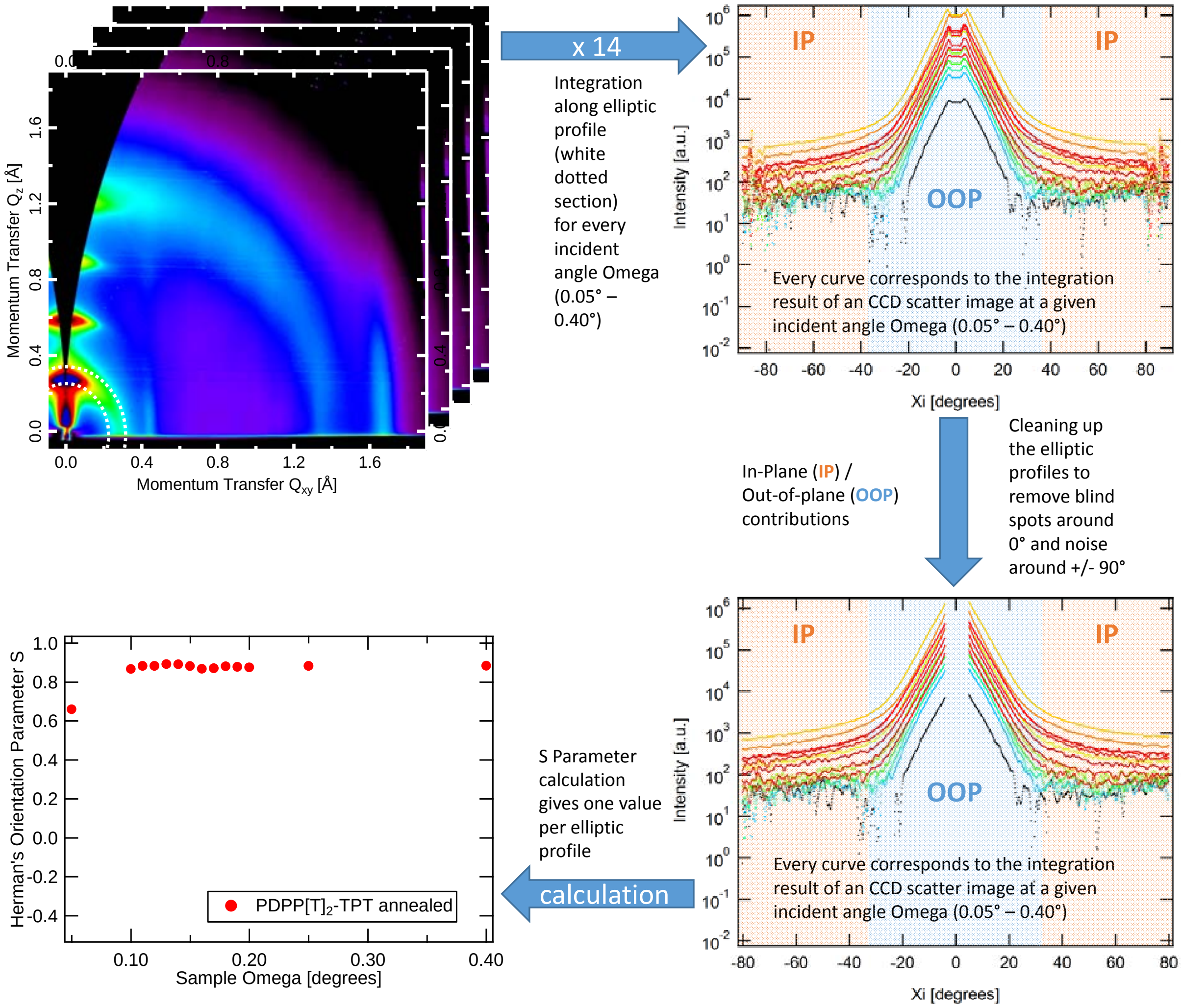


Figure S9. Exemplary S Parameter evaluation for PDPP[T]$_2$-TPT (annealed) starting from two-dimensional scatter plots. Integration of an elliptic profile along the <100> peak (white dotted section) results in one curve per X-ray incident angle (Sample Omega) for angles between 0.05° and 0.40°. Deleting data points in the centered range around 0° due to the geometric limitations of the grazing incidence setup and around ±90° due to noise and eventual wave guiding effects in the film at large Xi angles. S parameters were finally calculated on a point-by-point basis using the cleaned elliptic profiles to obtain one S Parameter value per incident angle Omega.

6 Additional OFET *I-V* curves

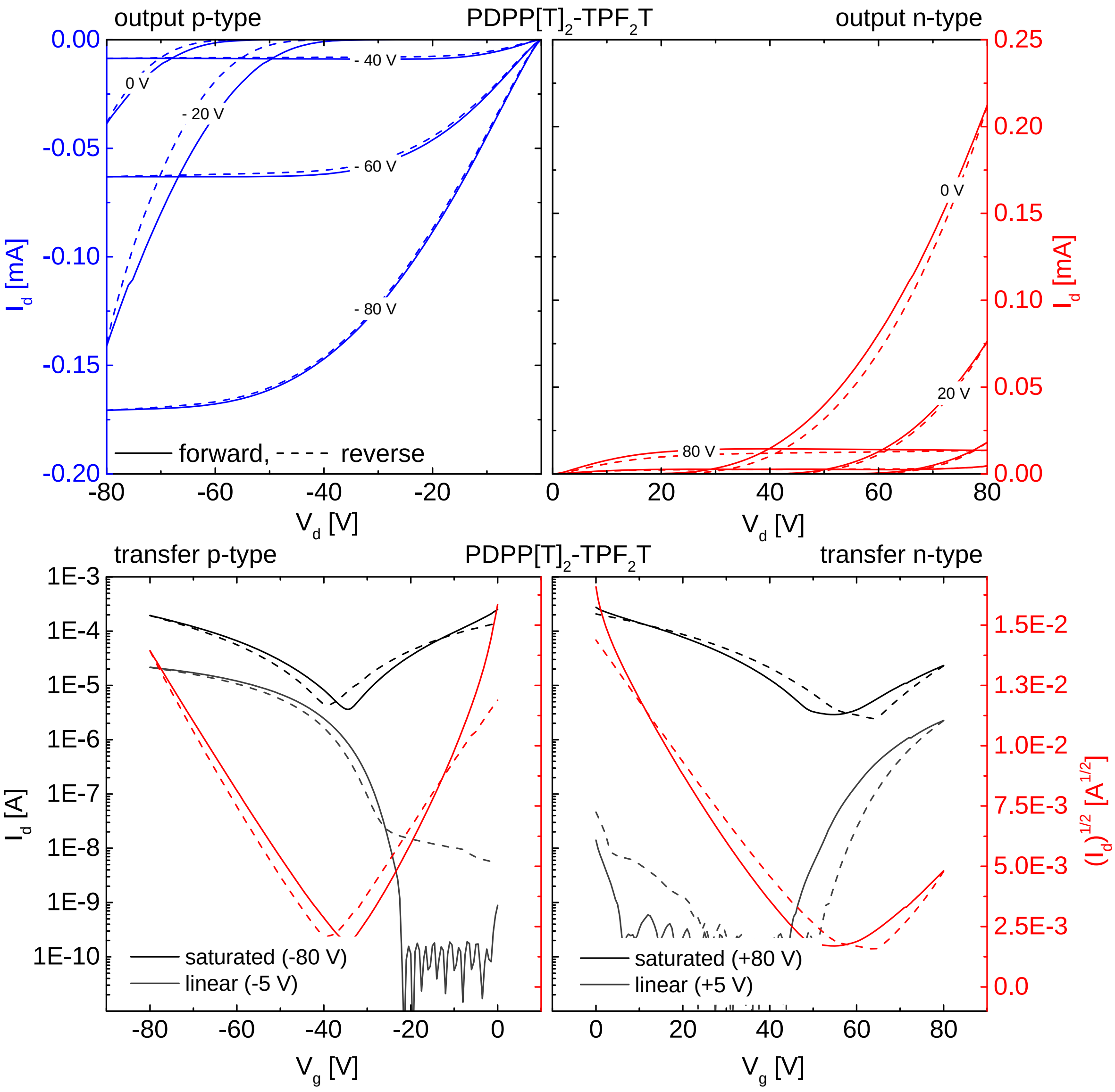


Figure S10. Representative OFET *I-V* curves in p-channel (blue output) and n-channel (red output) operation for the difluorinated PDPP[T]$_2$-TPF$_2$T after annealing at 350 °C. Solid lines represent forward scans, dashed lines the reverse scans in all graphs. In transfer curves (bottom), the black and gray plots indicate the transfer characteristics in the saturation and linear operation regime, respectively.

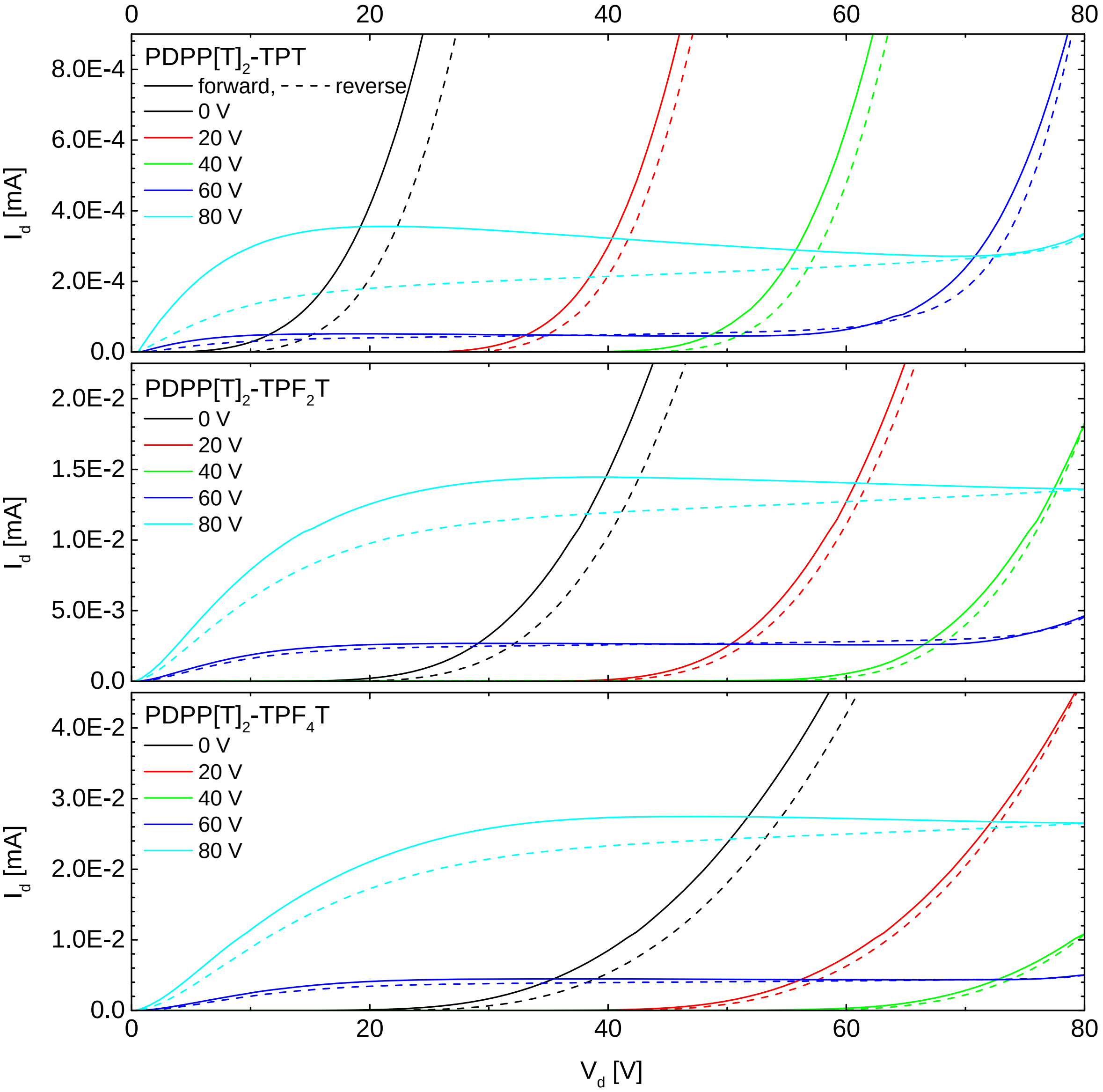


Figure S11. Output characteristics for the n-channel operation of OFET devices comparing all three polymers after annealing at 350 °C.

Table S2. OFET on/off ratios in different operation regimes. For ambipolar materials, the on/off ratio decreases in the saturation regime when high drain voltages are applied. All values were averaged over a minimum of 8 individual devices.

	On/Off ratio				Threshold Voltage	
	$I_{on/off}$ p-type lin.	$I_{on/off}$ p-type sat.	$I_{on/off}$ n-type lin.	$I_{on/off}$ n-type sat.	V_T [V] p-type sat.	V_T [V] n-type sat.
As cast						
PDPP[T]$_2$-TPT	>10^6	>10^6	-	-	0 ± 2	-
PDPP[T]$_2$-TPF$_2$T	>10^6	>10^5	-	-	0 ± 3	-
PDPP[T]$_2$-TPF$_4$T	>10^5	>10^3	-	-	0 ± 5	-
Annealed 200 °C						
PDPP[T]$_2$-TPT	>10^6	>10^6	-	-	-31 ± 10	-
PDPP[T]$_2$-TPF$_2$T	>10^6	>10^6	-	-	-25 ± 11	-
PDPP[T]$_2$-TPF$_4$T	>10^6	>10^6	-	-	-28 ± 9	-
Annealed 250 °C						
PDPP[T]$_2$-TPT	>10^6	>10^6	-	-	-38 ± 11	-
PDPP[T]$_2$-TPF$_2$T	>10^6	>10^6	-	-	-38 ± 8	-
PDPP[T]$_2$-TPF$_4$T	>10^6	>10^6	-	-	-38 ± 8	-
Annealed 300 °C						
PDPP[T]$_2$-TPT	>10^6	>10^6	-	-	-19 ± 7	-
PDPP[T]$_2$-TPF$_2$T	>10^6	>10^6	-	-	-32 ± 5	-
PDPP[T]$_2$-TPF$_4$T	>10^6	>10^6	-	-	-28 ± 5	-
Annealed 350 °C						
PDPP[T]$_2$-TPT	>10^6	>10^2	>10^5	>4	-33 ± 4	54 ± 2
PDPP[T]$_2$-TPF$_2$T	>10^6	>10^2	>10^5	>8	-34 ± 6	52 ± 1
PDPP[T]$_2$-TPF$_4$T	>10^6	>10^3	>10^5	>10^1	-35 ± 4	51 ± 3

7 References

[1] D. J. Crouch, P. J. Skabara, M. Heeney, I. McCulloch, S. J. Coles, M. B. Hursthouse, *Chem. Commun.* **2005**, 1465.

[2] A. Facchetti, M. H. Yoon, C. L. Stern, H. E. Katz, T. J. Marks, *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 3900.

[3] M. H. Yoon, A. Facchetti, C. E. Stern, T. J. Marks, *J. Am. Chem. Soc.* **2006**, *128*, 5792.

[4] D. J. Crouch, P. J. Skabara, J. E. Lohr, J. J. W. McDouall, M. Heeney, I. McCulloch, D. Sparrowe, M. Shkunov, S. J. Coles, P. N. Horton, M. B. Hursthouse, *Chem. Mater.* **2005**, *17*, 6567.

[5] T. Yamao, Y. Taniguchi, K. Yamamoto, T. Miki, S. Ota, S. Hotta, M. Goto, R. Azumi, *Japanese Journal of Applied Physics* **2007**, *46*, 7478.

[6] C. J. Mueller, C. R. Singh, M. Fried, S. Huettner, M. Thelakkat, *Adv. Funct. Mater.* **2015**, *25*, 2725.