Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Exploring the Bonding in Alkaline Earth Halides AeX- (Ae=Be-Ba, X=F-I) from the Fermi Hole Localization and QTAIM Perspectives

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Figure S1: DFT and CCSD(T) delocalization index computed for the bonds in (a) AeX^- (Ae=Be-Ba, X=F) and (b) EX (E=B-Tl, X=F) systems.

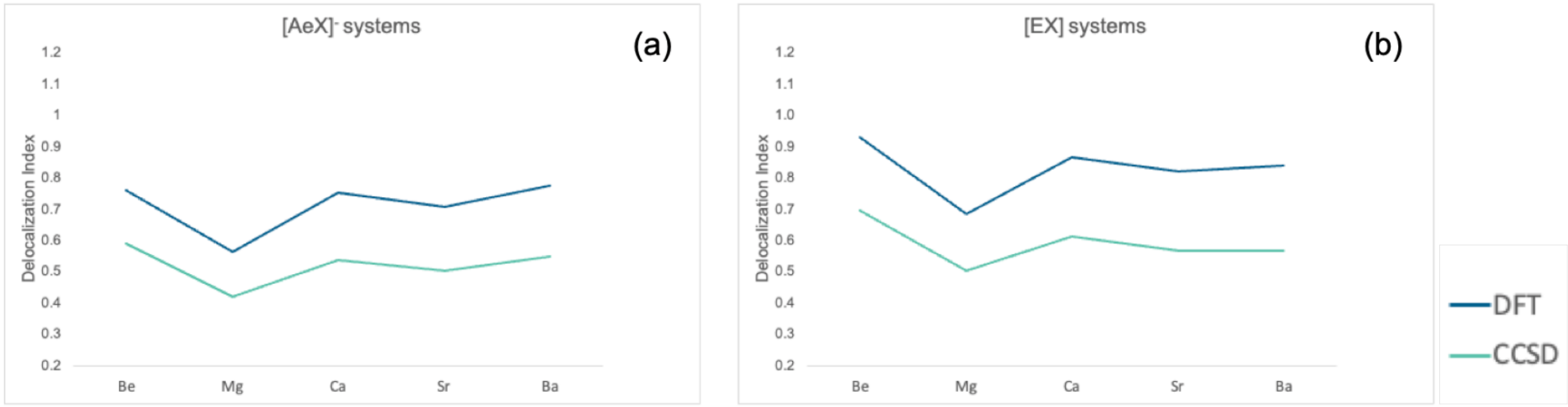

Figure S2: Comparison of the Fermi Hole Localization contours as obtained at the DFT and CCSD(T) levels for the AeX^- (Ae=Be-Ba, X=F) systems. Color scale values in bte.

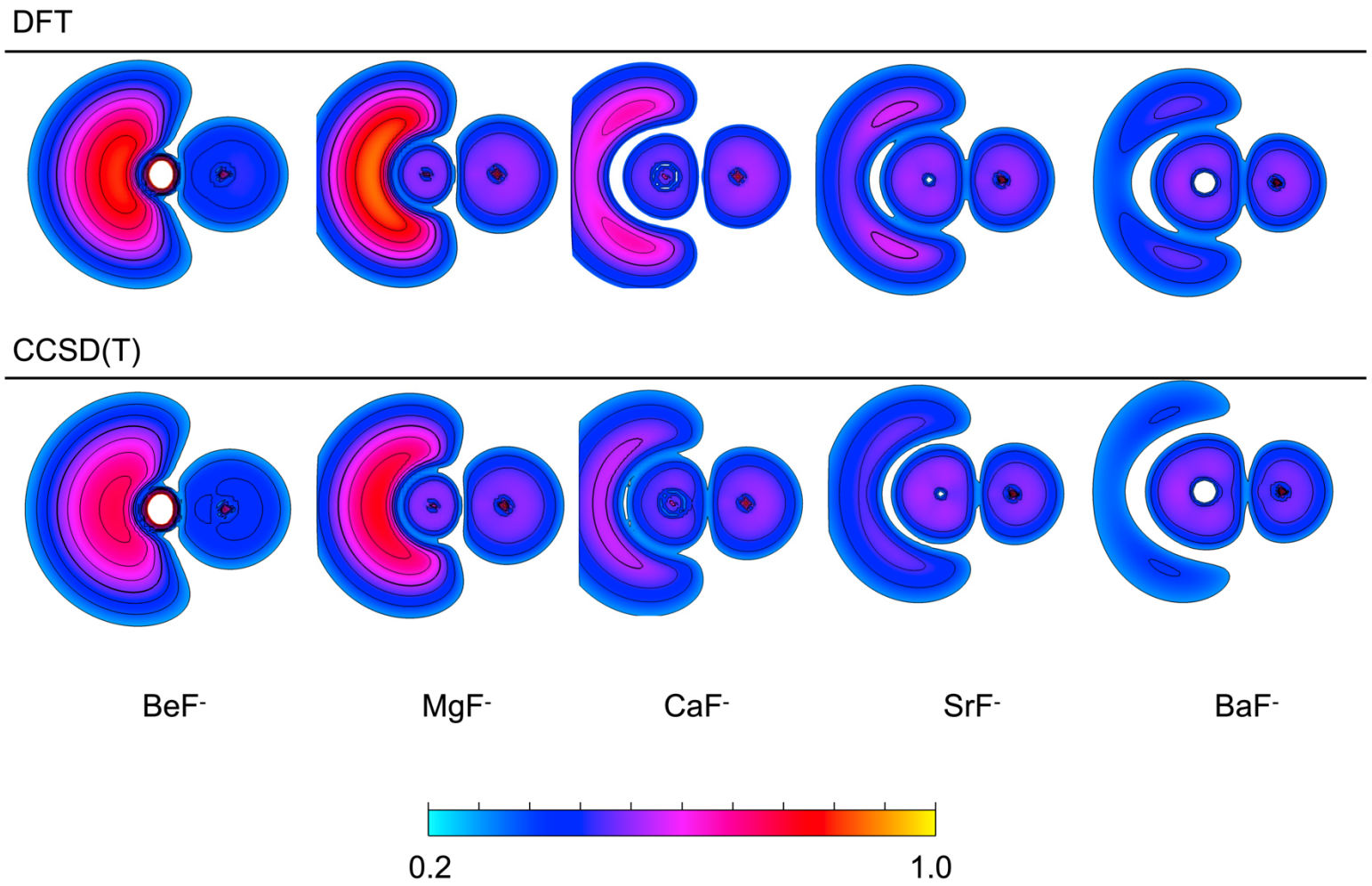

Figure S3: Comparison of the Fermi Hole Localization contours as obtained at the DFT and CCSD(T) levels for the EX (E=B-Tl, X=F) systems. Color scale values in bte.

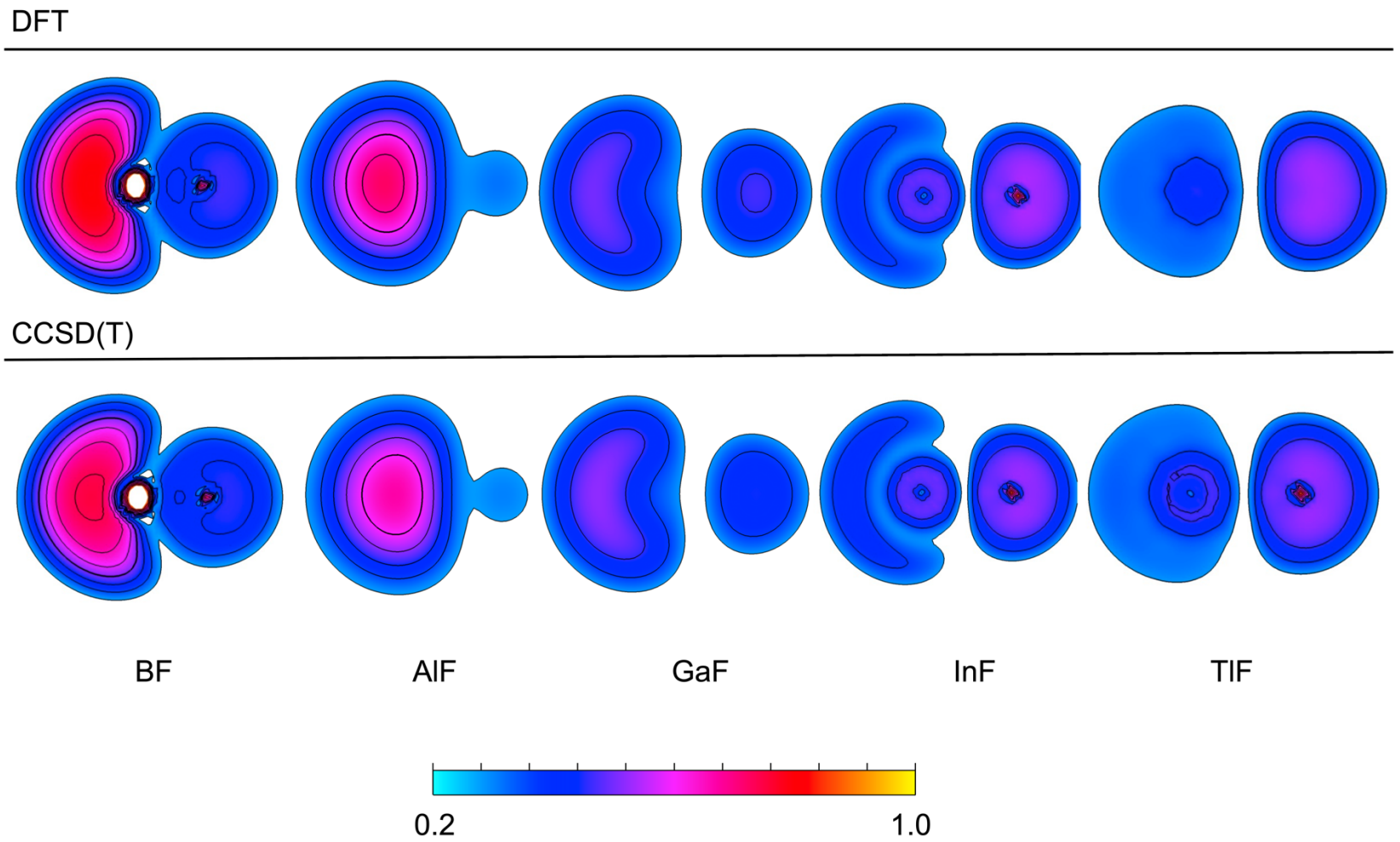

Figure S4: (a) Graphical representation of the Fermi hole localization (i.e., isovalue = 0.28125 bte) and (b) topological analysis obtained for the RhB molecule computed at the BP86/def2-QZVPP level of theory. The delocalization index has been also included in the figure as a value of reference.

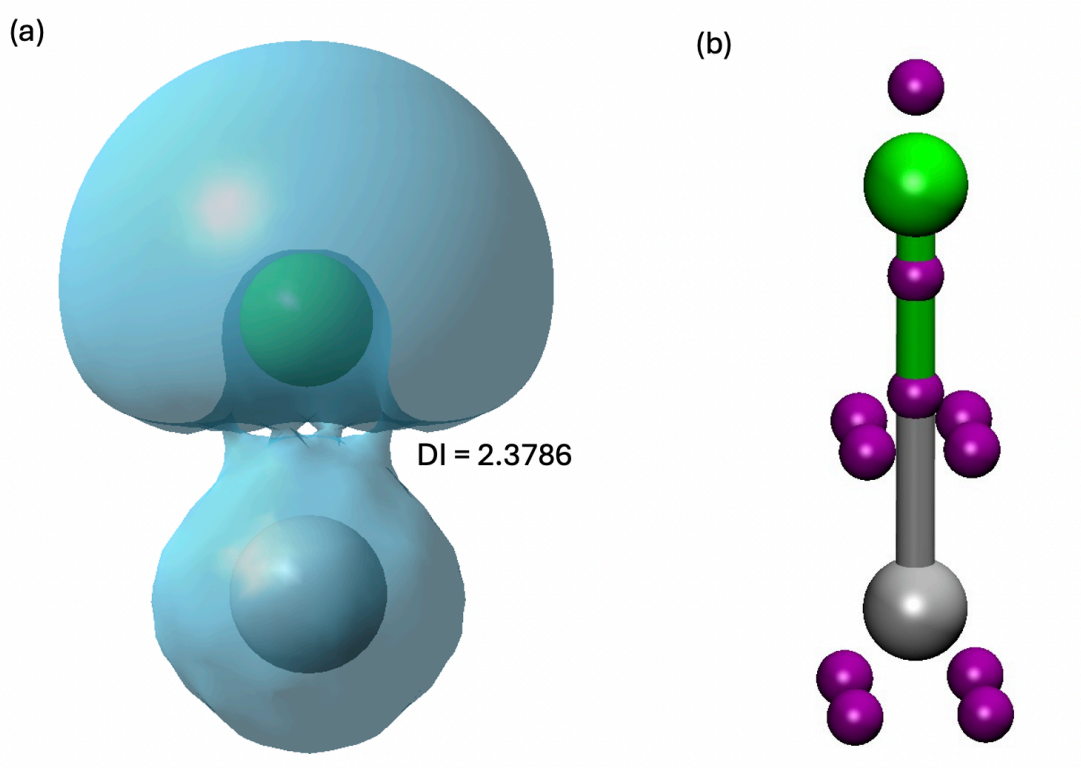

Table S1: Atomic partial charges (q) for $[AeX]^-$, Ae =Be-Ba and X = F-I calculated at BP86/def2-QZVPP.

	QTAIM		Hirshfeld		CM5	
[AeX]-	**q(Ae)**	**q(X)**	**q(Ae)**	**q(X)**	**q(Ae)**	**q(X)**
[BeF]-	0.05	-1.05	-0.65	-0.35	-0.50	-0.50
[BeCl]-	0.05	-1.05	-0.60	-0.40	-0.51	-0.49
[BeBr]-	0.03	-1.03	-0.55	-0.44	-0.49	-0.51
[BeI]-	0.01	-1.01	-0.48	-0.52	-0.44	-0.55
[MgF]-	-0.01	-0.99	-0.51	-0.49	-0.41	-0.59
[MgCl]-	-0.02	-0.98	-0.45	-0.55	-0.41	-0.59
[MgBr]-	-0.02	-0.98	-0.43	-0.57	-0.40	-0.60
[MgI]-	-0.04	-0.96	-0.38	-0.62	-0.37	-0.62
[CaF]-	-0.03	-0.97	-0.55	-0.45	-0.40	-0.59
[CaCl]-	-0.03	-0.97	-0.52	-0.48	-0.45	-0.55
[CaBr]-	-0.10	-0.90	-0.51	-0.49	-0.46	-0.53
[CaI]-	-0.10	-0.90	-0.49	-0.51	-0.46	-0.54
[SrF]-	-0.11	-0.89	-0.53	-0.47	-0.36	-0.63
[SrCl]-	-0.09	-0.91	-0.49	-0.51	-0.41	-0.59
[SrBr]-	-0.09	-0.91	-0.48	-0.52	-0.43	-0.57
[SrI]-	-0.09	-0.91	-0.46	-0.54	-0.43	-0.57
[BaF]-	-0.16	-0.84	-0.55	-0.45	-0.36	-0.63
[BaCl]-	-0.12	-0.88	-0.51	-0.48	-0.43	-0.57
[BaBr]-	-0.13	-0.87	-0.51	-0.49	-0.51	-0.49
[BaI]-	-0.12	-0.88	-0.49	-0.51	-0.47	-0.54

Table S2: Electron Density Properties in [AeX]- , with Ae = Be-Ba and X = F-I calculated in BCP at BP86/def2-QZVPP.

[AeX]-	ρ_{BCP} a.u.	$\nabla^2\rho_{BCP}$ a.u.	$\lvert V_{BCP}\rvert/G_{BCP}$	H_{BCP} a.u.	C(Ae) a.u.	V(Ae) a.u.	B(Ae,X) a.u.	V(X) a.u.	C(X) a.u.
[BeF]-	0.1201	1.0899	1.0004	-0.0001	2.04	2.03	1.83	5.92	2.02
[BeCl]-	0.0630	0.2603	1.1644	-0.0128	2.03	2.01	1.60	6.29	10.03
[BeBr]-	0.0499	0.1414	1.2679	-0.0129	2.03	2.00	1.42	6.72	27.73
[BeI]-	0.0382	0.0403	1.5720	-0.0135	2.03	1.99	1.13	5.36	46.06
[MgF]-	0.0655	0.5171	0.9367	+0.0077	10.04	1.99	1.28	6.53	2.14
[MgCl]-	0.0336	0.1448	0.9823	+0.0006	10.04	1.96	1.23	6.69	10.02
[MgBr]-	0.0271	0.0888	1.0271	-0.0006	10.05	1.95	1.08	7.10	27.64
[MgI]-	0.0209	0.0414	1.1432	-0.0017	10.03	1.95	0.79	7.53	44.35
[CaF]-	0.0901	0.4589	1.0729	-0.0090	18.14	1.90	0.51	7.19	2.15
[CaCl]-	0.0477	0.1550	1.0794	-0.0033	18.13	1.88	1.03	6.82	10.00
[CaBr]-	0.0390	0.1101	1.0788	-0.0024	18.08	1.87	1.49	6.63	27.35
[CaI]-	0.0295	0.0680	1.0876	-0.0016	18.09	1.96	1.73	6.54	44.46
[SrF]-	0.0785	0.3591	1.0841	-0.0082	35.62	1.88	0.42	7.29	2.15
[SrCl]-	0.0418	0.1282	1.0704	-0.0024	35.35	1.86	0.04	7.82	10.02
[SrBr]-	0.0343	0.0923	1.0715	-0.0018	35.49	1.85	1.41	6.63	27.18
[SrI]-	0.0262	0.0581	1.0830	-0.0013	35.55	1.85	1.73	6.54	44.22
[BaF]-	0.0818	0.2970	1.1889	-0.0166	52.78	1.86	1.43	6.20	2.15
[BaCl]-	0.0443	0.1163	1.1320	-0.0044	52.74	1.84	1.03	6.80	10.00
[BaBr]-	0.0367	0.0873	1.1134	-0.0028	52.73	1.83	1.35	6.74	27.17
[BaI]-	0.0285	0.0580	1.1021	-0.0016	52.85	1.78	1.71	6.60	44.21

Note: *'V', 'C', and 'B' indicate the average occupation numbers in the χ_{xc} (Valence, Core, and Bonding) basins, respectively. 'ρ_{BCP}' denotes the electron density at the bond critical point. '$\nabla^2\rho$' signifies the Laplacian evaluated at the bond critical point. '$\lvert V_{BCP}\rvert/G_{BCP}$' represents the ratio of potential to kinetic energy density, also evaluated at the bond critical point.*

Table S3: Atomic partial charges (q) for EX, E=B-Tl and X = F-I calculated at BP86/def2-QZVPP.

	QTAIM		Hirshfeld		CM5	
EX	**q(E)**	**q(X)**	**q(E)**	**q(X)**	**q(E)**	**q(X)**
BF	0.88	-0.88	0.05	-0.05	0.00	0.00
BCl	0.72	-0.72	-0.01	0.01	-0.08	0.08
BBr	0.57	-0.57	-0.01	0.01	-0.10	0.10
BI	0.21	-0.21	0.00	0.00	-0.09	0.09
AlF	0.91	-0.91	0.30	-0.30	0.28	-0.28
AlCl	0.83	-0.83	0.24	-0.24	0.21	-0.21
AlBr	0.79	-0.79	0.22	-0.22	0.17	-0.17
AlI	0.73	-0.73	0.21	-0.21	0.16	-0.16
GaF	0.73	-0.73	0.33	-0.33	0.34	-0.34
GaCl	0.63	-0.63	0.28	-0.28	0.27	-0.27
GaBr	0.57	-0.57	0.26	-0.26	0.24	-0.24
GaI	0.50	-0.50	0.24	-0.24	0.21	-0.21
InF	0.74	-0.74	0.38	-0.38	0.41	-0.41
InCl	0.64	-0.64	0.34	-0.34	0.34	-0.34
InBr	0.60	-0.60	0.31	-0.31	0.31	-0.31
InI	0.53	-0.53	0.29	-0.29	0.27	-0.27
TlF	0.71	-0.71	0.41	-0.41	0.44	-0.44
TlCl	0.62	-0.62	0.38	-0.38	0.39	-0.39
TlBr	0.57	-0.57	0.35	-0.35	0.36	-0.36
TlI	0.51	-0.51	0.33	-0.33	0.33	-0.33

Table S4: Electron Density Properties in EX systems, with E = B-Tl and X = F-I calculated in BCP at BP86/def2-QZVPP.

EX	ρ_{BCP} a.u.	$\nabla^2\rho_{BCP}$ a.u.	$\lvert V_{BCP}\rvert/G_{BCP}$	H_{BCP} a.u.	C(Ae) a.u.	V(Ae) a.u.	B(E,X) a.u.	V(X) a.u.	C(X) a.u.
BF	0.2405	1.3951	1.3709	-0.2056	2.05	2.15	1.44	5.96	2.15
BCl	0.1567	-0.0718	2.1214	-0.1657	2.05	2.13	1.58	6.17	10.00
BBr	0.1359	-0.2931	3.0986	-0.1400	2.04	2.12	1.50	6.53	27.34
BI	0.1118	-0.1446	3.1931	-0.0665	2.04	2.10	1.46	6.71	44.25
AlF	0.1057	0.8311	1.0459	-0.0100	10.04	2.02	1.04	6.73	2.15
AlCl	0.0674	0.2354	1.2336	-0.0179	10.04	2.02	1.14	6.71	10.03
AlBr	0.0591	0.1898	1.3476	-0.0187	10.03	2.02	1.11	7.00	27.21
AlI	0.0516	0.0529	1.5940	-0.0193	10.03	2.02	1.15	7.10	44.40
GaF	0.1209	0.6610	1.1934	-0.0396	27.25	2.39	0.01	7.72	2.14
GaCl	0.0834	0.1750	1.4044	-0.0297	27.34	2.36	1.12	6.73	10.02
GaBr	0.0726	0.1029	1.4951	-0.0252	27.24	2.35	1.13	7.02	27.38
GaI	0.0614	0.0444	1.6497	-0.0206	27.38	2.33	1.18	7.21	44.46
InF	0.0977	0.4910	1.1556	-0.0226	45.34	2.22	0.89	6.77	2.15
InCl	0.0694	0.1724	1.2851	-0.0172	44.66	2.20	1.07	6.68	10.02
InBr	0.0611	0.2735	1.3298	-0.0146	45.52	2.21	0.93	6.85	27.63
InI	0.0522	0.0689	1.4174	-0.0123	45.39	2.24	1.14	7.76	44.28
TlF	0.0910	0.4063	1.1630	-0.0197	76.74	2.00	1.48	5.89	2.14
TlCl	0.0666	0.1612	1.2651	-0.0145	76.68	1.70	1.70	5.97	10.02
TlBr	0.0593	0.1182	1.2943	-0.0123	76.85	1.67	1.14	6.77	27.36
Tll	0.0513	0.0757	1.3580	-0.0105	76.88	1.65	2.01	6.02	44.37

Note: *'V', 'C', and 'B' indicate the average occupation numbers in the χ_{xc} (Valence, Core, and Bonding) basins, respectively. 'ρ_{BCP}' denotes the electron density at the bond critical point. '$\nabla^2\rho$' signifies the Laplacian evaluated at the bond critical point. '$\lvert V_{BCP}\rvert/G_{BCP}$' represents the ratio of potential to kinetic energy density, also evaluated at the bond critical point.*

Table S5: Atomic partial charges (q) for $[AeX]^-$, Ae =Be-Ba and X = F calculated at CCSD(T)/def2-QZVPP.

	QTAIM		Hirshfeld		CM5	
EX	**q(Ae)**	**q(X)**	**q(Ae)**	**q(X)**	**q(Ae)**	**q(X)**
[BeF]-	0.09	-1.09	-0.62	-0.38	-0.47	-0.53
[MgF]-	0.01	-1.01	-0.47	-0.53	-0.37	-0.63
[CaF]-	0.02	-1.02	-0.41	-0.59	-0.26	-0.74
[SrF]-	-0.07	-0.93	-0.46	-0.54	-0.30	-0.70
[BaF]-	-0.17	-0.83	-0.53	-0.47	-0.35	-0.65

Table S6: Electron Density Properties in [AeX]- , with Ae = Be-Ba and X = F, calculated at CCSD(T)/def2-QZVPP.

EX	**ρ_{BCP} a.u.**	**$\nabla^2\rho_{BCP}$ a.u.**	**$\lvert V_{BCP}\rvert/G_{BCP}$**	**H_{BCP} a.u.**	**C(Ae) a.u.**	**V(Ae) a.u.**	**B(Ae,X) a.u.**	**V(X) a.u.**	**C(X) a.u.**
[BeF]-	0.1194	1.1873	0.9871	+0.0038	2.04	2.00	1.78	6.03	2.15
[MgF]-	0.0670	0.5885	0.9296	+0.0097	10.04	1.96	1.42	6.40	2.15
[CaF]-	0.0822	0.5143	1.0613	-0.0084	17.96	1.90	1.94	5.87	2.15
[SrF]-	0.0733	0.3975	1.0657	-0.0069	35.33	1.88	1.27	6.51	2.15
[BaF]-	0.0737	0.3459	1.1381	-0.0134	52.45	1.87	1.35	6.31	2.12

Note: *'V', 'C', and 'B' indicate the average occupation numbers in the χ_{xc} (Valence, Core, and Bonding) basins, respectively. 'ρ_{BCP}' denotes the electron density at the bond critical point. '$\nabla^2\rho$' signifies the Laplacian evaluated at the bond critical point. '$\lvert V_{BCP}\rvert/G_{BCP}$' represents the ratio of potential to kinetic energy density, also evaluated at the bond critical point.*

Table S7: Atomic partial charges (q) for EX, E = B-Tl and X = F calculated at CCSD(T)/def2-QZVPP.

	QTAIM		Hirshfeld		CM5	
EX	**q(E)**	**q(X)**	**q(E)**	**q(X)**	**q(E)**	**q(X)**
BF	0.94	-0.94	0.10	-0.10	0.04	-0.04
AlF	0.95	-0.95	0.34	-0.34	0.32	-0.32
GaF	0.80	-0.80	0.38	-0.38	0.39	-0.39
InF	0.81	-0.81	0.44	-0.44	0.47	-0.47
TlF	0.79	-0.79	0.49	-0.49	0.52	-0.52

Table S8: Electron Density Properties in EX systems, with E = B-Tl and X = F, calculated at CCSD(T)/def2-QZVPP.

EX	**ρ_{BCP} a.u.**	**$\nabla^2\rho_{BCP}$ a.u.**	**$\lvert V_{BCP}\rvert/G_{BCP}$**	**H_{BCP} a.u.**	**C(E) a.u.**	**V(E) a.u.**	**B(E,X) a.u.**	**V(X) a.u.**	**C(X) a.u.**
BF	0.2361	1.5783	1.3278	-0.1925	2.05	2.08	1.65	6.07	2.14
AlF	0.1026	0.8997	1.0225	-0.0052	10.05	1.97	1.07	6.75	2.14
GaF	0.1184	0.7069	1.1855	-0.0402	27.53	2.22	0.06	7.74	2.14
InF	0.0950	0.5276	1.1403	-0.0215	44.87	2.04	0.82	6.93	2.14
TlF	0.0891	0.4306	1.1597	-0.0204	76.71	1.69	1.36	6.34	2.14

Note: *'V', 'C', and 'B' indicate the average occupation numbers in the χ_{xc} (Valence, Core, and Bonding) basins, respectively. 'ρ_{BCP}' denotes the electron density at the bond critical point. '$\nabla^2\rho$' signifies the Laplacian evaluated at the bond critical point. '$\lvert V_{BCP}\rvert/G_{BCP}$' represents the ratio of potential to kinetic energy density, also evaluated at the bond critical point.*