Electronic Supplementary Material (ESI) for Dalton Transactions.

Electrocatalytic Hydrogen Evolution Mediated by an Organotelluroxane Macrocycle Stabilized through Secondary Interactions

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Table of contents

Section – 1: Crystallographic information of compounds 2-5

Table S1. Crystallographic information of compounds 2-5.

	$C_{56}H_{56}B_4F_{16}O_{10}Te_4$	$C_{56}H_{56}Cl_4O_{26}Te_4$	$C_{21}H_{21}BF_4O_3Te$	$C_{21}H_{21}ClO_7Te$
F.wt g/mol^{-1}	1746.65	1797.24	535.79	548.43
T, K	100.0(2)	100.0(2)	106(9)	285
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group (number)	*P*2$_1$/*c* (14)	*P*2$_1$/*c* (14)	*P -1 (2)*	*P -1 (2)*
Crystal size mm^3	0.32 × 0.25 × 0.16	0.1 × 0.08 × 0.08	0.8 × 0.12 ×0.1	0.09 × 0.08 × 0.06
a, Å	17.0516(2)	17.1420(1)	10.2455(2)	10.3196(4)
b, Å	17.0082(3)	17.2042(1)	10.5162(2)	10.7682(5)
c, Å	26.0700(4)	26.0805(2)	10.9830(2)	11.1672(5)
α, deg	90	90	110.245(2)	111.398(1)
β, deg	97.065(1)	97.420(1)	97.955(1)	96.830(1)
γ, deg	90	90	104.283(1)	104.125(1)
V, Å^3	7503.2(2)	7627.13(9)	1042.82(4)	1090.36(8)
Z	4	4	2	2
D_{calcd} Mg/m^3	1.720	1.735	1.706	1.670
μ, mm^{-1}	1.635	1.734	1.482	1.526
F(000)	3800.0	3924.0	528.0	544.0
Theta range, deg	3.72 to 49.998	3.94 to 53.874	4.078 to 53.924	5.878 to 61.102
Index ranges	-20 ≤ h ≤ 20 -20 ≤ k ≤ 20 -30 ≤ l ≤ 30	-21 ≤ h ≤ 21 -21 ≤ k ≤ 21 -32 ≤ l ≤ 32	-13 ≤ h ≤ 13 -13 ≤ k ≤ 13 -13 ≤ l ≤ 13	-14 ≤ h ≤ 14 -15 ≤ k ≤ 15 -15 ≤ l ≤ 15
Total reflns	67629	80531	15561	58169
Ind. reflns / R(int)	13201/0.0817	15871/0.0230	4326/0.0318	6644/0.0298
Data/restraints/parameters	13201/0/954	15871/0/954	4326/0/274	6644/0/274
Completeness to θ_{max}, %	100	96.1	95.4	99.6
GooF(F^2)	1.040	1.141	1.051	1.043
R_1/wR_2 [I>2σ(I)]	R_1 = 0.0594, wR_2 = 0.1427	R_1 = 0.0246, wR_2 = 0.0521	R_1 = 0.0267, wR_2 = 0.0597	R_1 = 0.0223, wR_2 = 0.0550

R_1/wR_2 [all data]	R_1 = 0.0741, wR_2 = 0.1499	R_1 = 0.0266, wR_2 = 0.0528	R_1 = 0.0294, wR_2 = 0.0610	R_1 = 0.0281, wR_2 = 0.0574
Largest diff peak/hole, e.Å^{-3}	3.36/-1.45	1.28/-1.02	1.30/-0.72	0.44/-0.51

Section – 2: ORTEP diagram of compound 2

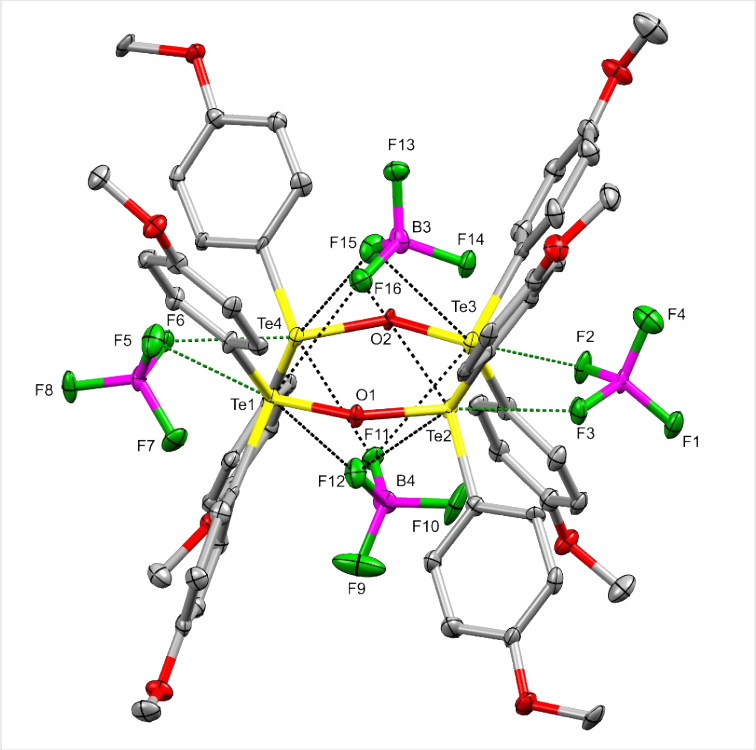


Figure S1. ORTEP diagram of **2**. The thermal ellipsoids are shown at a 40% probability level. Solvent molecule and all hydrogen atoms were omitted for clarity.

Section – 3: Te-F (BF_4) interaction distances of compound 2

Table S2. Bridging anion Interaction with Tellurium [Å].

Te(1)-F(5)	3.020
Te(2)-F(3)	2.640
Te(3)-F(2)	2.607
Te(4)-F(6)	2.620

Table S3. Capping anion Interaction with Tellurium [Å].

Te(1)-F(12)	2.800
Te(1)-F(16)	2.890

Te(2)-F(12)	2.940
Te(2)-F(16)	2.940
Te(3)-F(15)	3.080
Te(3)-F(11)	2.940
Te(4)-F(11)	2.840
Te(4)-F(15)	3.030

Section – 3.1: Bond lengths and bond angles for compound 2

Table S4. Selected bond lengths [Å] and angles [°] for **2**.

Te(1)-O(1)	1.940(4)
Te(2)-O(1)	1.960(4)
Te(3)-O(2)	1.960(4)
Te(4)-O(2)	1.950(4)
Te(1)-O(1)-Te(2)	125.2(2)
Te(3)-O(2)-Te(4)	122.2(2)

Section – 4: Cyclic voltammetry and bulky electrolysis

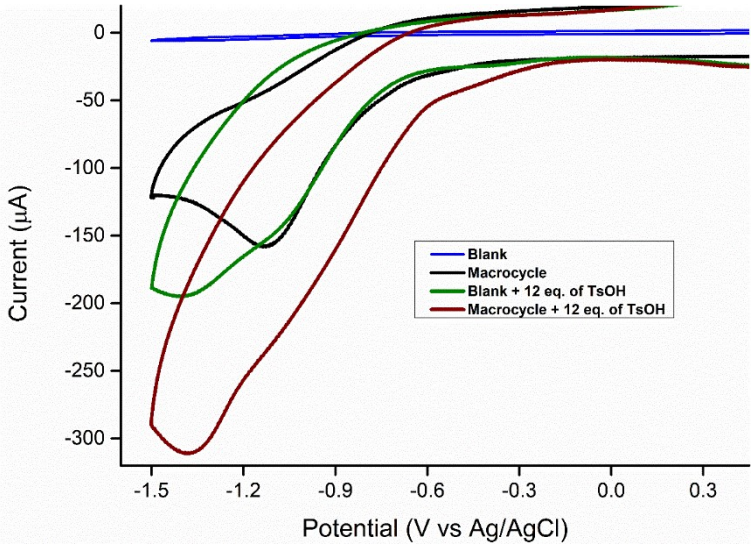


Fig. S2. Cyclic voltammogram of **Blank** (blue)**, macrocycle 2** (black), blank with 12 eq. equivalents of para-Toluene sulfonic acid as a proton source, and Macrocycle 2 with 12 eq. of TsOH. Electrocatalytic conditions 1 mM of the 2 in acetonitrile in the presence of 100 mM TBAP as supporting electrolyte at a scan rate of 100 mV s^{-} in an inert atmosphere using a three-electrode configuration.

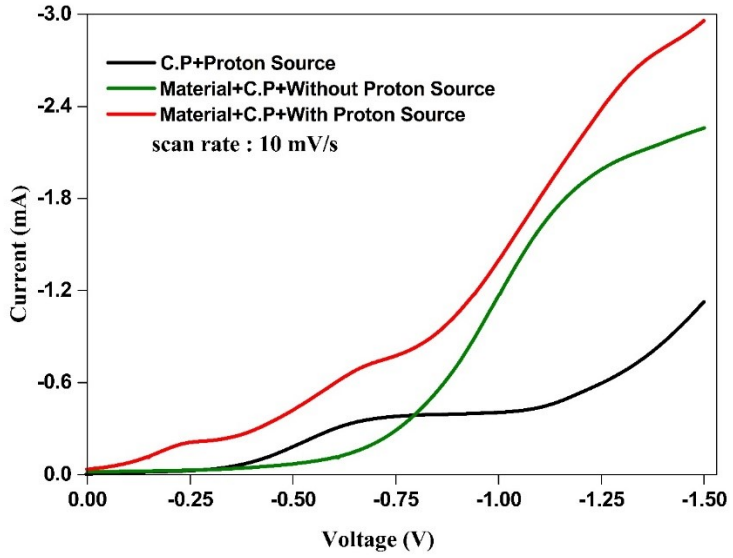


Fig. S3: (a) Linear sweep voltammetry of solution carbon paper (c.p) with proton source para-toluene sulfonic acid (black), macrocycle 2 (green), macrocycle 2 with proton source (red). Electrocatalytic conditions 1 mM of the macrocycle 2 in acetonitrile in the presence of 100 mM TBAP as supporting electrolyte at a scan rate of 10 mV s^{-} in an inert atmosphere using a homemade three-electrode configuration.

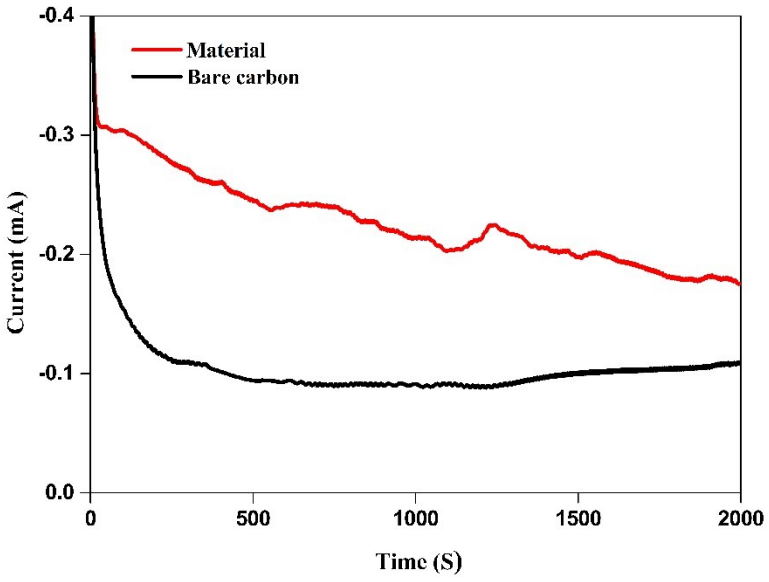


Fig. S4: Chronoamperometry profile of the same solution while holding the potential at -0.68 V vs Ag/Ag^{+}.

Section – 5: Homogeneous System H_2 calculation

$$H_2 = \frac{Area}{Slope} * 2 * empty\ volume$$

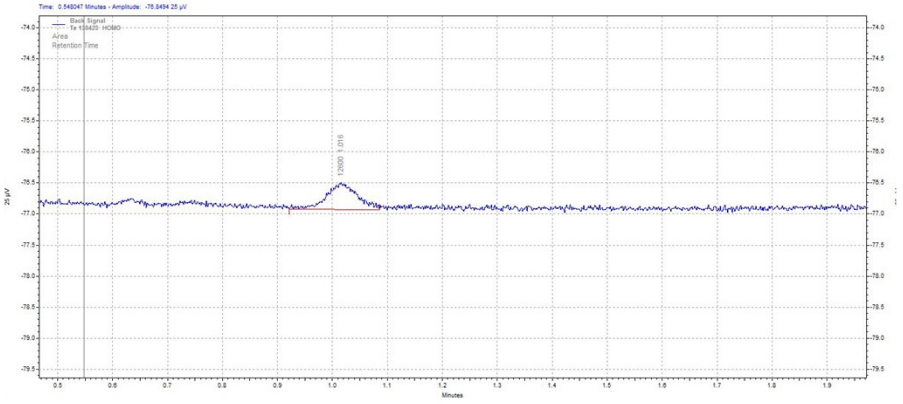
$$H_2 = \frac{12500}{22886976} * 2 * 10$$

$$H_2 = 0.01\ \mu\ mol$$

H_2 Slope calibration value = 22886976 µ mol

Area % Report

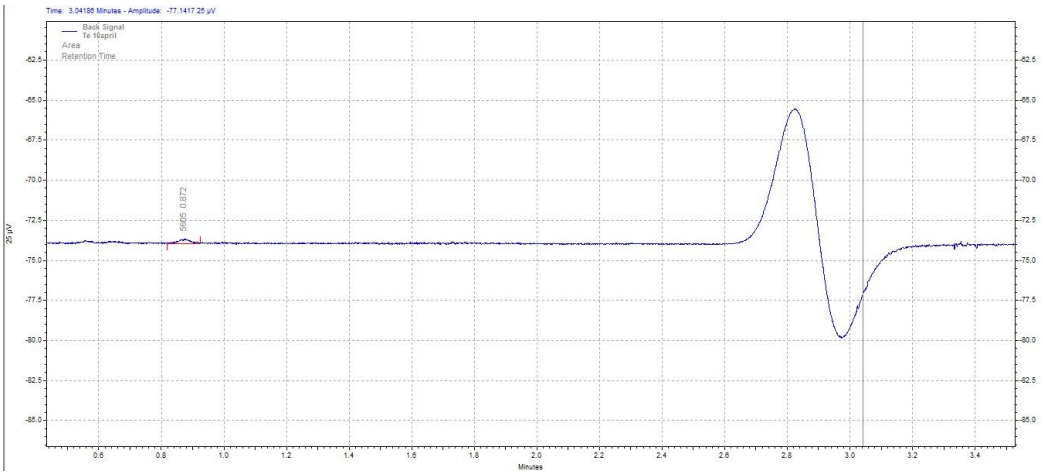
Data File: E:\Sathish KK\Te 130423 HOMO
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\sleep mode.met
Acquired: 4/13/2023 7:52:27 PM
Printed: 8/9/2023 10:49:34 AM



Back Signal
Results

Retention Time	Area	Area %	Height	Height %
1.016	12600	100.00	3272	100.00
Totals	12600	100.00	3272	100.00

(**a**). HER activity for the tellurium complex in homogenous system



(**b**). HER activity for the tellurium complex in heterogeneous system

Fig. S5. (a) and **(b)** are gas chromatography of evolved H_2 gas during bulk electrolysis in homogeneous and heterogeneous systems respectively

Section – 6: ESI mass spectral analysis of compound 2

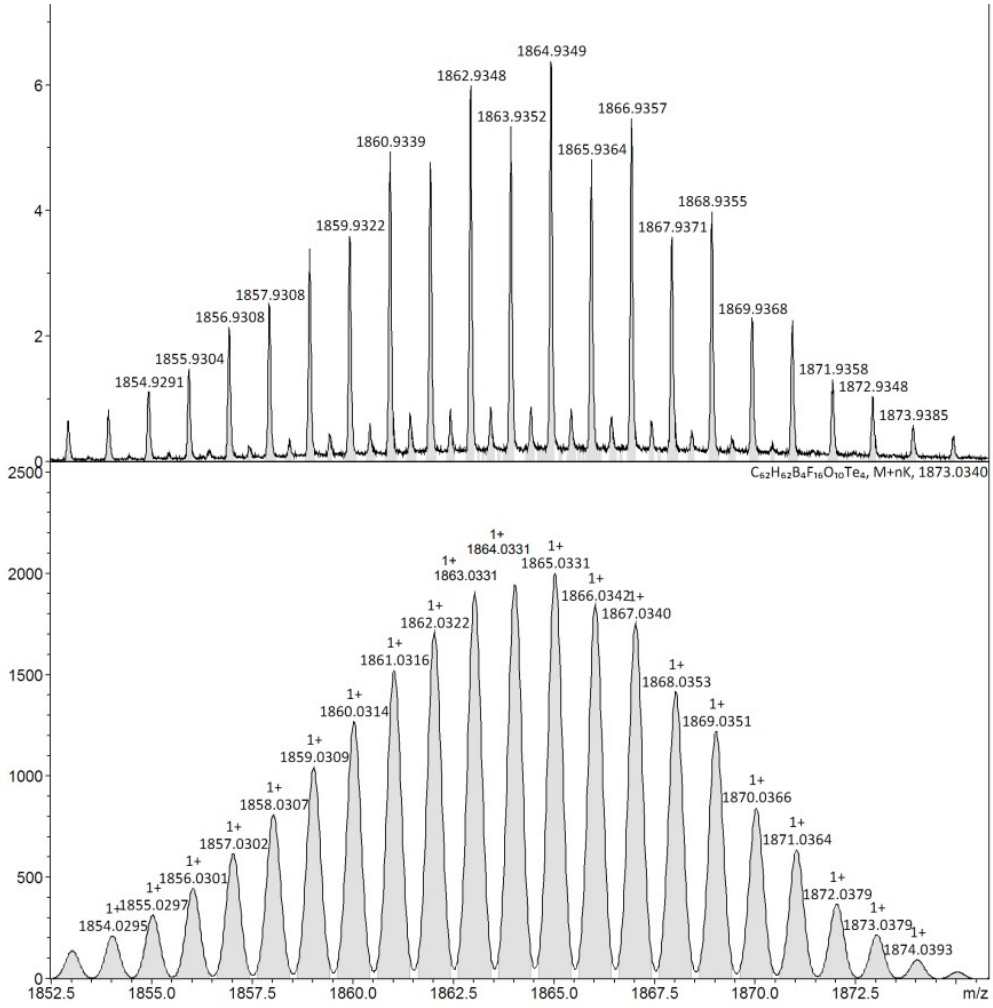


Fig. S6. ESI mass spectra of **2.**

Section – 7: ^{125}Te, ^{19}F, ^{11}B, ^{1}H, ^{13}C NMR spectral analysis of compound 2

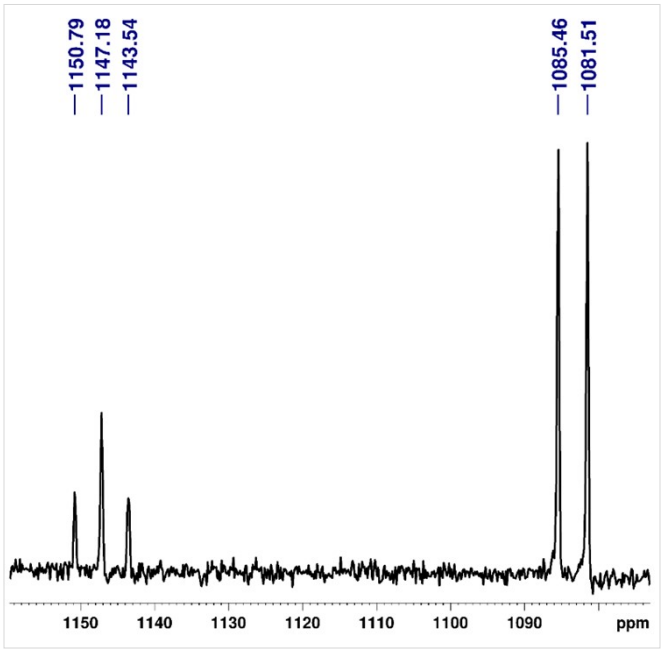


Fig. S7. ^{125}Te NMR spectrum of **2** in $CDCl_3$ at room temperature.

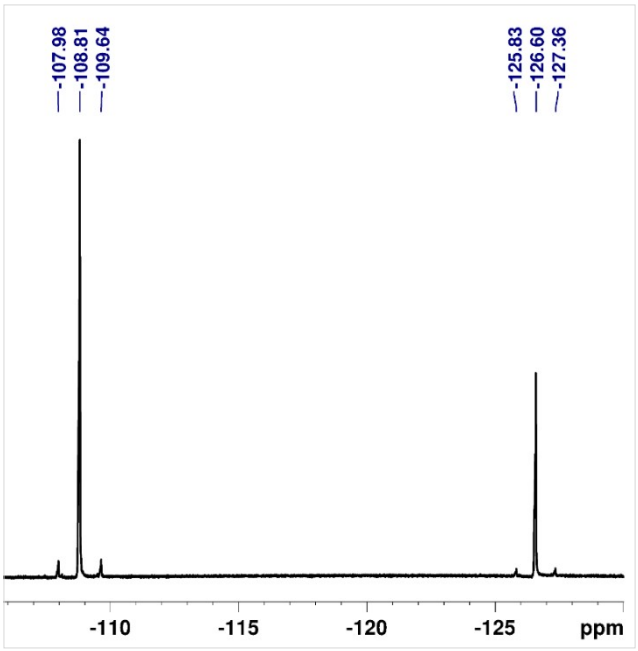


Fig. S8. ^{19}F NMR spectrum of **2** in $CDCl_3$ at room temperature.

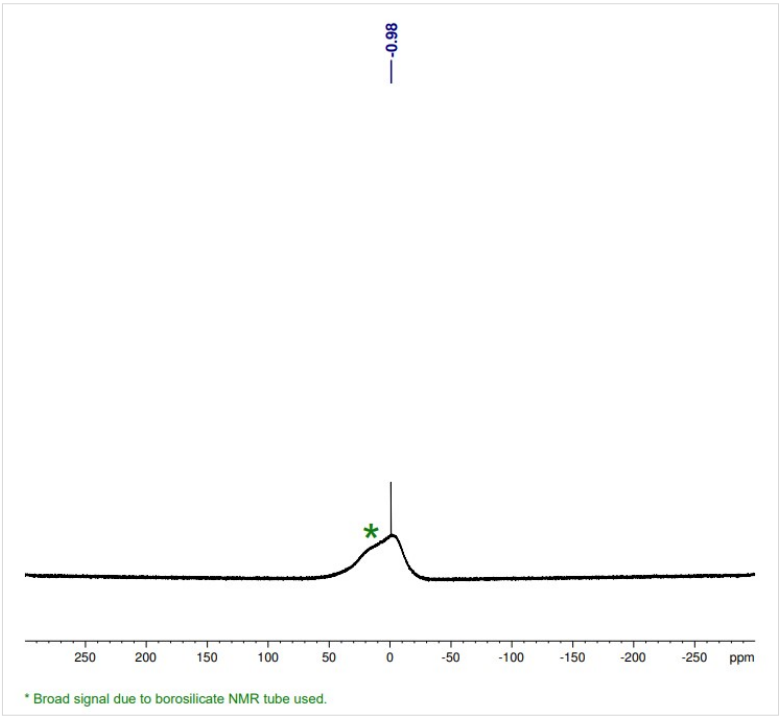


Fig. S9. ^{11}B NMR spectrum of **2** in $CDCl_3$ at room temperature.

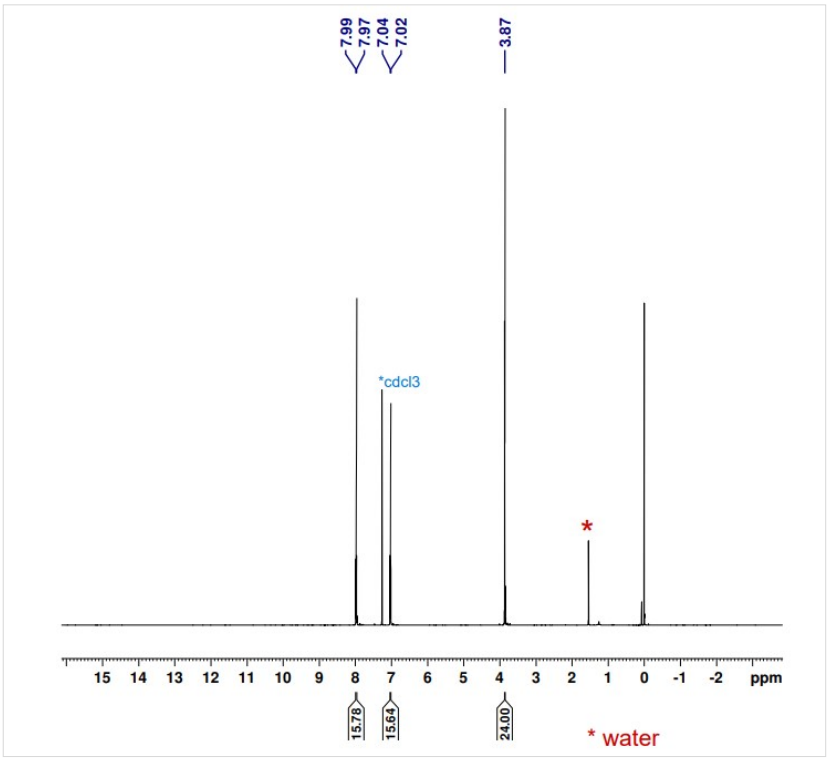


Fig. S10. ^{1}H NMR spectrum of **2** in $CDCl_3$ at room temperature.

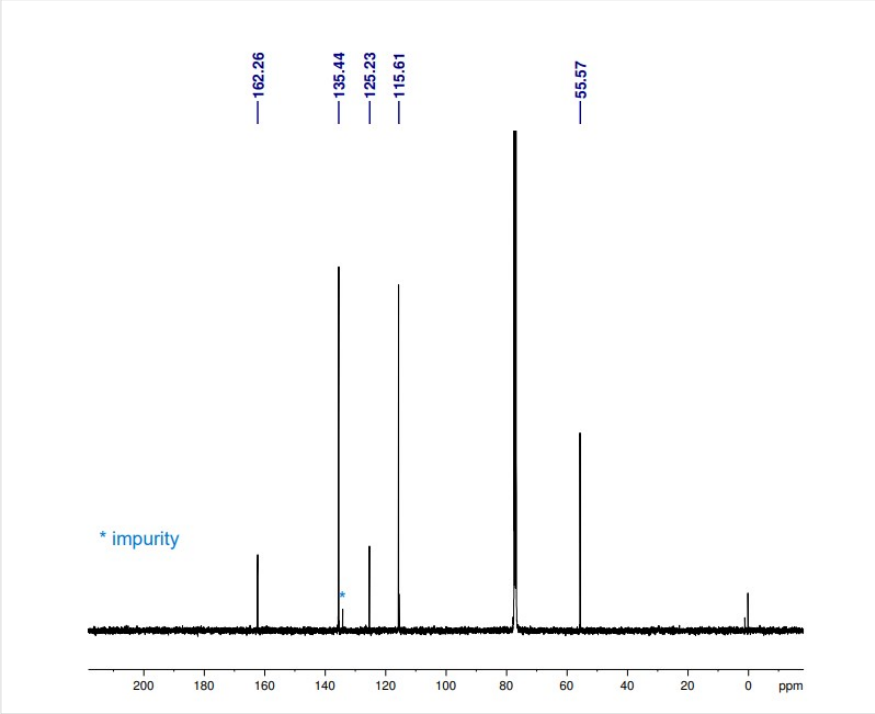


Fig. S11. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$ at room temperature.

Section – 8: powder XRD data and FT-IR spectral analysis of compound 2

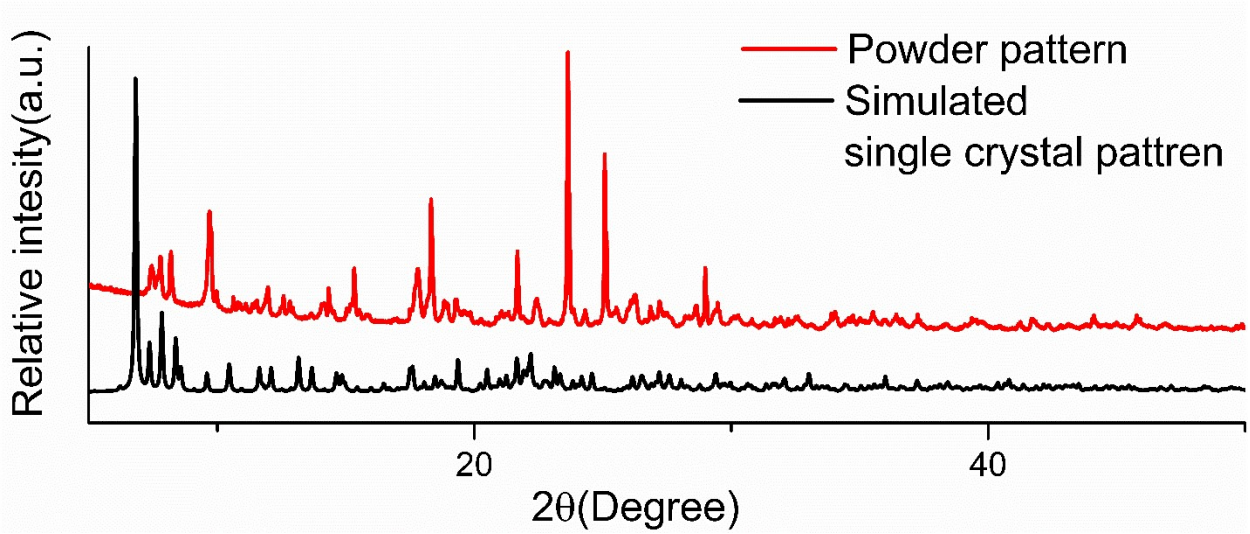


Fig. S12. Powder XRD-pattern for compound **2**.

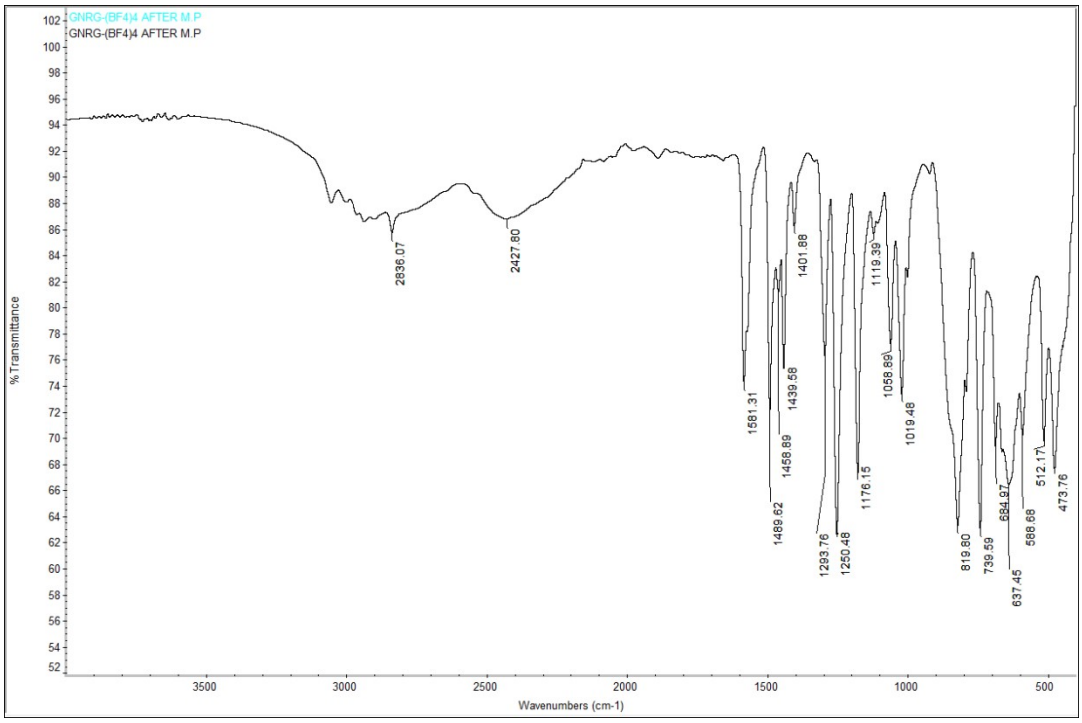


Fig. S13. FT-IR spectrum of compound **2**.

Section – 9: EDAX spectrum and elemental analysis for compound 2.

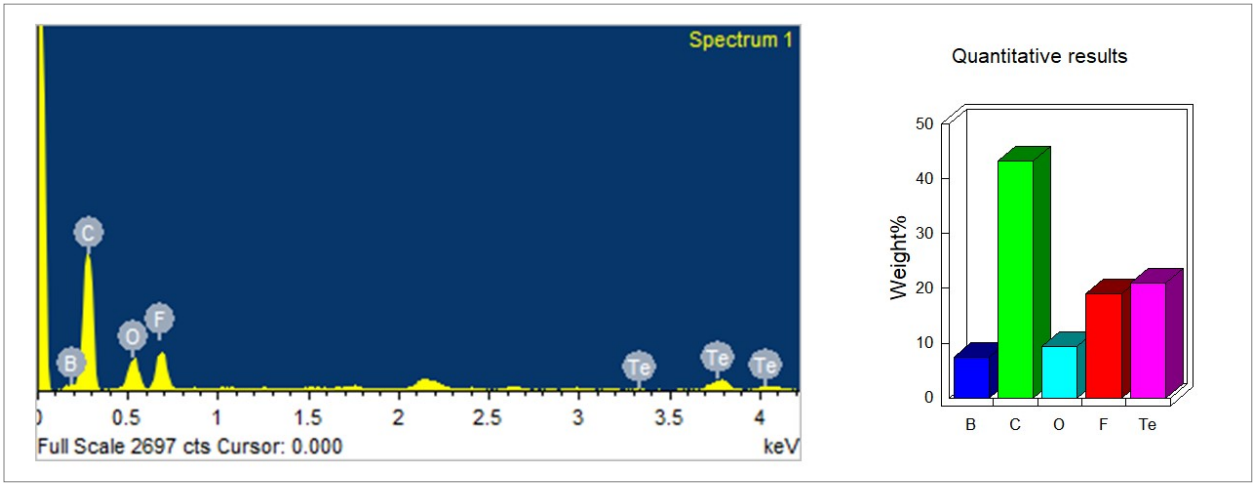


Fig. S14. EDAX spectrum of compound 2

Element	Calculated Weight%	Measured weight% from EDAX analysis
B	2.48	3.32
C	38.51	42.58
O	9.16	9.80
F	17.40	18.95
Te	29.22	25.35
H	3.23	Not detected
	100	--------

Table S5. EDAX elemental analysis of compound 2.

Section – 10: ORTEP diagram of compound 3

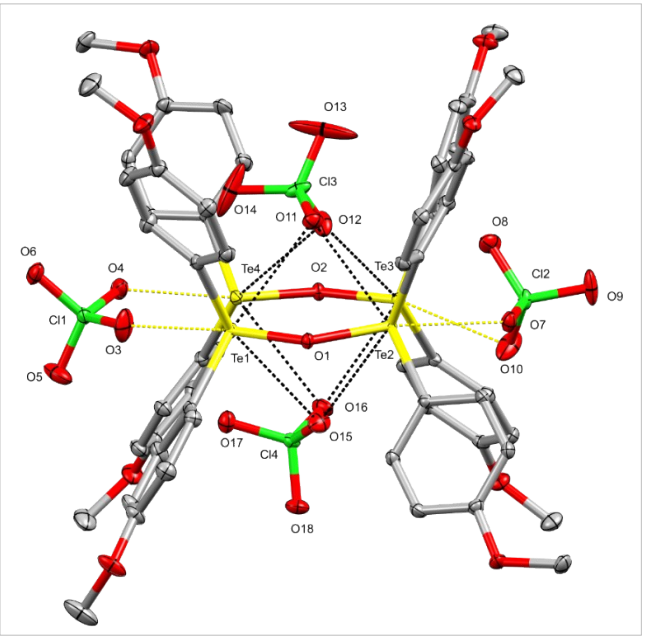


Fig. S15. ORTEP diagram of **3**. The thermal ellipsoids are shown at a 40% probability level. Solvent molecule and all hydrogen atoms were omitted for clarity.

Section – 11: Te-O (perchlorate) interaction distances of compound 3

Table S6. Bridging anion (perchlorate) Interaction with Tellurium [Å].

	Distance in [Å]
Te(1)-O(3)	2.658
Te(2)-O(7)	2.636
Te(3)-O(11)	3.084
Te(4)-O(4)	2.685

Table S7. Capping anion (perchlorate) Interaction with Tellurium [Å].

Te(1)-O(11)	2.970
Te(1)-O(15)	3.100
Te(2)-O(11)	2.885
Te(2)-O(15)	3.085
Te(2)-O(15)	2.840
Te(3)-O(16)	2.912
Te(4)-O(12)	2.960
Te(4)-O(16)	3.080

Section – 12: Bond lengths and bond angles of compound 3

Table S8. Selected bond lengths [Å] and angles [°] for **3**.

Te(1)-O(1)	1.9490(18)
Te(2)-O(1)	1.9602(17)
Te(3)-O(2)	1.9434(18)
Te(4)-O(2)	1.9680(17)
Te(1)-O(1)-Te(2)	122.02(9)
Te(3)-O(2)-Te(4)	124.80(9)

Section – 13: ESI mass spectral analysis of compound 3

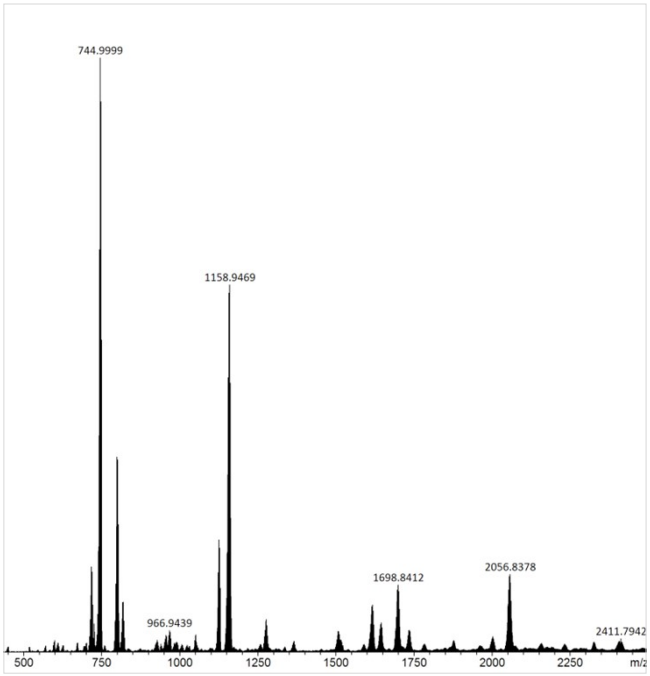


Fig. S16. ESI mass spectra of **3.**

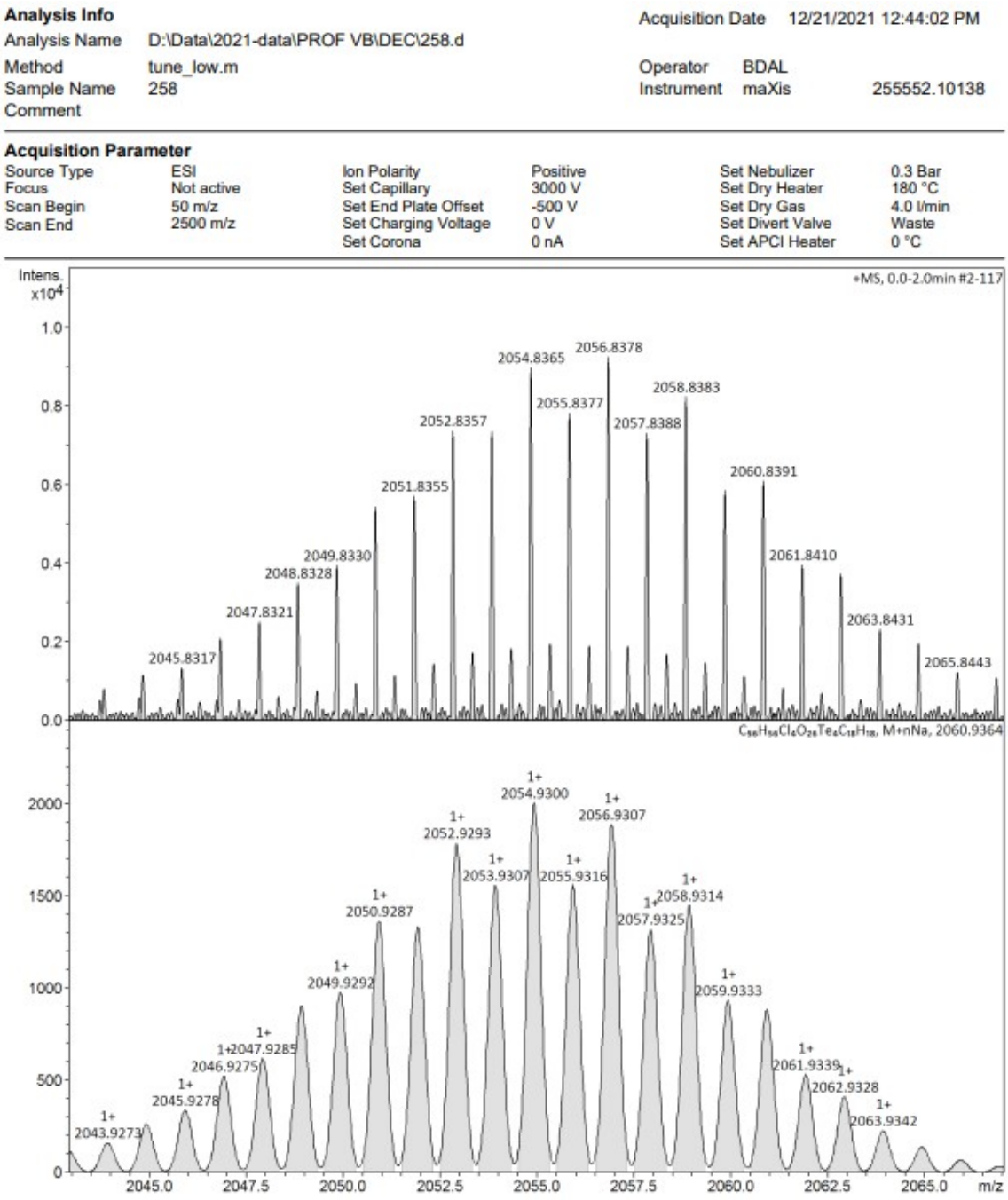


Fig. S16a. ESI mass spectra of **3** experimental above and simulated below

Section – 14: ^{1}H, ^{13}C NMR spectral analysis of compound 3

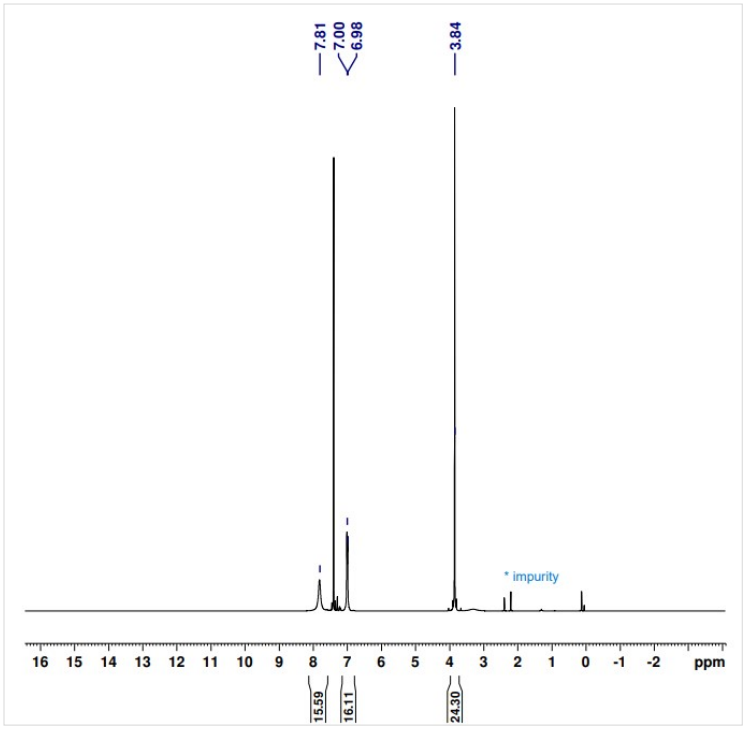


Fig. S17. ^{1}H NMR spectrum of **3** in $CDCl_3$ at room temperature.

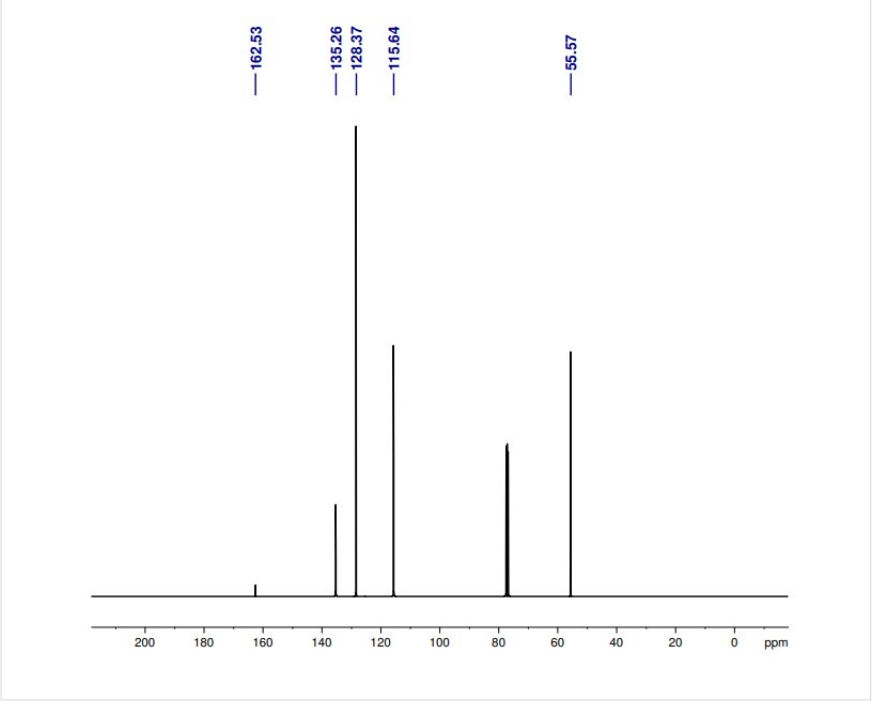


Fig. S18. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$ at room temperature.

Section – 15: Powder and FT-IR spectral analysis of compound 3

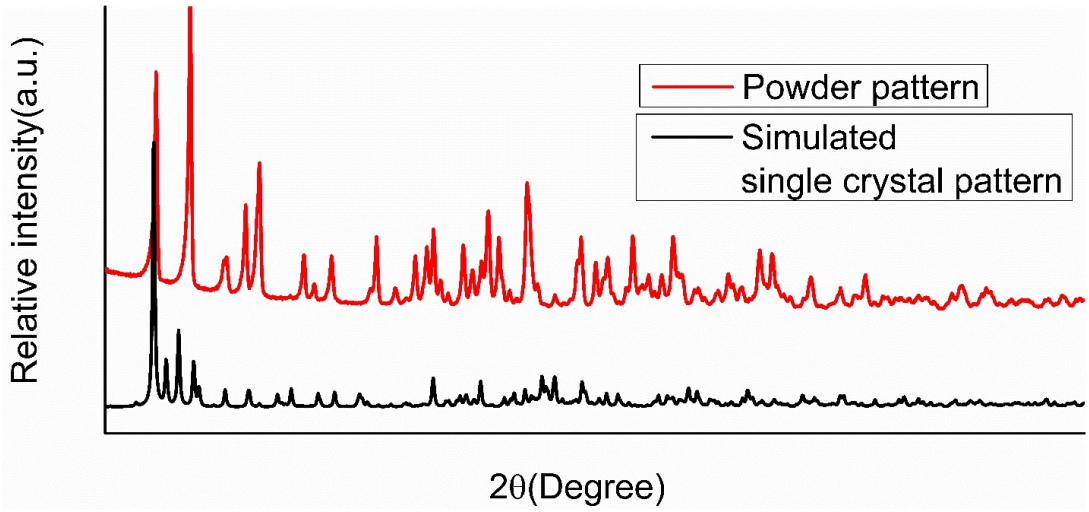


Fig. S19. Powder XRD-pattern for compound 3.

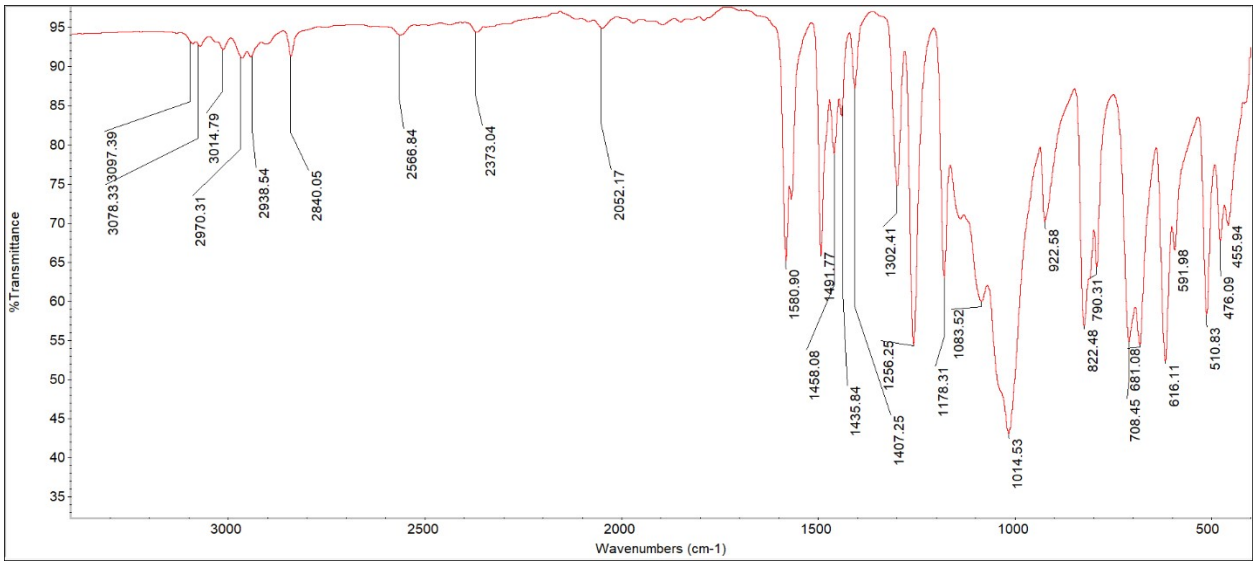


Fig. S20. FT-IR spectrum of compound **3**.

Section – 16: EDAX spectrum and elemental analysis for compound 2.

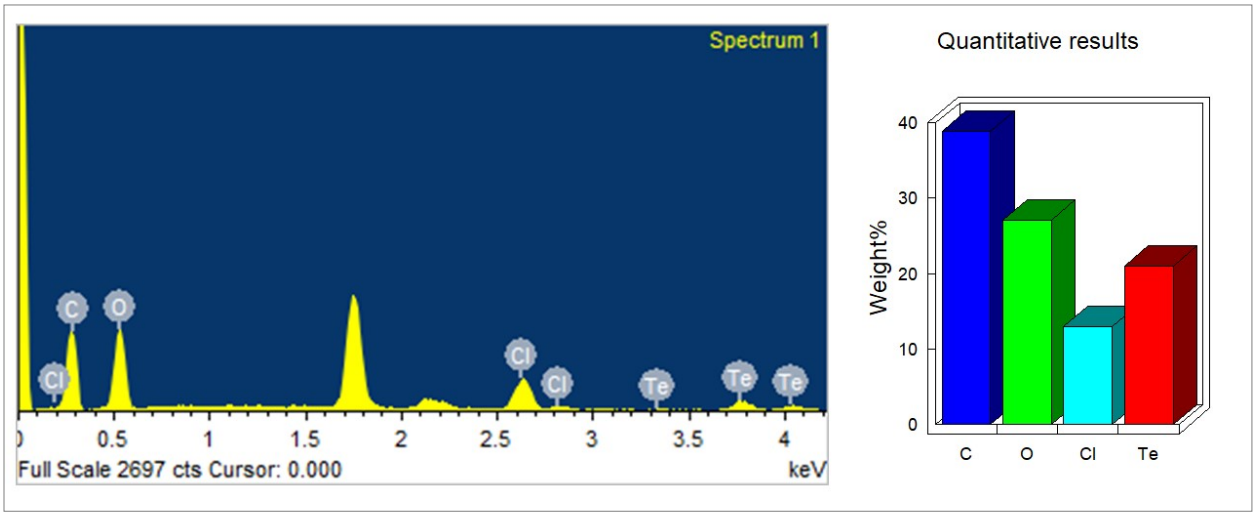


Fig. S21. EDAX spectrum of compound 3.

Element	Calculated Weight%	Measured weight% from EDAX analysis
C	37.42	38.90
O	23.15	25.13
Cl	7.89	11.95
Te	28.40	24.02
H	3.14	Not detected
	100	--------

Table S9. EDAX elemental analysis of compound 3.

Section – 17: ORTEP diagram of compound 4

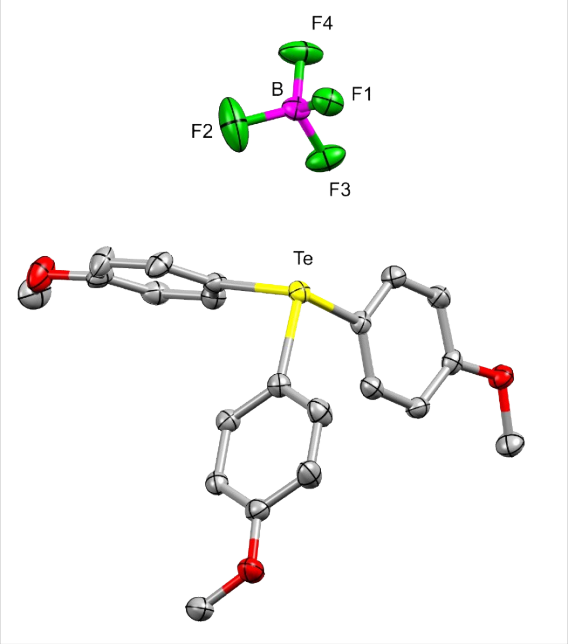


Fig. S22. ORTEP diagram of **4.** The thermal ellipsoids are shown at a 40% probability level. All hydrogen atoms omitted for clarity.

Section – 18: Te-F (BF_4) interaction distances, bond lengths and bond angles of compound 4

Table S10. Interaction [Å], Bond lengths [Å] and angles [°] for **4.**

Te(1)--F(1))	3.030
Te(1)-C(1))	2.100(3)
Te(1)-C(8))	2.100(3)
Te(1)-C(15))	2.120(3)
C(1)-Te(1)-C(8)	95.30(10)
C(1)-Te(1)-C(15)	97.45(10)
C(8)-Te(1)-C(15)	94.95(10)

Section – 19: ESI mass spectral analysis of compound 4

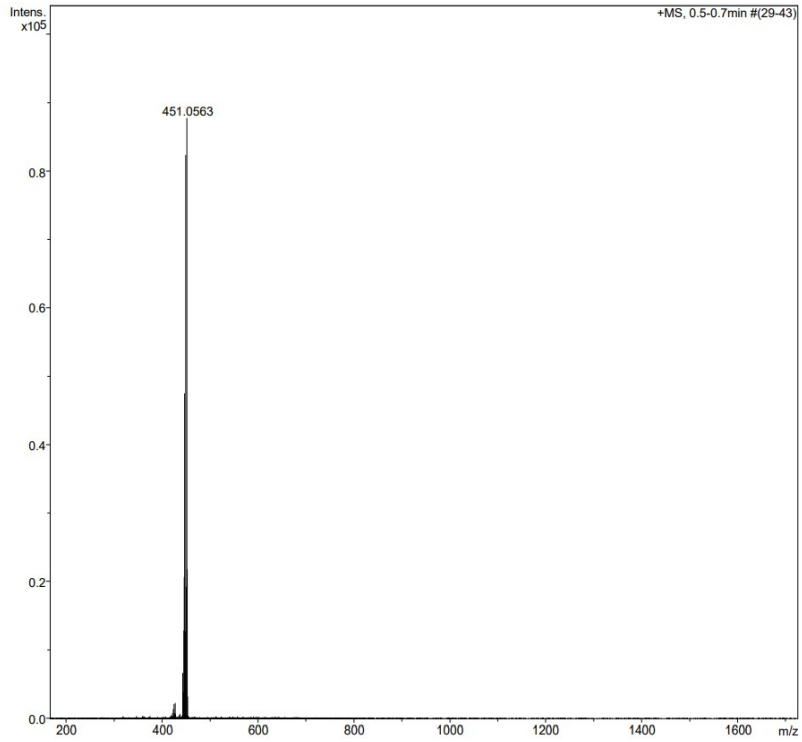


Fig. S23. ESI mass spectra of **4** (experimental)

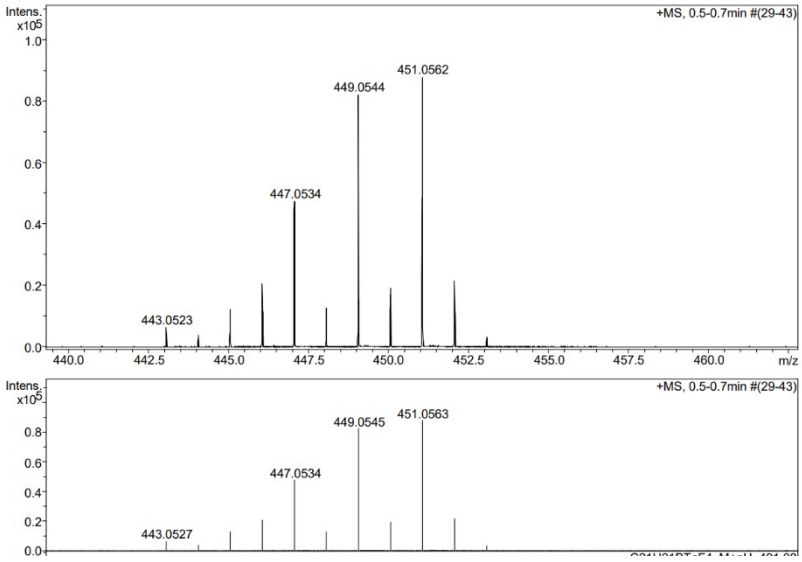


Fig. S24. ESI mass spectra of **4** experimental above and simulated below

Section – 20: ^{125}Te ^{19}F, ^{11}B, ^{1}H, ^{13}C NMR spectral analysis of compound

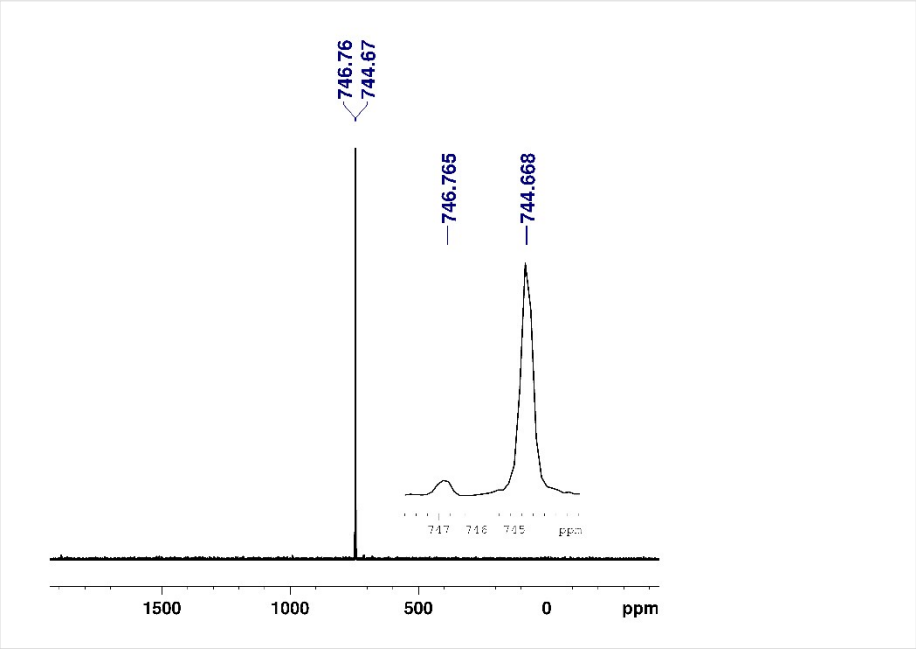


Fig.S22. ^{125}Te NMR spectrum of **4** in $CDCl_3$ at room temperature.

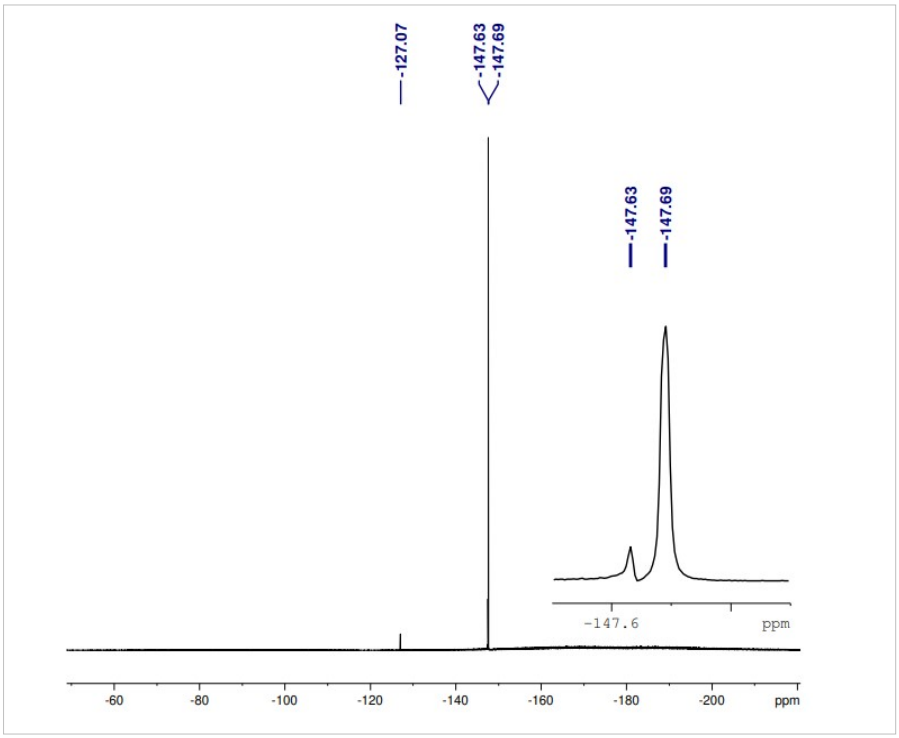


Fig. S23. ^{19}F NMR spectrum of **4** in $CDCl_3$ at room temperature.

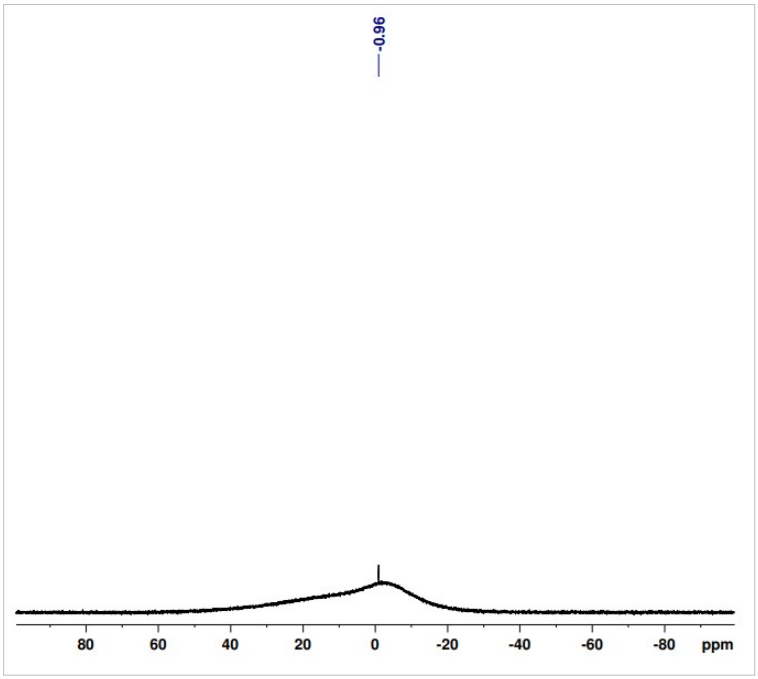


Fig. S24. ^{11}B NMR spectrum of **4** in $CDCl_3$ at room temperature.

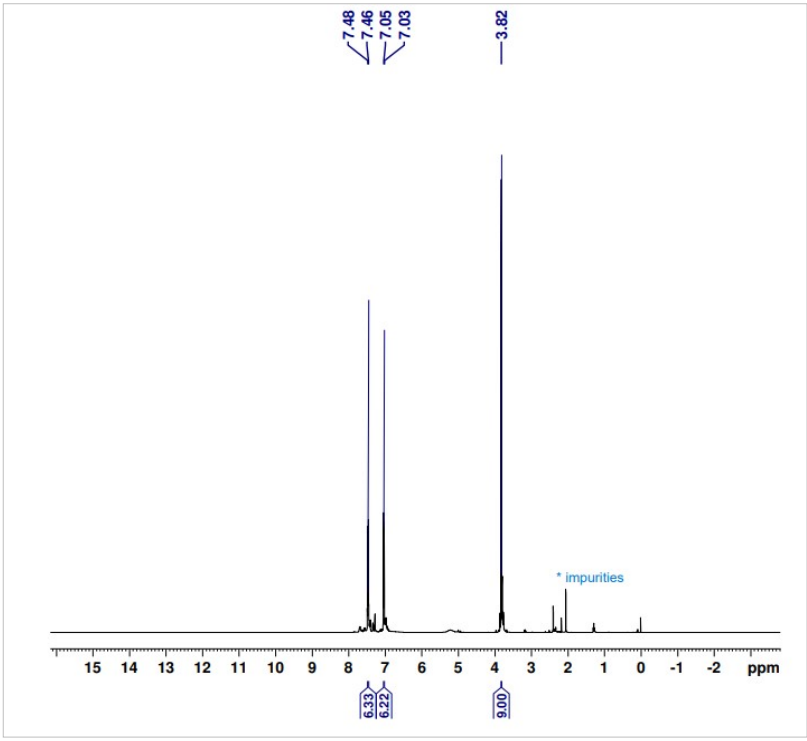


Fig. S25. ^{1}H NMR spectrum of **4** in $CDCl_3$ at room temperature.

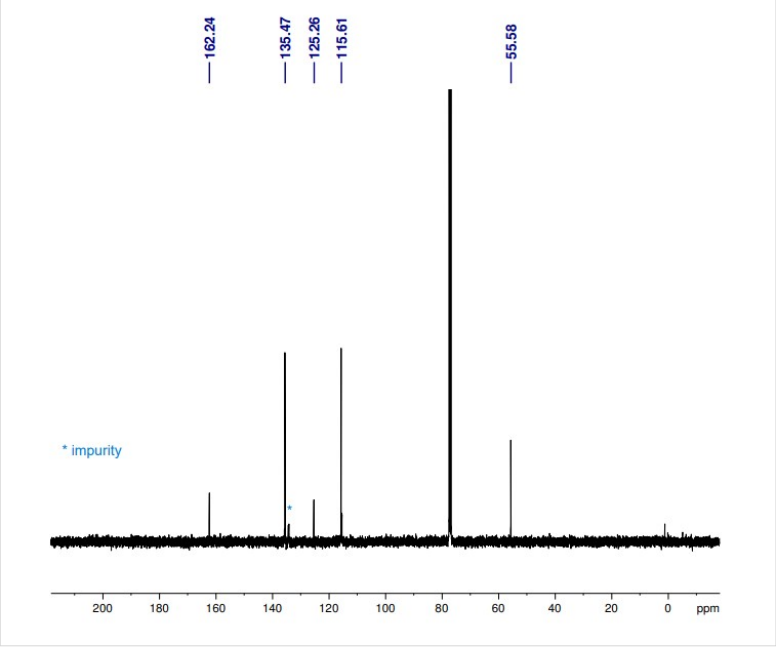


Fig. S26. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$ at room temperature.

Section – 21: Powder and FT-IR spectral analysis of compound 4

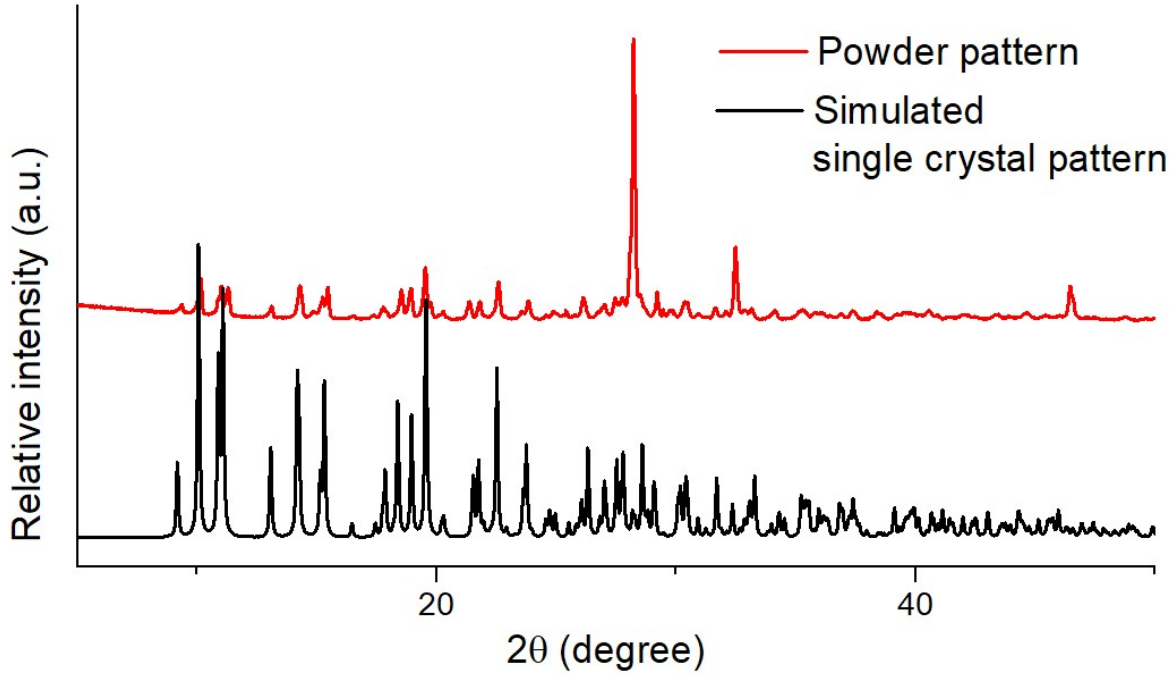


Fig. S27. Powder XRD-pattern for compound **4**.

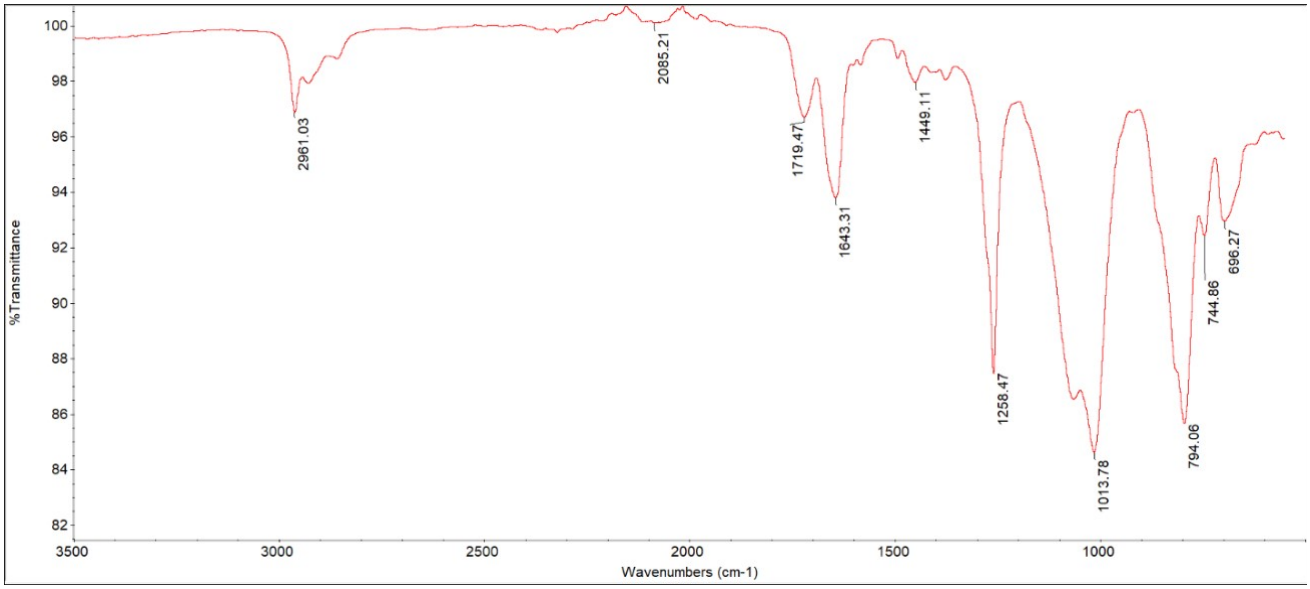


Fig. S28. IR spectrum of compound **4**.

Section – 22: EDAX spectrum and elemental analysis for compound 4.

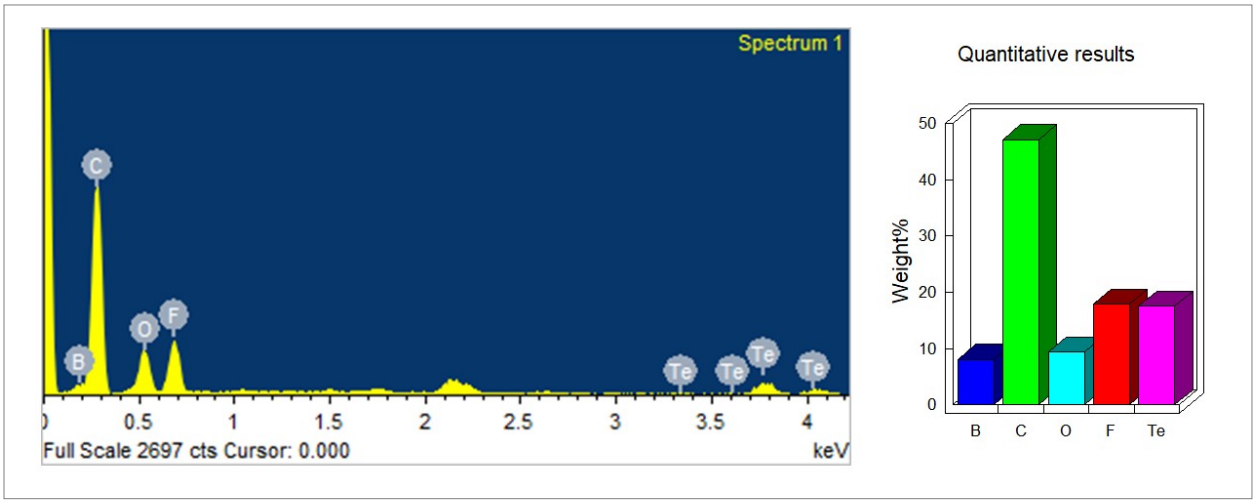


Fig. S29. EDAX spectrum of compound 4.

Element	Calculated Weight%	Measured weight% from EDAX analysis
B	2.02	3.45
C	47.08	47.52
O	8.96	9.37
F	14.18	20.25
Te	23.82	20.04
H	3.95	Not detected
	100	--------

Table S10. EDAX elemental analysis of compound 4.

Section – 23: ORTEP diagram of compound 5

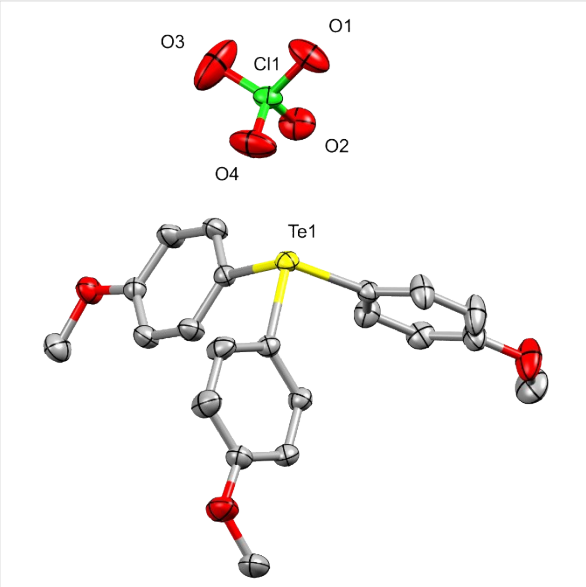


Fig. S29. ORTEP diagram of **5**. The thermal ellipsoids are shown at a 40% probability level. All hydrogen atoms omitted for clarity.

Section – 24: Te-O (perchlorate) interaction distances, bond lengths and bond angles of compound 5

Table S11. Interactions [Å], selected bond lengths [Å] and angles [°] for **5.**

Te(1)--O(2)	3.160
Te(1)-C(7)	2.1025(16)
Te(1)-C(1)	2.1034(16)
Te(1)-C(15)	2.1190(16)
C(7)-Te(1)-C(1)	95.60(6)
C(7)-Te(1)-C(15)	95.20(6)
C(1)-Te(1)-C(15)	97.50(6)

Section – 25: ESI mass spectral analysis of compound 5

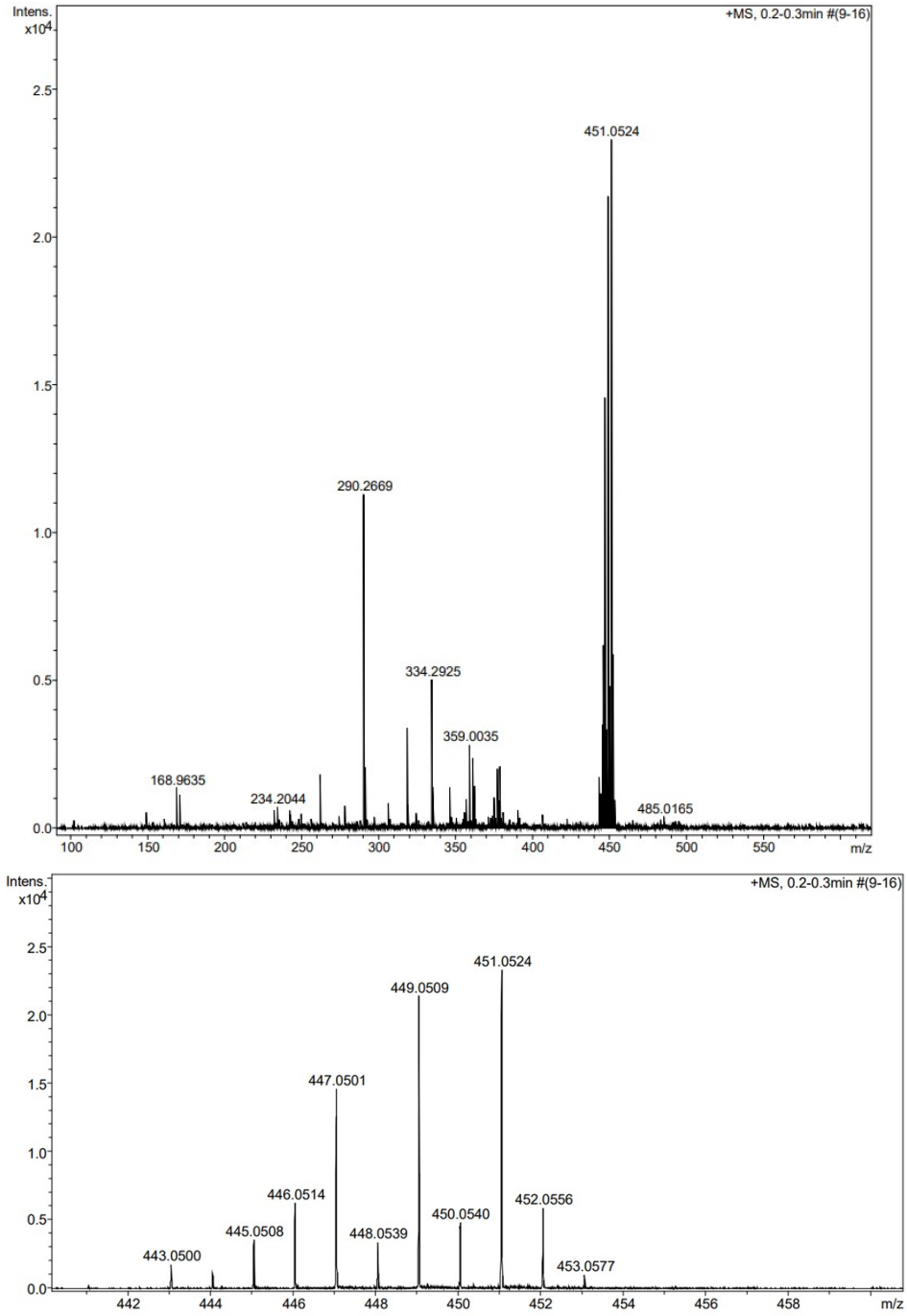


Figure S30. ESI mass spectra of **5**.

Section – 26: ^{125}Te NMR spectral analysis of compound 5

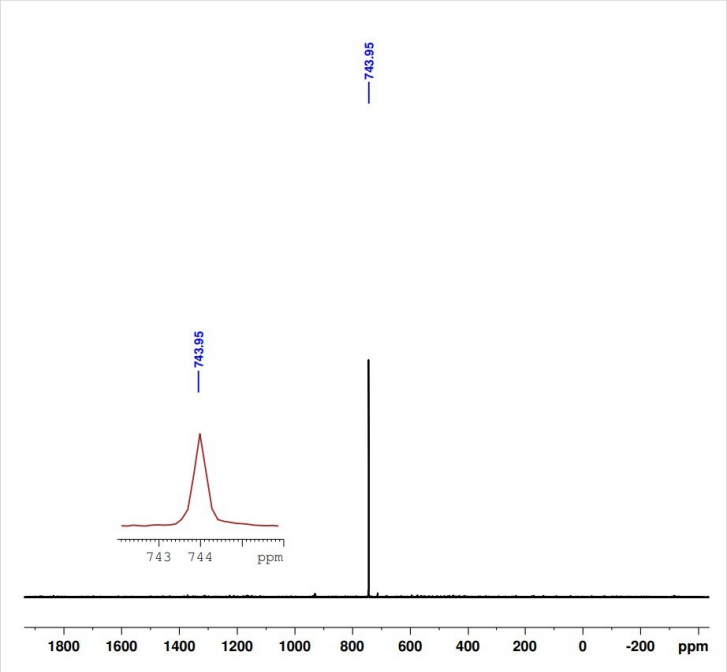


Fig. S31. ^{125}Te NMR spectral analysis of compound **5**

Section – 27: Powder and FT-IR spectral analysis of compound 5

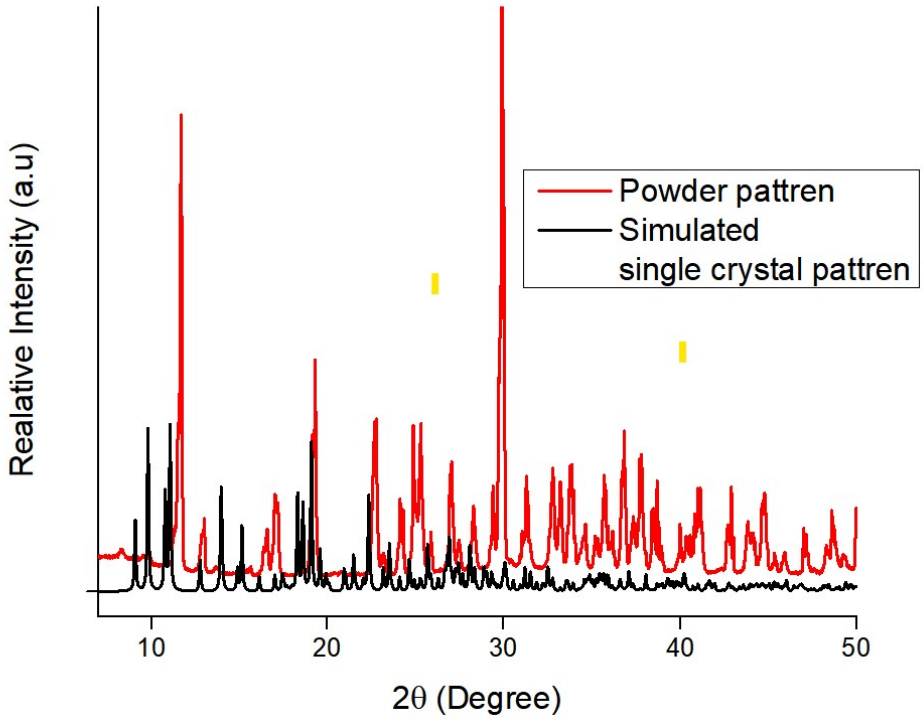


Fig. S32. Powder XRD-pattern for compound **5**.

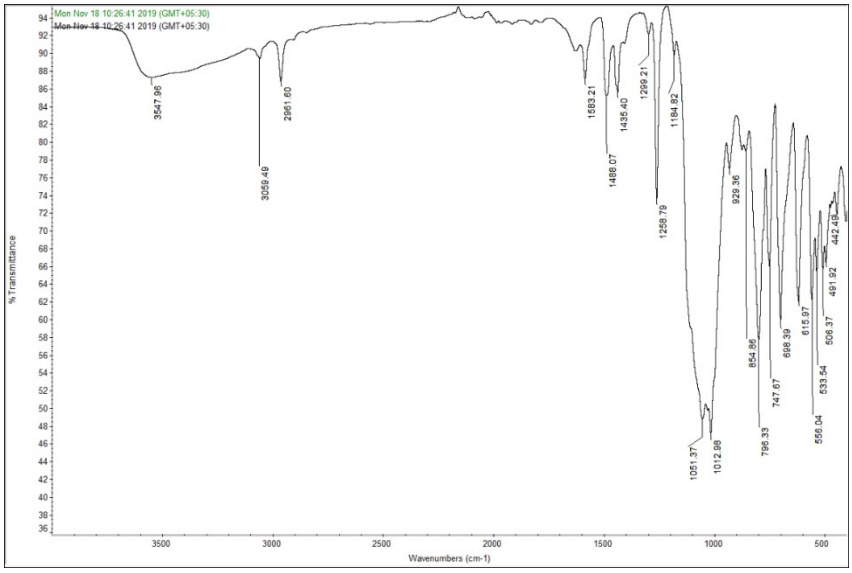


Fig. S33. FT-IR spectrum of compound **5**.

Section – 28: EDAX spectrum and elemental analysis for compound 5.

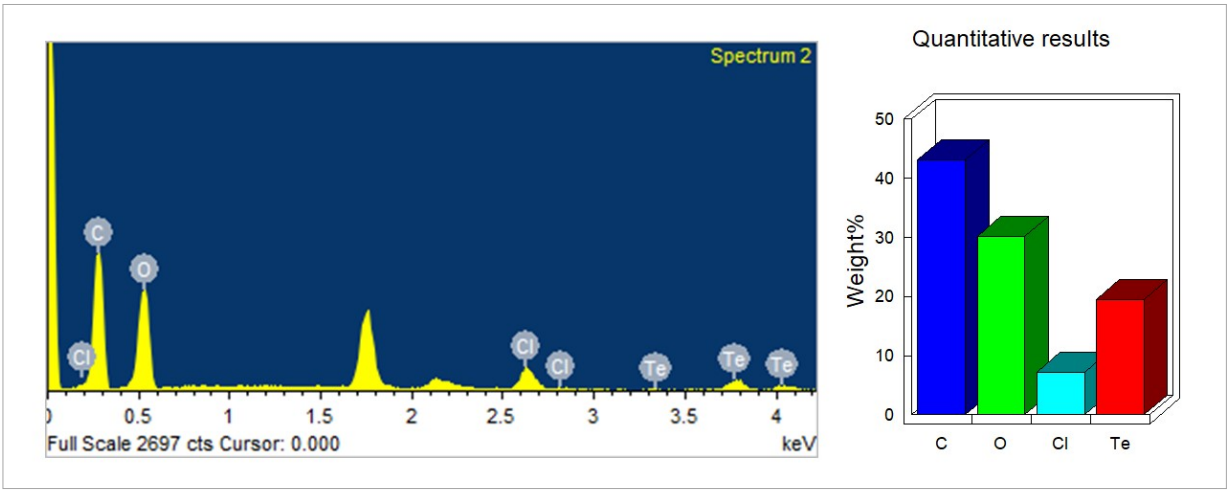


Fig. S34. EDAX spectrum of compound 2

Element	Calculated Weight%	Measured weight% from EDAX analysis
C	45.99	45.11
O	20.42	26.19
Cl	6.46	6.20
Te	23.27	22.50
H	3.86	Not detected
	100	----------

Table S11. EDAX elemental analysis of compound 5.

Disclaimer: Powder X-ray diffraction was performed to evaluate the bulk purity of the produced compounds 2-5. The small variation observed between the powder XRD data and simulated pattern may be due to the reason that the PXRD data was collected at room temperature whereas the simulated pattern is obtained from SCXRD data collected at 100 K. The SCXRD simulated powder data would also have contributions from the solvent of crystallization whereas the PXRD data was collected in samples which were kept under high vacuum, hence there could be a minor variation in the patterns observed.

The difference between the expected weight percentage and the starting stoichiometric ratio of the studied samples can be attributed to many parameters. The most significant are the time constant (Tc), acquisition time (AT), dead time (DT), work distance (WD), and acceleration voltage (AV), because they have a direct impact on energy resolution, natural width of characteristic X-ray lines, and peak intensity.[1]

1. J. I. Goldstein, D. E. Newbury, J. R. Michael, N. W. Ritchie, J. H. J. Scott and D. C. Joy, *Scanning electron microscopy and X-ray microanalysis*, springer, 2017.

Section – 29: Bond valence Sum calculation

Bond valence sum calculation. Numbers in brackets

after atom symbols are at.no., r and c -

see O"Keeffe and Brese, J.A.C.S. 1991, 113, 3226

[{(*p*-OMeC$_6$H$_4$)$_2$Te}$_2$(μ-O)(μ-BF$_4$)(μ-BF$_4$)]$_2$

.....Te1

Te (52, 1.40, 2.72)	Rij	Dij	Vij
-O (8, .63, 3.15)	2.03	1.94	1.26
-C (6, .78, 2.00)	2.17	2.09	1.23
-C (6, .78, 2.00)	2.17	2.08	1.26

Bond valence sum for Te 3.76

.....Te2

Te (52, 1.40, 2.72)	Rij	Dij	Vij
-O (8, .63, 3.15)	2.03	1.96	1.20
-C (6, .78, 2.00)	2.17	2.10	1.22
-C (6, .78, 2.00)	2.17	2.07	1.30

Bond valence sum for Te 3.72

.....Te3

Te (52, 1.40, 2.72) Rij Dij Vij

-O (8, .63, 3.15) 2.03 1.96 1.21

-C (6, .78, 2.00) 2.17 2.10 1.21

-C (6, .78, 2.00) 2.17 2.10 1.22

Bond valence sum for Te 3.64

.....Te4

Te (52, 1.40, 2.72) Rij Dij Vij

-O (8, .63, 3.15) 2.03 1.95 1.24

-C (6, .78, 2.00) 2.17 2.11 1.17

-C (6, .78, 2.00) 2.17 2.07 1.31

Bond valence sum for Te 3.7

[{(*p*-OMeC$_6$H$_4$)$_2$Te}$_2$(μ-O)(μ-ClO$_4$)(μ-ClO$_4$)]$_2$

.....Te1

Te (52, 1.40, 2.72) Rij Dij Vij

-O (8, .63, 3.15) 2.03 1.95 1.24

-C (6, .78, 2.00) 2.17 2.10 1.22

-C (6, .78, 2.00) 2.17 2.11 1.18

Bond valence sum for Te 3.64

.....Te2

Te (52, 1.40, 2.72) Rij Dij Vij

-O (8, .63, 3.15) 2.03 1.96 1.20

-C (6, .78, 2.00) 2.17 2.10 1.21

-C (6, .78, 2.00) 2.17 2.08 1.27

Bond valence sum for Te 3.69

.....Te3

Te (52, 1.40, 2.72) Rij Dij Vij

-O (8, .63, 3.15) 2.03 1.94 1.26

-C (6, .78, 2.00) 2.17 2.10 1.20

-C (6, .78, 2.00) 2.17 2.09 1.24

Bond valence sum for Te 3.70

.....Te4

Te (52, 1.40, 2.72) Rij Dij Vij

-O (8, .63, 3.15) 2.03 1.97 1.17

-C (6, .78, 2.00) 2.17 2.09 1.25

-C (6, .78, 2.00) 2.17 2.10 1.20

Bond valence sum for Te 3.63

(*p*-OMeC$_6$H$_4$)$_3$TeBF$_4$

.....Te1

Te (52, 1.40, 2.72) Rij Dij Vij

-C (6, .78, 2.00) 2.17 2.10 1.20

-C (6, .78, 2.00) 2.17 2.10 1.20

-C (6, .78, 2.00) 2.17 2.12 1.15

Bond valence sum for Te 3.56

(*p*-OMe C$_6$H$_4$)$_3$TeClO$_4$

.....Te1

Te (52, 1.40, 2.72) Rij Dij Vij

-C (6, .78, 2.00) 2.17 2.10 1.19

-C (6, .78, 2.00) 2.17 2.10 1.19

-C (6, .78, 2.00) 2.17 2.12 1.14

Bond valence sum for Te 3.53

……The End……..…….