1. ESR analysis

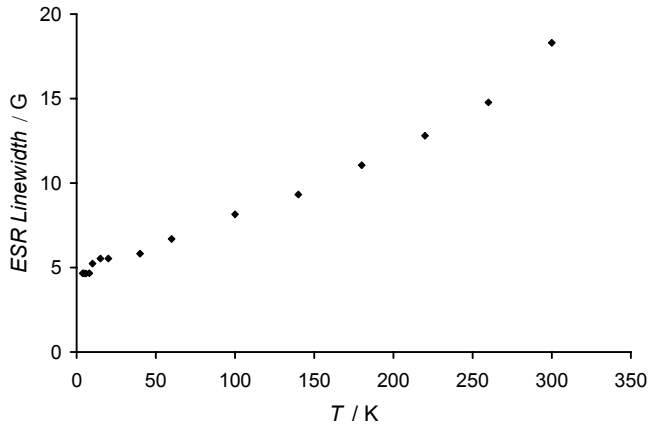

Figure S1. The linewidth of ESR signal of SSP-PEDOT as a function of temperature (3.9 K to 300 K). (The linewidth measured as a peak to peak separation).

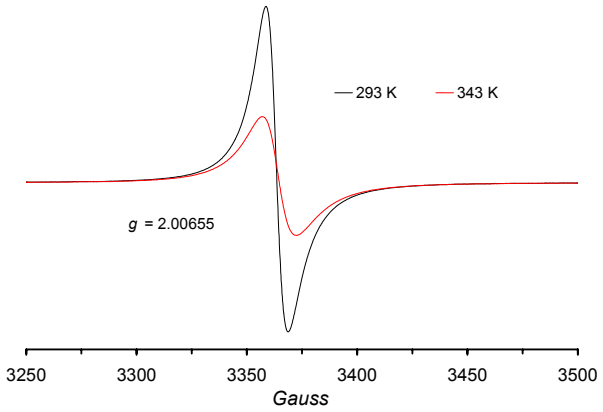

Figure S2. Residual ESR signal of dedoped SSP-PEDOT (note symmetric Lorentzian line shape of the signal).

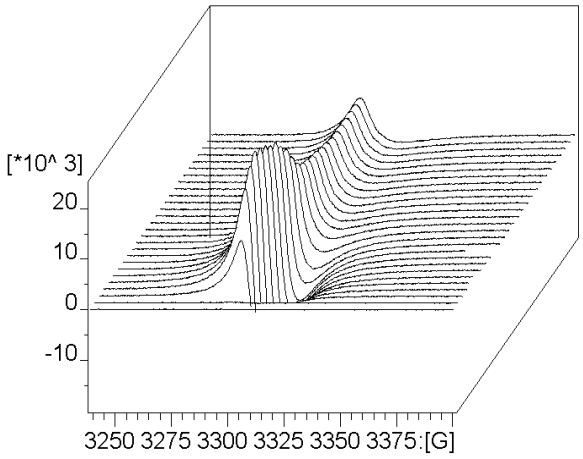

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Figure S3 In-situ monitoring of SSP of the DBEDOT (from front to back; a 3 mg polycrystalline sample) in the ESR cavity at 343 K. Similar behavior was observed at all studied temperatures.

2. TGA analysis

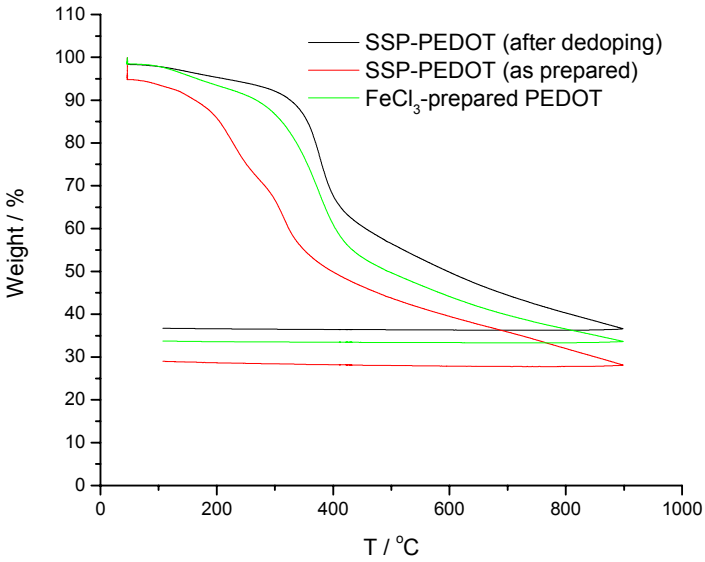


Figure S4 Thermal gravimetric analysis of the SSP-PEDOT and $FeCl_3$-PEDOT.

3. Thermomicroscopy analysis.

The thermomicroscopic analysis was performed on the a crystalline powder of DEBDOT, obtained by recrystallization (DBEDOT-1) and very thin single crystals or crystal twins, obtained by vacuum sublimation (DBEDOT-2).The behavior of both samples was essentially the same, but sample DBEDOT-2 is preferred in microscopic observation of SSP due to absence of light scattering. The supporting files show the slow-time movie records of the performed experiments as follows:
6.avi – heating large sample of DBEDOT-1 at 10 deg/min from 100 to 150 °C and holding at 150 °C for 10 min. The movie recorded at 5 sec/frame.
7.avi – heating small sample of DBEDOT-1 at 10 deg/min from 100 to 150 °C and holding at 150 °C for 2 h (only first 45 min are shown, continuing monitoring shows no essential changes). The movie recorded at 5 sec/frame
2.avi – holding a thin single crystal DBEDOT-2 sample (prepared by vacuum sublimation) at 92 °C for 2.5 h (only first 50 min are shown). The movie recorded at 10 sec/frame.
8.avi – holding a thick crystal DBEDOT-1 sample at 87 °C for 2.5 h (only first 50 min are shown). The movie recorded at 20 sec/frame.

4. X-ray analysis

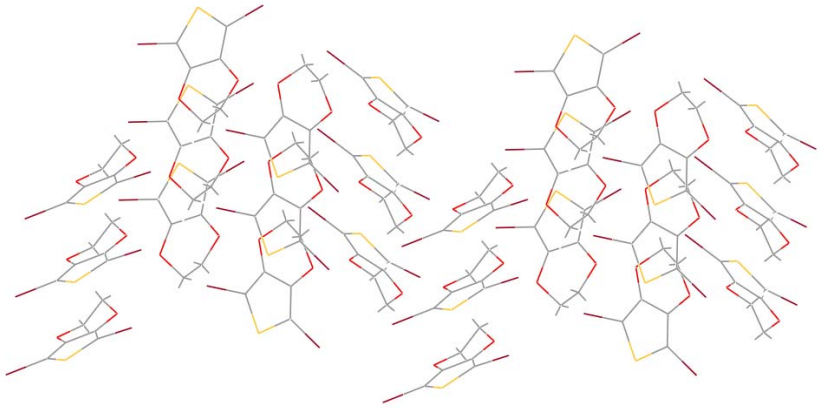


Figure S5. Crystal packing in DBEDOT.

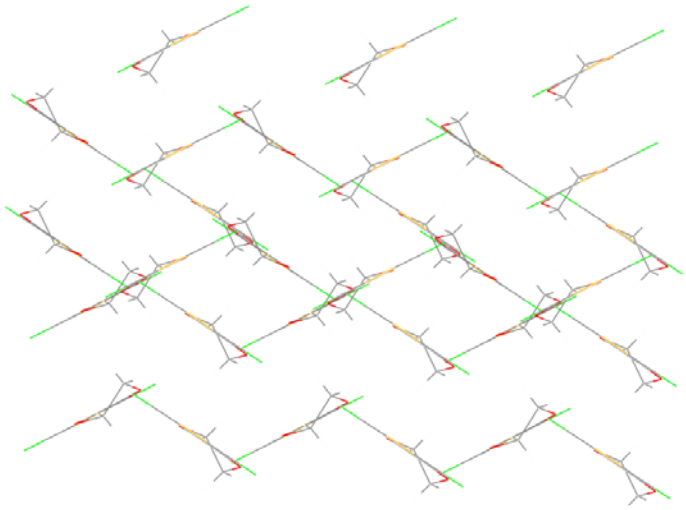


Figure S6. Crystal packing of DCEDOT

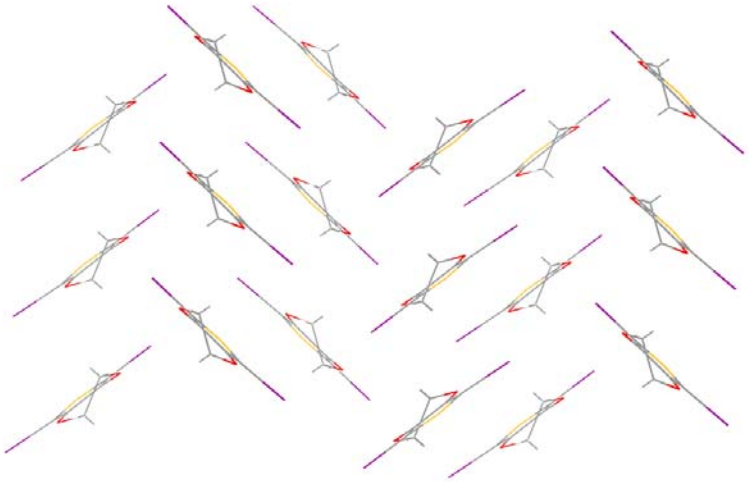


Figure S7. Crystal packing of DIEDOT.

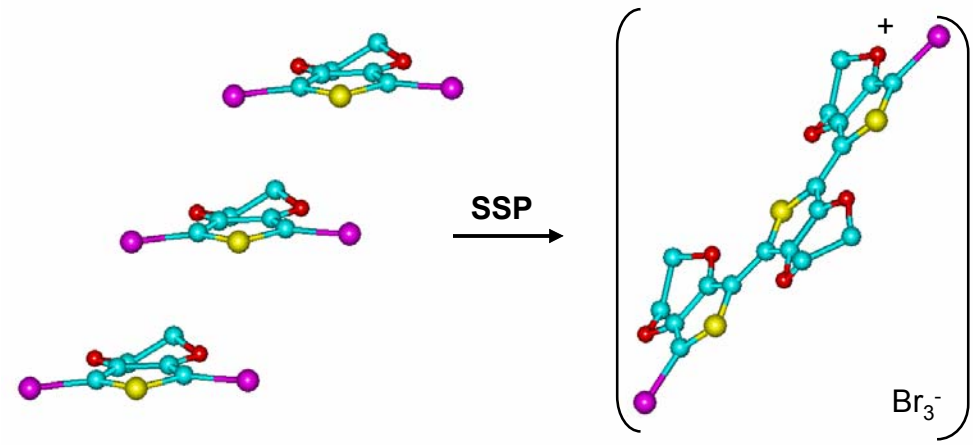


Figure S8. Most probable direction of the polymerization in the DBEDOT crystal (along the stack axis).

5. Electrochemistry

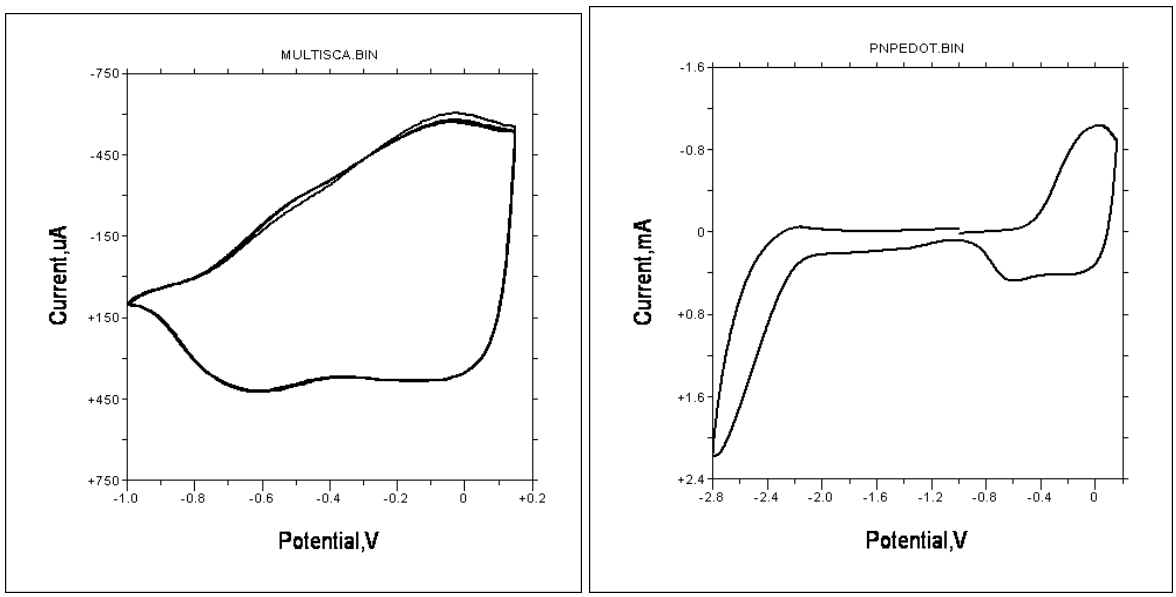


Figure S9 CV of a solid-state polymerized thin film deposited on a platinum plate: (left) multiple scanning in the positive direction and (right) the scanning in both positive and negative direction, showing *p*-doping (reversible) and *n*-doping (irreversible) processes. 0.1M Bu_4NPF_6 in MeCN; scan rate 50 mVs^{-1}; reference Ag/Ag^+.

Table S1. Crystal data and structure refinement for DBEDOT.

Empirical formula	C6 H4 Br2 O2 S	
Formula weight	299.97	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 25.270(6) Å	α= 90°.
	b = 5.0127(12) Å	β= 123.959(4)°.
	c = 15.667(4) Å	γ = 90°.
Volume	1646.1(7) $Å^3$	
Z	8	
Density (calculated)	2.421 Mg/m^3	
Absorption coefficient	10.045 mm^{-1}	
F(000)	1136	
Crystal size	0.01 x 0.18 x 0.2 mm^3	
Theta range for data collection	1.94 to 28.26°.	
Index ranges	-17<=h<=32, -6<=k<=6, -20<=l<=19	
Reflections collected	5067	
Independent reflections	2583 [R(int) = 0.0691]	
Completeness to theta = 28.26°	96.8 %	
Absorption correction	Empirical	
Max. and min. transmission	1.0000 and 0.3343	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2583 / 2 / 200	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.1186	
R indices (all data)	R1 = 0.0479, wR2 = 0.1196	
Absolute structure parameter	0.090(15)	
Extinction coefficient	0.0010(2)	
Largest diff. peak and hole	1.822 and -2.151 e.$Å^{-3}$	

Table S2. Crystal data and structure refinement for DCEDOT.

Empirical formula	C6 H4 Cl2 O2 S	
Formula weight	211.05	
Temperature	298(2) K	
Wavelength	0.71073 E	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 5.1098(8) E	α= 90°.
	b = 7.7988(12) E	β= 93.751(3)°.
	c = 20.306(3) E	γ = 90°.
Volume	807.5(2) E^3	
Z	4	
Density (calculated)	1.736 Mg/m^3	
Absorption coefficient	1.003 mm^{-1}	
F(000)	424	
Crystal size	0.6 x 0.4 x 0.4 mm^3	
Theta range for data collection	2.01 to 28.31°.	
Index ranges	-6<=h<=4, -8<=k<=10, -27<=l<=26	
Reflections collected	5066	
Independent reflections	1943 [R(int) = 0.0303]	
Completeness to theta = 28.31°	96.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.5257	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1943 / 0 / 101	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0968	
R indices (all data)	R1 = 0.0465, wR2 = 0.1038	
Extinction coefficient	0.010(2)	
Largest diff. peak and hole	0.342 and -0.388 $e.E^{-3}$	

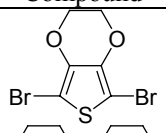
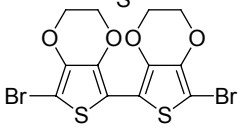
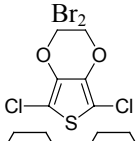
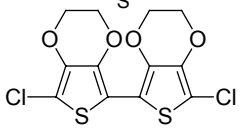
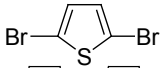
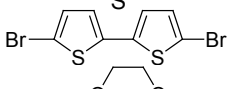
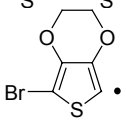
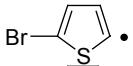
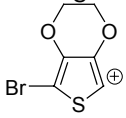
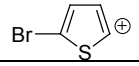
Table S3. Crystal data and structure refinement for DIEDOT.

Empirical formula	C6 H4 I2 O2 S	
Formula weight	393.95	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.432(3) Å	α= 90°.
	b = 4.9022(14) Å	β= 96.396(6)°.
	c = 15.932(5) Å	γ = 90°.
Volume	887.4(4) $Å^3$	
Z	4	
Density (calculated)	2.949 Mg/m^3	
Absorption coefficient	7.270 mm^{-1}	
F(000)	712	
Crystal size	0.4 x 0.05 x 0.05 mm^3	
Theta range for data collection	1.79 to 28.27°.	
Index ranges	-14<=h<=8, -6<=k<=6, -20<=l<=19	
Reflections collected	4717	
Independent reflections	1911 [R(int) = 0.0386]	
Completeness to theta = 28.27°	86.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.502	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1911 / 0 / 101
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0297, wR2 = 0.0800
R indices (all data)	R1 = 0.0321, wR2 = 0.0811
Extinction coefficient	0.0037(4)
Largest diff. peak and hole	1.353 and -1.319 e.$Å^{-3}$

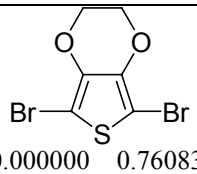
5. DFT calculations

Table S4. Calculated absolute energies at B3LYP/6-31G(d).[a]

Compound	B3LYP/6-31G(d)	ZPVE
	-5923.036601	58.18
	-6702.692684	116.41
Br_2	-5143.399112	0.47
	-1700.01673	58.94
	-2479.672637	117.18
Cl_2	-920.3498845	0.74
	-5695.199681	29.49
	-6247.014475	59.15
	-3351.241302	56.35
$Br^{\bullet}$	-2571.656918	0.0
	-3123.405605	27.76
	-3350.951371	56.25
Br^{-}	-2571.761339	0.0
	-3123.081783	26.88

[a] in Hartrees, ZPVE in kcal/mol.

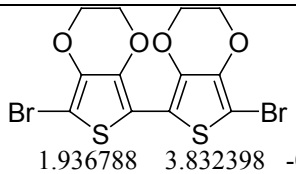
Table S5. Optimized geometries (at B3LYP/6-31G(d)).



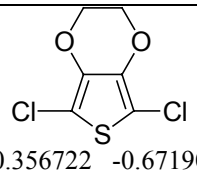
6	0.000000	0.760832	-3.131732
1	-0.531186	1.152270	-4.002311
1	-1.030559	-1.139829	-3.135829
1	1.030559	1.139829	-3.135829
8	-0.695197	1.270466	-1.983605
1	0.531186	-1.152270	-4.002311
6	-0.585601	1.097594	0.427233
6	0.000000	-0.760832	-3.131732
35	-1.451235	2.697463	0.885840
16	0.000000	0.000000	1.653722
6	0.585601	-1.097594	0.427233
6	0.337685	-0.635607	-0.833369
6	-0.337685	0.635607	-0.833369
35	1.451235	-2.697463	0.885840
8	0.695197	-1.270466	-1.983605

Br_2

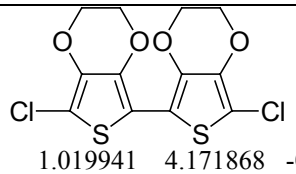
35	0.000000	0.000000	1.160839
35	0.000000	0.000000	-1.160839



8	1.936788	3.832398	-0.007966
16	-1.386428	1.757174	0.005199
6	-0.401053	3.195731	-0.002094
6	0.934385	2.909017	0.010319
6	1.179664	1.500638	0.023603
6	0.044870	0.718592	0.023900
6	-0.044870	-0.718592	0.023900
8	2.447844	0.986327	0.050376
35	-1.179664	4.902067	-0.026698
16	1.386428	-1.757174	0.005199
6	0.401053	-3.195731	-0.002094
6	-0.934385	-2.909017	0.010319
6	-1.179664	-1.500638	0.023603
35	1.179664	-4.902067	-0.026698
8	-1.936788	-3.832398	-0.007966
8	-2.447844	-0.986327	0.050376
6	3.204540	3.273926	0.364199
6	3.440506	1.945751	-0.340756
1	4.404182	1.516620	-0.057193
1	3.240829	3.134161	1.452868
1	3.956223	4.010686	0.071074
1	3.410151	2.082931	-1.429788
6	-3.204540	-3.273926	0.364199
6	-3.440506	-1.945751	-0.340756
1	-4.404182	-1.516620	-0.057193
1	-3.240829	-3.134161	1.452868
1	-3.410151	-2.082931	-1.429788
1	-3.956223	-4.010686	0.071074



6	-0.356722	-0.671908	-2.818452
1	-0.071290	-1.267064	-3.688826
1	1.444683	0.523775	-2.821973
1	-1.444683	-0.523775	-2.821973
8	0.018851	-1.447662	-1.669943
1	0.071290	1.267064	-3.688826
6	0.003386	-1.245372	0.740446
6	0.356722	0.671908	-2.818452
16	0.000000	0.000000	1.971635
6	-0.003386	1.245372	0.740446
6	0.000000	0.719902	-0.519821
6	0.000000	-0.719902	-0.519821
8	-0.018851	1.447662	-1.669943
17	0.013371	-2.918701	1.157896
17	-0.013371	2.918701	1.157896

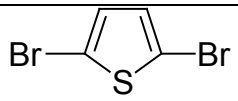


8	1.019941	4.171868	-0.015576
16	-1.748971	1.395961	0.000338
6	-1.113549	3.024426	-0.009351
6	0.252793	3.045680	0.004407
6	0.809276	1.729017	0.019382
6	-0.118434	0.710558	0.020279
6	0.118434	-0.710558	0.020279
8	2.161069	1.515868	0.047814
16	1.748971	-1.395961	0.000338
6	1.113549	-3.024426	-0.009351
6	-0.252793	-3.045680	0.004407
6	-0.809276	-1.729017	0.019382
8	-1.019941	-4.171868	-0.015576
8	-2.161069	-1.515868	0.047814
6	2.381459	3.915721	0.356295
6	2.910921	2.674033	-0.346768

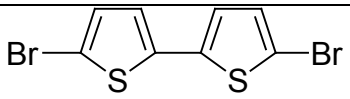
Cl_2

17	0.000000	0.000000	1.021319
17	0.000000	0.000000	-1.021319

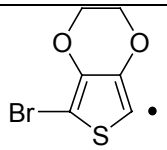
1	3.946950	2.474320	-0.064004
1	2.449118	3.790046	1.445158
1	2.946428	4.802984	0.060834
1	2.848978	2.798520	-1.435961
6	-2.381459	-3.915721	0.356295
6	-2.910921	-2.674033	-0.346768
1	-3.946950	-2.474320	-0.064004
1	-2.449118	-3.790046	1.445158
1	-2.848978	-2.798520	-1.435961
1	-2.946428	-4.802984	0.060834
17	2.161069	-4.395306	-0.031459
17	-2.161069	4.395306	-0.031459



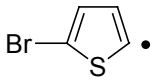
1	0.000000	1.323833	-2.465211
16	0.000000	0.000000	0.925989
6	0.000000	1.233804	-0.306136
6	0.000000	0.715207	-1.569000
6	0.000000	-0.715207	-1.569000
6	0.000000	-1.233804	-0.306136
35	0.000000	-3.053251	0.180232
1	0.000000	-1.323833	-2.465211
35	0.000000	3.053251	0.180232



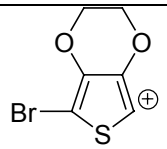
1	-2.007569	3.499882	0.419448
16	1.187103	1.849758	-0.128333
6	0.099211	3.197322	0.041470
6	-1.187103	2.805528	0.284470
6	-1.310369	1.388661	0.351594
6	-0.125029	0.713491	0.159193
6	0.125029	-0.713491	0.159193
1	-2.248229	0.883899	0.558532
35	0.746179	4.957757	-0.112715
16	-1.187103	-1.849758	-0.128333
6	-0.099211	-3.197322	0.041470
6	1.187103	-2.805528	0.284470
6	1.310369	-1.388661	0.351594
35	-0.746179	-4.957757	-0.112715
1	2.007569	-3.499882	0.419448
1	2.248229	-0.883899	0.558532



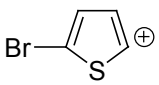
6	-2.288710	-1.716695	0.335418
1	-2.515042	-2.736107	0.014974
1	-3.133709	-0.792801	-1.427512
1	-2.382264	-1.649744	1.427102
8	-0.922904	-1.477971	-0.041813
1	-4.255336	-0.888413	-0.040293
6	0.693920	0.317851	0.103694
6	-3.218112	-0.713940	-0.335496
35	2.259591	-0.706764	-0.045120
16	0.727396	2.075860	0.077685
6	-0.986626	2.118866	-0.118604
6	-1.573339	0.889991	0.004353
6	-0.590915	-0.161529	0.028405
8	-2.908969	0.625821	0.073733



1	-1.298585	1.998417	0.000000
16	1.728945	-0.045833	0.000000
6	0.000000	0.271512	0.000000
6	-0.287837	1.606210	0.000000
6	0.896142	2.430307	0.000000
6	2.004168	1.653045	0.000000
1	0.882605	3.513980	0.000000
35	-1.226342	-1.158443	0.000000



6	-2.331855	-1.715163	0.391286
1	-2.579125	-2.743572	0.124849
1	-3.134216	-0.886895	-1.469063



1	-0.450395	2.327612	0.005055
16	-1.173951	-1.304127	-0.090403
6	-0.181648	0.153793	-0.192154

1	-2.454778	-1.578709	1.471498	6	-0.928319	1.357762	-0.104305
8	-0.935491	-1.539162	0.049895	6	-2.314054	1.123982	-0.045750
1	-4.244953	-0.768325	-0.071165	6	-2.374434	-0.175243	0.390864
6	0.709008	0.242363	-0.035263	1	-3.119659	1.846265	-0.120021
6	-3.201916	-0.743930	-0.387246	35	1.632686	0.055154	0.036271
35	2.261011	-0.701046	-0.045857				
16	0.639326	2.133131	0.023069				
6	-0.989483	2.220059	0.217335				
6	-1.504602	0.829738	0.054336				
6	-0.568135	-0.247286	0.070240				
8	-2.768214	0.647827	-0.135437				