12-Membered Inorganic Macrocycle Stabilizing Anions of varying Geometry

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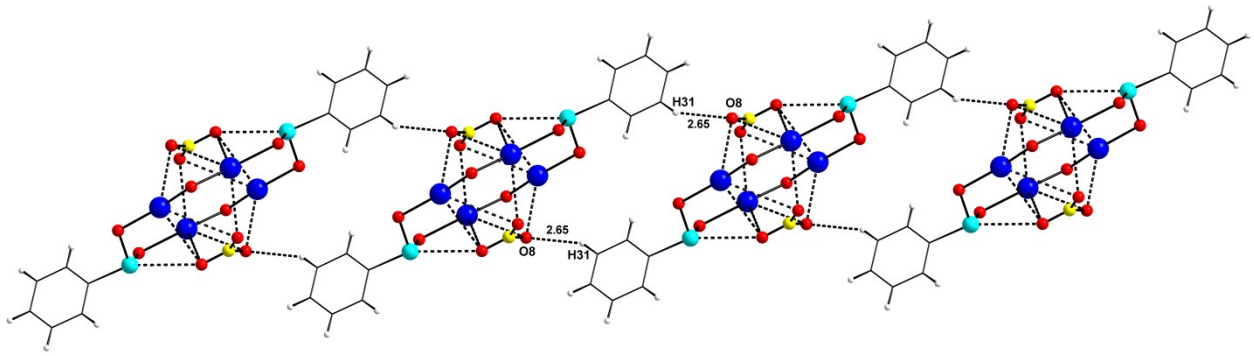
Supporting information:

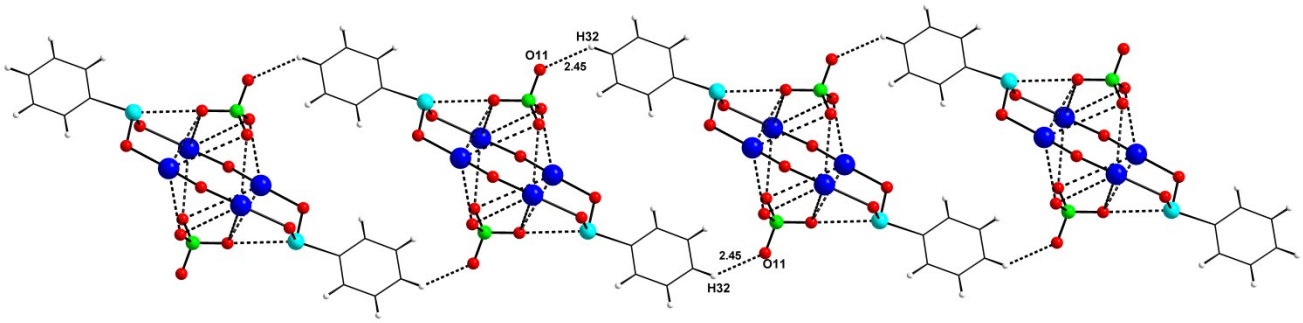
C-H…O and C-H…F interactions:

Apart from the strong Te-O and Se-O interactions in **2**, **3** and Te-F, Se-F interactions in **4**, we have also found some weak intermolecular C-H…O interactions in **2**, **3** and C-H…F interactions in **4** respectively. The C-H…O interactions in **2**, **3** arises between selenium attached phenyl CH of one macrocycle with one of the oxygens of nitrate anion (or) one of the oxygens of perchlorate anion of the another macrocycle respectively. The C-H…F interactions in **4** arises between selenium attached phenyl CH of one macrocycle with one of the fluorine atoms of tetrafluoroborate anion of another macrocycle. These weak interactions have led to the formation of interesting polymeric supramolecular assemblies in solid state (Figure S1). The C-H…O, C-H…F distances and the angles at hydrogen in **2**-**4** were given in the below table.[6]

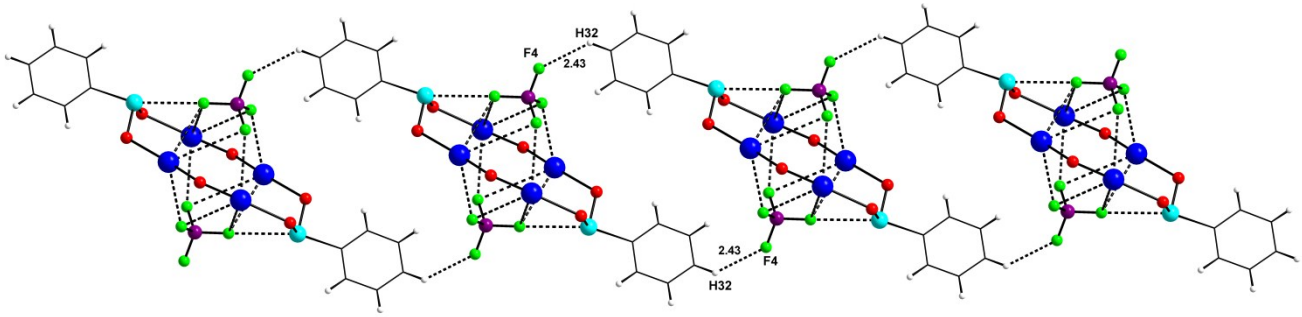
	H…O(Å)	C…O(Å)	C-H…O(deg)
Compound **2**	2.65	3.50	154
Compound **3**	2.45	3.13	130
	H…F(Å)	C…F(Å)	C-H…F(deg)
Compound **4**	2.43	3.10	128



(a)



(b)



(c)

Figure S1: Supramolecular assemblies showing C-H…O interactions in **2**(a), **3**(b) and C-H…F interactions in **4**(c). Anisyl rings attached to tellurium are omitted for clarity.

Table S1: Deviation of each atom from the mean plane (Å) in 12-membered $Te_4Se_2O_6$ ring

label	**2**	**3**	**4**
Te1	± 0.0894(4)	± 0.1188(4)	± 0.1204(3)
Te2	± 0.1006(4)	± 0.1050(4)	± 0.1108(3)
Se1	± 0.6304(4)	± 0.6221(5)	± 0.6244(3)
O1	± 0.2203(17)	± 0.1757(17)	± 0.1850(14)
O2	± 0.5391(17)	± 0.4585(18)	± 0.4704(15)
O3	± 0.0791(18)	± 0.1309(18)	± 0.1170(14)

Table S2: Torsion angles list in **2-4**

	2	**3**	**4**
At Se1			
C30-C29-Se1-O3	45.8(2)[+sc]	-76.8(3)[-sc]	-75.65(19)[-sc]
C30-C29-Se1-O2	-59.7(2)[-sc]	176.3(3)[+ap]	177.57(18)[+ap]
C34-C29-Se1-O2	121.17(18)[+ac]	-1.9(2)[-sp]	-0.66(17)[-sp]
C34-C29-Se1-O3	-133.32(18)[-ac]	105.0(2)[+ac]	106.12(17)[+ac]
At Te1			
C2-C1-Te1-O2	29.8(2)[+sp]	-135.6(2)[-ac]	-135.92(18)[-ac]
C2-C1-Te1-O1	-153.8(2)[-ap]	38.4(2)[+sc]	37.84(18)[+sc]
C6-C1-Te1-O1	29.0(2)[+sp]	-141.3(2)[-ac]	-140.75(18)[-ac]
C6-C1-Te1-O2	-147.4(2)[-ac]	44.8(2)[+sc]	45.49(17)[+sc]
C9-C8-Te1-O2	39.29(18)[+sc]	-142.1(2)[-ac]	-140.84(17)[-ac]
C9-C8-Te1-O1	-134.17(18)[-ac]	44.4(2)[+sc]	45.97(16)[+sc]
C13-C8-Te1-O1	46.14(19)[+sc]	-138.0(2)[-ac]	-135.65(17)[-ac]
C13-C8-Te1-O2	-140.40(-ac]	35.6(2)[+sc]	37.54(17)[+sc]
At Te2			
C16-C15-Te2-O3	-148.0(2)[-ac]	136.1(3)[+ac]	136.17(19)[+ac]
C16-C15-Te2-O1	42.5(2)[+sc]	-35.4(3)[-sc]	-35.56(18)[-sc]
C20-C15-Te2-O1	-140.1(2)[-ac]	145.1(3)[+ac]	143.06(19)[+ac]
C20-C15-Te2-O3	29.38(19)[+sp]	-43.5(3)[-sc]	-45.21(18)[-sc]
C23-C22-Te2-O3	-132.1(2)[-ac]	31.9(2)[+sc]	29.77(17)[+sp]
C23-C22-Te2-O1	39.1(2)[+sc]	-155.2(2)[-ap]	-157.68(18)[-ap]
C27-C22-Te2-O1	-141.1(2)[-ac]	21.7(2)[+sp]	19.83(17)[+sp]
C27-C22-Te2-O3	47.77(19)[+sc]	-151.2(3)[-ap]	-152.72(17)[-ap]

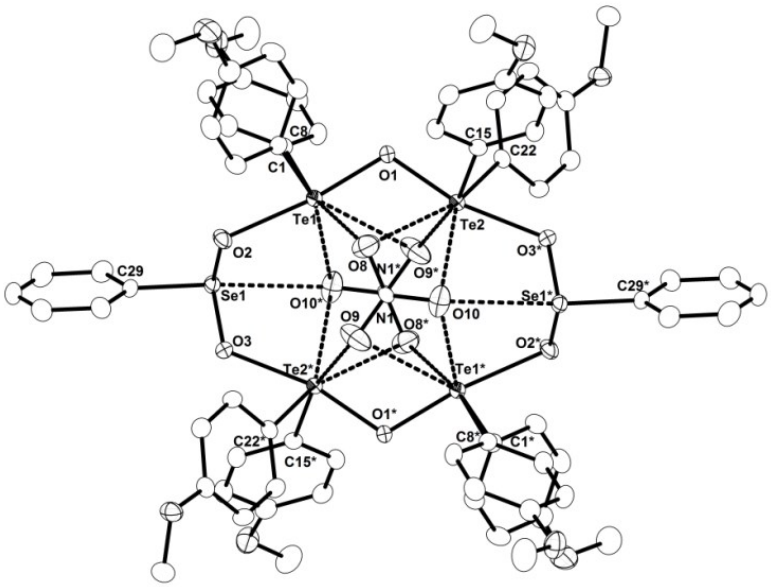
Table S3: crystallographic data for **2**-**4**

	2	**3**	**4**
Formula	$C_{80}H_{78}N_2O_{20}Se2Te_4$	$C_{86}H_{84}Cl_2O_{22}Se_2Te_4$	$C_{86}H_{84}B_2F_8O_{14}Se_2Te_4$
fw	2055.76	2208.75	2183.47
Temperature [K]	100	100	100
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Crystal size [mm]	0.40 x 0.28 x 0.12	0.80 x 0.46 x 0.28	0.40 x 0.30 x 0.14
a [Å]	11.9793(8)	12.2163	12.1225(9)
b [Å]	13.0047(9)	14.8089(13)	14.7726(11)
c [Å]	14.3277(10)	15.9691(14)	15.9277(12)
α [º]	107.5360(10)	71.3950(10)	71.2340(10)
β [º]	109.9690(10)	70.1130(10)	70.0790(10)
γ [º]	92.5130(10)	82.3580(10)	82.4160(10)
V [Å^3]	1973.4(2)	2573.7(4)	2538.3(3)
Z	1	1	1
$d_{calcd.}$ [Mgm^{-3}]	1.730	1.425	1.428
μ [mm^{-1}]	2.459	1.942	1.922
F (000)	1008	1086	1070
θ range for data collection [º]	1.61 to 25.01	1.42 to 26.37	1.42 to 25.50
index ranges	-14<=h<=14 -15<=k<=15 -17<=l<=17	-15<=h<=15 -18<=k<=18 -19<=l<=19	-14<=h<=14 -17<=k<=17 -19<=l<=19
Reflections collected/unique	18995/6948	27402/10449	25469/9431
R(int.)	0.0171	0.0260	0.0182
Data/restraints/parameters	6948 / 0 / 491	10449 / 0 / 527	9431 / 0 / 527
GoF on F^2	1.091	1.035	1.028
R_1/wR_2 [I>2σ(I)]	0.0198/0.0493	0.0275/0.0730	0.0196/0.0500
R_1/wR_2 [all data]	0.0208/0.0498	0.0293/0.0740	0.0210/0.0506
Largest diff peak/hole [eÅ^{-3}]	0.614/-0.480	1.832/-0.641	0.573/-0.369

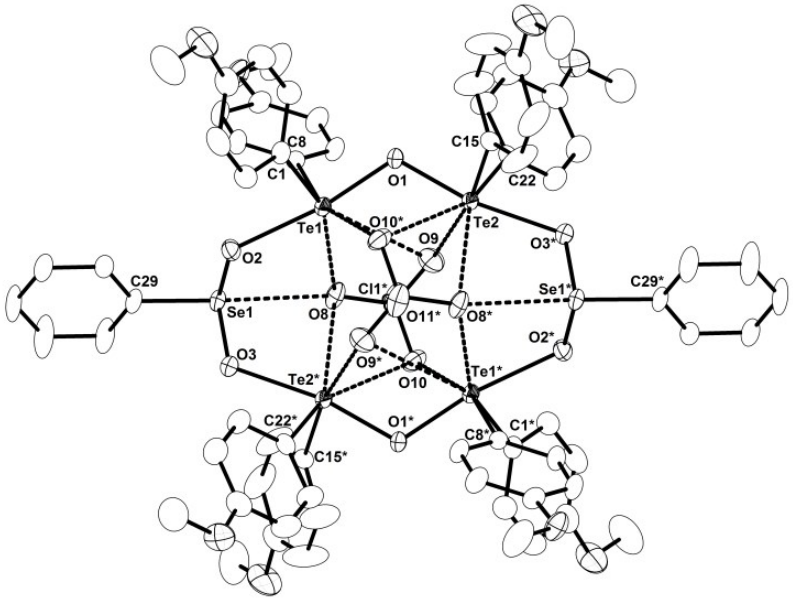
Table S4. selected bond lengths and bond angles in **2**-**4**

2		**3**		**4**	
Te1-O1	1.9952(14)	Te1-O1	1.9925(16)	Te1-O1	1.9917(13)
Te1-O2	2.3475(15)	Te1-O2	2.3294(16)	Te1-O2	2.3260(13)
Te2-O1	2.0105(15)	Te2-O1	2.0025(15)	Te2-O1	2.0032(12)
Te2-O3*	2.2909(15)	Te2-O3*	2.3083(16)	Te2-O3	2.3102(13)
Te1-C1	2.108(2)	Te1-C1	2.101(2)	Te1-C1	2.0996(19)
Te1-C8	2.100(2)	Te1-C8	2.099(2)	Te1-C8	2.1021(18)
Te2-C15	2.110(2)	Te2-C15	2.106(2)	Te2-C15	2.1117(19)
Te2-C22	2.101(2)	Te2-C22	2.108(2)	Te2-C22	2.1037(18)
Se1-O2	1.6989(15)	Se1-O2	1.6934(17)	Se1-O2	1.6974(13)
Se1-O3	1.6961(15	Se1-O3	1.7018(17)	Se1*-O3	1.7060(13)
Se1-C29	1.919(2)	Se1-C29	1.925(2)	Se1-C29	1.9280(19)
O2-Se1-O3	103.91(8)	O2-Se1-O3	105.29(9)	O2-Se1-O3*	105.16(7)
O1-Te1-O2	172.73(6)	O1-Te1-O2	171.68(6)	O1-Te1-O2	171.26(5)
O1-Te2-O3*	167.11(6)	O1-Te2-O3*	169.64(6)	O1-Te2-O3	169.65(7)
Te1-O1-Te2	114.39(7)	Te1-O1-Te2	116.63(8)	Te1-O1-Te2	116.86(6)
Te1-O2-Se1	112.12(7)	Te1-O2-Se1	118.23(8)	Te1-O2-Se1	118.00(7)
Se1-O3-Te2*	122.68(8)	Se1-O3-Te2*	119.72(8)	Se1*-O3-Te2	119.24(7)

ORTEP diagrams:



(a)



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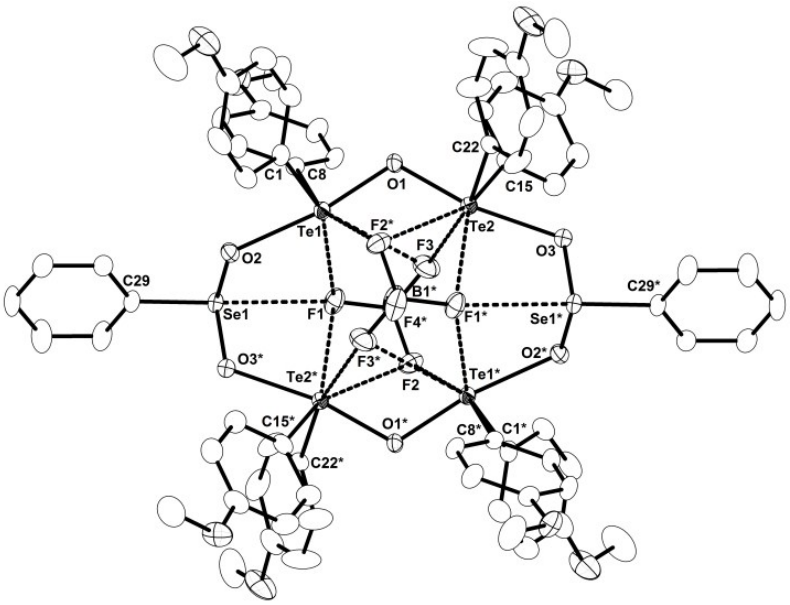
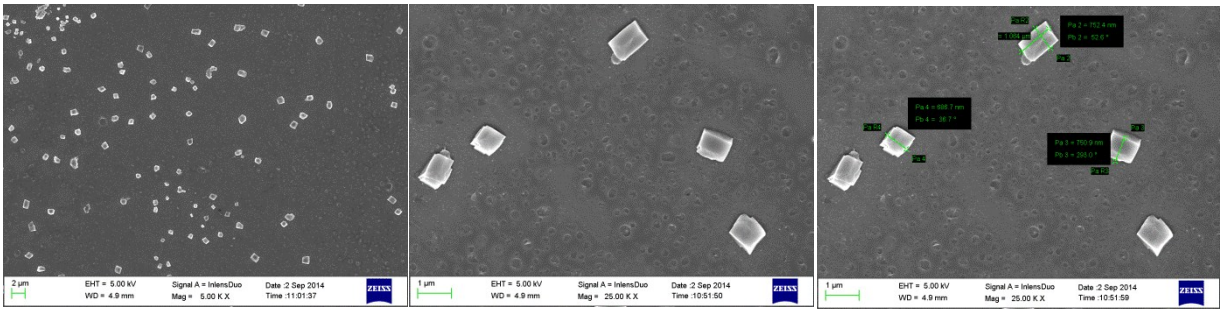
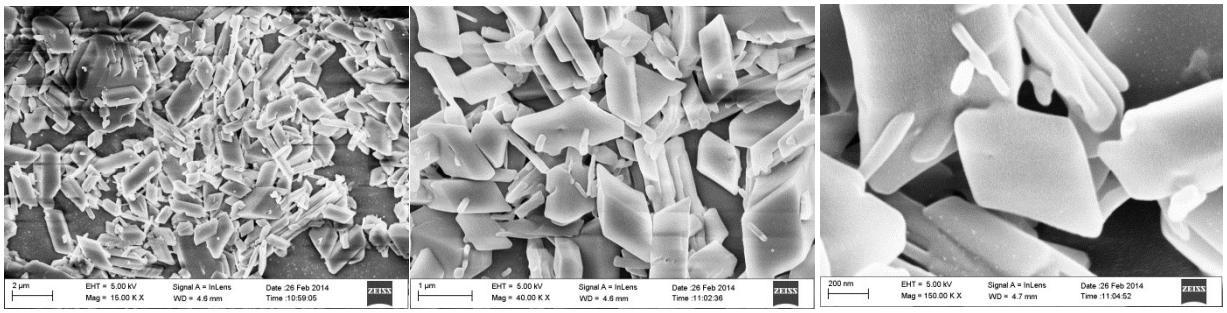


(c)

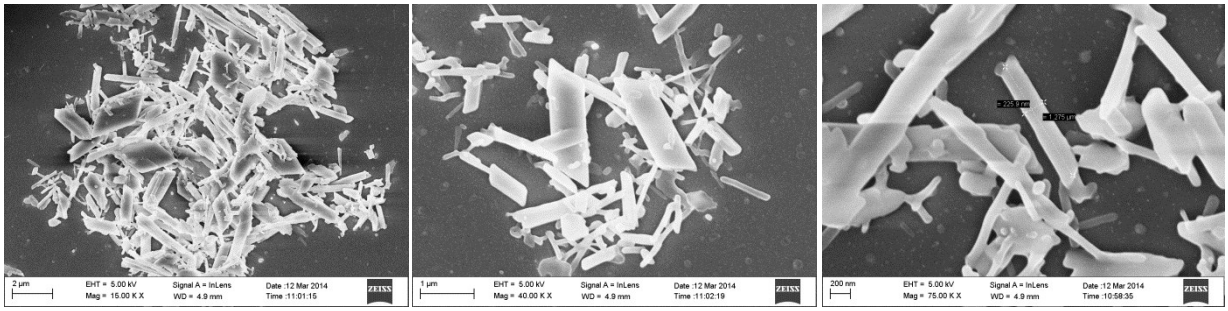
Figure S2: ORTEP representations of **2**(a), **3**(b) and **4**(c) with the thermal ellipsoids shown at 50% probability levels. Hydrogen atoms and benzene solvates are omitted for clarity.



(a)



(b)



(c)

Figure S3: FE-SEM images of **2**(a), **3**(b) and **4**(c) at varying magnifications. Samples were prepared by dispersing the compounds in toluene and drop casted on a glass plate.

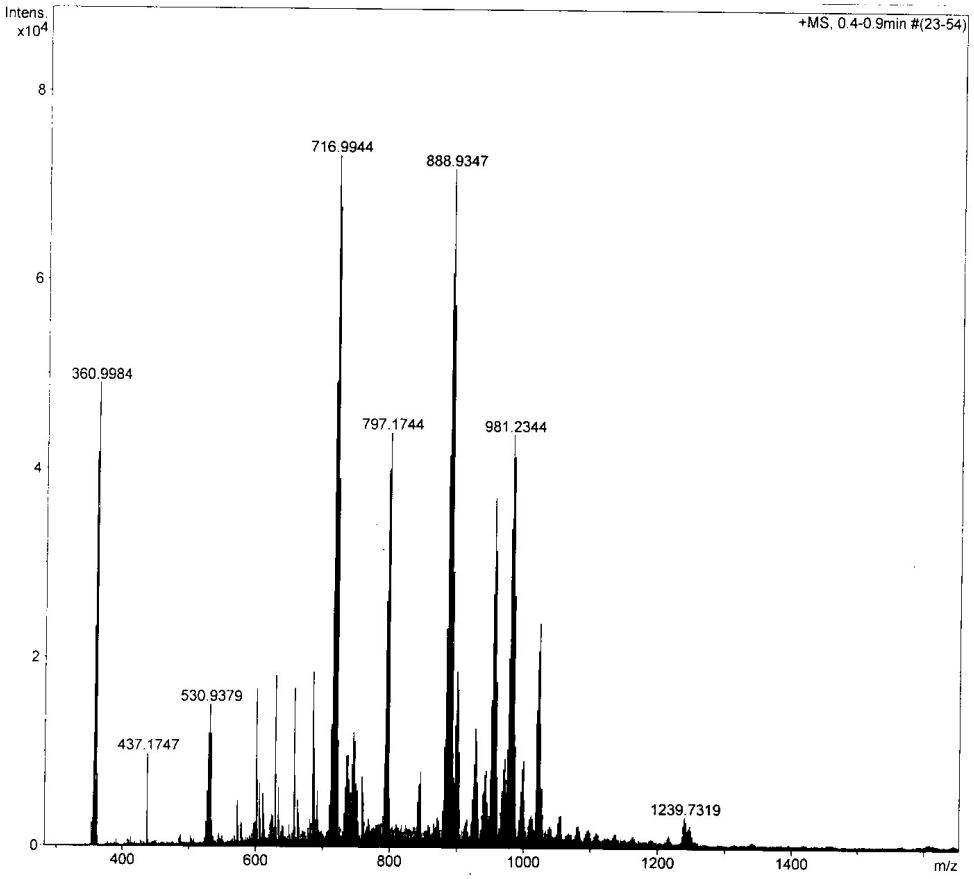


Figure S4: ESI-MS (positive ion mode in acetonitrile) of **4**.

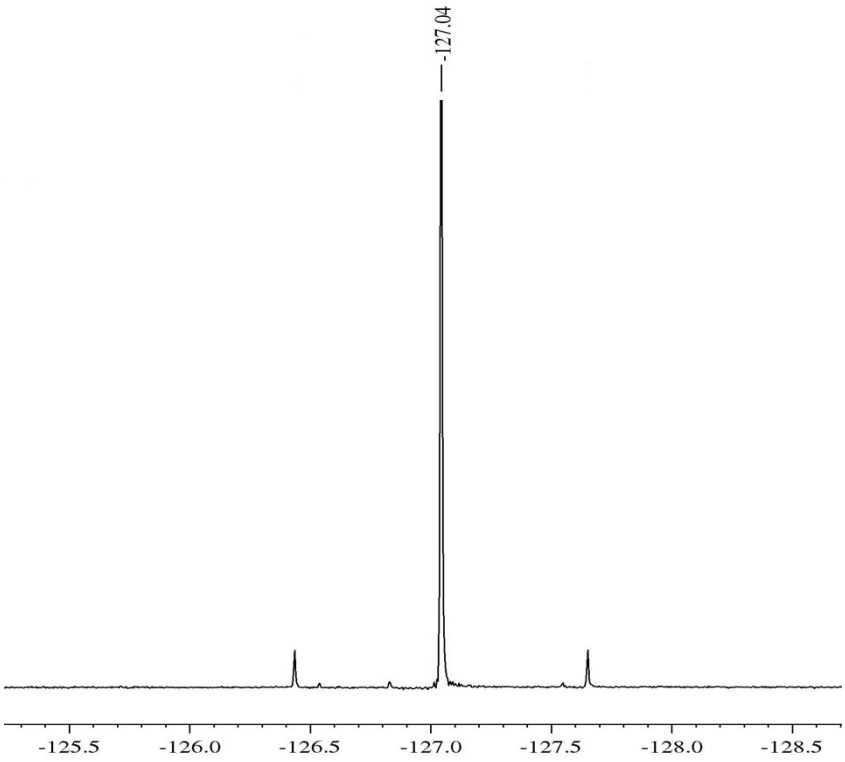


Figure S5: Solution ^{19}F NMR of compound **4** showing a resonance at -127 ppm with Te satellites on both sides.