Supplementary Information

Structural Assignment, Electronic and Magnetic Properties of Lanthanide Metal Doped Silicon Heptamers $Si_7M^{0/-}$ with M = Pr, Gd and Ho

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Tables contain natural electron configuration, charge, magnetic moment (μ_B) of 6*s*, 4*f*, 5*d*, 6*p* and 6*d* states of M atoms with M = Pr, Gd, Ho, along with total magnetic moment of the ground state structure of $Si_7M^{0/-}$ clusters (PBE) and Cartesian coordinates of the ground state structures of the clusters considered. Figures display the shapes, electronic states and relative energies of the most stable forms of the neutral and anionic $Si_7M^{0/-}$ clusters using the B3LYP, PBE, BPW91, BP86 and TPSSh functionals.

Table S1. The first VDE and ADE of the anionic $Si_7M^{0/-}$ clusters with M = Pr, Gd, Ho obtained using B3LYP, PBE, BPW91, BP86 and TPSSh functionals.

Species	ADE						VDE					
	B3LYP	PBE	BPW91	BP86	TPSSh	Exp	B3LYP	PBE	BPW91	BP86	TPSSh	Exp
$PrSi_7^-$	2.50	2.39	2.48	2.51	2.42	2.4 ± 0.1	2.70	2.64	2.74	2.76	2.85	2.60
$GdSi_7^-$	2.42	2.44	2.42	2.53	2.49	2.3 ± 0.1	2.62	2.69	2.69	2.70	2.75	2.55
$HoSi_7^-$	2.42	2.37	2.50	2.55	2.31	2.4 ± 0.1	2.69	2.65	2.54	2.66	2.53	2.60

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Table S2. Natural electron configuration and net charge of M atom of the ground state structure of $Si_7M^{0/-}$ clusters with M = Pr, Gd, Ho, along with total magnetic moments (PBE).

Clusters	Electron configuration	Charge
$PrSi_7$	[core]$6s^{0.35}4f^{2.66}5d^{1.12}6p^{0.08}6d^{0.01}$	1.18
$PrSi_7^-$	[core]$6s^{0.44}4f^{2.37}5d^{1.95}6p^{0.19}6d^{0.01}$	0.88
$GdSi_7$	[core]$6s^{1.06}4f^{7.02}5d^{1.02}6p^{0.15}6d^{0.01}$	0.44
$GdSi_7^-$	[core]$6s^{0.90}4f^{7.02}5d^{1.69}6p^{0.26}6d^{0.02}$	0.35
$HoSi_7$	[core]$6s^{0.53}4f^{10.91}5d^{0.51}6p^{0.10}6d^{0.01}$	0.72
$HoSi_7^-$	[core]$6s^{0.60}4f^{10.43}5d^{1.43}6p^{0.25}6d^{0.02}$	0.35

Table S3. Magnetic moment (μ_B) of 6s, 4f, 5d, 6p and 6d states of M atom with M = Pr, Gd, Ho, along with total magnetic moment of the ground state structure of $Si_7M^{0/-}$ clusters (PBE).

Clusters	Magnetic moment of M atoms						Molecule (μ_B)
	6s	4f	5d	6p	6d	Total	
$PrSi_7$	0.01	2.60	0.16	0.00	0.01	2.78	3
$PrSi_7^-$	0.01	2.19	0.07	0.00	0.01	2.28	2
$GdSi_7$	0.79	6.97	0.28	0.03	0.01	8.08	8
$GdSi_7^-$	0.44	6.96	0.23	0.01	0.00	7.64	7
$HoSi_7$	0.03	3.07	0.02	0.00	0.00	3.12	3
$HoSi_7^-$	0.02	3.56	0.15	0.01	0.00	3.74	4

Table S4. Cartesian Coordinates (angstrom) of the most stable neutrals and anions $Si_7M^{0/-}$ using B3LYP functional.

Structure	Geometry (Cartesian Coordinates)			
$PrSi_7$	14	0.099494000	1.340607000	-1.358769000
	14	0.543037000	1.009280000	1.100445000
	14	0.944951000	-1.001393000	-0.603210000
	14	2.174305000	-0.602201000	1.620952000
	14	3.285801000	-1.128141000	-0.549954000
	14	-1.314567000	2.183186000	0.435381000
	14	2.401222000	1.079125000	-0.526878000
	59	-1.930159000	-0.683500000	-0.027992000
$PrSi_7^-$	14	2.193521000	-2.322666000	0.000099000
	14	1.619988000	0.000001000	-0.000012000
	14	0.252435000	1.655748000	-1.265984000
	14	0.252512000	-1.655842000	-1.265983000
	14	0.252515000	1.655830000	1.265988000
	14	0.252443000	-1.655736000	1.265989000
	14	2.193516000	2.322671000	-0.000096000
	59	-1.665034000	-0.000001000	0.000000000
$GdSi_7$	14	0.564372000	1.875067000	-1.109465000
	14	0.452321000	0.932929000	1.196596000
	14	1.048348000	-0.563482000	-1.062542000
	14	1.375054000	-1.265266000	1.311517000
	14	3.176531000	-1.270151000	-0.426302000
	14	-1.271601000	2.215778000	0.448192000
	14	2.618123000	0.997591000	0.159605000
	64	-1.741939000	-0.639290000	-0.113225000
$GdSi_7^-$	14	0.564372000	1.875067000	-1.109465000
	14	0.452321000	0.932929000	1.196596000
	14	1.048348000	-0.563482000	-1.062542000
	14	1.375054000	-1.265266000	1.311517000
	14	3.176531000	-1.270151000	-0.426302000
	14	-1.271601000	2.215778000	0.448192000
	14	2.618123000	0.997591000	0.159605000
	64	-1.741939000	-0.639290000	-0.113225000
$HoSi_7$	14	-2.245781000	-0.630681000	1.616023000
	14	-1.032097000	-0.985361000	-0.640175000
	14	-0.601363000	0.961652000	1.125262000
	14	-0.244913000	1.398408000	-1.341354000

	14	-2.482172000	1.070816000	-0.472742000
	14	-3.386410000	-1.113056000	-0.562213000
	14	1.225726000	2.207721000	0.436767000
	67	1.831912000	-0.607955000	-0.033761000
$HoSi_7^-$	14	-2.194717000	2.336579000	0.000011000
	14	-1.687142000	0.000322000	-0.000035000
	14	-0.291262000	-1.629326000	-1.292776000
	14	-0.290409000	1.629595000	-1.292620000
	14	-0.291266000	-1.629345000	1.292756000
	14	-0.290435000	1.629528000	1.292656000
	14	-2.195670000	-2.335737000	0.000002000
	67	1.513024000	-0.000338000	0.000002000

Figure S1. Equilibrium shapes of the lowest-energy isomers for $Si_7M^{0/-}$ clusters using DFT calculations. The red and blue balls denote Si and M atoms, respectively.

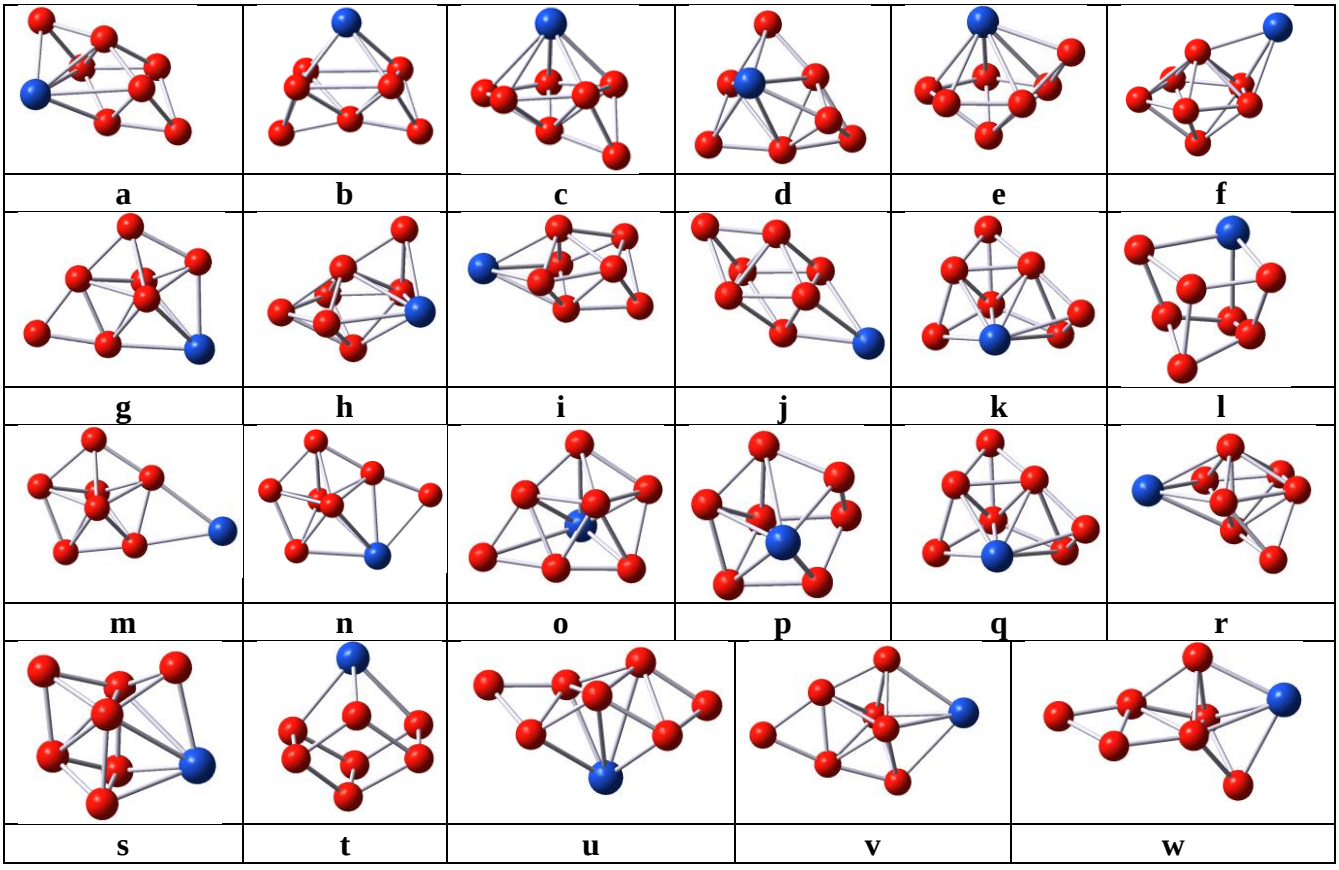
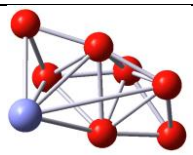
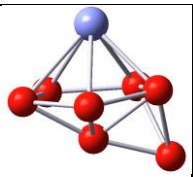
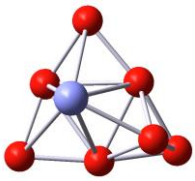
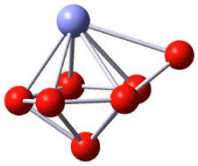
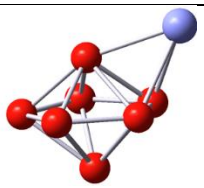
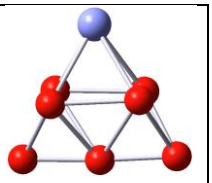


Figure S2. Shapes, electronic states and relative energies of the most stable forms of the neutral and anionic $Si_7Pr^{0/-}$ clusters using B3LYP, PBE, BPW91, BP86 and TPSSh functionals.

Neutral						
Functional	**Pr-n-1** (C_1, ^4A)	**Pr-n-2** (C_1, ^4A)	**Pr-n-3** (C_1, ^4A)	**Pr-n-4** (C_1, ^4A)	**Pr-n-5** (C_1, ^4A)	**Pr-n-6** (C_1, ^4A)
B3lyp	0.0	1.2	1.3	3.6	5.6	6.0
PBE	0.0	0.2	3.1	2.8	5.4	5.0
BPW91	0.0	0.3	2.2	2.2	4.8	4.9
TPSSh	0.0	1.8	2.9	8.6	4.0	5.0
BP86	0.1	0.0	1.9	1.3	5.4	5.3

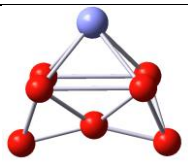
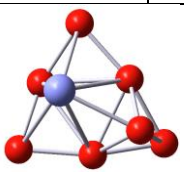
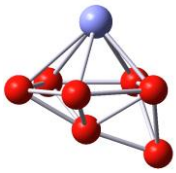
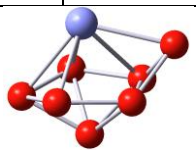
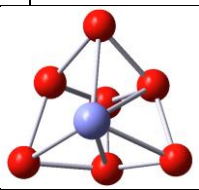
Anion					
Functional	**Pr-a-1** (C_{2v}, $^3A_2$)	**Pr-a-2** (C_1, ^3A)	**Pr-a-3** (C_1, ^3A)	**Pr-a-4** (C_1, ^5A)	**Pr-a-5** (C_1, ^5A)
B3lyp	0.0	0.5	1.0	5.5	8.6
PBE	0.0	1.1	0.5	5.2	12.6
BPW91	0.0	7.8	0.7	5.4	12.1
TPSSH	0.0	2.0	17.9	6.1	10.5
BP86	0.0	0.1	13.4	2.8	8.9

Figure S3. Shapes, electronic states and relative energies of the most stable forms of the neutral and anionic $Si_7Gd^{0/-}$ clusters using B3LYP, PBE, BPW91, BP86 and TPSSH functionals.

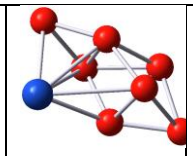
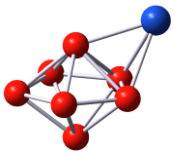
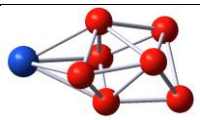
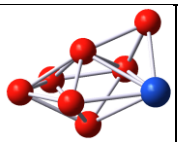
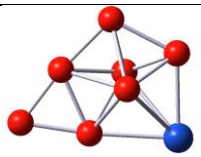
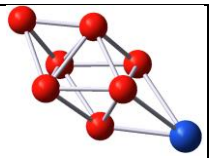
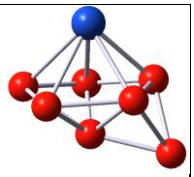
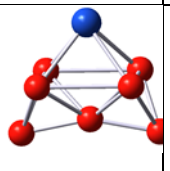
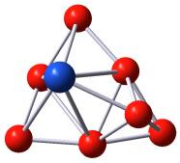
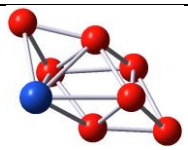
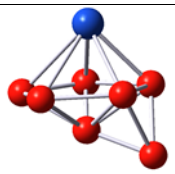
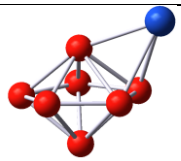
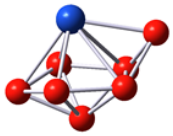
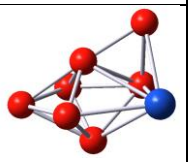
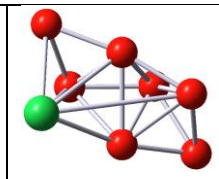
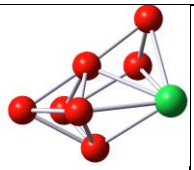
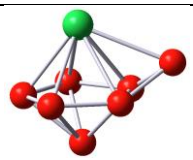
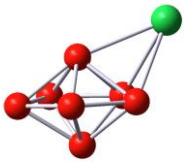
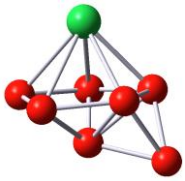
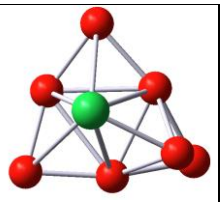
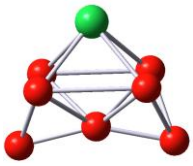
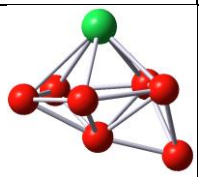
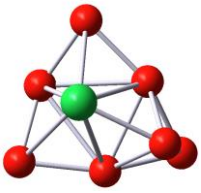
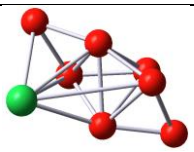
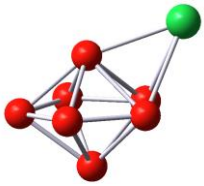
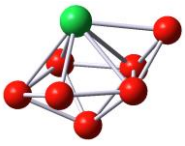
Neutral							
Functional	**Gd-n-1** (C_1, ^9A)	**Gd-n-2** (C_1, ^9A)	**Gd-n-3** (C_1, ^9A)	**Gd-n-4** (C_1, ^9A)	**Gd-n-5** (C_1, ^9A)	**Gd-n-6** (C_1, ^9A)	**Gd-n-7** (C_1, ^9A)
B3lyp	0.0	2.9	6.1	7.9	8.8	7.9	9.6
PBE	0.0	2.0	4.4	5.8	6.4	7.0	8.4
BPW91	0.0	2.0	4.2	6.0	6.2	7.0	6.9
TPSSH	0.0	1.8	3.7	5.6	6.9	6.8	7.9
BP86	0.0	2.3	4.6	6.1	6.4	7.3	6.9
Anion							
Functional	**Gd-a-1** (C_{2v}, $^8A_2$)	**Gd-a-2** (C_1, ^{10}A)	**Gd-a-3** (C_1, ^{10}A)	**Gd-a-4** (C_1, ^{10}A)	**Gd-a-5** (C_1, ^{10}A)	**Gd-a-6** (C_1, ^8A)	**Gd-a-7** (C_1, ^8A)
B3LYP	0.0	1.3	1.5	2.9	4.0	4.9	6.2
PBE	0.0	3.6	1.5	1.8	6.1	4.1	4.6
BPW91	0.0	2.7	1.3	1.8	6.3	2.9	5.0
TPSSH	0.0	5.1	3.6	3.6	9.8	3.5	5.2
BP86	0.0	2.2	1.0	1.6	5.4	2.2	5.1

Figure S4. Shapes, electronic states and relative energies of the most stable forms of the neutral and anionic $Si_7Ho^{0/-}$ clusters using B3LYP, PBE, BPW91, BP86 and TPSSH functionals.

Neutral						
Functional	**Ho-n-1** (C_1, ^4A)	**Ho-n-2** (C_1, ^4A)	**Ho-n-3** (C_1, ^4A)	**Ho-n-4** (C_1, ^6A)	**Ho-n-5** (C_1, ^4A)	**Ho-n-6** (C_1, ^4A)
B3LYP	0.0	7.6	9.1	9.4	9.7	11.7
PBE	0.0	5.6	8.4	9.8	7.4	8.4
BPW91	0.0	6.0	4.9	9.7	6.2	7.9
TPSSH	0.0	6.1	7.3	11.0	4.0	6.4
BP86	0.0	6.1	4.1	9.8	8.0	8.2
Anion						
Functional	**Ho-a-1** (C_1, $^5B_2$)	**Ho-a-2** (C_1, ^5A)	**Ho-a-3** (C_1, ^5A)	**Ho-a-4** (C_1, ^5A)	**Ho-a-5** (C_1, ^5A)	**Ho-a-6** (C_1, ^5A)
B3LYP	0.0	0.6	1.0	1.3	4.0	2.5
PBE	1.1	0.0	2.5	3.8	3.8	10.8
BPW91	1.8	0.0	1.0	2.7	6.5	10.6
TPSSH	1.7	1.3	0.0	8.2	4.0	1.7
BP86	2.0	0.0	0.8	3.7	6.8	10.5