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SUPPORTING INFORMATION

Unusual Electronic Structure of Ambipolar Dicyanovinyl-Substituted Diketopyrrolopyrrole Derivatives

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General Information.

Materials and instruments

All the chemicals were purchased from commercial suppliers and used without further purification. Compounds DPPT and *N*,*N*-alkylated DPPT were obtained as previously described.[i]

Toluene was freshly distilled over sodium/benzophenone under nitrogen before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on BrukerAvance 300 and AMX 500 MHz spectrometers. Chemical shifts are reported in ppm and referenced to the residual non-deuterated solvent frequencies ($CDCl_3$: δ 7.26 ppm for ^{1}H, δ 77.0 ppm for ^{13}C, $C_2D_2Cl_4$: δ 5.90 ppm for ^{1}H, δ 73.8 ppm for ^{13}C). UV–vis absorption spectra of the polymers in HPLC dichloromethane solutions at 20 °C were recorded on a Varian Cary 50 UV–vis spectrophotometer. Mass spectra were recorded on a MAT95 XP (FAB) or Bruker Reflex 2 (MALDI-TOF). Cyclic voltammograms were recorded in an inert atmosphere in electrochemical workstation at a scan rate of 100 $mV\cdot s^{-1}$ at 20 °C using tetrabutylammoniumhexafluoro phosphate (TBAHFP, 0.1 mol L^{-1}) as supporting electrolyte in dichloromethane. Polymer-precoated platinum electrodes, platinum–wire electrodes, and Ag/Ag^{+} electrodes were used as the working electrode, an auxiliary electrode, and the reference electrode, respectively. Potentials were recorded versus Fc/Fc$^+$.

UV-Vis absorption spectra of **DPP-4T-2DCV** and **2DPP-6T-2DCV** dichloromethane solutions were recorded on an Agilent 8453 instrument equipped with a diode array detection system. Emission and excitation spectra were measured using a spectrofluorometer from Edinburgh Analytical Instrument (FLS920P) equipped with a pulsed xenon flash-lamp, Xe900, of 400 mW. The transient absorption spectra were measured with an spectrometer from Luzchem (FLP-111) which includes a ceramic xenon light source of 300 W, 125 mm monochromator and Tektronix digitizer TDS-3000 series with 300 MHz bandwidth. A Nd:YAGLotis TII LS-2132 UTF laser working at 355 nm was employed for excitation.

FT-Raman spectra with 1064 nm excitation were recorded using a FT Raman accessory kit (FRA/106-S) of a Bruker Equinox 55 FT-IR interferometer and a continuous-wave Nd:YAG laser. A germanium detector operating at liquid-nitrogen temperature was used and the Raman scattering radiation was collected in a back-scattering configuration with a 4 cm^{-1} spectral resolution. An average of 1000 scans was used in the reported spectra.

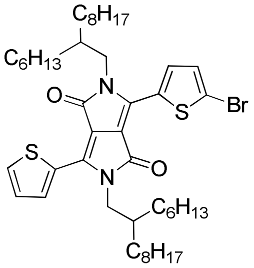
DFT calculations were performed using the B3LYP functional[ii] and 6-31G** basis set[iii]as implemented in Gaussian 09.[iv]Optimal geometries were determined on isolated entities. From the resulting ground-state optimized structures, relevant molecular parameters such as bond lengths and angles, molecular orbital energies and topologies, and atomic charge distributions were estimated.Radical cations, radical anions and dications were also calculated for the two semiconductors. Radical cations and anionswere treated as open-shell systems and computed using spin-unrestricted UB3LYP wavefunctions. For all the molecules, the maximum value obtained for the spin contamination $<S^2>$ was ~0.75-0.77, close to the 0.75 theoretically expected for a doublet, showing that spin contamination is almost absent. From the optimized radical cation, radical anion and dianion structures, atomic charge distributions were estimated.

OFET Fabrication and Characterization. Heavily doped Silicon substrates with a 300 nm thick thermally grown SiO_2layer were coated with an octadecyltrichlorosilane(OTS) monolayer. Around 80 nm thick films of **1** and **2**were spin-cast on the treated substrates from 10mg/mL semiconductor solutions in chloroform. Thin film AFM images were recorded in the tapping mode on aVeeco ICON PT system. The crystallinity and long range packing order of the **DPP-4T-2DCV** and **2DPP-6T-2DCV**thin films were studied by out of planediffraction of grazing incidence X-ray (GI-XRD) in a Rigaku ATX-G diffractometer with monochromatedCuKα radiation.

Top Au contacts (30 nm) were then deposited by thermal evaporation through a shadow mask to complete bottom-gate, top contact OFET devices. The resulting devices had channel lengths and widths of 50 and 1000 µm, respectively. Devices were tested in the dark and under vacuum using an Agilent B1500 semiconductor parameter analyzer. Hole and electron mobilities were extracted from saturated regimes from at least three separate devices from each substrate.

Synthesis of compounds:

DPP-2T-Br



To a solution of **DPP-2T** (500 mg, 0.67 mmol) in 36 mL of chloroform was very slowly added NBS (119 mg, 0.67 mmol) at 0°C. Then, the mixture was allowed to reach room temperature and stirred overnight in the dark. The solvent was removed under reduced pressure and the crude reaction was chromatographed on silica gel (hexanes:diethyl ether 9.5:0.5) to yield 287 mg (56%) of **DPP-2T-Br as** a red-pink solid, together with dibromoderivative**DPP-2T-2Br** 103 mg (17%) and starting material.

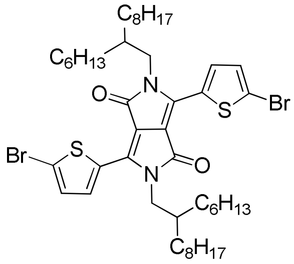
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.88 (m, 1H), 7.63 (dd, *J* = 5 Hz, *J* = 1.1 Hz, 1H), 7.26 (m, 2H), 7.21 (d, *J* = 4.2 Hz, 1H), 4.01 (d, *J* = 7.7 Hz, 2H), 3.93 (d, *J* = 7.7 Hz, 2H), 1.89 (bs, 2H), 1.33-1.11 (m, 96H), 0.92-0.82 (m, 24H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 161.8, 161.6, 141.0, 139.1, 135.6, 135.2, 131.5, 131.4, 130.9, 129.9, 128.6, 108.3, 107.9, 46.4, 37.9, 32.0, 31.9, 31.3, 29.8, 29.6, 29.4, 26.3, 22.8, 14.3, 14.2.

FTIR (CH_2Cl_2) ν (cm^{-1}) = 2925, 2854, 1666, 1560, 1457, 1400, 1102.

MS MALDI (m/z): calc. 826.414; found (M^+) 826.169.

DPP-2T-2Br



To a solution of **DPP-2T** (136 mg, 0.18 mmol) in 10 mL of chloroform was added NBS (67 mg, 0.38 mmol). Then the mixture was stirred 48 h in the dark. The solution was washed with water and extracted with dichloromethane. The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under pressure. The crude is purified on column chromatography (hexane:diethylether 9:1) to obtain 100 mg (61%) of a pink solid.

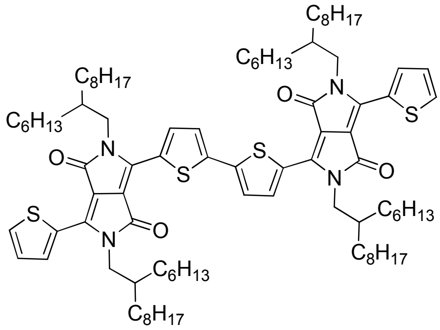
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.62 (d, *J* = 4.2 Hz, 2H), 7.21 (d, *J* = 4.2 Hz, 2H),3.92 (d, *J* = 7.2 Hz, 4H), 1.87 (bs, 2H), 1.30 -1.16 (m, 96H), 0.90-0.82 (m, 24H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 161.5, 139.5, 135.5, 131.6, 131.3, 119.1, 108.1, 46.5, 37.9, 32.0, 31.9, 31.3, 30.1, 29.8, 29.6, 29.4, 26.3, 22.8, 14.3.

FTIR (CH_2Cl_2) ν (cm^{-1}) = 3086, 2925, 2854, 1658, 1554, 1407, 1356.

MS MALDI (m/z):calc. 904.325; found (M^+) 904.353

2DPP-4T



A mixture of **DPP-2T-Br** (180 mg, 0.22 mmol), bis-tributyltin (183 mg, 0.31 mmol) and catalytic amount of Pd(PPh_3)$_4$ (10%) in 25 mL of degassed anhydrous toluene was refluxed under stirring for 24 h under argon. Then, the mixture was cooled to room temperature, the solvent was removed under reduced pressure and the crude reaction was chromatographied on silica gel to yield 105 mg (64 %) of a dark blue solid.

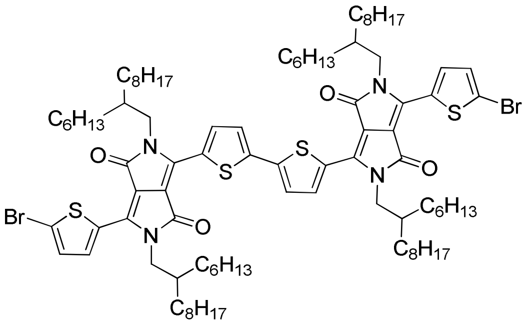
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.92 (m, 4H), 7.63 (dd, *J* = 5 Hz, *J* = 1.1 Hz, 2H), 7.41 (d, *J* = 4.2 Hz, 2H), 7.28 (t, *J* = 4.1 Hz, 2H), 4.04 (d, *J* = 7.6 Hz, 8H), 1.93 (m, 4H), 1.35-1.22 (m, 96H), 0.89-0.82 (m, 24H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 161.6, 140.8, 140.6, 139.1, 136.5, 135.5, 130.7, 129.8, 129.7, 128.5, 126.0, 125.3, 108.9, 108.2, 46.3, 38.0, 37.7, 31.8, 31.7, 31.2, 31.1, 30.0, 29.7, 29.5, 29.3, 26.2, 26.1, 22.6, 14.1.

FTIR (CH_2Cl_2) ν (cm^{-1}) = 2924, 2854, 1712, 1668, 1556, 1461.

MS FAB (m/z) = calc. 1495.0; found (M+H$^+$) 1496.2.

2DPP-4T-2Br



To a solution of **2DPP-4T** (134 mg, 0.089 mmol) in 20 mL of chloroform was very slowly added NBS (35 mg, 0.19 mmol) at -15^{o}C. Then, the mixture was let to reach room temperature and stirred overnight in the dark. The solvent was removed under reduced pressure and the crude reaction was chromatographied on silica gel to yield 81 mg (55 %) of a dark blue solid.

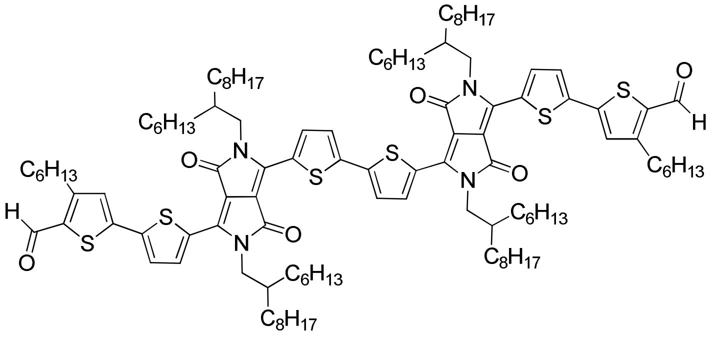
^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) = 8.87 (d, *J* = 4.2 Hz, 2H), 8.61 (d, *J* = 4.2 Hz, 2H), 7.37 (d, *J* = 4.2 Hz, 2H), 7.18 (d, *J* = 4.2 Hz, 2H), 4.01 (d, *J* = 7.6 Hz , 4H), 3.94 (d, *J* = 7.6 Hz, 4H), 1.90 (bs, 4H), 1.43-1.11 (m, 96H), 0.88-0.81 (m, 24H).

^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm) = 161.3, 161.2, 141.1, 139.4, 139.0, 136.6, 135.3, 131.3, 131.2, 129.7, 126.0, 119.0, 108.6, 108.2, 46.3, 37.9, 37.7, 31.9, 31.8, 31.2, 31.1, 30.0, 29.7, 29.6, 29.5, 29.3, 26.2, 26.1, 22.7, 22.6, 14.1.

FTIR (CH$_2$Cl$_2$) ν (cm^{-1}) = 2920, 2852, 1722, 1668, 1554, 1460, 1375.

MS FAB (m/z) = calc. 1650.8; found (M$^+$ 1650.9).

2DPP-6T-2CHO



A solution of **2DPP-4T-2Br** (67 mg, 0.04 mmol), (5-(1,3-Dioxolan-2-yl)-4-hexylthiophen-2-yl)tributylstannane (86 mg, 0.16 mmol) and Pd(PPh_3)$_4$ (10 %) was refluxed under argon atmosphere for 48 h. The solvent was removed under reduced pressure and the crude purified on flash column chromatography (hexanes/DCM mixtures) obtaining a dark green solid. Then, the product was dissolved on 10 mL of diethyl ether, 10 mL of HCl (30 % aqueous solution) were added and the mixture was stirred 2 h at room temperature. Afterwards, the mixture was washed with $NaHCO_3$, water, and the organic layer was dried over $MgSO_4$. The desiccant was filtered off and the solvent eliminated. A dark green solid was obtained 48 mg (62 %).

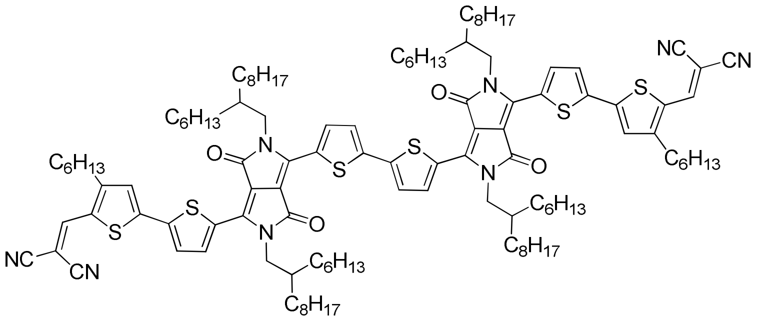
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 10.00, (s, 2H), 8.91 (bs, 2H), 8.81 (bs, 2H), 7.37 (bs, 4H), 7.15 (s, 2H), 4.03 (d, J = 7.6 Hz, 8H), 2.94 (t, J = 7.7, 4H), 1.91 (bs, 4H), 1.73-1.21 (m, H), 0.91-0.82 (m, 30H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 181.4, 161.4, 161.3, 153.7, 144.1, 141.3, 140.9, 139.4, 139.0, 137.2, 137.2, 136.9, 136.3, 130.4, 129.7, 127.6, 126.7, 126.1, 109.2, 109.0, 46.4, 37.9, 31.9, 31.8, 31.4, 31.3, 30.1, 29.7, 29.6, 29.5, 29.3, 29.0, 28.6, 26.4, 26.3, 26.2, 22.7, 22.6, 22.5, 14.1, 14.0.

FTIR (CH_2Cl_2) ν (cm^{-1}) = 2924, 2854, 1738, 1660, 1549, 1438, 1380, 1219

MALDI-HRMS (m/z): cal. 1883.1445; found ($M+H^+$) 1884.1486.

2DPP-6T-2DCV



A solution of **2DPP-6T-2CHO** (38 mg, 0.02 mmol), malononitrile (5.3 mg, 0.08 mmol) and β-alanine (5.4 mg, 0.06 mmol) in a mixture of dichloroethane (8 mL) and ethanol (3 mL) was stirred under reflux for 48 h. After the removal of the solvent under reduced pressure the crude product was filtered and washed with water and hot methanol obtaining 28 mg (70 %) of a dark green solid.

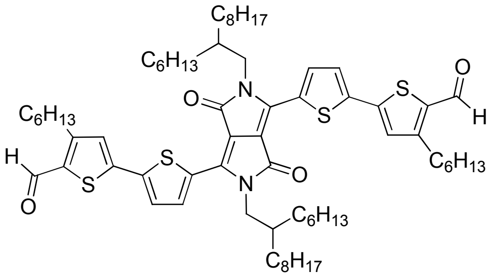
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.93 (d, *J* = 4.0 Hz, 2H), 8.78 (d, *J* = 4.3 Hz, 2H), 7.82 (s, 2H), 7.37 (d, *J* = 4.2 Hz, 2H), 7.34 (d, *J* = 4.3 Hz 2H), 7.21 (s, 2H), 4.02 (bs, 8H), 2.77 (t, *J* = 7.8 Hz, 4H), 1.90 (bs, 4H), 1.67 (bs, 4H), 1.4-1.1 (m, 112H), 0.96-0.76 (m, 30H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 161.4, 161.2, 157.1, 147.2, 145.6, 141.6, 139.8, 139.5, 138.3, 137.3, 136.2, 131.7, 130.0, 129.8, 127.8, 127.0, 126.2, 114.7, 113.6, 109.8, 109.0, 108.6, 75.3, 46.4, 38.0, 37.9, 31.9, 31.8, 31.5, 31.4, 31.3, 30.0, 29.7, 29.6, 29.4, 29.2, 26.4, 26.3, 26.2, 22.7, 22.6, 22.5, 14.1, 14.0.

FTIR (CH_2Cl_2) ν (cm^{-1}) = 2923, 2853, 2221, 1668, 1545, 1487.

MALDI-HRMS (m/z): cal. 1979.1669; found (M^{+}) 1979.1758.

DPP-4T-2CHO



A toluene (30 mL) solution of 100 mg (0.11 mmol) **DPP-2T-2Br**, 184 mg (0.35 mmol) of (5-(1,3-Dioxolan-2-yl)-4-hexylthiophen-2-yl)tributylstannane and 6.3 mg ($5.5\cdot10^{-3}$mmol) of $Pd(PPh_3)_4$ was stirred at 120°C under argon atmosphere overnight. The solvent is removed under reduced pressure and the crude is purified on column chromatography (Hexane/Diethyl Ether 8:2). After the removal de solvent the product were dissolved on dichloromethane and stirred 20 min with 2 mL of HCl cc. The solution was washed with water and extracted with dichloromethane. The organic phase was dried over $MgSO_4$, filtered and finally removed solvent by rotary evaporation. We obtained 60 mg (48 %) of a deep blue solid.

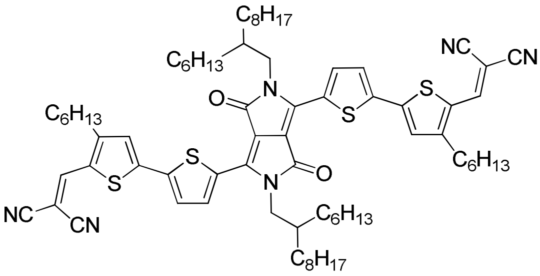
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 10.02 (s, 2H), 8.86 (d, *J* = 4.3 Hz, 2H), 7.45 (d, *J* =4.3 Hz 2H,), 7.19 (s, 2H), 4.03 (d, *J* = 7.5 Hz 4H,), 2.95 (t, *J* =7.8 Hz, 4H), 1.92 (bs, 2H), 1.71 (m, 4H), 1.45-1.15 (m, 60H), 0.95-0.80 (m, 18H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 181.6, 161.5, 153.8, 144.1, 141.2, 139.5, 137.3, 136.5, 130.3, 127.8, 126.9, 109.2, 46.4, 38.0, 32.0, 31.9, 31.6, 29.8, 29.4, 29.1, 22.8, 22.7, 22.6, 14.2.

FTIR (CH_2Cl_2) ν (cm^{-1}) = 2955, 2923, 2852, 1734, 1669, 1652, 1551, 1435, 1407.

MALDI HRMS (m/z): cal. 1136.6566; found (M+H$^+$) 1137.6675.

DPP-4T-2DCV



A solution of the **DPP-4T-2CHO** (50 mg, 0.044 mmol), malononitrile (8.7 mg, 0.13 mmol) and β-alanine (5.8 mg, 0.066 mmol) in a mixture of dichloroethane (15 mL) and ethanol (6 mL) was stirred under reflux for 2 days. After the removal of the solvent under reduced pressure the crude product was filtered and washed with water and hot methanol obtaining 37 mg (68%) of a deep green solid.

^{1}H NMR (500 MHz, CD_2Cl_4) δ (ppm) = 8.82 (d, *J* = 4.3 Hz, 2H), 7.86 (s, 2H), 7.54 (d, *J* = 4.3 Hz, 2H), 7.26 (s, 2H), 4.03 (d, *J* = 7.8 Hz, 4H), 2.76 (t, *J* =7.8 Hz, 4H), 1.90 (bs, 2H), 1.64 (m, 4H), 1.45-1.15 (m, 60H), 0.95-0.80 (m, 18H).

^{13}C NMR (125 MHz, CD_2Cl_4) δ (ppm) = 161.2, 157.3, 147.4, 145.4, 139.8, 139.2, 136.3, 131.3, 129.9, 127.9, 127.2, 120.2, 114.9, 113.6, 109.7, 75.0, 46.2, 37.8, 31.8, 31.7, 31.4, 31.2, 29.4, 29.2, 29.0, 22.6, 22.6, 22.5, 14.1, 14.1, 14.0.

FTIR (CH_2Cl_2) ν (cm^{-1}) = 2926, 2855, 2222, 1670, 1549, 1487.

MALDI-HRMS (m/z): cal. 1232.6791; found (M+H$^+$) 1233.6810.

UV and Cyclic Voltammetric Data

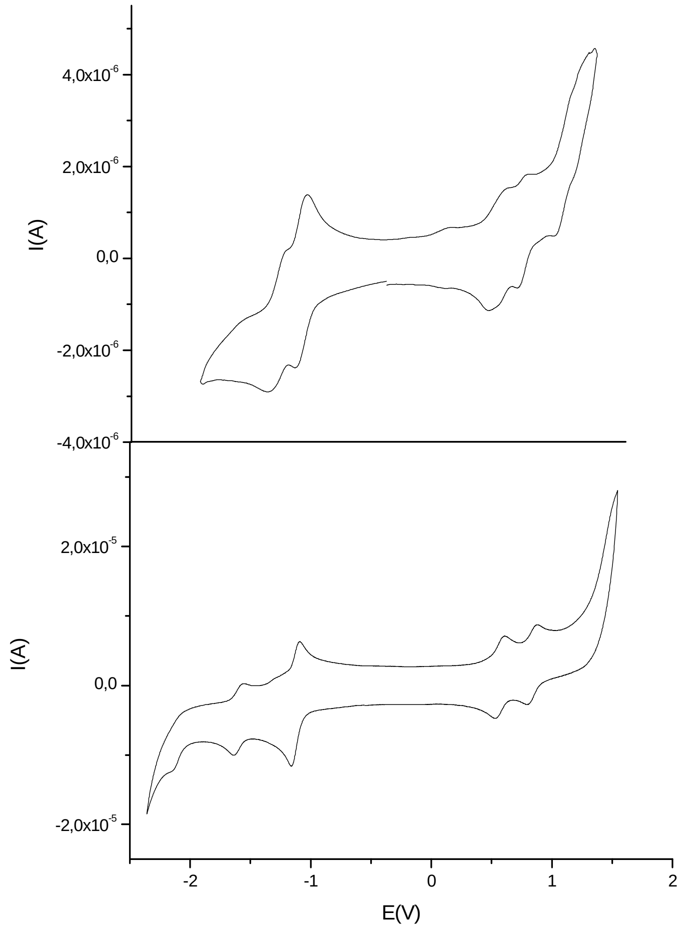
Table S1. UV/Vis absorption onsets (λ_{ons}), maxima (λ_{max}), optical band gap (E_{GAP}^{OPT}), reduction (E_{red}) and oxidation (E_{ox}) potentials, E_{HOMO} and E_{LUMO}.* Electrochemical band gaps (E_{GAP}^{ELEC}) measured in CH_2Cl_2 solution (potentials are relative to ferrocene).

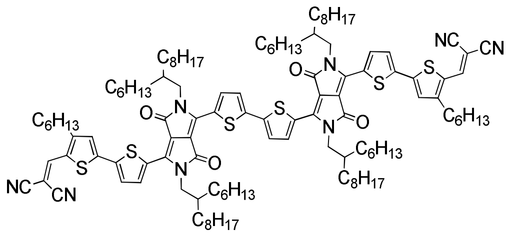
* Values calculated according to the following equations:

$$E_{GAP}^{OPT} = \frac{E}{\lambda ons} = \frac{h \cdot c \cdot Q}{\lambda ons} \quad h = 6.626 \cdot 10^{-34}\ J \cdot s^{-1} \quad c = 2.998 \cdot 10^{8} m \cdot s \quad Q = -1.6 \cdot 10^{-19}\ eV$$

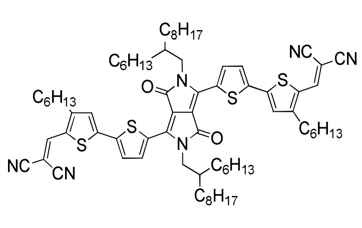
E_{LUMO}: $-(E_{red}+4.80)$ (eV)E_{HOMO}: $-(E_{ox}+4.80)$ (eV)$E_{GAP}^{ELEC} = E_{LUMO} - E_{HOMO}$

	λ_{ons} nm	λ_{max} nm	E_{GAP}^{OPT} eV	$E_{red(I)}^{1/2}$ V	$E_{red(II)}^{1/2}$ V	$E_{ox(I)}^{1/2}$ V	$E_{ox(II)}^{1/2}$ V	E_{HOMO} V	E_{LUMO} V	E_{GAP}^{ELEC} eV
DPP-4T-2DCV	771	645	1.60	-1.12	-1.60	0.57	0.84	-5.45	-3.68	1.69
2DPP-6T-2DCV	867	705	1.43	-1.12	-1.32	0.47	0.66	-5.27	-3.68	1.59

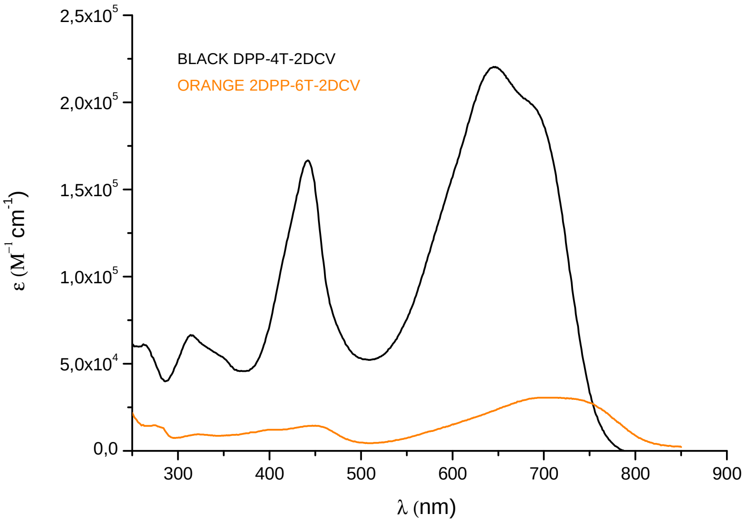




2DPP-6T-2DCV



DPP-4T-2DCV


BLACK DPP-4T-2DCV
ORANGE 2DPP-6T-2DCV
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2,0x10^5
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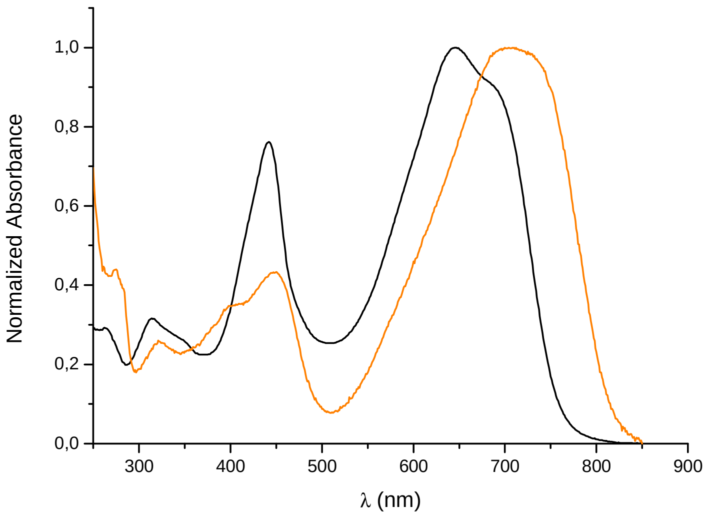
1,0x10^5
5,0x10^4
0,0
300
400
500
600
700
800
900
λ (nm)


Normalized Absorbance
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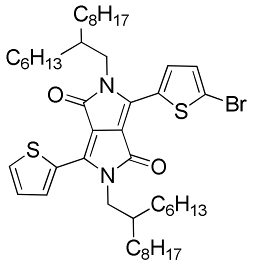
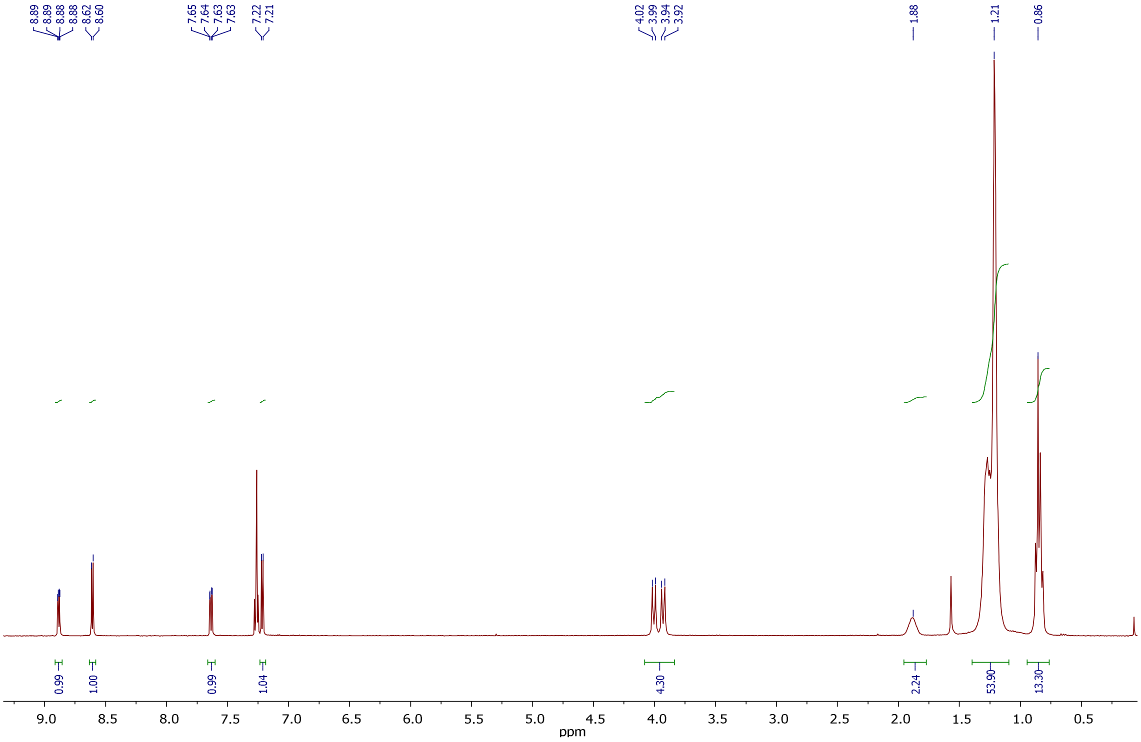
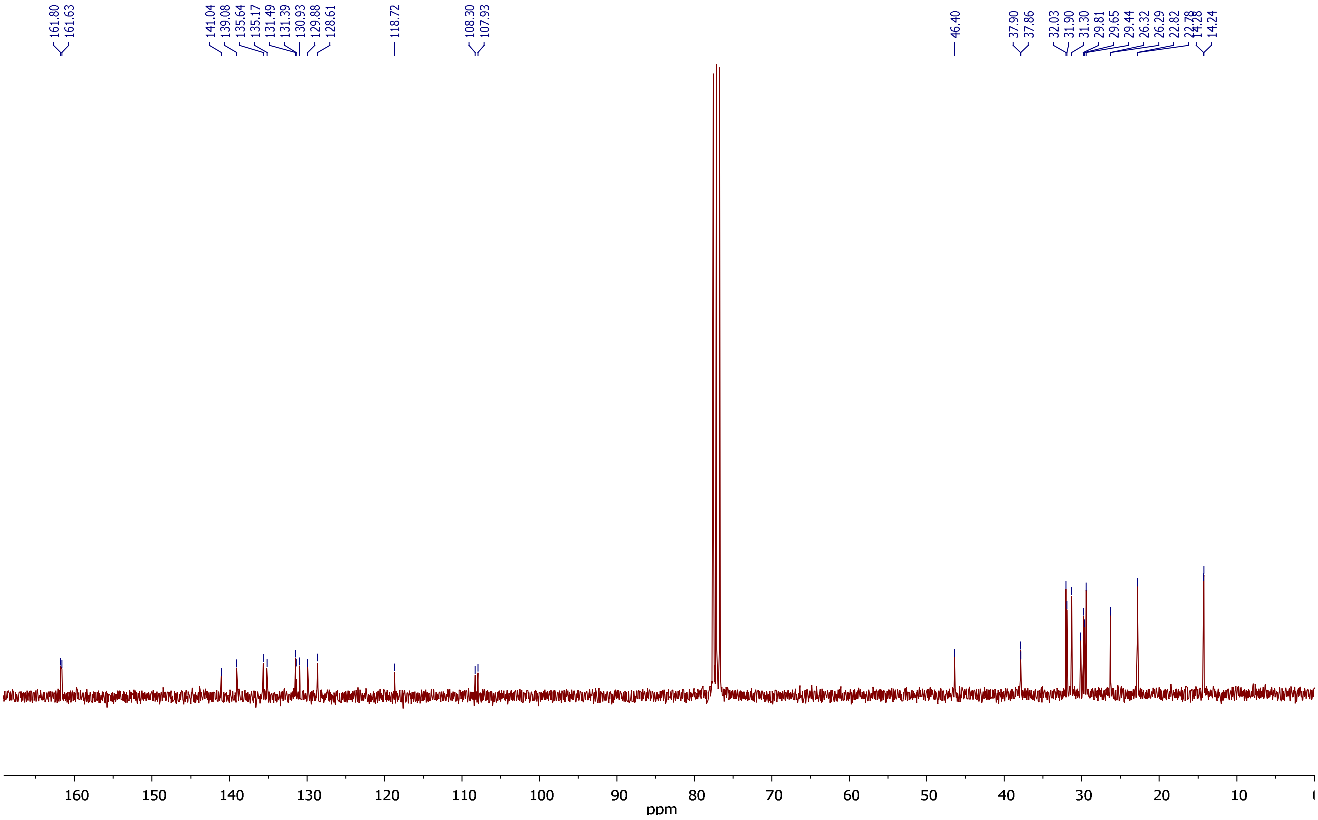
400
500
600
700
800
900
λ (nm)

Spectra of compounds:

DPP-2T-Br






161.80
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37.86
32.03
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31.30
29.81
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14.28
14.24
160
150
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130
120
110
100
90
80
70
60
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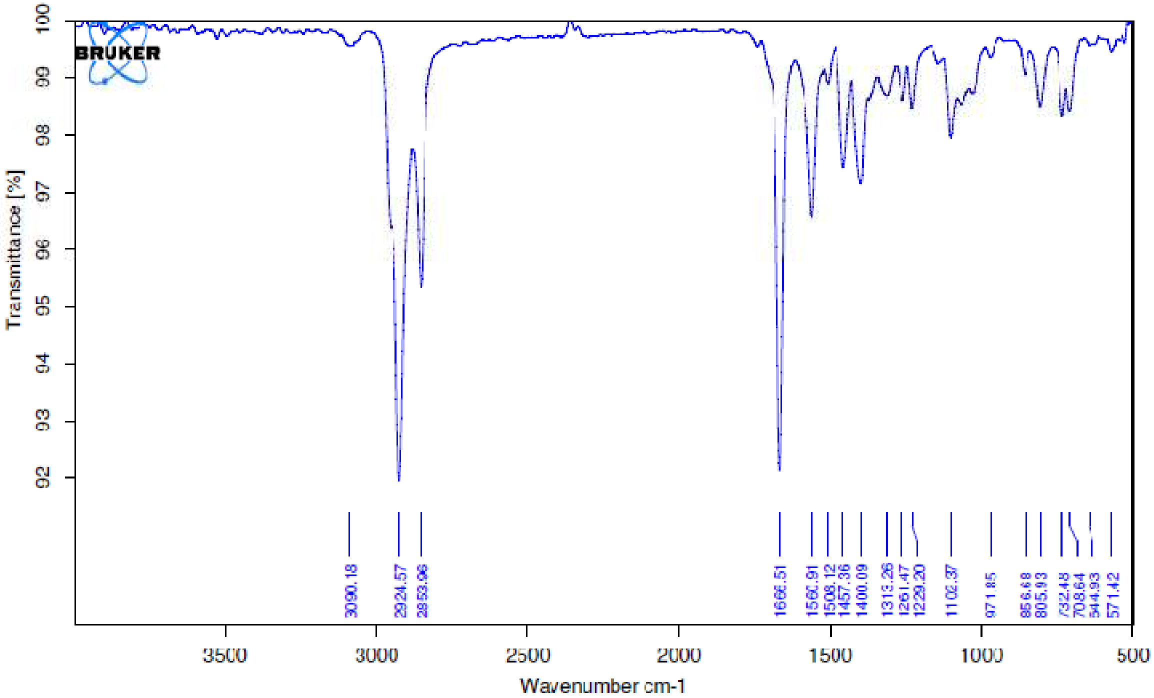
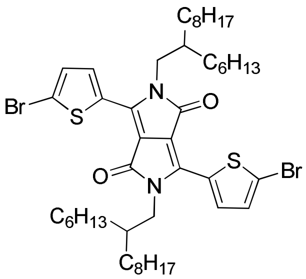
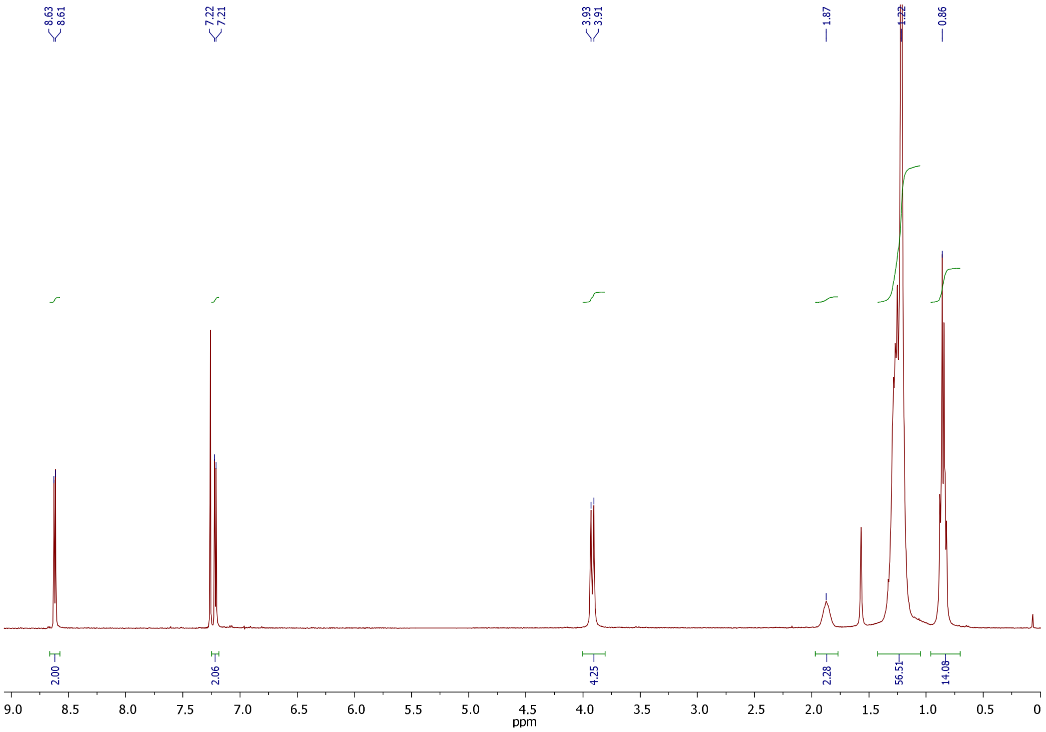
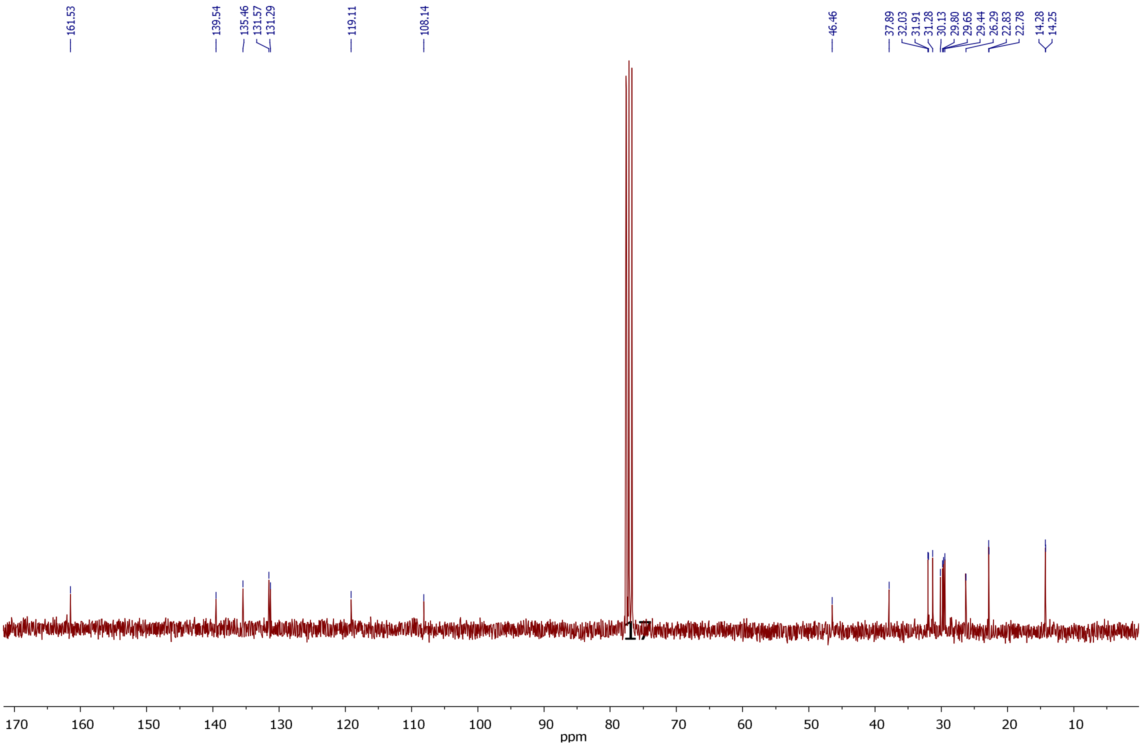
10
ppm

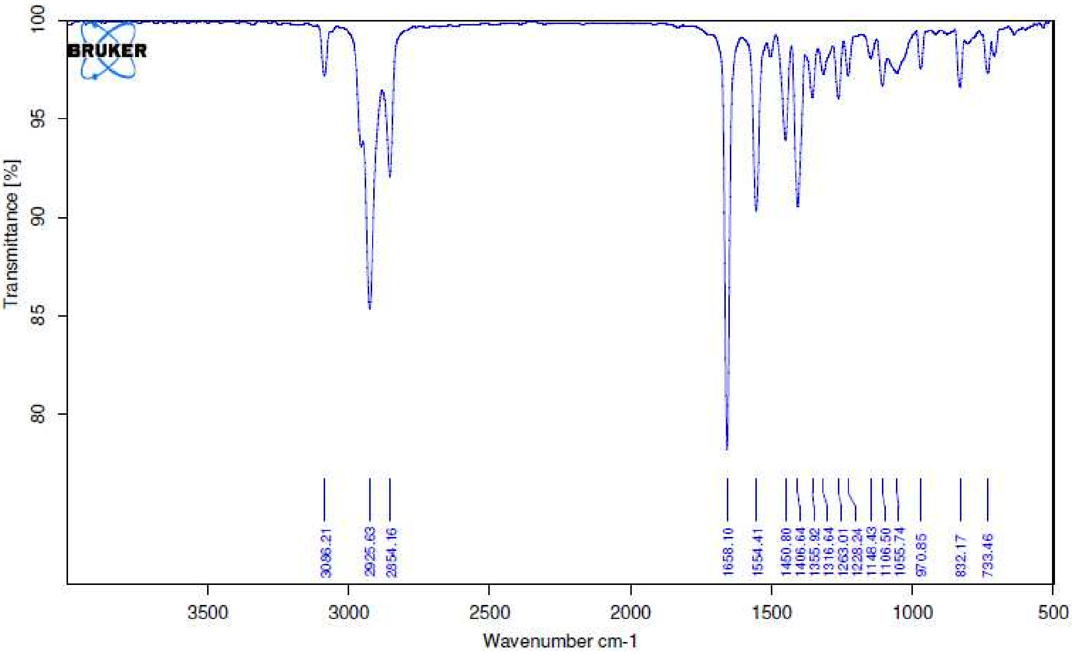

BRUKER
Transmittance [%]
100
99
98
97
96
95
94
93
92
3090.18
2924.57
2853.96
1666.51
1560.91
1508.12
1457.36
1400.09
1313.26
1261.47
1229.20
1102.37
971.85
856.68
805.93
732.48
708.64
644.93
571.42
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

DPP-2T-Br$_2$

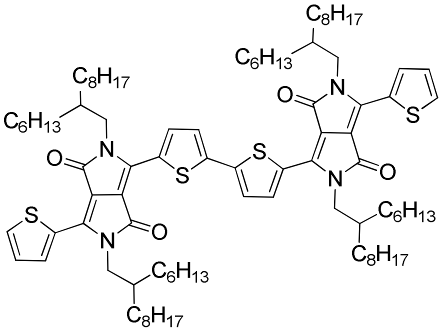

C8H17
C6H13
N
O
Br
S
S
Br
O
N
C6H13
C8H17

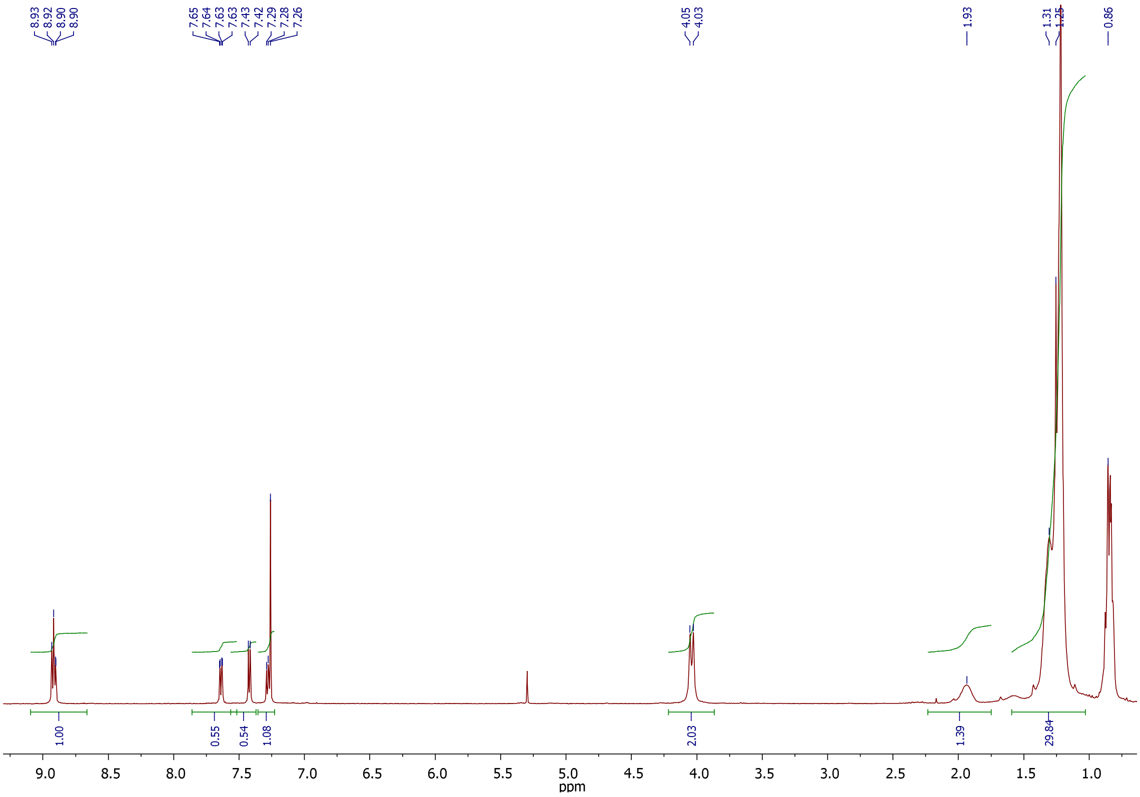

8.63
8.61
7.22
7.21
3.93
3.91
1.87
1.22
0.86
2.00
2.06
4.25
2.28
56.51
14.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
ppm

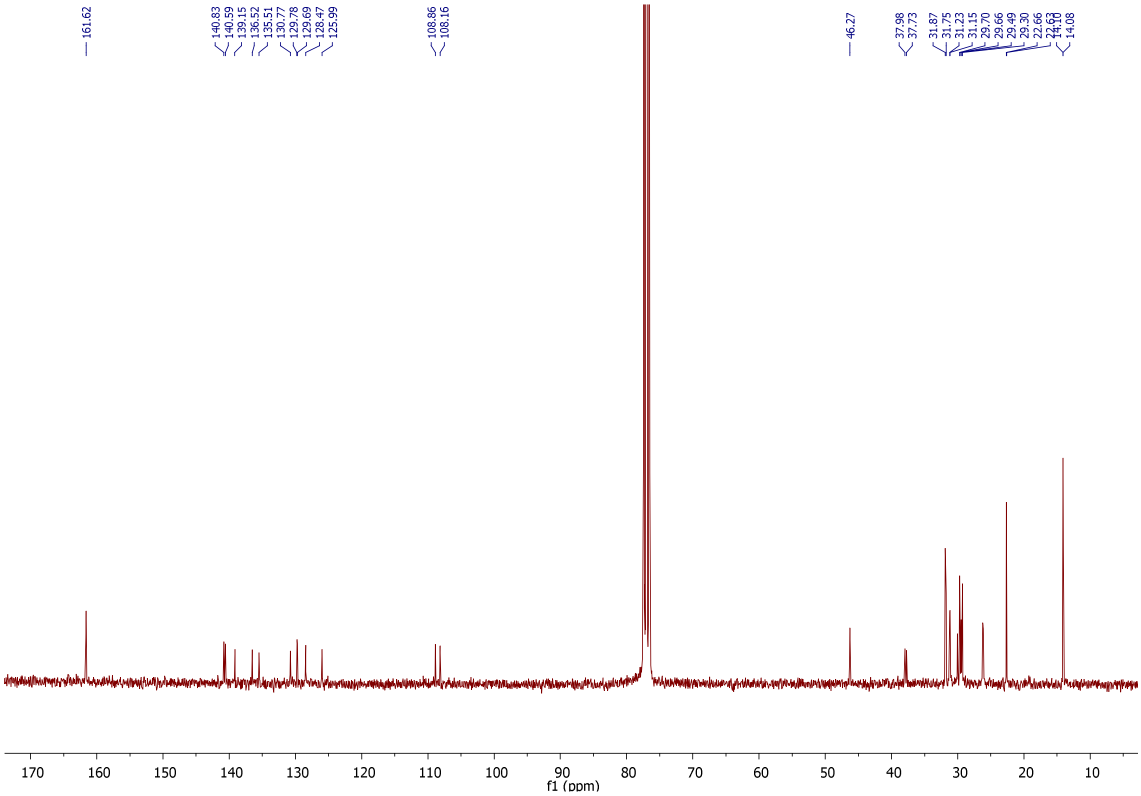

161.53
139.54
135.46
131.57
131.29
119.11
108.14
46.46
37.89
32.03
31.91
31.28
30.13
29.80
29.65
29.44
26.29
22.83
22.78
14.28
14.25
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

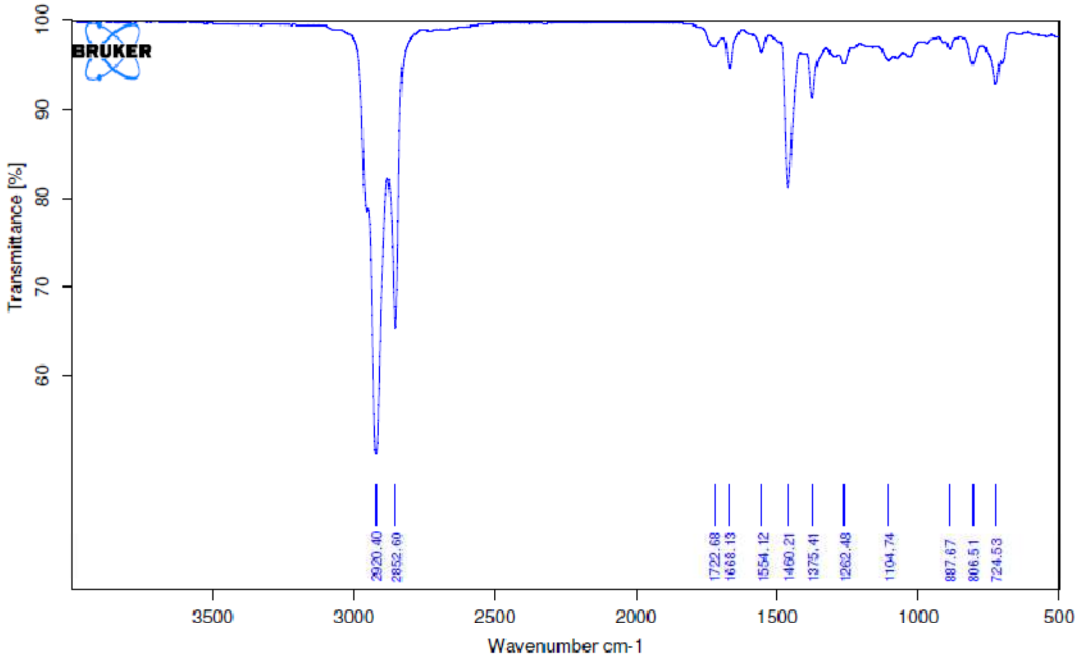

BRUKER
Transmittance [%]
100
95
90
85
80
3086.21
2925.63
2854.16
1658.10
1554.41
1450.80
1406.64
1355.92
1316.64
1263.01
1228.24
1148.43
1106.50
1055.74
970.85
832.17
733.46
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

2DPP-4T

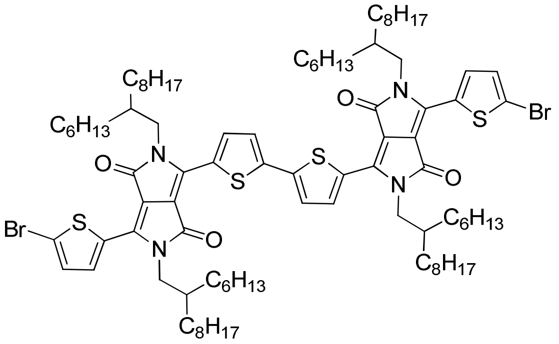

C8H17
C6H13
C8H17
C6H13
O
N
S
S
S
O
N
O
S
N
O
N
C6H13
C8H17
C6H13
C8H17

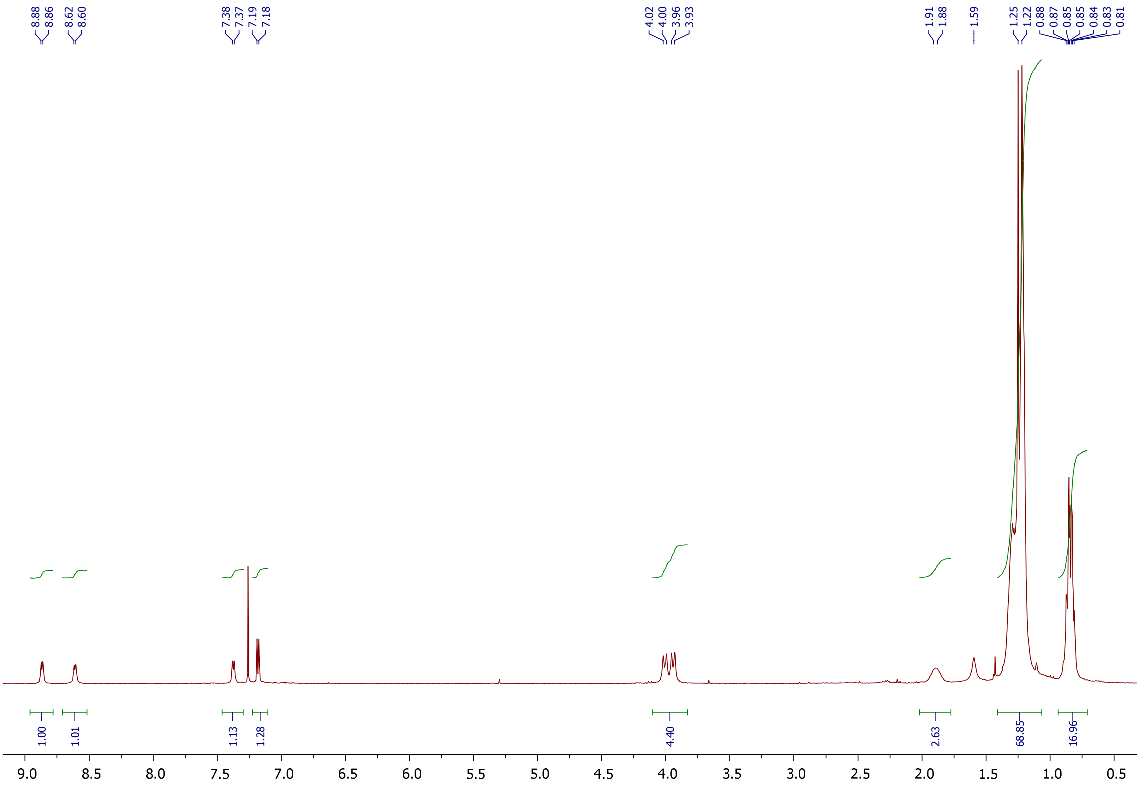

8.93
8.92
8.90
8.90
7.65
7.64
7.63
7.63
7.43
7.42
7.29
7.28
7.26
4.05
4.03
1.93
1.31
1.25
0.86
1.00
0.55
0.54
1.08
2.03
1.39
29.84
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

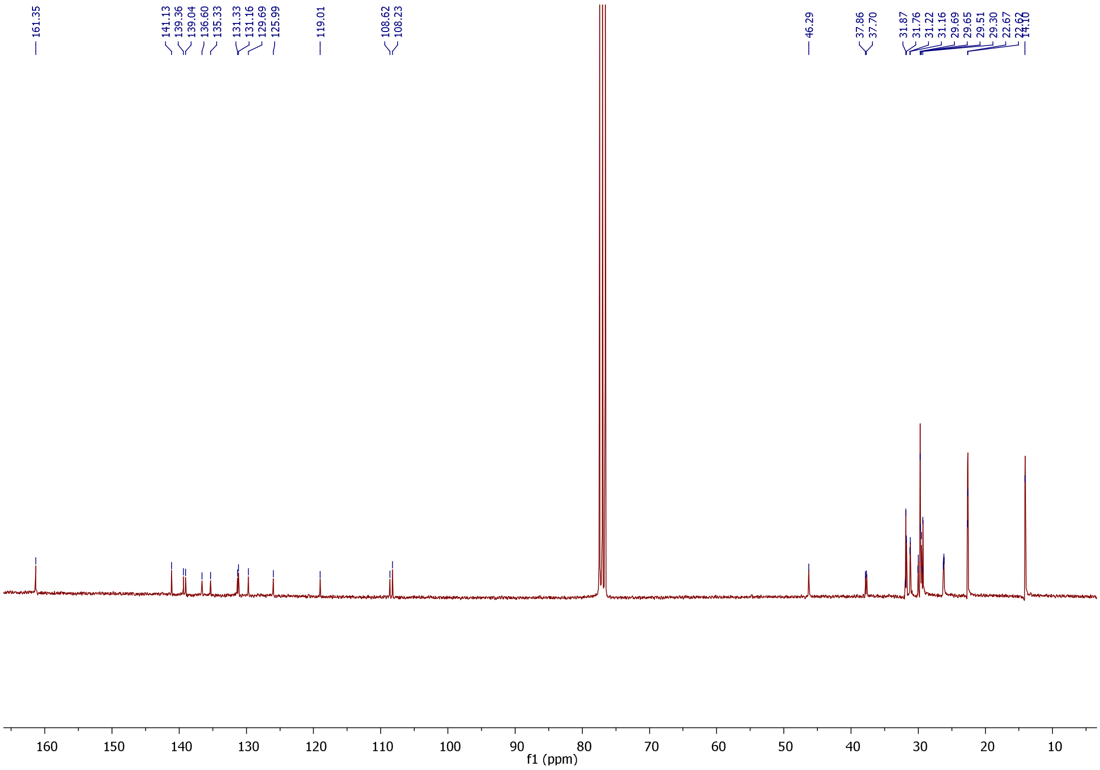

161.62
140.83
140.59
139.15
136.52
135.51
130.77
129.78
129.69
128.47
125.99
108.86
108.16
46.27
37.98
37.73
31.87
31.75
31.23
31.15
29.70
29.66
29.49
29.30
22.66
22.63
14.10
14.08
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

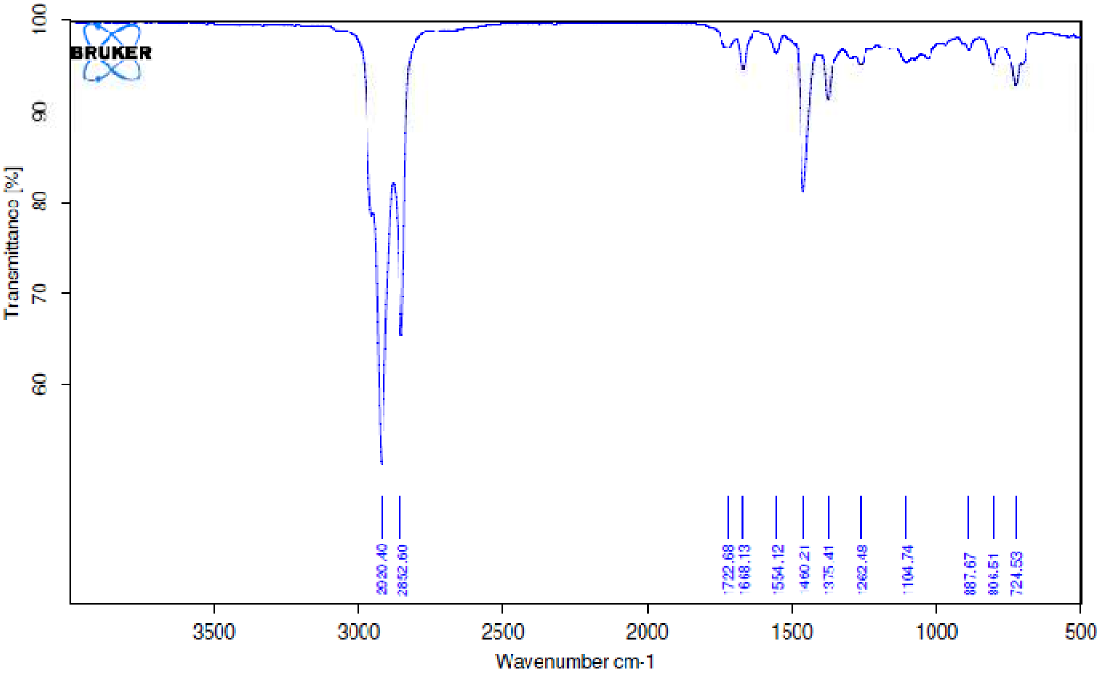

BRUKER
Transmittance [%]
100
90
80
70
60
2920.40
2852.69
1722.68
1668.13
1554.12
1460.21
1375.41
1262.48
1104.74
887.67
806.51
724.53
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

2DPP-4T-2Br

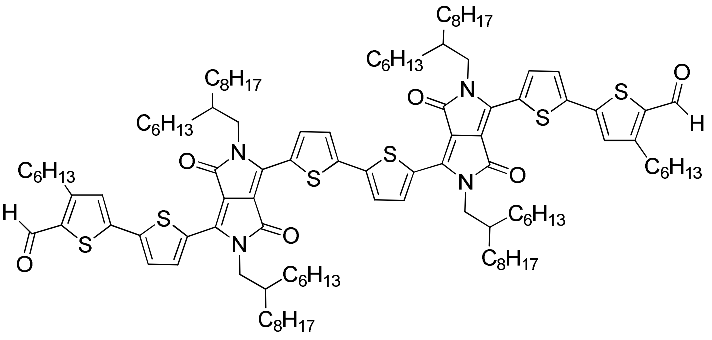

C8H17
C6H13
N
O
S
Br
C8H17
C6H13
N
O
S
S
N
O
C6H13
C8H17
Br
S
N
O
C6H13
C8H17

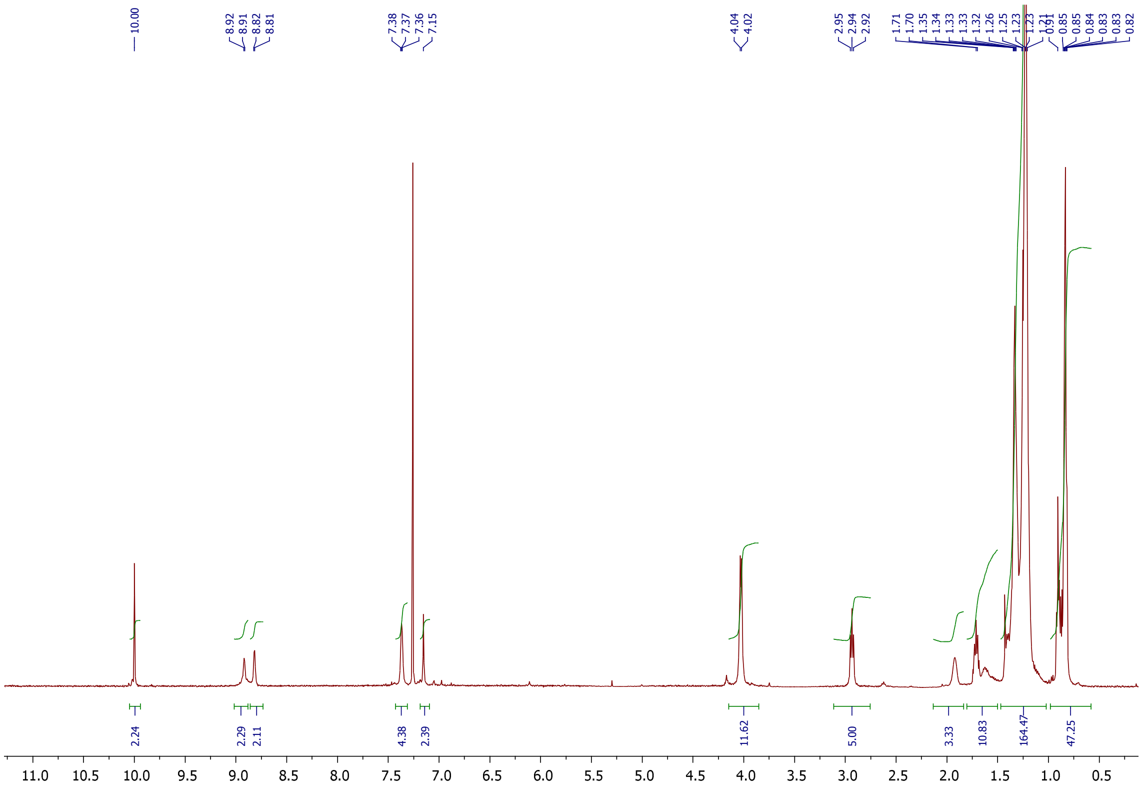

8.88
8.86
8.62
8.60
7.38
7.37
7.19
7.18
4.02
4.00
3.96
3.93
1.91
1.88
1.59
1.25
1.22
0.88
0.87
0.85
0.85
0.84
0.83
0.81
1.00
1.01
1.13
1.28
4.40
2.63
68.85
16.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

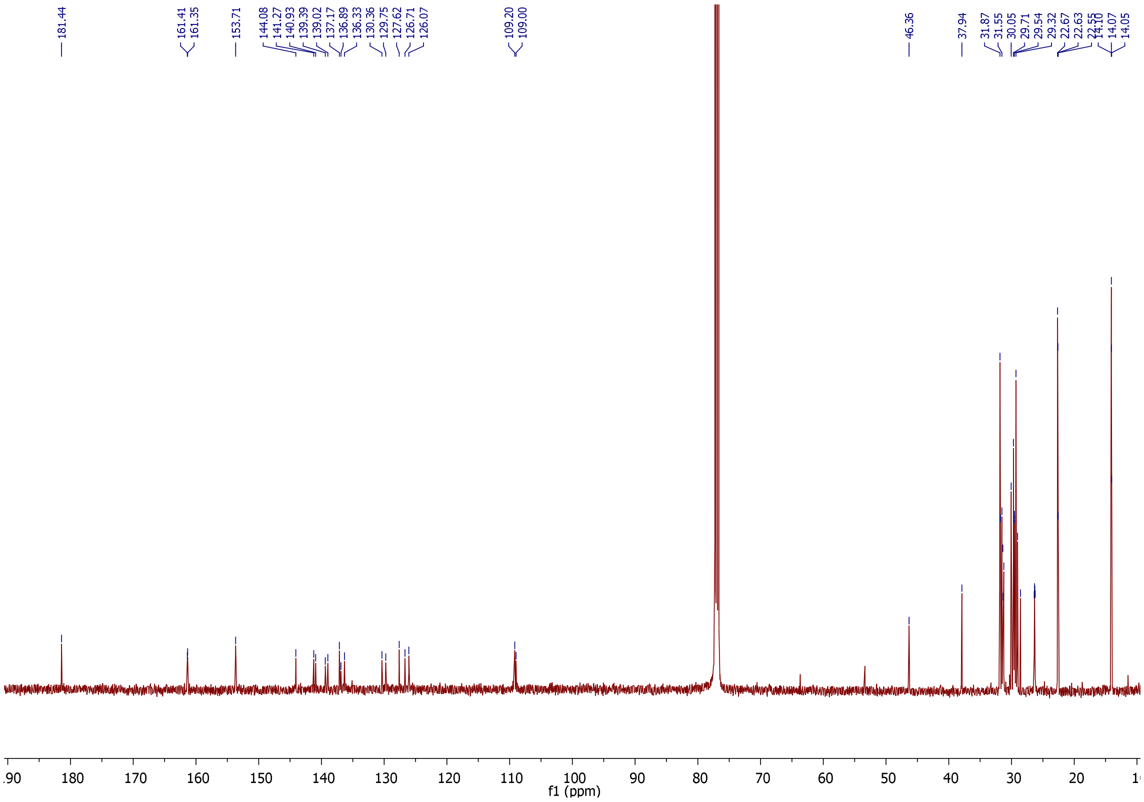

161.35
141.13
139.36
139.04
136.60
135.33
131.33
131.16
129.69
125.99
119.01
108.62
108.23
46.29
37.86
37.70
31.87
31.76
31.22
31.16
29.69
29.65
29.51
29.30
22.67
22.62
14.10
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

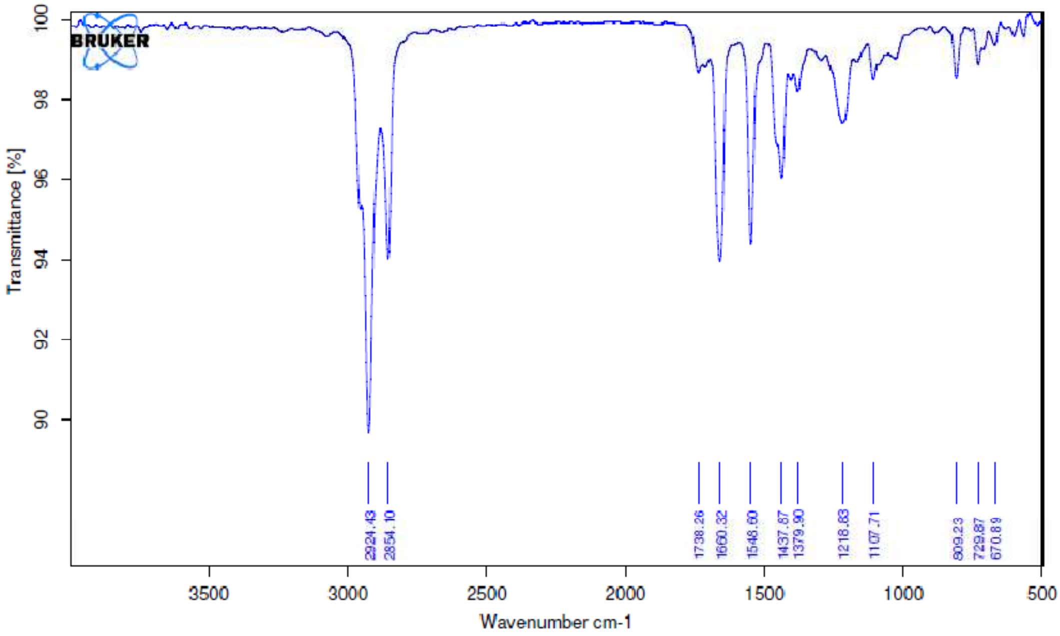

BRUKER
Transmittance [%]
100
90
80
70
60
2920.40
2852.60
1722.68
1668.13
1554.12
1460.21
1375.41
1262.48
1104.74
887.67
806.51
724.53
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

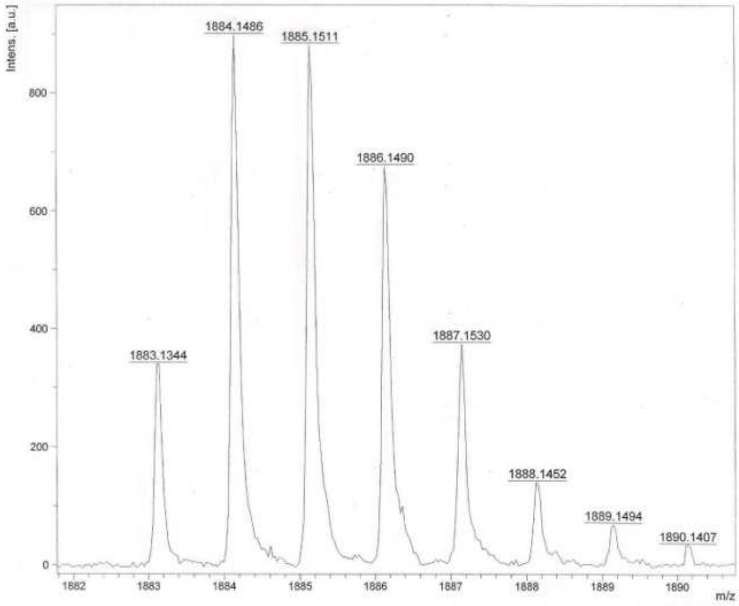
2DPP-6T-2CHO


C$_8$H$_{17}$
C$_6$H$_{13}$
O
N
S
S
H
C$_6$H$_{13}$
C$_8$H$_{17}$
C$_6$H$_{13}$
O
N
S
S
O
C$_6$H$_{13}$
H
S
S
N
O
C$_6$H$_{13}$
O
N
O
C$_6$H$_{13}$
C$_8$H$_{17}$
C$_8$H$_{17}$

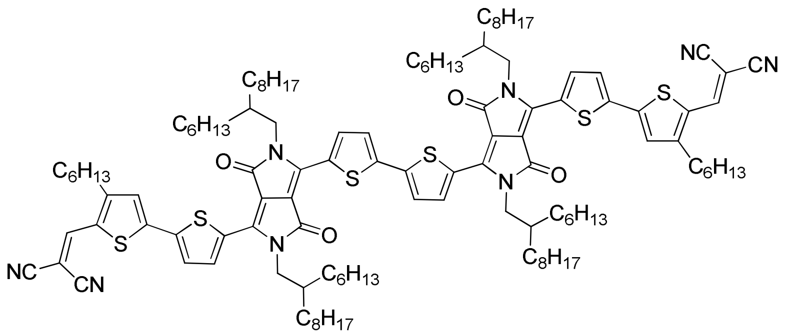

10.00
8.92
8.91
8.82
8.81
7.38
7.37
7.36
7.15
4.04
4.02
2.95
2.94
2.92
1.71
1.70
1.35
1.34
1.33
1.33
1.32
1.26
1.25
1.23
1.23
1.21
0.91
0.85
0.85
0.84
0.83
0.83
0.82
2.24
2.29
2.11
4.38
2.39
11.62
5.00
3.33
10.83
164.47
47.25
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

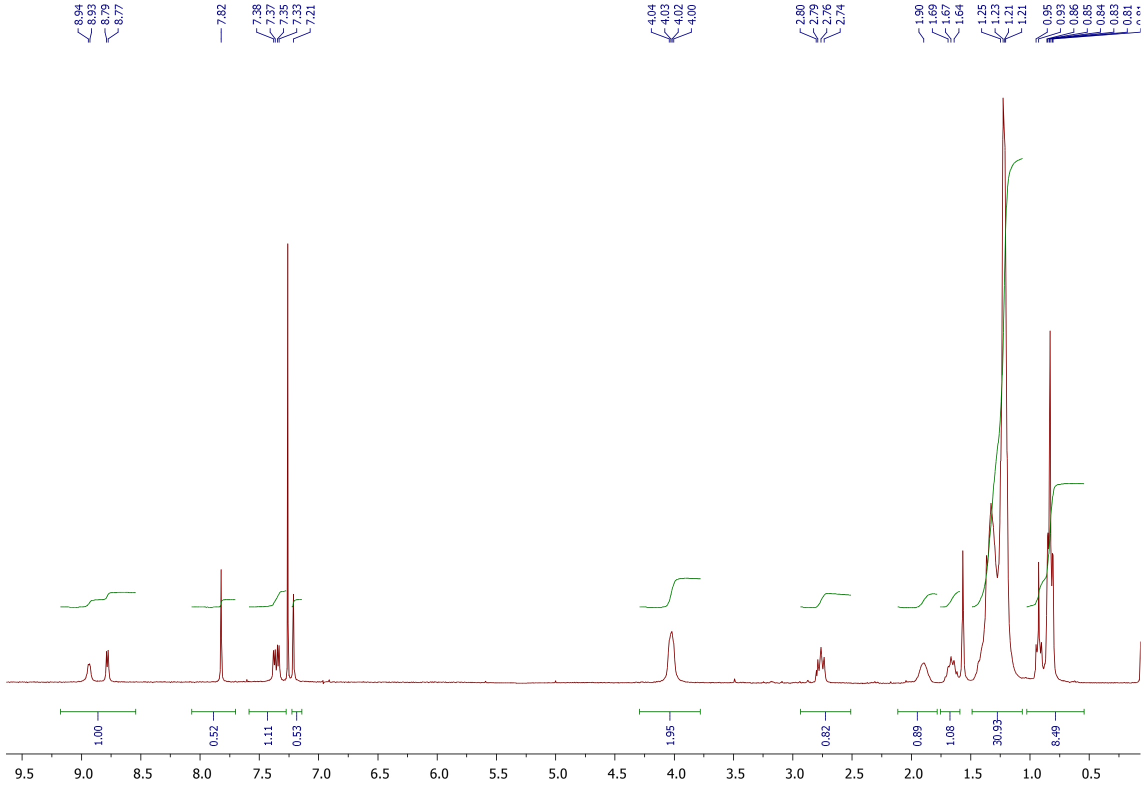

181.44
161.41
161.35
153.71
144.08
141.27
140.93
139.39
139.02
137.17
136.89
136.33
130.36
129.75
127.62
126.71
126.07
109.20
109.00
46.36
37.94
31.87
31.55
30.05
29.71
29.54
29.32
22.67
22.63
22.55
14.10
14.07
14.05
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

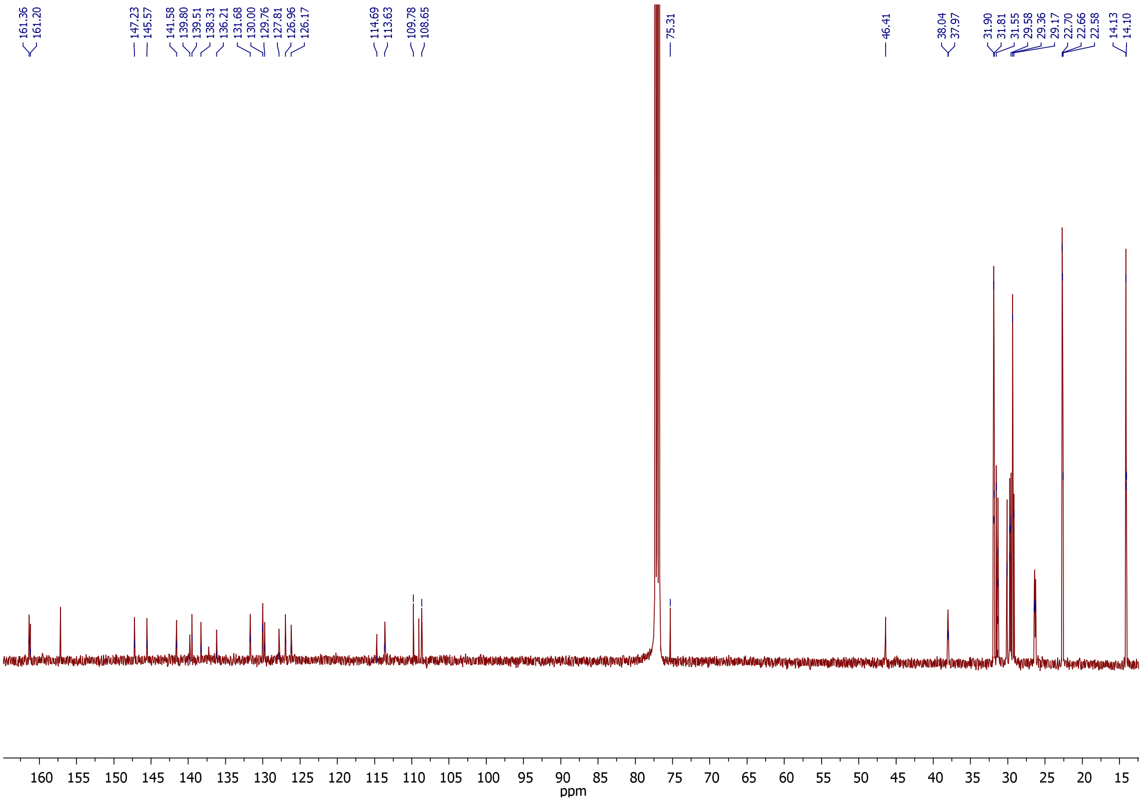

BRUKER
Transmittance [%]
100
98
96
94
92
90
2924.43
2854.10
1738.26
1660.32
1548.60
1437.87
1379.90
1218.83
1107.71
809.23
729.87
670.89
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

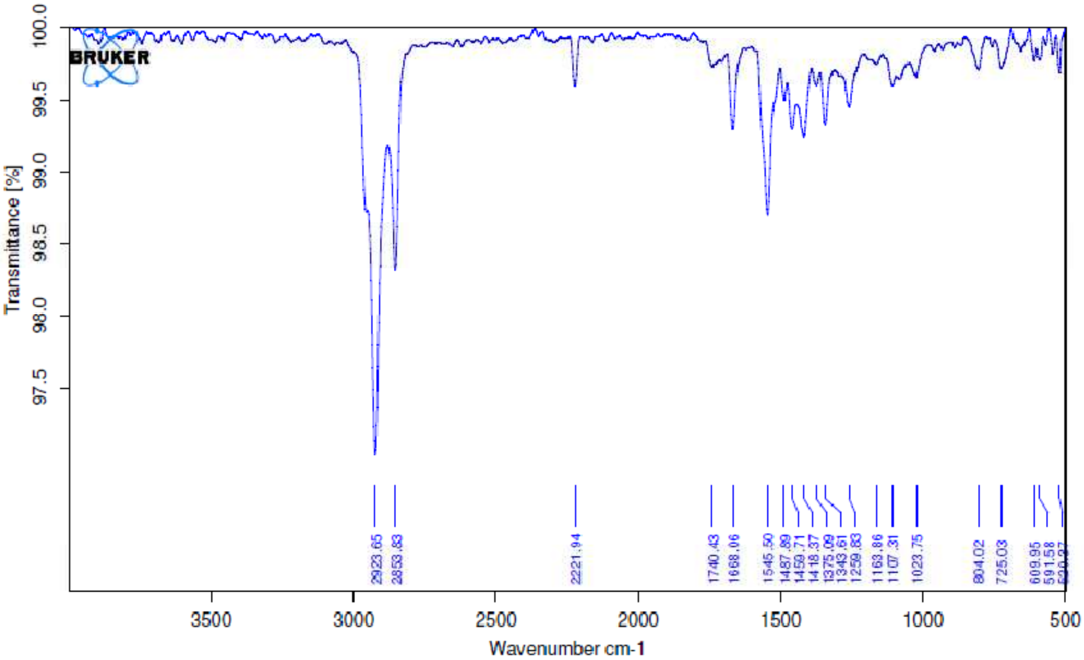

Intens. [a.u.]
800
600
400
200
0
1883.1344
1884.1486
1885.1511
1886.1490
1887.1530
1888.1452
1889.1494
1890.1407
1882
1883
1884
1885
1886
1887
1888
1889
1890
m/z

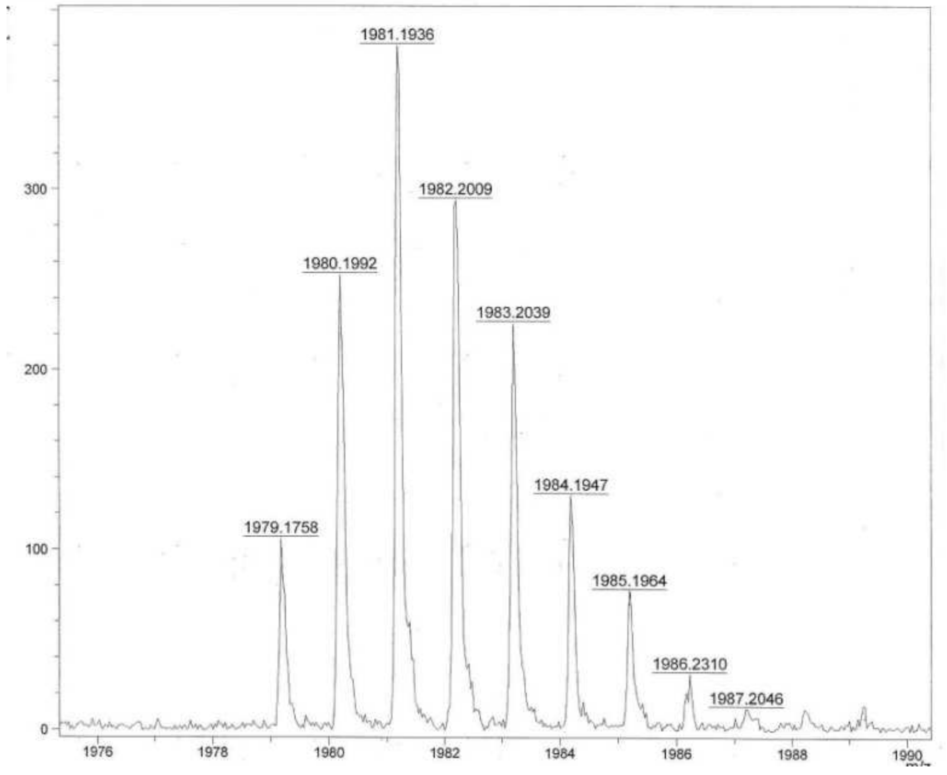
2DPP-6T-2DCV


C8H17
C6H13
NC
CN
O
N
S
C6H13
C8H17
NC
CN

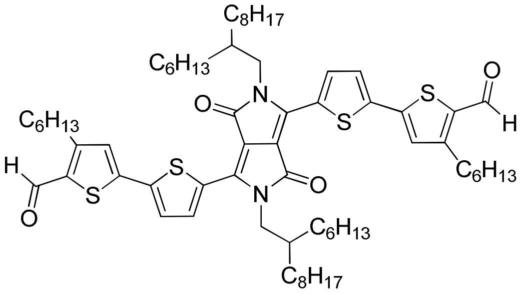

8.94
8.93
8.79
8.77
7.82
7.38
7.37
7.35
7.33
7.21
4.04
4.03
4.02
4.00
2.80
2.79
2.76
2.74
1.90
1.69
1.67
1.64
1.25
1.23
1.21
1.21
0.95
0.93
0.86
0.85
0.84
0.83
0.81
1.00
0.52
1.11
0.53
1.95
0.82
0.89
1.08
30.93
8.49
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


161.36
161.20
147.23
145.57
141.58
139.80
139.51
138.31
136.21
131.68
130.00
129.76
127.81
126.96
126.17
114.69
113.63
109.78
108.65
75.31
46.41
38.04
37.97
31.90
31.81
31.55
29.58
29.36
29.17
22.70
22.66
22.58
14.13
14.10
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
ppm

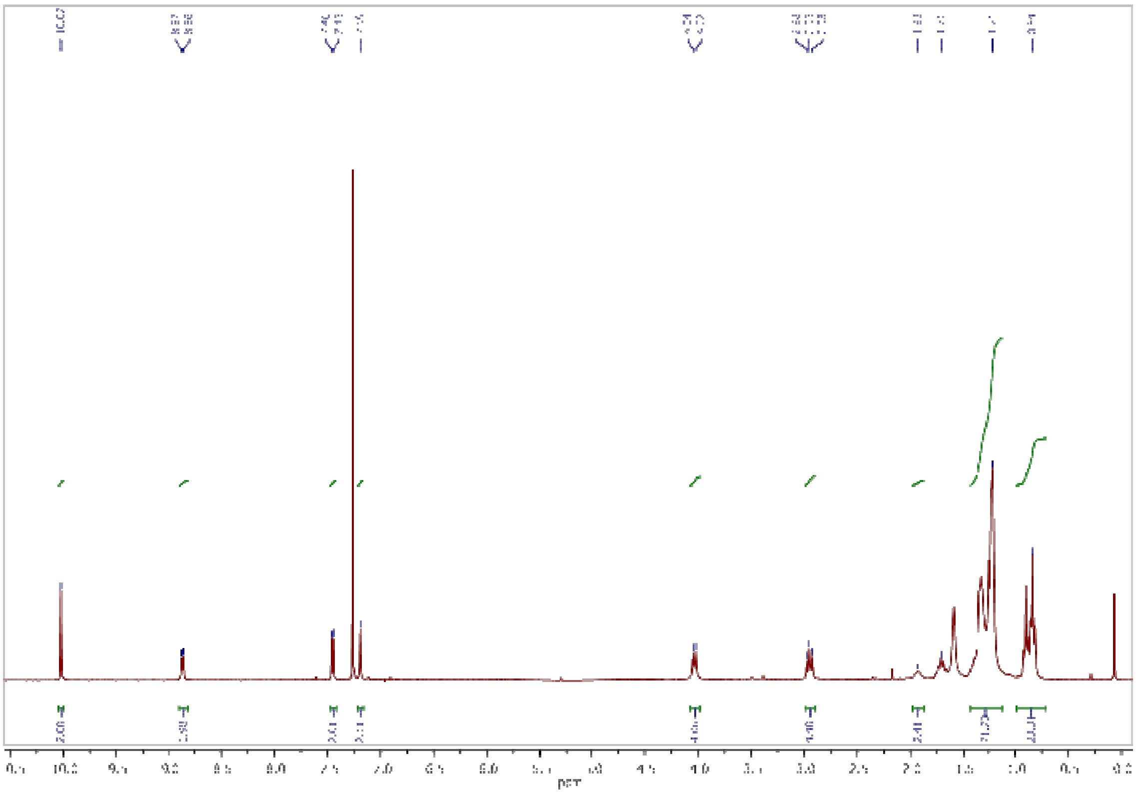

Transmittance [%]
100.0
99.5
99.0
98.5
98.0
97.5
BRUKER
2923.65
2853.83
2221.94
1740.43
1668.06
1545.50
1487.89
1459.71
1418.37
1375.09
1343.61
1259.83
1163.86
1107.31
1023.75
804.02
725.03
609.95
591.58
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


1981.1936
1982.2009
1980.1992
1983.2039
1984.1947
1979.1758
1985.1964
1986.2310
1987.2046
300
200
100
0
1976
1978
1980
1982
1984
1986
1988
1990
m/z

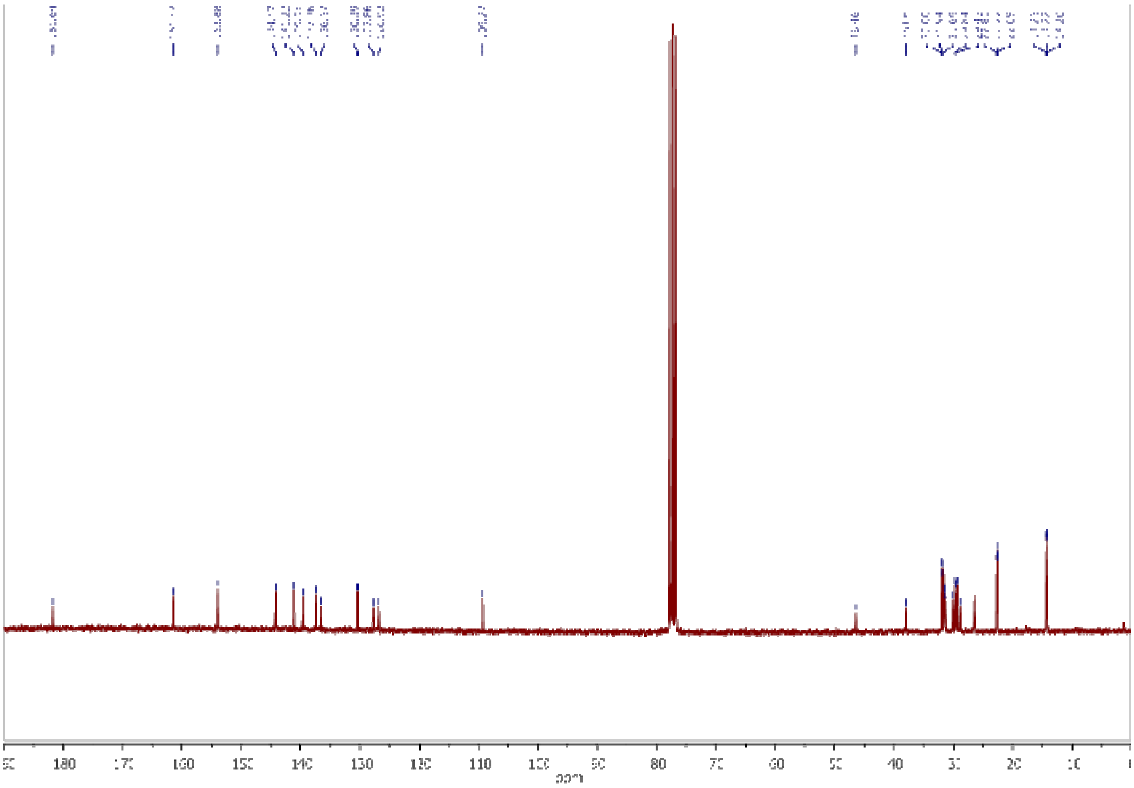
DPP-4T-2CHO



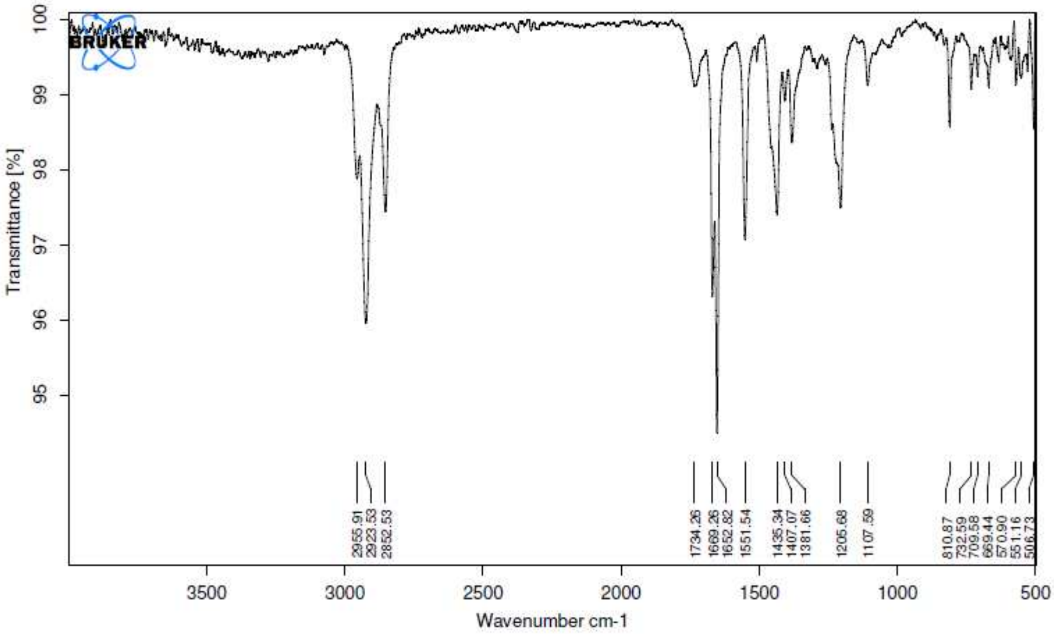
C8H17
C6H13
N
O
S
O
H
C6H13
S
H
S
O
S
N
O
C6H13
C8H17
C6H13



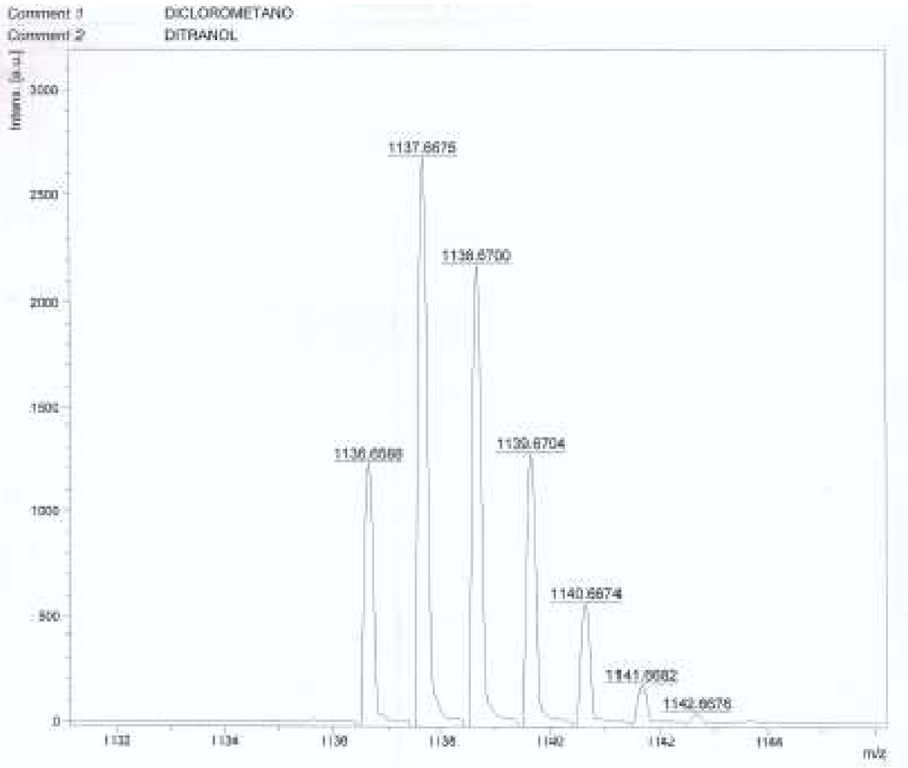
2.00
1.98
2.01
2.11
4.00
4.16
2.41
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



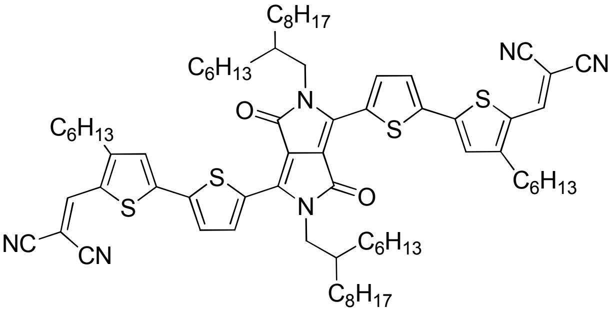
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

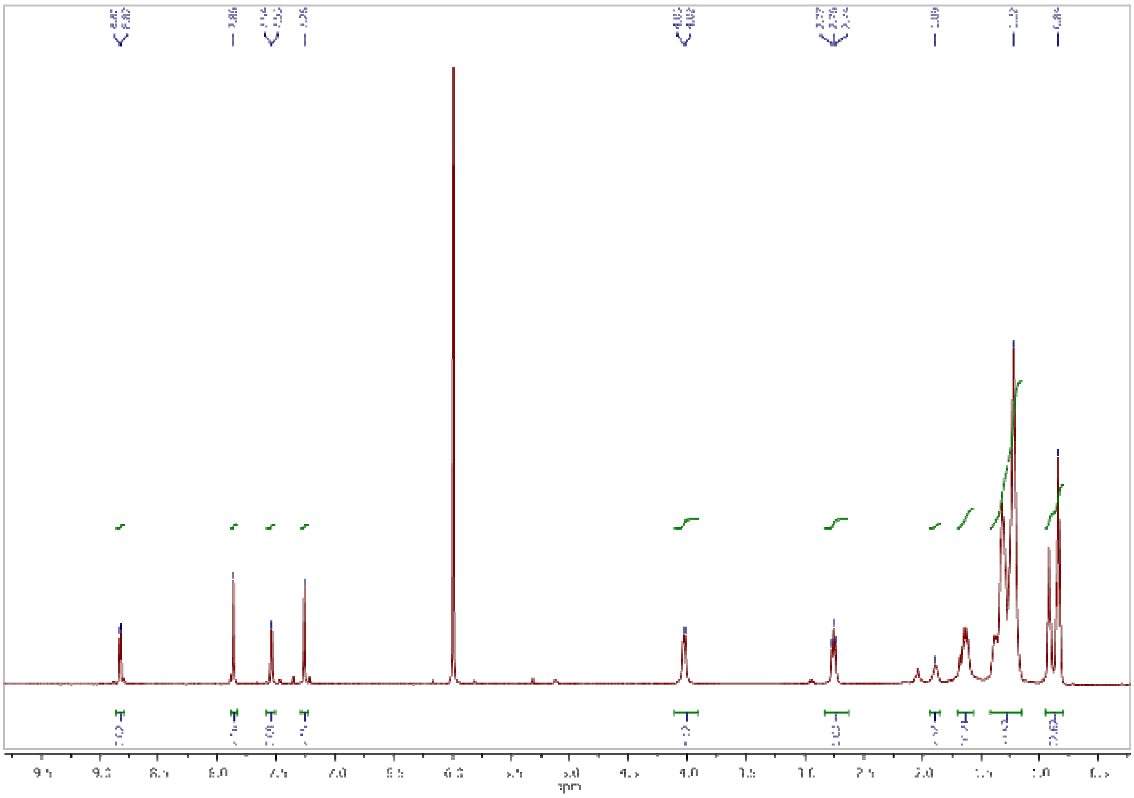


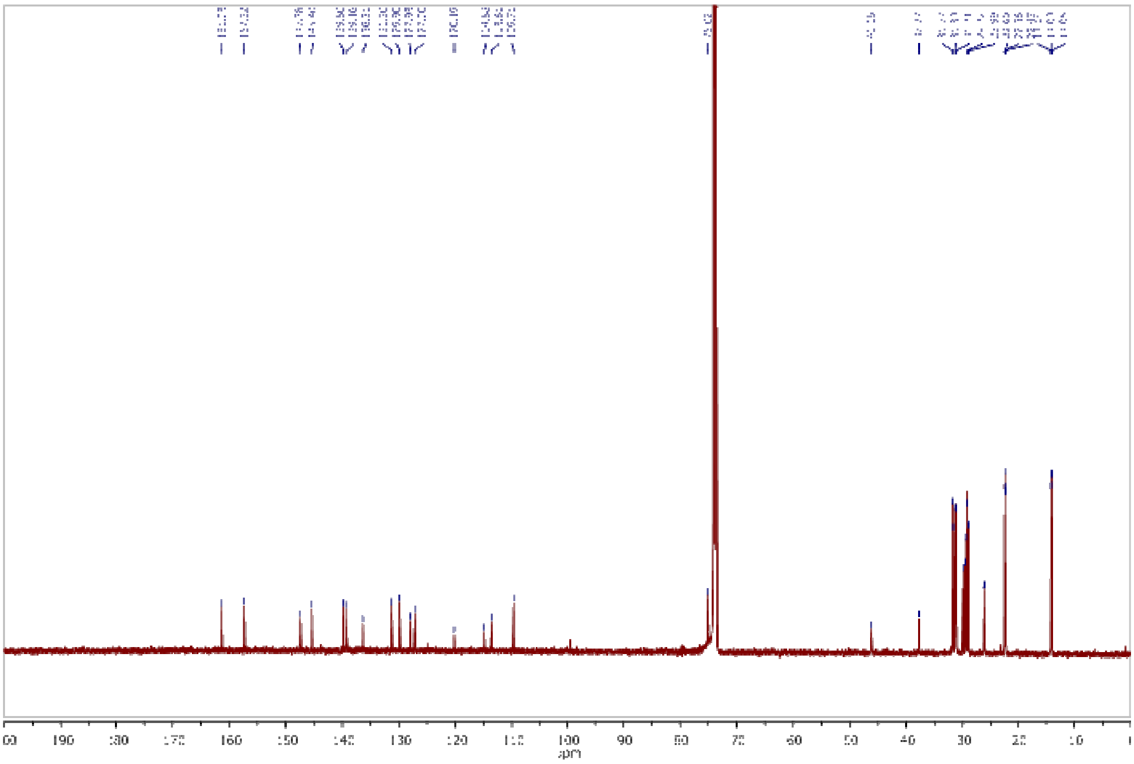
BRUKER
Transmittance [%]
100
99
98
97
96
95
2955.91
2923.53
2852.53
1734.26
1669.26
1652.82
1551.54
1435.34
1407.07
1381.66
1205.68
1107.59
810.87
732.59
709.58
669.44
570.90
551.16
506.73
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

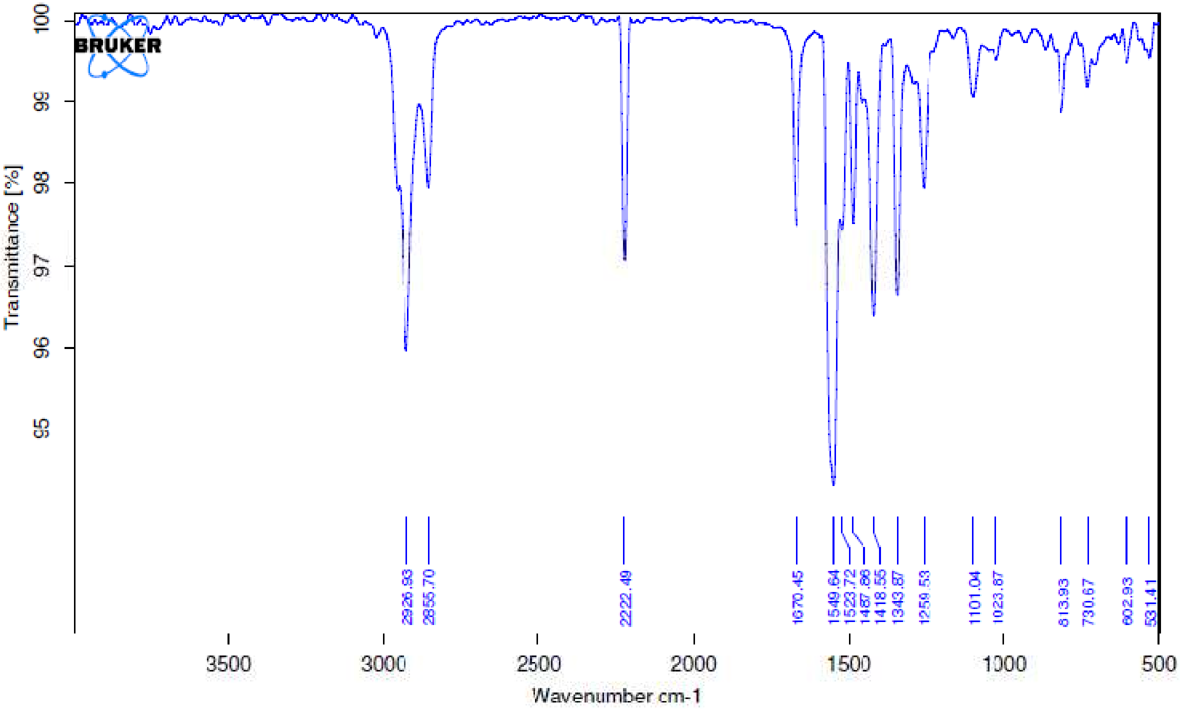

Comment 1
DICLOROMETANO
Comment 2
DITRANOL
Intens. [a.u.]
3000
2500
2000
1500
1000
500
0
1137.6675
1138.6700
1136.6688
1139.6704
1140.6674
1141.6682
1142.6676
1132
1134
1136
1138
1140
1142
1144
m/z

DPP-4T-2DCV


C$_8$H$_{17}$
C$_6$H$_{13}$
NC
CN
N
O
S
C$_6$H$_{13}$
S
C$_6$H$_{13}$
S
S
N
O
C$_6$H$_{13}$
C$_8$H$_{17}$
NC
CN


9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


BRUKER
Transmittance [%]
100
99
98
97
96
95
2926.93
2855.70
2222.49
1670.45
1549.64
1523.72
1487.86
1418.55
1343.87
1259.53
1101.04
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730.67
602.93
531.41
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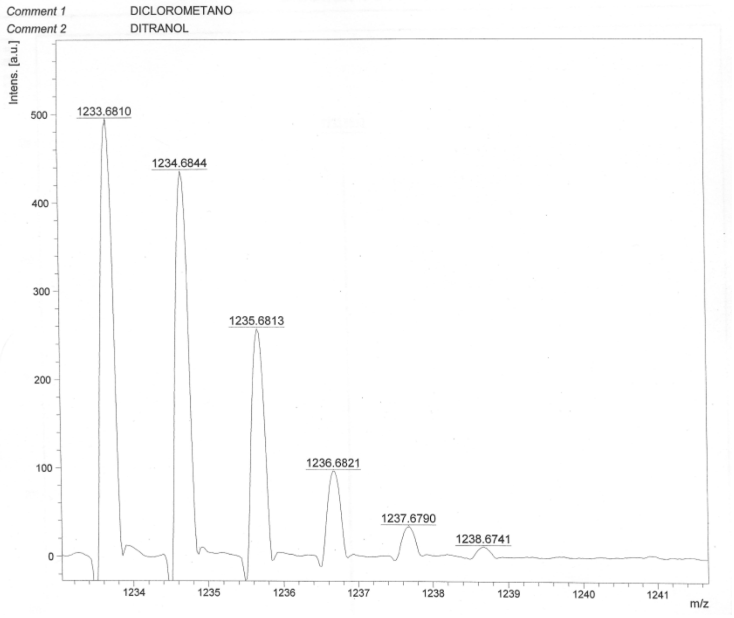
3000
2500
2000
1500
1000
500
Wavenumber cm-1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Comment 2 DITRANOL
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1236
1237
1238
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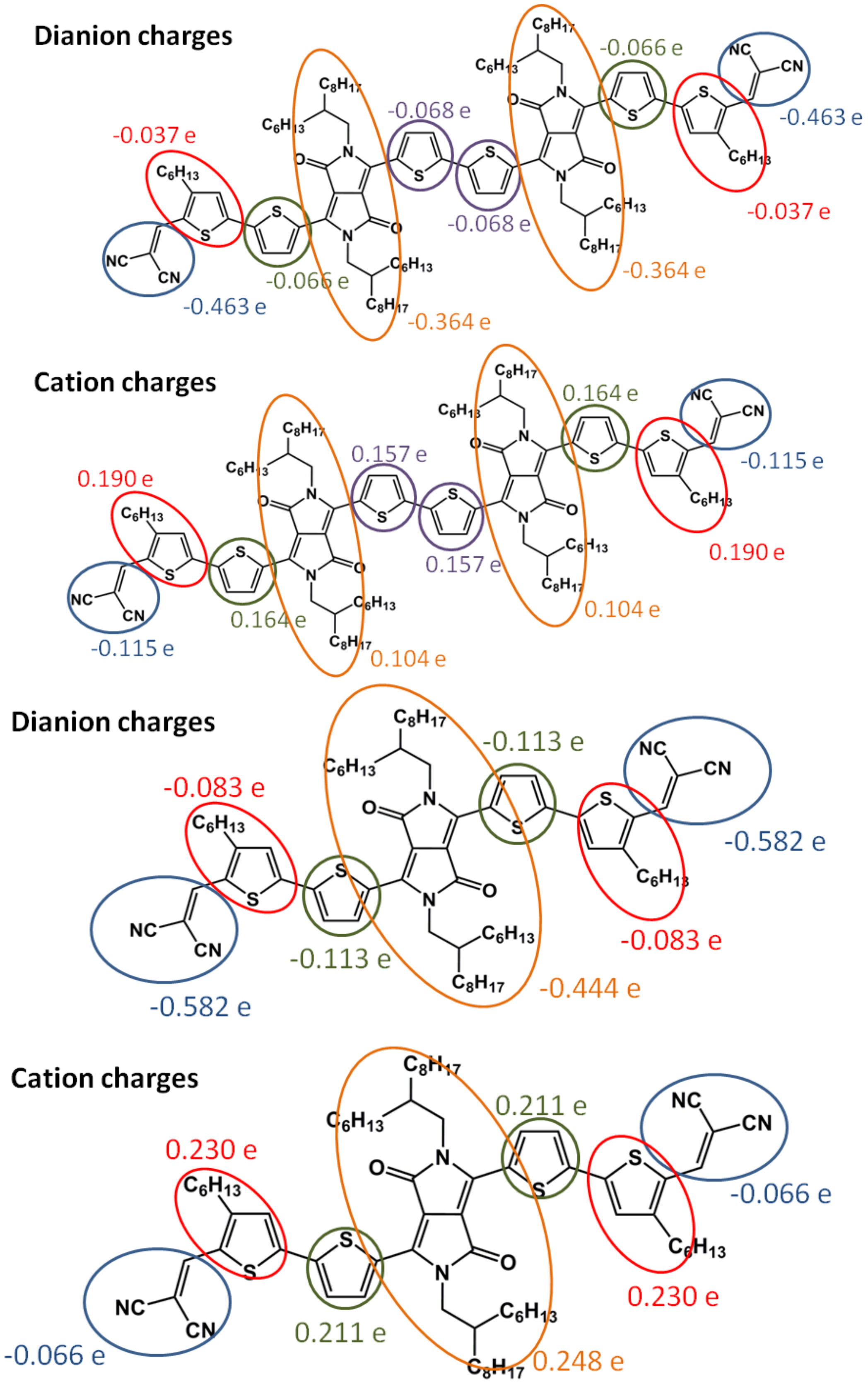
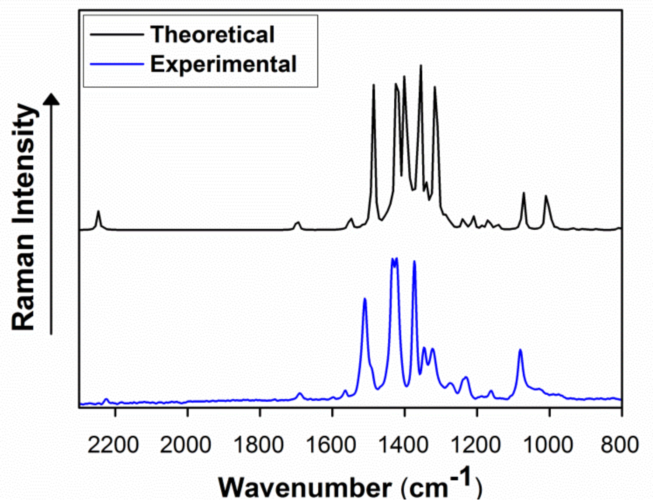
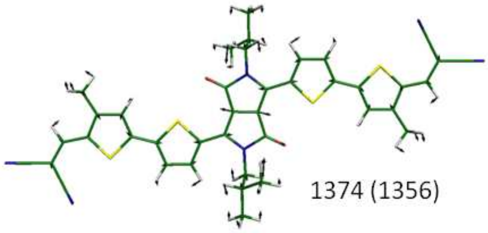
m/z

DFT//B3LYP/6-31G derived charge distributions for DPP-4T-2DCV and 2DPP-6T-2DCV dianion and radical anion species.**



Comparison between experimental and DFT //B3LYP/6-31G Raman spectra of DPP-4T-2DCV and selected eigenvectors (the wavenumbers shown are experimental values; theoretical ones are shown between brackets).**

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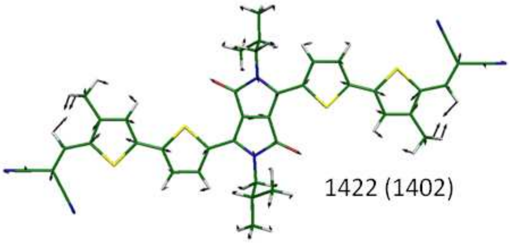
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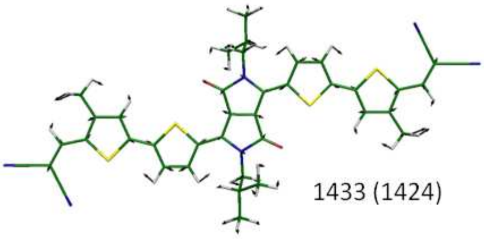
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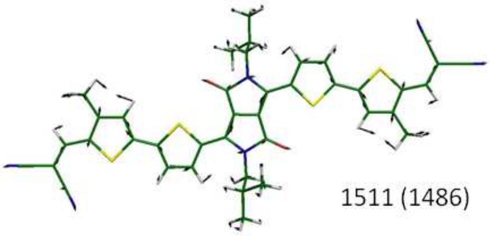
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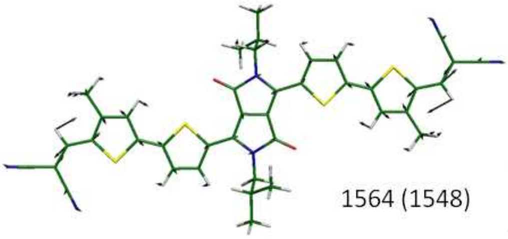
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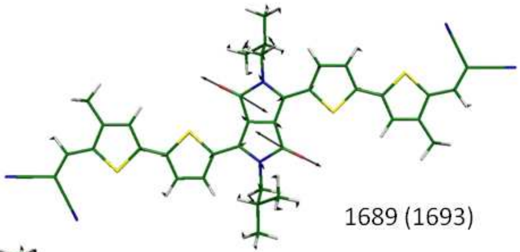
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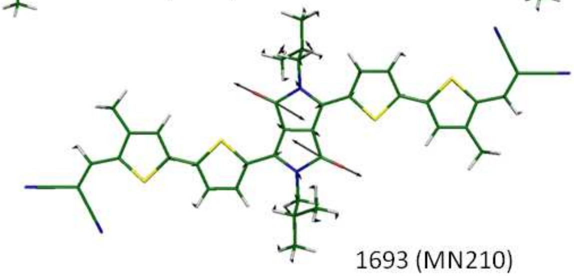
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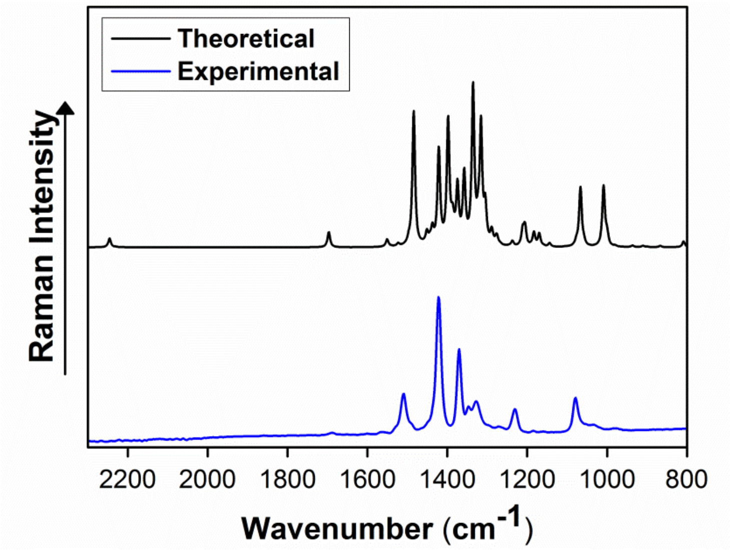
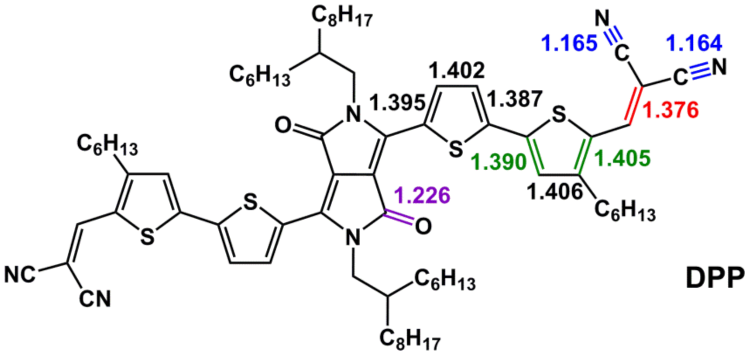
Comparison between experimental and DFT //B3LYP/6-31G** Raman spectra of 2DPP-6T-2DCV



DFT//B3LYP/6-31G** bond lengths for selected bonds



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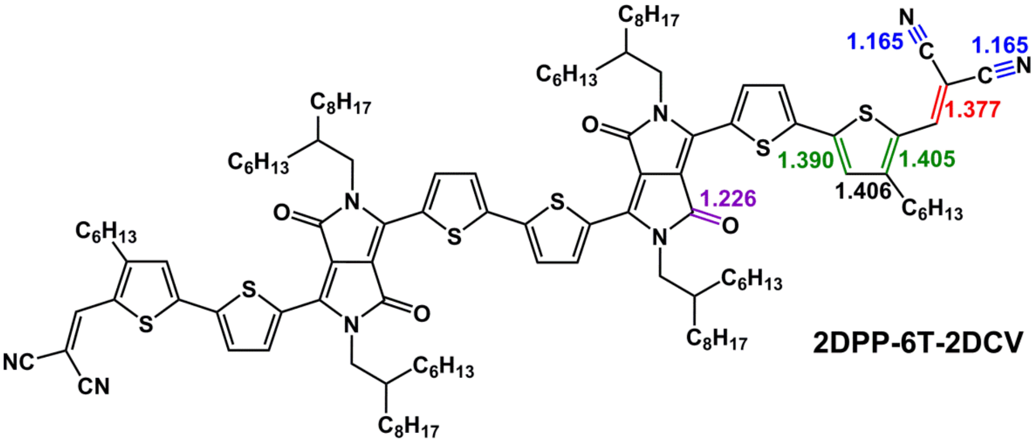


2DPP-6T-2DCV

Solar Cell Fabrication and Performance

Solar Cells were fabricated on patterned ITO-coated glass (280 nm thick; resistivity <10 Ω/sq; Think Film Device, Inc.). The substrates were cleaned by sonicating with hexane, soap/water, DI water, methanol, isopropanol and acetone, successively at 50°C for 30 min each. After the final sonication step, the substrates were dried with a stream of N_2 and UV/Ozone treated for 30 min. PEDOT:PSS (Clevios P VP Al 4083) was then spun-cast at 5000 rpm for 30 sec and annealed at 150°C for 15 min. The substrates were then transferred into a N_2 filled glove box for the remainder of the device fabrication procedure. Active layer solutions were prepared with total concentration of 15 mg/mL and the two constituents were combined in 1:1 ratio by weight. These solutions were spun-cast on the substrates to afford ~70 nm thick active layer films (Stylus DektakProfilometer, Vecco). They were then thermally annealed at various temperatures for 10 min and loaded onto the evaporation chamber. LiF(1.0 nm) and Al(100 nm) were sequentially evaporated through a shadow mask at a base pressure of ~10^{-6}torr to obtain devices with area of 0.06 cm^2. The substrates were encapsulated with epoxy and a glass cover slide and brought out the glove box for testing. Current versus potential (J−V) measurements were recorded with a Keithley 2400 digital source meter. Spectra-Nova Class A Solar Simulator with AM1.5G light (100 mW/cm2) from a Xe arc lamp was used as the light source and it has been calibrated with an NREL-certified Si diode equipped with a KG3 filter to bring spectral mismatch to unity. External quantum efficiency (EQE) was measured using an Oriel Model QE-PV-SI (Newport Instruments) equipped with a NIST (National Institute of Standards and Technology)-certified Si-diode and a Merlin lock-in amplifier and optical chopper. Monochromatic light was generated from a 300 W Xe arc lamp.

Device performance parameters of **DPP-4T-2CNV** and **2DPP-6T-2CNV** devices fabricated under various conditions are summarized in Table S2. Their ability to act as the acceptor of the bulk heterojunction was investigated by blending them with regioregular polymer P3HT (Rieke Metals, Inc.) in various solvents. On the other hand, their ability to act as the donor in the bulk heterojunction was investigated by blending them with $PC_{71}BM$ (American Dye Source, Inc.). Both **DPP-4T-2CNV** and **2DPP-6T-2CNV** performed better as the acceptor of the bulk heterojunction with PCE of 0.08 and 0.09 %, respectively. However, PCE of even 0.1% could not be obtained with these materials under any conditions.

Table S2.- Device performance of **DPP-4T-2CNV** and **2DPP-6T-2CNV**as both donors and acceptors in bulk heterojunction solar cells. [a]oDCB=1,2-dichlorobenzene; [b]No photoresponse.

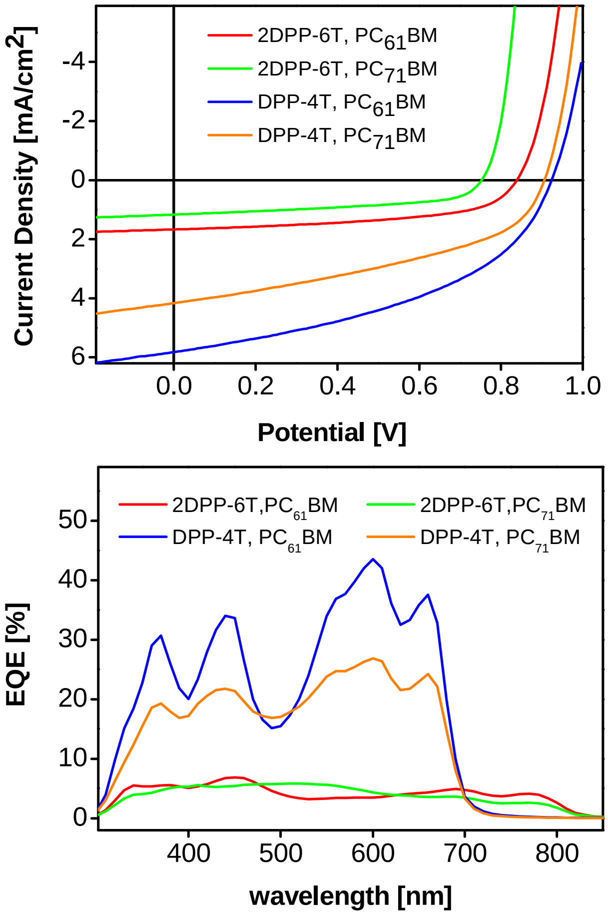
Donor	**Acceptor**	**Solvent**	**V_{oc} [V]**	**J_{sc}[mA/cm^2]**	**FF [%]**	**PCE [%]**
P3HT	**DPP-4T-2CNV**	p-xylene	0.53	0.03	61	0.01
P3HT	**DPP-4T-2CNV**	oDCB[a]	0.53	0.24	59	0.08
P3HT	**DPP-4T-2CNV**	$CHCl_3$	0.60	0.006	51	0.002
P3HT	**2DPP-6T-2CNV**	oDCB	0.53	0.40	41	0.09
P3HT	**2DPP-6T-2CNV**	$CHCl_3$	0.51	0.05	39	0.01
DPP-4T-2CNV	$PC_{71}BM$	$CHCl_3$	-	-	-	-[b]
2DPP-6T-2CNV	$PC_{71}BM$	$CHCl_3$	0.48	0.25	34	0.04

Solar Cells were also fabricated with **DPP-4T** and **2DPP-6T** as the donors in the bulk heterojunction while blended with $PC_{61}BM$ and $PC_{71}BM$. Films were cast from chloroform and were annealed at various temperatures before electrode deposition. The performance parameters are summarized in Table S3. Device performance decreases under annealing for **DPP-4T** and sees slight improvement under annealing for **2DPP-6T**. PCE of up to 2.36% was achieved for **DPP-4T** blended with $PC_{61}BM$ while only 0.52% could be achieved for **2DPP-6T**, also blended with $PC_{61}BM$.

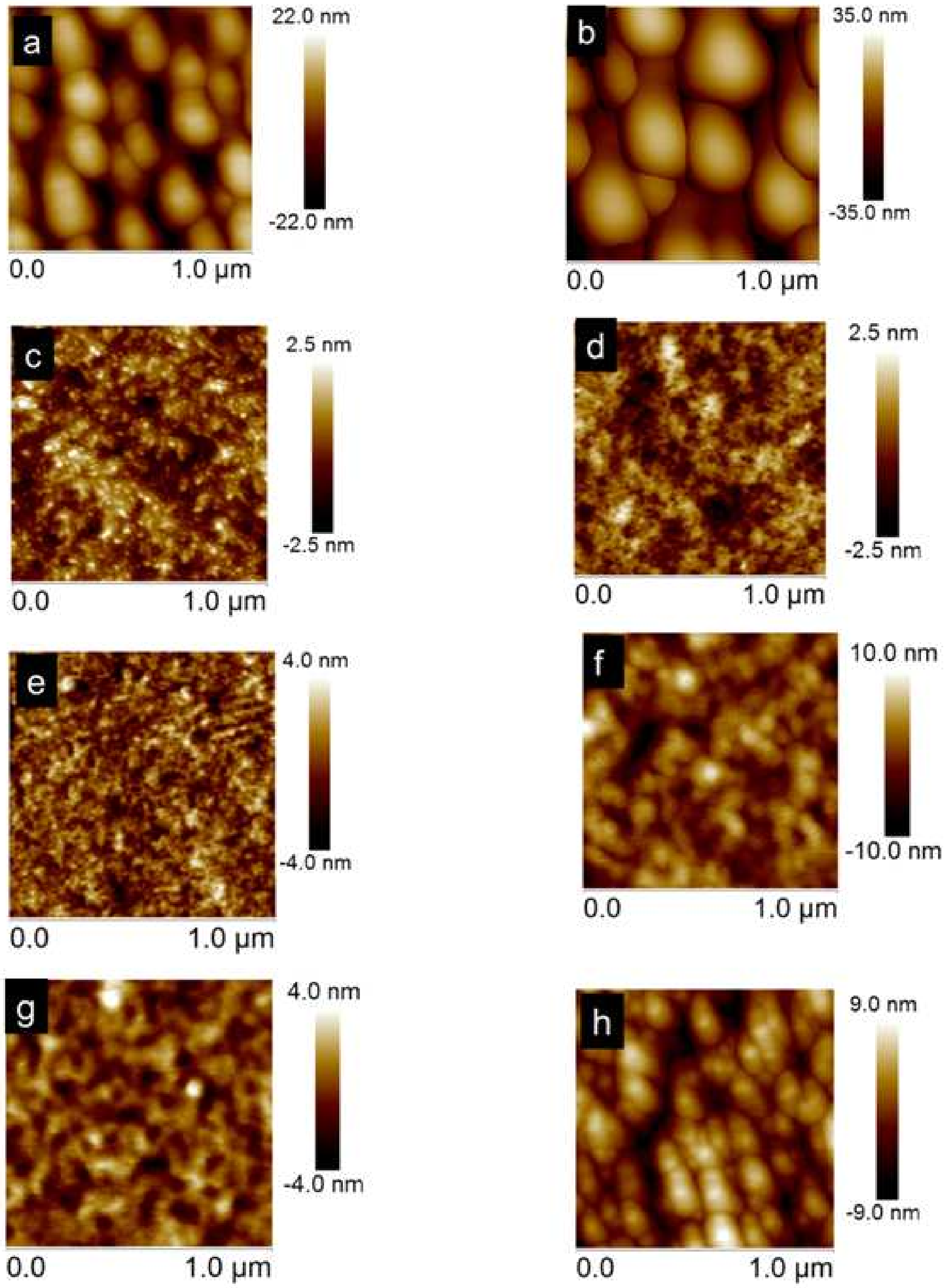
Table S3.- Device performance of **2DPP-6T** and **DPP-4T** as the donors of bulk heterojunction.

Donor	**Acceptor**	**Anneal [°C]**	**V_{oc} [V]**	**J_{sc} [mA/cm^2]**	**FF [%]**	**PCE [%]**
2DPP-6T	$PC_{61}BM$	-	0.743	1.26	55.5	0.52
2DPP-6T	$PC_{61}BM$	70	0.808	1.17	55.2	0.52
2DPP-6T	$PC_{61}BM$	135	0.853	1.13	48.5	0.47
2DPP-6T	$PC_{71}BM$	-	0.751	1.06	51.6	0.41
2DPP-6T	$PC_{71}BM$	70	0.747	1.16	51.8	0.45
2DPP-6T	$PC_{71}BM$	135	0.761	0.90	40.2	0.28
DPP-4T	$PC_{61}BM$	-	0.930	5.82	43.6	2.36
DPP-4T	$PC_{61}BM$	70	0.932	4.56	39.2	1.67
DPP-4T	$PC_{71}BM$	-	0.903	4.16	42.6	1.60
DPP-4T	$PC_{71}BM$	70	0.910	2.95	32.7	0.88

J-V and EQE curves for the blends 2DPP-6T/PC$_{61}$BM (Annealed 70°C); and 2DPP-6T/PC$_{71}$BM(Annealed70°C); DPP-4T/PC$_{61}$BM (As Cast) and DPP-4T/PC$_{71}$BM (As Cast).



AFM images of OPV active layers cast films, with the RMS roughness given in parenthesis. a) DPP-4T-2CNV+PCB$_{71}$M blend(6.3 nm); b) 2DPP-6T-2CNV+PC$_{71}$BM blend (10 nm); c) DPP-4T-2CNV+P3HT blend (0.6 nm); d) 2DPP-6T-2CNV+P3HT blend (0.6 nm); e) DPP-4T+PCB$_{61}$M blend (0.8 nm); f) DPP-4T +PC$_{71}$BM blend (2.0 nm); g) 2DPP-6T+PC$_{61}$BM blend (0.8 nm); h) 2DPP-6T+ PC$_{71}$BM blend (1.9 nm).



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