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

Supporting Information:

Exploring The Water Adsorption And Reactivity In Series Of Doped Aluminum Cluster Anions.

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Table S1: Properties of central-doped $Al_{12}V^-$ cluster optimized in different spin states sorted by decreasing stability, all distances given in Å

S	ΔE(eV)	symmetry	H-L gap	X-Al[a]	d(X-Al)[b]
nonet	0.00	I_h	0.96	2.684	0.001
quintet	0.24	C_2	0.47	2.800	0.564
triplet	0.31	C_1	0.53	2.817	0.634
septet	0.35	C_1	0.34	2.743	0.499
singlet[c]	0.64	C_1	0.23	2.845	0.710

[a] average X-Al distance

[b] difference between the longest and the shortest X-Al distance

[c] spin-restricted calculation (see Table S2 for unrestricted result)

Table S2: Total energies (a.u.) and spin contaminations (ΔS^2) of central-doped $Al_{12}X^-$ clusters optimized in different spin states (S) at TPSS/def2-TZVP. States highlighted in bold were used for energy evaluations in main text.

X	Sc			Ti			V			Cr			Mn		
S	$< S^2 >$	ΔS^2	Energy	S	$< S^2 >$	ΔS^2	Energy	S	$< S^2 >$	ΔS^2	Energy	S	$< S^2 >$	ΔS^2	Energy	S	$< S^2 >$	ΔS^2	Energy
1	3.37	3.37	-3670.407990	2*	2.44	1.69	-3759.223484	1	2.13	2.13	-3853.797376	2	1.99	1.24	-3954.282903	1	3.21	3.21	-4060.823422
3	**2.05**	**0.05**	**-3670.461734**	4*	5.07	1.32	-3759.211928	3	2.82	0.82	-3853.802266	4	4.28	0.53	-3954.288456	3	3.27	1.27	-4060.838135
5	6.07	0.07	-3670.449312	6	10.20	1.45	-3759.203963	5	6.17	0.17	-3853.804967	6	9.19	0.44	-3954.293175	5	6.92	0.92	-4060.832131
7	12.06	0.06	-3670.429659	**8**	**15.86**	**0.11**	**-3759.224623**	7	12.18	0.18	-3853.800785	**8**	**15.94**	**0.19**	**-3954.301701**	**7**	**12.48**	**0.48**	**-4060.847313**
9	20.06	0.06	-3670.403939					**9**	**20.08**	**0.08**	**-3853.813808**					9	20.27	0.27	-4060.810350
				10	24.84	0.09	-3759.206980	11	30.09	0.09	-3853.750835	10	24.87	0.12	-3954.266247				

X	Fe			Co			Ni			Cu			Zn		
S	$< S^2 >$	ΔS^2	Energy	S	$< S^2 >$	ΔS^2	Energy	S	$< S^2 >$	ΔS^2	Energy	S	$< S^2 >$	ΔS^2	Energy	S	$< S^2 >$	ΔS^2	Energy
2	2.04	1.29	-4173.574778	1	1.59	1.59	-4292.685210	2	1.65	0.90	-4418.265748	1	0.00	0.00	-4550.410596	**2**	**0.76**	**0.01**	**-4689.218840**
4	5.13	1.38	-4173.570649	3	2.10	0.10	-4292.685647	**4**	**3.79**	**0.04**	**-4418.269244**	**3**	**2.01**	**0.01**	**-4550.412645**	4	3.77	0.02	-4689.169325
6	**8.78**	**0.03**	**-4173.587969**	**5**	**6.19**	**0.19**	**-4292.685539**	6	8.84	0.09	-4418.215045	5	6.03	0.03	-4550.367363	6	8.80	0.05	-4689.123974
8	15.84	0.09	-4173.543409	7	12.10	0.10	-4292.641463	8	15.83	0.08	-4418.159794	7	12.07	0.07	-4550.319525	8	15.81	0.06	-4689.078450
				9	20.08	0.08	-4292.576748					9	20.07	0.07	-4550.274719				

	Co			Ni			Cu		
	1	0.00	0.00	-4290.747927	2	1.74	0.99	-4416.353003	1	0.00	0.00	-4548.528235
D3-PBE0/Def2-TZVP[a]	3	3.23	1.23	-4290.754859	**4**	3.85	0.10	**-4416.357089**	**3**	**2.03**	**0.03**	**-4548.531981**
	5	**6.66**	**0.66**	**-4290.757613**								
	1				2	(17,10)		-4409.244335	1	(18,10)		-4541.473491
CASSCF/DZ[b]	3				**4**	**(17,10)**		**-4409.260914**	**3**	**(18,10)**		**-4541.483569**
	5											

* optimization not completed due to convergence problems

[a] Some of the clusters ($Al_{12}Co^-$, $Al_{12}Ni^-$, $Al_{12}Cu^-$) with small energy differences between spin-states were reoptimized using a hybrid PBE0 functional with D3 empirical dispersion correction in Def2-TZVP basis set.

[b] CASSCF calculations were done using MOLCAS software[S1] in geometry of the lowest structure as obtained from TPPS/Def2-TZVP. 1F and 1P shells (10 orbitals) were included in active space (17,10) or (18,10) for $Al_{12}Ni^-$ and $Al_{12}Cu^-$, respectively. $Al_{12}Co^-$ was unattainable because of excessively large active space.

Table S3: Total energies (a.u.) and spin contaminations (ΔS^2) of surface-doped $Al_{12}X^-$ clusters optimized in different spin states (S) at TPSS/def2-TZVP. States highlighted in bold were used for energy evaluations in main text.

X	Sc			Ti			V			Cr			Mn		
S	$< S^2 >$	ΔS^2	Energy	$< S^2 >$	ΔS^2	Energy	$< S^2 >$	ΔS^2	Energy	$< S^2 >$	ΔS^2	Energy	$< S^2 >$	ΔS^2	Energy
1	**0.00**	**0.00**	**-3670.553231**	0.84	0.09	-3759.283444	0.00	0.00	-3853.795673	2.68	1.93	-3954.279764	0.00	0.00	-4060.794097
3	2.03	0.03	-3670.534854	**3.83**	**0.08**	**-3759.280190**	2.48	0.48	-3853.820817	5.05	1.30	-3954.308701	3.81	1.81	-4060.833386
5	6.05	0.05	-3670.497210	8.85	0.10	-3759.251193	**6.19**	**0.19**	**-3853.828222**	**9.03**	**0.28**	**-3954.316559**	6.91	0.91	-4060.865297
7	12.05	0.05	-3670.460332	15.88	0.13	-3759.214678	12.15	0.15	-3853.805006	15.81	0.06	-3954.307507	**12.07**	**0.07**	**-4060.873907**
9	20.06	0.06	-3670.420516				20.10	0.10	-3853.772825				20.08	0.08	-4060.829240

* optimization not completed due to convergence problems

Table S4: Computed spin densities (μ_B) of central-doped $Al_{12}X^-$ clusters.

	Mg	B	Al	Ga	Si	P	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
X	0.34	0.00	0.00	0.00	0.04	0.03	0.81	3.49	4.78	4.99	3.92	2.59	-0.10	0.67	-0.58	0.33
Al	0.11	0.00	0.00	0.00	0.02	0.05	0.26	0.18	0.27	0.10	0.07	0.20	-0.17	0.20	-0.14	0.11
Al	0.11	0.00	0.00	0.00	0.02	0.03	0.01	0.12	0.27	0.22	-0.12	0.20	-0.48	0.20	-0.14	0.11
Al	-0.00	0.00	0.00	0.00	0.02	0.03	0.00	0.40	0.27	0.26	0.41	0.20	-0.48	0.19	-0.13	-0.00
Al	0.11	0.00	0.00	0.00	0.02	0.05	0.33	0.34	0.27	0.37	0.59	0.20	-0.17	0.20	-0.14	0.11
Al	0.11	0.00	0.00	0.00	0.02	0.03	-0.00	0.15	0.27	0.17	0.41	0.20	-0.48	0.20	-0.14	0.12
Al	-0.00	0.00	0.00	0.00	0.02	0.41	0.22	0.36	0.27	0.26	0.40	0.20	-0.17	0.19	-0.16	-0.00
Al	-0.00	0.00	0.00	0.00	0.38	0.41	-0.03	0.27	0.27	0.38	0.40	0.20	-0.17	0.19	0.03	-0.00
Al	0.11	0.00	0.00	0.00	0.02	0.05	0.01	0.39	0.27	0.18	-0.12	0.20	-0.48	0.20	-0.17	0.11
Al	-0.00	0.00	0.00	0.00	0.02	0.03	0.02	0.43	0.27	-0.06	-0.12	0.20	-0.48	0.19	-0.13	-0.00
Al	-0.00	0.00	0.00	0.00	0.38	0.41	0.22	0.21	0.27	0.07	-0.12	0.20	-0.17	0.19	0.03	-0.00
Al	0.11	0.00	0.00	0.00	0.02	0.05	0.04	0.44	0.27	0.13	0.41	0.20	-0.48	0.20	-0.17	0.11
Al	-0.00	0.00	0.00	0.00	0.02	0.41	0.12	0.21	0.27	-0.06	-0.12	0.20	-0.17	0.19	-0.16	-0.00

Table S5: Computed spin densities (μ_B) of surface-doped $Al_{12}X^-$ clusters.

	Mg	B	Al	Ga	Si	P	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
X	0.46	0.00	0.00	0.00	0.20	0.24	-0.00	2.02	3.20	4.37	4.73	3.45	2.18	0.77	0.39	0.34
Al	0.02	0.00	-0.00	-0.00	-0.02	-0.03	-0.00	-0.05	-0.09	-0.19	-0.05	0.02	0.10	0.07	0.03	0.11
Al	-0.01	-0.00	0.00	-0.00	0.05	0.03	0.00	-0.01	-0.05	-0.04	0.03	0.03	0.03	0.22	0.17	-0.00
Al	0.02	-0.00	0.00	0.00	0.02	0.12	0.00	0.08	0.14	0.16	0.13	0.17	0.15	0.00	0.01	0.00
Al	0.47	-0.00	-0.00	0.00	0.49	0.71	-0.00	0.49	0.42	0.19	0.55	0.43	0.61	0.76	0.85	0.55
Al	0.02	-0.00	-0.00	-0.00	0.02	0.02	-0.00	0.15	0.20	0.16	0.13	0.17	0.24	0.24	0.10	0.00
Al	0.02	-0.00	0.00	0.00	0.02	0.29	0.00	0.08	0.13	0.16	0.13	0.19	0.16	0.00	0.00	0.00
Al	0.02	-0.00	-0.00	-0.00	0.02	0.02	0.00	0.20	0.08	0.16	0.13	0.18	0.16	0.25	0.06	0.01
Al	-0.01	0.00	-0.00	0.00	0.05	0.08	0.00	-0.01	-0.05	-0.04	0.03	0.06	0.03	0.22	0.17	-0.00
Al	-0.01	0.00	-0.00	-0.00	0.05	0.10	-0.00	-0.03	-0.05	-0.04	0.03	0.03	0.03	0.03	0.01	-0.01
Al	-0.01	-0.00	0.00	-0.00	0.05	0.03	-0.00	-0.03	-0.06	-0.04	0.03	0.04	0.03	0.15	0.09	-0.00
Al	0.02	-0.00	0.00	-0.00	0.02	0.10	-0.00	0.14	0.20	0.16	0.13	0.20	0.24	0.24	0.10	0.00
Al	-0.01	0.00	-0.00	0.00	0.05	0.28	-0.00	-0.03	-0.05	-0.04	0.03	0.05	0.04	0.03	0.01	-0.01

Table S6: CM5 charges of central-doped $Al_{12}X^-$ calculated at TPSS/Def2-TZVP level.

	Mg	B	Al	Ga	Si	P	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
X	-0.82	-0.12	-0.14	-0.03	-0.27	-0.22	0.58	0.61	0.61	0.68	0.40	0.35	0.22	0.39	0.67	0.50
Al	0.00	-0.07	-0.07	-0.08	-0.05	-0.05	-0.11	-0.11	-0.13	-0.11	-0.08	-0.11	-0.11	-0.12	-0.14	-0.12
Al	0.00	-0.07	-0.07	-0.08	-0.05	-0.04	-0.08	-0.11	-0.13	-0.14	-0.12	-0.11	-0.10	-0.12	-0.14	-0.12
Al	-0.03	-0.07	-0.07	-0.08	-0.05	-0.04	-0.11	-0.14	-0.13	-0.15	-0.12	-0.11	-0.10	-0.12	-0.14	-0.13
Al	0.00	-0.07	-0.07	-0.08	-0.05	-0.05	-0.16	-0.16	-0.13	-0.14	-0.12	-0.11	-0.11	-0.12	-0.14	-0.12
Al	0.00	-0.07	-0.07	-0.08	-0.05	-0.04	-0.19	-0.14	-0.13	-0.14	-0.12	-0.11	-0.10	-0.12	-0.14	-0.12
Al	-0.03	-0.07	-0.07	-0.08	-0.05	-0.11	-0.12	-0.16	-0.13	-0.15	-0.12	-0.11	-0.11	-0.12	-0.13	-0.13
Al	-0.03	-0.07	-0.07	-0.08	-0.12	-0.11	-0.09	-0.13	-0.13	-0.14	-0.12	-0.11	-0.11	-0.12	-0.16	-0.13
Al	0.00	-0.07	-0.07	-0.08	-0.05	-0.05	-0.07	-0.14	-0.13	-0.14	-0.12	-0.11	-0.10	-0.12	-0.13	-0.12
Al	-0.03	-0.07	-0.07	-0.08	-0.05	-0.04	-0.12	-0.15	-0.13	-0.16	-0.12	-0.11	-0.10	-0.12	-0.14	-0.13
Al	-0.03	-0.07	-0.07	-0.08	-0.12	-0.11	-0.18	-0.12	-0.13	-0.11	-0.13	-0.11	-0.11	-0.12	-0.16	-0.13
Al	0.00	-0.07	-0.07	-0.08	-0.05	-0.05	-0.20	-0.15	-0.13	-0.14	-0.12	-0.11	-0.10	-0.12	-0.13	-0.12
Al	-0.03	-0.07	-0.07	-0.08	-0.05	-0.11	-0.14	-0.11	-0.13	-0.16	-0.13	-0.11	-0.11	-0.12	-0.13	-0.13

Table S7: CM5 charges of surface-doped $Al_{12}X^-$ calculated at TPSS/Def2-TZVP level.

	Mg	B	Al	Ga	Si	P	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Al	-0.21	-0.10	-0.14	-0.13	-0.13	-0.13	-0.08	-0.08	-0.06	-0.08	-0.08	-0.06	-0.04	-0.05	-0.07	-0.08
X	0.01	-0.22	-0.07	-0.13	-0.23	-0.25	0.40	0.25	0.19	0.30	0.10	0.08	-0.01	0.08	0.20	0.13
Al	-0.07	-0.05	-0.07	-0.06	-0.04	-0.03	-0.17	-0.14	-0.14	-0.15	-0.12	-0.12	-0.11	-0.11	-0.13	-0.12
Al	-0.08	-0.07	-0.07	-0.07	-0.07	-0.07	-0.06	-0.07	-0.08	-0.09	-0.07	-0.07	-0.07	-0.09	-0.09	-0.08
Al	-0.05	-0.07	-0.07	-0.06	-0.08	-0.06	-0.14	-0.08	-0.07	-0.04	-0.07	-0.09	-0.07	-0.05	-0.04	-0.03
Al	-0.08	-0.07	-0.07	-0.07	-0.07	-0.06	-0.06	-0.08	-0.08	-0.09	-0.07	-0.07	-0.07	-0.08	-0.08	-0.08
Al	-0.08	-0.07	-0.07	-0.07	-0.07	-0.10	-0.06	-0.07	-0.08	-0.09	-0.07	-0.07	-0.07	-0.09	-0.09	-0.08
Al	-0.08	-0.07	-0.07	-0.07	-0.07	-0.06	-0.06	-0.08	-0.08	-0.09	-0.07	-0.07	-0.07	-0.07	-0.08	-0.08
Al	-0.07	-0.05	-0.07	-0.06	-0.04	-0.04	-0.17	-0.14	-0.14	-0.15	-0.12	-0.12	-0.11	-0.11	-0.13	-0.12
Al	-0.07	-0.05	-0.07	-0.06	-0.04	-0.04	-0.17	-0.15	-0.13	-0.15	-0.12	-0.12	-0.11	-0.13	-0.15	-0.12
Al	-0.07	-0.05	-0.07	-0.06	-0.04	-0.03	-0.17	-0.14	-0.12	-0.15	-0.12	-0.12	-0.10	-0.10	-0.13	-0.12
Al	-0.08	-0.07	-0.07	-0.07	-0.07	-0.07	-0.06	-0.08	-0.08	-0.09	-0.07	-0.07	-0.07	-0.08	-0.08	-0.08
Al	-0.07	-0.05	-0.07	-0.06	-0.04	-0.07	-0.17	-0.15	-0.13	-0.15	-0.12	-0.12	-0.11	-0.13	-0.15	-0.12

Density of states

Central-doped clusters

To further inspect the electronic structure, electronic (partial) density of states (DOS) was calculated for all clusters. Figure S1 shows side by side comparison of the molecular orbitals diagram of central-doped $Al_{12}Fe^-$ cluster and the corresponding spin-resolved and total DOS, allowing for more convenient interpretation of DOS. As discussed in the main text, the spin state and high symmetry of the cluster is explained by crystal-field splitting of the 3d shell of iron. The splitting is also confirmed by density of states, as the p- and d- contributions to DOS (red and blue lines in Fig. S1, respectively) for the lowest unoccupied orbitals as well as their ordering can be clearly mapped to the corresponding orbital levels.

Figure S2 plots the (P)DOS of $Al_{12}X^-$ clusters with free (left panel) and adsorbed water molecule (right panel). Upon adsorption, molecular orbitals of water (within the displayed energy window these are $1b_2$, $3a_1$ and $1b_1$) are greatly shifted to the negative region, and the shift in energy correlates well with the adsorption energy. As seen in right panel, water interacts with clusters via $3a_1$ and $1b_1$ orbitals, which overlap with 1S and 1P superatomic orbitals of a cluster. Additional peak(s) appear in DOS due to this interaction. In the case of pure aluminum cluster or boron-doped cluster, there is no overlap with the 1S orbitals of a cluster as these are energetically too far to overlap with $3a_1$ orbital of water. The doping atom modifies the DOS of a cluster by means of shifting the energy levels or splitting them due to Jahn-Teller distortions, and in case of TM-doping also introduction of 3d orbitals. By proper heteroatom doping we are able to alter the position of superatomic shells and thus control the overlap of the frontier orbitals.

Surface-doped clusters

PDOS in combination with orbital analysis (Figure S3) show that the water molecule interacts mostly with $1P_z$ superatomic orbital of a cluster via $1b_1$ orbital in a way similar

Figure S1: Shell structure of central-doped $Al_{12}Fe^-$ cluster (left panel) compared to the spin-resolved DOS (panel in the middle) and the resulting total DOS (right panel). Grey area represents occupied orbitals, the area filled with orange and green represents alpha and beta unoccupied orbitals (middle panel), respectively. Black, red and blue lines show s, p and d contributions, respectively.

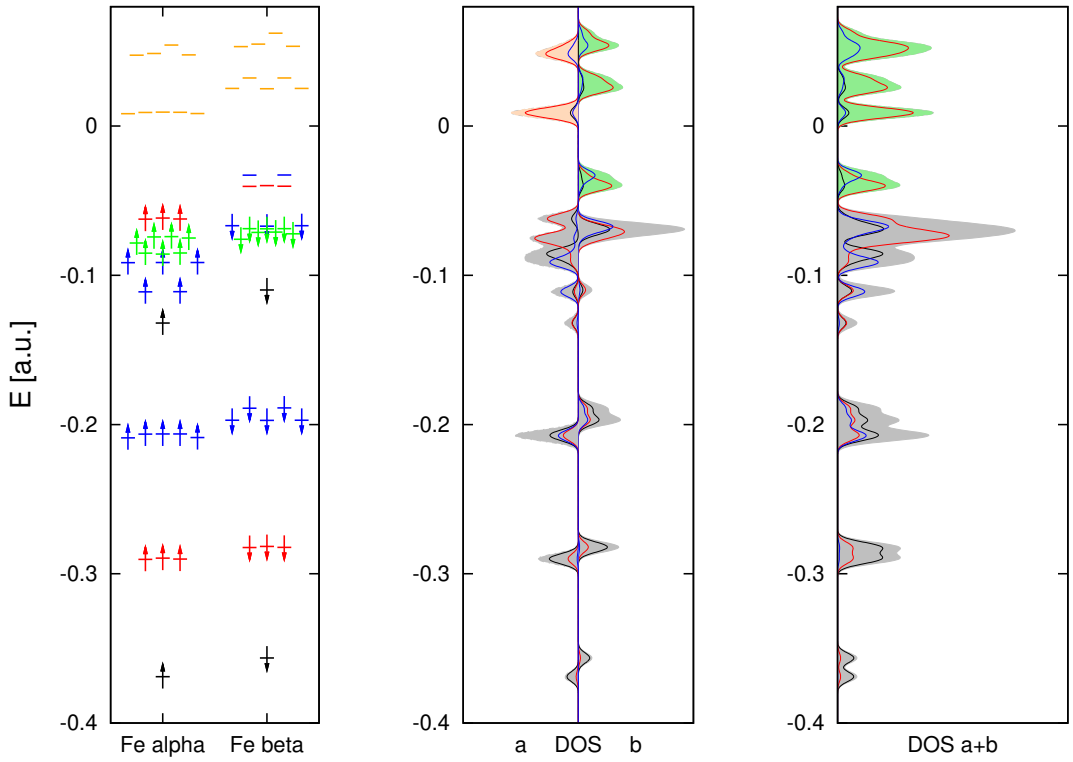
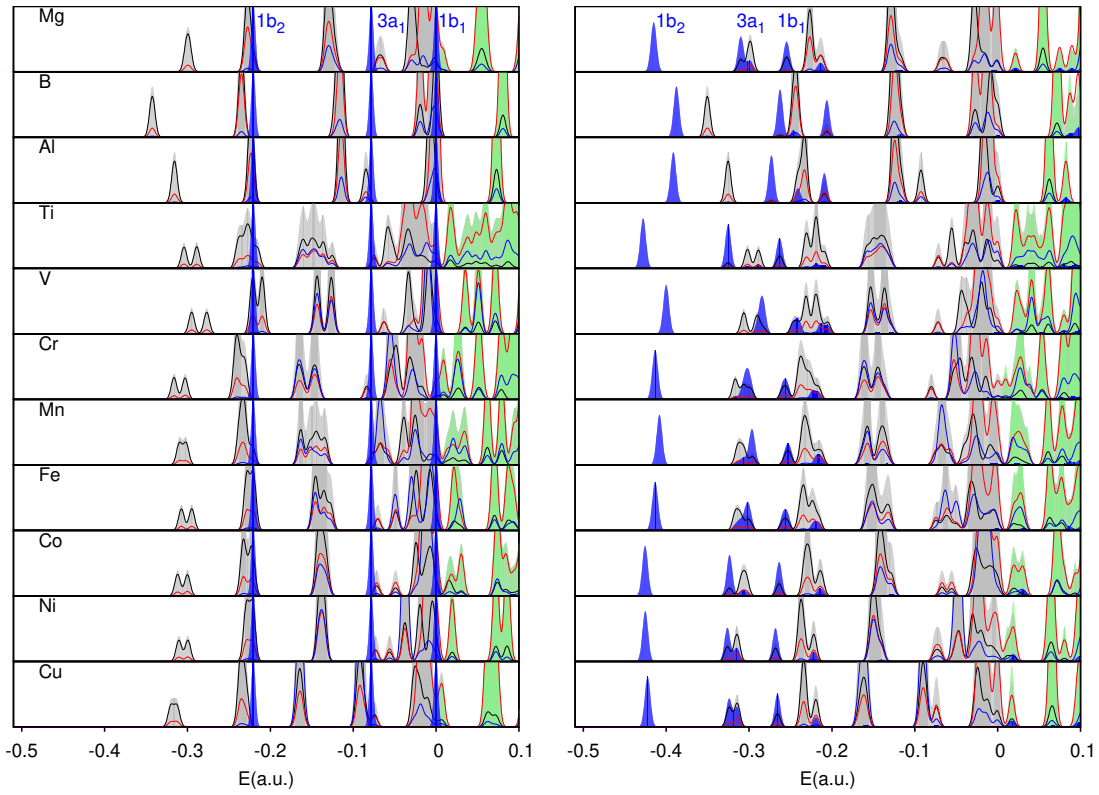
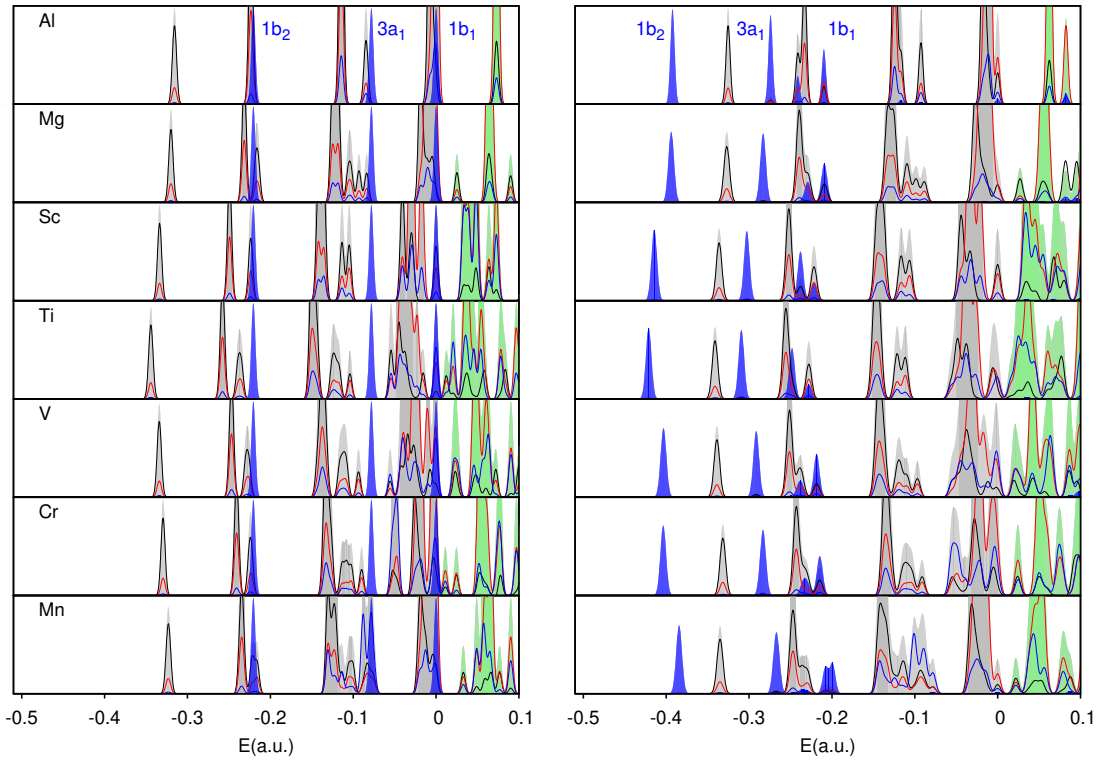


Figure S2: (P)DOS of bare central-doped $Al_{12}X^-$ (left) and $Al_{12}X^-$ with adsorbed water (right). Grey area represents occupied orbitals, the area filled with green represents unoccupied orbitals. Blue area shows orbitals of free and adsorbed water. Black, red and blue lines show s, p and d contributions, respectively. Fermi level is set to zero.



to pure Al cluster, while there is no interaction with $3a_1$ orbital as seen in central-doped clusters. Molecular orbitals of water are shifted from Fermi level more to the negative region in accordance with the adsorption energy. As was discussed in the main text, surface doping causes degeneracy breaking of superatomic shells by strong destabilization of $1P_z$, $1D_{z^2}$ and $1F_{z^3}$ orbitals. Nonetheless, it seems that this splitting gives rise to greater overlap with $1b_1$ orbital of water and the adsorption energy (on X-site) is proportional to the position of the $1P_z$ orbital (Figure S3).

Figure S3: (P)DOS of bare surface-doped $Al_{12}X^-$ (left) and $Al_{12}X^-$ with adsorbed water (right). Grey area represents occupied orbitals, the area filled with green represents unoccupied orbitals. Blue area shows orbitals of free and adsorbed water. Black, red and blue lines show s, p and d contributions, respectively. Fermi level is set to zero.



Reaction profiles of water dissociation

Table S8: Reaction profiles (eV) of water dissociation on central-doped $Al_{12}X^-$ clusters, (*) represents a given cluster

			*H_2O				TS					*OH + *H			
X	S	GAP[a]	S	ΔH_0	ΔH_{298}	ΔG_{298}	S	$\Delta H_0^{\ddagger}$	$\Delta H_{298}^{\ddagger}$	$\Delta G_{298}^{\ddagger}$	[b]ΔG_{298}^{act}	S	ΔH_0	ΔH_{298}	ΔG_{298}
Mg	2	0.24	2	-0.42	-0.45	-0.01	2	-0.26	-0.32	0.22	0.23	2	-1.83	-1.86	-1.41
B	1	2.20	1	-0.13	-0.13	0.20	1	0.18	0.14	0.61	0.41	1	-1.27	-1.29	-0.90
Al	1	1.99	1	-0.16	-0.17	0.17	1	0.06	0.02	0.50	0.33	1	-1.13	-1.14	-0.76
Ga	1	2.09	1	-0.14	-0.15	0.19	1	0.10	0.06	0.53	0.34	1	-1.29	-1.31	-0.90
Si	2	0.56	2	-0.19	-0.20	0.19	2	0.03	-0.01	0.48	0.29	2	-1.80	-1.82	-1.40
P	3	0.65	3	-0.26	-0.28	0.14	3	0.04	-0.01	0.50	0.36	3	-1.88	-1.91	-1.45
Ti	8	0.42	8	-0.43	-0.45	-0.02	8	-0.30	-0.35	0.16	0.18	8	-2.39	-2.42	-1.94
V	9	0.96	9	-0.15	-0.17	0.20	9	0.06	0.01	0.49	0.29	9	-1.36	-1.38	-0.95
Cr	8	0.24	8	-0.30	-0.32	0.12	8	-0.15	-0.21	0.37	0.25	8	-1.87	-1.91	-1.40
Mn	7	0.36	7	-0.35	-0.36	0.03	7	-0.19	-0.23	0.24	0.21	7	-1.97	-1.99	-1.61
Fe	6	0.58	6	-0.43	-0.49	0.05	6	-0.30	-0.39	0.23	0.19	6	-2.11	-2.15	-1.66
Co	5	0.40	3	-0.63	-0.65	-0.24	3	-0.55	-0.61	-0.10	0.14	3	-2.64	-2.66	-2.27
Ni	4	0.53	2	-0.36	-0.40	0.06	2	-0.30	-0.37	0.18	0.12	2	-2.24	-2.27	-1.81
Cu	3	0.19	1	-0.44	-0.49	0.03	1	-0.33	-0.41	0.18	0.16	1	-2.08	-2.12	-1.60
Zn	2	0.35	2	-0.46	-0.49	-0.04	2	-0.31	-0.37	0.17	0.22	2	-1.66	-1.68	-1.24

[a] HOMO-LUMO gap

[b] activation energy ΔG_{298}^{act} is defined as the energy difference between the TS and the adsorbed complex with water

Table S9: Reaction profiles (eV) of water dissociation on X-site of surface-doped $Al_{12}X^-$ clusters, (*) represents a given cluster

			*H_2O				TS					*OH + *H			
X	S	GAP[a]	S	ΔH_0	ΔH_{298}	ΔG_{298}	S	$\Delta H_0^{\ddagger}$	$\Delta H_{298}^{\ddagger}$	$\Delta G_{298}^{\ddagger}$	[b]ΔG_{298}^{act}	S	ΔH_0	ΔH_{298}	ΔG_{298}
Mg	2	0.69	2	-0.77	-0.79	-0.38	2	-0.49	-0.54	-0.05	0.33	2	-1.33	-1.34	-0.98
Sc	1	0.91	1	-0.90	-0.91	-0.53	1	-0.84	-0.88	-0.41	0.12	1	-2.53	-2.55	-2.15
Ti	4	0.34	4	-0.90	-0.92	-0.48	4	-0.70	-0.75	-0.25	0.23	4	-2.30	-2.31	-1.91
V	5	0.57	5	-0.81	-0.84	-0.38	5	-0.57	-0.61	-0.11	0.27	5	-1.92	-1.95	-1.55
Cr	6	0.30	6	-0.85	-0.87	-0.47	6	-0.49	-0.54	-0.05	0.42	6	-1.54	-1.56	-1.15
Mn	7	0.90	7	-0.53	-0.55	-0.15	7	-0.13	-0.17	0.30	0.45	7	-1.09	-1.10	-0.71

[a] HOMO-LUMO gap
[b] activation energy ΔG_{298}^{act} is defined as the energy difference between the TS and the adsorbed complex with water

Table S10: Reaction profiles (eV) of water dissociation on ortho-Al site of surface-doped $Al_{12}X^-$ clusters, (*) represents a given cluster

			*H_2O				TS					*OH + *H			
X	S	GAP[a]	S	ΔH_0	ΔH_{298}	ΔG_{298}	S	$\Delta H_0^{\ddagger}$	$\Delta H_{298}^{\ddagger}$	$\Delta G_{298}^{\ddagger}$	[b]ΔG_{298}^{act}	S	ΔH_0	ΔH_{298}	ΔG_{298}
Mg	2	0.69	2	-0.18	-0.20	0.20	2	-0.06	-0.10	0.38	0.17	2	-1.36	-1.36	-1.00
Sc	1	0.91	1	-0.20	-0.21	0.16	1	-0.01	-0.05	0.43	0.26	1	-1.21	-1.23	-0.83
Ti	4	0.34	4	-0.25	-0.27	0.16	4	-0.12	-0.17	0.34	0.18	4	-1.52	-1.54	-1.12
V	5	0.57	5	-0.28	-0.30	0.12	5	-0.15	-0.20	0.32	0.20	5	-1.51	-1.53	-1.10
Cr	6	0.30	6	-0.27	-0.30	0.13	6	-0.18	-0.24	0.27	0.14	6	-1.57	-1.58	-1.18
Mn	7	0.90	7	-0.22	-0.23	0.12	7	-0.06	-0.10	0.38	0.25	7	-1.30	-1.30	-0.92

[a] HOMO-LUMO gap
[b] activation energy ΔG_{298}^{act} is defined as the energy difference between the TS and the adsorbed complex with water

Table S11: Reaction profiles (eV) of water dissociation on meta-Al site of surface-doped $Al_{12}X^-$ clusters, (*) represents a given cluster

			*H_2O				TS					*OH + *H			
X	S	GAP[a]	S	ΔH_0	ΔH_{298}	ΔG_{298}	S	$\Delta H_0^{\ddagger}$	$\Delta H_{298}^{\ddagger}$	$\Delta G_{298}^{\ddagger}$	[b]ΔG_{298}^{act}	S	ΔH_0	ΔH_{298}	ΔG_{298}
Mg	2	0.69	2	-0.16	-0.18	0.23	2	-0.02	-0.06	0.41	0.18	2	-1.36	-1.37	-0.99
Sc	1	0.91	1	-0.27	-0.29	0.13	1	-0.16	-0.21	0.29	0.16	1	-1.99	-2.02	-1.56
Ti	4	0.34	4	-0.30	-0.32	0.11	4	-0.23	-0.29	0.23	0.12	4	-1.79	-1.81	-1.37
V	5	0.57	5	-0.25	-0.28	0.16	5	-0.18	-0.23	0.29	0.12	5	-1.75	-1.77	-1.36
Cr	6	0.30	6	-0.30	-0.32	0.09	6	-0.26	-0.31	0.18	0.09	6	-1.94	-1.96	-1.55
Mn	7	0.90	7	-0.21	-0.22	0.15	7	-0.10	-0.15	0.33	0.18	7	-1.66	-1.68	-1.28

[a] HOMO-LUMO gap
[b] activation energy ΔG_{298}^{act} is defined as the energy difference between the TS and the adsorbed complex with water

Table S12: Reaction profiles (eV) of water dissociation on para-Al site of surface-doped $Al_{12}X^-$ clusters (*) represents a given cluster

			*H_2O				TS					*OH + *H			
X	S	GAP[a]	S	ΔH_0	ΔH_{298}	ΔG_{298}	S	$\Delta H_0^{\ddagger}$	$\Delta H_{298}^{\ddagger}$	$\Delta G_{298}^{\ddagger}$	[b]ΔG_{298}^{act}	S	ΔH_0	ΔH_{298}	ΔG_{298}
Mg	2	0.69	2	-0.36	-0.38	0.00	2	-0.20	-0.25	0.24	0.24	2	-1.56	-1.58	-1.15
Sc	1	0.91	3	0.30	0.29	0.66	3	0.43	0.39	0.86	0.20	3	-1.18	-1.20	-0.78
Ti	4	0.34	4	-0.17	-0.19	0.20	4	-0.12	-0.17	0.34	0.14	4	-1.68	-1.71	-1.25
V	5	0.57	5	-0.31	-0.34	0.08	5	-0.21	-0.26	0.25	0.17	5	-1.67	-1.69	-1.23
Cr	6	0.30	6	-0.68	-0.71	-0.28	6	-0.58	-0.64	-0.12	0.16	6	-1.94	-1.96	-1.54
Mn	7	0.90	7	-0.22	-0.23	0.13	7	-0.04	-0.08	0.39	0.26	7	-1.53	-1.55	-1.13

[a] HOMO-LUMO gap
[b] activation energy ΔG_{298}^{act} is defined as the energy difference between the TS and the adsorbed complex with water

Table S13: Contributions of D3 dispersion corrections along the ΔG_{298} reaction profiles (eV) of water dissociation on central- and surface-doped $Al_{12}X^-$ clusters. IS is the initial state with water adsorbed on a cluster, FS is the final state after dissociation.

	central-doped $Al_{12}X^-$			surface doped $Al_{12}X^-$											
				X-site			ortho-Al			meta-Al			para-Al		
X	ΔG_{298}^{IS}	ΔG_{298}^{TS}	ΔG_{298}^{FS}	ΔG_{298}^{IS}	ΔG_{298}^{TS}	ΔG_{298}^{FS}	ΔG_{298}^{IS}	ΔG_{298}^{TS}	ΔG_{298}^{FS}	ΔG_{298}^{IS}	ΔG_{298}^{TS}	ΔG_{298}^{FS}	ΔG_{298}^{IS}	ΔG_{298}^{TS}	ΔG_{298}^{FS}
Mg	-0.09	-0.10	-0.09	-0.10	-0.11	-0.09	-0.09	-0.09	-0.08	-0.09	-0.10	-0.08	-0.09	-0.10	-0.10
B	-0.08	-0.10	-0.10												
Al	-0.08	-0.09	-0.10												
Ga	-0.08	-0.10	-0.10												
Si	-0.07	-0.09	-0.08												
P	-0.09	-0.10	-0.08												
Sc	-0.10	-0.11	-0.10	-0.08	-0.08	-0.07	-0.09	-0.09	-0.09	-0.09	-0.11	-0.09	-0.09	-0.10	-0.10
Ti	-0.10	-0.09	-0.08	-0.10	-0.11	-0.09	-0.09	-0.10	-0.10	-0.09	-0.11	-0.10	-0.09	-0.10	-0.09
V	-0.09	-0.11	-0.10	-0.11	-0.10	-0.09	-0.09	-0.10	-0.08	-0.09	-0.11	-0.10	-0.10	-0.11	-0.09
Cr	-0.08	-0.10	-0.10	-0.08	-0.09	-0.10	-0.09	-0.09	-0.08	-0.10	-0.11	-0.10	-0.10	-0.10	-0.10
Mn	-0.09	-0.10	-0.11	-0.11	-0.11	-0.12	-0.09	-0.10	-0.10	-0.08	-0.11	-0.10	-0.08	-0.09	-0.10
Fe	-0.09	-0.10	-0.09												
Co	-0.11	-0.11	-0.10												
Ni	-0.09	-0.10	-0.09												
Cu	-0.09	-0.11	-0.09												
Zn	-0.09	-0.11	-0.10												

Coordinates of central- and surface-doped clusters and transition states of water dissociation

Table S14: Coordinates (Å) of central-doped $Al_{12}X^-$ clusters

$Al_{12}Mg^-$	Mg	0.0000	0.0000	0.0001
	Al	0.0290	-1.4517	-2.2419
	Al	0.0334	1.4526	-2.2412
	Al	1.4292	2.3053	-0.0067
	Al	-0.0289	1.4514	2.2421
	Al	-0.0335	-1.4521	2.2415
	Al	-2.3019	0.0034	1.4348
	Al	-1.4222	2.3096	0.0081
	Al	-2.3138	0.0035	-1.3344
	Al	-1.4293	-2.3054	0.0073
	Al	1.4222	-2.3097	-0.0079
	Al	2.3142	-0.0039	1.3337
	Al	2.3014	-0.0031	-1.4354
$Al_{12}B^-$	B	-0.0010	0.0011	0.0002
	Al	-0.0117	-1.3362	-2.1632
	Al	-0.0078	1.3369	-2.1623
	Al	1.3397	2.1607	-0.0056
	Al	0.0118	1.3357	2.1628
	Al	0.0076	-1.3368	2.1627
	Al	-2.1567	0.0032	1.3456
	Al	-1.3330	2.1643	0.0066
	Al	-2.1681	0.0036	-1.3273
	Al	-1.3401	-2.1608	0.0059
	Al	1.3336	-2.1653	-0.0065
	Al	2.1687	-0.0035	1.3272
	Al	2.1572	-0.0028	-1.3464
Al_{13}	Al	-0.0000	0.0000	0.0000
	Al	-0.0119	-1.3947	-2.2569
	Al	-0.0078	1.3955	-2.2564
	Al	1.3983	2.2547	-0.0050
	Al	0.0123	1.3942	2.2570
	Al	0.0078	-1.3951	2.2566
	Al	-2.2506	0.0034	1.4049

	Al	-1.3915	2.2588	0.0063
	Al	-2.2629	0.0034	-1.3851
	Al	-1.3985	-2.2547	0.0058
	Al	1.3915	-2.2589	-0.0063
	Al	2.2630	-0.0039	1.3845
	Al	2.2503	-0.0028	-1.4054
$Al_{12}Ga^-$	Ga	-0.0000	0.0000	-0.0000
	Al	-0.0119	-1.3911	-2.2514
	Al	-0.0078	1.3920	-2.2509
	Al	1.3948	2.2493	-0.0055
	Al	0.0120	1.3911	2.2518
	Al	0.0077	-1.3921	2.2513
	Al	-2.2453	0.0033	1.4011
	Al	-1.3880	2.2533	0.0065
	Al	-2.2573	0.0035	-1.3816
	Al	-1.3949	-2.2491	0.0059
	Al	1.3880	-2.2534	-0.0067
	Al	2.2580	-0.0039	1.3812
	Al	2.2449	-0.0028	-1.4016
$Al_{12}Si^-$	Si	-0.0000	0.0000	-0.0000
	Al	0.0043	-1.3894	-2.2074
	Al	-0.0238	1.3893	-2.2065
	Al	1.3513	2.2305	-0.0053
	Al	-0.0041	1.3891	2.2077
	Al	0.0237	-1.3891	2.2066
	Al	-2.2165	0.0285	1.3742
	Al	-1.4834	2.4076	0.0055
	Al	-2.2289	0.0273	-1.3538
	Al	-1.3513	-2.2305	0.0058
	Al	1.4834	-2.4075	-0.0056
	Al	2.2291	-0.0279	1.3533
	Al	2.2163	-0.0280	-1.3747
$Al_{12}P^-$	P	-0.0003	0.0002	0.0001
	Al	0.0462	-1.3668	-2.1760
	Al	-0.0003	1.3628	-2.1851
	Al	1.3542	2.1905	-0.0171
	Al	-0.0460	1.3668	2.1763
	Al	0.0004	-1.3627	2.1852

	Al	-2.3998	0.0258	1.4899
	Al	-1.4975	2.3953	0.0202
	Al	-2.2174	0.0394	-1.2993
	Al	-1.3542	-2.1905	0.0173
	Al	1.4974	-2.3956	-0.0202
	Al	2.2173	-0.0397	1.2988
	Al	2.3999	-0.0255	-1.4902
$Al_{12}Sc^-$	Sc	0.7404	-0.4828	0.8568
	Al	0.1828	-1.3552	-1.9572
	Al	-0.0564	1.2219	-2.2603
	Al	1.1471	2.4891	-0.3276
	Al	0.2156	1.9645	2.1451
	Al	-0.7941	-2.4869	2.0894
	Al	-1.9696	0.0352	1.3590
	Al	-1.4510	2.1664	-0.0284
	Al	-2.1599	0.0905	-1.3839
	Al	-1.7932	-2.1456	-0.2687
	Al	0.7267	-3.1632	-0.0964
	Al	2.8546	1.3122	1.2089
	Al	2.3569	0.3539	-1.3366
$Al_{12}Ti^-$	Ti	-0.0806	-0.0270	0.3963
	Al	-0.0725	-1.3637	-2.2620
	Al	0.0909	1.2852	-2.3132
	Al	1.4404	2.2459	-0.0448
	Al	-0.0418	1.7192	2.3120
	Al	0.3402	-1.8654	2.1742
	Al	-2.4473	0.1836	1.4450
	Al	-1.3295	2.3184	-0.2066
	Al	-2.2328	0.0013	-1.3820
	Al	-1.4746	-2.2866	0.0378
	Al	1.4831	-2.2381	-0.2700
	Al	2.3544	0.0381	1.4669
	Al	2.2645	0.0519	-1.3935
$Al_{12}V^-$	V	0.0000	0.0004	0.0001
	Al	-0.0119	-1.4110	-2.2832
	Al	-0.0078	1.4118	-2.2827
	Al	1.4149	2.2810	-0.0049
	Al	0.0122	1.4109	2.2835

	Al	0.0077	-1.4119	2.2829
	Al	-2.2769	0.0033	1.4219
	Al	-1.4080	2.2854	0.0058
	Al	-2.2895	0.0035	-1.4010
	Al	-1.4149	-2.2811	0.0052
	Al	1.4080	-2.2853	-0.0061
	Al	2.2898	-0.0040	1.4006
	Al	2.2764	-0.0030	-1.4221
$Al_{12}Cr^-$	Cr	-0.0828	0.2064	0.0951
	Al	-0.0035	-1.3741	-2.1868
	Al	0.0642	1.3682	-2.2773
	Al	1.5046	2.2626	-0.0556
	Al	0.0339	1.4101	2.3257
	Al	-0.0172	-1.4406	2.2082
	Al	-2.3108	-0.0899	1.4105
	Al	-1.4445	2.3285	-0.0201
	Al	-2.2737	-0.0751	-1.3807
	Al	-1.4070	-2.2767	0.0023
	Al	1.3542	-2.1928	-0.0252
	Al	2.3017	-0.0146	1.3163
	Al	2.2807	-0.0063	-1.4124
$Al_{12}Mn^-$	Mn	-0.0011	0.1947	0.3297
	Al	-0.0225	-1.3023	-2.1093
	Al	-0.0129	1.3500	-2.2557
	Al	1.4363	2.2213	-0.1555
	Al	0.0027	1.4524	2.3725
	Al	-0.0048	-1.5444	2.1690
	Al	-2.3280	-0.0968	1.2924
	Al	-1.4385	2.2290	-0.1421
	Al	-2.2361	-0.0171	-1.3988
	Al	-1.3882	-2.2470	-0.0364
	Al	1.3587	-2.2568	-0.0506
	Al	2.3243	-0.1113	1.2749
	Al	2.2087	-0.0347	-1.4224
$Al_{12}Fe^-$	Fe	0.0004	0.0002	0.0001
	Al	-0.0299	-1.3568	-2.2439
	Al	0.0228	1.3884	-2.2249
	Al	1.3580	2.2441	0.0244

	Al	0.0297	1.3565	2.2441
	Al	-0.0226	-1.3883	2.2250
	Al	-2.2175	0.0336	1.3984
	Al	-1.3820	2.2292	-0.0345
	Al	-2.2561	-0.0144	-1.3377
	Al	-1.3583	-2.2437	-0.0243
	Al	1.3815	-2.2295	0.0346
	Al	2.2564	0.0144	1.3374
	Al	2.2175	-0.0338	-1.3986
$Al_{12}Co^-$	Co	0.0006	0.0011	-0.0005
	Al	0.0436	-1.4163	-2.2558
	Al	0.0215	1.2752	-2.1395
	Al	1.2778	2.1379	0.0226
	Al	-0.0443	1.4148	2.2563
	Al	-0.0198	-1.2765	2.1383
	Al	-2.2504	0.0558	1.4240
	Al	-1.4136	2.2576	0.0605
	Al	-2.1430	0.0303	-1.2682
	Al	-1.2793	-2.1361	-0.0221
	Al	1.4120	-2.2572	-0.0591
	Al	2.1439	-0.0291	1.2679
	Al	2.2512	-0.0576	-1.4243
$Al_{12}Ni^-$	Ni	-0.0000	-0.0000	-0.0000
	Al	-0.0115	-1.3676	-2.2128
	Al	-0.0073	1.3684	-2.2122
	Al	1.3724	2.2135	-0.0062
	Al	0.0115	1.3676	2.2128
	Al	0.0073	-1.3684	2.2121
	Al	-2.2097	0.0032	1.3785
	Al	-1.3658	2.2177	0.0072
	Al	-2.2191	0.0035	-1.3573
	Al	-1.3723	-2.2135	0.0063
	Al	1.3657	-2.2176	-0.0072
	Al	2.2192	-0.0036	1.3573
	Al	2.2097	-0.0032	-1.3785
$Al_{12}Cu^-$	Cu	0.0001	0.0001	0.0001
	Al	0.0102	-1.4065	-2.1998
	Al	-0.0285	1.4065	-2.1981

	Al	1.3376	2.2469	-0.0045
	Al	-0.0103	1.4065	2.1995
	Al	0.0284	-1.4065	2.1980
	Al	-2.2117	0.0432	1.3709
	Al	-1.3991	2.2805	0.0074
	Al	-2.2227	0.0433	-1.3492
	Al	-1.3377	-2.2470	0.0044
	Al	1.3992	-2.2805	-0.0073
	Al	2.2225	-0.0431	1.3493
	Al	2.2119	-0.0432	-1.3708
$Al_{12}Zn^-$	Zn	0.0000	0.0002	0.0001
	Al	0.0415	-1.4325	-2.1786
	Al	0.0458	1.4327	-2.1772
	Al	1.4129	2.2663	0.0149
	Al	-0.0414	1.4321	2.1788
	Al	-0.0459	-1.4321	2.1775
	Al	-2.2545	0.0037	1.4317
	Al	-1.4065	2.2707	-0.0131
	Al	-2.2693	0.0034	-1.2831
	Al	-1.4131	-2.2664	-0.0142
	Al	1.4065	-2.2709	0.0133
	Al	2.2699	-0.0039	1.2823
	Al	2.2542	-0.0032	-1.4324

Table S15: Transition states coordinates (Å) of water dissociation on central-doped clusters $Al_{12}X^-$

$[Al_{12}Mg^-+H_2O]^‡$	Al	0.2186	-2.1977	1.7432
	Mg	0.0502	-0.2190	0.0728
	Al	-2.3170	1.0866	-0.0013
	Al	-2.2126	-1.6543	0.3751
	Al	0.0159	-2.7723	-0.9155
	Al	-1.4457	-0.7066	-2.1121
	Al	-0.1497	1.7414	-1.6834
	Al	0.0229	2.2920	1.0635
	Al	2.2930	1.2120	-0.3937
	Al	1.3725	-0.7285	-2.1893
	Al	2.4248	-1.5372	0.2440
	Al	1.6538	0.3324	2.1588
	Al	-1.2295	0.1903	2.3844
	O	-0.2063	-2.6470	3.5355
	H	-0.7816	-1.4971	3.4278
	H	0.5468	-2.4655	4.1302
$[Al_{12}B^-+H_2O]^‡$	Al	0.2193	-2.1456	1.7765
	B	0.0425	-0.1949	0.0636
	Al	-2.1447	1.0302	-0.0486
	Al	-2.0638	-1.5874	0.4224
	Al	0.0415	-2.6340	-0.7983
	Al	-1.3601	-0.6367	-1.9635
	Al	-0.1325	1.7739	-1.7638
	Al	0.0274	2.1464	0.9417
	Al	2.1170	1.1469	-0.3648
	Al	1.2670	-0.6581	-2.0667
	Al	2.2567	-1.4931	0.2479
	Al	1.5270	0.2671	2.0761
	Al	-1.1500	0.1541	2.2456
	O	-0.2064	-2.7006	3.5599
	H	-0.7280	-1.5198	3.3521
	H	0.5433	-2.5192	4.1598
$[Al_{13}^-+H_2O]^‡$	Al	0.2196	-2.2282	1.7860
	Al	0.0465	-0.1967	0.0513
	Al	-2.2552	1.0903	-0.0208
	Al	-2.1798	-1.6163	0.3909

	Al	0.0061	-2.7284	-0.8449
	Al	-1.4078	-0.6205	-2.0998
	Al	-0.1406	1.8308	-1.8213
	Al	-0.0010	2.2589	0.9964
	Al	2.2091	1.2295	-0.4273
	Al	1.3749	-0.7559	-2.1515
	Al	2.3493	-1.5370	0.2959
	Al	1.6036	0.3419	2.1373
	Al	-1.1930	0.1416	2.3604
	O	-0.1976	-2.7017	3.5812
	H	-0.7428	-1.5424	3.4349
	H	0.5648	-2.5367	4.1712
$[Al_{12}Ga^{-}+H_2O]^{\ddagger}$	Al	0.2209	-2.2272	1.7908
	Ga	0.0462	-0.1949	0.0499
	Al	-2.2505	1.0874	-0.0275
	Al	-2.1684	-1.6199	0.3998
	Al	0.0144	-2.7230	-0.8417
	Al	-1.4099	-0.6277	-2.0880
	Al	-0.1396	1.8292	-1.8195
	Al	0.0049	2.2545	0.9920
	Al	2.2078	1.2223	-0.4164
	Al	1.3619	-0.7355	-2.1531
	Al	2.3423	-1.5371	0.2871
	Al	1.5972	0.3288	2.1373
	Al	-1.1941	0.1508	2.3493
	O	-0.2003	-2.7051	3.5860
	H	-0.7365	-1.5388	3.4168
	H	0.5598	-2.5345	4.1772
$[Al_{12}Si^{-}+H_2O]^{\ddagger}$	Al	0.0899	-1.2468	-2.3819
	Al	2.3672	0.0716	-1.4317
	Al	2.1375	-0.1905	1.3864
	Al	1.3566	-2.2741	-0.1550
	Al	-1.3596	-2.2905	-0.2945
	Al	-2.2037	0.0205	-1.4806
	Al	-1.4355	2.1080	0.1133
	Al	-2.4058	-0.2058	1.2872
	Al	-0.1240	-1.6301	2.0964
	Al	-0.1056	1.0829	2.2659

	Al	1.3316	2.1398	0.1673
	Al	0.0356	1.5671	-2.2580
	Si	-0.0189	-0.0593	-0.0844
	O	-1.3115	-2.2925	3.4446
	H	-2.1168	-1.4790	2.8053
	H	-1.6552	-3.1759	3.2087
$[Al_{12}P^{-}+H_2O]^{\ddagger}$	Al	-0.4728	-1.3167	2.2324
	Al	1.8927	-0.2175	1.5257
	Al	2.1395	-0.2571	-1.1617
	Al	-0.1540	-1.4073	-2.0259
	Al	1.0440	-2.5079	0.1979
	Al	-1.8179	-2.1117	0.0068
	Al	-2.2527	0.2374	-1.4523
	Al	-2.3388	0.3683	1.2338
	Al	-1.2813	2.6082	-0.1665
	Al	0.1548	1.3995	-2.3594
	Al	1.5638	2.2404	0.0121
	Al	-0.0865	1.5034	2.1878
	P	-0.1073	0.2456	-0.0390
	O	-1.3049	-2.8126	3.0886
	H	-1.7939	-2.8792	1.8550
	H	-0.7042	-3.5814	3.1224
$[Al_{12}Ti^{-}+H_2O]^{\ddagger}$	O	-0.3654	-2.5211	3.7836
	Al	0.1823	-2.1729	1.9812
	Ti	0.2388	-0.6111	0.0301
	Al	-2.2316	0.9941	-0.0070
	Al	-2.1470	-1.7780	0.3822
	Al	0.1467	-2.8378	-1.2919
	Al	-1.5024	-0.6072	-2.0916
	Al	-0.2220	1.8175	-1.5811
	Al	0.0855	2.1723	1.0442
	Al	2.2304	1.2547	-0.3804
	Al	1.2635	-0.3398	-2.4504
	Al	2.6365	-1.5923	-0.0994
	Al	1.7187	0.2017	2.1382
	Al	-1.2057	0.2008	2.3381
	H	-0.9145	-1.4189	3.6138
	H	0.3423	-2.3328	4.4303

$[Al_{12}V^{-}+H_2O]^{‡}$	Al	0.2516	-2.2095	1.7736
	V	0.0757	-0.2137	0.0157
	Al	-2.2982	1.0962	-0.0057
	Al	-2.1556	-1.6574	0.4199
	Al	0.0543	-2.7714	-0.8713
	Al	-1.4622	-0.6760	-2.1059
	Al	-0.1523	1.7718	-1.7236
	Al	0.0124	2.2901	1.0478
	Al	2.2682	1.2312	-0.3917
	Al	1.3649	-0.6819	-2.2590
	Al	2.3983	-1.5747	0.2333
	Al	1.6167	0.2868	2.1541
	Al	-1.2061	0.1632	2.3733
	O	-0.2258	-2.6486	3.5574
	H	-0.8035	-1.4856	3.4492
	H	0.5178	-2.4913	4.1726
$[Al_{12}Cr^{-}+H_2O]^{‡}$	Al	0.2286	-2.1605	1.7254
	Cr	0.2775	-0.1083	0.1319
	Al	-2.2828	1.0467	-0.0125
	Al	-2.0439	-1.6020	0.3985
	Al	0.0188	-2.7548	-0.9255
	Al	-1.4287	-0.6991	-2.0588
	Al	-0.1797	1.6921	-1.6941
	Al	-0.1102	2.2932	1.0732
	Al	2.3334	1.2269	-0.4156
	Al	1.2519	-0.7368	-2.2399
	Al	2.3751	-1.6703	0.1562
	Al	1.6115	0.3232	2.2291
	Al	-1.2547	0.1462	2.3632
	O	-0.2249	-2.6179	3.5141
	H	-0.8384	-1.4930	3.4716
	H	0.5226	-2.4563	4.1232
$[Al_{12}Mn^{-}+H_2O]^{‡}$	Al	0.2210	-2.0510	1.7147
	Mn	-0.0220	0.0945	0.1914
	Al	-2.3509	0.9924	-0.0598
	Al	-2.1027	-1.6939	0.3765
	Al	0.0631	-2.6449	-0.8243
	Al	-1.3994	-0.7706	-2.0641

	Al	-0.0970	1.6645	-1.7357
	Al	0.0609	2.3333	1.1164
	Al	2.3381	1.0749	-0.4435
	Al	1.2943	-0.7051	-2.1532
	Al	2.3504	-1.5492	0.1851
	Al	1.7103	0.2091	2.0989
	Al	-1.2881	0.1066	2.4017
	O	-0.1972	-2.6373	3.4766
	H	-0.8727	-1.5496	3.4800
	H	0.5481	-2.4443	4.0792
$[Al_{12}Fe^{-}+H_2O]^{\ddagger}$	Al	0.2732	-2.0285	1.7211
	Fe	0.0358	0.0500	0.3059
	Al	-2.3081	0.9359	-0.1455
	Al	-2.1285	-1.6808	0.3878
	Al	0.0536	-2.5469	-0.7831
	Al	-1.4119	-0.7121	-2.0376
	Al	-0.0965	1.6246	-1.6613
	Al	0.0240	2.2537	1.1497
	Al	2.3009	1.0565	-0.4789
	Al	1.2723	-0.6729	-2.1603
	Al	2.3844	-1.5770	0.1345
	Al	1.8307	0.2012	2.0470
	Al	-1.3863	0.0739	2.3501
	O	-0.1900	-2.6074	3.4707
	H	-0.9198	-1.5620	3.4393
	H	0.5224	-2.3789	4.1004
$[Al_{12}Co^{-}+H_2O]^{\ddagger}$	Al	0.4984	-1.9170	1.7877
	Co	0.0116	-0.3640	0.1791
	Al	-2.3260	1.1154	-0.0413
	Al	-2.1052	-1.4853	0.3715
	Al	0.0726	-2.5557	-0.8761
	Al	-1.5051	-0.7263	-2.1267
	Al	-0.1759	1.4206	-1.5227
	Al	0.0390	2.0854	0.9996
	Al	2.1190	1.0529	-0.3187
	Al	1.2847	-0.6572	-2.2174
	Al	2.4992	-1.4979	0.1352
	Al	1.7115	0.3684	2.1941

	Al	-1.1576	0.2292	2.3618
	O	-0.2483	-2.6145	3.3932
	H	-0.8376	-1.5119	3.3857
	H	0.3761	-2.5129	4.1349
$[Al_{12}Ni^{-}+H_2O]^{\ddagger}$	Al	0.0250	-1.2647	-2.2269
	Al	2.1911	-0.0112	-1.1920
	Al	2.1904	-0.1912	1.4303
	Al	1.3739	-2.3916	-0.2082
	Al	-1.4700	-2.3287	-0.3546
	Al	-2.2933	0.0191	-1.5103
	Al	-1.5351	2.1922	0.1019
	Al	-2.3784	-0.1866	1.1328
	Al	-0.0354	-1.6106	1.8529
	Al	-0.1110	1.1640	2.1208
	Al	1.4149	2.1612	0.2299
	Al	0.0015	1.3491	-1.8268
	Ni	-0.0993	-0.1342	0.0605
	O	-1.1635	-2.1723	3.2774
	H	-1.9851	-1.4003	2.7161
	H	-1.5442	-3.0489	3.0851
$[Al_{12}Cu^{-}+H_2O]^{\ddagger}$	Al	0.0381	-1.3553	-2.3587
	Al	2.1780	-0.0597	-1.2152
	Al	2.1926	-0.1194	1.4618
	Al	1.3076	-2.3594	-0.1627
	Al	-1.4456	-2.2860	-0.3391
	Al	-2.2971	-0.0086	-1.4875
	Al	-1.4424	2.1956	0.1268
	Al	-2.3541	-0.0862	1.2107
	Al	0.0082	-1.4621	2.0095
	Al	-0.1055	1.2277	2.2699
	Al	1.3417	2.1185	0.2189
	Al	-0.0282	1.2545	-1.9233
	Cu	-0.0954	-0.1329	0.0477
	O	-1.2003	-2.2472	3.2423
	H	-1.9977	-1.4278	2.6799
	H	-1.5184	-3.1063	2.9079
$[Al_{12}Zn^{-}+H_2O]^{\ddagger}$	Al	0.2149	-2.1766	1.6963
	Zn	0.0465	-0.2363	0.0988

Al	-2.2630	1.0561	-0.0250
Al	-2.1665	-1.6403	0.4001
Al	0.0296	-2.7311	-0.8973
Al	-1.4319	-0.7050	-2.0405
Al	-0.1284	1.6719	-1.6160
Al	0.0396	2.2348	1.0380
Al	2.2479	1.1766	-0.3415
Al	1.3205	-0.6851	-2.1283
Al	2.3717	-1.5304	0.2334
Al	1.6023	0.2899	2.1482
Al	-1.2258	0.1992	2.3301
O	-0.1935	-2.6153	3.4956
H	-0.7774	-1.4687	3.3777
H	0.5697	-2.4105	4.0702

Table S16: Coordinates (Å) of surface-doped $Al_{12}X^-$ clusters

$Al_{12}Mg^-$	Al	-0.0005	-0.0258	-0.0424
	Mg	-0.0098	-1.4619	-2.3588
	Al	-0.0082	1.4565	-2.2491
	Al	1.3980	2.2637	0.0070
	Al	0.0125	1.3431	2.1765
	Al	0.0078	-1.3898	2.2679
	Al	-2.2514	0.0118	1.4177
	Al	-1.3923	2.2678	0.0184
	Al	-2.3085	0.0371	-1.3599
	Al	-1.4282	-2.2660	0.0600
	Al	1.4198	-2.2715	0.0467
	Al	2.2643	0.0027	1.3957
	Al	2.2964	0.0323	-1.3798
$Al_{12}B^-$	Al	0.0014	0.0653	0.1076
	B	-0.0068	-1.0726	-1.7281
	Al	-0.0042	1.2150	-2.2860
	Al	1.4161	2.2426	-0.0793
	Al	-0.0005	1.4799	2.3633
	Al	0.0056	-1.4453	2.2267
	Al	-2.2838	-0.0404	1.3508
	Al	-1.4129	2.2443	-0.0720
	Al	-2.1342	-0.0984	-1.4622
	Al	-1.3149	-2.2262	-0.1437
	Al	1.3172	-2.2256	-0.1472
	Al	2.2894	-0.0359	1.3445
	Al	2.1276	-0.1028	-1.4744
Al_{13}^-	Al	-0.0000	0.0000	0.0000
	Al	-0.0119	-1.3947	-2.2569
	Al	-0.0078	1.3955	-2.2564
	Al	1.3983	2.2547	-0.0050
	Al	0.0123	1.3942	2.2570
	Al	0.0078	-1.3951	2.2566
	Al	-2.2506	0.0034	1.4049
	Al	-1.3915	2.2588	0.0063
	Al	-2.2629	0.0034	-1.3851
	Al	-1.3985	-2.2547	0.0058
	Al	1.3915	-2.2589	-0.0063

	Al	2.2630	-0.0039	1.3845
	Al	2.2503	-0.0028	-1.4054
$Al_{12}Ga^-$	Al	-0.0002	-0.0028	-0.0051
	Ga	-0.0093	-1.4045	-2.2660
	Al	-0.0100	1.4005	-2.2554
	Al	1.3959	2.2557	-0.0029
	Al	0.0145	1.3800	2.2404
	Al	0.0060	-1.3920	2.2577
	Al	-2.2495	0.0065	1.4059
	Al	-1.3893	2.2603	0.0144
	Al	-2.2658	0.0081	-1.3838
	Al	-1.4015	-2.2542	0.0100
	Al	1.3945	-2.2584	0.0024
	Al	2.2616	-0.0004	1.3855
	Al	2.2532	0.0011	-1.4032
$Al_{12}Si^-$	Al	-0.0000	0.0030	0.0048
	Si	-0.0135	-1.3593	-2.2056
	Al	-0.0062	1.3597	-2.2548
	Al	1.3915	2.2338	-0.0197
	Al	0.0090	1.4695	2.3684
	Al	0.0093	-1.3966	2.2331
	Al	-2.2387	-0.0063	1.3839
	Al	-1.3850	2.2372	-0.0116
	Al	-2.2341	-0.0150	-1.3935
	Al	-1.3807	-2.2443	-0.0206
	Al	1.3733	-2.2487	-0.0372
	Al	2.2516	-0.0128	1.3665
	Al	2.2237	-0.0201	-1.4136
$Al_{12}P^-$	Al	-0.0058	0.0123	0.0230
	P	0.0174	-1.2602	-2.0481
	Al	-0.0021	1.3792	-2.2336
	Al	1.4354	2.2231	-0.0442
	Al	0.0285	1.4396	2.3298
	Al	-0.0353	-1.3865	2.2143
	Al	-2.3381	-0.0292	1.4074
	Al	-1.4027	2.2050	0.0040
	Al	-2.2600	-0.0398	-1.4126
	Al	-1.4112	-2.2694	-0.0493

	Al	1.3838	-2.2306	0.0002
	Al	2.2836	0.0053	1.3245
	Al	2.3066	-0.0489	-1.5155
$Al_{12}Sc^-$	Al	-0.0001	-0.0246	-0.0396
	Sc	-0.0118	-1.5096	-2.4402
	Al	-0.0069	1.3888	-2.2497
	Al	1.3820	2.2435	0.0129
	Al	0.0109	1.4959	2.4158
	Al	0.0075	-1.3664	2.2533
	Al	-2.2275	0.0165	1.4077
	Al	-1.3772	2.2468	0.0241
	Al	-2.2545	0.0015	-1.3810
	Al	-1.3920	-2.2475	0.0081
	Al	1.3874	-2.2509	-0.0043
	Al	2.2384	0.0097	1.3907
	Al	2.2439	-0.0038	-1.3978
$Al_{12}Ti^-$	Al	-0.0008	-0.0092	-0.0168
	Ti	-0.0073	-1.4248	-2.2926
	Al	-0.0202	1.3953	-2.2385
	Al	1.4053	2.2447	-0.0144
	Al	0.0143	1.3700	2.2232
	Al	-0.0062	-1.3872	2.2743
	Al	-2.2491	-0.0103	1.3968
	Al	-1.3956	2.2851	0.0390
	Al	-2.2496	0.0189	-1.3775
	Al	-1.3845	-2.2459	-0.0011
	Al	1.3890	-2.2414	0.0161
	Al	2.2693	0.0162	1.3928
	Al	2.2353	-0.0115	-1.4014
$Al_{12}V^-$	Al	-0.0007	-0.0047	-0.0091
	V	-0.0551	-1.3317	-2.2594
	Al	0.0181	1.3757	-2.2570
	Al	1.3772	2.2793	-0.0158
	Al	0.0238	1.3559	2.2229
	Al	-0.0206	-1.4141	2.2628
	Al	-2.2679	0.0296	1.3953
	Al	-1.3893	2.2680	0.0308
	Al	-2.2550	-0.0250	-1.3798

	Al	-1.3525	-2.2638	0.0078
	Al	1.3876	-2.2370	0.0123
	Al	2.2896	0.0093	1.3710
	Al	2.2450	-0.0415	-1.3819
$Al_{12}Cr^-$	Al	-0.0000	-0.0227	-0.0363
	Cr	-0.0132	-1.3638	-2.2113
	Al	-0.0079	1.4172	-2.2535
	Al	1.4070	2.2669	-0.0048
	Al	0.0111	1.3358	2.1611
	Al	0.0085	-1.4029	2.2695
	Al	-2.2628	0.0025	1.4137
	Al	-1.3990	2.2718	0.0074
	Al	-2.2790	0.0156	-1.3756
	Al	-1.4075	-2.2596	0.0234
	Al	1.4011	-2.2642	0.0101
	Al	2.2755	-0.0040	1.3932
	Al	2.2663	0.0075	-1.3968
$Al_{12}Mn^-$	Al	-0.0005	-0.0111	-0.0191
	Mn	-0.0110	-1.3664	-2.2094
	Al	-0.0096	1.3922	-2.2522
	Al	1.3950	2.2498	-0.0033
	Al	0.0130	1.3713	2.2225
	Al	0.0067	-1.3901	2.2530
	Al	-2.2446	0.0041	1.4034
	Al	-1.3867	2.2551	0.0125
	Al	-2.2577	0.0047	-1.3832
	Al	-1.3947	-2.2504	0.0037
	Al	1.3877	-2.2534	-0.0074
	Al	2.2574	-0.0014	1.3830
	Al	2.2450	-0.0043	-1.4035
$Al_{12}Fe^-$	Al	-0.0000	0.0088	0.0138
	Fe	-0.0130	-1.2803	-2.0712
	Al	-0.0062	1.3326	-2.2895
	Al	1.3978	2.2609	-0.0374
	Al	0.0124	1.4224	2.2989
	Al	0.0022	-1.4244	2.2461
	Al	-2.2468	-0.0142	1.4067
	Al	-1.3809	2.2661	-0.0141

	Al	-2.2331	-0.0165	-1.3997
	Al	-1.3747	-2.2614	-0.0528
	Al	1.3667	-2.2599	-0.0531
	Al	2.2582	-0.0073	1.3824
	Al	2.2175	-0.0267	-1.4300
$Al_{12}Co^-$	Al	-0.0075	0.0139	0.0008
	Co	-0.0226	-1.2266	-2.0355
	Al	0.0178	1.3020	-2.3074
	Al	1.3516	2.2984	-0.0078
	Al	0.0495	1.3589	2.3086
	Al	-0.0276	-1.4195	2.2279
	Al	-2.2757	0.0622	1.3878
	Al	-1.3885	2.2828	0.0374
	Al	-2.2240	-0.0869	-1.4370
	Al	-1.3518	-2.2732	-0.0376
	Al	1.3672	-2.2549	-0.0496
	Al	2.2820	0.0123	1.3356
	Al	2.2295	-0.0693	-1.4231
$Al_{12}Ni^-$	Al	0.0247	0.0112	0.0818
	Ni	-0.0083	-1.2059	-1.9470
	Al	0.0780	1.2891	-2.2419
	Al	1.4127	2.3273	-0.0809
	Al	0.0369	1.3826	2.3011
	Al	-0.3072	-1.4991	2.2372
	Al	-2.3519	0.0044	1.3741
	Al	-1.3557	2.2727	0.1215
	Al	-2.1964	-0.1146	-1.3628
	Al	-1.3523	-2.3171	-0.1388
	Al	1.3721	-2.2264	-0.0048
	Al	2.4337	0.1918	1.1777
	Al	2.2138	-0.1161	-1.5172
$Al_{12}Cu^-$	Al	0.0046	0.0141	0.0343
	Cu	-0.0246	-1.2243	-2.0182
	Al	0.0793	1.4148	-2.2406
	Al	1.4618	2.2502	0.0191
	Al	-0.0534	1.4518	2.1789
	Al	-0.0439	-1.4772	2.2321
	Al	-2.2539	-0.0427	1.4554

	Al	-1.4319	2.2594	-0.0972
	Al	-2.2974	-0.0519	-1.3218
	Al	-1.4085	-2.2783	-0.0654
	Al	1.3985	-2.2764	-0.0158
	Al	2.3325	-0.0109	1.3136
	Al	2.2369	-0.0287	-1.4744
$Al_{12}Zn^-$	Al	-0.0009	0.0036	0.0032
	Zn	0.0034	-1.3365	-2.1239
	Al	-0.0116	1.4216	-2.2665
	Al	1.4092	2.2617	-0.0220
	Al	0.0085	1.3584	2.1895
	Al	0.0076	-1.4235	2.2469
	Al	-2.2678	-0.0073	1.3993
	Al	-1.4021	2.2698	-0.0034
	Al	-2.2880	0.0168	-1.3866
	Al	-1.4191	-2.2708	0.0119
	Al	1.4067	-2.2806	-0.0017
	Al	2.2809	-0.0208	1.3684
	Al	2.2732	0.0076	-1.4152

Table S17: Transition states coordinates (Å) of water dissociation on X-site of surface-doped $Al_{12}X^-$ clusters

$[Al_{12}Mg^-+H_2O]^‡$	O	-0.2675	-2.6521	3.7281
	Mg	0.2910	-2.4366	1.8518
	Al	-1.1793	0.1376	2.3426
	Al	1.7392	0.2945	2.0647
	Al	2.4268	-1.5135	0.0917
	Al	1.3066	-0.5930	-2.2565
	Al	2.2144	1.2522	-0.4635
	Al	0.0502	2.2184	1.0607
	Al	-0.1867	1.7612	-1.6156
	Al	-1.4247	-0.6047	-2.1196
	Al	0.0667	-2.7123	-1.0053
	Al	-2.1697	-1.6894	0.2852
	Al	-2.2626	1.0434	0.0055
	Al	0.0749	-0.2819	0.0822
	H	-0.8078	-1.4025	3.3875
	H	0.3847	-2.3920	4.4004
$[Al_{12}Sc^-+H_2O]^‡$	O	-0.2324	-2.6879	3.9147
	Sc	0.2561	-2.4073	1.8878
	Al	-1.1690	0.0520	2.2920
	Al	1.6742	0.2373	2.0310
	Al	2.3624	-1.5513	0.0683
	Al	1.3347	-0.6060	-2.2994
	Al	2.1974	1.2410	-0.4895
	Al	0.0219	2.2152	1.0439
	Al	-0.1862	1.9714	-1.7832
	Al	-1.3956	-0.5349	-2.1685
	Al	0.0700	-2.6817	-1.0243
	Al	-2.1334	-1.6641	0.2539
	Al	-2.2568	1.0790	-0.0287
	Al	0.0671	-0.2481	0.0132
	H	-0.7349	-1.6108	3.5257
	H	0.3805	-2.3744	4.6028
$[Al_{12}Ti^-+H_2O]^‡$	O	-0.1666	-2.6383	3.7462
	Ti	0.1259	-2.3926	1.7442
	Al	-1.2020	0.1252	2.2994
	Al	1.5879	0.2342	2.1160

	Al	2.3298	-1.5832	0.2404
	Al	1.3640	-0.5844	-2.1957
	Al	2.2880	1.2013	-0.3633
	Al	0.0119	2.2577	1.0312
	Al	-0.1157	1.7113	-1.6679
	Al	-1.4503	-0.5718	-2.1143
	Al	0.0310	-2.6625	-1.0430
	Al	-2.1712	-1.6705	0.3585
	Al	-2.3144	1.0580	-0.0575
	Al	0.0458	-0.2578	0.0646
	H	-0.6763	-1.4869	3.3849
	H	0.5684	-2.3106	4.2963
$[Al_{12}V^{-}+H_2O]^{\ddagger}$	O	-0.0814	-2.5986	3.7617
	V	0.0469	-2.2832	1.7895
	Al	-1.2836	0.0942	2.2791
	Al	1.5562	0.1713	2.1495
	Al	2.2666	-1.6476	0.2521
	Al	1.4189	-0.5894	-2.1802
	Al	2.2609	1.1919	-0.3001
	Al	0.0003	2.2379	1.0321
	Al	-0.0951	1.7026	-1.6582
	Al	-1.4480	-0.5739	-2.1423
	Al	0.0148	-2.6511	-1.0420
	Al	-2.1948	-1.6671	0.2858
	Al	-2.3075	1.0774	-0.0784
	Al	0.0277	-0.2617	0.0628
	H	-0.6514	-1.4653	3.4040
	H	0.7256	-2.3079	4.2246
$[Al_{12}Cr^{-}+H_2O]^{\ddagger}$	O	-1.3354	-2.3955	3.5074
	Cr	-0.1803	-1.5895	2.0854
	Al	-0.0288	-0.0820	-0.0255
	Al	-0.0186	1.2243	2.2789
	Al	1.3535	2.2019	0.0894
	Al	-0.0522	1.4474	-2.1094
	Al	-1.4465	2.2070	0.1177
	Al	-2.3120	-0.1367	1.2312
	Al	-2.2863	-0.0147	-1.5105
	Al	-1.3426	-2.3465	-0.3774

	Al	1.3871	-2.3195	-0.1304
	Al	2.1763	-0.1729	1.4524
	Al	2.2565	0.0453	-1.3424
	Al	0.0935	-1.2407	-2.4449
	H	-1.9415	-1.4684	2.6959
	H	-1.7412	-3.2142	3.1711
$[Al_{12}Mn^{-}+H_2O]^{\ddagger}$	O	-0.2479	-2.6590	3.7051
	Mn	0.2557	-2.2566	1.7853
	Al	-1.1876	0.1160	2.3415
	Al	1.7006	0.2344	2.0819
	Al	2.3698	-1.5509	0.1228
	Al	1.3136	-0.6143	-2.2613
	Al	2.2125	1.2246	-0.4424
	Al	0.0563	2.1915	1.0822
	Al	-0.1853	1.7826	-1.6152
	Al	-1.4090	-0.6107	-2.1154
	Al	0.0816	-2.7085	-0.9309
	Al	-2.1331	-1.7019	0.3123
	Al	-2.2566	1.0258	0.0042
	Al	0.0704	-0.2708	0.0716
	H	-0.8324	-1.4144	3.3809
	H	0.4476	-2.3586	4.3171

Table S18: Transition states coordinates (Å) of water dissociation on ortho-Al site of surface-doped $Al_{12}X^-$ clusters

$[Al_{12}Mg^-+H_2O]^‡$	O	-2.5903	-3.5457	0.0230
	Al	-1.2770	-2.5057	-0.8663
	Al	0.0080	-1.9600	1.9819
	Al	-0.2841	0.7388	2.4225
	Al	1.0420	2.0148	0.3671
	Al	-0.0685	1.4929	-2.0599
	Al	-1.6939	1.8385	0.2463
	Al	-2.3720	-0.6022	1.2274
	Al	-2.2858	-0.0772	-1.6271
	Al	-0.1201	-0.3027	-0.0916
	Al	1.4026	-2.4776	-0.3289
	Al	2.2024	-0.0065	-1.3200
	Al	2.1134	-0.3278	1.3825
	Mg	0.1648	-1.2522	-2.8659
	H	-2.7878	-2.4750	0.7115
	H	-2.1640	-4.1323	0.6782
$[Al_{12}Sc^-+H_2O]^‡$	O	-2.3043	-3.9105	0.1838
	Al	-1.4724	-2.4563	-0.7320
	Sc	0.0140	-1.3032	-2.8124
	Al	-0.0850	1.4698	-2.1434
	Al	1.4276	1.9875	0.3277
	Al	-0.1900	0.8215	2.4896
	Al	-0.3047	-1.9496	1.8267
	Al	-2.4112	-0.2657	1.1405
	Al	-1.3421	2.0755	0.1736
	Al	-2.3351	-0.0308	-1.5718
	Al	-0.1050	-0.2352	-0.1672
	Al	1.3063	-2.4375	-0.4836
	Al	2.1944	0.0246	-1.3829
	Al	1.9977	-0.5657	1.3883
	H	-3.2113	-3.6602	0.4514
	H	-1.5805	-3.3681	1.0890
$[Al_{12}Ti^-+H_2O]^‡$	O	-2.4334	-3.7372	0.2642
	Al	-1.7106	-2.2905	-0.7368
	Ti	-0.0408	-1.2341	-2.5906
	Al	0.1075	1.4936	-2.1062

	Al	1.4208	1.9235	0.4018
	Al	-0.3196	0.8820	2.2901
	Al	-0.5363	-1.8077	1.9555
	Al	-2.5875	-0.0918	1.0573
	Al	-1.3881	2.1679	0.0599
	Al	-2.2981	0.1645	-1.6832
	Al	-0.1939	-0.1931	-0.1118
	Al	1.0838	-2.4654	-0.3748
	Al	2.1790	-0.0934	-1.2647
	Al	1.8829	-0.6124	1.4879
	H	-1.7966	-3.1810	1.2217
	H	-1.9473	-4.5645	0.0768
$[Al_{12}V^{-}+H_2O]^{\ddagger}$	O	-2.4069	-3.7214	0.2476
	Al	-1.7416	-2.2535	-0.7652
	Al	1.0679	-2.4844	-0.3894
	Al	1.8816	-0.6362	1.4971
	Al	2.1532	-0.1065	-1.3277
	Al	-0.1975	-0.1938	-0.1018
	Al	-2.3262	0.1829	-1.6552
	Al	-1.3730	2.2100	0.0784
	Al	-2.5924	-0.1194	1.0420
	Al	-0.5317	-1.8081	1.9791
	Al	-0.3177	0.8923	2.2846
	Al	1.4760	1.8587	0.3961
	Al	0.0192	1.4756	-2.1180
	V	-0.0027	-1.2354	-2.5077
	H	-1.7996	-3.1606	1.2192
	H	-1.8925	-4.5321	0.0647
$[Al_{12}Cr^{-}+H_2O]^{\ddagger}$	O	-2.3109	-3.7883	0.1864
	Al	-1.8698	-2.1203	-0.6128
	Cr	-0.3278	-0.7567	-2.3097
	Al	-0.4666	1.8646	-1.5527
	Al	0.9240	2.0181	0.9348
	Al	-0.6988	0.7330	2.7329
	Al	-0.6326	-1.8986	2.1149
	Al	-2.8796	-0.3144	1.4014
	Al	-1.9345	2.1578	0.6977
	Al	-2.7180	0.3189	-1.2858

	Al	-0.5116	-0.0649	0.2199
	Al	1.0056	-2.1507	-0.3501
	Al	1.8321	0.3645	-0.9825
	Al	1.6554	-0.4746	1.7319
	H	-1.7648	-3.2874	1.2208
	H	-1.6880	-4.4823	-0.1049
$[Al_{12}Mn^{-}+H_2O]^{\ddagger}$	O	-2.0642	-3.9861	0.0485
	Al	-1.3153	-2.5014	-0.8703
	Mn	0.0548	-1.1352	-2.5920
	Al	-0.1173	1.5160	-2.0868
	Al	1.3277	1.9670	0.3992
	Al	-0.1881	0.6419	2.3335
	Al	-0.1737	-2.0505	1.7889
	Al	-2.4016	-0.4723	1.1351
	Al	-1.4698	1.9671	0.2380
	Al	-2.3181	-0.0804	-1.5688
	Al	-0.0865	-0.2613	-0.1449
	Al	1.4363	-2.3793	-0.5763
	Al	2.1881	0.1462	-1.4193
	Al	2.0945	-0.5474	1.3395
	H	-2.9886	-3.7923	0.3019
	H	-1.3913	-3.4531	1.0030

Table S19: Transition states coordinates (Å) of water dissociation on meta-Al site of surface-doped $Al_{12}X^-$ clusters

$[Al_{12}Mg^-+H_2O]^‡$	O	3.9315	-0.1969	2.0349
	Al	2.4012	0.7129	1.3742
	Al	1.3305	2.5670	-0.1778
	Al	-0.0594	1.3314	-2.2406
	Al	-1.3393	2.1895	0.0669
	Al	0.1105	1.7039	2.3444
	Al	0.3901	-1.0474	2.4928
	Al	-1.9703	-0.0411	1.5756
	Al	-2.0075	-0.3901	-1.1806
	Al	-0.8060	-2.3322	0.3717
	Al	1.9314	-1.9289	0.1902
	Al	2.4014	0.3442	-1.4475
	Al	0.2429	0.0977	0.0979
	Mg	0.4078	-1.5849	-2.2244
	H	3.7774	-0.4782	2.9581
	H	3.4017	-1.1326	1.3506
$[Al_{12}Sc^-+H_2O]^‡$	O	3.7103	0.0701	2.5292
	Al	2.6288	-0.5447	1.0821
	Al	1.9421	1.9361	-0.1061
	Al	0.2071	1.3744	-2.1498
	Sc	-0.3160	-1.4082	-2.4226
	Al	-2.2103	0.3119	-1.0382
	Al	-1.7283	0.1075	1.7481
	Al	0.7167	1.2056	2.4229
	Al	0.3631	-1.6497	2.1750
	Al	-1.3828	-2.1566	0.1225
	Al	1.3064	-2.5315	-0.2574
	Al	2.3131	-0.3291	-1.6266
	Al	0.2349	-0.1183	-0.0130
	Al	-0.7579	2.3067	0.3289
	H	2.6198	0.6678	2.8233
	H	4.2787	0.8065	2.2255
$[Al_{12}Ti^-+H_2O]^‡$	O	3.6954	0.0364	2.4711
	Al	2.6461	-0.6214	1.0253
	Al	1.9019	2.0294	-0.0597
	Al	0.2071	1.3939	-2.1364

	Ti	-0.2266	-1.3245	-2.2715
	Al	-2.0965	0.2715	-1.0815
	Al	-1.7800	0.1272	1.7311
	Al	0.7037	1.1424	2.3496
	Al	0.2765	-1.6357	2.2374
	Al	-1.3922	-2.1386	0.0987
	Al	1.3033	-2.5277	-0.2382
	Al	2.3297	-0.2969	-1.5977
	Al	0.2642	-0.0853	0.0516
	Al	-0.8021	2.3262	0.3431
	H	2.6283	0.6280	2.7559
	H	4.2820	0.7556	2.1635
$[Al_{12}V^{-}+H_2O]^{\ddagger}$	O	3.6804	0.0598	2.4610
	Al	2.6520	-0.6848	1.0409
	Al	1.9188	2.0150	-0.0742
	Al	0.1955	1.3975	-2.1254
	V	-0.1515	-1.3176	-2.2136
	Al	-2.0520	0.3122	-1.0767
	Al	-1.7739	0.0897	1.7578
	Al	0.6934	1.1510	2.3563
	Al	0.2931	-1.6578	2.2196
	Al	-1.4458	-2.0865	0.0627
	Al	1.2439	-2.5599	-0.2580
	Al	2.3334	-0.2905	-1.5958
	Al	0.2772	-0.0835	0.0692
	Al	-0.7902	2.3391	0.3355
	H	2.6137	0.6496	2.7484
	H	4.2513	0.7768	2.1211
$[Al_{12}Cr^{-}+H_2O]^{\ddagger}$	O	3.6911	-0.2140	2.6258
	Al	2.6709	-0.4927	1.0455
	Al	2.7822	2.4254	0.2686
	Al	1.2692	2.4960	-2.0223
	Cr	0.2662	-0.0248	-2.4526
	Al	-1.2684	1.8858	-1.3102
	Al	-1.4233	1.3592	1.4737
	Al	1.1381	1.6475	2.4294
	Al	0.0282	-0.8911	1.9165
	Al	-1.4715	-0.6880	-0.4059

	Al	1.0275	-1.8281	-0.5615
	Al	2.8379	0.2384	-1.5238
	Al	0.7050	0.8008	-0.0222
	Al	0.2504	3.3791	0.4533
	H	2.8137	0.6104	2.9262
	H	4.4757	0.3367	2.4383
$[Al_{12}Mn^{-}+H_2O]^{\ddagger}$	O	3.7067	0.0215	2.4906
	Al	2.6342	-0.5979	1.0457
	Al	1.9033	1.9861	-0.0828
	Al	0.1630	1.3937	-2.1541
	Mn	-0.1409	-1.3141	-2.1822
	Al	-2.1406	0.2740	-1.1005
	Al	-1.7799	0.1486	1.7030
	Al	0.7219	1.1670	2.3413
	Al	0.2701	-1.6018	2.2157
	Al	-1.4293	-2.1212	0.0926
	Al	1.3083	-2.5340	-0.2290
	Al	2.3347	-0.3152	-1.6124
	Al	0.2539	-0.0840	0.0404
	Al	-0.7917	2.3162	0.3085
	H	2.6341	0.6372	2.7703
	H	4.3061	0.7317	2.1869

Table S20: Transition states coordinates (Å) of water dissociation on para-Al site of surface-doped $Al_{12}X^-$ clusters

$[Al_{12}Mg^-+H_2O]^‡$	O	-0.1979	2.2654	3.9605
	Al	-0.2694	2.0423	2.0721
	Al	1.2783	2.5882	-0.0312
	Al	0.0120	1.4188	-2.1646
	Al	-1.5989	2.4168	-0.1918
	Al	-2.3867	0.3406	1.4432
	Al	-0.0693	-0.7051	2.6624
	Al	-1.3112	-2.0475	0.5923
	Al	-2.2174	-0.0838	-1.2858
	Al	-0.0278	0.2293	0.1728
	Al	1.4705	-1.8870	0.6800
	Al	2.2912	0.1805	-1.1186
	Al	2.1911	0.6062	1.6147
	Mg	0.1604	-1.6568	-1.9484
	H	-0.1372	0.9912	3.8036
	H	0.7104	2.5021	4.2322
$[Al_{12}Sc^-+H_2O]^‡$	O	0.1775	2.4760	3.7219
	Al	-0.6040	1.8589	2.0993
	Al	1.1278	2.6081	-0.0360
	Al	0.1074	1.3045	-2.2916
	Sc	0.2379	-1.4971	-2.1089
	Al	-2.2595	-0.0144	-1.3129
	Al	-2.4418	0.1039	1.3892
	Al	-0.2743	-1.0562	2.5608
	Al	-1.2481	-2.1929	0.2054
	Al	1.4619	-1.8555	0.5795
	Al	2.3041	0.2946	-0.9051
	Al	1.9156	0.5878	1.8064
	Al	-0.0919	0.1836	0.1188
	Al	-1.5820	2.4053	-0.2871
	H	-0.1358	1.9282	4.4687
	H	1.1445	1.8251	3.2569
$[Al_{12}Ti^-+H_2O]^‡$	O	-0.0348	2.6626	3.5277
	Al	-0.6562	1.2001	2.4860
	Al	1.1669	2.4086	0.5778
	Al	0.1972	1.6294	-1.8692

	Ti	0.2659	-1.2240	-2.0747
	Al	-2.0613	0.1047	-1.5316
	Al	-2.6248	-0.0404	1.2561
	Al	-0.3170	-1.4358	2.4583
	Al	-1.3626	-2.1568	0.0130
	Al	1.4225	-2.0797	0.2528
	Al	2.3054	0.3035	-0.7857
	Al	1.9706	0.0107	1.9577
	Al	-0.0904	0.0977	0.2350
	Al	-1.6548	2.2891	0.0922
	H	0.6671	2.3512	4.1326
	H	0.5894	2.9234	2.4835
$[Al_{12}V^{-}+H_2O]^{\ddagger}$	O	0.1223	2.2781	3.7949
	Al	-0.7780	1.4251	2.3562
	Al	1.1527	2.5318	0.2845
	Al	0.1643	1.4748	-2.0623
	V	0.3182	-1.2157	-1.9811
	Al	-2.1428	0.0388	-1.3924
	Al	-2.6408	-0.1207	1.2784
	Al	-0.4082	-1.2966	2.4523
	Al	-1.3006	-2.2064	-0.0282
	Al	1.4044	-1.9661	0.5037
	Al	2.3066	0.2423	-0.8497
	Al	1.9032	0.3539	1.9131
	Al	-0.1107	0.1537	0.2175
	Al	-1.5741	2.3783	0.0026
	H	1.0686	1.5967	3.3167
	H	0.3560	3.1913	3.5375
$[Al_{12}Cr^{-}+H_2O]^{\ddagger}$	O	-0.2214	2.6090	3.6671
	Al	0.0105	1.6900	2.0246
	Al	0.1339	1.7736	-0.6096
	Al	-2.0081	0.2958	-1.5837
	Cr	-1.7827	-2.2878	-0.6746
	Al	-3.5614	-0.5871	0.5828
	Al	-2.3466	0.2834	2.9164
	Al	0.1740	-0.9855	3.0958
	Al	-2.0305	-2.3497	2.0642
	Al	0.4892	-2.5740	0.8524

	Al	0.5412	-0.8513	-1.3231
	Al	1.7469	-0.0686	1.0280
	Al	-0.9327	-0.3244	0.7658
	Al	-2.3647	1.9289	0.6150
	H	-1.2186	1.8155	3.6721
	H	0.3619	2.2111	4.3416
$[Al_{12}Mn^{-}+H_2O]^{\ddagger}$	O	-0.2250	2.2312	3.9064
	Al	-0.3023	2.0700	2.0121
	Al	1.2466	2.5519	-0.1314
	Al	-0.0022	1.3160	-2.2557
	Mn	0.1382	-1.5405	-1.8608
	Al	-2.1813	-0.1780	-1.3670
	Al	-2.3967	0.2932	1.3624
	Al	-0.0763	-0.7258	2.5954
	Al	-1.2834	-2.0744	0.4892
	Al	1.4399	-1.9032	0.5751
	Al	2.2392	0.1051	-1.2000
	Al	2.1803	0.5814	1.5332
	Al	-0.0425	0.2193	0.1251
	Al	-1.6137	2.3631	-0.2980
	H	-0.1585	0.9576	3.7474
	H	0.6795	2.4788	4.1842

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