

An unprecedented non-classical poly-interhalogen anion made of $[\text{I}_2\text{Cl}]^-$ and I_2 at the 2-(*p*-tolyl)selenopheno[2,3-*b*]pyridinim cation template†

M. Carla Aragoni, Enrico Podda, Massimiliano Arca, Anna Pintus, Vito Lippolis, Claudia Caltagirone, Ricardi H. Bartz, Eder J. Lenardão, Gelson Perin, Ricardo F. Schumacher, Simon J. Coles, James B. Orton

ELECTRONIC SUPPLEMENTARY INFORMATION

Table S1. Crystal data and structure refinement parameters for compounds **1** and **2**.

Compound	1	2
Formula	C ₁₄ H ₁₆ ClNO ₂ Se	C ₁₄ H ₁₂ ClI _{2.33} NSe
$\rho_{calc.}/\text{g cm}^{-3}$	1.577	2.401
μ/mm^{-1}	5.176	6.697
Formula Weight	344.69	604.76
Colour	colourless	dark red
Shape	lath	(cut) block-shaped
Size/mm ³	0.09×0.04×0.01	0.13×0.06×0.05
<i>T</i> /K	100(2)	100(2)
Crystal System	triclinic	triclinic
Space Group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	7.3040(2)	11.76310(10)
<i>b</i> /Å	9.1476(2)	14.0582(2)
<i>c</i> /Å	11.7026(2)	16.4528(2)
α /°	70.419(2)	94.0460(10)
β /°	80.430(2)	95.4730(10)
γ /°	88.427(2)	111.1560(10)
<i>V</i> /Å ³	726.09(3)	2509.62(5)
<i>Z</i>	2	6
<i>Z</i> '	1	3
Wavelength/Å	1.54184	0.71073
Radiation type	CuK α	MoK α
θ_{min} /°	4.066	1.563
θ_{max} /°	68.225	27.483
Measured Refl's.	13289	115623
Indep't Refl's	2632	11505
Refl's $I \geq 2\sigma(I)$	2466	10395
<i>R</i> _{int}	0.0296	0.0361
Parameters	189	556
Restraints	2	15
Largest Peak	0.626	1.010
Deepest Hole	-0.413	-1.237
GooF	1.074	1.108
<i>wR</i> ₂ (all data)	0.0711	0.0641
<i>wR</i> ₂	0.0700	0.0625
<i>R</i> ₁ (all data)	0.0301	0.0322
<i>R</i> ₁	0.0277	0.0272

Table S2. Bond lengths in Å for compounds **1** and **2**.

1			2		
Se1	C5	1.857(2)	I1	I2A	2.7976(8)
Se1	C7	1.909(2)	I1	I2B	2.783(9)
N1	C1	1.342(3)	I1	C11	2.6947(10)
N1	C5	1.350(3)	I3	I4A	2.826(3)
C1	C2	1.378(4)	I3	I4B	2.7097(15)
C2	C3	1.382(4)	I3	C12	2.7779(9)
C3	C4	1.397(3)	I5	I6A	2.830(6)
C4	C5	1.401(3)	I5	I6B	2.790(5)
C4	C6	1.435(3)	I5	C13	2.7019(9)
C6	C7	1.362(3)	I7	I7 ⁱ	2.7430(11)
C7	C8	1.468(3)	Se1	C5	1.866(3)
C8	C9	1.389(3)	Se1	C7	1.903(3)
C8	C13	1.398(3)	N1	C1	1.348(4)
C9	C10	1.388(3)	N1	C5	1.344(4)
C10	C11	1.398(3)	C1	C2	1.380(5)
C11	C12	1.383(4)	C2	C3	1.383(5)
C11	C14	1.515(3)	C3	C4	1.399(5)
C12	C13	1.395(3)	C4	C5	1.406(5)
			C4	C6	1.435(5)
			C6	C7	1.354(5)
			C7	C8	1.470(4)
			C8	C9	1.402(5)
			C8	C13	1.399(5)
			C9	C10	1.381(5)
			C10	C11	1.396(5)
			C11	C12	1.392(5)
			C11	C14	1.501(5)
			C12	C13	1.386(5)
			Se2	C19	1.859(3)
			Se2	C21	1.903(3)
			N2	C15	1.340(4)
			N2	C19	1.348(4)
			C15	C16	1.382(5)
			C16	C17	1.389(5)
			C17	C18	1.397(5)
			C18	C19	1.405(5)
			C18	C20	1.436(5)
			C20	C21	1.357(5)
			C21	C22	1.465(5)
			C22	C23	1.399(5)
			C22	C27	1.397(5)
			C23	C24	1.388(5)
			C24	C25	1.393(5)
			C25	C26	1.396(5)
			C25	C28	1.503(5)
			C26	C27	1.390(5)
			Se3	C33	1.862(3)
			Se3	C35	1.906(3)
			N3	C29	1.350(4)
			N3	C33	1.343(4)
			C29	C30	1.376(5)
			C30	C31	1.386(5)
			C31	C32	1.402(5)
			C32	C33	1.398(5)
			C32	C34	1.435(5)
			C34	C35	1.361(5)
			C35	C36	1.464(4)
			C36	C37	1.402(5)
			C36	C41	1.403(4)
			C37	C38	1.384(5)
			C38	C39	1.395(5)
			C39	C40	1.395(5)
			C39	C42	1.503(4)
			C40	C41	1.386(5)

Simmety code: $i -x, -y, -z.$

Table S3. Bond angles in ° for compounds **1** and **2**.

1				2			
C5	Se1	C7	85.52(10)	C11	I1	I2A	178.77(4)
C1	N1	C5	121.2(2)	C11	I1	I2B	169.9(5)
N1	C1	C2	120.2(2)	I4B	I3	C12	173.0(2)
C1	C2	C3	120.4(2)	C12	I3	I4A	172.55(14)
C2	C3	C4	119.2(2)	C13	I5	I6A	175.23(18)
C3	C4	C5	118.2(2)	C13	I5	I6B	174.92(18)
C3	C4	C6	129.0(2)	C5	Se1	C7	85.87(14)
C5	C4	C6	112.7(2)	C5	N1	C1	121.5(3)
N1	C5	Se1	125.27(19)	N1	C1	C2	120.2(3)
N1	C5	C4	120.7(2)	C1	C2	C3	120.0(3)
C4	C5	Se1	114.00(17)	C2	C3	C4	119.7(3)
C7	C6	C4	115.2(2)	C3	C4	C5	117.9(3)
C6	C7	Se1	112.55(17)	C3	C4	C6	129.3(3)
C6	C7	C8	128.0(2)	C5	C4	C6	112.8(3)
C8	C7	Se1	119.43(17)	N1	C5	Se1	126.1(2)
C9	C8	C7	120.3(2)	N1	C5	C4	120.7(3)
C9	C8	C13	118.1(2)	C4	C5	Se1	113.2(2)
C13	C8	C7	121.6(2)	C7	C6	C4	115.6(3)
C10	C9	C8	120.8(2)	C6	C7	Se1	112.5(2)
C9	C10	C11	121.4(2)	C6	C7	C8	127.9(3)
C10	C11	C14	120.0(2)	C8	C7	Se1	119.6(2)
C12	C11	C10	117.7(2)	C9	C8	C7	120.7(3)
C12	C11	C14	122.4(2)	C13	C8	C7	121.6(3)
C11	C12	C13	121.4(2)	C13	C8	C9	117.7(3)
C12	C13	C8	120.6(2)	C10	C9	C8	120.9(3)
				C9	C10	C11	121.3(3)
				C10	C11	C14	120.8(3)
				C12	C11	C10	117.9(3)
				C12	C11	C14	121.3(3)
				C13	C12	C11	121.1(3)
				C12	C13	C8	121.1(3)
				C19	Se2	C21	85.91(14)
				C15	N2	C19	121.7(3)
				N2	C15	C16	120.4(3)
				C15	C16	C17	119.7(3)
				C16	C17	C18	119.6(3)
				C17	C18	C19	118.3(3)
				C17	C18	C20	129.2(3)
				C19	C18	C20	112.5(3)
				N2	C19	Se2	126.2(2)
				N2	C19	C18	120.3(3)
				C18	C19	Se2	113.5(2)
				C21	C20	C18	115.7(3)
				C20	C21	Se2	112.3(2)
				C20	C21	C22	128.2(3)
				C22	C21	Se2	119.5(2)
				C23	C22	C21	120.0(3)
				C27	C22	C21	122.1(3)
				C27	C22	C23	118.0(3)
				C24	C23	C22	120.5(3)
				C23	C24	C25	121.7(3)
				C24	C25	C26	117.8(3)
				C24	C25	C28	120.2(3)
				C26	C25	C28	122.0(3)
				C27	C26	C25	120.9(3)
				C26	C27	C22	121.2(3)
				C33	Se3	C35	85.82(14)
				C33	N3	C29	121.2(3)
				N3	C29	C30	120.3(3)
				C29	C30	C31	120.0(3)
				C30	C31	C32	119.4(3)
				C31	C32	C34	128.7(3)

1	2			
	C33	C32	C31	118.0(3)
	C33	C32	C34	113.2(3)
	N3	C33	Se3	125.6(2)
	N3	C33	C32	121.0(3)
	C32	C33	Se3	113.4(2)
	C35	C34	C32	115.1(3)
	C34	C35	Se3	112.4(2)
	C34	C35	C36	128.9(3)
	C36	C35	Se3	118.7(2)
	C37	C36	C35	121.5(3)
	C37	C36	C41	117.9(3)
	C41	C36	C35	120.6(3)
	C38	C37	C36	120.5(3)
	C37	C38	C39	121.6(3)
	C38	C39	C42	121.5(3)
	C40	C39	C38	118.0(3)
	C40	C39	C42	120.5(3)
	C41	C40	C39	120.9(3)
	C40	C41	C36	121.1(3)

Table S4. Hydrogen bonding interactions found in compounds **1** and **2**. Distances and angles are reported in Å and °, respectively.

	1	2		
	N1–H1...Cl1	N1–H1...Cl1	N2–H2...Cl2	N3–H3...Cl3
d_{D-A}	3.022(2)	3.054(3)	3.066(3)	3.076(3)
d_{H-A}	2.011(19)	2.389(8)	2.254(8)	2.258(8)
$\alpha_{D-H...A}$	174(3)	153.97(18)	153.30(18)	154.62(18)
	O1–H1AA...Cl1			
d_{D-A}	3.209(2)			
d_{H-A}	2.363(6)			
$\alpha_{D-H...A}$	172.9(2)			
	O2–H2A...Cl1			
d_{D-A}	3.190(9)			
d_{H-A}	2.212(6)			
$\alpha_{D-H...A}$	167.8(2)			
	C1–H1A...Cl1 ⁱ			
d_{D-A}	3.484(2)			
d_{H-A}	2.580(6)			
$\alpha_{D-H...A}$	159.2(2)			

Symmetry code: ⁱ = $-x, 2-y, 2-z$.

Table S5. Optimised geometry calculated for **L** at DFT level (mPW1PW//LANL2DZ(d,p)) in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	<i>Z</i>	<i>x</i>	<i>y</i>	<i>z</i>
1	34	0.869306	-1.385345	0.145371
2	7	3.663004	-0.850941	0.078662
3	6	4.669798	0.021267	-0.017247
4	1	5.673861	-0.400849	0.028745
5	6	4.490235	1.406459	-0.170239
6	1	5.359539	2.056891	-0.243659
7	6	3.201971	1.925826	-0.226237
8	1	3.031516	2.995261	-0.346266
9	6	2.117915	1.038020	-0.124141
10	6	2.438154	-0.337223	0.024502
11	6	0.710046	1.314668	-0.158575
12	1	0.322923	2.321901	-0.301177
13	6	-0.113014	0.227785	-0.042553
14	6	-1.580453	0.228112	-0.037063
15	6	-2.319687	-0.885074	-0.466973
16	1	-1.799100	-1.771678	-0.829062
17	6	-3.714315	-0.865777	-0.465043
18	1	-4.260255	-1.743966	-0.809413
19	6	-4.425186	0.261332	-0.036735
20	6	-3.685262	1.373037	0.397972
21	1	-4.209766	2.261699	0.750222
22	6	-2.294278	1.358792	0.404394
23	1	-1.750213	2.224528	0.777647
24	6	-5.929311	0.285965	-0.031129
25	1	-6.314642	1.104229	-0.653381
26	1	-6.318751	0.438930	0.983983
27	1	-6.344131	-0.653057	-0.413069

Table S6. Optimised geometry calculated for [HL]⁺ at DFT level (mPW1PW//LANL2DZ(d,p)) in the gas phase (total charge = 1, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	<i>Z</i>	<i>x</i>	<i>y</i>	<i>z</i>
1	34	-0.812267	-1.363570	-0.182248
2	7	-3.640158	-0.775411	-0.107542
3	1	-3.822192	-1.768939	-0.222691
4	6	-4.700031	0.057155	-0.013464
5	1	-5.682250	-0.401599	-0.070818
6	6	-4.491974	1.418163	0.146786
7	1	-5.351471	2.078332	0.222699
8	6	-3.188909	1.917323	0.207467
9	1	-3.020237	2.985488	0.334719
10	6	-2.093487	1.044788	0.103734
11	6	-2.363084	-0.339790	-0.057516
12	6	-0.696025	1.345144	0.150064
13	1	-0.331647	2.357763	0.302398
14	6	0.149024	0.273974	0.032208
15	6	1.606210	0.253437	0.025375
16	6	2.326787	-0.905980	0.359907
17	1	1.802010	-1.815417	0.657154
18	6	3.718478	-0.905510	0.358132
19	1	4.253941	-1.814341	0.628370
20	6	4.441884	0.247621	0.022704
21	6	3.717535	1.404991	-0.316065
22	1	4.255528	2.310891	-0.593265
23	6	2.329347	1.413850	-0.318711
24	1	1.801002	2.317527	-0.616032
25	6	5.942806	0.255810	0.018525
26	1	6.330233	0.996418	0.729833
27	1	6.328778	0.526740	-0.972376
28	1	6.351112	-0.722858	0.288582

Table S7. Selected optimised bond lengths (Å) and angles (°) calculated at the DFT level (mPW1PW//LANL2DZ(d,p)) in the gas phase for **L** and [HL]⁺ and corresponding structural data; numbering scheme as in Figure S.

	L (calculated)	[HL] ⁺ (calculated)	[HL] ⁺ (experimental) ^a
N1-C1	1.336	1.351	1.344
N1-C5	1.329	1.350	1.347
Se1-C5	1.891	1.862	1.859
Se1-C7	1.898	1.911	1.906
C1-C2	1.405	1.386	1.379
C2-C3	1.390	1.397	1.386
C3-C4	1.405	1.404	1.399
C4-C5	1.420	1.420	1.401
C4-C6	1.435	1.430	1.435
C6-C7	1.368	1.369	1.360
C7-C8	1.468	1.457	1.466
C8-C9	1.408	1.410	1.397
C8-C13	1.404	1.406	1.399
C9-C10	1.391	1.388	1.387
C10-C11	1.404	1.407	1.395
C11-C12	1.400	1.402	1.392
C11-C14	1.504	1.501	1.507
C12-C13	1.395	1.392	1.390
N1-H1		1.017	
C1-N1-C5	116.06	122.72	121.37
N1-C5-Se1	123.21	127.42	125.69
C5-Se1-C7	87.25	86.58	85.75
Se1-C7-C8-C13	28.02	23.94	2.66
C1-N1-C5-Se1	179.82	179.65	179.51

^aAverage calculated on the three independent [HL]⁺ cations in the asymmetric unit of **2**.

Table S8. Optimised geometry calculated for $\{[\text{HL}]^+\cdots[\text{Cl-I-I}]^-\}$ (**I**) at DFT level (mPW1PW//LANL2DZ(d,p)) in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (Z = atomic number).

Atom number	Z	x	y	z
1	34	-1.587353	0.744517	0.901816
2	7	0.254055	2.768554	0.073610
3	1	0.745077	2.521551	1.007615
4	6	0.723225	3.695462	-0.769667
5	1	1.632969	4.204235	-0.464805
6	6	0.057947	3.959046	-1.963859
7	1	0.454759	4.712236	-2.638849
8	6	-1.101740	3.249124	-2.276911
9	1	-1.627447	3.443492	-3.210599
10	6	-1.588801	2.278418	-1.387568
11	6	-0.854751	2.065985	-0.193347
12	6	-2.734639	1.425587	-1.499470
13	1	-3.382192	1.438132	-2.372998
14	6	-2.920282	0.563883	-0.451902
15	6	-3.999911	-0.413771	-0.291622
16	6	-5.262148	-0.185690	-0.872381
17	1	-5.446379	0.740200	-1.414329
18	6	-6.286585	-1.115280	-0.732741
19	1	-7.256428	-0.911188	-1.186606
20	6	-6.099649	-2.303593	-0.006852
21	6	-4.845459	-2.524040	0.575278
22	1	-4.670022	-3.438498	1.140844
23	6	-3.812065	-1.598633	0.437999
24	1	-2.840600	-1.817789	0.881475
25	6	-7.217570	-3.298063	0.140714
26	1	-6.903297	-4.167076	0.728021
27	1	-7.558958	-3.655680	-0.839329
28	1	-8.083424	-2.845473	0.641254
29	53	2.667652	-0.180075	0.935505
30	53	4.015559	-1.881346	-0.780448
31	17	1.162160	1.673880	2.599301

Table S9. Selected optimised bond lengths (Å) and angles (°) calculated at the DFT level (mPW1PW//LANL2DZ(d,p)) in the gas phase for {[HL]⁺...[Cl-I-I]⁻} (**I**) and {[HL]⁺...[I-I-Cl]⁻} (**II**) with corresponding structural data and for {[HL]⁺...[I-I-Cl]⁻} (**III**); numbering scheme as in Figure S.

	{[HL] ⁺ ...[Cl-I-I] ⁻ } (calculated)	{[HL] ⁺ ...[Cl-I-I] ⁻ } (experimental) ^a	{[HL] ⁺ ...[I-I-Cl] ⁻ } (calculated)
N1-C1	1.338	1.346	1.340
N1-C5	1.340	1.345	1.341
Se1-C5	1.866	1.862	1.866
Se1-C7	1.908	1.904	1.910
N1-H1	1.084	/	1.056
H1-C11	1.851	/	/
H1-I1	/	/	2.331
N1-C11	2.899	3.066	/
N1-I1	/	/	3.352
C11-I1	2.911	2.725	/
I1-I2	2.767	2.820	3.047
I2-C11	/	/	2.501
C1-N1-C5	121.87	121.46	122.39
N1-C5-Se1	125.41	125.94	126.08
C5-Se1-C7	85.69	85.87	85.74
N1-H1-C11	161.37	/	/
^a N1-H1-I1	/	/	162.10
H1-C11-I1	85.22	/	/
H1-I1-I2	/	/	71.59
C11-I1-I2	176.49	175.52	/
I1-I2-C11	/	/	175.85
C1-N1-H1-C11	172.99	/	163.59
Se1-C7-C8-C13	29.54	2.66	29.75
C1-N1-C5-Se1	179.48	179.51	178.91

^aAverage calculated for the three independent [I₂Cl]⁻ systems in the unit cell of **2**.

Table S10. Optimised geometry calculated for $\{[\text{HL}]^+\cdots[\text{I-I-Cl}]^-\}$ (**II**) at DFT level (mPW1PW//LANL2DZ(d,p)) in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (Z = atomic number).

Atom number	Z	x	y	z
1	34	1.118284	0.029890	-0.810164
2	7	-1.046281	1.911960	-0.835683
3	1	-1.594679	1.142191	-1.306227
4	6	-1.621915	3.090898	-0.562454
5	1	-2.660932	3.195998	-0.859458
6	6	-0.895977	4.087663	0.079348
7	1	-1.377100	5.036039	0.300942
8	6	0.431543	3.849392	0.437461
9	1	1.007101	4.620074	0.947859
10	6	1.024680	2.611038	0.147672
11	6	0.225234	1.639653	-0.506482
12	6	2.348364	2.145207	0.436377
13	1	3.072801	2.757170	0.968412
14	6	2.611238	0.861562	0.042862
15	6	3.865604	0.122233	0.199853
16	6	5.096972	0.804750	0.224088
17	1	5.117350	1.884731	0.089423
18	6	6.290117	0.109642	0.384909
19	1	7.230516	0.660716	0.393582
20	6	6.307144	-1.288630	0.522376
21	6	5.081226	-1.964512	0.490978
22	1	5.063400	-3.048308	0.599695
23	6	3.879992	-1.275486	0.332828
24	1	2.942939	-1.832585	0.343348
25	6	7.605024	-2.027954	0.692415
26	1	7.440986	-3.106845	0.780995
27	1	8.135469	-1.689970	1.592046
28	1	8.271534	-1.854607	-0.162372
29	53	-2.866416	-0.811451	0.913247
30	17	-3.274887	-0.542384	3.366187
31	53	-2.250134	-0.951181	-2.095464

Table S11. Optimised geometry calculated for $[\text{Cl-I-I}]^- \cdots \text{I}_2 \cdots [\text{I-I-Cl}]^-$ (**III**) at DFT level (mPW1PW//LANL2DZ(d,p)) in the gas phase (total charge = -2, spin multiplicity = 1) in orthogonal Cartesian coordinate format (Z = atomic number).

Atom number	Z	x	y	z
1	53	1.378255	-0.025286	-0.005620
2	53	-1.374624	0.026560	0.005733
3	53	-6.913309	-0.888460	-0.020770
4	53	6.912219	0.888104	0.020720
5	17	-4.594800	0.384503	0.032085
6	17	4.595506	-0.388706	-0.032266
7	53	-9.520214	-2.229847	-0.076627
8	53	9.516921	2.233173	0.076753

Table S12. Selected optimised bond lengths (Å) and angles (°) calculated at the DFT level (mPW1PW//LANL2DZ(d,p)) in the gas phase for {[Cl–I–I][–]⋯I₂⋯[I–I–Cl][–]} (**III**) and {[I–I–Cl][–]⋯I₂⋯[Cl–I–I][–]} (**IV**) with corresponding structural data for {[Cl–I–I][–]⋯I₂⋯[I–I–Cl][–]} (**III**); numbering scheme as in Figure S9.

	{[Cl–I–I] [–] ⋯I ₂ ⋯[I–I–Cl] [–] } (calculated)	{[Cl–I–I] [–] ⋯I ₂ ⋯[I–I–Cl] [–] } (experimental)	{[I–I–Cl] [–] ⋯I ₂ ⋯[Cl–I–I] [–] } (calculated)
C11-I1	2.637	2.702	/
I1-I2	2.940	2.830	2.932
I2-C11	/	/	2.645
I2-I3	3.545	3.286	/
C11-I3	/	/	3.240
I3-I4	2.788	2.743	2.753
I4-I5	3.536	3.286	/
I5-I6	2.941	2.830	2.932
I6-C12	2.635	2.702	/
I4-C12	/	/	3.238
C12-I5	/	/	2.646
C11-I1-I2	178.29	175.24	/
I1-I2-C11	/	/	178.46
I1-I2-I3	130.23	99.94	/
I2-C11-I3	/	/	144.85
I2-I3-I4	172.42	172.59	/
C11-I3-I4	/	/	174.73
I3-I4-I5	172.58	172.59	/
I3-I4-C12	/	/	174.63
I4-I5-I6	129.37	99.94	/
I4-C12-I5	/	/	144.66
I5-I6-C12	178.32	175.24	/
C12-I4-I5	/	/	178.45

Table S13. Optimised geometry calculated for $\{[\text{I}-\text{I}-\text{Cl}]^- \cdots \text{I}_2 \cdots [\text{Cl}-\text{I}-\text{I}]^-\}$ (**IV**) at DFT level (mPW1PW//LANL2DZ(d,p)) in the gas phase (total charge = -2, spin multiplicity = 1) in orthogonal Cartesian coordinate format (Z = atomic number).

Atom number	Z	x	y	z
1	53	5.789309	10.120304	15.779151
2	53	4.448717	12.350462	16.779267
3	53	0.964511	16.022658	19.788451
4	53	2.990155	15.435764	17.739670
5	17	-0.847931	16.624970	21.606602
6	53	9.276868	6.511384	12.752001
7	53	7.250001	7.047771	14.814816
8	17	11.089571	5.955987	10.922043

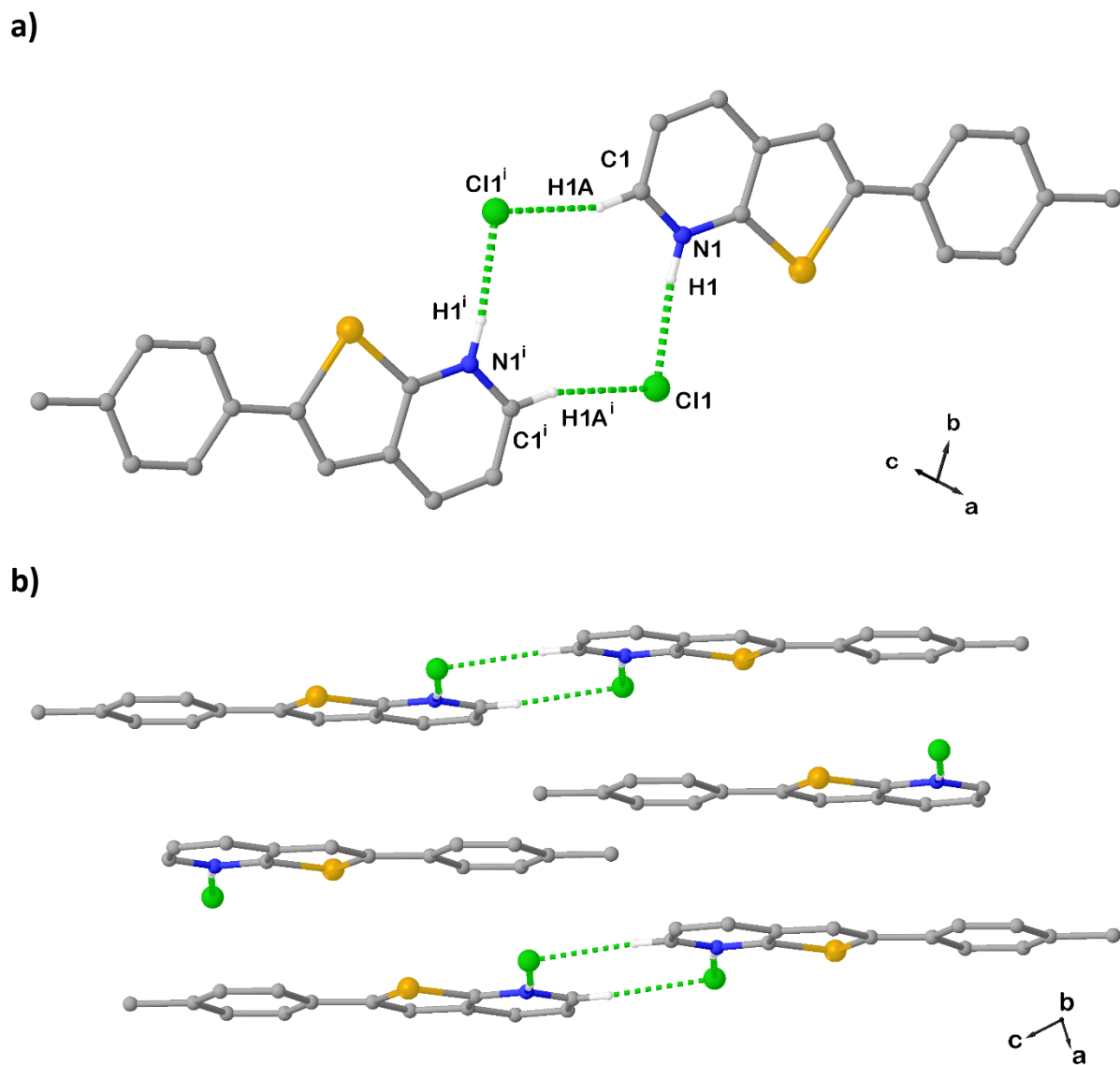
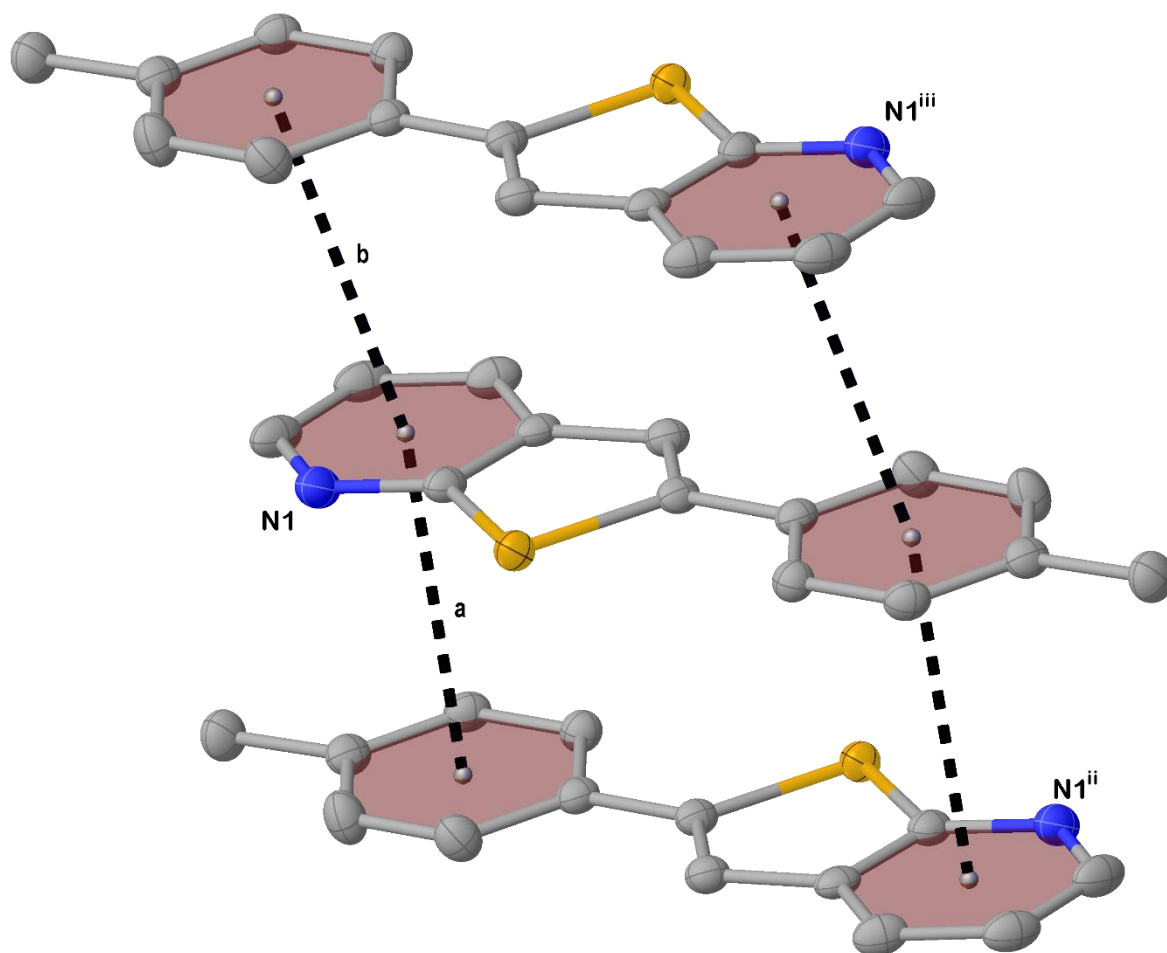


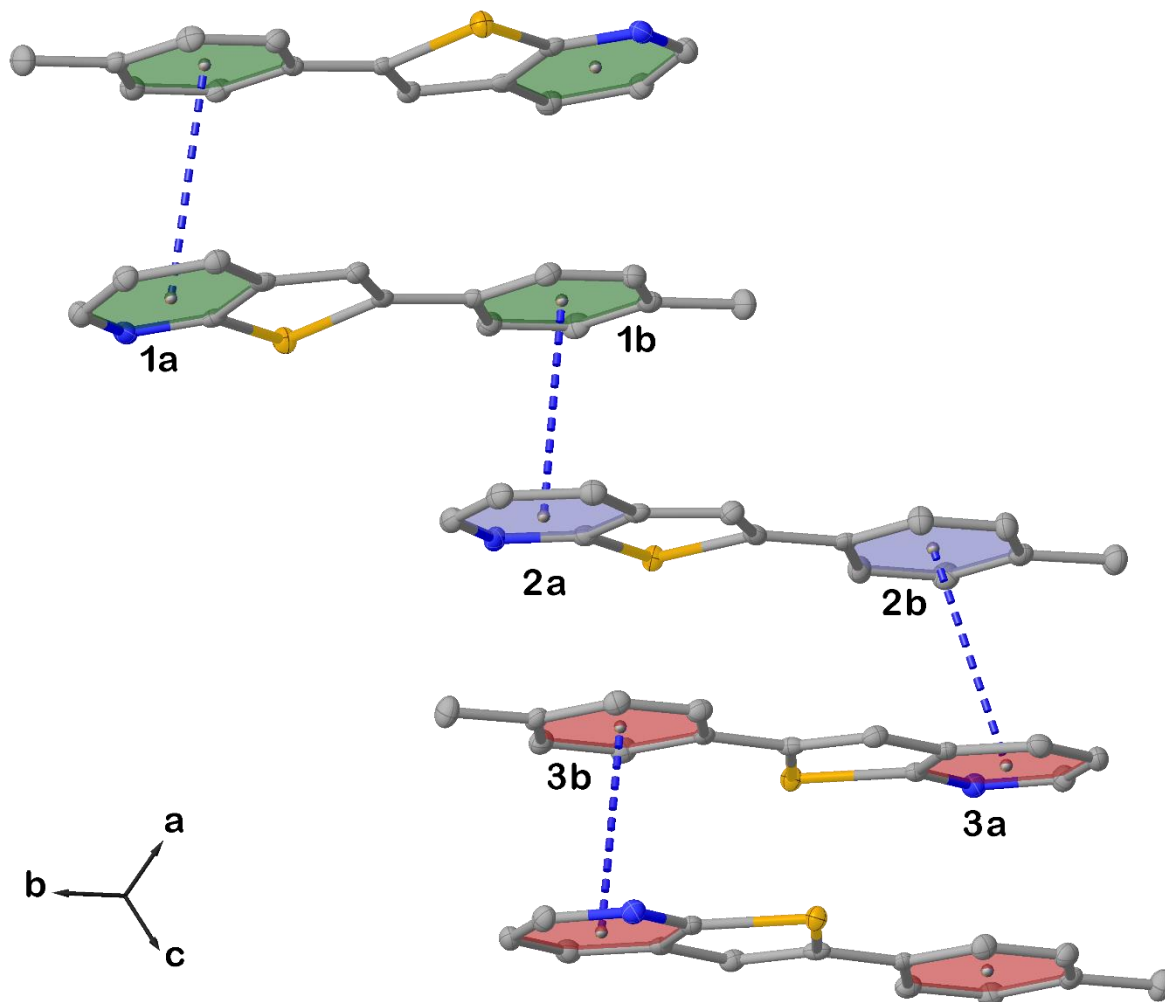
Figure S1. a) View along the [101] direction of the hydrogen-bonded dimeric arrangement found in **1**. Relevant bond lengths and angles are listed in Table S4. b) Packing diagram of **1** viewed along the *b* axis. Symmetry code: $i = -x, 2-y, 2-z$.



Interaction	Angle (°)	Centroid to centroid distance (Å)	Shift distance (Å)
a	1.24	3.61	1.17
b	2.65	3.74	1.51

Symmetry codes: ⁱⁱ = 1-x, 1-y, 1-z; ⁱⁱⁱ = 2-x, 1-y, 1-z.

Figure S2. Partial view along the [011] direction of a cationic π - π stacked layer found in compound **1** with relevant interactions are described below.



Planes	Angle (°)	Centroid to centroid distance (Å)	Shift distance (Å)
1a-1b ^{viii}	5.86	3.60	1.24
1b-2a	3.35	3.46	0.78
2b-3a ^{ix}	5.52	3.46	1.10
3a ^x -3b ^{ix}	2.37	3.54	1.14

Symmetry codes: ^{vii} = $2-x, 1-y, 1-z$; ^{ix} = $1-x, -y, 1-z$; ^x = $+x, +y, 1+z$.

Planes: **1a** = N1-C1-C2-C3-C4-C5; **1b** = C8-C9-C10-C11-C12-C13; **2a** = N2-C16-C17-C18-C19-C15; **2b** = C22-C23-C24-C25-C26-C27; **3a** = N3-C29-C30-C31-C32-C33; **3b** = C36-C37-C38-C39-C40-C41.

Figure S3. Partial view along the [111] direction of a cationic layer found in compound **2** with intermolecular π - π interactions.

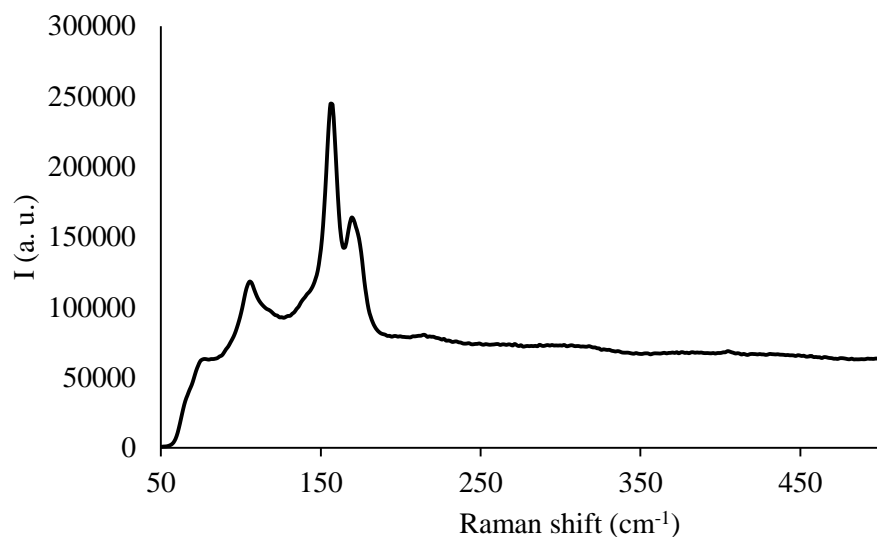


Figure S4. Raman spectrum of compound **2**.

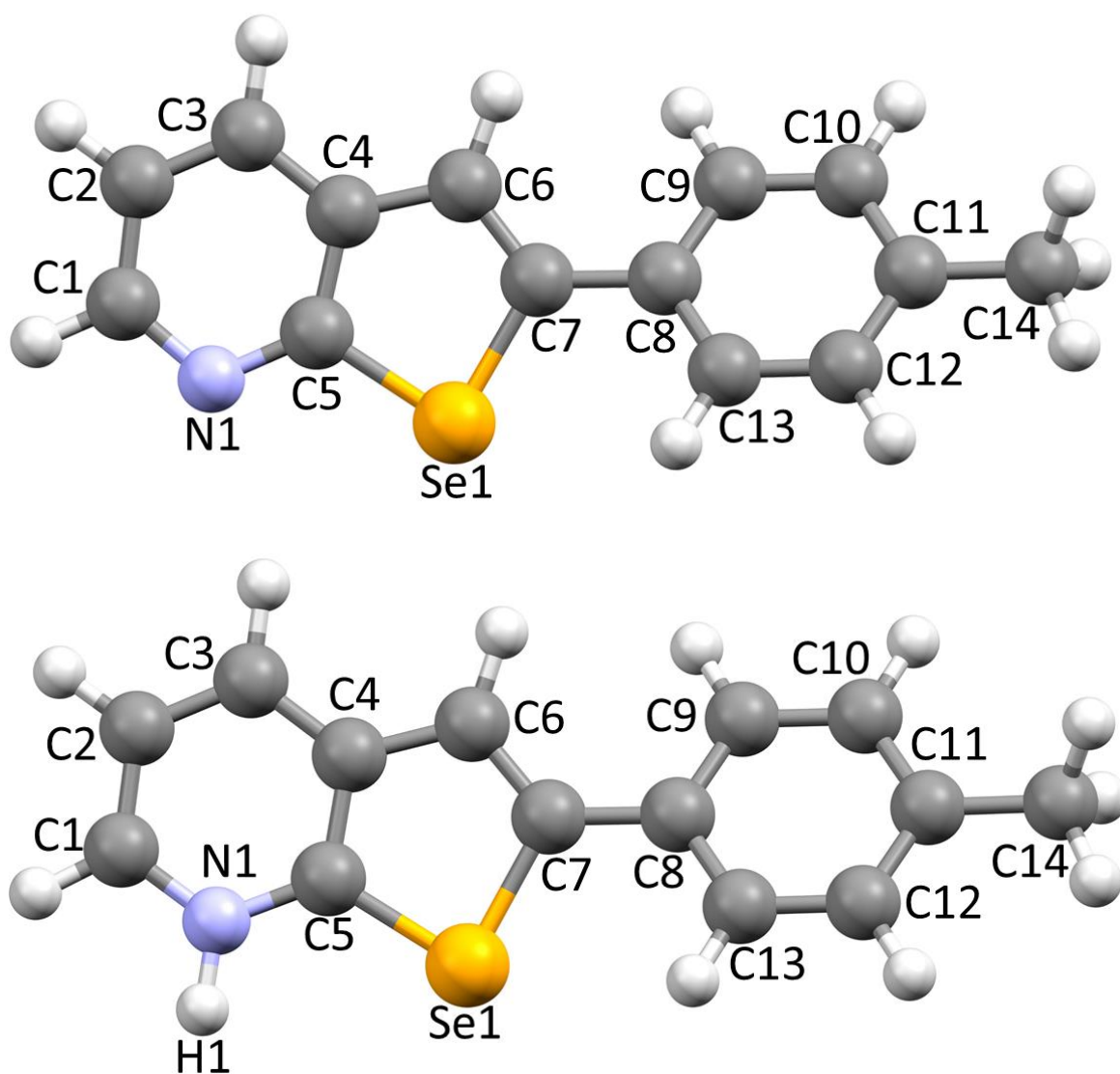


Figure S5. Molecular structure and atom labelling scheme calculated at the DFT level (mPW1PW//LANL2DZ(d,p)) in the gas phase for **L** (top) and **[HL]⁺** (bottom).

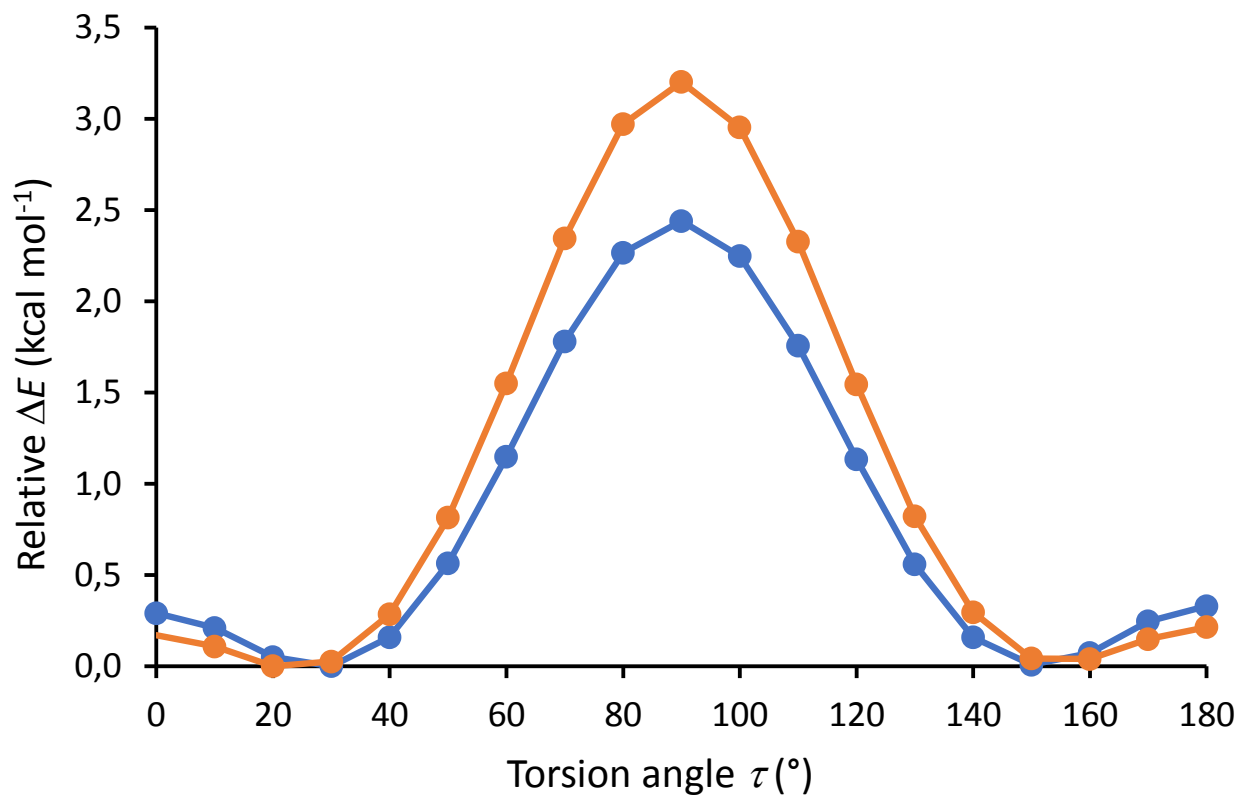
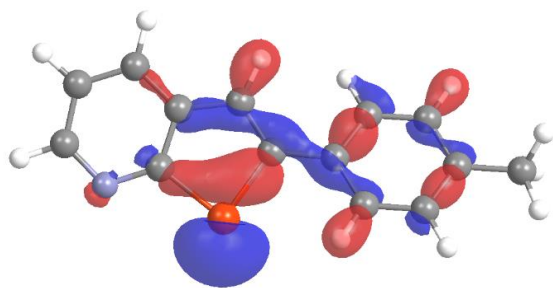
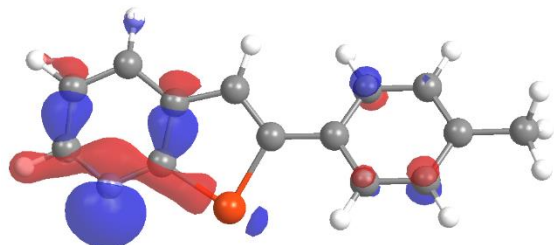


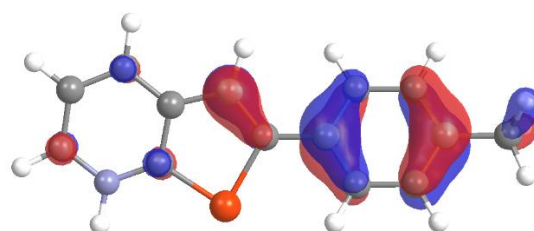
Figure S6. Relative energy variation ΔE of the total electronic energy as a function of torsion angle τ (Se1-C7-C8-C13; atom labelling scheme as in Figure S5) calculated for **L** (blue line) and **[HL]⁺** (orange line) at the DFT level (mPW1PW//LANL2DZ(d,p)).



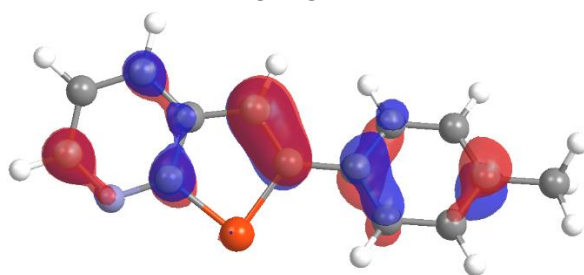
HOMO-6



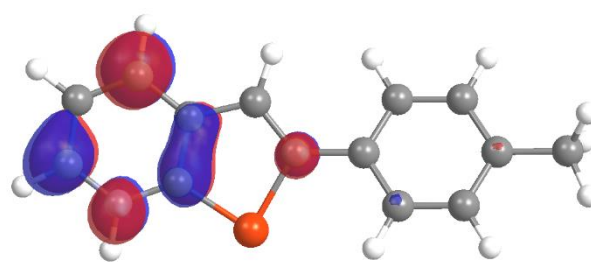
HOMO-4



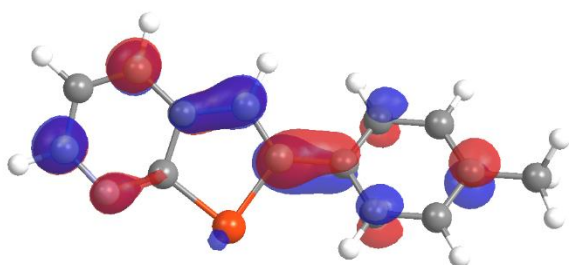
HOMO



HOMO



LUMO



LUMO

Figure S7. Isosurfaces of selected frontier KS-MOs calculated for **L** (left) and **[HL]⁺** (right) at the DFT level (mPW1PW// LANL2DZ(d,p)) in the gas phase; isovalue 0.05 |e|.

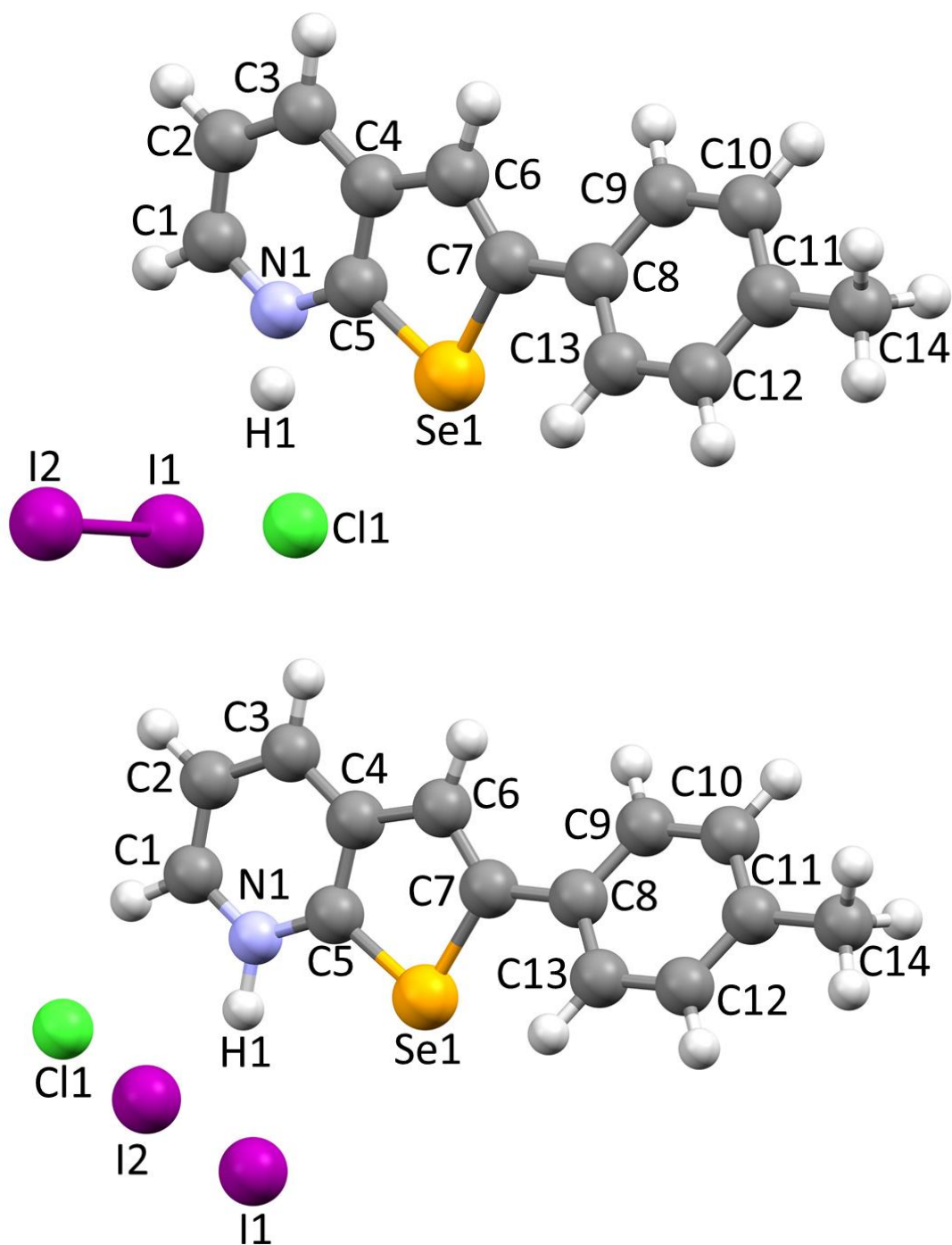


Figure S8. Molecular structure and atom labelling scheme calculated at the DFT level (mPW1PW//LANL2DZ(d,p)) in the gas phase for $\{[\text{LH}]^+\cdots[\text{Cl-I-I}]^-\}$ (**I**, top) and $\{[\text{LH}]^+\cdots[\text{I-I-Cl}]^-\}$ (**II**, bottom).

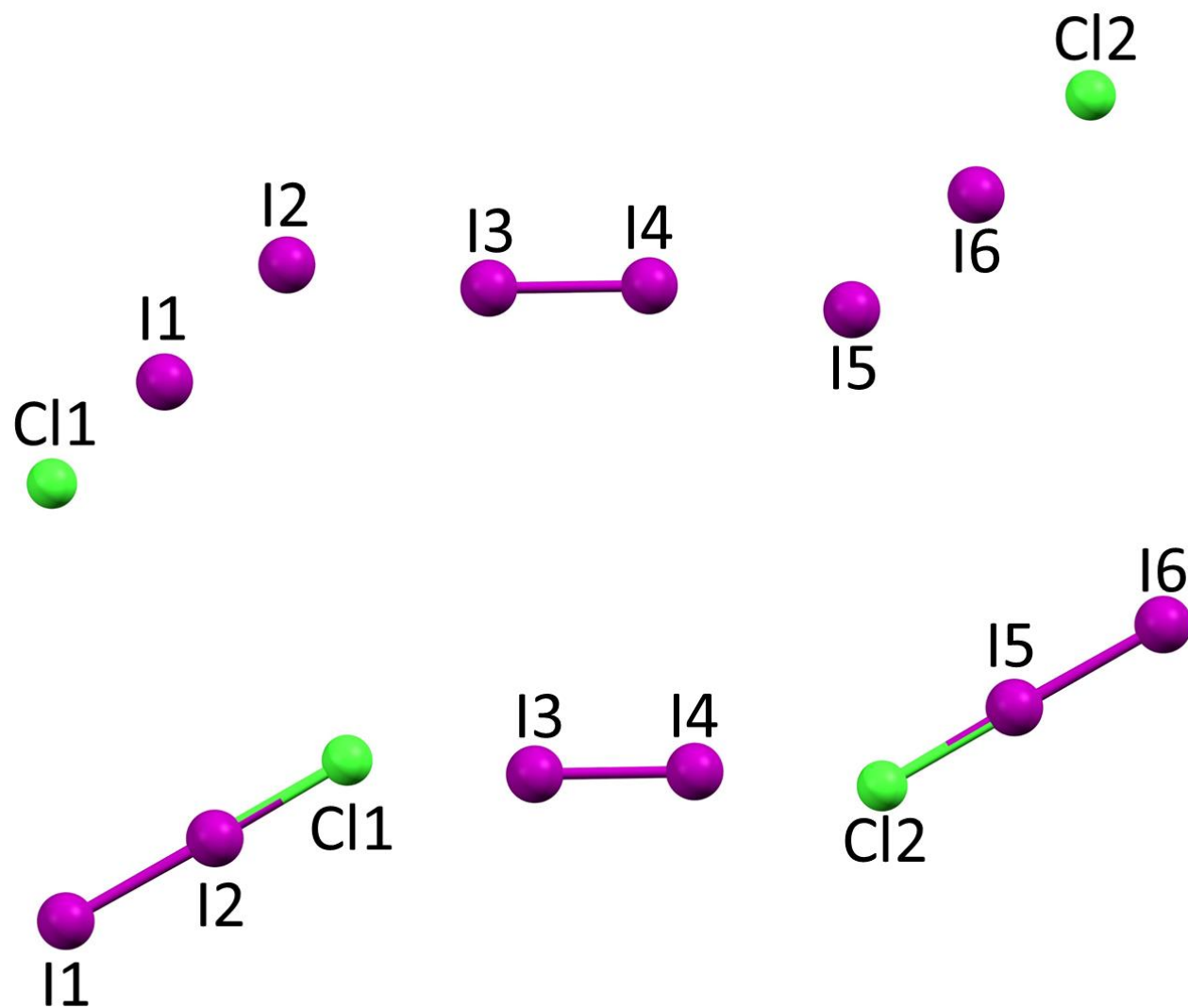


Figure S9. Molecular structure and atom labelling scheme calculated at the DFT level (mPW1PW//LANL2DZ(d,p)) in the gas phase for $\{[\text{Cl-I-I}]^- \cdots \text{I}_2 \cdots [\text{I-I-Cl}]^-\}$ (**III**, top) and $\{[\text{I-I-Cl}]^- \cdots \text{I}_2 \cdots [\text{Cl-I-I}]^-\}$ (**IV**, bottom).