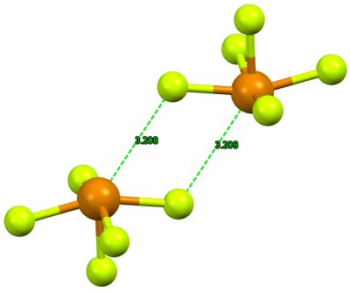
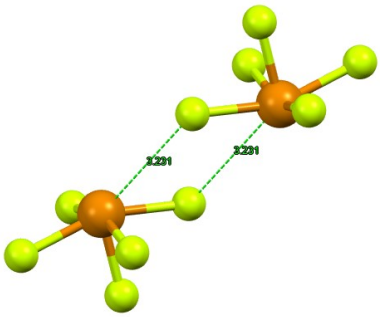
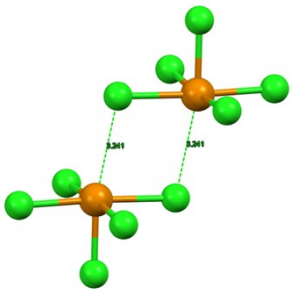
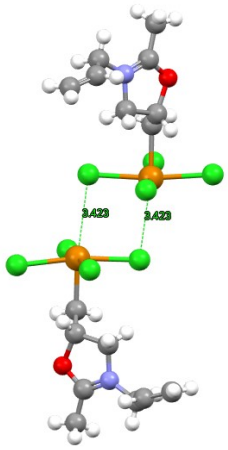
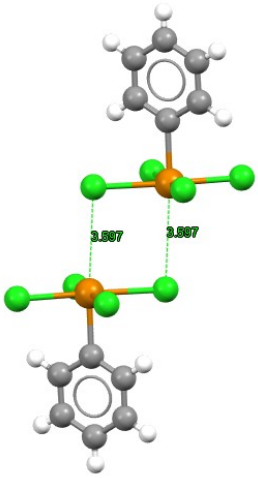
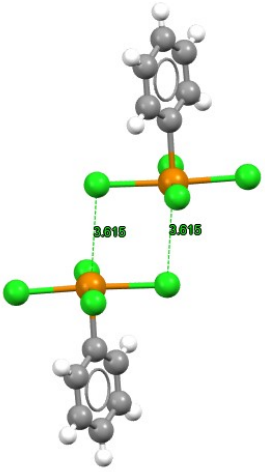
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

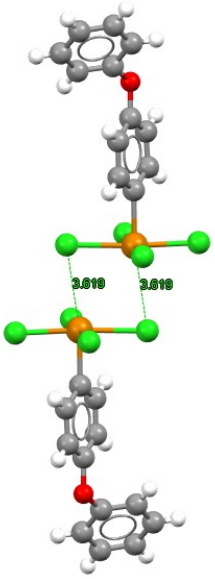
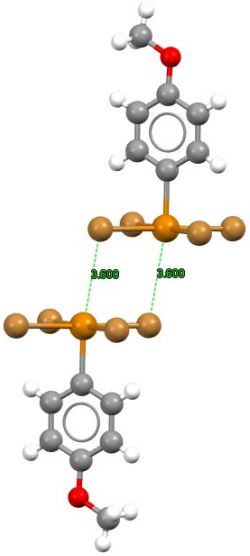
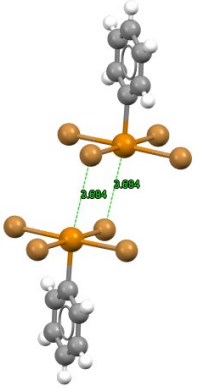
SUPPLEMENTARY INFORMATION

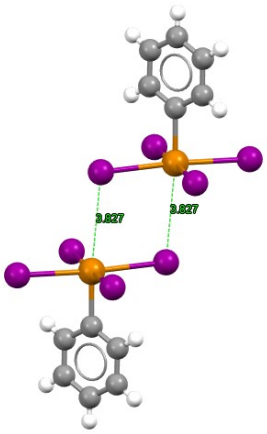
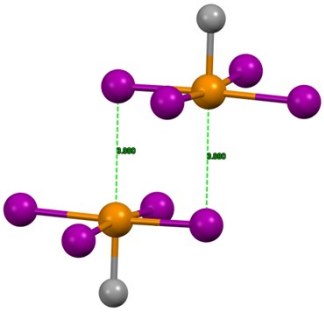
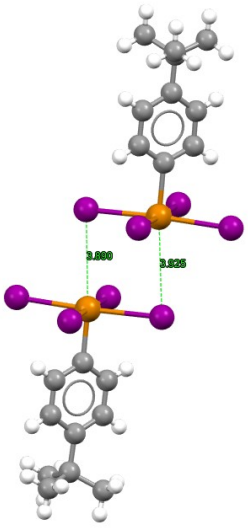
Anion···anion interaction within $Ch(CH_3)X_4^-$ (Ch = S, Se, Te; X=Cl, Br, I) dimers stabilized by chalcogen bonds

Rafał Wysokiński

CSD refcod	Ch···X [Å]	structures
YALRIM	Te···F 3.208	
WAMNON	Te···F 3.231	
JUCDAM	Te···Cl 3.241	

CITMAT	Te···Cl 3.423	
WUTJOK	Te···Cl 3.597	
CIFVOD	Te···Cl 3.615	

CUCGOW	Te···Cl 3.619	
ELAVAP	Te···Br 3.600	
CIFVUJ	Te···Br 3.684	

CIFWAQ	Te···I 3.827	
MTEMTE	Te···I 3.880	
ECOQIY	Te···I 3.890	

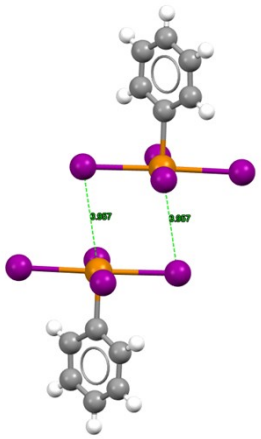
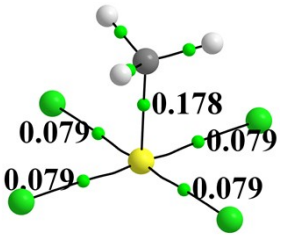
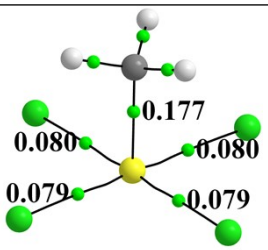
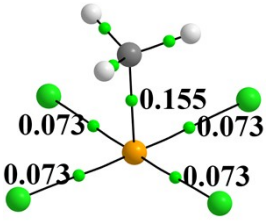
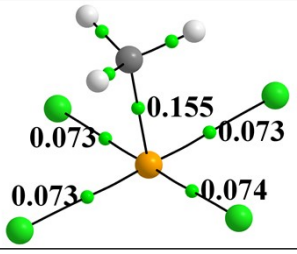
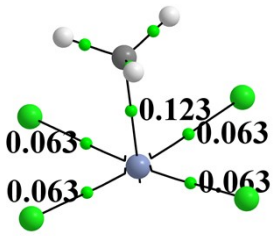
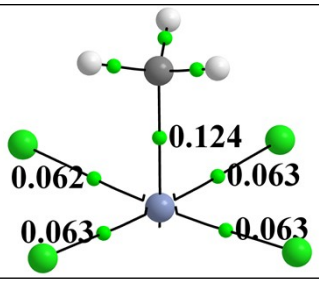
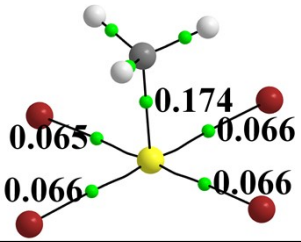
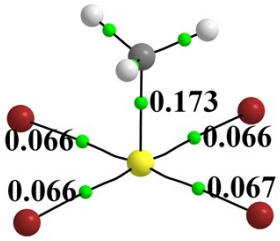
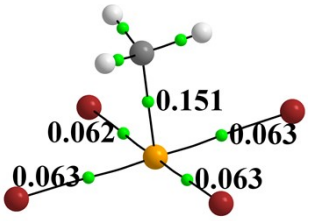
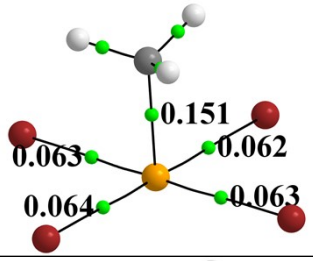
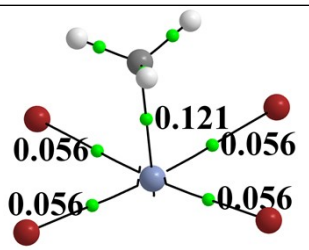
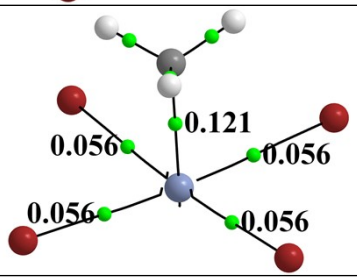
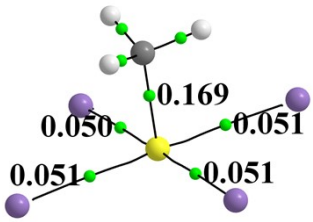
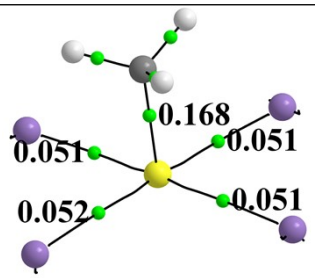
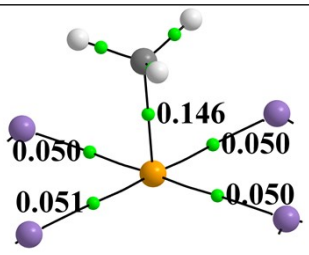
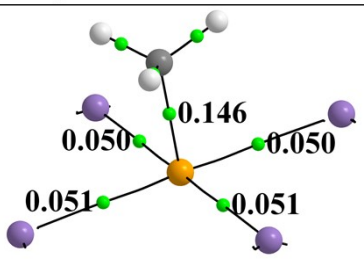
ECOQOE	Te···I 3.957	

Fig. S1. Examples drawn from the CSD database.

Monomers

	vacuum	water
$S(CH_3)Cl_4^-$		
$Se(CH_3)Cl_4^-$		

$Te(CH_3)Cl_4^-$		
$S(CH_3)Br_4^-$		
$Se(CH_3)Br_4^-$		
$Te(CH_3)Br_4^-$		
$S(CH_3)I_4^-$		
$Se(CH_3)I_4^-$		

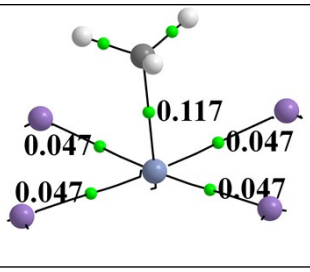
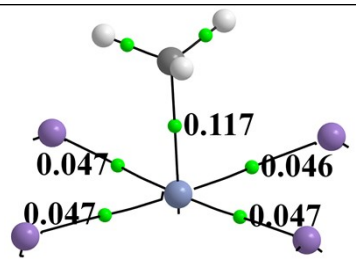
$Te(CH_3)I_4^-$		

Fig. S2. AIM molecular diagrams of MP2/aug-cc-pVDZ optimized complexes. Green dots represent bond critical points. Numbers refers to electron densities at BCPs (in au)

Table S1. Relative difference in dimers total energy (kcal/mol)[a] in vacuum and water solvent

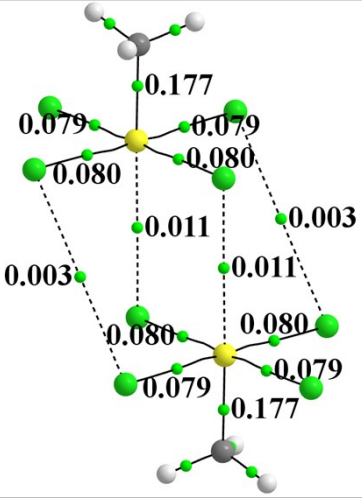
	water	vacuum
$S(CH_3)Cl_4^-$	0.00	-
$Se(CH_3)Cl_4^-$	0.00	150.24 (147.98)
$Te(CH_3)Cl_4^-$	0.00	143.83 (141.04)
$S(CH_3)Br_4^-$	0.00	144.05 (140.86)
$Se(CH_3)Br_4^-$	0.00	141.92 (140.15)
$Te(CH_3)Br_4^-$	0.00	136.43 (134.40)
$S(CH_3)I_4^-$	0.00	130.90 (129.52)
$Se(CH_3)I_4^-$	0.00	129.61 (128.01)
$Te(CH_3)I_4^-$	0.00	126.35 (123.65)

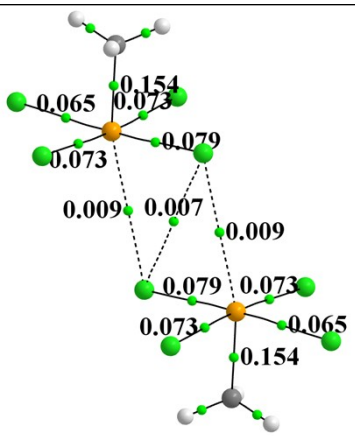
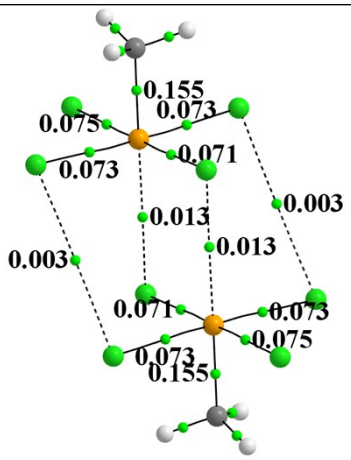
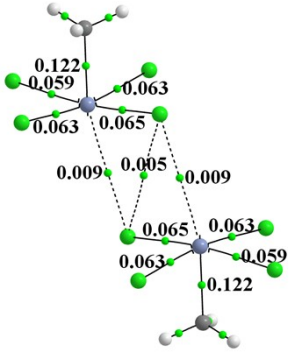
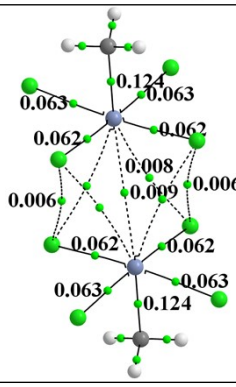
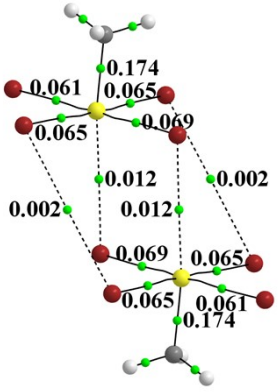
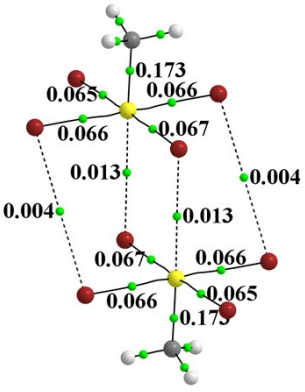
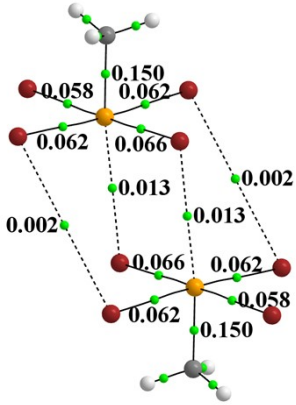
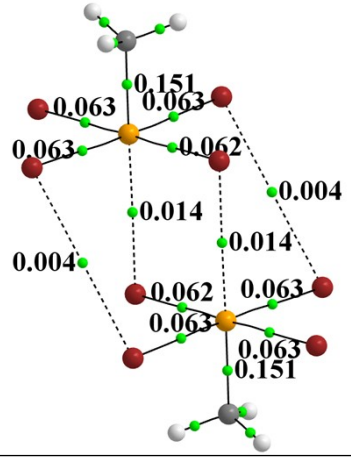
[a] Gibbs free energy differences in parentheses.

Tab. S2. AIM descriptors of the calculated complexes in vacuum. Bond critical point (BCP) properties: electron density ρ, Laplacian of electron density $\nabla^2\rho$ and total electron energy H and potential electron density energy V as well as kinetic electron density energy G, were obtained at the MP2/ aug-cc-pVDZ level. Data in atomic units.

	interaction	ρ	$\nabla^2\rho$	H	V	G
	vacuum					
$S(CH_3)Cl_4^-$	S-Cl	0.079	+0.067	-0.023	-0.063	+0.040
	S-C	0.178	-0.314	-0.129	-0.180	+0.051
$Se(CH_3)Cl_4^-$	Se-Cl	0.073	+0.066	-0.021	-0.059	+0.038
	Se-C	0.155	-0.232	-0.106	-0.154	+0.048
$Te(CH_3)Cl_4^-$	Te-Cl	0.063	+0.080	-0.017	-0.053	+0.036
	Te-C	0.123	-0.043	-0.070	-0.129	+0.059
$S(CH_3)Br_4^-$	S-Br	0.066	+0.062	-0.015	-0.046	+0.031

	S-C	0.174	-0.299	-0.125	-0.175	+0.050
$Se(CH_3)Br_4^-$	Se-Br	0.063	+0.051	-0.015	-0.043	+0.028
	Se-C	0.151	-0.215	-0.102	-0.150	+0.048
$Te(CH_3)Br_4^-$	Te-Br	0.056	+0.051	-0.014	-0.040	+0.026
	Te-C	0.121	-0.040	-0.068	-0.125	+0.058
$S(CH_3)I_4^-$	S-I	0.051	+0.051	-0.009	-0.031	+0.022
	S-C	0.169	-0.279	-0.119	-0.169	+0.050
$Se(CH_3)I_4^-$	Se-I	0.051	+0.040	-0.010	-0.030	+0.020
	Se-C	0.146	-0.193	-0.096	-0.144	+0.048
$Te(CH_3)I_4^-$	Te-I	0.047	+0.031	-0.010	-0.028	+0.018
	Te-C	0.117	-0.032	-0.064	-0.120	+0.056
	water					
$S(CH_3)Cl_4^-$	S-Cl	0.080	+0.067	-0.024	-0.064	+0.040
	S-C	0.177	-0.303	-0.127	-0.179	+0.052
$Se(CH_3)Cl_4^-$	Se-Cl	0.074	+0.066	-0.021	-0.059	+0.038
	Se-C	0.155	-0.234	-0.105	-0.152	+0.047
$Te(CH_3)Cl_4^-$	Te-Cl	0.063	+0.080	-0.016	-0.052	+0.036
	Te-C	0.124	-0.054	-0.071	-0.128	+0.057
$S(CH_3)Br_4^-$	S-Br	0.067	+0.061	-0.016	-0.047	+0.031
	S-C	0.173	-0.290	-0.123	-0.174	+0.051
$Se(CH_3)Br_4^-$	Se-Br	0.064	+0.051	-0.016	-0.044	+0.028
	Se-C	0.151	-0.218	-0.101	-0.148	+0.047
$Te(CH_3)Br_4^-$	Te-Br	0.056	+0.052	-0.013	-0.040	+0.026
	Te-C	0.121	-0.049	-0.068	-0.125	+0.056
$S(CH_3)I_4^-$	S-I	0.052	+0.051	-0.009	-0.032	+0.022
	S-C	0.168	-0.274	-0.118	-0.168	+0.050
$Se(CH_3)I_4^-$	Se-I	0.051	+0.040	-0.010	-0.030	+0.020
	Se-C	0.146	-0.197	-0.096	-0.143	+0.047
$Te(CH_3)I_4^-$	Te-I	0.047	+0.031	-0.010	-0.028	+0.018
	Te-C	0.117	-0.039	-0.065	-0.120	+0.055

	vacuum	water
$S(CH_3)Cl_4^-$	-	

$Se(CH_3)Cl_4^-$		
$Te(CH_3)Cl_4^-$		
$S(CH_3)Br_4^-$		
$Se(CH_3)Br_4^-$		

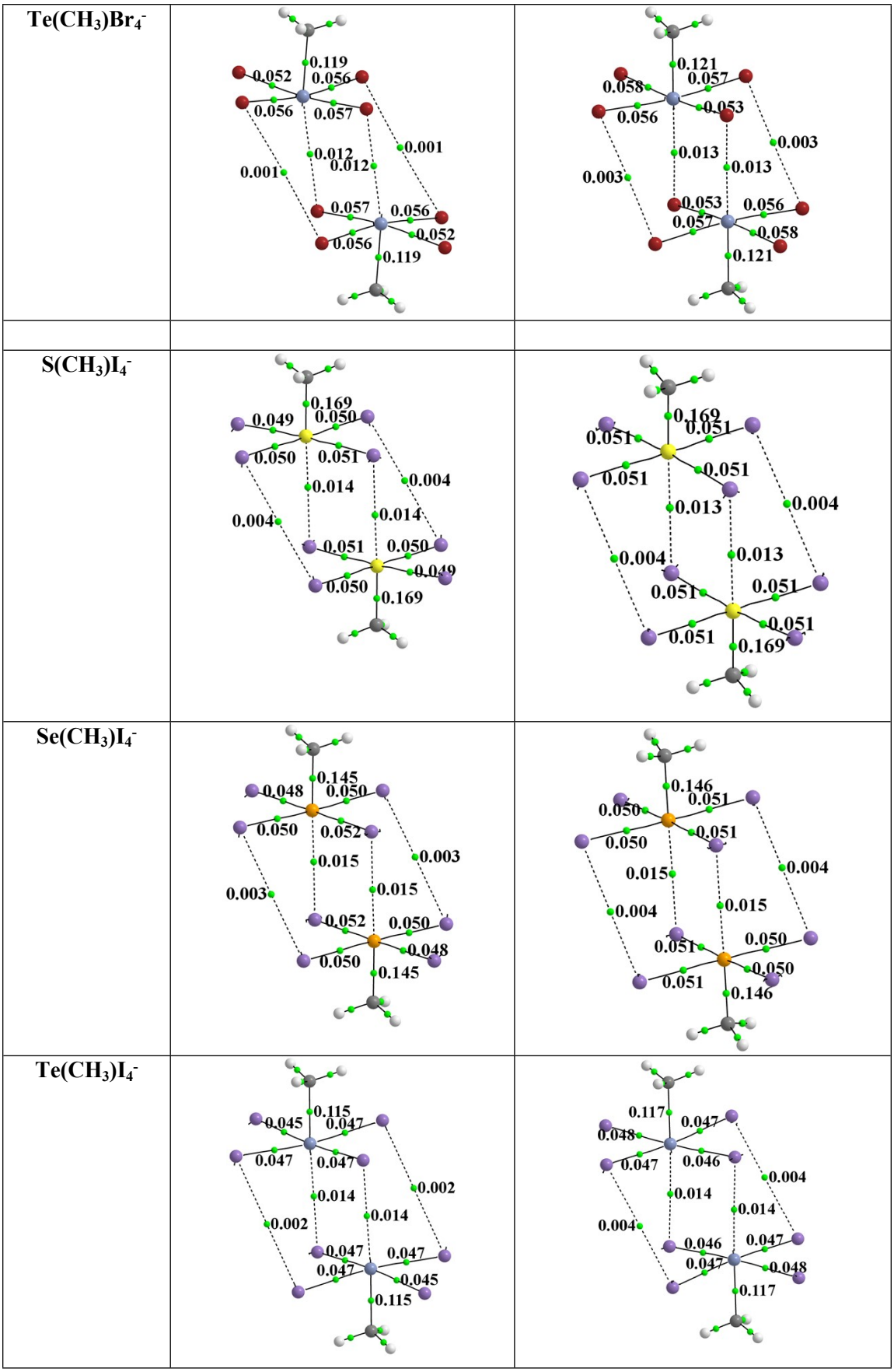


Fig. S3. AIM molecular diagrams of MP2/aug-cc-pVDZ optimized complexes. Green dots represent bond critical points. Numbers refers to electron densities at BCPs (in au)

Tab. S3. AIM descriptors of the calculated complexes in acetone. Bond critical point (BCP) properties: electron density ρ, Laplacian of electron density $\nabla^2\rho$ and total electron energy H and potential electron density energy V as well as kinetic electron density energy G, were obtained at the MP2/ aug-cc-pVDZ level. Data in atomic units.

	interaction	ρ	$\nabla^2\rho$	H	V	G
	vacuum					
$(S(CH_3)Cl_4^-)_2$	-	-	–	-	-	-
$(Se(CH_3)Cl_4^-)_2$	Se-Cl	0.078	+0.058	-0.025	-0.065	+0.040
	Se-C	0.154	-0.228	-0.105	-0.153	+0.048
	Se···Cl	0.009	+0.027	+0.001	-0.005	+0.006
	Cl···Cl	0.007	+0.019	+0.000	-0.004	+0.004
$(Te(CH_3)Cl_4^-)_2$	Te-Cl	0.065	+0.080	+0.018	-0.055	+0.038
	Te-C	0.122	-0.037	+0.069	-0.128	+0.059
	Te···Cl	0.009	+0.023	+0.001	-0.004	+0.005
	Cl···Cl	0.005	+0.014	+0.000	-0.003	+0.003
$(S(CH_3)Br_4^-)_2$	S-Br	0.069	+0.059	-0.017	-0.049	+0.032
	S-C	0.174	-0.302	-0.125	-0.174	+0.049
	S···Br	0.012	+0.034	+0.001	-0.006	+0.007
	Br···Br	0.002	+0.005	+0.000	-0.001	+0.001
$(Se(CH_3)Br_4^-)_2$	Se-Br	0.066	+0.048	-0.017	-0.046	+0.029
	Se-C	0.150	-0.211	-0.101	-0.150	+0.048
	Se···Br	0.013	+0.034	+0.001	-0.006	+0.007
	Br···Br	0.002	+0.004	+0.000	-0.001	+0.001
$(Te(CH_3)Br_4^-)_2$	Te-Br	0.057	+0.050	-0.014	-0.041	+0.027
	Te-C	0.119	-0.033	-0.066	-0.124	+0.058
	Te···Br	0.012	+0.027	+0.001	-0.005	+0.006
	Br···Br	0.001	+0.002	+0.000	-0.000	+0.000
$(S(CH_3)I_4^-)_2$	S-I	0.051	+0.053	-0.009	-0.031	+0.022
	S-C	0.169	-0.282	-0.119	-0.168	+0.049
	S···I	0.014	+0.034	+0.001	-0.007	+0.008
	I···I	0.004	+0.008	+0.000	-0.001	+0.002
$(Se(CH_3)I_4^-)_2$	Se-I	0.052	+0.040	-0.011	-0.031	+0.021
	Se-C	0.145	-0.185	-0.095	-0.144	+0.049
	Se···I	0.015	+0.034	+0.001	-0.007	+0.008
	I···I	0.003	+0.006	+0.000	-0.001	+0.001
$(Te(CH_3)I_4^-)_2$	Te-I	0.047	+0.031	-0.010	-0.028	+0.018
	Te-C	0.115	-0.023	-0.062	-0.119	+0.056
	Te···I	0.014	+0.028	+0.000	-0.006	+0.007
	I···I	0.002	+0.004	+0.000	-0.001	+0.001
	water					
$(S(CH_3)Cl_4^-)_2$	S-Cl	0.080	+0.069	-0.023	-0.064	+0.041
	S-C	0.177	-0.307	-0.128	-0.179	+0.051
	S···Cl	0.011	+0.034	+0.001	-0.006	+0.007
	Cl···Cl	0.003	+0.007	+0.000	-0.001	+0.002
$(Se(CH_3)Cl_4^-)_2$	Se-Cl	0.075	+0.064	-0.022	-0.060	+0.038
	Se-C	0.155	-0.235	-0.106	-0.153	+0.047
	Se···Cl	0.013	+0.037	+0.001	-0.007	+0.008
	Cl···Cl	0.003	+0.008	+0.000	-0.001	+0.002

$(Te(CH_3)Cl_4^-)_2$	Te-Cl	0.063	+0.080	-0.017	-0.054	+0.037
	Te-C	0.124	-0.054	-0.071	-0.129	+0.058
	Te···Cl	0.008	+0.021	+0.001	-0.004	+0.005
	Cl···Cl	0.006	+0.016	+0.000	-0.003	+0.004
	Te···Te	0.009	+0.025	+0.001	-0.004	+0.005
$(S(CH_3)Br_4^-)_2$	S-Br	0.067	+0.063	-0.016	-0.047	+0.031
	S-C	0.173	-0.295	-0.124	-0.174	+0.050
	S···Br	0.013	+0.035	+0.001	-0.007	+0.008
	Br···Br	0.004	+0.008	+0.000	-0.002	+0.002
$(Se(CH_3)Br_4^-)_2$	Se-Br	0.063	+0.051	-0.015	-0.044	+0.028
	Se-C	0.151	-0.218	-0.102	-0.149	+0.047
	Se···Br	0.014	+0.037	+0.001	-0.007	+0.008
	Br···Br	0.004	+0.008	+0.000	-0.002	+0.002
$(Te(CH_3)Br_4^-)_2$	Te-Br	0.058	+0.050	-0.015	-0.042	+0.027
	Te-C	0.121	-0.047	-0.068	-0.125	+0.057
	Te···Br	0.013	+0.029	+0.001	-0.006	+0.007
	Br···Br	0.003	+0.008	+0.000	-0.001	+0.002
$(S(CH_3)I_4^-)_2$	S-I	0.051	+0.053	-0.010	-0.031	+0.022
	S-C	0.169	-0.279	-0.119	-0.168	+0.049
	S···I	0.013	+0.033	+0.001	-0.006	+0.007
	I···I	0.004	+0.008	+0.000	-0.001	+0.002
$(Se(CH_3)I_4^-)_2$	Se-I	0.051	+0.041	+0.010	-0.030	+0.020
	Se-C	0.146	-0.193	+0.096	-0.143	+0.048
	Se···I	0.015	+0.033	-0.001	-0.007	+0.008
	I···I	0.004	+0.008	-0.000	-0.001	+0.002
$(Te(CH_3)I_4^-)_2$	Te-I	0.048	+0.030	+0.010	-0.028	+0.018
	Te-C	0.117	-0.033	+0.064	-0.120	+0.056
	Te···I	0.014	+0.029	-0.000	-0.006	+0.007
	I···I	0.004	+0.007	-0.000	-0.001	+0.002