Supporting Information

Selective Covalent Modification of Layered Double Hydroxide Nanoparticles with Tripodal Ligands on Outer and Interlayer Surfaces

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Table S1. Compositions of the LDHNP samples.

Entry	Sample name	M^{2+}/ (M^{2+}+Al)	Al/ (M^{2+}+Al)	M^{2+}/Al	Modifier/ (M^{2+}+Al)	CO_3^{2-}/ (M^{2+}+Al)
1	CoAl_Tris_inter(HT)	0.73	0.27	2.7	0.26	0.22
2	NiAl_Tris_inter(HT)	0.72	0.28	2.5	0.33	0.21
3	CoAl_Tris_outer	0.70	0.30	2.3	0.12	0.14
4	NiAl_Tris_outer	0.70	0.30	2.4	0.13	0.18
5	CoAl_Bis_outer	0.72	0.28	2.6	0.15	0.19
6	NiAl_Bis_outer	0.69	0.31	2.2	0.16	0.21
7	CoAl_Tris_outer(HT)	0.69	0.31	2.3	0.03	0.19
8	CoAl_Bis_outer(HT)	0.73	0.27	2.8	0.05	0.22
9	MgAl_Tris_inter	0.74	0.26	2.9	0.25	0.17
10	MgAl_Tris_outer	0.66	0.34	2.0	0.05	0.16
-	CoAl_none	0.75	0.25	3.0	-	0.16

All values are molar ratios. M^{2+} represents the divalent cation used.

Interpretation of the change in the d_{110} values of CoAl_Tris_inter(HT), CoAl_Tris_outer, and CoAl_none

The d_{110} values of CoAl_Tris_inter(HT) (Co/Al = 2.7), CoAl_Tris_outer (Co/Al = 2.3), and CoAl_none (Co/Al = 3.0) are 0.153, 0.152, and 0.154 nm, respectively (Figures 1 (a)–(c) in the main text). The variation in d_{110} values among the samples are mainly correlated with the variation in the Co/Al ratios. It is general for LDHs that a d_{110} value changes to be small when a M^{2+}/M^{3+} ratio decreases[S1]. Moreover, the covalent modification with Tris-NH_2 probably causes the lattice contraction of in-plane structure of LDHs because hybrid metal hydroxides modified with tripodal ligands show smaller d_{110} values than those of unmodified metal hydroxides.[S2]

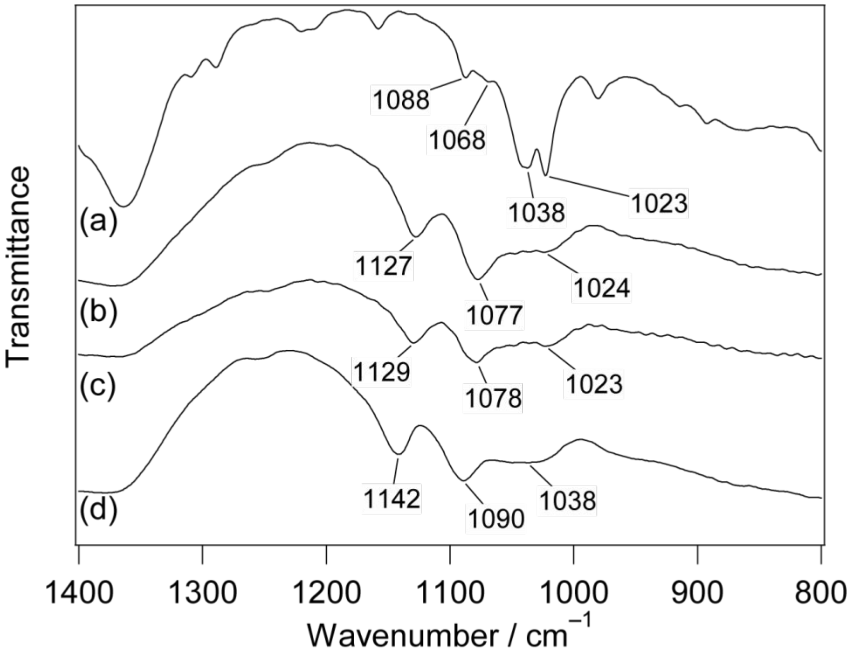

Figure S1. FTIR spectra of (a) a physical mixture of CoAl_none and Tris-NH_2, (b) CoAl_Tris_inter(HT), (c) NiAl_Tris_inter(HT), and (d) MgAl_Tris_inter at 1400–800 cm^{-1}.The mixture was prepared by mixing 30 mg of CoAl_none and 10 mg of Tris-NH_2.

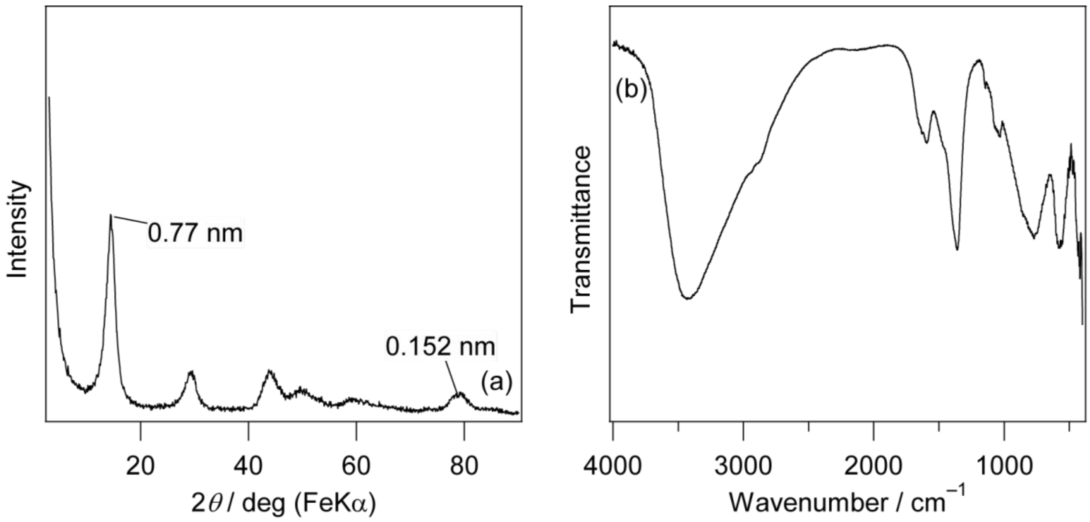

Figure S2. (a) XRD pattern and (b) FTIR spectrum of CoAl_Bis_outer.

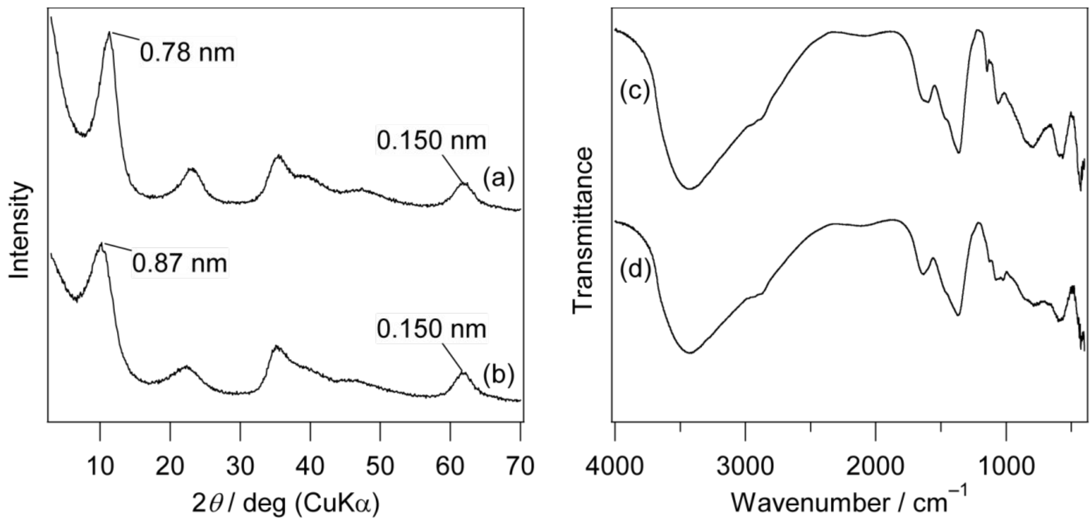

Figure S3. XRD patterns of (a) NiAl_Bis_outer and (b) NiAl_Tris_outer. FTIR spectra of (c) NiAl_Bis_outer and (d) NiAl_Tris_outer.

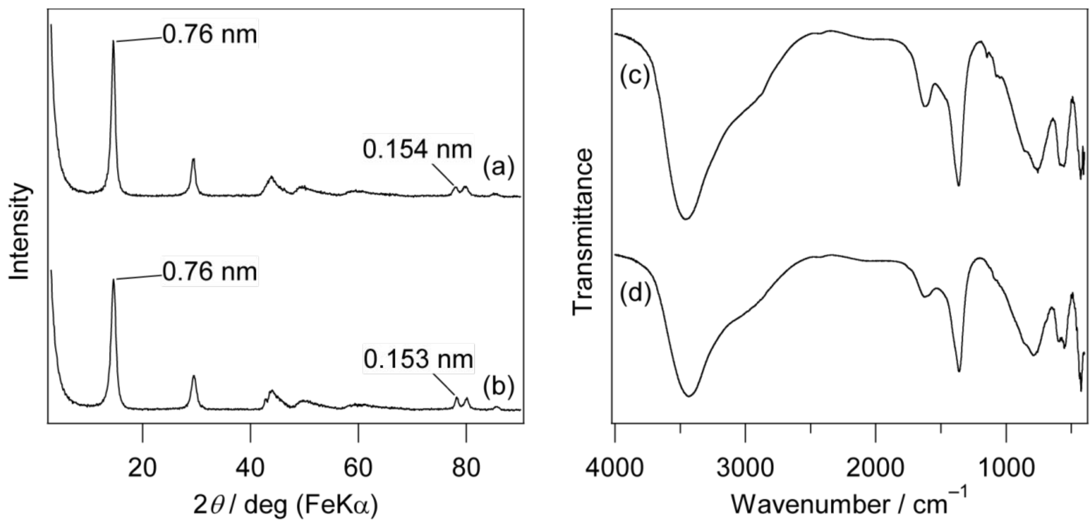

Figure S4. XRD patterns of (a) CoAl_Bis_outer(HT) and (b) CoAl_Tris_outer(HT). FTIR spectra of (c) CoAl_Bis_outer(HT) and (d) CoAl_Tris_outer(HT).

Table S2. Summary of the effect of the number of bonding sites in a modifier and reaction temperature on the resulted modification mode of organically modified CoAl LDHNPs.

		Number of bonding sites in a modifier	
		Tripodal (Tris-NH_2)	Dipodal (Bis-NH_2)
Reaction temperature	80 °C	no precipitate (entry 0)	outer (entry 5)
	180 °C	interlayer (entry 1)	outer (entry 8)

The constituent divalent metal cations, the concentration of both metal ions and modifiers, and reaction time are common among these experiments.

Table S3. Summary of the effect of the concentration of Tris-NH_2 and reaction temperature on the resulted modification mode of organically modified CoAl LDHNPs.

		Concentration of Tris-NH_2	
		0.5 M	0.1 M
Reaction temperature	80 °C	no precipitate (entry 0)	outer (entry 3)
	180 °C	interlayer (entry 1)	outer (entry 7)

The constituent divalent metal cations, the concentration of metal ions, the type of modifier, and reaction time are common among these experiments.

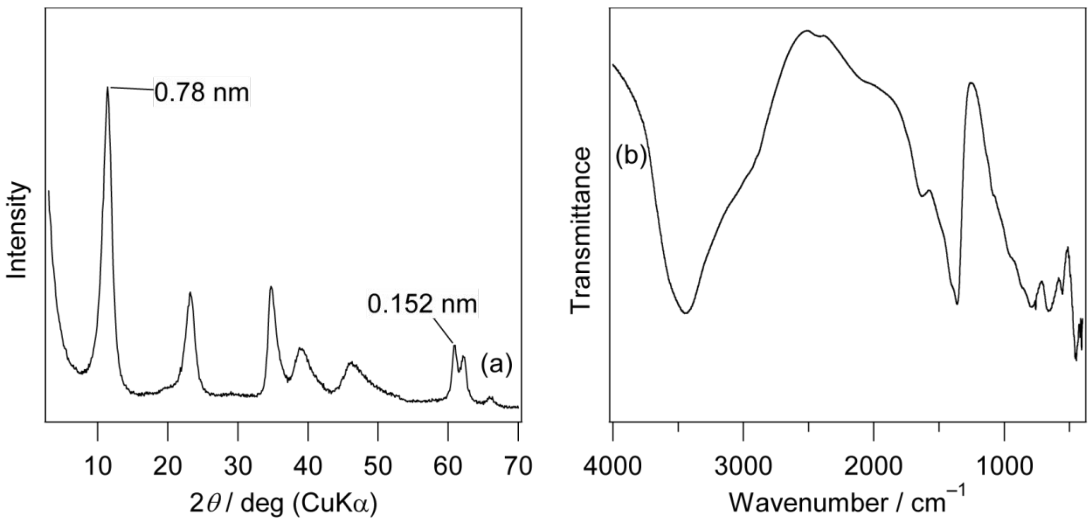

Figure S5. (a) XRD pattern and (b) FTIR spectrum of MgAl_Tris_outer.

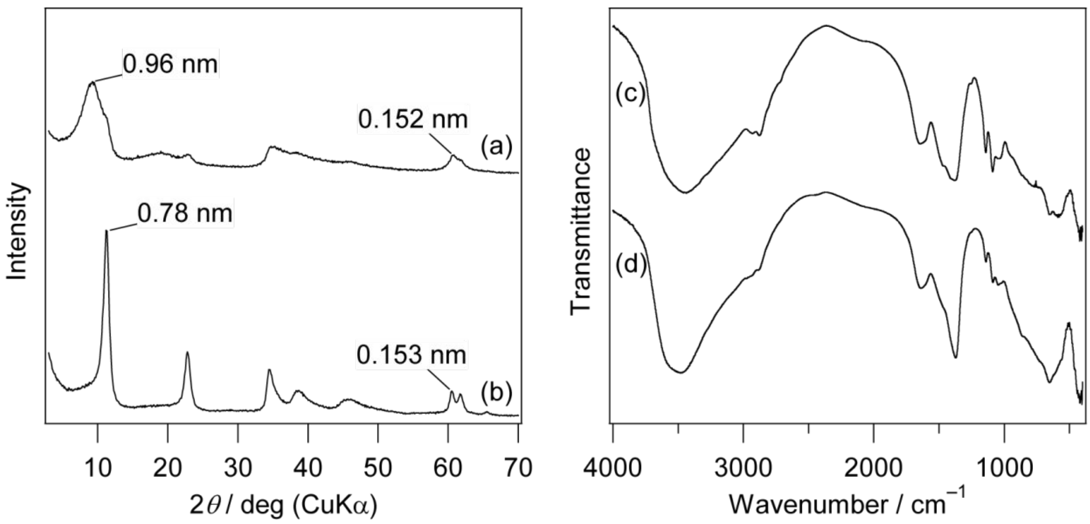

Figure S6. XRD patterns of MgAl_Tris_inter (a) before and (b) after dispersing in water for 24 h. FTIR spectra of MgAl_Tris_inter (c) before and (d) after dispersing in water for 24 h.

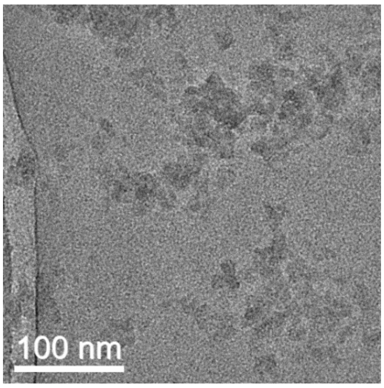

Figure S7. TEM image of the delaminated CoAl_Tris_inter(HT).

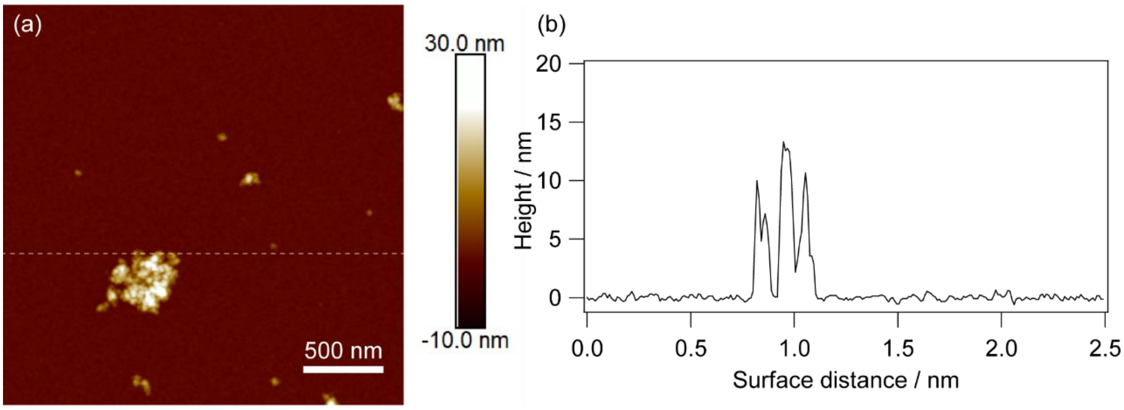

Figure S8. (a) AFM image of CoAl_Tris_inter(HT) before delamination. (b) The height profile on the lines indicated in (a). The dispersion of CoAl_Tris_inter(HT) during washing with water was mounted on a silicon substrate.

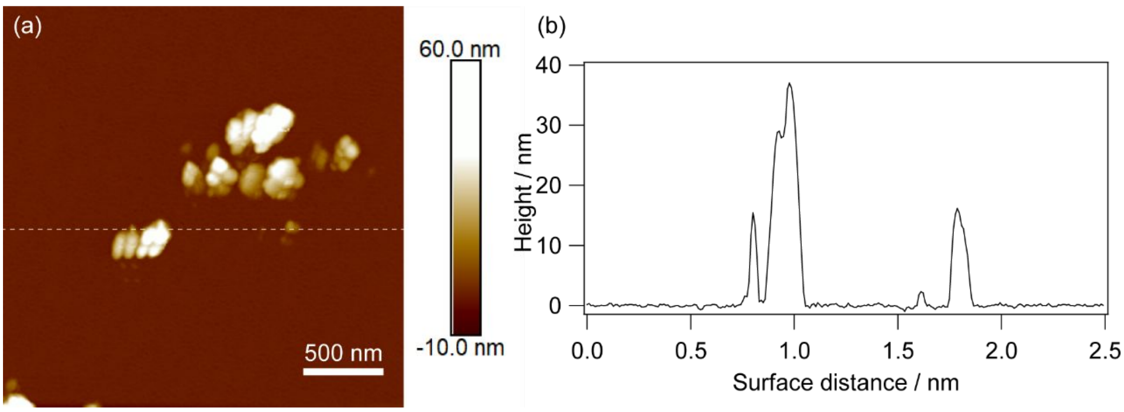

Figure S9. (a) AFM image of CoAl_none after ultrasonication in water for 2 h. (b) The height profile on the lines indicated in (a). The dispersion of CoAl_none after ultrasonication in water for 2 h was mounted on a silicon substrate.

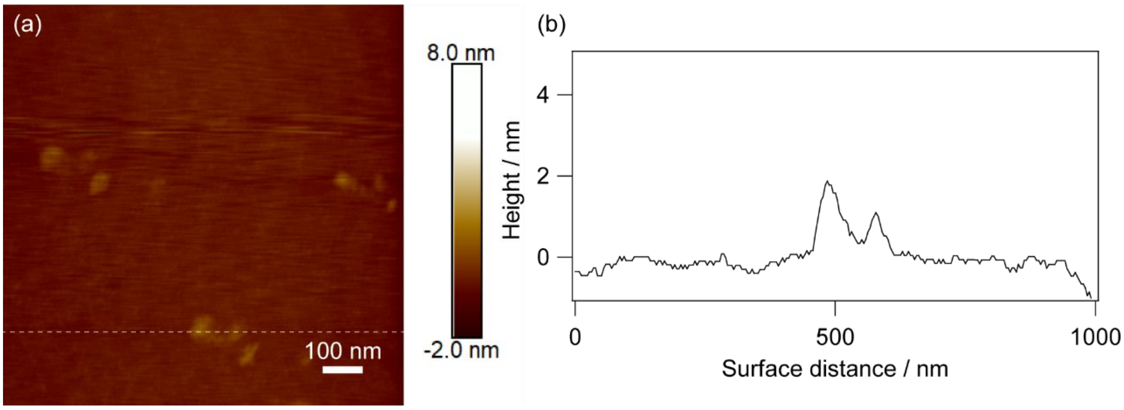

Figure S10. (a) AFM image of MgAl_Tris_inter after ultrasonication in water for 2 h. (b) The height profile on the lines indicated in (a). The dispersion of MgAl_Tris_inter after ultrasonication in water for 2 h was mounted on a silicon substrate.

References

[S1] Duan, X.; Evans, D. G., Eds. *Layered Double Hydroxides: Structure and Bonding;* Springer: Berlin/Heidelberg, Germany, 2006.

[S2] Kuroda, Y.; Koichi, T.; Muramatsu, K.; Yamaguchi, K.; Mizuno, N.; Shimojima, A.; Wada, H.; Kuroda, K., Direct Synthesis of Highly Designable Hybrid Metal Hydroxide Nanosheets by Using Tripodal Ligands as One-Size-Fits-All Modifiers. *Chem. Eur. J.* **2017**, *23*, 5023–5032.