Supplementary Information:

[11]Cycloparaphenylene incorporating a redox-active dithiafulvene moiety provides access to a carbon nanohoop with an unpaired electron along the core

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1. General Methods

Unless otherwise stated, commercially available materials were used without purification. Flash column chromatography was performed using silica gel (Silica gel 60 (43–60 µm) purchased from VWR). NMR spectra were recorded on a Bruker instrument equipped with an observe cryoprobe or a cryo-inverse probe instrument (Novo Nordisk Foundation NMR facility at the Department of Chemistry, University of Copenhagen (Grant: NNF21OC0067315)) at 500 MHz and 126 MHz for ^{1}H and ^{13}C NMR spectroscopy, respectively. Deuterated dichloromethane (CD_2Cl_2, ^{1}H = 5.32 ppm, ^{13}C = 53.84 ppm) was used as solvent and internal reference. Chemical shift values are referenced to the ppm scale; coupling constants are expressed in Hertz (Hz); and apparent multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), td (triplet of doublets) or m (multiplet). HRMS analysis was performed on a Bruker SolariX XR MALDI-FT-ICR instrument with dithranol as a matrix. All solvents used were HPLC grade from VWR and used without further purification. Anh. tetrahydrofuran (THF) was obtained after drying directly from the bottle over molecular sieves (3 Å). All water used was deionized. Compound **F[11]CPP** was prepared according to literature procedures.[1]

UV-Vis-NIR Absorption Spectroscopy

All measurements were carried out in 10-mm quartz cuvettes from Hellma. UV-Vis absorption measurements were carried out on a Varian Cary 50 UV-vis spectrophotometer (200-1100 nm). UV-Vis-NIR absorption measurements were carried out on an Agilent Cary 5000 UV-Vis-NIR spectrophotometer (200-3300 nm). A background of pure solvent was subtracted.

Electrochemistry

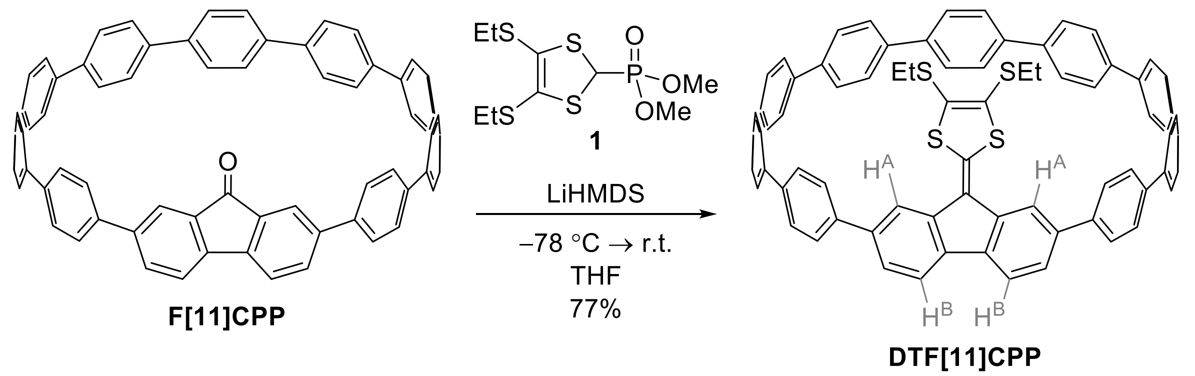
Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) were obtained using an Autolab PGSTAT12 instrument and Nova 1.11 software with a scan rate of 0.1 V/s for the CVs. A silver wire was used as the reference electrode, a Pt wire was used as the counter electrode, and a platinum disk electrode (diameter = 1.6 mm) was used as the working electrode. The reference electrode was separated from the solution containing the substrate by a ceramic frit. Measured potentials were referenced to the ferrocene/ferrocenium (Fc/Fc^{+}) redox couple, measured before and after the experiment for a 1.0 mM solution of Fc. A 0.1-M concentration of n-Bu_4NPF_6 was used as supporting electrolyte. All solutions were purged with argon prior to measurements. All compounds were measured at 0.5 mM concentrations in CH_2Cl_2.

ESR Spectroscopy

The sample was prepared by addition of 0.9 molar equivalents of ’magic blue’ (**MB**, tris(4-bromophenyl)ammoniumyl hexachloroantimonate) from a solution in anh. CD_2Cl_2 to a solution of **DTF[11]CPP** in CD_2Cl_2 under N_2, after which ≈25 µL of the resulting red solution was added to a flame-dried EPR tube under N_2. The EPR tube was degassed three times using by freeze-pump-thaw (N_2) and subsequently sealed. ESR measurements were performed at X-band (~9.6 GHz) using a Bruker Elexsys E580 spectrometer equipped with a Flexline MD5 dielectric resonator. Measurements were performed at room temperature using a 100 kHz modulation frequency, 0.1 G modulation amplitude, and a power of 0.15 mW. The measurements were performed at the Novo Nordisk Foundation Copenhagen Pulse EPR Facility.

For compound **F-DTF**: The sample was prepared by addition of approximately 1 molar equivalent of ’magic blue’ (**MB**, tris(4-bromophenyl)ammoniumyl hexachloroantimonate) from a freshly prepared solution in degassed anh. CD_2Cl_2 to a solution of **F-DTF** in degassed anh. CD_2Cl_2, after which the resulting red solution was added to a capillary tube (with one end capped), inserted into a EPR tube. ESR measurements were performed at X-band (~9.6 GHz) using a Bruker Elexsys spectrometer equipped with a dual mode resonator. Measurements were performed at room temperature using a 100 kHz modulation frequency, 1.0 G modulation amplitude, and a power of 20 mW. Measurements at 0.1 G modulation amplitude did not reveal any hyperfine coupling.

2. Synthetic Protocols



To a 50-mL flame-dried Schlenk-flask equipped with a magnetic stirrer bar was added phosphonate **1** (38 mg, 80 µmol, 3.0 equiv.); the flask was evacuated and backfilled with N_2 three times before anh. THF (10 mL) was added. The flask was cooled in a dry ice/acetone bath for 1 h before LiHMDS (0.12 mL, 0.12 mmol, 4.5 equiv.), from a 1.0 M solution in THF) was added dropwise via syringe, and the flask was left to stir for 1.5 h. In a separate 50-mL flame-dried Schlenk flask equipped with a magnetic stirrer bar was added ketone **F[11]CPP** (23 mg, 27 µmol), and the flask was evacuated and backfilled with N_2 three times before anh. THF (10 mL) was added. The flask was cooled in a dry ice/acetone bath for 30 min, before the deprotonated phosphonate **1** was cannulated into the flask over the course of approximately 2 min. The mixture was stirred in the cooling bath −78 °C and was allowed to reach room temperature overnight. The resulting clear yellow solution was quenched with sat. aq. NH_4Cl (1 mL) and H_2O (1 mL), and the organic volatiles were removed *in vacuo*. The mixture was extracted with CH_2Cl_2 (2 × 25 mL), and the organic phase was dried over $MgSO_4$, filtered and the volatiles removed *in vacuo*. The crude mixture was purified by a short column (SiO_2, CH_2Cl_2:heptane 3:1), followed by precipitation from CH_2Cl_2 by addition of pentane, which yielded **DTF[11]CPP** as a yellow powder(22 mg, 21 µmol, 77% yield).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.77 (d, *J* = 8.1 Hz, 2H, $\mathbf{H^B}$), 7.70–7.58 (m, 38H), 7.51 (d, *J* = 1.5 Hz, 2H, $\mathbf{H^A}$), 2.98 (q, *J* = 7.3 Hz, 4H, $-SC\mathbf{H_2}CH_3$), 1.36 (t, *J* = 7.3 Hz, 6H, $-SCH_2C\mathbf{H_3}$).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.77, 139.76, 139.61, 139.01, 138.95, 138.80, 138.67, 138.42, 138.36, 136.92, 136.48, 129.07, 128.29, 127.88, 127.84, 127.74, 127.71, 127.65, 127.62, 127.51, 127.48, 125.44, 123.24, 121.74, 121.12, 31.28, 15.30. Two sp^2-C signals are missing, presumably due to overlap.

HRMS (MALDI$^+$, FTICR) *m/z* = 1068.2941 $[M+H]^+$, calcd. for $C_{74}H_{52}S_4^+$ *m/z* = 1068.2946

3. NMR Spectra

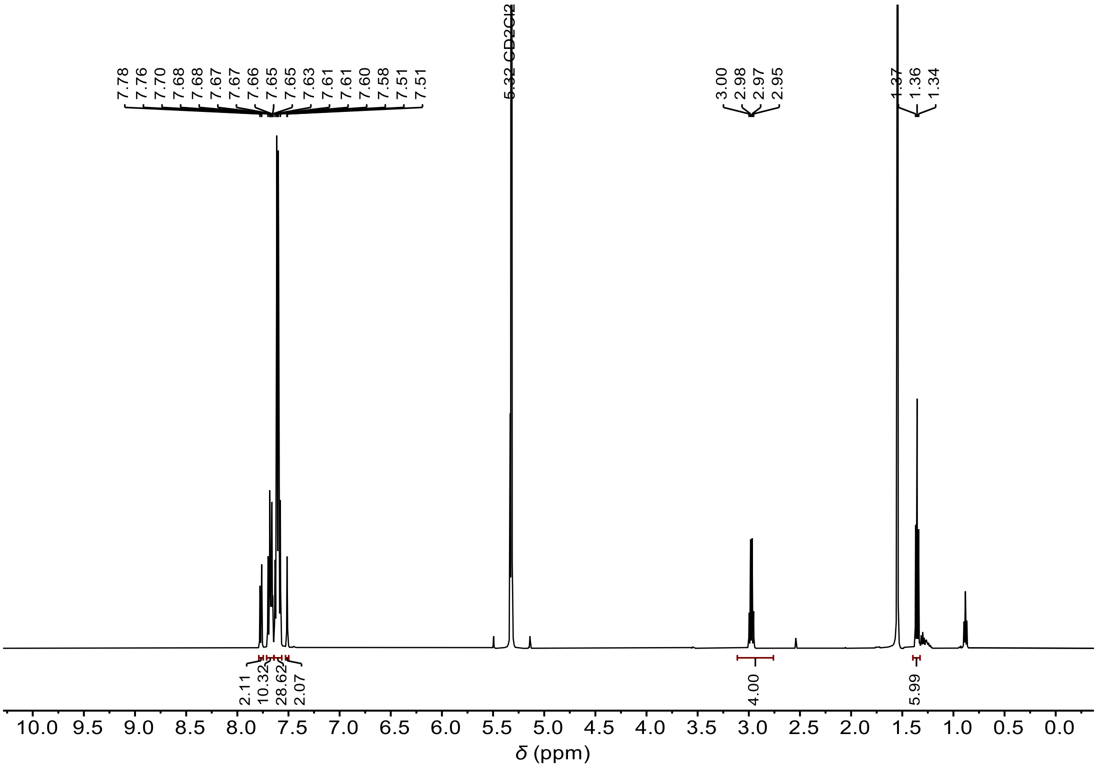


Figure S1. ^{1}H NMR (500 MHz) spectrum of compound **DTF[11]CPP** in CD_2Cl_2. Residual solvent (pentane) signals at 1.30 and 0.88 ppm.

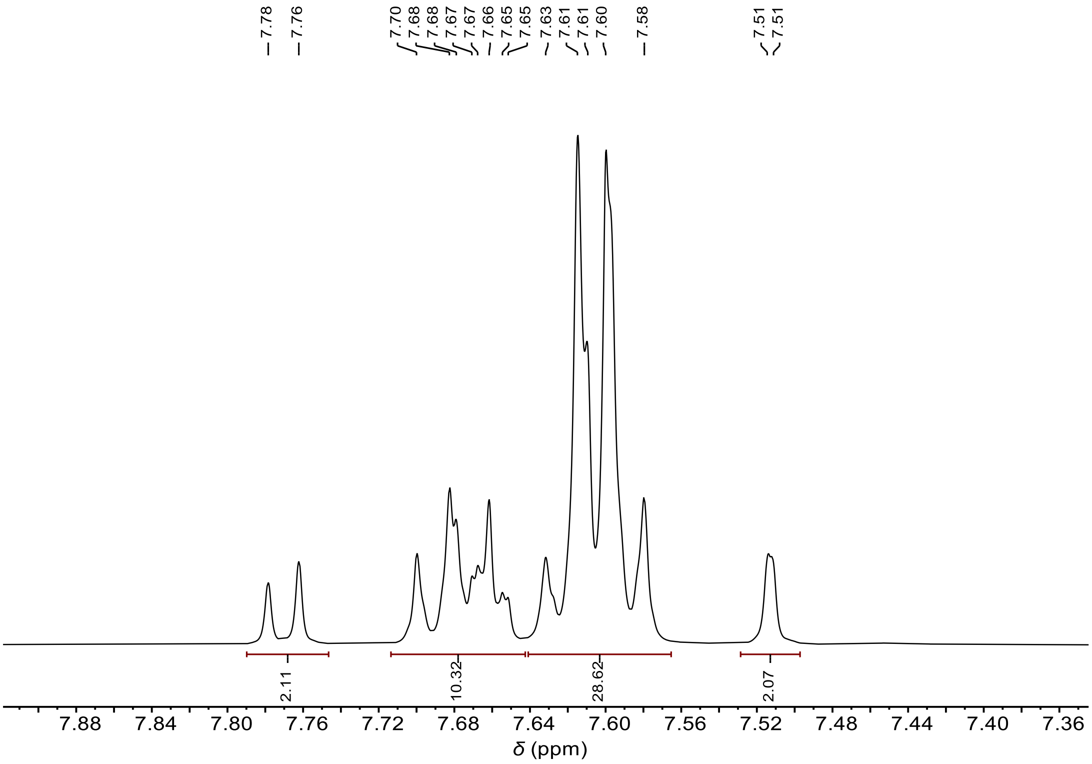


Figure S2. ^{1}H NMR (500 MHz) spectrum of compound **DTF[11]CPP** in CD_2Cl_2; selected region.

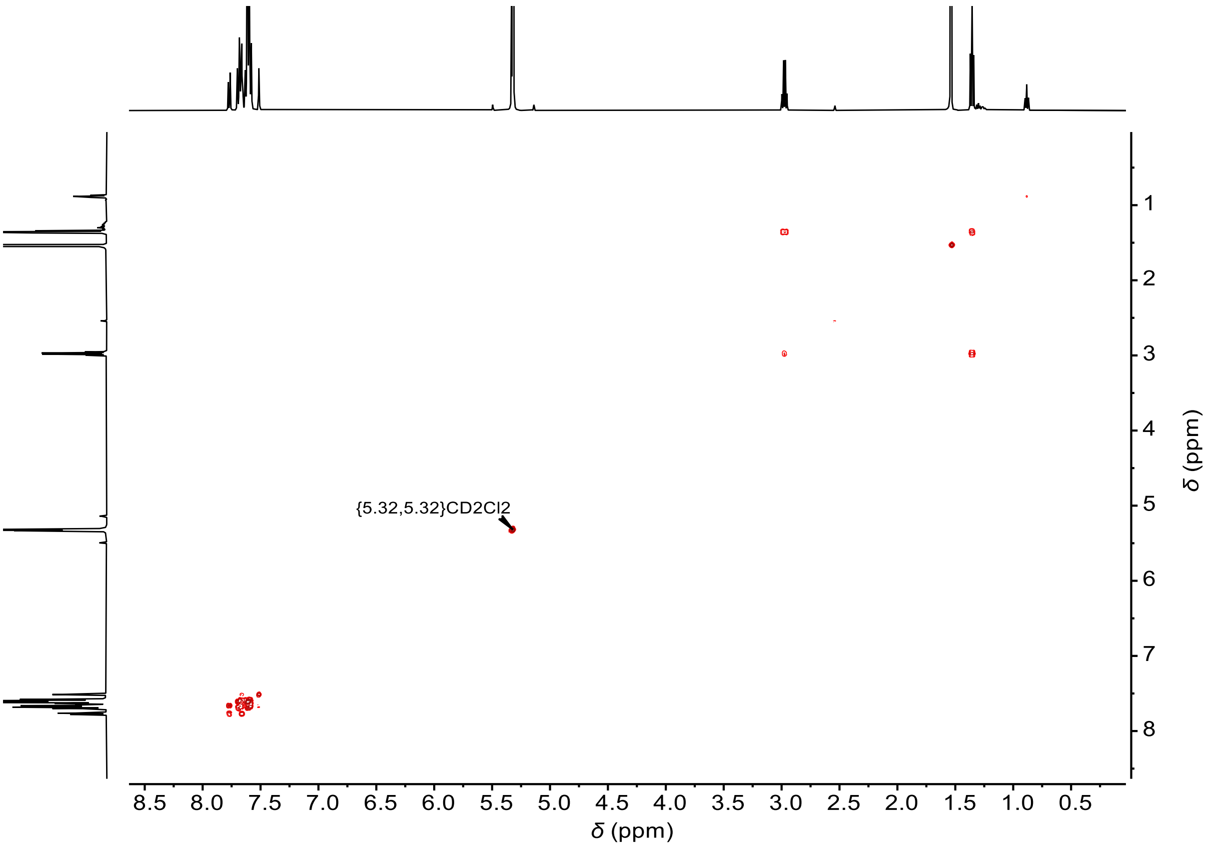


Figure S3. ^{1}H-^{1}H COSY NMR (500 MHz) spectrum of compound **DTF[11]CPP** in CD_2Cl_2.

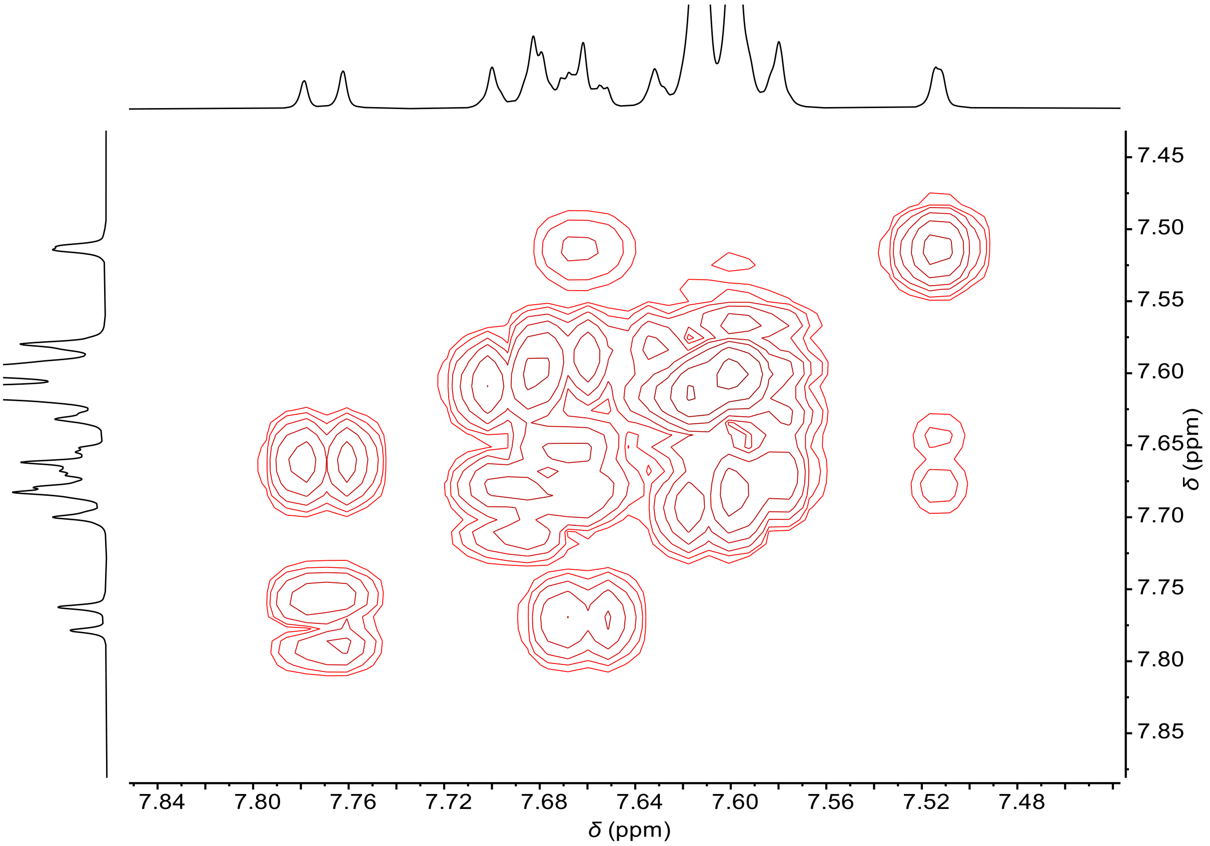


Figure S4. ^{1}H-^{1}H COSY NMR (500 MHz) spectrum of compound **DTF[11]CPP** in CD_2Cl_2; selected region.

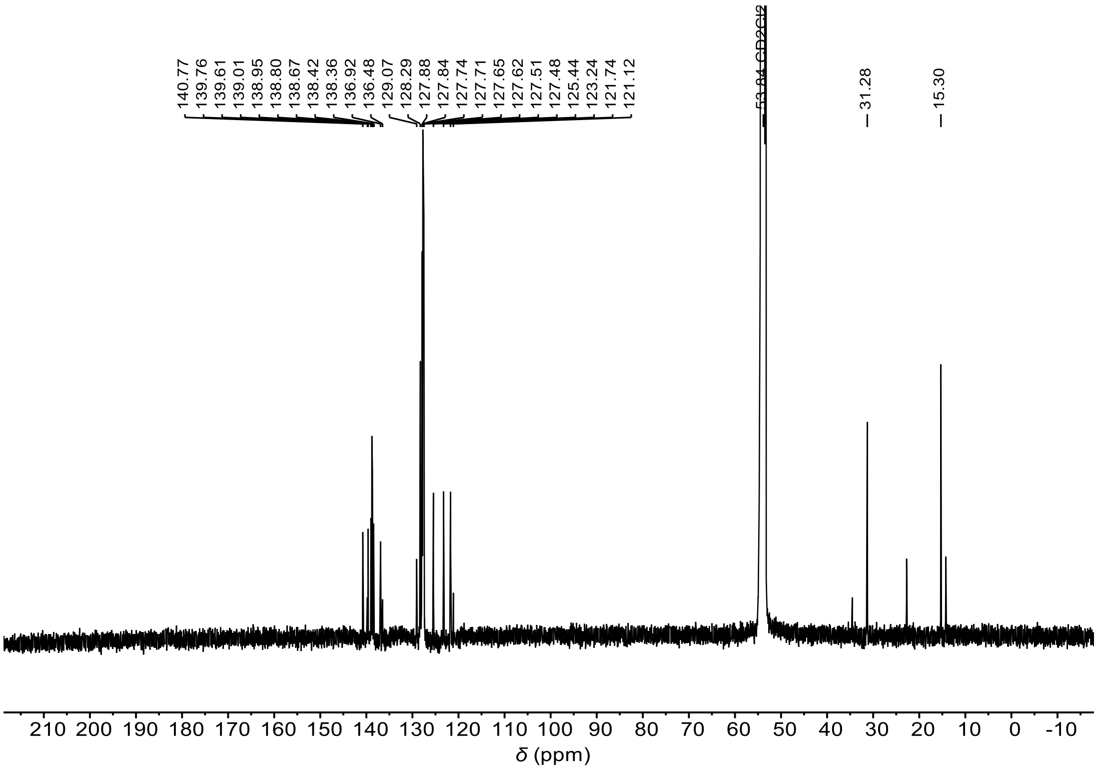


Figure S5. ^{13}C NMR (126 MHz) of compound **DTF[11]CPP** in CD_2Cl_2. Residual solvent (pentane) signals at 34.54, 22.75 and 14.22 ppm.

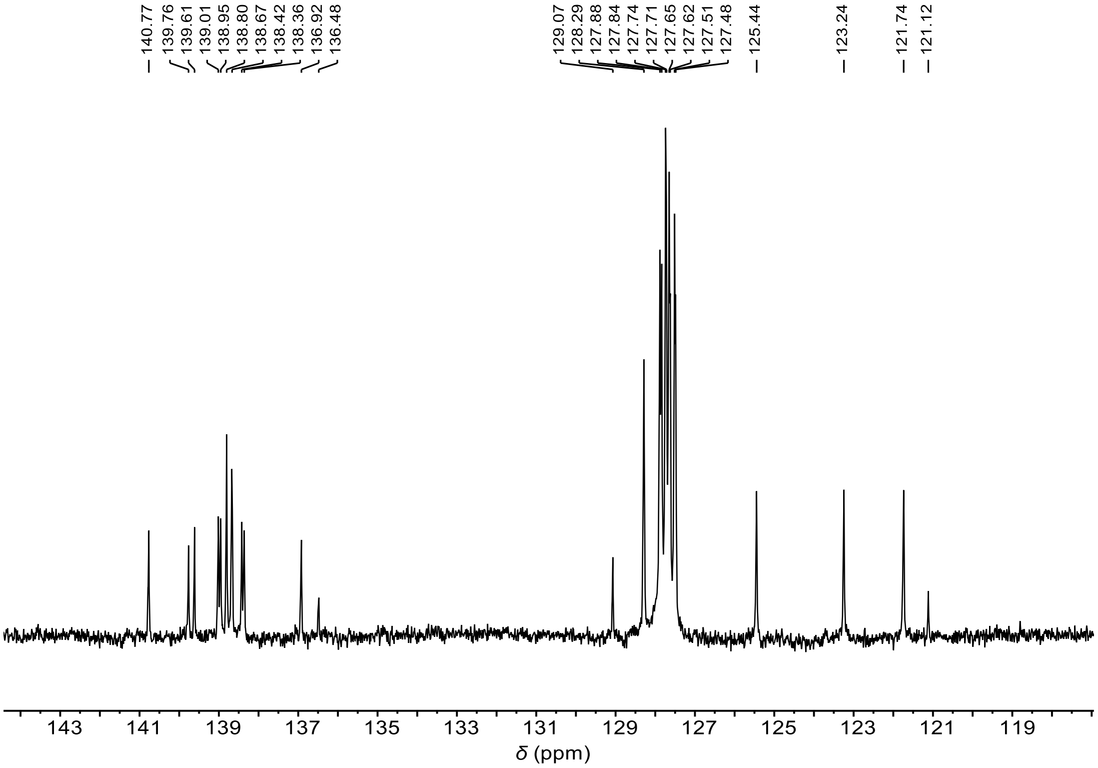


Figure S6. ^{13}C NMR (126 MHz) of compound **DTF[11]CPP** in CD_2Cl_2; selected region.

4. Electrochemistry

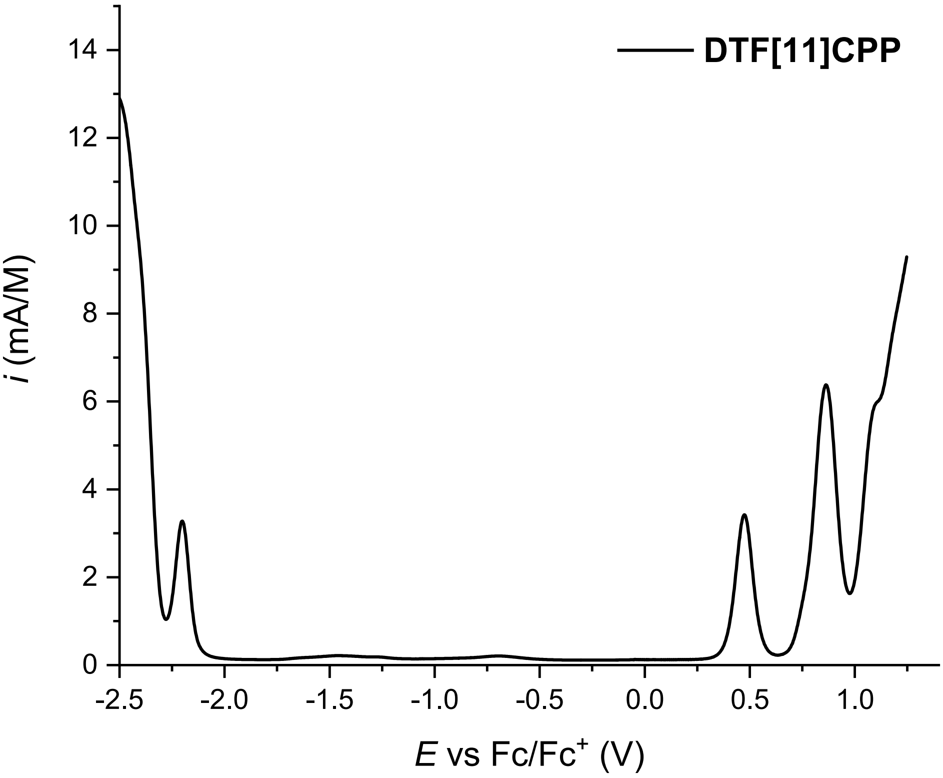


Figure S7. Differential pulse voltammogram of **DTF[11]CPP**. The voltammogram was recorded at 0.5 mM concentration in CH_2Cl_2 using *n*-Bu_4NPF_6 as the supporting electrolyte.

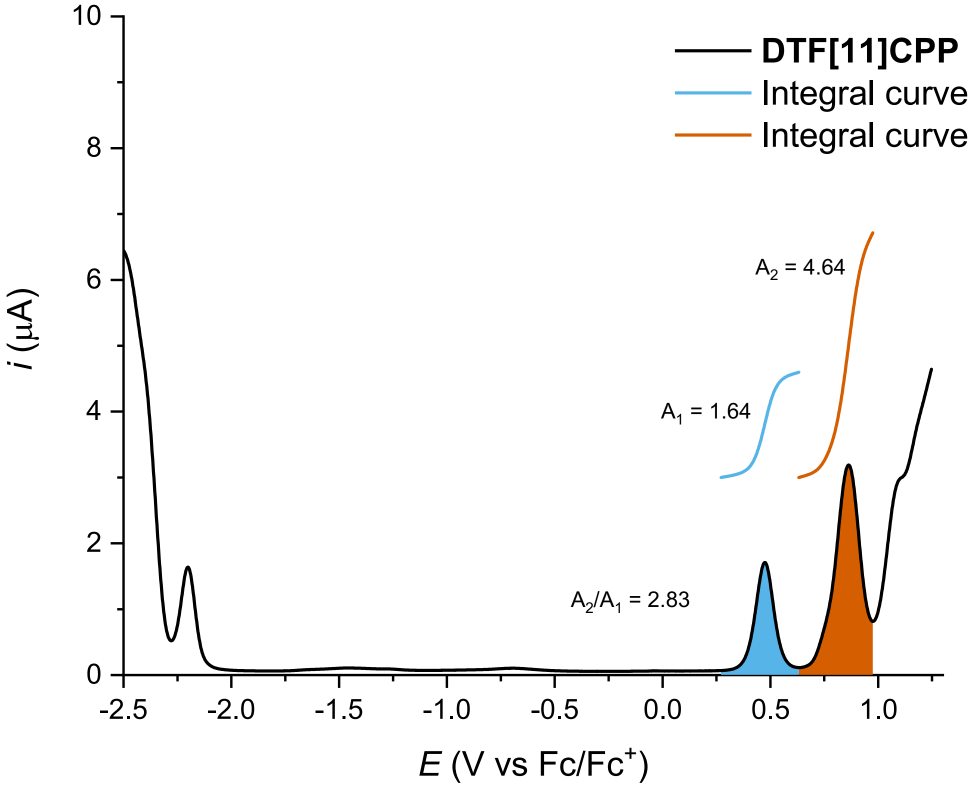


Figure S8. Differential pulse voltammogram of **DTF[11]CPP**. The voltammogram was recorded at 0.5 mM concentration in CH_2Cl_2 using *n*-Bu_4NPF_6 as the supporting electrolyte. Integral curves, integrals (a.u.), blue and orange, and integral ratio are shown.

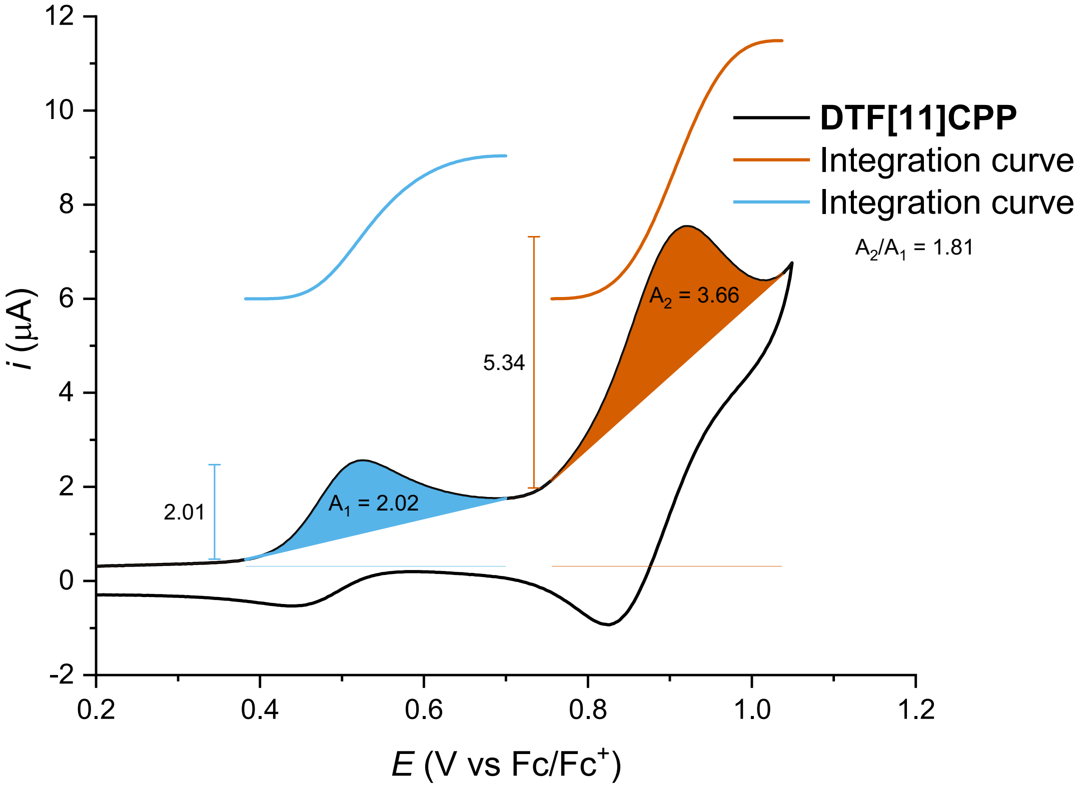
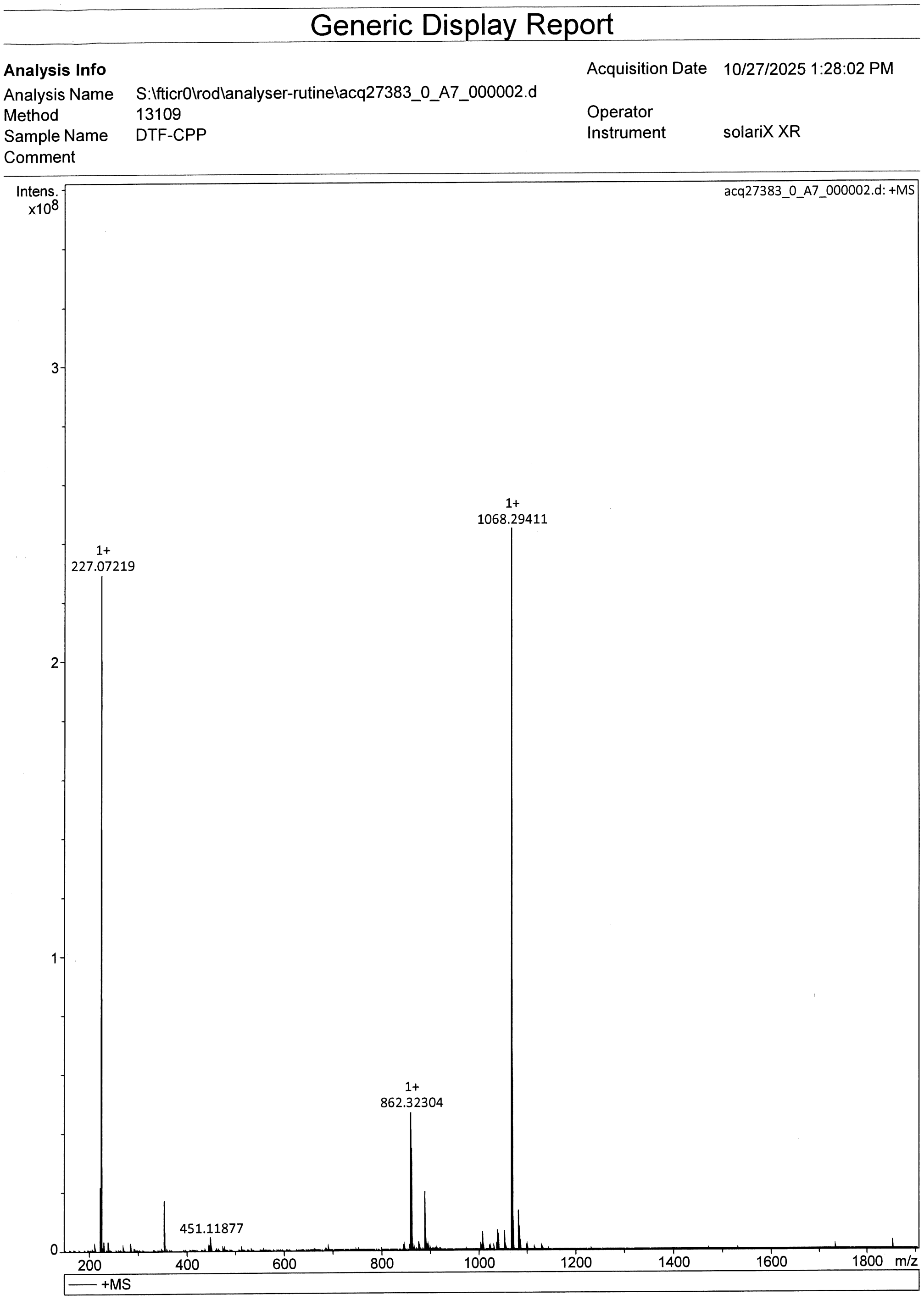


Figure S9. Cyclic voltammogram of **DTF[11]CPP**. The voltammogram was recorded at 0.5 mM concentration in CH_2Cl_2 using *n*-Bu_4NPF_6 as the supporting electrolyte at 0.1 V/s. Integral curves, integrals (a.u.), blue and orange, and integral ratio are shown.

5. HRMS Spectra



Generic Display Report

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Sample Name DTF-CPP
Comment

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Operator
Instrument solariX XR

Figure S10. HRMS spectrum of compound **DTF[11]CPP**.

Generic Display Report

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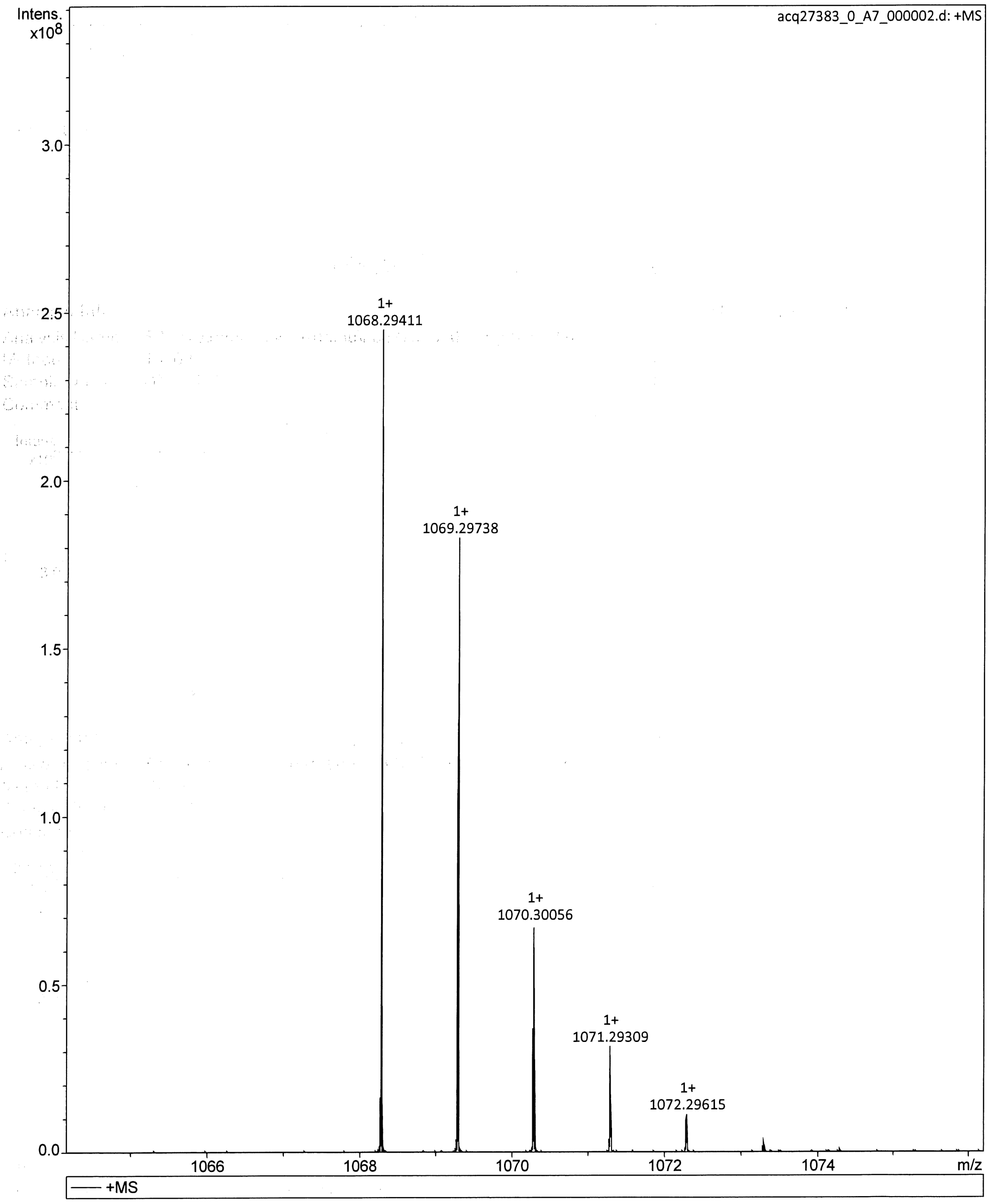

Figure S11. HRMS spectrum of compound **DTF[11]CPP**.

6. Computational

Table S1. The 20 calculated lowest energy transitions for **DTF[11]CPP.**

Transition	Energy (eV)	Energy (cm^{-1})	Wavelength (nm)	fosc (D^2)	D^2 (au^2)	DX (au)	DY (au)	DZ (au)
0-1A → 1-1A	3.393987	27374.4	365.3	0.788590612	9.48382	2.26798	0.09347	2.08118
0-1A → 2-1A	3.432373	27684.0	361.2	0.399475925	4.75049	−0.05946	2.17777	−0.06548
0-1A → 3-1A	3.774178	30440.8	328.5	0.352765056	3.81509	−0.02674	1.95193	−0.06588
0-1A → 4-1A	3.865014	31173.4	320.8	2.027424030	21.41092	−4.40799	0.02298	1.40713
0-1A → 5-1A	3.923303	31643.6	316.0	0.715166104	7.44041	2.26720	0.23060	−1.49901
0-1A → 6-1A	3.982100	32117.8	311.4	1.658905378	17.00401	−0.11963	4.12093	−0.08731
0-1A → 7-1A	4.060065	32746.6	305.4	0.037192313	0.37391	0.00323	0.50174	0.34950
0-1A → 8-1A	4.115978	33197.6	301.2	0.029059547	0.28818	−0.22586	−0.43621	0.21653
0-1A → 9-1A	4.360509	35169.9	284.3	0.262885491	2.46077	0.02016	−1.56794	0.04389
0-1A → 10-1A	4.476614	36106.3	277.0	0.029828137	0.27197	0.51971	0.03526	0.02504
0-1A → 11-1A	4.626910	37318.6	268.0	0.001903959	0.01680	−0.12818	−0.01109	−0.01562
0-1A → 12-1A	4.638526	37412.2	267.3	0.003309788	0.02912	0.01042	−0.17019	0.00712
0-1A → 13-1A	4.671963	37681.9	265.4	0.007659535	0.06692	0.04838	−0.13047	0.21807
0-1A → 14-1A	4.740899	38237.9	261.5	0.002534524	0.02182	0.03773	0.01769	0.14172
0-1A → 15-1A	4.771903	38488.0	259.8	0.001460405	0.01249	−0.07355	−0.01267	0.08320
0-1A → 16-1A	4.795088	38675.0	258.6	0.128999748	1.09808	−0.00541	−1.04712	0.03988
0-1A → 17-1A	4.802218	38732.5	258.2	0.019919921	0.16931	0.00087	−0.41118	0.01550
0-1A → 18-1A	4.843135	39062.5	256.0	0.000106847	0.00090	0.02737	0.01227	0.00095
0-1A → 19-1A	4.845108	39078.4	255.9	0.002944637	0.02481	−0.02634	0.15528	−0.00158
0-1A → 20-1A	4.899350	39515.9	253.1	0.007598504	0.06330	−0.02266	0.00435	−0.25054

Table S2. The 20 calculated lowest energy transitions for **DTF[11]CPP$^{\bullet+}$.**

Transition	Energy (eV)	Energy (cm^{-1})	Wavelength (nm)	fosc (D^2)	D^2 (au^2)	DX (au)	DY (au)	DZ (au)
0-2A → 1-2A	1.038123	8373.0	1194.3	0.000112660	0.00443	0.02898	−0.05791	0.01535
0-2A → 2-2A	1.734681	13991.1	714.7	0.229531319	5.40088	1.37167	−0.15676	1.86944
0-2A → 3-2A	2.041929	16469.3	607.2	0.001432799	0.02864	−0.07765	−0.02661	0.14800
0-2A → 4-2A	2.173862	17533.4	570.3	0.005799763	0.10890	0.03381	0.32494	0.04656
0-2A → 5-4A	2.339179	18866.8	530.0	0.018724078	0.32672	0.01188	0.57145	0.00500
0-2A → 6-2A	2.446981	19736.2	506.7	0.008572890	0.14300	0.14763	0.31777	0.14224
0-2A → 7-4A	2.453494	19788.8	505.3	0.010008143	0.16650	0.01335	−0.40706	−0.02502
0-2A → 8-4A	2.532147	20423.1	489.6	0.010545665	0.16999	0.08303	−0.39074	0.10206
0-2A → 9-4A	2.577084	20785.6	481.1	0.015996794	0.25336	−0.14463	−0.43888	−0.19957
0-2A → 10-2A	2.742932	22123.2	452.0	0.038229766	0.56889	−0.53568	−0.00266	−0.53097
0-2A → 11-2A	2.810816	22670.8	441.1	0.098257129	1.42683	−0.72243	−0.11166	−0.94470
0-2A → 12-4A	2.830798	22831.9	438.0	0.026537146	0.38264	−0.40148	0.02847	−0.46972
0-2A → 13-2A	2.887404	23288.5	429.4	0.017650603	0.24951	0.27256	0.26341	0.32533
0-2A → 14-4A	2.974596	23991.7	416.8	0.065007381	0.89202	0.64451	−0.04193	0.68911
0-2A → 15-2A	3.026089	24407.1	409.7	0.179619898	2.42278	1.04127	−0.33683	1.10684
0-2A → 16-4A	3.200491	25813.7	387.4	0.042497247	0.54198	−0.01296	−0.73264	0.07106
0-2A → 17-4A	3.300161	26617.6	375.7	0.017937662	0.22186	−0.33750	−0.11611	−0.30735
0-2A → 18-2A	3.348557	27007.9	370.3	0.031295354	0.38147	0.07330	0.61321	0.00821
0-2A → 19-2A	3.371030	27189.2	367.8	0.036124152	0.43740	0.18919	0.62011	0.13066
0-2A → 20-2A	3.381817	27276.2	366.6	0.061247537	0.73923	0.02151	0.84093	−0.17776

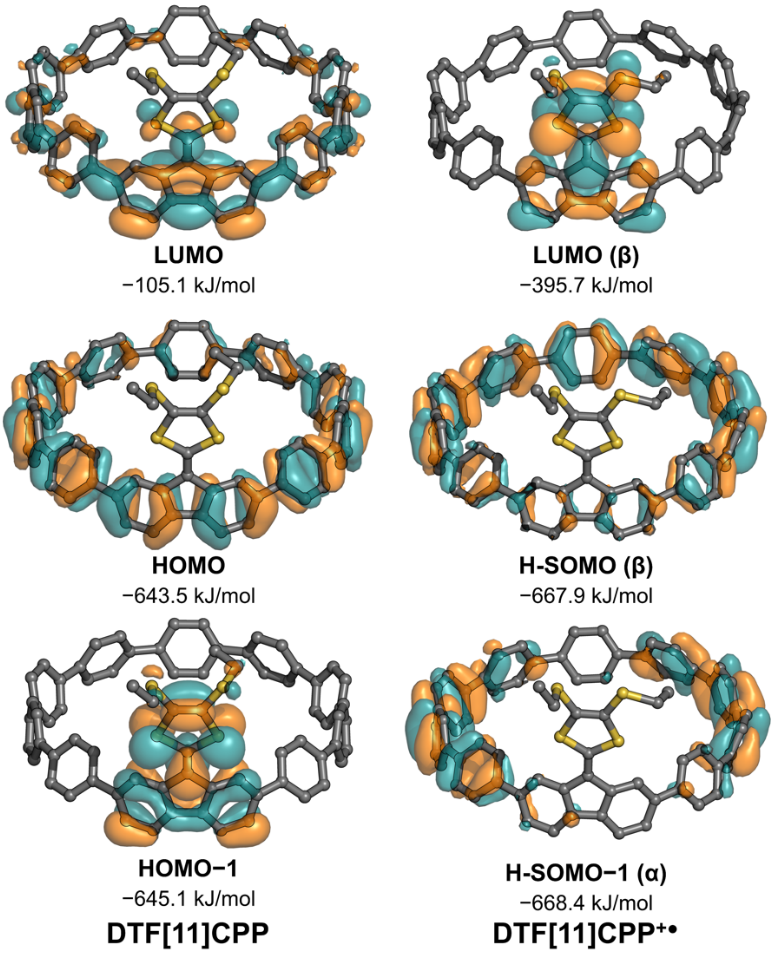

Figure S12. Frontier molecular orbitals for neutral **DTF[11]CPP** and radical cation **DTF[11]CPP$^{\bullet+}$** calculated using CAM-B3LYP/aug-pc-1; α and β denote the two different spin states of the orbitals for **DTF[11]CPP$^{\bullet+}$** (the unpaired electron is put in an α orbital). Isosurface levels set at 0.02. H-SOMO is the highest singly occupied molecular orbital and LUMO is the lowest unoccupied molecular

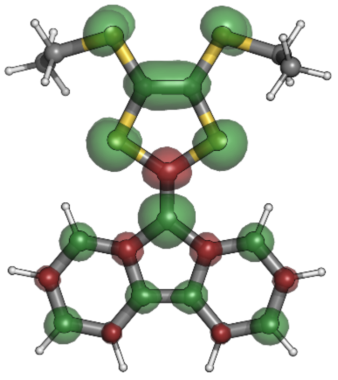

Figure S13. Spin density distribution of **F-DTF$^{\bullet+}$** in dichloromethane, calculated using CAM-B3LYP/pcJ-1 using C-PCM. Color code: positive spin density (green), negative spin density (red). Isosurface levels set at 0.002.

7. ESR spectrum of F-DTF

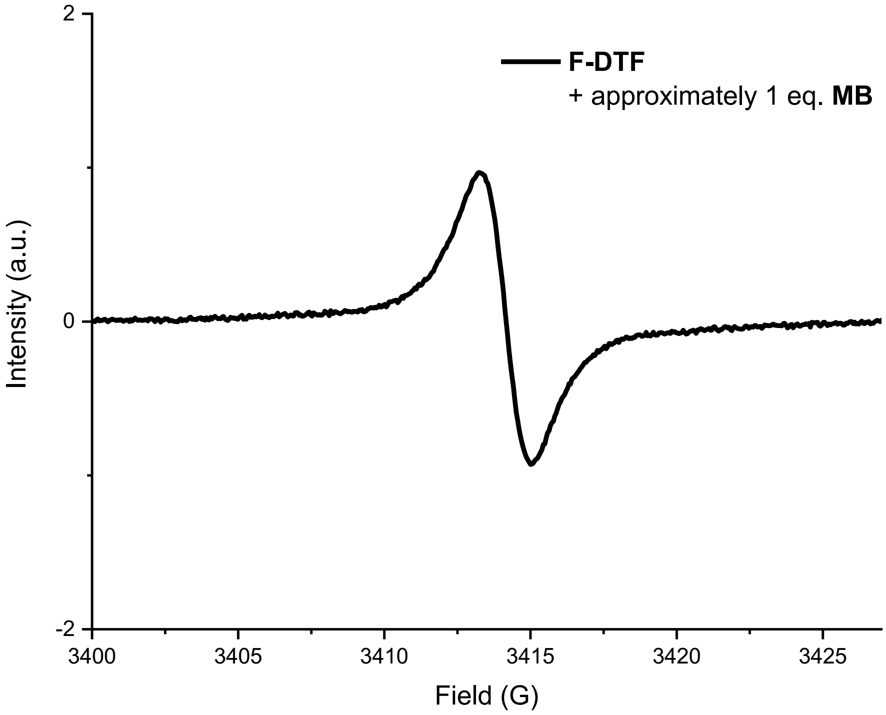

Figure S14. ESR spectrum of **F-DTF** treated with 'magic blue' (**MB**, tris(4-bromophenyl)ammoniumyl hexachloroantimonate) in CD_2Cl_2.

8. References

1. V. Bliksted Roug Pedersen, T. W. Price, N. Kofod, L. N. Zakharov, B. W. Laursen, R. Jasti and M. B. Nielsen, *Chem. Eur. J.*, 2024, **30**, e202303490.