

Supplementary Information for

Organotelluroxane molecular clusters assembled via Te \cdots X $^-$ (X = Cl $^-$, Br $^-$) chalcogen bonding anion template interactions

Andrew Docker,^{* [a]} Antonio J. Martínez Martínez^[b] Heike Kuhn^[a] and Paul Beer^{*[a]}

[a] A. Docker, H. Kuhn, Prof .P. D. Beer,

Department of Chemistry, University of Oxford, Chemistry Research Laboratory Mansfield Road, Oxford OX1 3T, UK.

E-mail: andrew.docker@chem.ox.ac.uk

paul.beer@chem.ox.ac.uk

[b] Dr. A. J. Martínez Martínez

Supramolecular Organometallic and Main Group Chemistry Laboratory, CIQSO-Center for Research in Sustainable Chemistry and Department of Chemistry University of Huelva, Campus El Carmen, ES-21007 Huelva, Spain.

Contents

Materials, Methods, Synthesis and Characterisation3
Crystal structure determination 17
References.....20

Materials, Methods, Synthesis and Characterisation

All solvents and reagents were purchased from commercial suppliers and used as received unless otherwise stated. Dry solvents were obtained by purging with nitrogen and then passing through an MBraun MPSP-800 column. H₂O was de-ionized and micro filtered using a Milli-Q ® Millipore machine. Column chromatography was carried out on Merck® silica gel 60 under a positive pressure of nitrogen. Routine NMR spectra were recorded on either a Varian Mercury 300, a Bruker AVIII 400 or a Bruker AVIII 500 spectrometer with ¹H NMR titrations recorded on a Bruker AVIII 500 spectrometer. Chemical shifts are quoted in parts per million relative to the residual solvent peak. Mass spectra were recorded on a Bruker μ TOF spectrometer. Fluorescence spectroscopic data were recorded using a Horiba Duetta fluorescence spectrophotometer, equipped with Peltier temperature controller and stirrer. UV-Vis spectra were recorded on a V-770 UV-Visible/NIR Spectrophotometer equipped with Peltier temperature controller and stirrer using quartz cuvettes of 1 cm path length. Experiments were conducted at 25°C unless otherwise stated. Tellurium tetrabromide, TeBr₄, was prepared by direct combination of Tellurium and Br₂.

Route A General Procedure

An Et₂O (30 ml) solution of 1,3-Bis(trifluoromethyl)-5-bromobenzene (6.45 g, 22 mmol) was cooled to -78 °C, to which an n-BuLi solution in hexanes (22.0 mmol) was added dropwise. The mixture was stirred for 1 hour at -78 °C, maintaining this temperature, a suspension of TeX₄ in Et₂O (ca. 50 ml) was added dropwise and left to stir for a further 30 minutes at -78 °C. The mixture was allowed to warm to ambient temperature after which time a saturated NH₄X_(aq) solution was added dropwise and left to stir for a further 20 minutes. The mixture was diluted with Et₂O (200 ml) and washed with H₂O (3 x 50 ml), the organic phase was dried over MgSO₄ and concentrated. The residue was subjected to purification by column chromatography, eluting with hexane, and the tellurium clusters isolated as white solids.

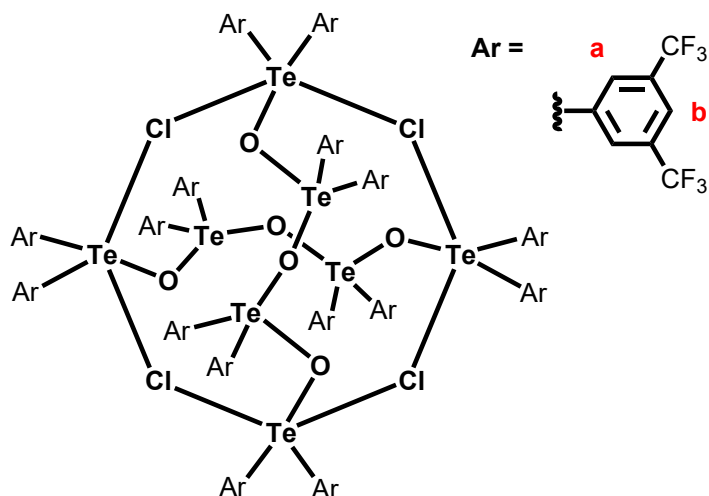
Route B General Procedure

An Et₂O (30 ml) solution of bis(3,5-bis(trifluoromethyl)phenyl)tellane (1.66 g, 3.00 mmol) was treated with a X₂ Et₂O solution (3.00 ml) and left to stir for 30 minutes. After which time a saturated NH₄X_(aq) solution was added dropwise and left to stir for a further 20 minutes. The mixture was diluted with Et₂O (200 ml) and washed with H₂O (3 x 50 ml), the organic phase was dried over MgSO₄ and concentrated. The residue was subjected to purification by column chromatography, eluting with hexane, and the tellurium clusters isolated as white solids.

Table S1. Summarised yields of **1·Cl** and **1·Br** via routes A and B.

Route	Yield	
	A	B
1·Cl	3 %	2 %
1·Br	4 %	2 %

1·Cl



¹H NMR (400 MHz, Acetone-d₆) δ 8.40 (d, *J* = 1.5 Hz, 32H), 8.03 (t, *J* = 1.5 Hz, 16H).

¹³C NMR (101 MHz, Acetone-d₆) δ 141.50, 132.91 (q, *J* = 33.4 Hz), 129.46 (d, *J* = 3.8 Hz), 125.77 (q, *J* = 272 Hz), 123.48 – 123.11 (m).

¹⁹F NMR (377 MHz, Acetone-d₆) δ -63.67.

¹²⁵Te NMR (126 MHz, Acetone-d₆) δ 820.48.

m.p. 45.0-45.5 °C

¹H NMR (400 MHz, CD₂Cl₂) δ 8.18 (s, 32H), 7.87 (s, 16H).

¹H NMR (400 MHz, Toluene-d₆) δ 7.71 (d, *J* = 1.6 Hz, 32H), 7.53 (t, *J* = 1.6 Hz, 16H).

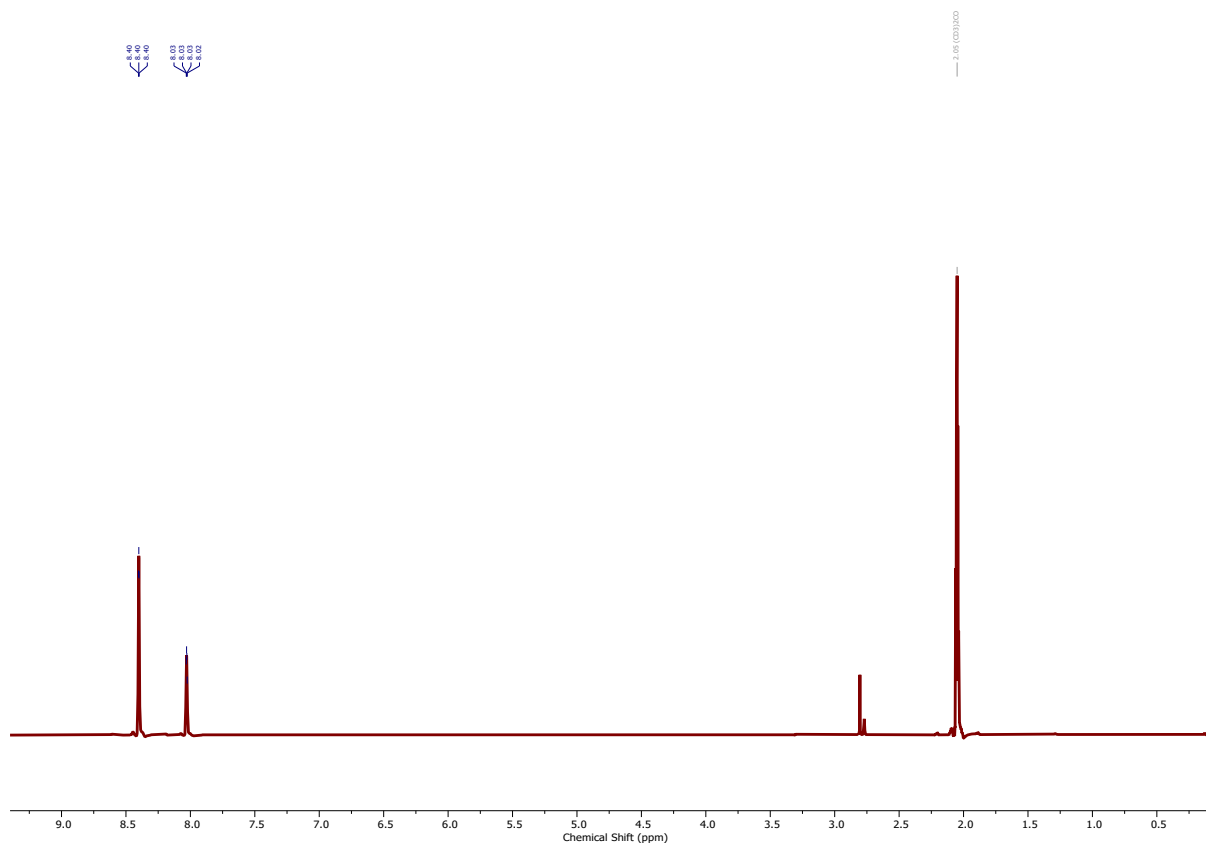


Figure S1. ^1H NMR Spectrum of **1·Cl** (Acetone- d_6 , 400 MHz, 298K).

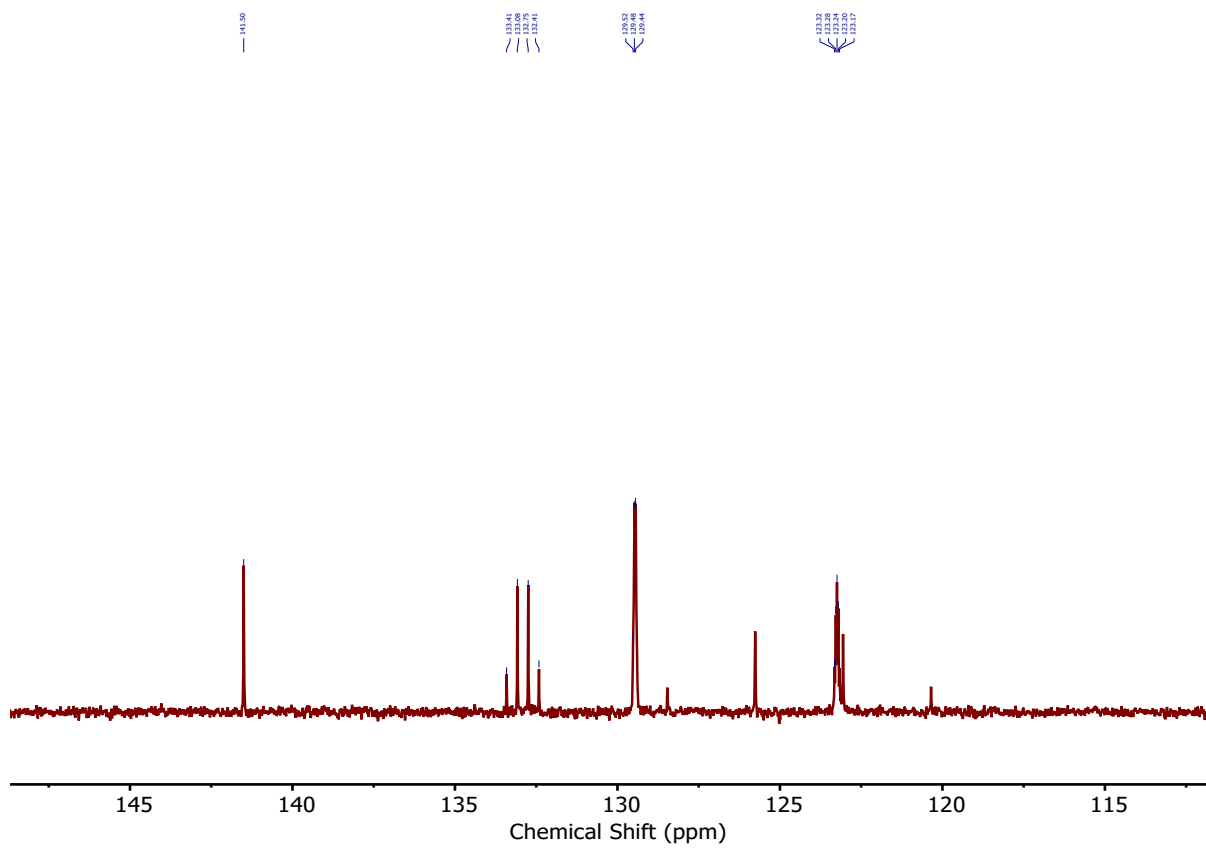


Figure S2. ^{13}C NMR Spectrum of **1·Cl** (Acetone- d_6 , 101 MHz, 298K).

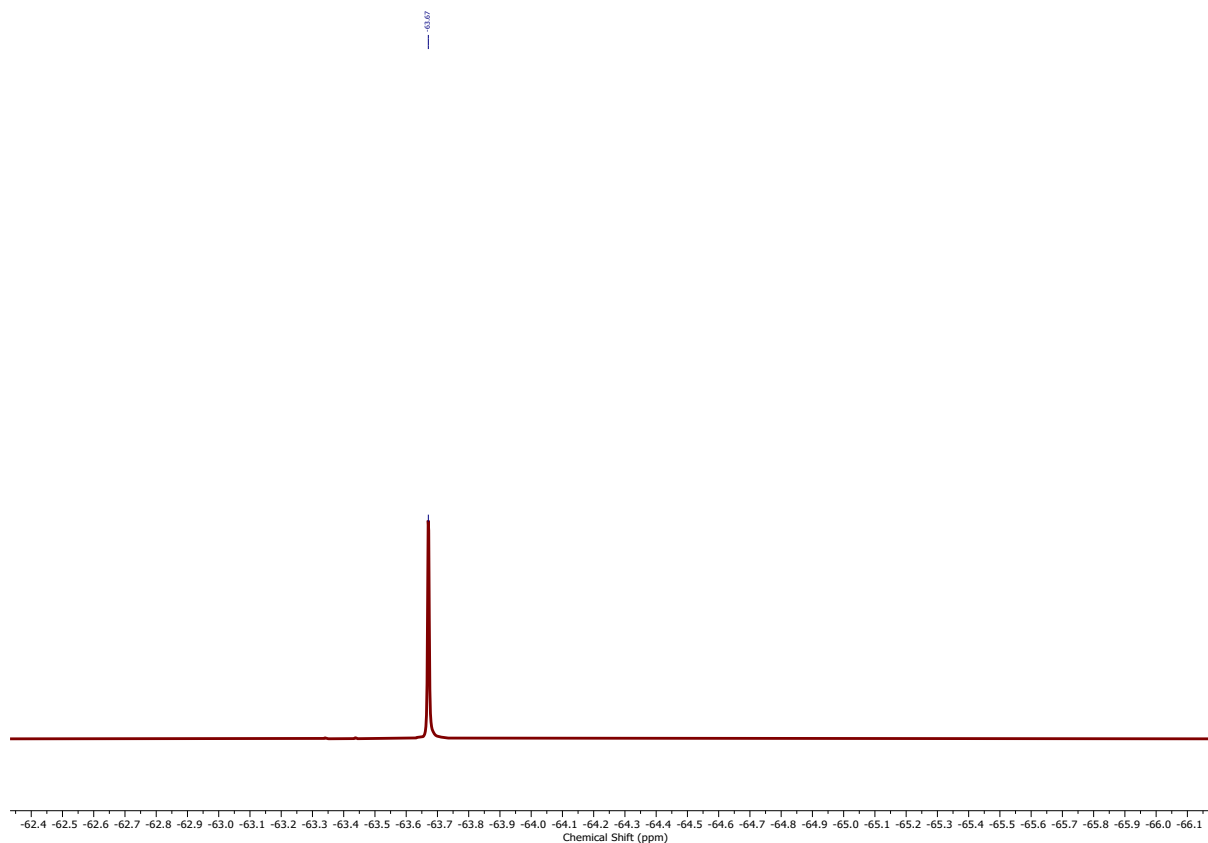


Figure S3. ^{19}F NMR Spectrum of **1-Cl** (Acetone- d_6 , 377 MHz, 298K).

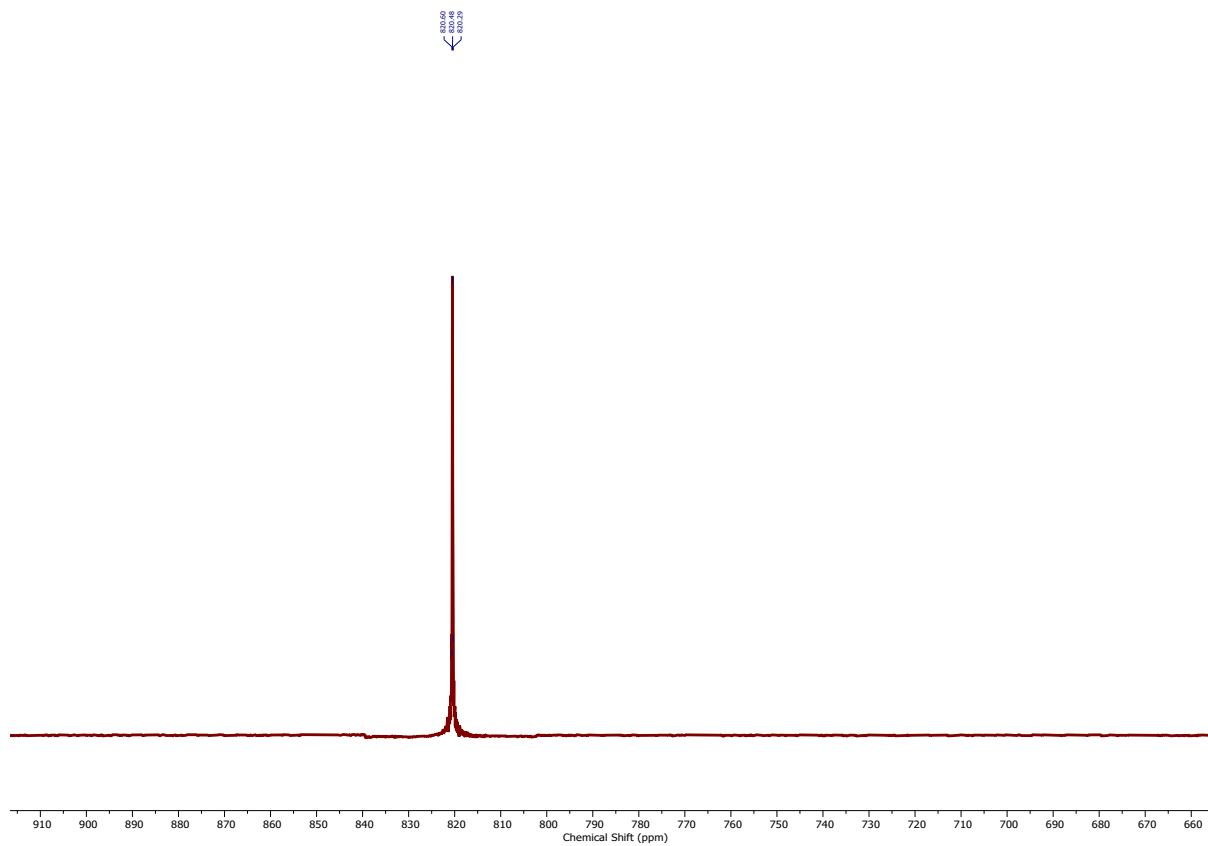


Figure S4. ^{125}Te NMR Spectrum of **1·Cl** (Acetone- d_6 , 126 MHz, 298K).

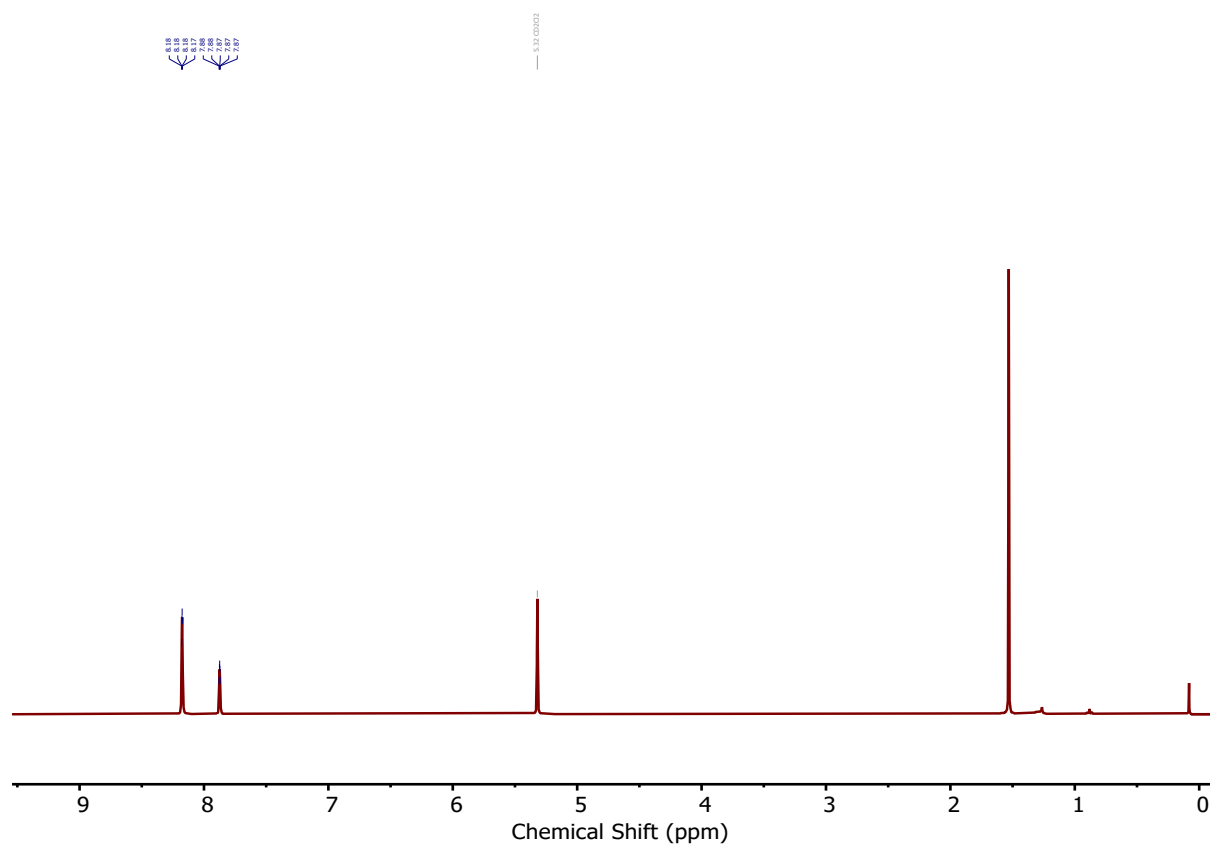


Figure S5. ^1H NMR Spectrum of **1·Cl** (CD_2Cl_2 , 400 MHz, 298K).

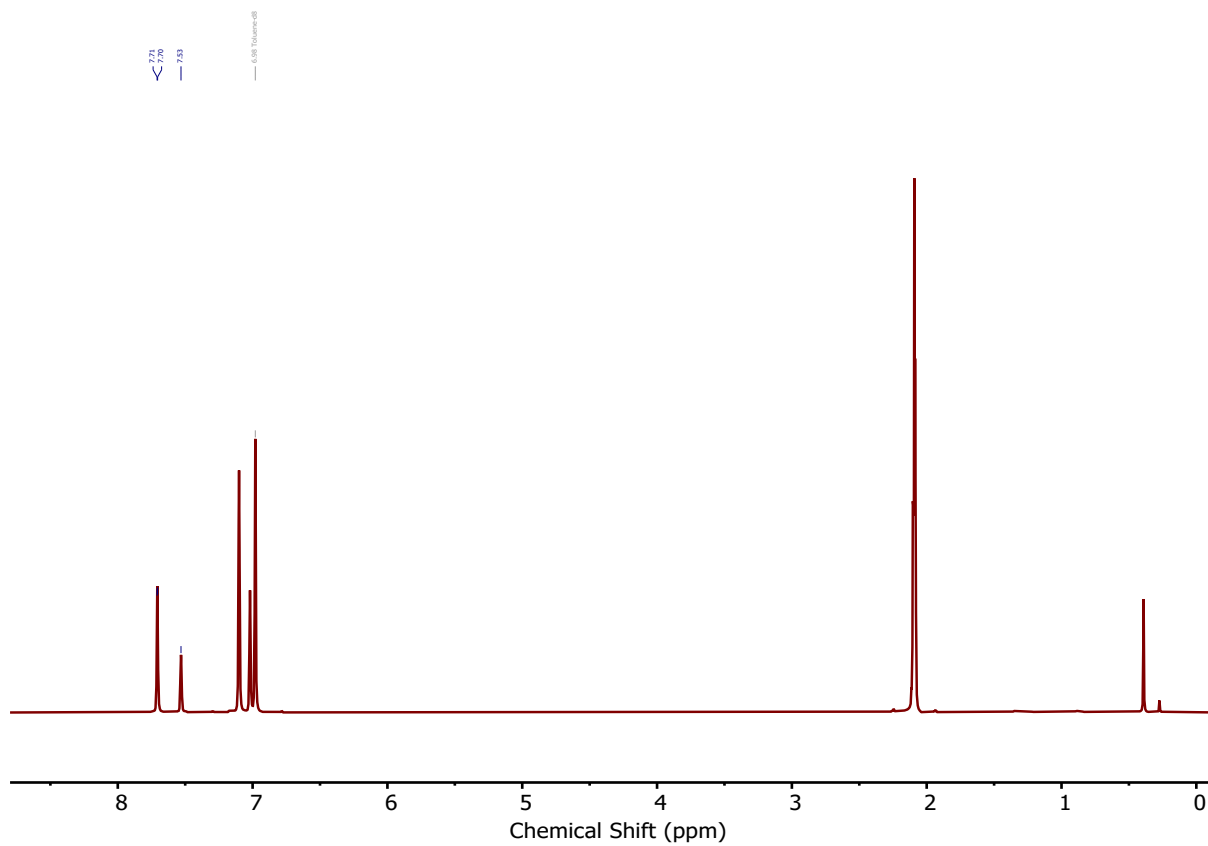


Figure S6. ^1H NMR Spectrum of **1-Cl** (Toluene-d_6 , 400 MHz, 298K).

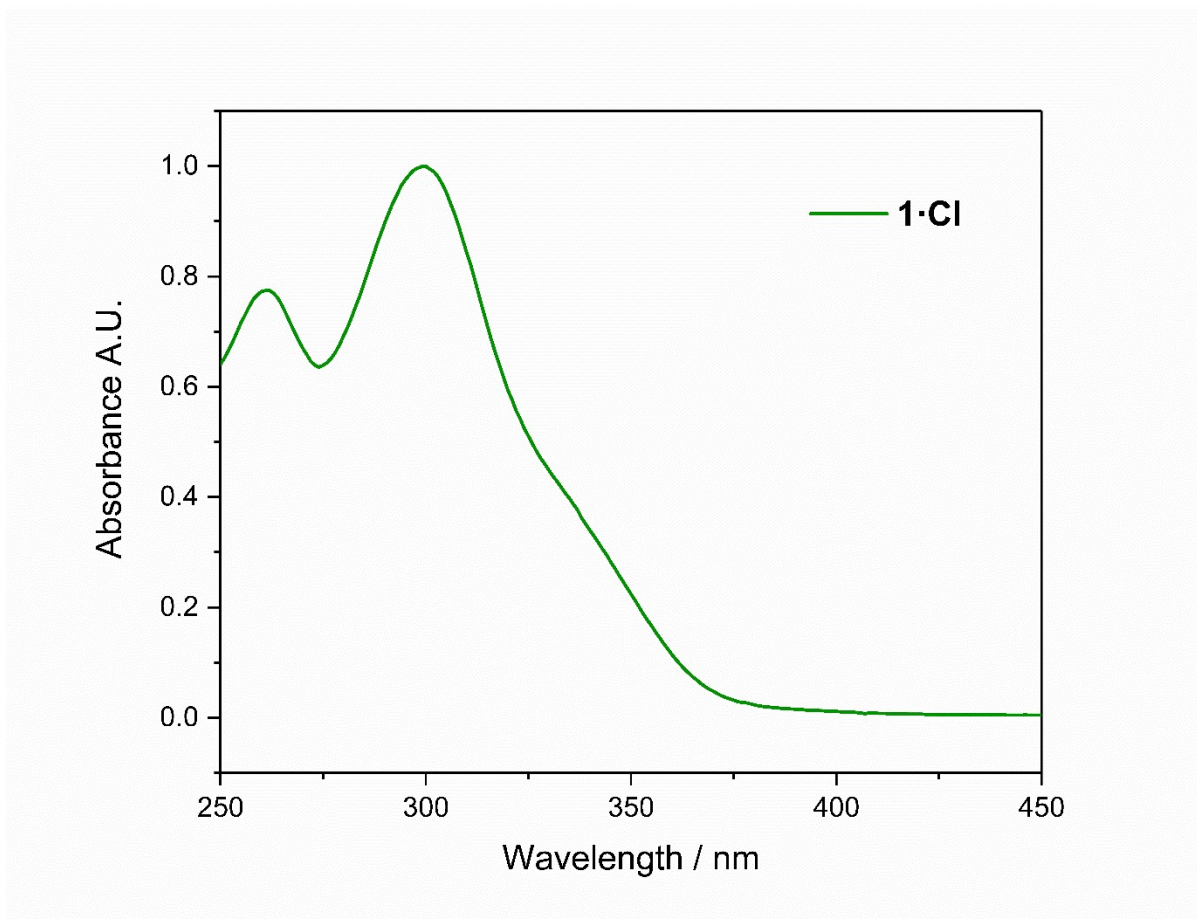


Figure S7. UV-Vis spectrum of **1·Cl** (10^{-5} M) in THF.

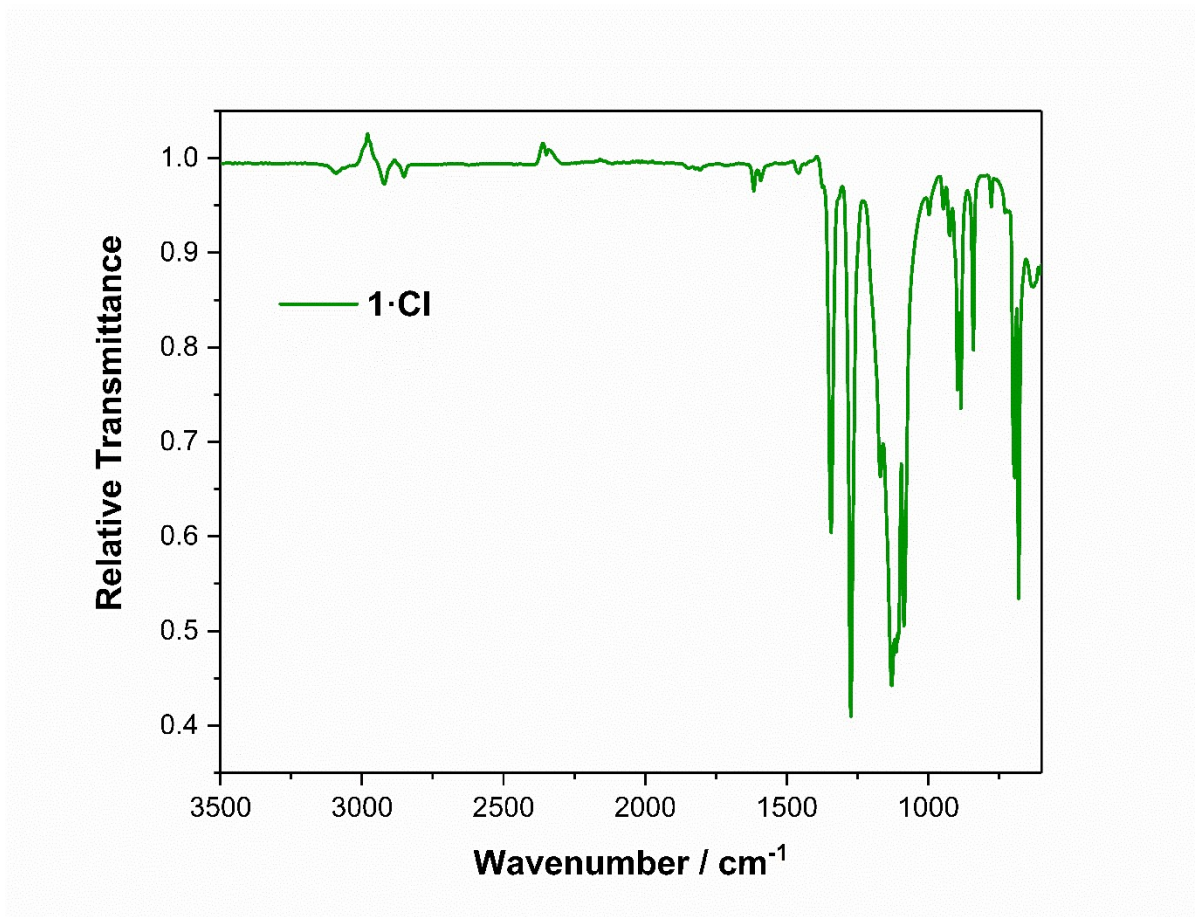


Figure S8. IR Spectrum of 1-Cl.

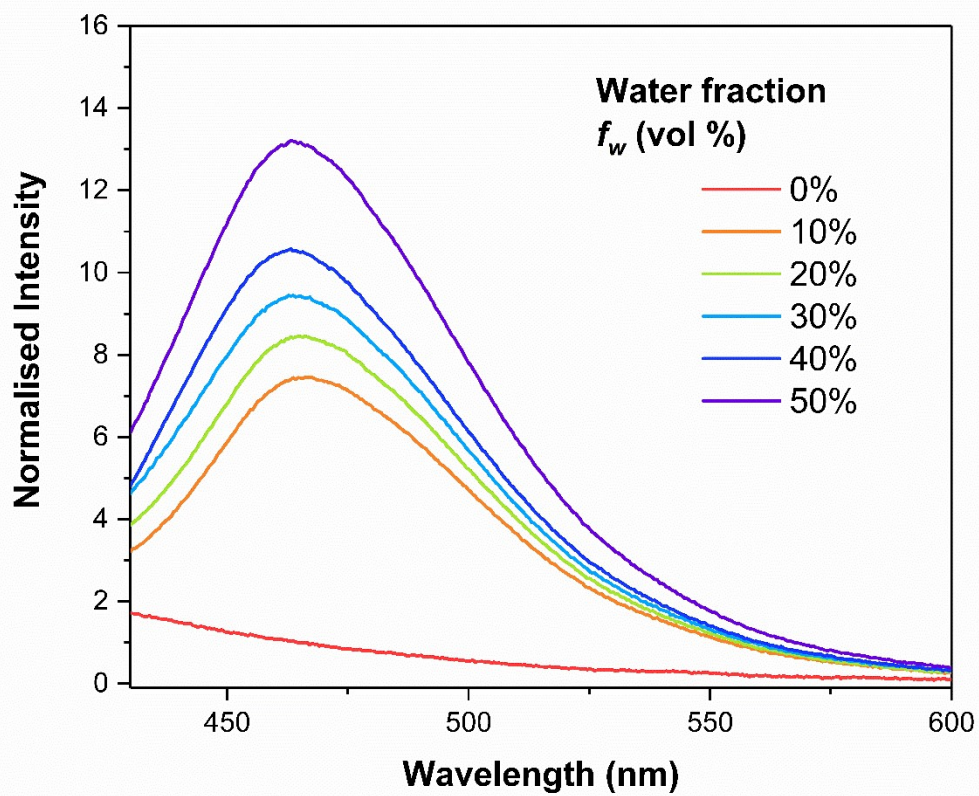
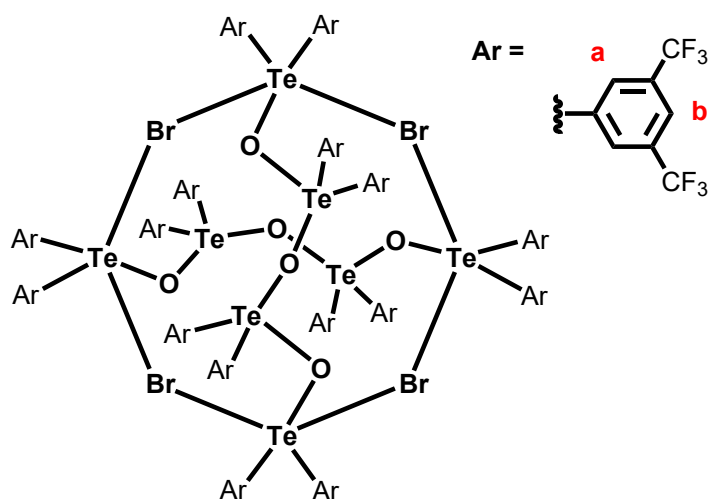


Figure S9. Fluorescence spectrum of **1·Cl** (THF, 10^{-5} M, $\lambda_{\text{ex}} = 350$ nm) with increasing water fraction (f_w).

1·Br



¹H NMR (400 MHz, Acetone-*d*₆) δ 8.58 (d, *J* = 1.5 Hz, 32H_a), 8.17 (t, *J* = 1.5 Hz, 16H_b).

¹³C NMR (101 MHz, Acetone-*d*₆) δ 141.50, 132.91 (q, *J* = 33.4 Hz), 129.46 (d, *J* = 3.8 Hz), 124.41 (q, *J* = 273 Hz), 123.24 (p, *J* = 3.9 Hz).

¹⁹F NMR (377 MHz, Acetone-*d*₆) δ -63.26.

¹²⁵Te NMR (126 MHz, Acetone-*d*₆) δ 820.48.

m.p. 48.5.0-49.5 °C

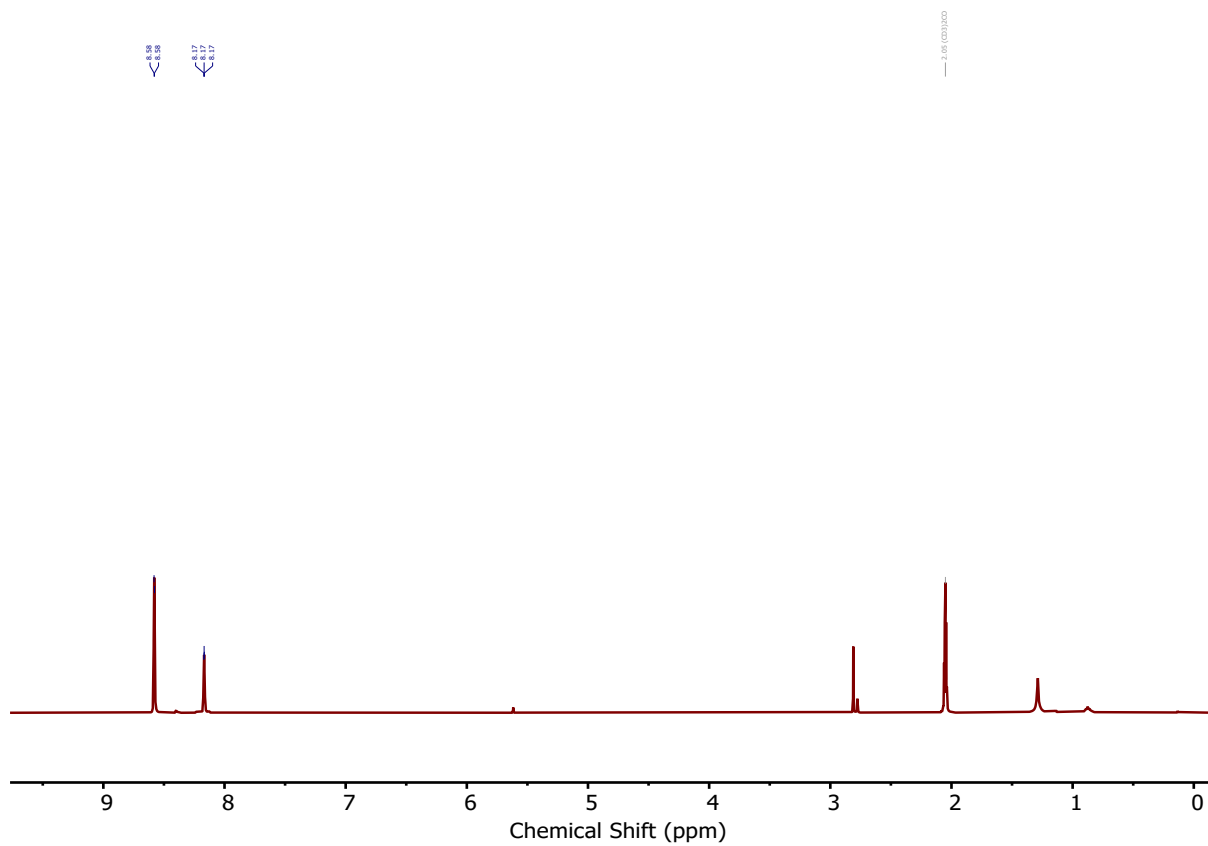


Figure S10. ^1H NMR Spectrum of **1-Br** (Acetone- d_6 , 400 MHz, 298K).

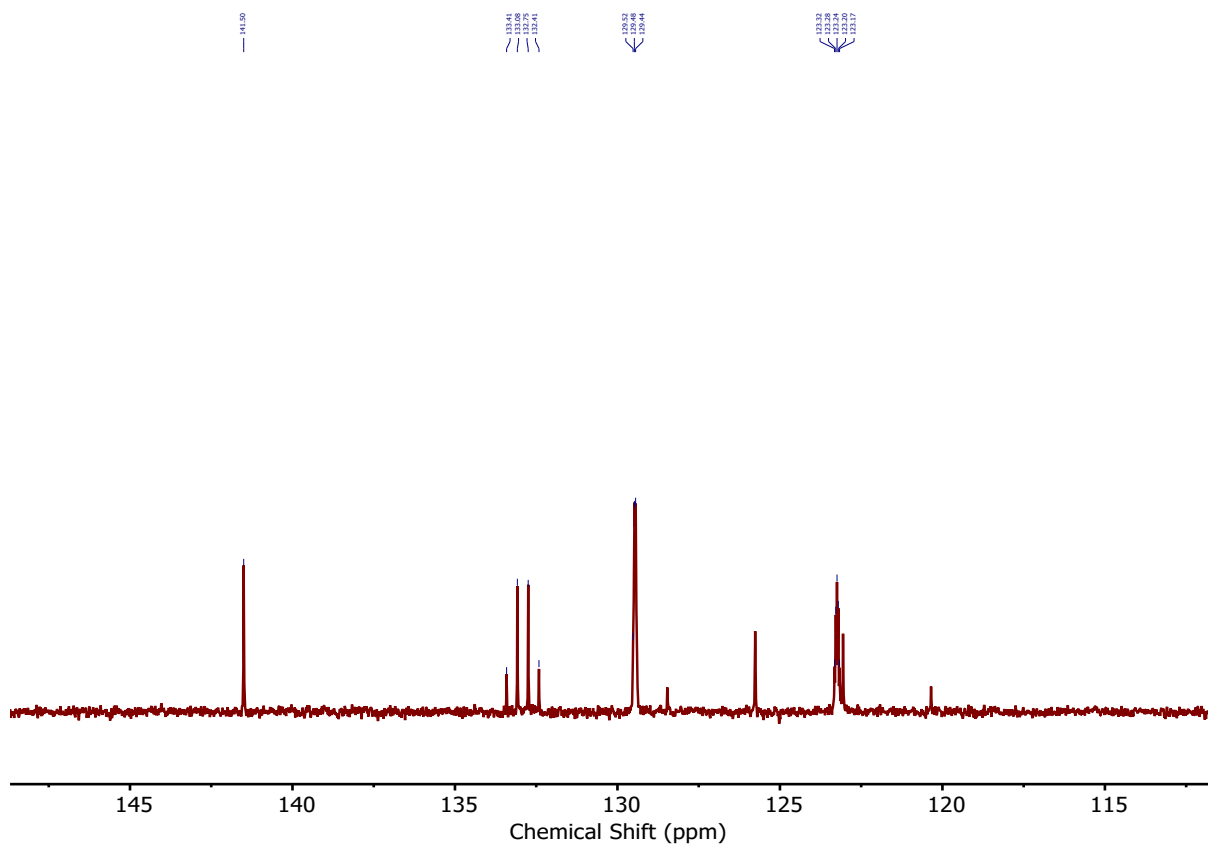


Figure S11. ^{13}C NMR Spectrum of **1·Br** (Acetone- d_6 , 101 MHz, 298K).

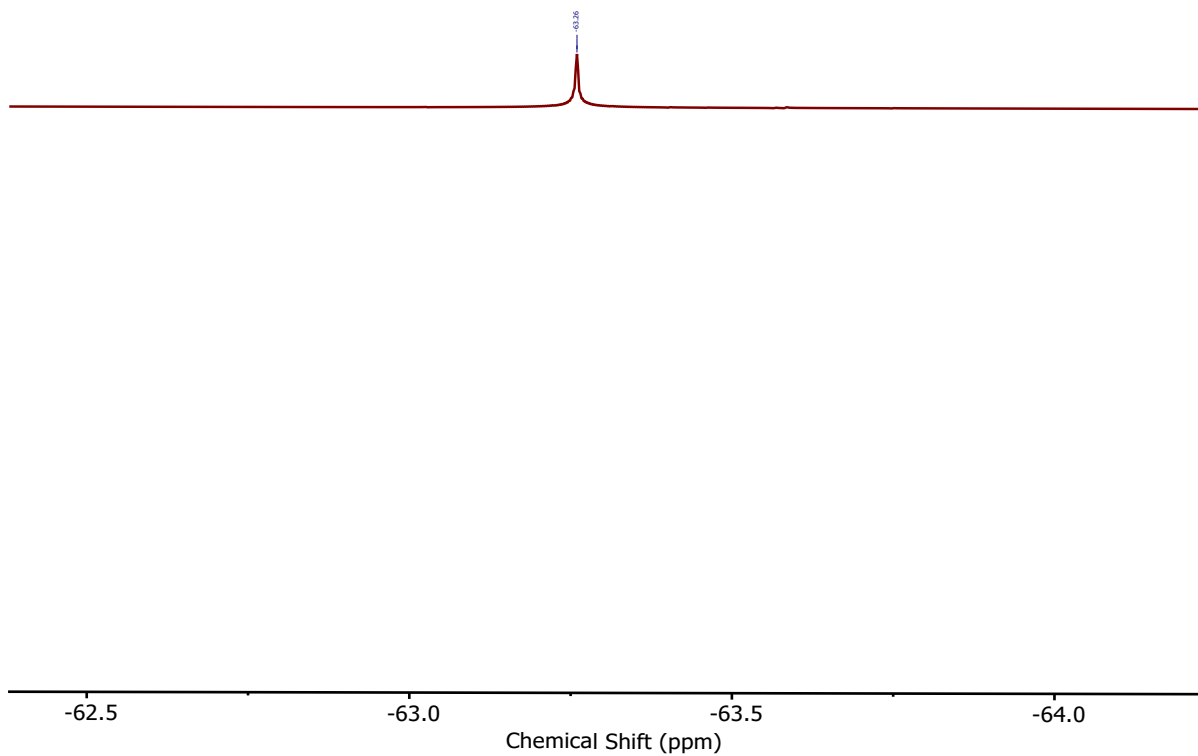


Figure S12. ^{19}F NMR Spectrum of **1·Br** (Acetone- d_6 , 377 MHz, 298K).

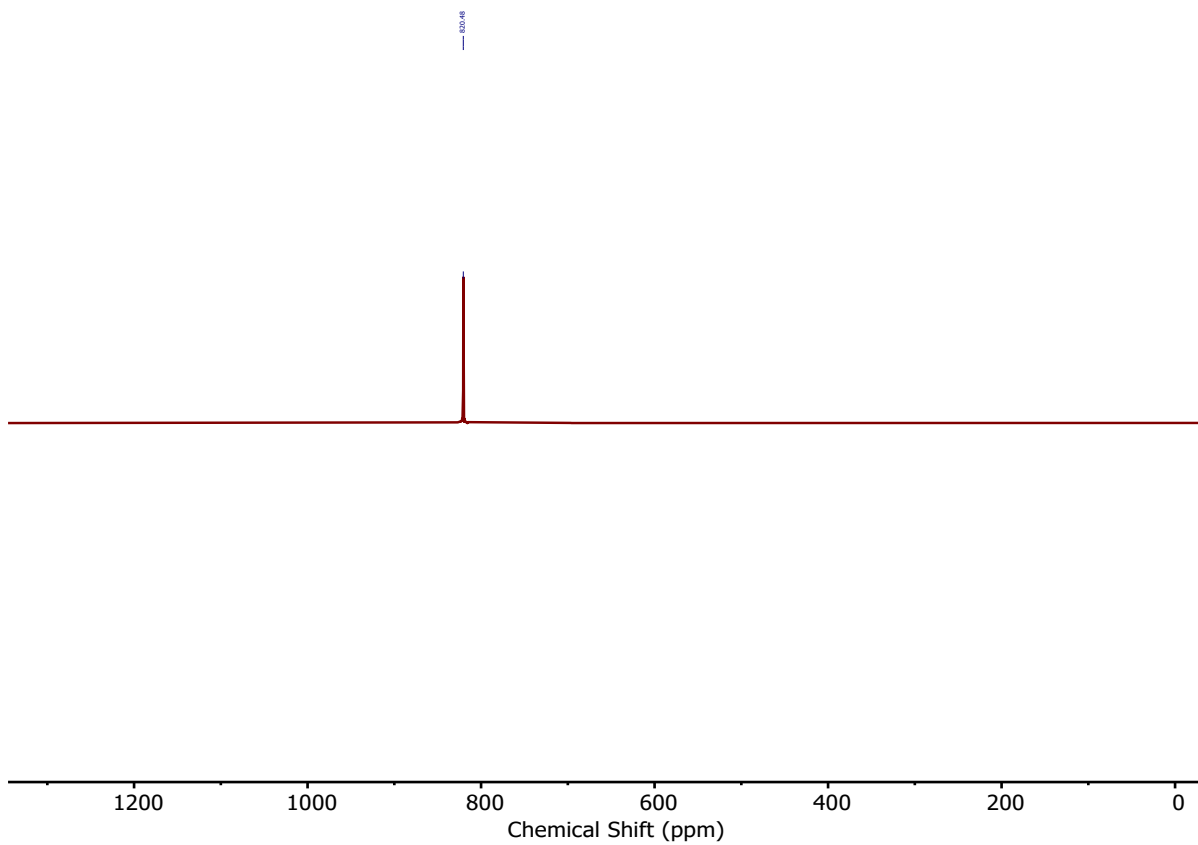


Figure S13. ^{125}Te NMR Spectrum of **1·Br** (Acetone- d_6 , 126 MHz, 298K).

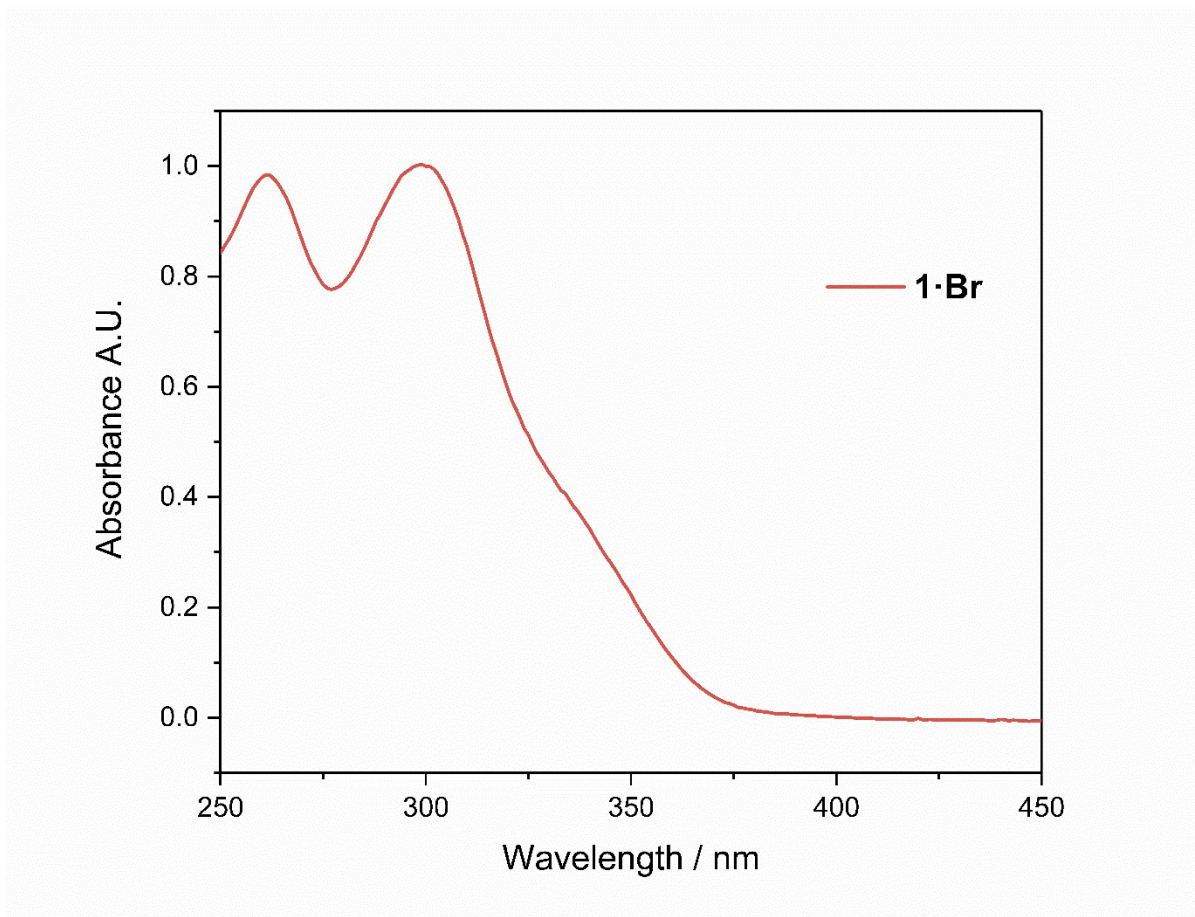


Figure S14. UV-Vis spectrum of **1-Br** (10^{-5} M) in THF.

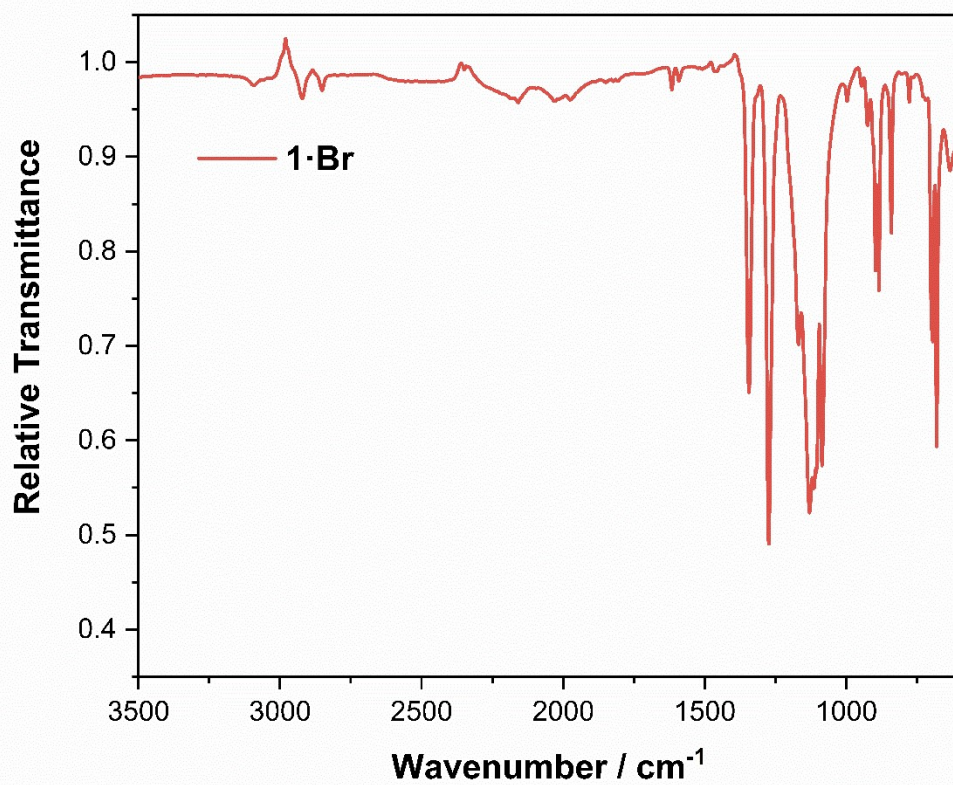


Figure S15. IR Spectrum of **1-Br**.

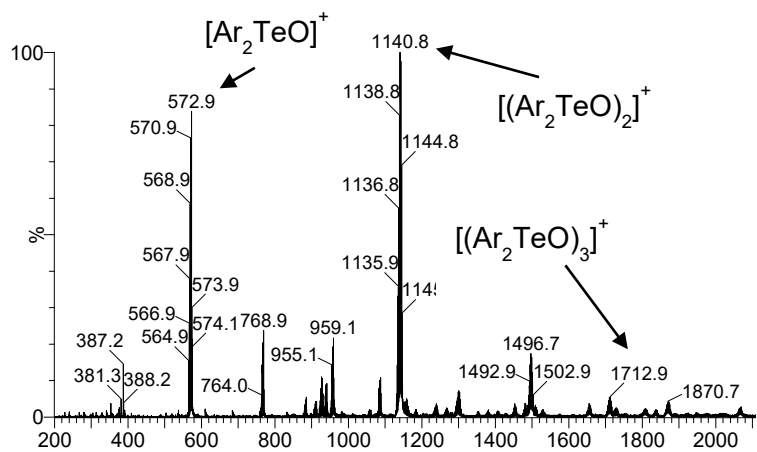


Figure S16. Truncated high resolution ESI spectrum.

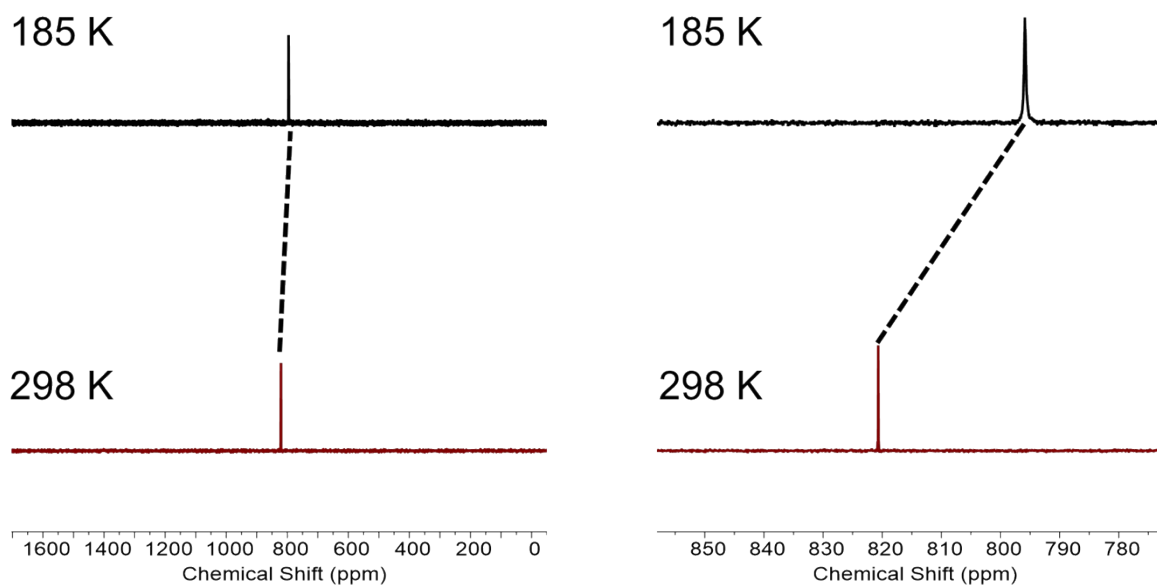


Figure S17. Variable Temperature ^{125}Te NMR spectrum of **1·Cl** (acetone- d_6 , 126 MHz).

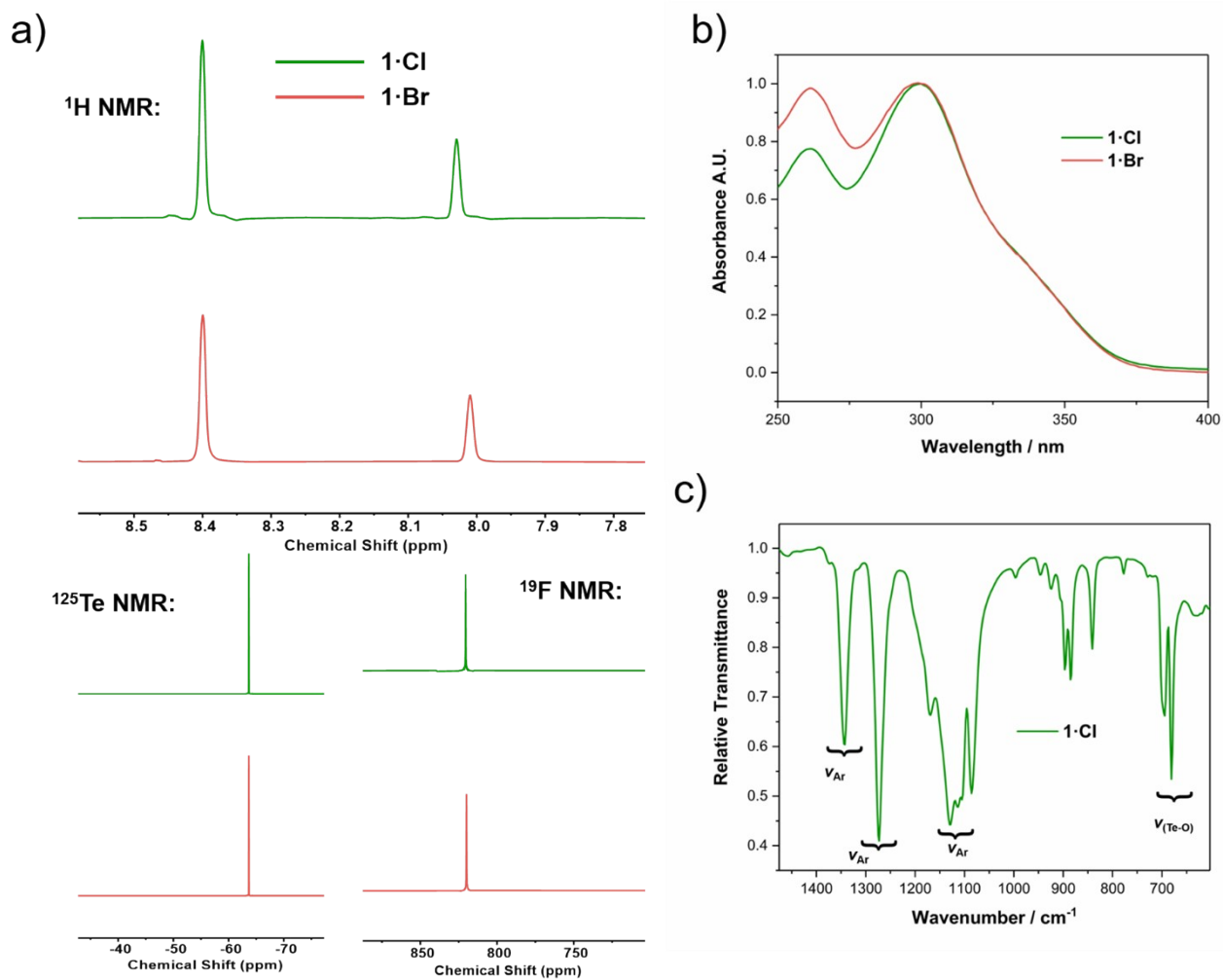


Figure S18. Summarised and representative characterisation data for **1-Cl** and **1-Br** a) Truncated ^1H , ^{125}Te and ^{19}F NMR spectra (400 MHz, 377 MHz and 126 MHz, 298 K, acetone- d_6). b) UV-Vis spectra (10^{-5} M, THF). c) Truncated IR spectrum of **1-Cl**.

Crystal structure determination

Single-crystal X-ray diffraction intensities for **1·Cl** and **1·Br** were collected at 150 K on Oxford Diffraction/Agilent SuperNovae diffractometers with Cu-K α ($\lambda = 1.54184$ Å) radiation equipped with nitrogen gas Oxford Cryosystems Cryostream unit.^[1] Raw frame data were reduced using CrysAlisPro.^[2] The structures were solved using SHELXT^[3] and refined to convergence on F^2 and against all independent reflections by full-matrix least-squares using SHELXL^[4] (version 2018/3) in combination with the GUI OLEX2 (version 1.5)^[5] program. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically placed and allowed to ride on their parent atoms. Selected crystallographic data for **1·Cl** and **1·Br** are summarized in the text. Full details for **1·Cl** are given in the supplementary deposited CIF file (CCDC 2131078) and details for **1·Br** are only given in the text. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Selected crystallographic and refinement data

X-ray crystal structure of **1·Cl**

Crystal data for 1·Cl: C₆₄H₂₄Cl₂F₄₈O₃Te₄, $M = 2334.13$ g/mol, triclinic, $P-1$, $a = 27.1854(2)$, $b = 27.3854(3)$, $c = 49.0741(3)$ Å, $\alpha = 90.1985(6)$, $\beta = 105.1120(6)$, $\gamma = 118.4449(9)^\circ$, $V = 30660.7(5)$ Å³, $Z = 16$, $\lambda(\text{Cu-K}\alpha) = 1.54184$ Å, $T = 150.0(3)$ K, dark yellow plate, 328174 reflections collected, 115222 independent measured reflections ($R_{\text{int}} = 0.1369$), F^2 refinement, $R_1(\text{obs}, I > 2\sigma(I)) = 0.1128$, $wR_2(\text{all data}) = 0.3473$, 72229 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta_{\text{max}} = 140.9^\circ$], 7181 restraints, 8300 parameters, GOF = 1.188 and residual electron density ($e \text{ \AA}^{-3}$) = 6.839/-4.103.

Additional details for 1·Cl: This compound was crystallised and collected several times with Cu-K α radiation (1.54184 Å) at different temperatures (298, 150 and 100 K). The crystals all showed modulated diffraction patterns. As the model does not account for this type of disorder, this is suspected to be the source of the long-range disorder present within the structure, the remaining residual electron density, and the large asymmetric unit found for this twinned data in $P-1$. When observed closely, the residual extra electron density appears to be around the heavy Te metal centres; thus, such residual electron density is likely not from unaccounted atom types. The quality of the collected data did not allow for a higher-quality model. Several restraints and constraints were also imposed over the multiple CF₃ groups as their positional disorder could not be appropriately modelled. In addition, alternative space groups and twin laws did not work. Reduced twin data was performed with CrysAlisPro over a two-component twin law and full details are given in the deposited CIF.

X-ray crystal structure of **1·Br**

Crystal data for 1·Br: C₁₂₈H₄₈Br₄F₉₆O₆Te₈, $M = 4846.10$ g/mol, triclinic, $P-1$, $a = 27.1049(3)$, $b = 27.3312(4)$, $c = 27.9868(4)$ Å, $\alpha = 119.1674(14)$, $\beta = 90.1053(10)$, $\gamma = 117.9086(12)^\circ$, $V = 15271.4(4)$ Å³, $Z = 4$, $\lambda(\text{Cu-K}\alpha) = 1.54184$ Å, $T = 150.0(3)$ K, dark yellow block, 227524 reflections collected, 53973 independent measured reflections ($R_{\text{int}} = 0.1329$), F^2 refinement, $R_1(\text{obs}, I > 2\sigma(I)) = 0.2368$, $wR_2(\text{all data}) = 0.6035$, 42358 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta_{\text{max}} = 133.2^\circ$], 9786 restraints, 4115 parameters, GOF = 1.607 and residual electron density ($e \text{ \AA}^{-3}$) = 17.232 /-5.367.

Additional details for 1·Br: This compound was crystallised and collected several times with Cu-K α radiation (1.54184 Å) at different temperatures (298, 150 and 100 K). The crystals all showed heavily modulated diffraction patterns that did not allow for a quality fitting between the model and the collected data. The collected data was not of sufficient quality for publication, however, it allowed to unequivocally establish the chemical nature and atom connectivity of this compound. Thus, the purpose of including this structure in this study is merely proof for formulation, preventing further structural discussions. Close exploration of alternative space groups and twin laws did not improve the model.

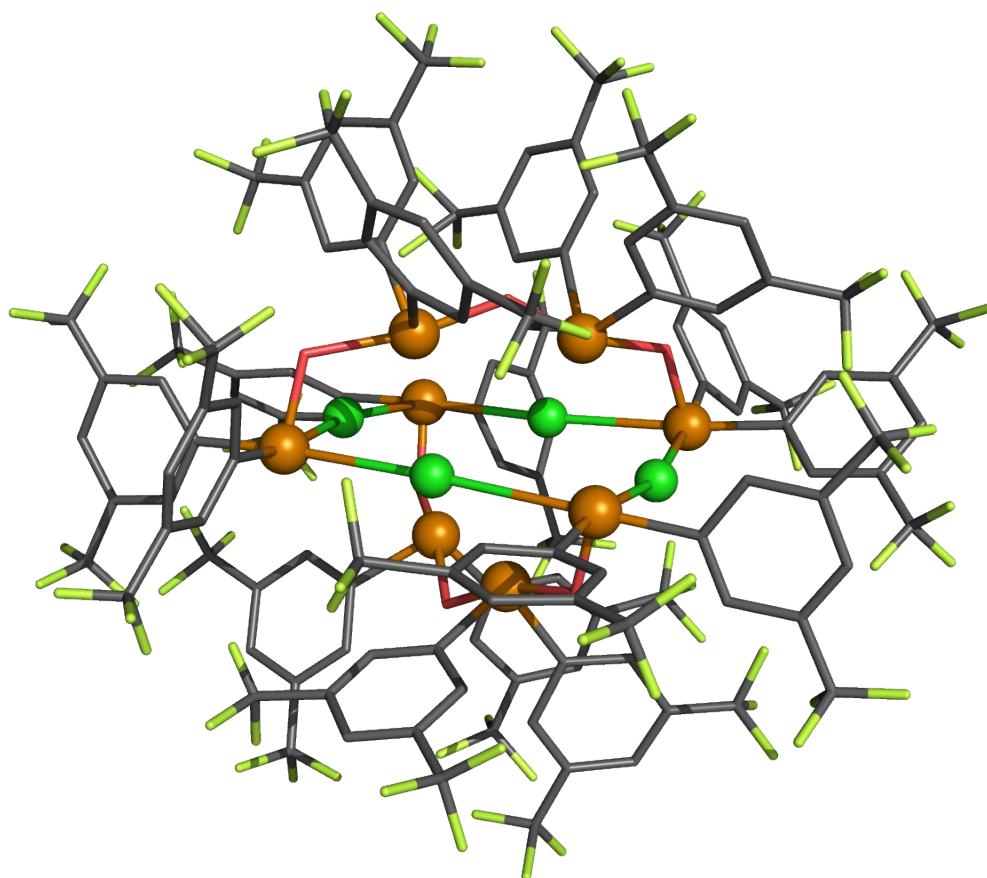


Figure S19. Wire frame representation solid state structure of the **1·Cl**. Grey = carbon, light green = fluorine, green = chloride, red = oxygen, orange = tellurium.

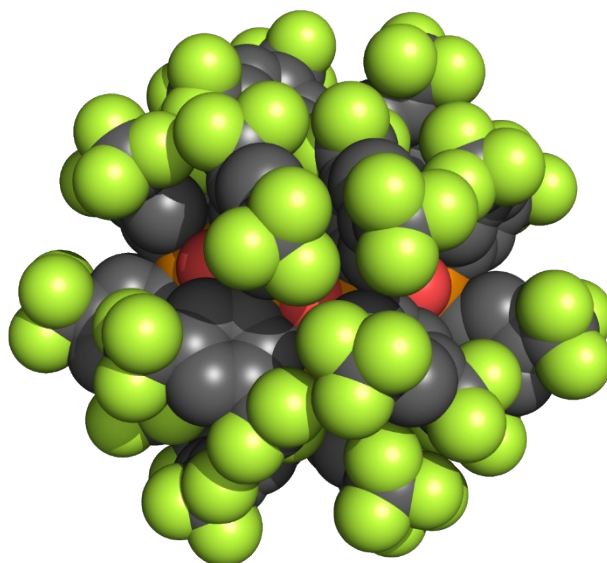


Figure S20. Solid state structure of the **1·Cl**. Grey = carbon, light green = fluorine, green = chloride, red = oxygen, orange = tellurium.

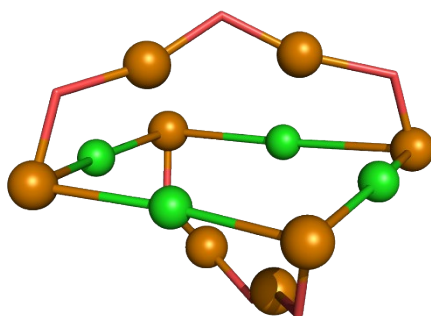


Figure S21. Truncated solid state structure of the **1·Cl**. Green = chloride, red = oxygen, orange = tellurium.

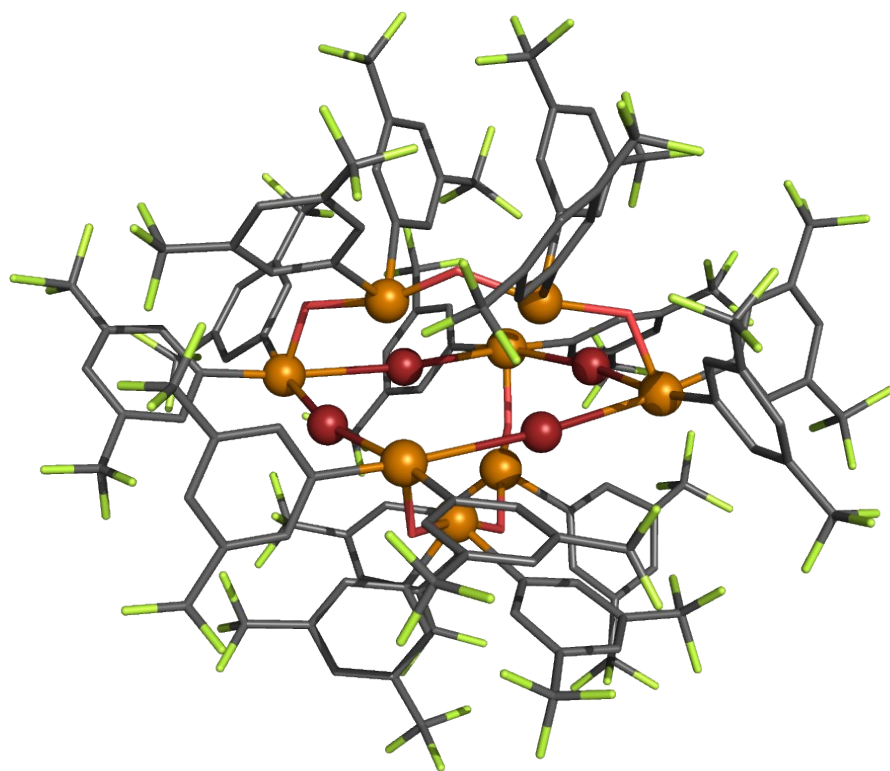


Figure S22. Wire frame representation solid state structure of the **1·Br**. Grey = carbon, light green = fluorine, brown = bromide, red = oxygen, orange = tellurium.

References

- [1] J. Cosier, A. M. Glazer, *J. Appl. Cryst.* 1986, 19, 105-107.
- [2] CrysAlisPRO, Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.
- [3] G. M. Sheldrick, *Acta Cryst. Sect. A* 2015, 71, 3-8.
- [4] G. M. Sheldrick, *Acta Cryst. Sect. A* 2008, 64, 112-122.
- [5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, 42, 339-341.