Supplementary Information

Pressure-Induced Evolution of Crystal and Electronic Structure of Neptunium Hydrides

Shichang Li, [a] Xiaoqiu Ye,[b] Chunbao Feng,[a] Yilin Wang,[a] Tao Gao,[c] Bingyun Ao,[b] Dengfeng Li [*a,d] and Gang Zhang[*e]

[a] School of Science, Chongqing University of Posts and Telecommunications, Chongqing, 400065, China. E-mail: lidf@cqupt.edu.cn

[b] Science and Technology on Surface Physics and Chemistry Laboratory, Jiangyou, 621908, China.

[c] Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, 610065, China.

[d] Institute for Advanced Sciences, Chongqing University of Posts and Telecommunications, Chongqing, 400065, China.

[e] Institute of High Performance Computing, A*STAR, 138632, Singapore. E-mail: zhangg@ihpc.a-star.edu.sg

Supplementary Figures

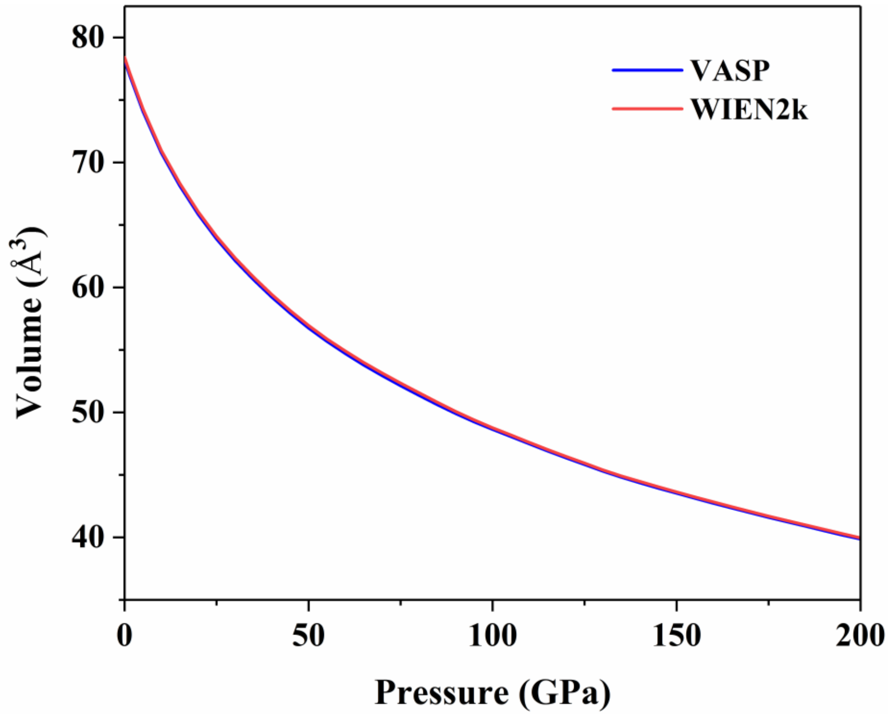

Fig. S1 Volumes as a function of pressures for $Fm\bar{3}m$ NpH3 calculated by using PAW potential in VASP calculationsand full-potential WIEN2k calculations.

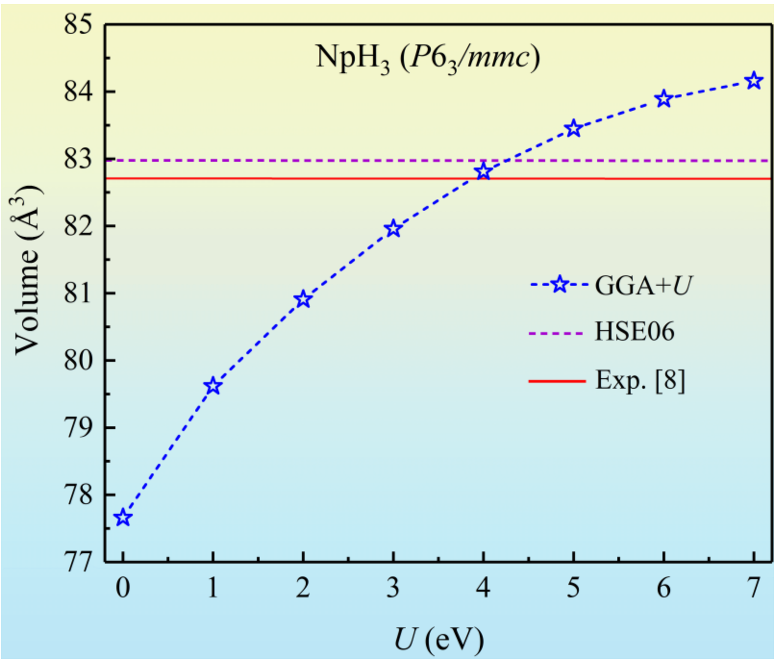

Fig. S2 Volume per formula unit as a function of U with respect to the $P6_3/mmc$ structure for static NpH_3 under atmospheric pressure.

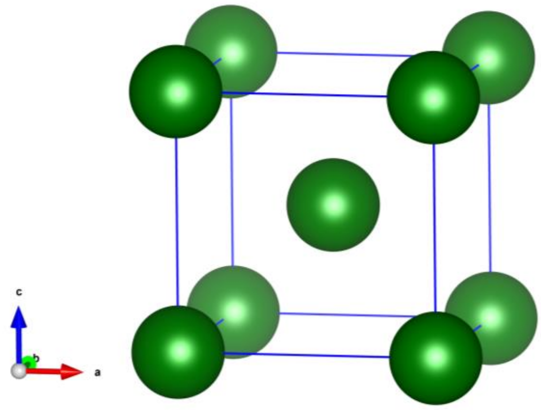

Fig. S3 Crystalline structures of the $Im\bar{3}m$ Np.

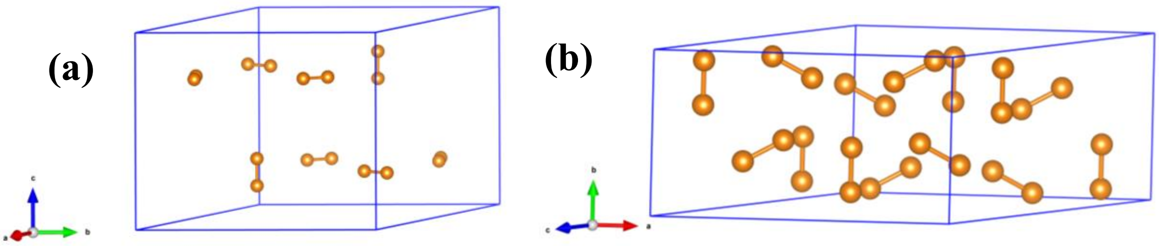

Fig. S4 Crystalline structures of the stable H_2. (a) $P6_3/m$ and (b) $C2/c$.

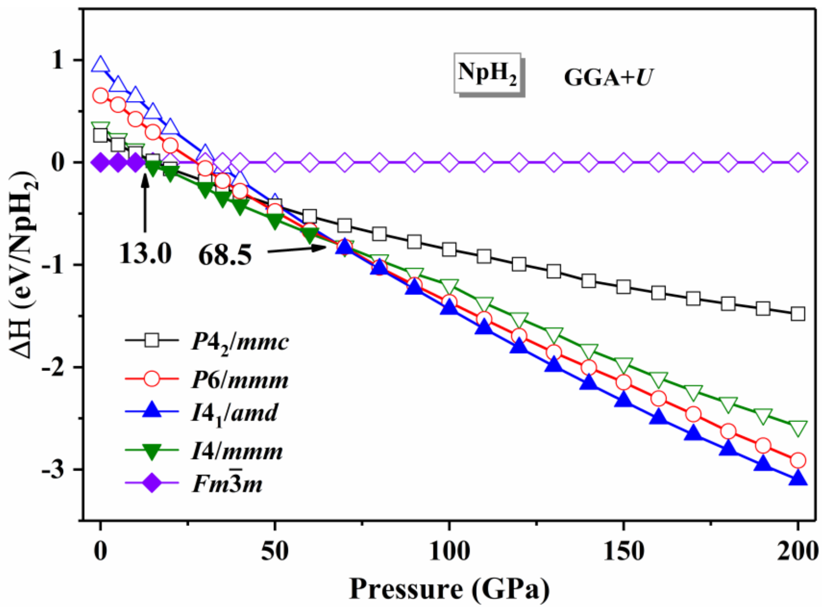

Fig. S5 Enthalpy curves per formula unit as a function of pressure with respect to the $Fm\bar{3}m$ structure for static NpH_2 in the high-pressure regime.

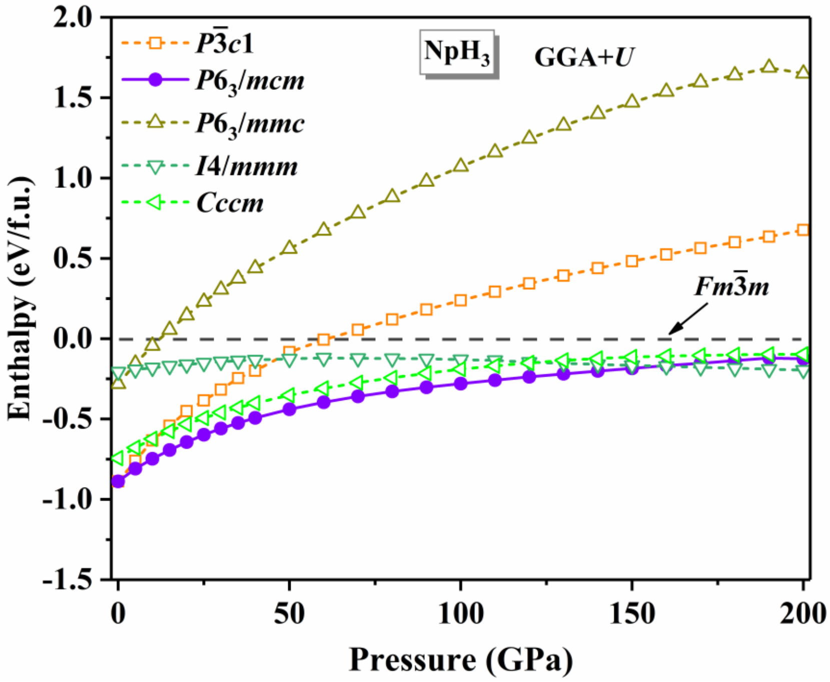

Fig. S6 Enthalpy curves per formula unit as a function of pressure with respect to the *Fm*$\bar{3}$*m* structure for static NpH_3 in the high-pressure regime.

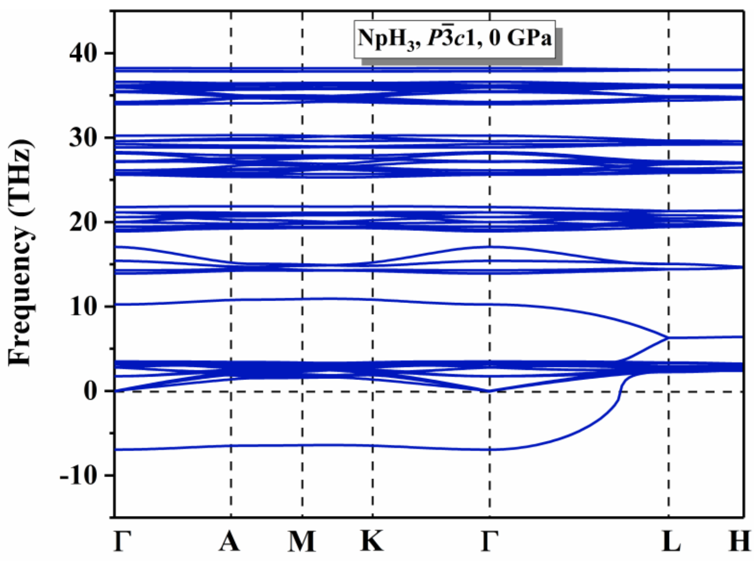

Fig. S7 Calculated phonon dispersion curves of *P*$\bar{3}$*c*1 NpH_3.

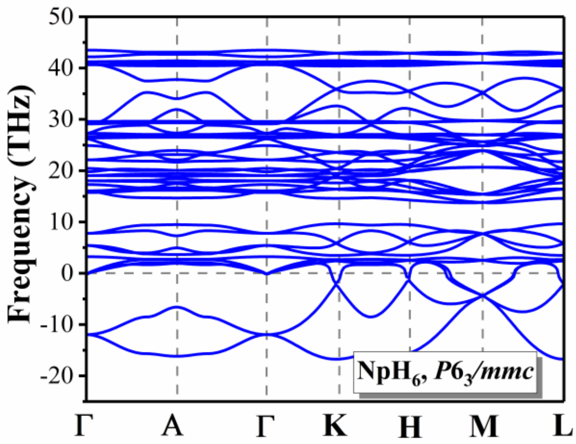

Fig. S8 The phonon dispersion curves of *P*6_3/*mmc* NpH_6.

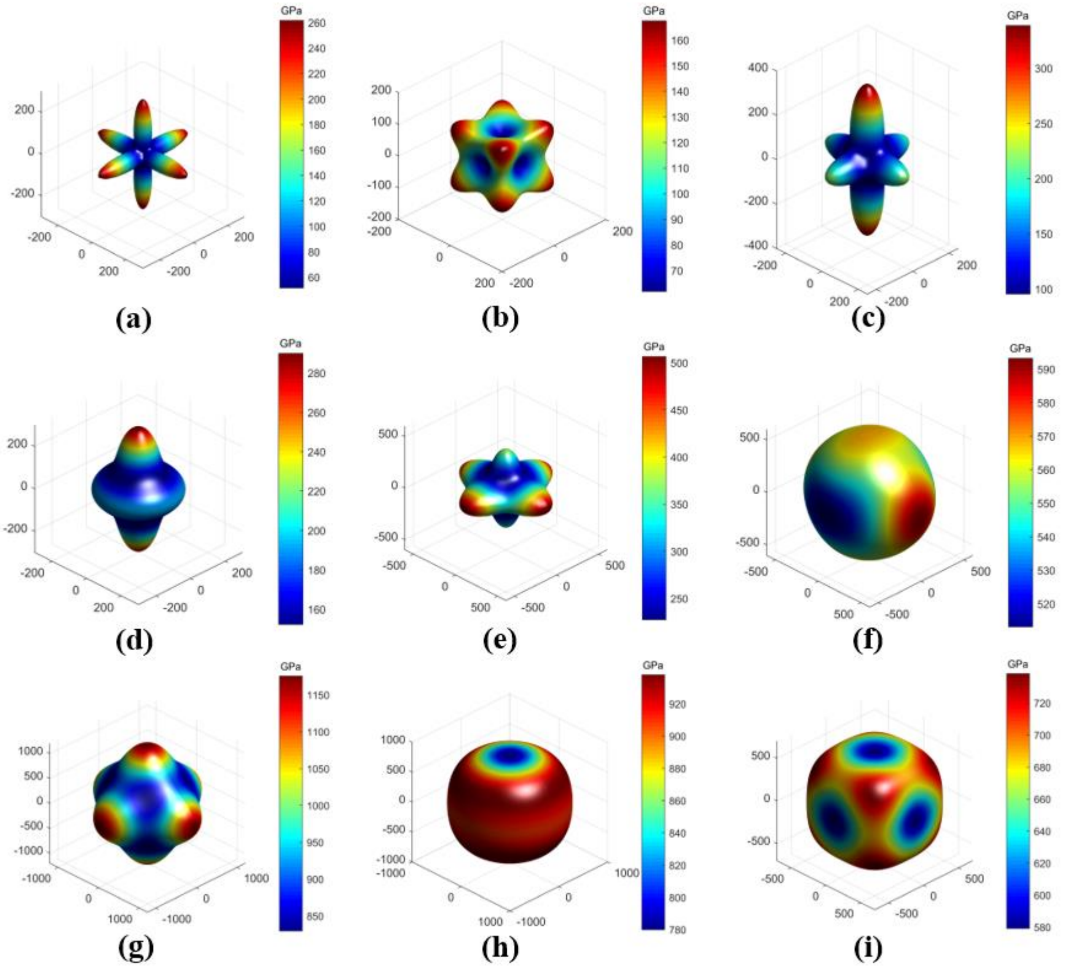

Fig. S9 Visualization of Young's modulus for NpH_x (x =1–10) at selected pressures. (a) *Fm*$\overline{3}$*m* structure of NpH at 100 GPa. (b) *Fm*$\overline{3}$*m* structure of NpH_2 at ambient pressure. (c) *I*4/*mmm* structure of NpH_2 at 25 GPa. (d) *P*6_3/*mcm* structure of NpH_3 at ambient pressure. (e) *P*4/*nmm* structure of NpH_5 at 100 GPa. (f) *Cmcm* structure of NpH_7 at 100 GPa. (g) *Fm*$\overline{3}$*m* structure of NpH_8 at 200 GPa. (h) *P*6_3/*mmc* structure of NpH_9 at 200 GPa. (i) *Fm*$\overline{3}$*m* structure of NpH_{10} at 200 GPa.

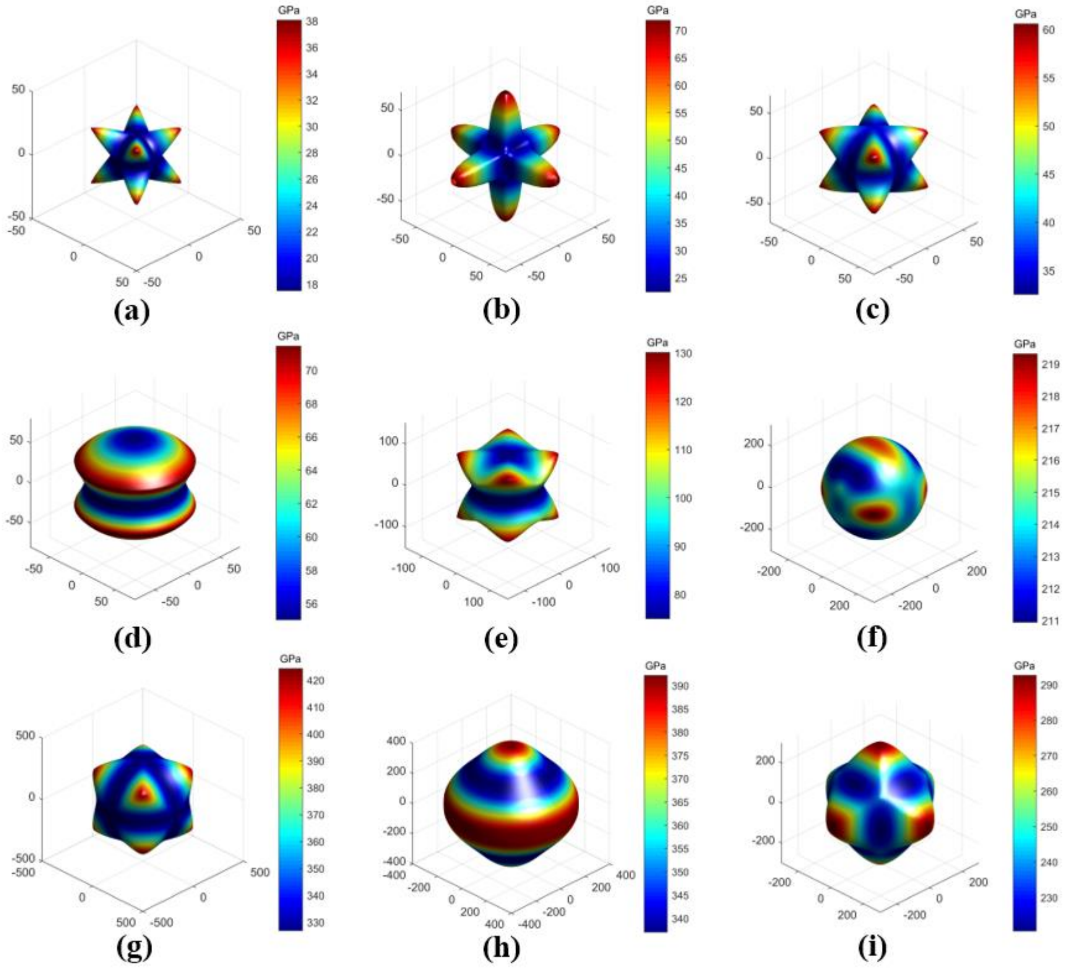

Fig. S10 Visualization of Shear modulus for NpH_x (x =1–10) at selected pressures. (a) $Fm\bar{3}m$ structure of NpH at 100 GPa. (b) $Fm\bar{3}m$ structure of NpH_2 at ambient pressure. (c) $I4/mmm$ structure of NpH_2 at 25 GPa. (d) $P6_3/mcm$ structure of NpH_3 at ambient pressure. (e) $P4/nmm$ structure of NpH_5 at 100 GPa. (f) *Cmcm* structure of NpH_7 at 100 GPa. (g) $Fm\bar{3}m$ structure of NpH_8 at 200 GPa. (h) $P6_3/mmc$ structure of NpH_9 at 200 GPa. (i) $Fm\bar{3}m$ structure of NpH_{10} at 200 GPa.

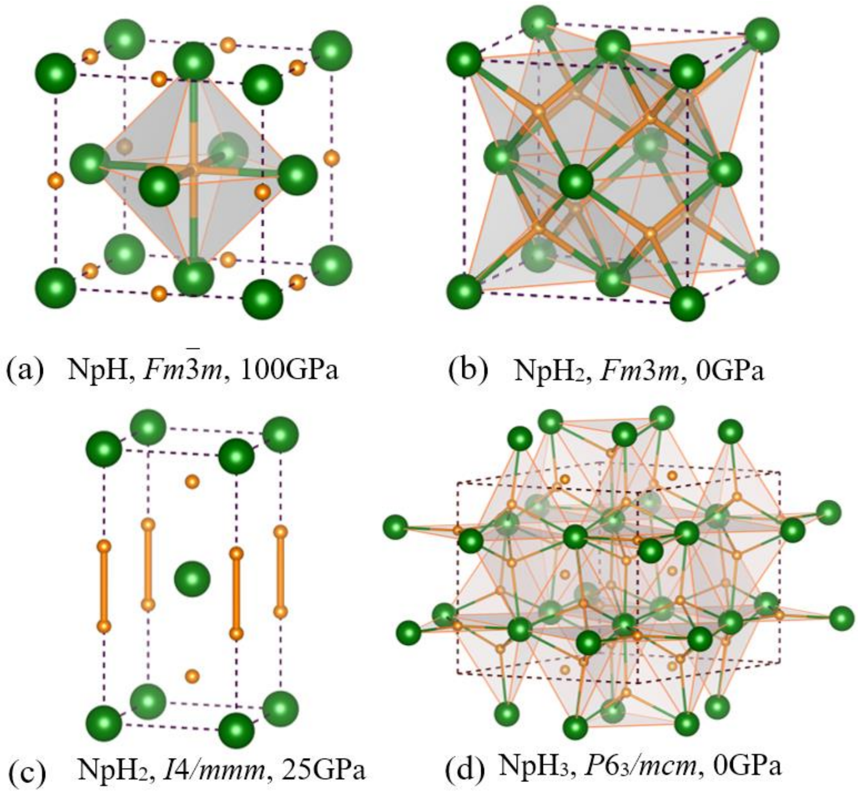

Fig. S11 Crystalline structures of the stable NpH, NpH_2, and NpH_3.

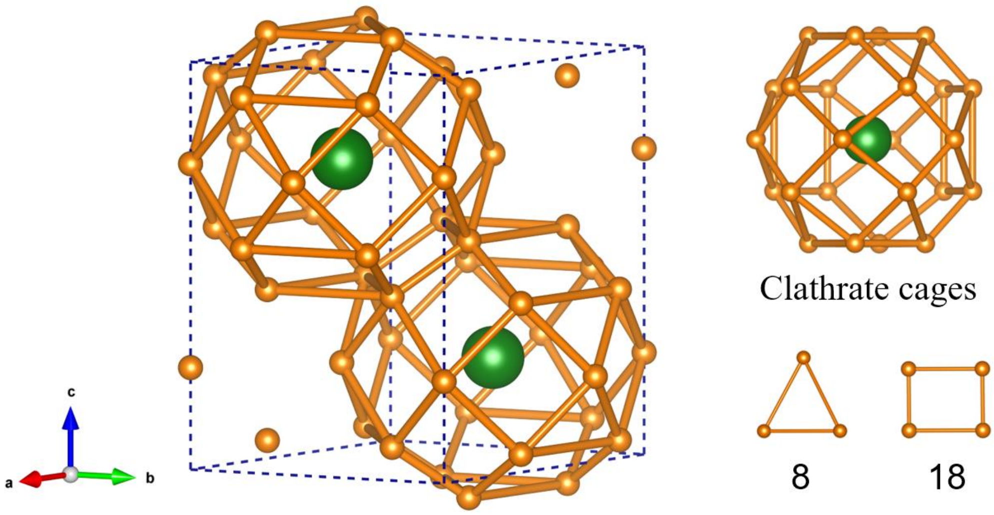

Fig. S12 Crystalline structures of the $P6_3/mmc$ NpH_8 with Np atoms at the center of the H_{24} cages.

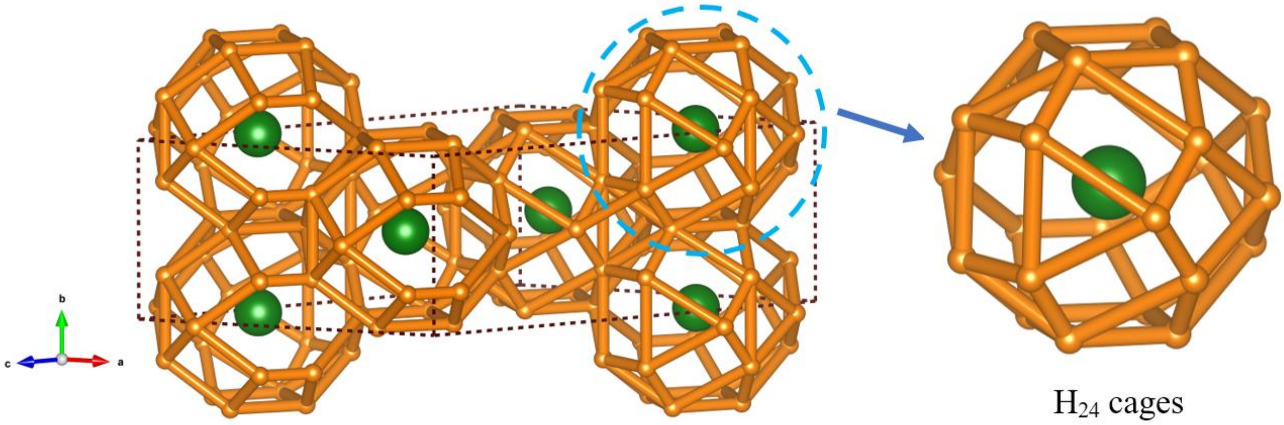

Fig. S13 Crystalline structures of the *C2/m* NpH_8 with Np atoms at the center of the H_{24} cages.

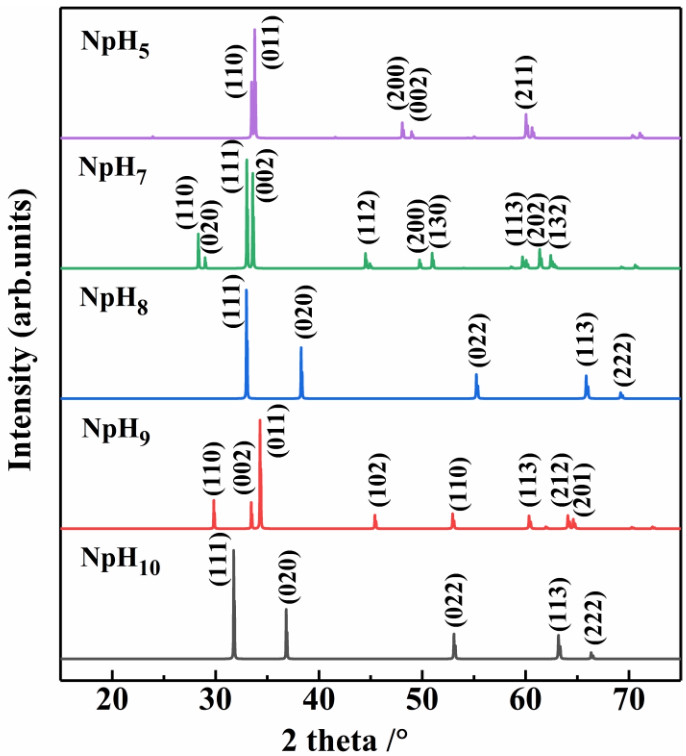

Fig. S14 X-ray powder diffraction patterns of NpH_5, NpH_7, NpH_8, NpH_9, and NpH_{10}. X-ray dispersion coefficients for λ = 0.154059 nm.

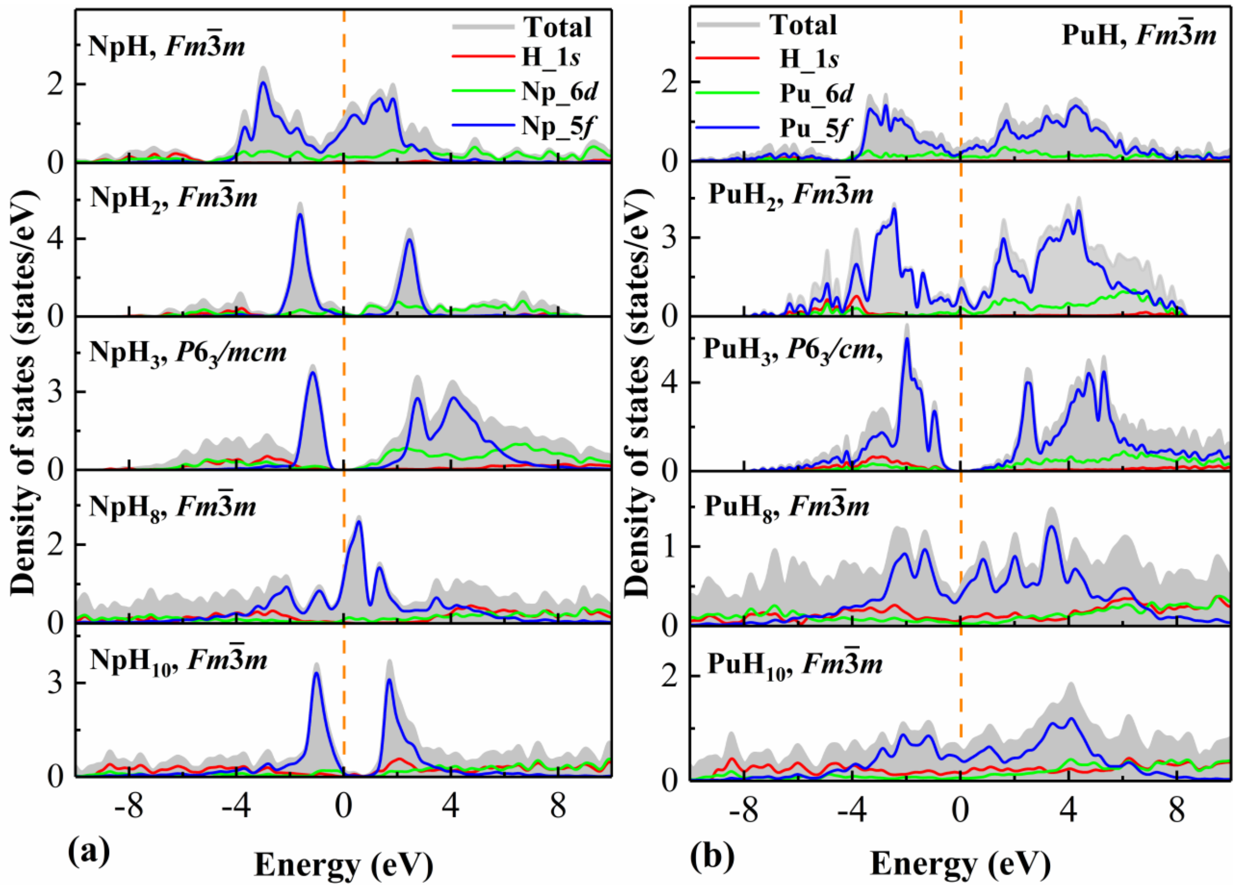

Fig. S15 The calculated DOS and PDOS for (a) NpH_x and (b) PuH_x. The DOS is projected onto 5*f*, 6*d*, and 1*s* orbitals. Energy is shifted so that the Fermi level E_F equals zero.

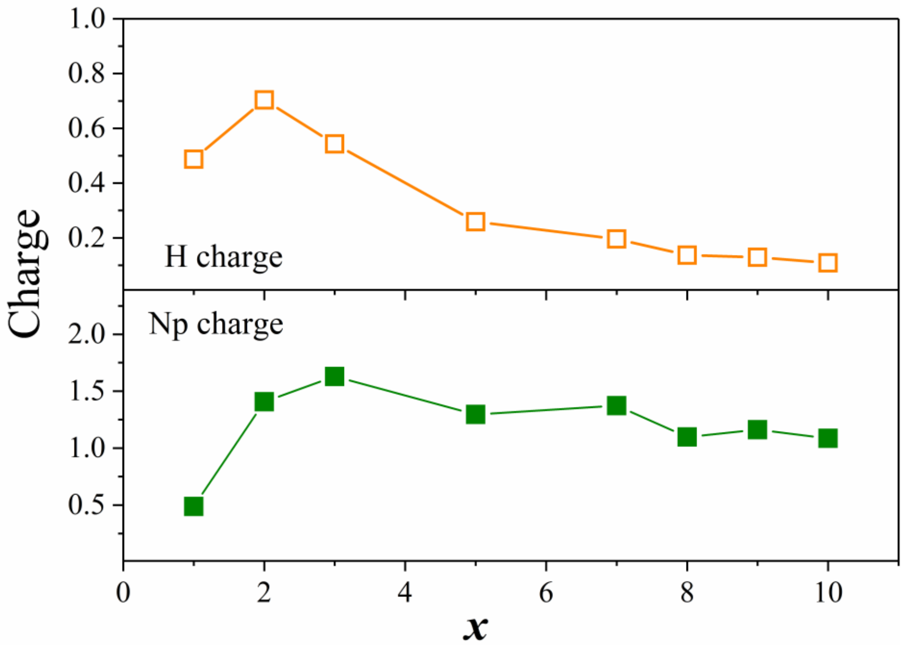

Fig. S16 The Bader charge analysis of Np-H systems. The anionic H and cationic Np charges are listed at selected pressures.

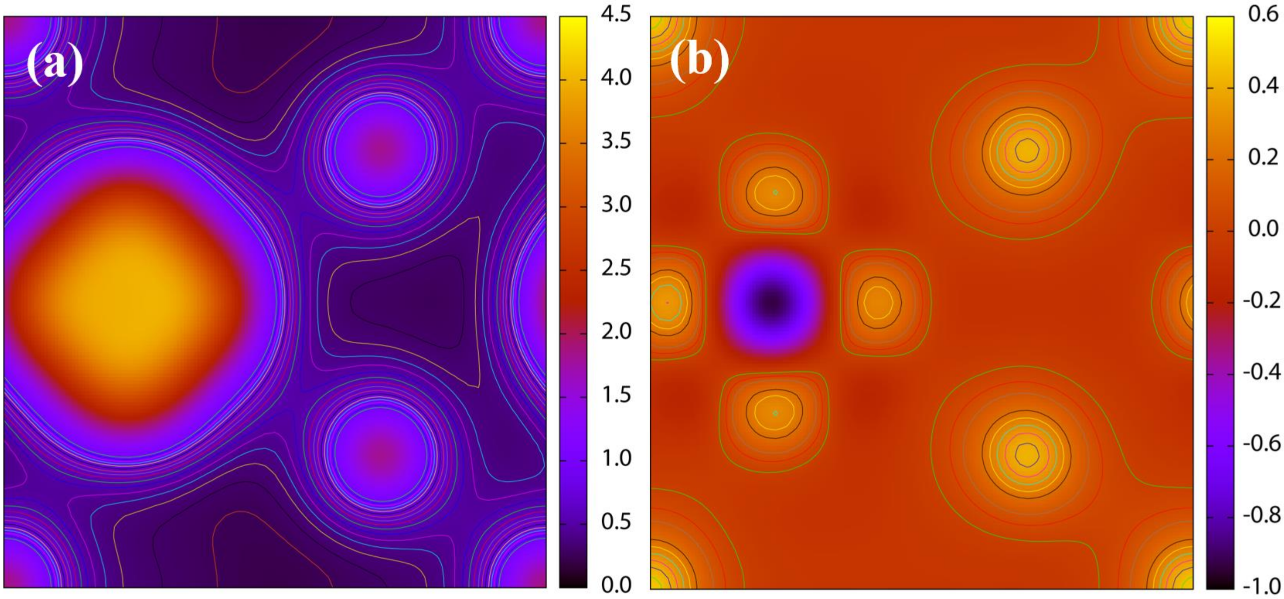

Fig. S17 (a) charge density and (b) charge-density difference along the (1 0 0) plane for the *P*4/*nmm* NpH_5 at 100 GPa.

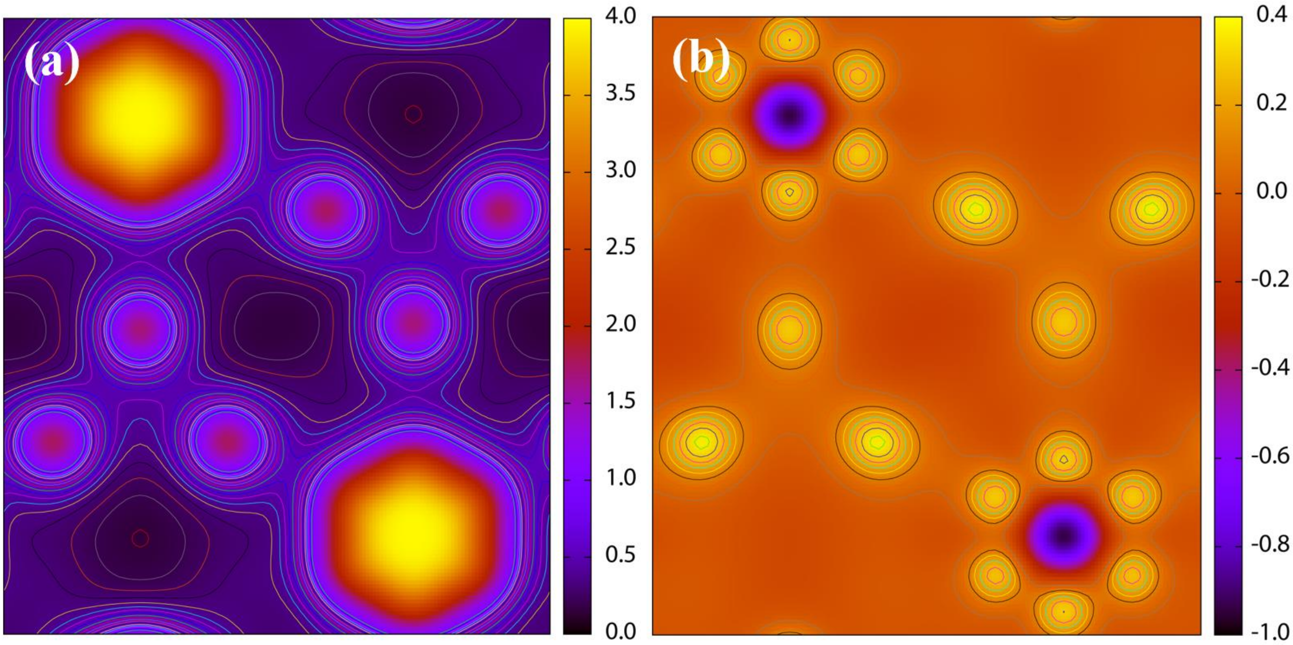

Fig. S18 (a) charge density and (b) charge-density difference along the (1 0 0) plane for the *Cmcm* NpH_7 at 100 GPa.

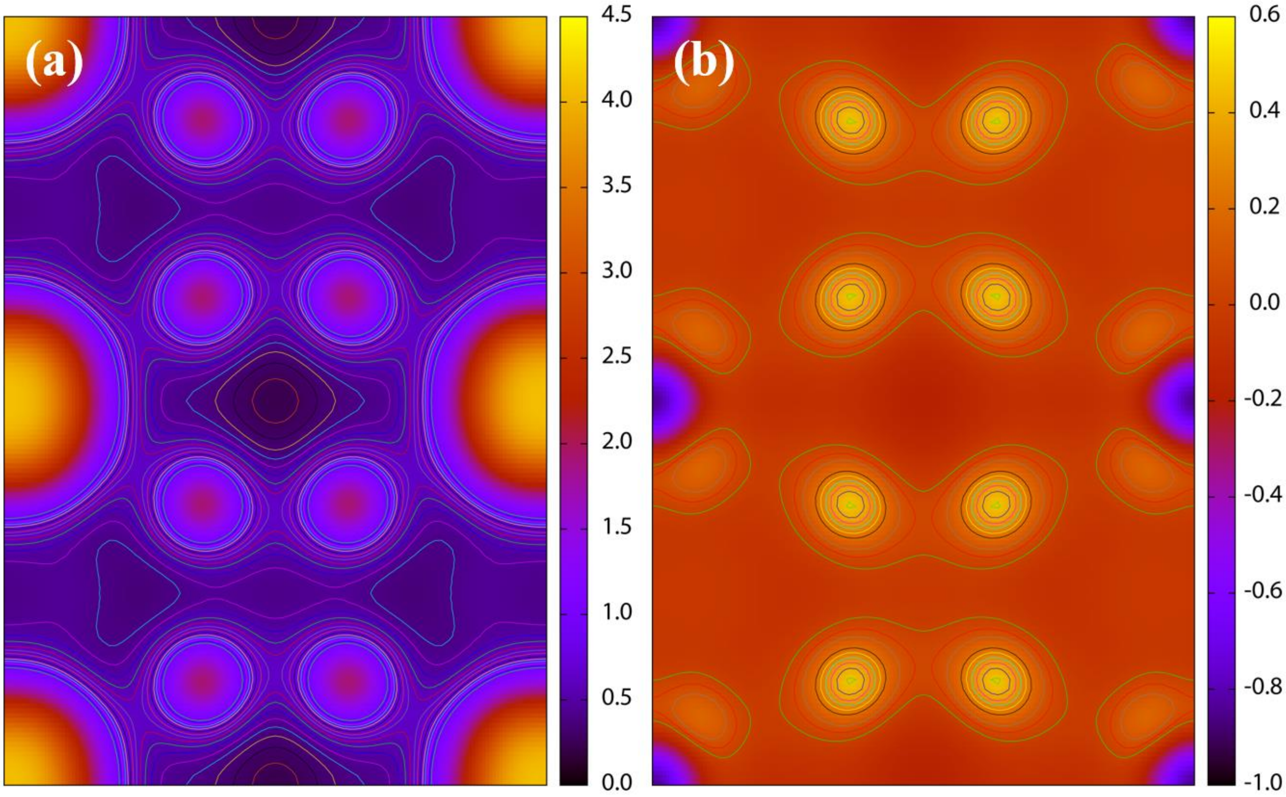

Fig. S19 (a) charge density and (b) charge-density difference along the (1 -1 0) plane for the *Fm*$\bar{3}$*m* NpH_8 at 200 GPa.

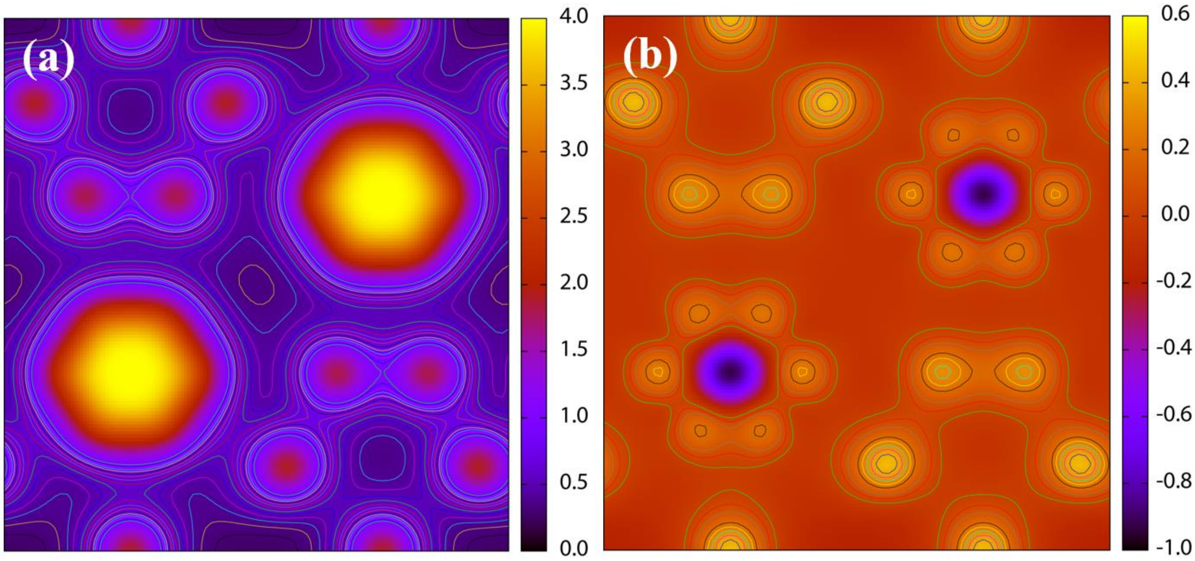

Fig. S20 (a) charge density and (b) charge-density difference along the (-1 -1 0) plane for the $P6_3/mmc$ NpH_9 at 200 GPa.

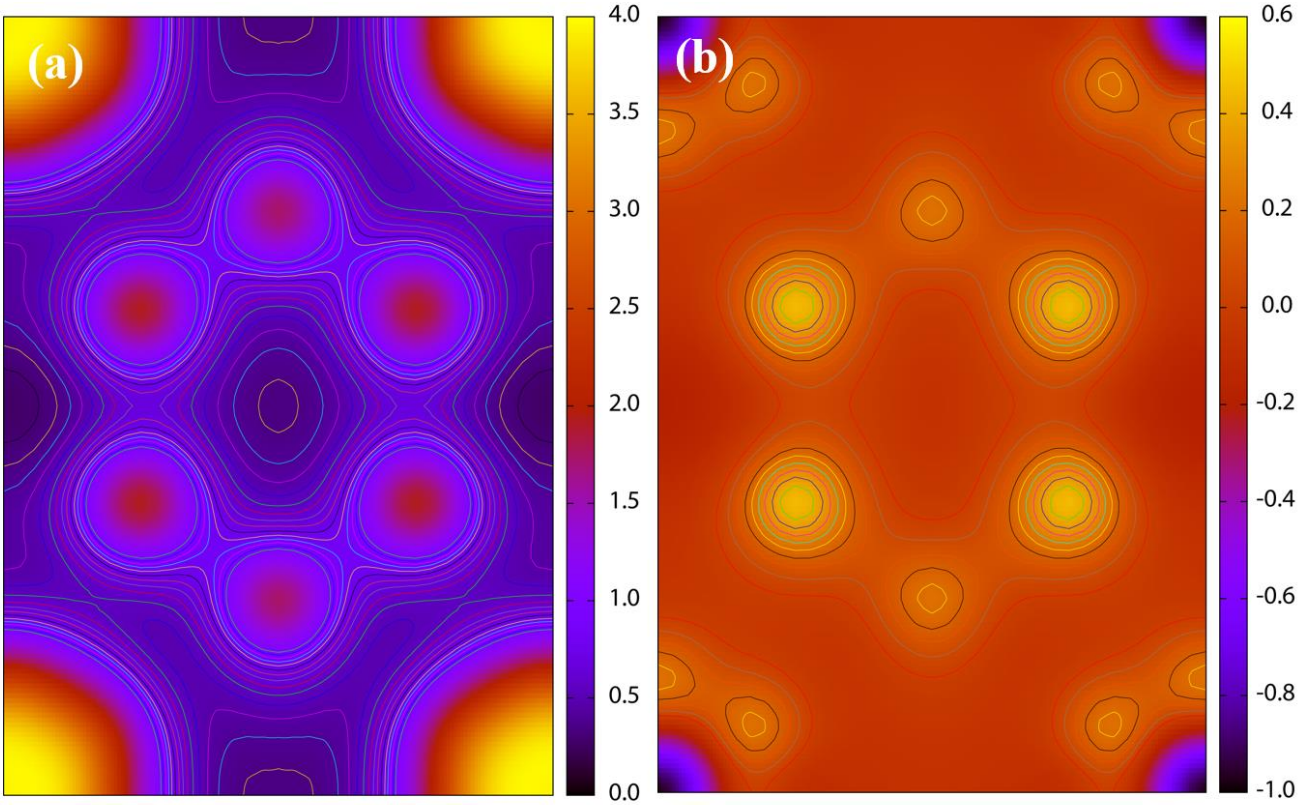

Fig. S21 (a) charge density and (b) charge-density difference along the (0 -1 -1) plane for the $Fm\bar{3}m$ NpH_{10} in the AFM magnetic state at 200 GPa.

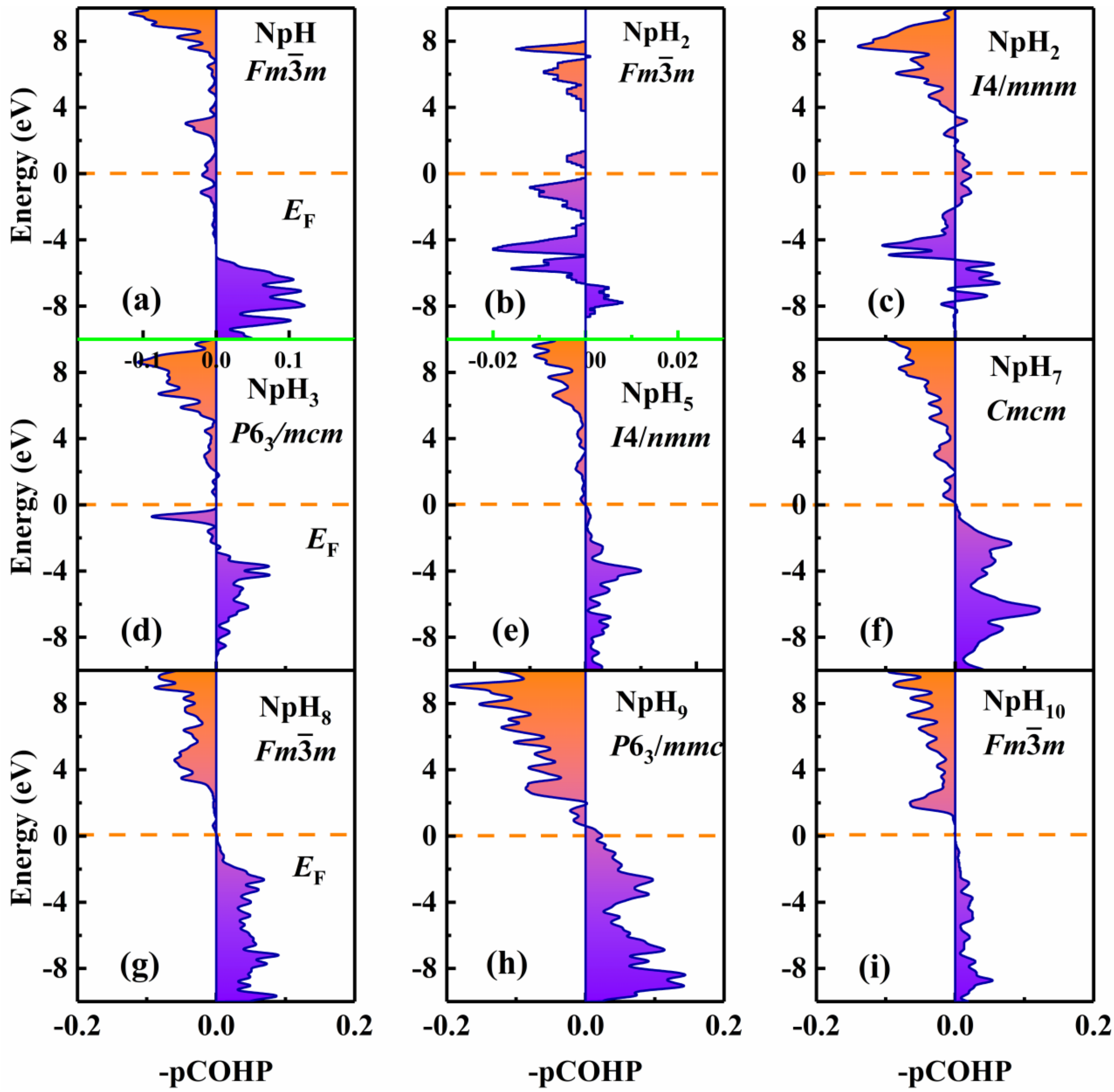

Fig. S22. pCOHP of the shortest Np−H bond in predicted stable Np−H phases. (a) $Fm\bar{3}m$ structure of NpH at 100 GPa. (b) $Fm\bar{3}m$ structure of NpH_2 at ambient pressure. (c) $I4/mmm$ structure of NpH_2 at 25 GPa. (d) $P6_3/mcm$ structure of NpH_3 at ambient pressure. (e) $P4/nmm$ structure of NpH_5 at 100 GPa. (f) $Cmcm$ structure of NpH_7 at 100 GPa. (g) $Fm\bar{3}m$ structure of NpH_8 at 200 GPa. (h) $P6_3/mmc$ structure of NpH_9 at 200 GPa. (i) $Fm\bar{3}m$ structure of NpH_{10} at 200 GPa.

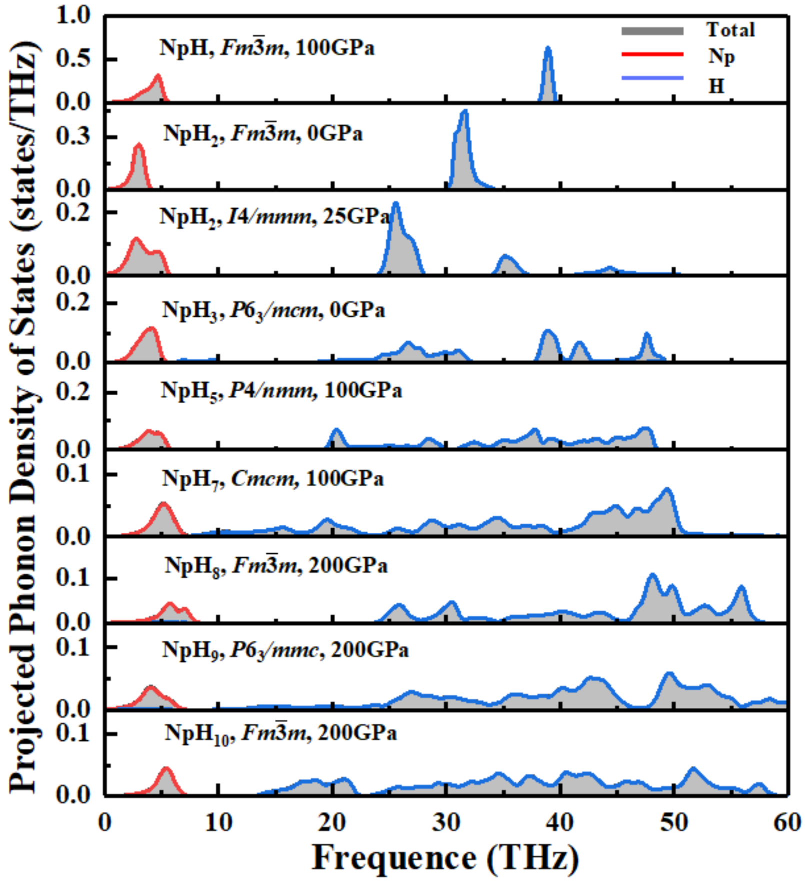

Fig. S23. Projected phonon DOS for NpH_x (x = 1–10) at selected pressures.

Supplementary Table

Table S1 Calculated elastic constants C_{ij} and bulk (B), shear (G), Young's (Y) moduli and Poisson's ratio (σ) of the stable phase of Np-H systems at selected pressures. All moduli are in GPa.

	NpH	NpH_2	NpH_2	NpH_3	NpH_5	NpH_7	NpH_8	NpH_9	NpH_{10}
	$Fm\bar{3}m$	$Fm\bar{3}m$	$I4/mmm$	$P6_3/mcm$	$P4/nmm$	$Cmcm$	$Fm\bar{3}m$	$P6_3/mmc$	$Fm\bar{3}m$
C_{11}	435.27	113.65	259.79	213.30	609.82	686.79	1266.72	1031.61	810.16
C_{12}	242.61	68.76	97.86	62.55	178.93	212.35	264.28	254.09	369.08
C_{13}	242.61	68.76	31.60	35.47	203.44	186.97	264.28	293.90	369.08
C_{22}	435.27	113.65	259.79	213.30	609.82	621.97	1266.72	1031.61	810.16
C_{23}	242.61	68.76	31.60	35.47	203.44	221.12	264.28	293.90	369.08
C_{33}	435.27	113.65	344.20	299.01	479.53	668.20	1266.72	914.32	810.16
C_{44}	17.51	71.77	35.56	55.04	75.10	217.88	326.87	392.15	292.64
C_{55}	17.51	71.77	36.04	55.01	74.96	231.50	326.87	392.15	292.64
C_{66}	17.51	71.77	32.53	75.38	116.18	212.82	326.87	388.76	292.64
B	306.83	83.72	131.73	109.77	317.65	357.47	598.43	517.58	516.11

G	37.53	45.12	57.54	73.42	117.64	222.43	388.17	375.85	261.30
B/G	8.18	1.85	2.29	1.50	2.70	1.61	1.54	1.38	1.98
Y	108.19	114.74	150.67	180.10	314.13	552.65	957.46	907.81	670.71
σ	0.4412	0.2716	0.3094	0.2265	0.3352	0.2423	0.233	0.2077	0.2834

Table S2 Predicted lattice constants, and atomic coordinates as referred to the conventional unit cells of NpH_x (x = 1 – 10) different pressures. Zero-point energies (ZPE) per formula unit are also listed.

System	Phase	Lattice parameter (Å, °)	Atom	Wyckoff position	Atomic coordinates (fractional) *x*	*y*	*z*	ZPE (meV)
NpH	$Fm\bar{3}m$	$a = b = c = 4.220$	Np	4a	0.000	0.000	0.000	266.36
	(*No*: 225, *Z* = 4)	$\alpha = \beta = \gamma = 90$	H	4b	0.50	0.000	0.000	
NpH_2	$Fm\bar{3}m$	$a = b = c = 5.263$	Np	4a	0.000	0.000	0.000	409.00
	(*No*: 225, *Z* = 4)	$\alpha = \beta = \gamma = 90$	H	8c	0.250	0.250	0.250	
	*I*4/*mmm*	$a = b = 3.060$	Np	2a	0.000	0.000	0.000	399.52
	(*No*: 139, *Z* = 2)	$c = 6.103$	H	4e	0.000	0.000	0.355	
		$\alpha = \beta = \gamma = 90$						
NpH_3	$P6_3/mcm$	$a = b = 6.252$	Np	6g	0.660	1.000	0.750	397.32
	(*No*:193, *Z* = 6)	$c = 6.328$	H_1	12k	0.305	1.000	0.597	
		$\alpha = \beta = 90$	H_2	2a	0.000	0.000	0.750	
		$\gamma = 120$	H_3	4d	0.333	0.667	0.000	
NpH_5	*P*4/*nmm*	$a = b = 3.783$	Np	2c	0.000	0.500	0.227	2314.45
	(*No*: 129, *Z* = 2)	$c = 3.717$	H_1	2a	0.500	0.500	0.000	
		$\alpha = \beta = \gamma = 90$	H_2	8i	0.500	0.731	0.304	
NpH_7	*Cmcm*	$a = 3.663$; $b = 6.157$	Np	4c	0.000	0.840	0.750	3266.15
	(*No*: 63, *Z* =4)	$c = 5.332$	H_1	12h	0.747	0.592	0.924	
		$\alpha = \beta = \gamma = 90$	H_2	8f	0.000	0.688	0.090	
			H_3	16c	0.000	0.505	0.250	
NpH_8	$Fm\bar{3}m$	$a = c = b = 4.700$	Np	4a	0.000	0.000	0.000	2225.16
	(*No*: 225, *Z* = 4)	$\alpha = \beta = \gamma = 90$	H	32f	0.365	0.635	0.365	
NpH_9	$P6_3/mmc$	$a = b = 3.456$	Np	2c	0.667	0.333	0.250	4697.55
	(*No*: 194, *Z* = 2)	$c = 5.354$	H_1	12k	0.157	0.843	0.439	
		$\alpha = \beta = 90$	H_2	4f	0.333	0.667	0.156	
		$\gamma = 120$	H_3	2b	0.000	0.000	0.750	
NpH_{10}	$Fm\bar{3}m$	$a = c = b = 4.877$	Np	4b	0.000	0.000	0.500	2400.22
	(*No*: 225, *Z* = 4)	$\alpha = \beta = \gamma = 90$	H_1	8c	0.750	0.750	0.750	
			H_2	32f	0.877	0.877	0.123	