Methylammonium Tetrel Halide Perovskite Ion pairs and Their Dimers: The Interplay Between the Hydrogen-, Pnictogen- and Tetrel-Bonding Interactions

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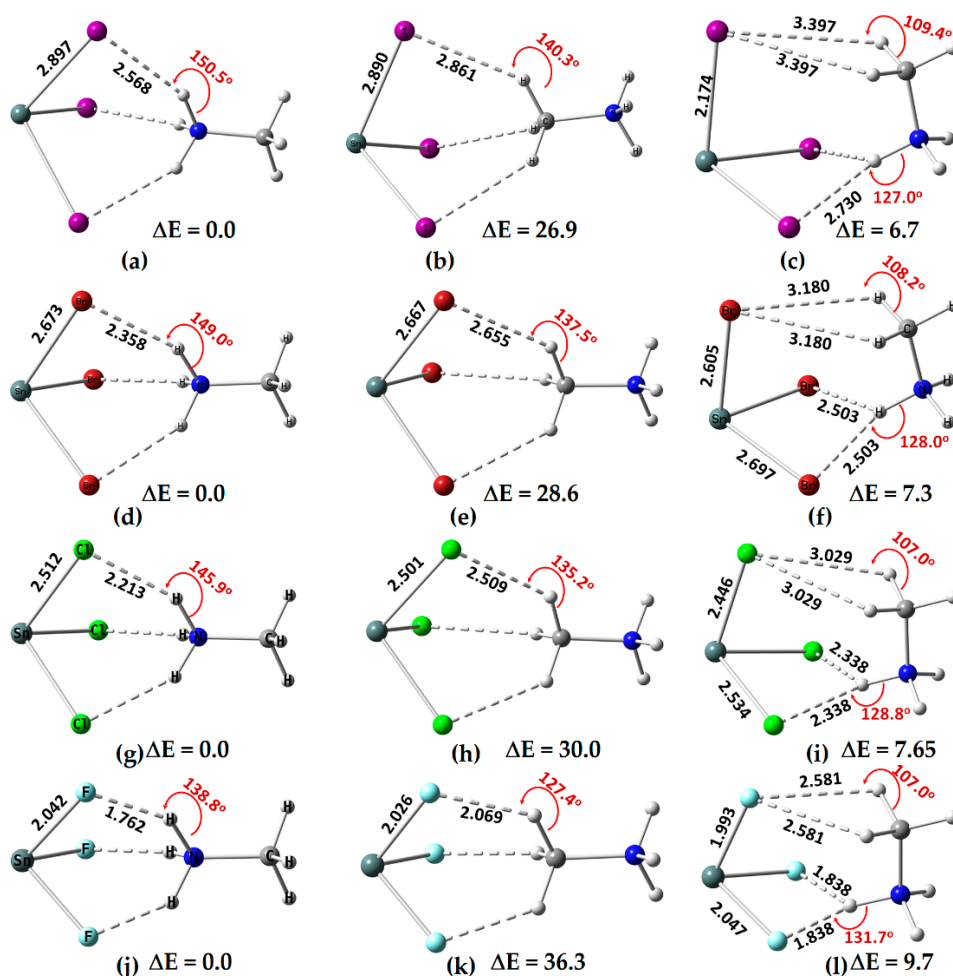
Electronic Supplementary Information

Figure S1. [ωB97XD/def2-TZVPPD] level fully-relaxed geometries of [CH$_3$NH$_3^+$•SnX$_3^-$] (X = F, Cl, Br, I) ion-pairs in the conformational space, including (a) [I$_3$Sn···NH$_3$CH$_3$]; (b)

[$I_3Sn\cdots CH_3NH_3$]; (c) [$Br_3Sn\cdots NH_3CH_3$]; (d) [$Br_3Sn\cdots CH_3NH_3$]; (e) [$Cl_3Sn\cdots NH_3CH_3$]; (f) [$Cl_3Sn\cdots CH_3NH_3$]; (g) [$Cl_3Sn\cdots H_3NCH_3$]. Shown are selected coordinate and hydrogen bond distances in Å and hydrogen bond angles in degrees. The relative energies (ΔE) with respect to the most stable conformer is shown in kcal mol^{-1}. Atom labeling is shown for selected systems.
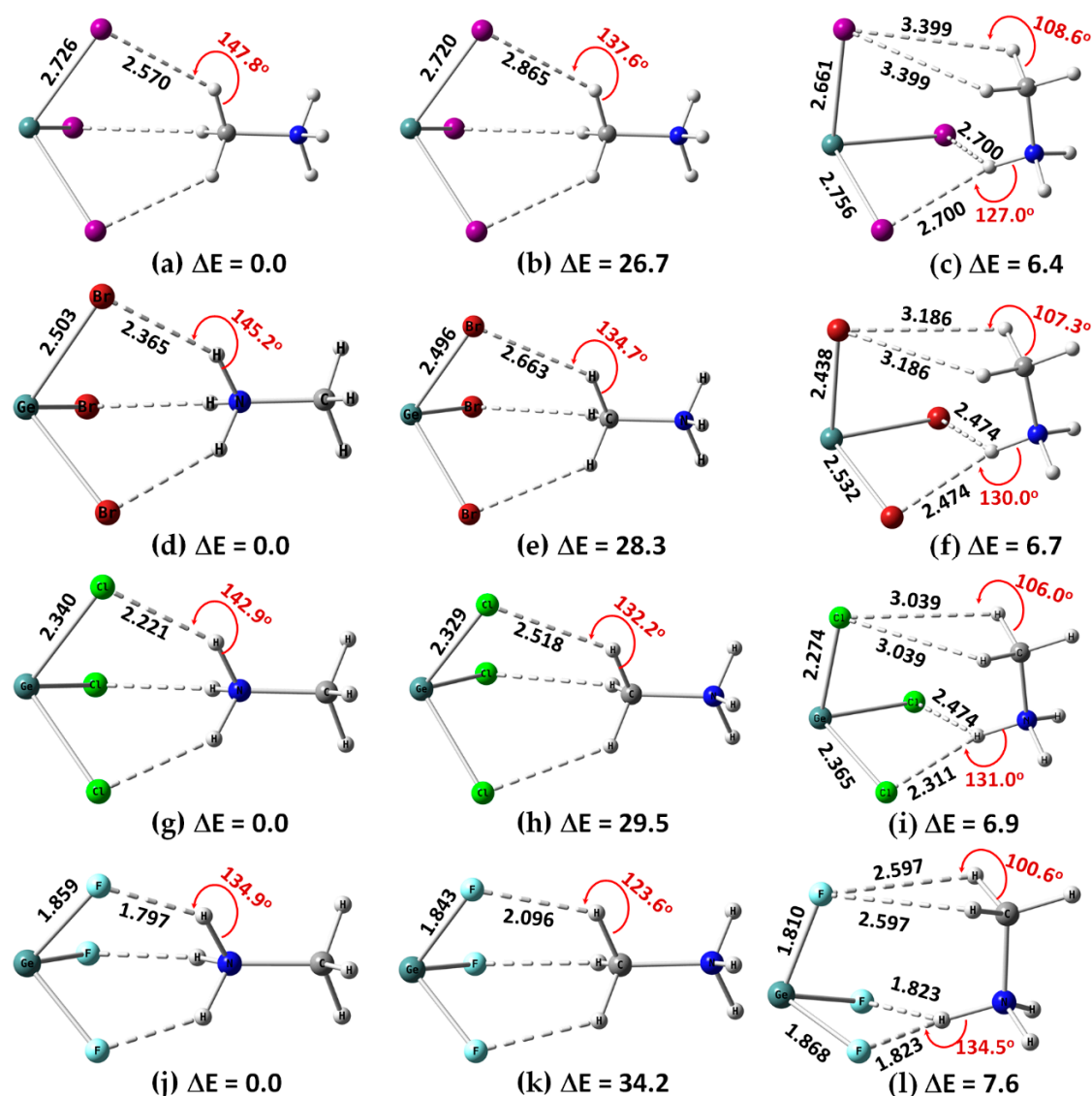
Figure S2. [ωB97XD/def2-TZVPPD] level fully-relaxed geometries of [CH₃NH₃⁺•GeX₃⁻] (X = F, Cl, Br, I) ion-pairs in the conformational space, including (a) [I₃Ge⋯NH₃CH₃]; (b) [I₃Ge⋯CH₃NH₃]; (c) [Br₃Ge⋯NH₃CH₃]; (d) [Br₃Ge⋯CH₃NH₃]; (e) [Cl₃Ge⋯NH₃CH₃]; (f) [Cl₃Ge⋯CH₃NH₃]; (g) [Cl₃Ge⋯H₃NCH₃]. Shown are selected coordinate and hydrogen bond distances in Å and hydrogen bond angles in degrees. The relative energies (Δ*E*) with respect to the most stable conformer is shown in kcal mol⁻¹. Atom labeling is shown for selected systems
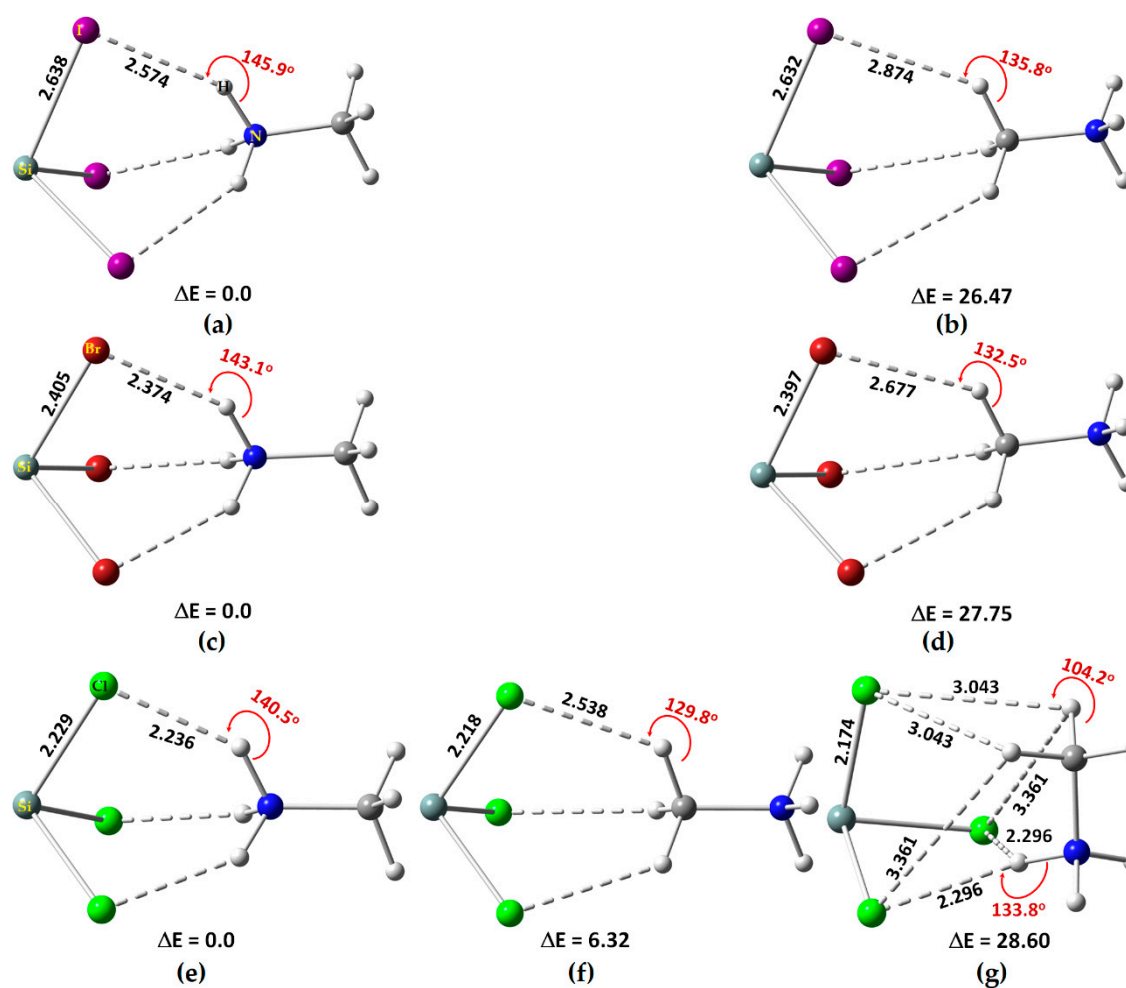
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Figure S3. [ωB97XD/def2-TZVPPD] level fully-relaxed geometries of [CH$_3$NH$_3{}^+\bullet$SiX$_3{}^-$] (X = Cl, Br, I) ion-pairs in the conformational space, including (a) [I$_3$Si$\cdots$NH$_3$CH$_3$]; (b) [I$_3$Si$\cdots$CH$_3$NH$_3$]; (c) [Br$_3$Si$\cdots$NH$_3$CH$_3$]; (d) [Br$_3$Si$\cdots$CH$_3$NH$_3$]; (e) [Cl$_3$Si$\cdots$NH$_3$CH$_3$]; (f) [Cl$_3$Si$\cdots$CH$_3$NH$_3$]; (g) [Cl$_3$Si$\cdots$H$_3$NCH$_3$]. Shown are selected coordinate and hydrogen bond distances in Å and hydrogen bond angles in degrees. The relative energies (ΔE) with respect to the most stable conformer is shown in kcal mol^{-1}. Atom labeling is shown for selected systems.
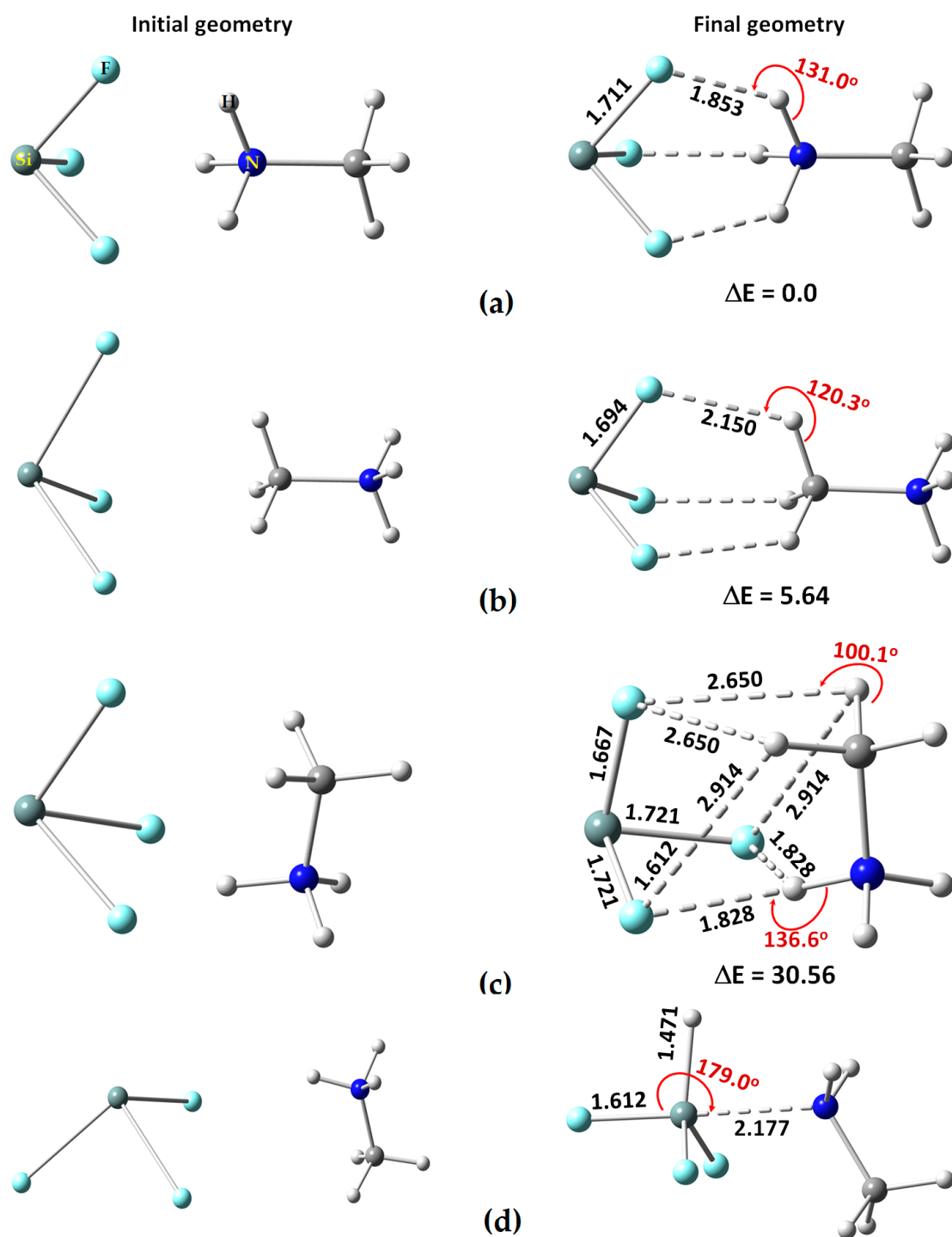
Figure S4. Initial (left) and final [ωB97XD/def2-TZVPPD] (right) configurations of [CH₃NH₃⁺•SiF₃⁻]. These include: (a) [F₃Si⋯NH₃CH₃]; (b) [F₃Si⋯CH₃NH₃]; (c) [F₃Si⋯H₃NCH₃]; (d) F₃HSi⋯NH₂CH₃. Shown (a)-(c) (right) are selected coordinate and hydrogen bond distances in Å and hydrogen bond angles in degrees. The relative energies (ΔE) with respect to the most stable conformer (a) is shown in kcal mol⁻¹. Atom labeling is shown in (a). Shown in (d) are selected coordinate bond and tetrel bond distances in Å and tetrel bond angle in degrees.
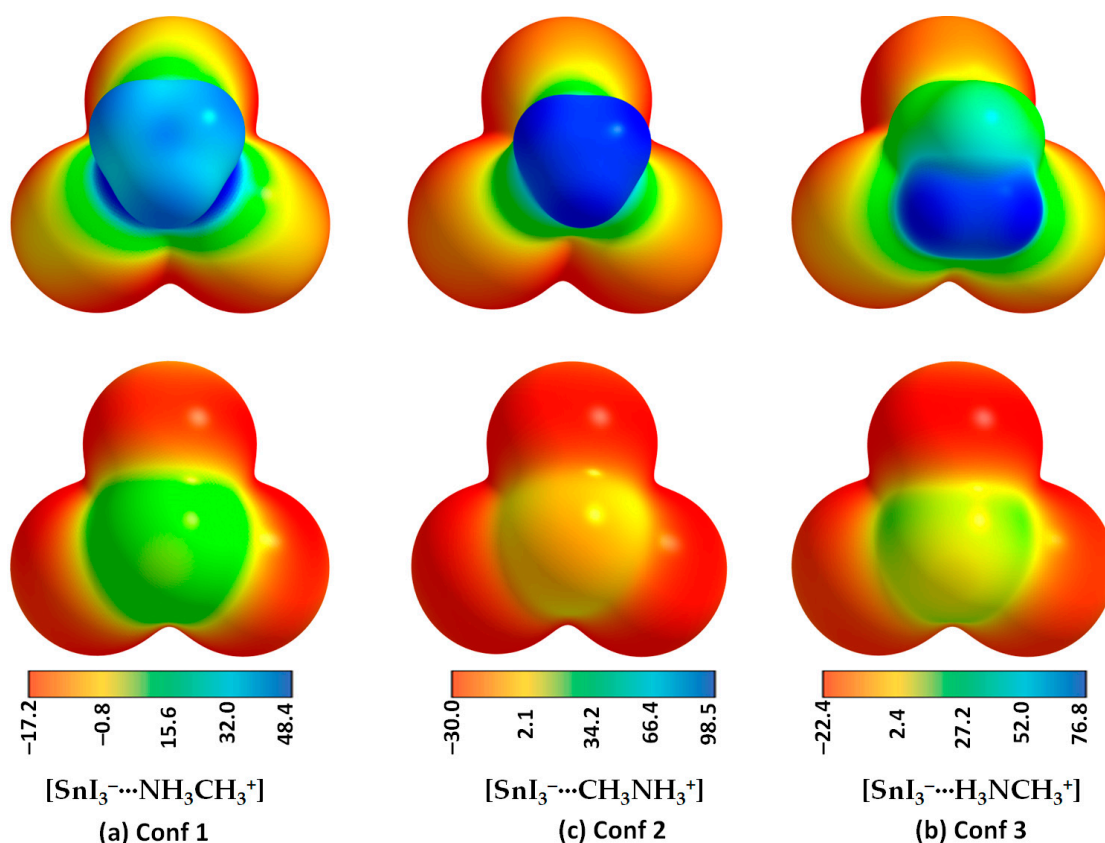
Figure S5. [ωB97XD/def2-TZVPPD] level potential on the electrostatic surface of the three conformations of [$CH_3NH_3^+ \bullet SnI_3^-$]: (a) [$SnI_3^- \cdots NH_3CH_3^+$]; (b) [$SnI_3^- \cdots CH_3NH_3^+$]; and (c) [$SnI_3^- \cdots H_3NCH_3^+$]. The methyl, ammonium and both groups of MA are facing the reader in the top panel of (a), (b) and (c), respectively. The Sn atom is facing the reader in the bottom panel of all the three MESP plots shown in (a)-(c). Values on the color bar are in kcal mol^{-1}. Atom labeling is shown for selected systems
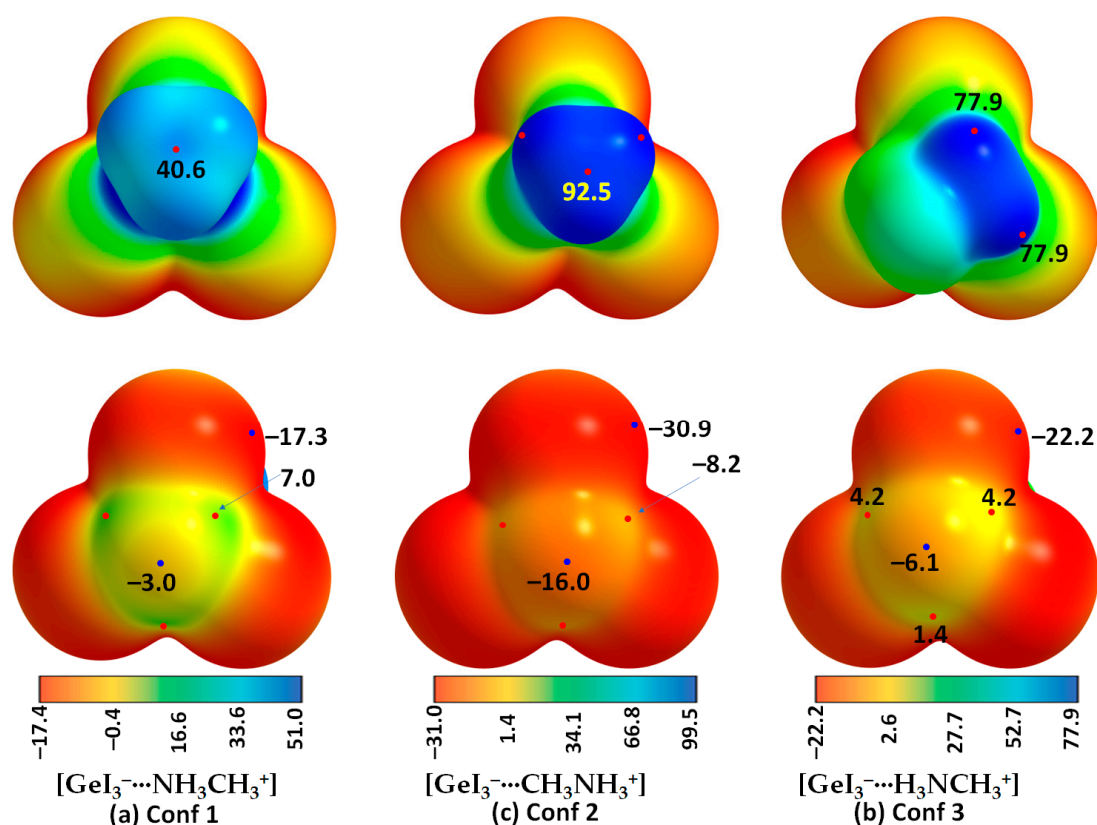
Figure S6. [ωB97XD/def2-TZVPPD] level potential on the electrostatic surface of the three conformations of [CH₃NH₃⁺•GeI₃⁻]: (a) [GeI₃⁻···NH₃CH₃⁺]; (b) [GeI₃⁻···CH₃NH₃⁺]; and (c) [GeI₃⁻···H₃NCH₃⁺]. The methyl, ammonium and both groups of MA are facing the reader in the top panel of (a), (b) and (c), respectively. The Sn atom is facing the reader in the bottom panel of all the three MESP plots shown in (a)-(c). Values on the color bar are in kcal mol⁻¹. Atom labeling is shown for selected systems.
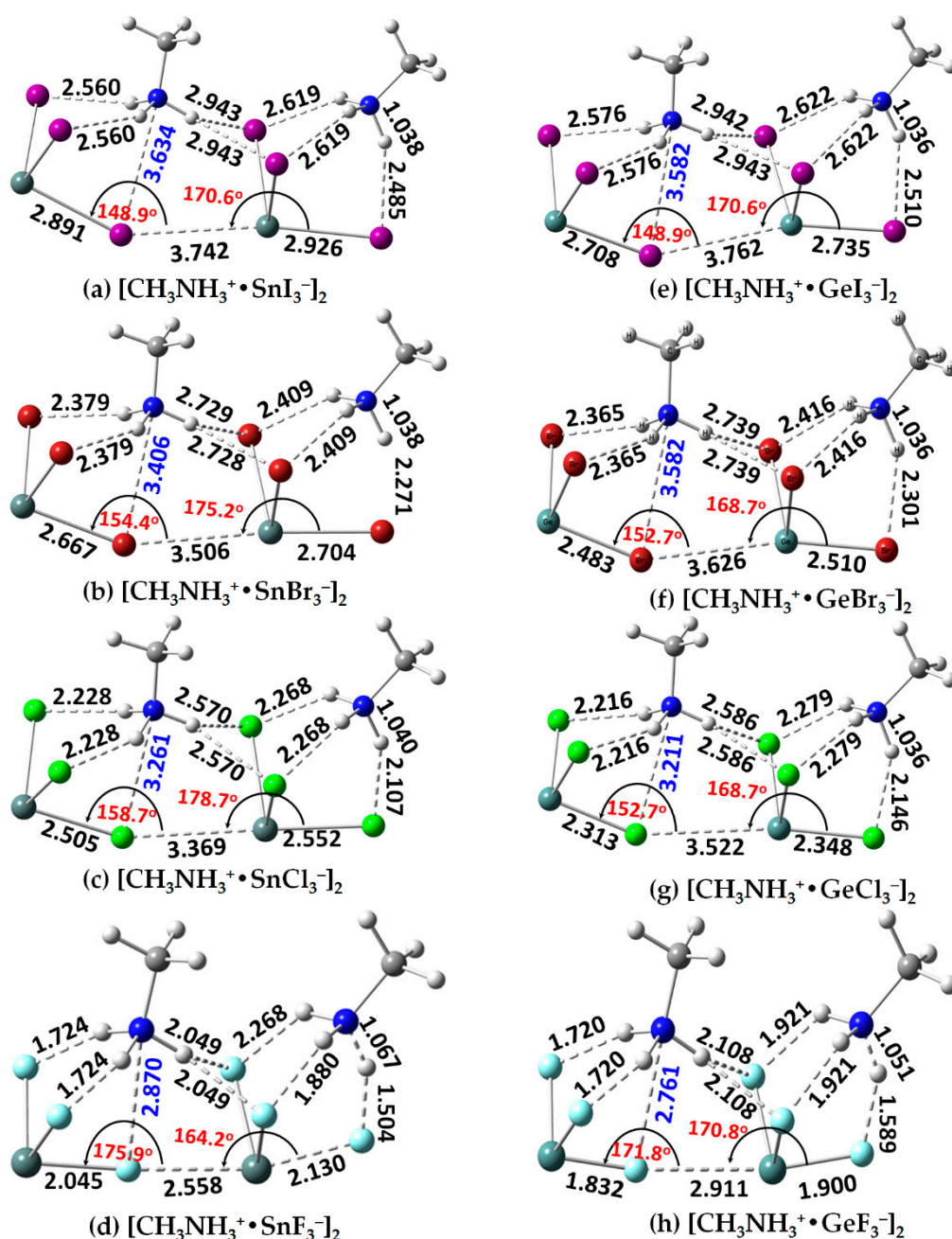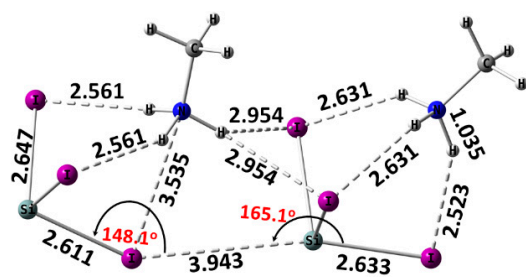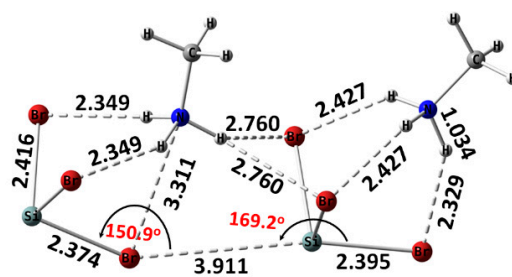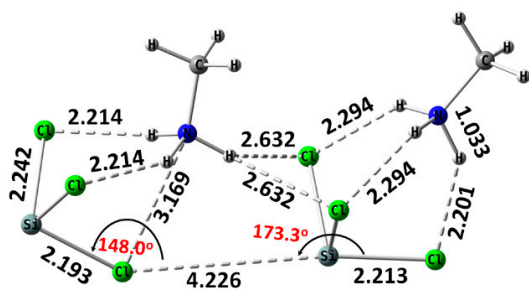
Figure S7. [*ω*B97XD/def2-TZVPPD] level fully relaxed gas-phase geometries of (a) [CH₃NH₃⁺•SnI₃⁻]₂; (b) [CH₃NH₃⁺•SnBr₃⁻]₂; (c) [CH₃NH₃⁺•SnCl₃⁻]₂; and (d) [CH₃NH₃⁺•SnF₃⁻]₂; (e) [CH₃NH₃⁺•GeI₃⁻]₂; (f) [CH₃NH₃⁺•GeBr₃⁻]₂; (g) [CH₃NH₃⁺•GeCl₃⁻]₂; and (d) [CH₃NH₃⁺•GeF₃⁻]₂. Selected bond lengths (Å) and bond angles (degrees) are shown in (a)-(h).
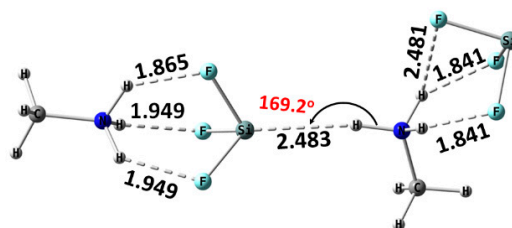
Figure S8. [ωB97XD/def2-TZVPPD] level fully relaxed gas-phase geometries of (a) [CH3NH3+•SiI3−]2; (b) [CH3NH3+•SiBr3−]2; (c) [CH3NH3+•SiCl3−]2; and (d) [CH3NH3+•SiF3−]2. Selected bond lengths (Å) and bond angles (degrees) are shown in (a)-(h). Atom labeling is shown for each case.
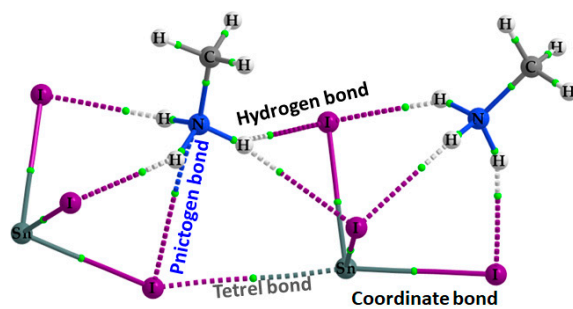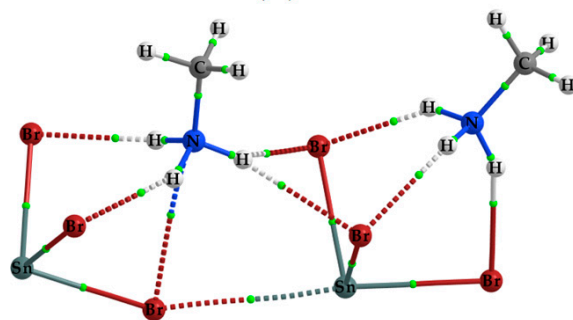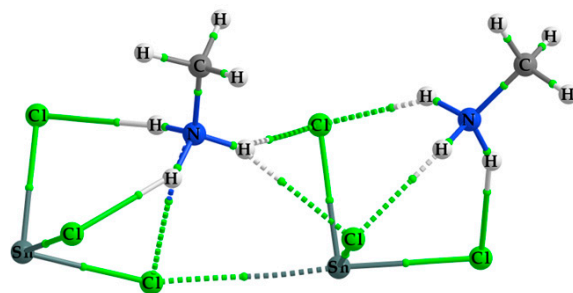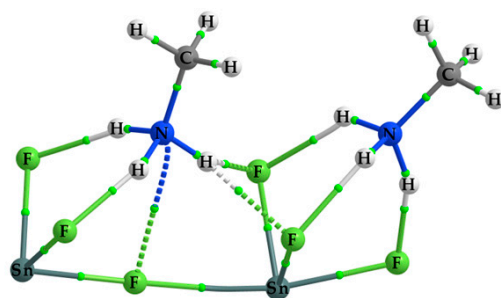
Figure S9. [ωB97XD/def2-TZVPPD] computed QTAIM based molecular graphs of a) [CH$_3$NH$_3$$^+$•SnI$_3$$^-$]$_2$; (b) [CH$_3NH_3$$^+$•SnBr$_3$$^-$]$_2$; (c) [CH$_3NH_3$$^+$•SnCl$_3$$^-$]$_2$; and (d) [CH$_3NH_3$$^+$•SnF$_3$$^-$]$_2$. The bond critical points between atomic basins are shown as tiny spheres in green, and bond paths as solid and lines in atom color. The values (in a.u.) of the charge density (ρ_b), the Laplacian of the charge density ($\nabla^2\rho_b$), and the total energy density (H_b) are given for selected bcps. Bond type and atom labeling is shown
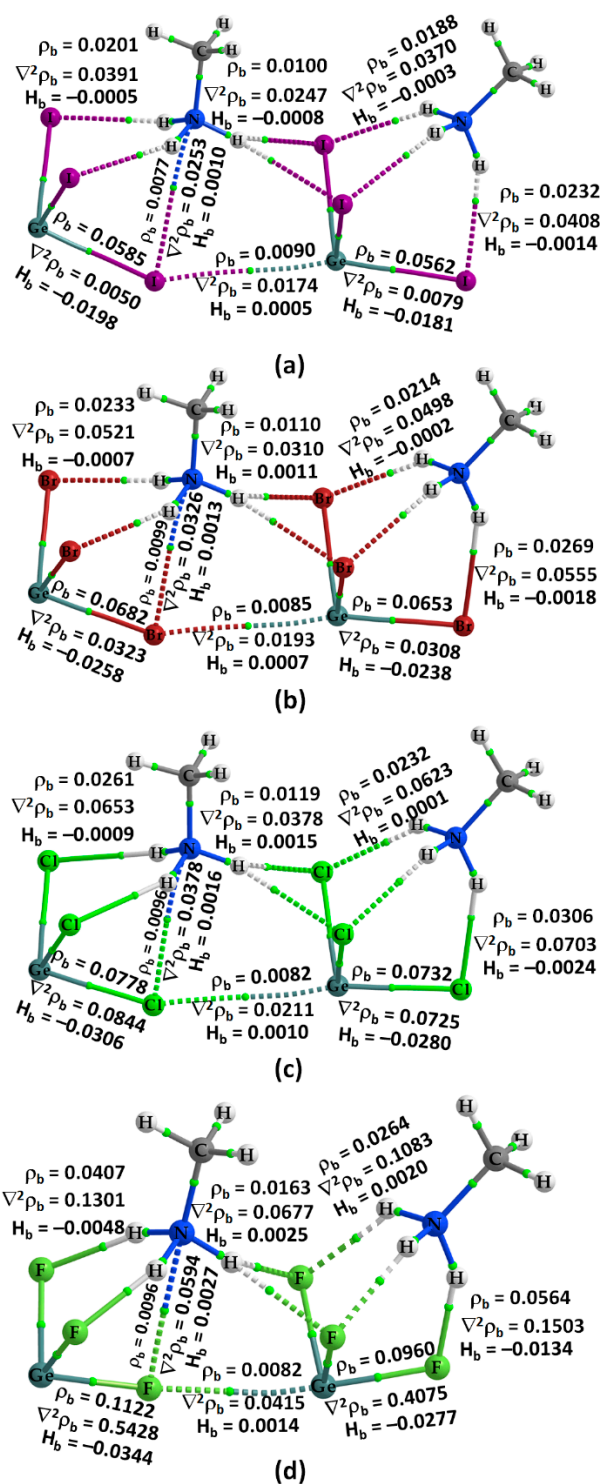
Figure S10. [ωB97XD/def2-TZVPPD] computed QTAIM based molecular graphs of a) [CH₃NH₃⁺•GeI₃⁻]₂; (b) [CH₃NH₃⁺•GeBr₃⁻]₂; (c) [CH₃NH₃⁺•GeCl₃⁻]₂; and (d) [CH₃NH₃⁺•GeF₃⁻]₂. The bond critical points between atomic basins are shown as tiny spheres in green, and bond paths as solid and lines in atom color. The values (in a.u.) of the charge density (ρ_b), the Laplacian of the charge density ($\nabla^2\rho_b$), and the total energy density (H_b) are given for selected bcps. Bond type and atom labeling is shown.
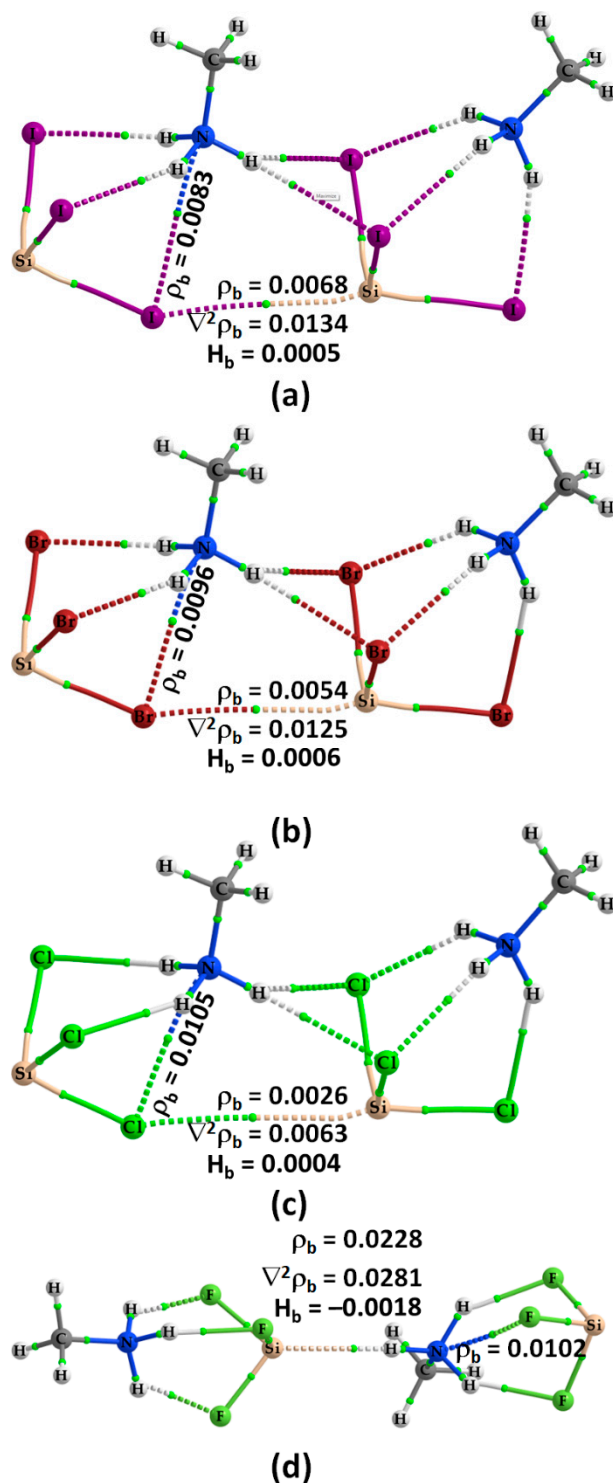
Figure S11. [ωB97XD/def2-TZVPPD] computed QTAIM based molecular graphs of a) [CH₃NH₃⁺•SiI₃⁻]₂; (b) [CH₃NH₃⁺•SiBr₃⁻]₂; (c) [CH₃NH₃⁺•SiCl₃⁻]₂; and (d) [CH₃NH₃⁺•SiF₃⁻]₂. The bond critical points between atomic basins are shown as tiny spheres in green, and bond paths as solid and lines in atom color. Bond type and atom labeling is shown. Charge density properties (ρ_b, $\nabla^2\rho_b$, and H_b) in a.u. are shown for selected bcps.

σ-hole region on Si

(a) [CH₃NH₃⁺•SiI₃⁻]₂

(b) [CH₃NH₃⁺•SiBr₃⁻]₂

(c) [CH₃NH₃⁺•SiCl₃⁻]₂

(c) [CH₃NH₃⁺•SiF₃⁻]₂

Figure S12. Two different views (left and right) of [ωB97XD/def2-TZVPPD] computed 0.001 a.u. mapped electrostatic potential on the molecular surfaces of a) [CH₃NH₃⁺•SiI₃⁻]₂; (b) [CH₃NH₃⁺•SiBr₃⁻]₂; (c) [CH₃NH₃⁺•SiCl₃⁻]₂; and (d) [CH₃NH₃⁺•SiF₃⁻]₂. Values on the color bar are in kcal mol⁻¹.

(a) o-MAPbI₃

(b) o-MAPbBr₃

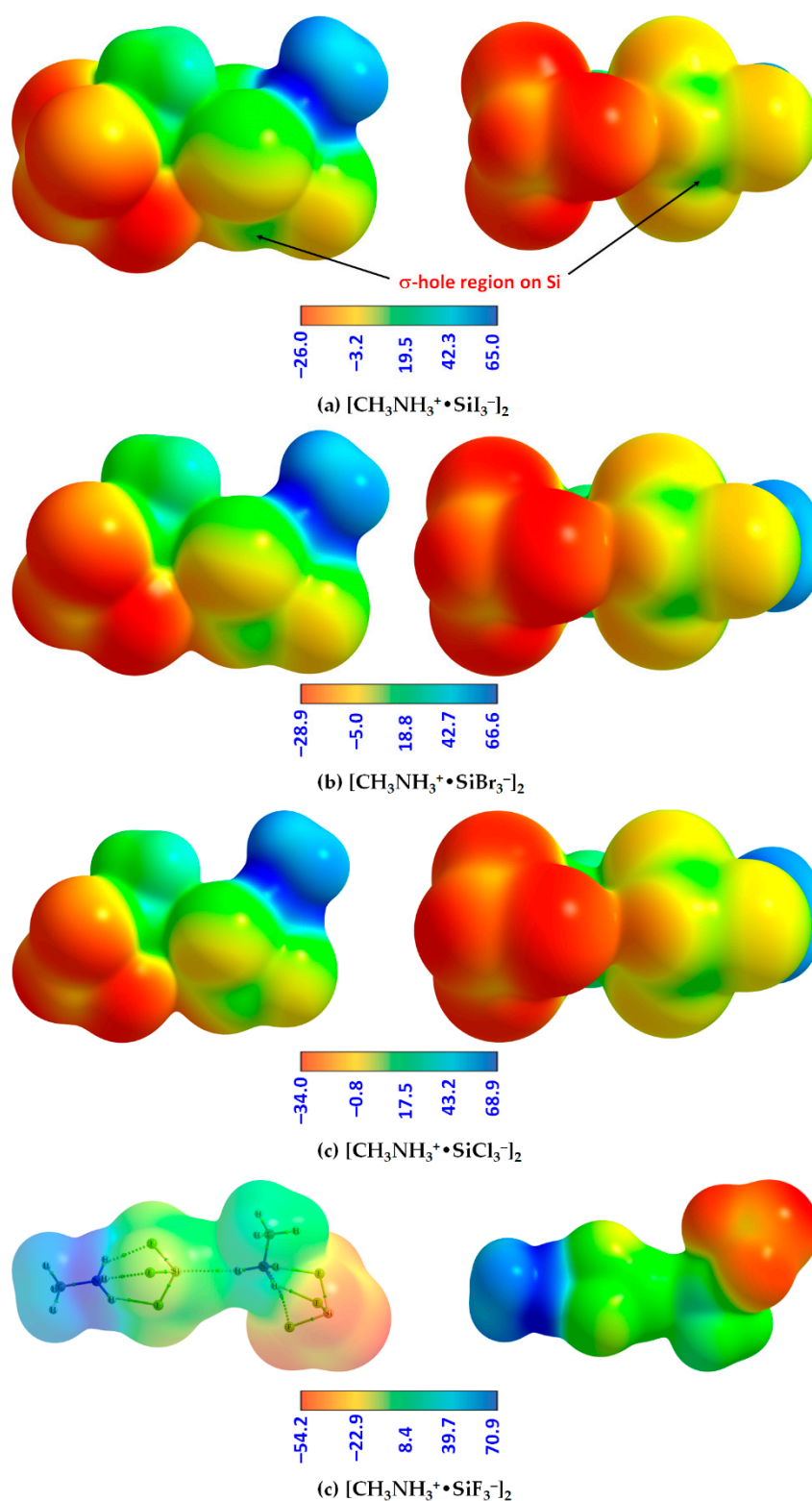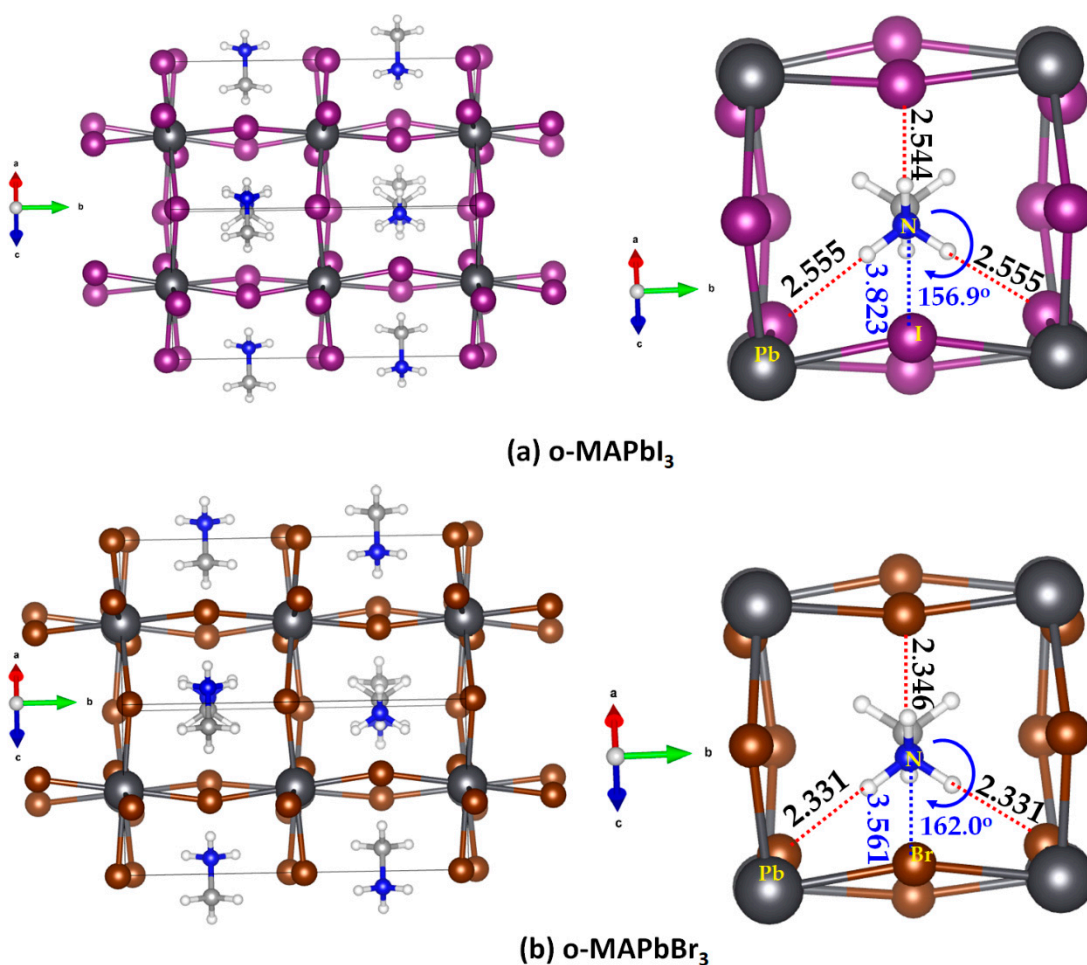**Figure S13.** (a) (left) [PBEsol/PAW] relaxed unit-cell geometry of MAPbI₃, showing (right) the nature of N–H⋯I hydrogen bond and C–N⋯I pnictogen bond. The pnictogen bond in the crystal (ICSD ref: 428898) of the corresponding has bond distance and bond angle of 3.786 Å and 152.6°, respectively, whereas the three N–H⋯I hydrogen bonds were 2.807, 2.807 and 2.613 Å. Shown in (b) is the [PBEsol/PAW] relaxed unit-cell geometry of MAPbBr₃, showing (right) the nature of N–H⋯Br hydrogen bond and C–N⋯Br pnictogen bond; the bond distance and bond angle of the latter contact in the crystal (ICSD ref: 268782), which has the H atoms in MA missing, were 3.570 Å and 155.0°, respectively. A k-mesh of 4 × 4 × 4, together with the global break condition for the electronic self-consistent and ionic relaxation loops were 10⁻⁶ and -10⁻² eV, respectively, was used. The VASP (version 5.4) code was used.

Table S1. Selected [MP2/def2-TZVPPD] computed 0.001 a.u. isoelectronic density envelope mapped maxima and minima of potential (kcal mol^{-1}) on the electrostatic surfaces of X$_3$Pb$^-$···MA ion-pairs, where X = I, Br, Cl, F, and MA = NH$_3$CH$_3^+$.[a]

Ion-pairs	$V_{S,max}$(X–Pb)	$V_{S,max}$(X–Pb)	$V_{S,max}$(X–Pb)	$V_{S,min}$(Pb)	$V_{S,max}$(N-C)/$V_{S,max}$(C-N)	$V_{S,min}$ (X)
I$_3$Pb···NH$_3$CH$_3$	25.7	25.7	25.7	23.8	36.2	-17.4
Br$_3$Pb···CH$_3$NH$_3$	27.3	27.3	27.3	25.0	35.0	-20.3
Cl$_3$Pb···H$_3$NCH$_3$	26.9	26.9	26.9	24.3	33.7	-23.2
F$_3$Pb···NH$_3$CH$_3$	24.4	24.4	24.4	19.6	27.0	-37.1

[a] The repetition of $V_{S,max}$(X–Pb) three times suggest that they belong to three equivalent σ-holes along the outer extensions of three Pb–X bonds of the inorganic anion of an ion-pair.

Table S2. Selected [MP2/aug-cc-pVTZ] computed 0.001 a.u. isoelectronic density envelope mapped maxima and minima of potential (kcal mol^{-1}) on the electrostatic surfaces of X$_3$Pb$^-$···MA ion-pairs, where X = I, Br, Cl, F, and MA = NH$_3$CH$_3^+$.[a,b]

Ion-pairs	$V_{S,max}$(X–Pb)	$V_{S,max}$(X–Pb)	$V_{S,max}$(X–Pb)	$V_{S,min}$(Pb)	$V_{S,max}$(N-C)/$V_{S,max}$(C-N)	$V_{S,min}$ (X)
I$_3$Pb···NH$_3$CH$_3$	23.4	23.4	23.4	19.6	36.0	-16.0
Br$_3$Pb···CH$_3$NH$_3$	24.5	24.5	24.5	19.7	34.9	-19.1
Cl$_3$Pb···H$_3$NCH$_3$	24.3	24.3	24.3	18.8	34.4	-22.4
F$_3$Pb···NH$_3$CH$_3$	22.3	22.3	22.3	14.8	27.9	-36.0

[a] The pseudo-potential aug-cc-pVTZ-PP was used for Pb and I.

[b] The repetition of $V_{S,max}$(X–Pb) three times suggest that they belong to three equivalent σ-holes along the outer extensions of three Pb–X bonds of the inorganic anion of an ion-pair.