Electronic supplementary information

New uranium(VI) and isothiouronium complexes: synthesis, crystal structure, spectroscopic characterization and a DFT study

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Table 1S Hydrogen bonds in the studied compounds**.**

Involved atoms	D-H [Å]	H---A [Å]	D---A [Å]	∠ D-H---A [°]
1_ac				
N1—H1A---O1	0.88	1.88	2.7567(19)	173
N1—H1B---O4	0.88	1.9	2.695(2)	150
N2—H2A---O2	0.88	1.91	2.7904(19)	174
N2—H2B---O3^{i}	0.88	1.91	2.7366(19)	155
N3—H3A---O4^{ii}	0.88	1.97	2.850(2)	175
N3—H3B---O2^{iii}	0.88	1.95	2.8256(19)	174
N4—H4C---O3^{ii}	0.88	1.9	2.7766(19)	179
N4—H4D---O1^{iv}	0.88	2.09	2.8551(19)	145
1_Cl				
N1—H1B---Cl1	0.90(3)	2.26(3)	3.151(2)	172(3)
N2—H2A---Cl1^{i}	0.86(3)	2.33(3)	3.146(2)	158(2)
N1—H1A---Cl1^{ii}	0.86(3)	2.57(3)	3.2994(19)	143(3)
N2—H2B---Cl1^{iii}	0.85(3)	2.38(3)	3.200(2)	161(2)
1_U				
N1—H1B---O9	0.88	1.97	2.771(6)	151
O9—H9A---O6	0.85	2.44	2.977(7)	122
O9—H9A---O10	0.85	1.87	2.684(5)	161
N1—H1A---O8^{i}	0.88	2	2.776(6)	147

N2—H2D---O3^{i}	0.88	2.05	2.906(5)	165
O9—H9B---O4^{ii}	0.85	2.64	3.192(6)	124
O9—H9B---O5^{ii}	0.85	2.27	3.078(7)	160
N2—H2E---O7^{iii}	0.88	2.02	2.880(6)	166
2_Cl				
N1—H1A---Cl1	0.92(8)	2.37(8)	3.183(5)	147(6)
N2—H2C---Cl1	0.91(6)	2.46(6)	3.301(5)	153(5)
N3—H3A---Cl2	0.84(5)	2.42(5)	3.194(5)	155(4)
N4—H4A---Cl2	0.83(9)	2.59(9)	3.229(5)	135(8)
N1—H1B---Cl2^{i}	0.81(6)	2.38(6)	3.168(5)	167(5)
N2—H2D---Cl2^{ii}	0.93(5)	2.23(6)	3.149(5)	167(4)
N3—H3B---Cl1^{iii}	0.76(6)	2.49(6)	3.179(5)	153(6)
N4—H4B---Cl1^{iv}	0.86(6)	2.31(6)	3.168(5)	176(5)
2_U				
N1—H1A---Cl1	0.81(7)	2.99(8)	3.684(9)	145(8)
N2—H2C---Cl1	0.87(6)	2.34(7)	3.212(8)	176(7)
N3—H3A---O8	0.86(7)	1.94(7)	2.782(9)	168(8)
N4—H4A---O3	0.82(7)	2.03(7)	2.828(9)	167(8)
N1—H1B---O6^{i}	0.79(7)	2.06(8)	2.795(9)	156(10)
N2—H2D---Cl1^{ii}	0.80(7)	2.45(8)	3.193(8)	155(8)
N3—H3B---Cl1^{iii}	0.87(7)	2.33(8)	3.142(7)	157(9)
N4—H4B---O1^{iv}	0.76(7)	2.57(9)	2.972(9)	115(8)
N4—H4B---O1^{v}	0.76(7)	2.28(8)	2.972(9)	152(9)

Symmetry operations for **1_ac**: ^{i} x–1, y, z; ^{ii} x, y+1, z; ^{iii} –x, –y+2, –z+1; ^{iv} –x+1, –y+2, –z+1
Symmetry operations for **1_U**: ^{i} x+1, y, z; ^{ii} –x+1.5, y+0.5, –z+0.5, z; ^{iii} x+0.5, –y+1.5, z–0.5
Symmetry operations for **1_Cl**: ^{i} x, y–1, z; ^{ii} –x+2, –y+1, –z+2; ^{iii} x–1, y–1, z
Symmetry operations for **2_Cl**: ^{i} –x+0.5, y–0.5, –z+1.5; ^{ii} –x, –y, –z+1; ^{iii} x, –y, z–0.5; ^{iv} x–1, –y, z–0.5
Symmetry operations for **2_U**: ^{i} x+1, y+2, z; ^{ii} –x+3.5, y–0.5, –z+1.5; ^{iii} x–1, y–1, z; ^{iv} x, y+1, z; ^{v} –x+2, –y+1, –z+2

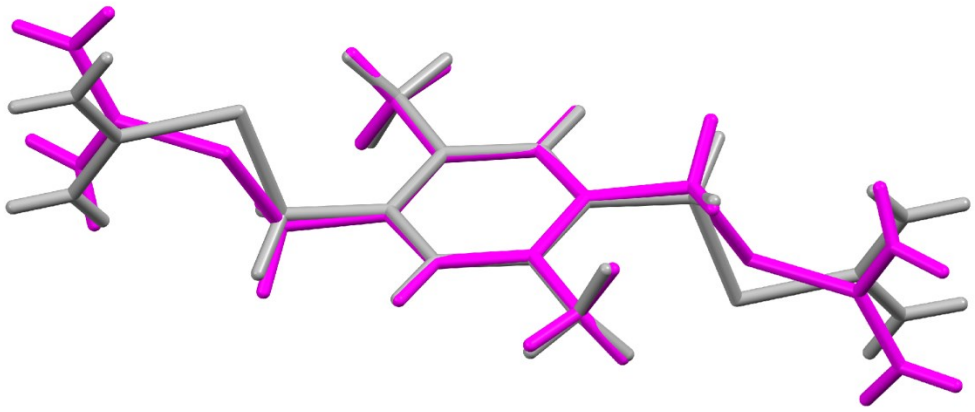

Figure 1S The overlay of the structures of isothiouronium cations in **1_ac** (acetate, grey) and **1_Cl** (chloride, magenta).

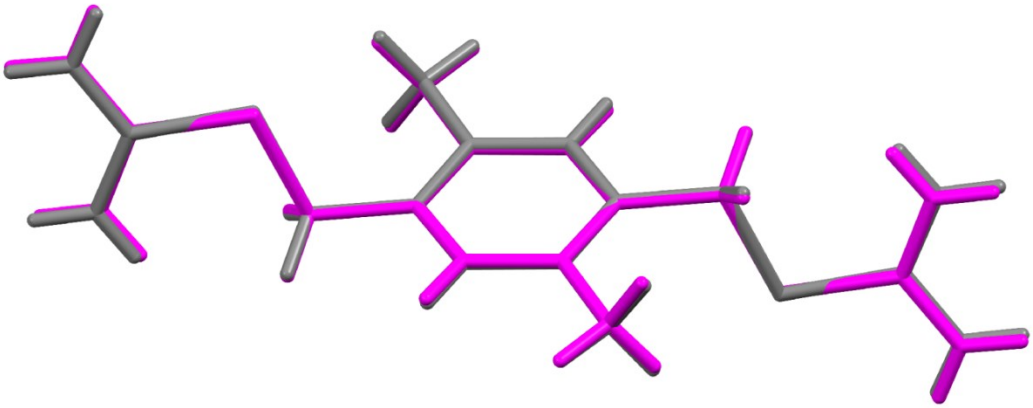

Figure 2S The overlay of the structures of isothiouronium cations in **1_ac**(acetate, grey) and **1_U** (magenta).

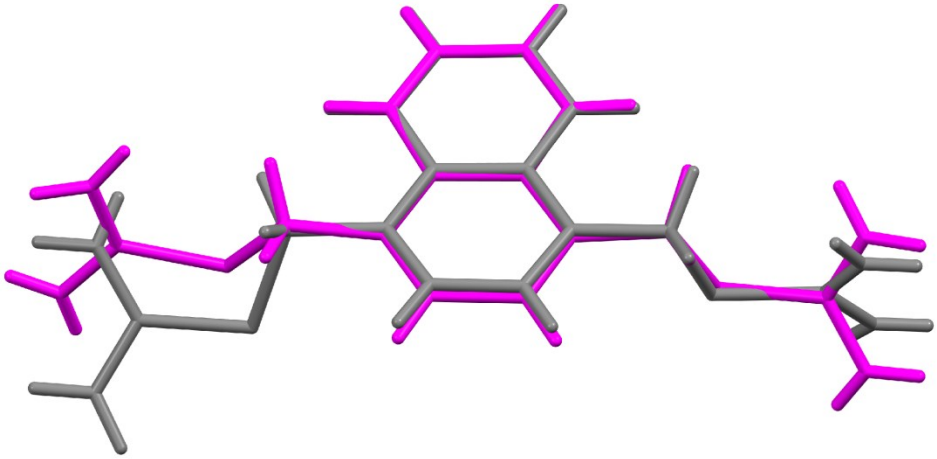

Figure 3S The overlay of the structures of isothiouronium cations in **2_Cl** (chloride, grey) and **2_U**(magenta).

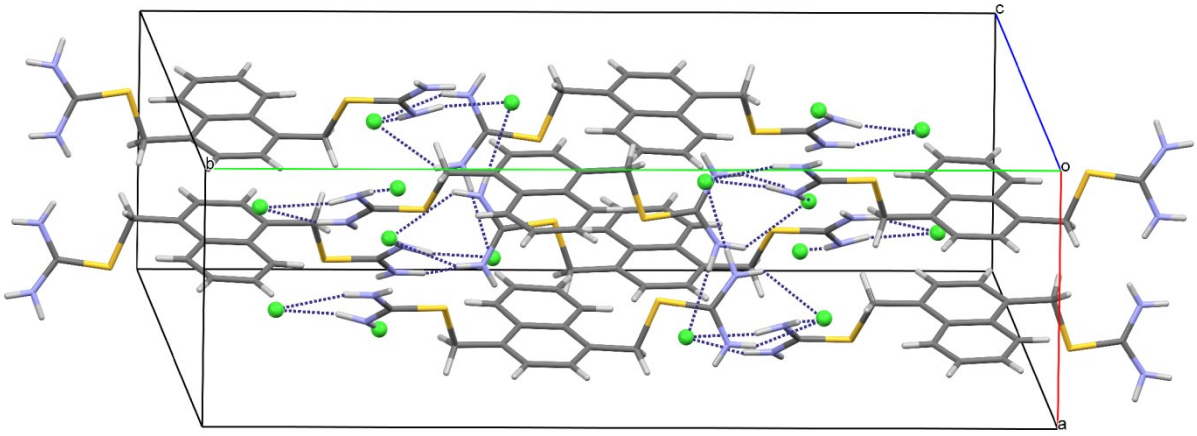

Figure 4S. Crystal packing of **2_Cl** approximately along the *c* axis. Chloride anions drawn as balls and isothiouronium cations as sticks. Hydrogen bonds drawn as dashed lines.

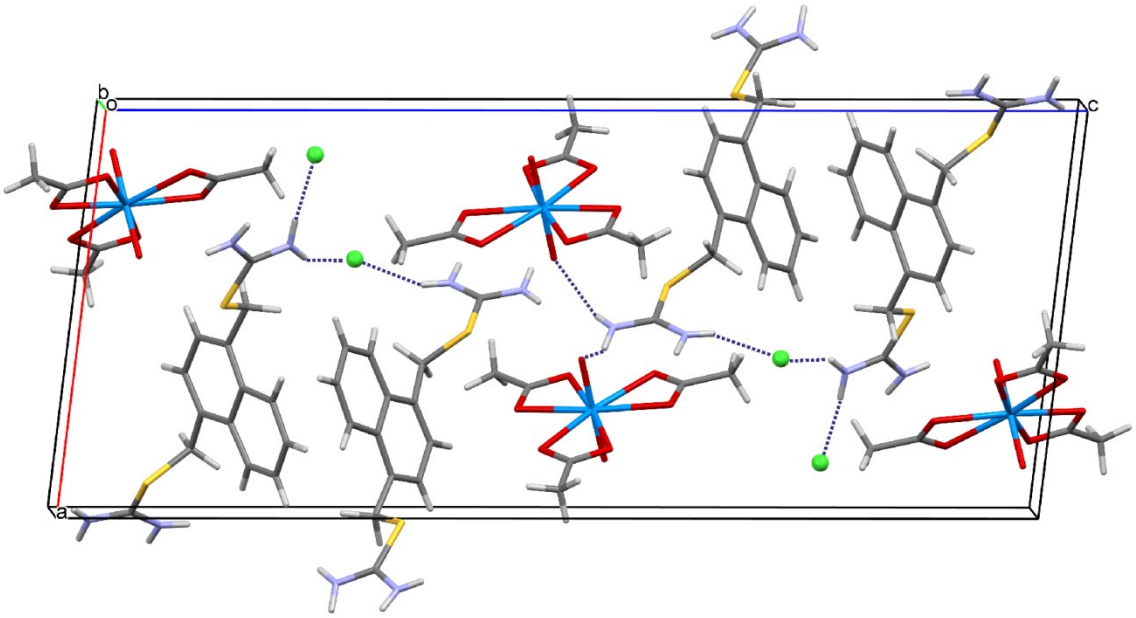

Figure 5S. Crystal packing of **2_U** approximately along the *b* axis. Chloride anions drawn as balls and the remaining ionic species as sticks. Hydrogen bonds drawn as dashed lines. Not all of H-bonds are visualized.

Table 2S. Calculated HOMO/LUMO energies, bond lengths and bond angles of **1o_ac, 1o_Cl, 1o_U, 2o_Cl,** and **2o_U** compounds.

Compound	Bond / angle	Bond length (Å)	Bond angle (°)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)
1o_ac	C(34)-N(3)	1.332	-	-3.868	-3.523	0.345
	C(34)-N(4)	1.306	-			
	C(34)-S(1)	1.799	-			
	C(37)-S(1)	1.844	-			
	N(3)-C(34)-N(4)	-	123.5			
	S(1)-C(34)-N(3)	-	121.6			
	S(1)-C(34)-N(4)	-	115.0			
	C(37)-S(1)-C(34)	-	102.4			
	N(3)-H(7)···O(52)	1.495	177.5			
	N(4)-H(9)···O(51)	1.711	175.7			
	N(4)-H(10)···O(50)	1.445	173.7			
1o_Cl	C(29)-N(5)	1.327	-	-5.535	-2.612	2.923
	C(29)-N(6)	1.323	-			
	C(29)-S(3)	1.764	-			
	C(33)-S(3)	1.850	-			
	N(5)-C(29)-N(6)	-	118.9			
	S(3)-C(29)-N(5)	-	117.2			
	S(3)-C(29)-N(6)	-	123.9			
	C(33)-S(3)-C(29)	-	102.8			

	N(5)-H(9)···Cl(2)	2.019	151.6			
	N(6)-H(11)···Cl(2)	1.967	154.0			
1o_U	C(14)-N(81)	1.327	-	-6.268	-3.66	2.608
	C(14)-N(82)	1.325	-			
	C(14)-S(84)	1.773	-			
	C(16)-S(84)	1.857	-			
	U(85)=O(29)	1.805	-			
	U(85)=O(30)	1.805	-			
	U(85)-O(25)	2.569	-			
	U(85)-O(26)	2.512	-			
	U(85)-O(27)	2.445	-			
	U(85)-O(28)	2.453	-			
	U(85)-O(31)	2.570	-			
	U(85)-O(32)	2.518	-			
	N(81)-C(14)-N(82)	-	121.5			
	S(84)-C(14)-N(81)	-	116.1			
	S(84)-C(14)-N(82)	-	122.3			
	C(14)-S(84)-C(16)	-	102.7			
	O(29)=U(85)=O(30)	-	178.0			
	N(81)-H(62)···O(25)	1.615	179.3			
	N(82)-H(64)···O(31)	1.590	178.7			
2o_Cl	C(23)-N(35)	1.323	-	-5.561	-3.218	2.343
	C(23)-N(36)	1.327	-			
	C(23)-S(40)	1.763	-			
	C(29)-S(40)	1.848	-			
	N(35)-C(23)-N(36)	-	118.6			
	S(40)-C(23)-N(35)	-	124.1			
	S(40)-C(23)-N(36)	-	117.3			
	C(23)-S(40)-C(29)	-	102.6			
	N(36)-H(1)···Cl(19)	2.014	152.2			
	N(35)-H(4)···Cl(19)	1.966	154.5			
	C(28)-N(37)	1.326	-			
	C(28)-N(38)	1.324	-			
	C(28)-S(39)	1.762	-			
	C(30)-S(39)	1.848	-			
	N(37)-C(28)-N(38)	-	118.7			
	S(39)-C(28)-N(37)	-	117.2			
	S(39)-C(28)-N(38)	-	124.0			
	C(28)-S(39)-C(30)	-	102.9			
	N(37)-H(2)···Cl(20)	2.010	152.3			
	N(38)-H(6)···Cl(20)	1.969	154.3			
2o_U	C(29)-N(61)	1.323	-	-5.556	-3.629	1.927
	C(29)-N(62)	1.326	-			
	C(29)-S(58)	1.763	-			
	C(28)-S(58)	1.849	-			

	N(62)-C(29)-N(61)	-	118.7			
	S(58)-C(29)-N(61)	-	124.2			
	S(58)-C(29)-N(62)	-	117.1			
	C(28)-S(58)-C(29)	-	102.9			
	N(61)-H(53)···Cl(63)	1.968	154.2			
	N(62)-H(55)···Cl(63)	2.008	152.2			
	C(27)-N(59)	1.323	-			
	C(27)-N(60)	1.325	-			
	C(27)-S(57)	1.765	-			
	C(19)-S(57)	1.850	-			
	U(1)=O(4)	1.801	-			
	U(1)=O(5)	1.801	-			
	U(1)-O(6)	2.577	-			
	U(1)-O(2)	2.516	-			
	U(1)-O(7)	2.452	-			
	U(1)-O(3)	2.453	-			
	U(1)-O(8)	2.515	-			
	U(1)-O(9)	2.569	-			
	N(59)-C(27)-N(60)	-	121.5			
	S(57)-C(27)-N(59)	-	122.8			
	S(57)-C(27)-N(60)	-	115.7			
	C(19)-S(57)-C(27)	-	103.3			
	O(4)=U(1)=O(5)	-	178.0			
	N(59)-H(47)···O(6)	1.600	178.7			
	N(60)-H(49)···O(9)	1.610	178.7			

Isothiouronium salts create a strong charge-assisted network of hydrogen bonds and ionic interactions. Calculated and experimental data agree well for 1_ac and 1o_ac, 1_Cl and 1o_Cl, and 1_U and 1o_U compounds (Tables 1, 1S, and 2S; Figs. 1, 3, 5 and 9). We can notice similar bond lengths C-N (range from 1.30 to 1.33 Å), C-S (range from 1.75 to 1.85) and bond angles N-C-N (range from 118 to 123°), S-C-N (range from 115 to 123°), and C-S-C (range from 101 to 103°). All ligand 1 compounds feature a *trans* configuration. Similarly to ligand 1 compounds, experimental and calculated bond lengths and bond angles of ligand 2 compounds correlates well; 2_Cl and 2o_Cl, and 2_U and 2o_U bond lengths C-N (range from 1.29 to 1.32 Å), C-S (range from 1.73 to 1.84) and bond angles N-C-N (range from 118 to 121°), S-C-N (range from 115 to 124°), C-S-C (range from 100 to 103°) (Tables 1, 1S, and 2S; Figs. 7, 8 and 10). All ligand 2 compounds feature a *cis* configuration. The biggest differences between experimental and calculated data we can observe for hydrogen bonds, due to very strong intermolecular interactions in crystals in comparison to single molecules (Tables 1S and 2S).

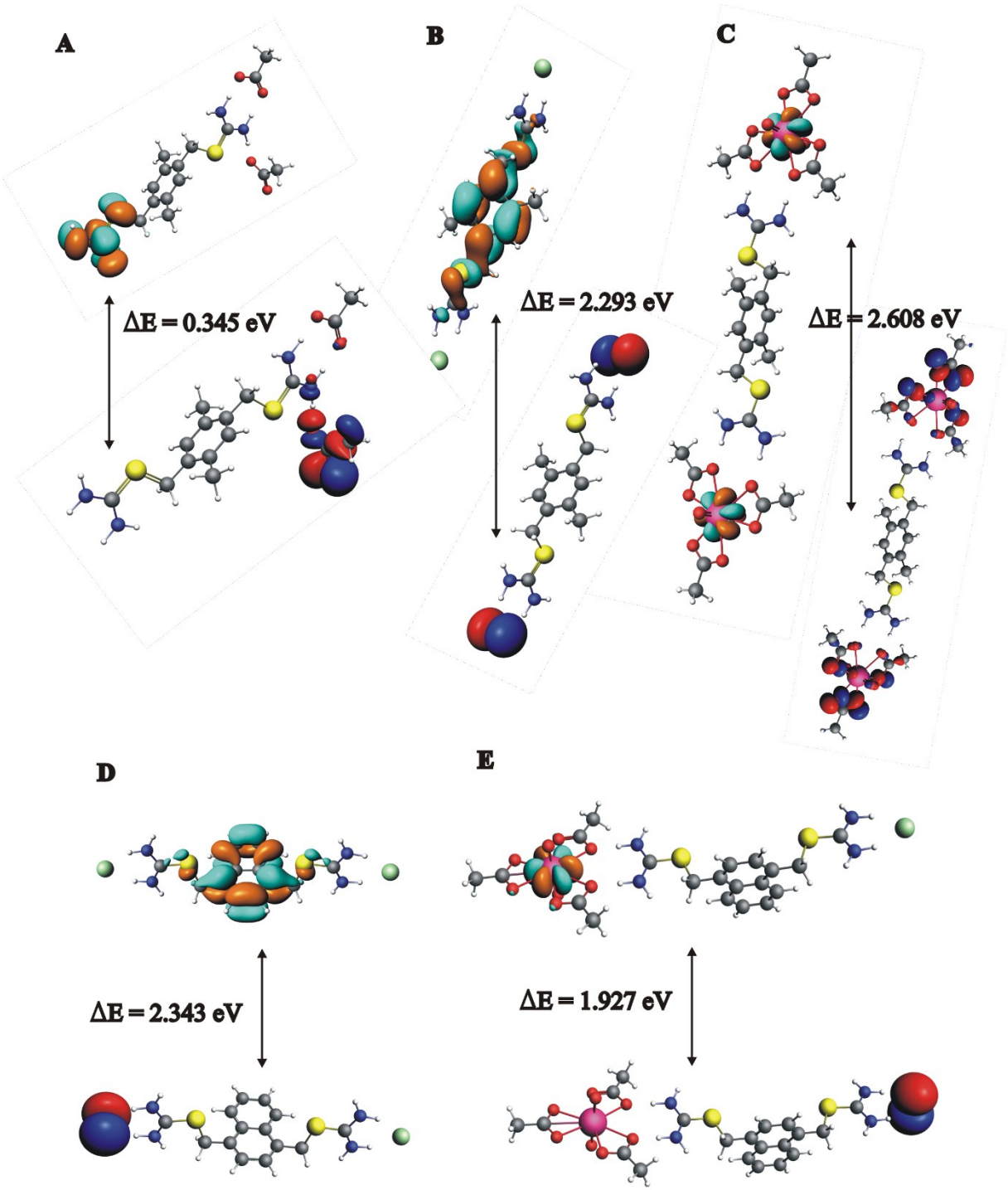

Figure 6S. Calculated frontier molecular orbitals of a) 1o_ac, b) 1o_Cl, c) 1o_U, d) 2o_Cl, and e) 2o_U.

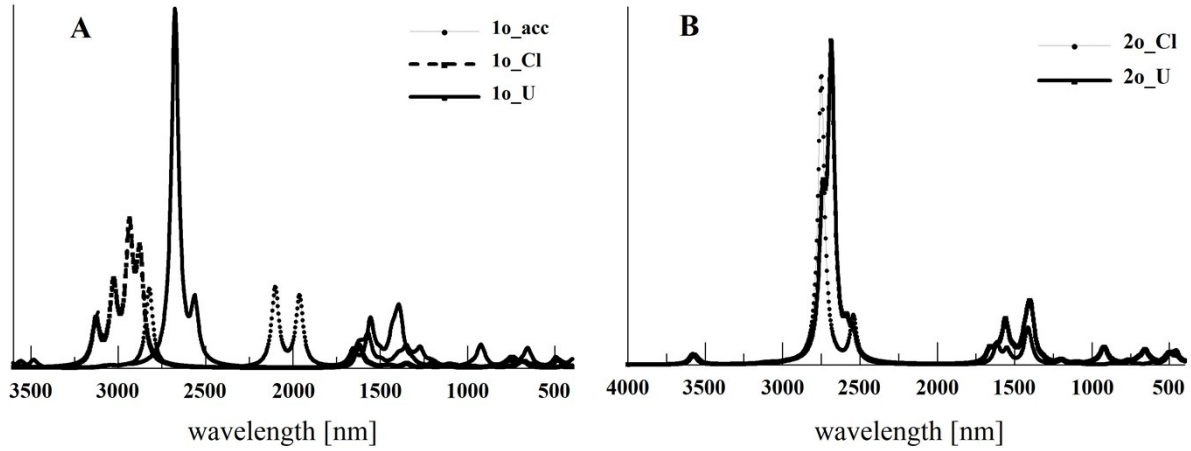

Figure 7S. Calculated IR spectra of a) 1o_ac, 1o_Cl and 1o_U, B) 2o_Cl and 2o_U.

Tab. 3S. Observed and calculated FTIR wavenumbers of 1_ac and 1o_ac.

Observed wavenumber [cm^{-1}]		**Calculated wavenumber [cm^{-1}]**	**Assignment**
596	m	549	ring deformation, C-H bending, N-H bending
		583	C-H bending, –COO deformation vibration
		585	ring deformation, C-H bending, N-H bending
		594	C-H bending, –COO deformation vibration, N-H bending
		622	C-H bending, N-H bending, N-C-N bending out-of-plane
683	w	627	N-H rocking, N-C-N bending in-plane, CS stretching, C-H bending, –COO deformation vibration
		632	N-H rocking, C-H bending, –COO deformation vibration
		660	ring deformation, C-H bending, N-H rocking, CS stretching
		677	ring deformation, C-H bending, N-H rocking, N-C-N bending in-plane, CS stretching
700	vs	687	ring deformation, C-H bending, N-H rocking
		690	N-H rocking, N-C-N bending in-plane, CS stretching, C-H bending, –COO deformation vibration
		723	ring deformation, C-H bending, N-H rocking, CS stretching
		735	ring deformation, C-H bending, CS stretching
773	w	762	ring deformation, C-H bending
795	vw	802	ring deformation, C-H bending
890	m	875	C-H bending, –COO deformation vibration, N-H bending
		878	ring deformation, C-H bending, –COO deformation vibration
		891	C-H bending, N-H bending
		892	ring deformation, C-H bending, N-H bending, –COO deformation vibration
994	w	953	N-H bending, C-H rocking
		972	N-H bending, C-H rocking
		978	C-H bending
		980	C-H bending
1009	w	1003	C-H bending
		1014	C-H rocking, N-H bending,
1042	w	1023	ring deformation, C-H bending

		1057	ring deformation, C-H bending, N-H rocking, CN stretching
1079	w	1067	N-H bending
		1089	N-H bending, C-H bending
1109	w	1104	N-H rocking
		1115	C-H rocking
1194	w	1175	C-H bending, ring deformation,
		1187	C-H bending, ring deformation,
		1190	N-H rocking, C-H bending
		1198	N-H rocking, C-H bending, ring deformation
		1200	N-H twisting, C-H bending
1242	s	1216	C-H bending, N-H rocking, CN stretching, CS stretching
1264	m	1258	ring deformation, C-H bending
		1267	ring deformation, C-H bending
		1271	C-H bending, N-H rocking, CN stretching, CS stretching, CO stretching
		1299	C-H bending, CO stretching
		1307	C-H bending, N-H bending, CO stretching
1386	m	1334	ring deformation, C-H bending
		1350	C-H bending, N-H rocking, CO stretching
		1360	C-H bending
		1384	ring deformation, C-H bending
		1391	N-H rocking, CS stretching, C-H bending
		1396	N-H rocking, CS stretching, C-H bending
1415	m	1408	N-H rocking, CS stretching, C-H bending
		1414	C-H bending,
		1423	C-H bending
		1425	N-H rocking, CS stretching, C-H bending, -COO symmetric stretching
		1427	C-H bending
		1432	C-H bending
		1435	C-H bending
1440	vw	1443	ring stretching, C-H bending
1455	vw	1453	ring stretching, C-H bending
1508	w	1489	ring stretching, C-H bending
		1496	N-H rocking, C-H bending, -COO asymmetric stretching, N-C-N asymmetric stretching vibrations
		1518	N-H bending, N-C-N asymmetric stretching vibrations
1532	w	1551	ring stretching, C-H rocking, C-H scissoring
		1568	N-H scissoring, C-H bending, -COO asymmetric stretching, N-C-N asymmetric stretching vibrations
1630	s	1603	N-H scissoring, N-C-N asymmetric stretching vibrations, ring stretching, C-H bending, -COO asymmetric stretching
		1606	N-H scissoring, N-C-N asymmetric stretching vibrations, ring stretching
		1622	N-H scissoring, N-C-N symmetric stretching vibrations
		1626	N-H scissoring, N-C-N asymmetric stretching vibrations
1644	s	1632	N-H scissoring, N-C-N asymmetric stretching vibrations
1707	m	1671	N-H scissoring, N-C-N asymmetric stretching vibrations
2698	w	1962	N-H stretching vibrations (bounded by hydrogen bond)
		2101	N-H stretching vibrations (bounded by hydrogen bond)
2723	w	2823	N-H stretching vibrations (bounded by hydrogen bond)
2990	m	2941	C-H symmetric stretching vibrations
		2943	C-H symmetric stretching vibrations
		2945	C-H symmetric stretching vibrations
		2953	C-H symmetric stretching vibrations
		2964	C-H symmetric stretching vibrations
		2977	C-H symmetric stretching vibrations

		3007	C-H asymmetric stretching vibrations
		3014	C-H asymmetric stretching vibrations
		3029	C-H asymmetric stretching vibrations
		3031	C-H asymmetric stretching vibrations
		3035	C-H asymmetric stretching vibrations
		3049	C-H asymmetric stretching vibrations
		3056	C-H asymmetric stretching vibrations
		3060	C-H asymmetric stretching vibrations
		3066	C-H asymmetric stretching vibrations
		3077	C-H asymmetric stretching vibrations
		3085	C-H asymmetric stretching vibrations
3181	m	3480	N-H asymmetric stretching vibrations
		3490	N-H asymmetric stretching vibrations
3232	m	3579	N-H asymmetric stretching vibrations
		3607	N-H asymmetric stretching vibrations
		3613	N-H asymmetric stretching vibrations

Tab. 4S. Observed and calculated FTIR wavenumbers of 1_Cl and 1o_Cl.

Observed wavenumber [cm^{-1}]		**Calculated wavenumber [cm^{-1}]**	**Assignment**
590	m	580	ring deformation, C-H bending, N-H rocking, N-C-N bending out-of-plane
		603	ring deformation, C-H bending, N-H rocking, N-C-N bending out-of-plane
699	s	672	CS stretching, N-C-N bending in-plane, N-H rocking
		683	ring deformation, C-H bending, N-H bending
758	vw	727	N-H rocking, CS stretching, C-H rocking, C-H scissoring, C-C ring deformation
		746	N-H rocking, CS stretching, C-H rocking, C-H scissoring, C-C ring deformation
		759	N-H bending, C-H rocking, C-H scissoring
		775	N-H bending
		799	N-H bending, C-H rocking, C-H scissoring
853	vw	836	N-H bending
		875	C-H rocking, ring deformation
890	vw	901	C-H rocking, ring deformation
991	vw	977	C-H bending, ring deformation
1038	vw	1018	C-H bending, ring deformation
1079	vw	1060	ring deformation
1109	vw	1103	ring deformation, C-H rocking, N-H rocking
		1112	C-H rocking, N-H rocking
1150	vw	1131	N-H rocking,
1196	vw	1175	ring deformation, C-H bending
		1195	ring deformation, C-H bending
1242	m	1229	C-H rocking, ring deformation, N-H rocking
1299	w	1326	ring stretching
		1347	C-H bending, N-H rocking, CS stretching
		1356	C-H bending, N-H rocking, CS stretching

1389	w	1378	C-H rocking, ring stretching
1422	s	1422	C-H scissoring, ring stretching
1457	w	1446	C-H scissoring, ring stretching
1496	w	1451	C-H scissoring, ring stretching
1534	vw	1483	C-H bending, ring stretching
1623	w	1555	N-H scissoring vibrations, N-C-N asymmetric stretching vibrations
1647	s	1607	N-H scissoring vibrations, N-C-N symmetric stretching vibrations
		1624	N-H scissoring vibrations, N-C-N asymmetric stretching vibrations
2700 2716	m	2875	N-H out-of-phase stretching vibrations (bounded by hydrogen bond) characteristic doublet
2994	vs	2924	C-H symmetric stretching vibrations
		2929	C-H symmetric stretching vibrations, N-H in-phase stretching vibrations (bounded by hydrogen bond)
		2936	C-H symmetric stretching vibrations, N-H in-phase stretching vibrations (bounded by hydrogen bond)
		2991	C-H asymmetric stretching vibrations
		3012	C-H asymmetric stretching vibrations
3175	s	3026	N-H asymmetric stretching vibrations, C-H asymmetric stretching vibrations
		3032	N-H asymmetric stretching vibrations, C-H asymmetric stretching vibrations
		3069	C-H asymmetric stretching vibrations
3237	s	3127	N-H asymmetric stretching vibrations

Tab. 5S. Observed and calculated FTIR wavenumbers of 1_U and 1o_U.

Observed wavenumber [cm^{-1}]		**Calculated wavenumber [cm^{-1}]**	**Assignment**
604	m	581	ring deformation, C-H bending, N-H bending
		586	C-H bending, –COO deformation vibration
		589	C-H bending, –COO deformation vibration
		593	C-H bending, –COO deformation vibration
674	vs	631	N-H rocking, N-C-N bending out-of-plane
		654	N-H rocking, C-H bending, –COO deformation vibration
		658	N-H rocking, C-H bending, –COO deformation vibration
		671	N-H rocking, C-H bending, –COO deformation vibration, C-S stretching
		679	N-H rocking, C-H bending, ring deformation
		697	N-H rocking, N-C-N bending in-plane, CS stretching
714	vw	727	N-H rocking, C-H bending, ring deformation
		802	C-H bending, C-C ring deformation
896	vw	872	N-H bending, C-H rocking, C-H scissoring, ring deformation
		887	N-H bending, C-H rocking, C-H scissoring
		896	N-H bending, C-H rocking, C-H scissoring
		908	C-H bending, –COO deformation vibration, N-H bending
		916	C-H bending, –COO deformation vibration, N-H bending
918	vs	922	U=O asymmetric stretching vibrations, N-H bending
		926	C-H bending, –COO deformation vibration, N-H bending
937	vw	935	N-H rocking,
950	vw	978	C-H bending, ring deformation

		979	C-H bending
		980	C-H bending
1008	w	1020	C-H bending, ring deformation
		1022	C-H bending
		1023	C-H bending
		1024	C-H bending
1044	w	1095	N-H rocking, CN stretching, C-H bending, ring deformation
1078	vw	1103	CN stretching, N-H bending, C-H bending
		1178	C-H rocking, C-H scissoring, ring deformation
		1192	C-H rocking, C-H scissoring, ring deformation
1241	vw	1204	C-H rocking, C-H scissoring, N-H rocking,
1251	vw	1258	C-H rocking, C-H scissoring, N-H rocking,
1345	vw	1317	C-H rocking, C-H scissoring
		1318	C-H rocking, C-H scissoring
		1319	C-H rocking, C-H scissoring
		1331	C-H rocking, C-H scissoring, ring deformation
		1361	C-H rocking, C-H scissoring, ring deformation
1403	s	1384	C-H bending, ring deformation, N-H rocking,
		1386	C-H bending, N-H rocking, -CO stretching
		1389	C-H bending, N-H rocking, -CO stretching
		1396	C-H bending, N-H rocking, -CO stretching
		1400	C-H bending, N-H rocking, -CO stretching
		1408	C-H bending, N-H rocking
		1410	C-H bending, N-H rocking
		1420	C-H bending
1454	s	1429	C-H bending, -COO symmetric stretching
		1431	C-H bending, -COO symmetric stretching
		1432	C-H bending, C-C ring deformation, N-H rocking, -COO symmetric stretching
		1434	C-H bending
		1454	C-H bending
		1489	C-H bending, ring stretching
1509	w	1504	C-H bending, -COO asymmetric stretching, N-H bending, N-C-N asymmetric stretching vibrations
1530	m	1542	C-H bending, -COO asymmetric stretching, N-H bending, N-C-N asymmetric stretching vibrations
		1557	C-H bending, -COO asymmetric stretching, N-H bending, N-C-N asymmetric stretching vibrations
1631	w	1655	N-H scissoring, N-C-N asymmetric stretching vibrations
1647	m	1658	N-H scissoring, N-C-N asymmetric stretching vibrations
1668	w		
2700	vw	2562	N-H out-of-phase stretching vibrations (bounded by hydrogen bond)
2729	vw		
2787	vw	2675	N-H in-phase stretching vibrations (bounded by hydrogen bond)
3002	m	2939	C-H symmetric stretching vibrations
		2956	C-H symmetric stretching vibrations
		2957	C-H symmetric stretching vibrations
		2968	C-H symmetric stretching vibrations
		3010	C-H asymmetric stretching vibrations
		3040	C-H asymmetric stretching vibrations
		3046	C-H asymmetric stretching vibrations

		3054	C-H asymmetric stretching vibrations
3059	m	3080	C-H asymmetric stretching vibrations
		3081	C-H asymmetric stretching vibrations
		3084	C-H asymmetric stretching vibrations
3240	m	3549	N-H asymmetric stretching vibrations
		3567	N-H asymmetric stretching vibrations

Tab. 6S. Observed and calculated FTIR wavenumbers of 2_Cl and 2o_Cl.

Observed wavenumber [cm^{-1}]		**Calculated wavenumber [cm^{-1}]**	**Assignment**
502	m	500	ring deformation, N-H bending, CS stretching
542	w	541	ring deformation
570	w	587	ring deformation, N-H bending, CS stretching
595	vw	610	N-H rocking, N-C-N bending out-of-plane
		611	N-H rocking, N-C-N bending out-of-plane
622	w	625	ring deformation, N-H bending, CS stretching
706	vw	691	ring deformation, C-H bending
		699	ring deformation, C-H bending, N-H rocking
		707	CS stretching, N-C-N bending in-plane, N-H rocking, C-H bending, ring deformation
		712	CS stretching, N-C-N bending in-plane, N-H rocking, C-H bending, ring deformation
766	s	755	C-H bending, ring deformation, N-H rocking
		761	C-H bending
		772	N-H bending
		774	N-H bending
786	w	790	C-H bending, ring deformation, N-H bending
845	vw	834	C-H bending out-of-plane
		869	N-H rocking, N-C-N bending out-of-plane
		870	N-H rocking, N-C-N bending out-of-plane
		875	C-H rocking, C-H scissoring
948	vw	938	C-H bending
		941	C-H bending
969	vw	975	C-H bending
994	vw	998	ring deformation, C-H rocking, C-H scissoring
		1036	ring deformation, C-H rocking, C-H scissoring
1077	m	1089	N-H rocking
		1091	N-H rocking
1111	w	1102	N-H rocking
		1114	C-H bending,
		1116	C-H bending,
1141	w	1149	C-H bending,
1164	w	1156	C-H bending,

1219	w	1196	C-H bending, N-H rocking
		1202	C-H bending, N-H rocking
		1227	C-H bending,
1247	m	1235	ring deformation, C-H rocking, C-H scissoring
		1261	ring deformation, C-H rocking, C-H scissoring
1338	w	1348	ring deformation, C-H rocking, C-H scissoring
1386	w	1378	ring deformation, C-H rocking, C-H scissoring
		1380	ring deformation, C-H rocking, C-H scissoring
1407	w	1402	N-H rocking, CN stretching, C-H rocking, C-H scissoring
		1403	N-H rocking, CN stretching
1424	m	1417	CN stretching, CS stretching, N-H rocking, C-H rocking, C-H scissoring
		1421	CS stretching, N-H rocking, C-H rocking, C-H scissoring
1439	m	1436	ring stretching, C-H scissoring, N-H bending
		1441	ring stretching, C-H scissoring, N-H bending
		1450	ring stretching,
1527	m	1511	ring stretching, C-H bending
		1549	N-H scissoring, N-C-N symmetric stretching vibrations
		1550	N-H scissoring, N-C-N symmetric stretching vibrations
1592	w	1575	ring stretching
		1586	ring stretching
		1609	ring stretching
1630	s	1615	N-H scissoring, N-C-N asymmetric stretching vibrations
1649	w		
2707	w	2540	N-H out-of-phase stretching vibrations (bounded by hydrogen bond)
		2545	N-H out-of-phase stretching vibrations (bounded by hydrogen bond)
2728	vw	2749	N-H in-phase stretching vibrations (bounded by hydrogen bond)
		2755	N-H in-phase stretching vibrations (bounded by hydrogen bond)
3032	vs	2973	C-H symmetric stretching vibrations
		2974	C-H symmetric stretching vibrations
		3045	C-H asymmetric stretching vibrations
		3046	C-H asymmetric stretching vibrations
		3094	C-H aromatic stretching vibrations
		3101	C-H aromatic stretching vibrations
		3109	C-H aromatic stretching vibrations
		3119	C-H aromatic stretching vibrations
		3127	C-H aromatic stretching vibrations
3212	s	3576	N-H asymmetric stretching vibrations
		3591	N-H asymmetric stretching vibrations

Tab. 7S. Observed and calculated FTIR wavenumbers of 2_U and 2o_U.

Observed wavenumber [cm^{-1}]	**Calculated wavenumber [cm^{-1}]**	**Assignment**

591	m	517	N-H bending
		541	ring deformation, C-H bending, N-H bending
		587	ring deformation, C-H bending, N-H bending, CS stretching
		588	C-H bending, –COO deformation vibration
		589	C-H bending, –COO deformation vibration
		590	C-H bending, –COO deformation vibration
672	vs	612	N-C-N bending out-of-plane
		625	ring deformation, C-H bending, N-H bending
		633	N-H bending, N-C-N bending out-of-plane
		656	N-H bending, C-H bending, –COO deformation vibration
		658	N-H bending, C-H bending, –COO deformation vibration
		671	N-H bending, C-H bending, –COO deformation vibration
695	w	691	ring deformation, N-H rocking, C-H bending,
		697	C-H bending, CS stretching, N-H rocking, N-C-N bending in-plane,
		703	C-H bending, CS stretching, N-H rocking, N-C-N bending in-plane,
		709	C-H bending, CS stretching, N-H rocking, N-C-N bending in-plane,
		711	C-H bending, ring deformation, CS stretching, N-H rocking, N-C-N bending in-plane,
769	m	754	ring deformation, C-H bending
		760	ring deformation, C-H bending
		772	N-H bending
790	w	790	C-H bending, ring deformation
837	w	832	C-H bending, ring deformation
850	w	851	C-H bending, ring deformation
876	w	867	N-H bending
		871	N-H bending, C-H bending, ring deformation
		886	N-H bending, C-H bending
		900	N-H bending, C-H bending
912	vs	909	C-H bending, –COO deformation vibration, N-H bending
		916	C-H bending, –COO deformation vibration, N-H bending
		919	U=O asymmetric stretching vibrations, N-H bending
		925	C-H bending, –COO deformation vibration, N-H bending
937	w	936	N-H bending, C-H bending
		937	N-H bending, C-H bending
950	vw	973	C-H bending, ring deformation
		978	C-H twisting
		979	C-H twisting
		980	C-H twisting
1013	w	999	C-H bending, ring deformation
1021	vw	1021	C-H bending
		1023	C-H bending
		1038	C-H bending, ring deformation
1044	w	1088	N-H rocking
		1094	N-H rocking

1128	vw	1101	N-H rocking, CN stretching
		1105	N-H rocking, CN stretching, CS stretching
		1115	C-H rocking, C-H scissoring
		1117	C-H rocking, C-H scissoring
		1150	C-H rocking, C-H scissoring
		1161	C-H rocking, C-H scissoring
		1197	C-H rocking
		1203	C-H rocking
1223	vw	1228	C-H bending, ring deformation
1238	w	1236	C-H bending, ring deformation
1259	w	1262	C-H bending, ring deformation
		1317	C-H rocking
		1318	C-H rocking
		1319	C-H rocking
1351	w	1348	C-H bending, ring deformation
1391	w	1381	C-H bending, ring deformation
		1388	-CO stretching, C-H bending, N-H rocking
		1392	-CO stretching, CS stretching, N-H rocking, C-H bending
		1399	-CO stretching, CS stretching, CN stretching, N-H bending, C-H bending
		1400	-CO stretching, CN stretching, N-H rocking, C-H bending
1407	m	1407	-CO stretching, N-H rocking, C-H rocking
		1408	-CO stretching, N-H rocking, C-H rocking
		1410	-COO symmetric stretching, N-H rocking, C-H bending
		1416	CS stretching, N-C-N symmetric stretching, N-H bending, C-H bending
		1420	C-H bending, ring stretching, CS stretching, N-C-N symmetric stretching, N-H rocking
1428	w	1427	C-H bending
		1428	C-H bending
1456	m	1434	C-H rocking, C-H scissoring, N-H rocking
		1437	C-H bending, -COO symmetric stretching
		1440	C-H bending, N-H bending
1525	s	1507	C-H bending, -COO asymmetric stretching, N-H bending,
		1510	C-H bending, ring deformation
		1547	C-H bending, -COO asymmetric stretching, N-H scissoring, N-C-N asymmetric stretching vibrations
		1548	N-H scissoring,
		1561	C-H bending, -COO asymmetric stretching, N-H scissoring, N-C-N asymmetric stretching vibrations
		1562	C-H bending, -COO asymmetric stretching, N-H scissoring, N-C-N asymmetric stretching vibrations
1644	w	1574	ring stretching
		1585	C-H bending, ring stretching
		1614	N-H scissoring , N-C-N asymmetric stretching vibrations
1658	m	1659	N-H scissoring, N-C-N asymmetric stretching vibrations
1672	w	1662	N-H scissoring, N-C-N asymmetric stretching vibrations

2688	vw	2541	N-H out-of-phase stretching vibrations (bounded by hydrogen bond)
		2584	N-H out-of-phase stretching vibrations (bounded by hydrogen bond)
2737	vw	2685 2742	N-H in-phase stretching vibrations (bounded by hydrogen bond)
2771	v		
3019	m	2960	C-H symmetric stretching vibrations
		2967	C-H symmetric stretching vibrations
		2971	C-H symmetric stretching vibrations
		3043	C-H symmetric stretching vibrations
		3050	C-H symmetric stretching vibrations
		3084	C-H asymmetric stretching vibrations
		3086	C-H asymmetric stretching vibrations
		3087	C-H asymmetric stretching vibrations
3122	m	3095	C-H aromatic stretching vibrations
		3110	C-H aromatic stretching vibrations
		3119	C-H aromatic stretching vibrations
		3126	C-H aromatic stretching vibrations
3365	m	3555	N-H asymmetric stretching vibrations
		3574	N-H asymmetric stretching vibrations
		3590	N-H asymmetric stretching vibrations

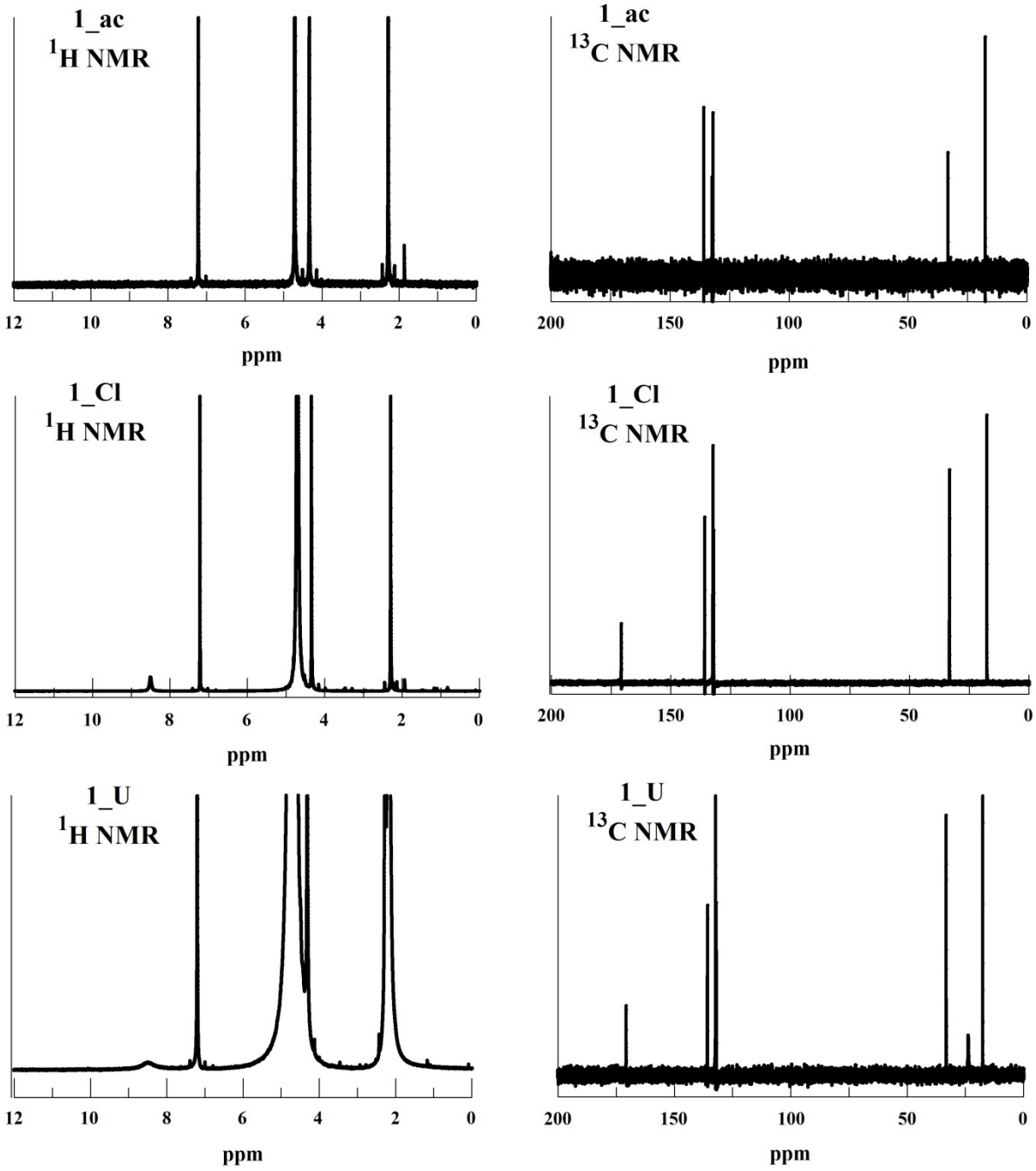

Figure 8S. NMR spectra of 1_ac, 1_Cl and 1_U.

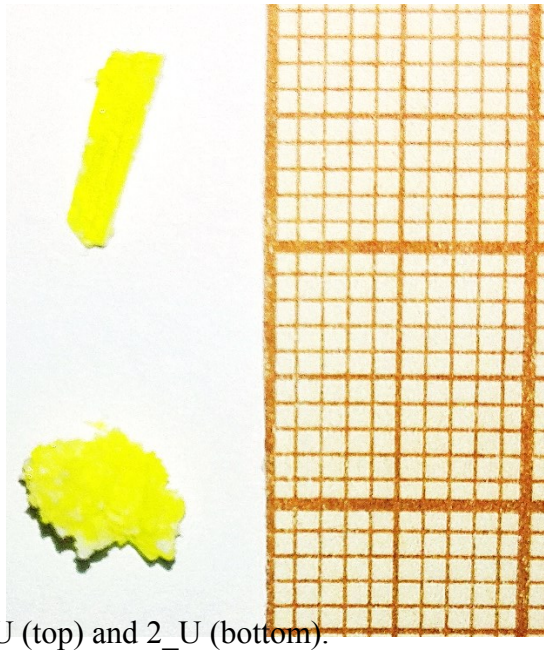

Figure 9S. Crystals of 1_U (top) and 2_U (bottom).

Cartesian coordinates (Å) for the species under study calculated by Amsterdam Density Functional package (ADF2019)

1o_ac

1.S	0.565980	7.910178	12.654652
2.N	-0.927483	8.245689	10.379402
3.H	-1.073209	8.445218	9.299485
4.H	-1.730578	8.206084	10.991662
5.N	1.385986	8.340454	10.190660
6.H	1.248798	8.549018	9.162995
7.H	2.390571	8.255045	10.675540
8.C	-1.049679	7.214212	14.719735
9.C	0.298093	8.193349	10.898036
10.C	-0.734558	5.566901	16.439473
11.H	-0.557686	4.529875	16.735226
12.C	-0.822132	5.868525	15.079399
13.C	-1.147537	7.630474	13.277255
14.H	-1.729850	8.558056	13.192352
15.H	-1.618758	6.842536	12.674413
16.C	-0.680415	4.784229	14.046436
17.H	-1.623298	4.627847	13.499482
18.H	-0.405566	3.830458	14.511920
19.H	0.088005	5.042898	13.303791
20.S	-2.459123	5.775874	19.475427
21.N	-1.050424	5.320472	21.735215
22.H	-0.941619	5.073542	22.714405
23.H	-0.207501	5.518755	21.210622
24.N	-3.344653	5.071719	21.847852
25.H	-3.308206	4.797719	22.824635
26.H	-4.257098	5.103771	21.405766
27.C	-0.853381	6.545782	17.433574

28.C	-2.245425	5.359253	21.151669
29.C	-1.167272	8.187427	15.717647
30.H	-1.335395	9.224356	15.418520
31.C	-1.078988	7.890894	17.079998
32.C	-0.737174	6.131607	18.872487
33.H	-0.152445	5.208290	18.969847
34.H	-0.323846	6.933467	19.497857
35.C	-1.204871	8.983163	18.108558
36.H	-0.270205	9.115778	18.675325
37.H	-1.433352	9.942374	17.630791
38.H	-2.003846	8.776827	18.836416
39.H	-1.194574	10.083162	5.554484
40.H	-1.138970	8.351523	5.212261
41.H	0.364875	9.324761	5.093435
42.O	5.422445	8.860125	12.484963
43.O	3.638074	8.020550	11.387494
44.C	4.353880	8.986962	11.857023
45.C	3.850033	10.421603	11.587270
46.H	4.014086	11.045400	12.475162
47.H	2.792995	10.455675	11.293244
48.H	4.446652	10.853470	10.770115
49.O	0.901119	8.876133	7.519694
50.O	-1.335642	8.713057	7.851892
51.C	-0.297950	8.901625	7.128028
52.C	-0.569372	9.184182	5.647771

1o_Cl

1.Cl	-4.718250	4.287546	-6.027589
2.Cl	4.718250	-4.287546	6.027589
3.S	2.494631	-0.810308	2.876262

4.N	2.758400	-3.267039	4.042793
5.H	3.294863	-3.897705	4.727007
6.H	1.902563	-3.556909	3.589788
7.N	4.296745	-1.680100	4.609529
8.H	4.707095	-2.424387	5.249566
9.H	4.709975	-0.763452	4.491964
10.C	3.223257	-2.034887	3.915716
11.C	0.586393	-0.856145	0.939654
12.C	1.151714	-0.769204	-0.348309
13.C	0.539009	0.090858	-1.262803
14.H	0.959475	0.171209	-2.267944
15.C	1.178510	-1.756689	1.988709
16.H	1.644198	-2.643976	1.541223
17.H	0.413247	-2.054575	2.716851
18.C	2.359472	-1.572504	-0.748941
19.H	3.200639	-1.415676	-0.058269
20.H	2.695021	-1.298043	-1.755803
21.H	2.140647	-2.651660	-0.758157
22.S	-2.494631	0.810308	-2.876262
23.N	-2.758400	3.267039	-4.042793
24.H	-3.294863	3.897705	-4.727007
25.H	-1.902563	3.556909	-3.589788
26.N	-4.296745	1.680100	-4.609529
27.H	-4.707095	2.424387	-5.249566
28.H	-4.709975	0.763452	-4.491964
29.C	-3.223257	2.034887	-3.915716
30.C	-0.586393	0.856145	-0.939654
31.C	-1.151714	0.769204	0.348309
32.C	-0.539009	-0.090858	1.262803
33.H	-0.959475	-0.171209	2.267944

34.C	-1.178510	1.756689	-1.988709
35.H	-1.644198	2.643976	-1.541223
36.H	-0.413247	2.054575	-2.716851
37.C	-2.359472	1.572504	0.748941
38.H	-3.200639	1.415676	0.058269
39.H	-2.695021	1.298043	1.755803
40.H	-2.140647	2.651660	0.758157

1o_U

1.C	-7.405672	6.818925	-0.847804
2.O	-6.895708	3.678818	-3.225694
3.O	-8.532793	3.545791	-4.698766
4.O	-10.493596	5.532381	-4.803970
5.O	-10.473415	7.180114	-3.330079
6.O	-9.674710	4.536251	-2.018672
7.O	-7.633141	6.491784	-4.263136
8.C	-6.841702	1.825352	-4.791802
9.H	-7.520569	1.356410	-5.511552
10.H	-5.904870	2.089042	-5.305462
11.H	-6.601751	1.116193	-3.987346
12.C	-7.465791	3.074449	-4.218557
13.C	-6.771516	7.488798	0.346579
14.H	-6.884982	6.844206	1.231029
15.H	-5.696640	7.634815	0.170008
16.H	-7.250794	8.453702	0.541919
17.C	-12.262881	7.181337	-4.952640
18.H	-13.082546	7.132611	-4.221152
19.H	-12.099065	8.241186	-5.189738
20.H	-12.542635	6.627450	-5.855428
21.C	-11.015279	6.601468	-4.335607

22.H	12.099065	-8.241186	5.189738
23.H	12.542635	-6.627450	5.855428
24.C	11.015279	-6.601468	4.335607
25.N	4.546187	-3.036395	2.153042
26.H	5.486696	-3.307869	2.588956
27.H	3.923383	-2.449666	2.695489
28.N	4.867182	-4.324000	0.257269
29.H	5.684321	-4.871817	0.669787
30.H	4.580927	-4.525522	-0.695444
31.C	4.159578	-3.442128	0.952753
32.C	1.076597	-0.673245	0.591152
33.S	2.670247	-2.858303	0.188329
34.C	2.195133	-1.421133	1.263949
35.H	1.860210	-1.812655	2.234043
36.H	3.085823	-0.791110	1.388738
37.C	-0.245779	-0.994000	0.921264
38.H	-0.429909	-1.782195	1.655930
39.C	-1.342938	-0.339683	0.353684
40.C	-2.746248	-0.728082	0.738742
41.H	-3.331327	0.140800	1.075159
42.H	-2.738638	-1.464758	1.551471
43.H	-3.285568	-1.179258	-0.109781
44.N	-4.546187	3.036395	-2.153042
45.H	-5.486696	3.307869	-2.588956
46.H	-3.923383	2.449666	-2.695489
47.N	-4.867182	4.324000	-0.257269
48.H	-5.684321	4.871817	-0.669787
49.H	-4.580927	4.525522	0.695444
50.C	-4.159578	3.442128	-0.952753
51.C	-1.076597	0.673245	-0.591152

52.S	-2.670247	2.858303	-0.188329
53.C	-2.195133	1.421133	-1.263949
54.H	-1.860210	1.812655	-2.234043
55.H	-3.085823	0.791110	-1.388738
56.C	0.245779	0.994000	-0.921264
57.H	0.429909	1.782195	-1.655930
58.C	1.342938	0.339683	-0.353684
59.C	2.746248	0.728082	-0.738742
60.H	3.331327	-0.140800	-1.075159
61.H	2.738638	1.464758	-1.551471
62.H	3.285568	1.179258	0.109781
63.C	6.841702	-1.825352	4.791802
64.H	7.520569	-1.356410	5.511552
65.H	5.904870	-2.089042	5.305462
66.H	6.601751	-1.116193	3.987346
67.C	7.465791	-3.074449	4.218557
68.C	6.771516	-7.488798	-0.346579
69.U	-8.679828	5.527600	-3.152592
70.O	-6.908083	5.714451	-1.301621
71.O	-8.421657	7.316740	-1.408809
72.C	12.262881	-7.181337	4.952640
73.H	5.696640	-7.634815	-0.170008
74.H	7.250794	-8.453702	-0.541919
75.H	13.082546	-7.132611	4.221152
76.H	6.884982	-6.844206	-1.231029
77.U	8.679828	-5.527600	3.152592
78.O	6.908083	-5.714451	1.301621
79.O	8.421657	-7.316740	1.408809
80.C	7.405672	-6.818925	0.847804
81.O	6.895708	-3.678818	3.225694

82.O	8.532793	-3.545791	4.698766
83.O	10.493596	-5.532381	4.803970
84.O	10.473415	-7.180114	3.330079
85.O	9.674710	-4.536251	2.018672
86.O	7.633141	-6.491784	4.263136

2o_Cl

1.H	2.630218	23.287231	6.282823
2.H	2.580802	9.192061	5.965124
3.H	0.255048	19.622639	4.015701
4.H	0.736635	23.219744	5.398045
5.H	3.600950	21.784058	6.649464
6.H	0.592284	9.302265	5.321352
7.Cl	1.548490	24.940667	5.892274
8.C	-0.245553	16.987566	5.984285
9.C	1.694548	17.629991	2.845295
10.C	1.783513	21.517251	5.759237
11.H	-0.535101	13.039757	5.728132
12.N	0.711621	22.149853	5.309495
13.C	1.024897	16.970561	3.909696
14.C	0.322583	14.851040	4.980789
15.S	1.874697	12.734904	5.705315
16.C	0.385908	17.685395	4.972358
17.H	1.608709	13.746199	2.831364
18.C	2.286668	16.920472	1.823298
19.H	-0.424741	19.536687	5.677629
20.H	0.100573	12.902278	4.052550
21.H	1.754115	18.717851	2.836024
22.C	1.681730	10.984537	5.644040
23.Cl	1.451001	7.560133	5.645350

24.N	2.773511	22.232817	6.277144
25.H	3.616702	10.676879	6.212973
26.C	0.378629	19.188490	5.016870
27.H	-0.784092	15.064845	6.804245
28.H	-0.283558	10.892290	5.092678
29.N	2.729795	10.246185	5.983590
30.C	0.263023	13.349589	5.042100
31.S	1.987696	19.766950	5.718521
32.C	1.613978	14.835475	2.843243
33.C	-0.274435	15.582156	5.990007
34.H	-0.060501	21.652982	4.887342
35.H	-0.736014	17.532054	6.792546
36.H	2.792419	17.449707	1.015468
37.C	2.244060	15.511183	1.821044
38.C	0.987594	15.530688	3.910911
39.N	0.562477	10.374657	5.287076
40.H	2.714966	14.954857	1.010327

2o_U

1.U	5.900862	1.501776	28.334842
2.O	6.662087	0.455396	26.177408
3.O	4.235475	0.443343	29.792597
4.O	4.610957	2.401601	27.457697
5.O	7.231407	0.647409	29.196632
6.O	7.585348	2.408097	26.607945
7.C	7.443626	1.381958	25.838762
8.C	8.207681	1.314831	24.538873
9.H	8.081456	0.333900	24.071051
10.H	9.274160	1.508914	24.714726
11.H	7.830111	2.087960	23.854354
12.O	4.735509	-0.615943	27.923069
13.C	3.056527	-1.616880	29.339892

14.H	2.876059	-1.653616	30.419580
15.H	3.395449	-2.589897	28.966418
16.H	2.108833	-1.374173	28.837581
17.C	4.064886	-0.546782	29.006464
18.O	5.457257	2.907767	30.372729
19.O	6.995956	3.720855	29.023240
20.C	6.300241	3.804159	30.106469
21.C	6.518461	4.966068	31.044238
22.H	5.747443	4.980838	31.820421
23.H	6.508048	5.912860	30.488356
24.H	7.503128	4.864842	31.523119
25.S	10.507096	6.797730	26.700162
26.S	15.927020	11.144396	25.112494
27.C	10.679852	9.163671	24.071991
28.H	9.838778	8.519874	24.326907
29.C	12.006770	8.686821	24.236664
30.C	12.292165	7.366194	24.707939
31.C	11.191509	6.393005	25.029454
32.H	11.591275	5.372824	25.069035
33.H	10.379982	6.451617	24.291369
34.C	14.442520	9.100762	24.071124
35.C	13.098924	9.567840	23.913158
36.C	12.799437	10.873231	23.442846
37.H	13.610550	11.561480	23.208638
38.C	13.604723	6.962913	24.861979
39.H	13.823691	5.956844	25.222113
40.C	14.670999	7.823215	24.545731
41.H	15.694461	7.466076	24.667409
42.C	11.497872	11.298943	23.291615
43.H	11.293824	12.306410	22.929101
44.C	10.428578	10.436868	23.609380
45.H	9.400727	10.779965	23.491840
46.N	9.058173	4.575447	26.103962
47.H	8.460607	3.714932	26.314981

48.H	9.347655	4.726975	25.146568
49.N	8.974172	5.359730	28.275855
50.H	8.195540	4.695261	28.572117
51.H	9.351534	5.998725	28.966367
52.C	9.420302	5.446760	27.031034
53.C	15.621929	9.966036	23.720960
54.H	15.441958	10.545865	22.806038
55.H	16.515432	9.341575	23.599885
56.N	17.924039	11.864942	23.388595
57.H	18.764470	12.502345	23.190083
58.H	17.624706	11.138524	22.753372
59.N	17.778977	13.018504	25.349275
60.H	18.625678	13.557639	24.992637
61.H	17.335692	13.207990	26.239250
62.C	17.319291	12.066303	24.548342
63.Cl	20.036223	13.941769	23.616420