Electronic Supplementary Information

for

Anion Exchange Behavior of $M^{II}Al$ Layered Double Hydroxides: a Molecular Dynamics and DFT Study

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14

Contents

Item	Title	Number
Figure	The total potential energy diagram of Mg_2Al-Cl-LDH under different simulation time	S1
	Snapshots of Mg_2Al-Cl-LDH at different simulation time, 200 ps (a), 400 ps (b), 800 ps (c), 1 ns (d), 10 ns (e), and 15 ns (f).	S2
	Snapshots of (a-i) Ni_2Al-A-LDHs (A= OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) after MD simulations of 2 ns.	S3
	Snapshots of (a-i) Zn_2Al-A-LDHs (A= OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) after MD simulations of 2 ns.	S4
	Snapshots of Mg_RAl-A-LDHs intercalated with different anions(A= OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, for monovalent anions and divalent anions, R = 1.6, 2.6, 3.5, 5.0 and 8.0; for trivalent anions, R = 1.4, 3.0, 5.0 and 8.0) after molecular dynamics simulations of 200 ps.	S5
	Snapshots of Ni_RAl-A-LDHs intercalated with different anions(A= OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, for monovalent anions and divalent anions, R = 1.6, 2.6, 3.5, 5.0 and 8.0; for trivalent anions, R = 1.4, 3.0, 5.0 and 8.0) after molecular dynamics simulations of 200 ps.	S6
	Snapshots of Zn_RAl-A-LDHs intercalated with different anions(A= OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, for monovalent anions and divalent anions, R = 1.6, 2.6, 3.5, 5.0 and 8.0; for trivalent anions, R = 1.4, 3.0, 5.0 and 8.0) after molecular dynamics simulations of 200 ps.	S7
	The van der Waals energies of (a) Mg_RAl-A-LDHs, (b) Ni_RAl-A-LDHs and (c) Zn_RAl-A-LDHs (A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) as a function of R.	S8
	The average distance (in Å) between the H atom of hydroxyl group in the layers and X or O atom in the interlayer anions ($L_{X...H}$ or $L_{O...H}$)) in Mg_2Al-A-LDHs (A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) from the side view.	S9
	The average distance (in Å) between the H atom of hydroxyl group in the layers and X or O atom in the interlayer anions ($L_{X...H}$ or $L_{O...H}$)) in Ni_2Al-A-LDHs (A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) from the side view.	S10
	The average distance (in Å) between the H atom of hydroxyl group in the layers and X or O atom in the interlayer anions ($L_{X...H}$ or $L_{O...H}$)) in Zn_2Al-A-LDHs (A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) from the side view.	S11
	The relationship between the relative binding energies and (a) the average distance (L) between the H atom of hydroxyl group in the layers and X or O atom in the interlayer anions (X…H or O…H) (b) the charge transfer (Δq) of anions or (c) the electronegativity of anions in Ni_2Al-A-LDHs (A = OH^-, Cl^-,	S12

	Br^-, NO_3^-, $HCOO^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}). Red solid line is the fitting line.	
	The relationship between the relative binding energies and (a) the average distance (L) between the H atom of hydroxyl group in the layers and X or O atom in the interlayer anions (X…H or O…H) (b) the charge transfer (Δq) of anions or (c) the electronegativity of anions in Zn_2Al-A-LDHs (A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}). Red solid line is the fitting line.	S13
	The schematic diagram of the distance between the oxygen or halide atoms in an anion and the hydrogen atom in the adjacent H_2O (d) under the top view, and the possibility of d (upper right) in Ni_2Al-A-LDHs after MD simulations of 2 ns.	S14
	The schematic diagram of the distance between the oxygen or halide atoms in an anion and the hydrogen atom in the adjacent H_2O (d) under the top view, and the possibility of d (upper right) in Zn_2Al-A-LDHs after MD simulations of 2 ns.	S15
	The linearly fitted mean square displacements (MSD) of eight anions for Ni_2Al-A-LDHs (A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-})	S16
	The linearly fitted mean square displacements (MSD) of eight anions for Zn_2Al-A-LDHs (A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-})	S17
Table	Lattice parameters of Mg_2Al-Cl-LDHs under different simulation time	S1
	The calculated energies of Mg_2Al-Cl-LDHs under the orbital cutoff ranging from 3.7 Å to 6.7 Å	S2
	Chemical formulae and lattice parameters of the calculated M^{II}_nAl-A-LDHs(M^{II} = Mg, Ni, Zn; R ranges from 1.4 to 8; A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}) after molecular dynamics simulation of 200 ps	S3
	The lattice parameter a of M^{II}_RAl-Cl-LDHs and $M^{II}(OH)_2$ (M^{II} = Mg, Ni, Zn) when R>4 after simulation of 200 ps	S4
	Energy composition of M^{II}_RAl-A-LDHs (M^{II} = Mg, Ni, Zn; R ranges from 1.4 to 8; A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}), where E_{tot}, E_a, E_c, $E_{non\text{-}bond}$, E_{vdW}, E_e, E_b represents the total potential energy, angle term, cross term, non-bond energy, van der waals energy, electrostatic energy and relative binding energy, respectively	S5
	Gibbs free energies of M^{II}_2Al-A-LDHs (M^{II}=Mg, Ni, Zn; A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}), along with those of the Mg_2Al-A-LDH with correction for non-covalent interaction (Mg_2Al-A-LDH-1)	S6
	Free energy change of anion-exchange reaction of Ni_2Al-A-LDHs	S7
	Free energy change of anion-exchange reaction of Zn_2Al-A-LDHs	S8
	Free energy change of anion-exchange reaction of Mg_2Al-A-LDHs with correction for non-covalent interaction	S9
	The calculated Mulliken charge (q) of the anion when it is introduced into M_2Al-A-LDHs (M^{II}=Mg, Ni, Zn) and the charge transfers	S10
	The frontier orbital energies, ionization potential, electron affinity	S11

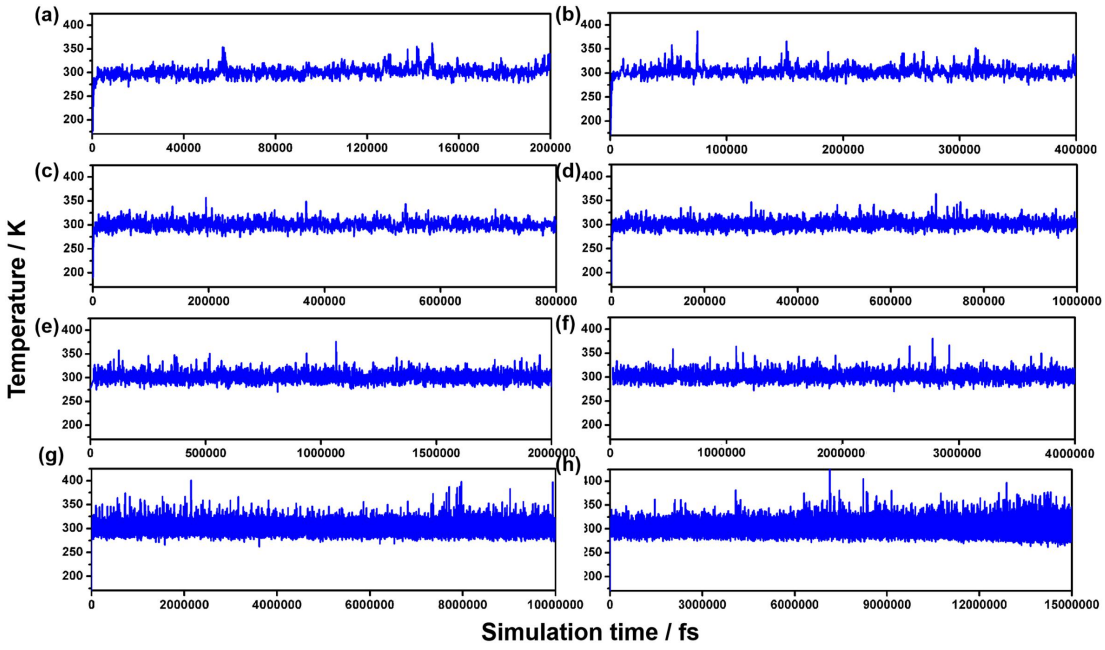

Fig. S1. The total potential energy diagram of Mg_2Al-Cl-LDH under different simulation time.

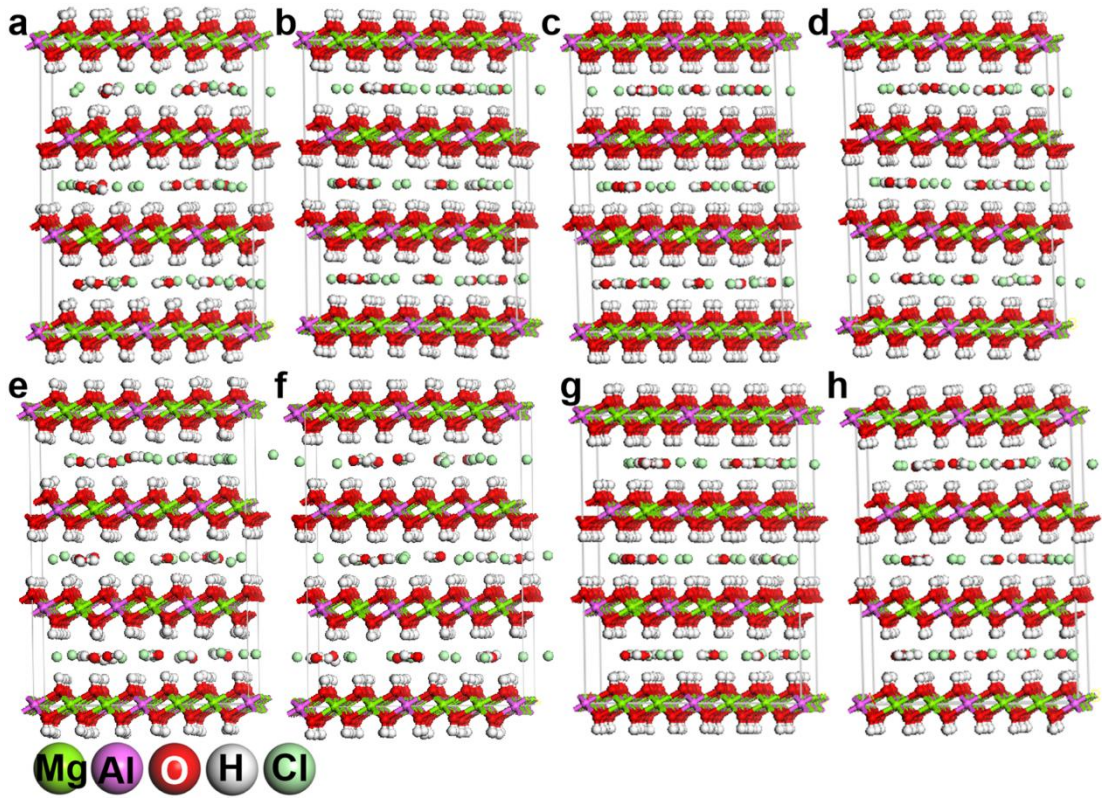

Fig. S2. Snapshots of Mg_2Al-Cl-LDH at different simulation time, 200 ps (a), 400 ps (b), 800 ps (c), 1 ns (d), 2 ns (e), 4 ns (f), 10 ns (g), and 15 ns (h).

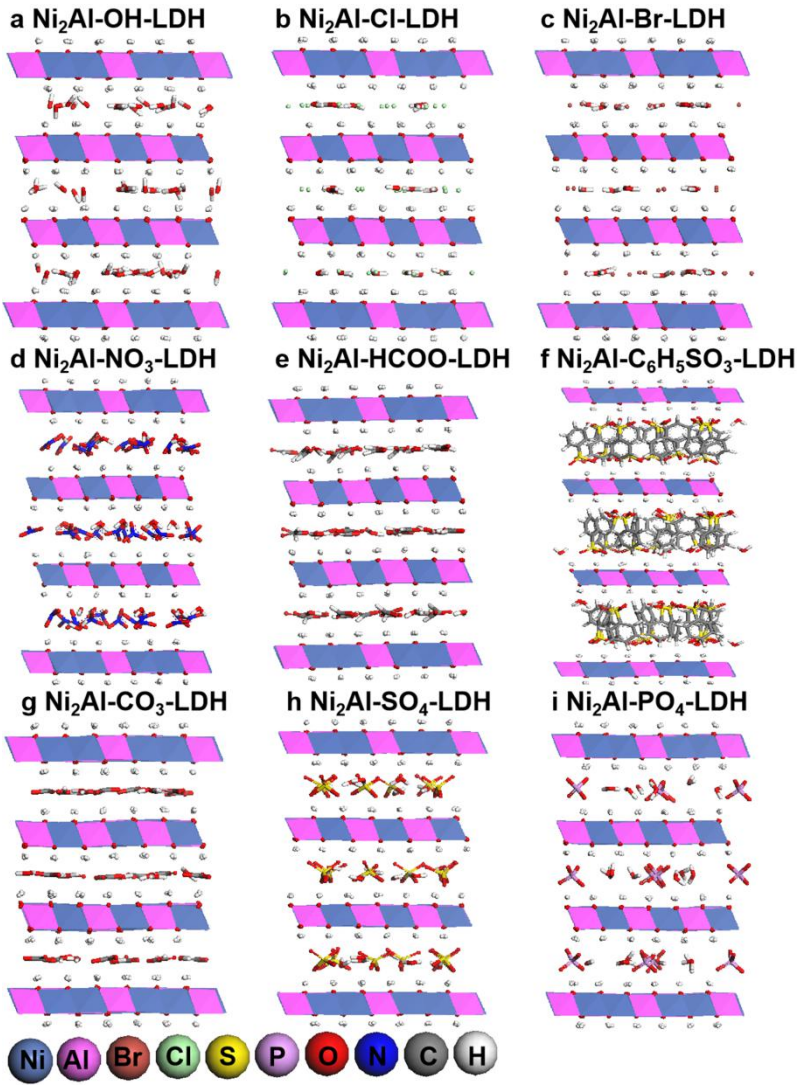

Fig. S3. Snapshots of (a-i) Ni_2Al-A-LDHs (A= OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) after MD simulations of 2 ns.

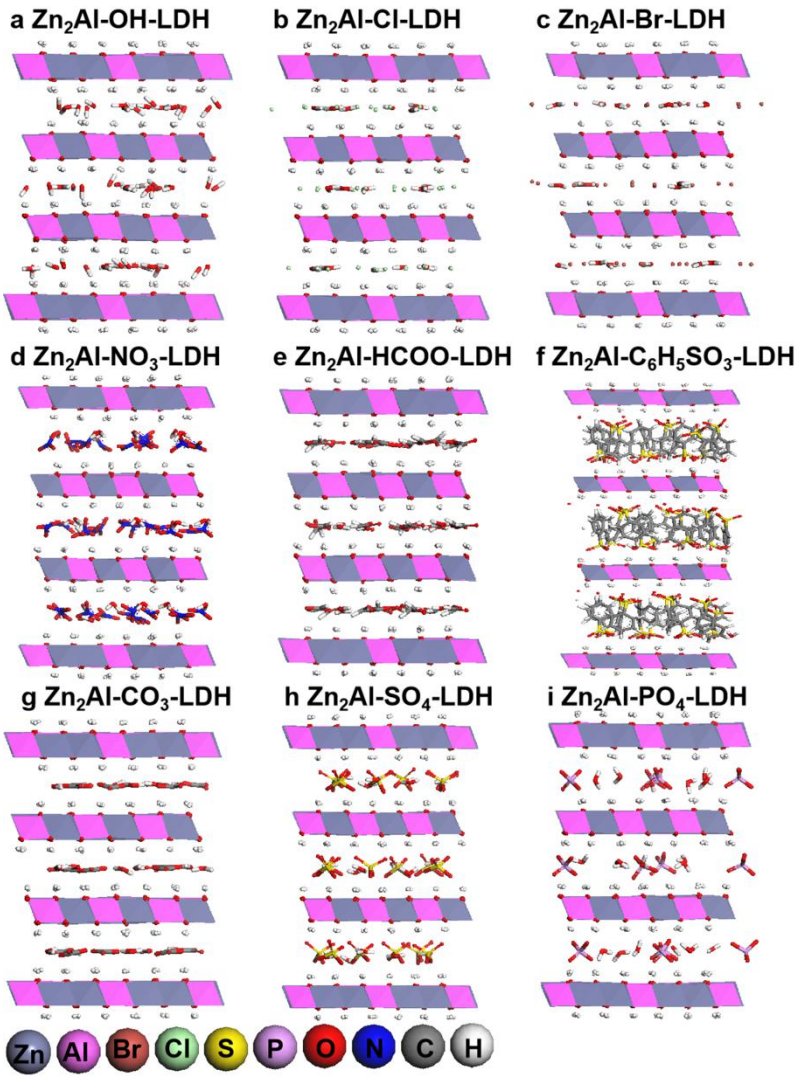

Fig. S4. Snapshots of (a-i) Zn_2Al-A-LDHs (A= OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) after MD simulations of 2 ns.


a $Mg_{22}Al_{14}$-OH-LDH
b $Mg_{26}Al_{10}$-OH-LDH
c $Mg_{28}Al_{8}$-OH-LDH
d $Mg_{30}Al_{6}$-OH-LDH
e $Mg_{32}Al_{4}$-OH-LDH
Mg Al O H
(A) MgAl-OH-LDH
a $Mg_{22}Al_{14}$-Cl-LDH
b $Mg_{26}Al_{10}$-Cl-LDH
c $Mg_{28}Al_{8}$-Cl-LDH
d $Mg_{30}Al_{6}$-Cl-LDH
e $Mg_{32}Al_{4}$-Cl-LDH
Mg Al Cl O H
(B) MgAl-Cl-LDH
a $Mg_{22}Al_{14}$-Br-LDH
b $Mg_{26}Al_{10}$-Br-LDH
c $Mg_{28}Al_{8}$-Br-LDH
d $Mg_{30}Al_{6}$-Br-LDH
e $Mg_{32}Al_{4}$-Br-LDH
Mg Al Br O H
(C) MgAl-Br-LDH
a $Mg_{22}Al_{14}$-NO_3-LDH
b $Mg_{26}Al_{10}$-NO_3-LDH
c $Mg_{28}Al_{8}$-NO_3-LDH
d $Mg_{30}Al_{6}$-NO_3-LDH
e $Mg_{32}Al_{4}$-NO_3-LDH
Mg Al O N H
(D) MgAl-NO_3-LDH
a $Mg_{22}Al_{14}$-HCOO-LDH
b $Mg_{26}Al_{10}$-HCOO-LDH
c $Mg_{28}Al_{8}$-HCOO-LDH
d $Mg_{30}Al_{6}$-HCOO-LDH
e $Mg_{32}Al_{4}$-HCOO-LDH
Mg Al O C H
(E) MgAl-HCOO-LDH

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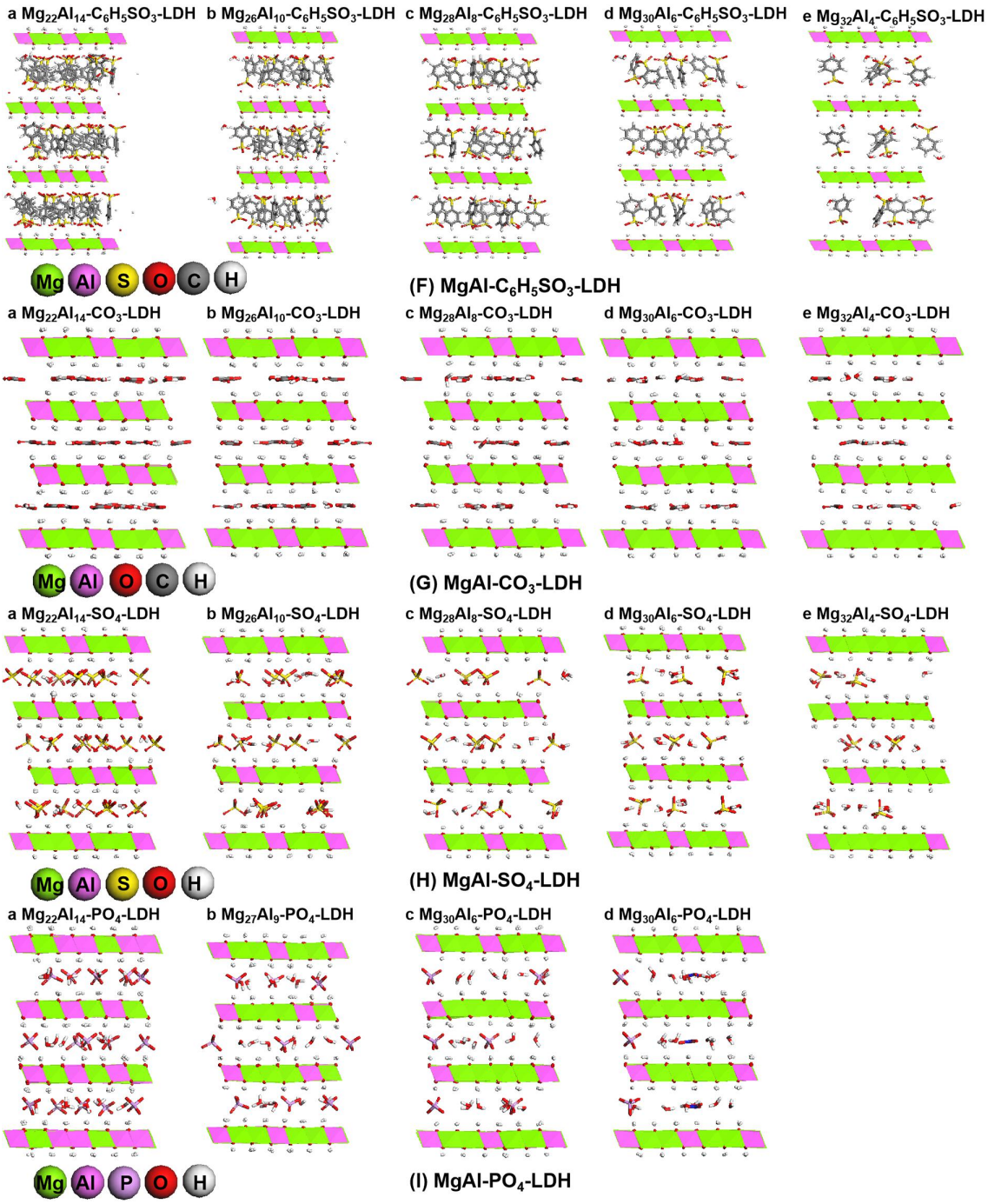
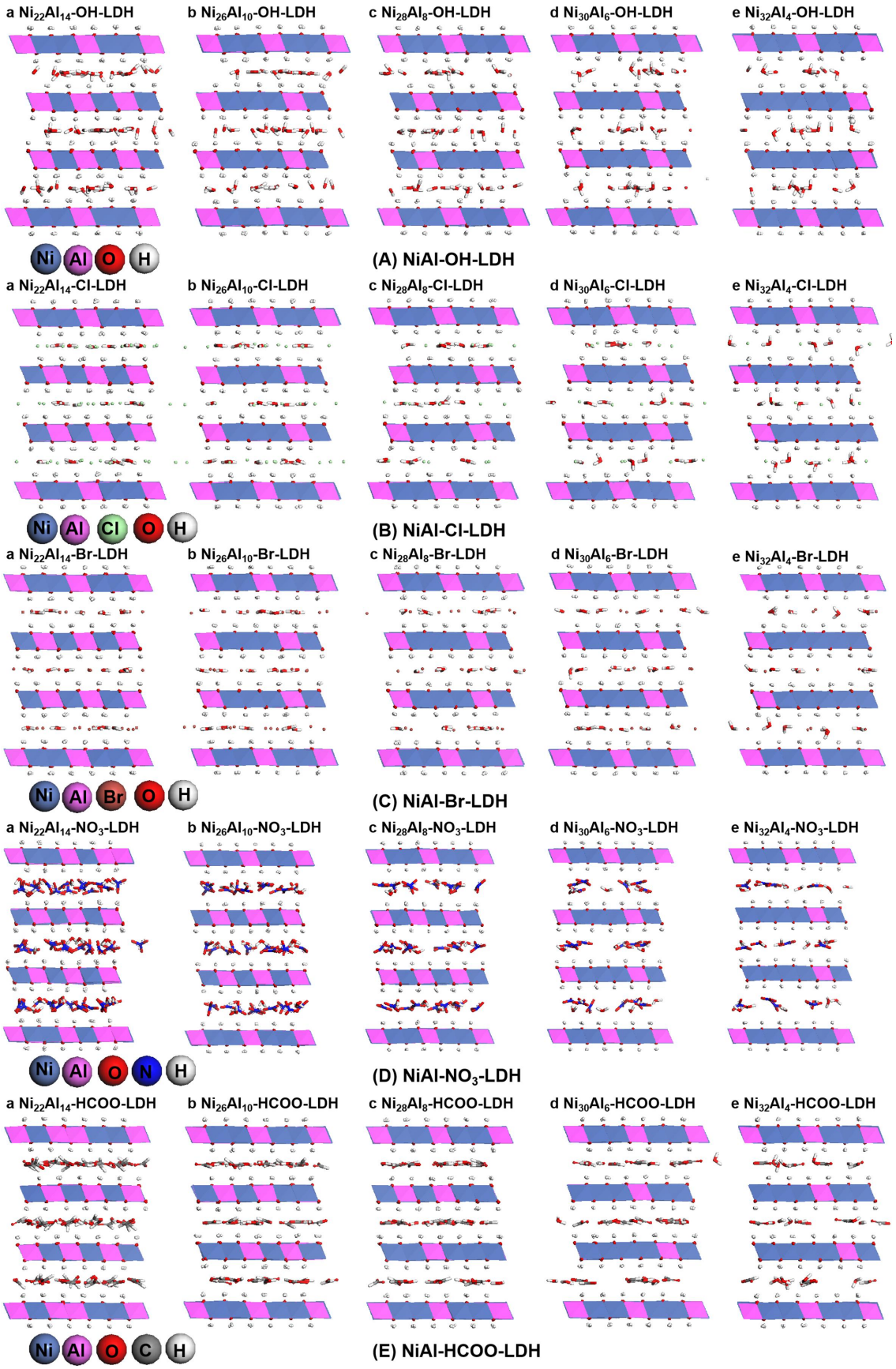


Fig. S5. Snapshots of Mg_RAl-A-LDHs intercalated with different anions (A= OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, for monovalent anions and divalent anions, R = 1.6, 2.6, 3.5, 5.0 and 8.0; for trivalent anions, R = 1.4, 3.0, 5.0 and 8.0) after molecular dynamics simulations of 200 ps.


a $Ni_{22}Al_{14}$-OH-LDH
b $Ni_{26}Al_{10}$-OH-LDH
c $Ni_{28}Al_{8}$-OH-LDH
d $Ni_{30}Al_{6}$-OH-LDH
e $Ni_{32}Al_{4}$-OH-LDH
Ni Al O H
(A) NiAl-OH-LDH
a $Ni_{22}Al_{14}$-Cl-LDH
b $Ni_{26}Al_{10}$-Cl-LDH
c $Ni_{28}Al_{8}$-Cl-LDH
d $Ni_{30}Al_{6}$-Cl-LDH
e $Ni_{32}Al_{4}$-Cl-LDH
Ni Al Cl O H
(B) NiAl-Cl-LDH
a $Ni_{22}Al_{14}$-Br-LDH
b $Ni_{26}Al_{10}$-Br-LDH
c $Ni_{28}Al_{8}$-Br-LDH
d $Ni_{30}Al_{6}$-Br-LDH
e $Ni_{32}Al_{4}$-Br-LDH
Ni Al Br O H
(C) NiAl-Br-LDH
a $Ni_{22}Al_{14}$-NO_3-LDH
b $Ni_{26}Al_{10}$-NO_3-LDH
c $Ni_{28}Al_{8}$-NO_3-LDH
d $Ni_{30}Al_{6}$-NO_3-LDH
e $Ni_{32}Al_{4}$-NO_3-LDH
Ni Al O N H
(D) NiAl-NO_3-LDH
a $Ni_{22}Al_{14}$-HCOO-LDH
b $Ni_{26}Al_{10}$-HCOO-LDH
c $Ni_{28}Al_{8}$-HCOO-LDH
d $Ni_{30}Al_{6}$-HCOO-LDH
e $Ni_{32}Al_{4}$-HCOO-LDH
Ni Al O C H
(E) NiAl-HCOO-LDH

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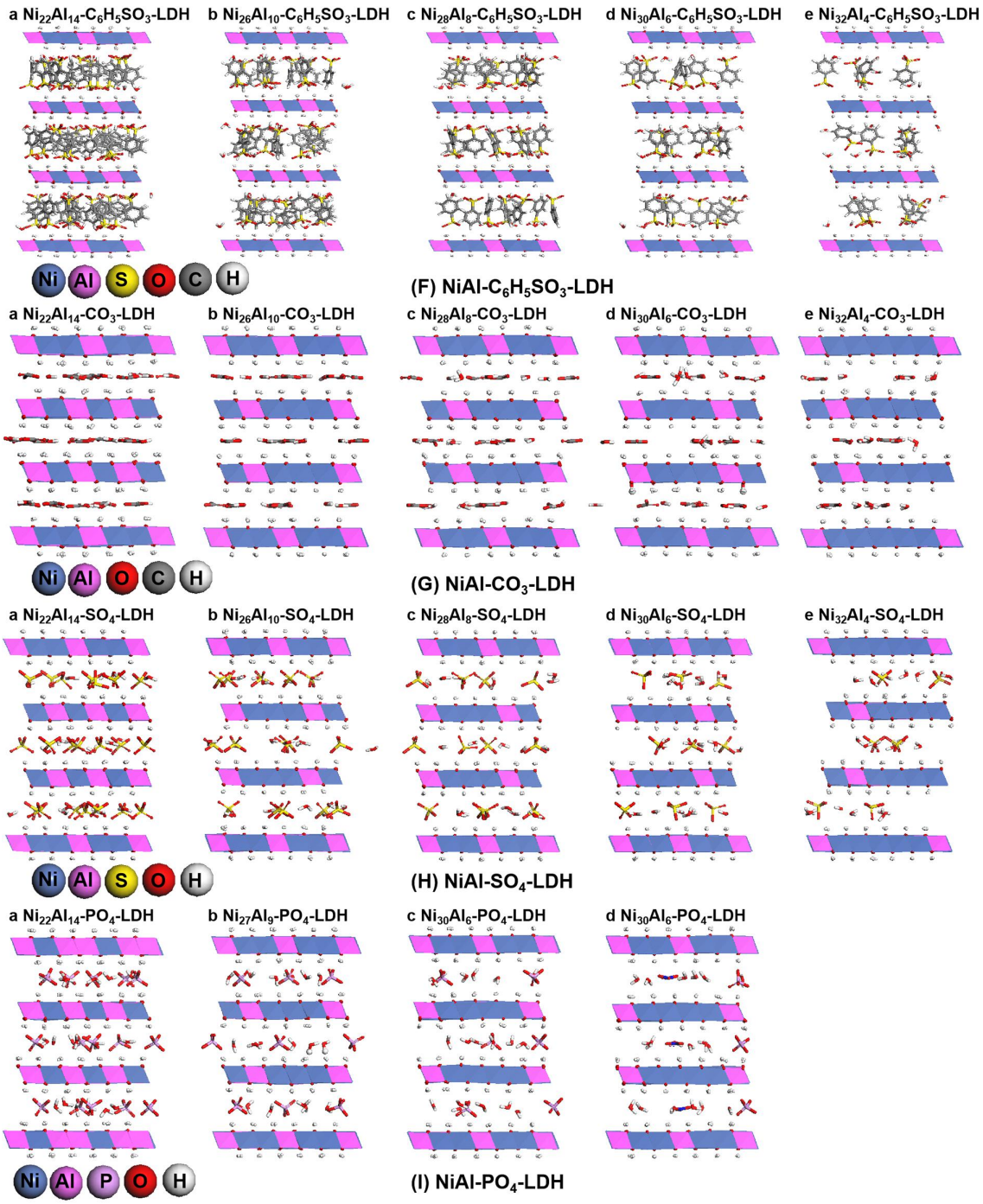
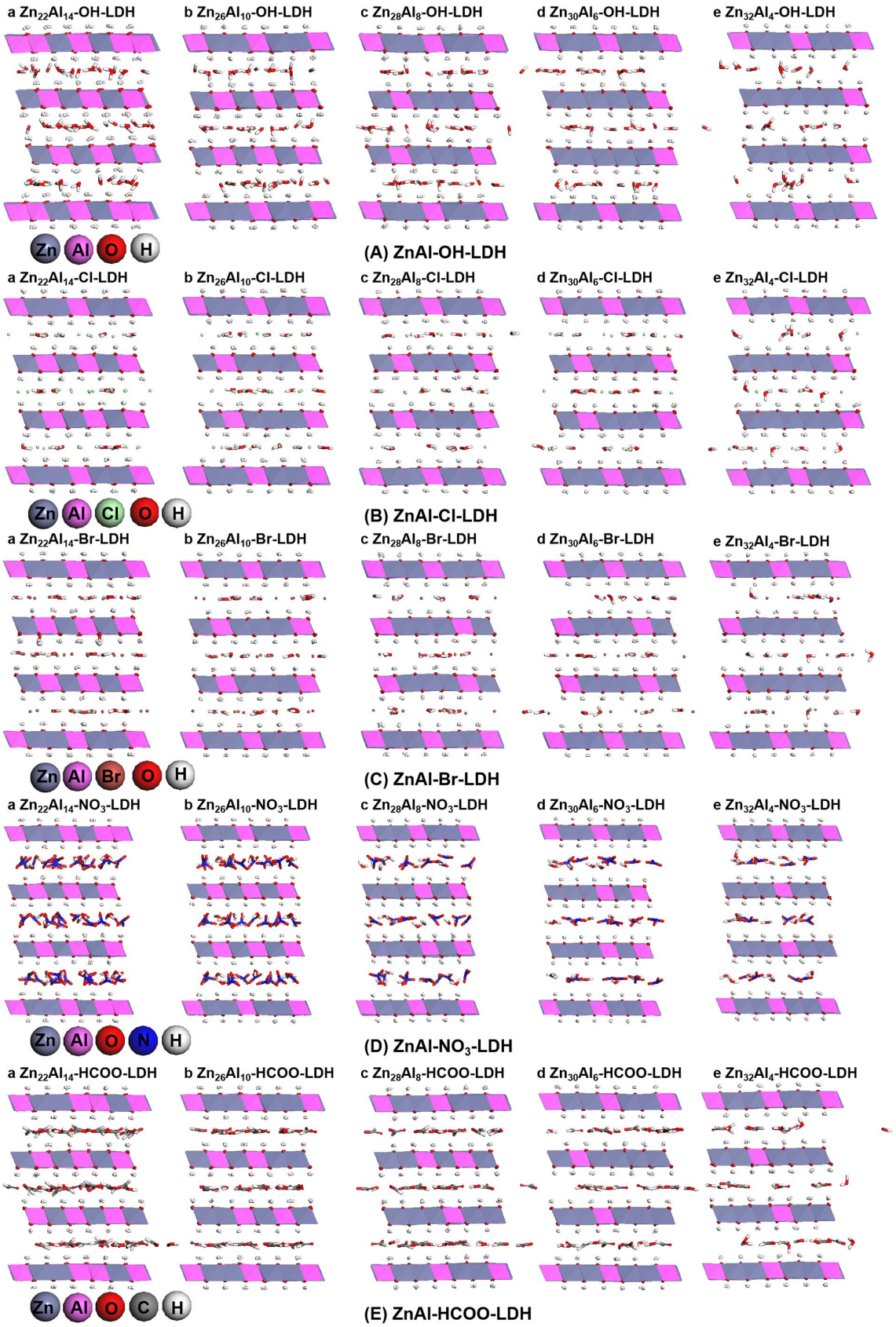


Fig. S6. Snapshots of Ni_RAl-A-LDHs intercalated with different anions (A= OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, for monovalent anions and divalent anions, R = 1.6, 2.6, 3.5, 5.0 and 8.0; for trivalent anions, R = 1.4, 3.0, 5.0 and 8.0) after molecular dynamics simulations of 200 ps.


a $Zn_{22}Al_{14}$-OH-LDH
b $Zn_{26}Al_{10}$-OH-LDH
c $Zn_{28}Al_{8}$-OH-LDH
d $Zn_{30}Al_{6}$-OH-LDH
e $Zn_{32}Al_{4}$-OH-LDH
Zn Al O H
(A) ZnAl-OH-LDH
a $Zn_{22}Al_{14}$-Cl-LDH
b $Zn_{26}Al_{10}$-Cl-LDH
c $Zn_{28}Al_{8}$-Cl-LDH
d $Zn_{30}Al_{6}$-Cl-LDH
e $Zn_{32}Al_{4}$-Cl-LDH
Zn Al Cl O H
(B) ZnAl-Cl-LDH
a $Zn_{22}Al_{14}$-Br-LDH
b $Zn_{26}Al_{10}$-Br-LDH
c $Zn_{28}Al_{8}$-Br-LDH
d $Zn_{30}Al_{6}$-Br-LDH
e $Zn_{32}Al_{4}$-Br-LDH
Zn Al Br O H
(C) ZnAl-Br-LDH
a $Zn_{22}Al_{14}$-NO_3-LDH
b $Zn_{26}Al_{10}$-NO_3-LDH
c $Zn_{28}Al_{8}$-NO_3-LDH
d $Zn_{30}Al_{6}$-NO_3-LDH
e $Zn_{32}Al_{4}$-NO_3-LDH
Zn Al O N H
(D) ZnAl-NO_3-LDH
a $Zn_{22}Al_{14}$-HCOO-LDH
b $Zn_{26}Al_{10}$-HCOO-LDH
c $Zn_{28}Al_{8}$-HCOO-LDH
d $Zn_{30}Al_{6}$-HCOO-LDH
e $Zn_{32}Al_{4}$-HCOO-LDH
Zn Al O C H
(E) ZnAl-HCOO-LDH

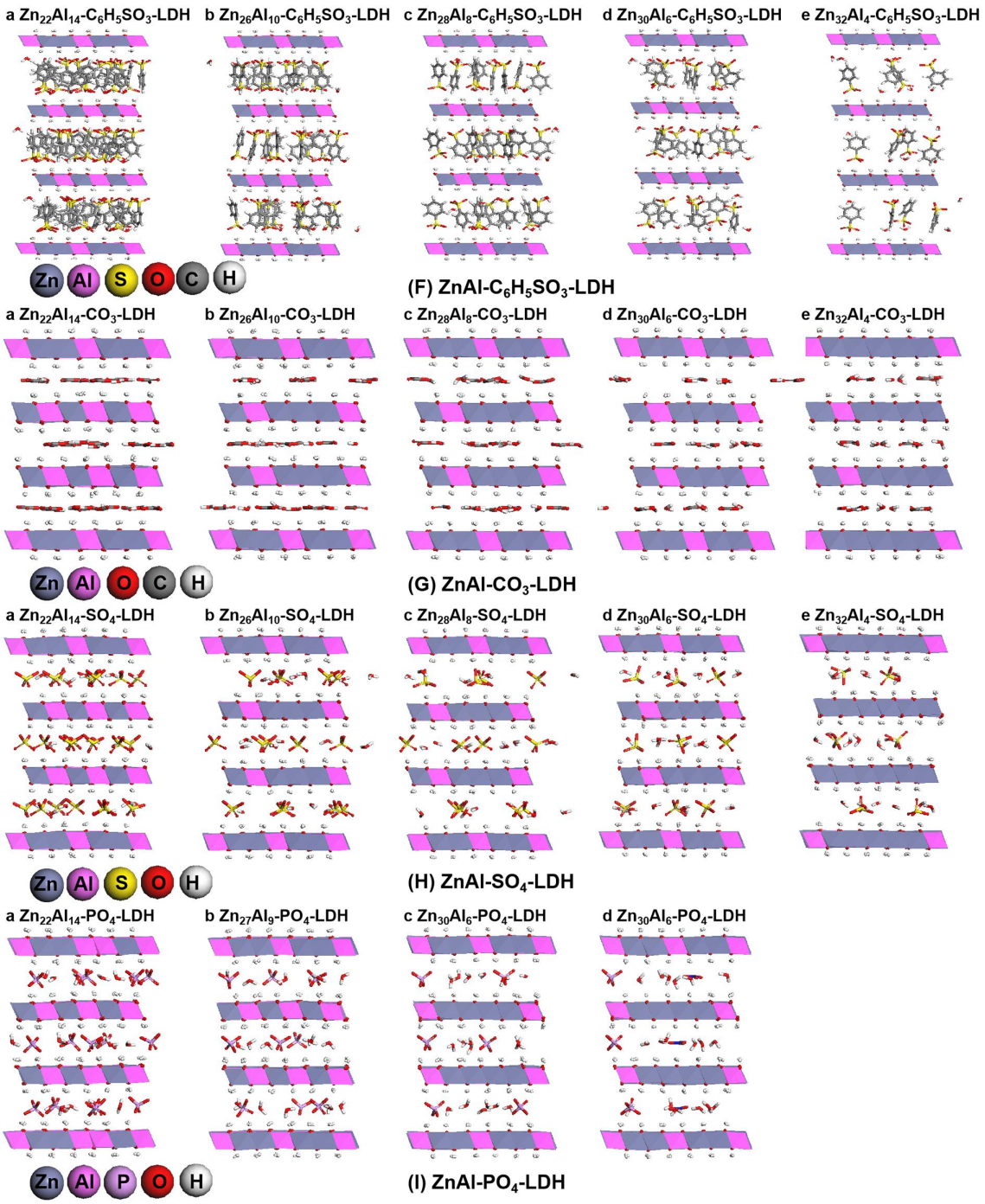
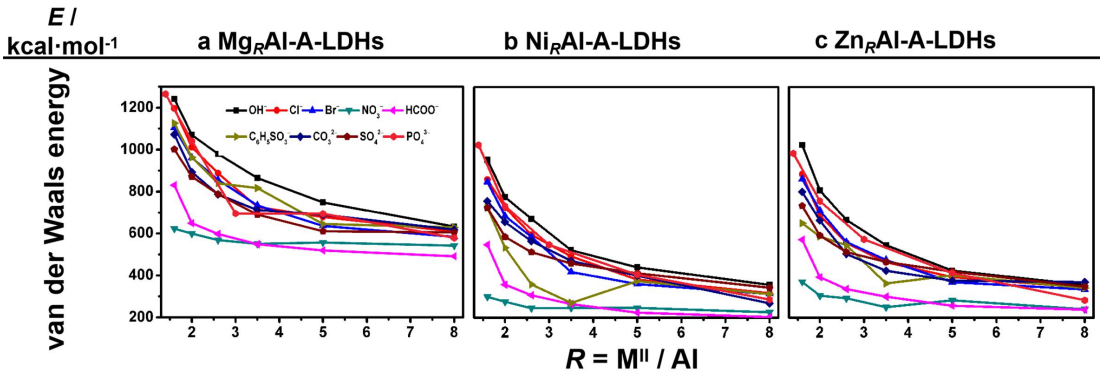


Fig. S7. Snapshots of Zn_RAl-A-LDHs intercalated with different anions(A= OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, for monovalent anions and divalent anions, R = 1.6, 2.6, 3.5, 5.0 and 8.0; for trivalent anions, R = 1.4, 3.0, 5.0 and 8.0) after molecular dynamics simulations of 200 ps.



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65 **Fig. S8.** The van der Waals energies of (a) Mg$_R$Al-A-LDHs, (b) Ni$_R$Al-A-LDHs and

66 (c) Zn$_R$Al-A-LDHs (A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-},

67 PO_4^{3-}) as a function of *R*.

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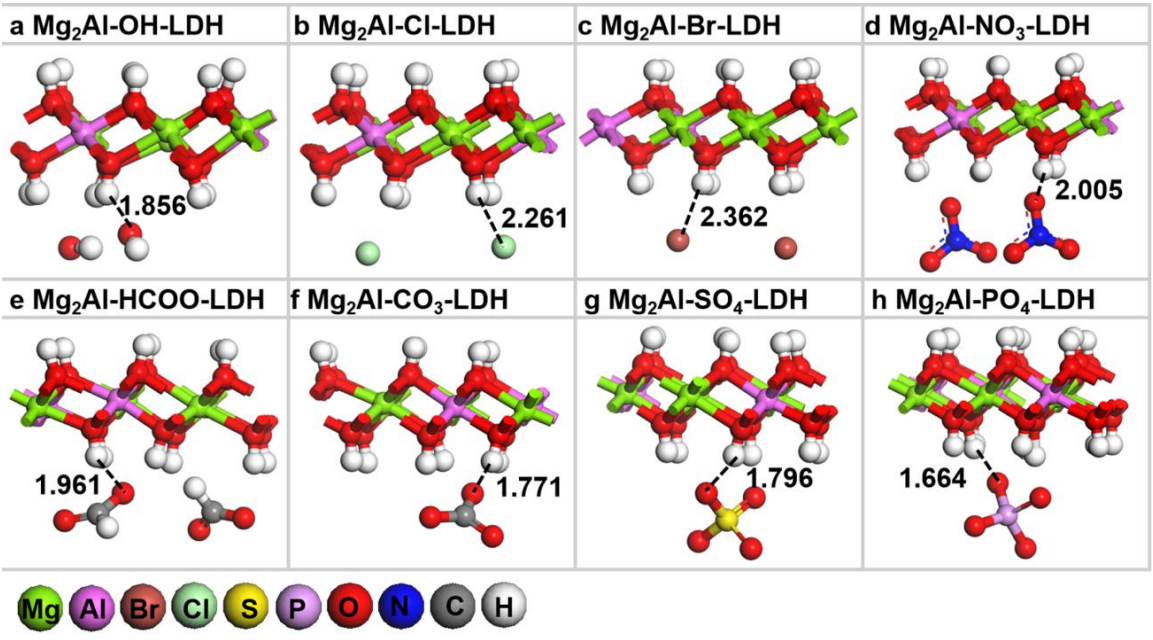

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71 **Fig. S9**. The average distance (in Å) between the H atom of hydroxyl group in the

72 layers and X or O atom in the interlayer anions ($L_{X...H}$ or $L_{O...H}$)) in Mg$_2$Al-A-LDHs (A

73 = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) from the side view.

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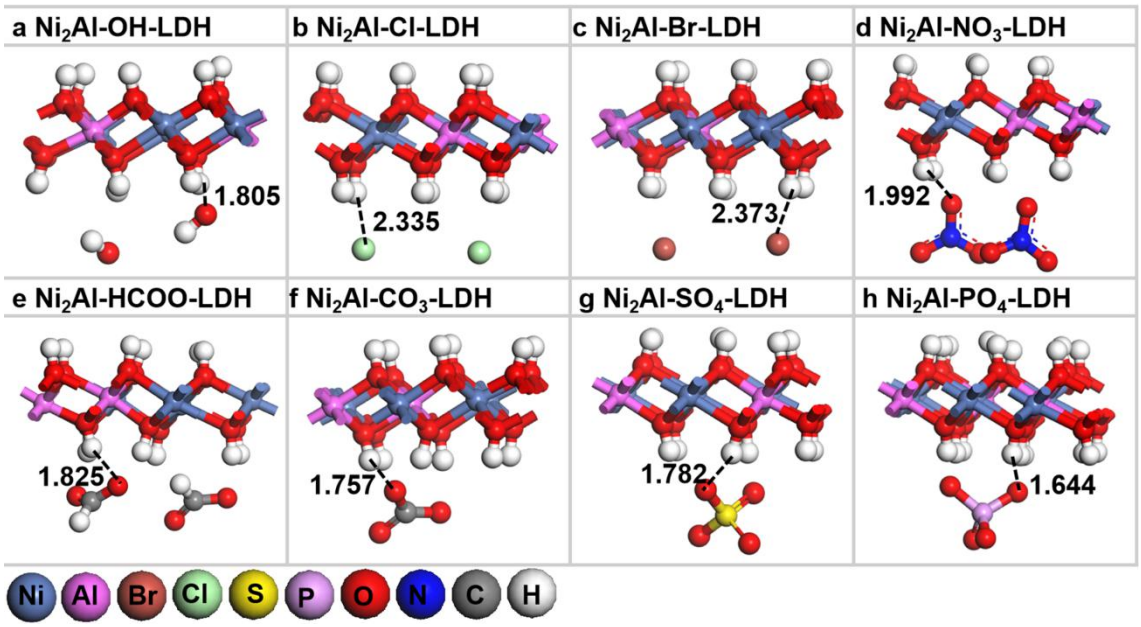


Fig. S10. The average distance (in Å) between the H atom of hydroxyl group in the layers and X or O atom in the interlayer anions ($L_{X...H}$ or $L_{O...H}$)) in Ni_2Al-A-LDHs (A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) from the side view.

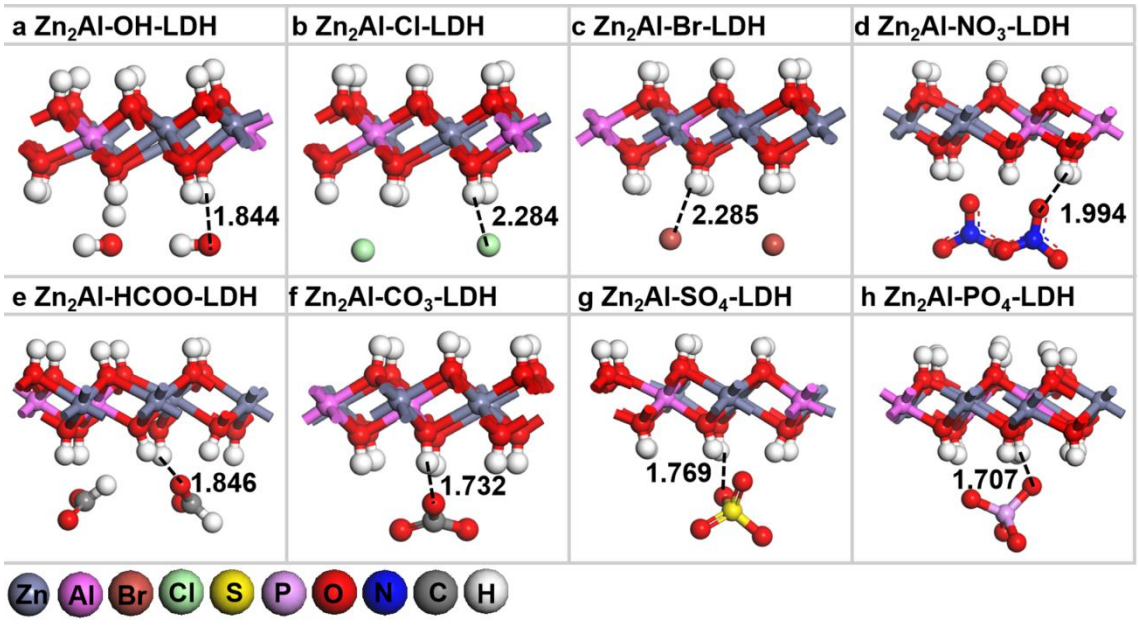


Fig. S11. The average distance (in Å) between the H atom of hydroxyl group in the layers and X or O atom in the interlayer anions ($L_{X...H}$ or $L_{O...H}$)) in Zn_2Al-A-LDHs (A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) from the side view.

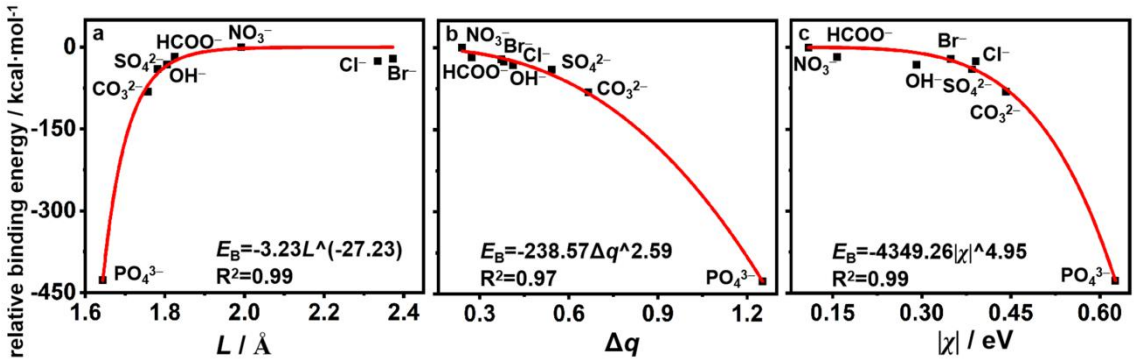


Fig. S12. The relationship between the relative binding energies and (a) the average distance (*L*) between the H atom of hydroxyl group in the layers and X or O atom in the interlayer anions (X…H or O…H) (b) the charge transfer (Δ*q*) of anions or (c) the electronegativity of anions in Ni_2Al-A-LDHs (A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}). Red solid line is the fitting line.

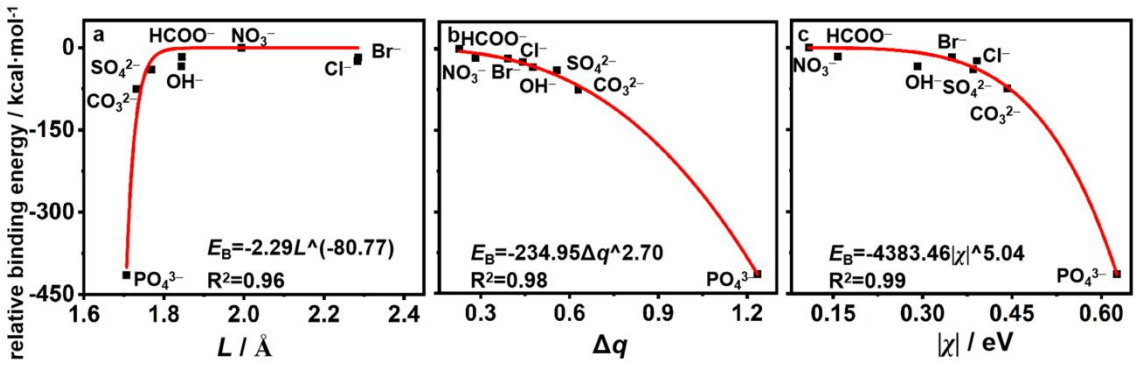


Fig. S13. The relationship between the relative binding energies and (a) the average distance (*L*) between the H atom of hydroxyl group in the layers and X or O atom in the interlayer anions (X…H or O…H) (b) the charge transfer (Δ*q*) of anions or (c) the electronegativity of anions in Zn_2Al-A-LDHs (A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}). Red solid line is the fitting line.

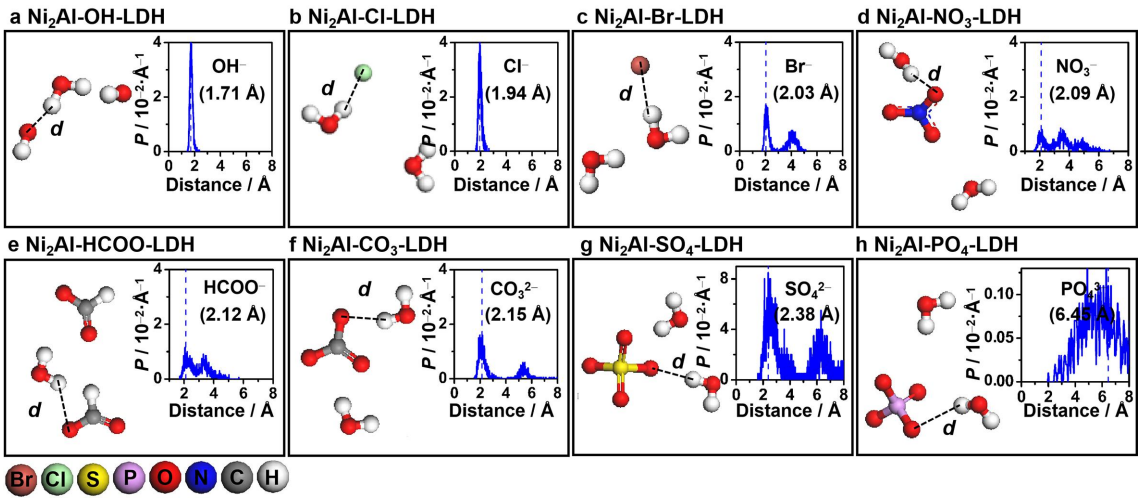


Fig. S14. The schematic diagram of the distance between the oxygen or halide atoms in an anion and the hydrogen atom in the adjacent H_2O (*d*) under the top view, and the possibility of *d* (upper right) in Ni_2Al-A-LDHs after MD simulations of 2 ns.

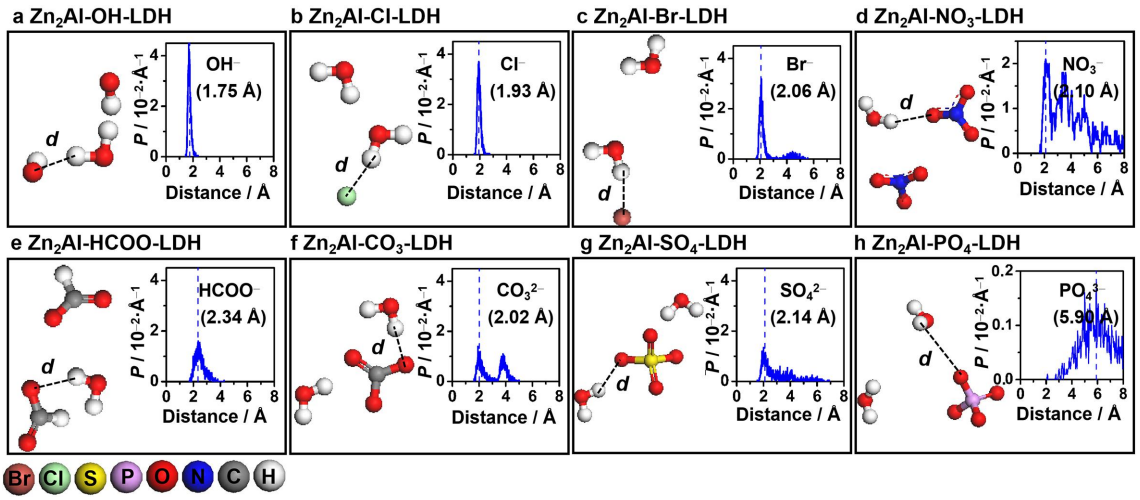
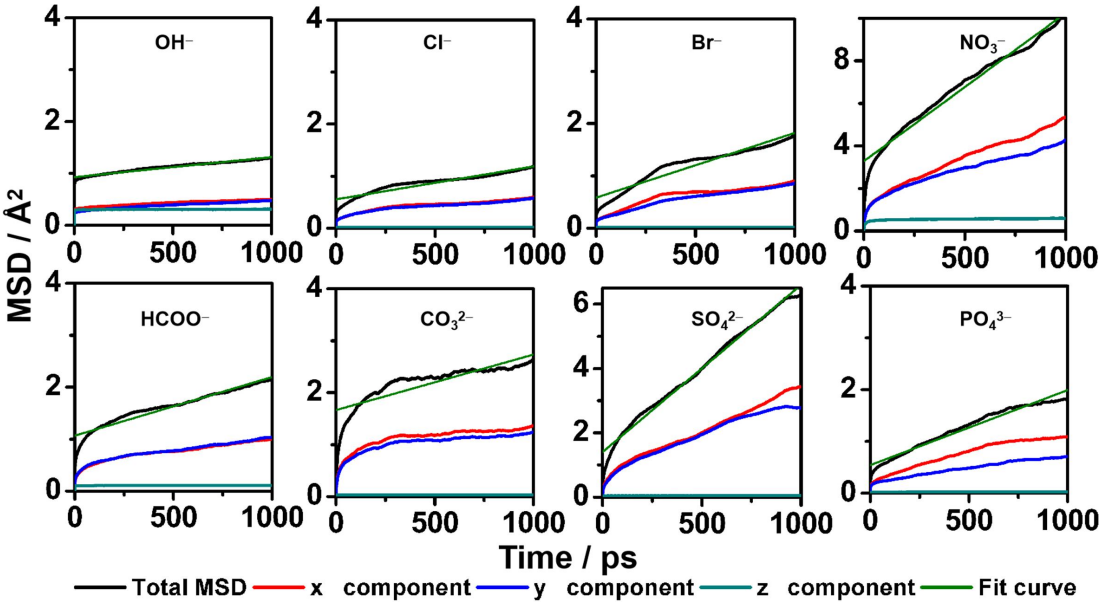


Fig. S15. The schematic diagram of the distance between the oxygen or halide atoms in an anion and the hydrogen atom in the adjacent H_2O (*d*) under the top view, and the possibility of *d* (upper right) in Zn_2Al-A-LDHs after MD simulations of 2 ns.



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113 **Fig. S16.** The linearly fitted mean square displacements (MSD) of eight anions for

114 Ni_2Al-A-LDHs (A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}).

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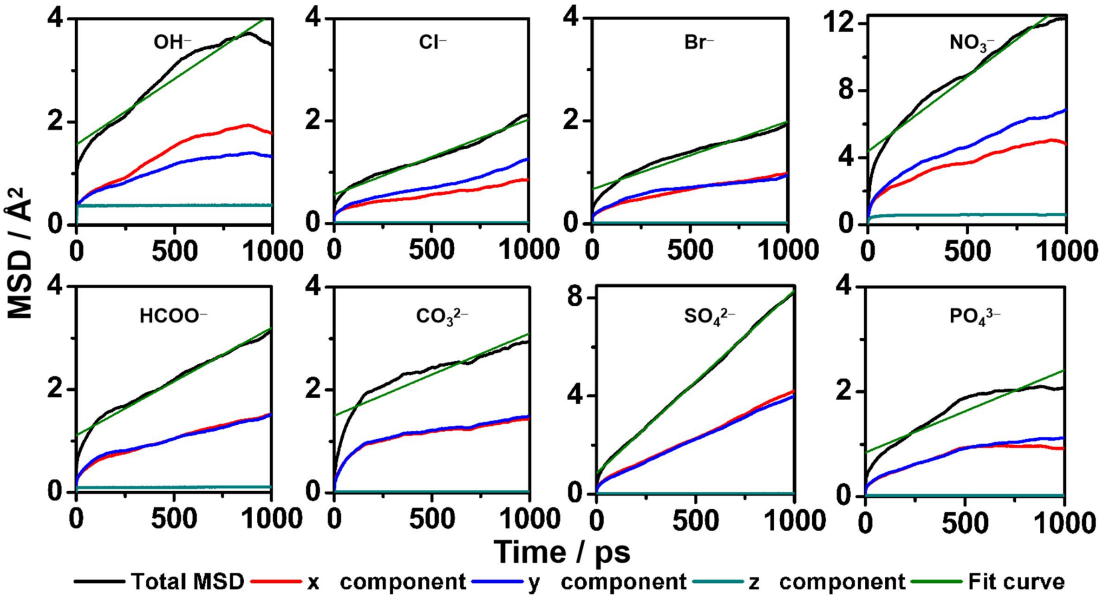

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118 **Fig. S17.** The linearly fitted mean square displacements (MSD) of eight anions for

119 Zn_2Al-A-LDHs (A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}).

120 **Table S1.** Lattice parameters of Mg_2Al-Cl-LDHs under different simulation time

Simulation time (ps)	lattice parameters					
	a (Å)	*b* (Å)	*c* (Å)	*α* (º)	*β* (º)	*γ* (º)
200	18.22	18.21	22.17	90.63	89.37	120.01
400	18.23	18.22	22.19	90.63	89.37	120.01
800	18.22	18.21	22.18	90.63	89.37	120.01
1000	18.23	18.22	22.19	90.63	89.37	120.01
2000	18.23	18.25	22.14	90.28	89.64	120.00
4000	18.20	18.23	22.12	90.28	89.64	120.00
10000	18.22	18.21	22.18	90.63	89.37	120.01
15000	18.21	18.21	21.99	91.44	89.55	120.00

The determination of the orbital cut−off

In this work, the geometry of model Mg_2Al-Cl-LDHs was optimized under the orbital cut-off ranging from 3.7 Å to 6.7 Å. The energy of Mg_2Al-Cl-LDHs is thus calculated to be −3115.426434 Ha with the cut−off 3.7 Å, and −3115.42842 Å with the cut-off 6.7 Å. Therefore, the difference of the calculation results under the cut-off of 3.7 Å and 6.7 Å is 0.001986 Ha. Given that the model of Mg_2Al-Cl-LDHs contains 32 atoms, the difference under the orbital cut-off of 3.7 Å and 6.7 Å is about 0.0000621 Ha/atom. Thus, in order to save the computational cost, the orbital cut-off of 3.7 Å is applied in this work.

Table S2. The calculated energies of Mg_2Al-Cl-LDHs under the orbital cutoff ranging from 3.7 Å to 6.7 Å

	Mg_2Al-Cl-LDHs				
cutoff /Å	3.7	4.3	4.9	5.5	6.7
E / Ha	−3115.426434	−3115.43238	−3115.431752	−3115.431223	−3115.42842

Table S3. Chemical formulae and lattice parameters of the calculated M^{II}_RAl-A-LDHs (M^{II} = Mg, Ni, Zn; *R* ranges from 1.4 to 8; A = OH^-, Cl^-, Br^-, NO_3^-,

136 $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}) after molecular dynamics simulation of

137 200 ps

model	anion	formula	α / º	β / º	γ / º	a / Å	b / Å	c /Å
Mg_RAl-A-LDHs	OH^-	$Mg_{66}Al_{42}(OH)_{216}42OH\cdot18H_2O$	92.2	89.1	120.0	18.1	18.1	21.2
		$Mg_{72}Al_{36}(OH)_{216}36OH\cdot18H_2O$	90.7	89.8	120.0	18.2	18.2	21.4
		$Mg_{78}Al_{30}(OH)_{216}30OH\cdot18H_2O$	91.2	89.5	120.0	18.3	18.3	21.7
		$Mg_{84}Al_{24}(OH)_{216}24OH\cdot18H_2O$	90.6	89.9	120.2	18.4	18.4	21.8
		$Mg_{90}Al_{18}(OH)_{216}18OH\cdot18H_2O$	89.5	90.3	119.9	18.5	18.5	22.3
		$Mg_{96}Al_{12}(OH)_{216}12OH\cdot18H_2O$	88.3	92.4	119.9	18.6	18.6	22.8
	Cl^-	$Mg_{66}Al_{42}(OH)_{216}42Cl\cdot18H_2O$	89.7	90.4	119.8	18.1	18.1	21.8
		$Mg_{72}Al_{36}(OH)_{216}36Cl\cdot18H_2O$	90.6	89.4	120.0	18.2	18.2	22.2
		$Mg_{78}Al_{30}(OH)_{216}30Cl\cdot18H_2O$	89.7	89.5	119.9	18.3	18.3	22.3
		$Mg_{84}Al_{24}(OH)_{216}24Cl\cdot18H_2O$	89.9	90.3	120.0	18.4	18.4	22.6
		$Mg_{90}Al_{18}(OH)_{216}18Cl\cdot18H_2O$	91.0	89.2	120.0	18.5	18.5	22.9
		$Mg_{96}Al_{12}(OH)_{216}12Cl\cdot18H_2O$	91.1	89.1	119.9	18.6	18.6	23.4
	Br^-	$Mg_{66}Al_{42}(OH)_{216}42Br\cdot18H_2O$	88.4	91.7	120.0	18.1	18.1	22.4
		$Mg_{72}Al_{36}(OH)_{216}36Br\cdot18H_2O$	89.7	90.5	120.0	18.2	18.2	22.7
		$Mg_{78}Al_{30}(OH)_{216}30Br\cdot18H_2O$	89.7	90.3	119.9	18.3	18.3	22.9
		$Mg_{84}Al_{24}(OH)_{216}24Br\cdot18H_2O$	90.0	90.2	119.9	18.4	18.4	23.2
		$Mg_{90}Al_{18}(OH)_{216}18Br\cdot18H_2O$	90.2	90.0	120.0	18.5	18.5	23.5
		$Mg_{96}Al_{12}(OH)_{216}12Br\cdot18H_2O$	90.2	90.0	120.0	18.6	18.6	23.9
	NO_3^-	$Mg_{66}Al_{42}(OH)_{216}42NO_3\cdot18H_2O$	89.5	91.2	120.0	18.2	18.2	26.4
		$Mg_{72}Al_{36}(OH)_{216}36NO_3\cdot18H_2O$	89.8	90.7	119.9	18.2	18.2	26.6
		$Mg_{78}Al_{30}(OH)_{216}30NO_3\cdot18H_2O$	90.2	90.1	119.9	18.3	18.3	27.2
		$Mg_{84}Al_{24}(OH)_{216}24NO_3\cdot18H_2O$	90.0	90.1	119.7	18.4	18.4	27.7
		$Mg_{90}Al_{18}(OH)_{216}18NO_3\cdot18H_2O$	90.4	89.8	120.0	18.5	18.5	27.5
		$Mg_{96}Al_{12}(OH)_{216}12NO_3\cdot18H_2O$	90.3	90.0	120.1	18.6	18.6	27.4
	$HCOO^-$	$Mg_{66}Al_{42}(OH)_{216}42HCOO\cdot18H_2O$	89.4	91.4	120.0	18.2	18.2	23.2
		$Mg_{72}Al_{36}(OH)_{216}36HCOO\cdot18H_2O$	90.0	90.4	119.9	18.2	18.2	23.1
		$Mg_{78}Al_{30}(OH)_{216}30HCOO\cdot18H_2O$	89.9	90.3	120.0	18.3	18.3	23.1
		$Mg_{84}Al_{24}(OH)_{216}24HCOO\cdot18H_2O$	89.6	90.2	120.0	18.4	18.4	23.4
		$Mg_{90}Al_{18}(OH)_{216}18HCOO\cdot18H_2O$	89.9	90.1	120.0	18.5	18.5	23.5
		$Mg_{96}Al_{12}(OH)_{216}12HCOO\cdot18H_2O$	90.2	89.7	119.9	18.6	18.6	23.7
	$C_6H_5SO_3^-$	$Mg_{66}Al_{42}(OH)_{216}42C_6H_5O_3S\cdot18H_2O$	88.1	96.7	120.8	18.4	18.5	43.2
		$Mg_{72}Al_{36}(OH)_{216}36C_6H_5O_3S\cdot18H_2O$	87.6	96.1	120.0	18.5	18.4	42.3
		$Mg_{78}Al_{30}(OH)_{216}30C_6H_5O_3S\cdot18H_2O$	88.8	94.4	120.4	18.4	18.4	42.9
		$Mg_{84}Al_{24}(OH)_{216}24C_6H_5O_3S\cdot18H_2O$	88.3	91.8	120.9	18.5	18.4	42.2
		$Mg_{90}Al_{18}(OH)_{216}18C_6H_5O_3S\cdot18H_2O$	88.6	92.1	120.1	18.6	18.6	42.7

		$Mg_{96}Al_{12}(OH)_{216}12C_6H_5O_3S\cdot18H_2O$	89.6	90.5	120.0	18.6	18.6	43.3
		$Mg_{66}Al_{42}(OH)_{216}21CO_3\cdot18H_2O$	90.6	89.9	120.1	18.1	18.1	21.9
		$Mg_{72}Al_{36}(OH)_{216}18CO_3\cdot18H_2O$	90.2	90.2	120.0	18.2	18.2	22.2
	CO_3^{2-}	$Mg_{78}Al_{30}(OH)_{216}15CO_3\cdot18H_2O$	89.2	90.9	119.9	18.3	18.3	22.4
		$Mg_{84}Al_{24}(OH)_{216}12CO_3\cdot18H_2O$	89.4	90.5	120.0	18.4	18.4	22.6
		$Mg_{90}Al_{18}(OH)_{216}9CO_3\cdot18H_2O$	89.9	89.9	119.8	18.5	18.5	22.7
		$Mg_{96}Al_{12}(OH)_{216}6CO_3\cdot18H_2O$	89.4	90.4	119.9	18.6	18.6	23.1
		$Mg_{66}Al_{42}(OH)_{216}21SO_4\cdot18H_2O$	87.7	92.1	120.1	18.1	18.1	25.6
		$Mg_{72}Al_{36}(OH)_{216}18SO_4\cdot18H_2O$	89.5	91.2	120.1	18.2	18.2	26.0
	SO_4^{2-}	$Mg_{78}Al_{30}(OH)_{216}15SO_4\cdot18H_2O$	88.4	92.6	119.9	18.3	18.3	26.1
		$Mg_{84}Al_{24}(OH)_{216}12SO_4\cdot18H_2O$	88.9	91.5	120.0	18.4	18.4	26.8
		$Mg_{90}Al_{18}(OH)_{216}9SO_4\cdot18H_2O$	88.6	91.3	120.0	18.5	18.5	27.1
		$Mg_{96}Al_{12}(OH)_{216}6SO_4\cdot18H_2O$	89.9	90.0	120.0	18.6	18.6	27.1
		$Mg_{63}Al_{45}(OH)_{216}15PO_4\cdot18H_2O$	93.4	86.4	119.9	18.0	18.0	24.5
		$Mg_{72}Al_{36}(OH)_{216}12PO_4\cdot18H_2O$	90.9	87.8	119.9	18.1	18.2	24.9
	PO_4^{3-}	$Mg_{81}Al_{27}(OH)_{216}9PO_4\cdot18H_2O$	90.3	89.4	119.9	18.0	18.0	24.9
		$Mg_{90}Al_{18}(OH)_{216}6PO_4\cdot18H_2O$	90.0	89.8	120.0	18.5	18.5	25.4
		$Mg_{96}Al_{12}(OH)_{216}4PO_4\cdot18H_2O$	89.6	90.4	120.0	18.6	18.6	25.0
		$Ni_{66}Al_{42}(OH)_{216}42OH\cdot18H_2O$	91.6	89.3	120.0	18.0	18.0	21.1
		$Ni_{72}Al_{36}(OH)_{216}36OH\cdot18H_2O$	90.7	89.9	120.0	18.1	18.1	21.3
	OH^-	$Ni_{78}Al_{30}(OH)_{216}30OH\cdot18H_2O$	90.5	89.7	120.1	18.2	18.2	21.6
		$Ni_{84}Al_{24}(OH)_{216}24OH\cdot18H_2O$	90.0	90.3	119.9	18.3	18.3	21.9
		$Ni_{90}Al_{18}(OH)_{216}18OH\cdot18H_2O$	92.0	89.0	120.1	18.4	18.4	22.3
		$Ni_{96}Al_{12}(OH)_{216}12OH\cdot18H_2O$	89.2	91.4	120.0	18.5	18.5	22.6
		$Ni_{66}Al_{42}(OH)_{216}42Cl\cdot18H_2O$	89.1	90.6	120.0	18.0	18.0	21.7
		$Ni_{72}Al_{36}(OH)_{216}36Cl\cdot18H_2O$	90.2	89.3	120.1	18.2	18.1	22.1
	Cl^-	$Ni_{78}Al_{30}(OH)_{216}30Cl\cdot18H_2O$	90.2	89.5	120.1	18.2	18.2	22.3
		$Ni_{84}Al_{24}(OH)_{216}24Cl\cdot18H_2O$	90.5	89.7	120.2	18.3	18.3	22.4
		$Ni_{90}Al_{18}(OH)_{216}18Cl\cdot18H_2O$	90.6	89.5	119.9	18.4	18.4	22.7
Ni_RAl-A-LDHs		$Ni_{96}Al_{12}(OH)_{216}12Cl\cdot18H_2O$	90.1	90.0	120.0	18.5	18.5	23.1
		$Ni_{66}Al_{42}(OH)_{216}42Br\cdot18H_2O$	89.8	90.3	120.0	18.1	18.1	22.3
		$Ni_{72}Al_{36}(OH)_{216}36Br\cdot18H_2O$	90.8	88.8	120.1	18.2	18.2	22.5
	Br^-	$Ni_{78}Al_{30}(OH)_{216}30Br\cdot18H_2O$	90.2	89.4	120.1	18.3	18.2	22.9
		$Ni_{84}Al_{24}(OH)_{216}24Br\cdot18H_2O$	90.0	90.0	120.1	18.3	18.3	23.1
		$Ni_{90}Al_{18}(OH)_{216}18Br\cdot18H_2O$	90.5	89.6	120.0	18.4	18.4	23.3
		$Ni_{96}Al_{12}(OH)_{216}12Br\cdot18H_2O$	90.2	89.9	120.0	18.5	18.5	23.5
		$Ni_{66}Al_{42}(OH)_{216}42NO_3\cdot18H_2O$	89.3	91.8	120.1	18.1	18.1	26.3
	NO_3^-	$Ni_{72}Al_{36}(OH)_{216}36NO_3\cdot18H_2O$	88.8	91.3	119.9	18.2	18.2	26.5
		$Ni_{78}Al_{30}(OH)_{216}30NO_3\cdot18H_2O$	89.2	91.0	120.0	18.2	18.2	26.5
		$Ni_{84}Al_{24}(OH)_{216}24NO_3\cdot18H_2O$	90.0	89.9	120.1	18.3	18.3	27.1

		$Ni_{90}Al_{18}(OH)_{216}18NO_3\cdot18H_2O$	90.2	90.0	120.2	18.4	18.4	27.8
		$Ni_{96}Al_{12}(OH)_{216}12NO_3\cdot18H_2O$	90.3	89.8	120.0	18.5	18.5	27.5
		$Ni_{66}Al_{42}(OH)_{216}42HCOO\cdot18H_2O$	90.2	90.1	120.0	18.1	18.1	23.2
		$Ni_{72}Al_{36}(OH)_{216}36HCOO\cdot18H_2O$	90.1	90.2	120.0	18.2	18.2	23.0
	$HCOO^-$	$Ni_{78}Al_{30}(OH)_{216}30HCOO\cdot18H_2O$	90.9	89.2	120.1	18.2	18.2	23.0
		$Ni_{84}Al_{24}(OH)_{216}24HCOO\cdot18H_2O$	89.9	90.1	120.3	18.3	18.4	23.3
		$Ni_{90}Al_{18}(OH)_{216}18HCOO\cdot18H_2O$	90.0	90.1	120.0	18.4	18.4	23.4
		$Ni_{96}Al_{12}(OH)_{216}12HCOO\cdot18H_2O$	90.5	89.5	120.0	18.5	18.5	23.5
		$Ni_{66}Al_{42}(OH)_{216}42C_6H_5O_3S\cdot18H_2O$	90.0	92.1	120.4	18.5	18.5	42.3
		$Ni_{72}Al_{36}(OH)_{216}36C_6H_5O_3S\cdot18H_2O$	89.7	92.5	120.3	18.3	18.5	41.5
	$C_6H_5SO_3^-$	$Ni_{78}Al_{30}(OH)_{216}30C_6H_5O_3S\cdot18H_2O$	90.3	90.7	120.4	18.3	18.3	42.4
		$Ni_{84}Al_{24}(OH)_{216}24C_6H_5O_3S\cdot18H_2O$	89.3	90.6	120.3	18.4	18.4	42.4
		$Ni_{90}Al_{18}(OH)_{216}18C_6H_5O_3S\cdot18H_2O$	90.5	90.0	120.2	18.4	18.4	42.7
		$Ni_{96}Al_{12}(OH)_{216}12C_6H_5O_3S\cdot18H_2O$	90.4	89.9	120.0	18.5	18.5	42.2
		$Ni_{66}Al_{42}(OH)_{216}21CO_3\cdot18H_2O$	90.3	89.6	120.3	18.0	18.0	21.9
		$Ni_{72}Al_{36}(OH)_{216}18CO_3\cdot18H_2O$	89.5	90.8	120.1	18.1	18.1	22.0
	CO_3^{2-}	$Ni_{78}Al_{30}(OH)_{216}15CO_3\cdot18H_2O$	89.7	90.2	120.0	18.2	18.2	22.4
		$Ni_{84}Al_{24}(OH)_{216}12CO_3\cdot18H_2O$	89.1	91.0	120.0	18.3	18.3	22.5
		$Ni_{90}Al_{18}(OH)_{216}9CO_3\cdot18H_2O$	90.1	90.0	119.9	18.4	18.3	22.6
		$Ni_{96}Al_{12}(OH)_{216}6CO_3\cdot18H_2O$	89.2	90.5	120.0	18.5	18.5	23.1
		$Ni_{66}Al_{42}(OH)_{216}21SO_4\cdot18H_2O$	89.1	90.7	120.1	18.1	18.1	25.6
		$Ni_{72}Al_{36}(OH)_{216}18SO_4\cdot18H_2O$	90.2	89.9	120.1	18.1	18.1	25.9
	SO_4^{2-}	$Ni_{78}Al_{30}(OH)_{216}15SO_4\cdot18H_2O$	90.4	89.8	120.0	18.2	18.2	26.1
		$Ni_{84}Al_{24}(OH)_{216}12SO_4\cdot18H_2O$	90.3	89.6	119.9	18.3	18.3	26.5
		$Ni_{90}Al_{18}(OH)_{216}9SO_4\cdot18H_2O$	90.1	89.9	120.1	18.4	18.4	26.7
		$Ni_{96}Al_{12}(OH)_{216}6SO_4\cdot18H_2O$	89.9	90.2	120.0	18.5	18.5	26.7
		$Ni_{63}Al_{45}(OH)_{216}15PO_4\cdot18H_2O$	94.0	85.8	119.9	17.9	18.0	24.3
		$Ni_{72}Al_{36}(OH)_{216}12PO_4\cdot18H_2O$	93.0	87.0	120.0	18.1	18.1	24.9
	PO_4^{3-}	$Ni_{81}Al_{27}(OH)_{216}9PO_4\cdot18H_2O$	90.0	89.5	120.0	18.2	18.2	25.1
		$Ni_{90}Al_{18}(OH)_{216}6PO_4\cdot18H_2O$	90.7	89.4	120.1	18.4	18.4	25.2
		$Ni_{96}Al_{12}(OH)_{216}4PO_4\cdot18H_2O$	90.0	90.0	119.9	18.5	18.5	25.0
		$Zn_{66}Al_{42}(OH)_{216}42OH\cdot18H_2O$	93.5	87.4	120.0	18.2	18.2	21.3
		$Zn_{72}Al_{36}(OH)_{216}36OH\cdot18H_2O$	92.1	89.0	120.0	18.4	18.4	21.4
	OH^-	$Zn_{78}Al_{30}(OH)_{216}30OH\cdot18H_2O$	91.0	89.7	119.8	18.4	18.4	21.9
		$Zn_{84}Al_{24}(OH)_{216}24OH\cdot18H_2O$	90.9	89.9	119.9	18.6	18.6	22.2
Zn_RAl-A-LDHs		$Zn_{90}Al_{18}(OH)_{216}18OH\cdot18H_2O$	90.5	89.8	120.0	18.7	18.7	22.9
		$Zn_{96}Al_{12}(OH)_{216}12OH\cdot18H_2O$	87.9	92.5	120.0	18.8	18.8	23.0
		$Zn_{66}Al_{42}(OH)_{216}42Cl\cdot18H_2O$	89.1	90.7	119.9	18.3	18.2	21.8
	Cl^-	$Zn_{72}Al_{36}(OH)_{216}36Cl\cdot18H_2O$	90.1	90.0	119.9	18.4	18.3	22.5
		$Zn_{78}Al_{30}(OH)_{216}30Cl\cdot18H_2O$	89.8	90.3	120.1	18.5	18.5	22.6

	$Zn_{84}Al_{24}(OH)_{216}24Cl\cdot18H_2O$	90.3	89.8	120.0	18.6	18.6	22.8
	$Zn_{90}Al_{18}(OH)_{216}18Cl\cdot18H_2O$	89.7	90.3	119.9	18.7	18.7	23.2
	$Zn_{96}Al_{12}(OH)_{216}12Cl\cdot18H_2O$	91.0	89.2	120.0	18.8	18.8	23.6
	$Zn_{66}Al_{42}(OH)_{216}42Br\cdot18H_2O$	89.8	90.4	119.9	18.3	18.3	22.4
	$Zn_{72}Al_{36}(OH)_{216}36Br\cdot18H_2O$	89.8	90.4	120.0	18.4	18.4	22.7
	$Zn_{78}Al_{30}(OH)_{216}30Br\cdot18H_2O$	89.8	90.3	120.0	18.5	18.5	23.1
Br^-	$Zn_{84}Al_{24}(OH)_{216}24Br\cdot18H_2O$	90.2	89.9	120.0	18.6	18.6	23.4
	$Zn_{90}Al_{18}(OH)_{216}18Br\cdot18H_2O$	90.3	89.8	119.9	18.7	18.7	23.8
	$Zn_{96}Al_{12}(OH)_{216}12Br\cdot18H_2O$	90.2	89.9	120.0	18.8	18.8	24.0
	$Zn_{66}Al_{42}(OH)_{216}42NO_3\cdot18H_2O$	89.1	91.5	119.8	18.3	18.3	26.3
	$Zn_{72}Al_{36}(OH)_{216}36NO_3\cdot18H_2O$	89.4	90.9	119.9	18.4	18.4	26.6
	$Zn_{78}Al_{30}(OH)_{216}30NO_3\cdot18H_2O$	89.1	91.1	119.9	18.5	18.5	26.6
NO_3^-	$Zn_{84}Al_{24}(OH)_{216}24NO_3\cdot18H_2O$	90.2	90.0	120.0	18.6	18.6	27.7
	$Zn_{90}Al_{18}(OH)_{216}18NO_3\cdot18H_2O$	90.8	89.6	120.0	18.7	18.7	27.4
	$Zn_{96}Al_{12}(OH)_{216}12NO_3\cdot18H_2O$	90.4	89.9	120.0	18.8	18.8	27.5
	$Zn_{66}Al_{42}(OH)_{216}42HCOO\cdot18H_2O$	89.6	90.9	119.9	18.3	18.3	23.2
	$Zn_{72}Al_{36}(OH)_{216}36HCOO\cdot18H_2O$	89.8	90.7	119.8	18.4	18.4	23.1
	$Zn_{78}Al_{30}(OH)_{216}30HCOO\cdot18H_2O$	89.9	90.4	119.9	18.5	18.5	23.2
$HCOO^-$	$Zn_{84}Al_{24}(OH)_{216}24HCOO\cdot18H_2O$	90.5	89.6	120.0	18.6	18.6	23.6
	$Zn_{90}Al_{18}(OH)_{216}18HCOO\cdot18H_2O$	89.8	90.2	120.0	18.7	18.7	23.8
	$Zn_{96}Al_{12}(OH)_{216}12HCOO\cdot18H_2O$	90.2	89.8	120.0	18.8	18.8	23.8
	$Zn_{66}Al_{42}(OH)_{216}42C_6H_5O_3S\cdot18H_2O$	88.1	94.8	120.3	18.7	18.6	42.4
	$Zn_{72}Al_{36}(OH)_{216}36C_6H_5O_3S\cdot18H_2O$	88.1	94.7	119.9	18.6	18.5	42.5
	$Zn_{78}Al_{30}(OH)_{216}30C_6H_5O_3S\cdot18H_2O$	88.6	94.2	120.2	18.5	18.6	42.1
$C_6H_5SO_3^-$	$Zn_{84}Al_{24}(OH)_{216}24C_6H_5O_3S\cdot18H_2O$	88.7	92.1	120.3	18.6	18.7	42.2
	$Zn_{90}Al_{18}(OH)_{216}18C_6H_5O_3S\cdot18H_2O$	88.8	91.3	120.3	18.8	18.7	44.0
	$Zn_{96}Al_{12}(OH)_{216}12C_6H_5O_3S\cdot18H_2O$	89.7	90.3	119.9	18.9	18.8	45.7
	$Zn_{66}Al_{42}(OH)_{216}21CO_3\cdot18H_2O$	89.8	90.0	119.9	18.2	18.2	22.1
	$Zn_{72}Al_{36}(OH)_{216}18CO_3\cdot18H_2O$	98.5	84.5	119.9	18.3	18.3	22.2
	$Zn_{78}Al_{30}(OH)_{216}15CO_3\cdot18H_2O$	89.4	90.8	119.8	18.4	18.4	22.5
CO_3^{2-}	$Zn_{84}Al_{24}(OH)_{216}12CO_3\cdot18H_2O$	88.9	91.0	119.8	18.5	18.5	22.9
	$Zn_{90}Al_{18}(OH)_{216}9CO_3\cdot18H_2O$	89.0	90.9	119.8	18.6	18.6	22.9
	$Zn_{96}Al_{12}(OH)_{216}6CO_3\cdot18H_2O$	89.5	90.4	119.9	18.8	18.8	23.5
	$Zn_{66}Al_{42}(OH)_{216}21SO_4\cdot18H_2O$	89.3	90.9	120.0	18.2	18.3	25.7
	$Zn_{72}Al_{36}(OH)_{216}18SO_4\cdot18H_2O$	89.5	91.0	119.9	18.4	18.3	25.9
	$Zn_{78}Al_{30}(OH)_{216}15SO_4\cdot18H_2O$	87.7	93.5	119.8	18.5	18.4	26.1
SO_4^{2-}	$Zn_{84}Al_{24}(OH)_{216}12SO_4\cdot18H_2O$	89.7	90.2	119.9	18.6	18.5	26.6
	$Zn_{90}Al_{18}(OH)_{216}9SO_4\cdot18H_2O$	89.8	90.2	119.9	18.7	18.7	26.7
	$Zn_{96}Al_{12}(OH)_{216}6SO_4\cdot18H_2O$	90.1	90.0	120.0	18.8	18.8	26.7
PO_4^{3-}	$Zn_{63}Al_{45}(OH)_{216}15PO_4\cdot18H_2O$	92.8	86.8	119.8	18.1	18.2	24.7

$Zn_{72}Al_{36}(OH)_{216}12PO_4 \cdot 18H_2O$	92.1	87.6	119.8	18.3	18.3	24.9
$Zn_{81}Al_{27}(OH)_{216}9PO_4 \cdot 18H_2O$	90.6	89.4	119.9	18.5	18.5	25.3
$Zn_{90}Al_{18}(OH)_{216}6PO_4 \cdot 18H_2O$	90.0	90.0	120.0	18.7	18.7	25.7
$Zn_{96}Al_{12}(OH)_{216}4PO_4 \cdot 18H_2O$	89.5	90.6	120.0	18.8	18.8	25.4

138

139 **Table S4.** The lattice parameter *a* of M^{II}_RAl-Cl-LDHs and $M^{II}(OH)_2$ (M^{II} = Mg, Ni,

140 Zn) when *R*>4 after simulation of 200 ps

$R = M^{2+}/Al^{3+}$	Lattice parameter *a*/ Å					
	Mg_RAl-Cl-LDH	$Mg(OH)_2$	Ni_RAl-Cl-LDH	$Ni(OH)_2$	Zn_RAl-Cl-LDH	$Zn(OH)_2$
5	3.08	3.14[S1]	3.07	3.09[S2]	3.11	3.19[S3]
8	3.10		3.08		3.13	

141

142 **Table S5.** Energy composition of $M^{II}_RM^{III}$-A-LDHs (M^{II} = Mg, Ni, Zn; M^{III} = Al; *R*

143 ranges from 1.4 to 8; A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, and

144 PO_4^{3-}), where E_{tot}, E_a, E_c, $E_{non\text{-}bond}$, E_{vdW}, E_e, E_b represents the total potential energy,

145 angle term, cross term, non-bond energy, van der waals energy, electrostatic energy

146 and relative binding energy, respectively

147

Model	Anion	*R*	E_{tot} / kcal·mol^{-1}	E_a / kcal·mol^{-1}	E_c / kcal·mol^{-1}	$E_{non\text{-}bond}$ / kcal·mol^{-1}	E_{vdW} / kcal·mol^{-1}	E_e / kcal·mol^{-1}	E_b / kcal·mol^{-1}
Mg_RAl-A-LDHs	OH^-	1.6	–105740.09	–13738.12	–1.00	–95071.22	1242.03	–96313.24	–36.38
		2.0	–105797.81	–13682.79	–1.26	–95340.65	1070.12	–96410.77	–34.21
		2.6	–106206.06	–13631.48	–3.20	–95900.58	979.64	–96880.22	–28.98
		3.5	–106625.78	–13583.88	–2.13	–96459.13	864.62	–97323.75	–13.92
		5.0	–107293.71	–13649.34	–2.44	–97114.37	748.90	–97863.27	–20.58
		8.0	–107983.57	–13653.45	–1.78	–97926.27	632.69	–98558.97	–19.10
	Cl^-	1.6	–105391.72	–13789.86	–1.53	–94681.70	1196.74	–95878.44	–28.53
		2.0	–105496.88	–13691.73	–1.74	–94967.06	1011.92	–95978.98	–26.30
		2.6	–106021.88	–13655.59	–1.71	–95688.42	887.64	–96576.06	–23.28
		3.5	–106480.86	–13643.29	–1.03	–96228.74	727.40	–96956.14	–8.32
		5.0	–107214.48	–13673.20	–1.42	–97008.06	678.51	–97686.57	–16.62
		8.0	–107920.27	–13688.30	–1.72	–97767.38	609.28	–98376.67	–14.26
	Br^-	1.6	–105105.80	–13839.83	–1.23	–94254.11	1105.16	–95359.27	–21.71
		2.0	–105336.28	–13770.06	–1.43	–94753.16	961.33	–95714.49	–21.83
		2.6	–105799.71	–13692.44	–1.51	–95381.56	855.83	–96237.39	–15.87
		3.5	–106399.41	–13683.03	–1.23	–96085.80	734.84	–96820.63	–4.92

		5.0	−107080.60	−13694.44	−1.17	−96836.58	635.90	−97472.48	−9.17
		8.0	−107865.77	−13688.78	−1.08	−97684.45	584.11	−98268.57	−9.71
		1.6	−104160.92	−13884.58	−0.37	−93262.89	622.90	−93885.79	0.00
		2.0	−104522.12	−13726.98	−0.21	−93946.06	599.36	−94545.42	0.00
	NO_3^-	2.6	−105300.06	−13723.12	−1.66	−94825.11	568.27	−95393.38	0.00
		3.5	−106262.41	−13647.62	−0.66	−96004.73	550.83	−96555.55	0.00
		5.0	−106901.33	−13711.80	−1.14	−96638.30	556.81	−97195.12	0.00
		8.0	−107739.76	−13708.20	−1.57	−97593.72	542.01	−98135.74	0.00
		1.6	−104680.00	−13892.52	−2.91	−93657.55	830.71	-94488.26	−12.37
		2.0	−105174.01	−13759.86	−2.87	−94511.38	648.88	-95160.26	−18.12
	$HCOO^-$	2.6	−105777.11	−13749.03	−2.51	−95307.64	597.26	-95904.89	−15.91
		3.5	−106369.23	−13698.20	−1.55	−96008.39	548.66	-96557.05	−4.46
		5.0	−106988.57	−13659.29	−2.21	−96797.89	518.75	-97316.64	−7.29
		8.0	−107829.21	−13682.51	−0.74	−97705.27	491.39	-98196.65	−7.47
		1.6	−98930.83	−13318.89	−36.54	−88901.15	1125.89	−85133.73	82.85
		2.0	−100086.45	−13550.65	−23.30	−89927.98	663.14	−90591.13	81.54
	$C_6H_5SO_3^-$	2.6	−102564.15	−13300.62	−34.11	−92986.92	839.76	−93826.68	49.52
		3.5	−102877.25	−13233.54	−13.04	−93783.28	817.19	−94600.47	99.37
		5.0	−104994.30	−13531.64	−16.07	−95095.95	644.93	−95740.88	64.27
		8.0	−106752.07	−13686.60	−0.41	−96773.29	628.97	−97402.25	40.63
		1.6	−107651.68	−13487.81	−2.34	−97235.50	1072.31	−98307.81	−42.14
		2.0	−107155.48	−13426.14	−2.94	−96953.06	893.03	−97846.09	−64.36
	CO_3^{2-}	2.6	−107269.68	−13436.73	−2.33	−97180.84	787.02	−97967.87	−49.37
		3.5	−107774.79	−13444.76	−3.02	−97341.09	712.54	−98476.73	−44.09
		5.0	−108171.07	−13481.24	−2.46	−98128.26	689.43	−98817.70	−59.14
		8.0	−108588.09	−13556.75	−2.68	−98527.45	618.05	−99145.50	−59.45
		1.6	−106571.61	−13736.43	−1.80	−95833.89	1010.77	−96844.66	−47.90
		2.0	−106592.25	−13635.25	−0.95	−96096.46	892.27	−96988.73	−48.11
	SO_4^{2-}	2.6	−106839.06	−13626.38	−0.80	−96499.51	800.68	−97300.19	−35.70
		3.5	−107273.96	−13643.24	−0.91	−97017.65	739.73	−97757.38	−17.40
		5.0	−107807.23	−13632.73	−1.19	−97626.67	684.54	−98311.21	−33.76
		8.0	−108378.99	−13654.87	−1.21	−98874.86	618.80	−98711.36	−39.64
		1.4	−108197.63	−13270.03	−0.01	−98058.11	1265.16	−99323.27	−421.22
		2.0	−107775.07	−13275.45	−0.03	−97868.87	1040.66	−98909.53	−432.47
	PO_4^{3-}	3.0	−110062.27	−15347.89	−0.07	−98522.53	695.36	−99217.89	−461.57
		5.0	−107937.13	−13387.29	0.00	−98088.01	694.30	−98782.31	−334.03
		8.0	−108445.06	−13575.87	−0.01	−98397.81	578.91	−98976.72	−337.72
		1.6	−99933.62	−15423.49	−1.63	−87393.84	953.71	−88347.56	−36.08
		2.0	−99417.69	−15536.85	−1.69	−86888.80	775.37	−87664.17	−32.08
	OH^-	2.6	−99366.20	−15692.88	−2.49	−86735.99	671.53	−87407.51	−22.56
Ni_RAl-A-LDHs		3.5	−99438.74	−15900.64	−1.06	−86585.64	522.23	−87107.87	−20.87
		5.0	−99467.81	−16077.44	−2.46	−86497.46	440.65	−86938.11	−23.09
		8.0	−99769.95	−16369.20	−1.42	−86519.53	356.50	−86876.02	−21.11
		1.6	−99541.34	−15472.51	−1.53	−86920.60	859.28	−87779.88	−27.18
	Cl^-	2.0	−99161.07	−15589.80	−2.26	−86508.38	725.80	−87234.18	−25.39

	2.6	–99161.80	–15727.18	–1.63	–86392.71	595.90	–86988.61	–16.19
	3.5	–99270.58	–15906.80	–1.42	–86387.45	492.85	–86880.29	–14.30
	5.0	–99450.42	–16169.18	–1.35	–86421.14	381.75	–86802.89	–20.13
	8.0	–99718.11	–16358.45	–1.40	–86465.37	316.67	–86782.05	–17.23
	1.6	–99232.91	–15488.64	–1.26	–86540.97	847.60	–87388.57	–19.83
	2.0	–99013.62	–15612.49	–1.64	–86280.86	685.52	–86966.38	–21.29
Br^-	2.6	–99048.75	–15799.98	–1.11	–86222.04	585.75	–86807.79	–12.42
	3.5	–99126.56	–15964.32	–0.88	–86191.33	418.57	–86609.91	–8.30
	5.0	–99375.87	–16143.63	–0.96	–86353.53	360.07	–86713.60	–15.98
	8.0	–99651.84	–16381.17	–1.18	–86406.40	313.28	–86719.68	–11.70
	1.6	–98366.87	–15582.76	–0.67	–85497.94	299.87	–85797.82	0.00
	2.0	–98218.91	–15633.99	–0.89	–85357.84	276.11	–85633.95	0.00
NO_3^-	2.6	–98652.62	–15828.59	–0.78	–85792.78	244.99	–86037.77	0.00
	3.5	–98908.60	–15980.75	–0.95	–85949.60	246.52	–86196.12	0.00
	5.0	–99074.13	–16175.20	–1.52	–86003.29	246.86	–86250.15	0.00
	8.0	–99501.97	–16402.55	–0.38	–86164.98	226.10	–86391.08	0.00
	1.6	–98828.69	–15589.45	–3.38	–85914.53	547.86	–86462.38	–11.01
	2.0	–98859.53	–15662.96	–2.94	–86079.51	357.60	–86437.12	–17.81
$HCOO^-$	2.6	–99020.36	–15802.16	–2.18	–99020.36	307.30	–86496.18	–12.27
	3.5	–99045.28	–15990.96	–2.62	–86105.87	265.22	–86371.09	–16.37
	5.0	–99339.09	–16181.92	–1.48	–86271.04	224.12	–86495.16	–14.73
	8.0	–99675.14	–16386.87	–1.13	–86380.22	203.51	–86583.73	–14.44
	1.6	–92317.73	–15276.92	–39.15	–79557.30	724.72	–80282.02	102.35
	2.0	–93293.16	–15211.07	–38.14	–81209.10	533.97	–81743.06	95.15
$C_6H_5SO_3^-$	2.6	–95028.92	–15483.31	–13.52	–82876.19	358.62	–83234.81	58.98
	3.5	–96142.59	–15700.16	–10.24	–83730.94	270.76	–84001.69	50.53
	5.0	–97339.84	–15978.50	–0.38	–84759.05	374.69	–85133.73	30.59
	8.0	–98649.85	–16390.54	–7.08	–85420.29	312.71	–85733.00	29.34
	1.6	–101843.29	–15184.17	–2.61	–89549.48	756.50	–90305.98	–83.60
	2.0	–101157.78	–15317.67	–2.54	–88831.24	656.27	–89487.51	–81.33
CO_3^{2-}	2.6	–101140.79	–15527.75	–3.03	–88245.82	565.57	–88811.39	–24.48
	3.5	–100589.09	–15717.20	–2.27	–87896.46	471.66	–88368.12	–29.05
	5.0	–100462.81	–15950.87	–2.13	–87318.04	400.51	–87954.01	–36.18
	8.0	–100165.57	–16222.74	–2.60	–87115.69	268.87	–87384.56	–28.66
	1.6	–100717.87	–15184.17	–2.61	–88099.88	724.16	–88824.05	–45.06
	2.0	–100144.65	–15317.67	–2.54	–87562.89	585.65	–88148.55	–40.09
SO_4^{2-}	2.6	–100059.08	–15527.75	–3.03	–87342.94	512.87	–87855.81	–26.87
	3.5	–100050.72	–15717.20	–2.27	–87176.60	458.99	–87635.59	–28.28
	5.0	–100080.33	–15950.87	–2.13	–87017.19	411.88	–87429.06	–44.90
	8.0	–100337.48	–16222.74	–2.60	–86894.41	343.15	–87237.56	–25.90
	1.4	–102530.09	–14835.31	–0.07	–90690.40	1024.15	–91714.55	–429.65
	2.0	–101407.90	–15154.17	–0.01	–89338.40	732.70	–90071.09	–427.14
PO_4^{3-}	3.0	–100595.30	–15482.20	–0.05	–88255.72	547.56	–88803.29	–392.73
	5.0	–100347.05	–15899.30	0.00	–87551.89	405.34	–87957.23	–373.55
	8.0	–100391.98	–16301.38	–0.01	–87188.56	286.39	–87474.95	–383.90

		1.6	−121353.35	−13562.34	−1.97	−111358.10	1024.44	−112382.55	−38.19
		2.0	−122878.25	−13541.01	−1.21	−113063.52	807.45	−113870.97	−33.68
	OH^-	2.6	−124690.39	−13599.72	−2.81	−114990.44	666.73	−115657.17	−24.74
		3.5	−126697.39	−13669.66	−1.22	−116970.48	546.19	−117516.67	−28.39
		5.0	−128681.47	−13800.45	−0.82	−118988.86	424.93	−119413.79	−12.76
		8.0	−131061.45	−13944.86	−0.90	−121346.83	356.17	−121703.00	−15.35
		1.6	−120889.06	−13609.17	−1.97	−110786.63	884.59	−111671.22	−27.58
		2.0	−122517.54	−13588.20	−1.03	−112666.94	688.56	−113355.50	−24.11
	Cl^-	2.6	−124430.21	−13626.88	−1.42	−114644.24	557.17	−115201.42	−16.52
		3.5	−126542.75	−13694.65	−0.92	−116848.45	465.33	−117313.78	−22.39
		5.0	−128699.48	−13837.61	−1.48	−118945.54	393.89	−119339.43	−14.20
		8.0	−131035.58	−13954.08	−2.30	−121706.36	343.68	−121706.36	−13.64
		1.6	−120551.72	−13656.24	−1.49	−110360.24	861.59	−111221.82	−19.54
		2.0	−122278.50	−13593.03	−0.73	−122278.50	711.28	−113064.50	−17.46
	Br^-	2.6	−124264.43	−13653.10	−0.79	−114384.60	561.02	−114945.61	−10.98
		3.5	−126444.98	−13729.60	−1.24	−116683.91	475.99	−117159.90	−18.31
		5.0	−128569.96	−13844.10	−1.10	−118847.62	369.57	−119217.19	−7.00
		8.0	−130991.42	−13975.44	−1.35	−121258.64	335.04	−121593.68	−9.95
		1.6	−119698.13	−13675.03	−0.90	−109443.79	370.92	−109814.71	0.00
		2.0	−121621.66	−13653.08	−0.67	−111545.40	305.11	−111850.52	0.00
	NO_3^-	2.6	−123911.39	−13713.42	−0.68	−113945.85	292.79	−114238.64	0.00
		3.5	−125986.63	−13786.78	−0.72	−116206.24	249.97	−116456.21	0.00
Zn_RAl-A-LDHs		5.0	−128429.81	−13904.59	−1.17	−118595.44	282.88	−118878.33	0.00
		8.0	−130862.58	−13995.71	−0.37	−121108.40	240.31	−121348.71	0.00
		1.6	−120255.56	−13746.46	−3.10	−109861.16	572.03	−110433.18	−13.28
		2.0	−122210.61	−13669.83	−2.26	−112135.15	393.31	−112528.46	−16.37
	$HCOO^-$	2.6	−124304.26	−13705.77	−2.39	−114348.58	336.43	−114685.02	−13.11
		3.5	−126332.88	−13753.17	−2.43	−116483.46	300.22	−116783.68	−14.44
		5.0	−128560.65	−13841.15	−1.39	−118896.84	257.02	−119153.86	−7.28
		8.0	−130960.44	−13952.43	−1.26	−121288.87	238.42	−121527.29	−8.17
		1.6	−113931.01	−13614.17	−58.00	−103765.16	650.78	−104415.94	95.64
		2.0	−116732.12	−13552.71	−41.69	−108587.00	587.67	−109174.67	94.15
	$C_6H_5SO_3^-$	2.6	−119699.39	−13539.79	−16.60	−110928.93	546.05	−111474.97	98.73
		3.5	−123241.32	−13471.51	−41.64	−114320.80	363.13	−114683.92	72.71
		5.0	−126330.67	−13563.29	−11.25	−117272.75	402.41	−117675.16	74.94
		8.0	−129636.20	−9405.36	−22.62	−120230.84	341.68	−120572.52	60.52
		1.6	−123099.69	−13333.82	−1.49	−113355.87	800.18	−114156.04	−80.04
		2.0	−124445.68	−13311.93	−1.53	−114883.80	663.70	−115547.50	−74.95
	CO_3^{2-}	2.6	−125764.60	−13359.79	−3.08	−116288.80	504.45	−116793.25	−41.61
		3.5	−127445.25	−13458.07	−3.26	−118007.77	424.69	−118432.46	−39.61
		5.0	−129596.17	−13580.38	−2.63	−120043.98	377.17	−120488.96	−47.65
		8.0	−131661.30	−13819.15	−1.98	−122078.51	369.68	−122448.19	−51.18
		1.6	−122018.01	−13538.77	−1.39	−111938.70	733.75	−112672.45	−43.57
	SO_4^{2-}	2.0	−123541.05	−13511.71	−1.09	−113701.20	592.17	−114293.38	−39.74
		2.6	−125317.55	−13563.57	−1.13	−115582.71	513.74	−116096.45	−26.85

	3.5	–127231.80	–13693.86	–0.61	–117528.07	466.34	–117994.41	–36.87
	5.0	–129307.00	–13769.63	–0.74	–119602.64	420.33	–120022.97	–30.57
	8.0	–131409.76	–13918.13	–1.04	–121717.70	347.96	–122065.66	–24.30
	1.4	–122916.40	–13035.91	–0.01	–113483.29	983.59	–114466.88	–366.65
	2.0	–124659.80	–13012.33	0.00	–115379.93	756.44	–116136.38	–414.57
PO_4^{3-}	3.0	–126669.01	–13171.50	0.24	–117451.65	573.76	–118025.41	–421.34
	5.0	–129366.77	–13527.42	0.00	–119982.61	412.81	–120395.42	–317.55
	8.0	–131329.84	–13823.28	–0.01	–121757.30	283.27	–122040.57	–92.74

Calculation of Gibbs free energy[S4,S5]

The Gibbs free energy (G) can be obtained by Eq 1:

$$G = H - TS \tag{1}$$

Where H is enthalpy, T is the temperature of the system and S is entropy.

For solids, entropy and enthalpy are almost independent of pressure. H and S can be calculated by Eqs 2 and 3:

$$H(T) = E_{\text{elec}} + E_{\text{ZPE}} + E_{\text{vib}}(T) \tag{2}$$

$$S(T) = S_{\text{conf}} + S_{\text{vib}}(T) \tag{3}$$

where E_{elec} is the total electronic energy at 0 K, E_{ZPE} is zero-point energy, $E_{\text{vib}}(T)$ is the vibration term, S_{conf} and $S_{\text{vib}}(T)$ are the configurational and vibrational entropy, respectively.

So, Eq (1) can be expressed as:

$$G = E_{\text{elec}} + E_{\text{ZPE}} + E_{\text{vib}}(T) - TS \tag{4}$$

According to statistical mechanics, the vibrational partition function can be obtained from Eq 5:

$$q_{\text{vib}} = \sum_i \frac{1}{1 - \exp(-hv_i / kT)} \tag{5}$$

Thus the E_{ZPE} and E_{vib} at the temperature T can be caculated by Eqs 6 and 7:

$$E_{\mathrm{ZPE}} = \frac{R}{k}\frac{1}{2}\sum_i h\nu_i \quad (6)$$

$$E_{\mathrm{vib}} = \frac{R}{k}\sum_i \frac{h\nu_i \exp(-h\nu_i / kT)}{1-\exp(-h\nu_i / kT)} \quad (7)$$

where k is Boltzmann's constant, R is the ideal gas constant, ν_i is the i-th normal vibration frequency, h is Planck's constant.

S_{conf} and $S_{\mathrm{vib}}(T)$ can be obtained by Eqs 8 and 9:

$$S_{\mathrm{conf}} = -RN_{\mathrm{T}}(X_{\mathrm{A}}\ln X_{\mathrm{A}} + X_{\mathrm{W}}\ln X_{\mathrm{W}} + X_{\mathrm{V}}\ln X_{\mathrm{V}}) \quad (8)$$

$$S_{\mathrm{vib}}(T) = R\sum_i \frac{h\nu_i / kT \exp(-h\nu_i / kT)}{1-\exp(-h\nu_i / kT)} - R\sum_i \ln[1-\exp(-h\nu_i / kT)] \quad (9)$$

where N_{T} is the total moles of mixing species, and X_{A}, X_{W}, and X_{V} are the mole fraction of anion, water molecule, and vacancy, respectively.

For solid, E_{vib} and S_{conf} are significantly smaller than E_{elec} and S_{vib}, respectively, they can be neglected in the calculation of G, Eq 4 can be expressed as

$$G = E_{\mathrm{elec}} + E_{\mathrm{ZPE}} - TS \quad (10)$$

Table S6. Gibbs free energies of M^{II}_2Al-A-LDHs (M^{II}=Mg, Ni, Zn; A = OH^-, Cl^-, Br^-, NO_3^-, $HCOO^-$, $C_6H_5SO_3^-$, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}), along with those of the Mg_2Al-A-LDH with correction for non-covalent interaction (Mg_2Al-A-LDH-1)

A	G / kcal·mol^{-1}			
	Mg_2Al-A-LDH	Mg_2Al-A-LDH-1	Ni_2Al-A-LDH	Zn_2Al-A-LDH
NO_3^-	–1729043.99	–1729110.91	–1656114.65	–1797069.72
$HCOO^-$	–1614671.87	–1614749.17	–1541754.71	–1682685.33
Br^-	–1394273.04	–1394344.25	–1321339.88	–1462277.91
Cl^-	–1954822.32	–1954891.99	–1881888.02	–2022827.82

OH^-	–1472456.23	–1472514.72	–1399527.75	–1540438.15
SO_4^{2-}	–1815920.35	–1815985.92	–1742989.73	–1883933.81
CO_3^{2-}	–1542866.61	–1542930.52	–1469939.19	–1610863.89
PO_4^{3-}	–2469004.08	–2469090.21	–2359622.03	–1610863.89
$C_6H_5SO_3^-$	–2450115.79	–2450229.69	–2377464.91	–2518407.12

Table S7. Free energy change of anion-exchange reaction of Ni_2Al-A-LDHs

anion-exchange reaction	ΔG / kcal·mol^{-1}
$Ni_4Al_2(OH)_{12}(NO_3)_2 + 2C_6H_5SO_3^- = Ni_4Al_2(OH)_{12}(C_6H_5SO_3)_2 + 2NO_3^-$	42.60
$Ni_4Al_2(OH)_{12}(NO_3)_2 + 2HCOO^- = Ni_4Al_2(OH)_{12}(HCOO)_2 + 2NO_3^-$	–27.94
$Ni_4Al_2(OH)_{12}(NO_3)_2 + 2Br^- = Ni_4Al_2(OH)_{12}(Br)_2 + 2NO_3^-$	–38.61
$Ni_4Al_2(OH)_{12}(NO_3)_2 + 2Cl^- = Ni_4Al_2(OH)_{12}(Cl)_2 + 2NO_3^-$	–39.30
$Ni_4Al_2(OH)_{12}(NO_3)_2 + 2OH^- = Ni_4Al_2(OH)_{12}(OH)_2 + 2NO_3^-$	–82.39
$Ni_4Al_2(OH)_{12}(NO_3)_2 + SO_4^{2-} = Ni_4Al_2(OH)_{12}(SO_4) + 2NO_3^-$	–82.66
$Ni_4Al_2(OH)_{12}(NO_3)_2 + CO_3^{2-} = Ni_4Al_2(OH)_{12}(CO_3) + 2NO_3^-$	–195.39
$3Ni_4Al_2(OH)_{12}(NO_3)_2 + 2PO_4^{3-} = 2Ni_6Al_3(OH)_{18}(PO_4) + 6NO_3^-$	–633.16

Table S8. Free energy change of anion-exchange reaction of Zn_2Al-A-LDHs

anion-exchange reaction	ΔG / kcal·mol^{-1}
$Zn_4Al_2(OH)_{12}(NO_3)_2 + 2C_6H_5SO_3^- = Zn_4Al_2(OH)_{12}(C_6H_5SO_3)_2 + 2NO_3^-$	55.47
$Zn_4Al_2(OH)_{12}(NO_3)_2 + 2HCOO^- = Zn_4Al_2(OH)_{12}(HCOO)_2 + 2NO_3^-$	–3.497
$Zn_4Al_2(OH)_{12}(NO_3)_2 + 2Br^- = Zn_4Al_2(OH)_{12}(Br)_2 + 2NO_3^-$	–21.57
$Zn_4Al_2(OH)_{12}(NO_3)_2 + 2Cl^- = Zn_4Al_2(OH)_{12}(Cl)_2 + 2NO_3^-$	–24.03
$Zn_4Al_2(OH)_{12}(NO_3)_2 + 2OH^- = Zn_4Al_2(OH)_{12}(OH)_2 + 2NO_3^-$	–37.73
$Zn_4Al_2(OH)_{12}(NO_3)_2 + SO_4^{2-} = Zn_4Al_2(OH)_{12}(SO_4) + 2NO_3^-$	–71.68
$Zn_4Al_2(OH)_{12}(NO_3)_2 + CO_3^{2-} = Zn_4Al_2(OH)_{12}(CO_3) + 2NO_3^-$	–165.01
$3Zn_4Al_2(OH)_{12}(NO_3)_2 + 2PO_4^{3-} = 2Zn_6Al_3(OH)_{18}(PO_4) + 6NO_3^-$	–563.59

Table S9. Free energy change of anion-exchange reaction of Mg_2Al-A-LDHs with correction for non-covalent interaction

anion-exchange reaction	ΔG / kcal·mol^{-1}
$Mg_4Al_2(OH)_{12}(NO_3)_2 + 2C_6H_5SO_3^- = Mg_4Al_2(OH)_{12}(C_6H_5SO_3)_2 + 2NO_3^-$	274.09
$Mg_4Al_2(OH)_{12}(NO_3)_2 + 2HCOO^- = Mg_4Al_2(OH)_{12}(HCOO)_2 + 2NO_3^-$	–26.14

$Mg_4Al_2(OH)_{12}(NO_3)_2 + 2Br^- = Mg_4Al_2(OH)_{12}(Br)_2 + 2NO_3^-$	–46.72
$Mg_4Al_2(OH)_{12}(NO_3)_2 + 2Cl^- = Mg_4Al_2(OH)_{12}(Cl)_2 + 2NO_3^-$	–47.01
$Mg_4Al_2(OH)_{12}(NO_3)_2 + 2OH^- = Mg_4Al_2(OH)_{12}(OH)_2 + 2NO_3^-$	–73.11
$Mg_4Al_2(OH)_{12}(NO_3)_2 + SO_4^{2-} = Mg_4Al_2(OH)_{12}(SO_4) + 2NO_3^-$	–82.60
$Mg_4Al_2(OH)_{12}(NO_3)_2 + CO_3^{2-} = Mg_4Al_2(OH)_{12}(CO_3) + 2NO_3^-$	–190.40
$3Mg_4Al_2(OH)_{12}(NO_3)_2 + 2PO_4^{3-} = 2Mg_6Al_3(OH)_{18}(PO_4) + 6NO_3^-$	–580.70

Table S10. The calculated Mulliken charge (q) of the anion when it is introduced into M_2Al-A-LDHs (M^{II}=Mg, Ni, Zn) and the charge transfers

	PO_4^{3-}		CO_3^{2-}		SO_4^{2-}		OH^-		Cl^-		Br^-		$HCOO^-$		NO_3^-	
	q	Δq	q	Δq	q	Δq	q	Δq	q	Δq	q	Δq	q	Δq	q	Δq
M^{II}=Mg	–1.815	1.185	–1.372	0.628	–1.495	0.505	–0.502	0.498	–0.61	0.390	–0.649	0.531	–0.732	0.268	–0.778	0.222
M^{II}=Ni	–1.748	1.252	–1.334	0.666	–1.458	0.542	–0.588	0.412	–0.619	0.381	–0.627	0.373	-0.717	0.283	–0.759	0.241
M^{II}=Zn	–1.765	1.235	–1.37	0.685	–1.442	0.558	–0.516	0.484	–0.557	0.443	–0.619	0.381	-0.717	0.283	–0.771	0.229

Table S11. The frontier orbital energies, ionization potential, electron affinity and electronegativity of anions

	HOMO /eV	I /eV	LUMO /eV	A /eV	χ
PO_4^{3-}	0.472	-0.472	0.78	-0.78	-0.626
CO_3^{2-}	0.344	-0.344	0.54	-0.54	-0.442
SO_4^{2-}	0.232	-0.232	0.538	-0.538	-0.385
OH^-	0.191	-0.191	0.392	-0.392	-0.2915
Cl^-	0.083	-0.083	0.699	-0.699	-0.391
Br^-	0.082	-0.082	0.616	-0.616	-0.349
$HCOO^-$	0.056	-0.056	0.260	-0.26	-0.158
NO_3^-	0.046	-0.046	0.173	-0.173	-0.1095

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