

Oxidation Pathways Involving a Sulfide Endcapped Donor-Acceptor-Donor π -Conjugated Molecule and Antimony(V) Chloride

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SUPPORTING INFORMATION

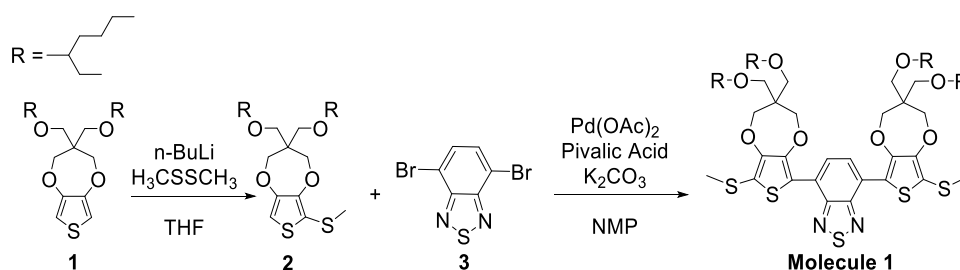
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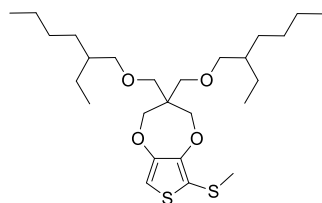
A. General Information

All reagents purchased from commercial suppliers were used without further purification. The antimony(V) chloride reagent was purchased from Acros Organics as a 1.0 M solution in dichloromethane. All reactions were carried out under a N₂ atmosphere, unless otherwise noted. ¹H- and ¹³C-NMR spectra were recorded using a Bruker ARX 400 MHz spectrometer in deuterated chloroform at 293 K and a Bruker ARX 500 MHz spectrometer in deuterated dichloromethane from a temperature range of 200 K to 293 K. High resolution electrospray ionization mass spectrometry was recorded on an Agilent 6320 LC-MS/MS. UV-vis-NIR absorption spectra were measured with an Agilent Technologies Cary 6000i spectrophotometer (350-1600 nm). All the electrochemistry related experiments (CV, DPV) were performed using BioLogic SP-150. Electron Paramagnetic Resonance (EPR) spectra were recorded on a Bruker EMX EPR spectrometer.

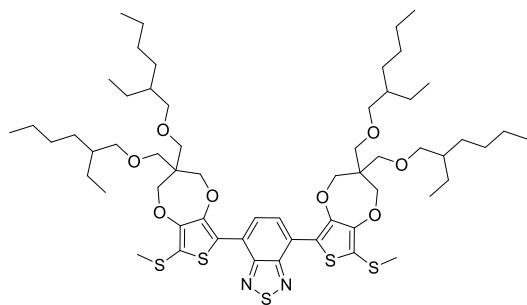
B. Synthetic Protocols



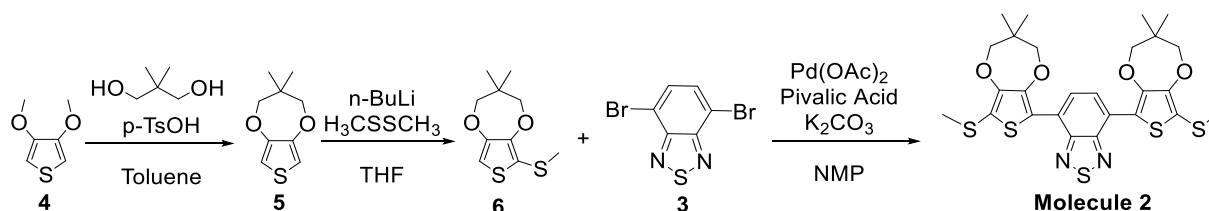
Scheme S1. Synthesis of molecule 1.



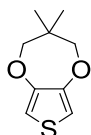
To a THF solution (75 mL) of **1** (2.00 g, 4.54 mmol) was added n-butyllithium (2.5 M, 5.0 mmol) in hexane at -78°C under N₂. After stirring for 120 min at 0°C, dimethyldisulfide (471 mg, 5.0 mmol) was added dropwise to the reaction mixture and then allowed to warm to room temperature. After stirring overnight, the reaction mixture was quenched with water and extracted with hexane and dried over Na₂SO₄. The crude product was concentrated under vacuum and passed through a short alumina column using hexanes:ethyl acetate (75:1). After solvent evaporation, the residue was separated by preparative HPLC (polystyrene/divinylbenzene stationary phase) with CHCl₃ to give **2** as a light yellow oil (1.77g, 80% yield). ¹H NMR (300 MHz, CDCl₃, ppm) δ: 6.44 (s, 1H), 4.09 (s, 2H), 4.00 (s, 2H), 3.47 (s, 4H), 3.27 (d, J = 5.7 Hz, 4H), 2.37 (s, 3H), 1.35 – 1.23 (m, 20H), 0.90 – 0.84 (m, 13H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ 150.63, 149.15, 106.15, 74.18, 73.93, 73.61, 69.73, 47.83, 39.51, 30.57, 29.03, 23.89, 23.00, 21.12, 14.02, 11.06. HRMS (ESI), [M+H]⁺ *m/z* calcd. for C₂₆H₄₇O₄S₂: 487.2910; found 487.2902



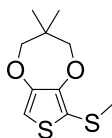
Molecule 1: Compound **2** (3.63 mmol, 1.77 g), **3** (0.73 mmol, 214 mg), Pd(OAc)₂ (2.0 mol %), pivalic acid (1.10 mmol, 111 mg) and (1.90 mmol, 263 mg) were all added to a 25 mL schlenk tube and vacuumed for 30 minutes, and then purged with N₂ three times. Anhydrous N-methyl-2-pyrrolidone (5 mL) was added to the mixture and the reaction was heated at 110°C in an oil bath for 2 h, or until benzothiadiazole was completely consumed per TLC analysis. Upon completion, the reaction mixture was quenched with water and extracted with hexane. The organic layer was washed with water twice, then once with brine. The organic layer was separated and dried over MgSO₄, then filtered and concentrated. The desired product was purified via SiO₂ column chromatography using hexanes:CH₂Cl₂ (3:1) to give molecule **1** as an orange viscous oil (331 mg, 41% yield). ¹H NMR (500 MHz, CD₂Cl₂, ppm) δ 8.33 (s, 2H), 4.21 (s, 4H), 4.15 (s, 4H), 3.54 (s, 8H), 3.32 (dd, *J* = 5.0 Hz, 8H), 2.45 (s, 6H), 1.43 – 1.27 (m, 34H), 0.87 (m, 22H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 151.92, 149.69, 147.47, 126.69, 122.98, 117.32, 115.89, 109.21, 73.48, 73.38, 73.20, 69.04, 54.33, 54.11, 53.89, 53.68, 53.46, 47.58, 39.24, 30.32, 28.91, 23.60, 23.55, 23.26, 20.32, 14.23, 10.94. HRMS (ESI), [M+H]⁺ *m/z* calcd. for C₅₈H₉₂N₂O₈S₅: 1104.5458; found 1104.5441. Elem. Anal. calcd. C, 63.01; H, 8.39; N, 2.53; found C, 63.25; H, 8.33; N, 2.60. Molar Absorption Coefficient: ε_{490nm} = 2.4 × 10⁴ cm⁻¹M⁻¹.



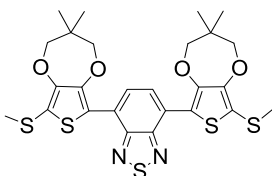
Scheme S2: Synthesis of Molecule **2**.



Compound **4** (0.023 mmol, 3.30 g), 2,2-dimethyl-1,3-propanediol (0.027 mmol, 2.86 g) and p-toluene sulfonic acid monohydrate (0.002 mmol, 435 mg) were added to a three-neck round bottom flask and purged with N₂. Toluene (60 mL) was added and the solution was refluxed overnight. The resulting mixture was filtered and the toluene soluble fraction was washed with water and concentrated under vacuum to yield a green viscous oil. The crude product was purified by SiO₂ column chromatography using hexanes:CH₂Cl₂ (2:1) to give **5** as a white solid product (2.36 g, 47% yield). ¹H NMR (400 MHz, CDCl₃, ppm) δ: 6.47 (s, 2H), 3.73 (s, 4H), 1.03 (s, 6H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ 149.90, 105.41, 79.99, 38.79, 21.58. HRMS (ESI), [M+H]⁺ *m/z* calcd. for C₉H₁₃O₂S: 185.0631; found 185.0635



To a THF solution (150 mL) of **5** (2.36 g, 12.8 mmol) was added n-butyllithium (14.1 mmol, 2.5 M) in hexane at -78°C under N₂. After stirring for 120 min at 0°C, dimethyldisulfide (14.1 mmol, 1.33 g) as added dropwise to the reaction mixture and then allowed to warm to room temperature. After stirring overnight, the reaction mixture was quenched with water and extracted with hexane and dried over Na₂SO₄. The crude product was concentrated under vacuum and passed through a short alumina column using hexanes:ethyl acetate (75:1). After solvent evaporation, the residue was separated by preparative HPLC (polystyrene/divinylbenzene stationary phase) with CHCl₃ to give **6** as a light yellow oil (1.04 g, 35% yeild). ¹H NMR (400 MHz, CDCl₃, ppm) δ 6.48 (s, 1H), 3.81 (s, 2H), 3.72 (s, 2H), 2.36 (s, 3H), 1.03 (s, 6H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ 150.92, 149.44, 114.69, 106.72, 80.03, 79.90, 38.88, 21.65, 21.19. HRMS (ESI), [M+H]⁺ *m/z* calcd. for C₁₀H₁₅O₂S₂: 231.0508; found 231.0505



Molecule 2: Compound **6** (4.52 mmol, 1.04 g), **3** (0.90 mmol, 265 mg), Pd(OAc)₂ (2.0 mol %), pivalic acid (1.35 mmol, 138 mg) and (1.80 mmol, 249 mg) were all added to a 25 mL schlenk tube and vacuumed for 30 minutes, and then purged with N₂ three times. Anhydrous N-methyl-2-pyrrolidone (3 mL) was added to the mixture and the reaction was heated at 110°C in an oil bath for 2 h, or until benzothiadiazole was completed consumed per TLC analysis. Upon completion, the reaction mixture was quenched with water and extracted with hexane. The organic layer was washed with water twice, then once with brine. The organic layer was separated and dried over MgSO₄, then filtered and concentrated. The desired product was purified via SiO₂ column chromatography using hexanes:CH₂Cl₂ (3:1) to give molecule **2** as an orange solid (197 mg, 37% yield). ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.28 (s, 2H), 3.93 (s, 8H), 2.48 (s, 6H), 1.11 (s, 12H). ¹³C NMR (101 MHz, CDCl₃, ppm) δ 152.45, 150.43, 147.74, 127.45, 123.73, 118.64, 116.95, 80.02, 79.87, 38.87, 21.81, 20.61. HRMS (ESI), [M+H]⁺ *m/z* calcd. for C₂₆H₂₉N₂O₄S₅: 592.0647; found 592.0629

C. Cyclic Voltammetry (CV)

Solution CV of molecule **1** was conducted under a nitrogen atmosphere at 1 mM in 0.2 M TBAPF₆/CH₂Cl₂ on a platinum button electrode and a platinum wire counter electrode. An Ag/AgCl wire was used as the pseudoreference electrode which was calibrated against a ferrocene/ferrocenium as an internal standard ($E_{1/2} = 0.51$ V). The voltage was scanned from -0.2 to 0.6 V vs. Fc⁺/Fc, at a 5 mV/s scan rate. The second cycle is reported in the main text figure.

D. Differential Pulse Voltammetry (DPV)

After CV, the same solution of neutral molecule **1** was used to conduct DPV. The voltage was scanned from -0.2 V to 0.6 V vs. Fc⁺/Fc, at a 200 mV/sec scan rate. A 5 mV pulse height, 10 ms pulse width, 5.0 mV step height, and 25 ms step time were used.

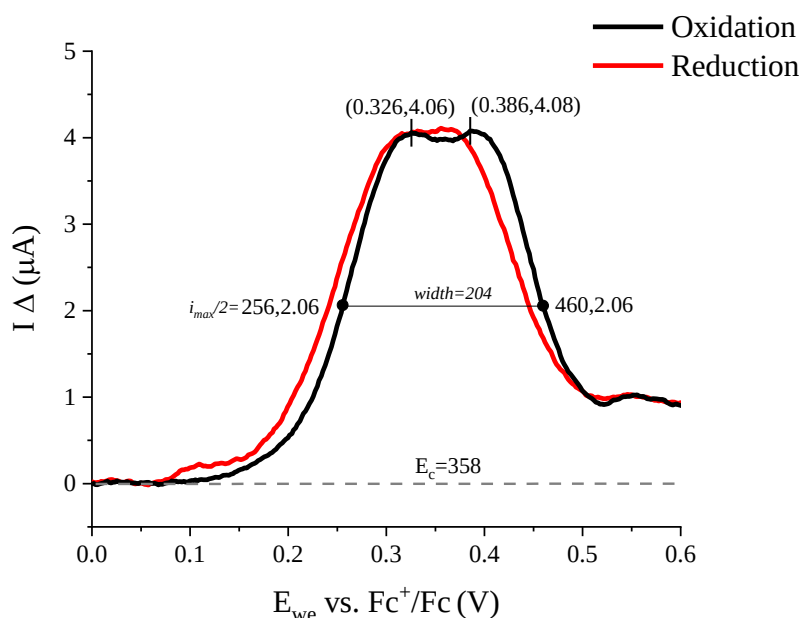


Figure S1: Differential Pulse Voltammetry (200 mV/s) of a 1 mM solution of molecule **1** in 0.2 M TBAPF₆/CH₂Cl₂ at a platinum button working electrode vs. Fc⁺/Fc as an internal standard ($E_{1/2} = 0.51$ V vs. Ag/AgCl). Separation of $E_{1/2}^1$ and $E_{1/2}^2$ calculated from a peak broadening method according to reference 27.

$$E_{1/2}^1 = E_c + \frac{\Delta E_{1/2} + E_{pul}}{2}$$

$$E_{pul} = \text{pulse amplitude} = 10 \text{ mV}$$

$$E_{1/2}^2 = 358 + \left(\frac{117 + 10}{2} \right) = 422 \text{ mV}$$

$$E_{1/2}^1 = 422 - 117 = 305 \text{ mV}$$

$$K_c = \exp \left[\frac{(E_1^o - E_2^o)n_1n_2F}{RT} \right] = \exp \left[\frac{(117)}{25.69} \right] = 95.04$$

E. Spectroelectrochemistry

Solution spectroelectrochemistry of molecule **1** was done in a three electrode honeycomb electrochemical cell supplied by Pine Research. A 12.5 x 12.5 x 45.0 mm³ quartz cuvette with a 1.7 mm path length was used as the cell, equipped with a polished platinum honeycomb electrode (working and counter) and Ag/AgCl pseudoreference electrode calibrated against a ferrocene/ferrocenium standard for which the $E_{1/2}$ is taken to be 0.51 V vs. Ag/AgCl. A homemade teflon cap was specially designed to keep the cell sealed from solvent evaporation and air contamination. In a nitrogen filled glove box, 4 x 10⁻⁴ M solution of PBP was prepared with 0.2 M TBAPF₆ in anhydrous DCM and transferred and sealed in the electrochemical quartz cell and sealed with teflon tape. During electrochemical oxidation, the voltage is increased from 0 to 1.2 V in 50 mV increments by linear scan voltammetry (LSV) at a 25 mV/s scan rate. The internal resistance was compensated for before every LSV reading by the EC-Lab software program. After the experiment was completed, a reduction potential of -0.1 V was applied to retrieve the neutral species. The time constant between each absorption spectrum measurement is 170 s; potential is applied for 10 seconds and the UV-vis-NIR absorption is taken immediately after from 250 to 1600 nm at a rate of 10 nm/sec (160 s).

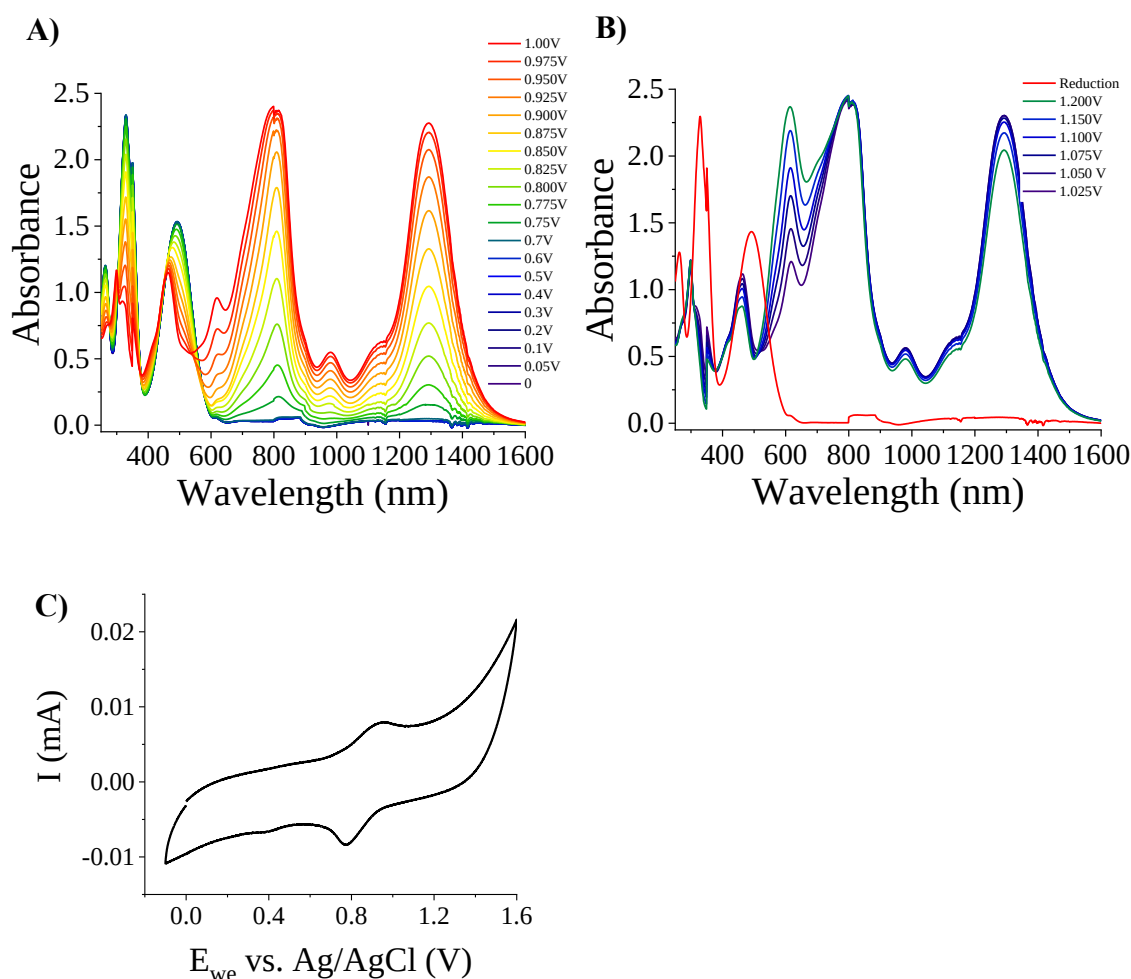


Figure S2: Spectroelectrochemistry of a 2.0 mM solution of molecule **1** in 0.2 M TBAPF₆/CH₂Cl₂ in an optically transparent thin layer quartz cuvette equipped with a platinum honeycomb electrode vs. Ag/AgCl. The spectra is divided into **A)** oxidation potential from 0 to 1.00 V and **B)** 1.025 to 1.200 V and reduction back to neutral. **C)** Cyclic voltammogram of molecule **1** at a platinum honeycomb electrode.

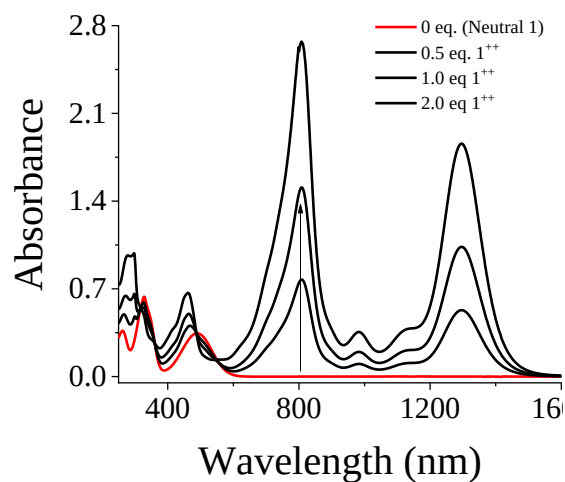
F. Comproportionation Reaction of **1** and **1⁺⁺**

Figure S3: Absorption spectra tracking the addition of **1⁺⁺** into a solution of **1**. This is a comproportionation reaction ($X + X^{++} \rightarrow X^{+}$) of **1** and isolated **1⁺⁺**(**SbCl₆**)₂ to generate **1⁺**. This experiment proves that the dication state should not be stable in the presence of the neutral state. For **Cl-2⁺**, this is not the case, as this 2e⁻ oxidized chlorine adduct is stable in the presence of neutral **1**.

G. Stability Measurement of Chlorine Adduct (Cl-2⁺) in Reaction Solution

A 3.1×10^{-3} solution of molecule **1** in CH₂Cl₂ was treated with 1.5 equivalent of 1.0 M SbCl₅ under an inert atmosphere. To measure the absorbance of the Cl-2⁺ adduct (dication) at 620 nm as a function of time, aliquots of the reaction solution were taken at specific time intervals and diluted to 3.1×10^{-5} M to allow measurements in a 10 mm pathlength cuvette. The purpose of this analysis is to show that Cl-2⁺ is stable in solution for several hours, even after dilution of the reaction solution from 3.1×10^{-3} M to 3.1×10^{-5} M. The mass spectroscopy experiment (Figure S5) that was conducted to detect Cl-2⁺ took about 30 minutes under ambient conditions and required a 100× dilution of the reaction mixture due to signal saturation. Since this type of adduct is expected to be extremely sensitive to moisture content or concentration, this stability experiment was used to confirm that dilution nor time was a problem in the timeframe used to detect Cl-2⁺.

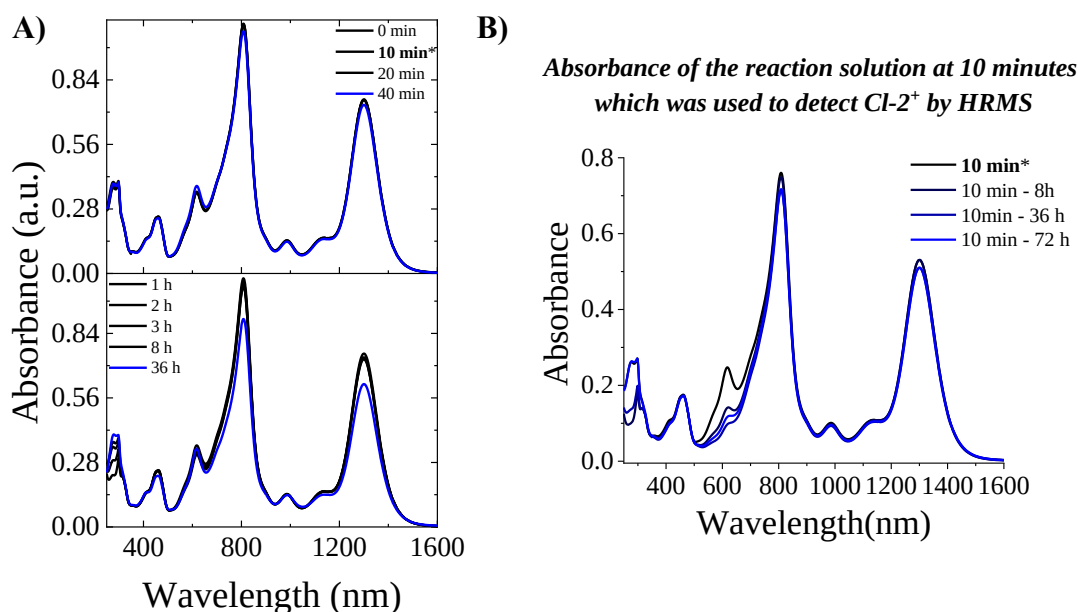


Figure S4. A) Absorption spectra depicting the consistency of the Chlorine adduct (Cl-2⁺) absorbance peak at 620 nm over the course of several hours to show its stability over several hours after dilution from 10^{-3} to 10^{-5} M. **B)** Absorption spectra of the reaction solution aliquot taken at 10 min* to run the mass spectroscopy experiment (shown in Figure S5) and its stability after several hours.

H. High Resolution Mass Spectroscopy (HR-MS) by Atmospheric Pressure Chemical Ionization (APCI)

A 0.0032 M solution of molecule **2** was prepared by dissolving 4.7 mg of **2** in 2.5 mL of anhydrous CH_2Cl_2 in a N_2 filled glove box. Chemical oxidation by 1.5 equivalent of SbCl_5 (0.012 mmol, 24 μL , 0.5 M) was added to the solution and $\sim 25 \mu\text{L}$ of the reaction solution was analyzed by APCI. The chloro-sulfonium cation was successfully detected by observation of the chlorine 35 and 37 isotope peaks of $2^{+\bullet}(\text{Cl})$ at 627 and 629 m/z , with a difference of 1.4 ppm compared to theoretical calculations.

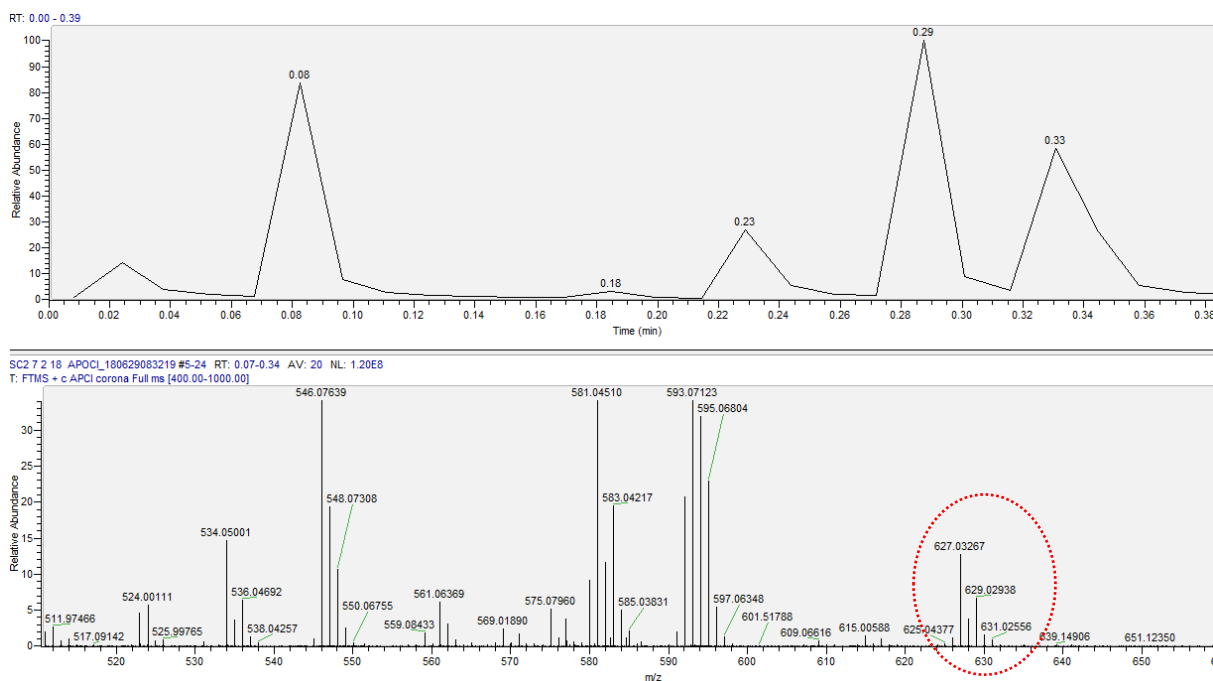


Figure S5: HR-APCI of a reaction solution of molecule **2** with SbCl_5 showing the chlorine isotope peaks of $\text{Cl}-2^+$ at 627 and 629 m/z .

I. Electrochemical and Chemical Oxidation of Molecule 2

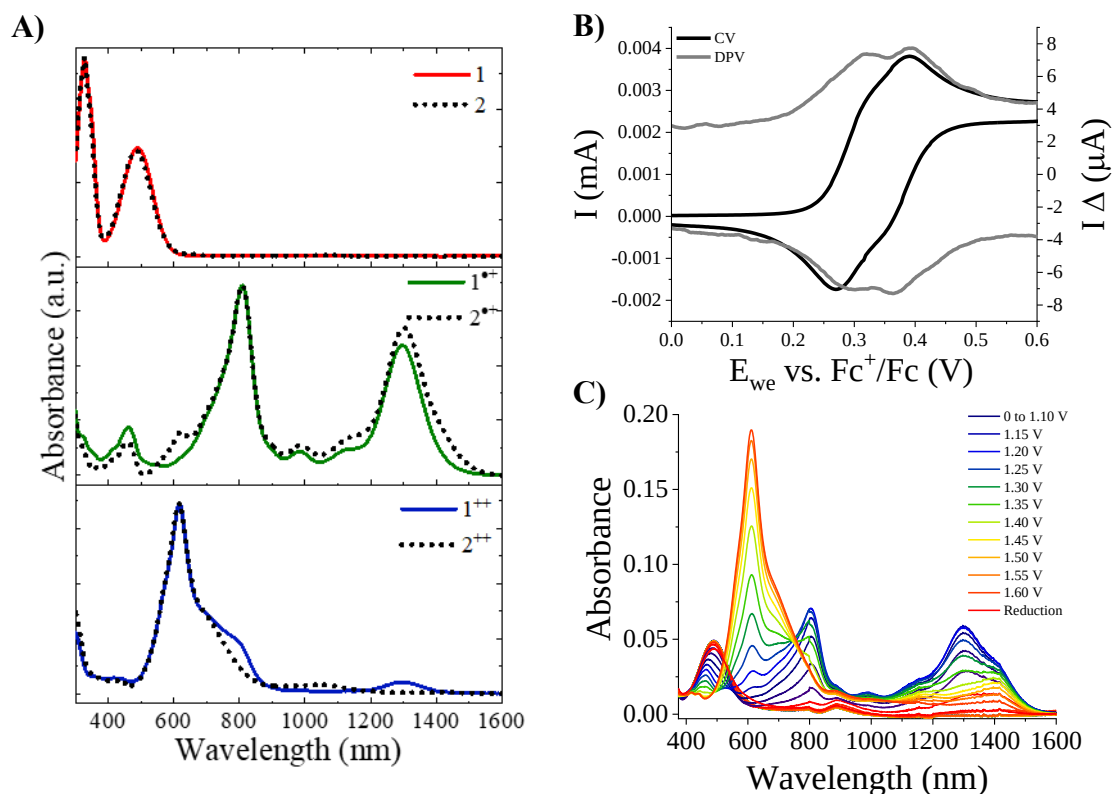


Figure S6: **A)** Comparison between absorption spectra of molecule 1 and 2 in the neutral, radical cation, and dication states as isolated SbCl₆ salts redissolved in anhydrous CH₂Cl₂. **B)** Cyclic voltammogram (scan rate: 5 mV/s) and differential pulse voltammogram (scan rate: 200 mV/s) of a 1 mM solution of molecule 2 in 0.2 M TBAPF₆/CH₂Cl₂ at a platinum button working electrode vs. Fc⁺/Fc as an internal standard ($E_{1/2} = 0.51$ V vs. Ag/AgCl). **C)** Spectroelectrochemistry of a 20 μ M solution of molecule 2 in 0.2 M TBAPF₆/CH₂Cl₂ in an optically transparent thin layer quartz cuvette equipped with a platinum honeycomb electrode vs. Ag/AgCl.

J. X-Ray Crystallography

The radical cation, $2^{+\bullet}[\text{SbCl}_6]$ was synthesized by SbCl_5 oxidation of **2**. After isolation of the radical cation salt, 10mg/ml solution of $2^{+\bullet}$ was prepared in o-dichlorobenzene (o-DCB), carefully layered with 1:1 mixture of o-DCB:n-hexane, and a final layer of n-hexane in an NMR tube under air at RT. Slow diffusion for one week led to the formation of two black crystal with distinct morphologies. Manual separation and single crystal analysis of the two morphologies revealed the formation of rod-shaped crystals of $2^{+\bullet}$ and a block-shaped crystal of a decomposition product with one ketone terminal group (**2'**).

Bond #	2 Bond Length (Å)	$2^{+\bullet}$ Bond Length (Å)	2^{++} Bond Length (Å)	2' Bond Length (Å)
1	(1.831)	1.804(5)/ (1.819)	(1.819)	*C=O
2	(1.758)	1.698(3)/ (1.730)	(1.700)	1.241(7)/ (1.208)
3	(1.375)	1.394(4)/ (1.390)	(1.410)	1.440(8)/ (1.470)
4	(1.437)	1.394(4)/ (1.409)	(1.390)	1.367(7)/ (1.365)
5	(1.385)	1.413(4)/ (1.419)	(1.453)	1.464(8)/ (1.466)
6	(1.747)	1.755(3)/ (1.767)	(1.779)	1.759(5)/ (1.766)
7	(1.737)	1.726(3)/ (1.735)	(1.734)	1.784(6)/ (1.812)
8	(1.462)	1.419(4)/ (1.417)	(1.378)	1.380(7)/ (1.385)
9	(1.383)	1.415(4)/ (1.416)	(1.450)	1.447(7)/ (1.443)
10	(1.420)	1.381(4)/ (1.387)	(1.356)	1.381(7)/ (1.368)
11	(1.383)	1.414(4)/ (1.416)	(1.450)	1.403(8)/ (1.436)
12	(1.438)	1.444(4)/ (1.448)	(1.460)	1.457(7)/ (1.457)
13	(1.450)	1.432(4)/ (1.443)	(1.434)	1.435(7)/ (1.440)
14	(1.438)	1.439(4)/ (1.448)	(1.460)	1.441(8)/ (1.457)
15	(1.462)	1.412(4)/ (1.417)	(1.378)	1.402(7)/ (1.395)
16	(1.385)	1.413(4)/ (1.419)	(1.454)	1.436(7)/ (1.435)
17	(1.437)	1.395(4)/ (1.409)	(1.390)	1.380(8)/ (1.402)
18	(1.375)	1.391(4)/ (1.390)	(1.410)	1.399(8)/ (1.396)
19	(1.737)	1.718(3)/ (1.735)	(1.734)	1.719(5)/ (1.730)
20	(1.747)	1.754(3)/ (1.767)	(1.779)	1.753(6)/ (1.775)
21	(1.758)	1.707(3)/ (1.730)	(1.700)	1.693(6) (1.720)
22	(1.831)	1.793(4)/ (1.819)	(1.818)	1.808(6)/ (1.818)

Table S1. Select geometric parameters extracted from the x-ray crystal structures (w/ esd) and, in parentheses, from DFT calculations at the OT- ω B97X-D/6-31+G(d,p) level of theory.

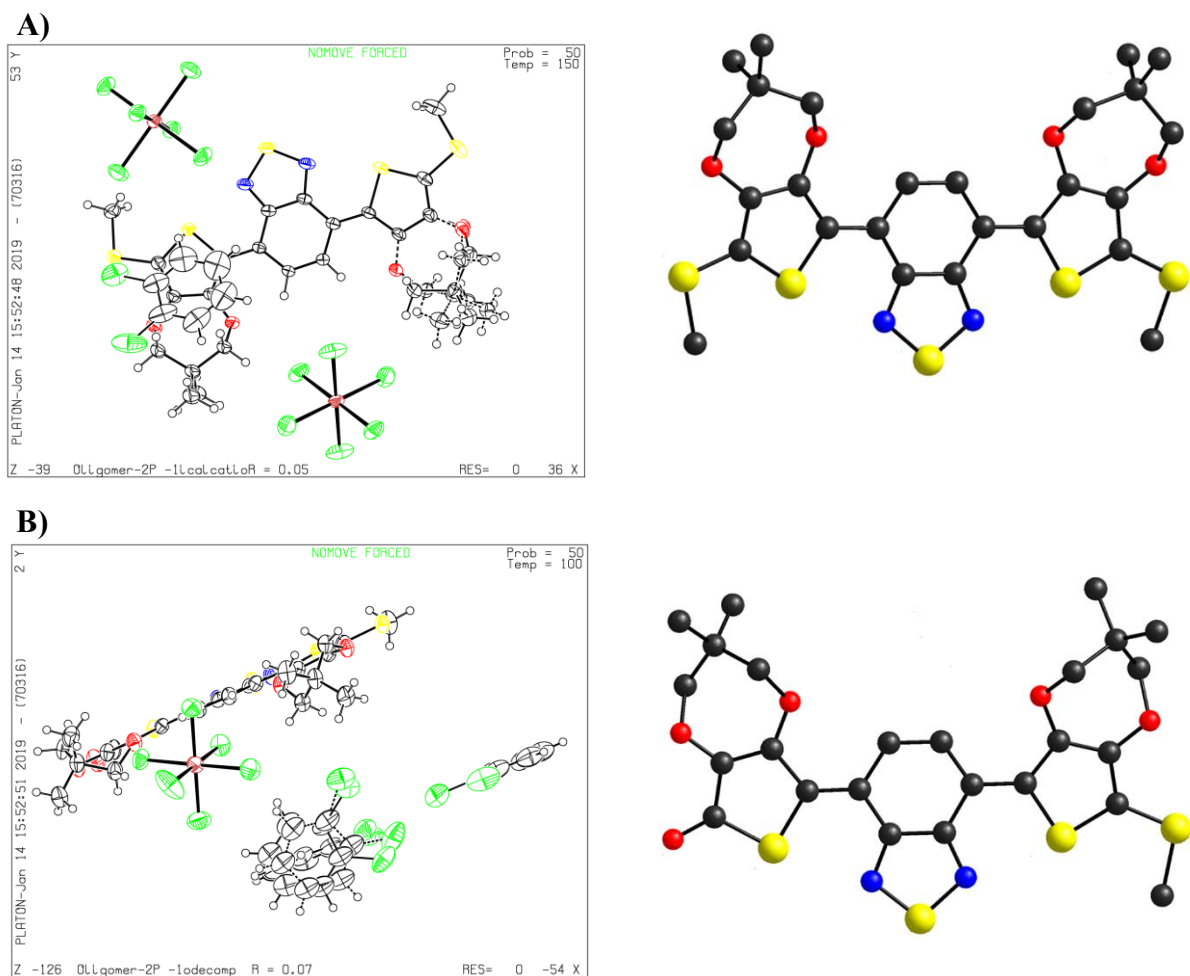


Figure S7. Perspective drawings from the X-ray crystal structure determination of **A) 2**** and **B) 2'** depicting all counter anions and solvent molecules.

K. DFT-derived Bond Lengths and Atomic Charges

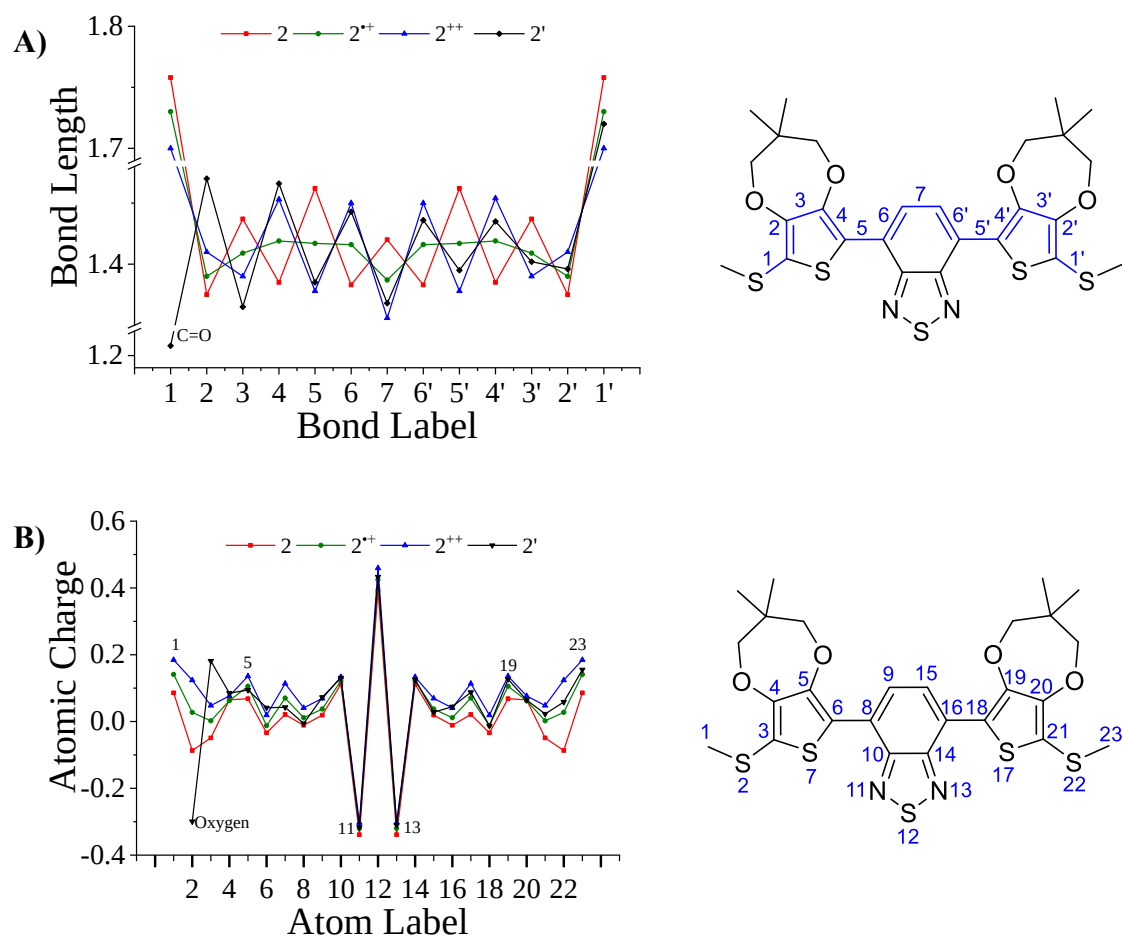


Figure S8. A) Select π -backbone bond lengths for **2**, **2⁺**, **2⁺⁺**, and **2'** with corresponding bond label scheme, and **B)** atomic charge distribution of **2**, **2⁺**, **2⁺⁺**, and **2'** with corresponding atom label scheme as determined at the OT- ω B97X-D/6-31+G(d,p) level of theory.

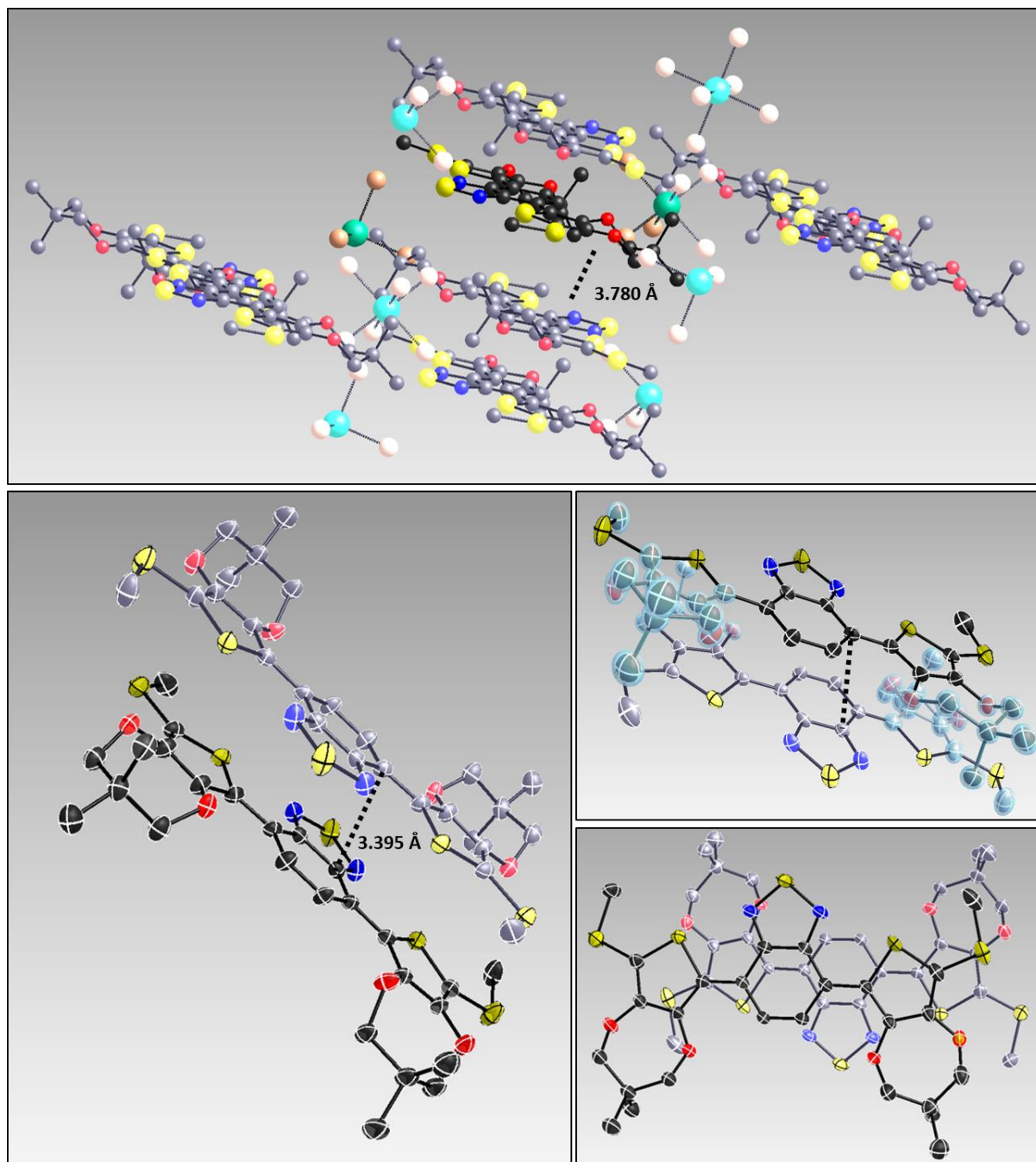
L. X-Ray Crystallography of $(2^{\bullet+})_2$ π -Dimer

Figure S9: Perspective drawings from the X-ray crystal structure determination of $2^{\bullet+}$ that highlight a π - π stacking distance of 3.395 Å between two radical molecules and a 3.780 Å distance between two π -dimers.

M. Low Temperature UV-vis-NIR Spectroscopy

Table S2. Low Temperature UV-vis-NIR and NMR spectroscopy of Molecule 1.

	UV-vis-NIR (nm)		¹ H NMR (ppm, proton)	
	RT	~200 K	RT	~200 K
1	328, 490	328, 490	A: 2.45, 6H C: 4.15, 4H and 4.21, 4H D: 8.33, 2H	A: 2.33, 6H C: 4.07, 4H and 4.16, 4H D: 8.18, 2H
1^{•+} (a)	808, 1295	624, 938 ^(a) , 1458 ^(c)	Alkyl side chain peaks at 0.5-1.5 and 3.0-3.6 ^(b)	A: 2.50, 3H and 2.89, 3H C: 4.03 – 4.57, 8 H D: 6.81-6.99, 2H
1⁺⁺	620	620	Alkyl side chain peaks at 0.5-1.5 and 3.0-3.6 ^(b)	A: 3.14, 6H C: 4.34 – 4.60, 8H D: 8.69, 2H

a – radical cation π -dimerization at 200 K in solution

b – paramagnetic line broadening effect

c – retrieved from solid state thin film

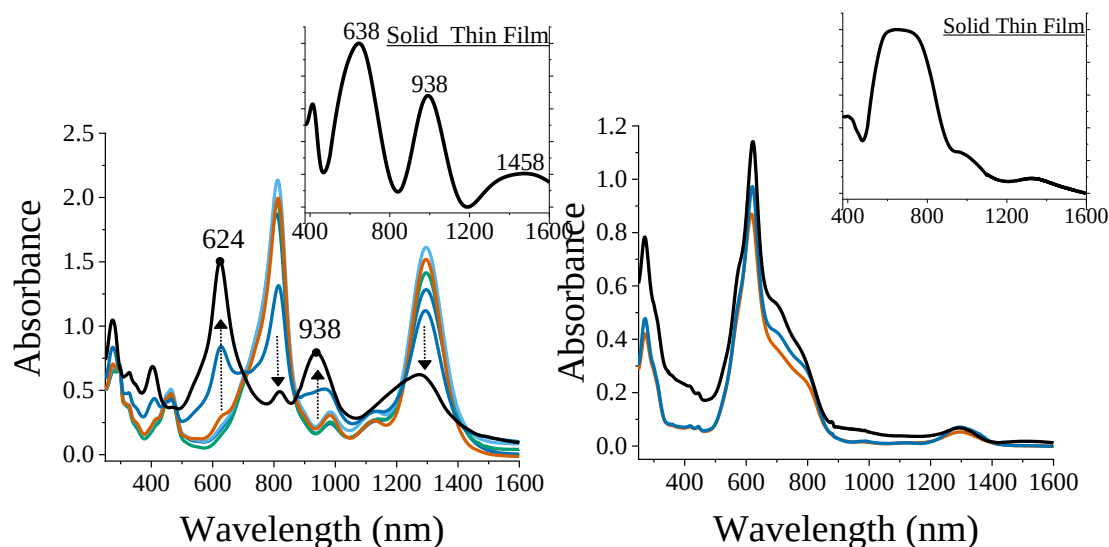


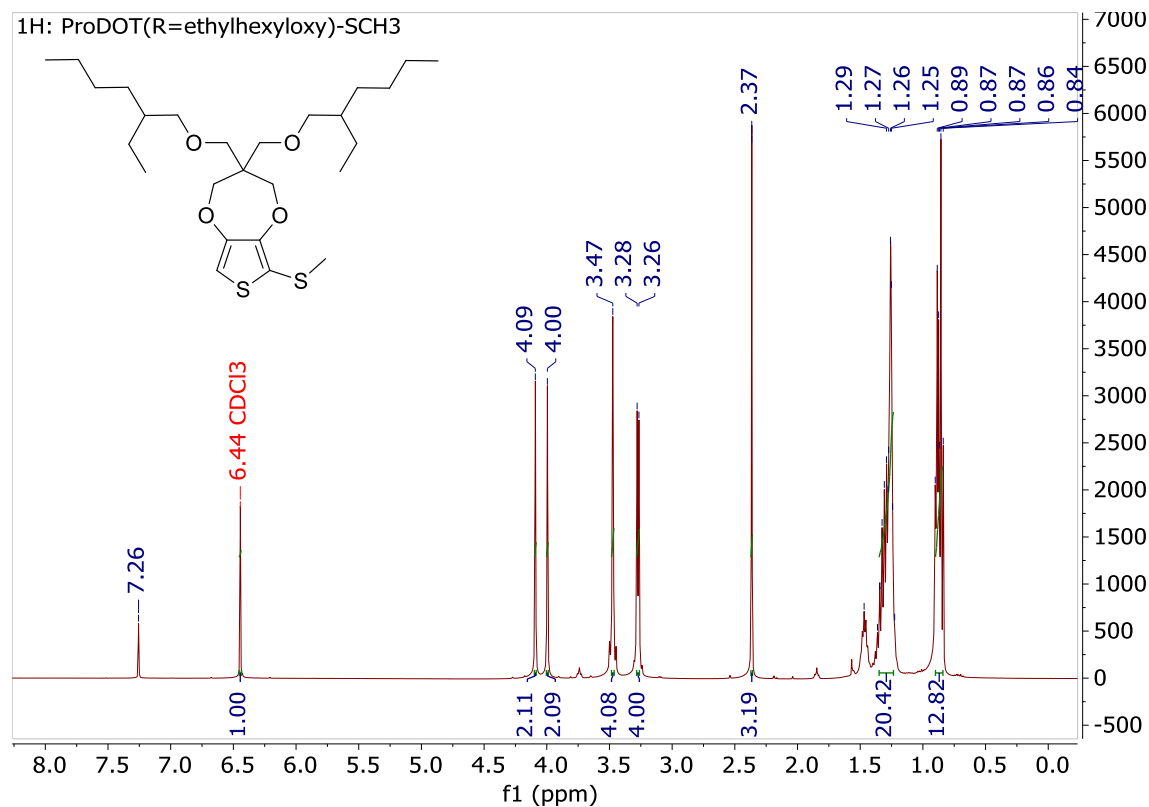
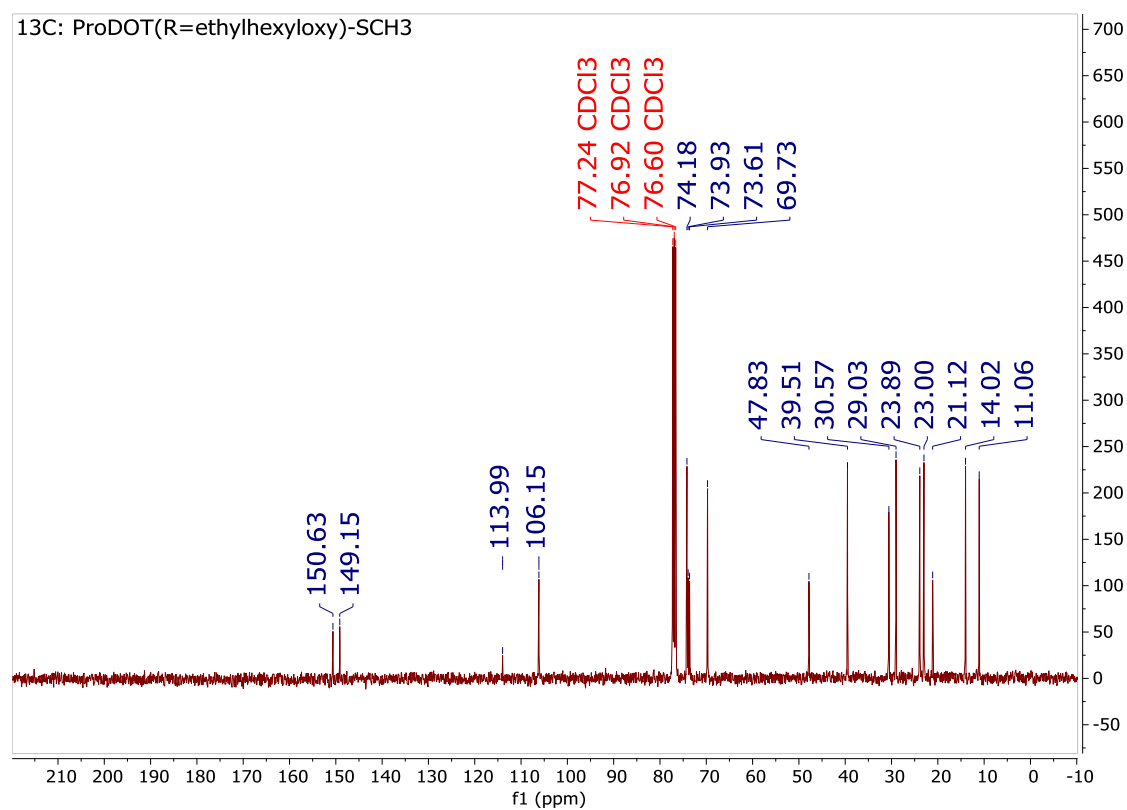
Figure S10. Temperature-modulated spectral change of the solution of **1^{•+}** and **1⁺⁺** (20 μ M in CH_2Cl_2). Temperature from (K): 290, 273, 243, 223, 203, 177. Inset: Solid thin-film spectra of isoalted **1^{•+}** and **1⁺⁺**.

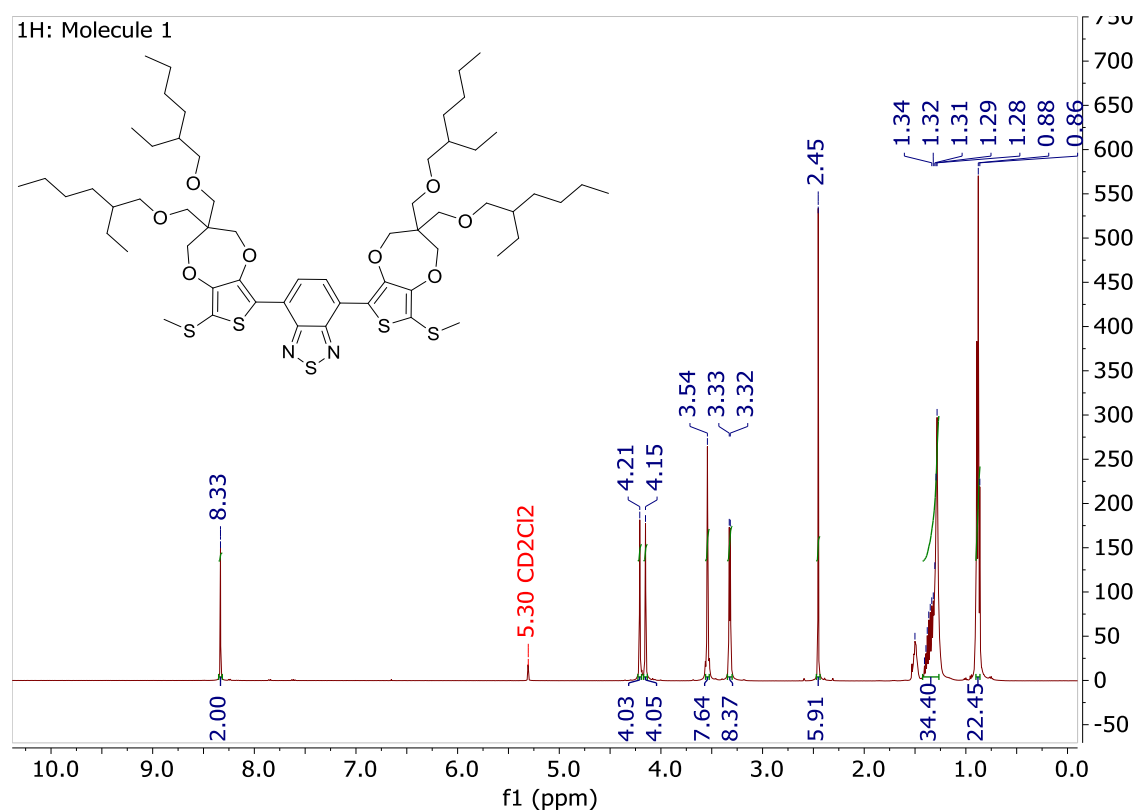
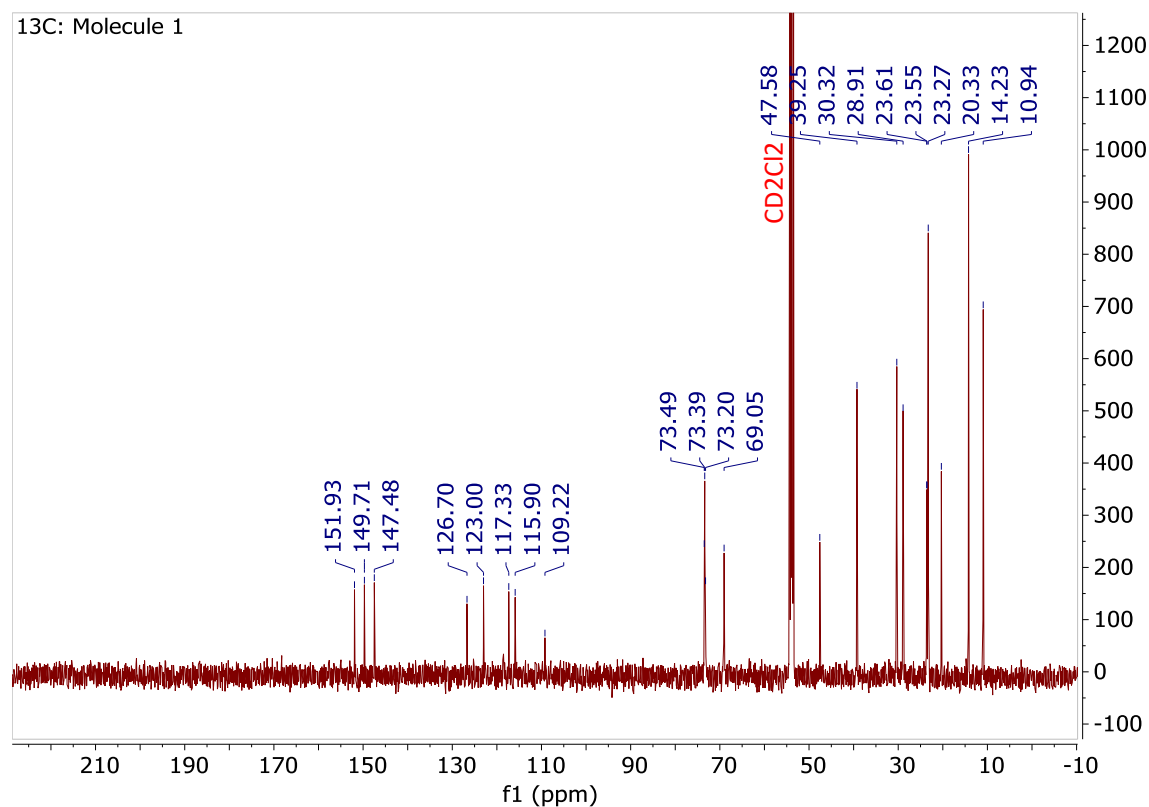
N. Low Temperature Electron Paramagnetic Resonance (EPR) Spectroscopy

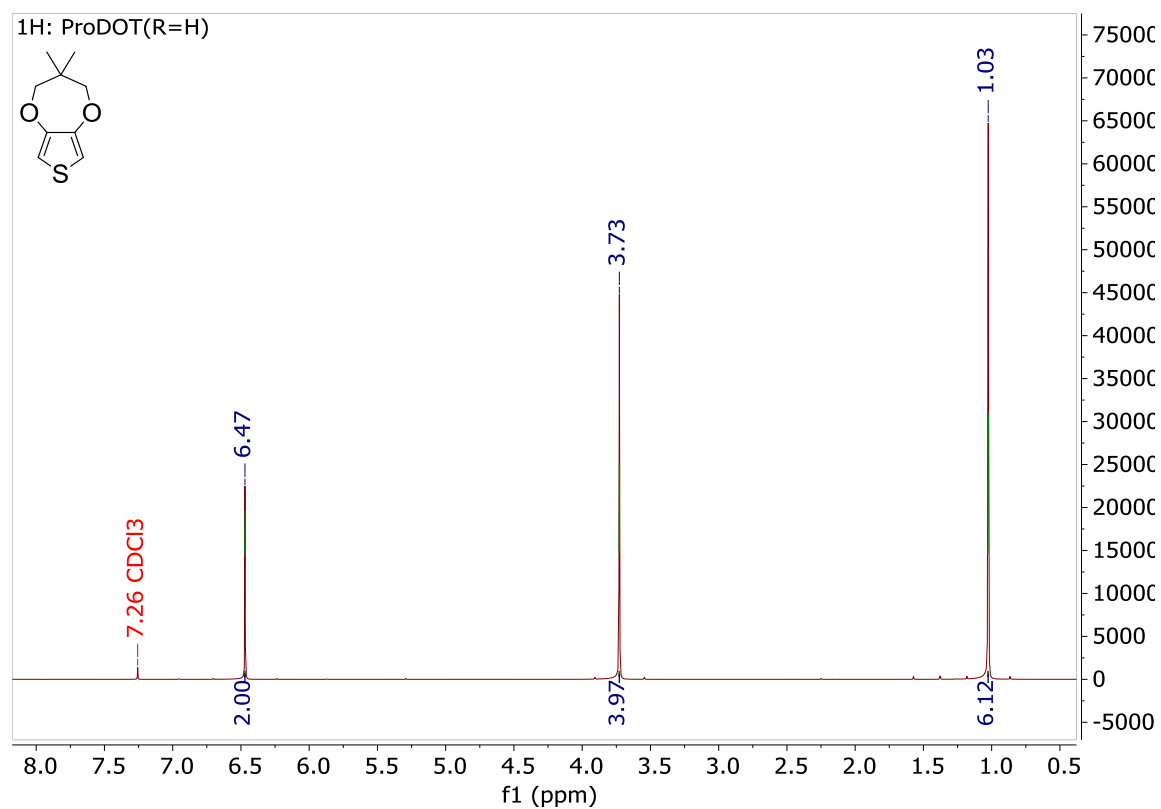
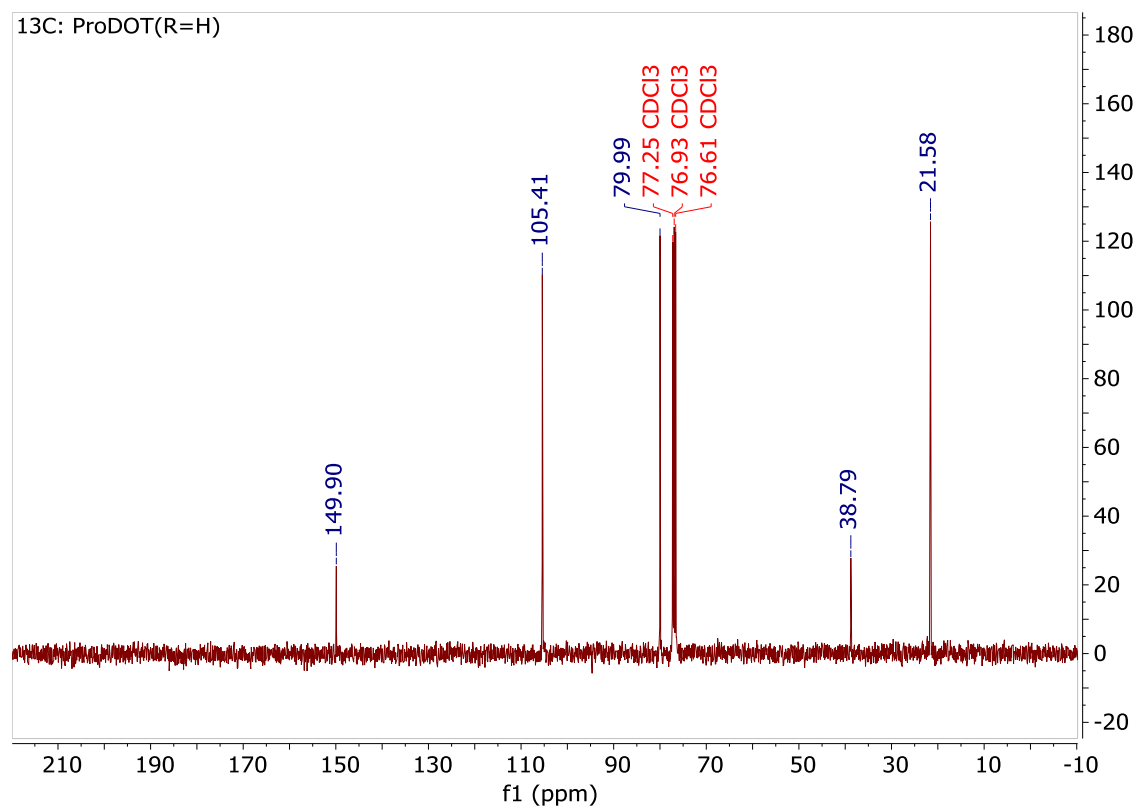
EPR spectroscopy was performed at a microwave bridge frequency of 9.49 GHz, 10.02 mW power, 100 kHz modulation frequency, 1.00 G modulation amplitude, and 2000 receiver gain. Solutions were prepared in a nitrogen filled glove box at a 300 μ M in anhydrous CH_2Cl_2 for room temperature measurements. Oven dried EPR tubes were transferred into the glove box and 0.3 ml of each sample was transferred into the tube and sealed. Low temperature EPR measurements were conducted in an anhydrous solution of 1:1 CH_2Cl_2 : CHCl_3 , with a sample volume of 0.3 ml. Measurements were taken at 290 K, decreased to 170 K and raised in increments of 20 K back to 290 K. At each temperature, the sample was allowed to equilibrate for $\sim$ 5 minutes before taking measurement.

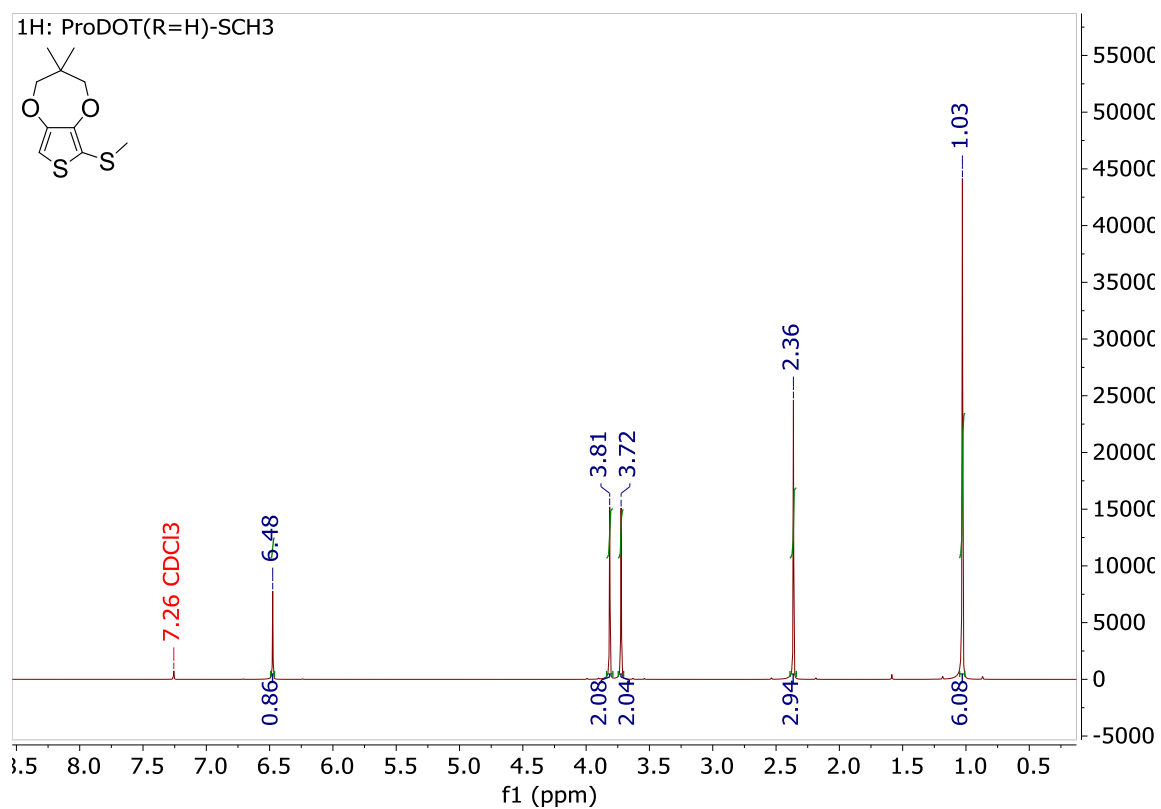
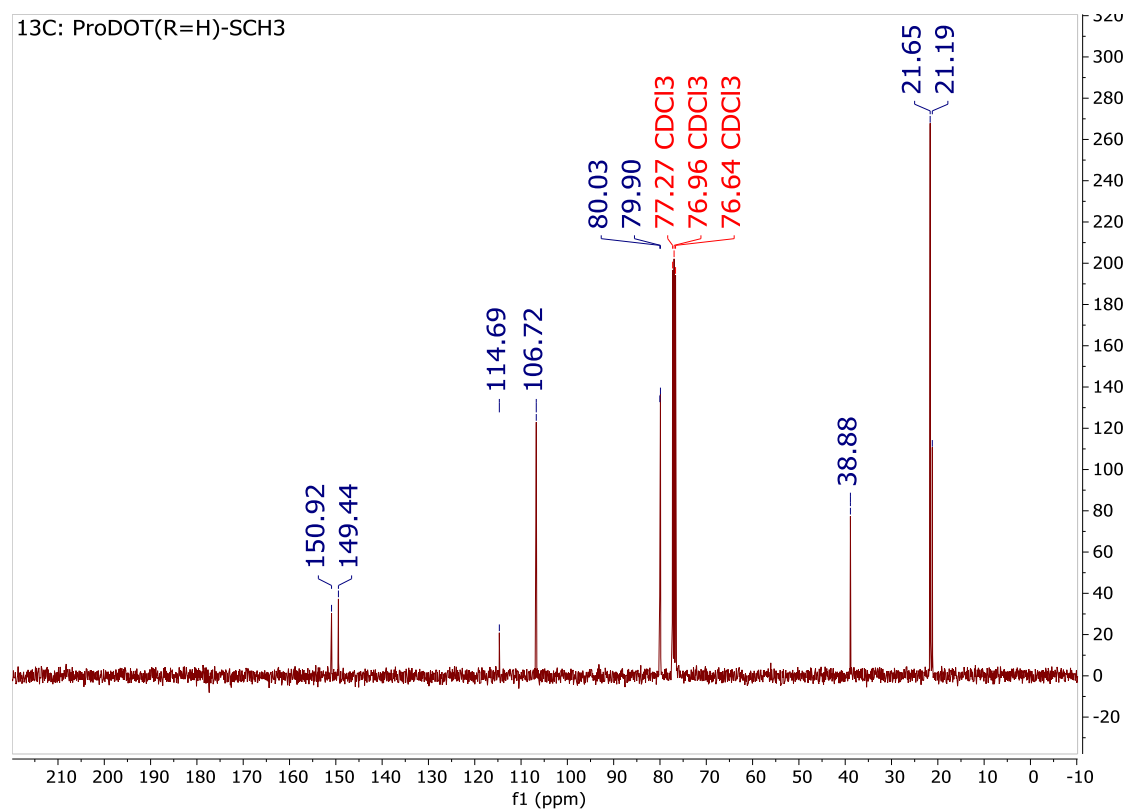
O. Low Temperature Nuclear Magnetic Resonance (NMR) Spectroscopy

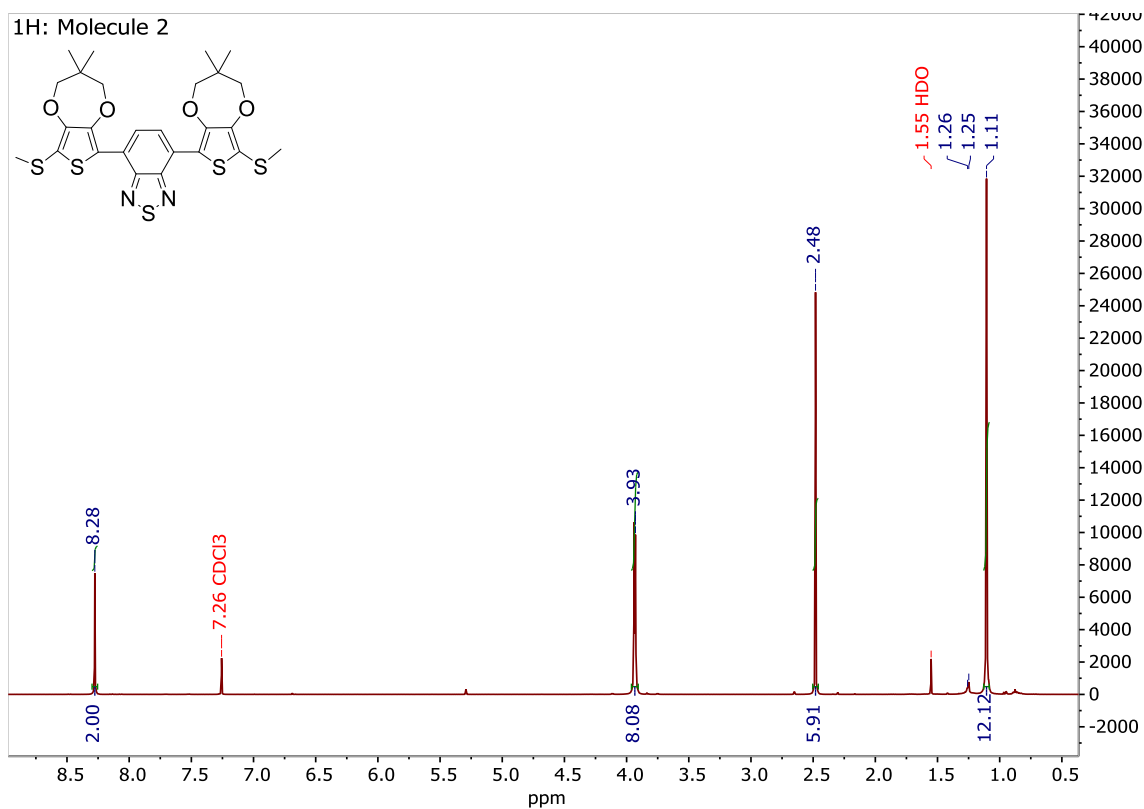
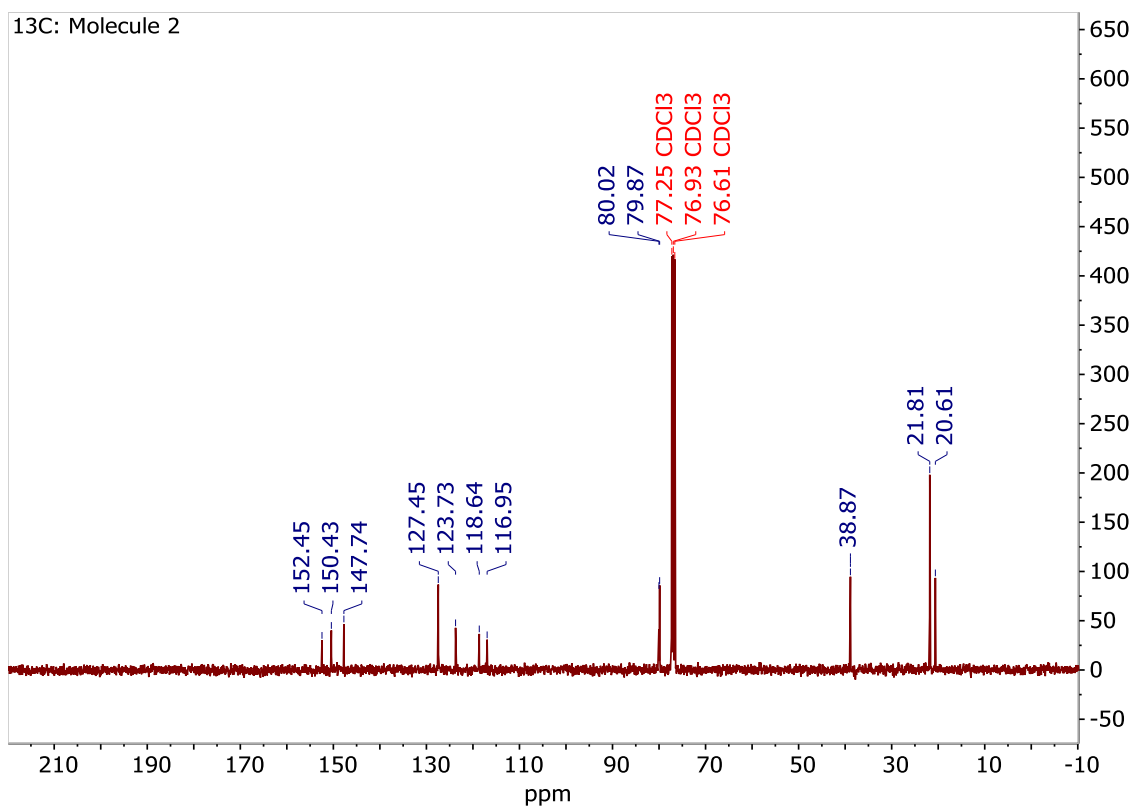
Low temperature NMR spectroscopy was performed on molecule **1**, **1^{••}** and **1⁺⁺**. In a nitrogen filled glove box, 30 mg of each sample is dissolved in 0.75 ml anhydrous CD_2Cl_2 and transferred into a valved NMR tube via needle and syringe. ^1H measurements were taken at 290 K, decreased to $\sim$ 200 K and raised in increments of $\sim$ 20 K back to 290 K.

P. ^1H - and ^{13}C -NMR Spectra



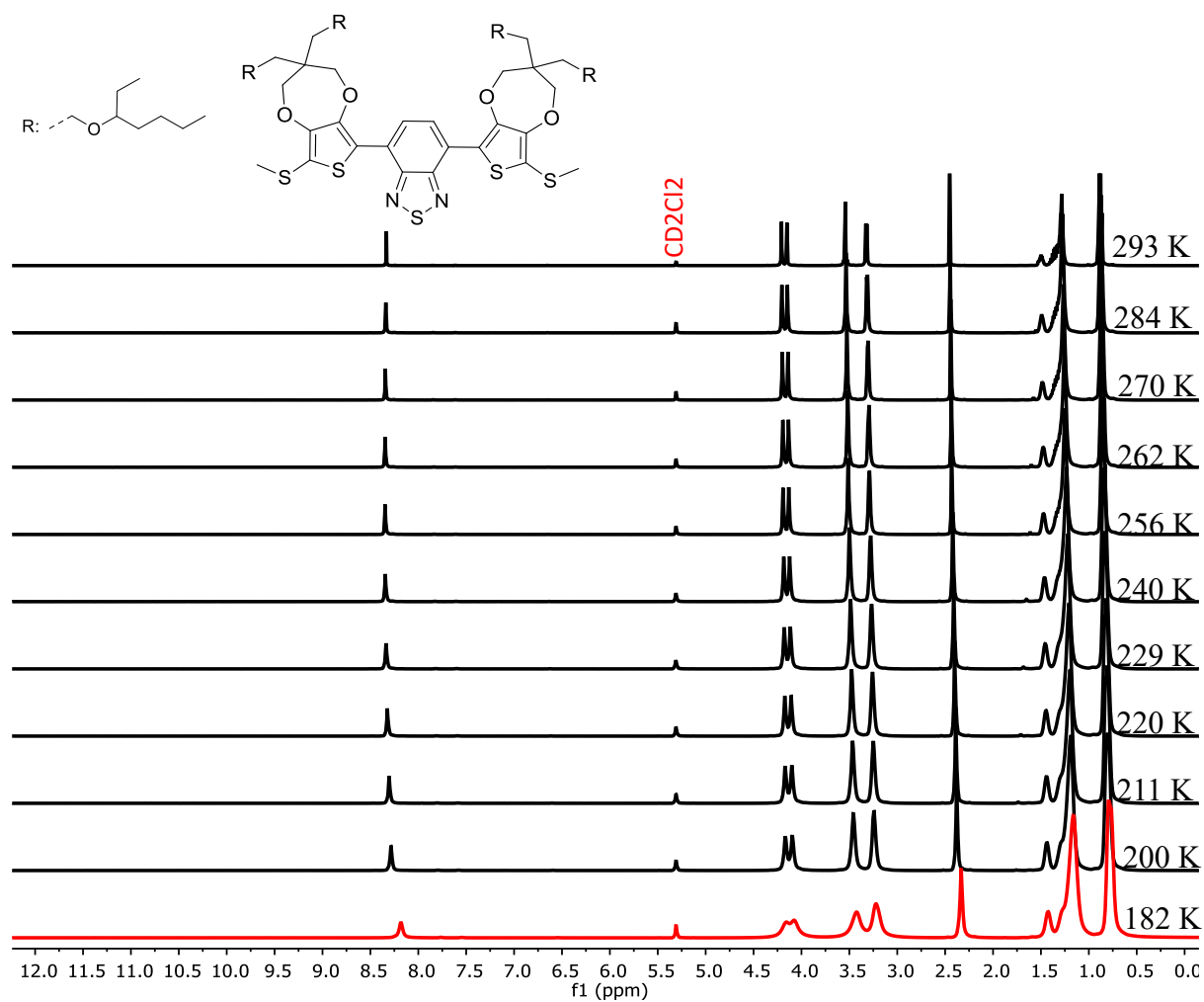


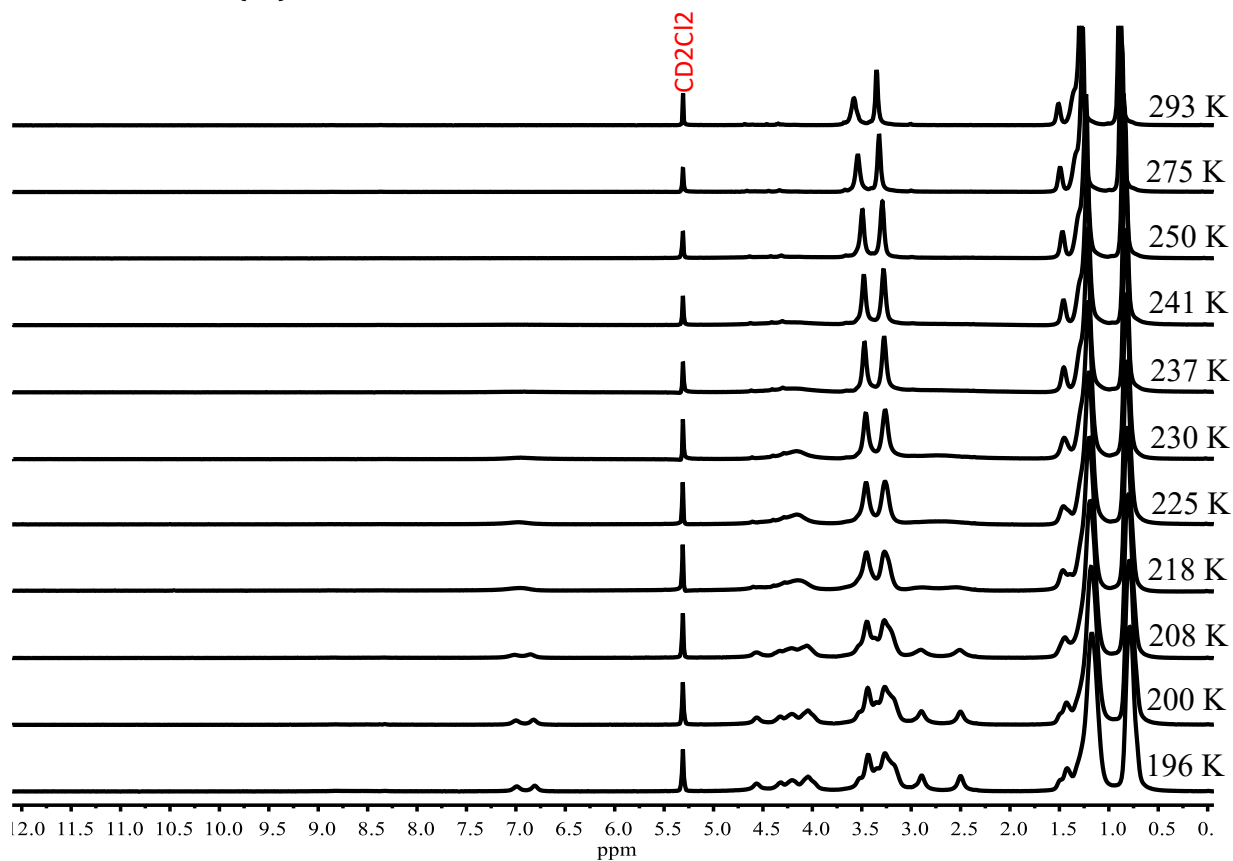




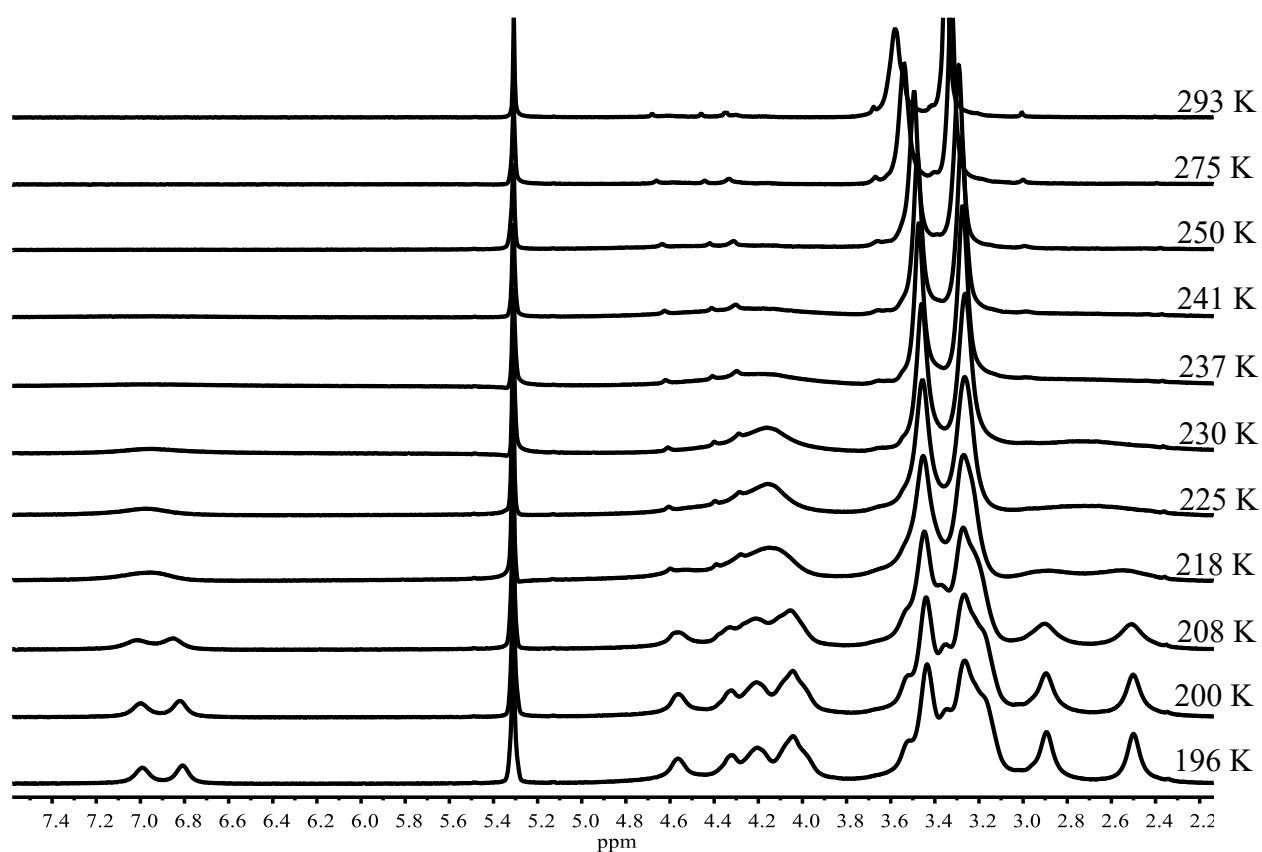
Q. Low Temperature NMR Spectra

1H: Neutral Molecule 1

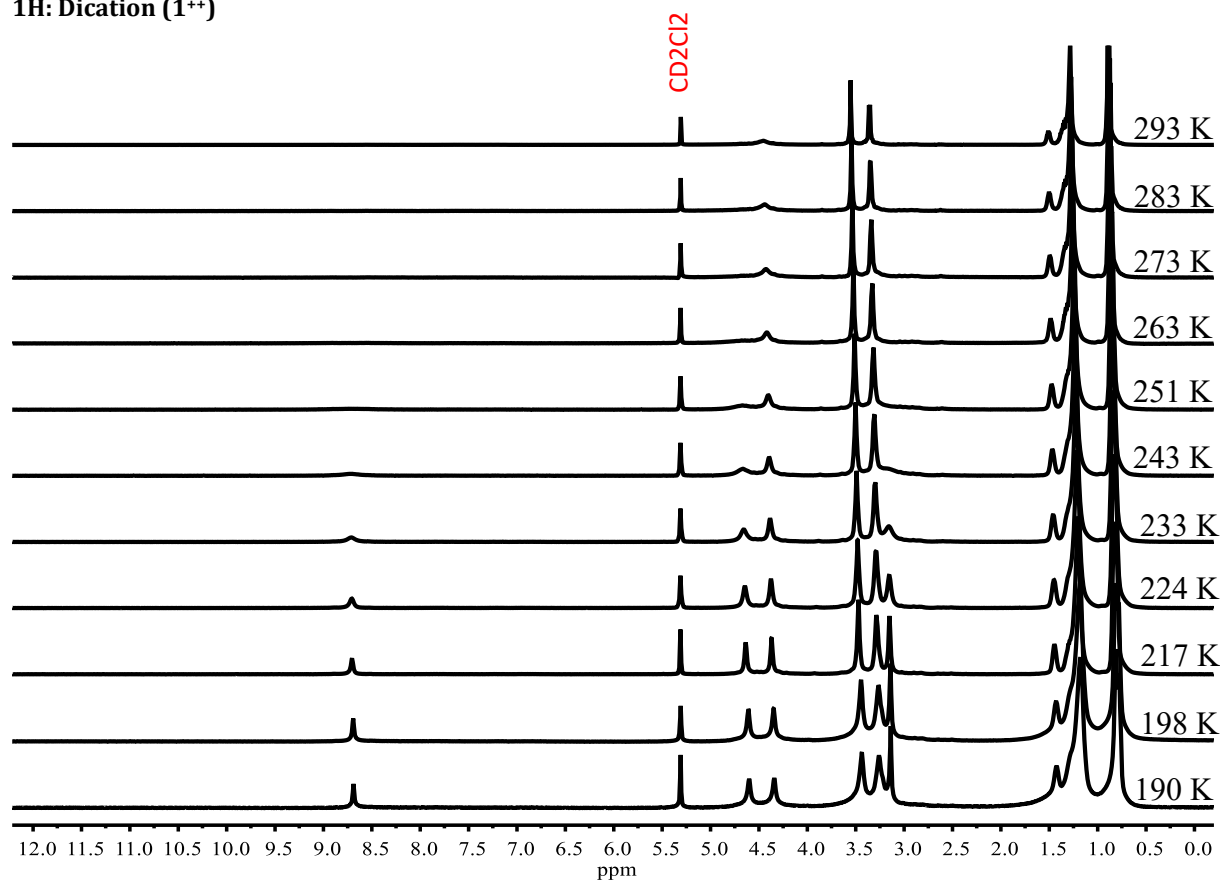


1H: Radical Cation (1^{•+})

[Zoom in of 1H spectrum]



¹H: Dication (1⁺⁺)



[Zoom in of ¹H spectrum]

