Supporting Information

Is Pentavalent Pr(V) Feasible in Solid $CsPrF_6$?

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I. $CsPrF_6$ Structure and Corresponding Properties

The crystal structure of $CsPrF_6$ is shown in Figure S1 and corresponding lattice parameters are listed in Table S1.

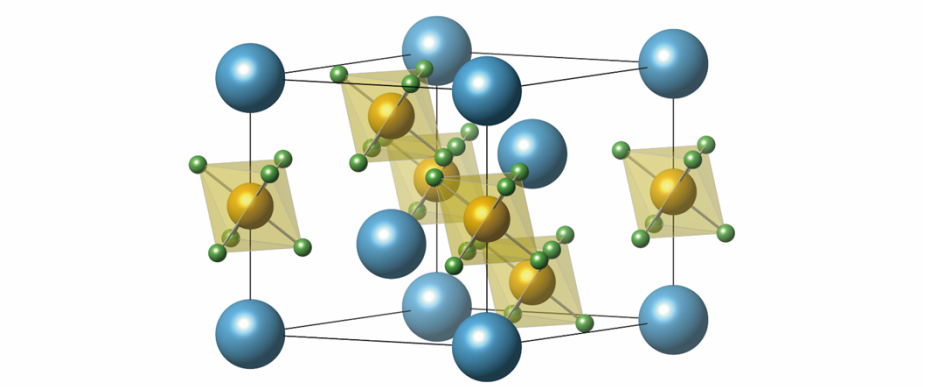

Figure S1. The structure of $CsPrF_6$ (Color scheme: Blue: Cs; Yellow: Pr; Green: F)

Table S1. The crystallographic parameters for prediction $CsPrF_6$ crystal structure

$CsPrF_6$ Lattice Parameter	
formula weight (g/ mol)	387.8
crystal system	Rhombohedral
space group	$R\bar{3}$(#148)
a = b (Å)	7.799
c (Å)	8.079
α = β (°)	90
γ (°)	120
Z	3
volume ($Å^3$)	421.31
density, calc (g/ cm^3)	4.585

The structure can be considered to consist four components as shown in Figure S2: (A) Cs^+ on the vertices of the crystal unit cell, (B) Cs+ on the body diagonal, (C) $[PrF_6]^-$ octahedra on the medium of the edge, and (D) $[PrF_6]^-$ octahedra within the tetrahedral of Cs^+

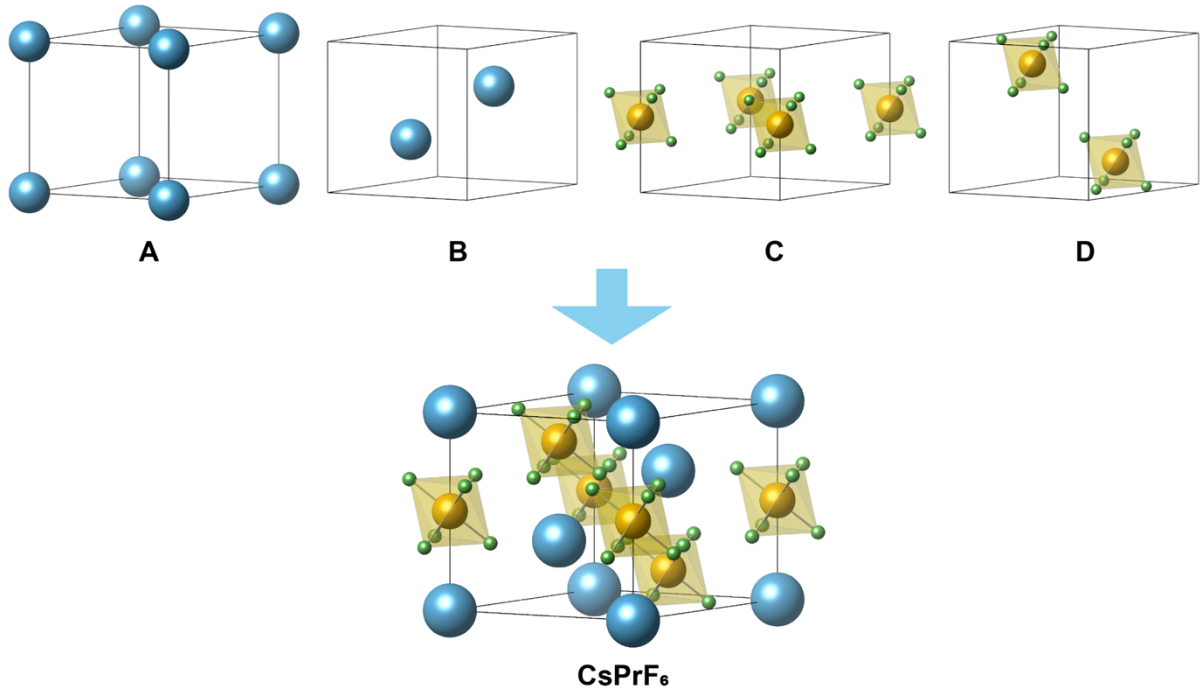

Figure S2. The components of $CsPrF_6$. (A) Cs^+ on the vertices, (B) Cs+ on the body diagonal, (C) $[PrF_6]^-$ octahedra on the medium of the edge, (D) $[PrF_6]^-$ octahedra within the tetrahedral of Cs^+ (Color scheme: Blue: Cs; Yellow: Pr; Green: F)

This optimal $CsPrF_6$ structure has been further confirmed to be stable by phonon spectrum calculations along the high-symmetry lines in the Brillouin zone. The spectrum was evaluated within the harmonic approximation by finite displacement method, and the spectra are constructed by using Phonopy program. A ($3 \times 3 \times 3$) supercell geometry was employed with a $1 \times 1 \times 1$ k-point grid for the $CsPrF_6$ cell. The phonon spectrum is shown in Figure S3. Therefore, we can validate the kinetic stability of $CsPrF_6$. And the thermodynamic free energies data with the entropy and zero-point energies corrected of F_2, CsF, PrF_3 and $CsPrF_6$ at ambient temperature and pressure (300K, 1 atm) are listed in Table S2.

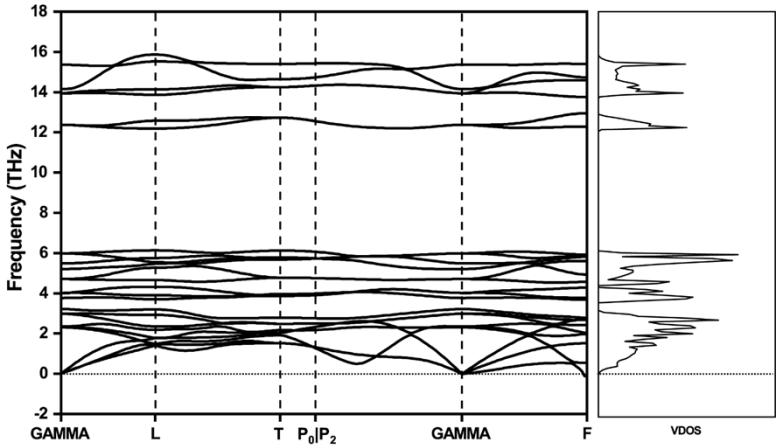

Figure S3. The calculated phonon spectrum of $CsPrF_6$ solid. The Gamma, L, T, P_0, P_2, F represent the k-points of (0, 0, 0), (0.5, 0, 0), (0.5, -0.5, 0.5), (0.403, -0.597, 0.403), (0.403, 0.403, 0.403) and (0.5, -0.5, 0) in the first Brillouin zone

Table S2. The Gibbs free energy with the entropy and zero-point energies (ZPE) corrected of F_2, CsF, PrF_3, Cs_2PrF_6 and $CsPrF_6$ at ambient temperature and pressure (300K, 1 atm)

Species	Pr-F Bond Length/ Å	E_{ele}/ eV	Correction/ eV	Gibbs Free Energy/ eV
F_2		− 3.709	− 0.476	− 4.186
CsF		− 8.033	− 0.144	− 8.178
PrF_3	2.422	− 28.236	0.036	− 28.201
Cs_2PrF_6	2.141	− 48.763	4.676	− 44.086
$CsPrF_6$	2.077	− 43.601	− 0.177	− 43.778

Plausible methods for synthesizing $CsPrF_6$ and its reaction energy are outlined in following reaction equation:

$$\mathbf{PrF_3(s) + F_2(g) + CsF(s) \rightarrow CsPrF_6(s)} \qquad \mathbf{\Delta G_{300K} = -74.1\ kcal/\ mol} \qquad \mathbf{(1)}$$

$$\mathbf{Cs_2PrF_6(s) + \frac{1}{2}\,F_2(g) \rightarrow CsPrF_6(s) + CsF(s)} \qquad \mathbf{\Delta G_{300K} = -133.2\ kcal/\ mol} \qquad \mathbf{(2)}$$

II. Structure and Corresponding Properties of Cs_2PrF_6, PrF_3, CsF and F_2

Cs_2PrF_6

The structure of Cs_2PrF_6 was obtained by OQMD with a space group ($Fm\bar{3}m$). The bond length between Pr and F after optimization is 2.141 Å. The crystal structure of Cs_2PrF_6 is shown in Figure S4 and corresponding lattice parameters are listed in Table S3. The phonon spectrum is shown in Figure S5. The phonon spectrum has no virtual frequency, which indicates the structure is stable.

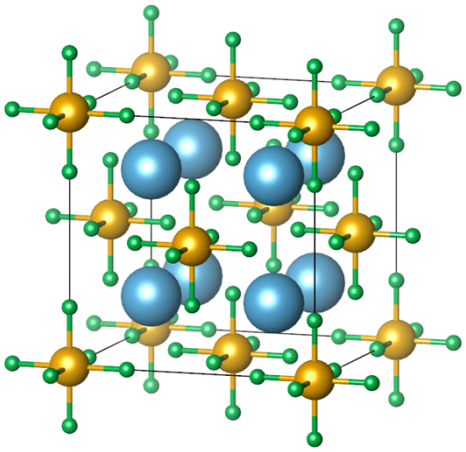

Figure S4. The structure of Cs_2PrF_6 after optimization (Color scheme: Blue: Cs; Yellow: Pr; Green: F)

Table S3. The lattice parameter of Cs_2PrF_6

Species	Space Group	Lattice Parameters		Bond Length
		a/ Å	α/ °	r(Pr-F)/ Å
Cs_2PrF_6	225 ($Fm\bar{3}m$)	9.184	90	2.141

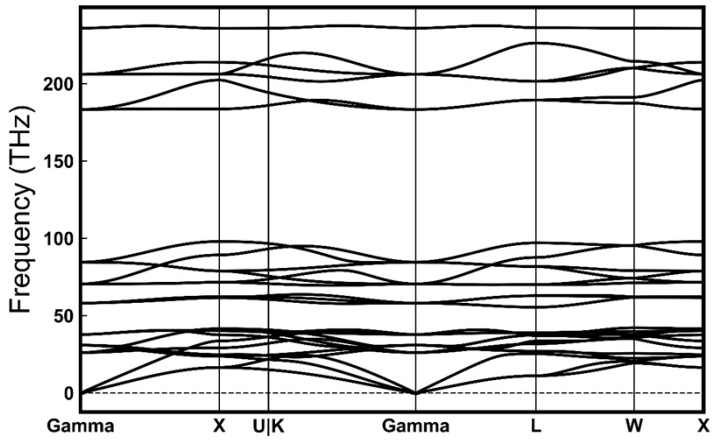

Figure S5. The calculated phonon spectrum of Cs_2PrF_6 solid. The Gamma, X, U, K, L and W represent the k-points of (0, 0, 0), (0.5, 0, 0.5), (0.625, 0.25, 0.625), (0.375, 0.375, 0.75), (0.5, 0.5, 0.5) and (0.5, 0.25, 0.75) in the first Brillouin zone.

PrF_3

The structure of PrF_3 was obtained by ICSD with a space group (P3c1). The bond length between Pr and F after optimization is 2.410 Å. The crystal structure of PrF_3 is shown in Figure S6 and corresponding lattice parameters are listed in Table S4. The phonon spectrum is shown in Figure S7. The phonon spectrum has no virtual frequency, which indicates the structure is stable.

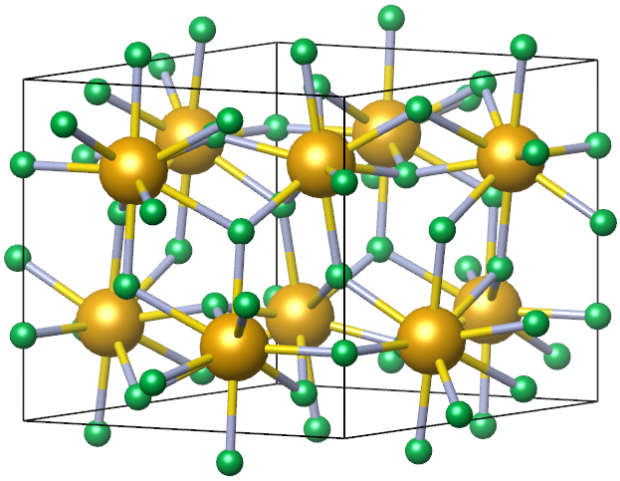

Figure S6. The structure of PrF_3 after optimization (Color scheme: Yellow: Pr; Green: F)

Table S4. The lattice parameter of PrF_3

Species	Space Group	Lattice Parameters				Bond Length
		a/ Å	c/ Å	α/ °	γ/ °	r(Pr-F)/ Å
PrF_3	165 (P3c1)	7.069	7.225	90	120	2.410

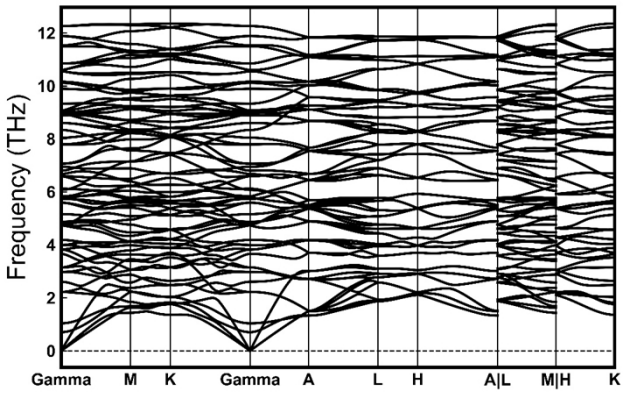

Figure S7. The calculated phonon spectrum of PrF_3 solid. The Gamma, M, K, A, L and H represent the k-points of (0, 0, 0), (0.5, 0, 0), (0.33, 0.33, 0), (0, 0, 0.5), (0.5, 0, 0.5) and (0.33, 0.33, 0.5) in the first Brillouin zone.

CsF

The structure of CsF was obtained by ICSD with a space group ($Fm\bar{3}m$). The crystal structure of CsF is shown in Figure S8 and corresponding lattice parameters are listed in Table S5. The phonon spectrum is shown in Figure S9. The phonon spectrum has no virtual frequency, which indicates the structure is stable.

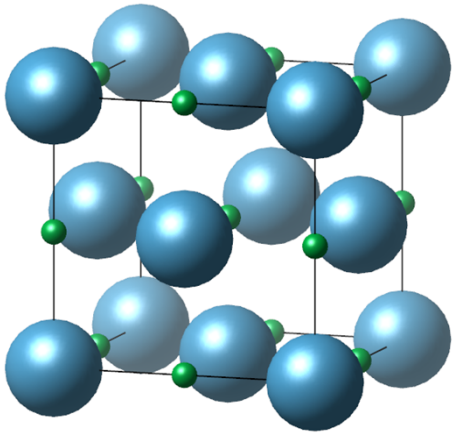

Figure S8. The structure of CsF after optimization (Color scheme: Blue: Cs; Green: F)

Table S5. The lattice parameter of CsF

Species	Space Group	Lattice Parameters	
		a/ Å	α/ °
CsF	225 ($Fm\bar{3}m$)	6.118	90

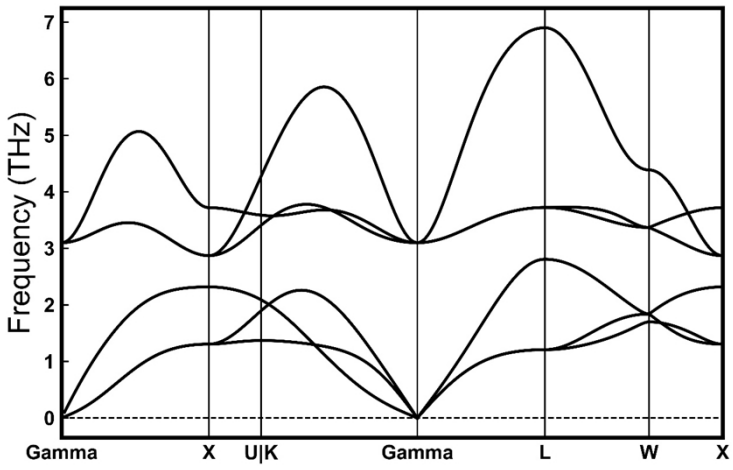

Figure S9. The calculated phonon spectrum of CsF solid. The Gamma, X, U, K, L and W represent the k-points of (0, 0, 0), (0.5, 0, 0.5), (0.625, 0.25, 0.625), (0.375, 0.375, 0.75), (0.5, 0.5, 0.5) and (0.5, 0.25, 0.75) in the first Brillouin zone.

F_2

For the free energy calculation of F_2 molecules, a cell of 20Å × 20Å × 20Å was constructed to obtain F_2 electron energy (Figure S10), and then performed a vibration analysis on it.

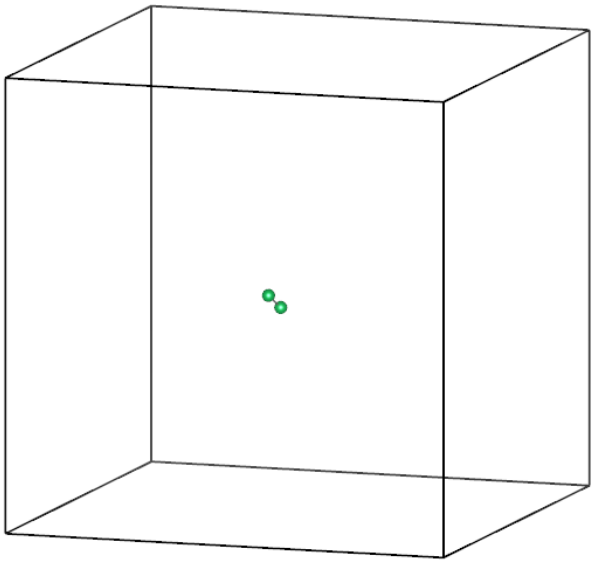

Figure S10. The ideal gas box of F_2 (Color scheme: Green: F)

III. HSE06 band structure of $CsPr^{II}F_3$, $Cs_3Pr^{III}F_6$, and $Cs_2Pr^{IV}F_6$ crystal.

The band structure of $CsPr^{II}F_3$, $Cs_3Pr^{III}F_6$, and $Cs_2Pr^{IV}F_6$ crystal was shown in Figure S11 - S13.

$CsPrF_3$

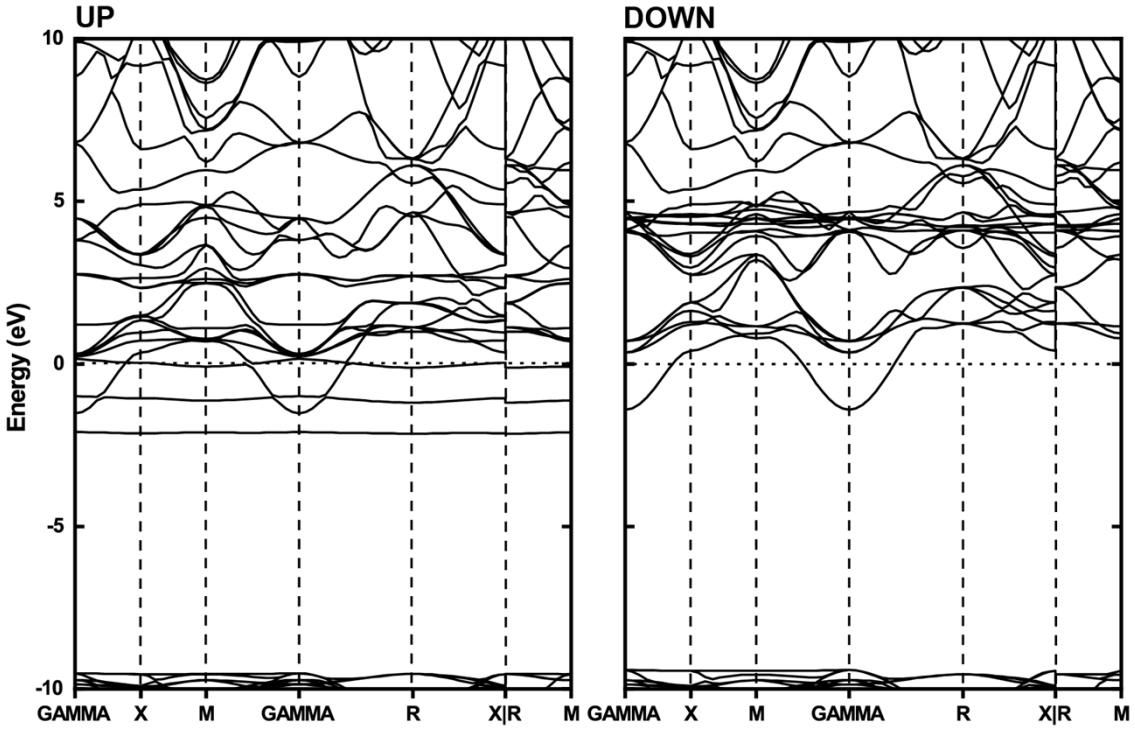

Figure S11. HSE06 band structure of $CsPr^{II}F_3$. The Fermi level is assigned at 0 eV. The four points of Gamma (0, 0, 0), X (0, 0.5, 0), M (0.5, 0.5, 0), and R (0.5, 0.5, 0.5) refer to high-symmetry points of the first Brillouin zone in reciprocal space.

Cs_3PrF_6

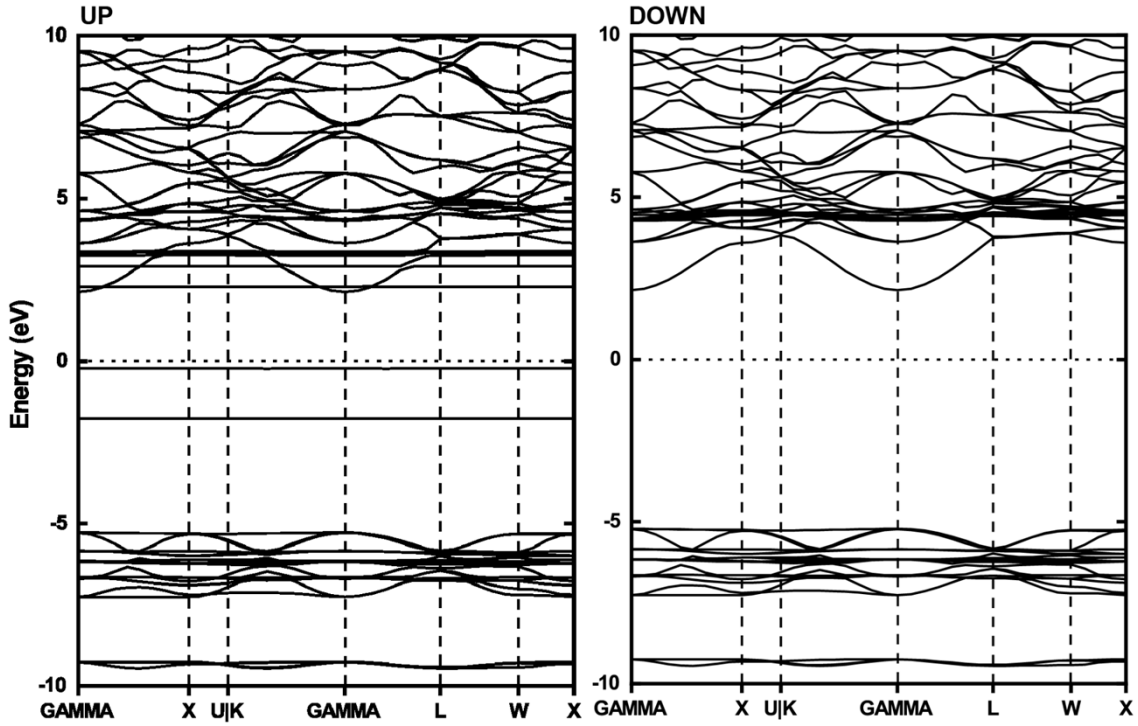

Figure S12. HSE06 band structure of $Cs_3Pr^{III}F_6$. The Fermi level is assigned at 0 eV. The six points of Gamma (0, 0, 0), X (0.5, 0, 0.5), U (0.625, 0.25, 0.625), K (0.375, 0.375, 0.75), L (0.5, 0.5, 0.5), and W (0.5, 0.25, 0.75) refer to high-symmetry points of the first Brillouin zone in reciprocal space.

Cs_2PrF_6

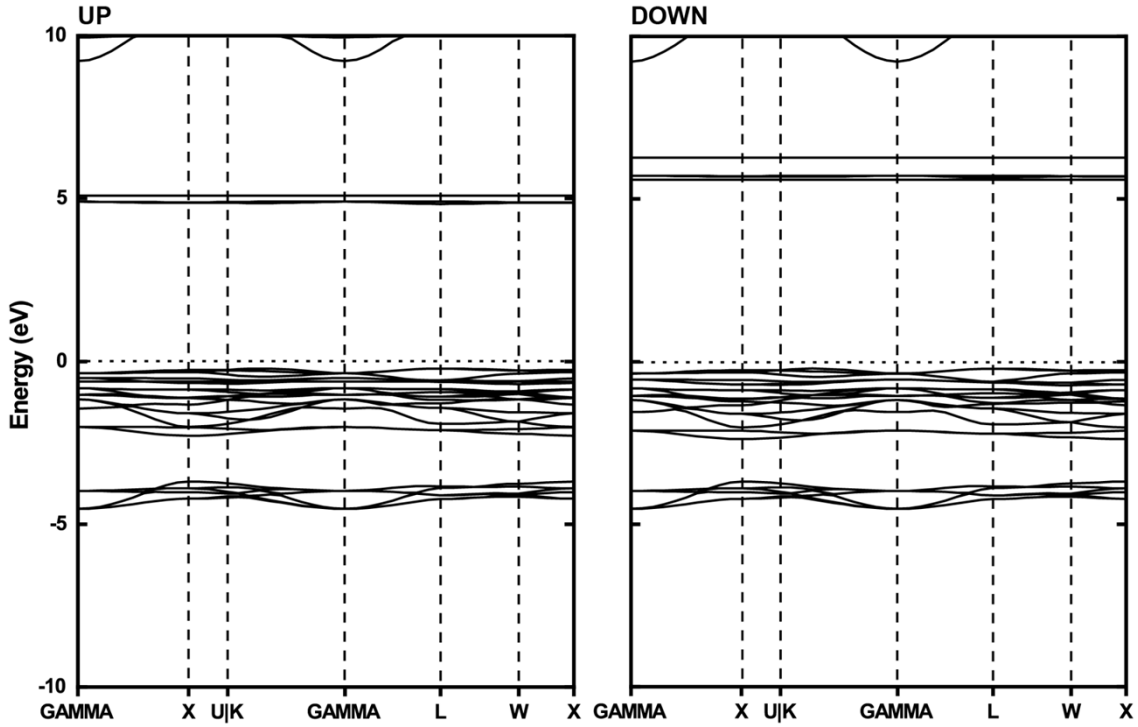

Figure S13. HSE06 band structure of $Cs_2Pr^{IV}F_6$. The Fermi level is assigned at 0 eV. The six points of Gamma (0, 0, 0), X (0.5, 0, 0.5), U (0.625, 0.25, 0.625), K (0.375, 0.375, 0.75), L (0.5, 0.5, 0.5), and W (0.5, 0.25, 0.75) refer to high-symmetry points of the first Brillouin zone in reciprocal space.

IV. The pDOS analysis of $CsPr^{II}F_3$, $Cs_3Pr^{III}F_6$, and $Cs_2Pr^{IV}F_6$ crystal.

The pDOS data of $CsPr^{II}F_3$, $Cs_3Pr^{III}F_6$, and $Cs_2Pr^{IV}F_6$ crystals are shown in Figure S14 - S16.

$CsPrF_3$

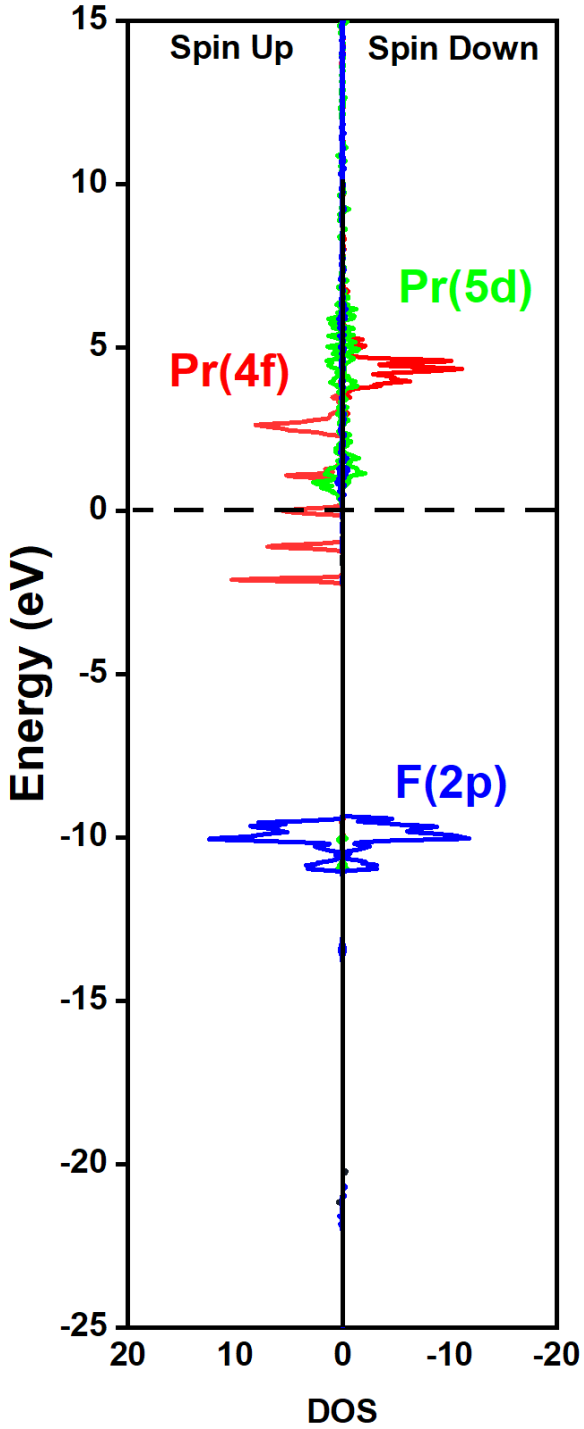

Figure S14. Partial density of states (PDOS) of $CsPr^{II}F_3$ crystal. The Fermi level is assigned at 0 eV.

Cs_3PrF_6

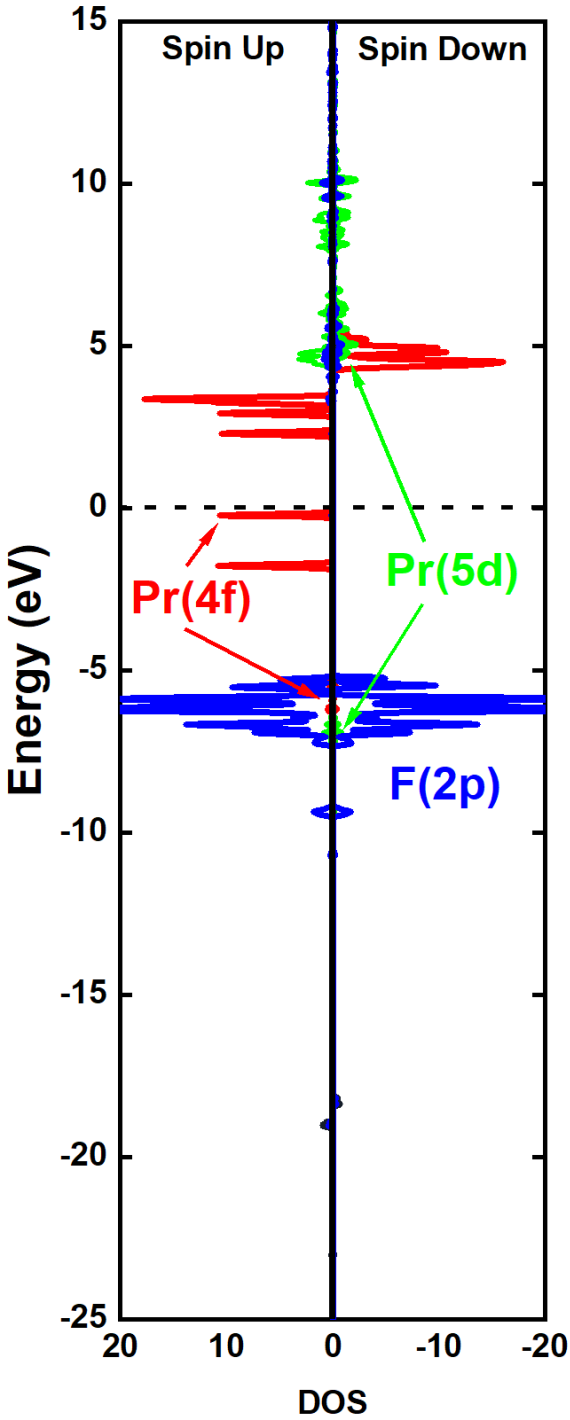

Figure S15. Partial density of states (PDOS) of $Cs_3Pr^{III}F_6$ crystal. The Fermi level is assigned at 0 eV.

Cs_2PrF_6

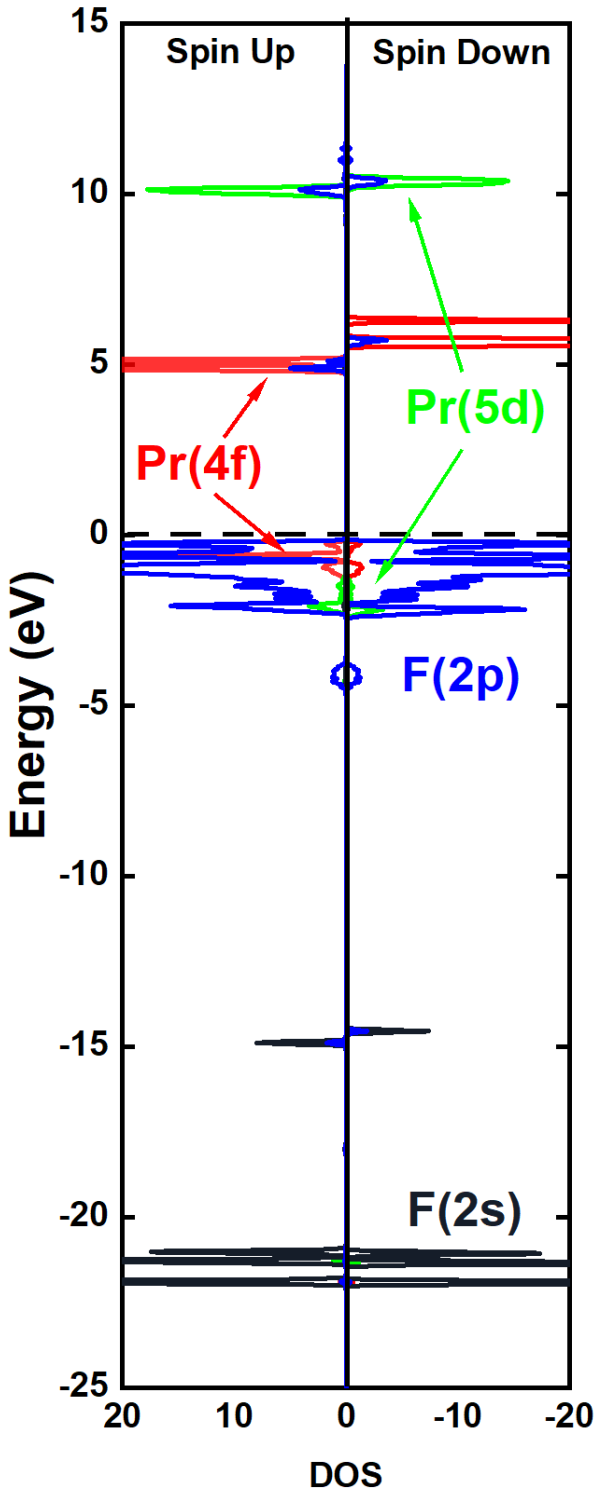

Figure S16. Partial density of states (PDOS) of $Cs_2Pr^{IV}F_6$ crystal. The Fermi level is assigned at 0 eV.

V. The spin density analysis of $CsPr^{II}F_3$, $Cs_3Pr^{III}F_6$, $Cs_2Pr^{IV}F_6$, and $CsPr^{V}F_6$ crystal.

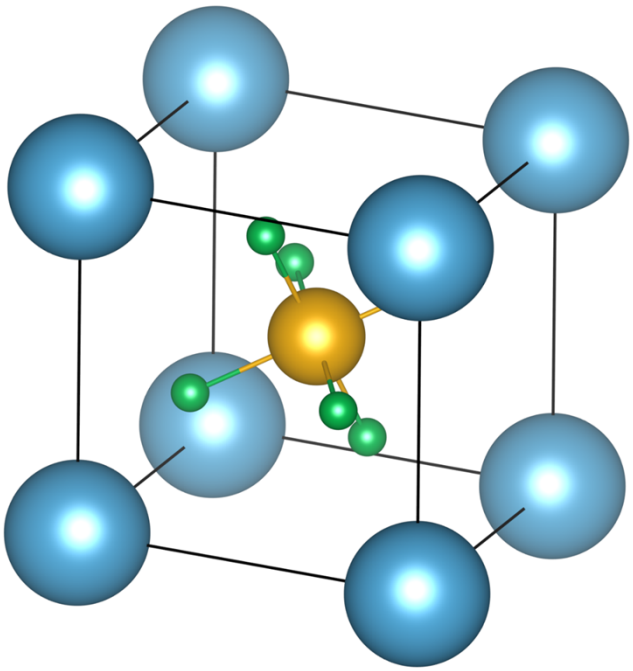

Figure S17. The spin density of primary $CsPr^{V}F_6$ cell. The isovalue is 0.002 e/Å^3.

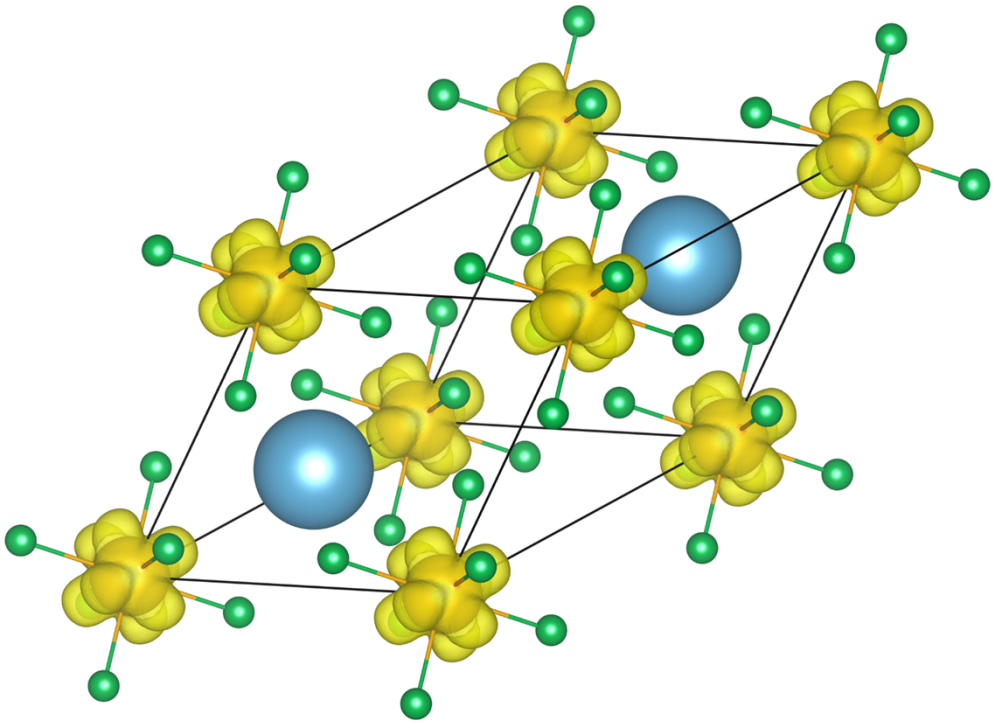

Figure S18. The spin density of primary $Cs_2Pr^{IV}F_6$ cell. The isovalue is 0.002 e/Å^3.

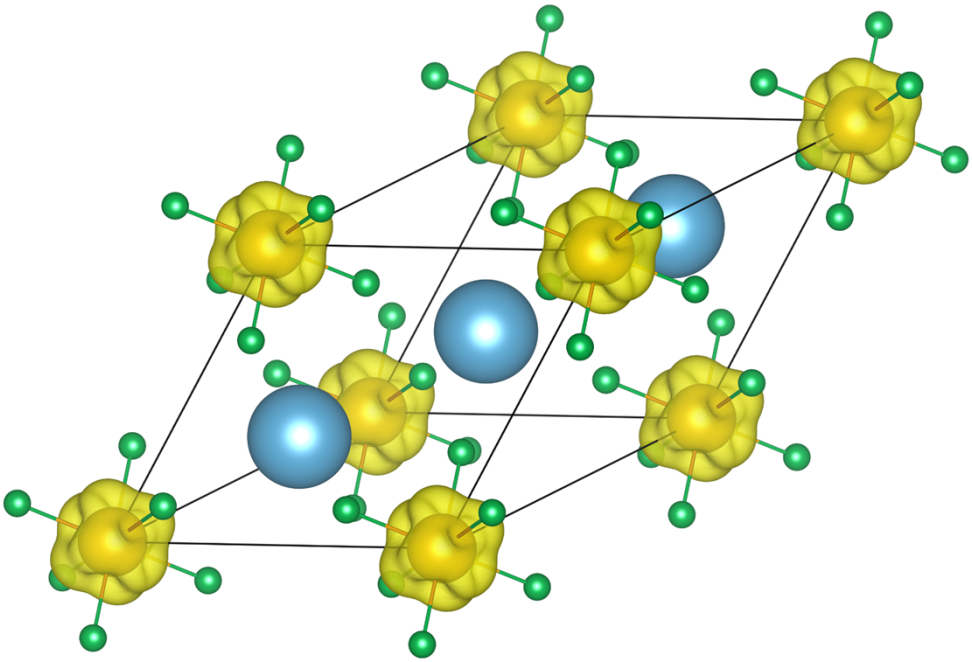

Figure S19. The spin density of primary $Cs_3Pr^{III}F_6$ cell. The isovalue is 0.002 e/Å^3.

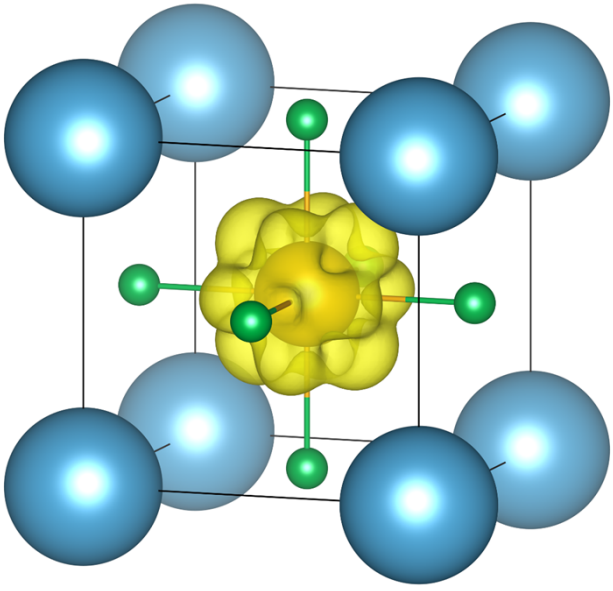

Figure S20. The spin density of primary $CsPr^{II}F_3$ cell. The isovalue is 0.002 e/Å^3.

VI. The COHP analysis of $CsPr^{II}F_3$, $Cs_3Pr^{III}F_6$, and $Cs_2Pr^{IV}F_6$ crystal.

The COHP data of $CsPr^{II}F_3$, $Cs_3Pr^{III}F_6$, and $Cs_2Pr^{IV}F_6$ crystal was shown in Figure S17 - S19.

$CsPrF_3$

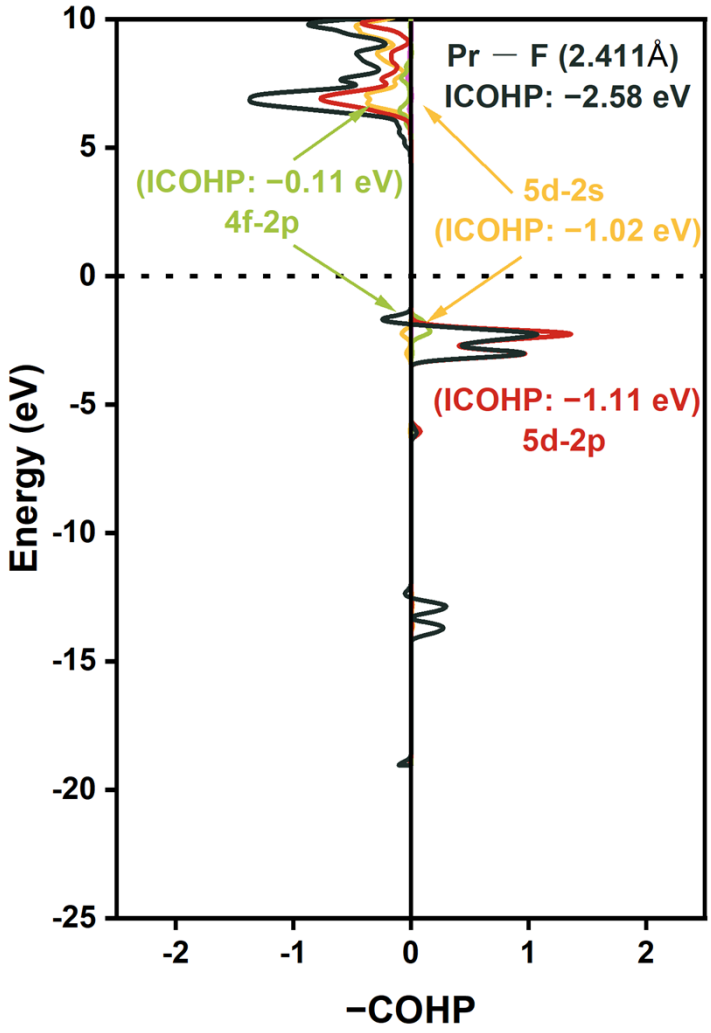

Figure S21. The crystal orbital Hamilton population (COHP) analysis of Pr–F interactions in solid-state $CsPr^{II}F_3$. Zero line (dotted) represents the Fermi level. The ICOHP values (in eV/bond) are listed here to show the corresponding interactions (black) and main orbital-pair contributions to these (colored).

Cs_3PrF_6

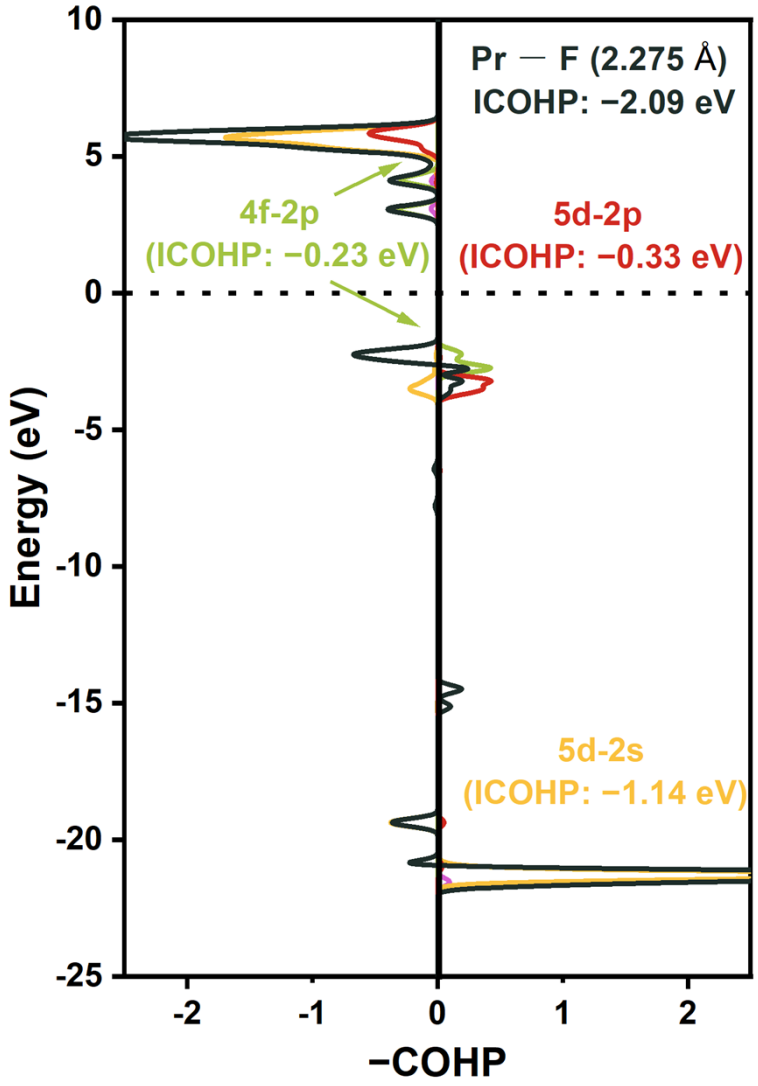

Figure S22. The crystal orbital Hamilton population (COHP) analysis of Pr–F interactions in solid-state $Cs_3Pr^{III}F_6$. Zero line (dotted) represents the Fermi level. The ICOHP values (in eV/bond) are listed here to show the corresponding interactions (black) and main orbital-pair contributions to these (colored).

Cs_2PrF_6

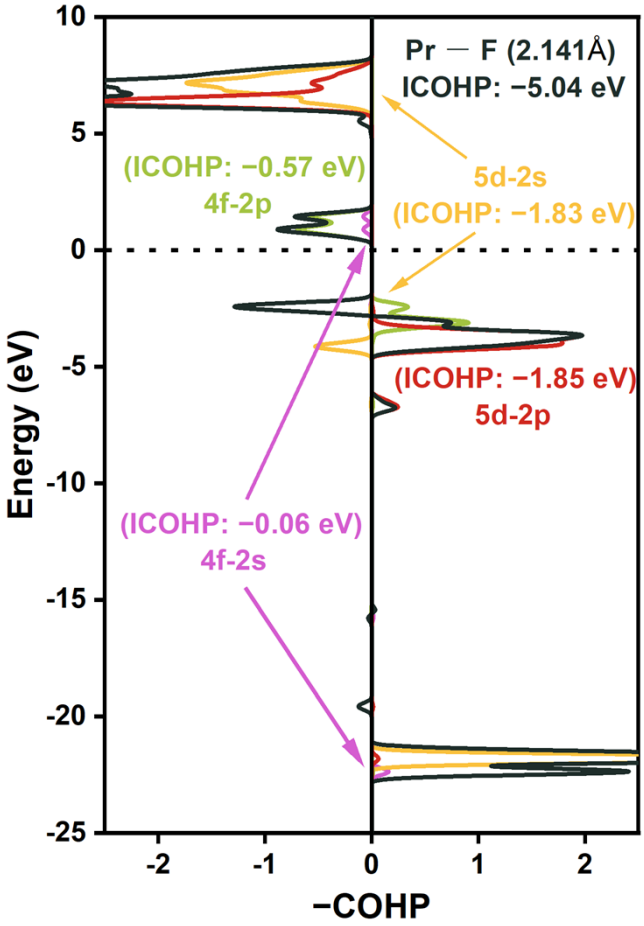

Figure S23. The crystal orbital Hamilton population (COHP) analysis of Pr–F interactions in solid-state $Cs_2Pr^{IV}F_6$. Zero line (dotted) represents the Fermi level. The ICOHP values (in eV/bond) are listed here to show the corresponding interactions (black) and main orbital-pair contributions to these (colored).

VII. $CsPrF_6$ Atom Coordinate Information

	$CsPrF_6$		
F	0.5635899899999970	0.7093999980000021	0.0098699930000024
F	0.4364100100000030	0.2906000019999979	0.9901300069999976
F	0.2906000019999979	0.8541899920000020	0.0098699930000024
F	0.7093999980000021	0.1458100079999980	0.9901300069999976
F	0.1458100079999980	0.4364100100000030	0.0098699930000024
F	0.8541899920000020	0.5635899899999970	0.9901300069999976
F	0.2302566620000022	0.0427333299999972	0.3432033360000020
F	0.1030766740000004	0.6239333150000022	0.3234633510000009
F	0.9572666879999971	0.1875233199999968	0.3432033360000020
F	0.3760666550000025	0.4791433509999976	0.3234633510000009
F	0.8124766950000009	0.7697433230000001	0.3432033360000020
F	0.5208566780000012	0.8969233039999978	0.3234633510000009
F	0.8969233039999978	0.3760666550000025	0.6765366790000016
F	0.7697433230000001	0.9572666879999971	0.6567966940000005
F	0.6239333150000022	0.5208566780000012	0.6765366790000016
F	0.0427333299999972	0.8124766950000009	0.6567966940000005
F	0.4791433509999976	0.1030766740000004	0.6765366790000016
F	0.1875233199999968	0.2302566620000022	0.6567966940000005
Cs	0.6666666870000029	0.3333333429999996	0.3333333730000021
Cs	0.3333333129999971	0.6666666269999979	0.6666666269999979
Cs	0.0000000000000000	0.0000000000000000	0.0000000000000000
Pr	0.0000000000000000	0.0000000000000000	0.5000000000000000
Pr	0.6666666870000029	0.3333333429999996	0.8333333129999971
Pr	0.3333333429999996	0.6666666870000029	0.1666666719999981