Supplementary Information to

Bifuran- and bithiophene-fused 4,6-dihydro-1,2,7-oxadiborepins as building blocks for conjugated copolymers

Jonas Bachmann, Andreas Drichel, Jonas Klopf, Abhishek Koner, Adam Slabon* and Holger Helten*

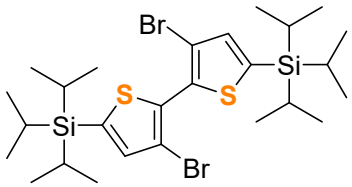
Table of Contents

1. Experimental Section

1.1 General procedures

All manipulations before the aqueous workup were performed under an atmosphere of dry argon using standard Schlenk techniques or in an MBraun glovebox. Solvents (CH_2Cl_2, toluene, Et_2O and THF) were dried and degassed by means of an Innovative Technology solvent purification system. $CDCl_3$ for NMR spectroscopy as well as *o*-xylene were dried and degassed at reflux over CaH_2 or Na, respectively, and freshly distilled prior to use. Solvents for aqueous work-up and chromatography (petroleum ether, Et_2O, CH_2Cl_2, THF, MeOH) were distilled prior use. Following chemicals were commercially purchased and used as received: *n*-butyllithium solutions (1.6 M and 2.5 M in *n*-hexane), *t*-butyllithium solutions (1.7 M and 2.5 M in *n*-pentane), BBr_3 solution (1 M in CH_2Cl_2), $SnMe_3Cl$ solution (1 M in THF), triisopropylsilyl chloride, iodine bromide, 1,3,5-tris-(trifluoromethyl)benzene, tetrakis(triphenylphosphine)palladium(0), tris(dibenzylideneacetone)dipalladium(0), tri-*tert*-butyl phosphine, [1,1'-Bis(diphenylphosphino)-ferrocene]palladium(II) dichloride and bis(triphenylphosphine)palladium chloride were commercially purchased and used as received. Trimethylsilyl chloride was purified by inert-gas distillation. 3,3',5,5'-tetrabromo-2,2'-bithiophene **1**,[1] 2,8-dibromo-4,6-bis(2,4,6-tris(trifluoromethyl)phenyl)-4,6-dihydrodi-furo[3,2-c:2',3'-e][1,2,7]oxadiborepin **7**,[2] (4,8-bis((2-octyldodecyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) **9**,[3] 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione **10**,[4] were prepared according to literature procedures. NMR spectra were recorded at 25 °C on a Bruker Avance III HD spectrometer operating at 300 MHz or on a Bruker Avance 500 spectrometer operating at 500 MHz. Chemical shifts were referenced to residual protic impurities in the solvent (^1H) or the deuterio solvent itself (^{13}C) and reported relative to external $SiMe_4$ (^1H, ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B) or $CFCl_3$ (^{19}F) standards. Microwave assisted reactions were performed using a Biotage Initiator 4.1.3 microwave system.

1.2 Syntheses

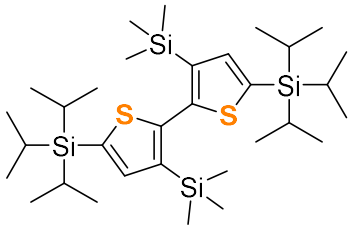


Synthesis of 2.

To a solution of **1** (4.90 g, 10.2 mmol) in THF (100 ml) *n*-butyllithium (2.5 M in *n*-hexane, 8.13 ml, 20.4 mmol) was added at –78 °C. The solution was stirred for 15 min at –78 °C. Tri*iso*propyl chloride (4.02 g, 20.8 mmol) was added at –78 °C and the mixture stirred at ambient temperature overnight. After column chromatography (SiO_2, eluent: petroleum ether), the product was obtained as a pale-yellow solid.

Yield: 5.72 g (8.98 mmol, 88 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.16 (s, 2H, Thi-C*H*) ppm, 1.34 (sept, $^3J_{HH}$ = 7.3 Hz, 6H, Si-C*H*-$(CH_3)_2$), 1.13 (d, $^3J_{HH}$ = 7.3 Hz, 36H, Si-CH-(C*H*$_3)_2$). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 138.5 (s, Thi-*C*H), 137.1 (s, Thi-C_q), 134.3 (s, Thi-C_q), 112.6 (s, Thi-*C*Br), 18.7 (s, Si-CH-

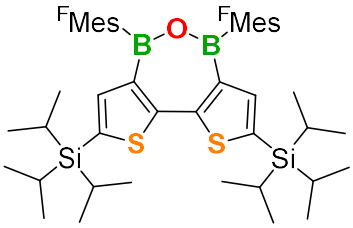
(CH_3)$_2$), 11.8 (s, Si-*C*H-(CH_3)$_2$) ppm. **HRMS** (ACPI neg): m/z ([M]$^-$ -H$^+$, $C_{26}H_{42}Br_2S_2Si_2$) = calcd. 635.0678; found 635.0696.



Synthesis of 3.

To a solution of **2** (5.09 g, 8.00 mmol) in THF (100 ml) *n*-butyllithium (1.6 M in *n*-hexane, 10.5 ml, 16.8 mmol) was added at –78 °C. The solution was stirred for 2 h at –78 °C. Trimethyl chloride (1.91g, 17.6 mmol) was added at –78 °C and the mixture stirred at ambient temperature overnight. After a short column chromatography plug (SiO_2, eluent: petroleum ether), the product was obtained as an oil. After solidifying at 4 °C, the pale-green solid was loosened up and dried *in vacuo*.

Yield: 4.79 g (7.68 mmol, 96 %). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.18 (s, 2H, Thi-C*H*) ppm, 1.33 (m, 6H, Si-C*H*-(CH_3)$_2$), 1.12 (d, $^3J_{HH}$ = 7.2 Hz, 36H, Si-CH-(C*H*$_3$)$_2$), 0.06 (s, 18H, Si-(C*H*$_3$)$_3$) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 148.2 (s, Thi-*C*$_q$), 142.1 (s, Thi-*C*$_q$), 141.4 (s, Thi-*C*H), 134.3 (s, Thi-*C*$_q$), 18.8 (s, Si-CH-(*C*H$_3$)$_2$), 12.0 (s, Si-*C*H-(CH_3)$_2$), 0.2 (s, Si-(*C*H$_3$)$_3$) ppm. **HRMS** (ACPI pos): m/z ([M]$^-$, $C_{32}H_{62}S_2Si_4$) = calcd. 622.3365; found 622.3359.

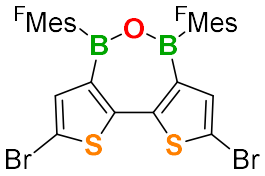


Synthesis of 4.

To a solution of **3** (1.25 g, 2.00 mmol) in CH_2Cl_2 (40 mL) BBr_3 (1 M in CH_2Cl_2; 16.0 mL, 16.0 mmol) was added dropwise at −78 ℃, stirred at −78 ℃ for 2 h, and then warmed up to ambient temperature overnight. To a solution of ^{F}MesH (1.88 g, 6.60 mmol) in Et_2O (15 mL) *n*-BuLi (1.6 M in *n*-hexane; 4.40 mL, 7.00 mmol) was added at −78℃ and stirred for 30 min, then it was stirred at ambient temperature for 3 h. All volatiles of both mixtures were removed *in vacuo* and the residues were dissolved in toluene (20 mL), respectively. To the solution mixture of [^{F}MesLi] the other mixture was dropped at −78℃ (+ washing with additional 20 mL of toluene). The resulting mixture was stirred at r.t. overnight. Afterwards, H_2O was added, stirred for 30 min, and all solvents was removed *in vacuo*, and the residue was extracted with CH_2Cl_2 (3×50 mL). All the organic extracts were dried over $MgSO_4$, the desiccant was filtered off and the solvent was removed *in vacuo*. Subsequently, the residue was purified by column chromatography (SiO_2, eluent: petroleum ether) to afford **4** as a yellow solid.

Yield: 851 mg (0.79 mmol, 40 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.10 (s, 4H, ^{F}Mes-C*H*), 6.91 (s, 2H, Thi-C*H*), 1.27 (sept, 6H, $^3J_{HH}$ = 7.4 Hz Si-C*H*-(CH_3)$_2$), 1.05 (d, 36H, $^3J_{HH}$ = 7.4 Hz, Si-CH-(C*H*$_3$)$_2$) ppm. **^{11}B NMR** (160 MHz, $CDCl_3$): δ = 42.0 ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 156.0 (s, Thi-*C*$_q$), 145.7(s, Thi-*C*H), 141.8 (br, ^{F}Mes-*C*-B), 135.9 (s, Thi-*C*$_q$), 135.4 (br, Thi-*C*-B), 134.6 (q, $^2J_{CF}$ = 33.6 Hz,

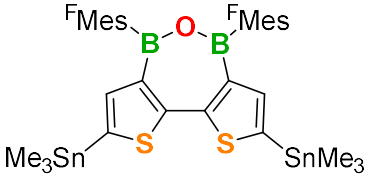
o-^{F}Mes-*C*-CF_3), 132.1 (q, $^{2}J_{CF}$ = 34.3 Hz, *p*-^{F}Mes-*C*-CF_3), 126.1 (br, ^{F}Mes-*C*H), 123.6 (q, $^{1}J_{CF}$ = 274.3 Hz, *o*-^{F}Mes-*C*F_3), 122.9 (q, $^{1}J_{CF}$ = 272.4 Hz, *p*-^{F}Mes-*C*F_3), 18.4 (s, Si-CH-(*C*H_3)$_2$), 11.9 (s, Si-*C*H-(CH_3)$_2$) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = –58.1 (s, 12F, *o*-^{F}Mes-C*F*$_3$), –63.1 (s, 6F, *p*-^{F}Mes-C*F*$_3$). **HRMS** (ACPI neg): m/z ([M]$^-$, $C_{44}H_{48}B_2F_{18}OS_2Si_2$) = calcd. 1076.2594; found 1076.2572.



Alternative Synthesis of 5.

To a solution of **4** (1.91 g, 1.77 mmol) in CH_2Cl_2 (80 mL) IBr (2.94 g, 14.2 mmol) in CH_2Cl_2 (140 mL) was added. The resulting solution was stirred in the dark at ambient temperature overnight. Afterwards, 40 mL aq. $Na_2S_2O_3$ was added, then it was extracted with CH_2Cl_2 (3×50 mL). All the organic extracts were dried over $MgSO_4$, the desiccant was filtered off and the solvent was removed *in vacuo*. The residue was purified by column chromatography (SiO_2, eluent: petroleum ether) to afford the product as a yellow solid.

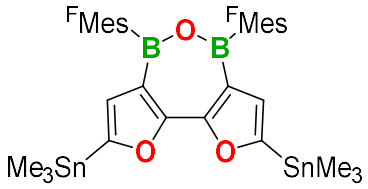
Yield: 1.51 g (1.63 mmol, 92 %). *The **NMR** and **HRMS** data are consistent with those reported in the literature.*[5]



Synthesis of 6.

5 (369 mg, 0.40 mmol) was dissolved in THF (10 mL) and cooled to −78℃. Then, *t*-BuLi (1.7 M in pentane; 0.48 mL, 0.82 mmol) was added and it was stirred at −78℃ for 40 min, followed by addition of $SnMe_3Cl$ (1 M in THF; 0.84 mL, 0.84 mmol) in the cold. The reaction mixture was allowed to warm to ambient temperature and stirred for overnight. The solvent was removed *in vacuo*, the residue was extracted with Et_2O (3×10 mL). All the organic extracts were dried over $MgSO_4$, and the solvent was removed *in vacuo* resulting in a pale-yellow solid.

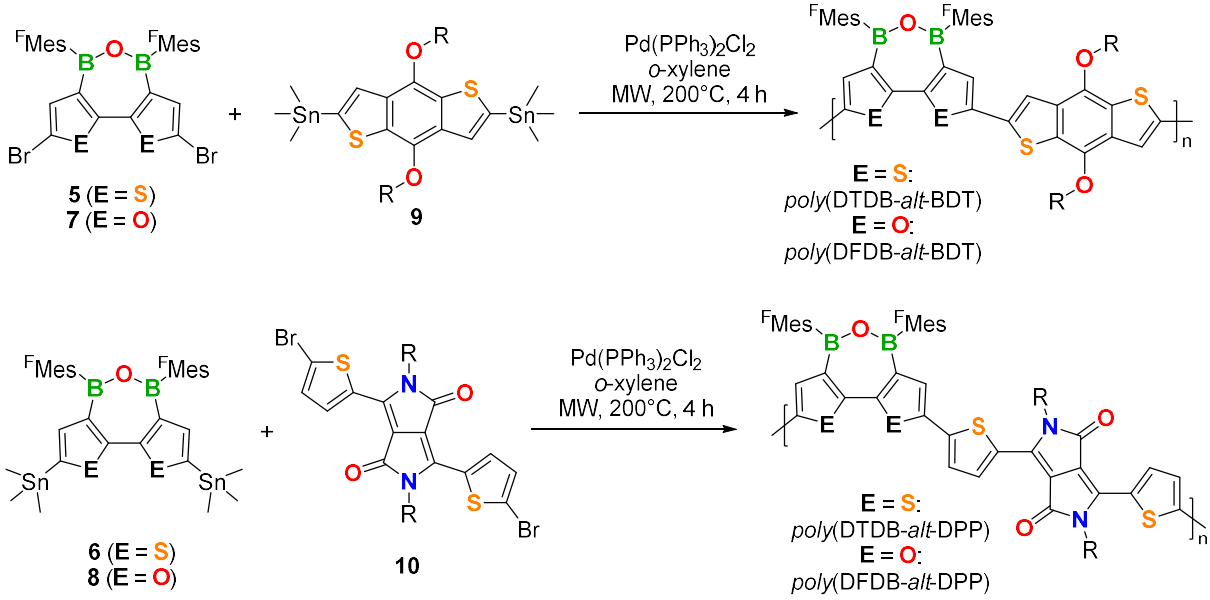
Yield: 367 mg (336 µmol, 84 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.10 (s, 4H, ^{F}Mes-C*H*), 6.85 (s, 2H, Thi-C*H*), 0.36 (s, 18H, Sn(C*H*$_3$)$_3$) ppm. **^{11}B NMR** (160 MHz, $CDCl_3$): δ = 42.0 ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 156.8 (s, Thi-*C*$_q$), 144.7 (s, Thi-*C*H), 141.9 (br, ^{F}Mes-*C*-B), 139.6 (s, Thi-*C*$_q$), 135.2 (br, Thi-*C*-B), 134.6 (q, $^{2}J_{CF}$ = 32.4 Hz, *o*-^{F}Mes-*C*-CF_3), 132.1 (q, $^{2}J_{CF}$ = 34.3 Hz, *p*-^{F}Mes-*C*-CF_3), 126.2 (br, ^{F}Mes-*C*H), 123.6 (q, $^{1}J_{CF}$ = 274.5 Hz, *o*-^{F}Mes-*C*F_3), 122.9 (q, $^{1}J_{CF}$ = 272.5 Hz, *p*-^{F}Mes-*C*F_3), –8.0 (s, Sn-*C*H_3) ppm. **^{19}F** (471 MHz, $CDCl_3$): δ = –58.1 (s, 12F, *o*-^{F}Mes-C*F*$_3$), –63.2 (s, 6F, *p*-^{F}Mes-C*F*$_3$) ppm. **HRMS** (ACPI neg): m/z ([M]$^-$, $C_{32}H_{24}B_2F_{18}OS_2Sn_2$) = calcd. 1089.9223; found 1089.9203.



Synthesis of 8.

To a solution of **7** (356 mg, 0.40 mmol) in THF (10 ml) *t*-butyllithium (1.7 M in *n*-pentane, 0.48 ml, 0.82 mmol) was added at –78 °C. After stirring for 40 min at –78 °C, Me_3SnCl (1 M in THF, 0.84 ml, 0.84 mmol) was added and the solution was allowed to warm up to ambient temperature and stirred overnight. All volatiles were removed *in vacuo.* The crude product was dissolved in *n*-hexane, the precipitated salt was filtered off and the solvent of the filtrate was removed *in vacuo*. The product was obtained as a colorless solid and stored under inert atmosphere. **Yield:** 265 mg (0.25 mmol, 63 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.10 (s, 4H, ^{F}Mes-C*H*), 6.44 (s, 2H, Fur-C*H*), 0.40 (s, 18H, Sn-CH_3). **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 43.0 ppm. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 163.5 (s, Fur-C_q), 158.6 (Fur- C_q), 141.4 (br, ^{F}Mes-*C*-B), 134.7 (q, $^2J_{CF}$ = 32.4 Hz, *o*-^{F}Mes-*C*-CF_3), 132.0 (q, $^2J_{CF}$ = 34.3 Hz, *p*-^{F}Mes-*C*-CF_3), 127.6 (s, Fur-*C*H), 126.0 (br, ^{F}Mes-*C*H), 123.6 (q, $^1J_{CF}$ = 274.5 Hz, *o*-^{F}Mes-*C*F_3), 122.9 (q, $^1J_{CF}$ = 272.5 Hz, *p*-^{F}Mes-*C*F_3), 118.0 (br, Fur-*C*-B), –8.7 (s, Sn-CH_3) ppm. **^{19}F** (471 MHz, $CDCl_3$): δ = –58.1 (s, 12F, *o*-^{F}Mes-CF_3), –63.2 (s, 6F, *p*-^{F}Mes-CF_3) ppm. **^{119}Sn NMR** (187 MHz, $CDCl_3$): δ = –45.5 ppm. **HRMS** (ACPI neg): m/z ([M]$^-$, $C_{32}H_{24}B_2F_{18}O_3Sn_2$) = calcd. 1057.9684; found 1057.9688.

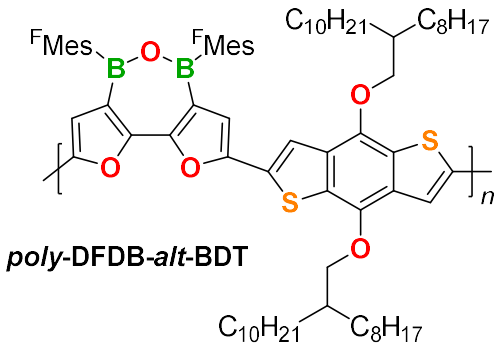
Polymer Synthesis



General Method for Polymerization:

In a glovebox, Br-Ar^1-Br (0.10 mmol, 1.0 eq.), Me_3Sn-Ar^2-$SnMe_3$ (0.10 mmol, 1.0 eq.) and $Pd(PPh_3)_2Cl_2$ (2.11 mg, 0.01 mmol, 0.1 eq.) were dissolved in *o*-xylene (1.5 mL) in a 2 mL microwave vial. Over a period of 30 min, the mixture was heated gradually to 200 °C in the microwave and then stirred at 200 °C for 4 h. After cooling to ambient temperature, the mixture was diluted with 20 mL THF, filtered through a SiO_2 pad, and the solvent was removed under *in vacuo*. The residue was dissolved in small amount

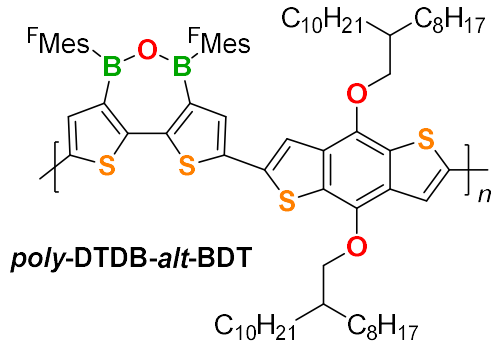
of THF, precipitated into cold methanol (0 °C, 8 mL) and centrifuged to remove the supernatant liquid. This process was repeated once, and the polymer was obtained as a powdered solid after drying in high vacuum.



***poly*-DFDB-*alt*-BDT**

Synthesis of *poly*-DFDB-*alt*-BDT:

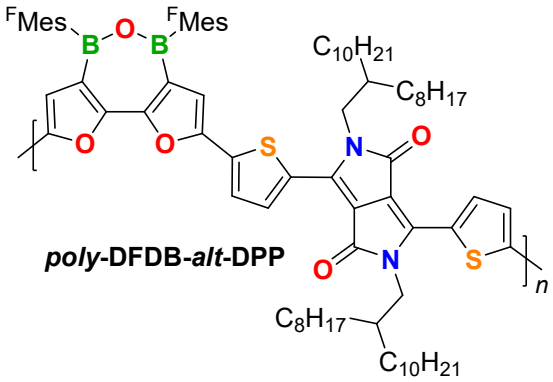
Br-Ar^1-Br = **7**, Me_3Sn-Ar^2-$SnMe_3$ = **9**. Black solid (orange in solution). **Yield:** 96.1 mg (63.6 µmol, 64 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.18 (m, 4H, ^{F}Mes-C*H*), 7.86 (m, 2H, BDT-C*H*), 6.61 (m, 2H, DFDB-C*H*), 4.25 (br s, 4H, O-CH_2-), 1.90 (br s, 2H, O-CH_2-C*H*-), 1.76 – 1.00 (m, 64H, -CH_2-), 0.79 (m, 12H, -CH_3) ppm. **^{11}B NMR** (160 MHz, $CDCl_3$): *no signal detectable*. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 153.0, 150.8, 145.1, 135.0, 134.7, 132.8, 129.8, 126.9, 126.3, 124.7, 123.9, 122.5, 121.7, 120.4, 118.2, 114.1, 39.4, 31.9, 31.4, 30.3, 29.8, 29.4. 27.2, 22.7 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = –58.0 (m, 12F, *o*-^{F}Mes-CF_3), –63.2 (s, 6F, *p*-^{F}Mes-CF_3), **GPC:** M_n = 8.2 kDa, M_w = 14.1 kDa; **UV–vis** (THF): $\lambda_{abs,max}$ = 478 (ε = 3.8 · 10^4 L mol^{-1} cm^{-1}), 514 (ε = 3.5 · 10^4 L mol^{-1} cm^{-1}) nm; **fluorescence** (THF): $\lambda_{em,max}$ = 538, 580 nm (Φ_f = 0.24).



***poly*-DTDB-*alt*-BDT**

Synthesis of *poly*-DTDB-*alt*-BDT:

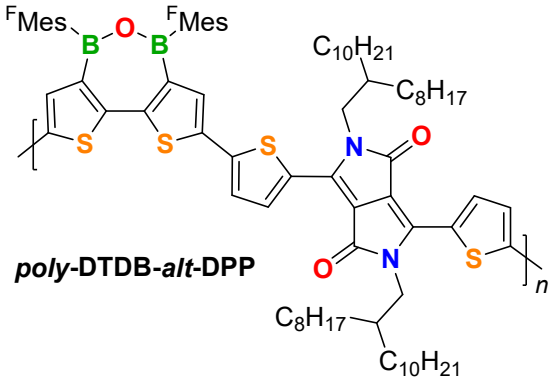
Br-Ar^1-Br = **5**, Me_3Sn-Ar^2-$SnMe_3$ = **9**. Black solid (red in solution). **Yield:** 126.1 mg (81.7 µmol, 82 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.17 (m, 4H, ^{F}Mes-C*H*), 7.57 (m, 2H, BDT-C*H*), 6.97 (m, 2H, DFDB-C*H*), 4.20 (m, 4H, O-CH_2-), 1.90 (m, 2H, O-CH_2-C*H*-), 1.72 – 1.12 (m, 64H, -CH_2-), 0.83 (m, 12H, -CH_3) ppm. **^{11}B NMR** (160 MHz, $CDCl_3$): *no signal detectable*. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 150.2, 144.7, 140.4, 137.0, 134.8, 132.8, 129.6, 126.9, 126.4, 124.8, 123.9, 122.6, 121.7, 120.4, 119.5, 118.4, 39.3, 32.1, 31.5, 30.2, 29.9, 29.5. 27.2, 22.8 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = –57.9 (m, 12F, *o*-^{F}Mes-CF_3), –63.2 (s, 6F, *p*-^{F}Mes-CF_3), **GPC:** M_n = 2.7 kDa, M_w = 8.5 kDa; **UV–vis** (THF): $\lambda_{abs,max}$ = 513 (ε = 4.5 · 10^4 L mol^{-1} cm^{-1}), 552 (ε = 3.7 · 10^4 L mol^{-1} cm^{-1}) nm; **fluorescence** (THF): $\lambda_{em,max}$ = 648 nm (Φ_f = 0.11).



***poly*-DFDB-*alt*-DPP**

Synthesis of *poly*-DFDB-*alt*-DPP:

Br-Ar^1-Br = **10**, Me$_3$Sn-Ar^2-SnMe$_3$ = **8**. Black solid (blue-green in solution). **Yield:** 123.4 mg (77.6 µmol, 78 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.90 (m, 2H, Thi-C*H*), 8.15 (m, 4H, ^{F}Mes-C*H*), 7.45 (m, 2H, Thi-C*H*), 6.85 (m, 2H, DFDB-C*H*), 4.06 (m, 4H, N-C*H*$_2$-), 1.95 (m, 2H, N-CH$_2$-C*H*-), 1.71 – 0.98 (m, 64H, -C*H*$_2$-), 0.84 (m, 12H, -C*H*$_3$) ppm. **^{11}B NMR** (160 MHz, $CDCl_3$): *no signal detectable*. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = *some signals are not visible due to limited solubility* 126.4, 124.7, 122.5, 32.0, 31.4, 30.2, 29.8, 29.5. 26.4, 14.2 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = –57.9 (m, 12F, *o*-^{F}Mes-C*F*$_3$), –63.2 (s, 6F, *p*-^{F}Mes-C*F*$_3$), **GPC:** M_n = 5.0 kDa, M_w = 10.8 kDa; **UV–vis** (THF): $\lambda_{abs,max}$ = 344 (ε = 2.3 · 10^4 L mol^{-1} cm^{-1}), 434 (ε = 2.2 · 10^4 L mol^{-1} cm^{-1}), 681 (ε = 4.5 · 10^4 L mol^{-1} cm^{-1}), 730 (*shoulder*, ε = 4.2 · 10^4 L mol^{-1} cm^{-1}) nm; **fluorescence** (THF): *not detected*.



***poly*-DTDB-*alt*-DPP**

Synthesis of *poly*-DFDB-*alt*-DPP:

Br-Ar^1-Br = **10**, Me$_3$Sn-Ar^2-SnMe$_3$ = **6**. Black solid (blue in solution). **Yield:** 123.9 mg (76.4 µmol, 76 %). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.87 (m, 2H, Thi-C*H*), 8.15 (m, 4H, ^{F}Mes-C*H*), 7.32 (m, 2H, Thi-C*H*), 6.84 (m, 2H, DTDB-C*H*), 4.00 (m, 4H, N-C*H*$_2$-), 1.95 (m, 2H, N-CH$_2$-C*H*-), 1.71 – 0.98 (m, 64H, -C*H*$_2$-), 0.84 (m, 12H, -C*H*$_3$) ppm. **^{11}B NMR** (160 MHz, $CDCl_3$): *no signal detectable*. **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = *some signals are not visible due to limited solubility* 126.4, 32.1, 30.2, 29.8, 29.5. 22.8, 14.2 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = –57.9 (m, 12F, *o*-^{F}Mes-C*F*$_3$), –63.1 (s, 6F, *p*-^{F}Mes-C*F*$_3$), **GPC:** M_n = 3.4 kDa, M_w = 10.2 kDa; **UV–vis** (THF): $\lambda_{abs,max}$ = 344 (ε = 1.6 · 10^4 L mol^{-1} cm^{-1}), 447 (ε = 2.1 · 10^4 L mol^{-1} cm^{-1}), 721 (ε = 5.3 · 10^4 L mol^{-1} cm^{-1}) nm; **fluorescence** (THF): *not detected.*

1.3 NMR spectra

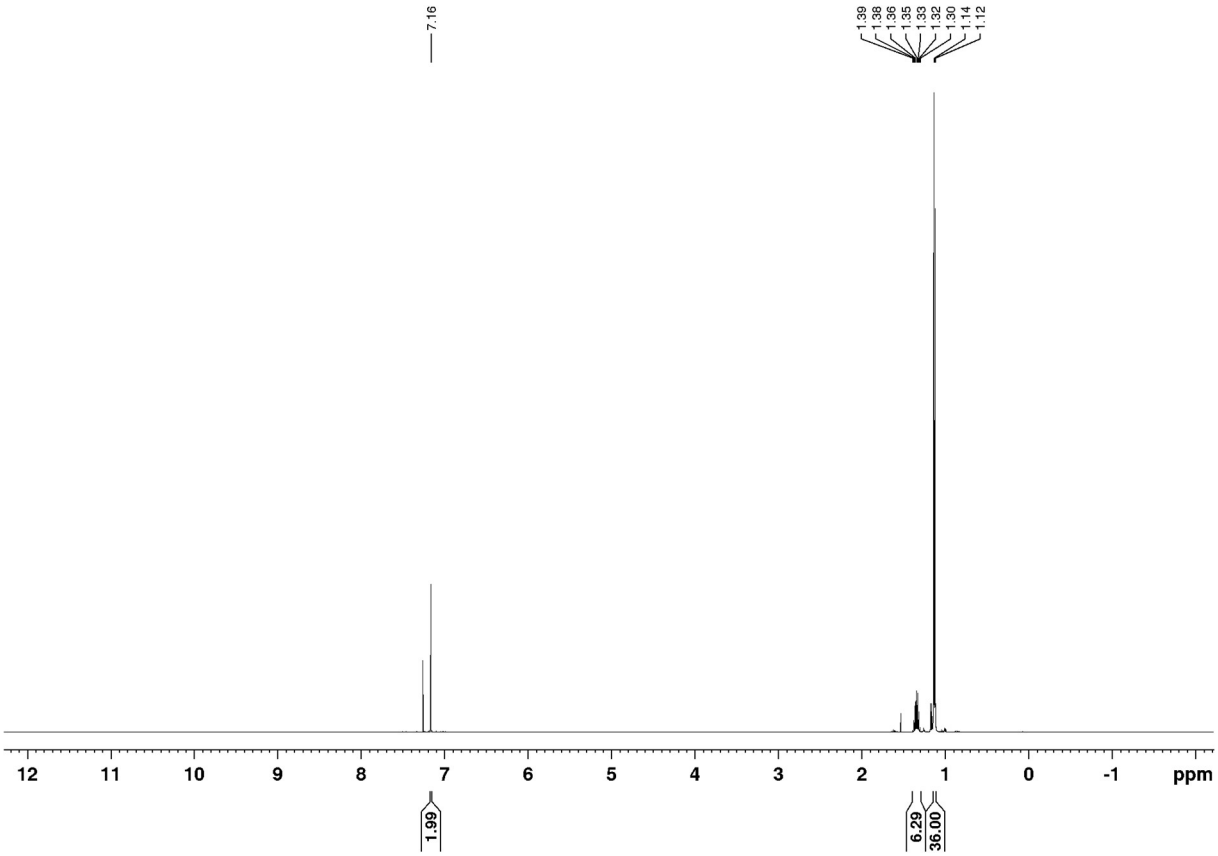


Figure S 1: ^{1}H NMR spectrum of **2** (500 MHz, in $CDCl_3$).

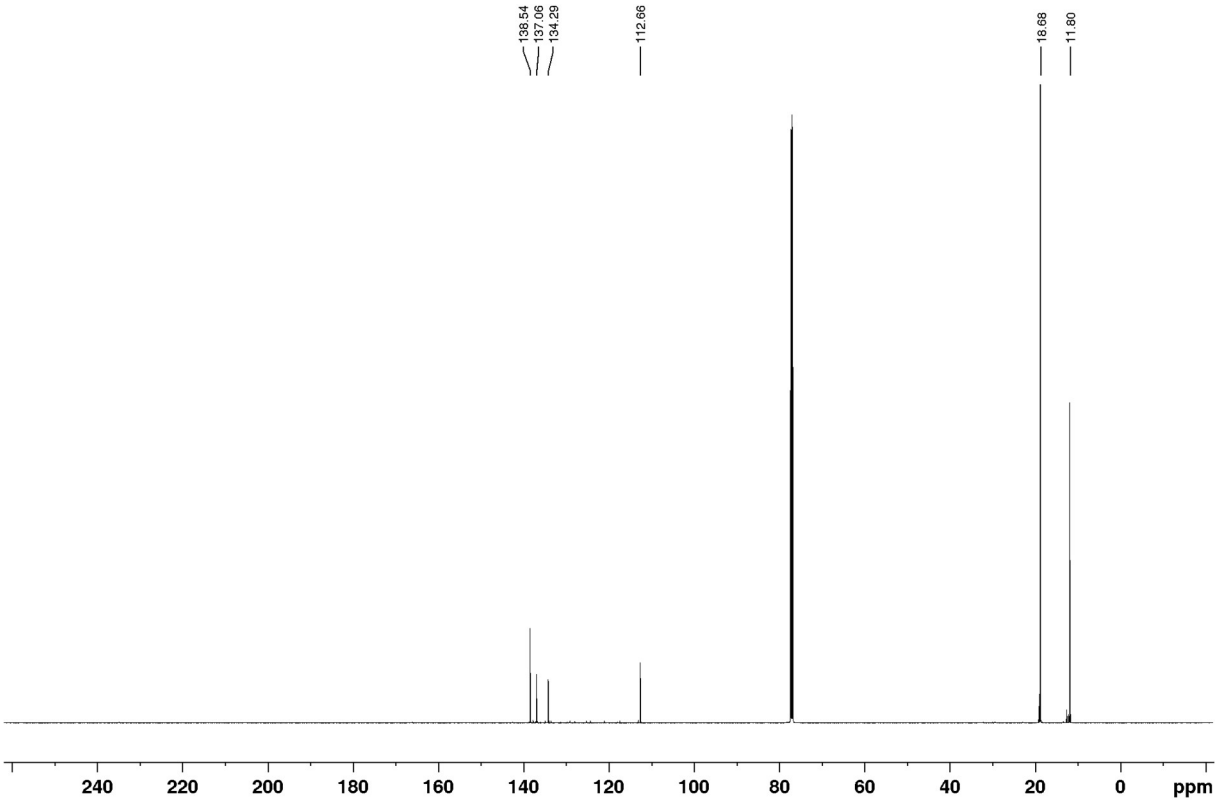


Figure S 2: $^{13}C\{^{1}H\}$ NMR spectrum of **2** (126 MHz, in $CDCl_3$).

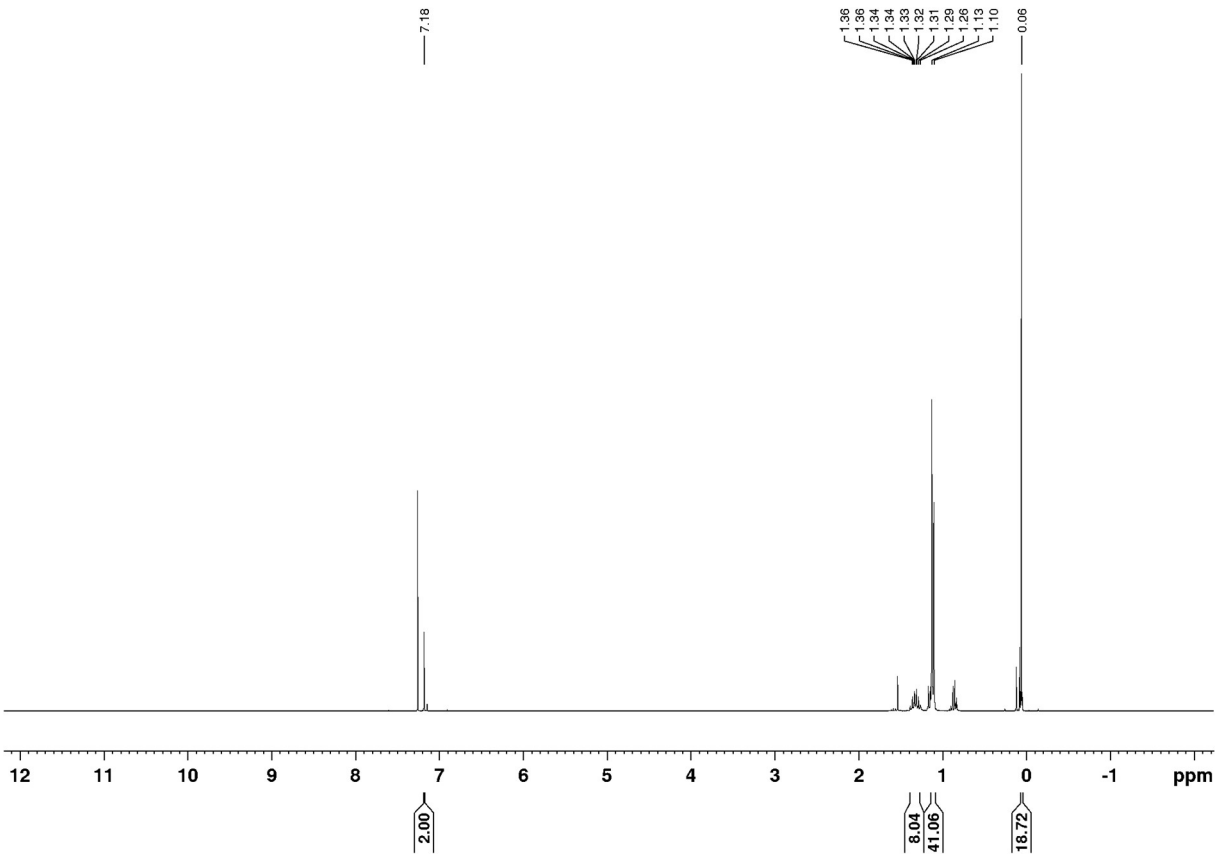


Figure S 3: ^{1}H NMR spectrum of **3** (300 MHz, in $CDCl_3$).

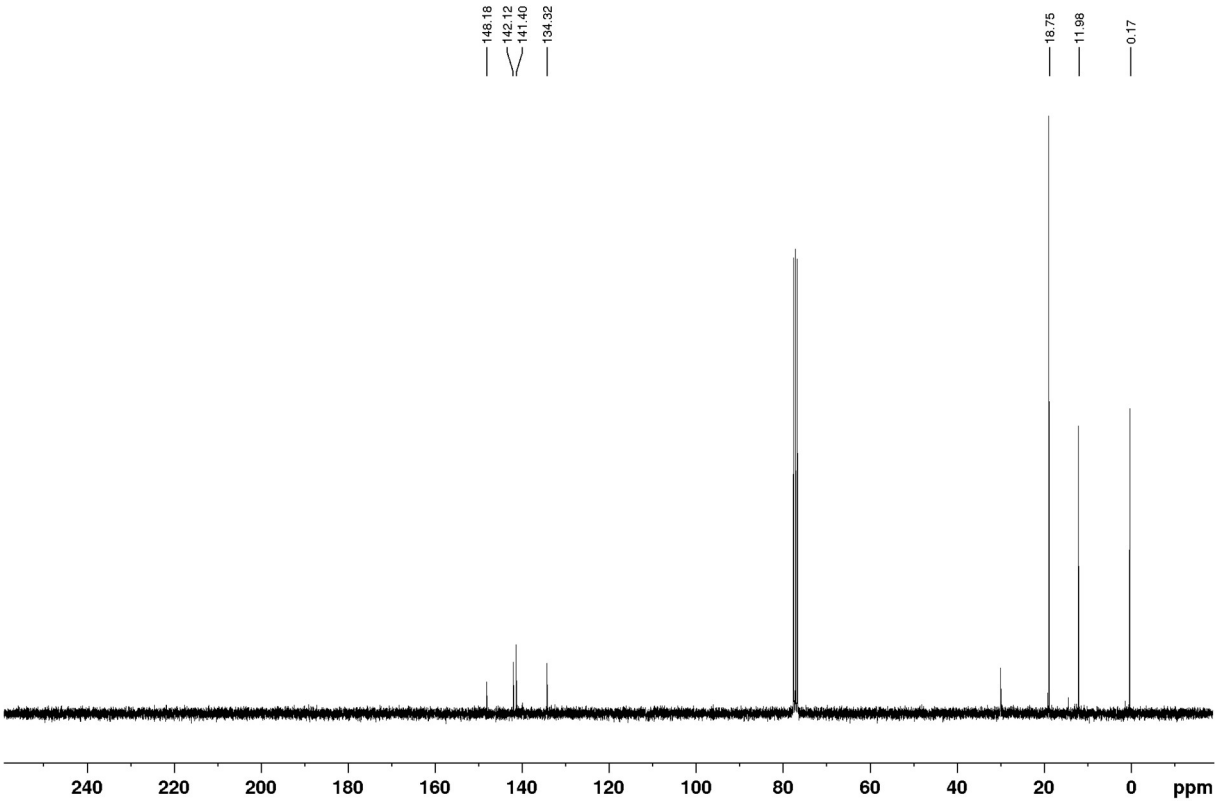


Figure S 4: $^{13}C\{^{1}H\}$ NMR spectrum of **3** (75 MHz, in $CDCl_3$).

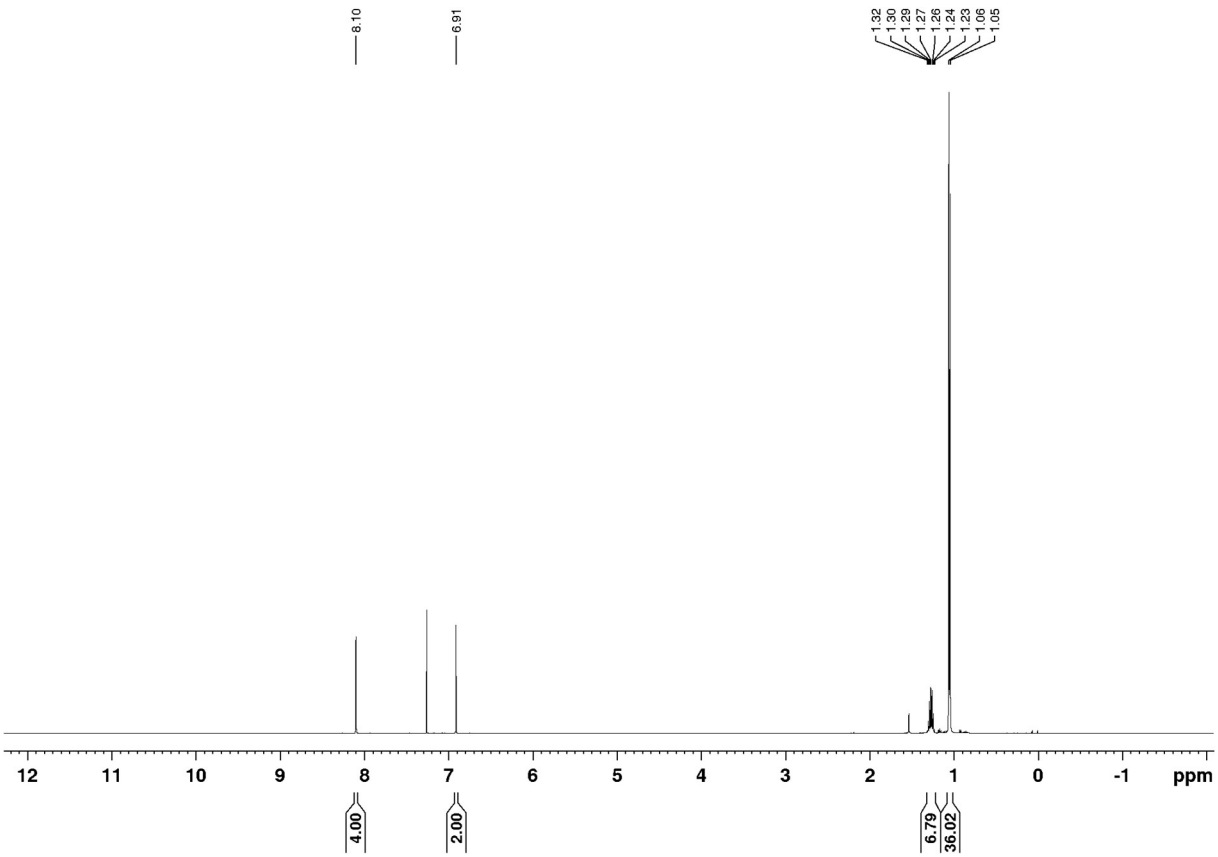


Figure S 5: ^{1}H NMR spectrum of **4** (500 MHz, in $CDCl_3$).

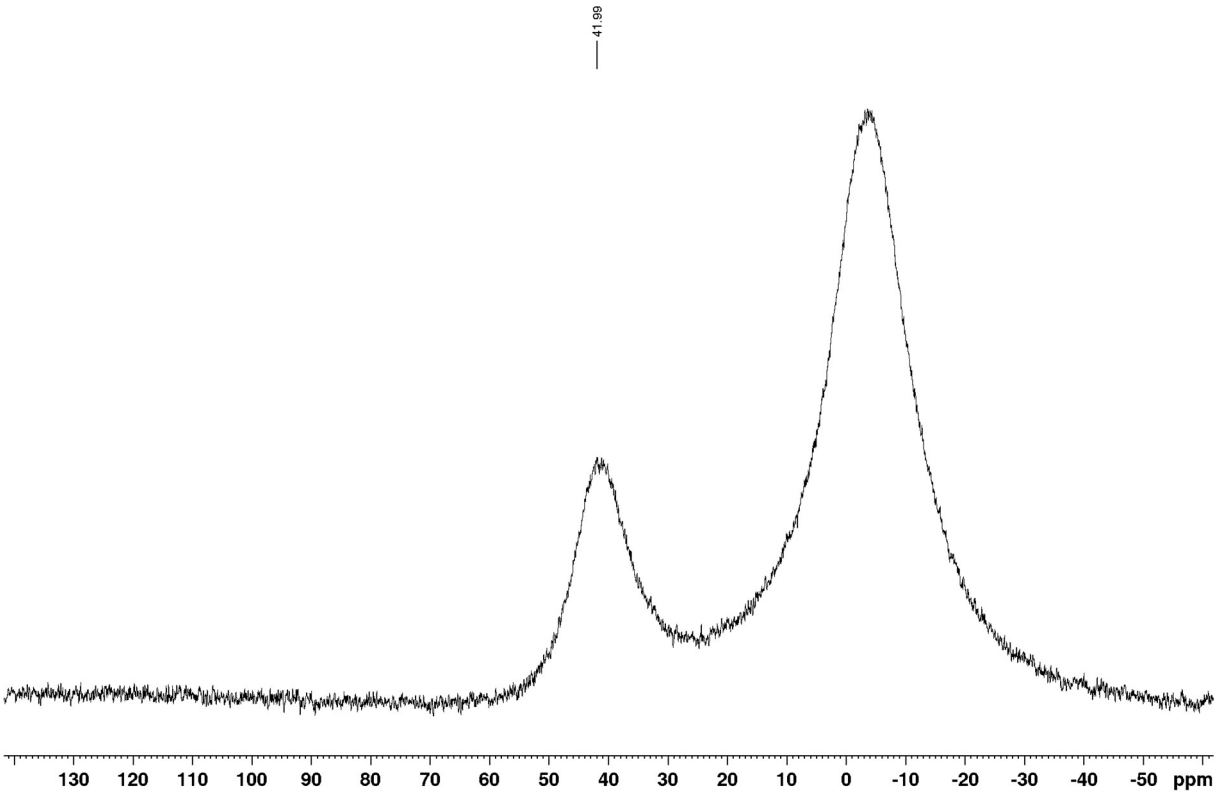


Figure S 6: ^{11}B NMR spectrum of **4** (160 MHz, in $CDCl_3$).

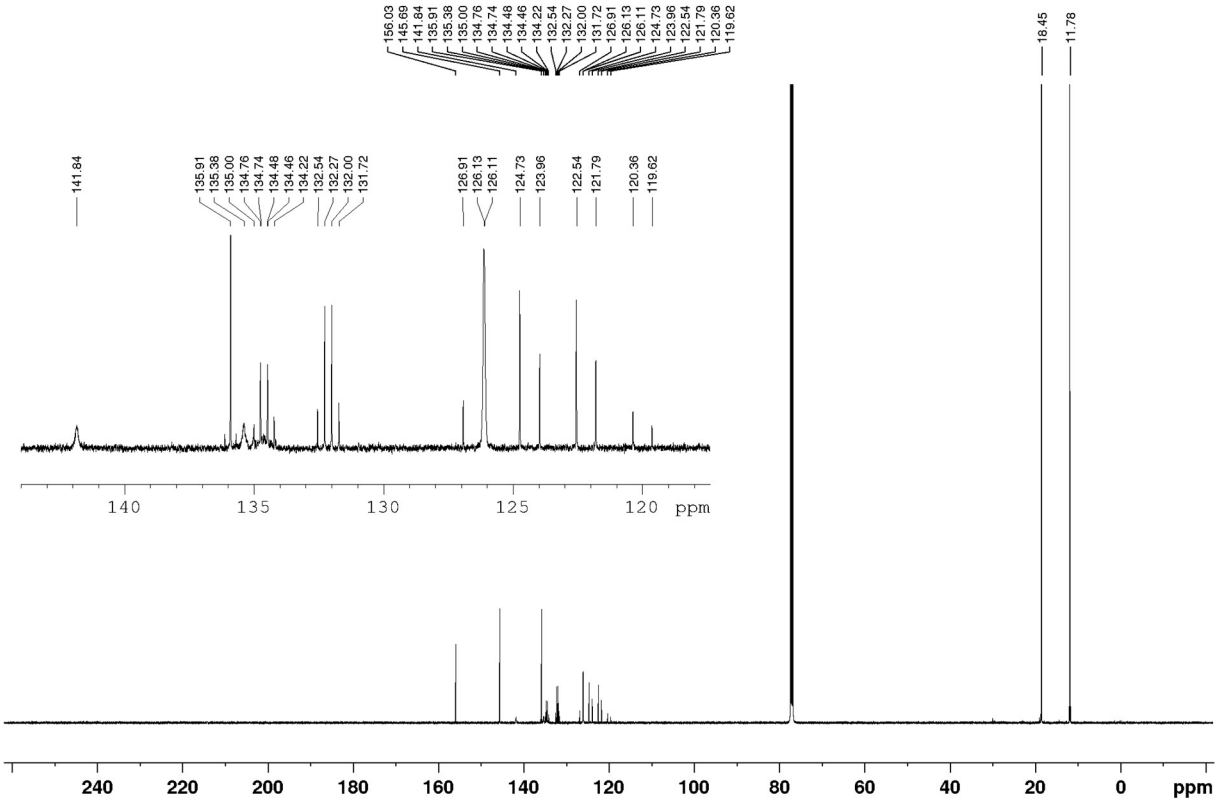


Figure S 7: $^{13}C\{^{1}H\}$ NMR spectrum of **4** (126 MHz, in $CDCl_3$).

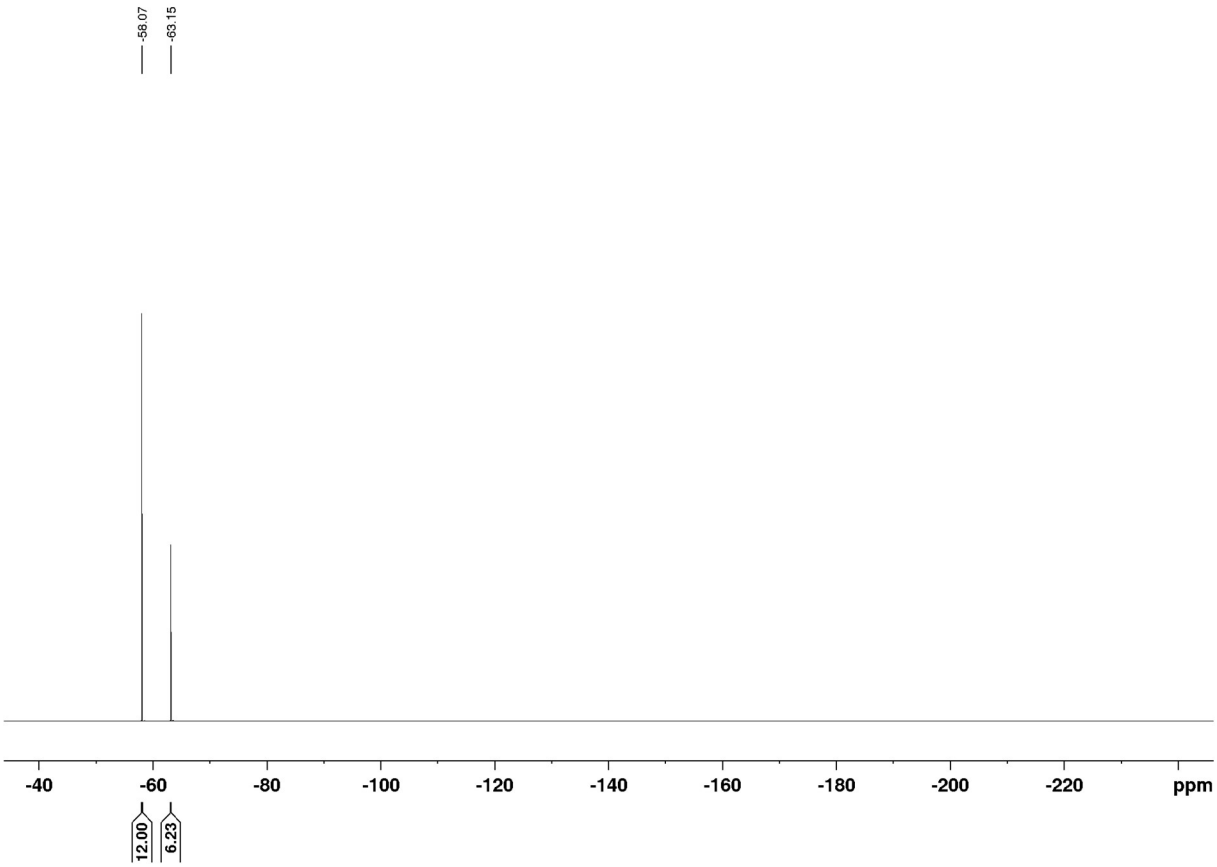


Figure S 8: ^{19}F NMR spectrum of **4** (471 MHz, in $CDCl_3$).

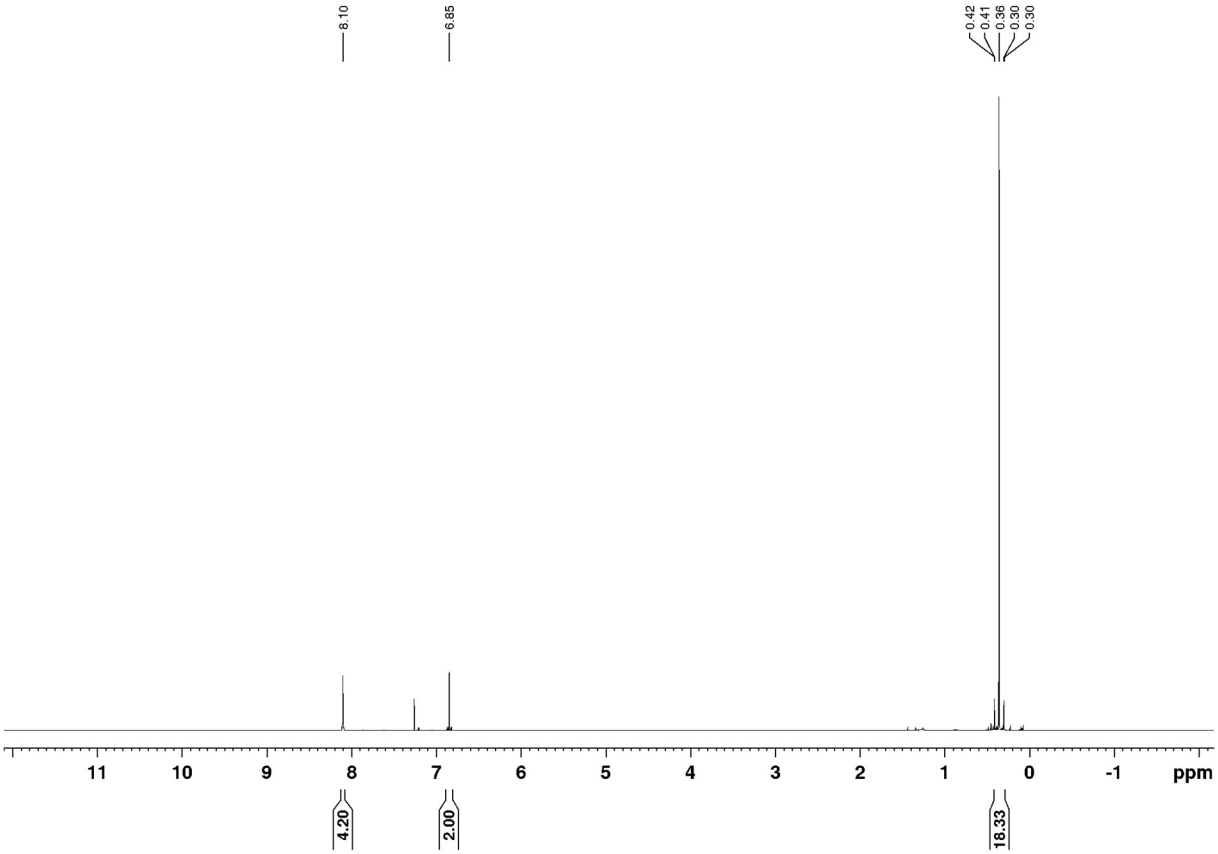


Figure S 9: ^{1}H NMR spectrum of **6** (500 MHz, in $CDCl_3$).

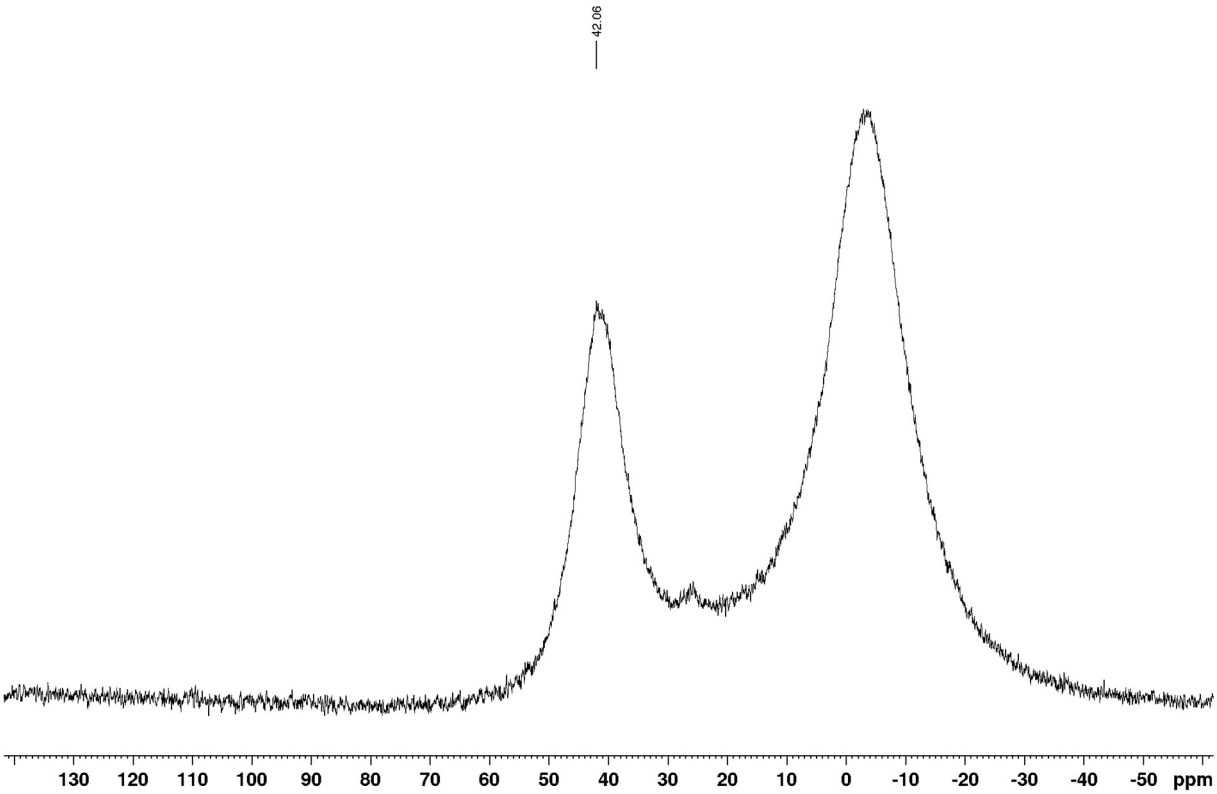


Figure S 10: ^{11}B NMR spectrum of **6** (160 MHz, in $CDCl_3$).

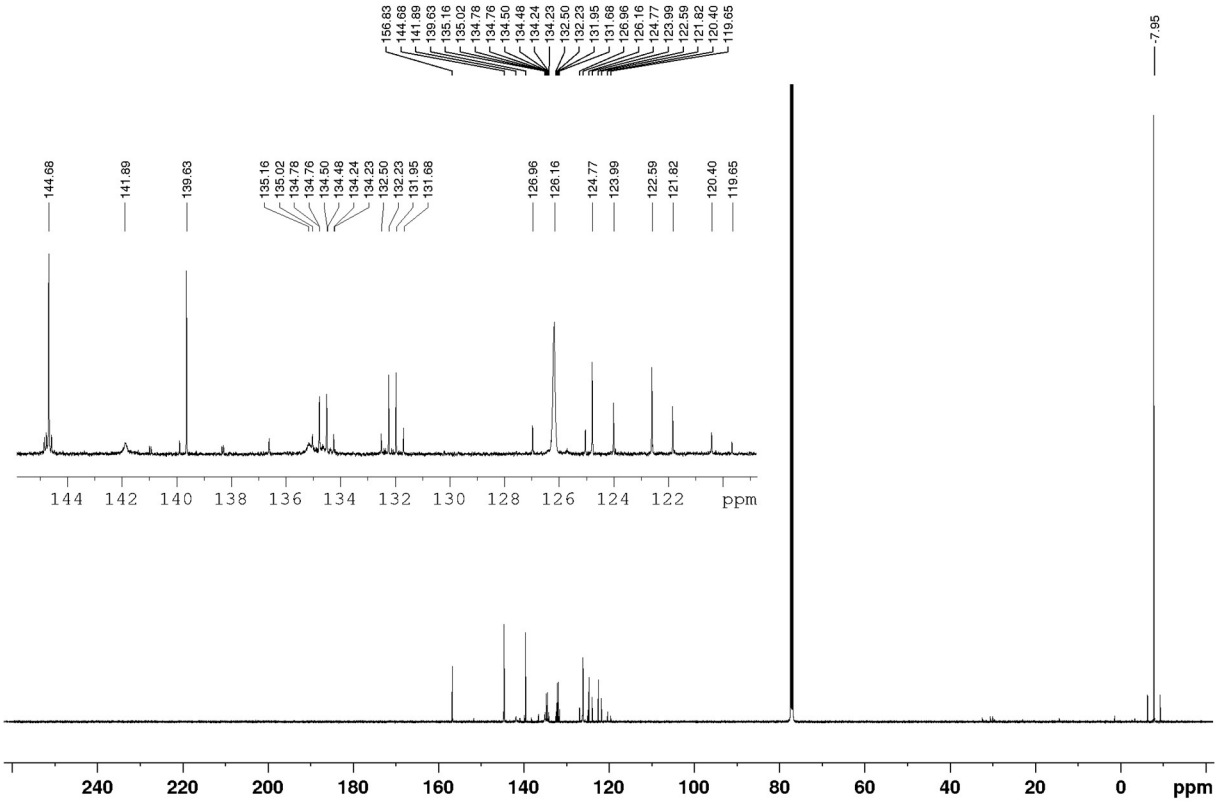


Figure S 11: $^{13}C\{^{1}H\}$ NMR spectrum of **6** (126 MHz, in $CDCl_3$).

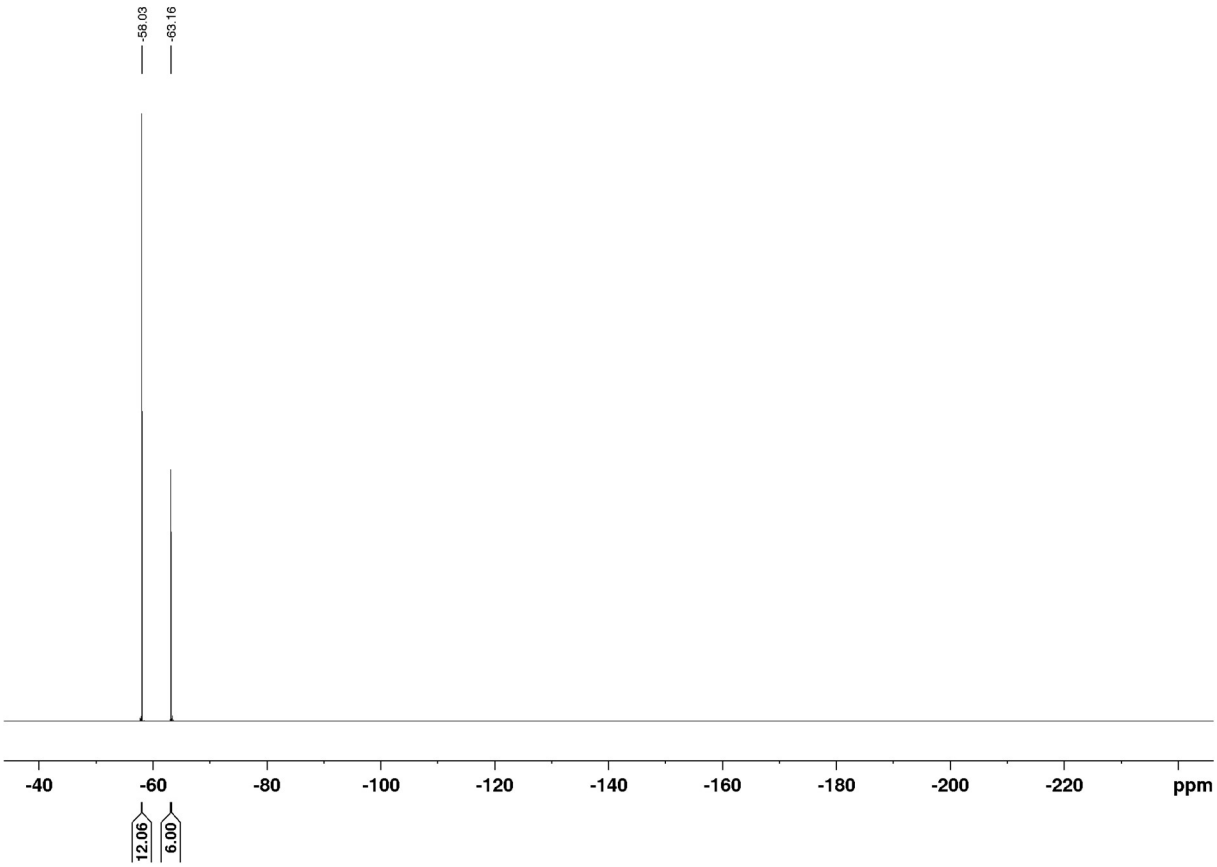


Figure S 12: ^{19}F NMR spectrum of **6** (471 MHz, in $CDCl_3$).

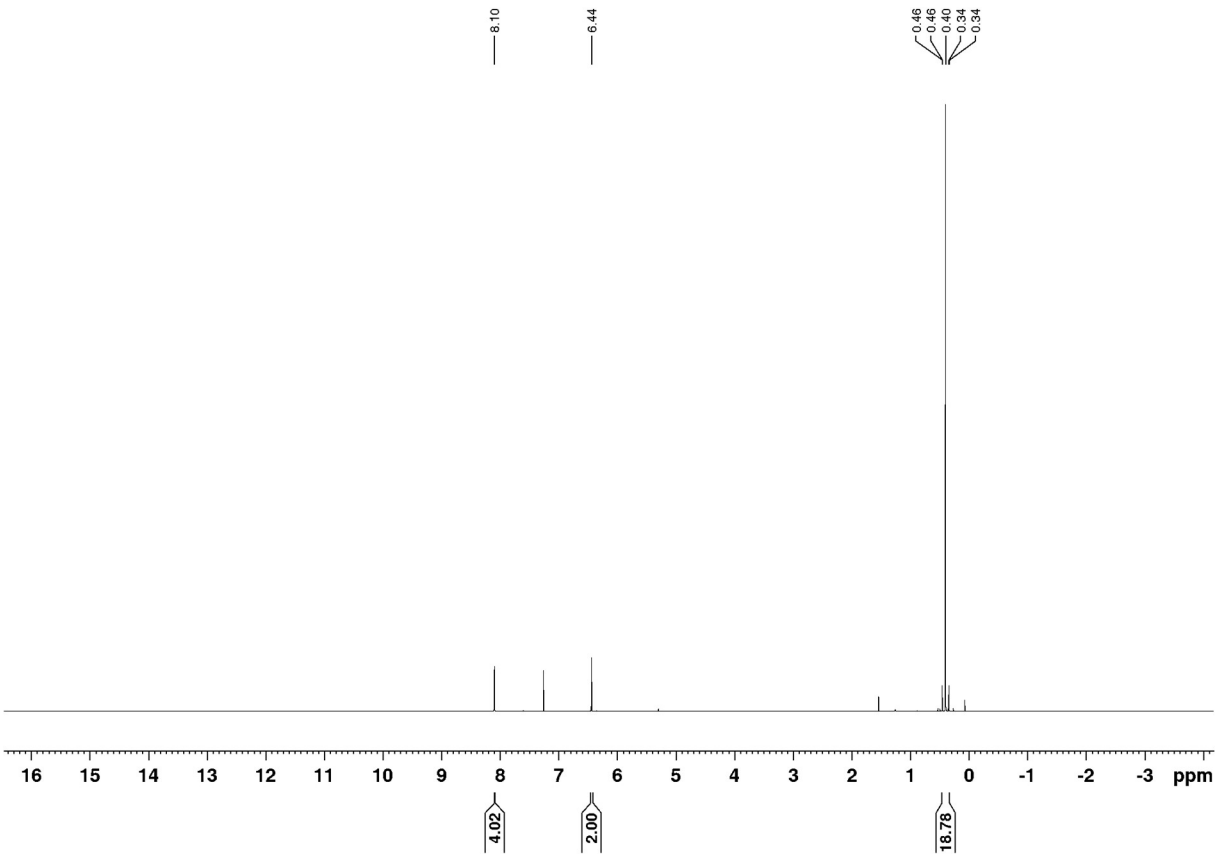


Figure S 13: ^{1}H NMR spectrum of **8** (500 MHz, in $CDCl_3$).

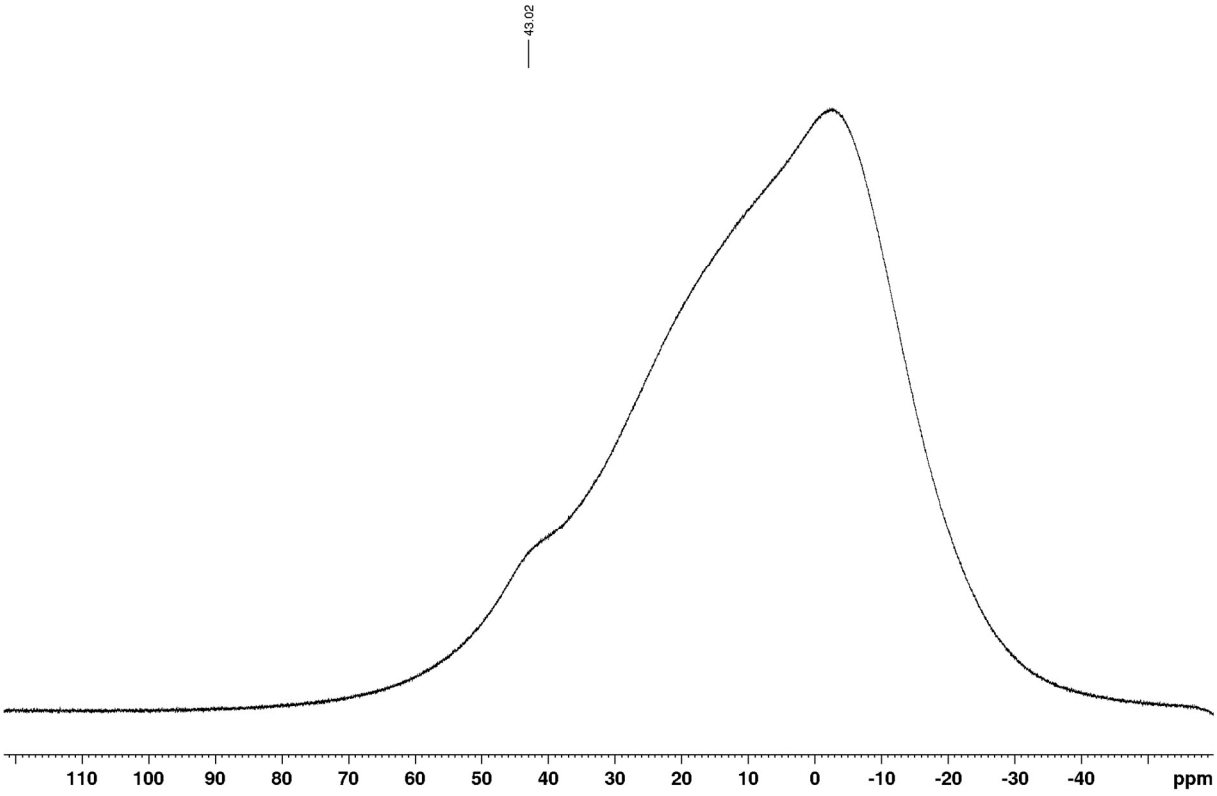


Figure S 14: ^{11}B NMR spectrum of **8** (160 MHz, in $CDCl_3$).

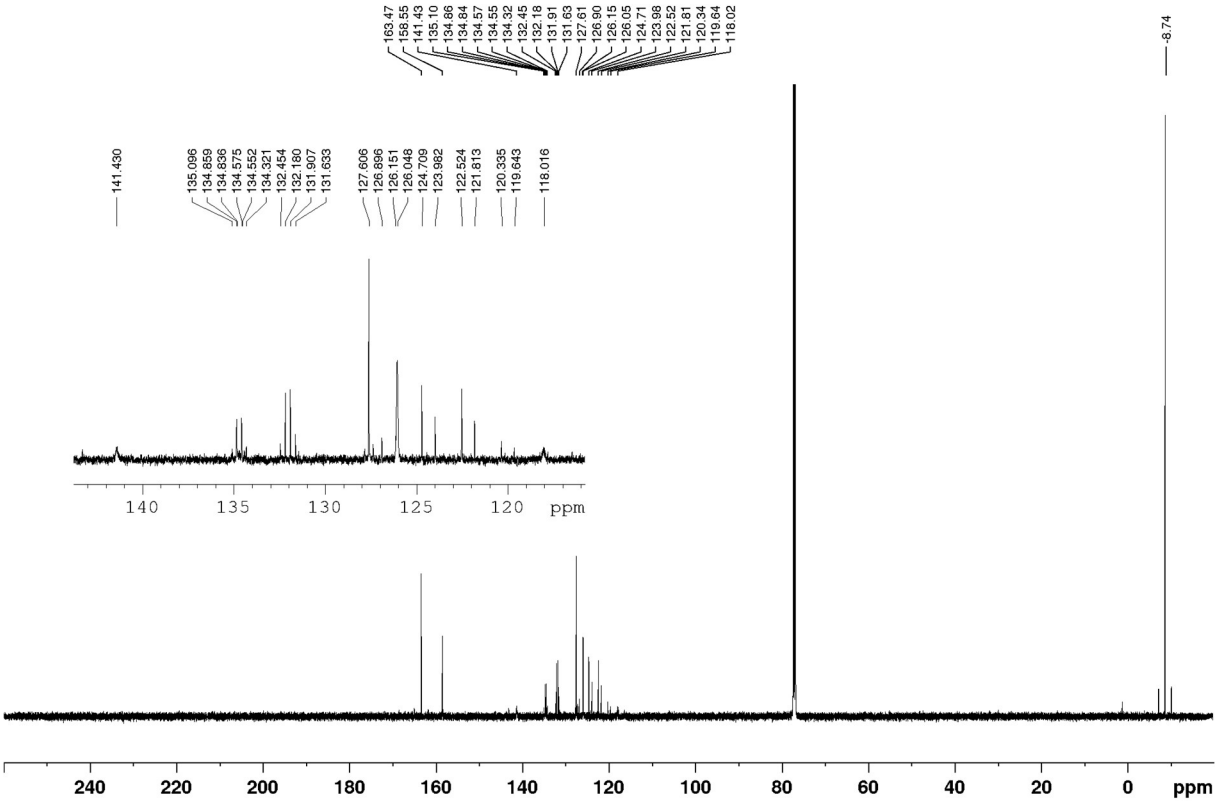


Figure S 15: $^{13}C\{^{1}H\}$ NMR spectrum of **8** (126 MHz, in $CDCl_3$).

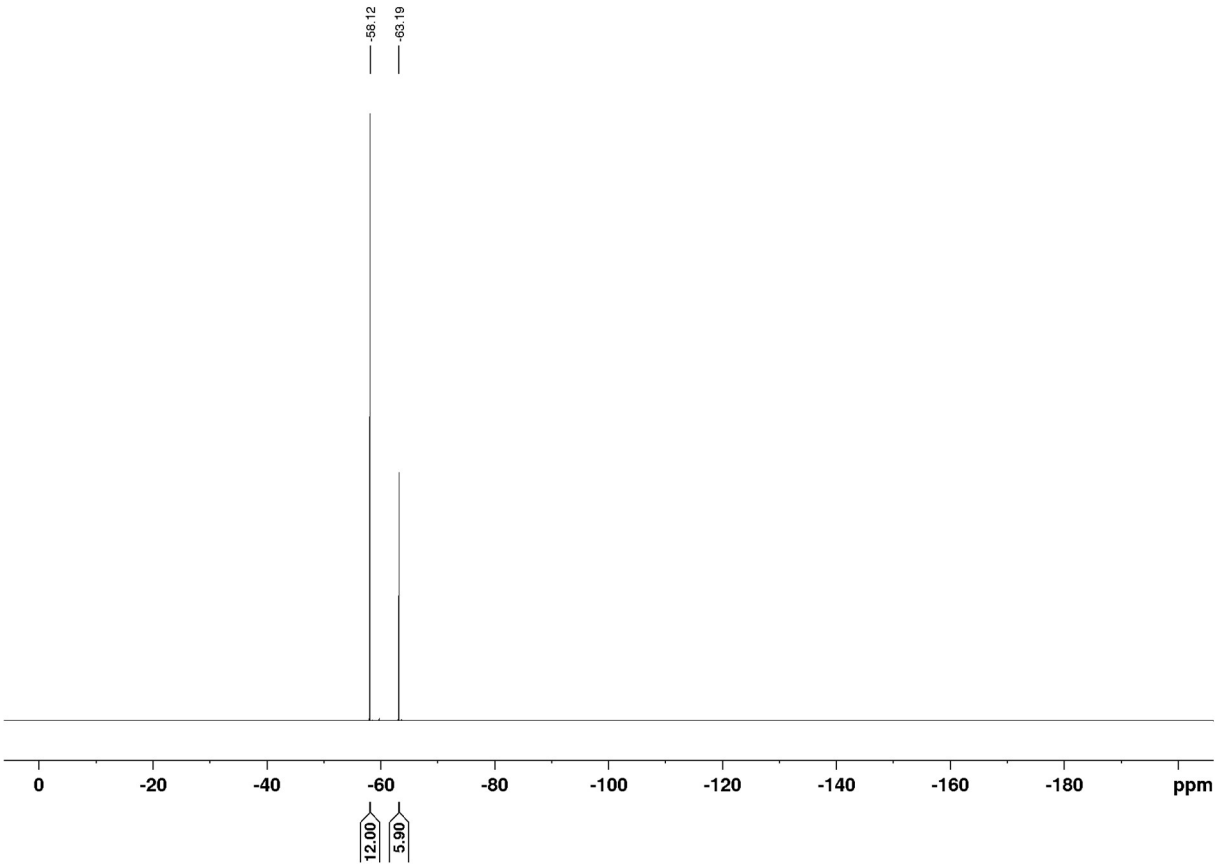


Figure S 16: ^{19}F NMR spectrum of **8** (471 MHz, in $CDCl_3$).

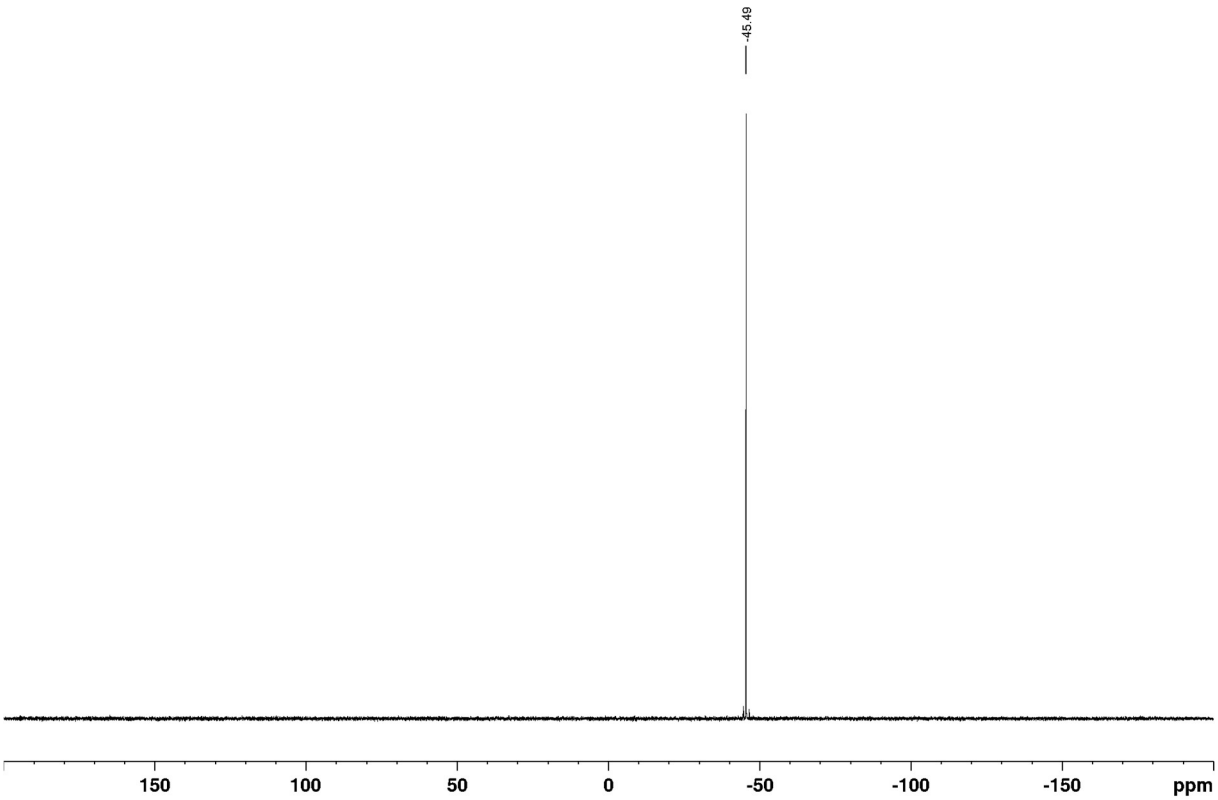


Figure S 17: ^{119}Sn NMR spectrum of **8** (187 MHz, in $CDCl_3$).

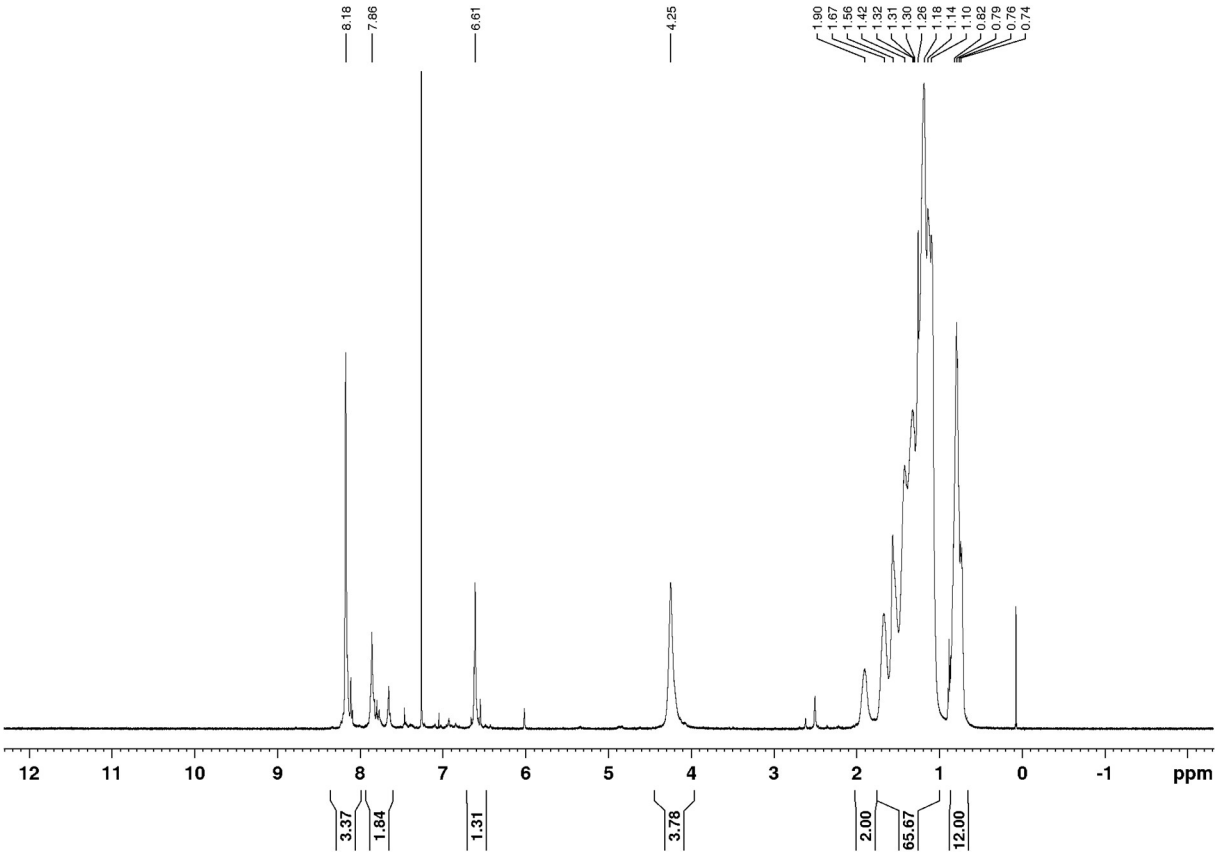


Figure S 18: ^{1}H NMR spectrum of ***poly*-DFDB-*alt*-BDT** (500 MHz, in $CDCl_3$).

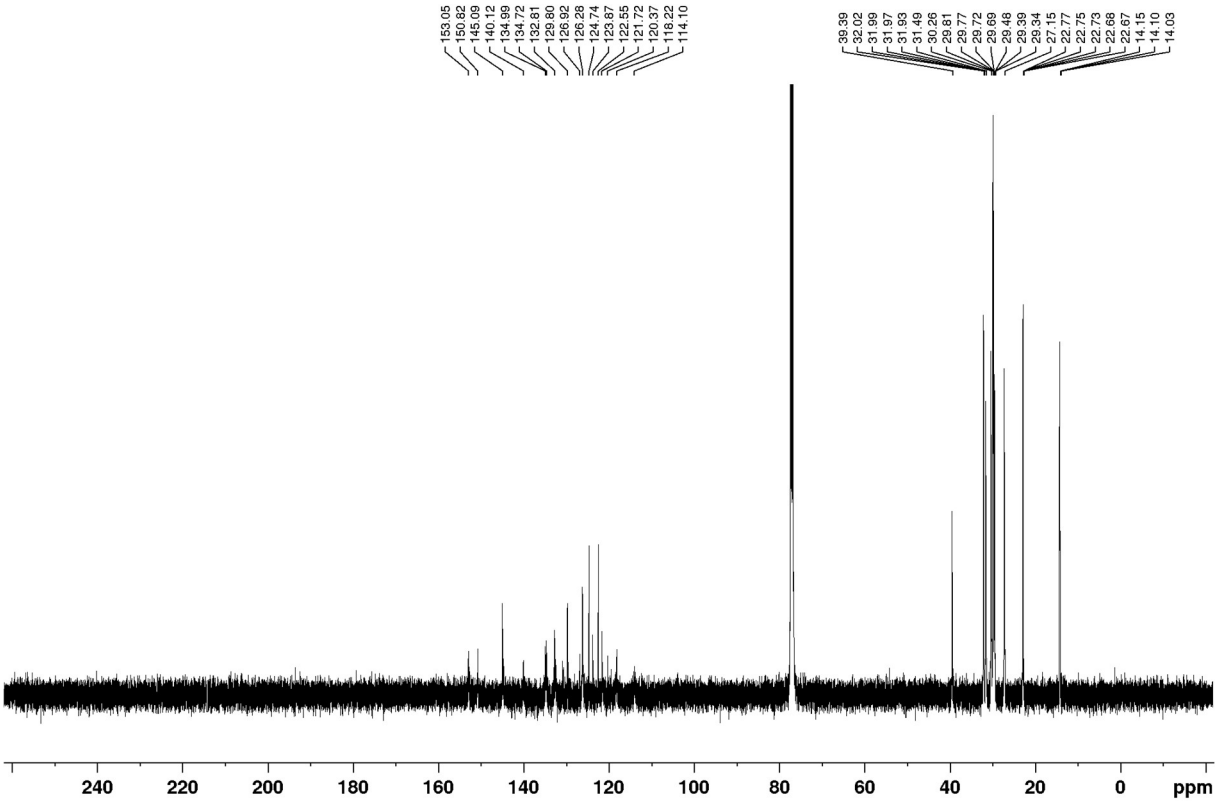


Figure S 19: $^{13}C\{^{1}H\}$ NMR spectrum of ***poly*-DFDB-*alt*-BDT** (126 MHz, in $CDCl_3$).

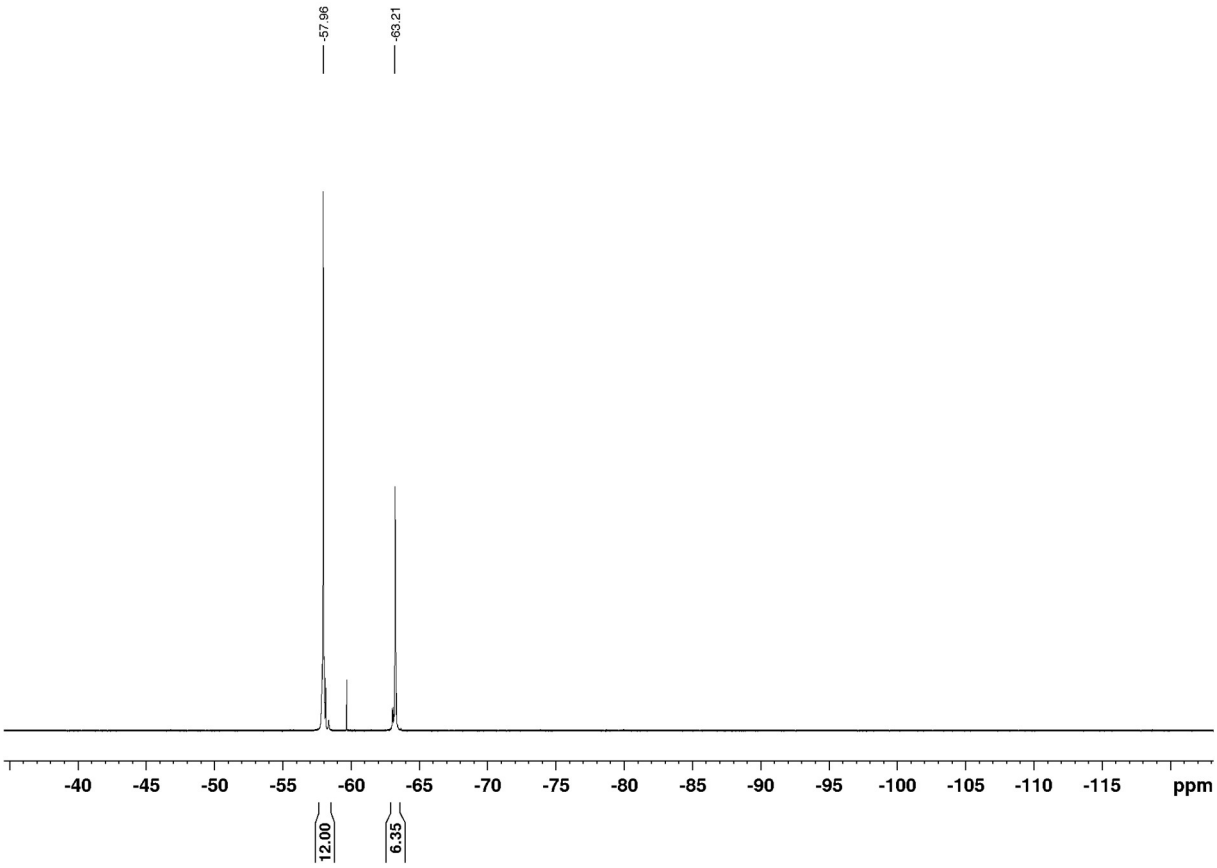


Figure S 20: ^{19}F NMR spectrum of ***poly*-DFDB-*alt*-BDT** (471 MHz, in $CDCl_3$).

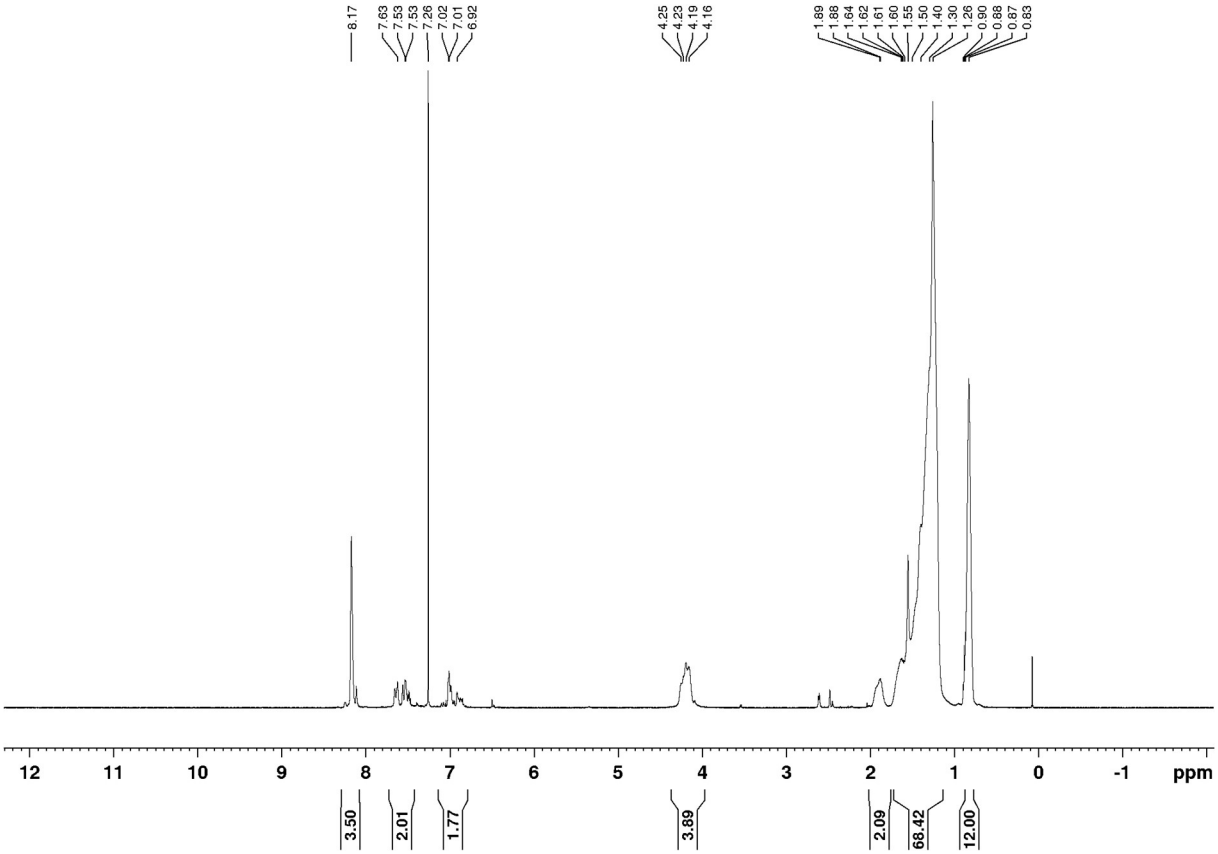


Figure S 21: ^{1}H NMR spectrum of ***poly*-DTDB-*alt*-BDT** (500 MHz, in $CDCl_3$).

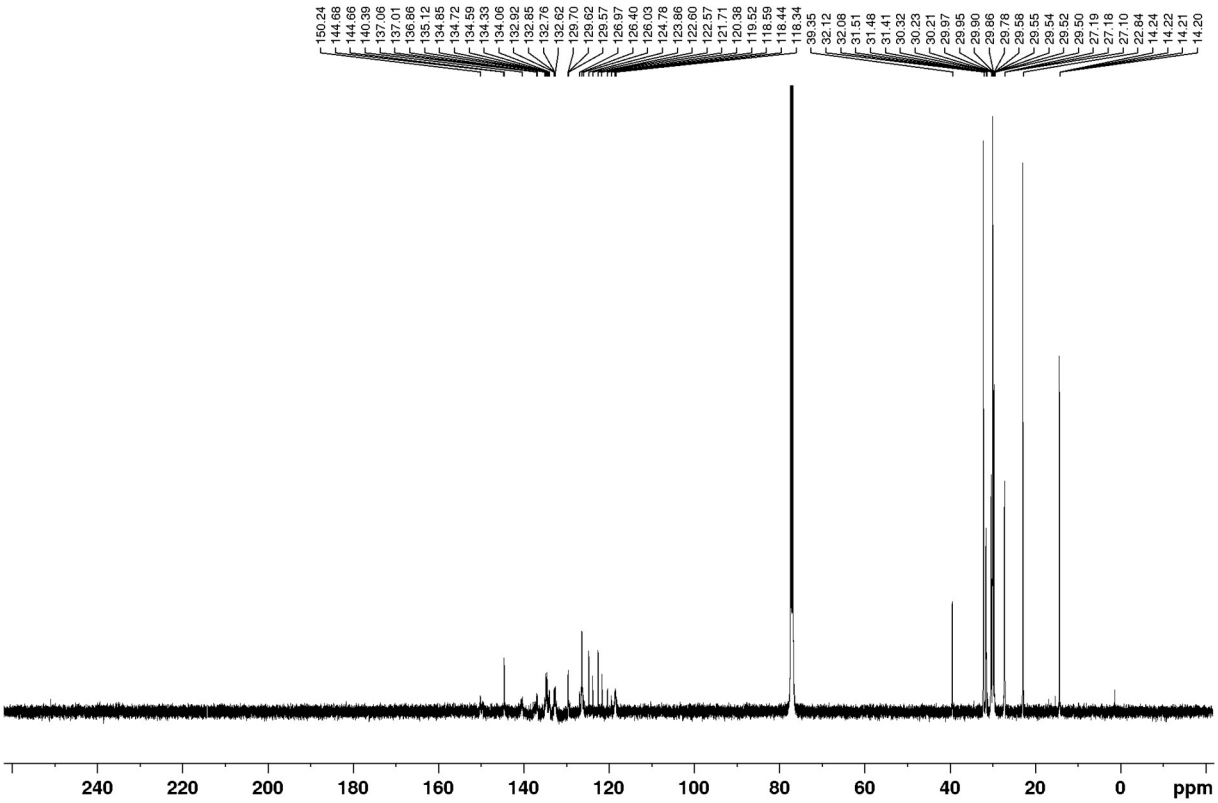


Figure S 22: $^{13}C\{^{1}H\}$ NMR spectrum of ***poly*-DTDB-*alt*-BDT** (126 MHz, in $CDCl_3$).

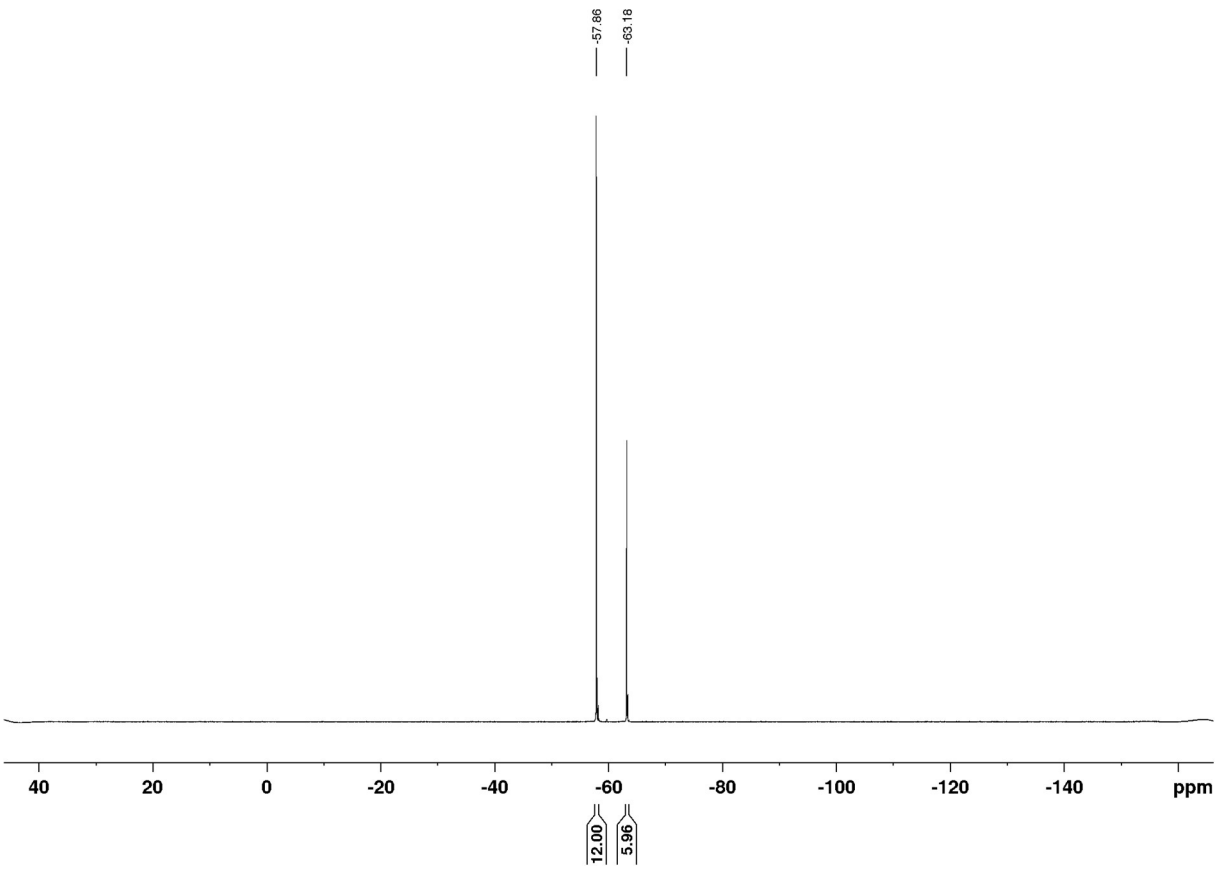


Figure S 23: ^{19}F NMR spectrum of ***poly*-DTDB-*alt*-BDT** (471 MHz, in $CDCl_3$).

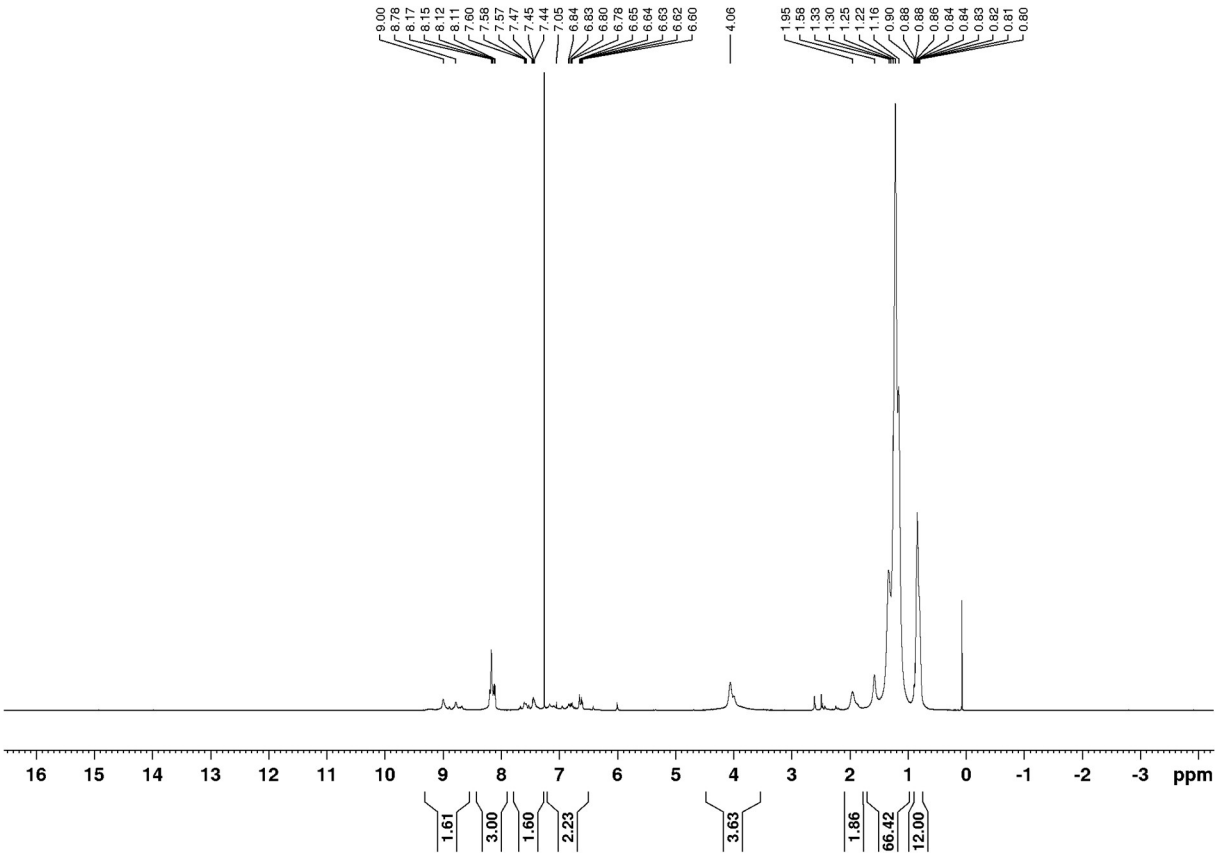


Figure S 24: ^{1}H NMR spectrum of ***poly*-DFDB-*alt*-DPP** (500 MHz, in $CDCl_3$).

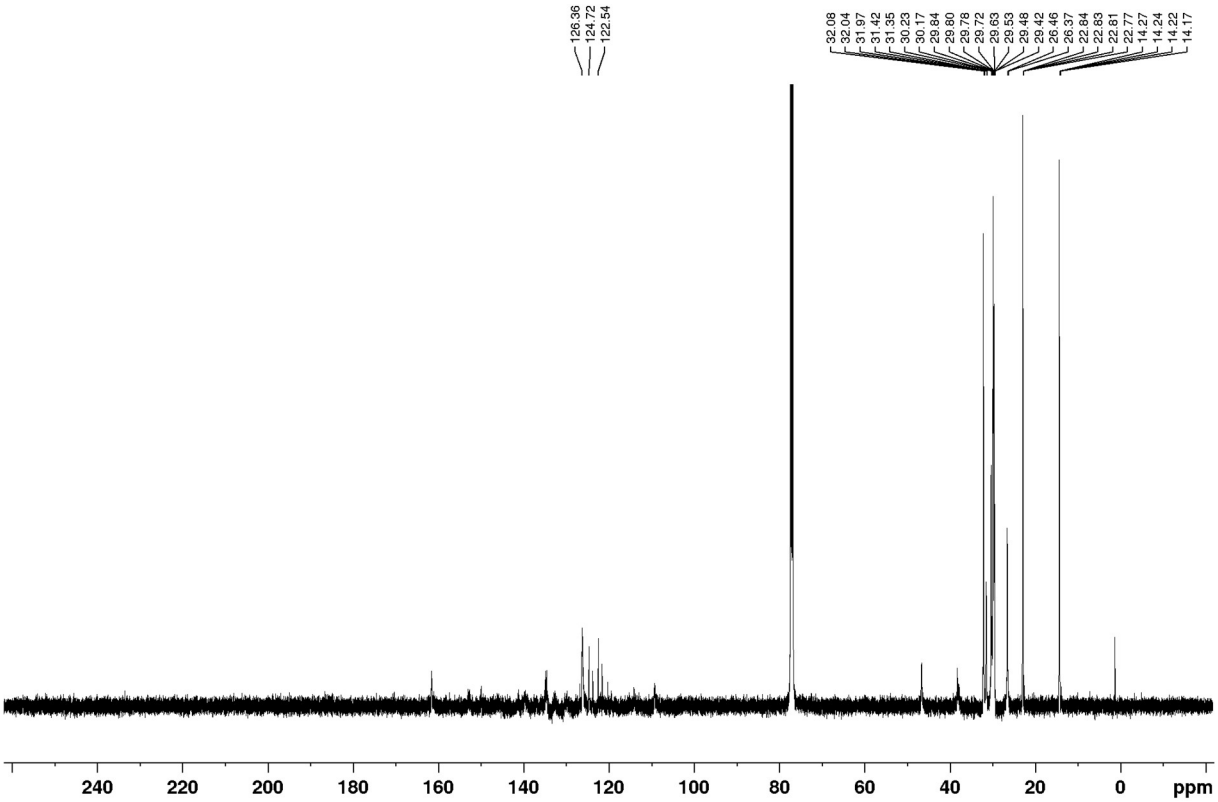


Figure S 25: $^{13}C\{^{1}H\}$ NMR spectrum of ***poly*-DFDB-*alt*-DPP** (126 MHz, in $CDCl_3$).

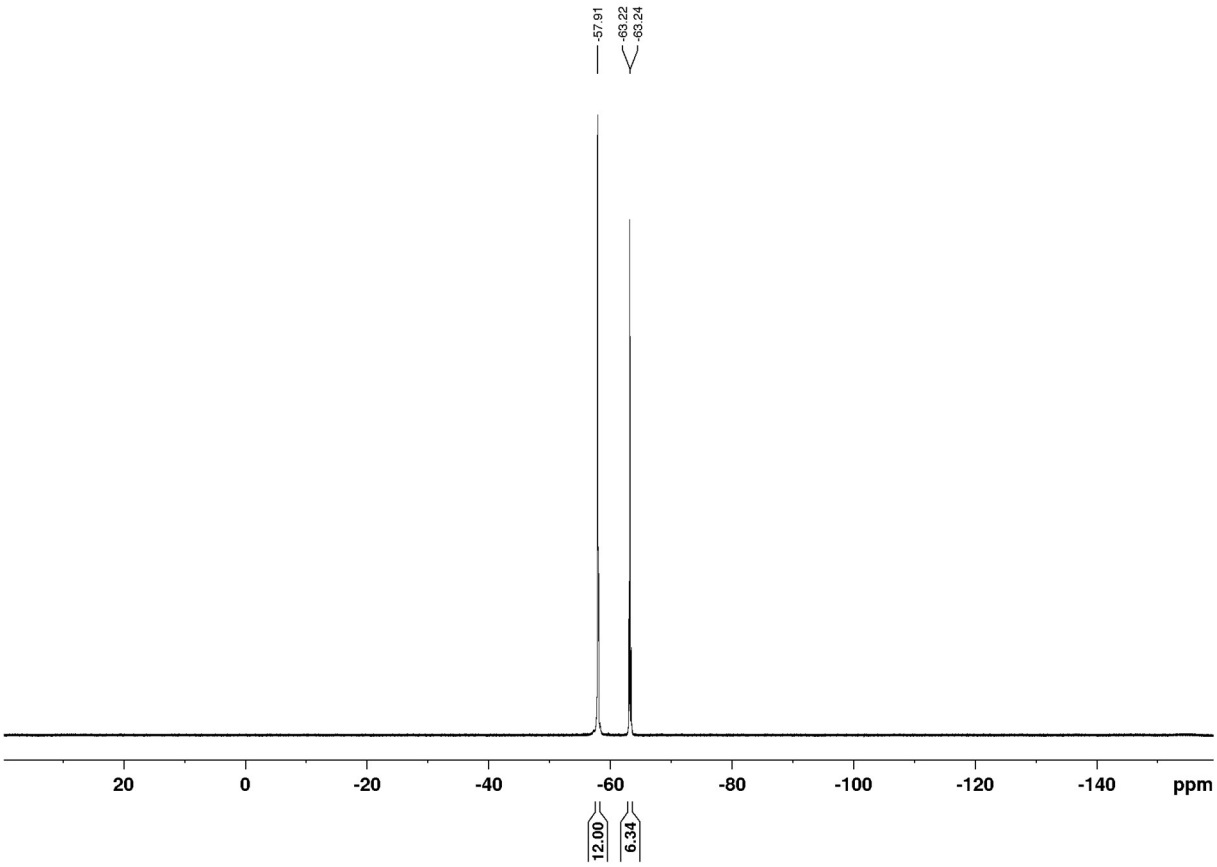


Figure S 26: ^{19}F NMR spectrum of ***poly*-DFDB-*alt*-DPP** (471 MHz, in $CDCl_3$).

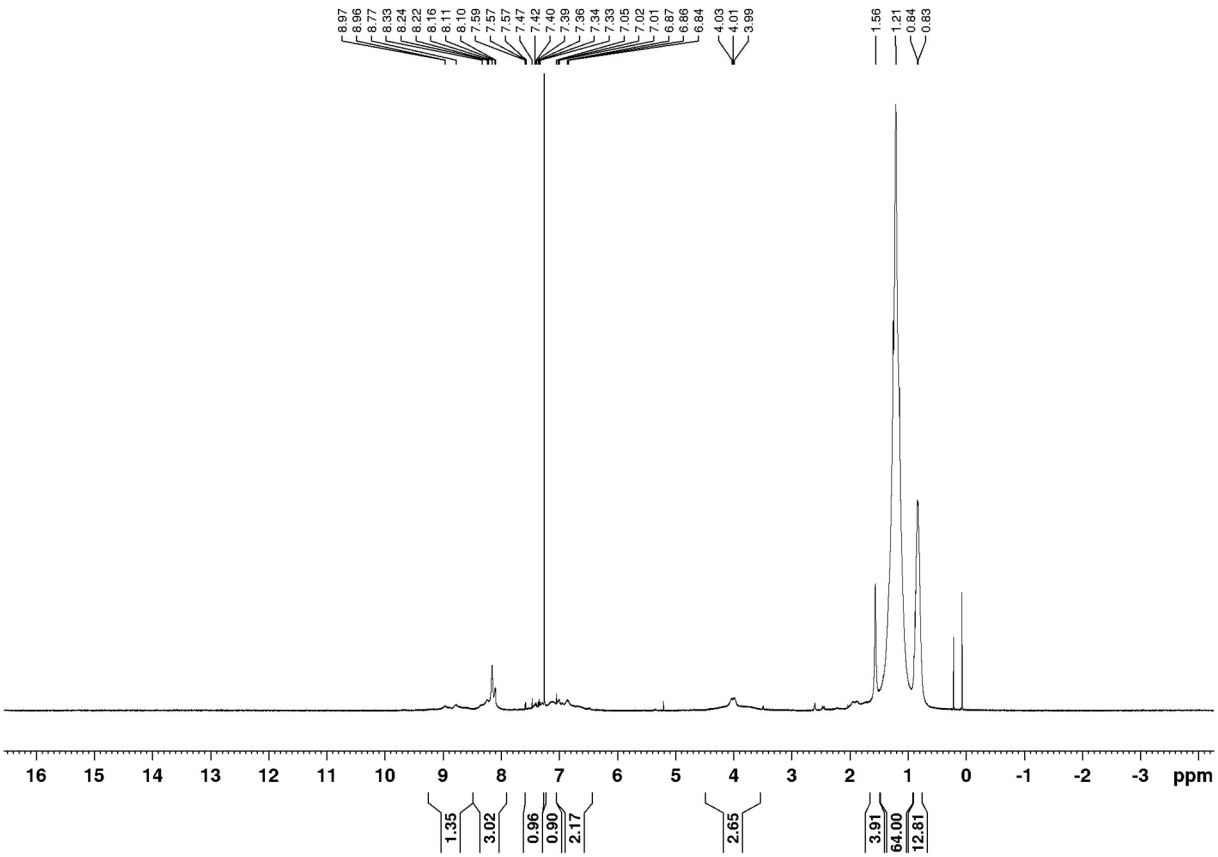


Figure S 27: ^{1}H NMR spectrum of ***poly*-DTDB-*alt*-DPP** (500 MHz, in $CDCl_3$).

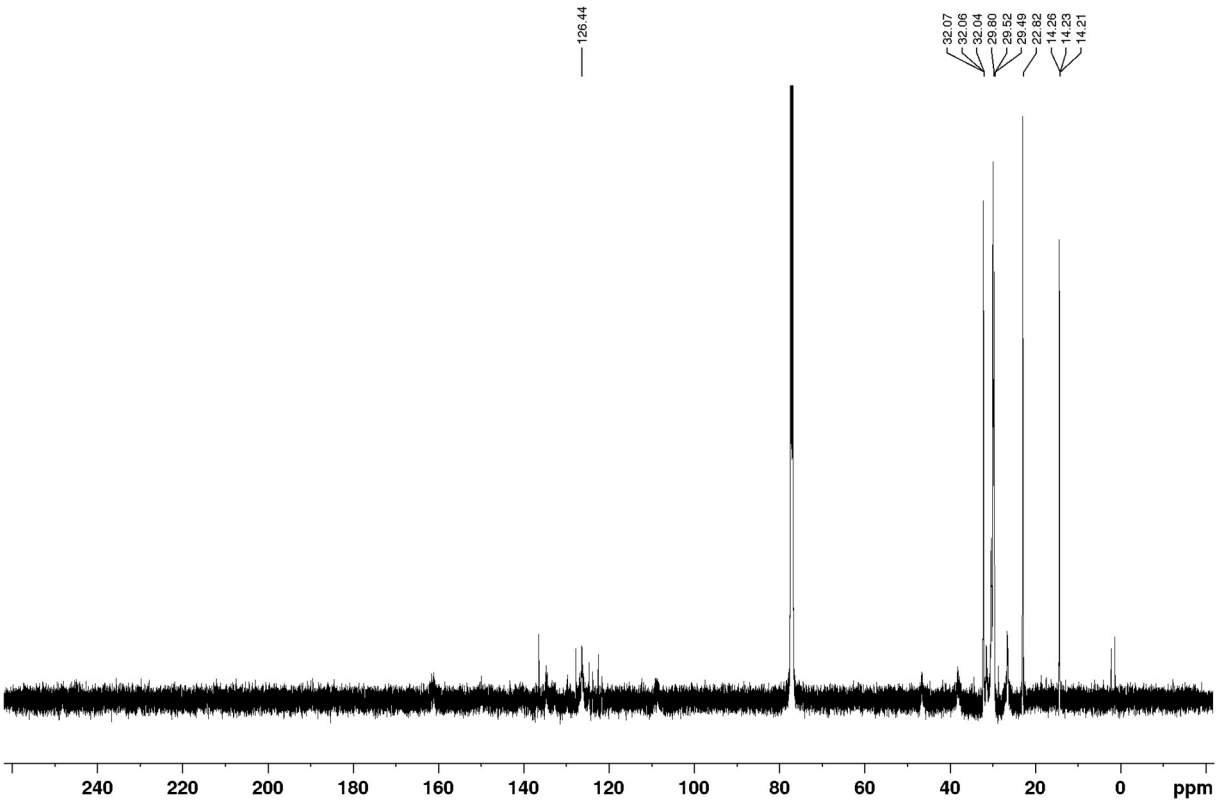


Figure S 28: $^{13}C\{^{1}H\}$ NMR spectrum of ***poly*-DTDB-*alt*-DPP** (126 MHz, in $CDCl_3$).

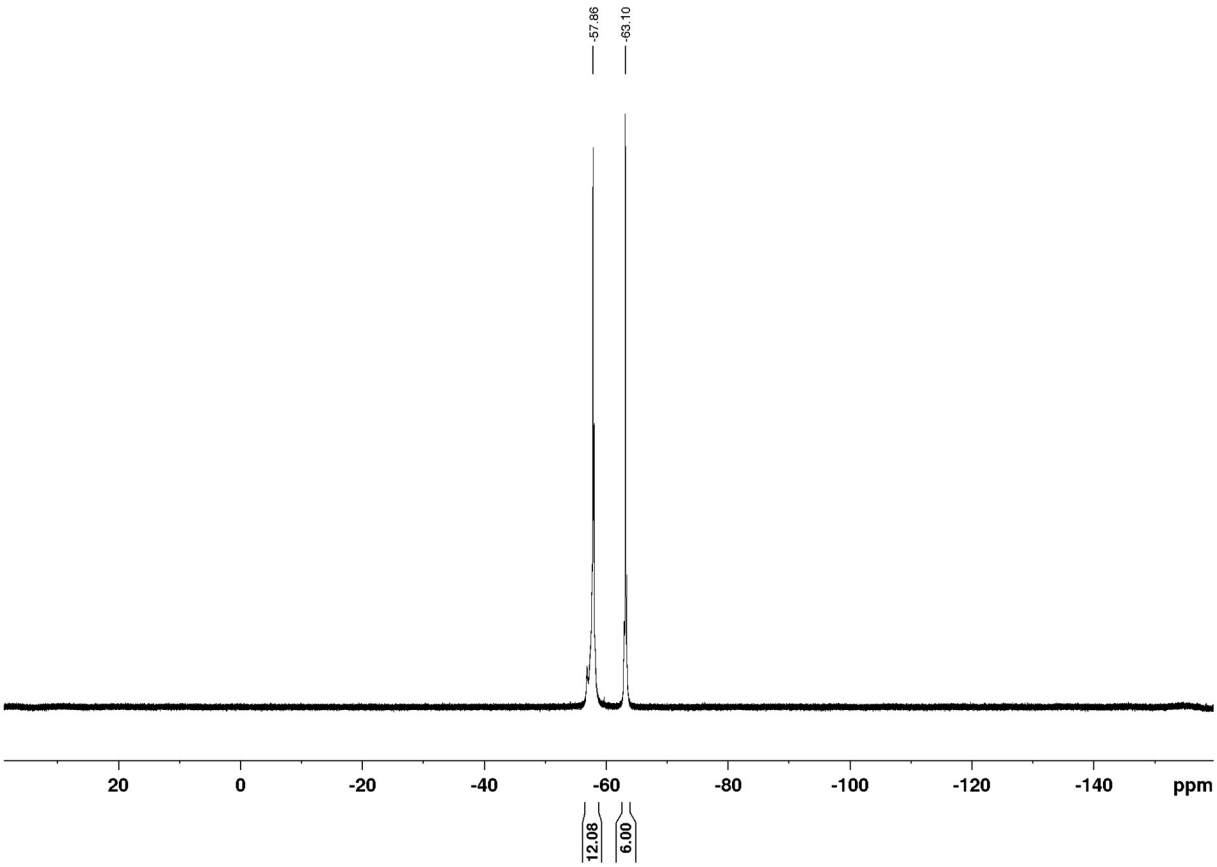


Figure S 29: ^{19}F NMR spectrum of ***poly*-DTDB-*alt*-DPP** (471 MHz, in $CDCl_3$).

1.4 High resolution mass spectrometry

Mass spectra were obtained with the use of a Thermo Scientific Exactive Plus Orbitrap MS system employing atmospheric pressure chemical ionization (APCI). The mass spectra were processed using the Qual Browser of the XCalibur software. The figures show the total spectrum in the upper part, the product peak with isotope distribution in the middle and a corresponding simulation in the lower part.

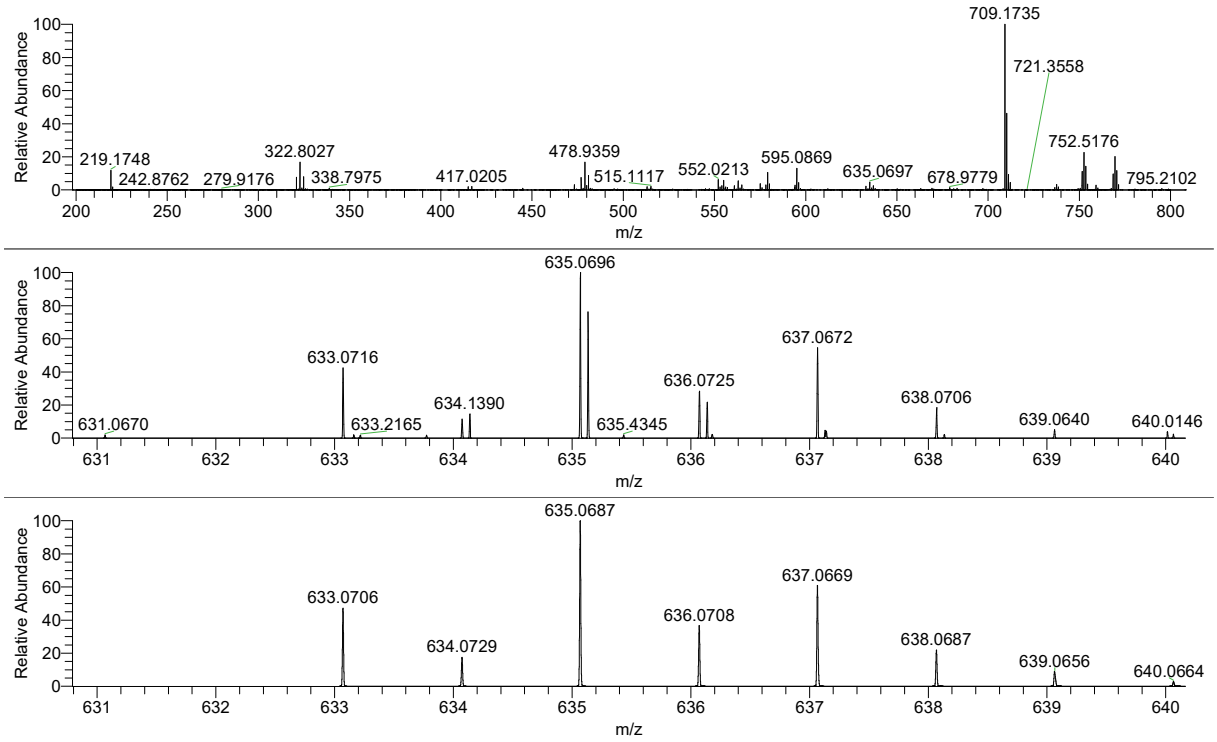


Figure S 30: High resolution mass spectrum (APCI neg) of **2**.

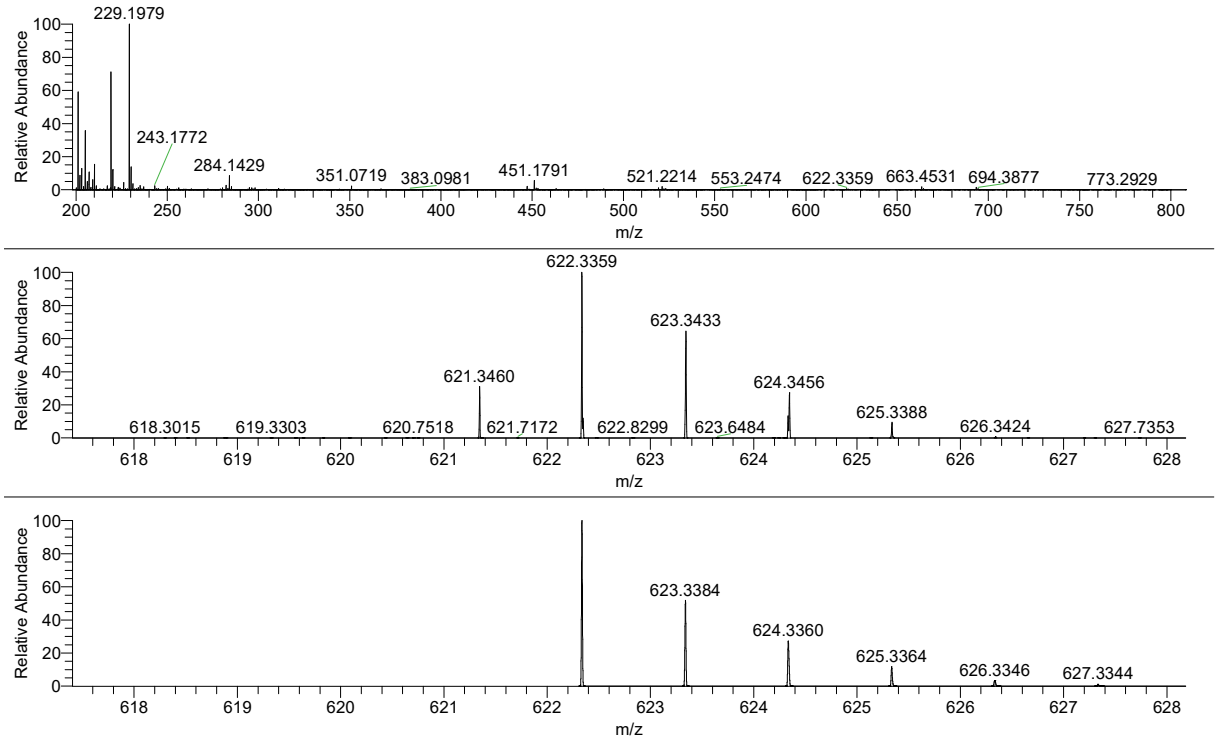


Figure S 31: High resolution mass spectrum (APCI pos) of **3**.

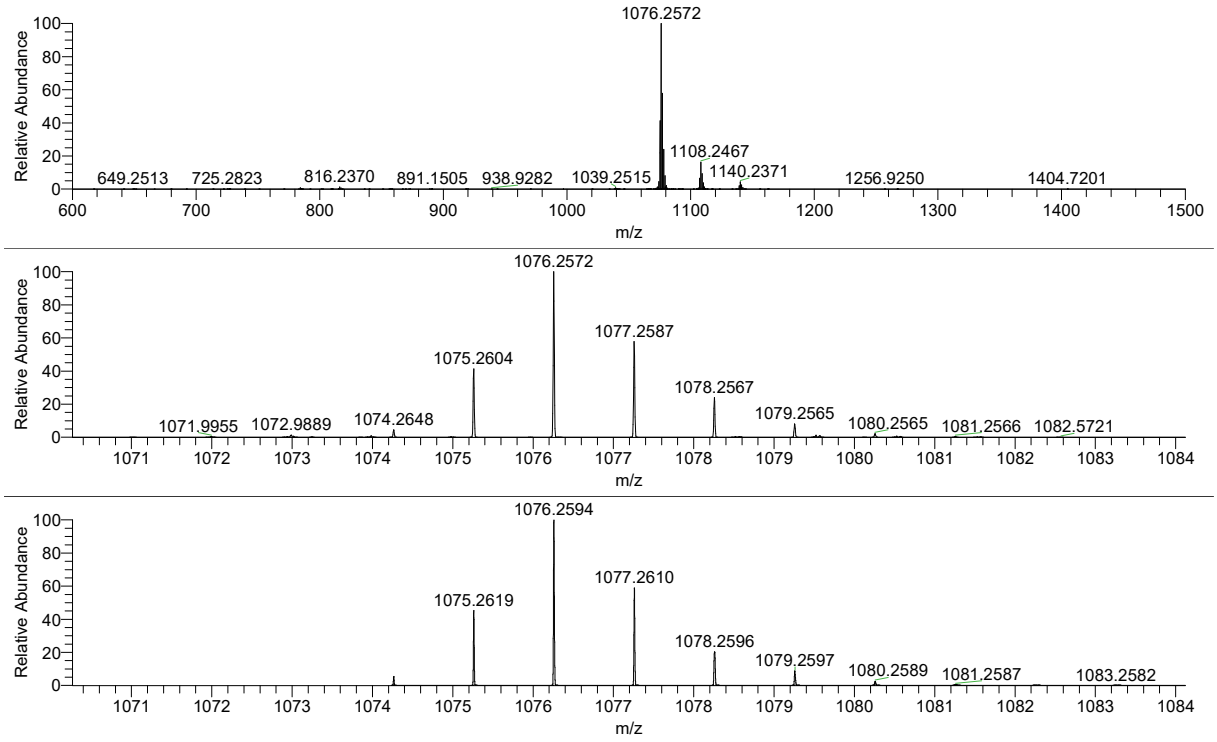


Figure S 32: High resolution mass spectrum (APCI neg) of **4**.

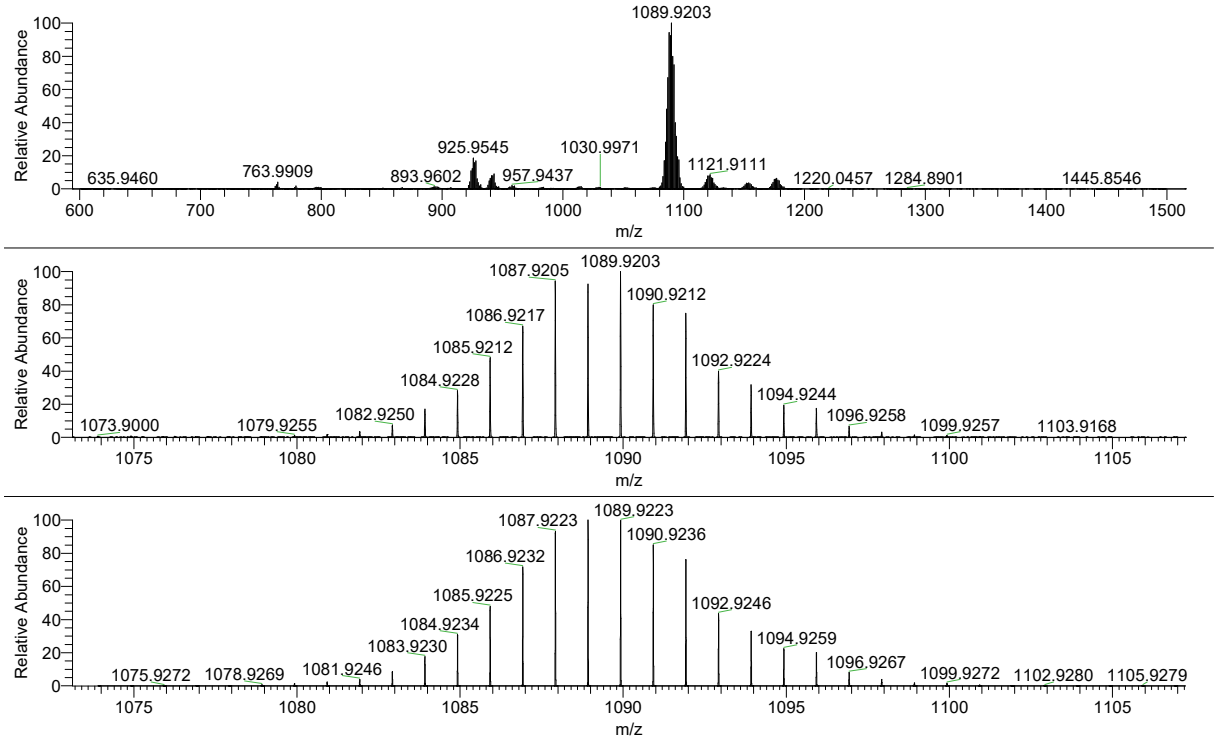


Figure S 33: High resolution mass spectrum (APCI neg) of **6**.

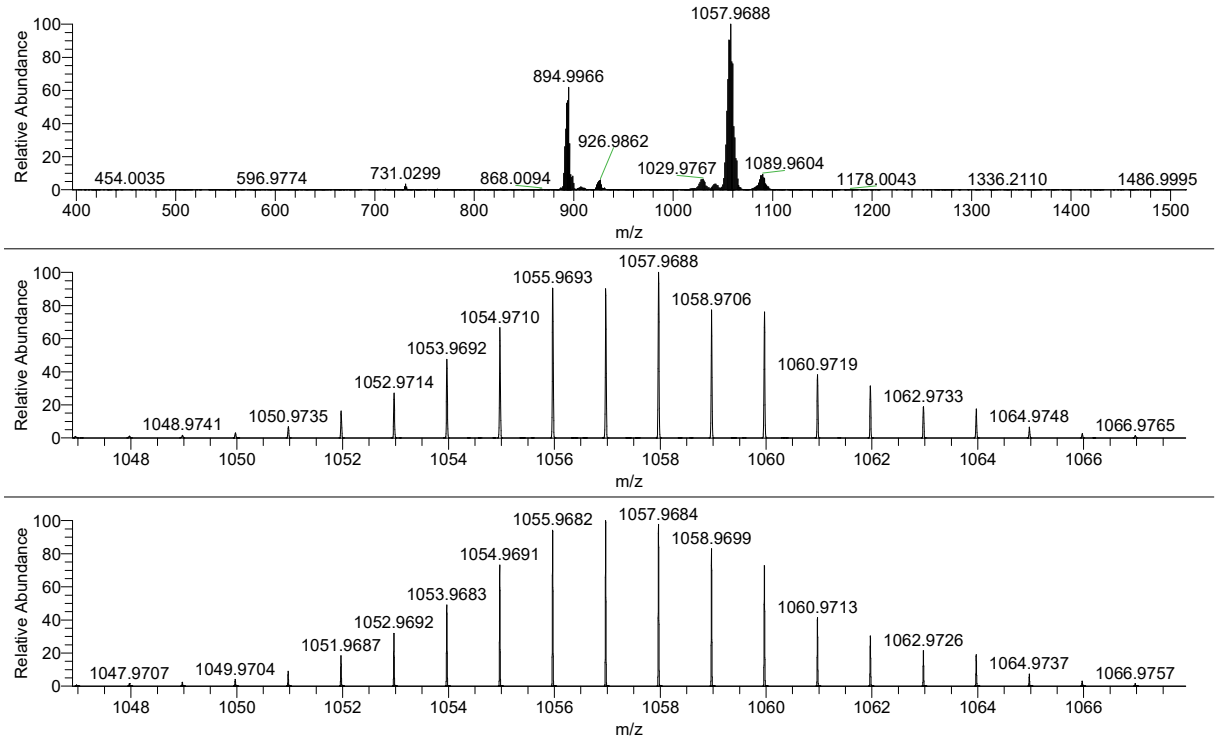
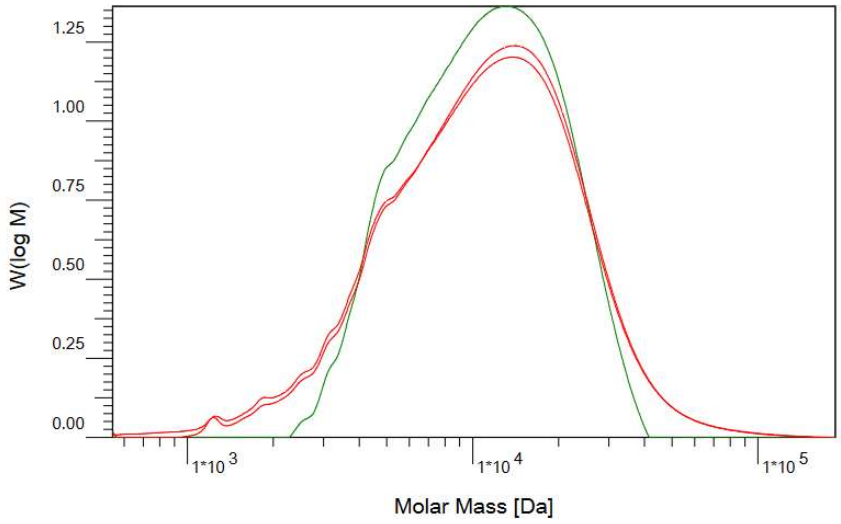


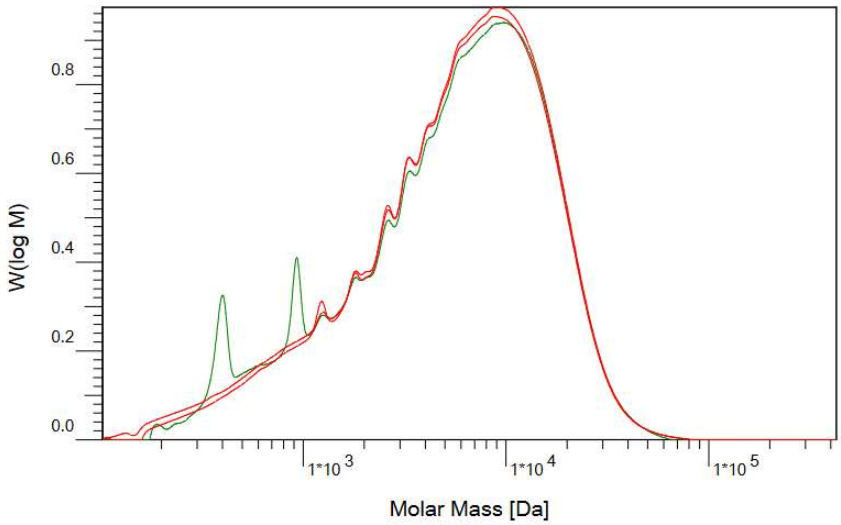
Figure S 34: High resolution mass spectrum (APCI neg) of **8**.

1.5 Gel permeation chromatography



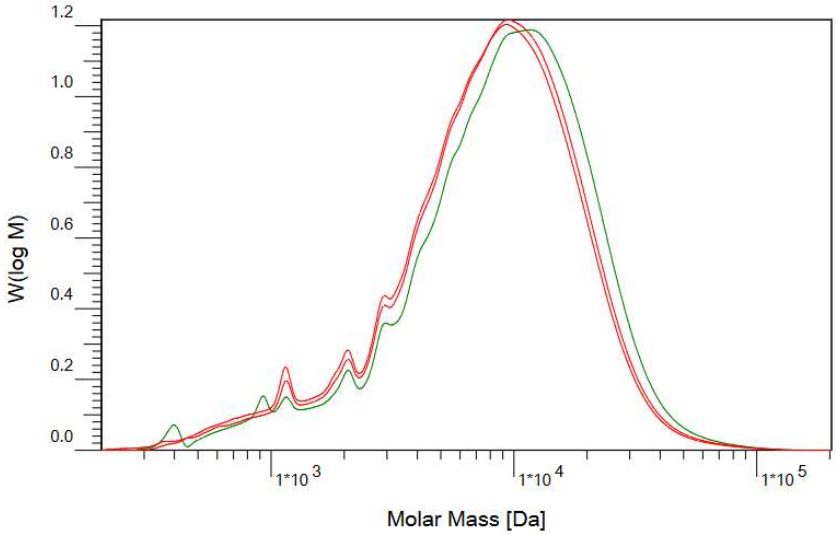
	I1: RID 1, RI Signal		I1: VWD 1, Signal A		I1: VWD 1, Signal B		
		Unsicherheit [%]		Unsicherheit [%]		Unsicherheit [%]	
Mn :	9.0591e3	100.49	8.1664e3	0.39	7.5700e3	0.17	g/mol
Mw :	1.2723e4	100.49	1.4068e4	0.38	1.3854e4	0.12	g/mol
Mz :	1.6851e4	100.49	2.2862e4	0.39	2.3345e4	0.16	g/mol
Mv :	0.000000	100.49	0.000000	0.39	0.000000	0.17	g/mol
D :	1.4045e0	142.11	1.7227e0	0.54	1.8302e0	0.20	
[n]:	0.000000	0.00	0.000000	0.00	0.000000	0.00	ml/g
Vp :	2.2405e1	100.49	2.2271e1	0.37	2.2288e1	0.11	ml
Mp :	1.3384e4	100.49	1.4145e4	0.40	1.4048e4	0.19	g/mol
FI :	5.7376e0	100.49	8.3723e2	0.37	6.4687e2	0.11	ml*V
< 545	0.00	100.49	0.00	0.37	0.00	0.11	
w% :	100.00	100.49	100.00	0.37	100.00	0.11	
> 186623	0.00	100.49	0.00	0.37	0.00	0.11	

Figure S 35: Original GPC data of ***poly*-DFDB-*alt*-BDT** (in THF, vs. polystyrene standard).



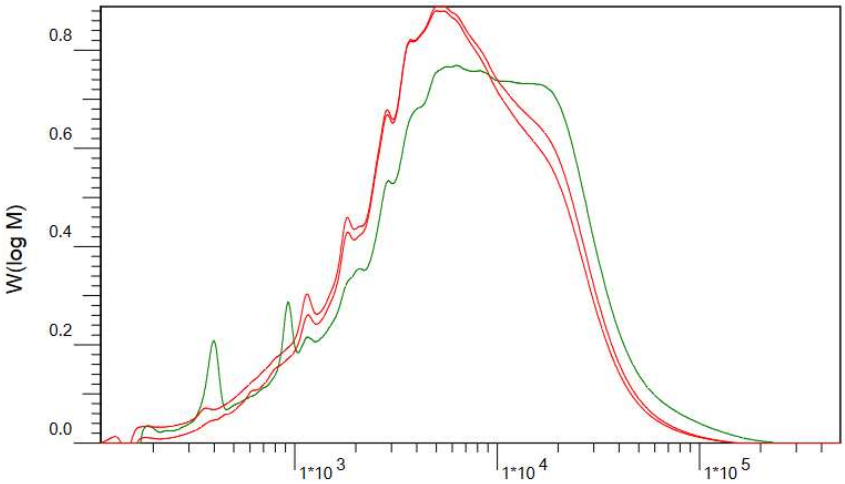
	I1: RID 1, RI Signal		I1: VWD 1, Signal A		I1: VWD 1, Signal B		
		Unsicherheit [%]		Unsicherheit [%]		Unsicherheit [%]	
Mn :	2.4221e3	12.98	2.6999e3	0.90	2.3986e3	1.26	g/mol
Mw :	8.2255e3	12.98	8.4643e3	0.89	8.2807e3	1.25	g/mol
Mz :	1.5029e4	12.98	1.5251e4	0.90	1.5219e4	1.26	g/mol
Mv :	0.000000	12.98	0.000000	0.90	0.000000	1.26	g/mol
D :	3.3960e0	18.35	3.1350e0	1.26	3.4523e0	1.77	
[n]:	0.000000	0.00	0.000000	0.00	0.000000	0.00	ml/g
Vp :	2.3215e1	12.95	2.3432e1	0.14	2.3449e1	0.12	ml
Mp :	9.6008e3	12.98	8.7788e3	0.90	8.7185e3	1.26	g/mol
FI :	8.7075e0	12.95	1.0137e3	0.14	8.2293e2	0.12	ml*V
< 102	0.00	12.95	0.00	0.14	0.00	0.12	
w% :	100.00	12.95	100.00	0.14	100.00	0.12	
> 425872	0.00	12.95	0.00	0.14	0.00	0.12	

Figure S 36: Original GPC data of ***poly*-DTDB-*alt*-BDT** (in THF, vs. polystyrene standard).



	I1: RID 1, RI Signal	Unsicherheit [%]	I1: VWD 1, Signal A	Unsicherheit [%]	I1: VWD 1, Signal B	Unsicherheit [%]	
Mn :	5.1516e3	4.12	4.9685e3	0.70	4.5609e3	0.50	g/mol
Mw :	1.1935e4	4.12	1.0835e4	0.69	1.0393e4	0.49	g/mol
Mz :	2.0270e4	4.12	1.8735e4	0.70	1.8135e4	0.50	g/mol
Mv :	0.000000	4.12	0.000000	0.70	0.000000	0.50	g/mol
D :	2.3168e0	5.82	2.1808e0	0.98	2.2787e0	0.70	
[n]:	0.000000	0.00	0.000000	0.00	0.000000	0.00	ml/g
Vp :	2.2745e1	4.12	2.3264e1	0.69	2.3298e1	0.47	ml
Mp :	1.1644e4	4.12	9.4075e3	0.71	9.2786e3	0.51	g/mol
FI :	2.8604e1	4.12	6.7024e2	0.69	5.8350e2	0.47	ml*V
< 200	0.00	4.12	0.00	0.69	0.00	0.47	
w% :	100.00	4.12	100.00	0.69	100.00	0.47	
> 203087	0.00	4.12	0.00	0.69	0.00	0.47	

Figure S 37: Original GPC data of ***poly*-DFDB-*alt*-DPP** (in THF, vs. polystyrene standard).



	I1: RID 1, RI Signal	Unsicherheit [%]	I1: VWD 1, Signal A	Unsicherheit [%]	I1: VWD 1, Signal B	Unsicherheit [%]	
Mn :	3.1352e3	12.42	3.4386e3	0.38	2.7921e3	0.80	g/mol
Mw :	1.2684e4	12.42	1.0224e4	0.36	9.5577e3	0.79	g/mol
Mz :	3.3744e4	12.42	2.3232e4	0.38	2.2420e4	0.80	g/mol
Mv :	0.000000	12.42	0.000000	0.38	0.000000	0.80	g/mol
D :	4.0456e0	17.56	2.9734e0	0.52	3.4232e0	1.12	
[n]:	0.000000	0.00	0.000000	0.00	0.000000	0.00	ml/g
Vp :	2.4236e1	12.40	2.4772e1	0.23	2.4772e1	0.20	ml
Mp :	6.3009e3	12.42	5.0464e3	0.39	5.0464e3	0.81	g/mol
FI :	1.1869e1	12.40	3.1242e2	0.23	2.7159e2	0.20	ml*V
< 110	0.00	12.40	0.00	0.23	0.00	0.20	
w% :	100.00	12.40	100.00	0.23	100.00	0.20	
> 495532	0.00	12.40	0.00	0.23	0.00	0.20	

Figure S 38: Original GPC data of ***poly*-DTDB-*alt*-DPP** (in THF, vs. polystyrene standard).

1.6 Photophysical data

UV–vis spectra were obtained using a Jasco V-630 spectrophotometer. Emission spectra were recorded using an Edinburgh Instruments FLSP920 spectrometer equipped with a double monochromator for both excitation and emission, operating in right-angle geometry mode, and all spectra were fully corrected for the spectral response of the instrument. Fluorescence quantum yields were measured using a calibrated integrating sphere from Edinburgh Instruments combined with the FLSP920 spectrometer described above.

Table S 1: Photophysical properties of the copolymers in THF.

Copolymer	$\lambda_{abs,\ max}$ [nm]	ε [L mol^{-1} cm^{-1}]	$\lambda_{em,\ max}$ [nm]	QY
***poly*-DFDB-*alt*-BDT**	**478**; 514	38000; 35000	538, 580	0.24
***poly*-DTDB-*alt*-BDT**	**513**; 552^{s}	45000; 37000	648	0.11
***poly*-DFDB-*alt*-DPP**	344; 434; **681**; 730^{s}	23000; 22000; 45000; 42000	n. d.	-
***poly*-DTDB-*alt*-DPP**	344; 447; **721**	16000; 21000; 53000	n. d.	-

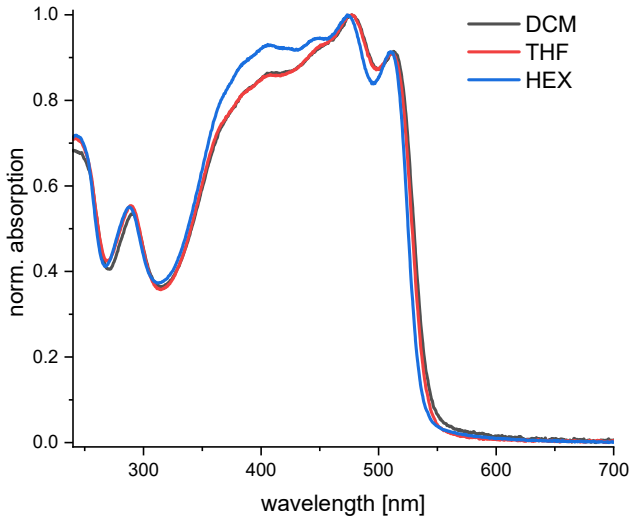


Figure S 39: Normalized absorption spectra of ***poly*-DFDB-*alt*-BDT** in DCM, THF and *n*-hexane.

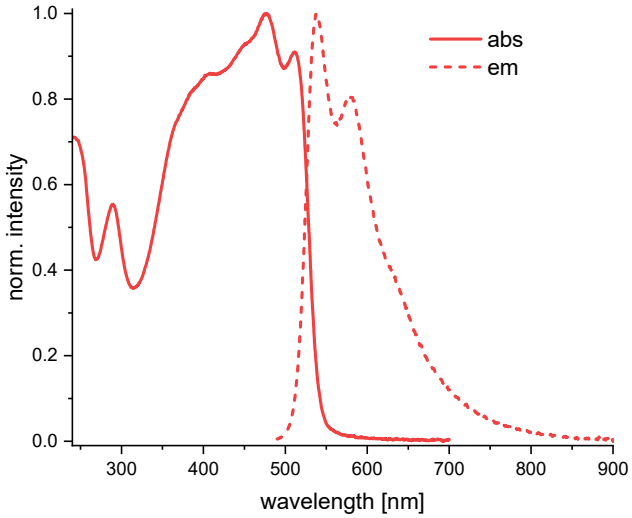


Figure S 40: Normalized absorption and emission spectra of ***poly*-DFDB-*alt*-BDT** in THF.

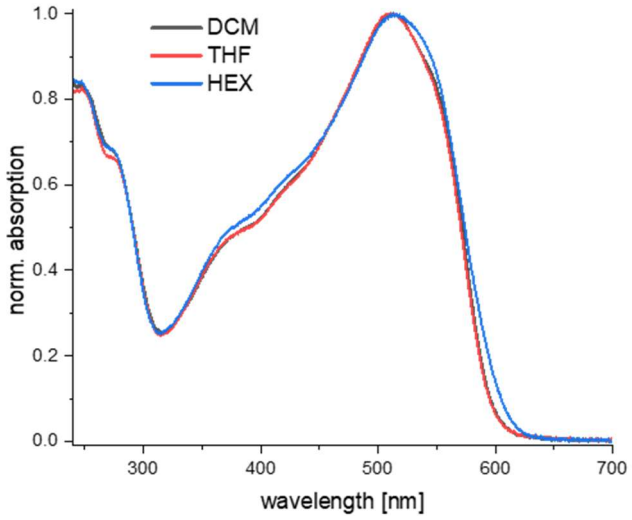


Figure S 41: Normalized absorption spectra of ***poly*-DTDB-*alt*-BDT** in DCM, THF and *n*-hexane.

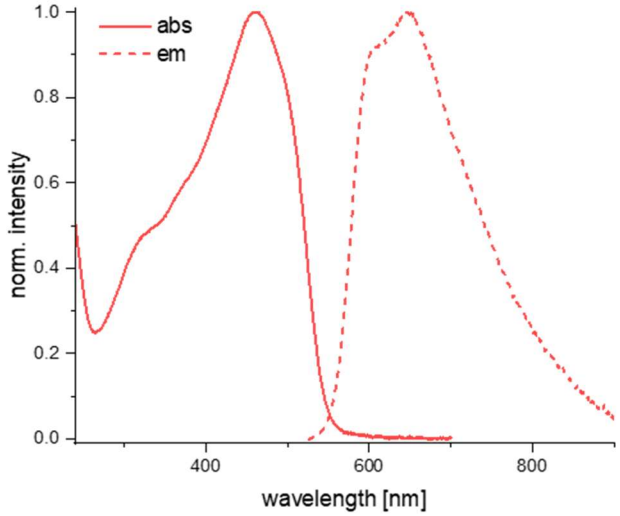


Figure S 42: Normalized absorption and emission spectra of ***poly*-DTDB-*alt*-BDT** in THF.

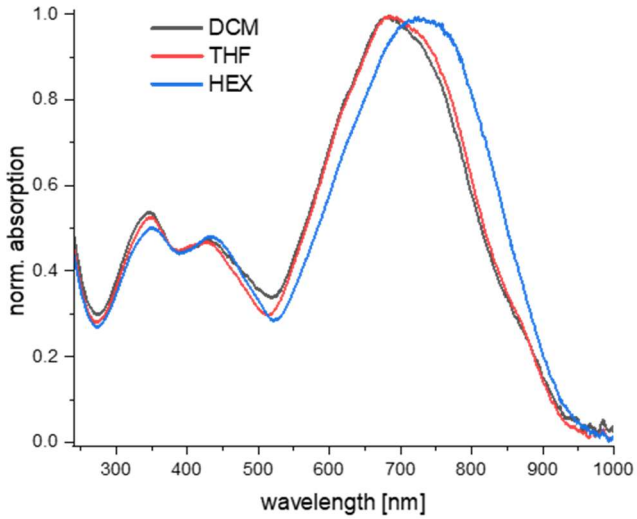


Figure S 43: Normalized absorption spectra of ***poly*-DFDB-*alt*-DPP** in DCM, THF and *n*-hexane.

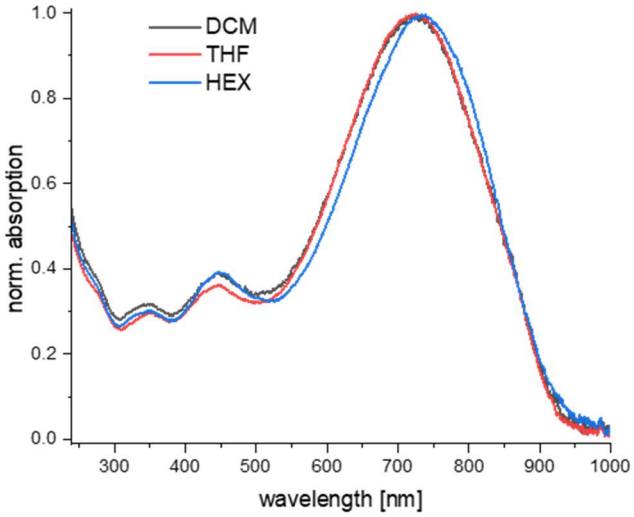


Figure S 44: Normalized absorption spectra of ***poly*-DTDB-*alt*-DPP** in DCM, THF and *n*-hexane.

1.7 Cyclic voltammetry

Cyclic voltammetry experiments were performed using a Gamry Instruments Reference 600 potentiostat. Tetra-n-butylammonium hexafluorophosphate ([n-Bu_4N][PF_6]) was employed as the supporting electrolyte. The scans were referenced after the addition of a small amount of ferrocene as internal standard. The potentials are reported relative to the ferrocene/ferrocenium couple.

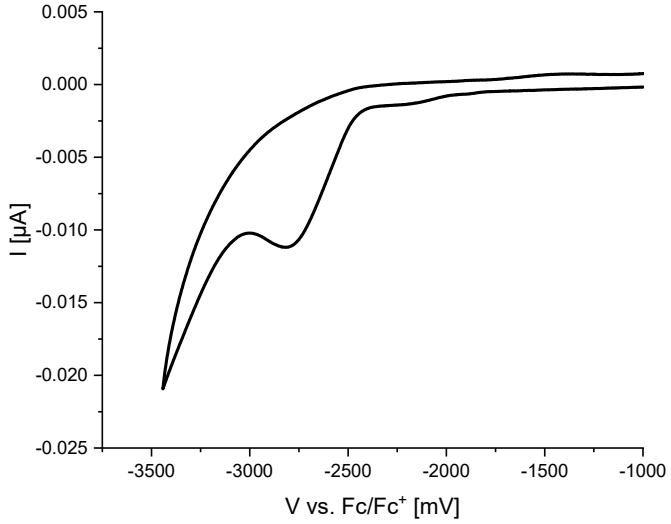


Figure S 45: Cyclic voltammogram of ***poly*-DFDB-*alt*-BDT** in THF (vs. $[Cp_2Fe]^{0/+}$, scan rate: 250 mVs^{-1}).

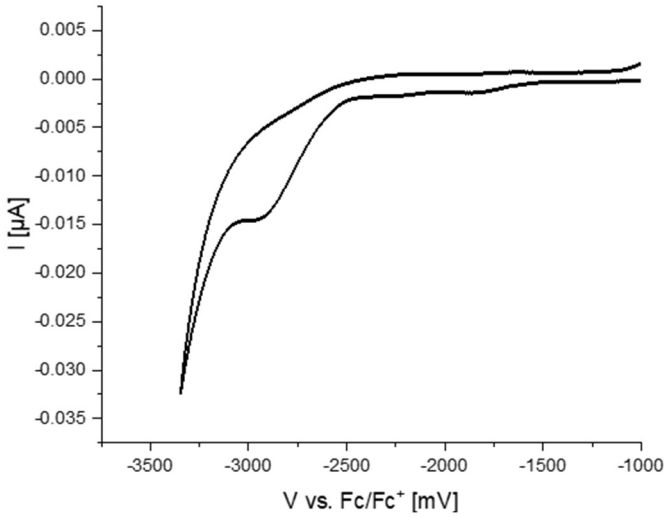


Figure S 46: Cyclic voltammogram of ***poly*-DTDB-*alt*-BDT** in THF (vs. $[Cp_2Fe]^{0/+}$, scan rate: 250 mVs^{-1}).

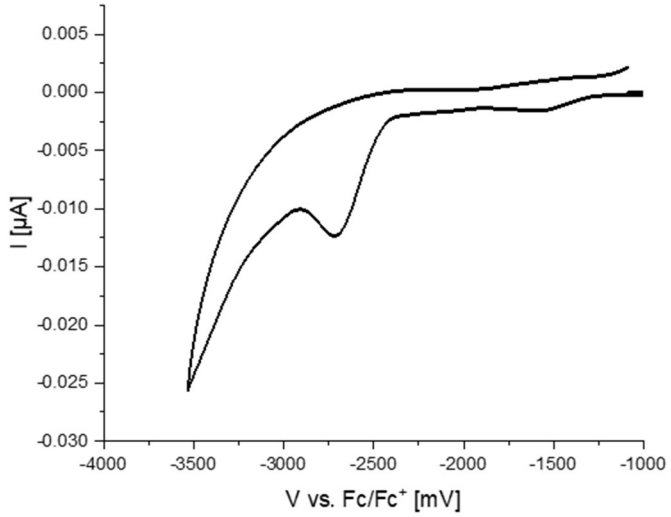


Figure S 47: Cyclic voltammogram of ***poly*-DFDB-*alt*-DPP** in THF (vs. $[Cp_2Fe]^{0/+}$, scan rate: 250 mVs^{-1}).

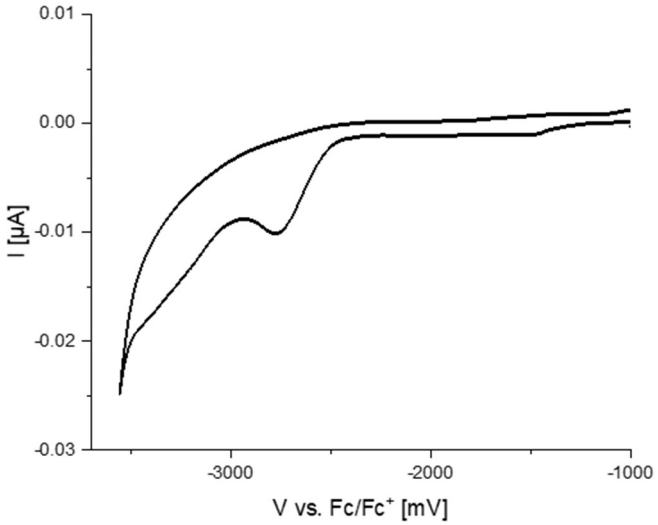


Figure S 48: Cyclic voltammogram of ***poly*-DTDB-*alt*-DPP** in THF (vs. $[Cp_2Fe]^{0/+}$, scan rate: 250 mVs^{-1}).

1.8 Photoelectrochemistry

Preparation: NiO on FTO:

Synthesis of NiO thin film electrodes NiO thin films were hydrothermally grown on fluorine−doped tin oxide (FTO) glasses (2.2 mm thick, Sigma−Aldrich) followed with an extra thermal treatment. Prior to the hydrothermal route, the FTO glasses were ultrasonically washed in acetone, ethanol, and deionized water for 2 min each, and were then dried at room−temperature. In a typical hydrothermal route, 2.34 g nickel acetate tetrahydrate (Alfa Aesar) and 1.32 g hexamethylenetetramine (Sigma−Aldrich) were firstly dissolved in 56 mL Milli−Q water under vigorous stirring for 30 min until a bottle green transparent solution was obtained. 10 mL of the mixed solution was then loaded into a Teflon−lined autoclave with 15 mL in volume. A cleaned FTO substrate was subsequently placed against the wall with the conducting side facing down. The hydrothermal reaction was performed at 110 °C for 6 h, with heating rate of 2°C min^{-1}. After the autoclaves were allowed to cool down, the resulting substrates with a light green coating were cautiously washed with deionized water, following by thermal treatment at 450 °C for 30 min to obtain the cubic phase of NiO.

Figure S 49: Nickeloxide−nanoflakes on the FTO−substrate before (left) and after dropcasting the Copolymers on a 0.785 cm^2 large area (right).

Table S 2: Summary of the photoelectrochemistry data.

Compound	Color(THF)	Type	Edge	Bandgap E_g	Other edge
***poly*-DFDB-*alt*-BDT**	orange	n	CBE: +0.05V	2.0 eV	VBE: +2.05V
***poly*-DTDB-*alt*-BDT**	red	p	VBE: +1.35V	1.5 eV	CBE: −0.15V
***poly*-DFDB-*alt*-DPP**	blue	p	VBE: +1.40V	1.8 eV	CBE: −0.40V
***poly*-DTDB-*alt*-DPP**	blue	p	VBE: +1.0V	1.1 eV	CBE: −0.1V

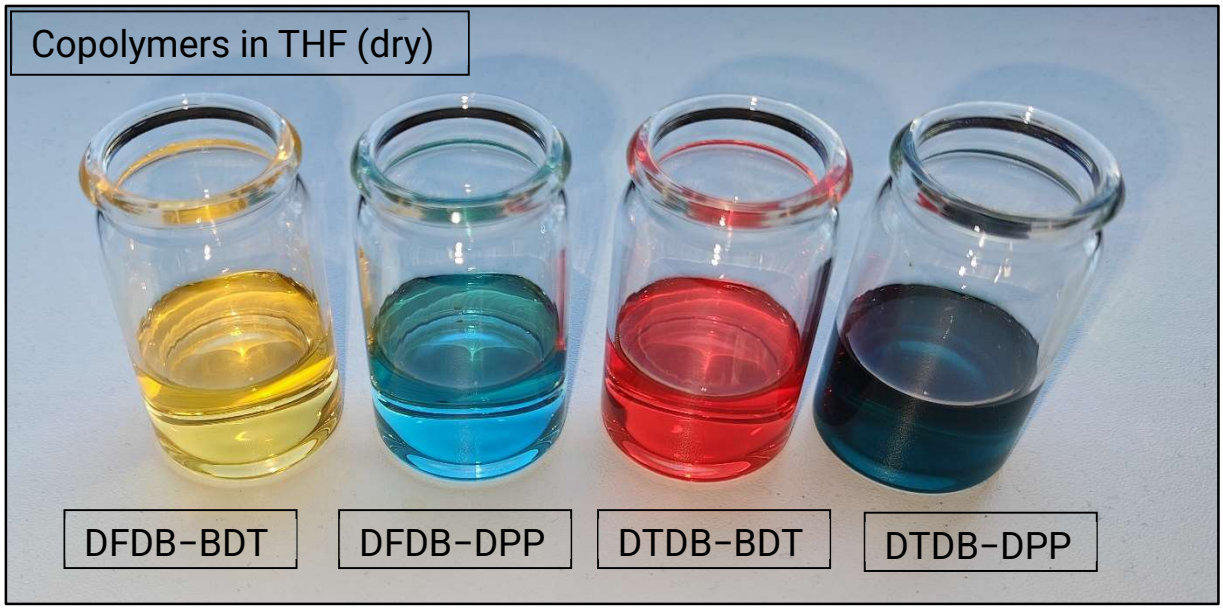


Figure S 50: Investigated copolymers.

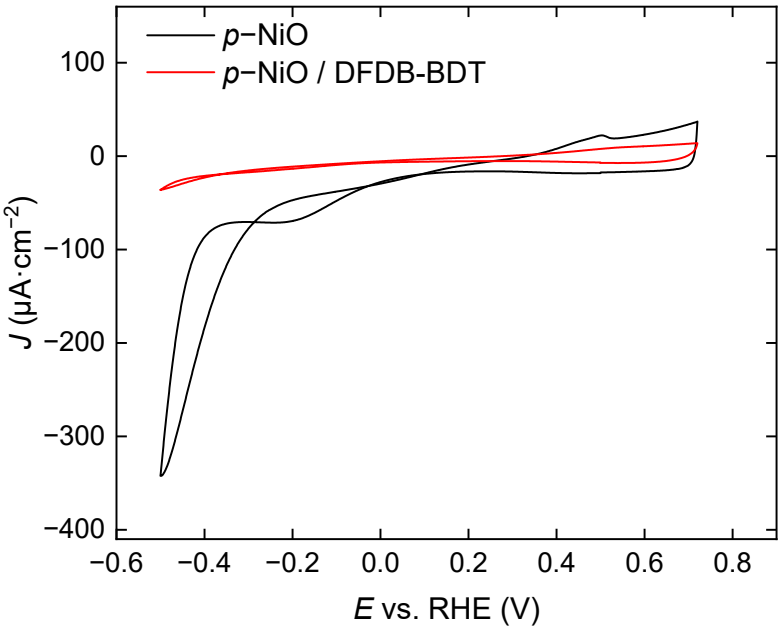


Figure S 51: Stable hysteresis of NiO/***poly*-DFDB-*alt*-BDT** on FTO−Substrate in in 0.1M KP_i−electrolyte (Sørensen) with pH 7.0 at a scan rate of 10 $mV \cdot s^{-1}$.

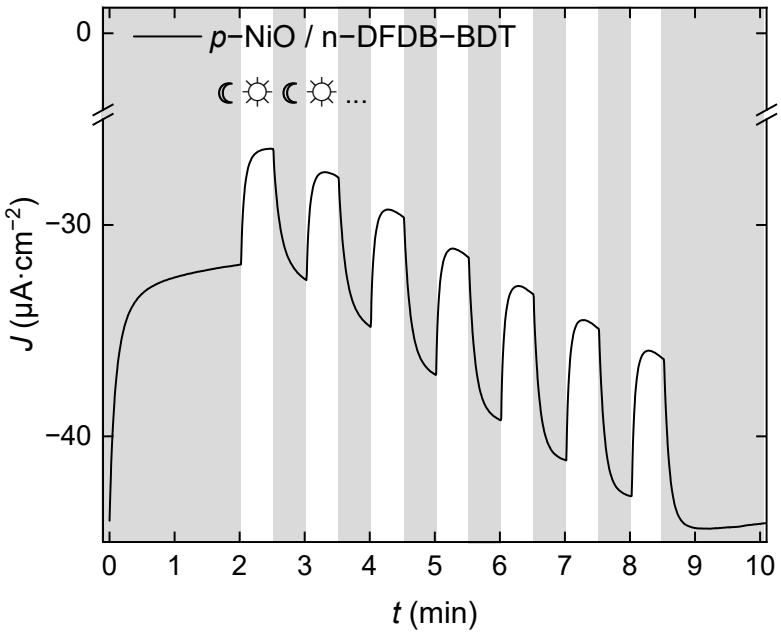


Figure S 52: CA curves recorded at −0.3 V vs. RHE of NiO/***poly*-DFDB-*alt*-BDT** in KP_i (pH 7.0) under interrupted AM 1.5G illumination.

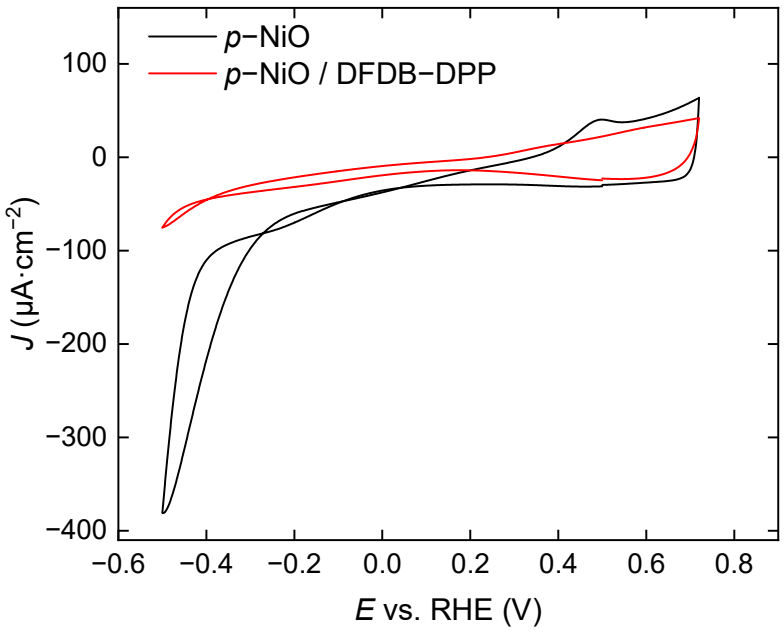


Figure S 53: Stable hysteresis of NiO/***poly*-DFDB-*alt*-DPP** on FTO−Substrate in in 0.1M KP_i−electrolyte (Sørensen) with pH 7.0 at a scan rate of 10 $mV \cdot s^{-1}$.

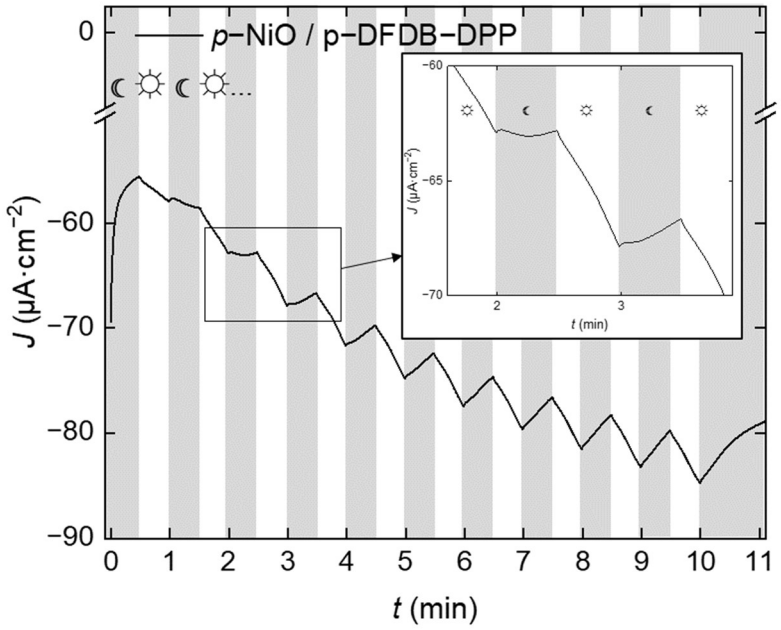


Figure S 54: CA curves recorded at −0.3 V vs. RHE of NiO/***poly*-DFDB-*alt*-DPP** in KP_i (pH 7.0) under interrupted AM 1.5G illumination. Inset: Zoomed region.

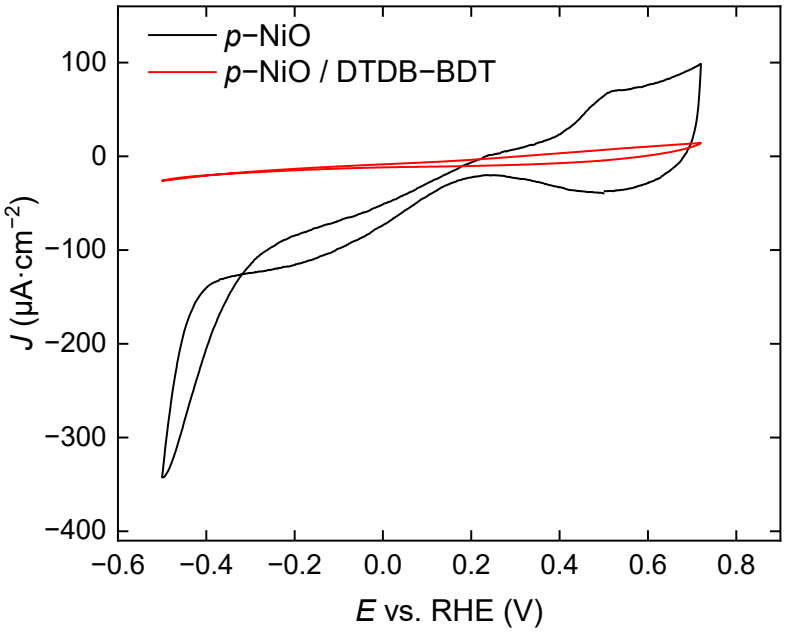


Figure S 55: Stable hysteresis of NiO/***poly*-DTDB-*alt*-BDT** on FTO–Substrate in in 0.1M KP_i–electrolyte (Sørensen) with pH 7.0 at a scan rate of 10 $mV \cdot s^{-1}$.

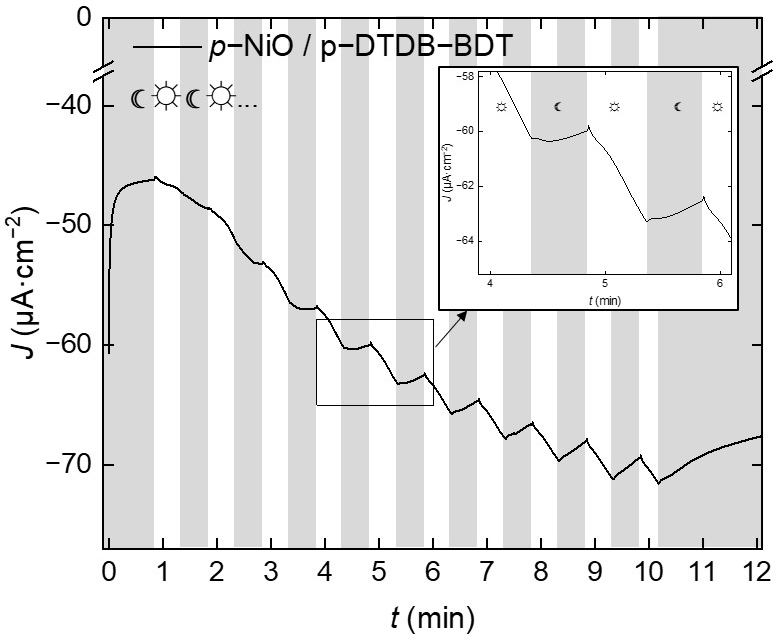


Figure S 56: CA curves recorded at −0.3 V vs. RHE of NiO/***poly*-DTDB-*alt*-BDT** in KP_i (pH 7.0) under interrupted AM 1.5G illumination. Inset: Zoomed region.

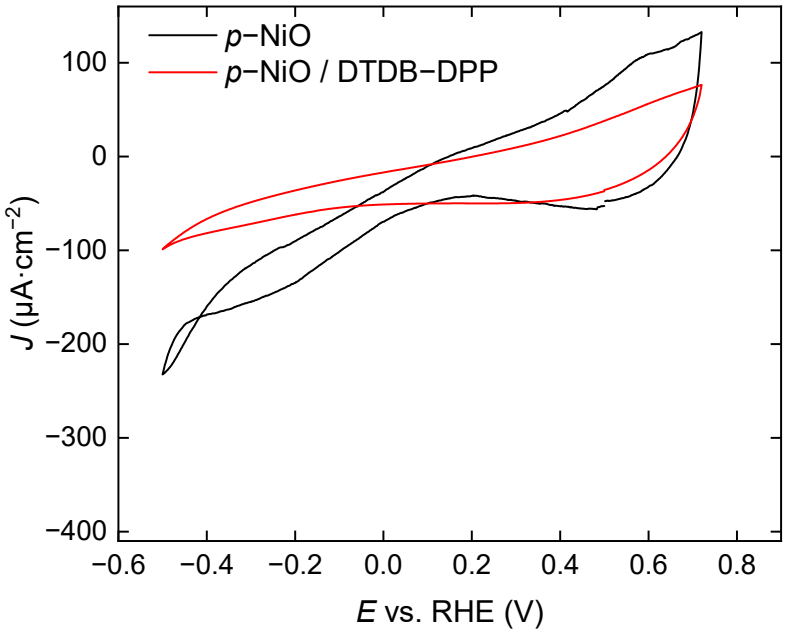


Figure S 57: Stable hysteresis of NiO/***poly*-DTDB-*alt*-DPP** on FTO−Substrate in in 0.1M KP_i−electrolyte (Sørensen) with pH 7.0 at a scan rate of 10 $mV \cdot s^{-1}$.

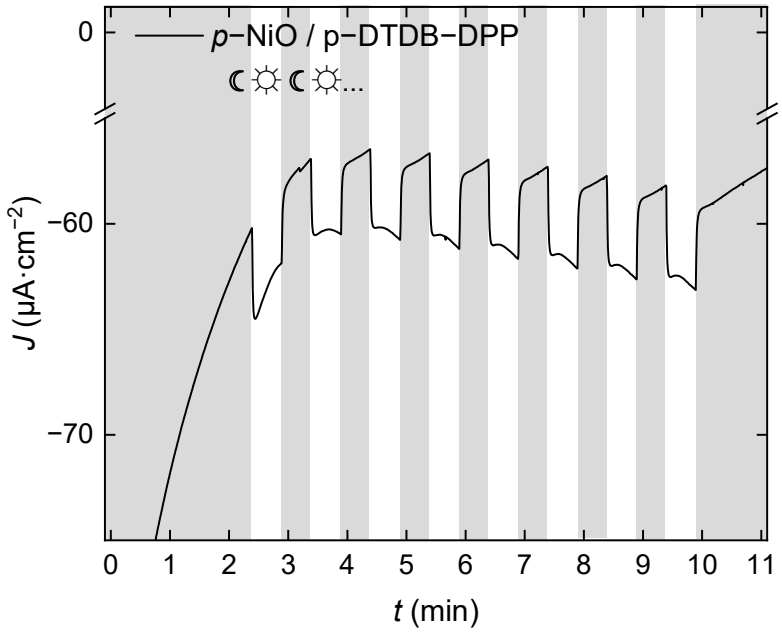


Figure S 58: CA curves recorded at −0.3 V vs. RHE of NiO/***poly*-DTDB-*alt*-DPP** in KP_i (pH 7.0) under interrupted AM 1.5G illumination.

***UV–Vis Spectroscopy*.** UV−vis spectra of **DFDB(DTDB)−BDT(DPP)** were recorded on a VWR UV−3100PC spectrophotometer. Tauc plots were calculated via the Kubelka Munk function $F(R_\infty) = (1-R)^2/2R$ to determine the bandgap size E_g. One of the most general forms of the Tauc plot is with $(F(R_\infty)h{\cdot}\nu)^{1/r}$ as the y−axis and $h{\cdot}\nu$ as the x−axis. The Bandgap of a direct and allowed transition was calculated by selecting r=½. The continuation of the tangent line at the inflection point was used to extrapolate E_g.

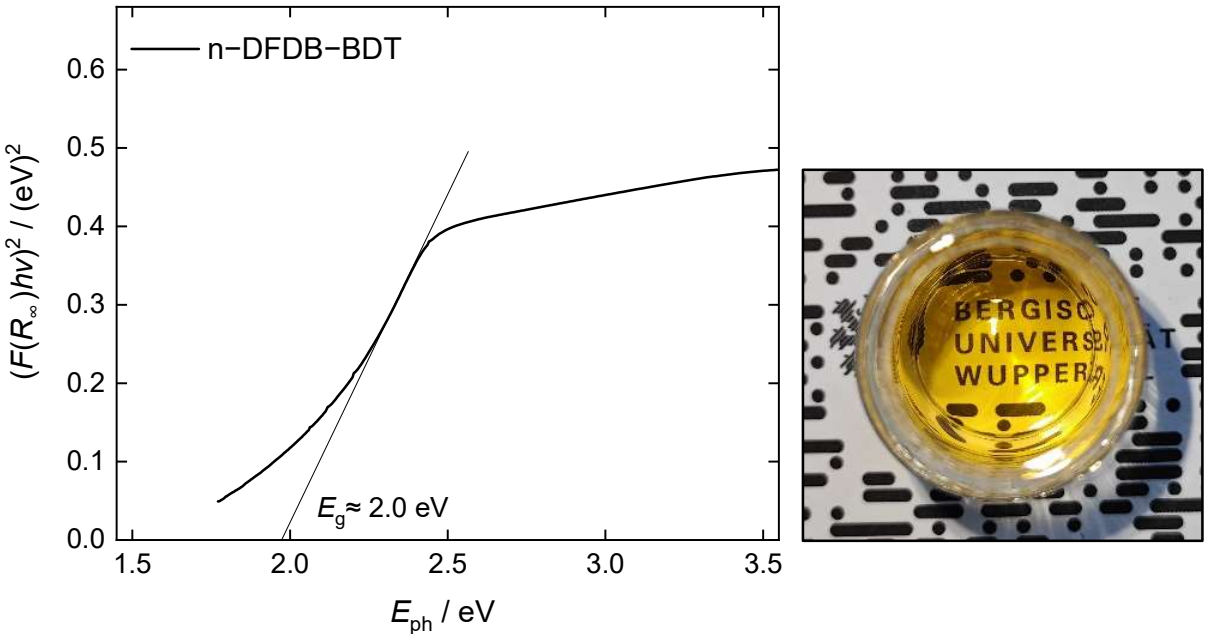


Figure S 59: Tauc plot obtained from Kubelka Munk function for **n−*poly*-DFDB-*alt*-BDT**. Inset: Copolymer solved in dried THF.

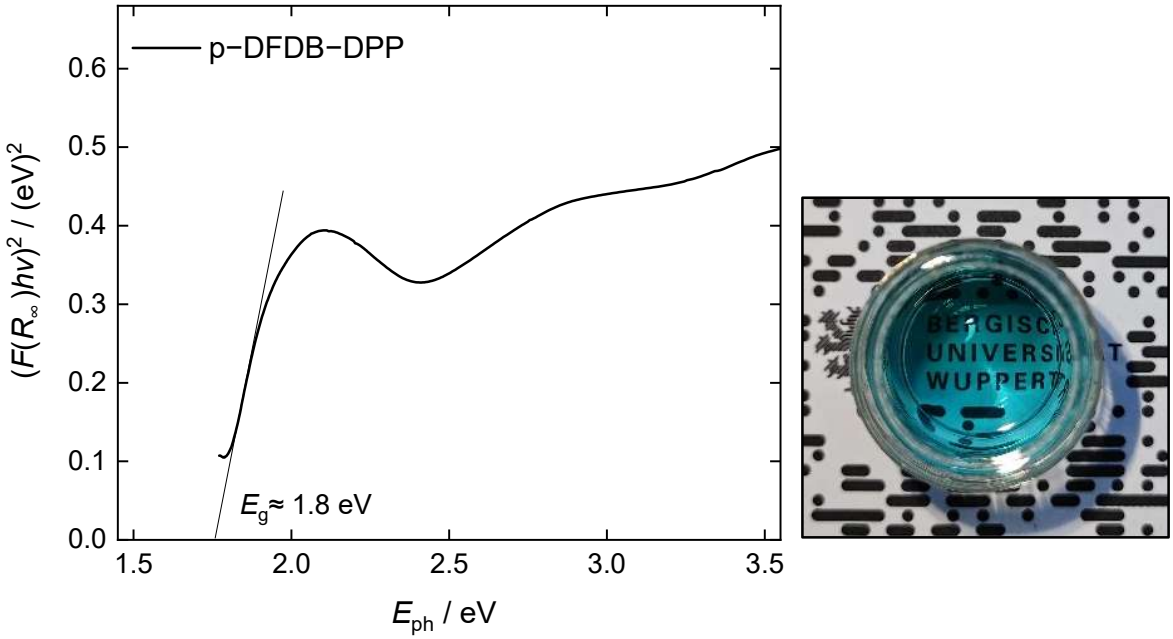


Figure S 60: Tauc plot obtained from Kubelka Munk function for **p–*poly*-DFDB-*alt*-DPP**. Inset: Copolymer solved in dried THF.

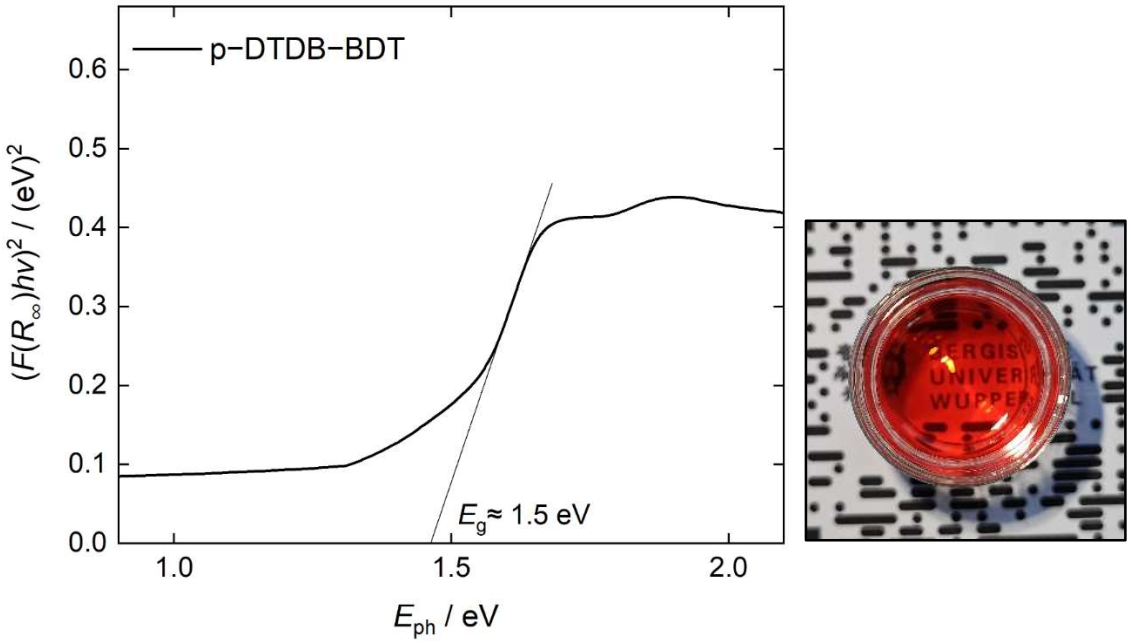


Figure S 61: Tauc plot obtained from Kubelka Munk function for **p–*poly*-DTDB-*alt*-BDT**. Inset: Copolymer solved in dried THF.

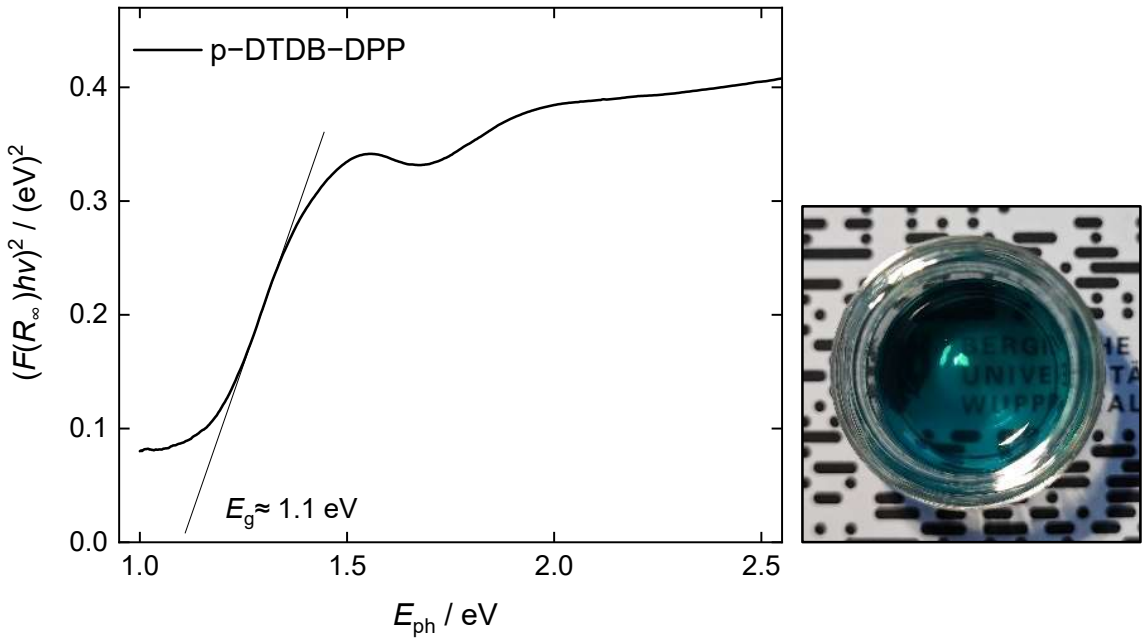


Figure S 62: Tauc plot obtained from Kubelka Munk function for **p−*poly*-DTDB-*alt*-DPP**. Inset: Copolymer solved in dried THF.

Mott−Schottky experiments. p−NiO / **DFDB**(or: **DTDB**)−**BDT**(or: **DPP**) electrodes were prepared by dropcasting a solution of the copolymers dissolved in dried THF onto the previously prepared p−NiO and evaporating the solvent in an ambient atmosphere. The Mott−Schottky (MS) measurements were performed in a potentiostat (BioLogic SP−300) operating in a three−electrode setup and floating ground. The fabricated electrode, an Ag/AgCl electrode in a sat. KCl solution and a platinum wire were used as a working electrode, a reference electrode, and a counter electrode, respectively. The measured potential was recorded vs. $E_{Ag/AgCl\ (KCl\ sat.)}$ (V) and then converted to E_{RHE}(V) according to the formula: E_{RHE}(V)= 0.197(V) + $E_{Ag|AgCl|KCl\ sat.}$ (V) + [0.059 ·pH] (V) at 25 °C. The measurements were performed in a 0.1M KP_i−electrolyte (Sørensen) with pH 7.0 in the dark at an AC amplitude of 10 mV with frequencies in the decadic distant range of 0.7 Hz to 700 Hz, to determine the band edge $E_{FB.}$

Capacitance measurement according to the MS function:

$$\frac{1}{{C_{sc}}^2} = \frac{2}{A^2 \varepsilon \varepsilon_0 q N_D}\left(E - E_{FB} - \frac{k_b T}{q}\right)$$

where C_{SC} is the capacitance in the Space−Charge−Layer, A is the electrode/ electrolyte interfacial area, ε is the dielectric constant of the material, ε_0 is the permittivity of free space, q is the electronic charge, N_D is the donor density (doping level), E is the applied potential, k_b is Boltzmann's constant, and T is the absolute temperature. A plot of $1/{C_{SC}}^2$ against E permits E_{FB} and $2/(A^2\varepsilon\varepsilon_0 q N_D)$ to be respectively determined from the x−axis intercept and the slope of the linear region. The semiconductor type was determined by the positive (or negative) slope of $2/(A^2\varepsilon\varepsilon_0 q N_D)$ for a n−type (or p−type) respectively. The obtained results for E_{FB} correspond approximately to the E_{CB} or E_{VB} of a n−type or p−type semiconductor respectively. When one of E_{VB} or E_{CB} potentials is defined, the other can be reasonably deduced based on $E_g = E_{VB} - E_{CB}$ analyzed via the methods above.

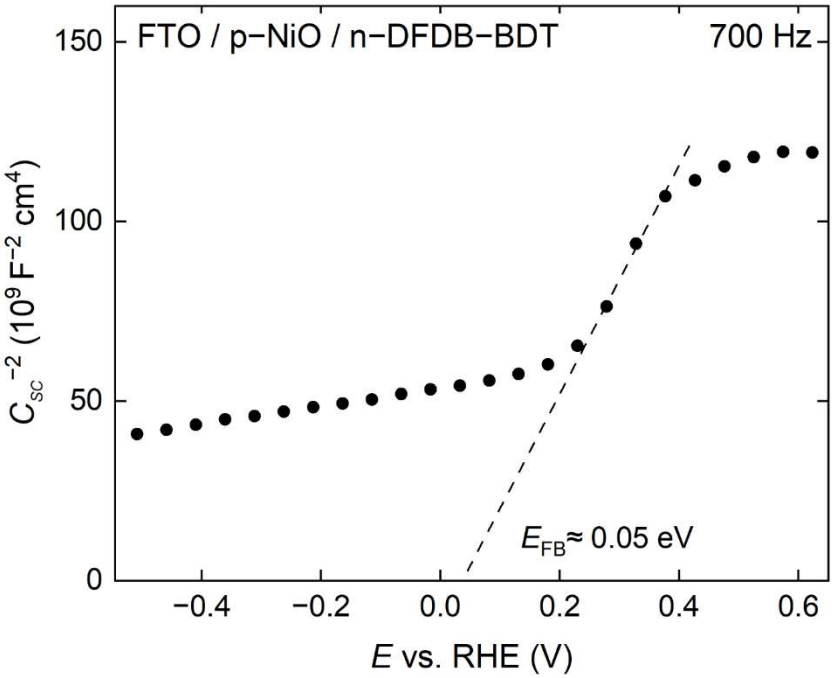


Figure S 63: Mott−Schottky plot of **n−*poly*-DFDB-*alt*-BDT** on FTO−Substrate in 0.1M KP_i−electrolyte (Sørensen) with pH 7.0 at a frequency of 700 Hz.

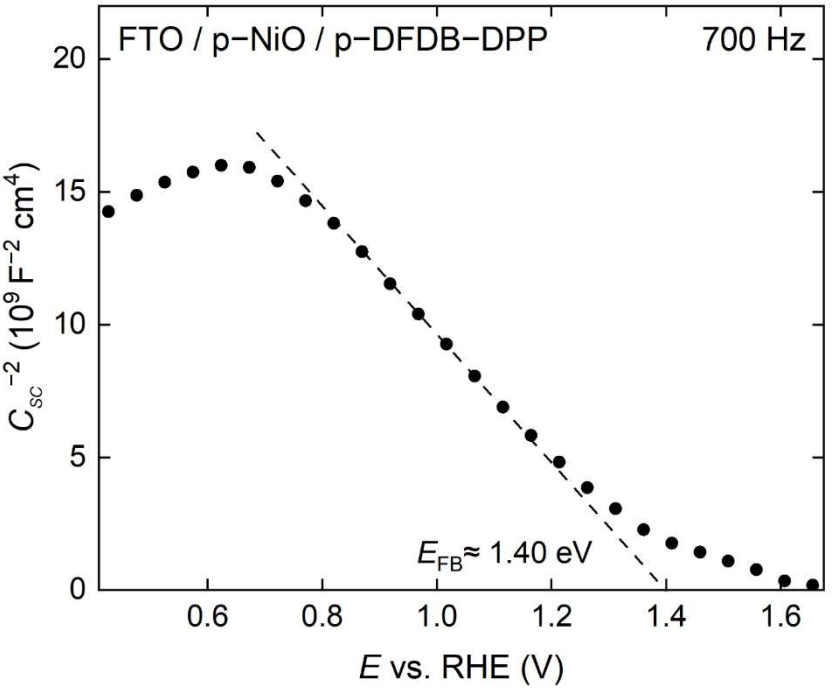


Figure S 64: Mott−Schottky plot of **p−*poly*-DFDB-*alt*-DPP** on FTO−Substrate in 0.1M KP_i−electrolyte (Sørensen) with pH 7.0 at a frequency of 700 Hz.

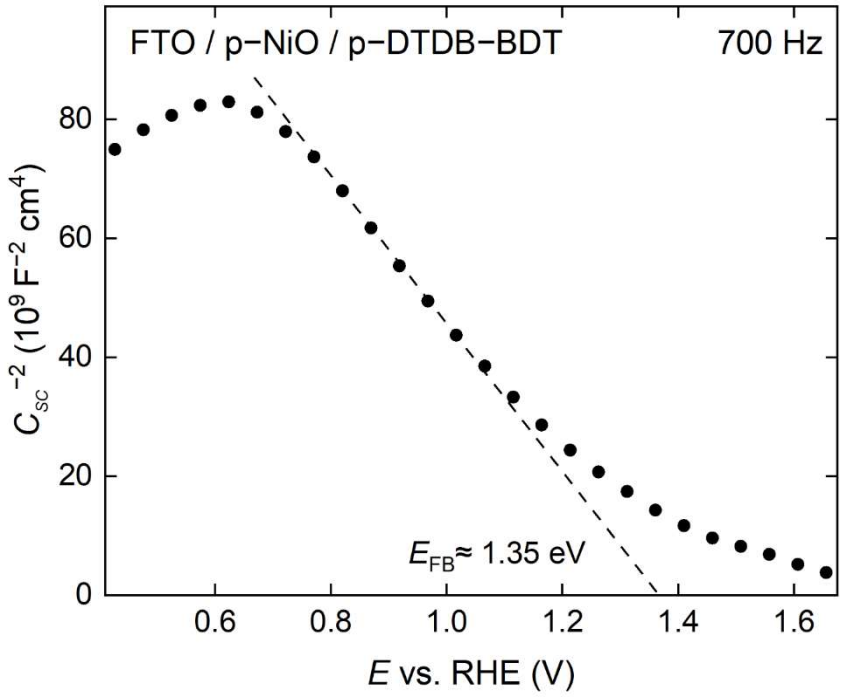


Figure S 65: Mott−Schottky plot of **p−*poly*-DTDB-*alt*-BDT** on FTO−Substrate in 0.1M KP_i−electrolyte (Sørensen) with pH 7.0 at a frequency of 700 Hz.

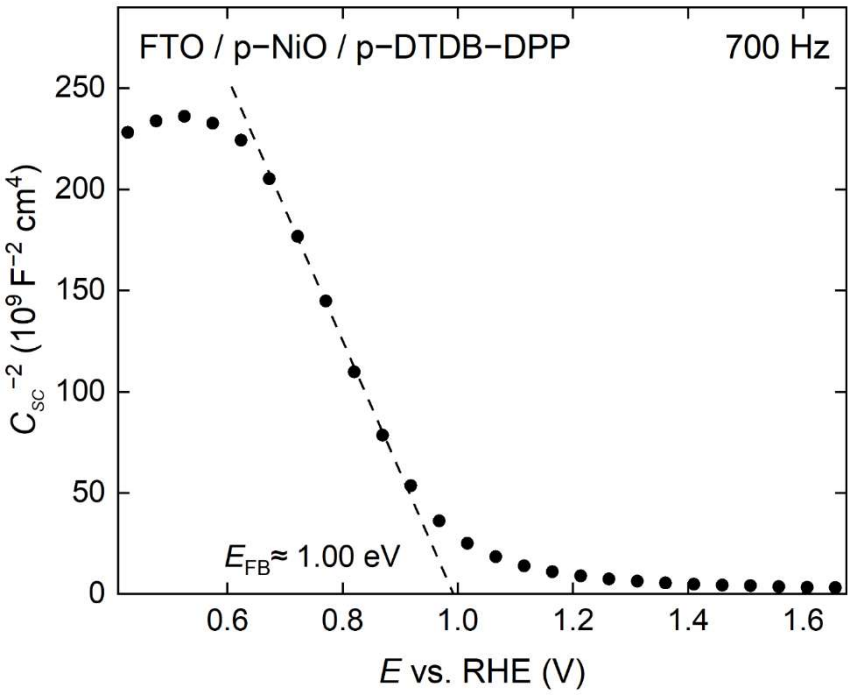


Figure S 66: Mott−Schottky plot of **p−*poly*-DTDB-*alt*-DPP** on FTO−Substrate in 0.1M KP_i−electrolyte (Sørensen) with pH 7.0 at a frequency of 700 Hz.

1.9 Electrochemical impedance spectroscopy (EIS)

For EIS, the frequency range has been extended to 0.07Hz to 700kHz. The ZFit software from BioLogic was used to fit the impedance values once a circuit model had been selected for the system.

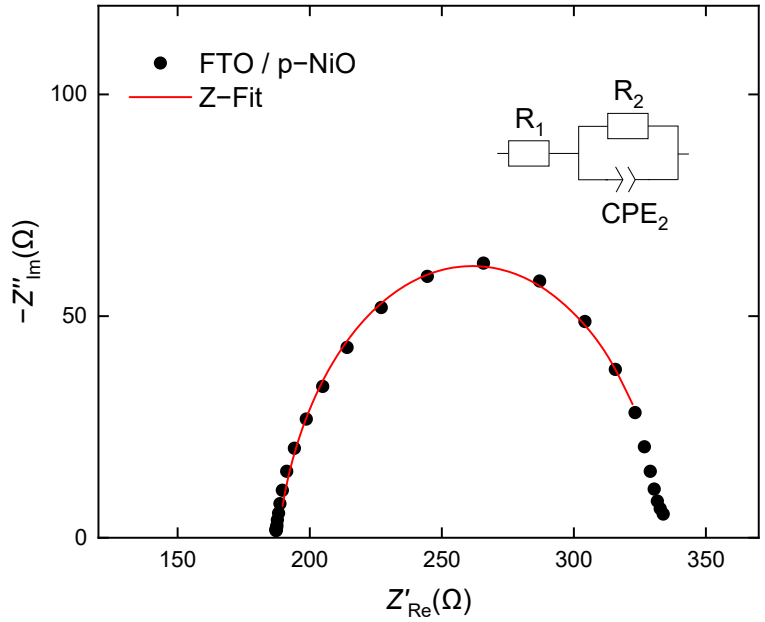


Figure S 67: Nyquist plot of FTO/ p-NiO in dark in 0.1M KP_i–electrolyte (Sørensen) with pH 7.0. The line represents the fit using the ideal equivalent circuit model.

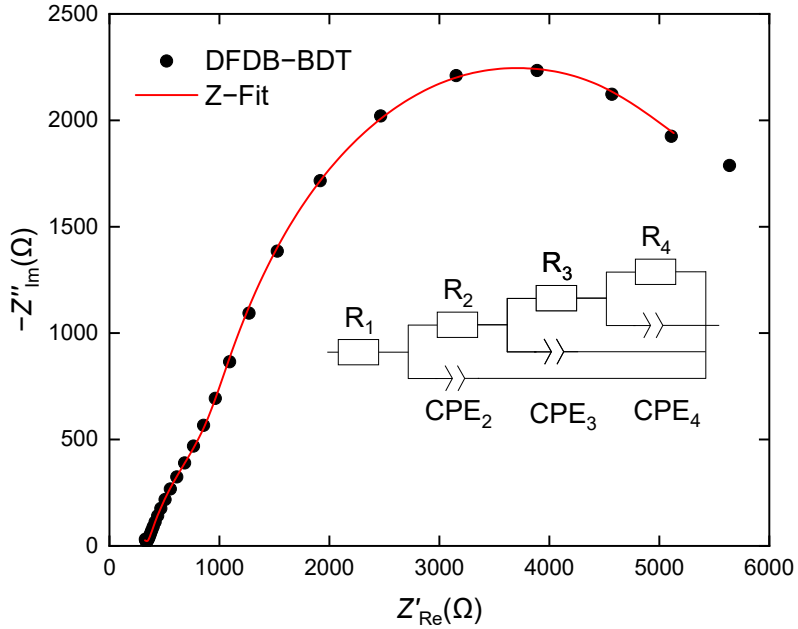


Figure S 68: Nyquist plot of FTO/ p-NiO/***poly*-DFDB-*alt*-BDT** in dark in 0.1M KP_i–electrolyte (Sørensen) with pH 7.0. The line represents the fit using the ideal equivalent circuit model.

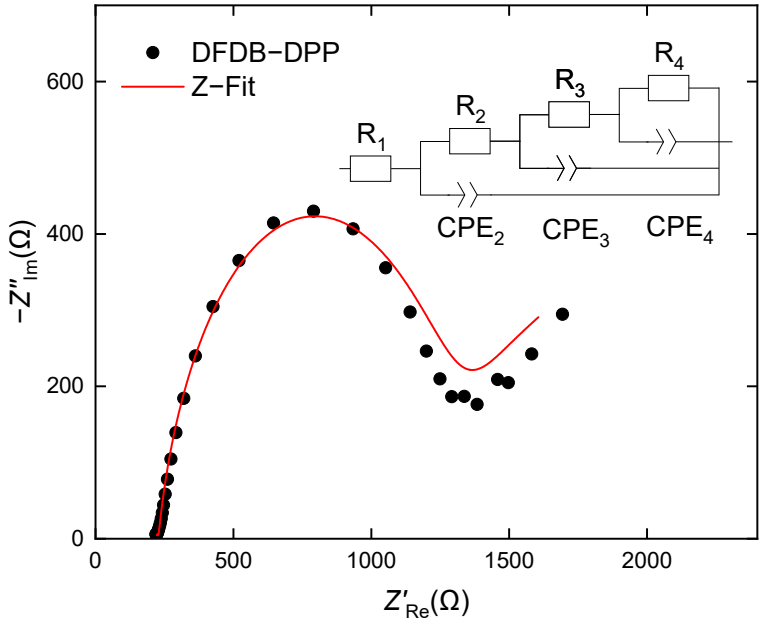


Figure S 69: Nyquist plot of FTO/ p-NiO/***poly*-DFDB-*alt*-DPP** in dark in 0.1M KP_i–electrolyte (Sørensen) with pH 7.0. The line represents the fit using the ideal equivalent circuit model.

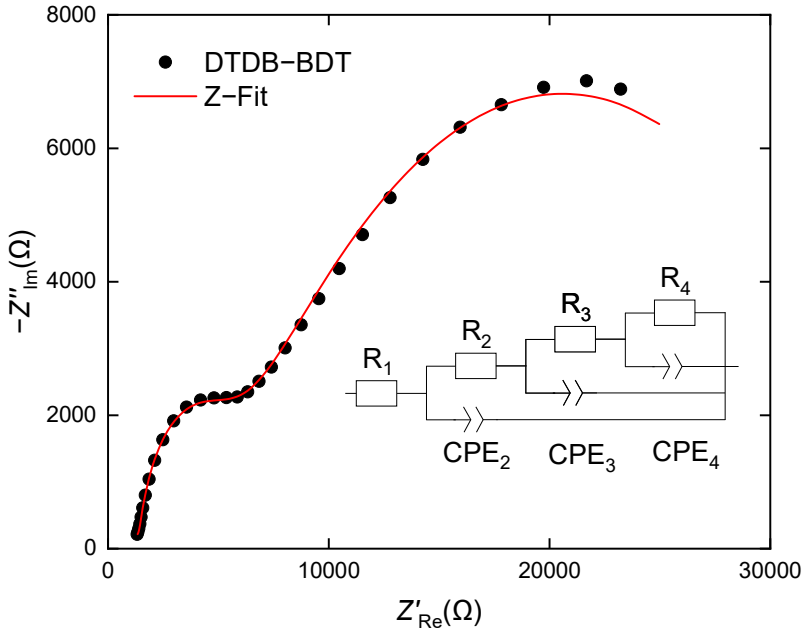


Figure S 70: Nyquist plot of FTO/ p-NiO/***poly*-DTDB-*alt*-BDT** in dark in 0.1M KP_i–electrolyte (Sørensen) with pH 7.0. The line represents the fit using the ideal equivalent circuit model.

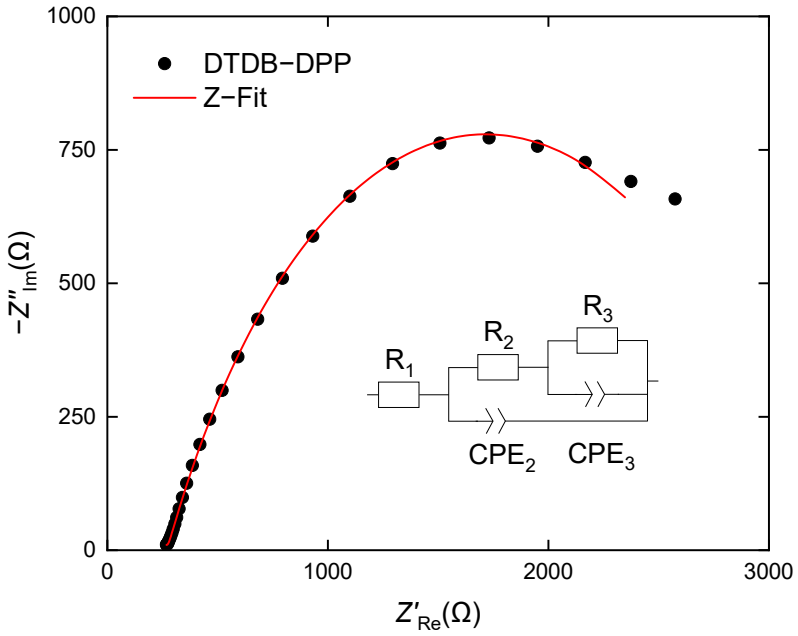


Figure S 71: Nyquist plot of FTO/ p-NiO/***poly*-DTDB-*alt*-DPP** in dark in 0.1M KP_i−electrolyte (Sørensen) with pH 7.0. The line represents the fit using the ideal equivalent circuit model.

Table S 3: Values for the corresponding components of the circuit model. Thickness (*d)* of the fabricated thin films and mass (*m)* of the coated copolymers.

		FTO/p−NiO	DFDB−BDT	DFDB−DPP	DTDB−BDT	DTDB−DPP	Unit
R_1		186	186	186	186	186	Ω
R_2		150	170	43	1400	90	Ω
R_3		–	1750	1100	4700	2900	Ω
R_4		–	5000	1100	> 30000*	0*	Ω
CPE_2	Q_2	43	2.6	4.0	2.0	4.6	$\mu F \cdot s^{(\alpha-1)}$
	α_2	0.87	0.5	0.55	0.4	0.45	1
CPE_3	Q_3	–	28	36	0.35	62	$\mu F \cdot s^{(\alpha-1)}$
	α_3	–	0.695	0.84	0.91	0.635	1
CPE_4	Q_4	–	9.9	> 3250*	30	0*	$\mu F \cdot s^{(\alpha-1)}$
	α_4	–	1.0*	0.65	0.535	0*	1
d(NiO)		13	14	12	13	16	µm
d(Polymer)		–	70	46	37	85	µm
m(Polymer)		–	≈ 3−5				mg/cm^2

*In the simulation, adjusting these parameters led to an improved fit quality (R^2). However, these adjustments primarily altered the behavior of the fit at the boundary regions and should, therefore, not be considered accurate. To achieve more reliable results, the frequency range would need to be extended. However, this would disproportionately increase the measurement time.

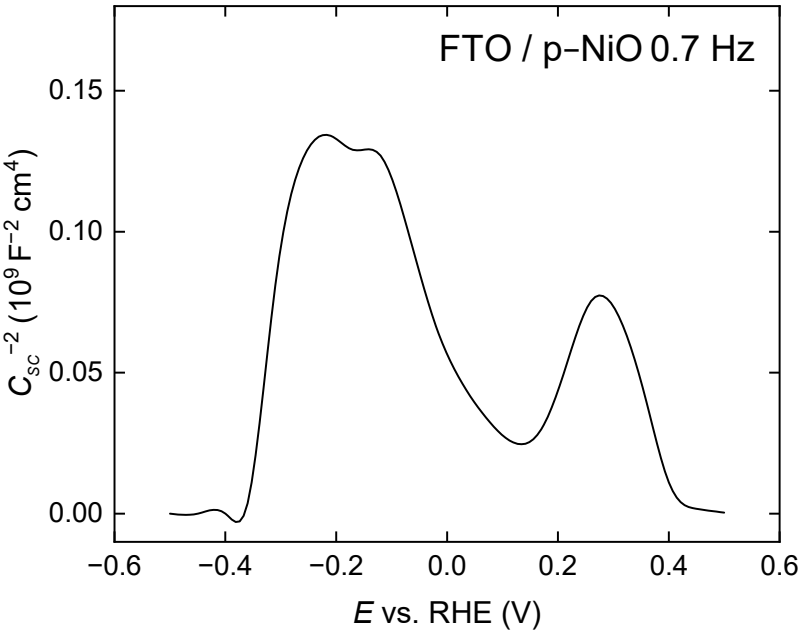


Figure S 72: Mott−Schottky plot of p−NiO on FTO−Substrate in 0.1M KP_i−electrolyte (Sørensen) with pH 7.0 at a frequency of 0.7 Hz.

2. Computational Information

Computational methods. DFT geometry optimizations and the subsequent NICS computations were carried out with the Gaussian 16, Revision C.01 program package[6] using the ωB97X-D[7] functional in combination with the 6-31G(d)[8-14] basis set in gas phase. The equilibrium geometries were characterized as minima by frequency computations. Vertical singlet excitations were calculated by means of time-dependent DFT with the program ORCA 5[15-16] using the ωB97X-D3[17] functional with optimal tuned ω parameters[18-19], the def2-SVP[20] basis set and the CPCM[21] solvation model mimicking tetrahydrofuran (ε= 7.25) as solvent.
The NICS[22] computations were done by defining a plane containing 7-membered BOB-ring. The NICS-Z values follow an imaginary vector perpendicular to this defined plane.

Table 4: Characterization of the electronically excited states using TD-DFT calculations with the ω_TB97X-D3/def2-SVP, CPCM (THF) level of theory for the relevant compounds. BF = bifuran, BT = bithiophene.

Compound	State	λ_{vert} / nm	E [eV]	Oscillator strength *f*	Orbital contributions	$\|c\|^2$ / %
DFDB-BDT^{Me}	S_1	382	3.25	1.207	HOMO -> LUMO	81.5
DFDB-BDT^{Me}	S_2	334	3.71	0.288	HOMO-1 -> LUMO	63.8
DFDB-BDT^{Me}	S_3	305	4.07	0.424	HOMO -> LUMO+1 HOMO-1 -> LUMO+1	39.3 19.6
BF-BDT^{Me}	S_1	361	3.43	1.244	HOMO -> LUMO	92.8
BF-BDT^{Me}	S_2	316	3.92	0.276	HOMO-1 -> LUMO	81.7
BF-BDT^{Me}	S_3	268	4.64	0.235	HOMO-2 -> LUMO HOMO-1 -> LUMO+2	25.3 15.4

					HOMO -> LUMO+1 HOMO -> LUMO+2	25.6 22.0
BF-BDT^{Me}		253	4.90	0.111	HOMO -> LUMO+1 HOMO -> LUMO+2	49.3 22.7
BF-BDT^{Me}		242	5.13	0.139	HOMO-2 -> LUMO HOMO-1 -> LUMO+1 HOMO -> LUMO+2	40.4 14.0 19.6
DTDB-BDT^{Me}	S_1	398	3.12	1.107	HOMO -> LUMO HOMO-1 -> LUMO	70.0 22.1
DTDB-BDT^{Me}	S_2	344	3.61	0.168	HOMO -> LUMO HOMO-1 -> LUMO	13.1 58.2
DTDB-BDT^{Me}	S_3	301	4.12	0.361	HOMO -> LUMO+1 HOMO-1 -> LUMO+1	29.2 19.5
BT-BDT^{Me}	S_1	357	3.48	1.225	HOMO -> LUMO	89.1
BT-BDT^{Me}	S_2	318	3.89	0.290	HOMO-1 -> LUMO	78.2
BT-BDT^{Me}	S_3	272	4.57	0.079	HOMO-2 -> LUMO HOMO-1 -> LUMO+1 HOMO -> LUMO+1 HOMO -> LUMO+2	32.8 50.0 19.2 19.2
DFDB-DPP^{Me}	S_1	535	2.32	1.255	HOMO -> LUMO	95.3
DFDB-DPP^{Me}	S_2	381	3.26	0.648	HOMO -> LUMO HOMO-1 -> LUMO	24.5 56.8
DFDB-DPP^{Me}	S_3	367	3.38	0.009	HOMO-2 -> LUMO	89.6
BF-DPP^{Me}	S_1	539	2.30	1.202	HOMO -> LUMO	92.6
BF-DPP^{Me}	S_2	388	3.20	0.437	HOMO-1 -> LUMO	77.3
BF-DPP^{Me}	S_3	364	3.41	0.006	HOMO-2 -> LUMO	93.1
DTDB-DPP^{Me}	S_1	533	2.33	1.261	HOMO -> LUMO	93.2
DTDB-DPP^{Me}	S_2	391	3.17	0.514	HOMO -> LUMO+1 HOMO-1 -> LUMO+1	37.4 13.6
DTDB-DPP^{Me}	S_3	367	3.38	0.000	HOMO-2 -> LUMO HOMO-2 -> LUMO+1	83.7 12.1
BT-DPP^{Me}	S_1	524	2.37	1.145	HOMO -> LUMO	95.0
BT-DPP^{Me}	S_2	368	3.37	0.514	HOMO-2 -> LUMO HOMO-1 -> LUMO HOMO -> LUMO+1	11.2 57.3 17.1
BT-DPP^{Me}	S_3	362	3.43	0.082	HOMO-2 -> LUMO	81.1

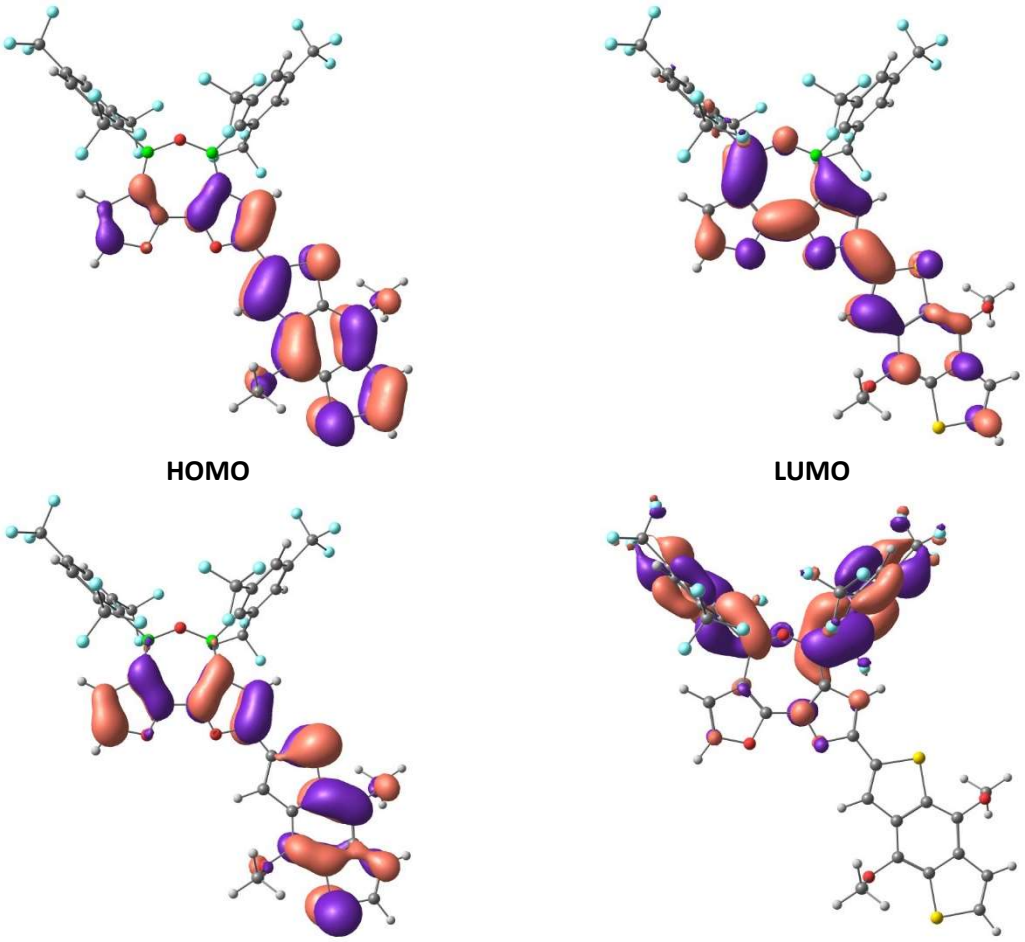
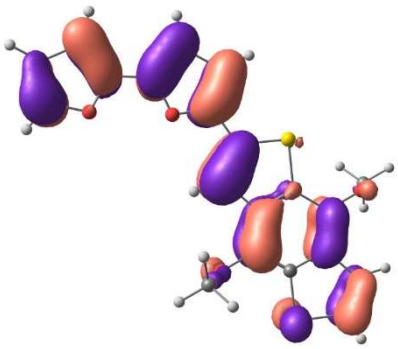
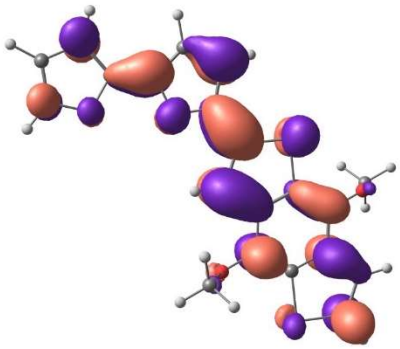


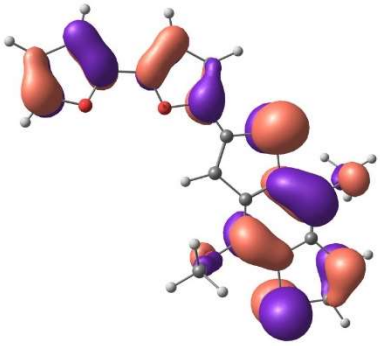
Figure S 73. Calculated frontier orbitals (isovalue 0.03 a.u.) of **DFDB-BDT^{Me}** (ω_TB97X-D3/def2-SVP, CPCM(THF), ω_T = 0.135).



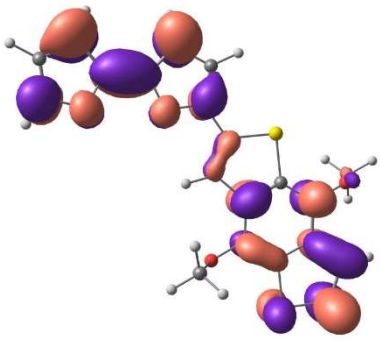
HOMO



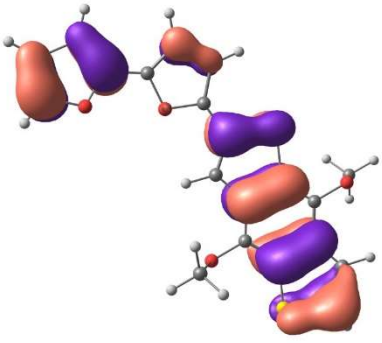
LUMO



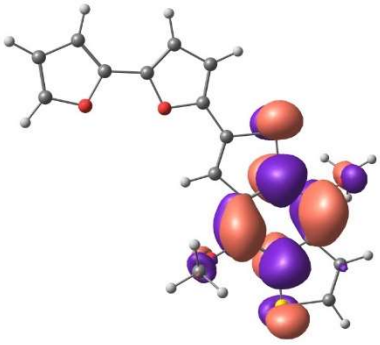
HOMO-1



LUMO+1



HOMO-2



LUMO+2

Figure S 74. Calculated frontier orbitals (isovalue 0.03 a.u.) of **BF-BDT^{Me}** (ω_TB97X-D3/def2-SVP, CPCM(THF), ω_T = 0.160).

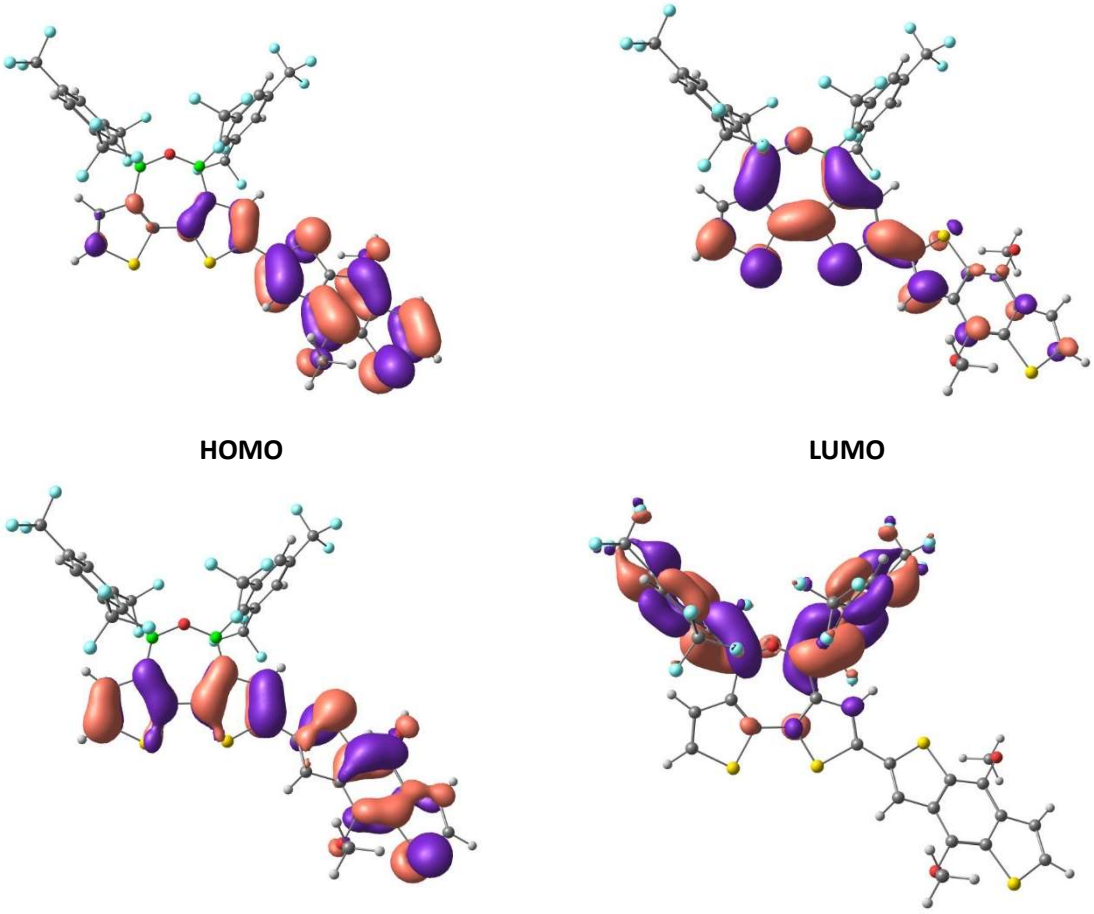
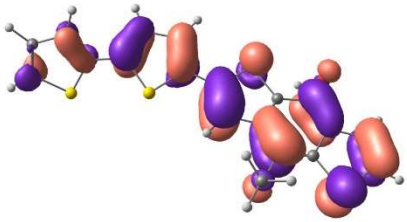
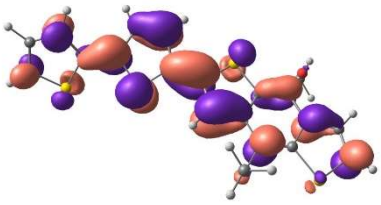


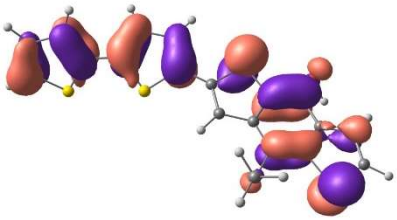
Figure S 75. Calculated frontier orbitals (isovalue 0.03 a.u.) of **DTDB-BDT^{Me}** (ω_TB97X-D3/def2-SVP, CPCM(THF), ω_T = 0.135).



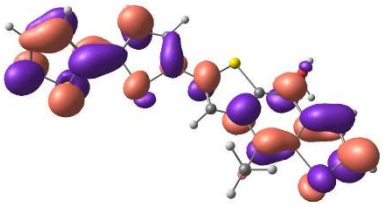
HOMO



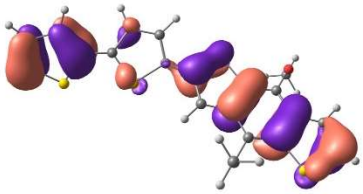
LUMO



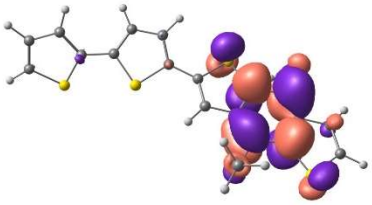
HOMO-1



LUMO+1

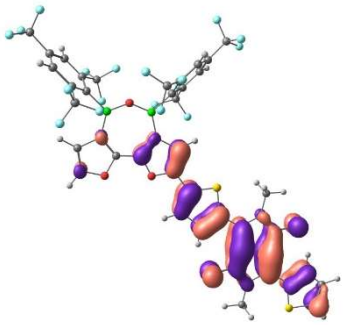


HOMO-2

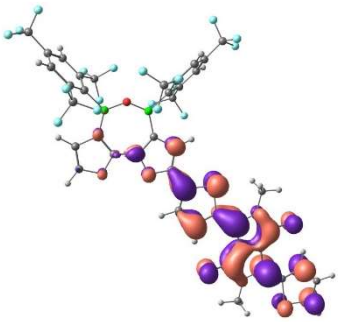


LUMO+2

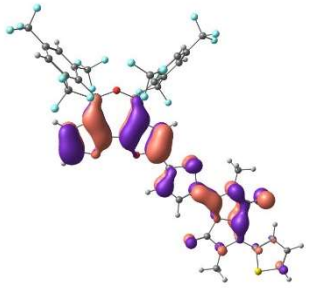
Figure S 76. Calculated frontier orbitals (isovalue 0.03 a.u.) of **BT-BDT^{Me}** (ω_TB97X-D3/def2-SVP, CPCM(THF), ω_T = 0.155).



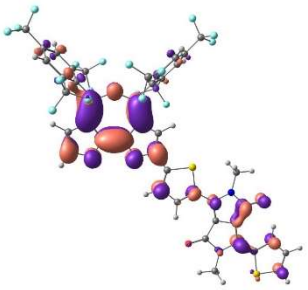
HOMO



LUMO

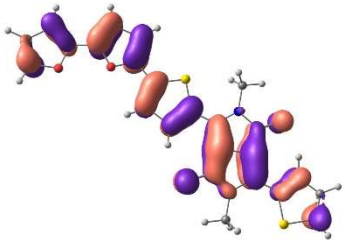


HOMO-1

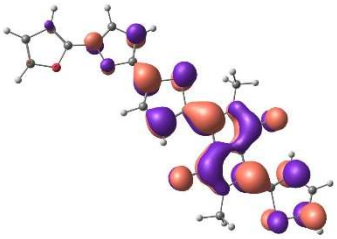


LUMO+1

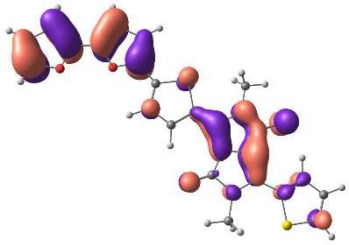
Figure S 77. Calculated frontier orbitals (isovalue 0.03 a.u.) of **DFDB-DPP^{Me}** (ω_TB97X-D3/def2-SVP, CPCM(THF), ω_T = 0.130).



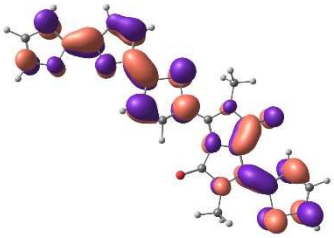
HOMO



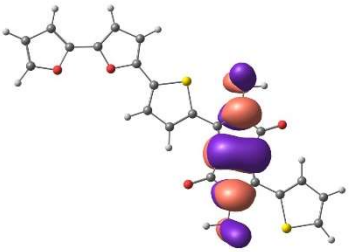
LUMO



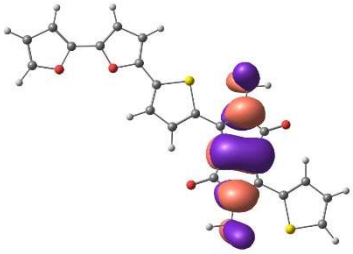
HOMO-1



LUMO+1

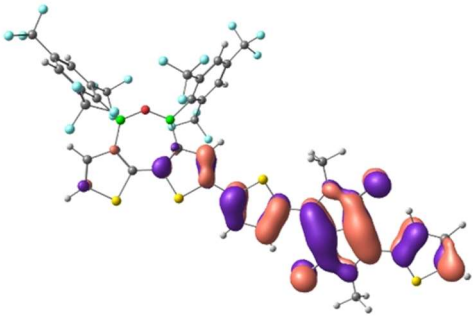


HOMO-1

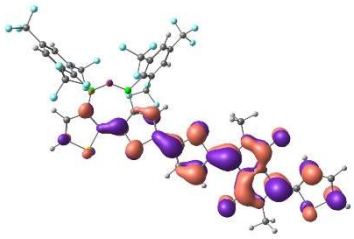


HOMO-2

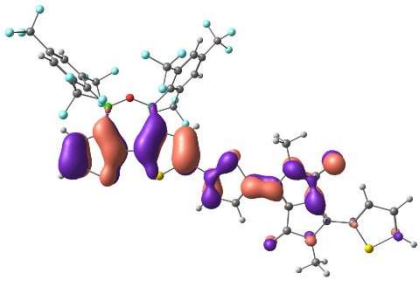
Figure S 78. Calculated frontier orbitals (isovalue 0.03 a.u.) of **BF-DPP^{Me}** (ω_TB97X-D3/def2-SVP, CPCM(THF), ω_T = 0.130).



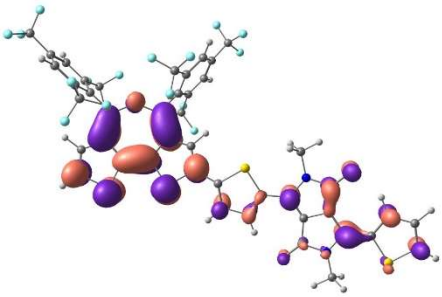
HOMO



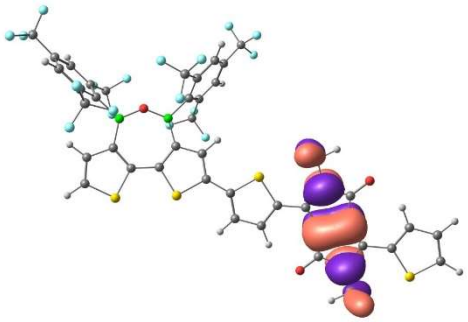
LUMO



HOMO-1

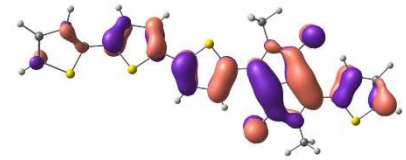


LUMO+1

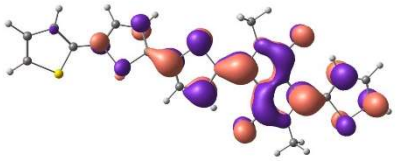


HOMO-2

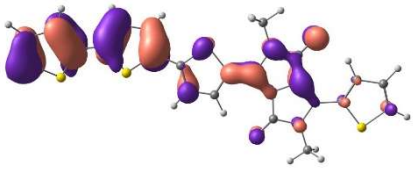
Figure S 79. Calculated frontier orbitals (isovalue 0.03 a.u.) of **DTDB-DPP^{Me}** (ω_TB97X-D3/def2-SVP, CPCM(THF), ω_T = 0.130).



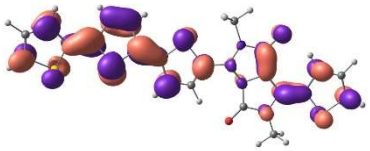
HOMO



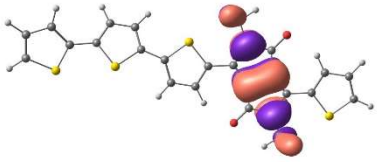
LUMO



HOMO-1



LUMO+1



HOMO-2

Figure S 80. Calculated frontier orbitals (isovalue 0.03 a.u.) of **BT-DPP^{Me}** (ω_TB97X-D3/def2-SVP, CPCM(THF), ω_T = 0.130).

Table 5: Calculated HOMO and LUMO energies (ω_TB97X-D3/def2-SVP, CPCM (THF)) for the relevant compounds.

Compound	HOMO energy (eV)	LUMO energy (eV)	HOMO-LUMO gap (eV)
DFDB-BDT^{Me}	-6.80	-0.87	5.92
BF-BDT^{Me}	-6.75	-0.35	6.40
DTDB-BDT^{Me}	-6.85	-1.16	5.69
BT-BDT^{Me}	-6.91	-0.52	6.39
DFDB-DPP^{Me}	-6.46	-1.64	4.82
BF-DPP^{Me}	-6.31	-1.55	4.76
DTDB-DPP^{Me}	-6.50	-1.68	4.82
BT-DPP^{Me}	-6.50	-1.53	4.97

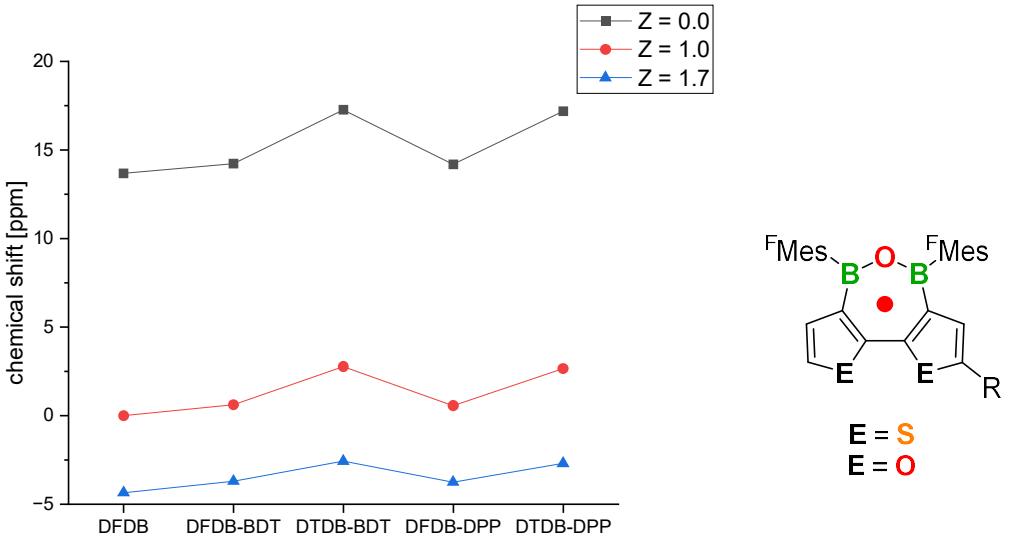


Figure S 81. Calculated Z-NICS values (out-of-plane component) of the relevant compounds for Z = 0.0, 1.0 and 1.7 Å. The observed dummy atom (red dot) was moved vertical to the mean plane of the 7-membered ring.

Cartesian coordinates (Å) and total energies (hartree) of optimized stationary points

Compound **DFDB-BDT^{Me}**:

Total energy (ωB97X-D/6-31G(d)): -4476.09901611

C	-4.931161000	-1.245934000	-1.310068000
C	-4.181158000	-1.627329000	-0.187768000
C	-4.892915000	-2.148962000	0.899071000
C	-6.275170000	-2.302768000	0.868402000
C	-6.982700000	-1.933431000	-0.266127000
C	-6.311080000	-1.398971000	-1.358080000
B	-2.596874000	-1.431876000	-0.160341000
O	-2.197723000	-0.130543000	-0.053526000
B	-1.013233000	0.544725000	-0.004084000
C	-1.162598000	2.125854000	0.154414000
C	-0.905765000	3.013436000	-0.896948000
C	-1.048476000	4.389649000	-0.750152000
C	-1.454498000	4.911956000	0.468796000
C	-1.730187000	4.059874000	1.530753000
C	-1.589716000	2.687836000	1.366684000
C	-0.432325000	2.496122000	-2.234048000
F	-0.822527000	3.290477000	-3.240269000
C	-1.660395000	6.396093000	0.625012000
F	-1.404297000	6.798562000	1.879117000
C	-1.961184000	1.790710000	2.524770000
F	-1.868160000	2.428169000	3.700478000
C	-4.165506000	-2.589885000	2.146495000
F	-4.932594000	-2.467404000	3.238434000
C	-8.484454000	-2.050194000	-0.288489000
F	-8.910952000	-3.070470000	0.471739000
C	-4.245729000	-0.599913000	-2.492150000
F	-4.954951000	-0.744769000	-3.620927000
C	-1.640644000	-2.623738000	-0.291640000
C	-0.261190000	-2.584681000	-0.292636000
O	0.265105000	-3.815398000	-0.439864000
C	-0.780970000	-4.680136000	-0.540370000

C	-1.956530000	-4.017306000	-0.458469000
C	0.632139000	-1.473316000	-0.168966000
O	1.956228000	-1.715511000	-0.161176000
C	2.585124000	-0.509812000	-0.029842000
C	1.660264000	0.485816000	0.045883000
C	0.367163000	-0.124682000	-0.046232000
F	0.908280000	2.419918000	-2.288125000
F	-0.910390000	1.263621000	-2.487759000
F	-0.865917000	7.094938000	-0.199929000
F	-2.927500000	6.743115000	0.347189000
F	-3.218749000	1.339212000	2.413721000
F	-1.156900000	0.711230000	2.592064000
F	-9.066404000	-0.934528000	0.179963000
F	-8.944873000	-2.246684000	-1.533302000
F	-3.790223000	-3.878609000	2.070784000
F	-3.051683000	-1.864248000	2.355510000
F	-4.066586000	0.714583000	-2.299262000
F	-3.030031000	-1.137670000	-2.714035000
H	1.865897000	1.542061000	0.145407000
H	-2.944011000	-4.452744000	-0.499817000
H	-0.513275000	-5.717378000	-0.664068000
H	-0.844979000	5.050266000	-1.584941000
H	-2.047126000	4.464848000	2.484716000
H	-6.797245000	-2.707088000	1.727961000
H	-6.860974000	-1.108547000	-2.245524000
S	4.925182000	0.964222000	0.171666000
C	6.436422000	0.089254000	0.101233000
C	6.226048000	-1.305067000	-0.031284000
C	4.828862000	-1.632082000	-0.093361000
H	4.450637000	-2.638936000	-0.217596000
C	4.028622000	-0.538077000	0.000019000
C	7.704391000	0.647791000	0.165402000
O	7.866327000	1.999635000	0.303845000
C	8.051209000	2.678160000	-0.933501000
H	8.155888000	3.736808000	-0.691530000
H	7.186642000	2.535816000	-1.593060000
H	8.955415000	2.325871000	-1.445012000
S	10.110680000	-2.476592000	-0.093094000
C	8.595765000	-1.608794000	-0.027699000
C	8.804667000	-0.214410000	0.104017000
C	10.206970000	0.111533000	0.166188000
H	10.579059000	1.121248000	0.288037000
C	10.995259000	-0.982447000	0.075366000
H	12.076667000	-1.011541000	0.098181000
C	7.325074000	-2.167246000	-0.093350000
O	7.159277000	-3.517410000	-0.233616000
C	6.970656000	-4.199016000	1.001597000
H	6.864227000	-5.256604000	0.756078000
H	7.834653000	-4.060180000	1.662542000
H	6.065968000	-3.846726000	1.512220000

Compound **BF-BDT^{Me}**:

Total energy (ωB97X-D/6-31G(d)): -1867.38095838

C	6.793963000	0.031238000	-0.102189000
C	5.441305000	0.215282000	-0.082681000
O	5.146934000	1.534186000	-0.198614000
C	6.323517000	2.197535000	-0.293354000
C	7.367402000	1.331376000	-0.239918000

C	4.338748000	-0.708620000	0.035486000
O	3.085190000	-0.196634000	-0.004177000
C	2.215904000	-1.234802000	0.120993000
C	2.908509000	-2.406511000	0.240963000
C	4.288098000	-2.065799000	0.186041000
H	2.483299000	-3.393513000	0.354991000
H	8.416602000	1.582281000	-0.292577000
H	6.248713000	3.268724000	-0.393295000
S	-0.390041000	-2.175598000	0.291437000
C	-1.680779000	-1.005630000	0.145282000
C	-1.175550000	0.307051000	-0.022387000
C	0.260609000	0.329470000	-0.049431000
H	0.847493000	1.227878000	-0.192621000
C	0.810525000	-0.903836000	0.102768000
C	-3.039329000	-1.281357000	0.185029000
O	-3.488499000	-2.563336000	0.357833000
C	-3.775159000	-3.231285000	-0.865039000
H	-4.107624000	-4.235491000	-0.597483000
H	-2.880877000	-3.296664000	-1.496638000
H	-4.569365000	-2.715839000	-1.419268000
S	-4.721673000	2.268394000	-0.242993000
C	-3.427538000	1.102698000	-0.103985000
C	-3.930989000	-0.209965000	0.062063000
C	-5.371725000	-0.229729000	0.088518000
H	-5.952333000	-1.133316000	0.227757000
C	-5.907805000	1.001964000	-0.059595000
H	-6.958650000	1.259549000	-0.072425000
C	-2.065985000	1.377848000	-0.145506000
O	-1.617579000	2.658464000	-0.320731000
C	-1.299228000	3.320766000	0.897741000
H	-0.970237000	4.324728000	0.625450000
H	-2.178574000	3.386338000	1.549931000
H	-0.493214000	2.801587000	1.430657000
H	5.132830000	-2.735843000	0.250088000
H	7.314034000	-0.912753000	-0.028951000

Compound **DTDB-BDT^{Me}**:

Total energy (ωB97X-D/6-31G(d)): -5122.05567472

C	-5.342828000	-0.485452000	-1.070512000
C	-4.543668000	-1.142202000	-0.123617000
C	-5.191278000	-1.643362000	1.011313000
C	-6.564591000	-1.515786000	1.192229000
C	-7.327449000	-0.876519000	0.225975000
C	-6.716312000	-0.355989000	-0.907817000
B	-2.961874000	-1.256047000	-0.321901000
O	-2.309909000	-0.076704000	-0.131104000
B	-1.006694000	0.311773000	-0.138772000
C	-0.802868000	1.878695000	0.097188000
C	-0.436230000	2.747558000	-0.936910000
C	-0.278819000	4.113774000	-0.729033000
C	-0.486496000	4.643877000	0.536065000
C	-0.861964000	3.812515000	1.583693000
C	-1.021441000	2.451045000	1.358451000
C	-0.167705000	2.207002000	-2.320646000
F	-0.434340000	3.114177000	-3.269911000
C	-0.368228000	6.128861000	0.760622000
F	0.025890000	6.407663000	2.012348000
C	-1.488353000	1.585711000	2.505963000

F	-1.192932000	2.129839000	3.694891000
C	-4.403365000	-2.375030000	2.070877000
F	-4.965132000	-2.255257000	3.281302000
C	-8.807784000	-0.688152000	0.432323000
F	-9.326653000	-1.655706000	1.203532000
C	-4.705087000	0.150535000	-2.284099000
F	-5.576757000	0.282234000	-3.294499000
C	-2.304939000	-2.582812000	-0.750152000
C	-0.945475000	-2.849931000	-0.867861000
S	-0.673353000	-4.479468000	-1.408575000
C	-2.360419000	-4.808950000	-1.476033000
C	-3.092003000	-3.727549000	-1.104914000
C	0.187423000	-1.983393000	-0.600754000
S	1.799377000	-2.631039000	-0.671199000
C	2.510780000	-1.098313000	-0.274721000
C	1.539770000	-0.152881000	-0.112636000
C	0.205275000	-0.628542000	-0.293656000
F	1.115937000	1.842088000	-2.469929000
F	-0.921963000	1.121033000	-2.580283000
F	0.514994000	6.686786000	-0.081204000
F	-1.545991000	6.744653000	0.567854000
F	-2.815012000	1.394462000	2.472470000
F	-0.912059000	0.367693000	2.469868000
F	-9.070295000	0.484059000	1.032073000
F	-9.470835000	-0.694570000	-0.734369000
F	-4.314900000	-3.688270000	1.802951000
F	-3.144944000	-1.903906000	2.163903000
F	-4.227191000	1.371934000	-2.007030000
F	-3.672385000	-0.584697000	-2.741273000
H	1.767165000	0.874755000	0.148624000
H	-4.175271000	-3.730638000	-1.077084000
H	-2.711102000	-5.783137000	-1.787339000
H	0.003845000	4.761076000	-1.551142000
H	-1.022550000	4.223532000	2.573470000
H	-7.035947000	-1.912173000	2.084068000
H	-7.309886000	0.143598000	-1.664578000
S	4.658300000	0.657803000	-0.352728000
C	6.257775000	0.009516000	-0.086946000
C	6.221837000	-1.388537000	0.135107000
C	4.882081000	-1.903388000	0.082124000
H	4.645644000	-2.950959000	0.229996000
C	3.950903000	-0.943813000	-0.161072000
C	7.443097000	0.730649000	-0.090152000
O	7.438315000	2.082983000	-0.299202000
C	7.652932000	2.447818000	-1.658088000
H	7.615084000	3.537541000	-1.693964000
H	6.871419000	2.031777000	-2.305317000
H	8.632796000	2.101216000	-2.008982000
S	10.202136000	-2.006363000	0.627819000
C	8.598910000	-1.361888000	0.369359000
C	8.634502000	0.036041000	0.144977000
C	9.978568000	0.552366000	0.206745000
H	10.219984000	1.600775000	0.082852000
C	10.891197000	-0.412953000	0.454440000
H	11.961843000	-0.290023000	0.551349000
C	7.411496000	-2.083568000	0.371980000
O	7.409187000	-3.435174000	0.581939000
C	7.217277000	-3.798198000	1.944872000
H	7.246015000	-4.888175000	1.979966000

H	8.014521000	-3.389104000	2.577009000
H	6.247170000	-3.442932000	2.313946000

Compound **BT-BDT^{Me}**:

Total energy (ωB97X-D/6-31G(d)): -2513.34414093

C	-6.649042000	0.273929000	0.892593000
C	-5.574893000	0.004939000	0.084532000
S	-6.049164000	-1.002984000	-1.250579000
C	-7.680451000	-1.059302000	-0.700156000
C	-7.854695000	-0.331656000	0.439601000
C	-4.211491000	0.489706000	0.248058000
S	-2.830774000	-0.476451000	-0.177581000
C	-1.726289000	0.762411000	0.339504000
C	-2.409535000	1.853036000	0.813154000
C	-3.818553000	1.700592000	0.756088000
H	-1.915356000	2.738859000	1.196590000
H	-8.806374000	-0.238875000	0.949165000
H	-8.418571000	-1.627148000	-1.249471000
S	0.774519000	1.973958000	0.253351000
C	2.180216000	0.945929000	0.120145000
C	1.818302000	-0.422130000	0.070321000
C	0.394842000	-0.601549000	0.140901000
H	-0.078888000	-1.576294000	0.119734000
C	-0.288978000	0.568692000	0.243881000
C	3.500620000	1.367573000	0.061944000
O	3.814022000	2.698915000	0.121233000
C	3.954287000	3.304637000	-1.158572000
H	4.189759000	4.354687000	-0.978568000
H	3.023140000	3.230551000	-1.733320000
H	4.766725000	2.837326000	-1.728782000
S	5.544944000	-2.002050000	-0.225628000
C	4.136954000	-0.976371000	-0.088109000
C	4.498031000	0.391910000	-0.041133000
C	5.926943000	0.569423000	-0.102834000
H	6.408840000	1.538366000	-0.060239000
C	6.589318000	-0.604500000	-0.199287000
H	7.660287000	-0.747292000	-0.257768000
C	2.814095000	-1.397980000	-0.030355000
O	2.497741000	-2.727914000	-0.088310000
C	2.361229000	-3.334920000	1.191536000
H	2.120583000	-4.383602000	1.010910000
H	3.295647000	-3.265274000	1.761461000
H	1.553273000	-2.865350000	1.766186000
H	-4.524823000	2.464052000	1.060333000
H	-6.566203000	0.866197000	1.796492000

Compound **DFDB-DPP^{Me}**:

Total energy (ωB97X-D/6-31G(d)): -4739.17168174

C	6.267675000	-1.133402000	1.235454000
C	5.529111000	-1.536347000	0.112775000
C	6.258906000	-1.970911000	-0.999642000
C	7.649506000	-2.020694000	-0.994781000
C	8.346496000	-1.633393000	0.139773000
C	7.655396000	-1.184255000	1.258235000
B	3.934591000	-1.460195000	0.114578000
O	3.435893000	-0.190359000	0.050610000
B	2.203387000	0.393478000	0.038426000

C	2.227632000	1.985067000	-0.080290000
C	1.922722000	2.823187000	0.998511000
C	1.956188000	4.209594000	0.886331000
C	2.298080000	4.792641000	-0.324775000
C	2.618725000	3.991683000	-1.413574000
C	2.587322000	2.609127000	-1.284025000
C	1.515252000	2.236778000	2.328726000
F	1.863841000	3.030810000	3.349807000
C	2.385734000	6.291988000	-0.443892000
F	2.086677000	6.704709000	-1.685052000
C	3.003770000	1.772761000	-2.471929000
F	2.840936000	2.431274000	-3.628201000
C	5.544629000	-2.430091000	-2.247971000
F	6.280546000	-2.219825000	-3.347719000
C	9.853016000	-1.635366000	0.143113000
F	10.349031000	-2.536625000	-0.717900000
C	5.555793000	-0.576547000	2.446732000
F	6.291514000	-0.702471000	3.560417000
C	3.073323000	-2.724732000	0.226538000
C	1.695245000	-2.791516000	0.251724000
O	1.266742000	-4.062224000	0.372977000
C	2.376932000	-4.846697000	0.431186000
C	3.497163000	-4.093921000	0.348391000
C	0.718351000	-1.748551000	0.174398000
O	-0.583560000	-2.090297000	0.181953000
C	-1.304001000	-0.933039000	0.094095000
C	-0.457710000	0.132069000	0.031057000
C	0.878409000	-0.380755000	0.085104000
F	0.184791000	2.058762000	2.403325000
F	2.088111000	1.037087000	2.539195000
F	1.546594000	6.904559000	0.405039000
F	3.624131000	6.730032000	-0.166442000
F	4.293138000	1.414450000	-2.394137000
F	2.280897000	0.637868000	-2.554275000
F	10.341517000	-0.435318000	-0.208898000
F	10.340155000	-1.920429000	1.360601000
F	5.267734000	-3.744804000	-2.203848000
F	4.375918000	-1.784465000	-2.417657000
F	5.276339000	0.726149000	2.297694000
F	4.386703000	-1.210001000	2.667844000
H	-0.742746000	1.172331000	-0.035907000
H	4.515403000	-4.453714000	0.360556000
H	2.191178000	-5.904380000	0.529374000
H	1.718019000	4.831147000	1.741735000
H	2.885731000	4.444036000	-2.361512000
H	8.185389000	-2.358320000	-1.874239000
H	8.197324000	-0.880548000	2.146322000
S	-3.769882000	0.306653000	-0.007474000
O	-8.929480000	2.342457000	-0.197215000
N	-6.950135000	1.125653000	-0.095212000
C	-8.844503000	-0.103492000	-0.059507000
C	-6.562304000	-0.205780000	-0.014277000
C	-6.118697000	2.308574000	-0.141677000
H	-5.507585000	2.403348000	0.760714000
H	-6.802190000	3.157618000	-0.196926000
H	-5.476896000	2.312161000	-1.027610000
C	-8.368717000	1.258391000	-0.127210000
C	-4.858639000	-2.025282000	0.118598000
H	-5.605160000	-2.812944000	0.155808000

C	-3.465034000	-2.242500000	0.148377000
H	-3.002129000	-3.219170000	0.212427000
C	-5.203512000	-0.691458000	0.034281000
C	-2.739368000	-1.078113000	0.086765000
S	-12.794953000	-1.375187000	-0.061827000
O	-7.628773000	-3.411587000	0.145736000
N	-9.609076000	-2.195630000	0.041602000
C	-7.714647000	-0.966193000	0.008707000
C	-9.996990000	-0.864895000	-0.039053000
C	-10.440976000	-3.378451000	0.090203000
H	-11.051038000	-3.474460000	-0.812580000
H	-9.758305000	-4.227803000	0.149109000
H	-11.084852000	-3.377696000	0.974422000
C	-8.190927000	-2.328353000	0.075132000
C	-11.701559000	0.951947000	-0.172700000
H	-10.955278000	1.740035000	-0.203208000
C	-13.101128000	1.165507000	-0.210490000
H	-13.558846000	2.145063000	-0.274111000
C	-11.358429000	-0.381932000	-0.091341000
C	-13.813597000	0.002072000	-0.157976000
H	-14.887649000	-0.124830000	-0.170509000

Compound **BF-DPP^{Me}**:

Total energy (ωB97X-D/6-31G(d)): -2130.45397440

C	8.809603000	-0.236350000	-0.000758000
C	7.463522000	-0.465201000	-0.000049000
O	7.215340000	-1.798445000	0.000257000
C	8.414671000	-2.425952000	-0.000196000
C	9.428315000	-1.522766000	-0.000892000
C	6.329047000	0.426506000	0.000423000
O	5.094549000	-0.129924000	0.000078000
C	4.188748000	0.884286000	0.000533000
C	4.840716000	2.086240000	0.001204000
C	6.230619000	1.790014000	0.001125000
H	4.382404000	3.065020000	0.001722000
H	10.486108000	-1.740792000	-0.001419000
H	8.377463000	-3.503742000	-0.000012000
S	1.542601000	1.684916000	0.000211000
O	-3.897875000	2.795407000	-0.000692000
N	-1.736157000	1.938838000	-0.000275000
C	-3.387315000	0.397727000	-0.000647000
C	-1.120153000	0.693283000	-0.000242000
C	-1.125302000	3.249929000	-0.000135000
H	-0.516924000	3.407789000	0.895229000
H	-1.948273000	3.966899000	-0.000103000
H	-0.516843000	3.407966000	-0.895418000
C	-3.156181000	1.823317000	-0.000506000
C	0.875340000	-0.803742000	-0.000129000
H	0.277330000	-1.710178000	-0.000306000
C	2.285286000	-0.777414000	0.000074000
H	2.911890000	-1.660268000	0.000067000
C	0.301563000	0.451875000	-0.000048000
C	2.799581000	0.497064000	0.000293000
S	-7.057102000	-1.540531000	0.001414000
O	-1.612064000	-2.654196000	-0.000156000
N	-3.774661000	-1.797242000	-0.000166000
C	-2.123387000	-0.257195000	-0.000521000
C	-4.389629000	-0.552315000	-0.000391000

C	-4.385515000	-3.108495000	-0.000531000
H	-4.994600000	-3.265592000	-0.895458000
H	-3.562545000	-3.825412000	-0.001006000
H	-4.994142000	-3.266352000	0.894580000
C	-2.353985000	-1.681967000	-0.000245000
C	-6.386810000	0.943884000	-0.001139000
H	-5.789325000	1.850473000	-0.002058000
C	-7.803016000	0.911674000	-0.000488000
H	-8.424928000	1.798465000	-0.001030000
C	-5.815578000	-0.311599000	-0.000258000
C	-8.301789000	-0.359093000	0.000917000
H	-9.337542000	-0.670650000	0.001653000
H	7.051241000	2.492200000	0.001587000
H	9.296732000	0.727868000	-0.001195000

Compound **DTDB-DPP^{Me}**:

Total energy (ωB97X-D/6-31G(d)): -5385.12836165

C	6.610094000	-0.316093000	0.675601000
C	5.741216000	-0.970539000	-0.208539000
C	6.264686000	-1.340724000	-1.452835000
C	7.587122000	-1.086950000	-1.799706000
C	8.424093000	-0.451169000	-0.893700000
C	7.935899000	-0.061469000	0.346839000
B	4.213720000	-1.231632000	0.178328000
O	3.454168000	-0.102017000	0.185942000
B	2.131966000	0.161487000	0.361018000
C	1.783259000	1.719540000	0.397436000
C	1.447527000	2.376998000	1.586298000
C	1.166315000	3.738721000	1.620215000
C	1.213026000	4.477941000	0.447178000
C	1.551058000	3.859586000	-0.750089000
C	1.836355000	2.500150000	-0.765979000
C	1.349948000	1.598504000	2.876043000
F	1.600186000	2.367524000	3.943660000
C	0.958138000	5.962627000	0.476408000
F	0.383281000	6.383873000	-0.660676000
C	2.256248000	1.871504000	-2.074418000
F	1.802401000	2.563663000	-3.129076000
C	5.392080000	-2.062824000	-2.450886000
F	5.797116000	-1.855920000	-3.710813000
C	9.843869000	-0.125969000	-1.278836000
F	10.332621000	-1.014828000	-2.157099000
C	6.096299000	0.175046000	2.009185000
F	7.085007000	0.316474000	2.903687000
C	3.717799000	-2.639110000	0.564095000
C	2.400975000	-3.041532000	0.753752000
S	2.317406000	-4.717174000	1.206998000
C	4.027950000	-4.887868000	1.137864000
C	4.629433000	-3.722207000	0.787889000
C	1.179273000	-2.273380000	0.605357000
S	-0.356036000	-3.087031000	0.627117000
C	-1.229556000	-1.595894000	0.458320000
C	-0.361478000	-0.544507000	0.374375000
C	1.018518000	-0.902271000	0.449998000
F	0.127147000	1.070280000	3.043483000
F	2.229480000	0.577313000	2.901245000
F	0.154208000	6.306412000	1.493691000
F	2.102456000	6.649542000	0.621351000

F	3.590134000	1.802720000	-2.184668000
F	1.783847000	0.614001000	-2.188940000
F	9.926941000	1.086063000	-1.850332000
F	10.654499000	-0.118219000	-0.209647000
F	5.396575000	-3.389463000	-2.244270000
F	4.110519000	-1.653674000	-2.368403000
F	5.485849000	1.363026000	1.896562000
F	5.200093000	-0.682406000	2.537065000
H	-0.696795000	0.482704000	0.280512000
H	5.703592000	-3.619597000	0.687307000
H	4.487576000	-5.840333000	1.362623000
H	0.912626000	4.219610000	2.557752000
H	1.585283000	4.434309000	-1.668327000
H	7.961909000	-1.382710000	-2.772694000
H	8.588109000	0.433307000	1.056965000
S	-3.522334000	-0.261860000	-0.318846000
O	-8.365693000	2.116353000	-1.627002000
N	-6.566038000	0.825507000	-0.917675000
C	-8.606704000	-0.049457000	-0.504321000
C	-6.358691000	-0.390413000	-0.279190000
C	-5.585275000	1.778629000	-1.389402000
H	-4.974425000	2.163522000	-0.567552000
H	-6.150926000	2.603156000	-1.826975000
H	-4.941182000	1.342762000	-2.158794000
C	-7.954230000	1.098604000	-1.089042000
C	-4.913481000	-2.179354000	0.688666000
H	-5.757980000	-2.785754000	1.001952000
C	-3.560954000	-2.523210000	0.896202000
H	-3.245256000	-3.426773000	1.405403000
C	-5.076044000	-0.969325000	0.045438000
C	-2.680104000	-1.584854000	0.415517000
S	-12.689902000	-0.747959000	-0.254294000
O	-7.841314000	-3.097911000	1.103586000
N	-9.641943000	-1.811427000	0.387761000
C	-7.601483000	-0.933477000	-0.020830000
C	-9.849778000	-0.595911000	-0.250462000
C	-10.622988000	-2.762538000	0.863665000
H	-11.227830000	-3.157216000	0.042154000
H	-10.058397000	-3.580909000	1.313740000
H	-11.273495000	-2.318538000	1.622684000
C	-8.254405000	-2.082428000	0.562594000
C	-11.297906000	1.192916000	-1.212995000
H	-10.453882000	1.809552000	-1.506824000
C	-12.656384000	1.531101000	-1.427425000
H	-12.980074000	2.445983000	-1.908344000
C	-11.134816000	-0.022886000	-0.581562000
C	-13.516630000	0.578451000	-0.962168000
H	-14.597718000	0.580904000	-0.995381000

Compound **DFDB**:

Total energy (ωB97X-D/6-31G(d)): -3067.42225016

C	-2.586171000	-0.717875000	1.329255000
C	-2.407985000	0.033774000	0.158199000
C	-3.252771000	-0.264862000	-0.917323000
C	-4.235877000	-1.245693000	-0.831679000
C	-4.396650000	-1.955865000	0.348713000
C	-3.567449000	-1.695499000	1.432371000
B	-1.266800000	1.147341000	0.068164000

O	0.000034000	0.643181000	0.000217000
B	1.266872000	1.147326000	-0.067750000
C	2.408046000	0.033766000	-0.157983000
C	3.253009000	-0.264920000	0.917388000
C	4.236055000	-1.245799000	0.831549000
C	4.396582000	-1.955965000	-0.348878000
C	3.567190000	-1.695556000	-1.432382000
C	2.585978000	-0.717892000	-1.329071000
C	3.136932000	0.500179000	2.213802000
F	3.512028000	-0.242507000	3.264461000
C	5.424369000	-3.053658000	-0.437697000
F	5.905200000	-3.176963000	-1.684438000
C	1.662126000	-0.511100000	-2.507214000
F	2.226633000	-0.903074000	-3.658832000
C	-3.136412000	0.500265000	-2.213689000
F	-3.511411000	-0.242354000	-3.264431000
C	-5.424506000	-3.053511000	0.437313000
F	-6.462855000	-2.825781000	-0.381422000
C	-1.662571000	-0.511121000	2.507604000
F	-2.227331000	-0.903138000	3.659083000
C	-1.604439000	2.642499000	0.106923000
C	-0.714688000	3.695260000	0.054752000
O	-1.350577000	4.879519000	0.126704000
C	-2.679951000	4.606407000	0.230322000
C	-2.893395000	3.271595000	0.224808000
C	0.714753000	3.695249000	-0.054917000
O	1.350632000	4.879494000	-0.127174000
C	2.680002000	4.606366000	-0.230801000
C	2.893455000	3.271557000	-0.224944000
C	1.604509000	2.642479000	-0.106858000
F	3.912000000	1.598581000	2.210768000
F	1.874276000	0.906455000	2.440362000
F	6.462797000	-2.826094000	0.380983000
F	4.899402000	-4.241061000	-0.094997000
F	0.522323000	-1.202621000	-2.366092000
F	1.324586000	0.785583000	-2.650551000
F	-4.899579000	-4.240898000	0.094496000
F	-5.905443000	-3.176951000	1.684000000
F	-3.911363000	1.598750000	-2.210738000
F	-1.873671000	0.906409000	-2.440024000
F	-0.522746000	-1.202657000	2.366708000
F	-1.325058000	0.785554000	2.651067000
H	3.849623000	2.773149000	-0.286436000
H	3.325109000	5.467900000	-0.297334000
H	-3.849560000	2.773196000	0.286400000
H	-3.325067000	5.467955000	0.296596000
H	4.872113000	-1.455601000	1.683667000
H	3.689642000	-2.248829000	-2.356170000
H	-4.871791000	-1.455457000	-1.683916000
H	-3.690104000	-2.248764000	2.356137000

3. References

[1] G. Lu, H. Usta, C. Risko, L. Wang, A. Facchetti, M. A. Ratner and T. J. Marks, Synthesis, Characterization, and Transistor Response of Semiconducting Silole Polymers with Substantial Hole Mobility and Air Stability. Experiment and Theory, *J. Am. Chem. Soc.*, 2008, **130**, 7670.

[2] J. Bachmann, A. Helbig, M. Crumbach, I. Krummenacher, H. Braunschweig and H. Helten, Fusion of Aza- and Oxadiborepins with Furans in a Reversible Ring-Opening Process Furnishes Versatile Building Blocks for Extended π-Conjugated Materials, *Chem. Eur. J.*, 2022, **28**, e202202455.

[3] X. Wang, Y. Sun, S. Chen, X. Guo, M. Zhang, X. Li, Y. Li and H. Wang, Effects of π-Conjugated Bridges on Photovoltaic Properties of Donor-π-Acceptor Conjugated Copolymers, *Macromolecules*, 2012, **45**, 1208.

[4] G. Conboy, R. G. D. Taylor, N. J. Findlay, A. L. Kanibolotsky, A. R. Inigo, S. S. Ghosh, B. Ebenhoch, L. K. Jagadamma, G. K. V. V. Thalluri, M. T. Sajjad, I. D. W. Samuel and P. J. Skabara, Novel 4,8-benzobisthiazole copolymers and their field-effect transistor and photovoltaic applications, *J. Mater. Chem. C*, 2017, **5**, 11927.

[5] Q. Yan, M. Yin, C. Chen and Y. Zhang, An Air-Stable Organoboron Compound, Dithienooxadiborepine: Preparation and Functionalization, *J. Org. Chem.*, 2018, **83**, 9096.

[6] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, M. C. X. Li, A. V. Marenich, B. G. J. J. Bloino, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. L. F. Ding, J. G. F. Egidi, A. P. B. Peng, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16 Revision C.01*, Gaussian, Inc., Wallingford CT, 2016.

[7] J.-D. Chai and M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615.

[8] J. D. Dill and J. A. Pople, Self-consistent molecular orbital methods. XV. Extended Gaussian-type basis sets for lithium, beryllium, and boron, *J. Chem. Phys.*, 1975, **62**, 2921.

[9] R. Ditchfield, W. J. Hehre and J. A. Pople, Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules, *J. Chem. Phys.*, 1971, **54**, 724.

[10] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements, *J. Chem. Phys.*, 1982, **77**, 3654.

[11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, M. C. X. Li, A. V. Marenich, B. G. J. J. Bloino, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. L. F. Ding, J. G. F. Egidi, A. P. B. Peng, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.

P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 09 Revision E.01*, Gaussian, Inc., Wallingford CT, 2009.

[12] M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro and W. J. Hehre, Self-consistent molecular-orbital methods. 22. Small split-valence basis sets for second-row elements, *Journal of the American Chemical Society*, 1982, **104**, 2797.

[13] P. C. Hariharan and J. A. Pople, The influence of polarization functions on molecular orbital hydrogenation energies, *Theor. Chim. Acta*, 1973, **28**, 213.

[14] W. J. Hehre, R. Ditchfield and J. A. Pople, Self—Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules, *J. Chem. Phys.*, 1972, **56**, 2257.

[15] F. Neese, F. Wennmohs, U. Becker and C. Riplinger, The ORCA quantum chemistry program package, *J. Chem. Phys.*, 2020, **152**, 224108.

[16] F. Neese, Software update: The ORCA program system—Version 5.0, *WIREs Computational Molecular Science*, 2022, **12**.

[17] Y. S. Lin, G. D. Li, S. P. Mao and J. D. Chai, Long-Range Corrected Hybrid Density Functionals with Improved Dispersion Corrections, *J. Chem. Theory Comput.*, 2013, **9**, 263.

[18] T. Stein, L. Kronik and R. Baer, Reliable prediction of charge transfer excitations in molecular complexes using time-dependent density functional theory, *J. Am. Chem. Soc.*, 2009, **131**, 2818.

[19] T. Stein, H. Eisenberg, L. Kronik and R. Baer, Fundamental gaps in finite systems from eigenvalues of a generalized Kohn-Sham method, *Phys. Rev. Lett.*, 2010, **105**, 266802.

[20] A. Karolewski, L. Kronik and S. Kummel, Using optimally tuned range separated hybrid functionals in ground-state calculations: consequences and caveats, *J. Chem. Phys.*, 2013, **138**, 204115.

[21] F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.

[22] V. Barone and M. Cossi, Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model, *J. Phys. Chem. A*, 1998, **102**, 1995.

[23] A. Stanger, Nucleus-independent chemical shifts (NICS): distance dependence and revised criteria for aromaticity and antiaromaticity, *J. Org. Chem.*, 2006, **71**, 883.