Electronic Supplementary Information

Organoselenium(II) Halides Containing the Pincer 2,6-$(Me_2NCH_2)_2C_6H_3$ Ligand – An Experimental and Theoretical Investigation

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[2,6-(Me_2NCH_2)$_2$$C_6H_3$]$_2$$Se_2$ (1). A solution of ^{n}BuLi in hexane (11.5 mL, 1.6M, 18.41 mmol) was added dropwise to a solution of 1,3-bis(dimethylaminomethyl)benzene (3.54 g, 18.41 mmol) in hexane (50 mL), then the reaction mixture was refluxed for 24 h to give a clear orange solution. The solvent was removed to dryness to give [2,6-(Me_2NCH_2)$_2$$C_6H_3$]Li as an orange oil, sensitive to moisture and soluble in hexane. The organolithium reagent was treated with selenium powder (1.45 g, 18.41 mmol) in anhydrous THF (80 mL), under argon atmosphere. After all elemental selenium was consumed, the reaction mixture containing the lithium selenolate was poured into water and left overnight in an efficient fume hood to complete the oxidation process to **1**.[8a] Purification of the diselenide was achieved as previously reported.[18] Anal. calcd. for $C_{24}H_{38}N_4Se_2$ (542.14): C 53.33, H 7.09, N 10.37; Found: C 53.53, H 7.10, N 10.35%. ^{1}H NMR ($CDCl_3$): δ 2.99 (24 H, s, H-8,10, CH_3), 4.20 (8 H, s, H-7,9, CH_2), 7.28 (6 H, m, H-3,4,5, C_6H_3). ^{13}C NMR ($CDCl_3$): δ 48.89 (s, C-8,10, CH_3), 63.98 (s, C-7,9, CH_2), 125.90 (s, C-3,5), 128.42 (s, C-4), 132.38 (s, C-2,6), 132.52 (s, C-1). ^{77}Se NMR ($CDCl_3$): δ 395.6. MS (ESI$^+$), *m/z* (%): 271 [2,6-(Me_2NCH_2)$_2$$C_6H_3Se^+$].

Table S1. Crystal data and structure refinement for **2**·H_2O, **2**·$2H_2O$ and **8**.

	2·H_2O	**2**·$2H_2O$	**8**
Empirical formula	$C_{12}H_{21}ClN_2OSe$	$C_{12}H_{23}ClN_2O_2Se$	$C_{24}H_{29}Cl_4N_2SbSe$
Formula weight [$gmol^{-1}$]	323.72	341.73	688.00
Temperature	297(2) K	297(2) K	298(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	C2/c	P-1	P-1
a [Å]	14.7558(18)	7.7651(14)	a = 9.4870(7)
b [Å]	11.3558(14)	9.6342(18)	12.6148(9)
c [Å]	18.666(2)	11.281(2)	12.9073(9)
α [°]	90.00	79.378(3)	109.2860(10)
β [°]	109.722(2)	70.513(3)	101.6220(10)
γ [°]	90.00	87.642(3)	104.8360(10)
V [$Å^3$]	2944.3(6)	781.8(2)	1338.37(17)
Z	8	2	2
ρ_{calcd} [gcm^{-3}]	1.461	1.452	1.707
μ [mm^{-1}]	2.720	2.570	2.806
F(000)	1328	352	680
Crystal size [mm]	0.39 x 0.27 x 0.24	0.38 x 0.31 x 0.20	0.52 x 0.48 x 0.47
Theta range for data collection [°]	2.32 to 25.00	1.95 to 26.37	1.76 to 25.00
Completeness to Θ_{max} [%]	100	99.4	98.9
Index ranges	-17<=h<=17	-9<=h<=9	-11<=h<=11
	-13<=k<=13	-12<=k<=12	-15<=k<=15
	-22<=l<=22	-14<=l<=14	-15<=l<=15
Reflections collected	13720	8347	11219
Independent reflections	2588 [R(int) = 0.0401]	3175 [R(int) = 0.0365]	4662 [R(int) = 0.0293]
Absorption correction	Multi-Scan[1]	Multi-Scan[1]	Multi-Scan[1]
Max. / min. transmission	0.5613 / 0.4168	0.627 / 0.442	0.3522 / 0.3232
Refinement method	Full-matrix least-squares on F^2		
Data / restrains / parameters	2588 / 3 / 167	3175 / 11 / 187	4662 / 0 / 293
Goodness-of-fit on F^2	1.027	1.046	1.177
Final *R* indices [$I>2\sigma(I)$]	*R*1 = 0.0292	*R*1 = 0.0424	*R*1 = 0.0307
	*wR*2 = 0.0690	*wR*2 = 0.1044	*wR*2 = 0.0739
R indices (all data)	*R*1 = 0.0347	*R*1 = 0.0477	*R*1 = 0.0341
	*wR*2 = 0.0710	*wR*2 = 0.1073	*wR*2 = 0.0754
Largest diff. peak and hole [$eÅ^{-3}$]	0.455 / -0.230	0.796 / -0.640	0.358 / -0.859

[1] G. M. Sheldrick, *SADABS, Program for area detector adsorption correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.

[{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}Se]$^+$Cl$^-$·H$_2$O (2·H$_2$O)

Table S2. Hydrogen bonds [Å] and angles [°] in the dimer association of **2**·H$_2$O.[a]

O(1b)–H(13b)	0.94(3)	O(1b)–H(13b)···Cl(2a)	168(3)
H(13b)···Cl(2a)	2.24(3)		
O(1b)···Cl(2a)	3.163(3)		
O(1b)–H(14b)	0.92(4)	O(1b)–H(14b)···Cl(1b)	170(5)
H(14b)···Cl(1b)	2.33(3)		
O(1b)···Cl(1b)	3.238(3)		
O(1b)–H(9C)	2.44	O(1b)–H(9C)···C(9)	166
O(1b)–H(8Af)	2.49	O(1b)–H(8Af)···C(8f)	155

[a] Symmetry equivalent atoms (–0.5+*x*, 0.5+*y*, *z*), (–0.5+*x*, –0.5+*y*, *z*) and (1–*x*, 1–*y*, 2–*z*) are given by "a", "b" and "f", respectively.

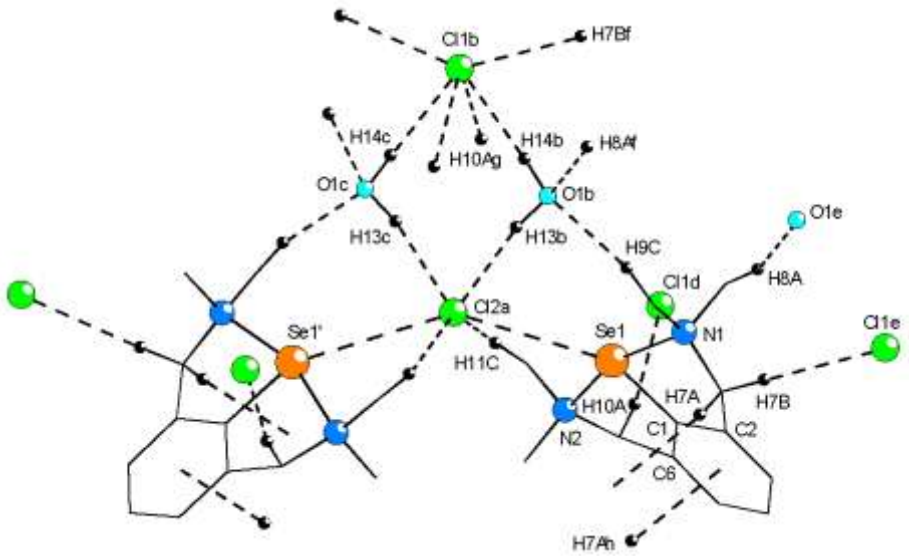


Figure S1. Dimer association of (R_{N1},R_{N2})-cations in **2**·H$_2$O, showing atom numbering scheme. The atoms are drawn with 50% probability ellipsoids [symmetry equivalent atoms (1–*x*, *y*, 1.5–*z*), (–0.5+*x*, 0.5+*y*, *z*), (–0.5+*x*, –0.5+*y*, *z*), (1.5–*x*, –0.5+*y*, 1.5–*z*), (–1+*x*, *y*, *z*), (1.5–*x*, 1.5–*y*, 2–*z*), (1–*x*, 1–*y*, 2–*z*), (0.5–*x*, –0.5+*y*, 1.5–*z*) and (1–*x*, 2–*y*, 2–*z*) are given by "prime", "a", "b", "c", "d", "e", "f", "g" and "h", respectively].

- interatomic distances Cl(2a)···H(11C)$_{methyl}$ 2.96 Å $\sum r_{vdW}$(Cl,H) 3.01 Å
  Cl(1b)···H(7Bf)$_{methylene}$ 2.91 Å
  Cl(1b)···H(10Ag)$_{methylene}$ 2.93 Å

- inter-cations distance C(7h)–H(7Ah)$_{methylene}$···Ar$_{centroid}${C(1)-C(6)} 2.92 Å

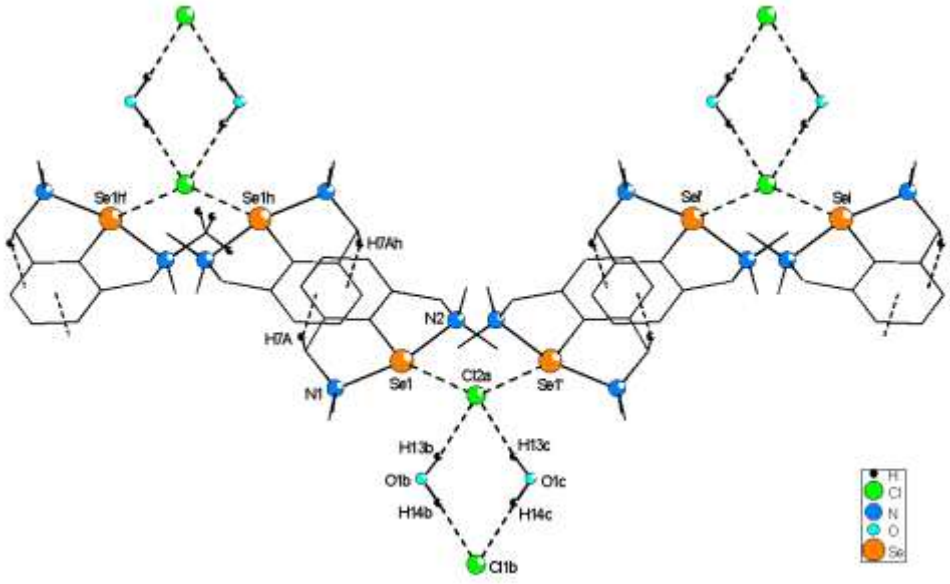


Figure S2a. View along *a* axis of the chain polymers of alternating (R_{N1},R_{N2})/(R_{N1},R_{N2}) and (S_{N1},S_{N2})/(S_{N1},S_{N2}) dimer units built through inter-cations C-H···π ($Aryl_{centroid}$) contacts (only hydrogen atoms involved in intra-cations contacts are shown) [symmetry equivalent atoms (1–*x*, *y*, 1.5–*z*), (–0.5+*x*, 0.5+*y*, *z*), (–0.5+*x*, –0.5+*y*, *z*), (1.5–*x*, –0.5+*y*, 1.5–*z*), (1–*x*, 2–*y*, 2–*z*), (*x*, 2–*y*, 0.5+*z*), (*x*, 2–*y*, –0.5+*z*) and (1–*x*, 2–*y*, 1–*z*) are given by "prime", "a", "b", "c", "h", "h prime", "i prime" and "i", respectively].

- inter-cations distance $C(7h)–H(7Ah)_{methylene}\cdots Ar_{centroid}\{C(1)\text{-}C(6)\}$ 2.92 Å

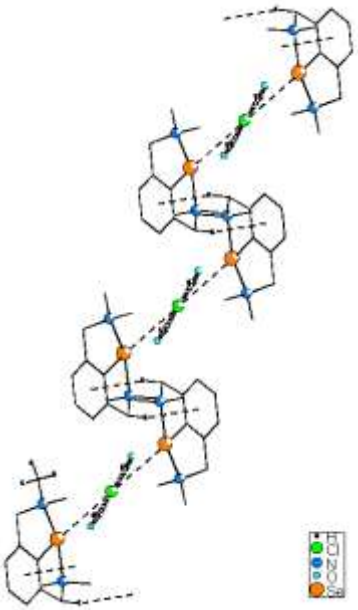


Figure S2b. View along *b* axis of the chain polymers of alternating (R_{N1},R_{N2})/(R_{N1},R_{N2}) and (S_{N1},S_{N2})/(S_{N1},S_{N2}) dimer units built through inter-cations C-H···π ($Aryl_{centroid}$) contacts (only hydrogen atoms involved in intra-cations contacts are shown).

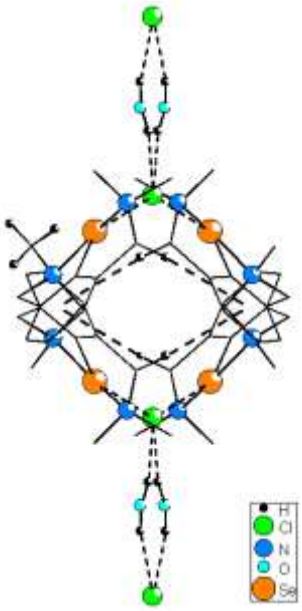


Figure S2c. View along *c* axis of the chain polymers of alternating (R_{N1},R_{N2})/(R_{N1},R_{N2}) and (S_{N1},S_{N2})/(S_{N1},S_{N2}) dimer units built through inter-cations C-H···π ($Aryl_{centroid}$) contacts (only hydrogen atoms involved in intra-cations contacts are shown).

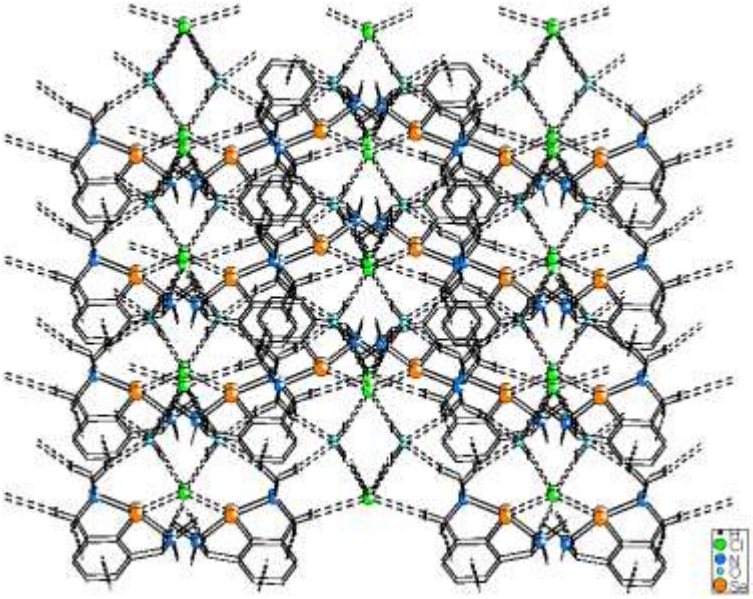


Figure S3a. View along *a* axis of the 3D architecture based on C-H···π ($Aryl_{centroid}$), Cl···H and O···H contacts in the crystal of **2**·H_2O (only hydrogen atoms involved in contacts are shown).

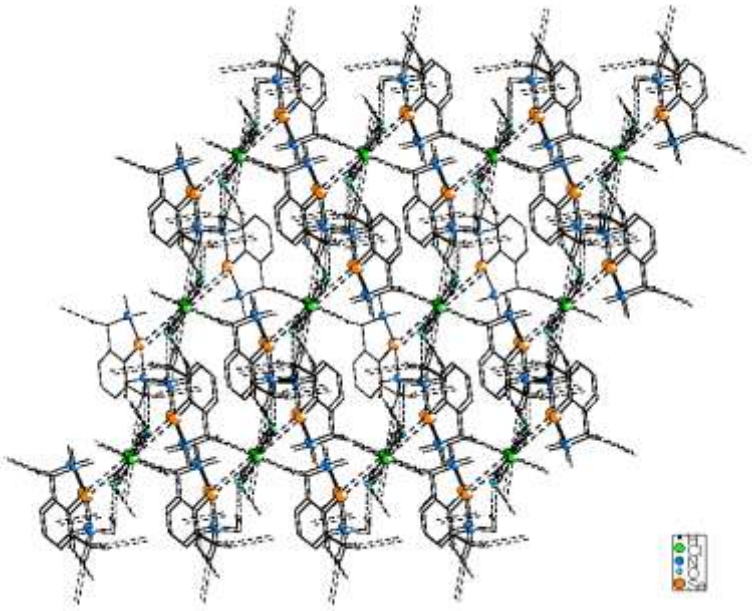


Figure S3b. View along *b* axis of the 3D architecture based on C-H···π ($Aryl_{centroid}$), Cl···H and O···H contacts in the crystal of **2**·H_2O (only hydrogen atoms involved in contacts are shown).

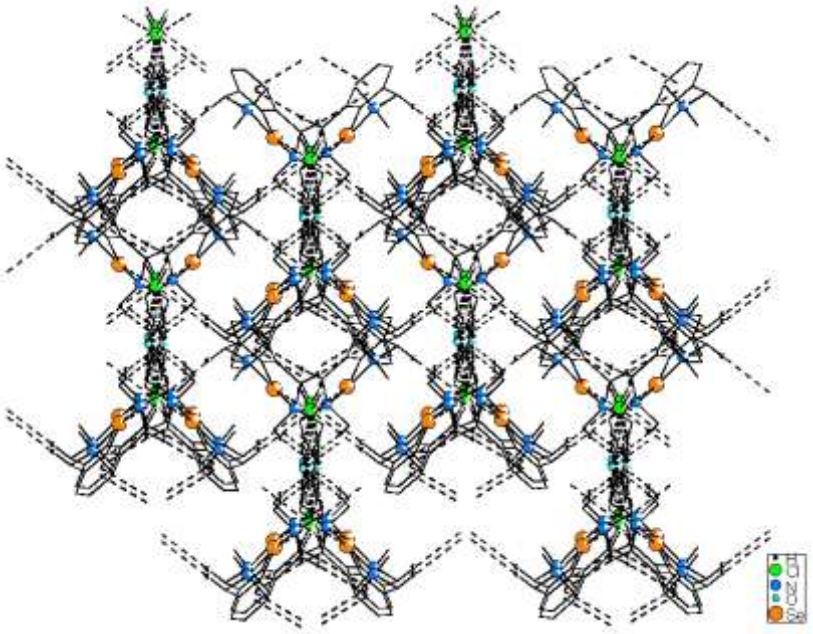


Figure S3c. View along *c* axis of the 3D architecture based on C-H···π ($Aryl_{centroid}$), Cl···H and O···H contacts in the crystal of **2**·H_2O (only hydrogen atoms involved in intra- and intermolecular contacts are shown).

$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Se]^+[Ph_2SbCl_4]^-$ (8)

Table S3. Selected bond distances [Å] and angles [°] for the anion in **8**.

Sb(1)–C(13)	2.143(3)	Sb(1)–C(19)	2.137(3)
Sb(1)–Cl(1)	2.4623(9)	Sb(1)–Cl(3)	2.4709(9)
Sb(1)–Cl(2)	2.4932(8)	Sb(1)–Cl(4)	2.4323(8)
C(13)–Sb(1)–C(19)	178.48(11)		
C(13)–Sb(1)–Cl(1)	90.44(9)	C(19)–Sb(1)–Cl(1)	90.40(9)
C(13)–Sb(1)–Cl(2)	88.93(9)	C(19)–Sb(1)–Cl(2)	89.81(9)
C(13)–Sb(1)–Cl(3)	89.80(9)	C(19)–Sb(1)–Cl(3)	89.37(9)
C(13)–Sb(1)–Cl(4)	90.91(9)	C(19)–Sb(1)–Cl(4)	90.35(9)
Cl(1)–Sb(1)–Cl(3)	179.49(3)	Cl(2)–Sb(1)–Cl(4)	179.53(3)
Cl(1)–Sb(1)–Cl(2)	90.14(3)	Cl(3)–Sb(1)–Cl(4)	90.12(4)
Cl(2)–Sb(1)–Cl(3)	90.32(3)	Cl(4)–Sb(1)–Cl(1)	89.43(3)

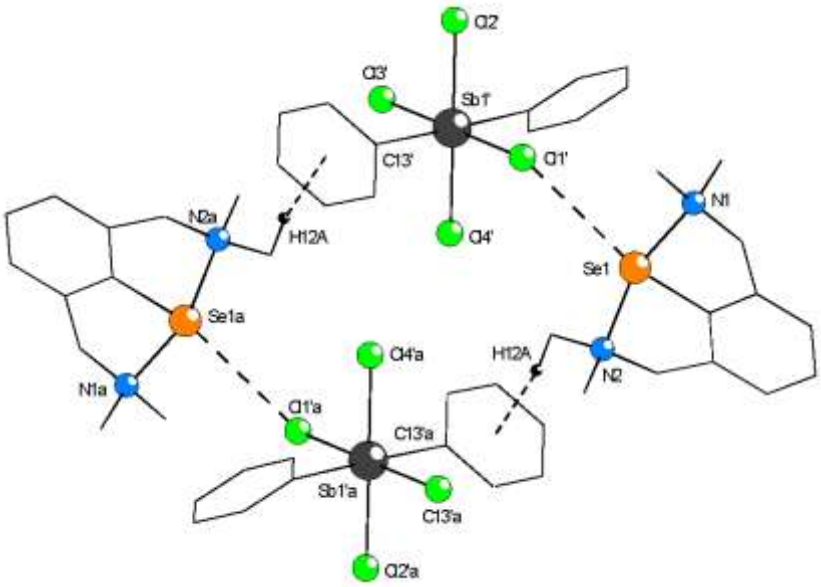


Figure S4. View of the dimer cation-anion association based on Se···Cl and C-H···π ($Ph_{centroid}$) contacts in the crystal of **8** [symmetry equivalent atoms (1–*x*, 2–*y*, 1–*z*), (2–*x*, 2–*y*, 1–*z*) and (1+*x*, *y*, *z*) are given by "prime", "a" and "prime a", respectively].

- cation-anion interaction Se(1)···Cl(1') 3.680(1) Å $\sum r_{vdW}$(Se,Cl) 3.81 Å
  $C(12)–H(12A)_{methyl}\cdots Ph_{centroid}\{C(13'a)\text{-}C(18'a)\}$ 2.68 Å

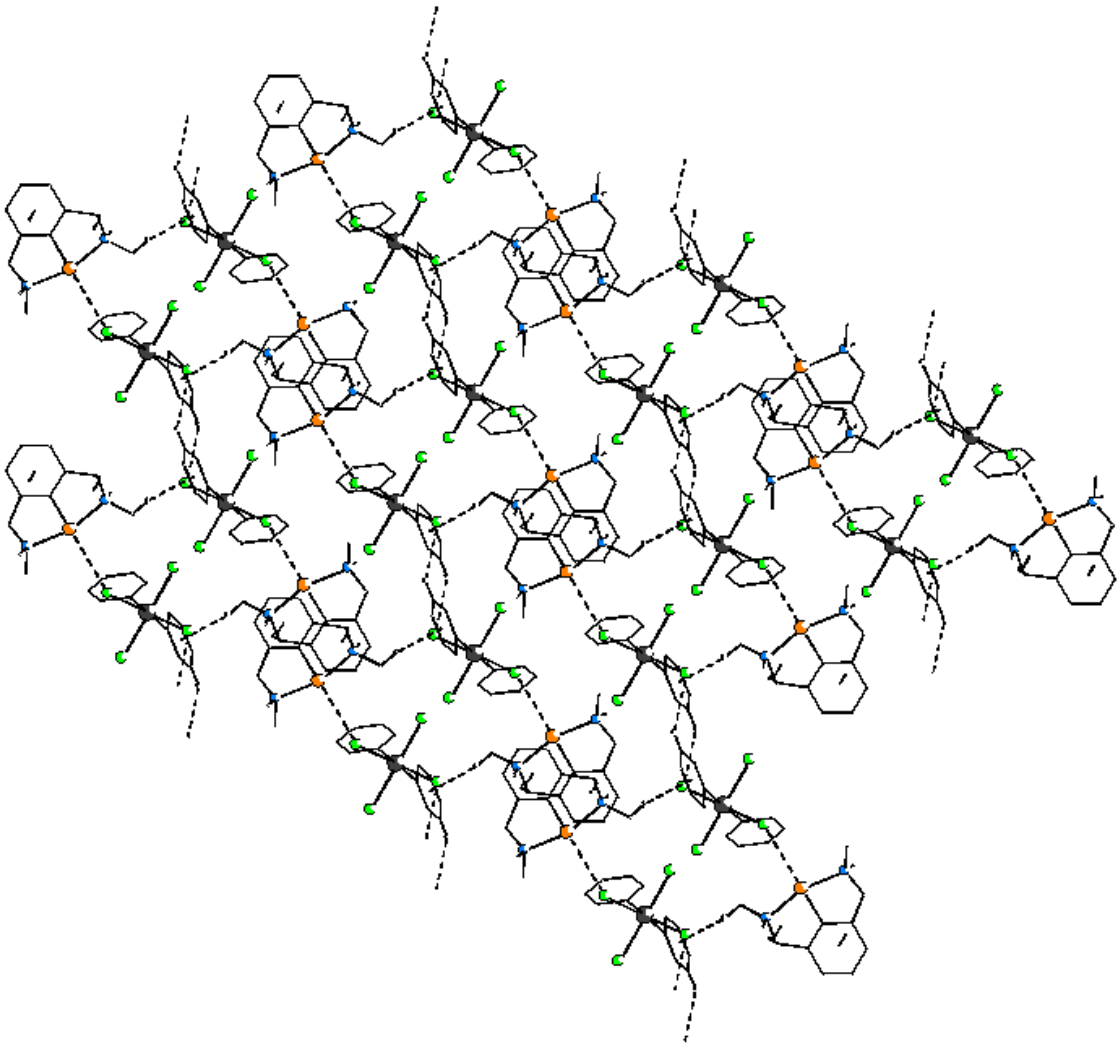


Figure S5a. View along *a* axis of the layer of dimer cation-anion associations based on Se···Cl, C-H_{methyl}···π ($Ph_{centroid}$), C-$H_{methylene}$···π ($Ar_{centroid}$) and H_{phenyl}···Cl contacts in the crystal of **8** [symmetry equivalent atoms (1–*x*, 2–*y*, 1–*z*), (2–*x*, 2–*y*, 1–*z*), (1+*x*, *y*, *z*), (1–*x*, 1–*y*, –*z*) and (1+*x*, 1+*y*, *z*) are given by "prime", "a", "prime a", "prime b" and "c", respectively].

- cation-anion interaction — Se(1)···Cl(1') 3.680(1) Å; $\sum r_{vdW}$(Se,Cl) 3.81 Å
  C(12)–$H(12A)_{methyl}$···$Ph_{centroid}${C(13'a)-C(18'a)} 2.68 Å, γ = 7.5°
- cation-cation interaction — $C(10)–H(10A)_{methylene}$···$Ar_{centroid}${C(1'b)-C(6'b)} 2.78 Å, γ = 3.1°
- anion-anion interaction — $Cl(3')···H(17c)_{phenyl}$ 2.87 Å; $\sum r_{vdW}$(Cl,H) 3.01 Å

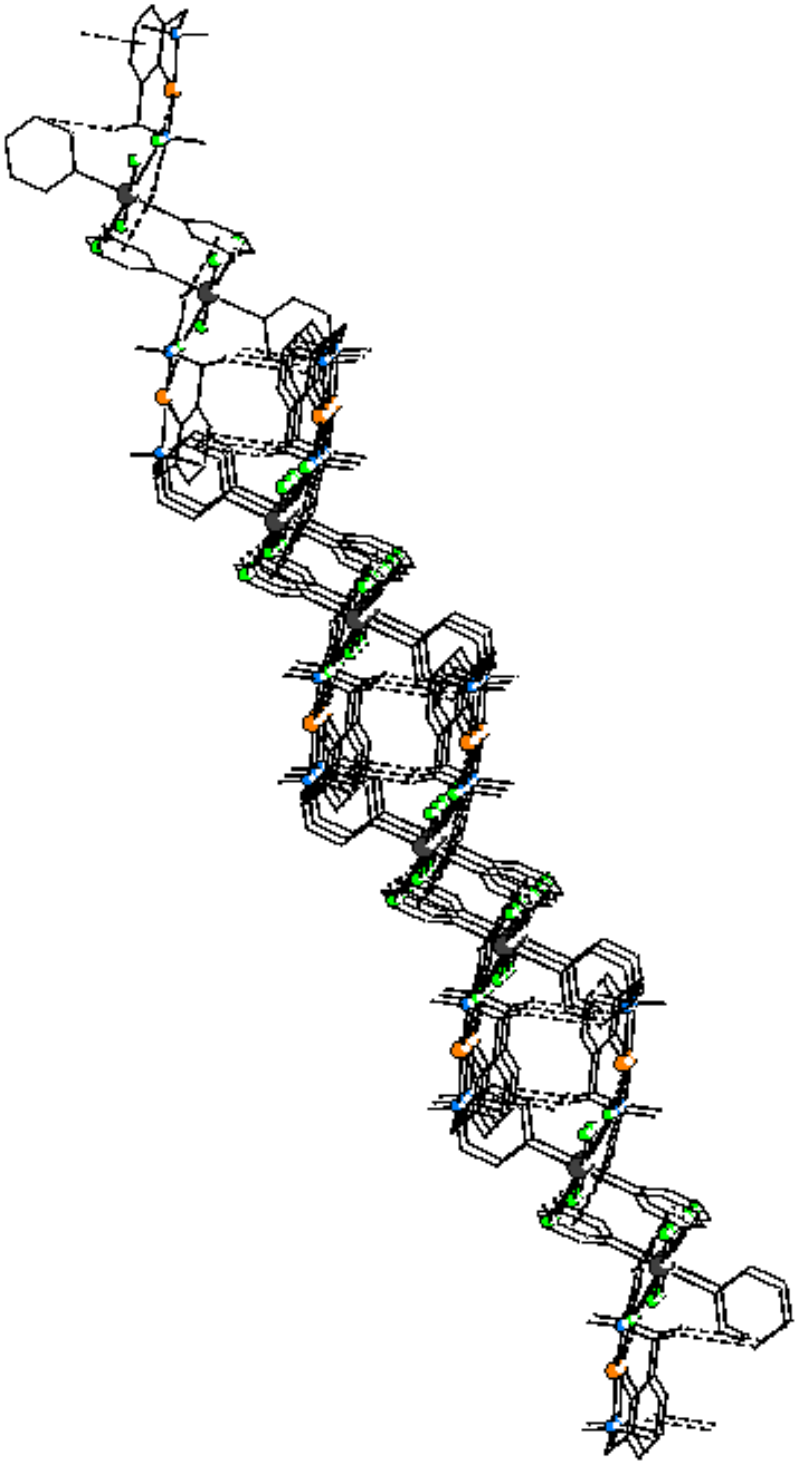


Figure S5b. View along *b* axis of the layer of dimer cation-anion associations based on Se···Cl, C-H_{methyl}···π ($Ph_{centroid}$), C-$H_{methylene}$···π ($Ar_{centroid}$) and H_{phenyl}···Cl contacts in the crystal of **8**.

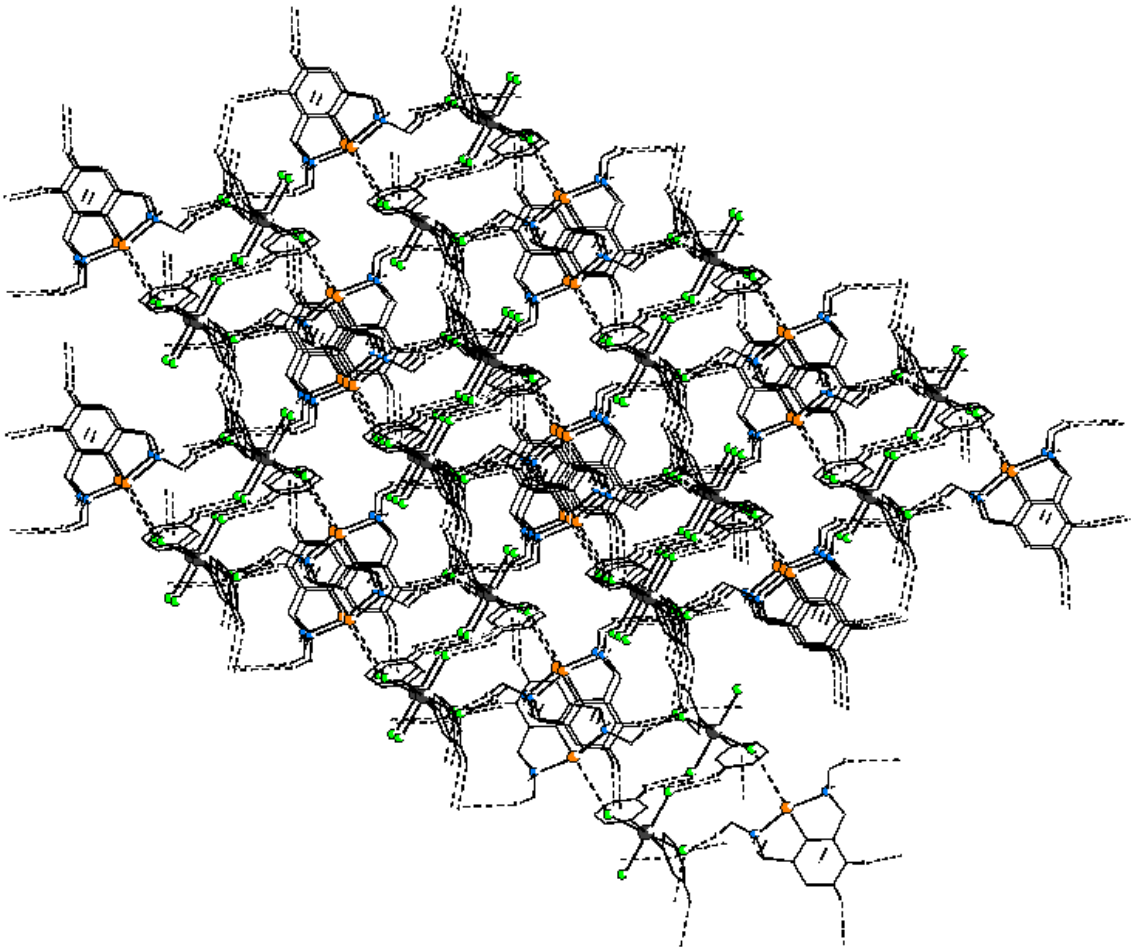


Figure S6a. View along *a* axis of the 3D architecture based on layers connected through C-$H_{aryl}\cdots\pi$ ($Ph_{centroid}$), C-$H_{methyl}\cdots\pi$ ($Ph_{centroid}$), $H_{aryl}\cdots$Cl and $H_{phenyl}\cdots$Cl contacts in the crystal of **8**.

- cation-anion interaction
  - C(4)–$H(4)_{aryl}\cdots Ph_{centroid}${C(19'b)-C(24'b)} 2.83 Å, γ = 11.0°
  - C(9)–$H(9C)_{methyl}\cdots Ph_{centroid}${C(13'd)-C(18'd)} 2.89 Å, γ = 19.4°
  - Cl(3'b)$\cdots H(3)_{aryl}$ 2.92 Å $\sum r_{vdW}$(Cl,H) 3.01 Å
- anion-anion interaction
  - Cl(4')$\cdots H(23)_{phenyl}$ 2.93 Å $\sum r_{vdW}$(Cl,H) 3.01 Å

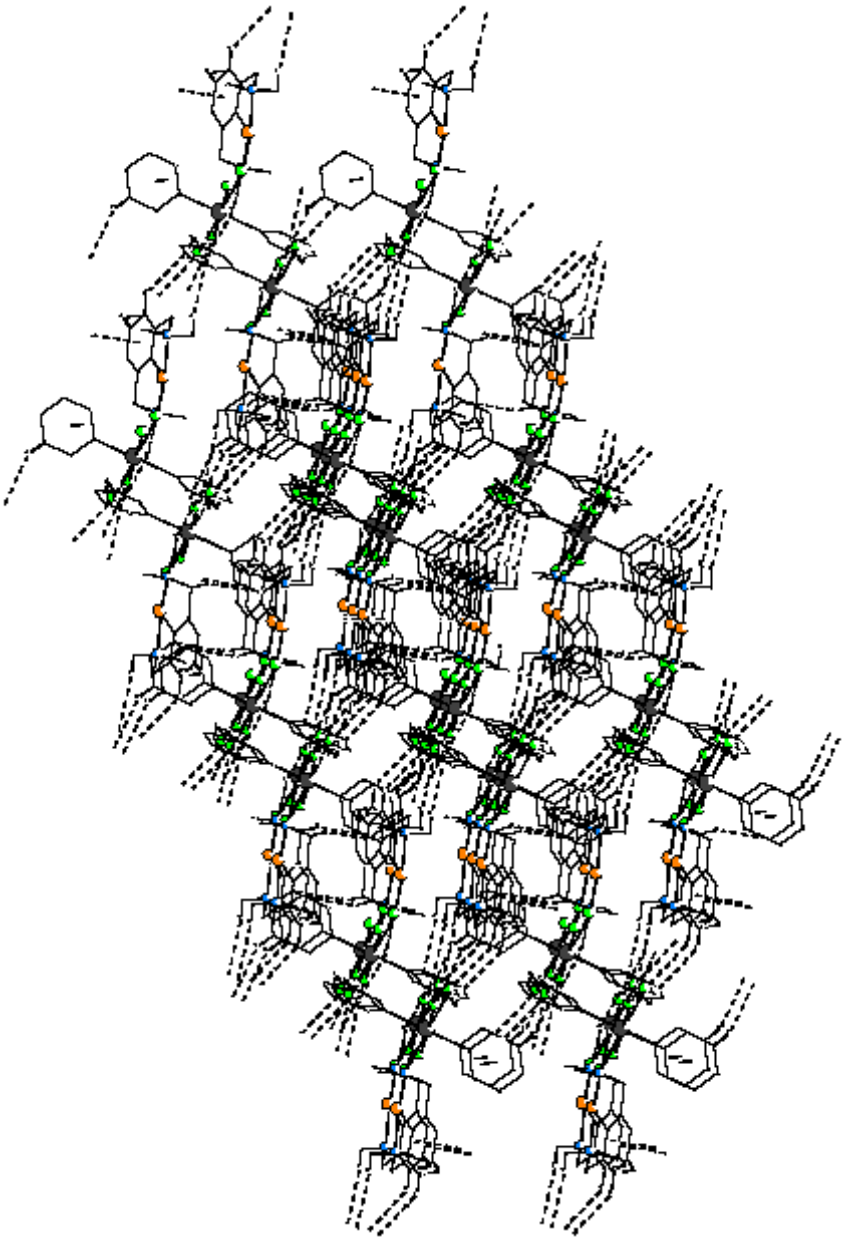


Figure S6b. View along *b* axis of the 3D architecture based on layers connected through C-H_{aryl}···π ($Ph_{centroid}$), C-H_{methyl}···π ($Ph_{centroid}$), H_{aryl}···Cl and H_{phenyl}···Cl contacts in the crystal of **8**.

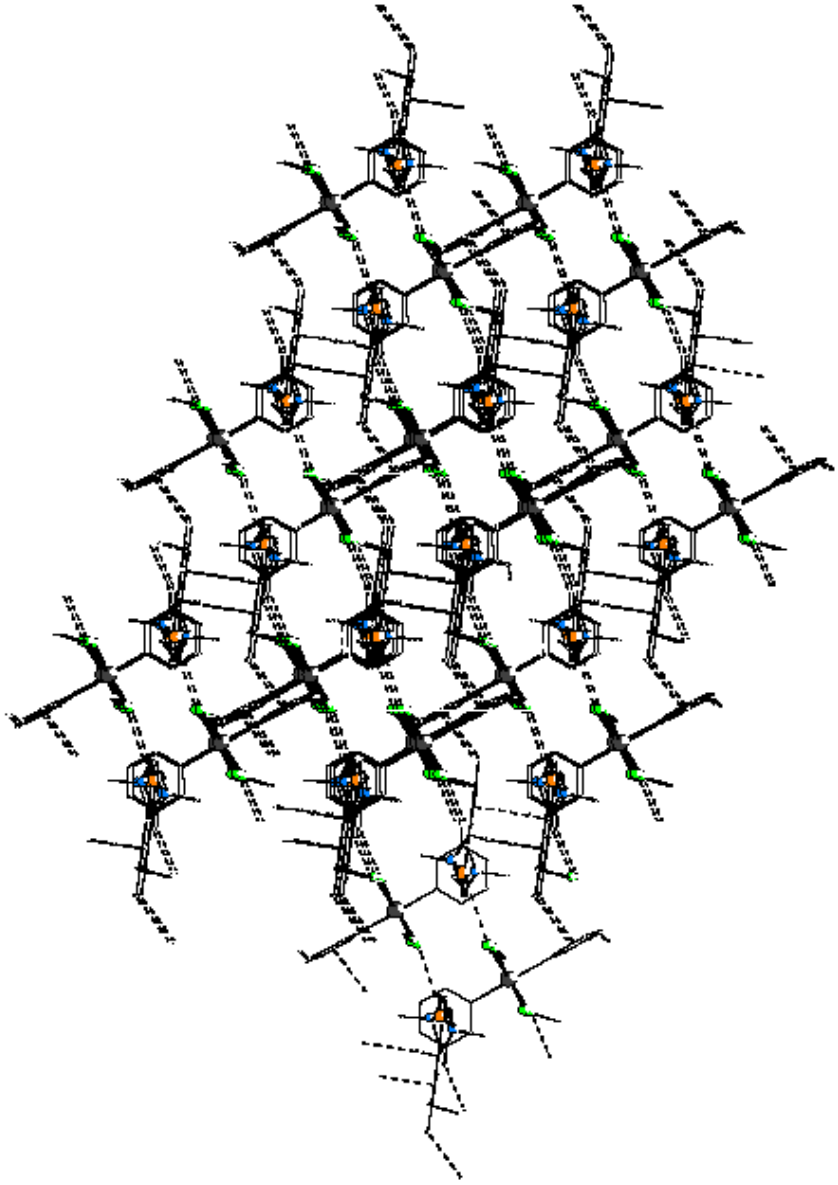


Figure S6c. View along *c* axis of the 3D architecture based on layers connected through C-H_{aryl}···π ($Ph_{centroid}$), C-H_{methyl}···π ($Ph_{centroid}$), H_{aryl}···Cl and H_{phenyl}···Cl contacts in the crystal of **8**.

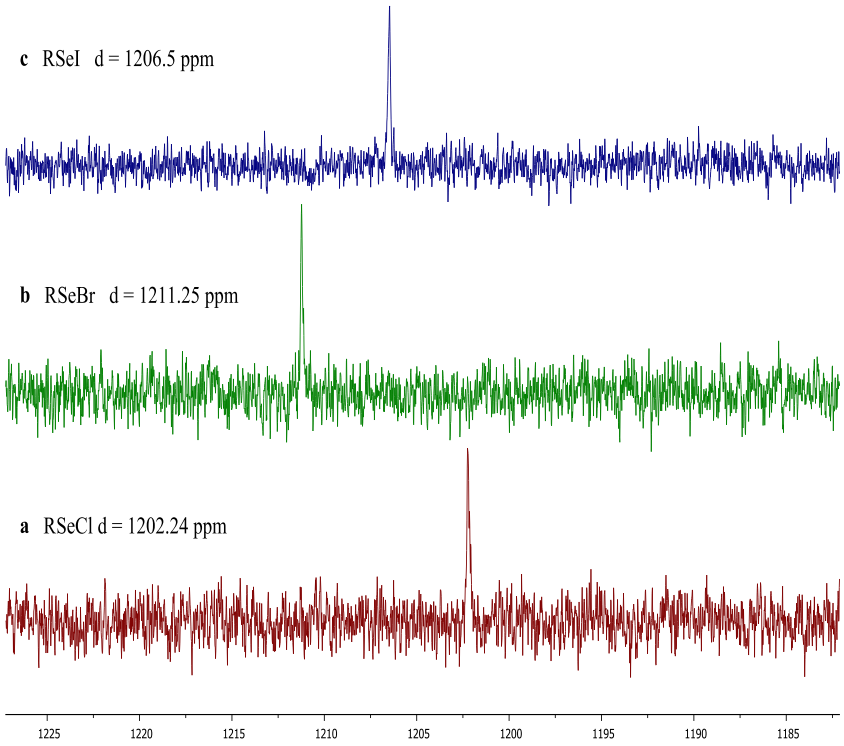


Figure S7. Stacked ^{77}Se NMR spectra recorded in $CDCl_3$ at room temperature for (a) chloride **2**, (b) bromide **3**, and (c) iodide **4**.

Z-matrices of optimized structures

- **2a**

Se	0.00004	-1.13456	0.00010
N	-2.18656	-0.77028	-0.04439
N	2.18646	-0.77030	0.04446
C	1.18948	1.42304	-0.27751
C	1.18555	2.81749	-0.26758
H	-0.00001	4.59591	-0.00019
H	-2.10198	3.37171	0.47841
H	2.10197	3.37168	-0.47876
C	-0.00000	3.50547	-0.00016
C	-2.35176	0.53717	0.62908
H	-2.36134	0.35469	1.71539
H	-3.32165	0.98352	0.35828
C	2.35173	0.53710	-0.62918
H	2.36132	0.35447	-1.71546
H	3.32166	0.98339	-0.35842
C	-1.18555	2.81751	0.26729
C	-1.18948	1.42305	0.27732
C	-2.59585	-0.69793	-1.45650
H	-2.35399	-1.64198	-1.95865
H	-3.67942	-0.51565	-1.52935
H	-2.05870	0.11897	-1.95348
C	-2.88110	-1.85791	0.65652
H	-3.96708	-1.67875	0.66628
H	-2.68747	-2.80789	0.14294
H	-2.51552	-1.92830	1.68784
C	2.88102	-1.85800	-0.65637
H	3.96696	-1.67866	-0.66638
H	2.68763	-2.80788	-0.14253
H	2.51519	-1.92867	-1.68758
C	2.59590	-0.69774	1.45654
H	2.35395	-1.64168	1.95888
H	3.67949	-0.51559	1.52924
H	2.05887	0.11932	1.95340
C	-0.00000	0.75915	-0.00006

- **2**

Se	0.63661	0.34445	0.12418
N	-0.67141	2.27194	0.14408
N	1.14802	-1.77458	0.13515
Cl	3.57365	0.68732	-0.42772
C	-1.29611	-1.75397	0.17693
C	-2.56261	-2.31445	0.01897
H	-4.64200	-1.93085	-0.40712
H	-4.32562	0.51129	-0.71966

H	-2.70823	-3.38919	0.14829
C	-3.64890	-1.49456	-0.29226
C	-1.86129	1.88182	-0.61923
H	-1.61333	1.98060	-1.68859
H	-2.70698	2.56284	-0.41532
C	-0.05826	-2.48804	0.60485
H	-0.01393	-2.51257	1.70523
H	-0.03644	-3.53108	0.24997
C	-3.47139	-0.11979	-0.46405
C	-2.20337	0.44483	-0.33134
C	-0.98450	2.56221	1.54028
H	-0.05335	2.69565	2.10468
H	-1.59427	3.47916	1.62647
H	-1.54105	1.72249	1.97586
C	0.10234	3.34444	-0.47772
H	-0.47070	4.28742	-0.50374
H	1.02974	3.50090	0.08754
H	0.38085	3.05549	-1.49818
C	2.30359	-2.01038	1.01725
H	2.57881	-3.07646	0.98456
H	3.13231	-1.37231	0.67050
H	2.03901	-1.72529	2.04241
C	1.49004	-2.10394	-1.25957
H	2.31300	-1.44181	-1.56571
H	1.79967	-3.15920	-1.32803
H	0.61540	-1.93471	-1.89996
C	-1.12888	-0.38145	0.00679

○ **3**

Se	0.25877	0.19789	0.19122
N	-0.69307	2.30191	0.17743
N	0.41645	-1.98481	0.17792
Br	3.41877	0.20544	-0.26925
C	-1.98965	-1.55828	0.14598
C	-3.32579	-1.89765	-0.06134
H	-5.29577	-1.16971	-0.55162
H	-4.56824	1.18766	-0.82375
H	-3.65358	-2.93373	0.04836
C	-4.24868	-0.90551	-0.39814
C	-1.90990	2.12490	-0.62518
H	-1.61661	2.18735	-1.68566
H	-2.63110	2.93962	-0.43612
C	-0.90532	-2.49209	0.60190
H	-0.90133	-2.53376	1.70267
H	-1.04684	-3.52089	0.23285
C	-3.84007	0.42188	-0.54718
C	-2.50107	0.76565	-0.36485
C	-0.99741	2.64596	1.56469
H	-0.07495	2.62597	2.15775

H	-1.44878	3.65159	1.63007
H	-1.69928	1.91221	1.98141
C	0.27139	3.22798	-0.41626
H	-0.13594	4.25266	-0.45549
H	1.19411	3.22542	0.17745
H	0.52875	2.89402	-1.42837
C	1.49022	-2.42152	1.08520
H	1.58065	-3.51876	1.04925
H	2.42940	-1.93948	0.77095
H	1.25420	-2.10065	2.10673
C	0.73566	-2.34742	-1.21328
H	1.66476	-1.83052	-1.49352
H	0.86673	-3.43848	-1.29469
H	-0.08089	-2.02562	-1.87160
C	-1.59342	-0.23115	-0.00179

○ **4**

Se	-0.12667	0.13504	0.21622
N	-0.88953	2.28625	0.19259
N	-0.13439	-2.06459	0.17999
I	3.28351	0.08749	-0.18315
C	-2.49824	-1.44806	0.12602
C	-3.85532	-1.67744	-0.09686
H	-5.75503	-0.79143	-0.60305
H	-4.83962	1.50129	-0.85678
H	-4.26663	-2.68409	0.00468
C	-4.69181	-0.61253	-0.43794
C	-2.11114	2.21958	-0.62277
H	-1.80370	2.26591	-1.67986
H	-2.75967	3.09184	-0.43029
C	-1.49567	-2.46758	0.58866
H	-1.50660	-2.51329	1.68928
H	-1.71606	-3.48040	0.21378
C	-4.17758	0.67896	-0.57660
C	-2.81756	0.91324	-0.37841
C	-1.17770	2.65720	1.57823
H	-0.26495	2.56396	2.17908
H	-1.54481	3.69655	1.63476
H	-1.94162	1.98475	1.98904
C	0.15708	3.13056	-0.38949
H	-0.16276	4.18565	-0.42203
H	1.07299	3.04181	0.20827
H	0.39089	2.78248	-1.40241
C	0.89620	-2.58804	1.08996
H	0.90667	-3.68882	1.04752
H	1.87332	-2.18049	0.78848
H	0.68098	-2.25761	2.11298
C	0.16424	-2.43750	-1.21223
H	1.13651	-2.00355	-1.48504

H	0.20077	-3.53478	-1.30780
H	-0.61463	-2.03786	-1.87352
C	-1.99883	-0.15539	-0.01181

- **2a'**

Se	0.82349	-1.25155	-0.39444
N	2.54918	-0.34904	0.25460
N	-3.35556	-0.46342	0.17260
C	-1.26798	0.74369	-0.35246
C	-1.69365	2.06870	-0.21208
H	-1.11580	4.12400	0.06491
H	1.32073	3.64683	0.09264
H	-2.76366	2.28167	-0.23148
C	-0.76718	3.09659	-0.04560
C	2.46919	1.05637	-0.25820
H	2.79904	1.03492	-1.30868
H	3.17404	1.67689	0.31394
C	-2.19054	-0.41585	-0.62556
H	-2.48083	-0.39998	-1.68870
H	-1.54085	-1.35785	-0.53108
C	0.60536	2.83123	-0.02746
C	1.04688	1.51896	-0.16777
C	2.55425	-0.36810	1.73890
H	2.51545	-1.40500	2.08923
H	3.47506	0.11282	2.09755
H	1.68109	0.18065	2.10935
C	3.72287	-1.07162	-0.28651
H	4.63912	-0.56232	0.04129
H	3.72649	-2.09936	0.09493
H	3.67350	-1.08406	-1.38080
C	-4.44020	-1.26124	-0.35363
H	-4.23822	-2.35028	-0.30633
H	-5.35544	-1.06549	0.22084
H	-4.63508	-0.99297	-1.40065
C	-3.13491	-0.62286	1.59089
H	-4.07116	-0.44636	2.13669
H	-2.77519	-1.63958	1.85225
H	-2.39547	0.10627	1.94875
C	0.09812	0.50397	-0.29956

- **2'**

Se	1.03201	-1.25492	0.05011
N	2.68256	0.37815	0.68517
N	-3.44129	0.26537	0.52795
Cl	-0.37958	-2.72023	-1.04854
C	-1.21189	0.64521	-0.46438

C	-1.65646	1.89254	-0.92658
H	-1.15138	3.85919	-1.64474
H	1.30765	3.48940	-1.39809
H	-2.73491	2.05766	-0.94330
C	-0.77183	2.89699	-1.29686
C	2.53202	1.16841	-0.53970
H	2.92287	0.55474	-1.36852
H	3.12307	2.10196	-0.50008
C	-2.23550	-0.35571	0.02303
H	-2.50683	-1.02028	-0.81061
H	-1.75898	-1.01921	0.77562
C	0.60066	2.68751	-1.17419
C	1.07388	1.44921	-0.75439
C	2.37164	1.12580	1.89443
H	2.36087	0.44398	2.75446
H	3.11606	1.92199	2.08186
H	1.38060	1.58730	1.80177
C	3.96195	-0.30405	0.77312
H	4.80294	0.40940	0.84361
H	3.97768	-0.94731	1.66296
H	4.10467	-0.93604	-0.11368
C	-4.57673	-0.62464	0.51235
H	-4.46500	-1.49675	1.19291
H	-5.48283	-0.08017	0.81664
H	-4.74226	-1.01210	-0.50291
C	-3.25493	0.88979	1.81573
H	-4.16391	1.43622	2.10742
H	-3.02325	0.15953	2.62215
H	-2.42975	1.61486	1.77333
C	0.17357	0.40929	-0.44943

○ **3'**

Se	-0.98300	0.99940	0.33326
N	-2.79442	-0.61244	0.68288
N	3.31722	-0.97330	0.59538
Br	0.57843	2.66531	-0.59808
C	1.09926	-0.97628	-0.48821
C	1.44666	-2.16231	-1.15173
H	0.79065	-3.92696	-2.19741
H	-1.63181	-3.38963	-1.90682
H	2.50703	-2.41748	-1.18738
C	0.48773	-3.00747	-1.69376
C	-2.67586	-1.15766	-0.67089
H	-2.99401	-0.36379	-1.36713
H	-3.34113	-2.02801	-0.82285
C	2.19451	-0.16654	0.16816
H	2.56010	0.58430	-0.54889
H	1.75581	0.41992	1.00340
C	-0.86416	-2.70123	-1.54649

C	-1.24066	-1.51526	-0.92572
C	-2.57012	-1.60068	1.72498
H	-2.52167	-1.10138	2.70139
H	-3.37935	-2.35491	1.75341
H	-1.61832	-2.11787	1.55017
C	-4.01400	0.14552	0.89198
H	-4.91423	-0.49197	0.81644
H	-3.99822	0.60421	1.88968
H	-4.08373	0.94710	0.14415
C	4.53006	-0.20794	0.75086
H	4.47521	0.55064	1.56196
H	5.36922	-0.88047	0.98233
H	4.76959	0.31898	-0.18370
C	3.02377	-1.77630	1.75805
H	3.86589	-2.44957	1.97582
H	2.83042	-1.16762	2.66866
H	2.13681	-2.39966	1.57670
C	-0.26067	-0.62408	-0.44320

○ **4'**

Se	0.76382	-0.96184	0.49240
N	3.05810	0.05702	0.66340
N	-2.65186	2.30612	0.60619
I	-1.34603	-2.29960	-0.39282
C	-0.60069	1.49659	-0.50274
C	-0.58050	2.66470	-1.27882
H	0.55849	4.01412	-2.51122
H	2.69035	2.75132	-2.19857
H	-1.50306	3.24551	-1.32650
C	0.57268	3.09750	-1.91913
C	3.02806	0.43799	-0.74795
H	3.03642	-0.49545	-1.33498
H	3.92095	1.02503	-1.03578
C	-1.86617	1.14627	0.24561
H	-2.48592	0.49401	-0.38919
H	-1.59979	0.52525	1.12791
C	1.75991	2.38443	-1.75961
C	1.76651	1.20360	-1.02497
C	3.20778	1.18378	1.56573
H	3.07755	0.84641	2.60239
H	4.20491	1.65675	1.47346
H	2.44404	1.94139	1.34835
C	3.98824	-1.01648	0.94949
H	5.03786	-0.71924	0.76418
H	3.89703	-1.31606	2.00223
H	3.75273	-1.88685	0.32162
C	-4.03786	1.99108	0.85237
H	-4.19306	1.33135	1.73381
H	-4.60599	2.91666	1.02704

H	-4.47487	1.48884	-0.02241
C	-2.06565	3.07371	1.67882
H	-2.63479	4.00194	1.83496
H	-2.04157	2.52266	2.64455
H	-1.03314	3.35437	1.42726
C	0.57405	0.72706	-0.44182

Table S4. Selected optimized structural parameters for **2a** and **2**–**4**.

	Calculated				Experimental		
	2a	**2**	**3**	**4**	**2**·2H$_2$O (**2**·H$_2$O) (this work)	**3**·H$_2$O (ref. 25)	**2a**[PF$_6$]$^-$ (ref. 24)
Se–N1	2.217	2.180	2.188	2.200	2.174 (2.183)	2.181	2.154
Se–N2	2.217	2.329	2.309	2.283	2.177 (2.184)	2.185	2.180
Se–C	1.894	1.912	1.911	1.908	1.884 (1.889)	1.887	1.874
Se–X	–	3.008	3.193	3.434	– (3.558)[a]	3.662	–
N1–Se–N2	161.1	159.4	159.8	160.2	161.99 (161.31)	161.6	161.9
X–Se–C	–	159.0	160.9	163.4	– (153.89)[a]	154.4	-
N2–Se–C–C	14.3	15.4	14.9	14.3	13.6 (12.2)	11.6	12.0
C–C–Se–X	–	52.2	57.6	64.8	– (71.2)[a]	71.1	–

[a] Only the value for **2**·H$_2$O is reported due to Cl/O disorder in **2**·2H$_2$O.

Table S5. Contribution of the main Atomic Orbital (AOs) to HOMOs and LUMOs calculated for **2a** and **2**–**4**.

	2a		**2**		**3**		**4**	
	Atom (%)	AO (%)	Atom (%)	AO (%)	Atom (%)	AO (%)	Atom (%)	AO (%)
	Se (51.8)	4p_z (51.0) 5p_z (0.7)	Cl (84.3)	3p_x (69.8) 3p_z (10.7) 4p_x (3.8)	Br (89.5)	4p_x (66.1) 4p_z (17.5) 4p_y (2.7) 5p_x (2.3) 5p_z (1.0)	I (94.0)	5p_x (50.3) 5p_z (37.4) 5p_y (3.0) 6p_x (1.5) 6p_z (1.8)
HOMO	C4 (15.1)	2p_z (14.4) 2p_x (0.6)	Se (8.3)	4s (1.5) 4p_z (6.2) 4d_{xz} (0.6)	Se (5.0)	4s (0.7) 4p_z (4.3)	Se (2.7)	4p_z (2.7)
	C1 (10.4)	2p_z (10.1) 2p_x (0.3)	N2 (0.8)	2p_y (0.8)	N2 (0.5)	2p_y (0.5)	N2 (0.4)	2p_y (0.4)
	Se (66.0)	4p_x (62.7) 5p_x (3.3)	Se (58.6)	4p_x (49.7) 4p_y (8.9)	Se (59.9)	4p_x (55.7) 4p_y (4.2)	Se (60.8)	4p_x (59.3) 4p_y (1.5)
LUMO	N1 (10.6)	2p_x (8.8) 2s (1.8)	N1 (11.3)	2p_x (9.2) 2s (2.1)	N1 (11.2)	2p_x (9.1) 2s (2.1)	N1 (10.9)	2p_x (8.9) 2s (2.0)
	N2 (10.6)	2p_x (8.8) 2s (1.8)	N2 (7.8)	2p_x (3.8) 2p_y (2.7) 2s (1.3)	N2 (8.3)	2p_x (5.2) 2p_y (1.7) 2s (1.4)	N2 (8.8)	2p_x (6.2) 2p_y (1.2) 2s (1.4)

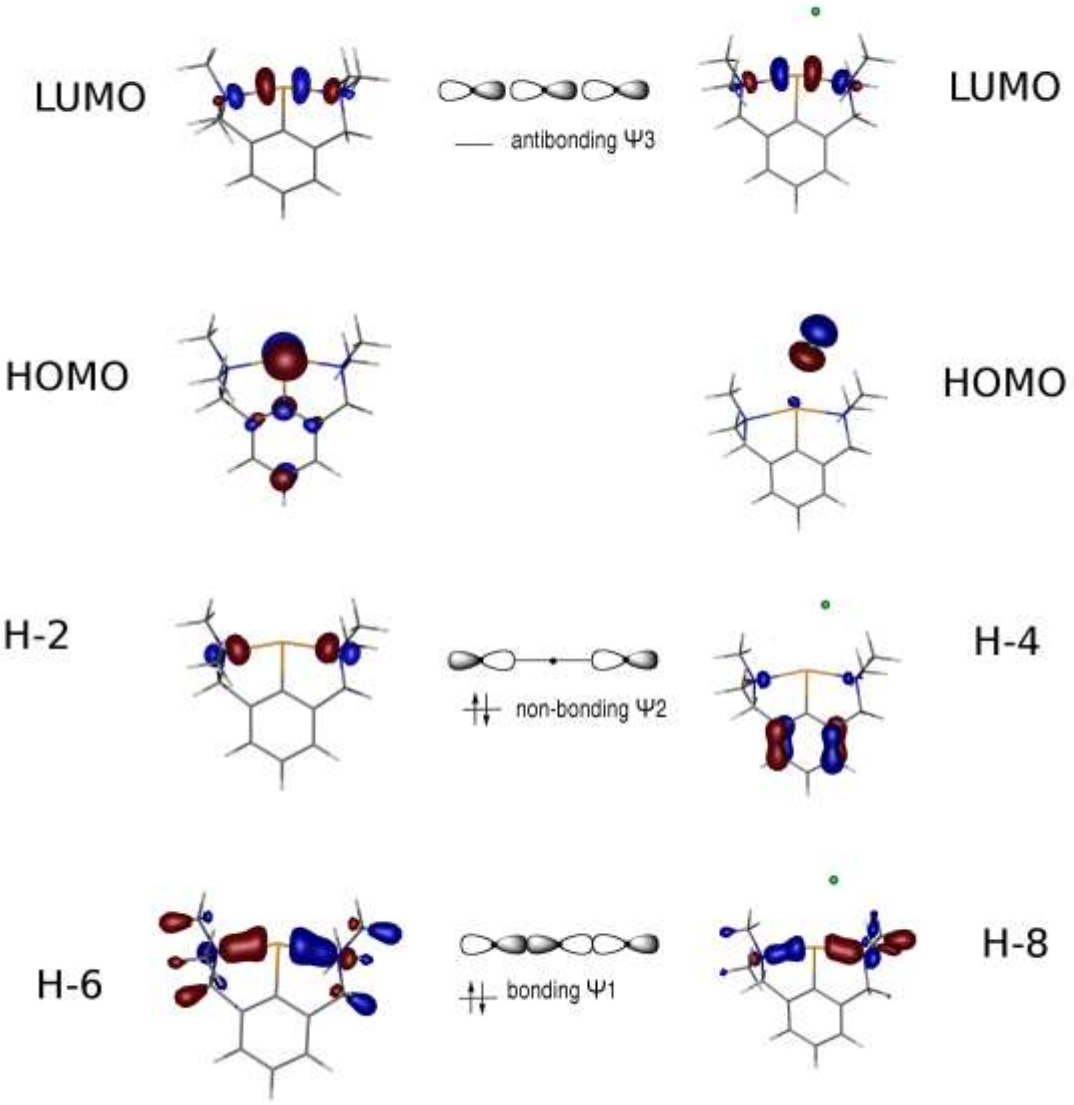


Figure S8. Isosurfaces of selected Kohn Sham MOs calculated for **2a** (left) and **2** (right) which show the 3c-4e bonding scheme for the N–Se–N fragment in them (cut-off value 45%).

Table S6. QTAIM electron density ρ, Laplacian of electron density $\nabla^2\rho$, bond ellipticity ε, electronic energy density H, AIM charges q,[a] and two-centre delocalization index δ[b] calculated at the BCPs of all A–B bond/interactions involving the Se atom in **2a** and **2**–**4**.

	A–B	ρ [au]	$\nabla^2\rho$ [au]	ε	H [au]	q(Se)[a]	q(N2)[a]	q(N1)[a]	q(X)[a]	δ(A,B)[b]
2a	Se–N2	0.0823	0.1517	0.0940	-0.0209					0.585
	Se–N1	0.0823	0.1517	0.0940	-0.0209	0.408	-1.099	-1.099		0.585
	Se–C	0.1743	-0.1666	0.1913	-0.1165					1.063
2	Se–N2	0.0647	0.1445	0.1045	-0.0112					0.464
	Se–N1	0.0888	0.1518	0.1144	-0.0249	0.518	-1.110	-1.084	-0.815	0.617
	Se–C	0.1694	-0.1266	0.2163	-0.1108					1.056
	Se–Cl	0.0232	0.0595	0.1466	0.0007					0.297
3	Se–N2	0.0675	0.1472	0.1058	-0.0125					0.482
	Se–N1	0.0872	0.1526	0.1116	-0.0238					0.608
	Se–C	0.1698	-0.1286	0.2144	-0.1112	0.499	-1.107	-1.086	-0.804	1.054
	Se–Br	0.0202	0.0485	0.1522	0.0008					0.297
4	Se–N2	0.0714	0.1506	0.1067	-0.0146					0.506
	Se–N1	0.0851	0.1532	0.1090	-0.0225	0.481	-1.104	-1.089	-0.800	0.596
	Se–C	0.1705	-0.1321	0.2122	-0.1121					1.053
	Se–I	0.0169	0.0373	0.1557	0.0007					0.286

[a] QTAIM net charge. The NBO charge [au] is shown in Table 4. Calculated QTAIM charges on C atoms bound to Se are -0.202, -0.212, -0.211 and -0.210 for **2a** and **2**–**4**, respectively. [b] Two-centre delocalization index. The Wiberg index (NBO) is shown in Table 2.

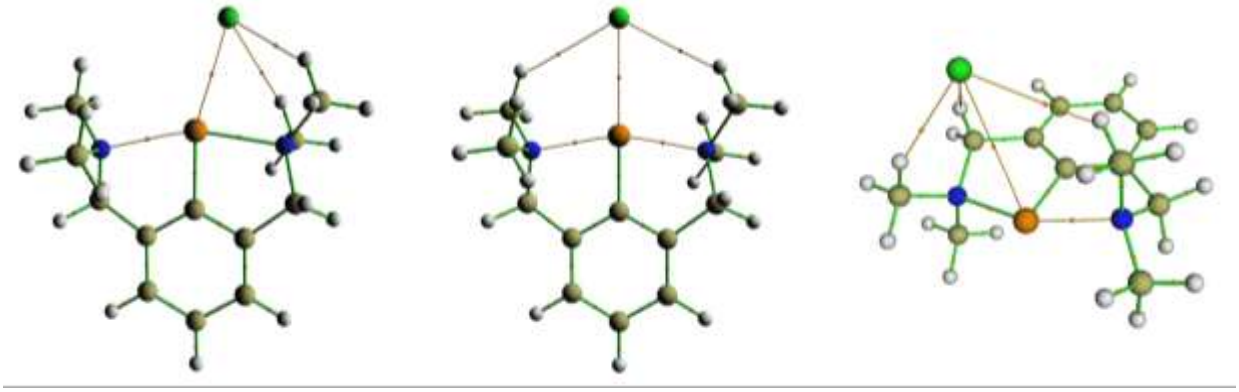
Although the quite low values for the ellipticity, ε, at the BCPs of the Se–N bonds indicate an axial symmetry for them, this parameter cannot be used to fully prove the hypervalent nature for the N–Se–N moiety in **2a** and **2**–**4**.[42]

The three-centre (3*c*) delocalization index δ(N,Se,N) is in accordance to a 3*c*-4*e* bonding nature for the N→Se(C)←N moiety in the compounds considered.[40] The maximum value for the δ(N,Se,N) correlation index is calculated for **2a.**

Table S7. Core and Valence Shell Population (number of electrons) of Se atom in compounds **2a** and **2**–**4**.

Compound	C(Se)	V(Se)	V(Se,N)	V(Se,C)	N_v(Se)[a]
2a	27.43	5.12	3.66	1.95	10.73
2	27.45	5.16	3.63	2.02	10.82
3	27.49	5.13	3.61	2.00	10.76
4	27.49	5.08	3.64	2.01	10.79

[a] $N_v(Se) = \sum V(Se)_i + V(Se,R)_j$, R = N, C, X (electrons in the valence shell, shared and unshared electrons)



(i) **(ii)** **(iii)**

Figure S9. BCPs in the structure corresponding to the global and local minima from PES scan [(**i**) and (**iii**), respectively, see Fig. 5a-c), and to the saddle point (**ii**) in Figure 5a.

Table S8. Relative electronic energy and energy interaction for the H···Cl bonds in structure (**i**), (**ii**) and (**iii**) in Figure S9.

Structure	Electronic Energy difference (kcal/mol)	EML energy(kcal/mol)[a]
(**i**)	0	-2.03
		-3.89
		-5.92
(**ii**)	2.11	-1.59
		-1.60
		-3.19
(**iii**)	0.71	-3.09
		-4.52
		-0.92
		-8.54

[a] EML = Espinosa-Molins-Lacomte equation

The sum of the H···Cl interaction energies for structure (**i**) is higher than that calculated for (**ii**); interestingly, H···Cl interaction energy difference between structures (**i**) and (**ii**) is roughly similar to the electronic energy difference between the two structures, indicating a major contribution of the H···Cl interactions in stabilizing structure (**i**) with respect structure (**ii**). On the other hand, on the base of the H···Cl interaction energies calculated, structure (**iii**) should be more stable than structure (**ii**), the overall higher stability of the latter should be related to a different energy for the Se···Cl and Se–N interactions.

Table S9. Sum of electronic and thermal enthalpies and Zero-Point correction energies (au) calculated for **2a**, **2a'**, **2**-**4** and **2'**-**4'**, and relative enthalpies ΔH_f, kcal/mol.

	RSeX	X'	$[RSe]^+$	Cation Relative Stability (ΔH_f, kcal/mol)
2a	-586.3962	0.0000	-586.3962	84.9
2	-601.5671	-15.0428	-586.5243	4.5
3	-599.7866	-13.2682	-586.5184	8.2
4	-598.0076	-11.4969	-586.5106	13.1
2a'	-586.3556	0.0000	-586.3556	110.4
2'	-601.5743	-15.0428	-586.5315	0.0
3'	-599.7935	-13.2682	-586.5253	3.9
4'	-598.0142	-11.4969	-586.5172	9.0