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

Supplementary Information

Potential Rules for Stable Transition Metal Hexafluoride with High Oxidation State Under Pressures

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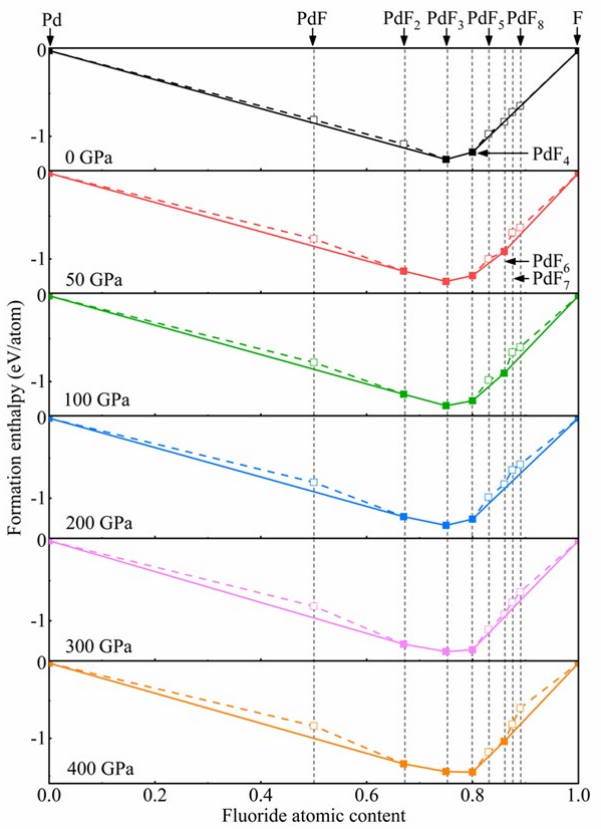

Fig. S1 Convex hulls of the Pd-F system with respect to solid Pd and F at selected pressures. Solid points connected by a solid line denote thermodynamically stable phases, while empty points connected by a dotted line represent unstable/metastable structures.

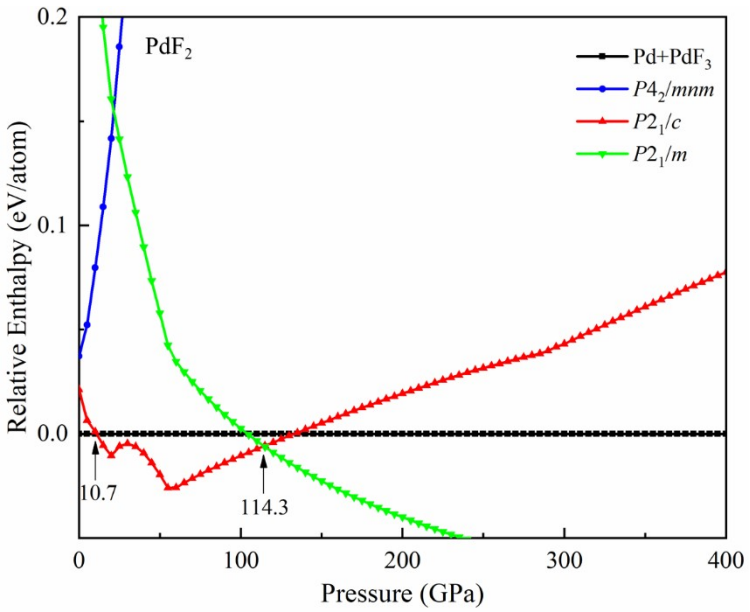

Fig. S2 Enthalpies of various predicted PdF_2 phases with respect to Pd and PdF_3 as a function of pressures.

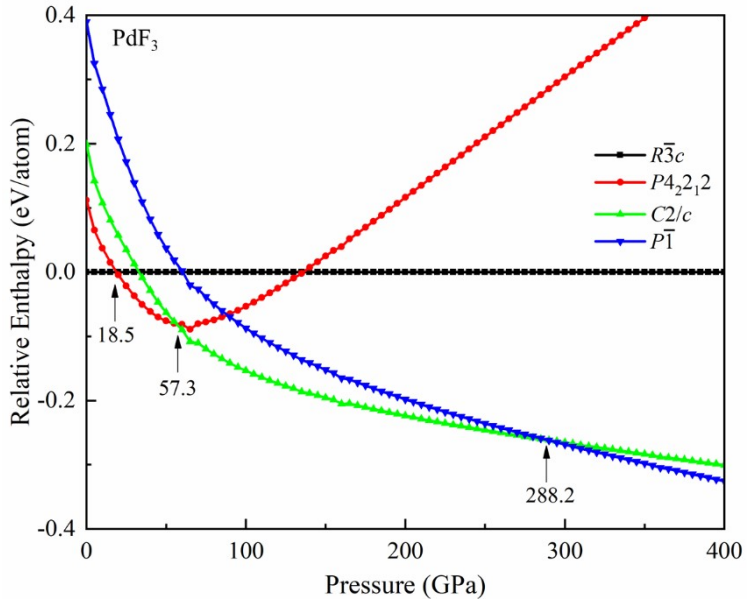

Fig. S3 Enthalpies (relative to $R\bar{3}c$ phase) of various predicted PdF_3 phases as a function of pressures.

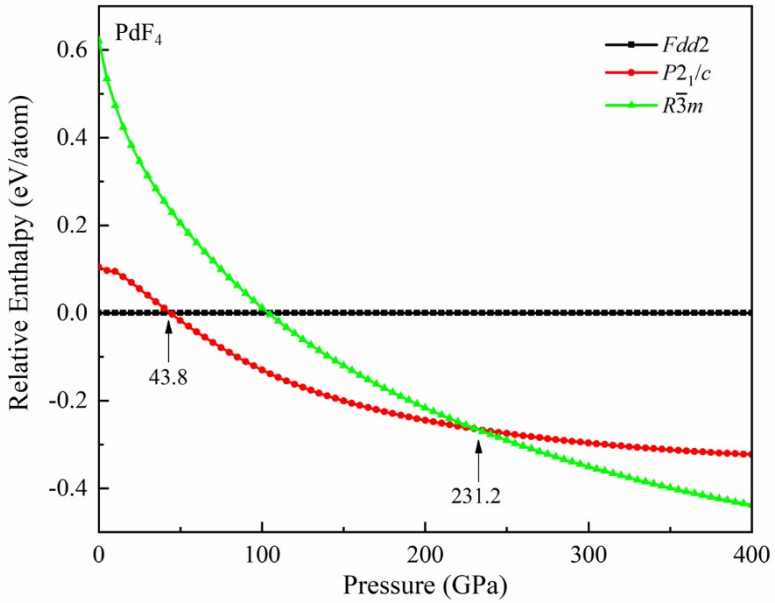

Fig. S4 Enthalpies (relative to *Fdd*2 phase) of various predicted PdF_4 phases as a function of pressures.

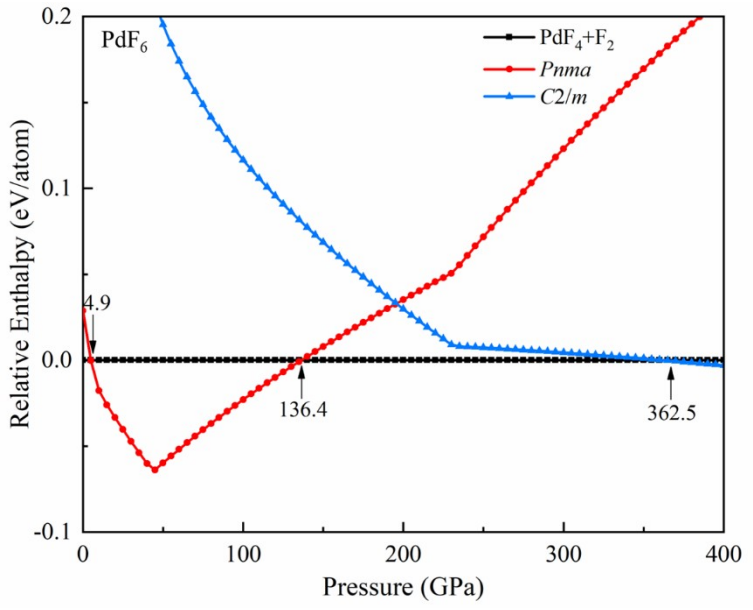

Fig. S5 Enthalpies of various predicted PdF_6 phases with respect to PdF_4 and F_2 as a function of pressures using PBE functional.

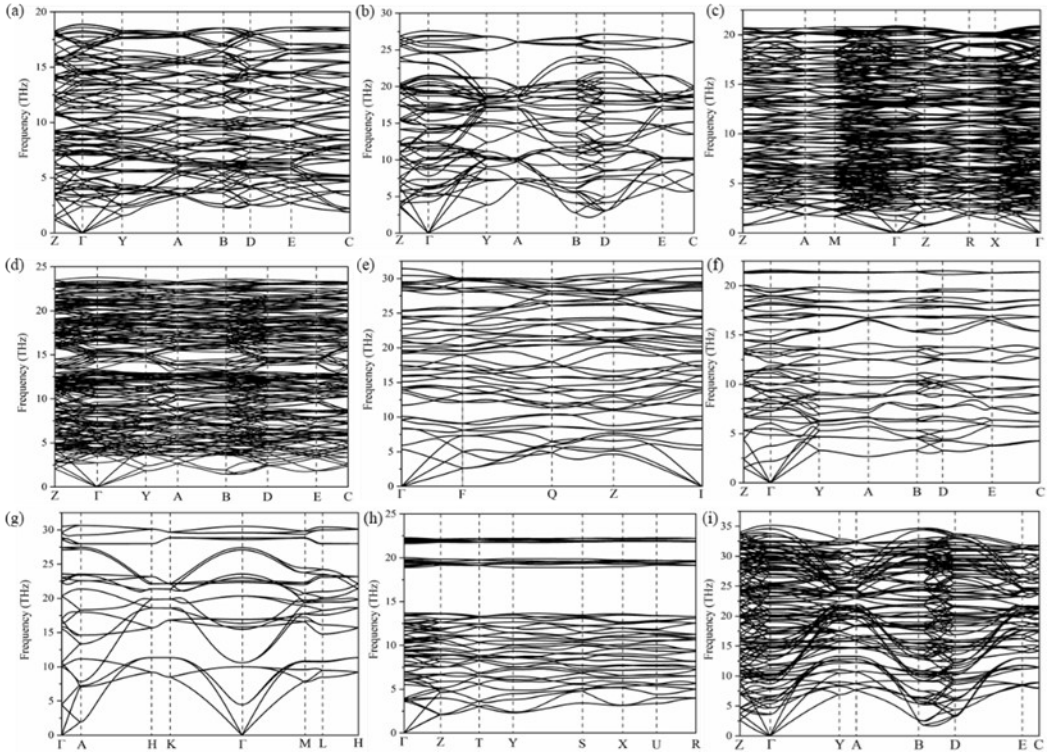

Fig. S6 Phonon dispersion curves of the predicted Pd-F binary compounds. (a) $P2_1/c$ PdF_2 at 50 GPa. (b) $P2_1/m$ PdF_2 at 200 GPa. (c) $P4_22_12$ PdF_3 at 50 GPa. (d) $C2/c$ PdF_3 at 100 GPa. (e) $P\bar{1}$ PdF_3 at 300 GPa. (f) $P2_1/c$ PdF_4 at 50 GPa. (g) $R\bar{3}m$ PdF_4 at 300 GPa. (h) *Pnma* PdF_6 at 50 GPa. (i) $C2/m$ PdF_6 at

400 GPa.

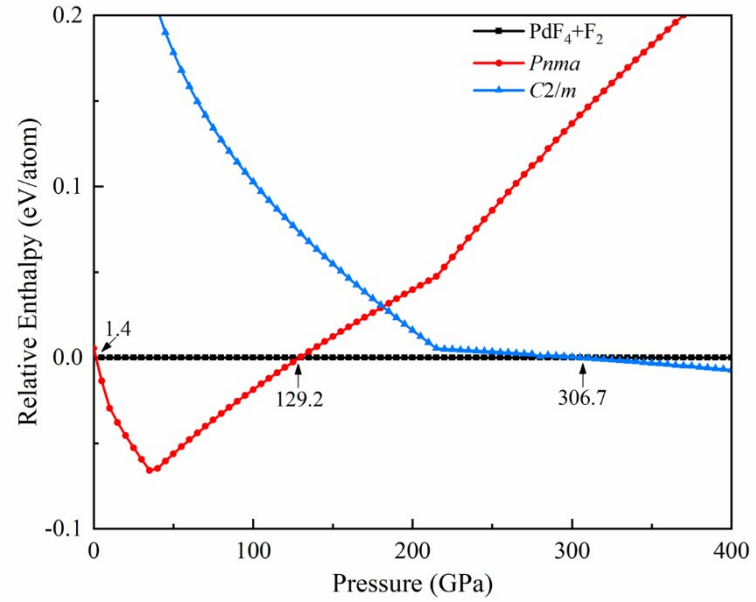

Fig. S7 Enthalpies of various predicted PdF_6 phases with respect to PdF_4 and F_2 as a function of pressures using optB88-vdW functional.[1-2]

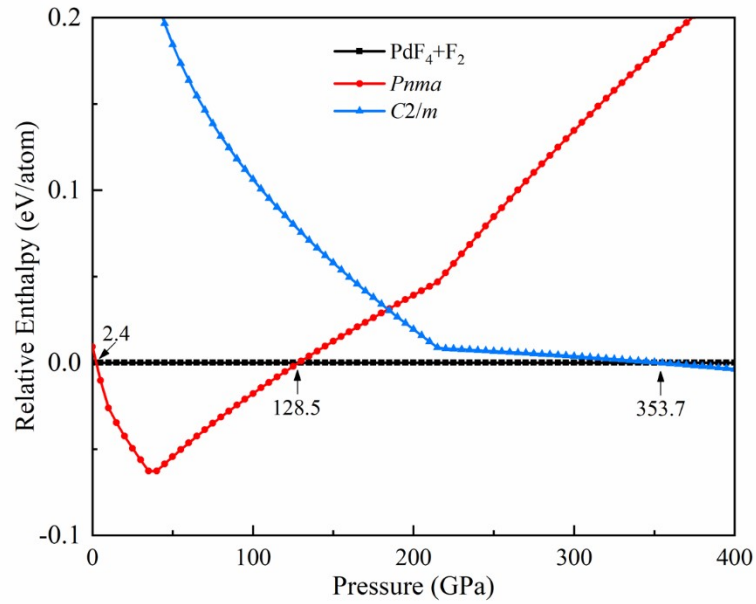

Fig. S8 Enthalpies of various predicted PdF_6 phases with respect to PdF_4 and F_2 as a function of pressures using optPBE-vdW functional.[1-2]

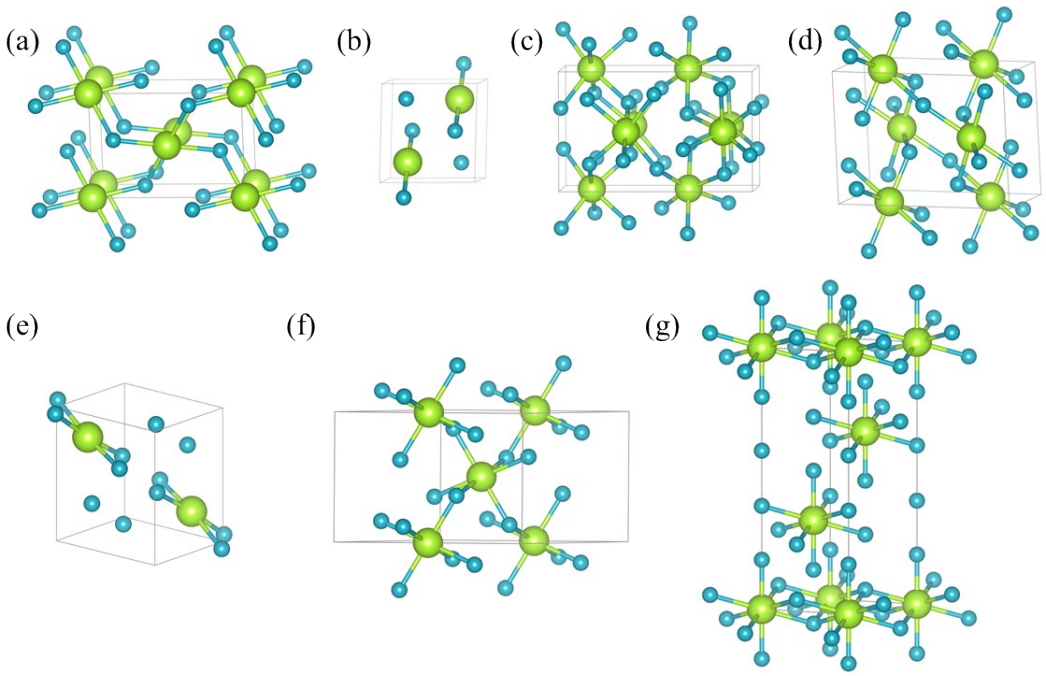

Fig. S9 Crystalline structures of the predicted stable Pd-F phases. (a) $P2_1/c$ structure of PdF_2 at 50 GPa. (b) $P2_1/m$ structure of PdF_2 at 200 GPa. (c) $P4_22_12$ structure of PdF_3 at 50 GPa. (d) $C2/c$ structure of PdF_3 at 100 GPa. (e) $P\bar{1}$ structure of PdF_3 at 300 GPa. (f) $P2_1/c$ structure of PdF_4 at 50 GPa. (g) $R\bar{3}m$ structure of PdF_4 at 300 GPa.

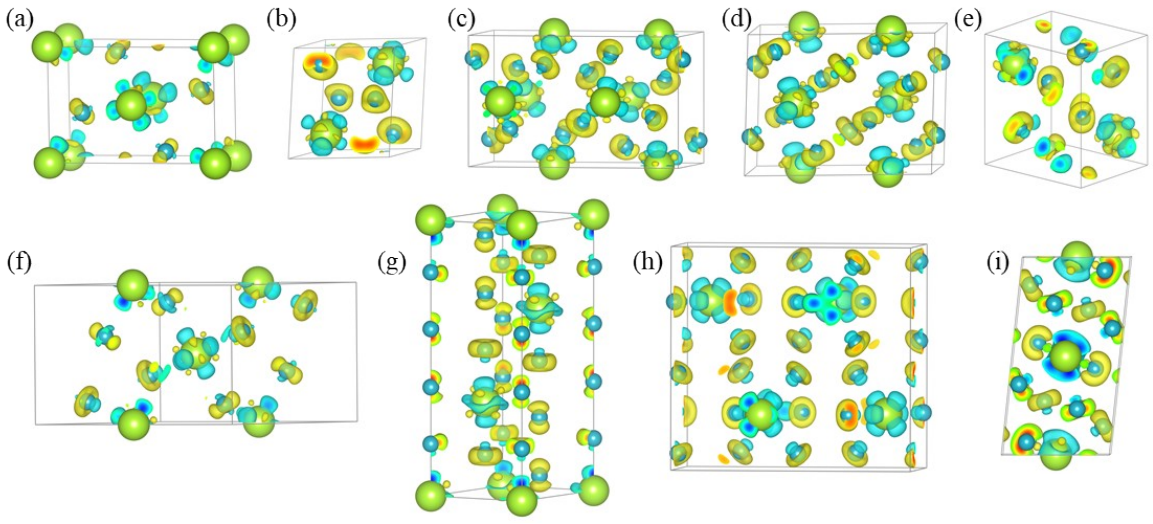

Fig. S10 Three-dimensional charge density difference for (a) $P2_1/c$ PdF_2 at 50 GPa; (b) $P2_1/m$ PdF_2 at 200 GPa; (c) $P4_22_12$ PdF_3 at 50 GPa; (d) $C2/c$ PdF_3 at 100 GPa; (e) $P\bar{1}$ PdF_3 at 300 GPa; (f) $P2_1/c$ PdF_4 at 50 GPa; (g) $R\bar{3}m$ PdF_4 at 300 GPa; (h) *Pnma* PdF_6 at 50 GPa and (i) $C2/m$ PdF_6 at 400 GPa with an

isosurface value of 0.03 *e*/Bohr^3. Blue and yellow colors represent losing and gaining electrons, respectively.

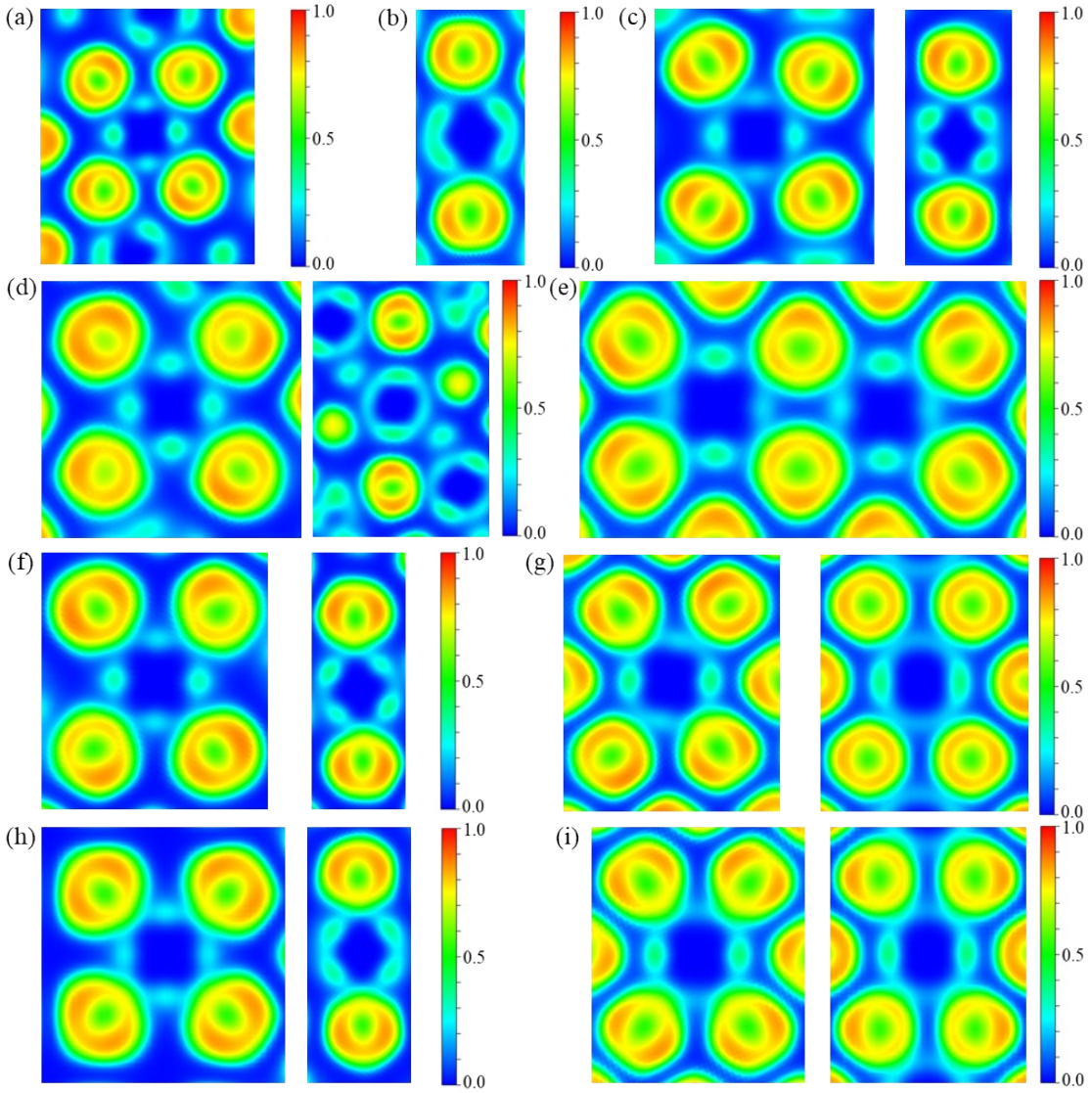

Fig. S11 Electron function localization (ELF) maps for (a) $P2_1/c$ PdF_2 on the (1.78132, -1.51638, 1) plane at 50 GPa; (b) $P2_1/m$ PdF_2 on the (0, 1, 0) plane at 200 GPa; (c) $P4_22_12$ PdF_3 on the (1, 1.78629, 0) and (2.6609, 1, 2309.73) plane at 50 GPa; (d) $C2/c$ PdF_3 on the (4.90199, 1.75107, -1) and (-1, -1.9651, 1.9651) plane at 100 GPa; (e) $P\bar{1}$ PdF_3 on the (1, -1.0398, -2.03364) plane at 300 GPa; (f) $P2_1/c$ PdF_4 on the (-4.46078, -2.16113, 1) and (-1, -2.212, 0) plane at 50 GPa; (g) $R\bar{3}m$ PdF_4 on the (-1, 2, 0) and (-1, 0, 5.44173) plane at 300 GPa; (h) *Pnma* PdF_6 on the (1.21664, 0, -1) and (0, 1, 0) plane at 50 GPa; (i) $C2/m$ PdF_6 on the (0, 1, 0) and (4.24799, 0, 1) plane at 400 GPa.

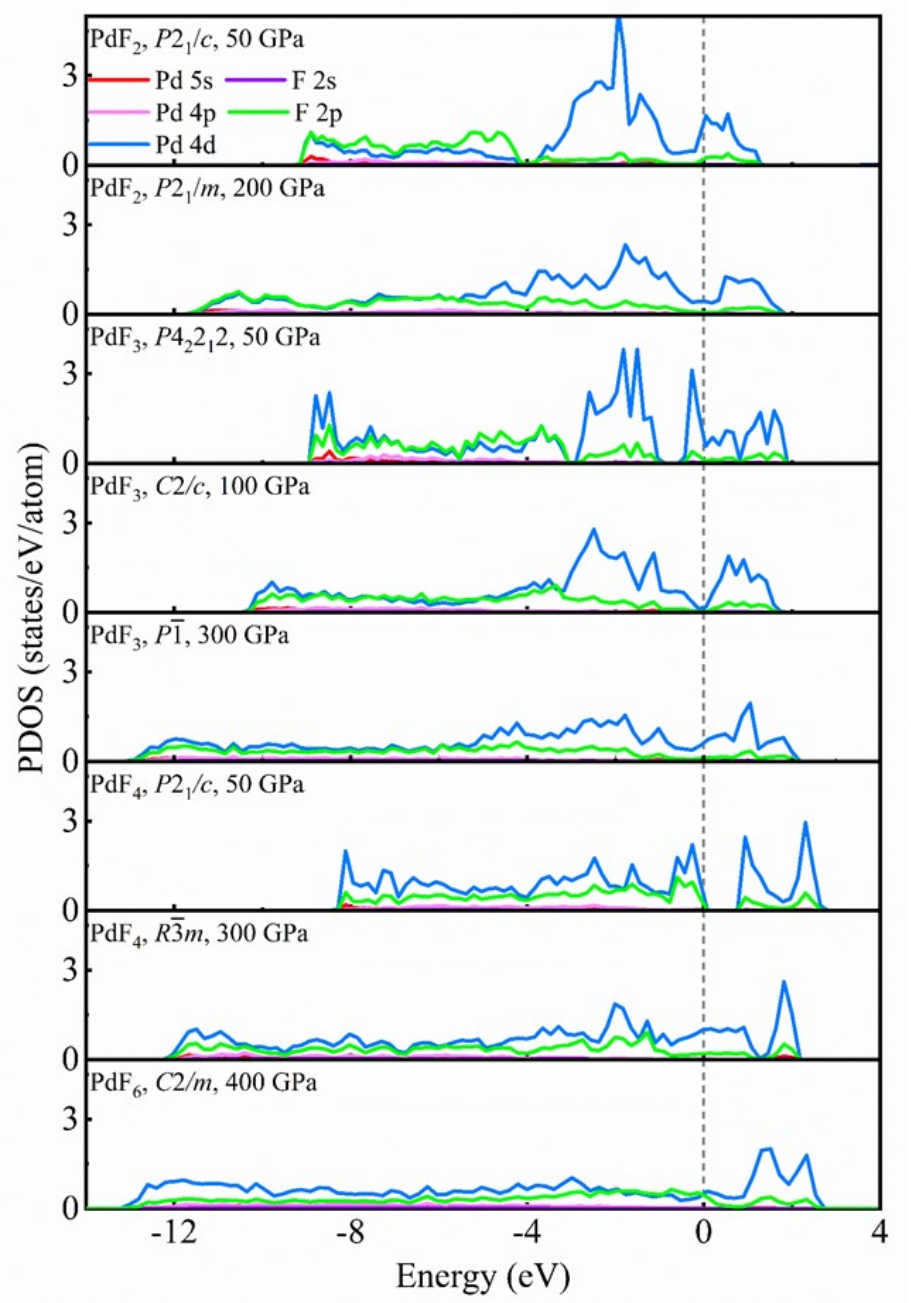

Fig. S12 Projected density of states (PDOS) of the stable Pd-F compounds at selected pressures. Energy is shifted so that the Fermi level E_F equals zero.

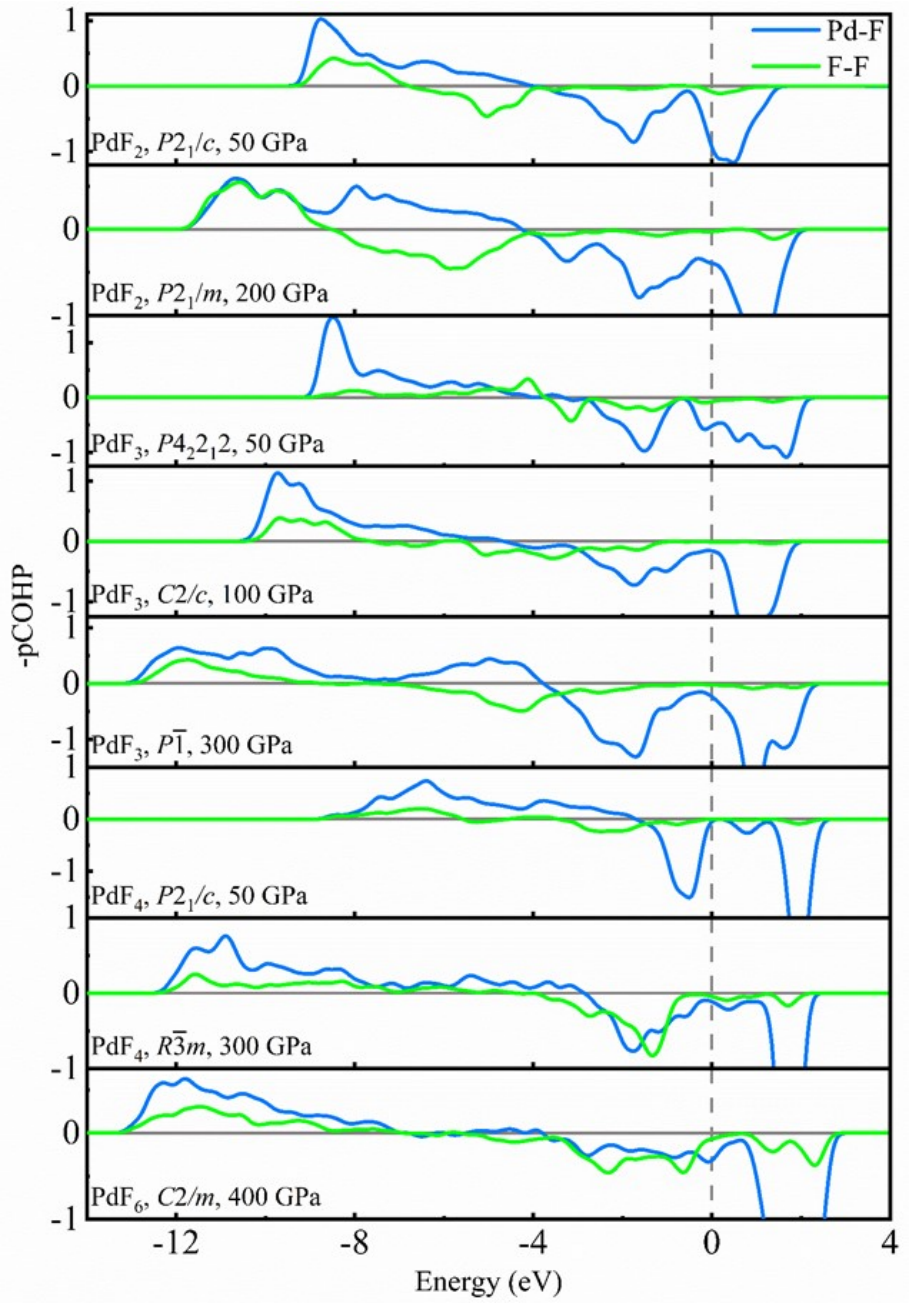

Fig. S13 Crystal orbital Hamilton populations (COHP) for the nearest Pd-F and F-F pairs of the stable Pd-F compounds at selected pressures. Positive and negative denote bonding and antibonding orbital interactions, respectively. Energy is shifted so that the Fermi level E_F equals zero.

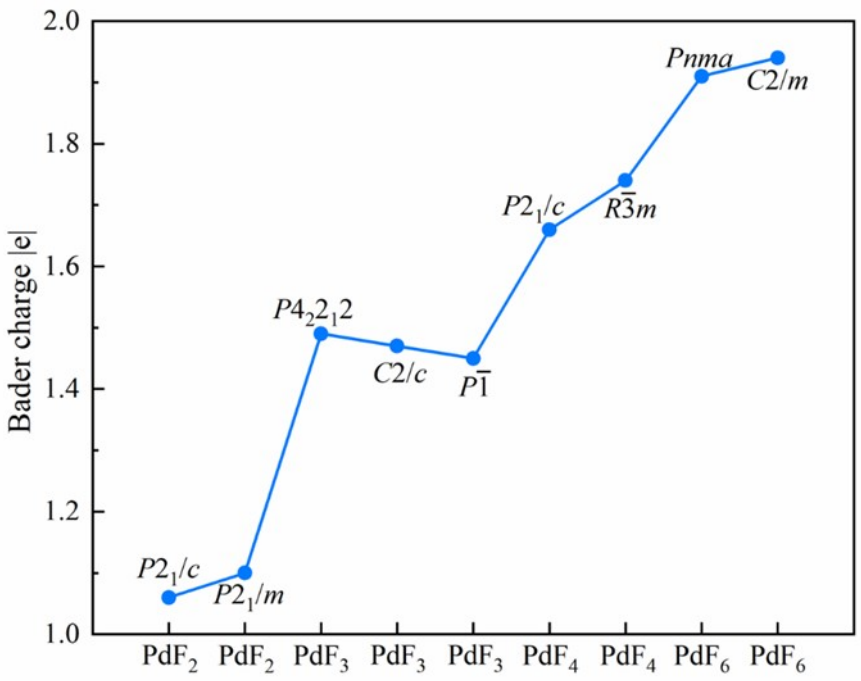

Fig. S14 Bader charge transfer of Pd atom in the stable Pd-F compounds.

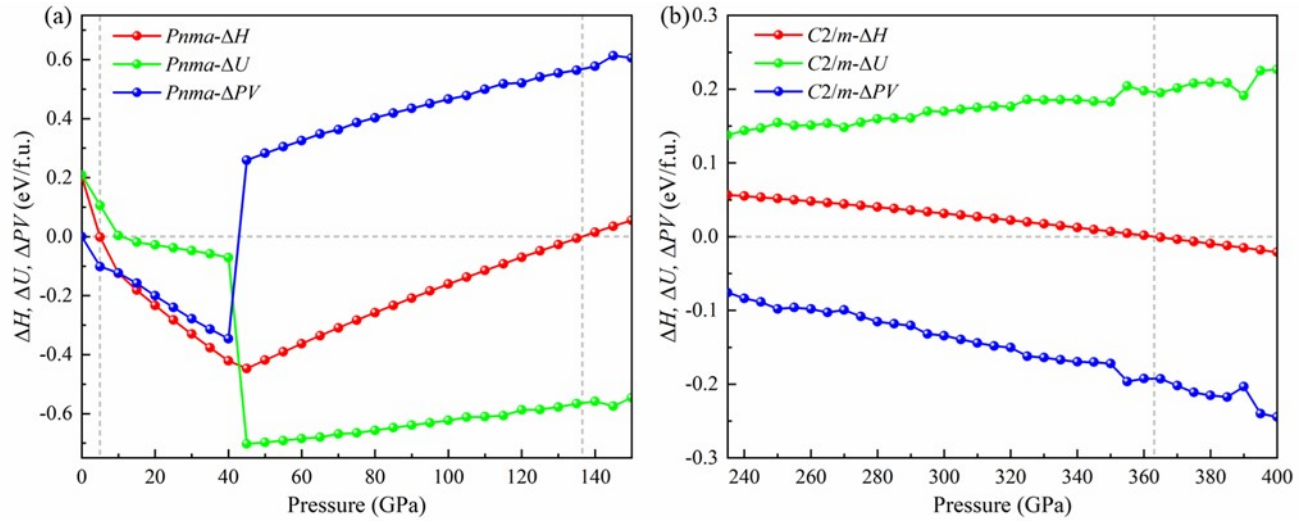

Fig. S15 Relationship between Δ*H*, Δ*U*, and Δ*PV* with pressure of (a) *Pnma* PdF_6 and (b) *C*2/*m* PdF_6 with respect to PdF_4 plus F_2. The changes of enthalpy (Δ*H*), internal energy (Δ*U*), and (Δ*PV*) are defined as $\Delta H = H(PdF_6) - (H(PdF_4) + H(F_2))$, $\Delta U = U(PdF_6) - (U(PdF_4) + U(F_2))$, $\Delta PV = PV(PdF_6) - (PV(PdF_4) + PV(F_2))$, respectively.

Table S1. Calculated structural parameters of the predicted stable TM-F compounds.

	Space group	Lattice Parameters (Å, °)	Atoms	Atomic coordinates (fractional) X	Y	Z
PdF_2 (50 GPa)	$P2_1/c$	a=2.57850 b=3.81920 c=5.58190 α=γ=90.0000 β=88.5446	Pd (2a) F (4e)	0.00000 0.74248	0.50000 0.91487	0.50000 0.32964
PdF_2 (200 GPa)	$P2_1/m$	a=3.37130 b=3.43570 c=3.67800 α=γ=90.0000 β=73.1054	Pd (2e) F1 (2e) F3 (2e)	0.36848 0.72219 0.92419	0.75000 0.75000 0.25000	0.19062 0.49336 0.15656
PdF_3 (50 GPa)	$P4_22_12$	a=b= 4.44900 c=7.21520 α=β=γ=90.0000	Pd (4d) F1 (8g) F9 (4f)	0.50000 0.13477 0.17945	0.00000 0.22240 0.17945	1.15186 1.15347 0.50000
PdF_3 (100 GPa)	$C2/c$	a=6.25010 b=4.07430 c=4.71700 α=γ=90.0000 β=92.4330	Pd (4c) F1 (8f) F9 (4e)	0.25000 0.36298 0.50000	0.25000 0.64277 0.87278	1.00000 0.86606 1.25000
PdF_3 (300 GPa)	$P\bar{1}$	a=3.28680 b=3.53610 c=4.52870 α=100.6174 β=97.2066 γ=113.7740	Pd (2i) F1 (2i) F3 (2i) F7 (2i)	0.87218 0.39081 0.88834 0.64267	0.22896 0.24675 0.28246 0.76473	0.79331 0.57084 0.30974 0.94673
PdF_4 (50 GPa)	$P2_1/c$	a=6.48130 b=4.49200	Pd (2d) F1 (4e)	0.50000 0.30491	0.00000 0.86568	0.50000 0.92003

		c=4.54160	F5 (4e)	0.85507	0.66052	1.18750
		α=γ=90.0000				
		β=141.0896				
PdF_4	$R\bar{3}m$	a=b=3.19650	Pd (3a)	0.00000	0.00000	0.00000
(300 GPa)		c=9.29580	F1 (6c)	0.33333	0.66667	0.85564
		α=β=90.0000	F7 (6c)	0.00000	0.00000	0.60541
		γ=120.0000				
PdF_6	*Pnma*	a=7.75110	Pd (4c)	0.62909	0.75000	0.42417
(50 GPa)		b=7.15950	F1 (8d)	0.76873	0.92899	0.59784
		c=4.12080	F9 (8d)	1.48619	0.57166	0.25409
		α=β=γ=90.0000	F17 (4c)	1.23838	0.25000	0.94347
			F21 (4c)	1.49869	0.25000	0.20390
PdF_6	*C*2/*m*	a=6.41910	Pd (2d)	0.00000	0.50000	0.50000
(400 GPa)		b=3.04890	F1 (4i)	0.93427	0.00000	0.77922
		c=3.50030	F5 (4i)	0.76690	0.00000	0.34187
		α=γ=90.0000	F9 (4i)	0.64181	0.00000	0.90677
		β=83.9461				
CoF_6	*Pnma*	a=6.80090	Co (4c)	0.63064	0.75000	0.42682
(200 GPa)		b=6.32760	F1 (4c)	0.23434	0.25000	0.94422
		c=3.63240	F5 (8d)	0.77071	0.93167	0.60482
		α=β=γ=90.0000	F9 (8d)	0.48415	0.56973	0.25708
			F21 (4c)	0.49709	0.25000	0.19343
CrF_6	*Pnma*	a=6.91630	Cr (4c)	0.12798	0.75000	0.42095
(200 GPa)		b=6.37400	F1 (4c)	-0.26523	0.25000	0.94312
		c=3.66670	F5 (8d)	0.26664	0.93059	0.59996
		α=β=γ=90.0000	F9 (8d)	-0.01474	0.56905	0.25111
			F21 (4c)	0.00148	0.25000	0.20390
HfF_6	*Pnma*	a=7.67010	Hf (4c)	0.15008	0.75000	0.46004
(200 GPa)		b=6.60180	F1 (4c)	-0.30420	0.25000	0.98733

		c=3.32130	F5 (8d)	0.31835	0.96650	0.60367
		α=β=γ=90.0000	F9 (8d)	-0.05811	0.51436	0.31216
			F21 (4c)	-0.01585	0.25000	0.03093
MnF_6	*Pnma*	a=6.88760	Mn (4c)	0.62864	0.75000	0.42251
(200 GPa)		b=6.35520	F1 (4c)	0.23331	0.25000	0.94165
		c=3.64300	F5 (8d)	0.76849	0.93060	0.60129
		α=β=γ=90.0000	F9 (8d)	0.48489	0.56860	0.25417
			F21 (4c)	0.49953	0.25000	0.19881
YF_6	*Pnma*	a=6.40450	Y (4c)	1.16541	0.75000	0.49833
(200 GPa)		b=7.06350	F1 (4c)	0.66572	0.25000	0.00008
		c=3.77180	F5 (8d)	1.31185	-0.00163	0.71373
		α=β=γ=90.0000	F9 (8d)	0.94064	0.50236	0.25932
			F21 (4c)	0.99855	0.25000	0.00350

Table S2. Calculated Bader charge analysis of the stable Pd-F compounds. ΔQ is the charge transfer in e per atom. The number in parentheses is the Wyckoff sites corresponding to the atoms.

Phase	Pressure (GPa)	Q (Pd/e)	ΔQ (Pd/e)	Q (F/e)	ΔQ (F/e)
$P2_1/c$ PdF_2	50	8.94 (2a)	-1.06	7.53 (4e)	+0.53 (F1)
$P2_1/m$ PdF_2	200	8.90 (2e)	-1.10	7.53 (2e)	+0.53 (F1)
				7.57 (2e)	+0.57 (F3)
$P4_22_12$ PdF_3	50	8.51 (4d)	-1.49	7.49 (8g)	+0.49 (F1)
				7.51 (4f)	+0.51 (F9)
$C2/c$ PdF_3	100	8.53 (4c)	-1.47	7.46 (8f)	+0.46 (F1)
				7.55 (4e)	+0.55 (F9)
$P\bar{1}$ PdF_3	300	8.55 (2i)	-1.45	7.45 (2i)	+0.45 (F1)
				7.51 (2i)	+0.51 (F3)
				7.49 (2i)	+0.49 (F7)

$P2_1/c$ PdF_4	50	8.34 (2d)	-1.66	7.38 (4e)	+0.38 (F1)
				7.45 (4e)	+0.45 (F5)
$R\bar{3}m$ PdF_4	300	8.26 (3a)	-1.74	7.46 (6c)	+0.46 (F1)
				7.41 (6c)	+0.41 (F7)
Pnma PdF_6	50	8.09 (4c)	-1.91	7.32 (8d)	+0.32 (F1)
				7.31 (8d)	+0.31 (F9)
				7.33 (4c)	+0.33 (F17)
				7.32 (4c)	+0.32 (F21)
$C2/m$ PdF_6	400	8.06 (2d)	-1.94	7.33 (4i)	+0.33 (F1)
				7.34 (4i)	+0.34 (F5)
				7.30 (4i)	+0.30 (F9)

References

1. J. Klimeš, D. R. Bowler and A. Michaelides, *J. Phys-Condens. Mat.*, 2009, **22**, 022201.
2. T. Thonhauser, V. R. Cooper, S. Li, A. Puzder, P. Hyldgaard and D. C. Langreth, *Phys. Rev. B*, 2007,

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