

Supporting Information

Degradation Pathways of Conjugated Radical Cations

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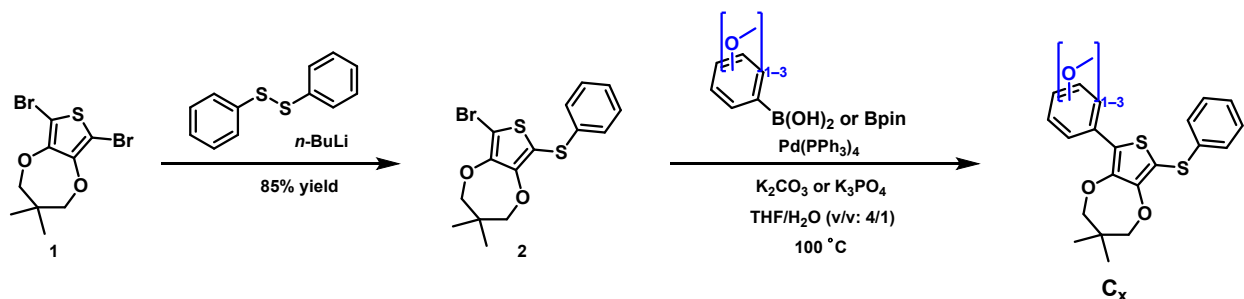
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1. Materials and synthesis

Compound **1** was prepared according to the reported literature.¹ The corresponding boric acids or pinacol borates were purchased from Combi-Blocks (San Diego, CA).



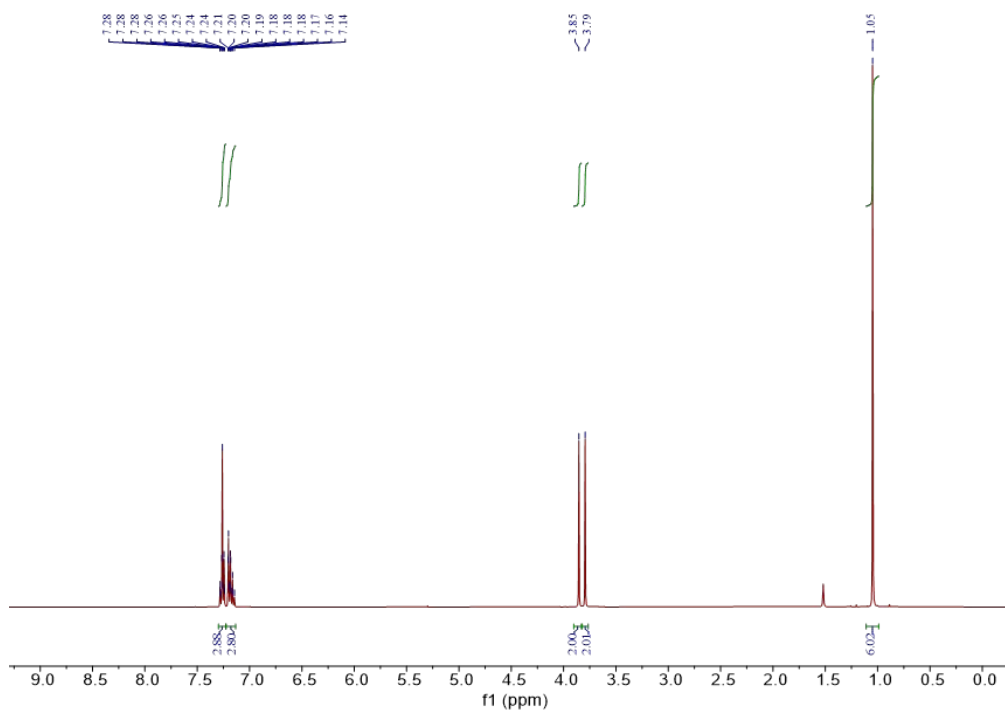
To a THF solution (75 mL) of **1** (2.00 g, 4.54 mmol) n -butyllithium (2.5 M, 5.0 mmol) in hexane was added at -78°C under N_2 . After stirring for 30 min at -78°C , 1,2-diphenyldisulfane (471 mg, 5.0 mmol) was added dropwise to the reaction mixture and then allowed to warm to room temperature. After stirring for 2 h, the reaction mixture was quenched with water and extracted with hexane and dried over Na_2SO_4 . 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 CHCl_3 to give **2** as a light-yellow oil (1.77g, 85% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.28 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 3.85 (s, 2H), 3.79 (s, 1H), 1.05 (s, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 152.2, 147.6, 137.4, 128.9, 126.9, 126.1, 108.9, 96.9, 80.2, 38.9, 21.7.

General procedure for the synthesis of target compounds C_x via Suzuki coupling

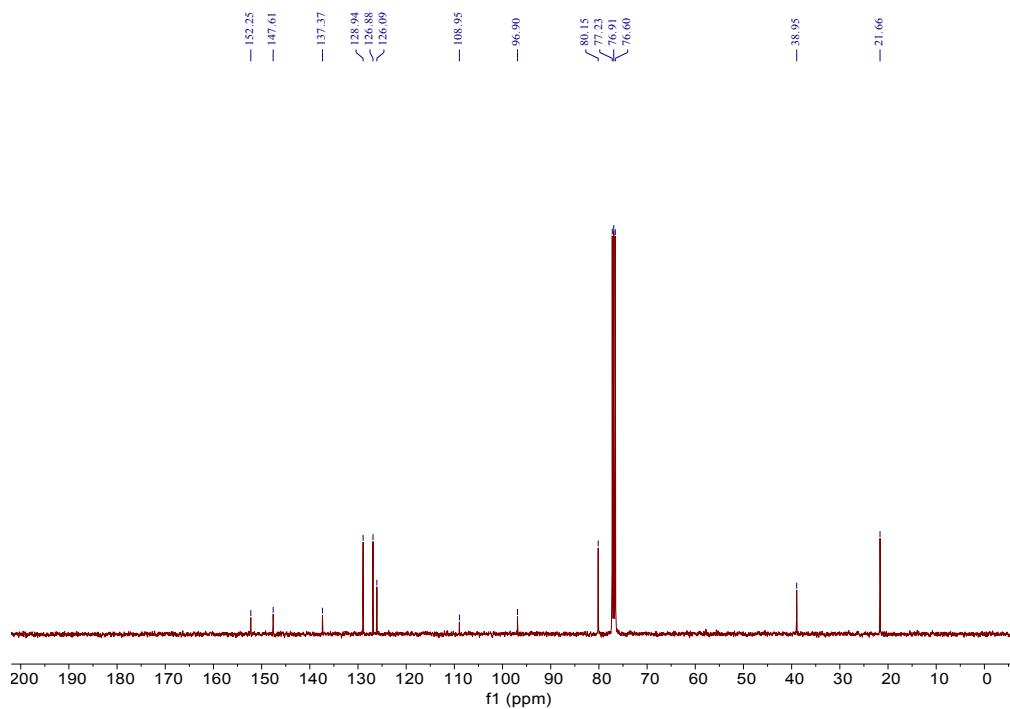
Compound **2** (4.52 mmol, 1.04 g), the corresponding boric acids or pinacol borates (0.90 mmol), $\text{Pd(PPh}_3)_4$ (2.0 mol %), and K_2CO_3 or K_3PO_4 (for boric acids or pinacol borates, respectively) (1.80

mmol) were all added to a 25 mL Schlenk tube and vacuumed for 30 minutes, and then purged with N₂ three times. Anhydrous THF (3 mL) was added to the mixture and the reaction was heated at 100 °C in an oil bath for 2 h. Upon completion, the reaction mixture was quenched with water and extracted with dichloromethane. 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 to give molecules **C_x** with 50%–95% yields.

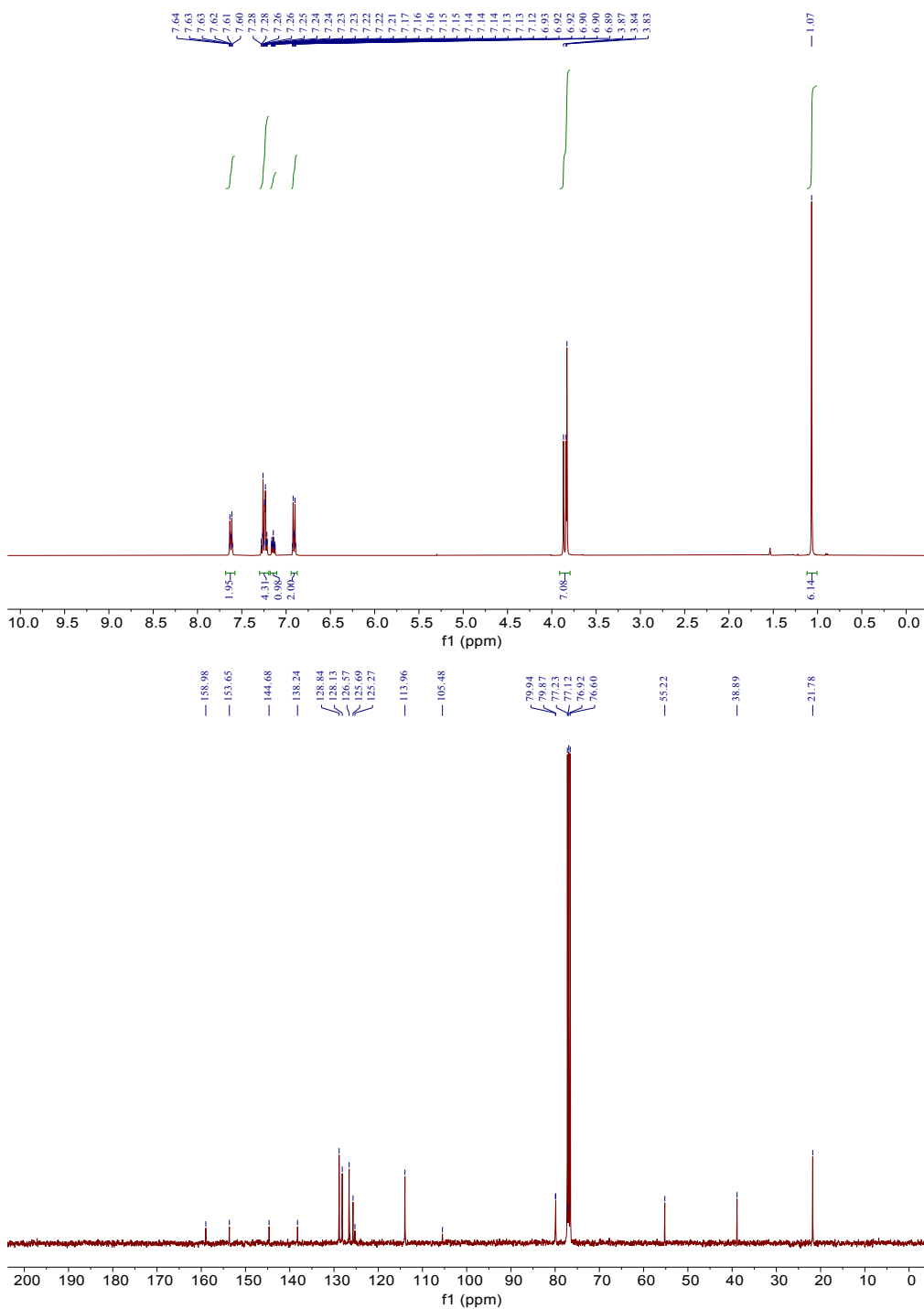
Compound **2** – ¹H NMR



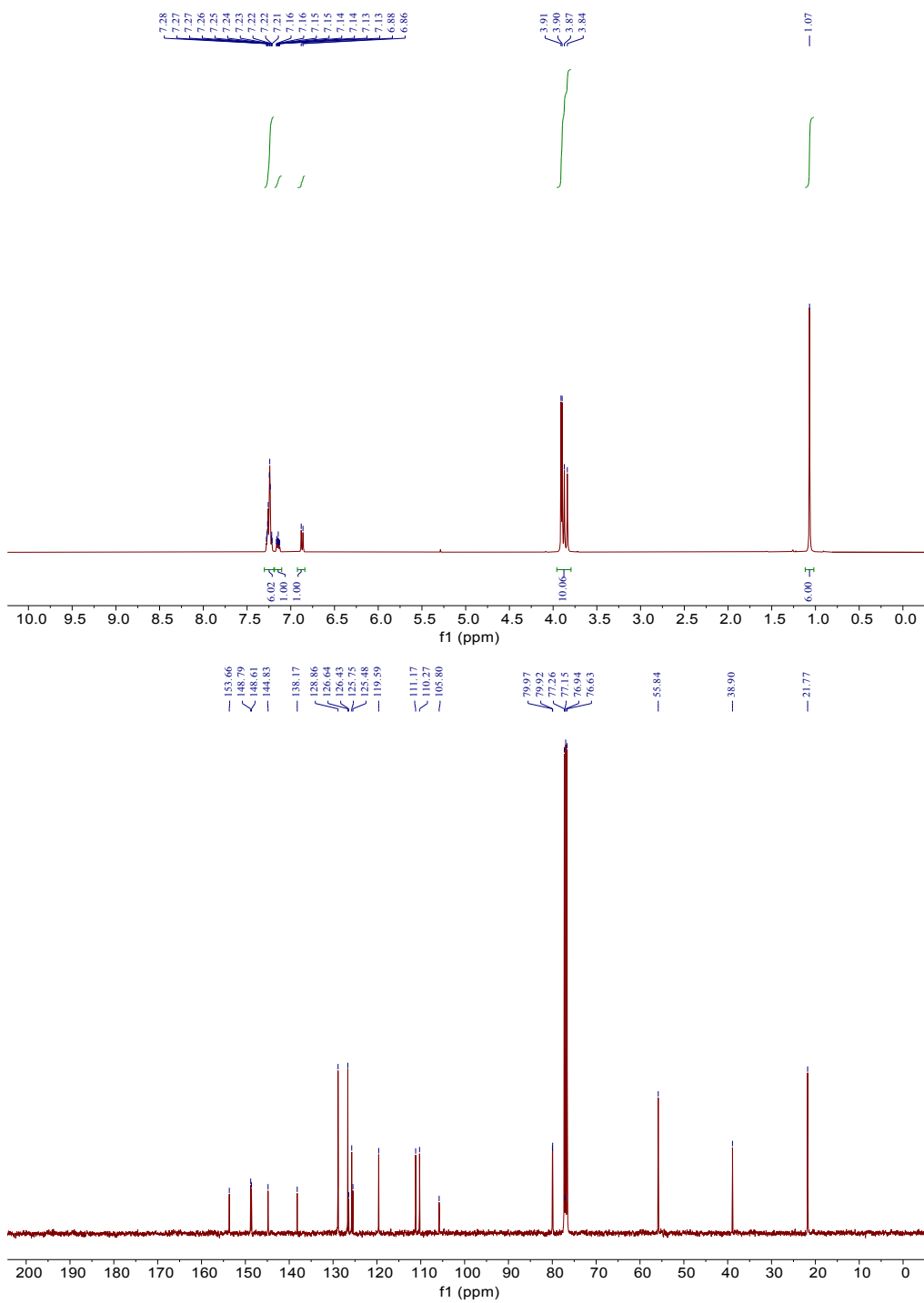
Compound **2** – ¹³C NMR



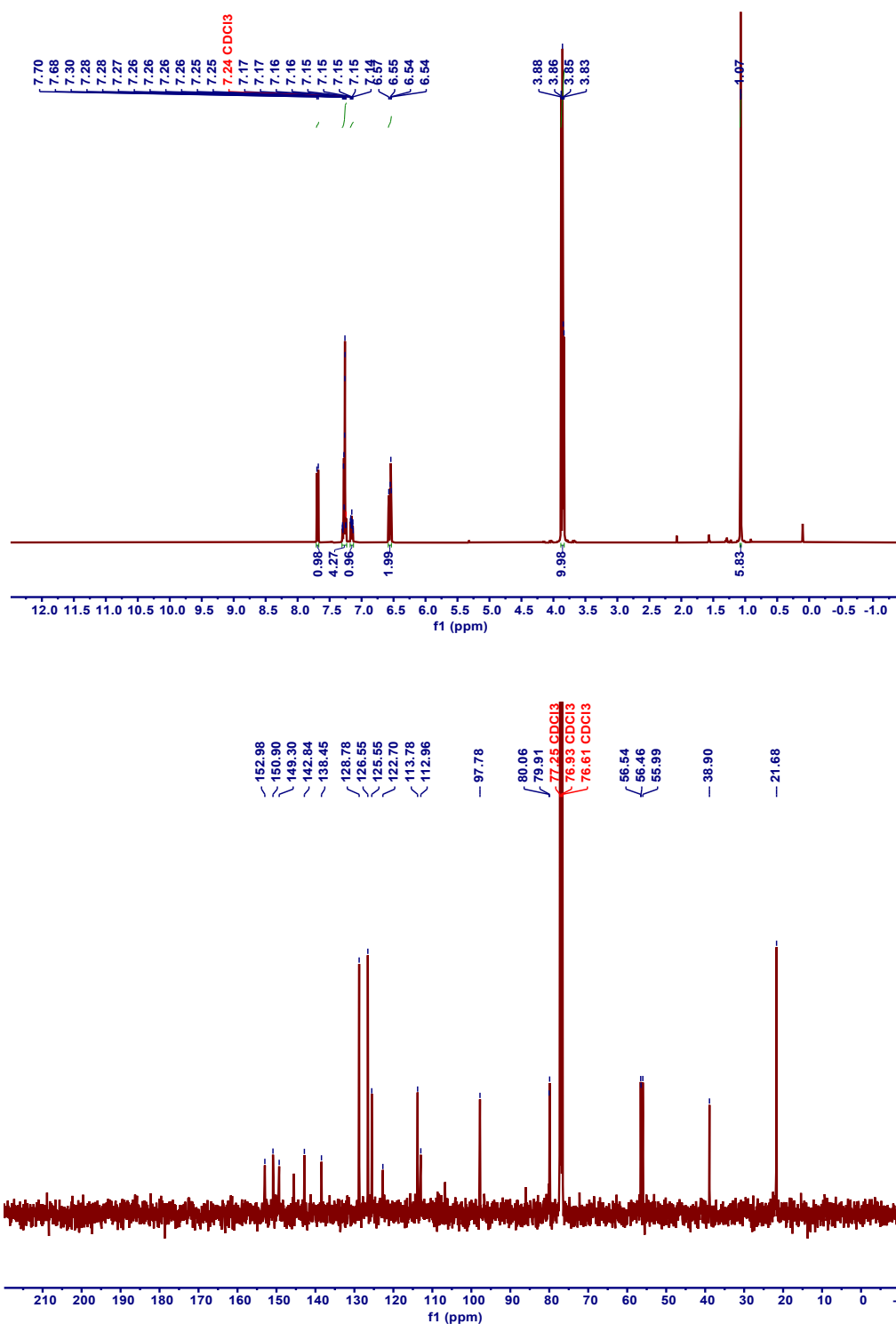
C₁: white solid. 81% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.64-7.60 (m, 2H), 7.28 – 7.21 (m, 4H), 7.17 – 7.12 (m, 1H), 6.93 – 6.89 (m, 2H), 3.87 – 3.83 (m, 7H), 1.07 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 153.6, 144.7, 138.2, 128.8, 128.1, 126.6, 125.7, 125.3, 114.1, 105.5, 79.9, 79.9, 55.2, 38.9, 21.8.



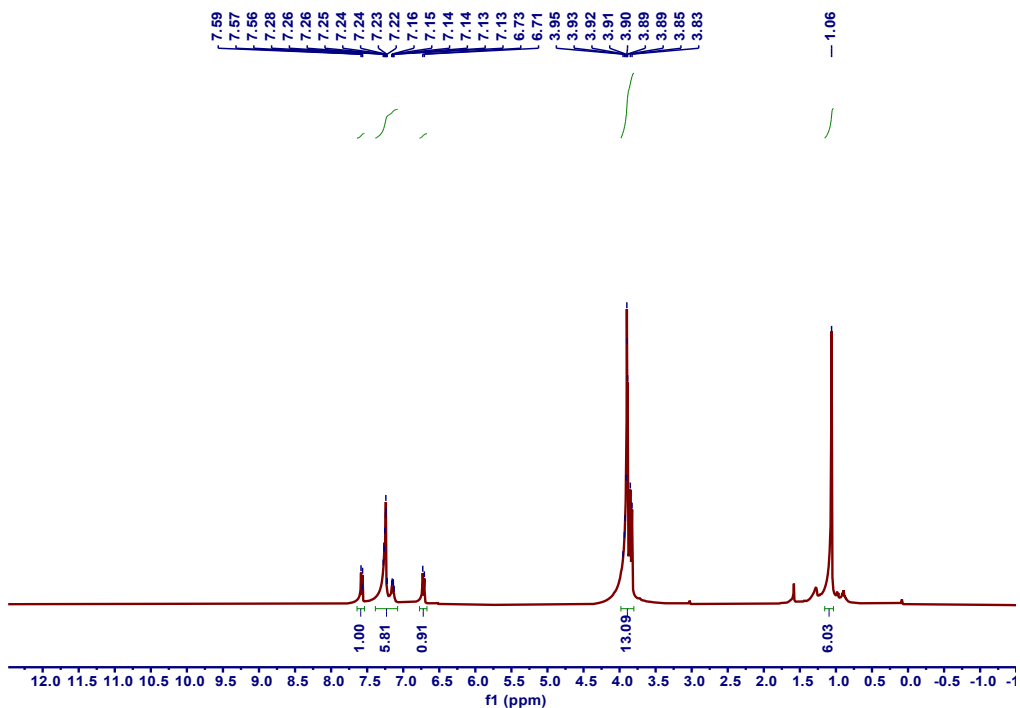
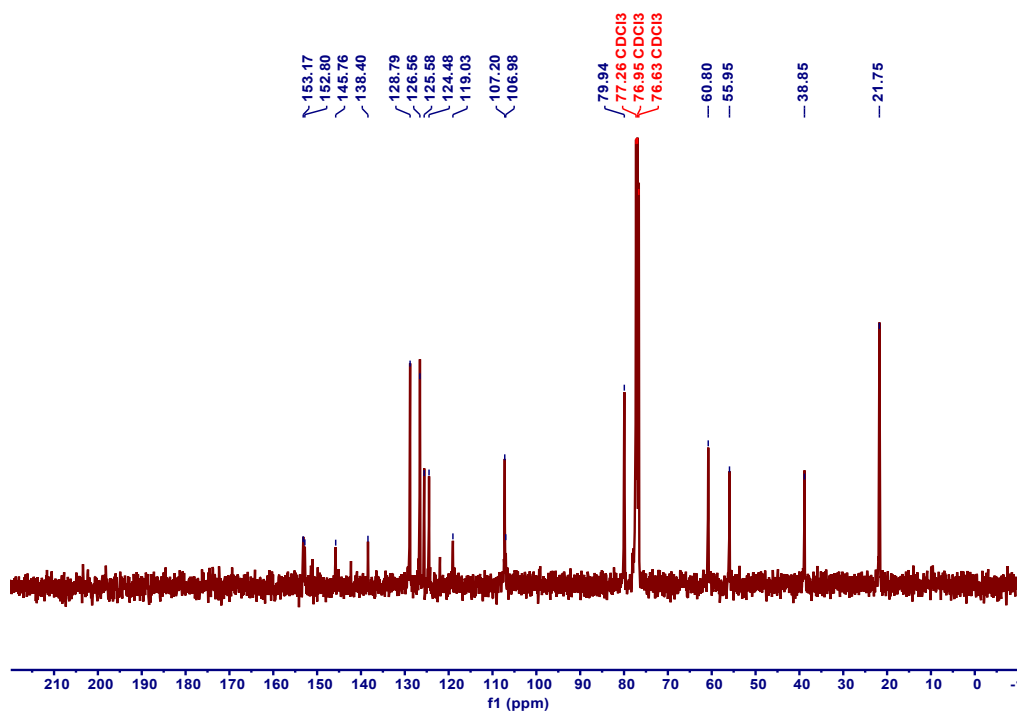
C₁₂: white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.21 (m, 6H), 7.16 – 7.13 (m, 1H), 6.88 (d, J = 8.0 Hz, 1H), 3.91 – 3.83 (m, 10H), 1.07 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 153.7, 148.8, 148.6, 144.8, 138.2, 128.9, 126.6, 126.4, 125.7, 125.5, 119.6, 111.2, 110.3, 105.8, 80.0, 79.9, 55.8, 38.9, 21.



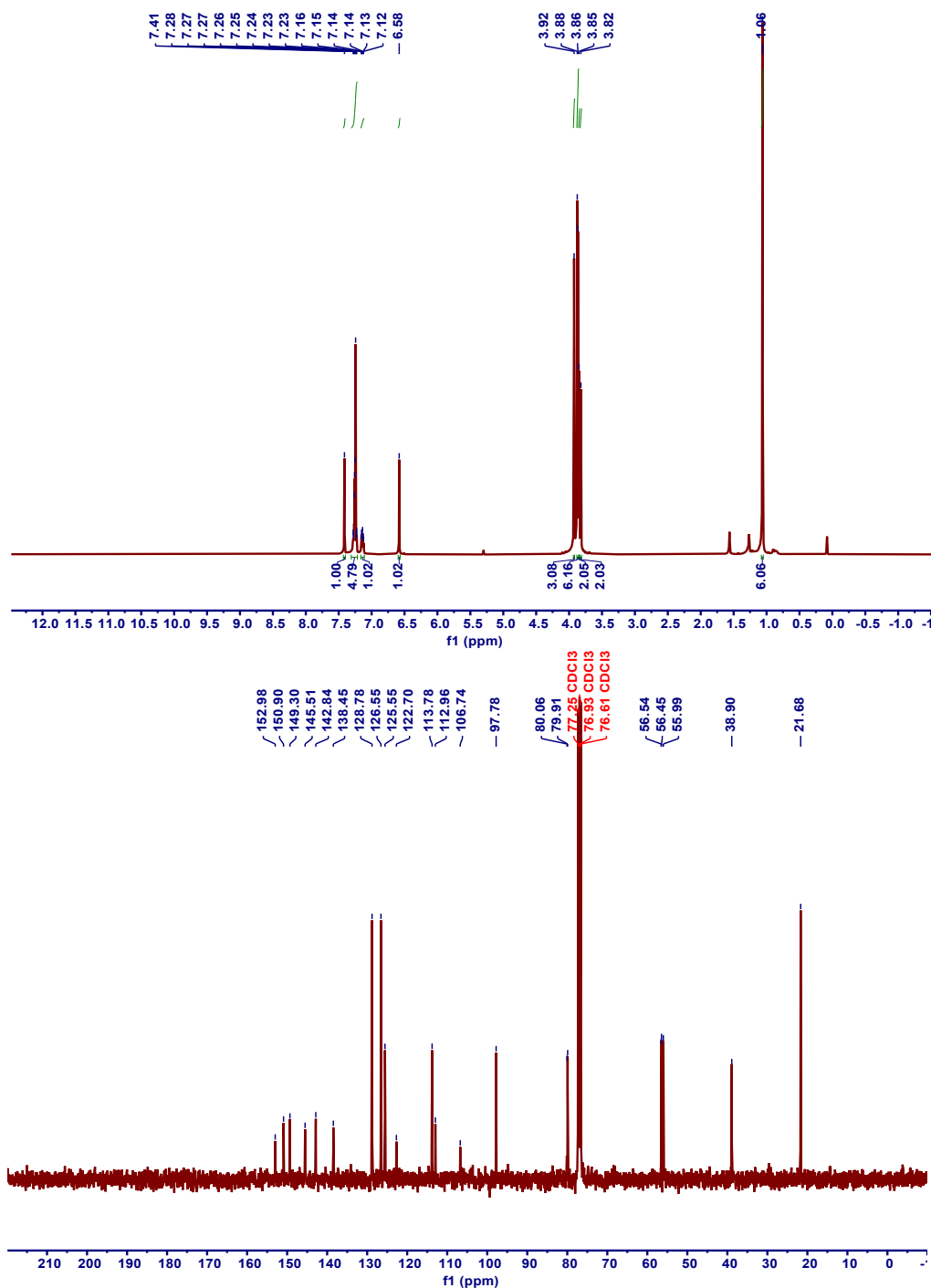
C₁₃: white solid. 85% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 8.5 Hz, 1H), 7.31 – 7.23 (m, 4H), 7.18 – 7.13 (m, 1H), 6.58 – 6.53 (m, 2H), 3.88 – 3.83 (m, 10H), 1.07 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 153.0, 150.9, 149.3, 142.8, 138.4, 128.8, 126.5, 125.5, 122.7, 113.8, 113.1, 97.8, 80.1, 79.9, 56.5, 56.5, 56.1, 38.9, 21.7.



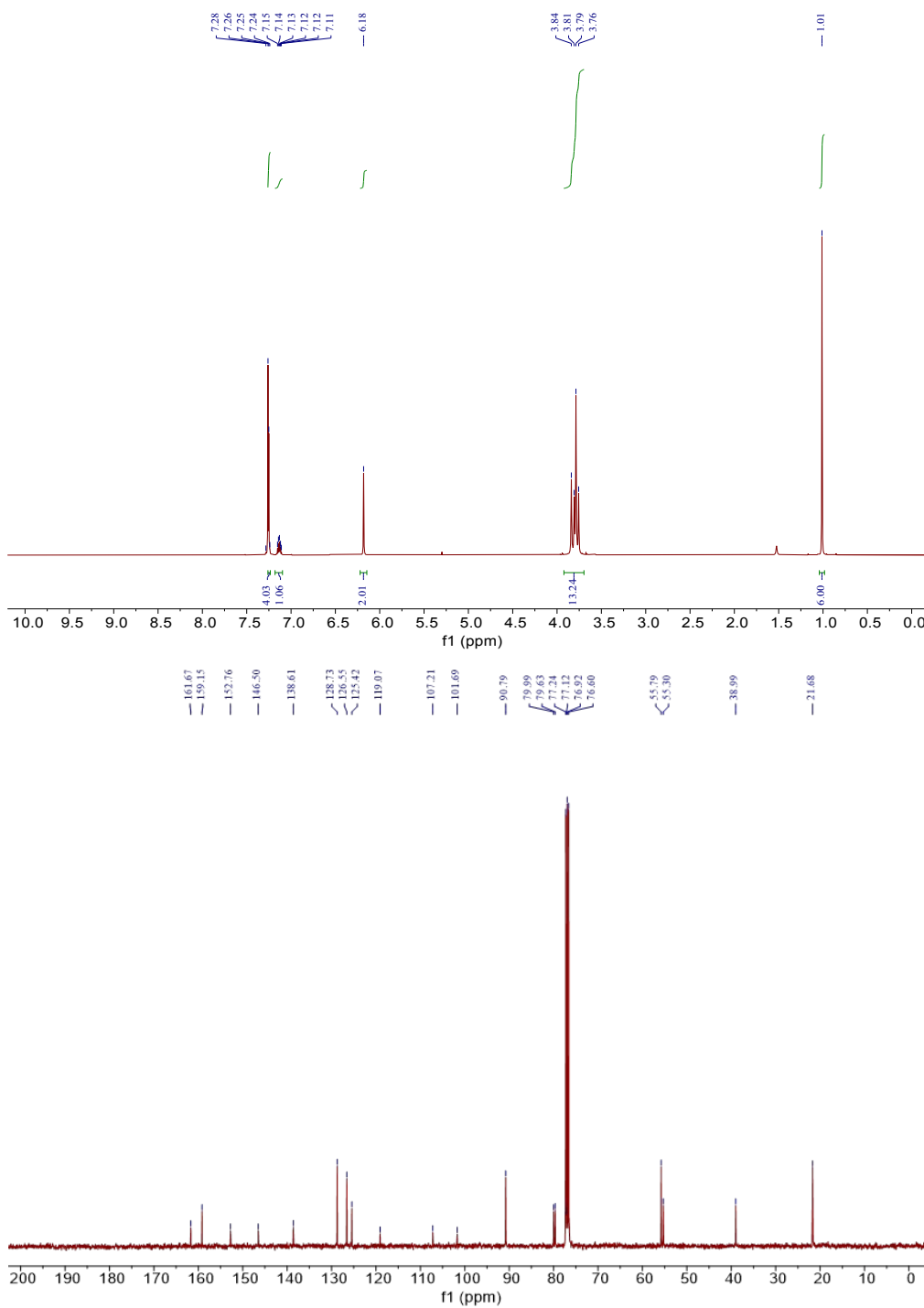
C₁₂₃: colorless oil. 68% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.54 (m, 1H), 7.39 – 7.08 (m, 6H), 6.72 (d, J = 8.9 Hz, 1H), 3.98 – 3.80 (m, 13H), 1.06 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 153.2, 152.8, 145.8, 138.4, 128.8, 126.6, 125.6, 124.5, 119.0, 107.2, 107.1, 79.9, 60.8, 56.0, 38.8, 21.7.



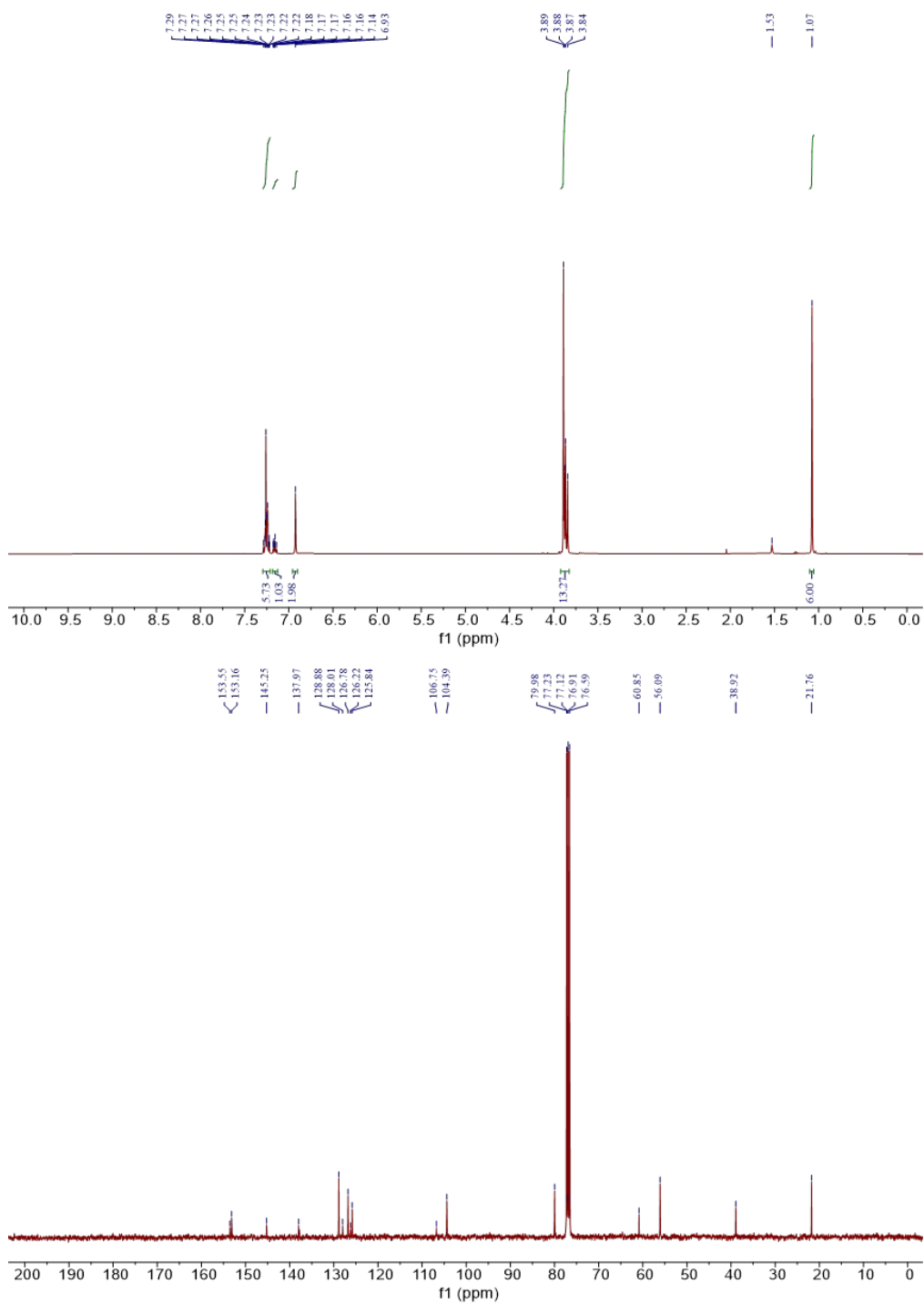
C₁₂₃: white solid. 59% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (s, 1H), 7.31 – 7.22 (m, 5H), 7.14 (td, J = 6.0, 2.7 Hz, 1H), 6.58 (s, 1H), 3.92 (s, 3H), 3.87 (d, J = 4.6 Hz, 6H), 3.85 (s, 2H), 3.82 (s, 2H), 1.06 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 153.0, 150.9, 149.3, 145.5, 142.8, 138.4, 128.8, 126.5, 125.5, 122.7, 113.8, 113.0, 106.7, 97.8, 80.1, 79.9, 56.5, 56.4, 56.0, 38.9, 21.7.



C₁₃₃: white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.24 (m, 4H), 7.15 – 7.11 (m, 1H), 6.18 (s, 2H), 3.84 – 3.76 (m, 13H), 1.01 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 161.7, 159.2, 152.8, 146.5, 138.6, 128.7, 126.5, 125.4, 119.1, 107.2, 101.7, 90.8, 80.0, 79.6, 55.8, 55.3, 39.0, 21.7.



C₁₂₂:- white solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.29 – 7.22 (m, 4H), 7.18 – 7.14 (m, 1H), 6.93 (s, 2H), 3.89 – 3.84 (m, 13H), 1.07 (s, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 153.5, 153.2, 145.2, 138.0, 128.9, 128.0, 126.8, 126.2, 125.8, 106.7, 104.4, 80.0, 60.8, 56.1, 38.9, 21.8.

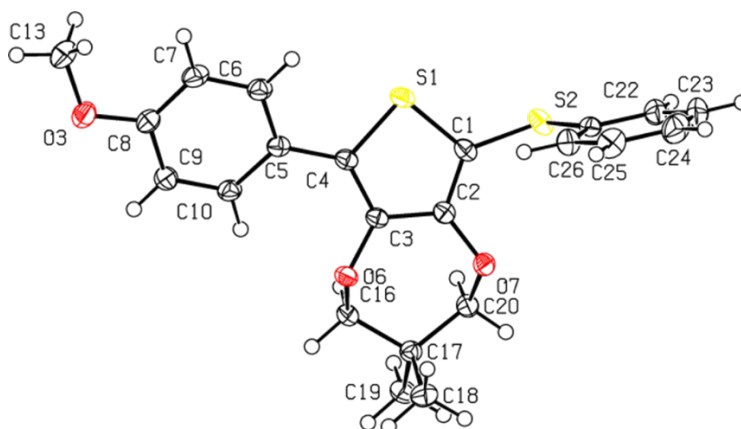


2. Single crystal X-ray structure determination

General Procedure

A single crystal of each analyzed compound was mounted on a Mitegen micromesh in a random orientation. Data were collected from a shock-cooled single crystal at 150(2) K on either a Bruker AXS D8 Quest three circle diffractometer with a fine focus sealed tube X-ray source using a Triumph curved graphite crystal as monochromator and a PhotonII charge-integrating pixel array (CPAD) detector with MoK α radiation ($\lambda = 0.71073$ Å) (C_1 , C_{12} , $C_{133'}$, $C_{123'}$, $C_{122'}$, C_{13} and $C_{123'-a^{2+}}$) or an AXS D8 Quest four circle diffractometer with a microfocus sealed tube X-ray source using laterally graded multilayer (Goebel) mirrors for monochromatization and a PhotonIII charge-integrating and photon counting pixel array detector with CuK α radiation ($\lambda = 1.54178$ Å) (C_1-a^{+} , $C_{122'-f^{2+}}$, $C_{13-a^{2+}}$ and $C_{123-a^{2+}}$). All data were integrated with SAINT V8.40B and a multi-scan absorption correction using SADABS 2016/2 was applied.² The structures were solved by dual methods with SHELXT and refined by full-matrix least-squares methods against F² using SHELXL-2018/3.^{3,4} All non-hydrogen atoms were refined with anisotropic displacement parameters. Carbon bound hydrogen atoms and alcohol hydroxyl H atoms were refined isotropically on calculated positions using a riding model. Methyl CH₃, and hydroxyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. X-H and H...H distances were restrained to expected target values and were further restrained based on hydrogen bonding considerations. U_{iso} values were constrained to 1.5 times the U_{eq} of their pivot atoms for methyl, and hydroxyl groups and 1.2 times for all other hydrogen atoms.

Reports and cif files were generated using FinalCif.⁵

(i) C₁**Figure S1** Thermal ellipsoid plot of C1

Empirical formula	C ₂₂ H ₂₂ O ₃ S ₂
Formula weight	398.51
Temperature [K]	150(2)
Crystal system	orthorhombic
Space group (number)	<i>Pna</i> 2 ₁ (33)
<i>a</i> [Å]	17.5465(18)
<i>b</i> [Å]	5.9077(5)
<i>c</i> [Å]	18.6884(12)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å ³]	1937.2(3)
<i>Z</i>	4
ρ_{calc} [gcm ⁻³]	1.366
μ [mm ⁻¹]	0.295
<i>F</i> (000)	840
Crystal size [mm ³]	0.090×0.170×0.190
Crystal colour	colourless
Crystal shape	plate
Radiation	MoK α (λ =0.71073 Å)
2 θ range [°]	6.37 to 66.27 (0.65 Å)
Index ranges	-26 ≤ <i>h</i> ≤ 26 -8 ≤ <i>k</i> ≤ 8 -26 ≤ <i>l</i> ≤ 28
Reflections collected	28181
Independent reflections	7020 <i>R</i> _{int} = 0.0599 <i>R</i> _{sigma} = 0.0536

Completeness to $\theta = 25.242^\circ$	99.3 %
Data / Restraints / Parameters	7020 / 1 / 247
Goodness-of-fit on F^2	1.027
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0363$ $wR_2 = 0.0696$
Final R indexes [all data]	$R_1 = 0.0602$ $wR_2 = 0.0783$
Largest peak/hole [$\text{e}\text{\AA}^{-3}$]	0.30/−0.30
Flack X parameter	−0.05(3)

(ii) C_{12}

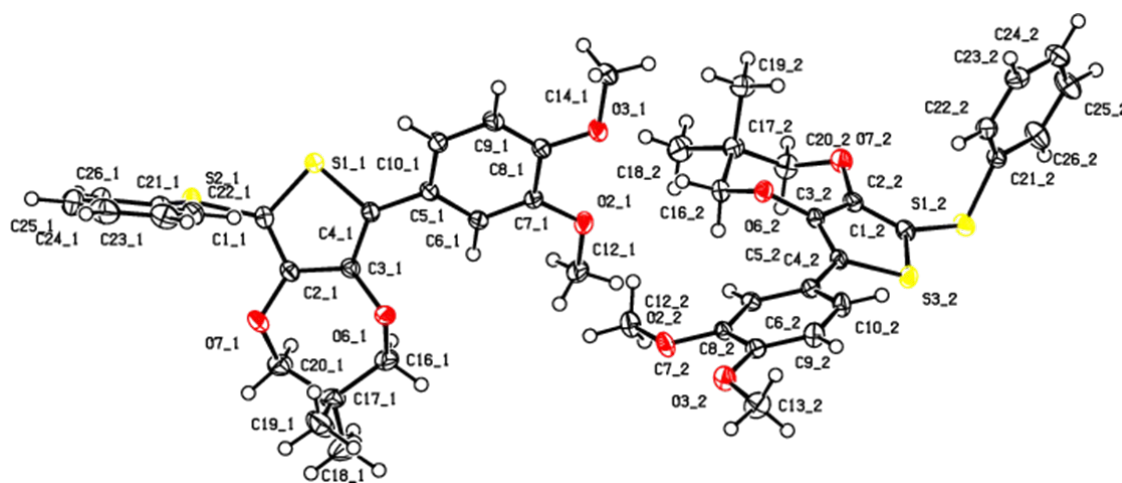


Figure S2 Thermal ellipsoid plots of the two crystallographically unique molecules present in the crystal of C_{12} .

Empirical formula	$\text{C}_{23}\text{H}_{24}\text{O}_4\text{S}_2$
Formula weight	428.54
Temperature [K]	150(2)
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [$\text{\AA}$]	5.8185(2)
b [$\text{\AA}$]	15.2949(5)
c [$\text{\AA}$]	24.8319(9)
α [$^\circ$]	103.9653(16)
β [$^\circ$]	94.8428(17)
γ [$^\circ$]	92.9395(16)
Volume [$\text{\AA}^3$]	2131.02(13)
Z	4
ρ_{calc} [gcm^{-3}]	1.336
μ [mm^{-1}]	0.277

$F(000)$	904
Crystal size [mm ³]	0.030×0.030×0.550
Crystal colour	yellow
Crystal shape	needle
Radiation	MoK $_{\alpha}$ ($\lambda=0.71073$ Å)
2 θ range [°]	4.87 to 66.46 (0.65 Å)
Index ranges	$-8 \leq h \leq 8$ $-23 \leq k \leq 23$ $-38 \leq l \leq 38$
Reflections collected	45960
Independent reflections	15384 $R_{\text{int}} = 0.0606$ $R_{\text{sigma}} = 0.0648$
Completeness to $\theta = 25.242^{\circ}$	99.9 %
Data / Restraints / Parameters	15384 / 0 / 531
Goodness-of-fit on F^2	1.015
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0451$ $wR_2 = 0.0922$
Final R indexes [all data]	$R_1 = 0.0891$ $wR_2 = 0.1072$
Largest peak/hole [eÅ ⁻³]	0.45/−0.31

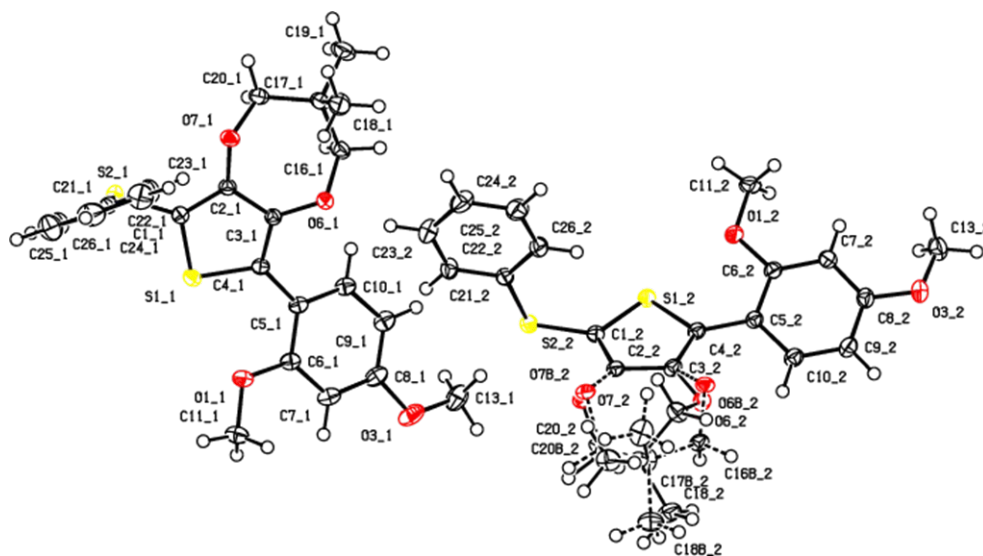
(iii) C_{13} 

Figure S3 Thermal ellipsoid plots of the two crystallographically unique molecules present in the crystal of C_{13} .

The 2,2-dimethylpropane unit of one of the molecules was refined as disordered. The two flanking oxygen atoms were included in the disorder. The two disordered moieties were restrained to have similar geometries as the not disordered equivalent moiety in the other molecule. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.814(2) to 0.186(2).

Empirical formula	$C_{23}H_{24}O_4S_2$
Formula weight	428.54
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	$P2_1/n$ (14)
a [Å]	18.922(5)
b [Å]	12.7062(16)
c [Å]	19.913(3)
α [°]	90
β [°]	118.078(16)
γ [°]	90
Volume [Å ³]	4224.3(15)
Z	8
ρ_{calc} [gcm ⁻³]	1.348
μ [mm ⁻¹]	0.279

$F(000)$	1808
Crystal size [mm ³]	0.220×0.390×0.480
Crystal colour	yellow
Crystal shape	block
Radiation	MoK $_{\alpha}$ ($\lambda=0.71073$ Å)
2 θ range [°]	4.03 to 66.40 (0.65 Å)
Index ranges	$-26 \leq h \leq 29$ $-17 \leq k \leq 19$ $-30 \leq l \leq 28$
Reflections collected	118075
Independent reflections	16160 $R_{\text{int}} = 0.0514$ $R_{\text{sigma}} = 0.0278$
Completeness to $\theta = 25.242^{\circ}$	99.9 %
Data / Restraints / Parameters	16160 / 240 / 597
Goodness-of-fit on F^2	1.036
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0303$ $wR_2 = 0.0850$
Final R indexes [all data]	$R_1 = 0.0436$ $wR_2 = 0.0906$
Largest peak/hole [eÅ ⁻³]	0.45/−0.37

(iv) $C_{133'}$

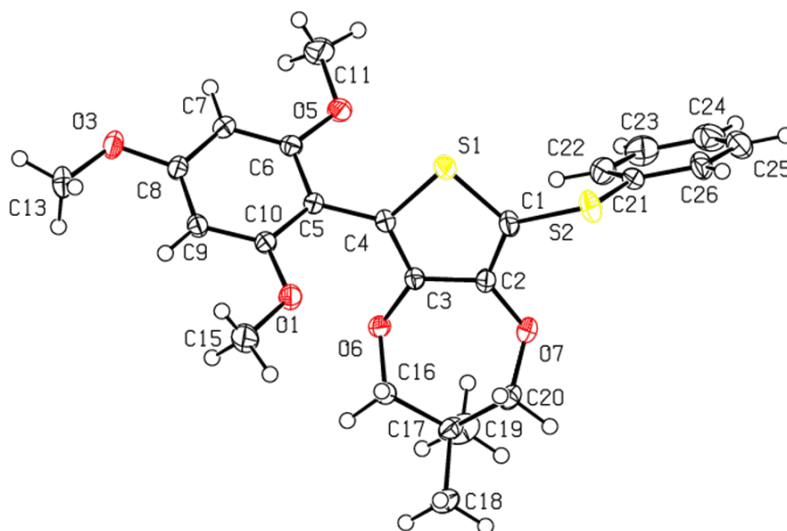


Figure S4 Thermal ellipsoid plot of $C_{133'}$

Empirical formula	$C_{24}H_{26}O_5S_2$
Formula weight	458.57
Temperature [K]	149(2)
Crystal system	orthorhombic
Space group (number)	$P2_12_12_1$ (19)
a [Å]	9.8534(4)
b [Å]	15.0462(5)
c [Å]	15.6234(6)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å ³]	2316.27(15)
Z	4
ρ_{calc} [gcm ⁻³]	1.315
μ [mm ⁻¹]	0.262
$F(000)$	968
Crystal size [mm ³]	0.120×0.150×0.440
Crystal colour	colourless
Crystal shape	rod
Radiation	MoK_α ($\lambda=0.71073$ Å)
2θ range [°]	4.94 to 66.37 (0.65 Å)
Index ranges	$-15 \leq h \leq 11$ $-18 \leq k \leq 23$ $-24 \leq l \leq 23$
Reflections collected	34866

Independent reflections	8848 $R_{\text{int}} = 0.0306$ $R_{\text{sigma}} = 0.0285$
Completeness to $\theta = 25.242^\circ$	99.7 %
Data / Restraints / Parameters	8848 / 0 / 286
Goodness-of-fit on F^2	1.053
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0303$ $wR_2 = 0.0760$
Final R indexes [all data]	$R_1 = 0.0367$ $wR_2 = 0.0795$
Largest peak/hole [$\text{e}\text{\AA}^{-3}$]	0.29/−0.31
Flack X parameter	0.41(5)

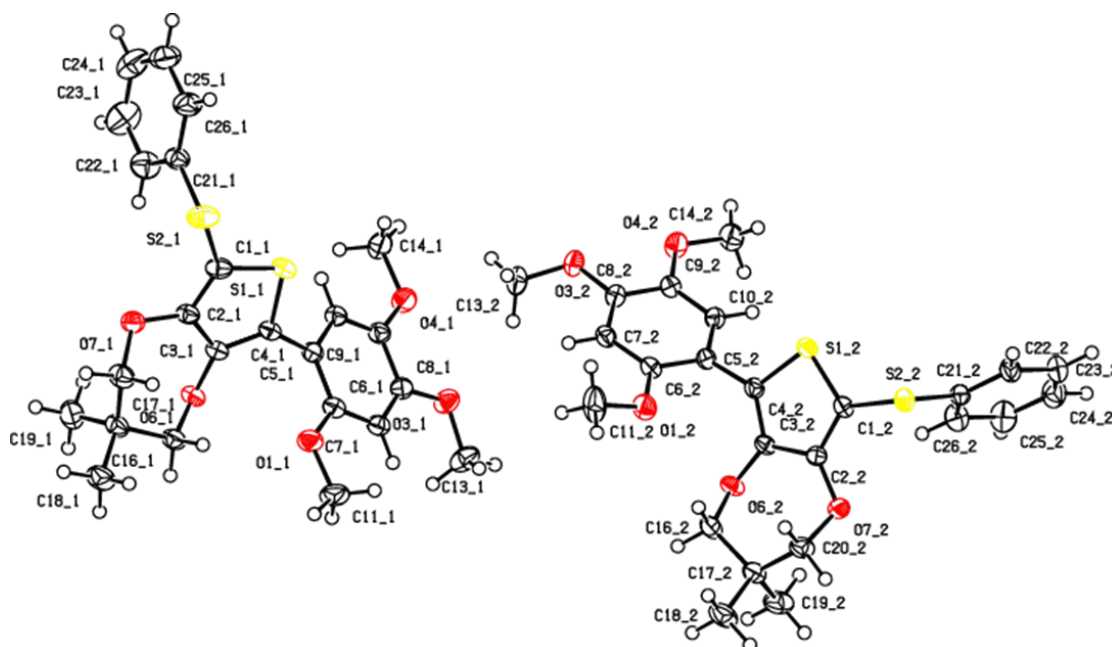
(v) $C_{123'}$ 

Figure S5 Thermal ellipsoid plots of the two crystallographically unique molecules present in the $C_{123'}$ crystal.

The structure fits a metrically orthorhombic C-centered lattice with twice the volume and is twinned by this symmetry. Application of the transformation matrix $\begin{pmatrix} 1 & 0 & 0.966 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$ (two-fold rotation around $(1\ 0\ 0)$) yielded a BASF value of 0.193(1).

Empirical formula	$C_{24}H_{26}O_5S_2$
Formula weight	458.57
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	25.249(3)
b [Å]	9.9398(11)
c [Å]	19.739(3)
α [°]	90
β [°]	112.195(4)
γ [°]	90
Volume [Å ³]	4586.7(10)
Z	8
ρ_{calc} [gcm ⁻³]	1.328
μ [mm ⁻¹]	0.265

$F(000)$	1936
Crystal size [mm ³]	0.030×0.280×0.440
Crystal colour	colourless
Crystal shape	plate
Radiation	MoK $_{\alpha}$ ($\lambda=0.71073$ Å)
2 θ range [°]	4.10 to 56.78 (0.75 Å)
Index ranges	$-32 \leq h \leq 33$ $-13 \leq k \leq 13$ $-25 \leq l \leq 26$
Reflections collected	41827
Independent reflections	11374 $R_{\text{int}} = 0.0600$ $R_{\text{sigma}} = 0.0647$
Completeness to $\theta = 25.242^{\circ}$	99.3 %
Data / Restraints / Parameters	11374 / 0 / 571
Goodness-of-fit on F^2	1.066
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0624$ $wR_2 = 0.1735$
Final R indexes [all data]	$R_1 = 0.0772$ $wR_2 = 0.1885$
Largest peak/hole [eÅ ⁻³]	0.43/−0.57
Extinction coefficient	0.0022(5)

(vi) C₁₂₂'

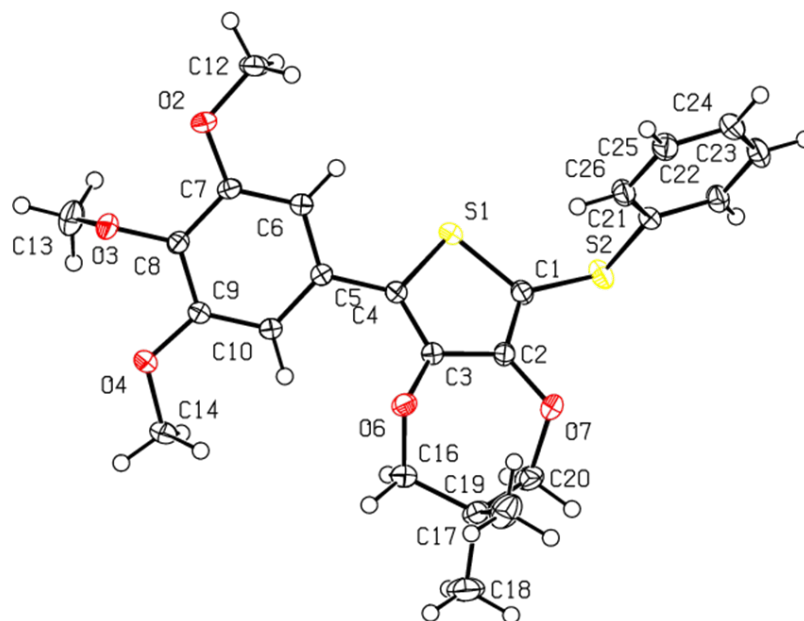


Figure S6 Thermal ellipsoid plot of C₁₂₂'

Empirical formula	C ₂₄ H ₂₆ O ₅ S ₂
Formula weight	458.57
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>n</i> (14)
<i>a</i> [Å]	13.8570(4)
<i>b</i> [Å]	9.7143(3)
<i>c</i> [Å]	17.9710(6)
α [°]	90
β [°]	109.8903(12)
γ [°]	90
Volume [Å ³]	2274.79(12)
<i>Z</i>	4
ρ_{calc} [gcm ⁻³]	1.339
μ [mm ⁻¹]	0.267
<i>F</i> (000)	968
Crystal size [mm ³]	0.390×0.520×0.540
Crystal colour	yellow
Crystal shape	block
Radiation	MoK α (λ =0.71073 Å)
2 θ range [°]	4.82 to 66.33 (0.65 Å)

Index ranges	$-21 \leq h \leq 20$ $-14 \leq k \leq 14$ $-27 \leq l \leq 26$
Reflections collected	69523
Independent reflections	8634 $R_{\text{int}} = 0.0408$ $R_{\text{sigma}} = 0.0230$
Completeness to $\theta = 25.242^\circ$	99.6 %
Data / Restraints / Parameters	8634 / 0 / 285
Goodness-of-fit on F^2	1.038
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0321$ $wR_2 = 0.0849$
Final R indexes [all data]	$R_1 = 0.0438$ $wR_2 = 0.0918$
Largest peak/hole [$\text{e}\text{\AA}^{-3}$]	0.47/−0.32

Electrochemical Doping and Characterization

Redox properties of the molecules (4 mM solutions prepared in 0.2 M LiTFSI electrolyte dissolved in dichloromethane) were tested in a three-electrode cell using a Pt-button working electrode, a Ag/AgCl reference electrode and a Pt wire counter electrode. Cyclic voltammetry was performed at a scan rate of 20 mV s⁻¹, unless specified otherwise. Differential pulse voltammetry was also done over the same potential range. All measurements were performed under inert conditions.

In situ-spectroelectrochemical characterization during electrochemical doping of 0.4 mM solutions (dissolved in either 0.2 M LiTFSI in dichloromethane or 0.2 M LiTFSI in propylene carbonate) were carried out in a cuvette of 1 mm path length using a honeycomb-electrode with a built-in counter electrode. The same Ag/AgCl reference electrode used for the CV and DPV measurements were used in these experiments. The absorbance of the neutral solution was recorded and then the applied potential was gradually increased in 0.05 V steps. The potential was held constant for 30 seconds before recording the absorbance spectrum at each potential step. Smaller potential steps were chosen as the oxidation potential was approached.

Chemical doping and characterization

AgSbF₆ was used as an oxidant. Equal volumes of a 2 mM stock solution of the respective electrochromes and a 3 mM stock solution of AgSbF₆ (1.5 eq) were mixed and stirred for 30 minutes inside a N₂ filled glovebox. The chemically doped solutions were then filtered using a 0.2 micron plastic filter to remove the solid Ag residue. A 300 uL aliquot of this sample was diluted to 3 mL using dichloromethane to prepare 0.1 mM solutions and the absorbance was measured immediately. A further 100 uL aliquot of the doped solution was diluted using 900 uL of anhydrous acetonitrile and tested immediately using electro-spray ionization mass spectrometry. The filtered stock solutions were kept inside the glovebox and portions were analyzed at different time intervals to follow the degradation. Where specified, the above-mentioned concentrations and dopant equivalents were altered as required to study degradation products under different conditions.

Electron-paramagnetic resonance (EPR) of the chemically doped solutions (0.2 mM solutions) were measured at room temperature on a Bruker EMX EPR Spectrometer using WinEPR Acquisition Software.

ESI-Mass spectrometric measurements

ESI-MS were acquired using an Agilent 6560 IM Q-ToF mass spectrometer (Santa Clara, CA, USA) fitted with a custom-designed electrospray ionization (ESI) source. A 100 μ M solution of sample species was infused into the inlet of the instrument via a fused-silica capillary (50 μ m ID, 150 μ m OD) at a flow rate of 1 μ L/min. ESI conditions include a spray voltage of 3.5 kV and inlet temperature of 250 °C. Positive ions were analyzed in the mass range of m/z 100 – 3200. The resolution ($m/\Delta m$) at m/z 428 was 19,000. The solvent composition was a mixture of acetonitrile-dichloromethane (90:10, %v/v). The instrument also includes a collision cell filled with nitrogen where select precursor ions underwent collision induced dissociation (CID) to form product (fragment) ions. The collision energy value was set to 30 eV.

Crystallization of degradation products

Single crystals of the degraded radical cations were grown by following a similar chemical doping procedure. The molecular electrochrome (10 mM in dichloromethane, 1.5 mL) and oxidant (15 mM AgSbF₆ in dichloromethane, 1.5 mL) were mixed and stirred under inert conditions for 30 minutes, filtered to a 20 mL glass vial and left undisturbed inside the glovebox for three days. Dark blue, needle-shaped crystals were formed. In the case of C₁₂₃, crystals of the degraded product were formed at the solvent interface during very slow addition of n-hexane antisolvent. For C_{122'}, the demethylated product (red/purple crystals) was obtained using *o*-dichlorobenzene antisolvent, upon slow solvent evaporation overnight. The C_{122'} dimer (orange-brown crystals) was formed only formed in a 1 mM chemically doped solution, that was left undisturbed for more than a week.

Theoretical calculations

Geometry Optimization and Time-dependent density functional theory (DFT) to simulate the absorption spectra were done using Range-separated hybrid Functional with dispersion correction ω -B97XD with a correlation-consistent basis set, cc-pVDZ due to its reliability with modeling the charge transfer behavior characteristic of conjugated systems.⁶ The Gaussian16, Revision B.01 program suite was used to execute the DFT calculations. To minimize user error in the input structures for the geometry optimization, initial structures – neutral and charged species – were prepared by GFN2-xTB, a semiempirical quantum method in the xTB program developed by the Grimme group.⁷ The crude structure was used as a starting point for CREST (Conformer-Rotamer

Ensemble Sampling Tool) to find the lowest energy conformer and the initial guess for DFT optimization. Fractional spin density was extracted from Natural Bond Orbital Analysis (NBO) on the radical species. Atomic charges were calculated from the electrostatic potential (ESP) difference between the neutral and first oxidation states^{8,9} Implicit solvation of dichloromethane (DCM) was incorporated in xTB and Gaussian16 through the Analytical Linearized Poisson-Boltzmann (ALPB) model and Polarizable Continuum Model (PCM), respectively, to reflect solvation effects from experiments.^{10,11}

3. DFT calculations of neutral molecules

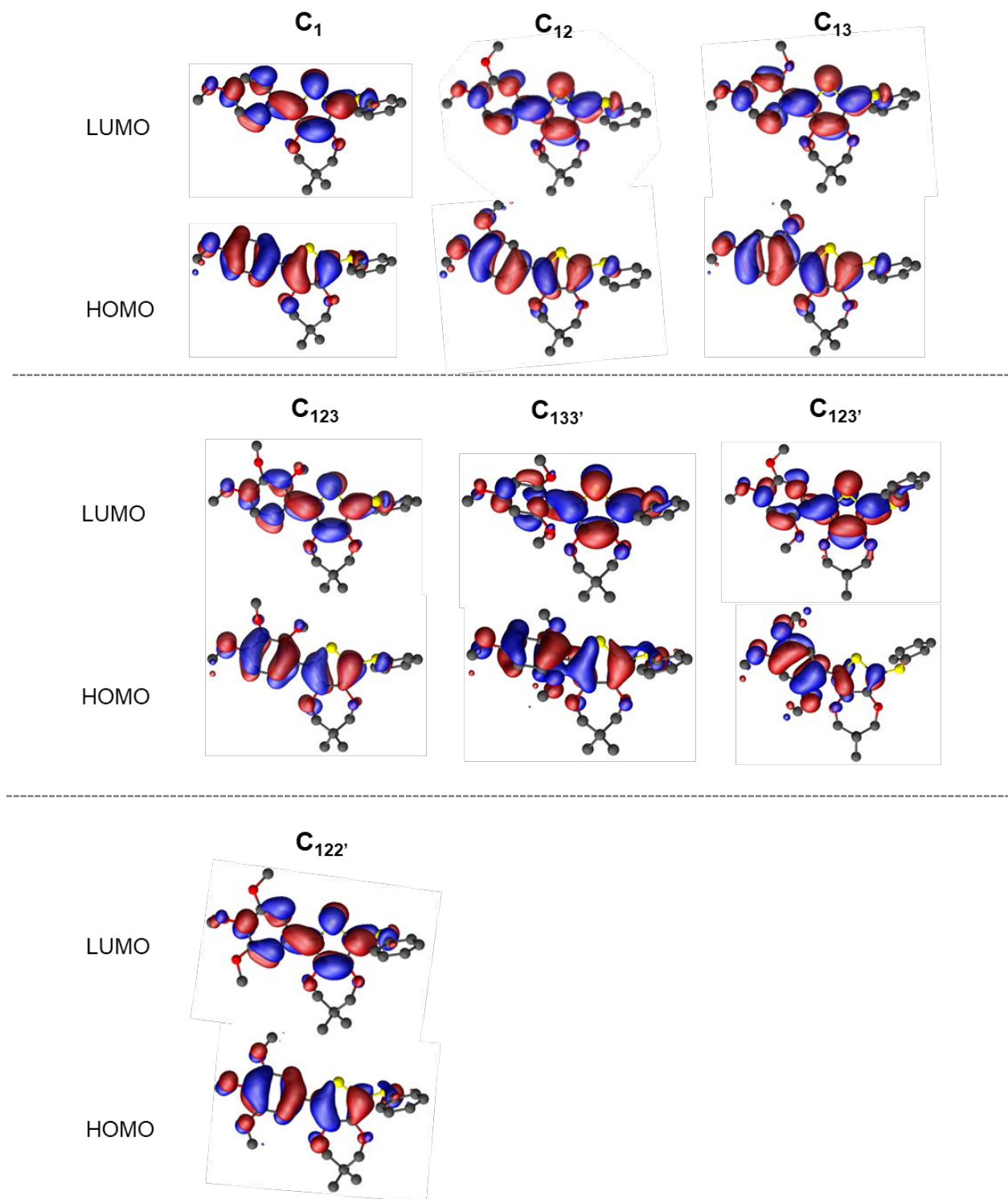


Figure S7 The HOMO and LUMO of neutral molecules computed at ω B97XD/cc-PVTZ level of theory with implicit DCM solvation.

4. Theoretically computed molecular geometries and energy levels

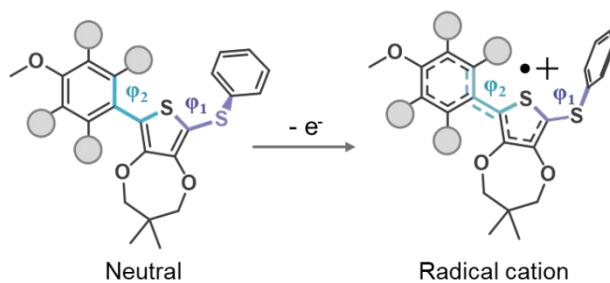


Table S1 Computed dihedrals for the neutral and radical cation states

Molecule	ϕ_1		ϕ_2	
	Neutral	Radical cation	Neutral	Radical cation
C₁	95.7	1.1	29.2	5.5
C₁₂	95.5	1.0	28.4	3.5
C₁₃	93.7	0.2	29.3	4.8
C₁₂₃	96.0	1.5	27.7	3.4
C_{133'}	92.5	0.3	63.9	33.5
C_{123'}	95.5	1.2	23.5	3.7
C_{122'}	97.4	0.9	26.8	3.0

Table S2 Energy levels calculated from DFT for neutral molecules solvated in dichloromethane

Molecule	HOMO (eV)	LUMO (eV)	$\Delta_{\text{HOMO-LUMO}}$
C₁	-7.47	0.48	7.95
C₁₂	-7.31	0.47	7.78
C₁₃	-7.32	0.56	7.88
C₁₂₃	-7.44	0.49	7.92
C_{133'}	-7.52	0.91	8.44
C_{123'}	-7.22	0.42	7.63
C_{122'}	-7.52	0.34	7.86

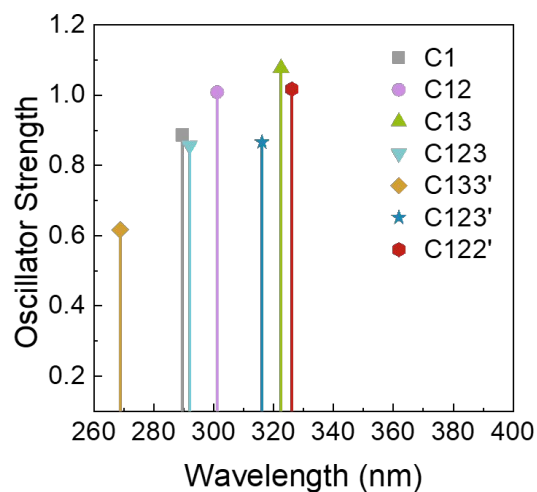


Figure S8 Wavelengths of maximum absorption for calculated using TD-DFT for neutral molecules in dichloromethane solvent.

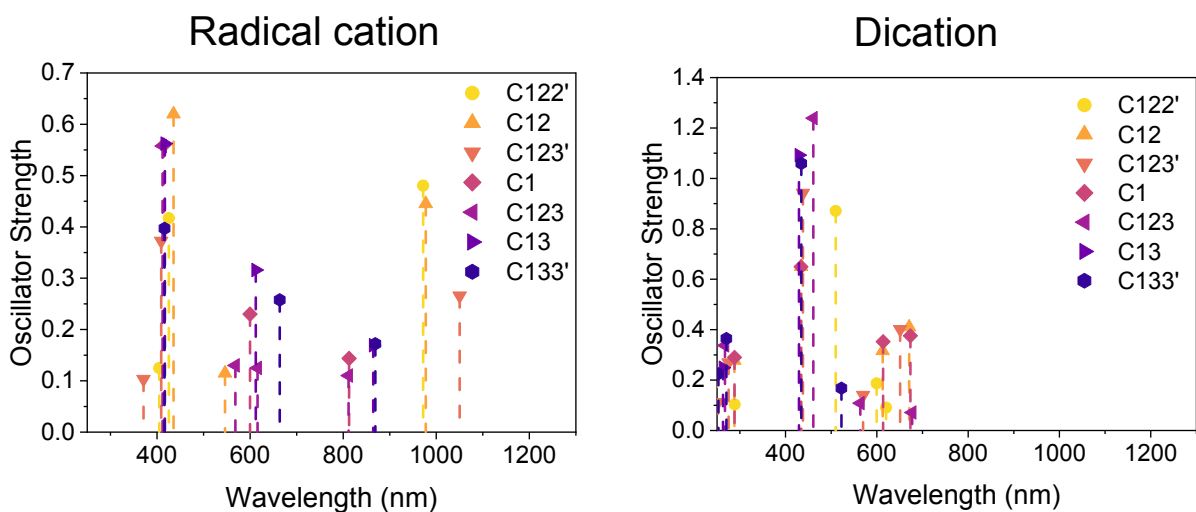


Figure S9 Prominent absorption peaks for radical cationic and dicationic states as calculated using TD-DFT in dichloromethane solvent.

5. Electrochemical doping

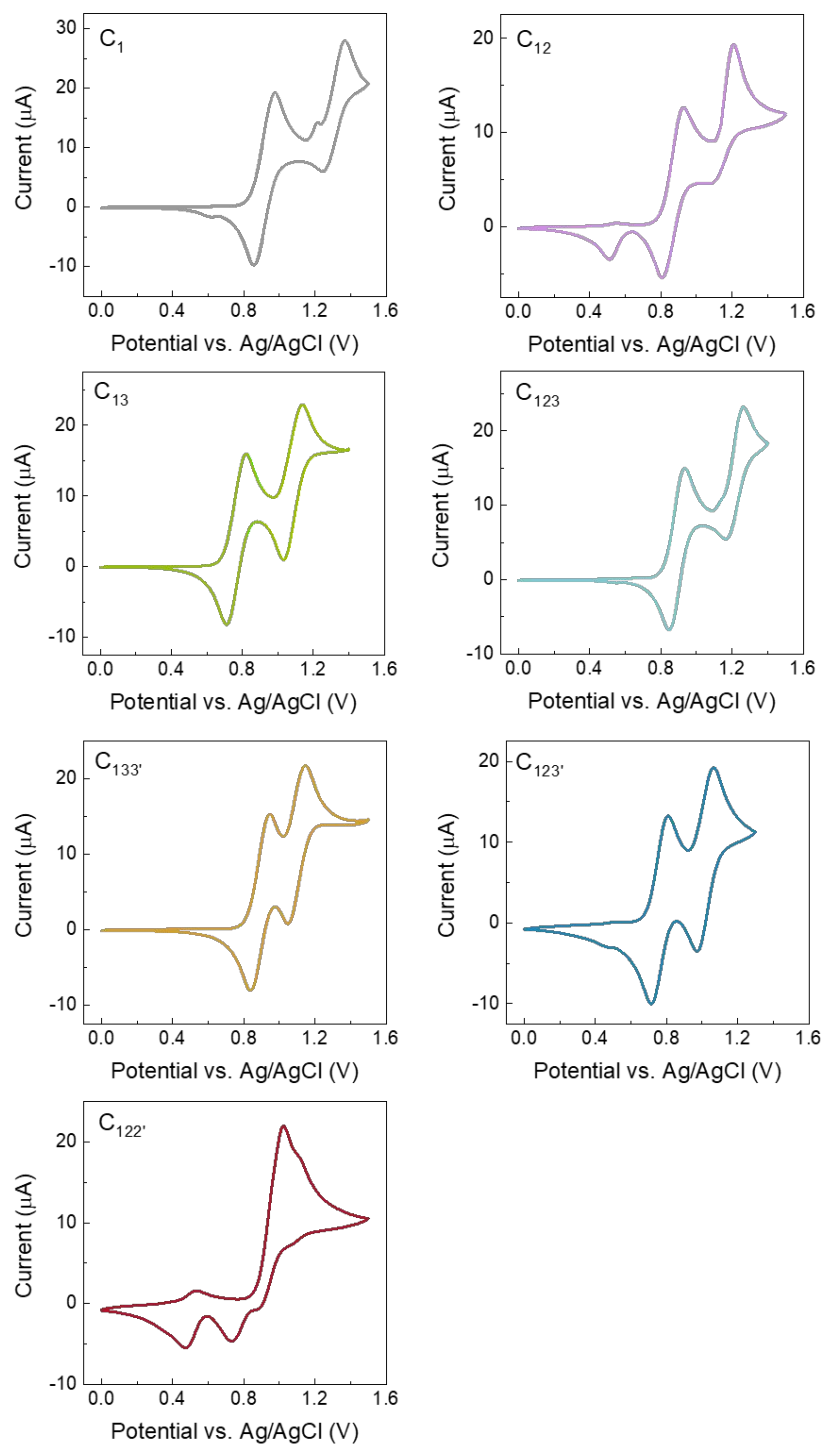


Figure S10 Cyclic voltammetry of 4 mM solutions of neutral molecules dissolved in an electrolyte of 0.2 M LiTFSI prepared in a solvent mixture of 90% dichloromethane and 10% propylene carbonate.

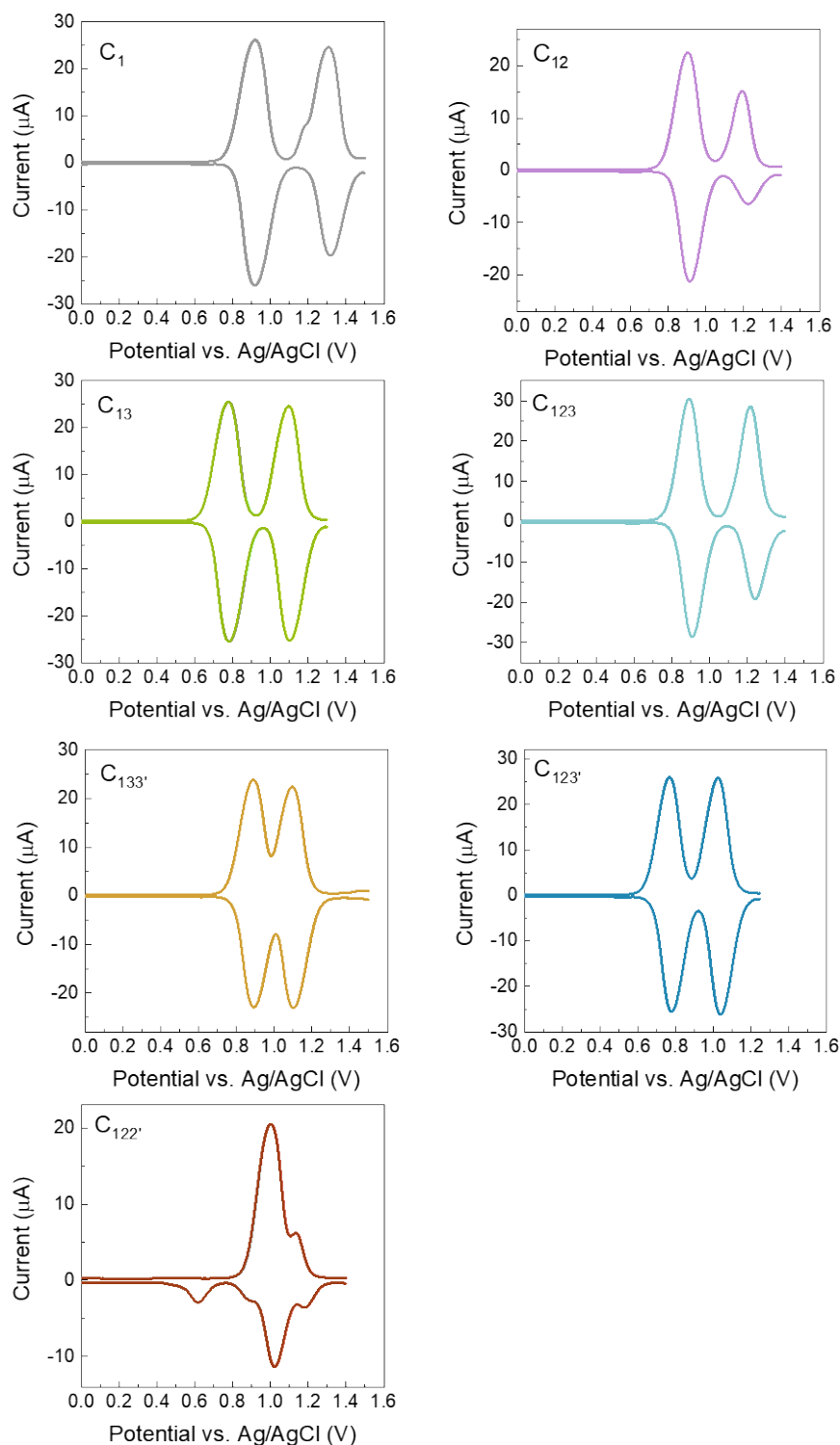


Figure S11 Differential pulse voltammetry of 4 mM solutions of neutral molecules dissolved in an electrolyte of 0.2 M LiTFSI prepared in a solvent mixture of 90% dichloromethane and 10% propylene carbonate.

Table S3 Half-wave potentials for the 1st and 2nd oxidations (measured vs. Ag/AgCl)

Molecule	E ¹ _{1/2} (V)	E ² _{1/2} (V)	ΔE(V)
C ₁	0.92	1.31	0.39
C ₁₂	0.90	1.19	0.29
C ₁₃	0.77	1.08	0.31
C ₁₂₃	0.89	1.22	0.33
C _{133'}	0.89	1.10	0.21
C _{123'}	0.76	1.02	0.26
C _{122'}	1.00 ^a	-	-

^aValue extracted from DPV experiment**Table S4** Experimentally derived HOMO and LUMO levels

Molecule	Oxidation onset vs. Ag/AgCl (V)	HOMO (eV)	Absorption onset (nm)	Optical bandgap (eV)	LUMO (eV)
C ₁	0.83	-5.16	355	3.49	-1.67
C ₁₂	0.80	-5.13	361	3.43	-1.70
C ₁₃	0.69	-5.02	356	3.48	-1.54
C ₁₂₃	0.81	-5.14	351	3.53	-1.60
C _{133'}	0.815	-5.14	333	3.72	-1.42
C _{123'}	0.685	-5.01	369	3.36	-1.65
C _{122'}	0.877	-5.20	359	3.45	-1.75

*The oxidation onsets were obtained from the cyclic voltammetry data.

6. Radical cation absorption spectra

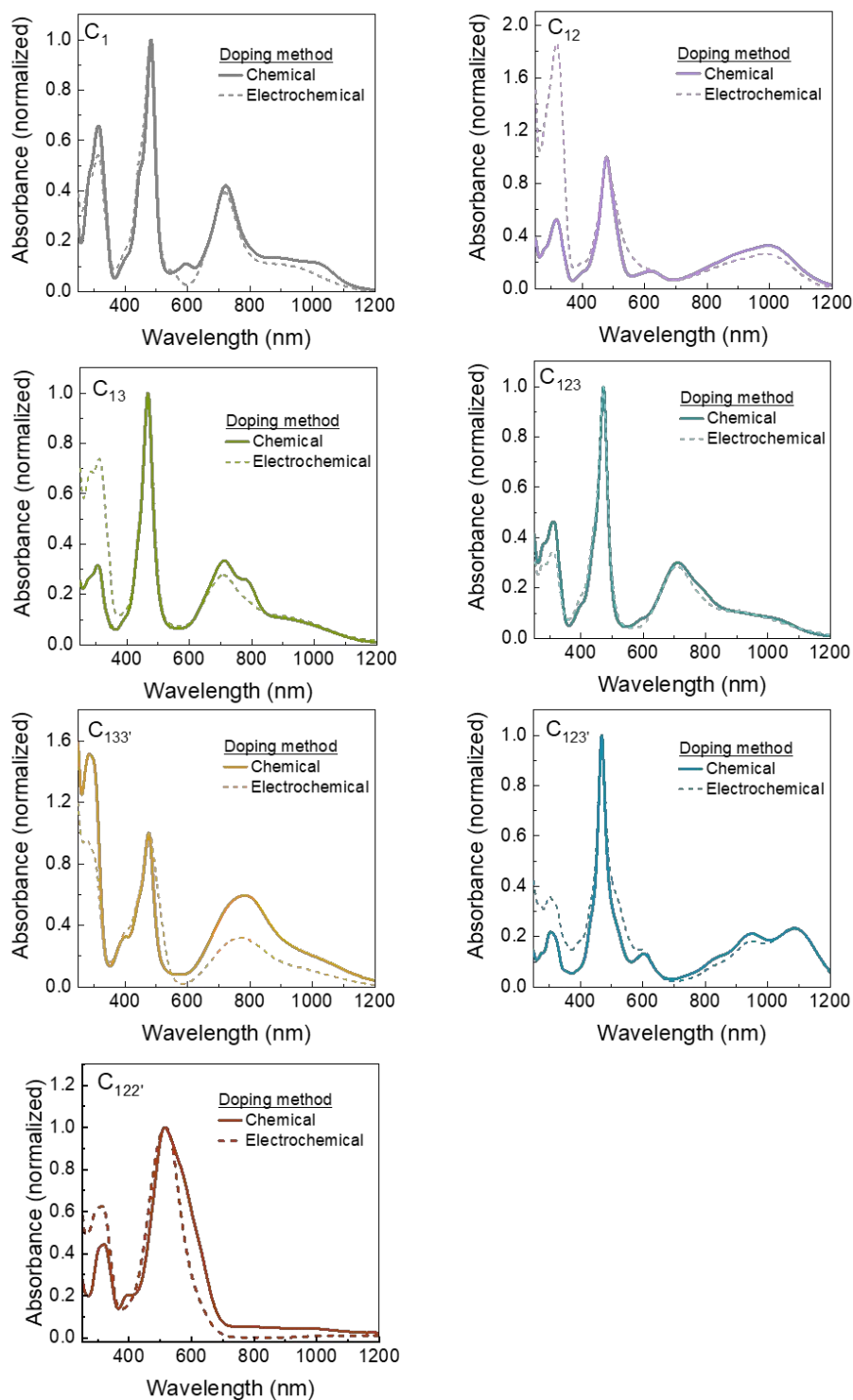


Figure S12 Comparison of absorption spectra of electrochemically and chemically doped Ph(OMe)_x-ProDOT species.

7. TD-DFT calculations – Radical cations

Table S5. A list of excited states with oscillator strengths greater than 0.1 and the dominant (i.e., highest coefficient) transition for the radical cations, presented in terms of wavelength, oscillator strength and corresponding orbital transitions.

ACE Molecule	Excited State	f	Wavelength (nm)	Corresponding Orbital Transition
C₁	1	0.1436	812	SOMO-1 --> SOMO
	2	0.2301	600	SOMO-2 --> SOMO
	4	0.5596	415	SOMO --> LUMO
C₁₂	1	0.4451	977	SOMO-1 --> SOMO
	3	0.1149	546	SOMO-5 --> SOMO
	4	0.6199	436	SOMO --> LUMO
C₁₃	1	0.1692	865	SOMO-1 --> SOMO
	2	0.316	612	SOMO-2 --> SOMO
	4	0.5622	417	SOMO --> LUMO
C₁₂₃	1	0.1103	811	SOMO-1 --> SOMO
	2	0.125	616	SOMO-2 --> SOMO
	3	0.13	568	SOMO-3 --> SOMO
	4	0.5575	412	SOMO --> LUMO
C_{133'}	1	0.1721	869	SOMO-1 --> SOMO
	2	0.2577	664	SOMO-2 --> SOMO
	4	0.3971	416	SOMO --> LUMO
C_{123'}	1	0.1103	811	SOMO-1 --> SOMO
	3	0.125	616	SOMO-2 --> SOMO
	4	0.5575	412	SOMO --> LUMO
C_{122'}	1	0.4804	972	SOMO-1 --> SOMO
	4	0.417	425	SOMO --> LUMO
	5	0.1249	405	SOMO-4 --> SOMO

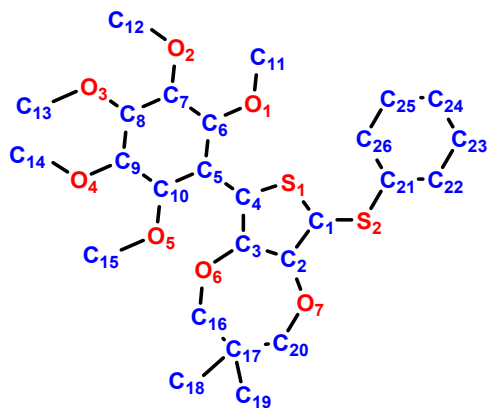


Table S6 Calculated electrostatic potentials (ESP) of select atoms in ACE molecules.

Atom #	Molecule						
	C ₁	C ₁₂	C ₁₃	C ₁₂₃	C _{133'}	C _{123'}	C _{122'}
S1	0.014	-0.005	-0.047	-0.063	0.02	0.014	-0.017
S2	0	-0.078	-0.03	-0.028	-0.027	-0.116	-0.099
O1	---	---	-0.033	-0.047	-0.151	-0.085	---
O2	---	-0.298	---	-0.214	---	---	-0.29
O3	-0.302	-0.265	-0.284	-0.128	-0.27	-0.237	-0.197
O4	---	---	---	---	---	-0.189	-0.157
O5	---	---	---	---	-0.161	---	---
C1	-0.132	-0.095	-0.105	-0.103	-0.184	-0.137	-0.085
C2	0.308	0.249	0.268	0.249	0.367	0.406	0.197
C3	0.185	0.186	0.167	0.131	-0.009	-0.031	0.218
C4	-0.095	-0.086	-0.021	0.044	0.066	-0.091	-0.111
C5	0.103	0.172	-0.109	-0.034	-0.346	0.006	0.123
C6	0.077	-0.125	0.35	0.167	0.528	0.288	-0.105
C7	-0.125	0.252	-0.339	-0.012	-0.427	-0.222	0.273
C8	0.51	0.331	0.557	0.259	0.579	0.4	0.192
C9	-0.182	-0.072	-0.203	-0.09	-0.332	0.146	0.214
C15	---	---	---	---	0.187	---	---
C10	0.115	-0.003	0.144	0.031	0.412	0.031	-0.149
C11	---	---	0.175	0.179	0.2	0.23	---
C12	---	0.255	---	0.178	---	---	0.252
C13	0.256	0.262	0.239	0.19	0.237	0.275	0.244
C14	---	---	---	---	---	0.283	0.193

*The atom with the highest positive charge is highlighted in pale blue.

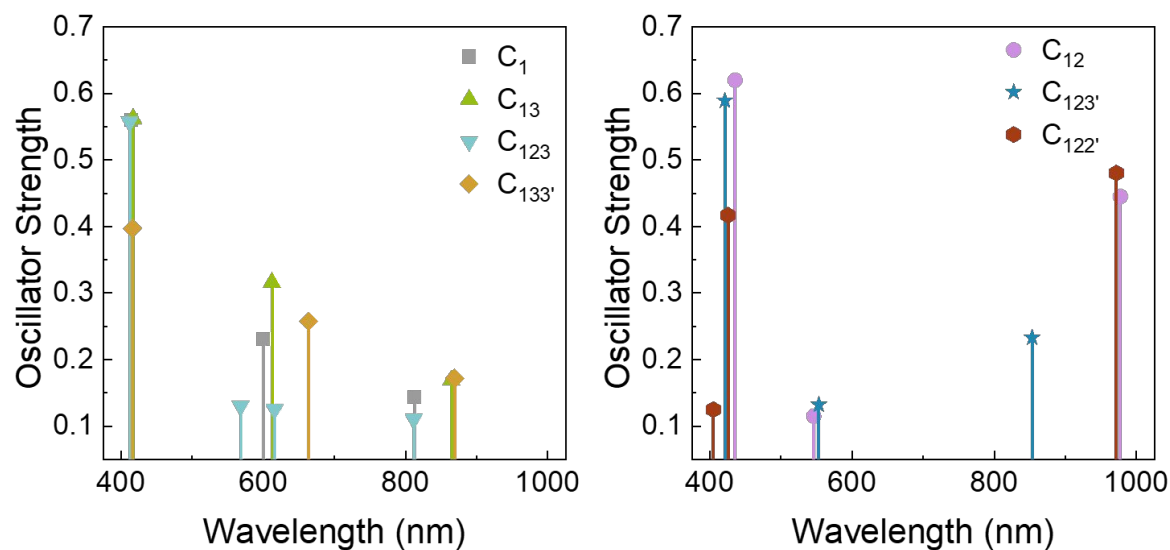


Figure S13 Dominant absorption peaks of the radical cations as calculated from TD-DFT, categorized according to the position of the low-energy peak.

8. Instability of radical cations

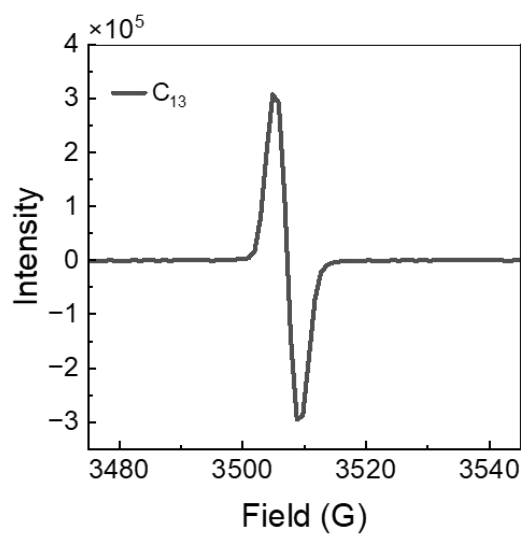


Figure S14 EPR spectrum of a C_{13} solution (in DCM) doped with 1.5 eq of $AgSbF_6$. The spectrum was measured 1 hr after doping.

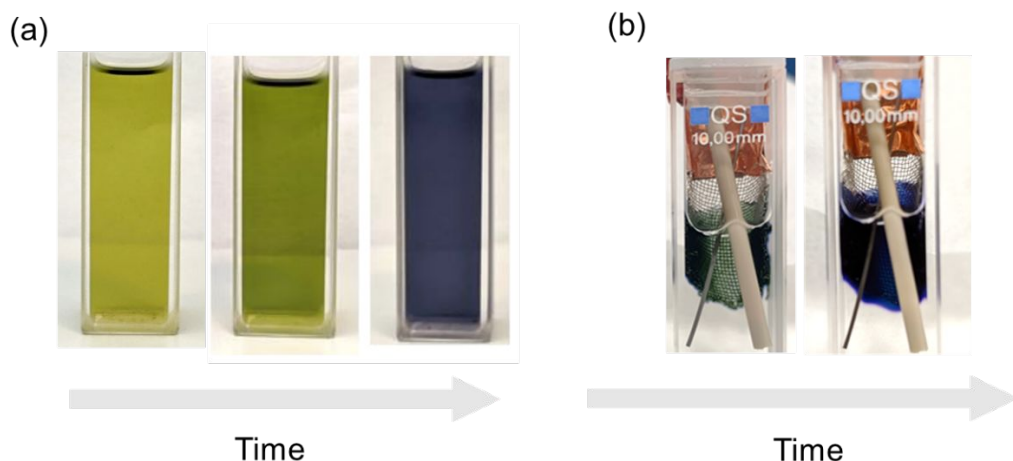


Figure S15 Degradation observed visually in (a) chemically doped C_{13} solutions over timer and (b) during electrochemical doping at a Pt mesh electrode using a constant potential of +0.9 V vs. Ag/AgCl reference electrode.

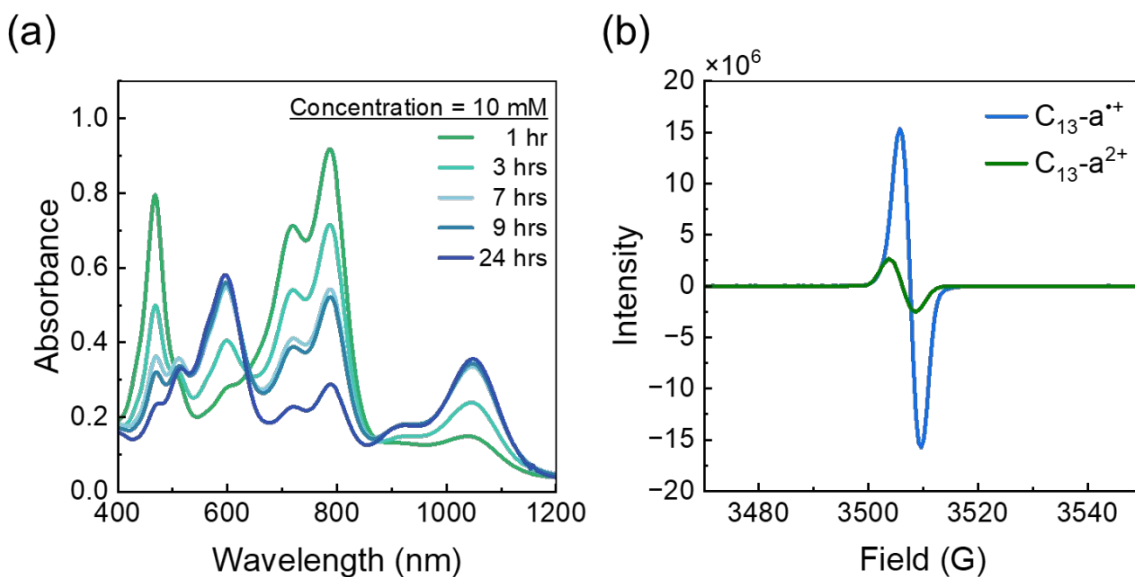


Figure S16 Degradation of the $C_{13}^{\bullet+}$ radical cation as observed over time in a concentrated solution. (b) EPR spectra of degraded solutions predominantly containing the dimer radical cation($C_{13}-a^{\bullet+}$) or the dimer dication ($C_{13}-a^{2+}$).

9. Absorption changes of chemically doped solutions

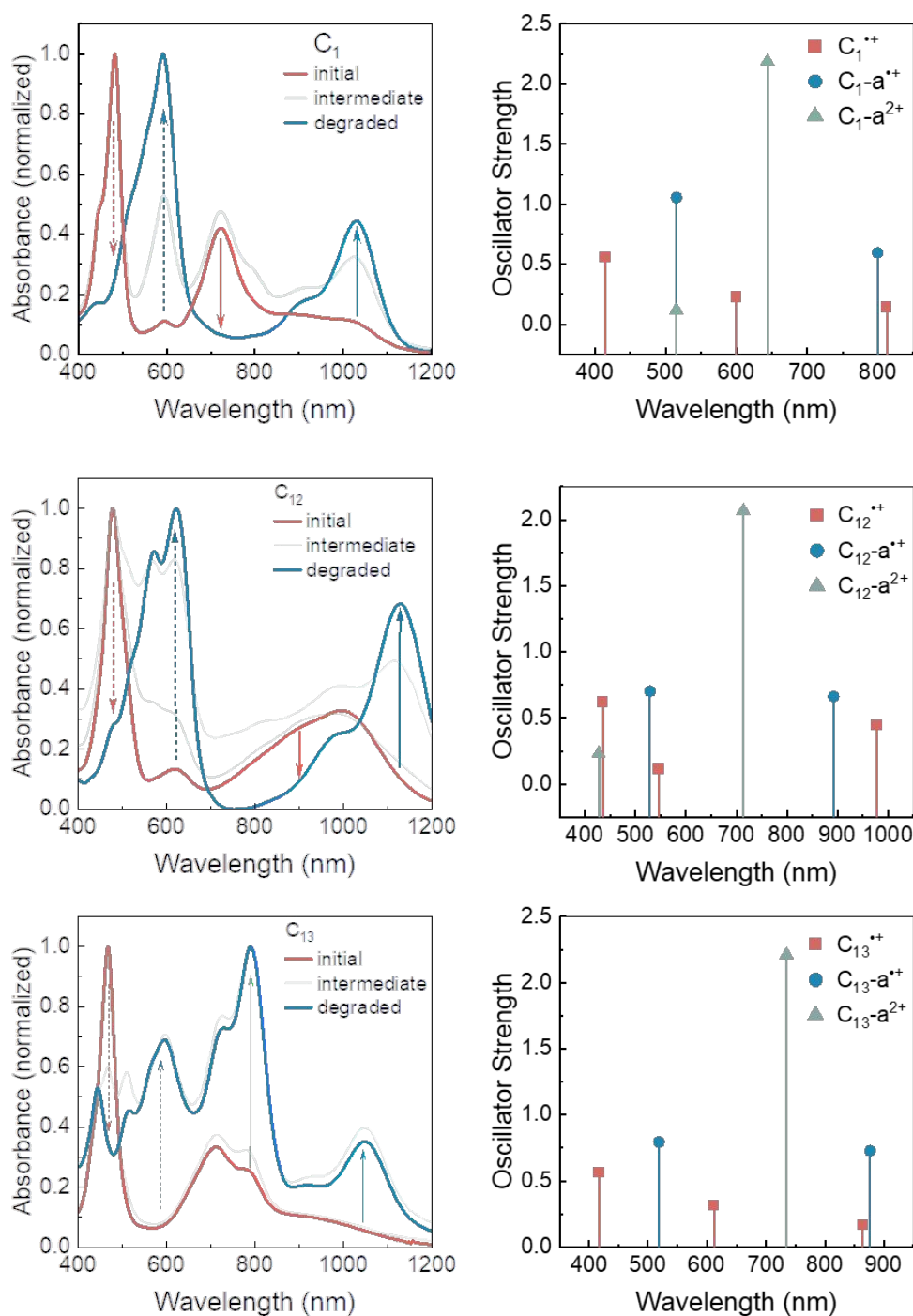
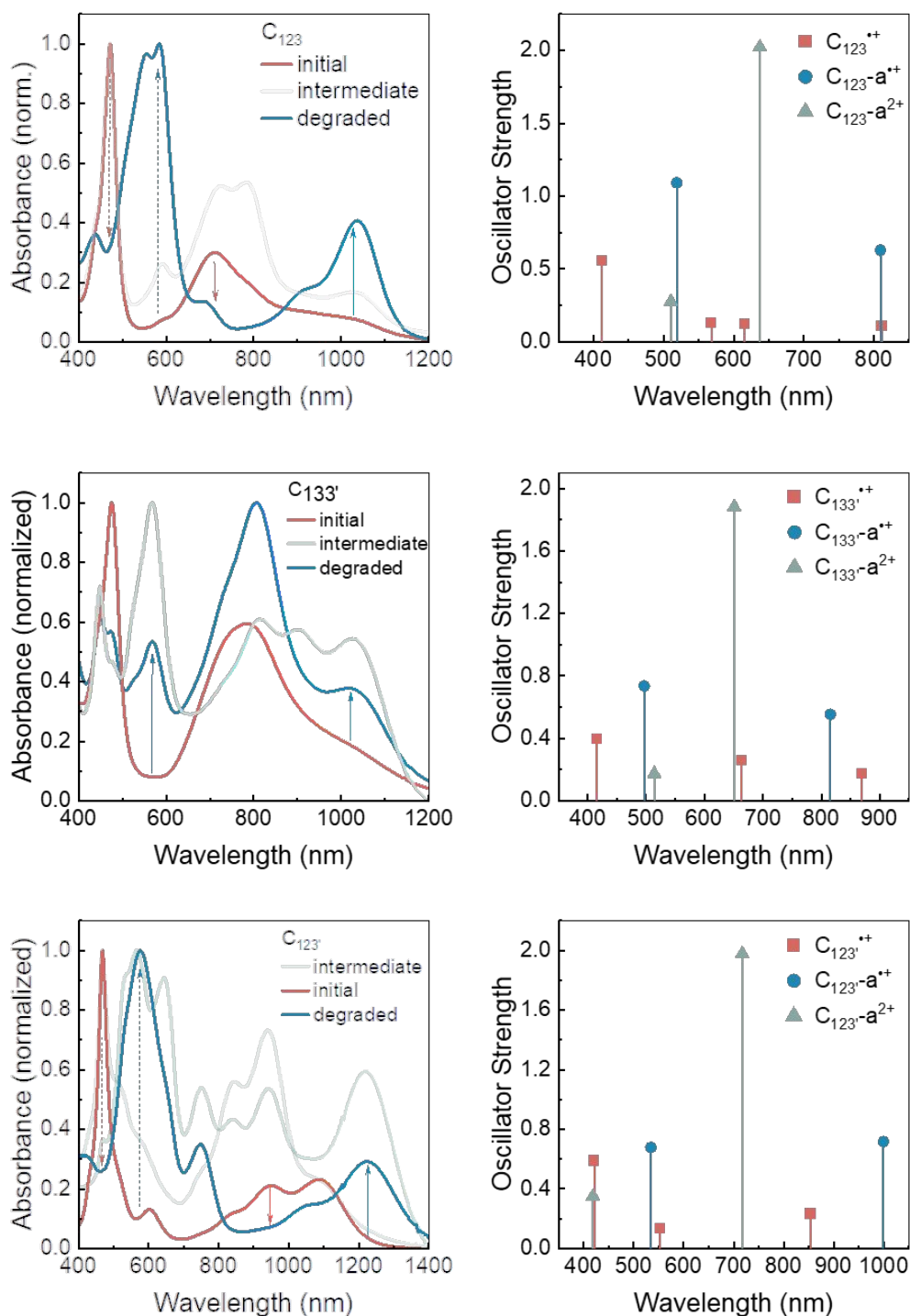


Figure S17 Comparison of experimentally observed spectra and TD-DFT predicted results for dimerization.

Figure S17 Continued



10. Dimerization of $C_{123}^{+\bullet}$

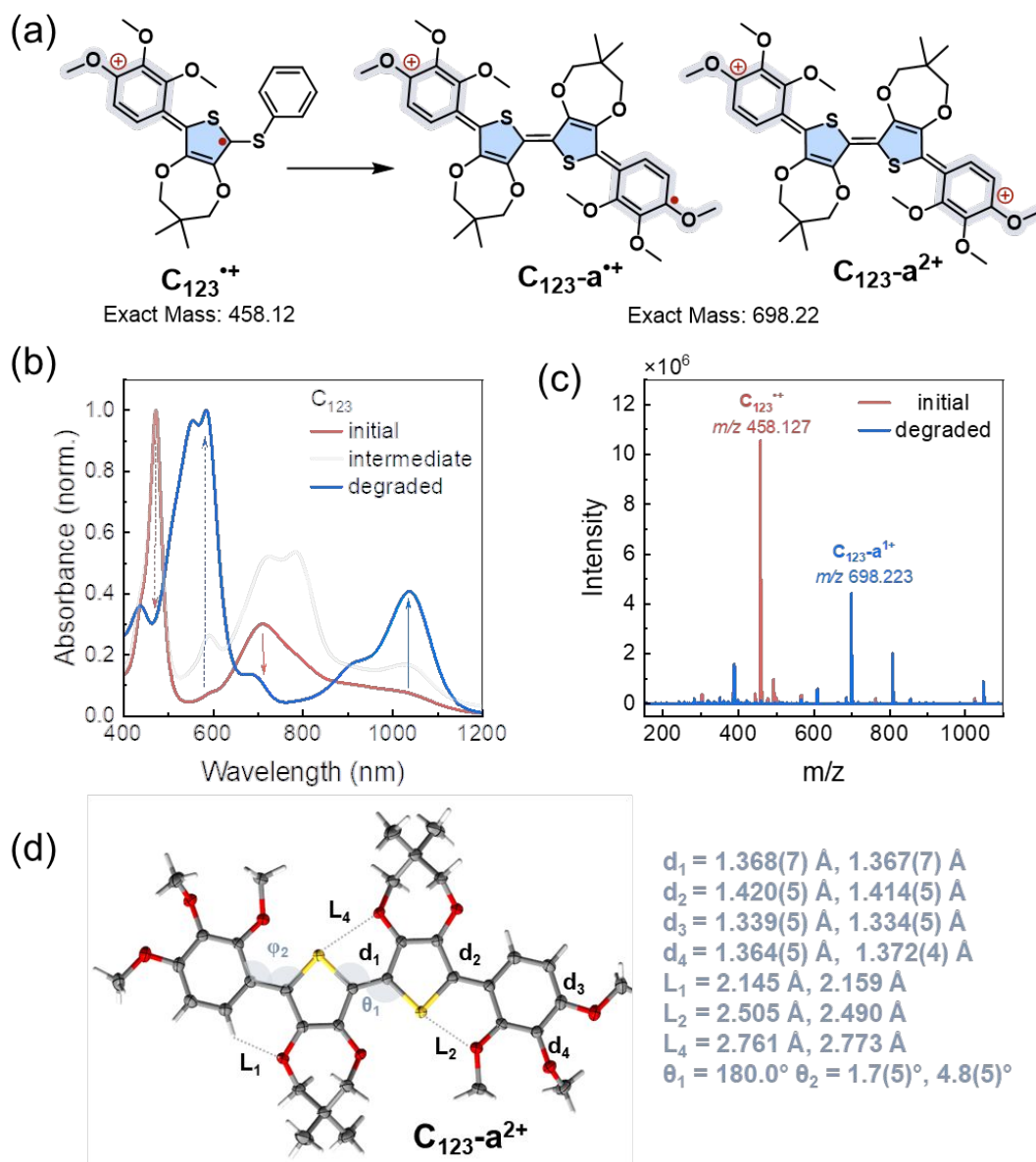


Figure S18 (a) Degradation of C_{123} radical cations, (b) Absorbance spectra showing evolution of decomposition products, (c) Mass spectra of doped C_{123} solutions before and after decomposition, (d) Structure of $C_{123}-a^{2+}$ from crystallographic data.

11. Mass spectrometric analyses of degradation products

Chemically-oxidized solutions of conjugated small molecules (1 mM in dichloromethane + 1.5 eq of AgSbF_6 oxidant) were stirred in the glovebox for 30 minutes, and filtered using a 0.45 micron plastic syringe filter. For the initial measurement, the filtered stock solutions were diluted 10 times using anhydrous DCM, and analyzed using the ESI-MS within 2 hours of doping. The filtered stock solutions were diluted and tested again after 24 hrs.

The results analyzed below indicate the formation of several types of degradation products over time.

i) C_1^{+} degradation

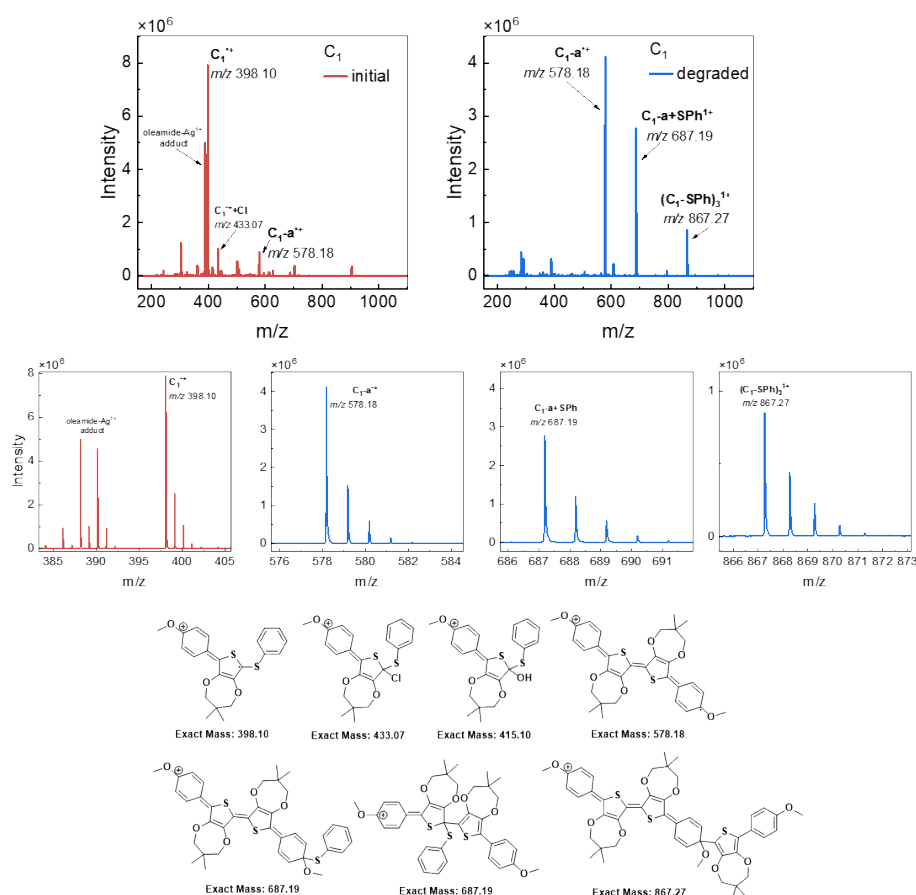


Figure S19: Mass spectra and predicted molecular structures for C_1 degradation

Initially, doped C_1 solution mainly consists of C_1^{+} (m/z 398.1) and its chloro (m/z 433.07) and hydroxy (m/z 415.10) adducts. Traces of $\text{C}_1\text{-a}^{+}$ dimer radical cation (m/z 578.18) are also observed in the initial sample. Over time, the radical cation completely disappears and the degraded dimer ($\text{C}_1\text{-a}^{+}$) and its thiophenyl adduct (m/z 687.19) are observed as positively charged molecules. A trimer of C_1 that has lost their SPh end capping groups is detected at m/z 867.27.

ii) C_{13}^{+} degradation

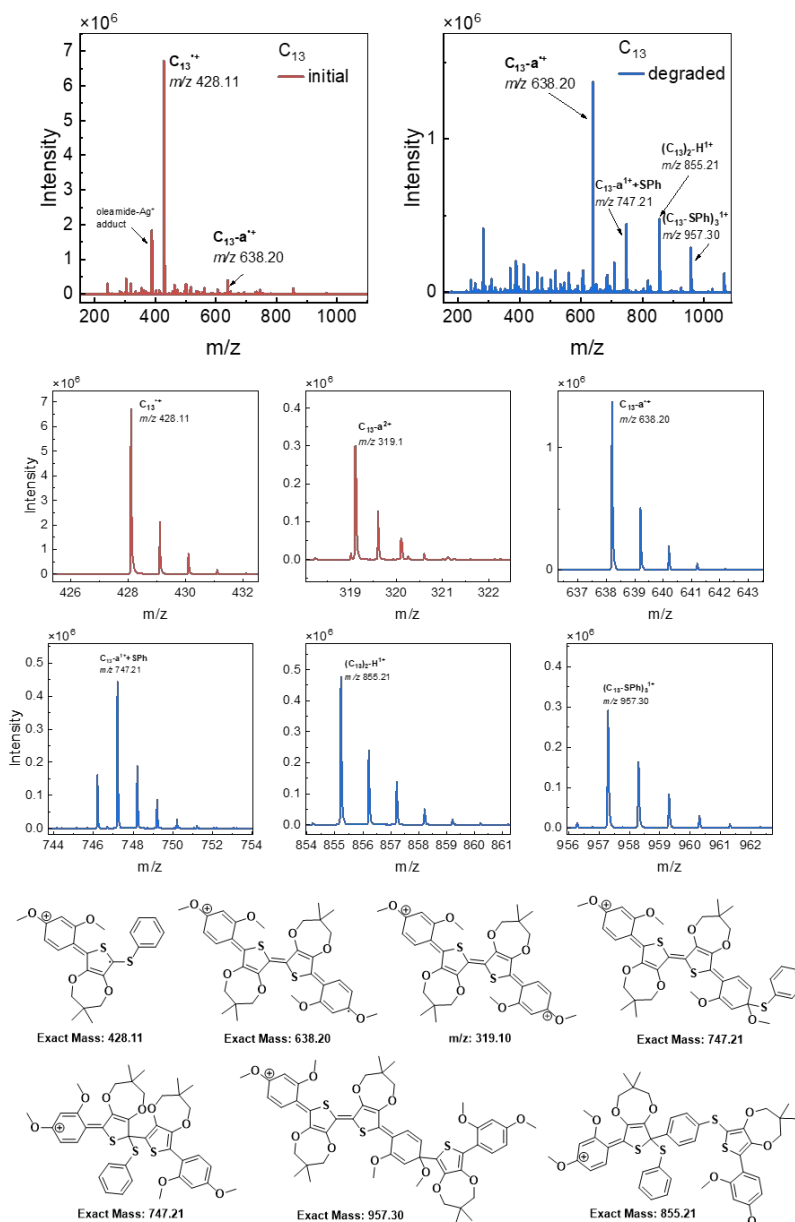


Figure S20: Mass spectra and predicted molecular structures for C_{13} degradation

Initially, doped C_{13} solution mainly consists of C_{13}^{+} (m/z 428.11) and traces of C_1-a^{+} dimer radical cation (m/z 638.20). The dimer dication $C_{13}-a^{2+}$ (m/z 319.1) can also be detected in the initial sample, where the peaks are separated by 0.5 amu confirming its +2 charge. Over time, the radical cation decreases, and the degraded dimer ($C_{13}-a^{+}$) dominates. Similar to C_1 , the thiophenyl adduct

(m/z 747.21) and trimer (m/z 957.30) are also observed. Another prominent peak at m/z 855.21 represents C_{133} dimer with the SPh groups intact.

iii) $C_{133}^{\cdot+}$ degradation

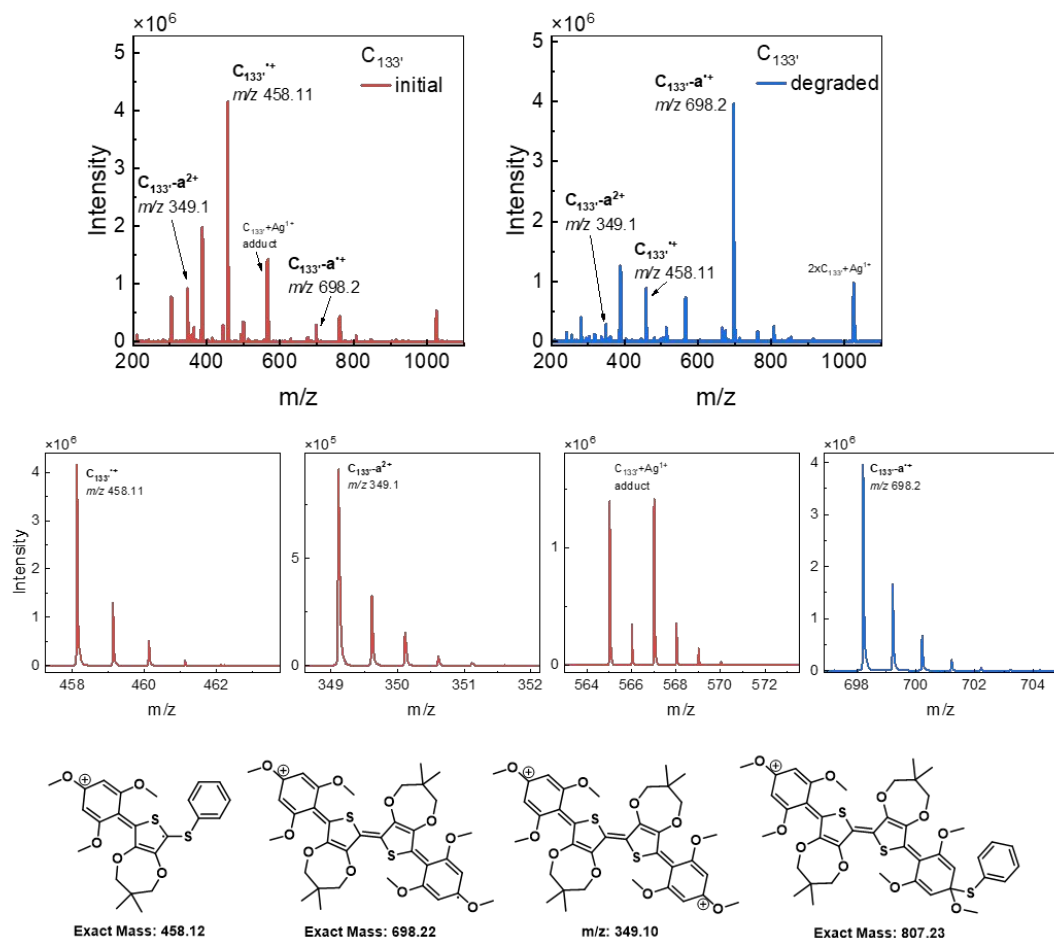


Figure S21: Mass spectra and predicted molecular structures for $C_{133}^{\cdot+}$ degradation.

Initially, doped $C_{133}^{\cdot+}$ solution consists of $C_{133}^{\cdot+}$ (m/z 458.12) and traces of $C_{133}^{\cdot+}$ dimer radical cation (m/z 698.22). The dimer dication $C_{133}^{\cdot+}$ (m/z 349.1) can also be detected in the initial sample, where the peaks are separated by 0.5 amu confirming its +2 charge. Although the radical cation decreases with time, it is still detected in the degraded sample, which is now dominated by the dimer radical cation ($C_{133}^{\cdot+}$). The presence $C_{133}^{\cdot+}$ adducts with Ag^+ indicate the presence of neutral $C_{133}^{\cdot+}$ in the doped mixture, showing the chemical doping with 1.5 eq of $AgSbF_6$ has not been efficient.

iv) $C_{123}^{\cdot+}$ degradation

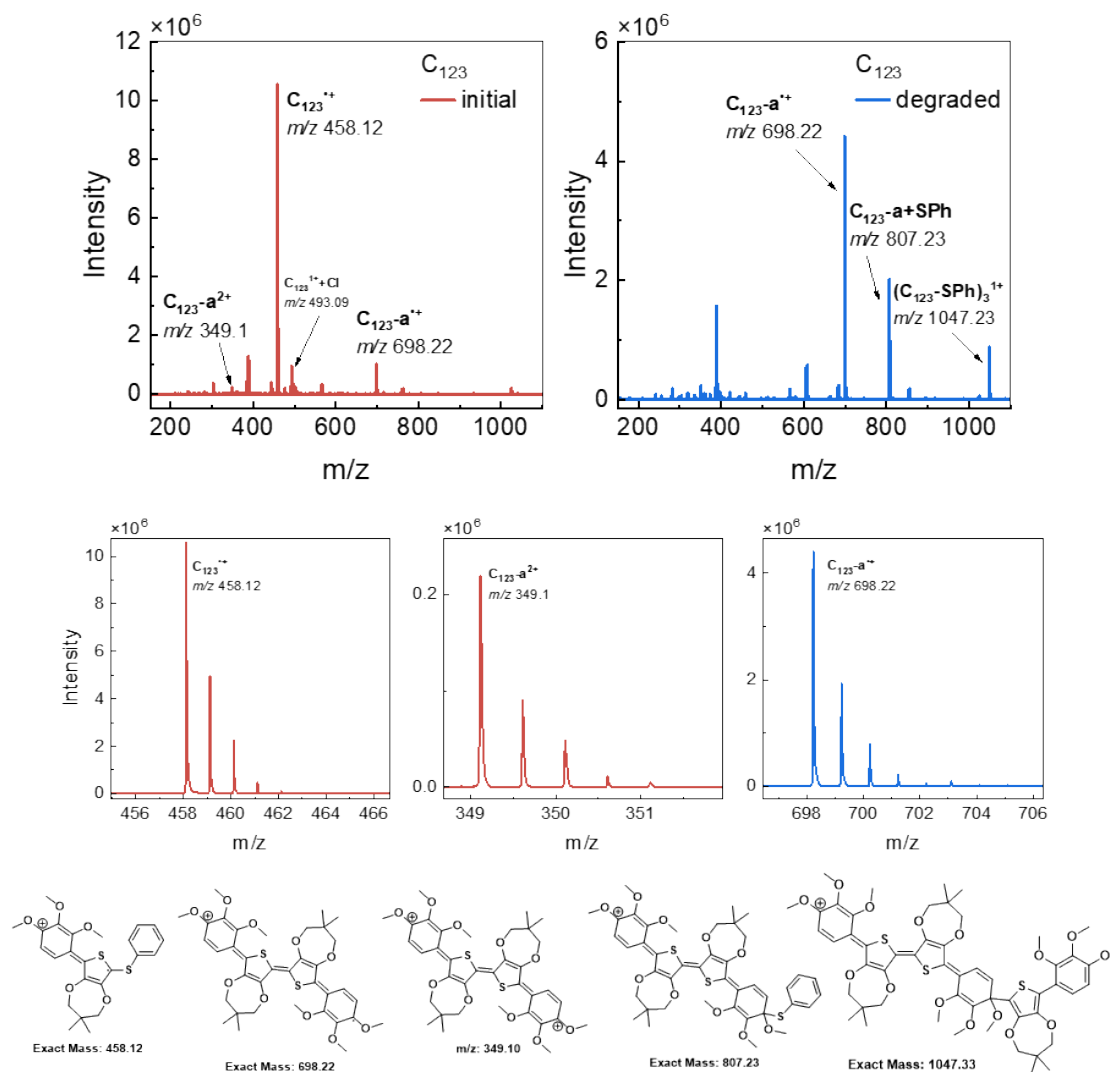


Figure S22: Mass spectra and predicted molecular structures for C_{123} degradation

Chemically doped C_{123} solution consists of the radical cation $C_{123}^{\cdot+}$ (m/z 458.12) and traces of the dimer radical cation $C_{123}-a^+$ (m/z 698.22) and dimer dication $C_{123}-a^{2+}$ (m/z 349.1). In the degraded samples are characterized by the familiar $C_{123}-a^+$, its SPh adduct (m/z 807.23) and the degraded trimer (m/z 1047.23).

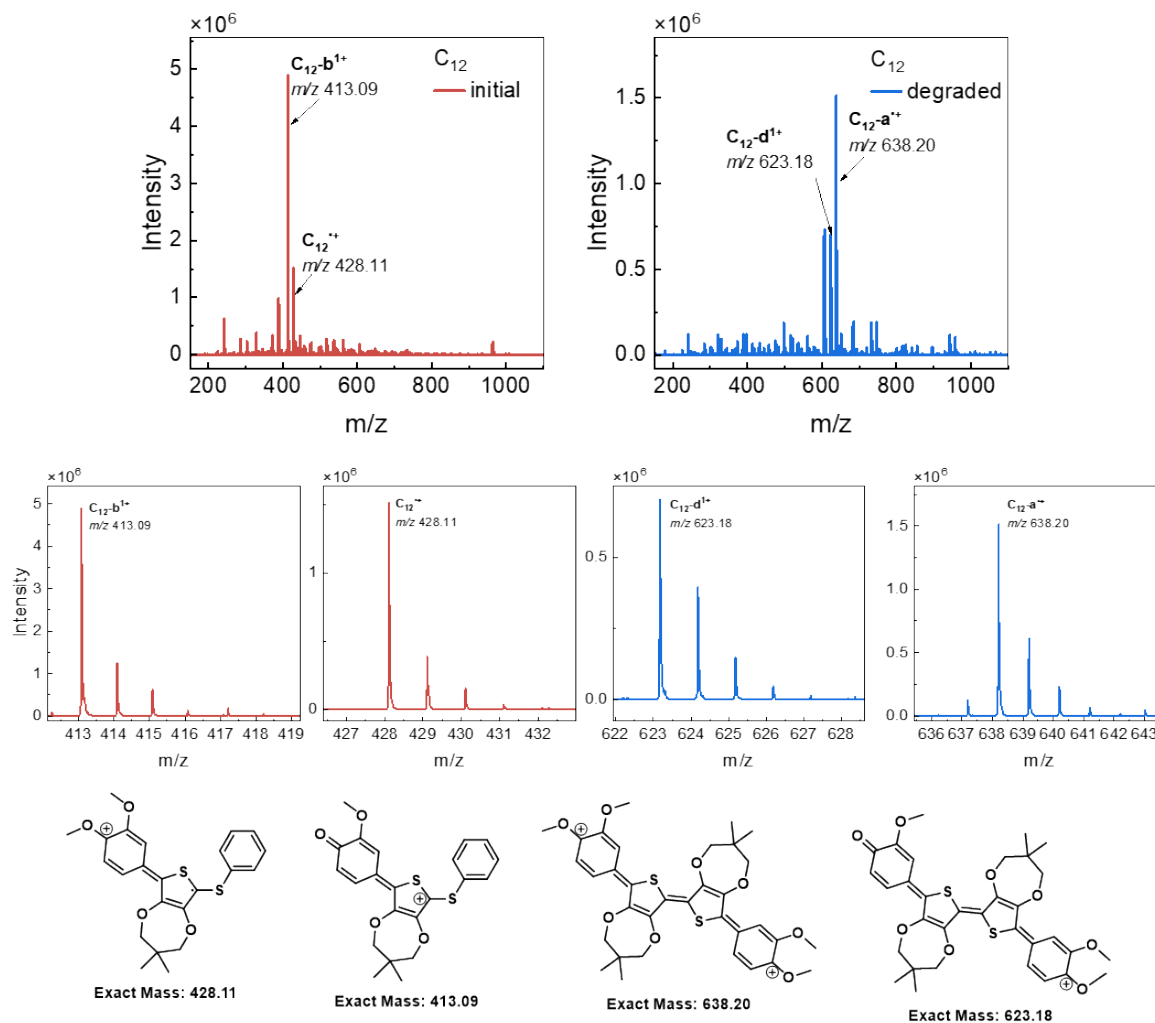
v) $C_{12}^{\cdot+}$ degradation

Figure S23: Mass spectra and predicted molecular structures for C_{12} degradation.

Doped C_{12} solutions have a prominent peak denoting a methyl loss from the original radical cation at m/z 413.09. This compound is named $C_{12}-b^{1+}$. The undegraded $C_{12}^{\cdot+}$ is also detected at m/z 428.11. In the degraded samples, both $C_{12}-a^{+}$ and its dealkylated version ($C_{12}-d^{1+}$, m/z 623.18) are present.

CID of m/z 606 at 30eV

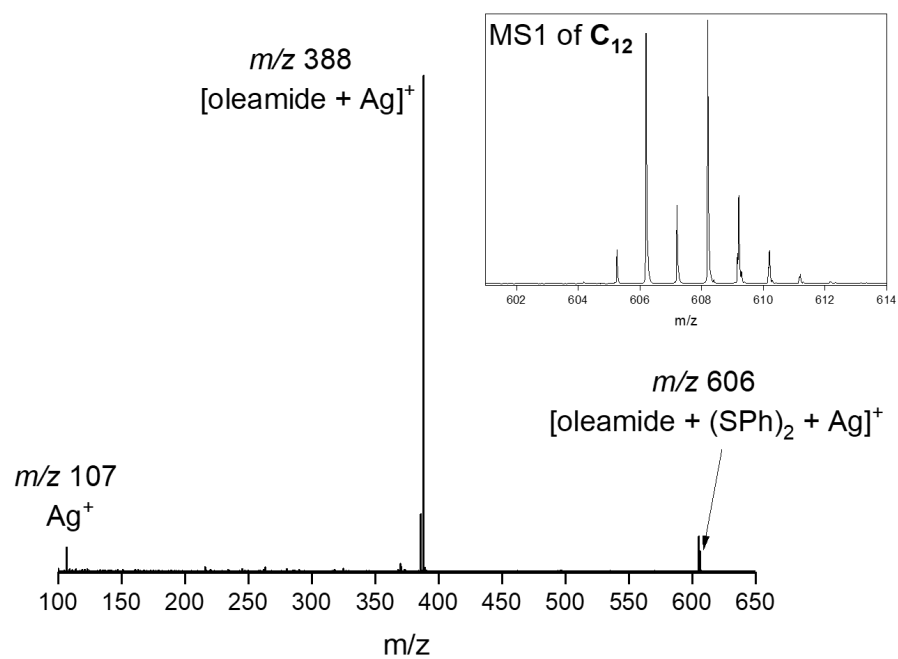
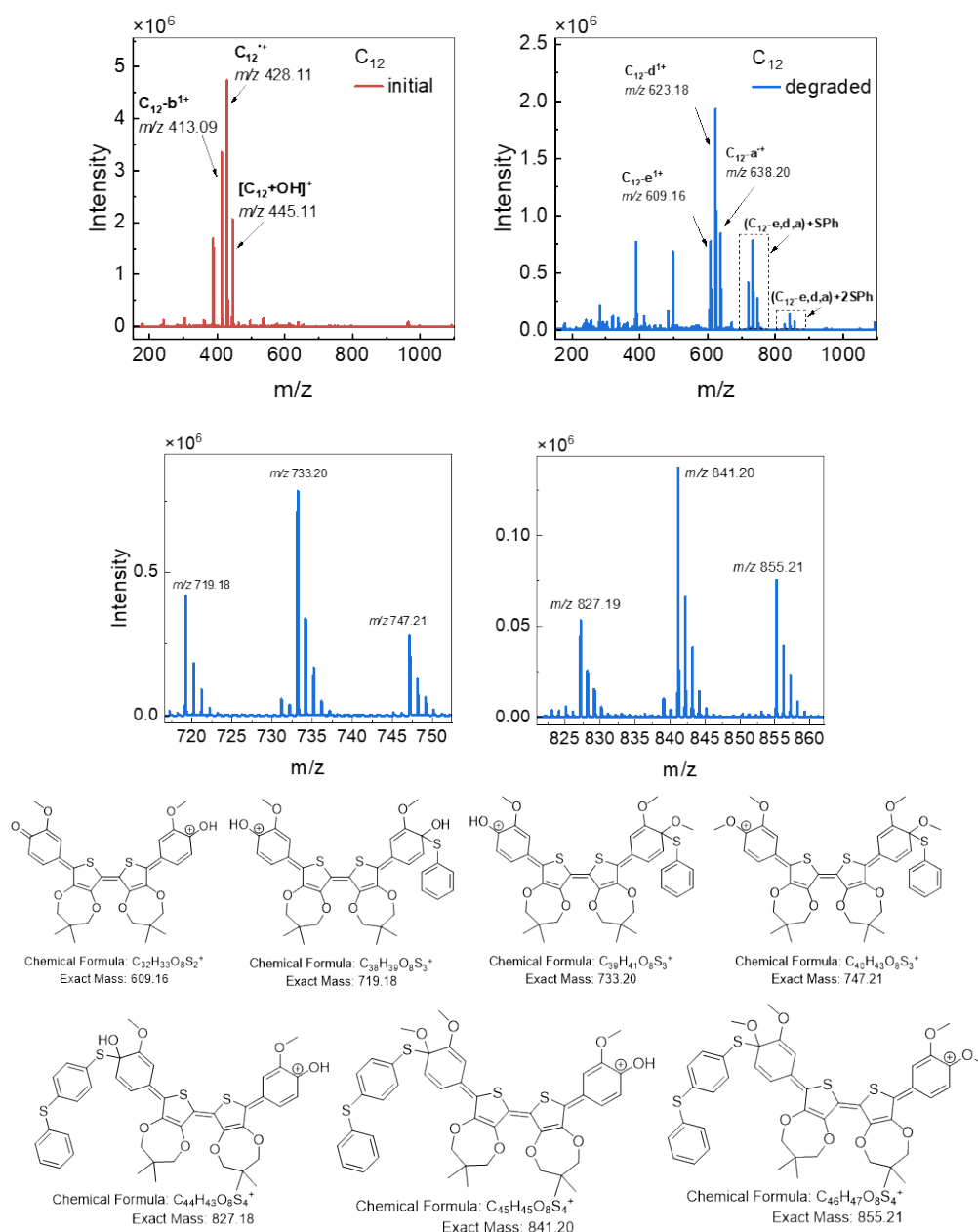


Figure S24 Collision Induced Dissociation (CID) mass spectra of P^* (m/z 606).

An array of degradation products for C_{12} can be observed when the doped solutions are exposed to trace amounts of water:



In addition to the compounds discussed in the previous section, the hydroxylated C_{12}^{++} adduct is detected at m/z 445.11 in the initial stages. In the degraded mixture, the dimer is present in three forms; non-dealkylated (m/z 638.20), once-dealkylated (m/z 623.18) and twice-dealkylated (m/z 609.16). The thiophenyl and dithiophenyl adducts of the above three forms are also observed. Although the above chemical structures are proposed with covalent links, they may as well be strongly bound aggregates formed between the dimers and thiophenyl compounds.

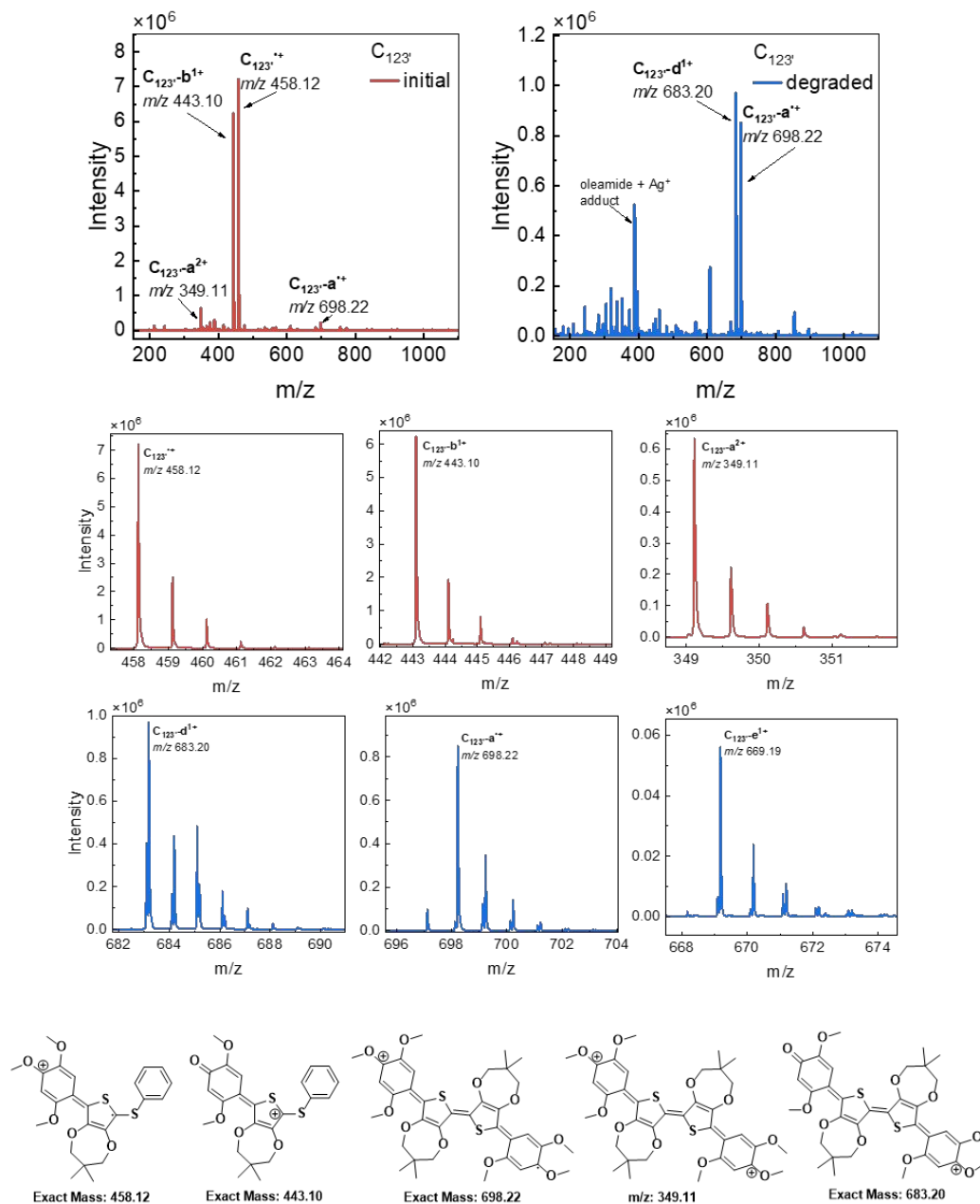
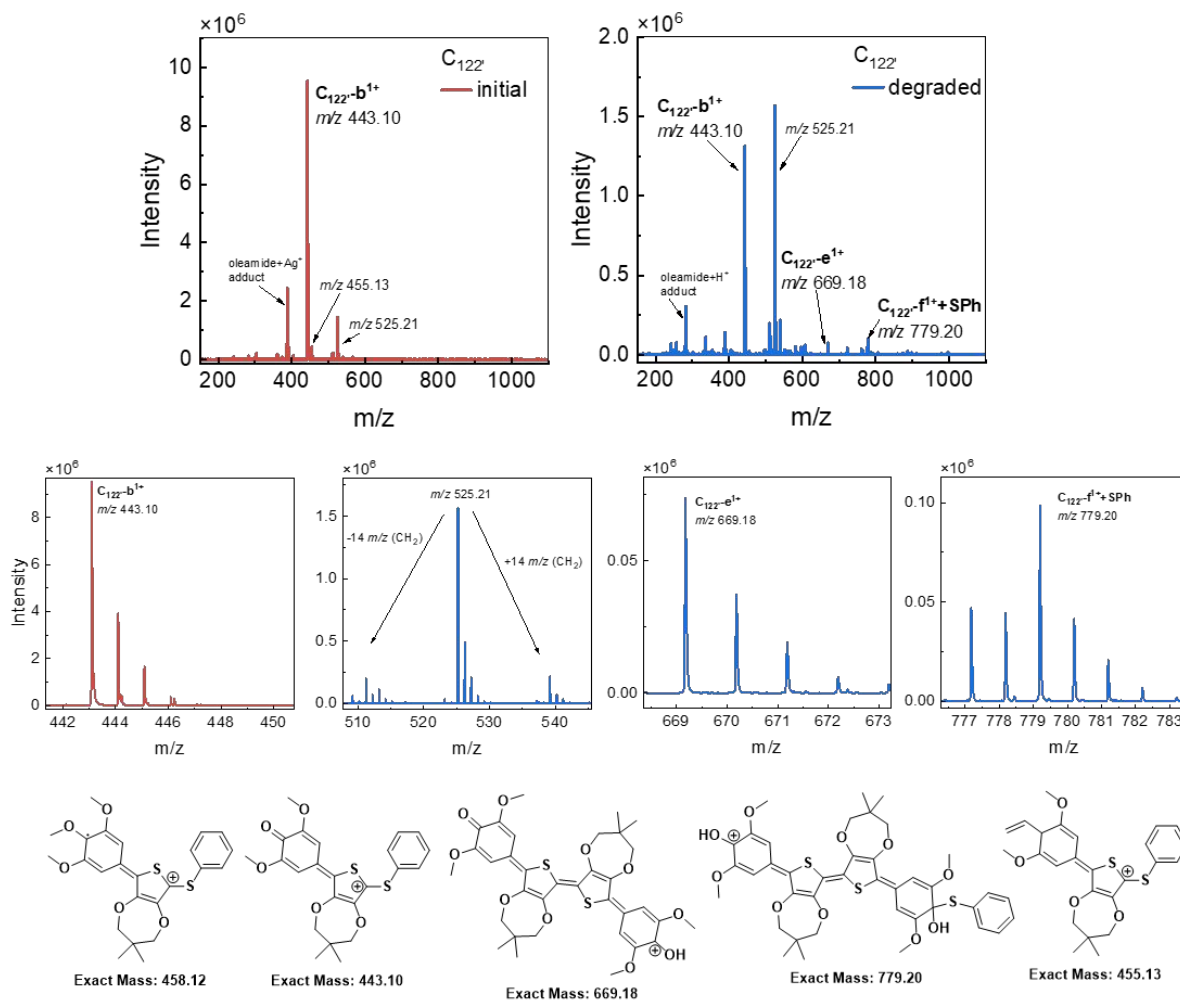
vi) $C_{123}^{\cdot+}$ degradation

Figure S25: Mass spectra and predicted molecular structures for $C_{123}^{\cdot+}$ degradation

The dealkylated form of the $C_{123}^{\cdot+}$ radical cation is detected at m/z 443.10 ($C_{123}^{\cdot+}-b^{1+}$) in the initial solution. The dimer dication $C_{123}^{\cdot+}-a^{2+}$ (m/z 349.11) is also visible. In the degraded mixture the dimer radical cation ($C_{123}^{\cdot+}-a^{+}$, m/z 698.22) is present with its dealkylated form ($C_{123}^{\cdot+}-d^{1+}$, m/z 638.20) and a trace of the twice-dealkylated product ($C_{123}^{\cdot+}-e^{1+}$, m/z 669.188) is observed.

vii) $C_{122}^{\cdot+}$ degradation**Figure S26:** Mass spectra and predicted molecular structures for $C_{122}^{\cdot+}$ degradation

The $C_{122}^{\cdot+}$ radical cation cannot be detected using HR-MS. Only its dealkylated product $C_{122}^{\cdot+}$ is seen at m/z 433.10. Two other species at m/z 455.13 and 525.21 are also included in the mass spectrum, however their structures remain unresolved. The intensity of the $C_{122}^{\cdot+}$ peak decreases with time. New peaks emerge at m/z 669.18 and 779.20, representing dimerized products of dealkylated $C_{122}^{\cdot+}$. We assume the formation of CH_2 radicals during the dealkylation process, which gives rise to various byproducts that are separated by m/z 14 units.

12. Comparison of degradation products as detected by HR-MS

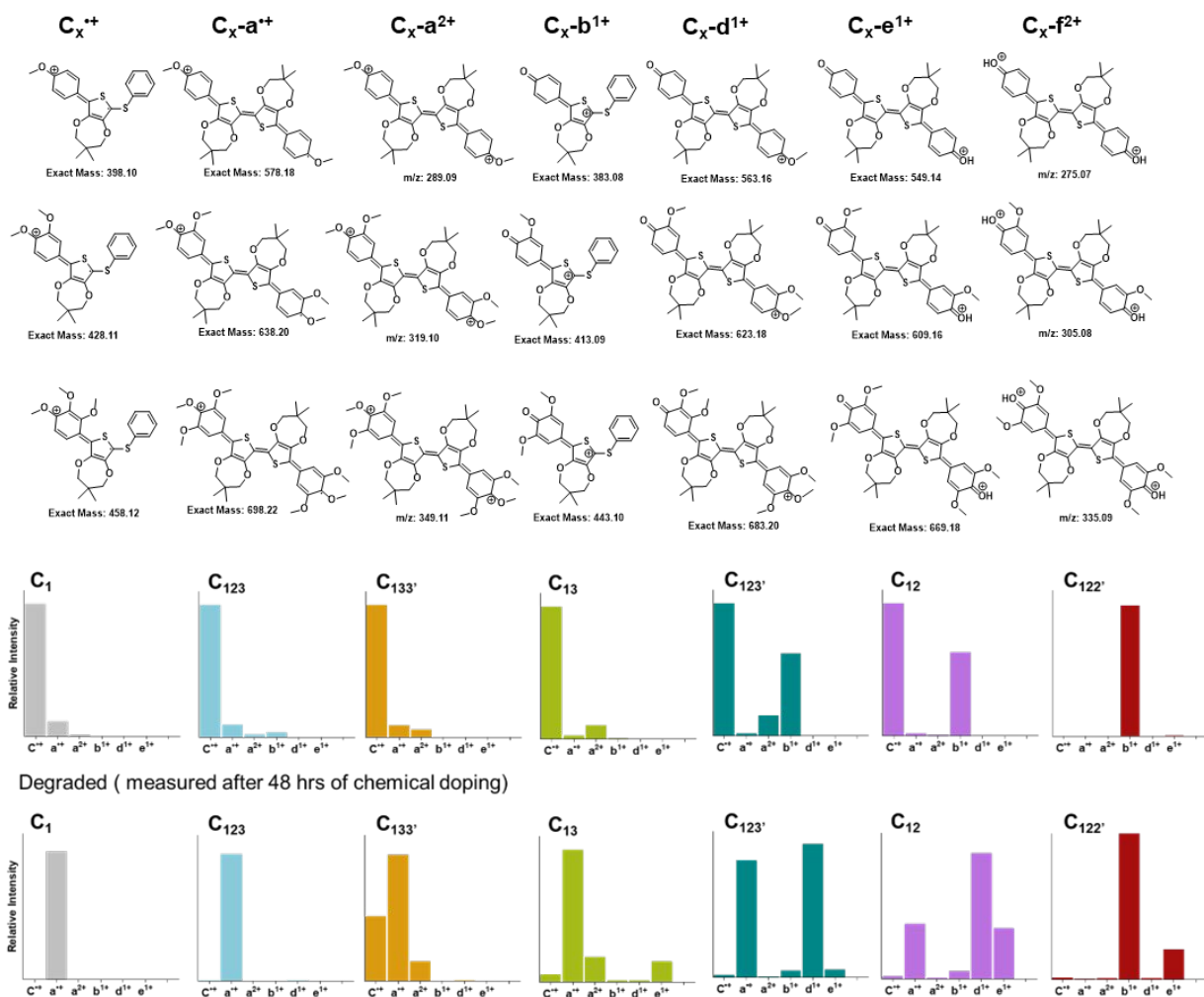


Figure S27: Expected m/z values for all possible degradation products and the relative intensity for each peak in the ESI-MS, calculated with respect to the radical cation.

13. Absorption spectra of Ph-ProDOT molecules with different end-capping groups

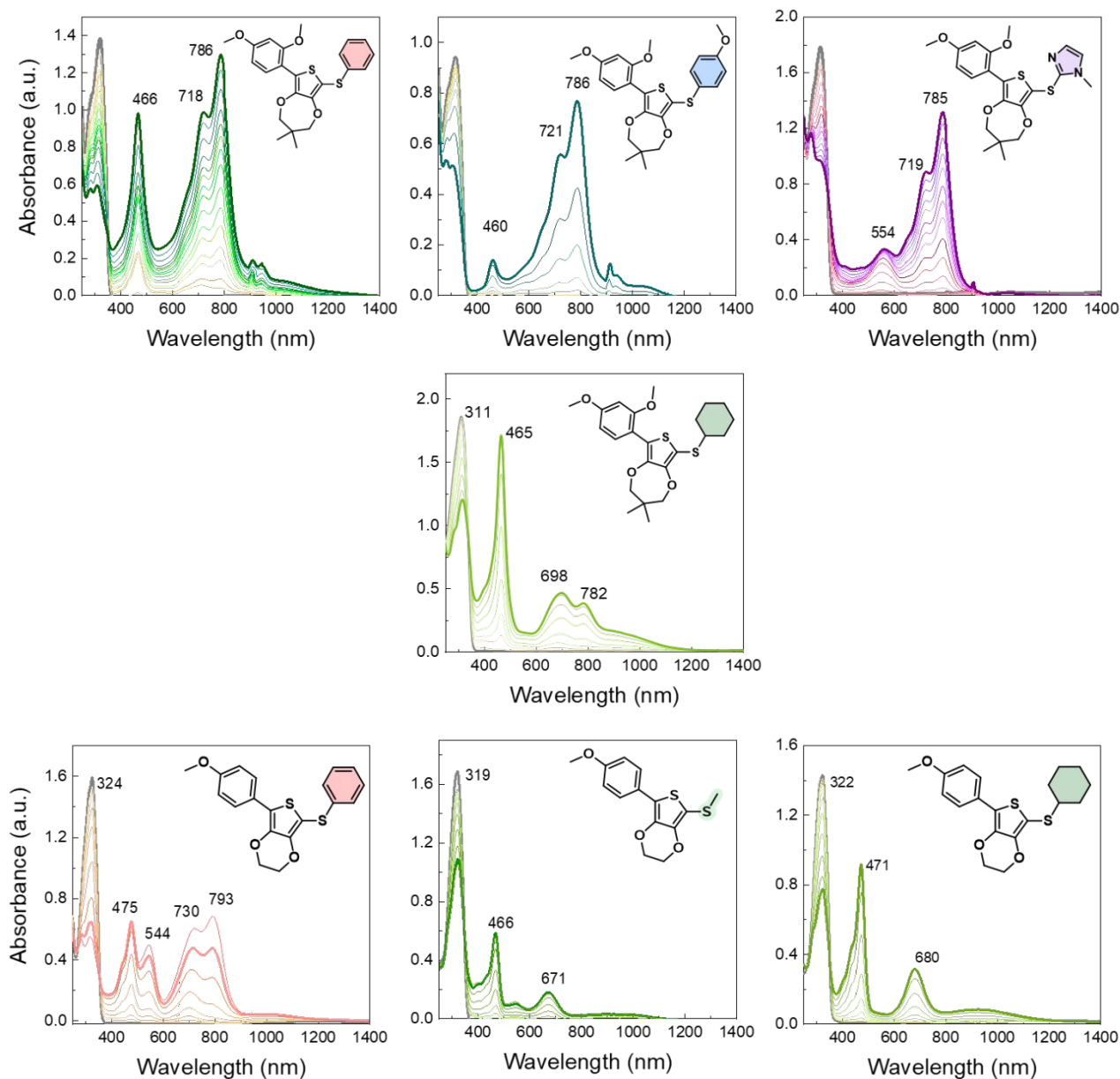


Figure S28 Absorbance changes measured during in-situ electrochemical doping of Ph-dioxothiophene compounds with different S-end capping groups. Electrolyte: 0.2 M LiTFSI prepared in propylene carbonate.

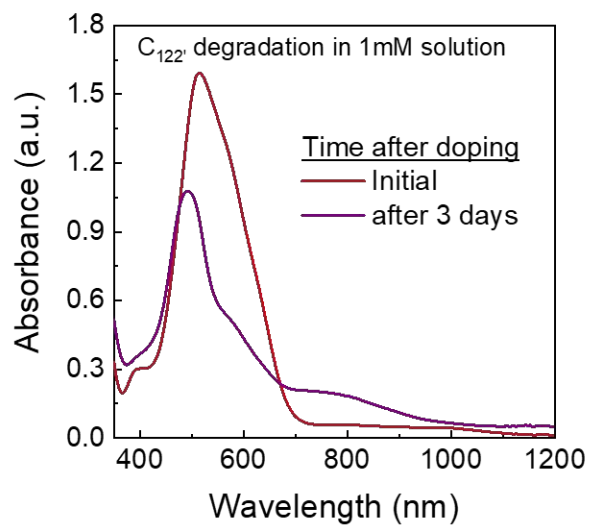
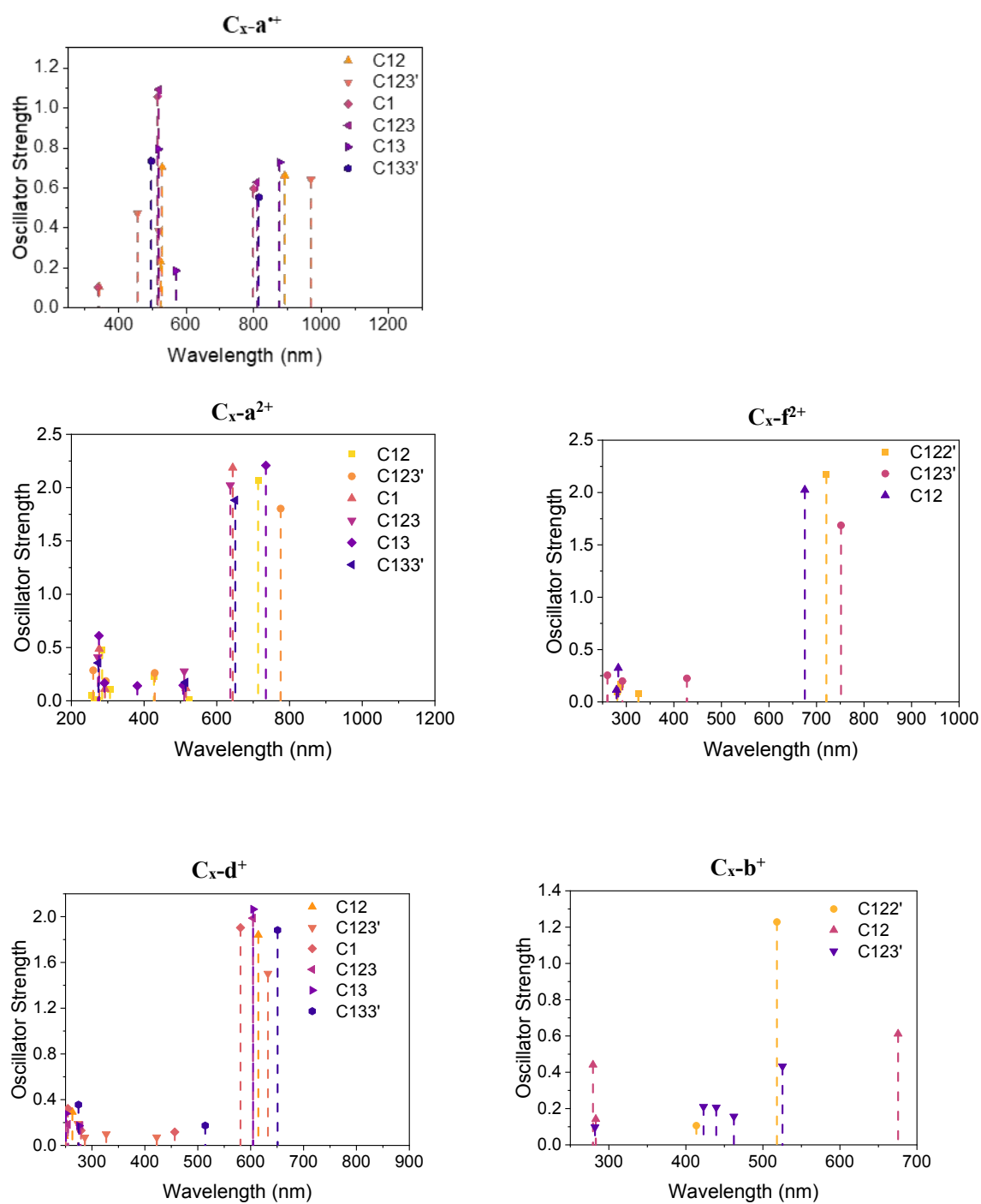


Figure S29 Absorbance changes over time of a chemically-doped C_{122}' solution.

Table S7 $\langle S^2 \rangle$ values of the radical species, calculated before and after annihilation.

		$\langle S^2 \rangle$ (Before annihilation)	$\langle S^2 \rangle$ (After annihilation)
C_1	$C_1^{\bullet+}$	0.7843	0.7506
	$C_1\text{-}a^{\bullet+}$	0.8065	0.7521
C_{12}	$C_{12}^{\bullet+}$	0.7741	0.7504
	$C_{12}\text{-}a^{\bullet+}$	0.8128	0.7526
C_{13}	$C_{13}^{\bullet+}$	0.7789	0.7504
	$C_{13}\text{-}a^{\bullet+}$	0.8037	0.7517
C_{123}	$C_{123}^{\bullet+}$	0.7817	0.7505
	$C_{123}\text{-}a^{\bullet+}$	0.8077	0.7522
C_{133}'	$C_{133}'^{\bullet+}$	0.7736	0.7503
	$C_{133}'\text{-}a^{\bullet+}$	0.7959	0.7512
C_{123}'	$C_{123}'^{\bullet+}$	0.7911	0.7509
	$C_{123}'\text{-}a^{\bullet+}$	0.8137	0.7525
C_{122}'	$C_{122}'^{\bullet+}$	0.7931	0.7506

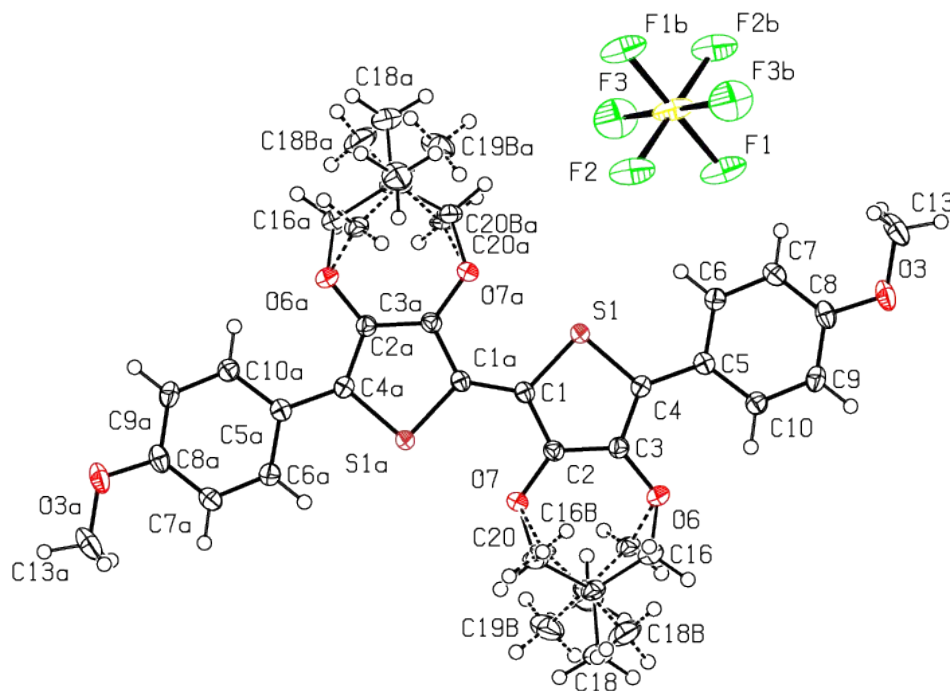
14. Comparison of TD-DFT calculated absorption peaks



15. Degradation Products – Crystal structures

C1 dimer radical cation ($C_1\text{-a}^{\bullet+}$)

Polymorph 1

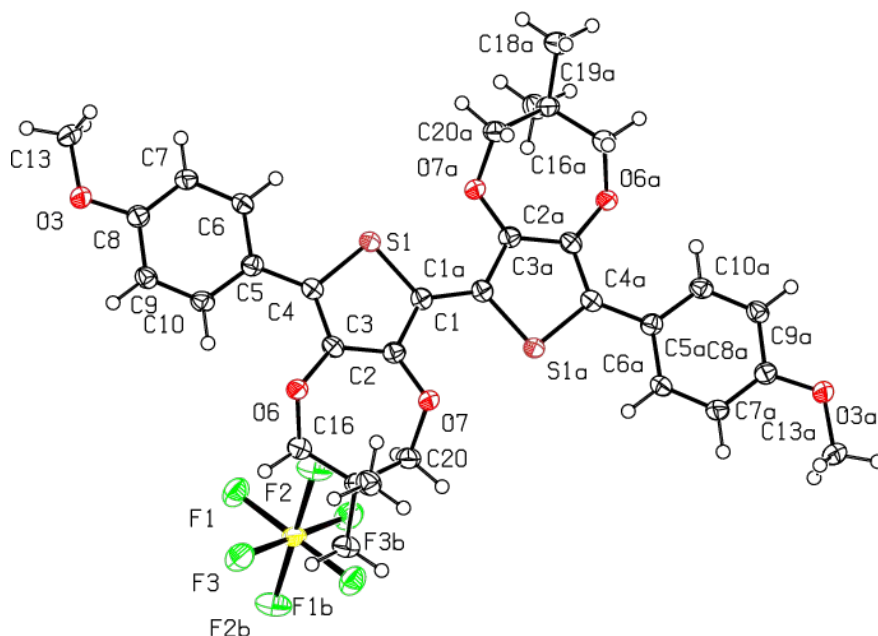


The 1,4 dioxepin ring was found to be disordered. The two disordered moieties were restrained to have similar geometries. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.752(5) to 0.248(5).

Empirical formula	$C_{32}H_{34}F_6O_6S_2Sb$
Formula weight	814.46
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	12.8425(4)
b [Å]	6.8164(2)
c [Å]	19.1720(5)
α [°]	90
β [°]	101.094(2)
γ [°]	90

Volume [$\text{\AA}^3$]	1646.95(8)
<i>Z</i>	2
ρ_{calc} [gcm^{-3}]	1.642
μ [mm^{-1}]	8.519
<i>F</i> (000)	822
Crystal size [mm^3]	0.080×0.090×0.150
Crystal colour	rod
Crystal shape	dark blue
Radiation	$\text{CuK}\alpha$ ($\lambda=1.54178 \text{ \AA}$)
2 θ range [$^\circ$]	7.01 to 159.31 (0.78 $\text{\AA}$)
Index ranges	$-16 \leq h \leq 15$ $-8 \leq k \leq 6$ $-22 \leq l \leq 24$
Reflections collected	11820
Independent reflections	3388 $R_{\text{int}} = 0.0324$ $R_{\text{sigma}} = 0.0324$
Completeness to $\theta = 67.679^\circ$	99.4 %
Data / Restraints / Parameters	3388 / 154 / 265
Goodness-of-fit on F^2	1.076
Final <i>R</i> indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0279$ $wR_2 = 0.0720$
Final <i>R</i> indexes [all data]	$R_1 = 0.0294$ $wR_2 = 0.0732$
Largest peak/hole [$\text{e}\text{\AA}^{-3}$]	0.60/−0.48

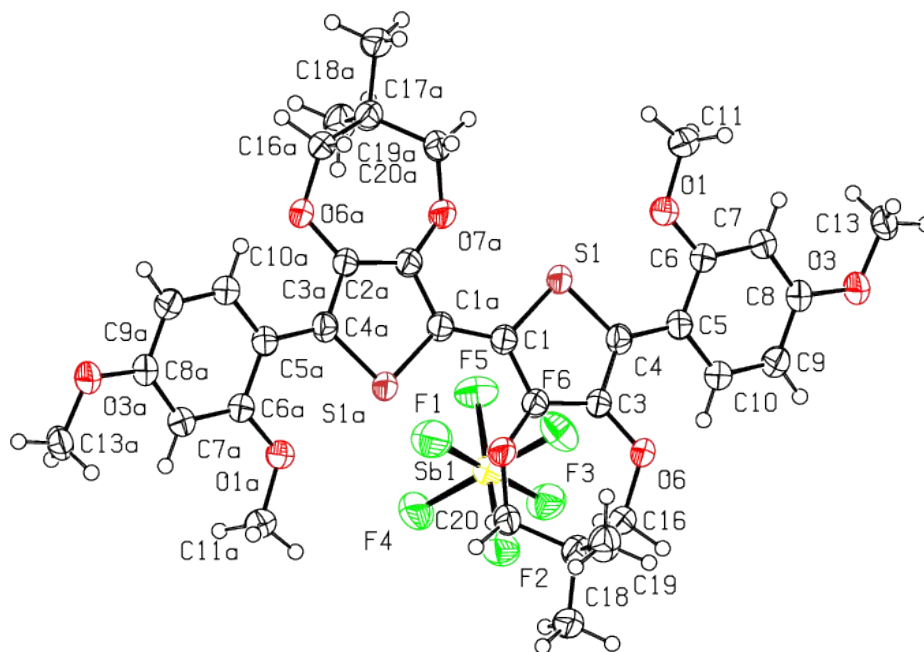
Polymorph 2



Empirical formula	C ₃₂ H ₃₄ F ₆ O ₆ S ₂ Sb
Formula weight	814.46
Temperature [K]	150(2)
Crystal system	triclinic
Space group (number)	<i>P</i> $\bar{1}$ (2)
<i>a</i> [Å]	6.4190(3)
<i>b</i> [Å]	10.7976(4)
<i>c</i> [Å]	12.6498(5)
α [°]	93.340(2)
β [°]	98.998(2)
γ [°]	105.246(2)
Volume [Å ³]	830.93(6)
<i>Z</i>	1
ρ_{calc} [gcm ^{−3}]	1.628
μ [mm ^{−1}]	8.442
<i>F</i> (000)	411
Crystal size [mm ³]	0.020×0.040×0.330
Crystal colour	black
Crystal shape	needle
Radiation	CuK α (λ =1.54178 Å)
2 θ range [°]	7.11 to 159.06 (0.78 Å)
Index ranges	−6 ≤ <i>h</i> ≤ 7 −13 ≤ <i>k</i> ≤ 12 −16 ≤ <i>l</i> ≤ 15
Reflections collected	8247

Independent reflections	3245 $R_{\text{int}} = 0.0445$ $R_{\text{sigma}} = 0.0431$
Completeness to $\theta = 67.679^\circ$	97.2 %
Data / Restraints / Parameters	3245 / 0 / 217
Goodness-of-fit on F^2	1.065
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0307$ $wR_2 = 0.0690$
Final R indexes [all data]	$R_1 = 0.0347$ $wR_2 = 0.0710$
Largest peak/hole [$\text{e}\text{\AA}^{-3}$]	0.56/−0.53

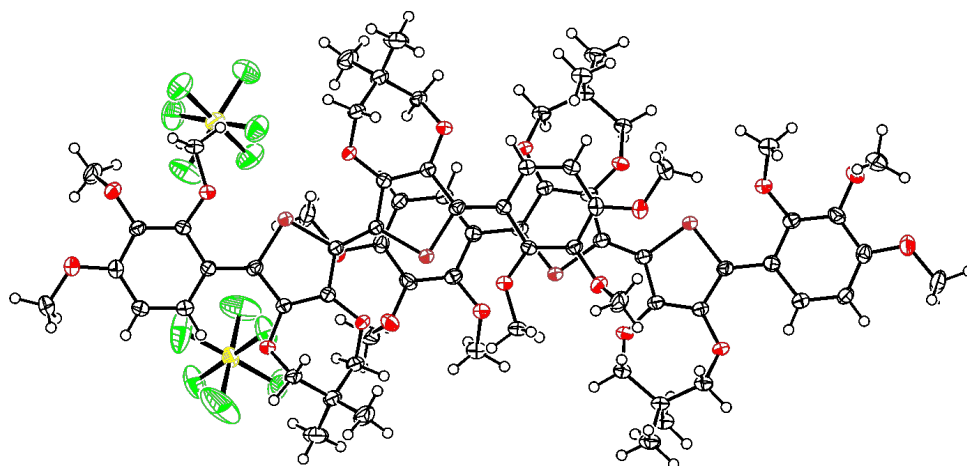
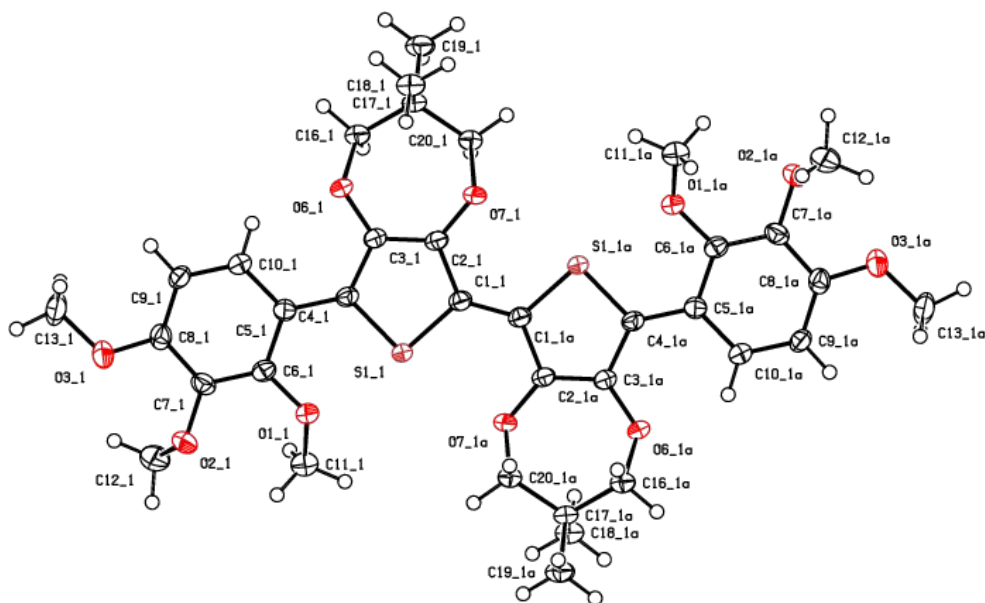
C₁₃ dimer dication (C₁₃-a²⁺)



Empirical formula	C ₃₄ H ₃₈ F ₁₂ O ₈ S ₂ Sb ₂
Formula weight	1110.26
Temperature [K]	150(2)
Crystal system	triclinic
Space group (number)	<i>P</i> $\bar{1}$ (2)
<i>a</i> [Å]	8.7107(3)
<i>b</i> [Å]	10.7527(5)
<i>c</i> [Å]	11.1875(4)
α [°]	103.493(2)
β [°]	97.147(2)
γ [°]	104.143(2)
Volume [Å ³]	969.59(7)
<i>Z</i>	1
ρ_{calc} [gcm ⁻³]	1.901
μ [mm ⁻¹]	13.039
<i>F</i> (000)	548
Crystal size [mm ³]	0.030×0.300×0.400
Crystal colour	black
Crystal shape	plate
Radiation	CuK α (λ =1.54178 Å)
2 θ range [°]	10.32 to 159.05 (0.78 Å)
Index ranges	−11 ≤ <i>h</i> ≤ 11 −13 ≤ <i>k</i> ≤ 13 −14 ≤ <i>l</i> ≤ 14
Reflections collected	36319

Independent reflections	4160 $R_{\text{int}} = 0.0874$ $R_{\text{sigma}} = 0.0664$
Completeness to $\theta = 67.679^\circ$	99.3 %
Data / Restraints / Parameters	4160 / 0 / 266
Goodness-of-fit on F^2	1.130
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0439$ $wR_2 = 0.1249$
Final R indexes [all data]	$R_1 = 0.0443$ $wR_2 = 0.1255$
Largest peak/hole [$\text{e}\text{\AA}^{-3}$]	0.99/−1.53

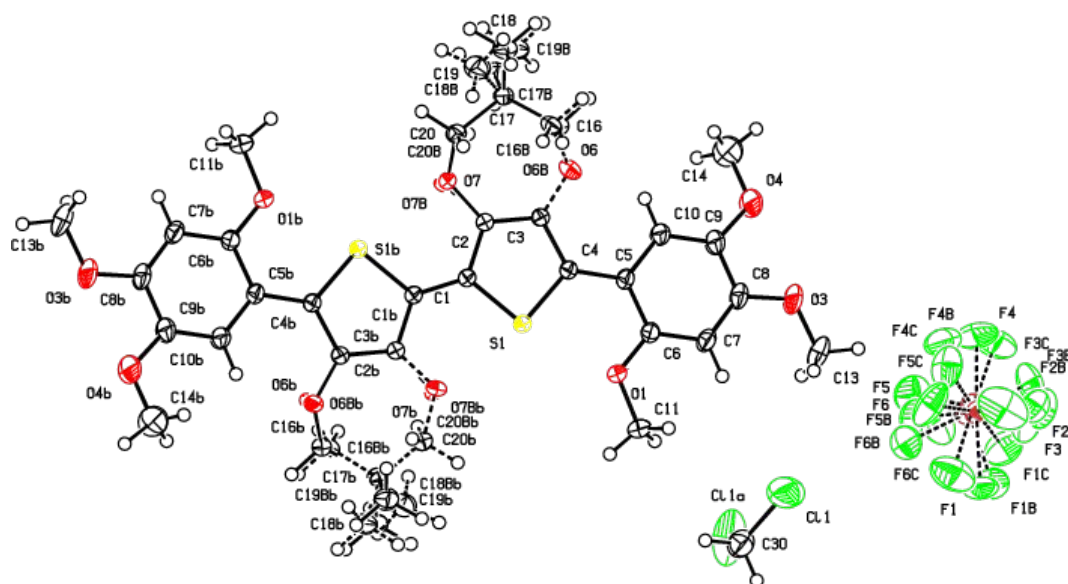
C₁₂₃ dimer dication (C₁₂₃-a²⁺)



Empirical formula	C ₃₆ H ₄₂ F ₁₂ O ₁₀ S ₂ Sb ₂
Formula weight	1170.31
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>c</i> (14)
<i>a</i> [Å]	16.9963(7)
<i>b</i> [Å]	22.1049(11)
<i>c</i> [Å]	12.1322(6)
α [°]	90
β [°]	108.646(2)

γ [°]	90
Volume [Å ³]	4318.8(4)
<i>Z</i>	4
ρ_{calc} [gcm ⁻³]	1.800
μ [mm ⁻¹]	11.783
<i>F</i> (000)	2320
Crystal size [mm ³]	0.030×0.070×0.310
Crystal colour	black
Crystal shape	blade
Radiation	CuK $_{\alpha}$ (λ =1.54178 Å)
2 θ range [°]	6.79 to 159.29 (0.78 Å)
Index ranges	−17 ≤ <i>h</i> ≤ 20 −22 ≤ <i>k</i> ≤ 27 −15 ≤ <i>l</i> ≤ 14
Reflections collected	29473
Independent reflections	8797 <i>R</i> _{int} = 0.0567 <i>R</i> _{sigma} = 0.0502
Completeness to θ = 67.679°	98.5 %
Data / Restraints / Parameters	8797 / 0 / 569
Goodness-of-fit on <i>F</i> ²	1.038
Final <i>R</i> indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0378 <i>wR</i> ₂ = 0.0803
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0559 <i>wR</i> ₂ = 0.0876
Largest peak/hole [eÅ ⁻³]	0.75/−0.80

C_{123'} dimer dication (C_{123'}-a²⁺)

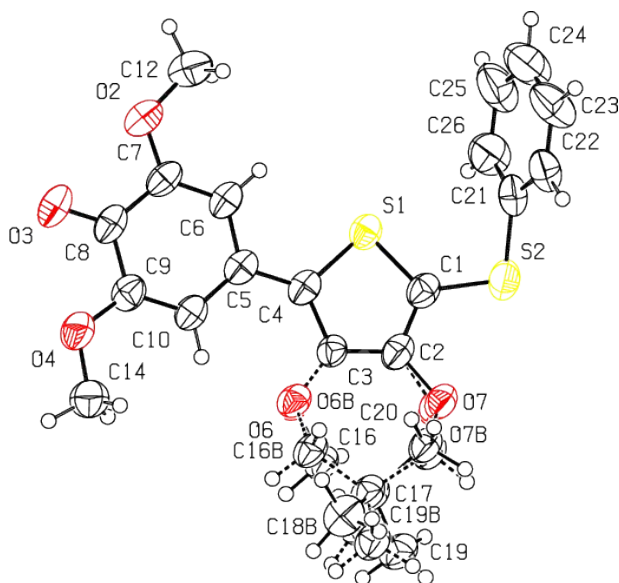


The dihydro-1,4-dioxepine ring was refined as disordered. The two disordered moieties were restrained to have similar geometries. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.857(4) to 0.143(4). The hexafluoroantimonate anion was refined as three-fold disordered. The three disordered moieties were restrained to have similar geometries. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.446(3) to 0.319(2) to 0.235(3).

Empirical formula	C ₃₇ H ₄₄ Cl ₂ F ₁₂ O ₁₀ S ₂ Sb ₂
Formula weight	1255.24
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	C2/c (15)
<i>a</i> [Å]	28.4590(15)
<i>b</i> [Å]	9.0120(5)
<i>c</i> [Å]	18.8151(10)
α [°]	90
β [°]	106.443(2)
γ [°]	90
Volume [Å ³]	4628.2(4)
<i>Z</i>	4
ρ_{calc} [gcm ⁻³]	1.801

μ [mm ⁻¹]	1.474
$F(000)$	2488
Crystal size [mm ³]	0.040×0.180×0.260
Crystal colour	brown
Crystal shape	plate
Radiation	MoK $_{\alpha}$ (λ =0.71073 Å)
2 θ range [°]	4.76 to 61.10 (0.70 Å)
Index ranges	-40 ≤ h ≤ 40 -12 ≤ k ≤ 12 -26 ≤ l ≤ 26
Reflections collected	62854
Independent reflections	7079 $R_{\text{int}} = 0.0386$ $R_{\text{sigma}} = 0.0199$
Completeness to $\theta = 25.242^{\circ}$	99.9 %
Data / Restraints / Parameters	7079 / 780 / 494
Goodness-of-fit on F^2	1.021
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0314$ $wR_2 = 0.0784$
Final R indexes [all data]	$R_1 = 0.0439$ $wR_2 = 0.0865$
Largest peak/hole [eÅ ⁻³]	0.75/-0.99

C₁₂₂⁺ cation (C₁₂₂-b¹⁺)

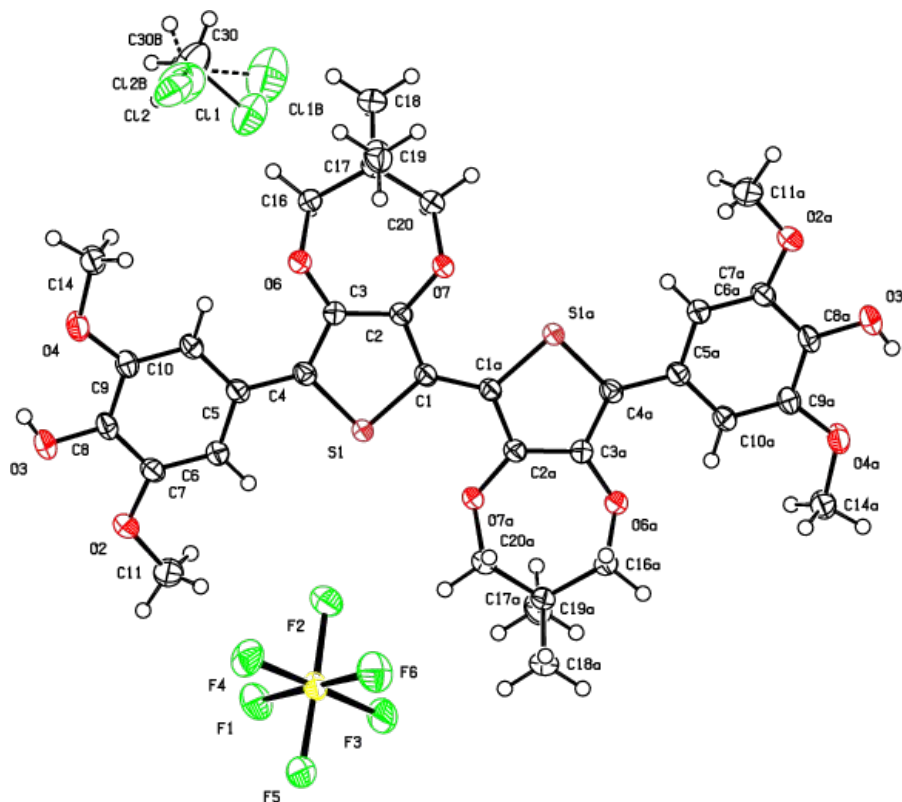


The 2,2-dimethylpropylene unit was refined as disordered by a pseudo- mirror operation. The disorder extends to the two terminal oxygen atoms. The disordered moieties were restrained to have similar geometries. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.609(8) to 0.391(8). The dichlorobenzene solvate molecule was refined as disordered by a slight rotation. The two disordered moieties were restrained to have similar geometries. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.730(4) to 0.270(4). The SbF₆ anion was refined as disordered by a swinging motion. The two disordered moieties were restrained to have similar geometries. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.680(7) to 0.320(7).

Empirical formula	C ₂₉ H ₂₇ Cl ₂ F ₆ O ₅ S ₂ Sb
Formula weight	826.27
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>c</i> (14)
<i>a</i> [Å]	9.944(4)
<i>b</i> [Å]	24.191(12)
<i>c</i> [Å]	14.0302(15)
α [°]	90
β [°]	104.954(18)

γ [°]	90
Volume [Å ³]	3261(2)
<i>Z</i>	4
ρ_{calc} [gcm ⁻³]	1.683
μ [mm ⁻¹]	1.210
<i>F</i> (000)	1648
Crystal size [mm ³]	0.050×0.150×0.450
Crystal colour	black
Crystal shape	plate
Radiation	MoK α (λ =0.71073 Å)
2 θ range [°]	4.51 to 56.74 (0.75 Å)
Index ranges	−13 ≤ <i>h</i> ≤ 13 −32 ≤ <i>k</i> ≤ 32 −18 ≤ <i>l</i> ≤ 18
Reflections collected	47282
Independent reflections	8096 $R_{\text{int}} = 0.0584$ $R_{\text{sigma}} = 0.0395$
Completeness to $\theta = 25.242^\circ$	99.4 %
Data / Restraints / Parameters	8096 / 671 / 613
Goodness-of-fit on F^2	1.120
Final <i>R</i> indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0956$ $wR_2 = 0.1934$
Final <i>R</i> indexes [all data]	$R_1 = 0.1168$ $wR_2 = 0.2028$
Largest peak/hole [eÅ ⁻³]	0.71/−0.72

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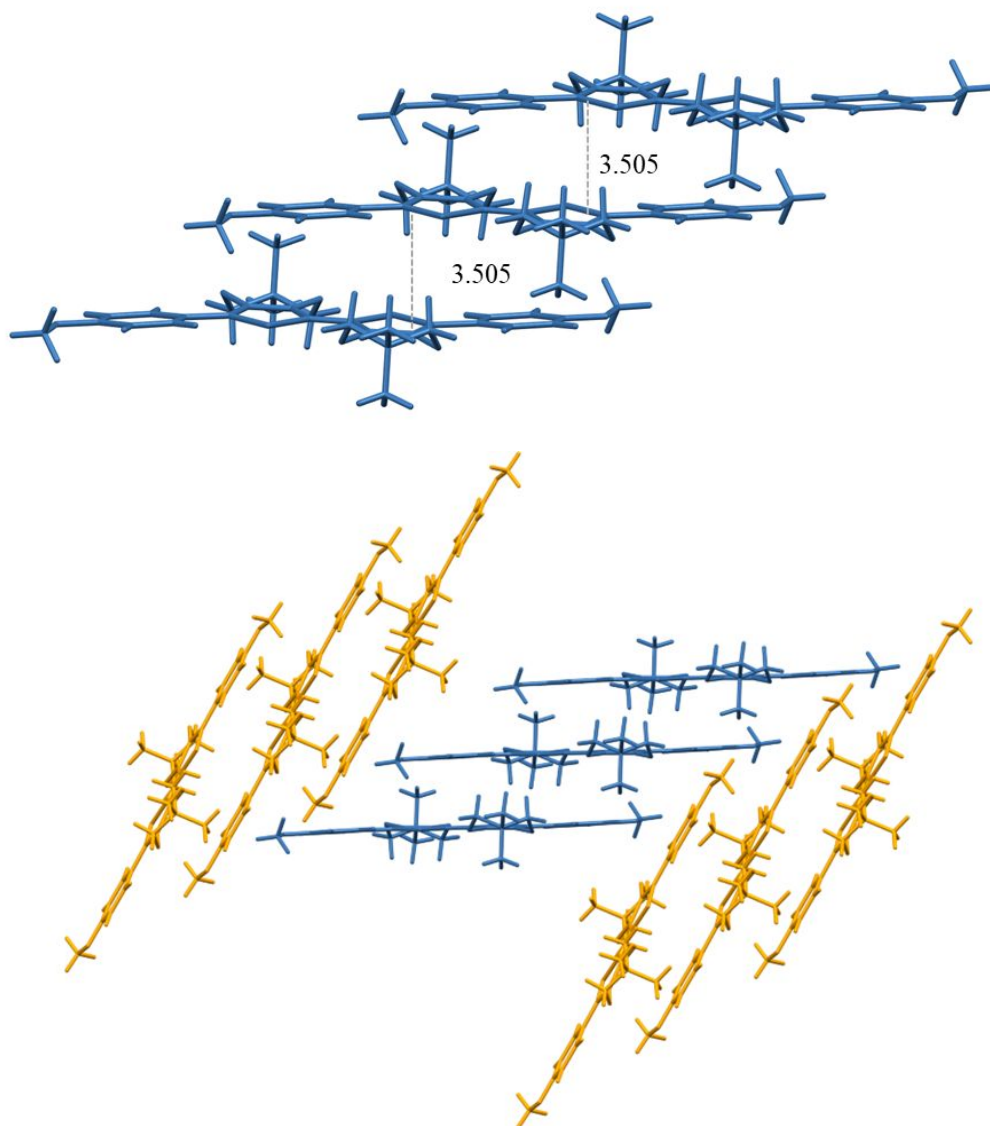
A CH₂Cl₂ molecule was refined as disordered. The two disordered moieties were restrained to have similar geometries. Uij components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.799(9) to 0.201(9). The position of the phenolic hydrogen atom was freely refined.

Empirical formula	C ₃₆ H ₄₂ Cl ₄ F ₁₂ O ₁₀ S ₂ Sb ₂
Formula weight	1312.11
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>n</i> (14)
<i>a</i> [Å]	10.6292(4)
<i>b</i> [Å]	17.4277(7)
<i>c</i> [Å]	13.4259(4)
α [°]	90
β [°]	105.993(2)
γ [°]	90
Volume [Å ³]	2390.79(15)
<i>Z</i>	2

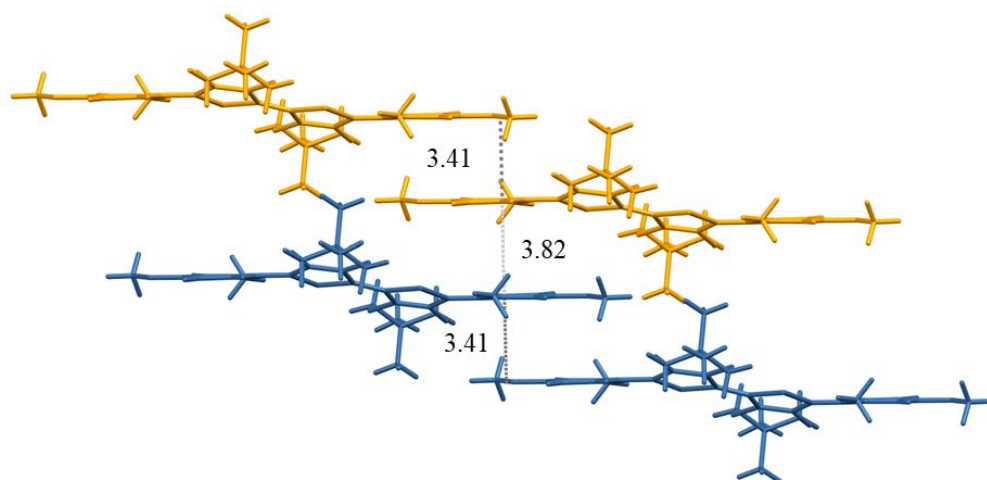
ρ_{calc} [gcm ⁻³]	1.823
μ [mm ⁻¹]	12.731
$F(000)$	1296
Crystal size [mm ³]	0.020×0.050×0.310
Crystal colour	black
Crystal shape	needle
Radiation	CuK α (λ =1.54178 Å)
2 θ range [°]	8.52 to 159.39 (0.78 Å)
Index ranges	-13 ≤ h ≤ 10 -21 ≤ k ≤ 21 -13 ≤ l ≤ 16
Reflections collected	24604
Independent reflections	5013 $R_{\text{int}} = 0.0457$ $R_{\text{sigma}} = 0.0327$
Completeness to $\theta = 67.679^\circ$	99.8 %
Data / Restraints / Parameters	5013 / 63 / 333
Goodness-of-fit on F^2	1.061
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0297$ $wR_2 = 0.0655$
Final R indexes [all data]	$R_1 = 0.0378$ $wR_2 = 0.0690$
Largest peak/hole [eÅ ⁻³]	0.48/-0.57

16. Crystal packing arrangements

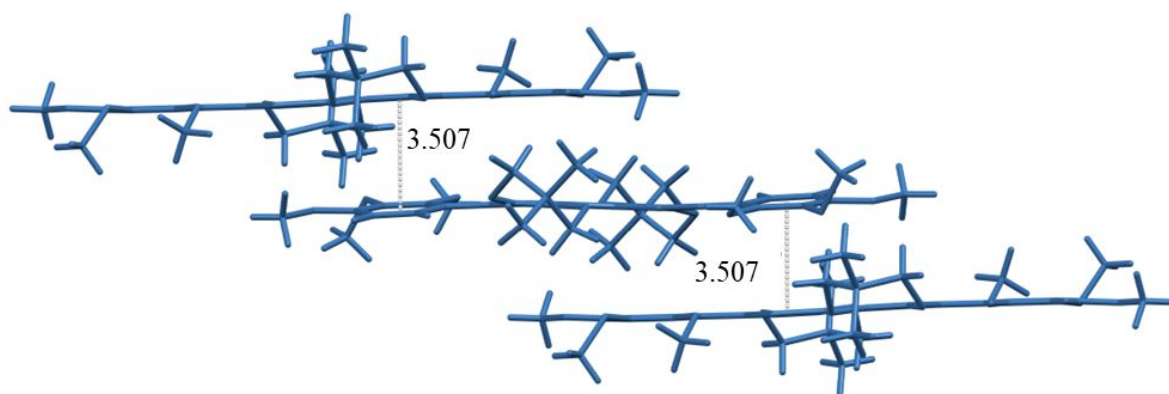
C_1 radical cation



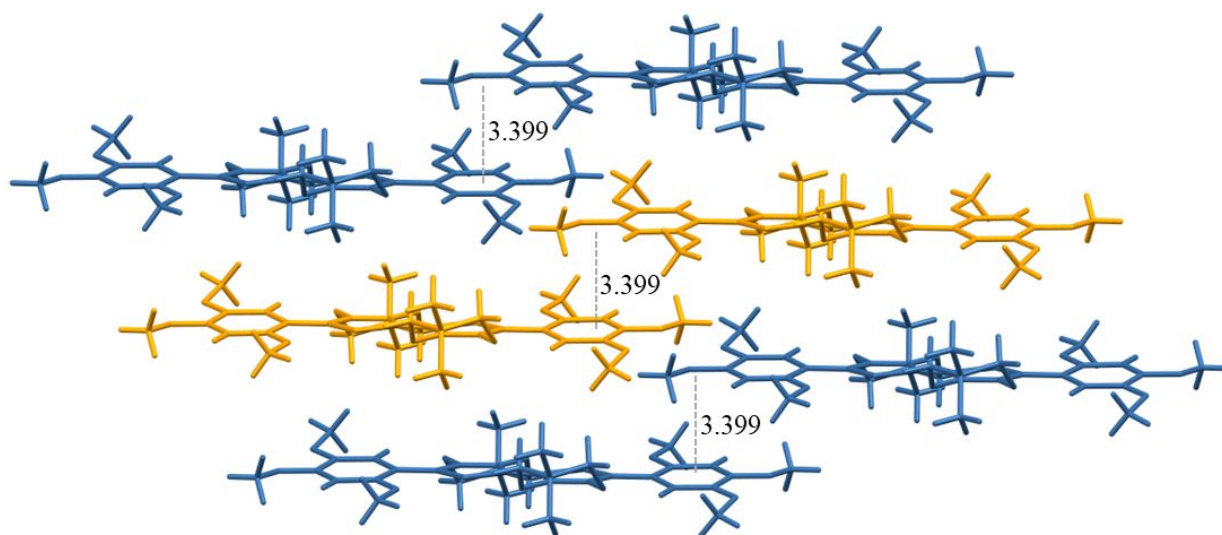
C_{13} dimer dication



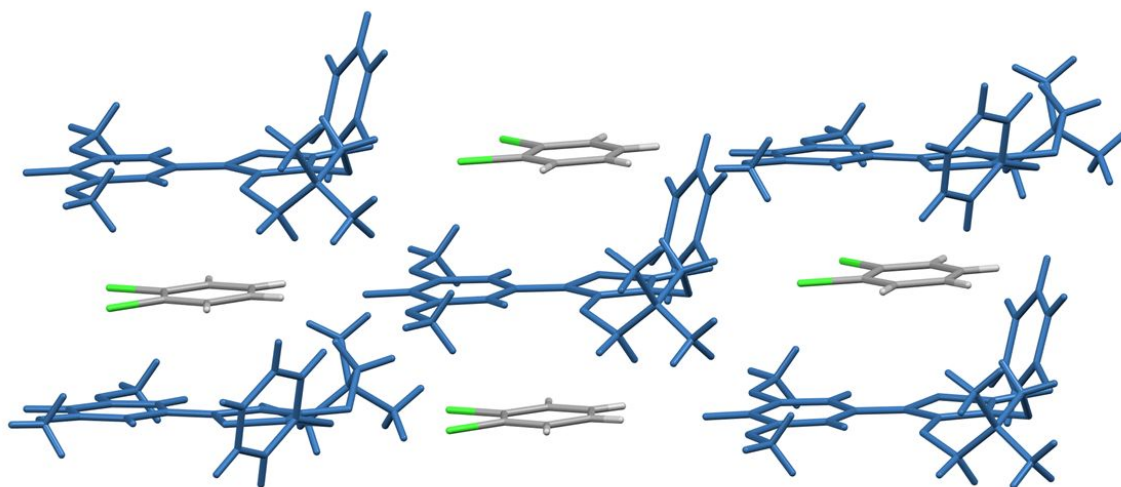
C_{123} dimer dication



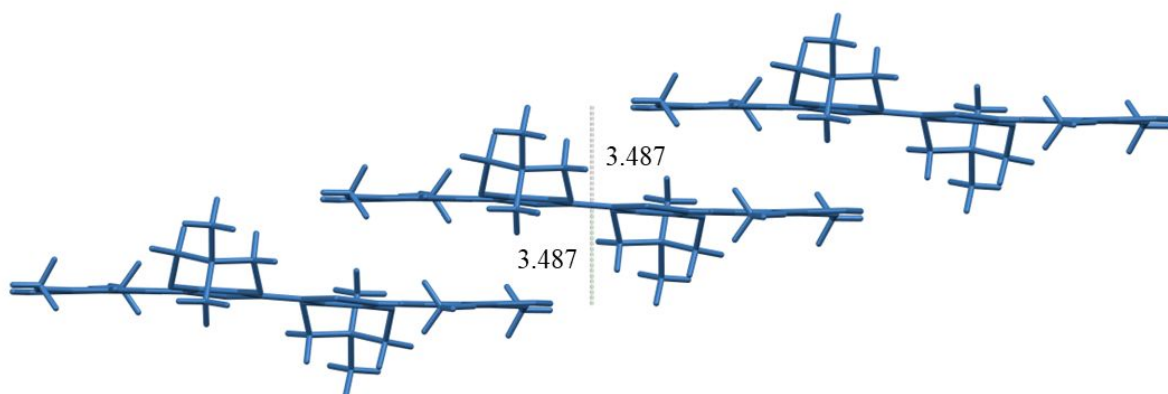
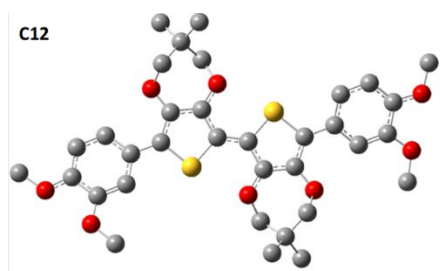
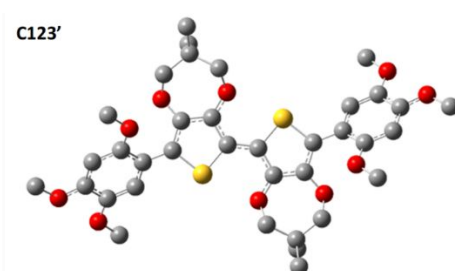
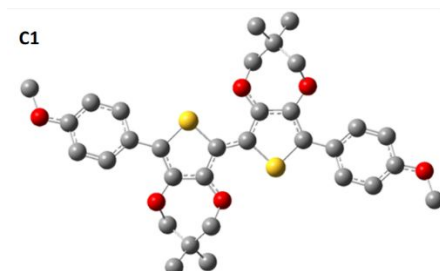
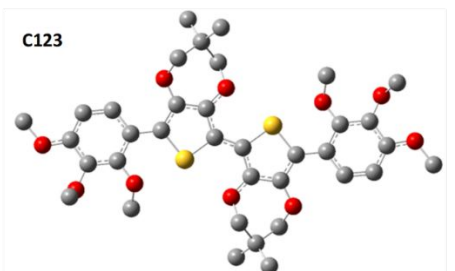
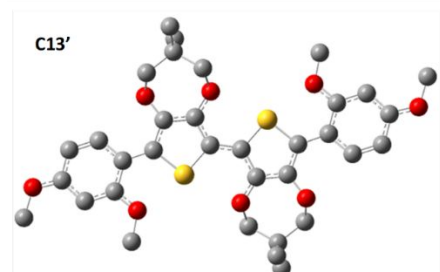
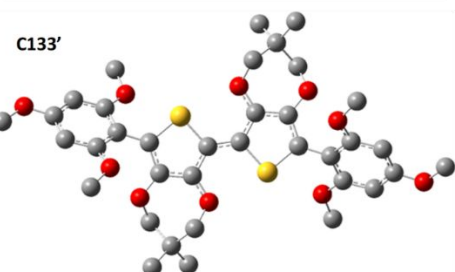
C₁₂₃' dimer dication



C₁₂₂' cation (C₁₂₂'-b¹⁺)



C_{122} dimer dication (C_{122}^{2+})



Computed geometries of dimerized radical cations ($C_x\text{-a}^{++}$) with hydrogens omitted for simplicity.

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