Electronic Supplementary Information

Nature of the Interaction between Rare Gas Atoms and Transition Metal Doped Silicon Clusters: The Role of Shielding Effects

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Part 1. Analysis of the mass spectra

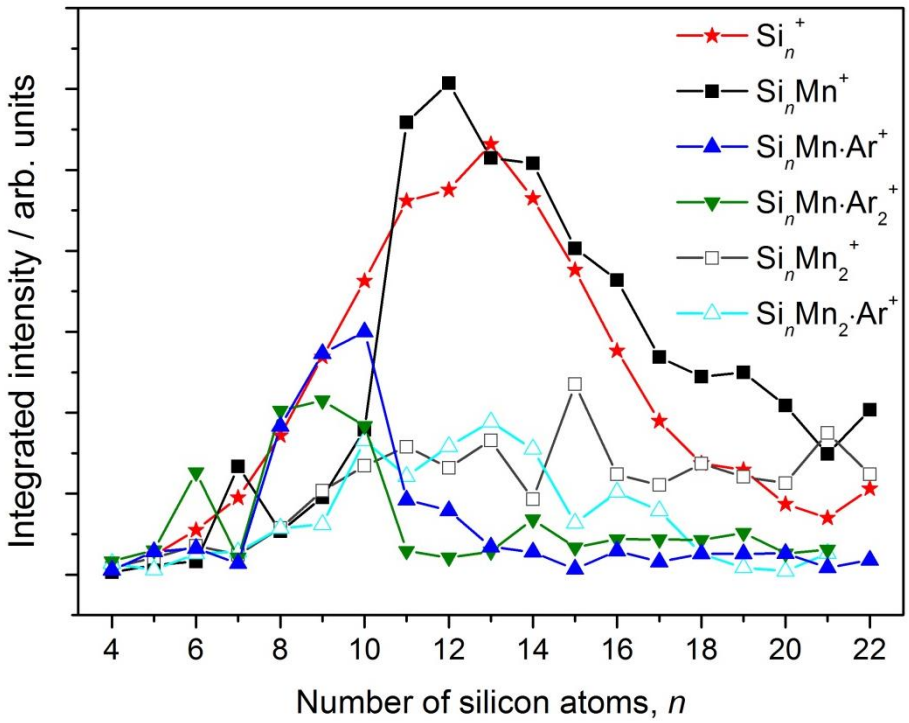


Figure S1. The intensities of Si_n^+, Si_nMn^+, $Si_nMn_2^+$, $Si_nMn^+\cdot Ar$, $Si_nMn^+\cdot Ar_2$, and $Si_nMn_2^+\cdot Ar$, obtained by fitting the natural isotope distribution of those species to the mass spectrum presented in Fig. 1a of the main text.

The mass spectra of $Si_nMn^+\cdot RG$ (such as the one shown in Fig. 1) are congested due to the large number of possible compositions and due to the natural isotope distributions of silicon. The intensity of each species can be extracted from the mass spectra by deconvolution. The abundance of each cluster is than obtained by fitting the corresponding isotope distribution to the measured mass spectra. The result of such analysis for $Si_nMn_m^+\cdot Ar$ is shown in Fig. S1 where the intensities of Si_n^+, Si_nMn^+, $Si_nMn_2^+$, $Si_nMn^+\cdot Ar$, $Si_nMn^+\cdot Ar_2$, and $Si_nMn_2^+\cdot Ar$ are plotted as a function of *n*.

Part 2. Dependence of the cluster-RG binding energy on the used functionals

Table S1. The cluster-RG binding energies (eV) calculated using B3P36 and M06 functionals with the basis set 6-311+G(d) for Ar, Si and TM atoms, aug-cc-pVdZ for Xe atom.

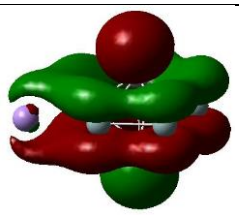
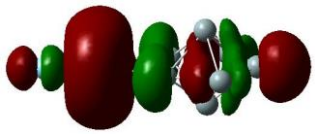
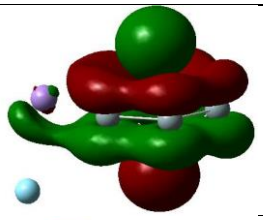
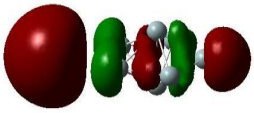
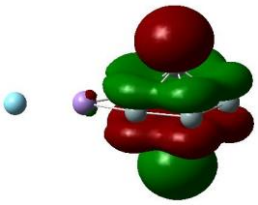
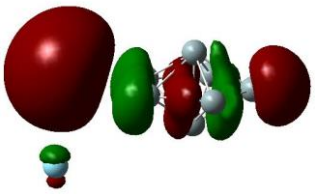
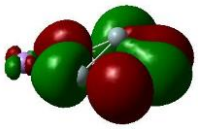
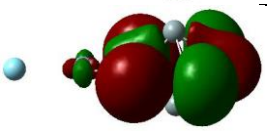
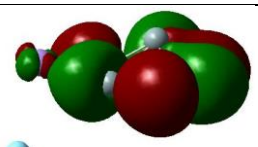
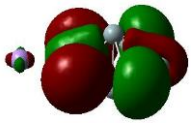
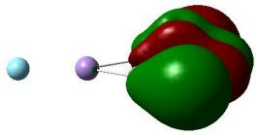
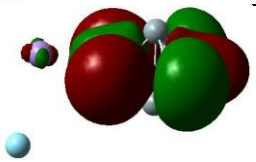
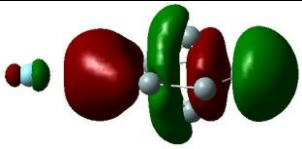
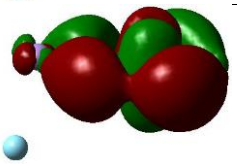
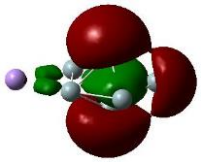
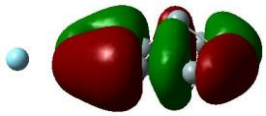
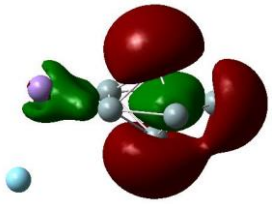
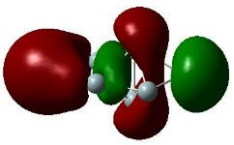
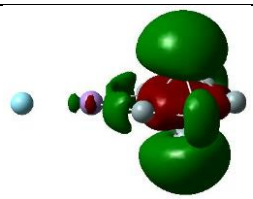
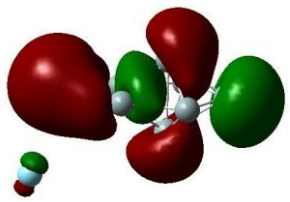
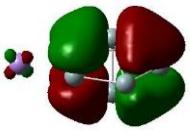
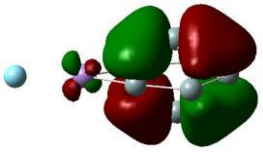
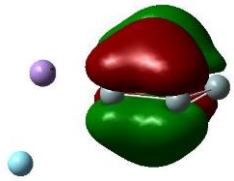
Complex		**B3P86**	**M06**
Si_7Cr^+.Ar	**Com-A**	0.189	0.205
Si_7Cr^+.Xe	**Com-A**	0.417	0.513
Si_7Mn^+.Ar	**Com-A**	-0.248	-0.202
	Com-B	0.017	0.110
Si_7Mn^+.Xe	**Com-A**	0.028	0.128
	Com-B	0.143	0.309
Si_7Cu^+.Ar	**Com-A**	0.216	0.264
Si_7Cu^+.Xe	**Com-A**	0.507	0.615
Si_7Zn^+.Ar	**Com-A**	-0.399	-0.596
	Com-B	0.005	0.060
Si_7Zn^+.Xe	**Com-A**	-0.111	-0.291
	Com-B	0.097	0.207

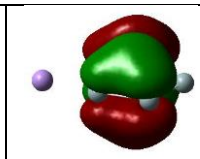
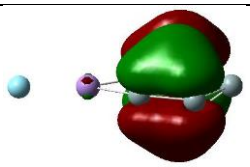
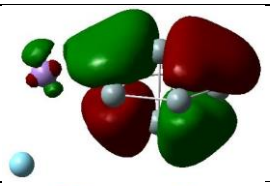
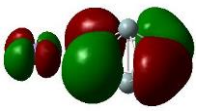
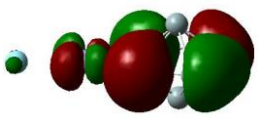
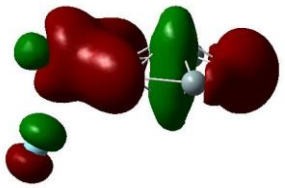
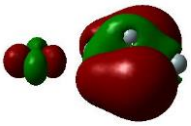
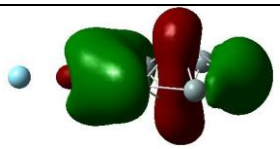
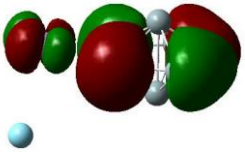
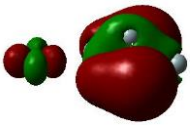
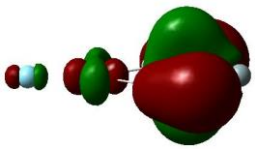
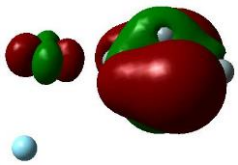
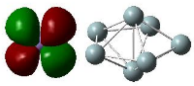
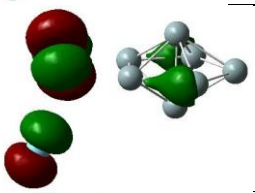
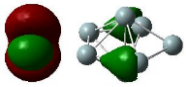
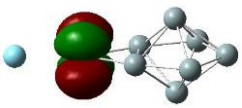
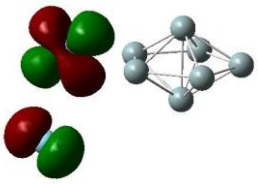
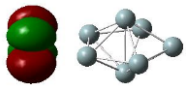
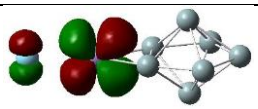
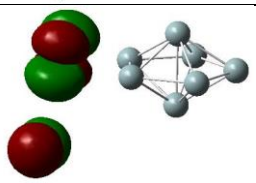
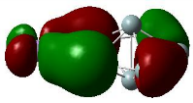
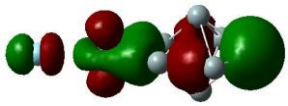
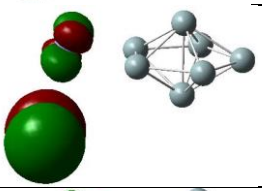
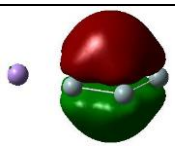
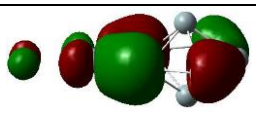
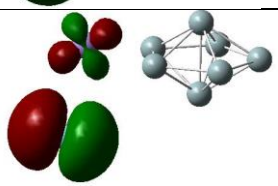
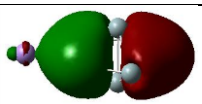
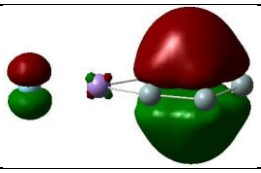
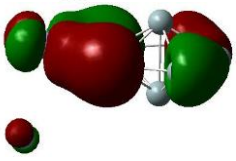
Part 3. Interaction of Si_nMn^+ (n = 6-10) with rare gas atoms (Ar, Xe)

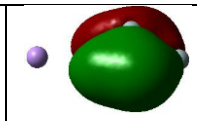
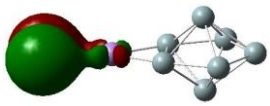
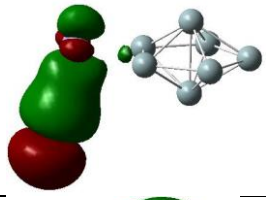
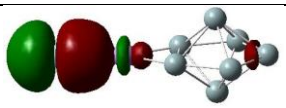
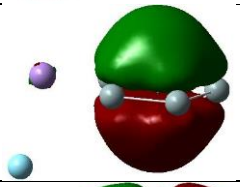
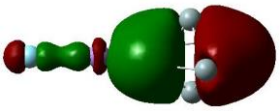
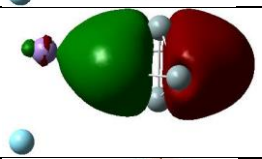
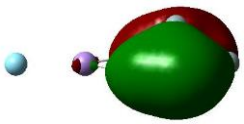
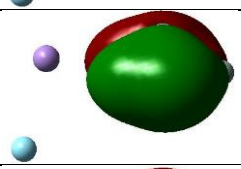
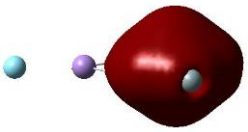
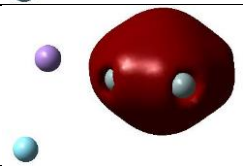
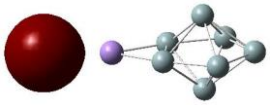
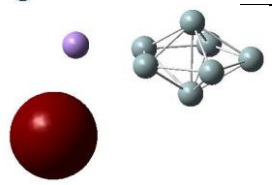
Table S2. Some selected bond lengths (d, in Å), atomic charge and charge transfer (CT, in e) in Si_nMn^+ clusters and their RG complexes, as obtained at the B3P86/6-311+G(d) level of theory.

	Si_nMn^+		$Si_nMn^+ \cdot Ar$		$Si_nMn^+ \cdot Xe$	
	Shortest d(Si-Mn)	Charge on Mn (e)	d (Mn-Ar)	CT (Ar→Mn)	d (Mn-Xe)	CT (Xe→Mn)
Si_6Mn^+	2.480	0.96	2.634	0.09	2.848	0.18
Si_7Mn^+(**Com-A**)	2.787	0.83	2.719	0.07	2.906	0.14
Si_7Mn^+(**Com-B**)	2.787	0.83	3.436	0.01	3.240	0.07
Si_8Mn^+	2.477	0.93	2.622	0.10	2.837	0.19
Si_9Mn^+	2.458	0.80	2.640	0.10	2.850	0.20
$Si_{10}Mn^+$	2.450	1.01	2.634	0.08	2.844	0.17

Table S3. Shapes of molecular orbitals (for spin up) of Si_7Mn^+ cluster and the Si_7Mn^+·Ar complexes (**Com-A** and **Com-B**)

	Si_7Mn^+	**Com-A**	**Com-B**
LUMO			
HOMO			
HOMO-1			
HOMO-2			
HOMO-3			
HOMO-4			
HOMO-5			
HOMO-6			

HOMO-7			
HOMO-8			
HOMO-9			
HOMO-10			
HOMO-11			
HOMO-12			
HOMO-13			
HOMO-14			
HOMO-15			
HOMO-16			

HOMO-18			
HOMO-19			
HOMO-20			
HOMO-21			
HOMO-22			
HOMO-23			

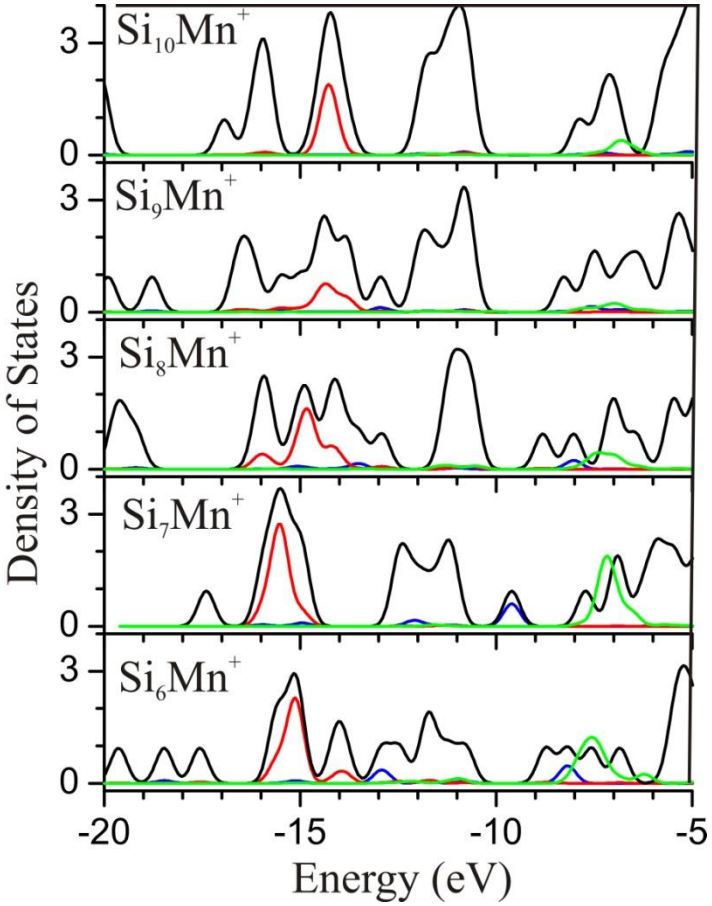


Figure S2. Total density of states (TDOS) for *alpha* orbitals (black line) together with the partial density of states (pDOS) for *alpha* and *beta* Mn *3d* (red and green line, respectively) and *alpha* Mn 4*s* orbital (blue line) of Si_nMn^+ (n = 6-10).

Part 4. Interaction of Si_7TM^+ (TM = Cr, Mn, Cu and Zn) with rare gas atoms (Ar, Xe)

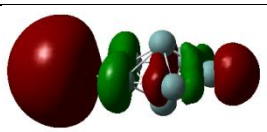
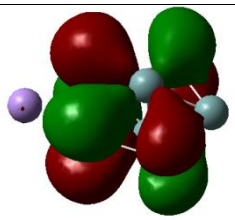
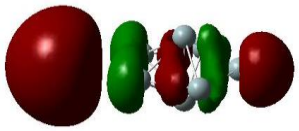
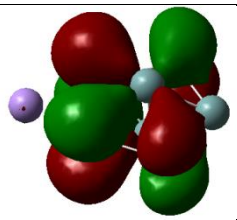
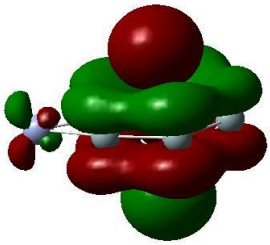
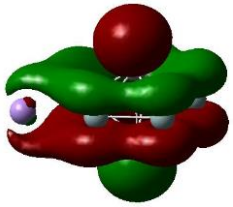
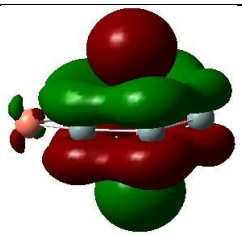
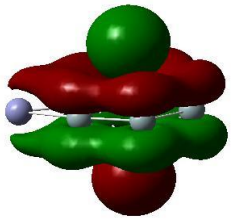
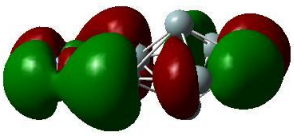
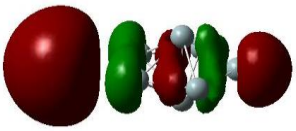
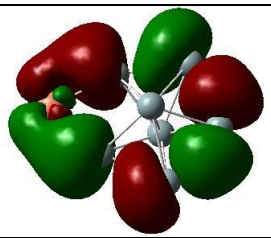
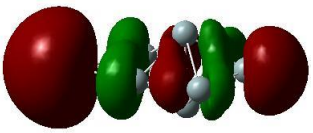
Table S4. Electronic state, electron configuration, charge on the dopant atom (in e), HOMO-LUMO gap (in eV) and average Si-dopant bond distance (in Å) of the Si_7TM^+ (TM = Cr, Mn, Cu and Zn) calculated at the B3P86/6-311+G(d) level. Electron analysis is obtained from the NBO 5.G program.

Cluster	Electronic state	Electron configuration of TM	Charge on TM, e	HOMO-LUMO gap, eV	averaged *d* (Si-TM), Å
Si_7Cr^+	$^6A_1$	$3d^{4.96}\ 4s^{0.20}\ 4p^{0.01}$	+0.83	2.541	2.5782
Si_7Mn^+	$^7A_1$	$3d^{5.10}\ 4s^{1.04}\ 4p^{0.03}$	+0.83	1.885	2.7870
Si_7Cu^+	$^1A_1$	$3d^{9.91}\ 4s^{0.34}\ 4p^{0.01}$	+0.73	3.376	2.3098
Si_7Zn^+	$^2A_1$	$3d^{9.99}\ 4s^{1.22}\ 4p^{0.14}$	+0.64	2.166	2.6809

Table S5. Transition metal-rare gas bond distance, average Si-dopant bond distance (in Å), charge transfer from rare gas to metal atom (*CT*, e), dissociation energy of the metal-rare gas bond (*BDE*, in eV), HOMO-LUMO gap (in eV) and electron configuration of metal atom of the Si_7TM^+·RG (TM = Cr, Mn, Cu and Zn; RG = Ar, Xe) complexes calculated at the B3P86/6-311+G(d) level. Electron analysis is obtained from the NBO 5.G program.

Complex	**Structure**	***d*(TM-RG), Å**	**average *d*(TM-Si), Å**	***CT*, e**	**BE, eV**	**HOMO-LUMO gap, eV**	**Electron Configuration on TM**
Si_7Cr^+.Ar	**Com-A**	2.8169	2.5629	0.066	0.189	2.559	$3d^{4.97}\ 4s^{0.26}\ 4p^{0.01}$
Si_7Cr^+.Xe	**Com-A**	2.8618	2.5906	0.131	0.417	2.522	$3d^{5.00}\ 4s^{0.30}\ 4p^{0.01}\ 4d^{0.02}$
Si_7Mn^+.Ar	**Com-A**	2.7188	2.4779	0.067	-0.248	1.678	$3d^{5.34}\ 4s^{0.47}\ 4p^{0.03}\ 4d^{0.01}$
	Com-B	3.4363	2.7786	0.012	0.017	1.871	$3d^{5.11}\ 4s^{1.03}\ 4p^{0.03}$
Si_7Mn^+.Xe	**Com-A**	2.9057	2.4813	0.144	0.028	1.863	$3d^{5.36}\ 4s^{0.49}\ 4p^{0.04}\ 4d^{0.02}$
	Com-B	3.2402	2.7391	0.065	0.143	1.804	$3d^{5.13}\ 4s^{0.99}\ 4p^{0.04}\ 4d^{0.01}$
Si_7Cu^+.Ar	**Com-A**	2.4573	2.3343	0.074	0.216	3.351	$3d^{9.91}\ 4s^{0.34}\ 4p^{0.02}$
Si_7Cu^+.Xe	**Com-A**	2.6389	2.3462	0.150	0.507	3.324	$3d^{9.92}\ 4s^{0.44}\ 4p^{0.02}\ 4d^{0.01}$
Si_7Zn^+.Ar	**Com-A**	2.7305	2.4269	0.054	-0.399	1.518	$3d^{9.99}\ 4s^{0.88}\ 4p^{0.05}$
	Com-B	3.6126	2.6799	0.005	0.005	2.126	$3d^{9.99}\ 4s^{1.23}\ 4p^{0.05}\ 5s^{0.01}$
Si_7Zn^+.Xe	**Com-A**	2.8311	2.4213	0.143	-0.111	1.669	$3d^{9.99}\ 4s^{0.86}\ 4p^{0.07}\ 4d^{0.01}$
	Com-B	3.2534	2.6676	0.050	0.097	2.033	$3d^{9.99}\ 4s^{1.21}\ 4p^{0.05}\ 5s^{0.01}$

Table S6. Shapes of some selected frontier orbitals of Si_7TM^+ (TM = Cr, Mn, Cu and Zn)

MO	Cr	Mn	Cu	Zn
LUMO+1				
LUMO				
HOMO				

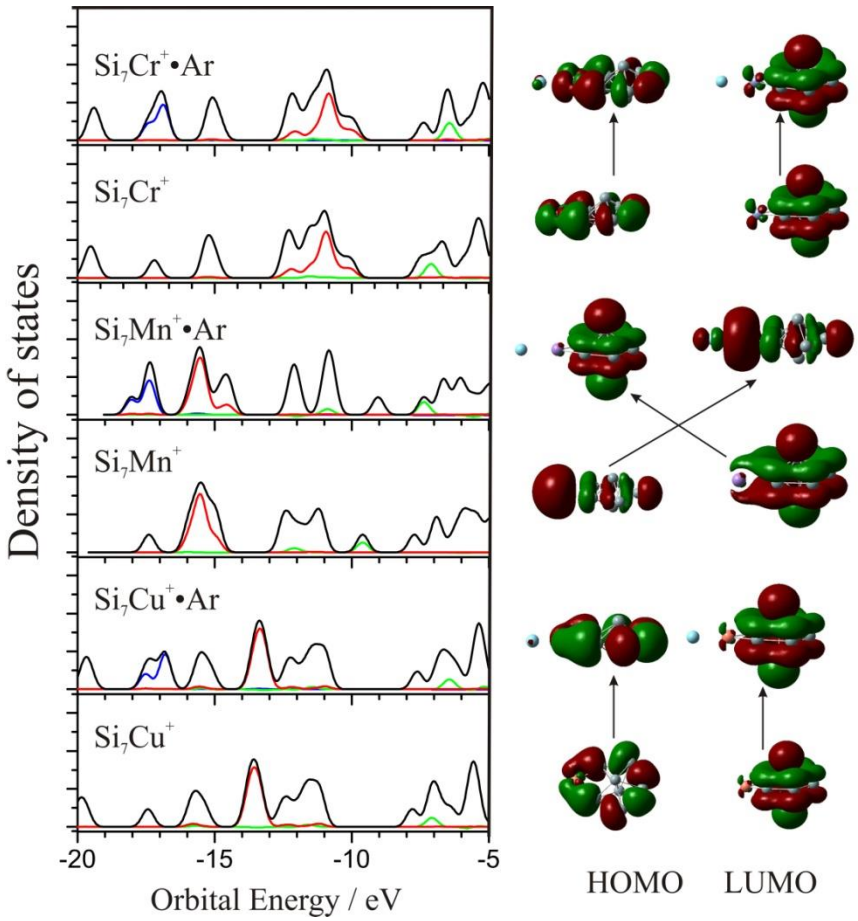


Figure S3. Black curve is TDOS of Si_nTM^+ (TM = Cr, Mn, Cu) and their Ar-complexes (**Com-A)**. Red curve is pDOS of 3*d* (TM); green curve is pDOS of 4*s* (TM); blue curve is pDOS of 3*p* (Ar). The DOS are plotted based on *alpha* orbitals. HOMO and LUMO orbital are depicted on the right.

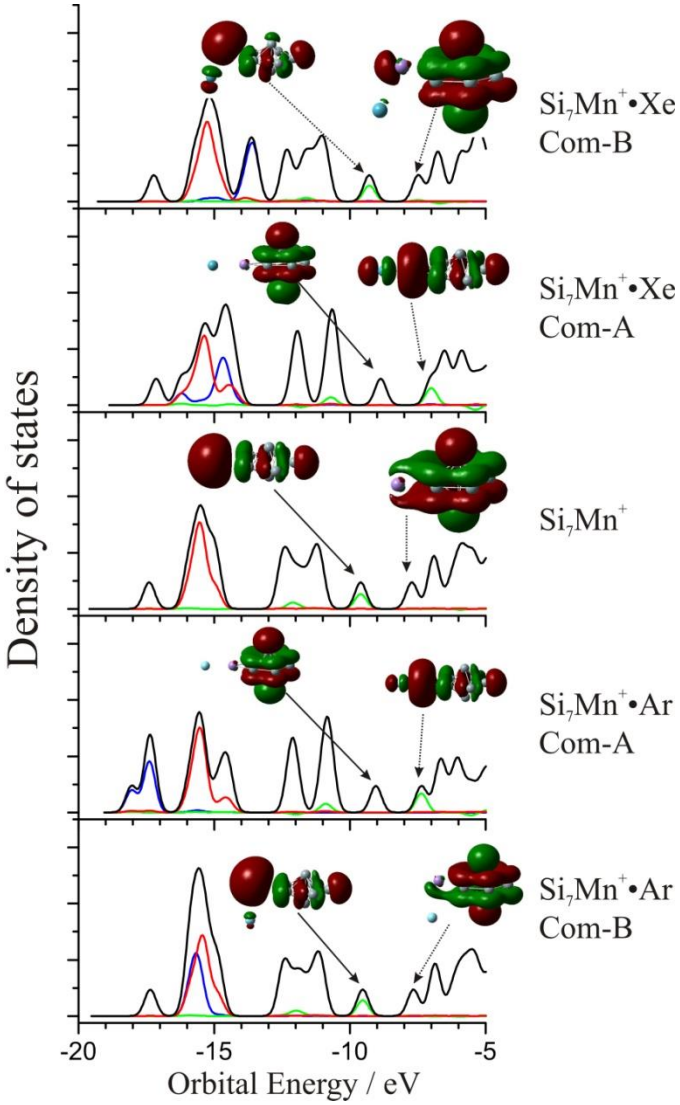


Figure S4. TDOS of Si_7Mn^+ (middle panel) and its **Com-A**, **Com-B** complexes with Ar (lower panels) and Xe (upper panels). Red curve is pDOS of 3*d* (Mn); green curve is pDOS of 4*s* (Mn); blue curve is pDOS of either 3*p* orbitals (Ar) or 5*p* (Xe) in the complexes. The DOS are plotted based on *alpha* orbitals. The solid arrow indicates the position of the HOMO the dashed arrow the position of the LUMO.