SUPPLEMENTARY MATERIAL

A structural approach to the strength evaluation of linear chalcogen bonds

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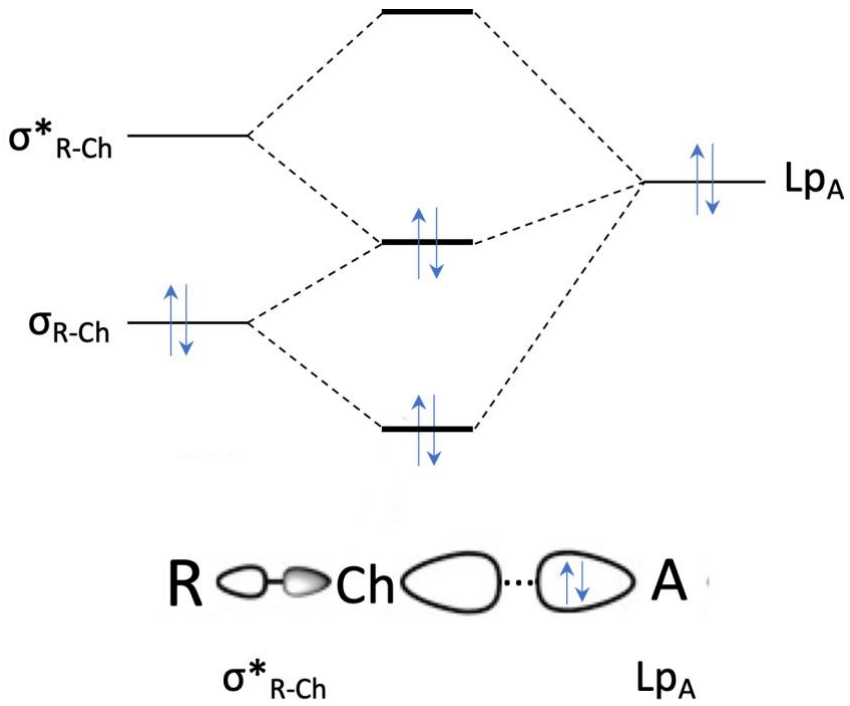

Scheme S1: Perturbation molecular orbital scheme showing the σ-interaction between the ChB acceptor A and the σ^*_{R-Ch} orbital of the ChB donor fragment.

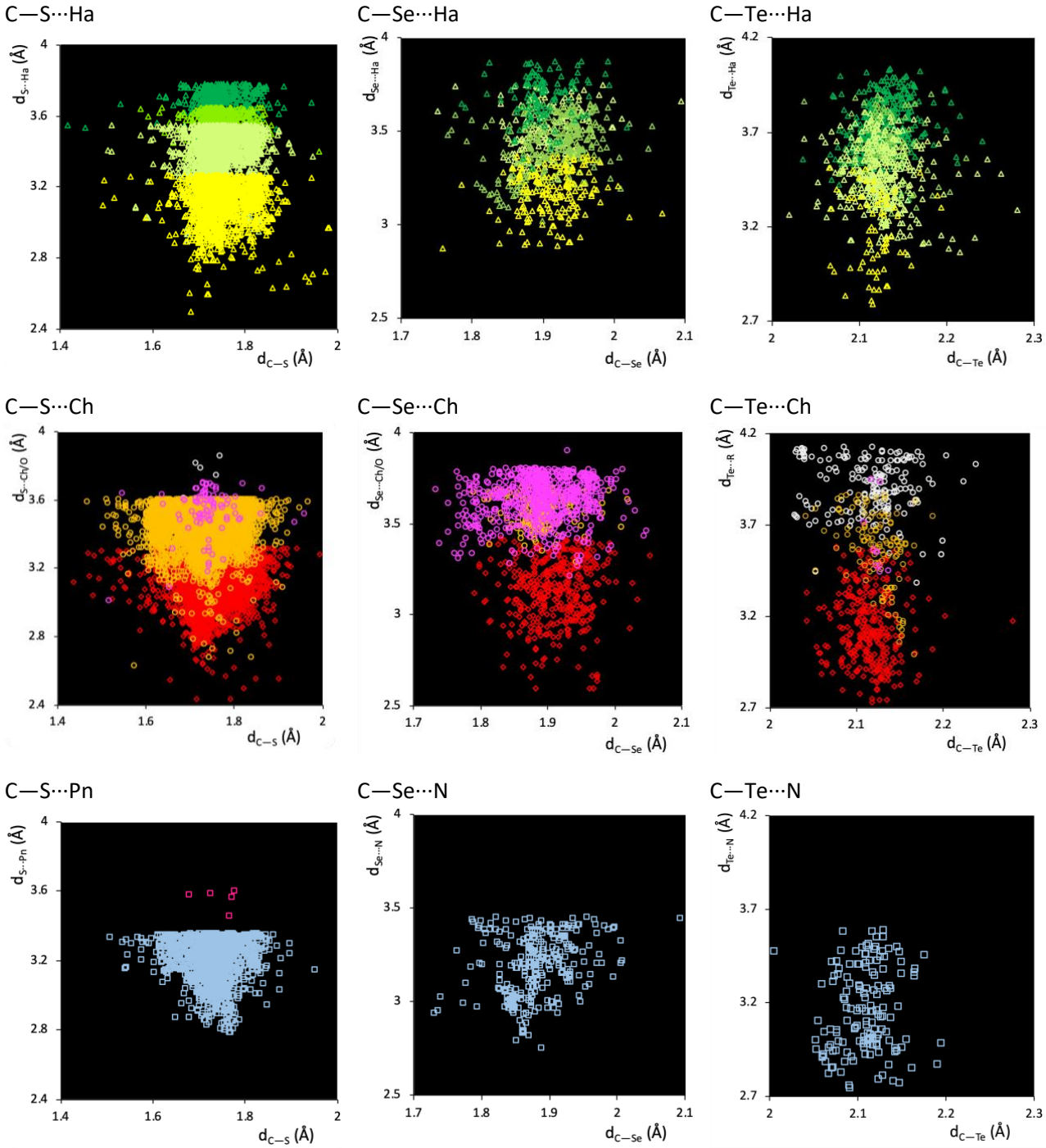

Figure S1: Scatterplot of the $d_{Ch\cdots A}$ *vs* d_{C-Ch} distances within the fragments C—Ch···A. A = Ha [triangles: F (lemon yellow), Cl (light green), Br (apple green), I (dark green)]; Ch/O [Ch = circles: S (yellow), Se (magenta), Te (white); O = rhombs (red)]; Pn [squares: N (light blue) P (purple)].

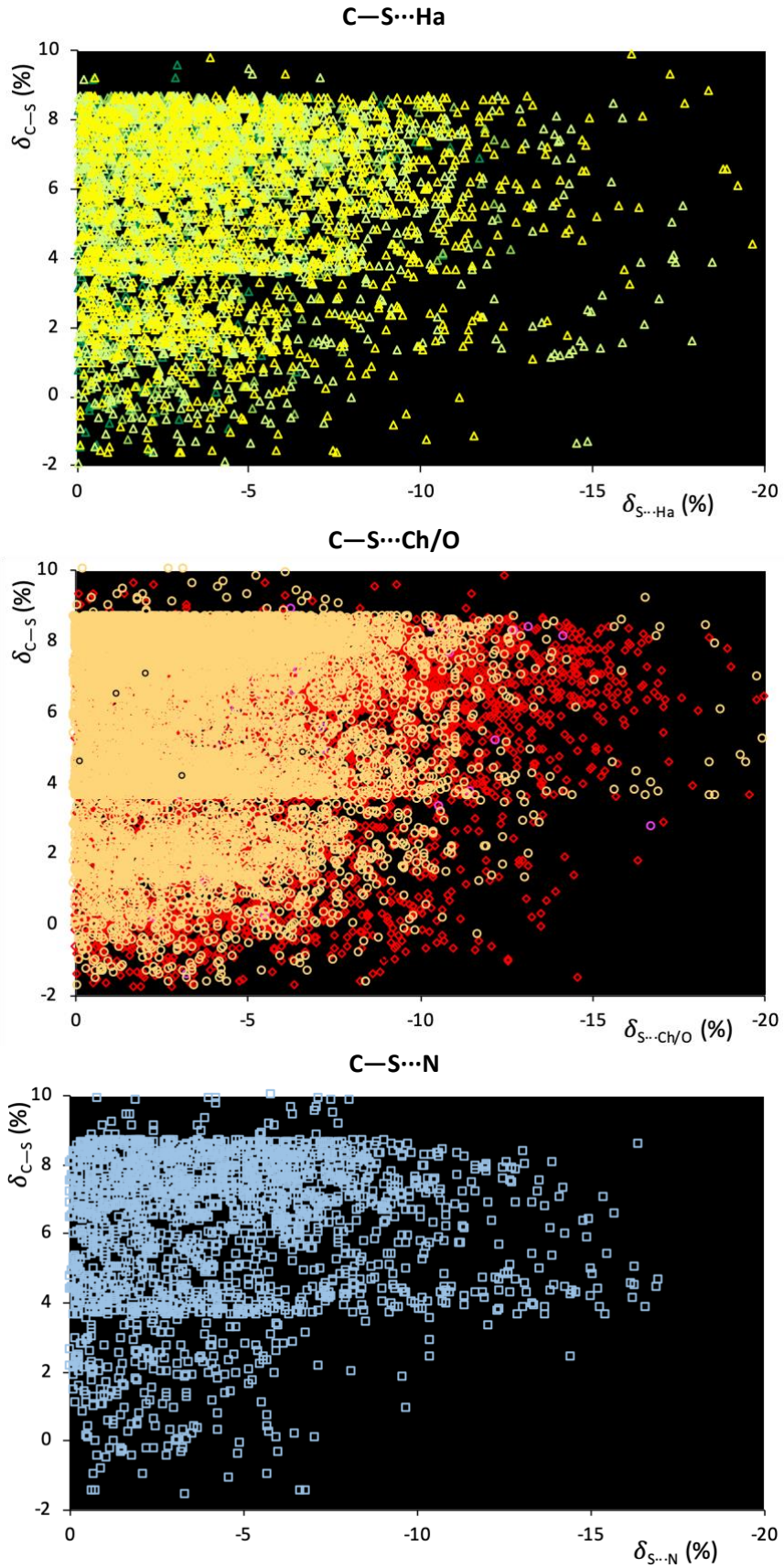

Figure S2: Scatterplots of the $d_{Ch\cdots A}$ *vs* d_{C-Ch} values calculated for the fragments C—S···A. A = Ha [triangles: F (lemon yellow), Cl (light green), Br (apple green), I (dark green)]; Ch/O [Ch = circles: S (yellow), Se (magenta), Te (white); O = rhombs (red)]; N (light blue squares).

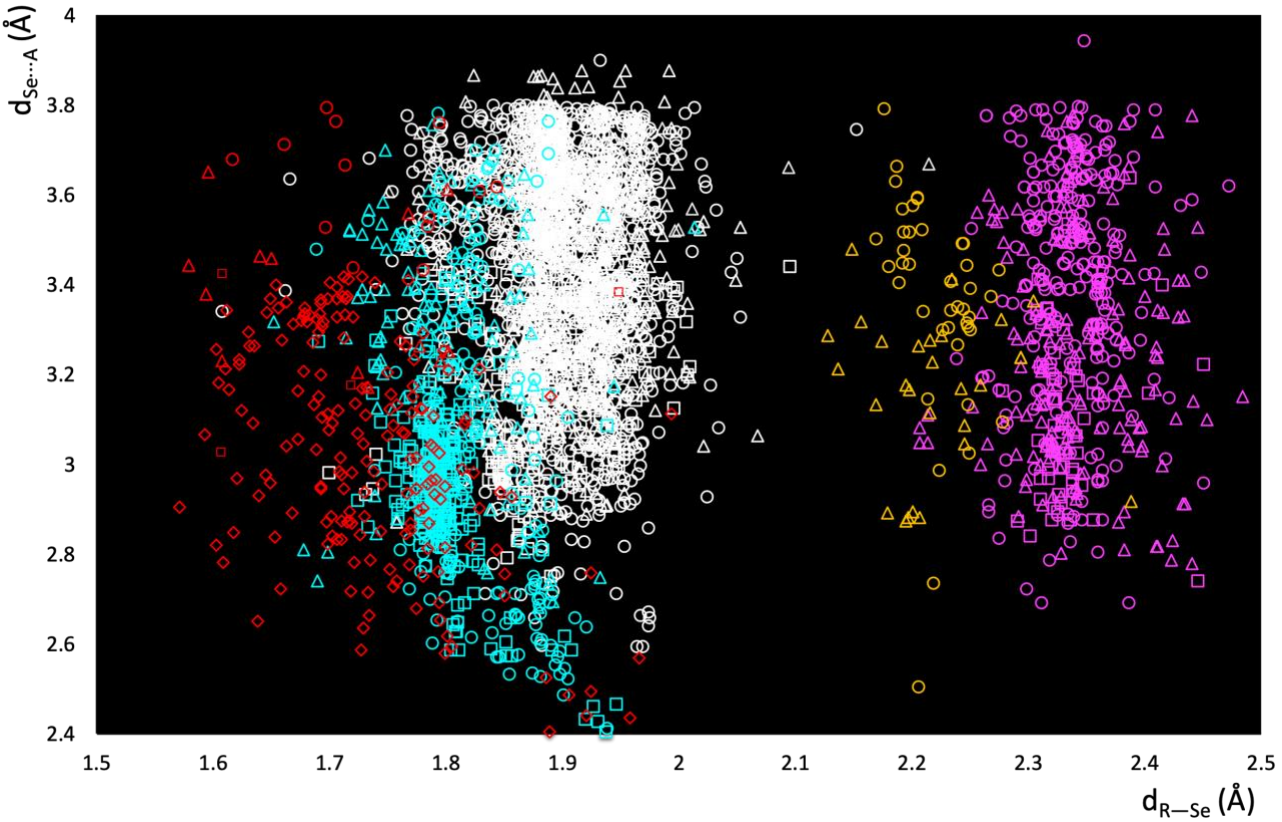

Figure S3: Scatterplot of $d_{Se\cdots A}$ *vs* d_{R-Se} distances within the fragments R—Se···A. R = C (white), O (red), N (cyano), S (yellow); Se (magenta); A = N (square), Ch (circle), O (rhombus), Ha (triangle).

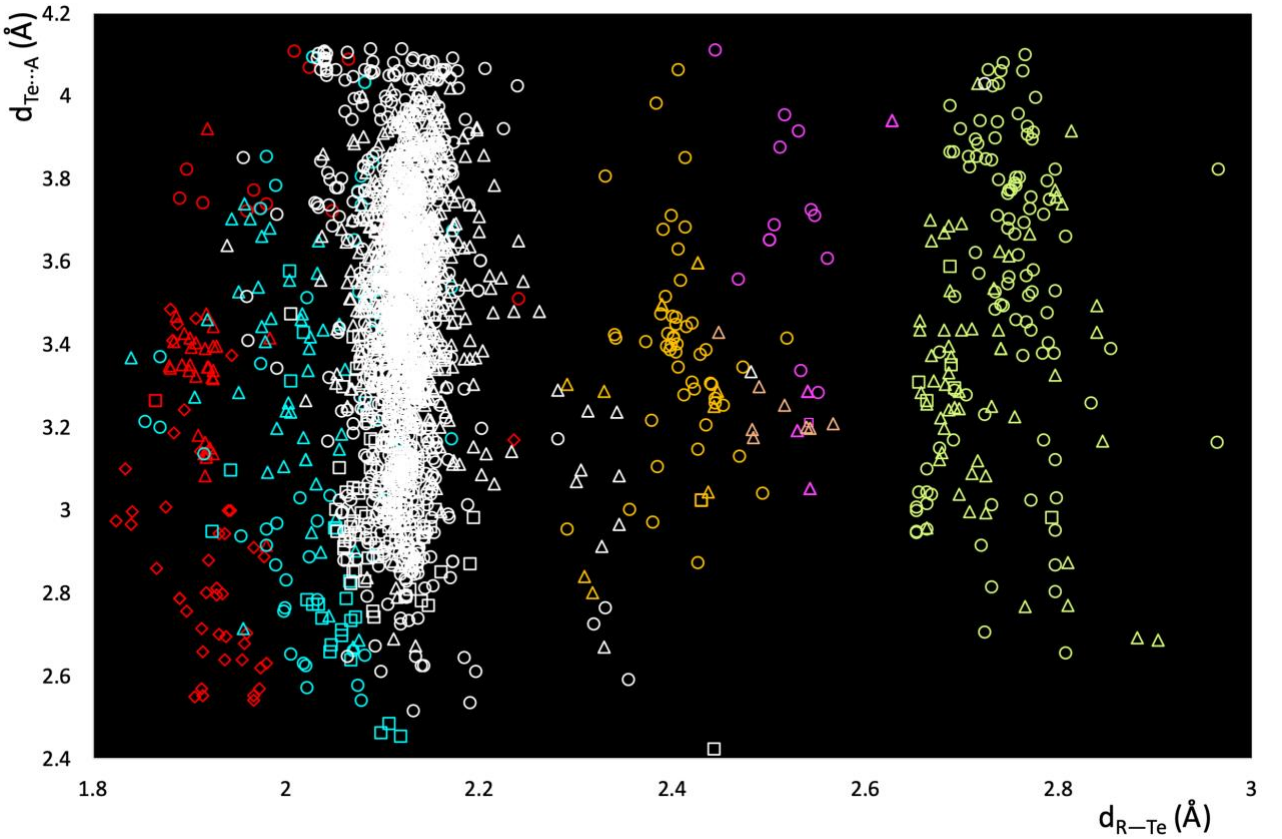

Figure S4: Scatterplot of the $d_{Te\cdots A}$ *vs* d_{R-Te} distances within the fragments R—Te···A. R = C (white), O (red), N (cyano), S (yellow); Se (magenta); Te (acid green). A = N (square), Ch (circle), O (rhomb), Ha (triangle).

Table S1: Occurrence of the linear 27763 fragments R–S···A featuring a ChB sorted by the nature of the involved atoms. R = B, C, Si, N, P, As, Sb, O, S, Se, Te, F, Cl, Br, and I; A = N, P, As, Sb, O, S, Se, Te, F, Cl, Br, and I.

R–S···A	N	P	As	Sb	O	S	Se	Te	F	Cl	Br	I
B	0	0	0	0	5	2	0	0	6	9	0	0
C	1975	5	0	1	6537	8784	87	9	1511	1871	661	552
Si	4	0	0	0	0	1	0	0	0	0	0	0
N	1116	0	0	0	363	341	3	0	244	297	27	35
P	6	1	0	0	17	163	2	1	12	23	5	1
As	0	0	12	0	1	24	0	0	1	12	0	1
Sb	11	0	0	91	0	32	0	0	0	3	0	0
O	36	0	0	0	836	29	2	2	71	101	18	6
S	180	0	0	0	199	642	4	0	145	177	186	69
Se	5	0	0	0	1	2	8	0	0	12	12	1
Te	0	0	0	0	1	6	1	4	1	3	3	2
F	13	0	0	0	22	0	0	0	59	0	0	0
Cl	2	0	0	0	4	1	0	0	10	11	0	0
Br	0	0	0	0	0	0	0	0	1	0	6	0
I	0	0	0	0	0	1	0	0	0	0	1	2

Table S2: Occurrence of the linear 4109 fragments R–Se···A featuring a ChB sorted by the nature of the involved atoms. R = B, C, Si, N, P, As, Sb, O, S, Se, Te, F, Cl, Br, and I; A = N, P, As, Sb, O, S, Se, Te, F, Cl, Br, and I.

R–Se···A	N	P	As	Sb	O	S	Se	Te	F	Cl	Br	I
B	0	0	0	0	0	0	1	0	0	0	1	0
C	272	1	0	0	424	186	718	1	171	292	182	116
Si	0	0	0	0	0	0	1	0	0	0	0	0
N	253	0	0	0	118	11	57	0	28	70	13	23
P	1	9	0	0	9	4	141	1	9	15	5	21
As	3	0	3	0	1	0	11	0	0	0	0	0
Sb	6	0	0	1	0	0	4	0	0	0	0	0
O	4	0	0	0	189	0	13	0	0	13	0	1
S	28	0	0	0	5	20	16	0	0	19	5	4
Se	54	1	1	0	44	26	209	1	41	46	48	33
Te	0	0	0	0	0	0	1	3	2	3	2	1
F	0	0	0	0	0	0	0	0	2	0	0	0
Cl	5	0	0	0	6	0	2	0	23	32	0	0
Br	0	0	0	0	0	0	1	0	0	0	16	0
I	0	0	0	0	0	0	1	0	0	1	0	4

Table S3: Occurrence of the linear 2318 fragments R–Te···A featuring a ChB sorted by the nature of the involved atoms. R = B, C, Si, N, P, As, Sb, O, S, Se, Te, F, Cl, Br, and I; A = N, P, As, Sb, O, S, Se, Te, F, Cl, Br, and I.

R–Te···A	N	P	As	Sb	O	S	Se	Te	F	Cl	Br	I
B	0	0	0	0	1	0	0	0	3	0	0	1
C	155	1	0	0	332	127	10	185	66	352	165	376
Si	0	0	0	0	0	0	0	1	0	0	0	0
N	28	0	0	0	28	14	0	2	13	23	3	9
P	0	2	0	0	3	2	0	9	0	3	4	5
As	0	0	0	0	3	1	0	0	0	0	0	0
Sb	0	0	0	2	0	0	0	0	0	0	0	0
O	1	0	0	0	50	7	0	7	0	4	8	21
S	1	0	0	0	5	38	0	7	4	2	3	8
Se	1	0	0	0	0	1	3	8	1	1	1	1
Te	6	0	0	1	34	4	0	67	20	13	10	17
F	0	0	0	0	0	0	0	0	0	0	0	0
Cl	1	0	0	0	3	0	0	1	1	9	0	0
Br	0	0	0	0	1	0	0	0	2	0	16	0
I	0	0	0	0	0	0	0	0	1	3	0	12