

Supporting Information

Hexagonal ordering of racemic Ni(II) complexes in the interlayer
space of a clay mineral

Jun Yoshida,* Kazunori Tateyama, Hidetaka Yuge, and Mitsuo Hara*

Materials and methods

All solvents employed were reagent grade. Sodium-montmorillonite clay (**Na-Mt**) was purchased from Kunimine Industries Co., Ltd as a specimen of the Clay Science Society of Japan (JCSS-3101). The elemental composition and cation-exchange capacity are $(\text{Na}_{0.47}\text{Ca}_{0.04})(\text{Al}_{1.51}\text{Mg}_{0.35}\text{Fe}_{0.13})(\text{Si}_{3.78}\text{Al}_{0.22})\text{O}_{10}(\text{OH})_2$ and 1.19 meq per gram, respectively. $[\text{Ni}(\text{phen})_3]\text{Cl}_2$ was prepared according to the reported procedure.¹ The intercalated and intersalated compounds of a montmorillonite clay with $[\text{Ni}(\text{phen})_3]^{2+}$ were prepared by adding an aqueous solution of $[\text{Ni}(\text{phen})_3]\text{Cl}_2$ into an aqueous suspension of **Na-Mt**. After the decantation, the suspension was filtered with a membrane filter. The precipitate was dried under air. The actual amount of adsorbed Ni complexes was determined by the UV-Vis spectra of the filtrate. The obtained adsorption isotherm is shown in Fig. S1.

UV-Vis spectra were recorded with V-570 (JASCO Corp.). Thermogravimetric (TG) analysis was performed with a Thermo plus EVO2 TG-DTA 8122 (Rigaku Corp.). FT-IR spectroscopy was performed with a JASCO FT/IR-4200 with an ATR unit (diamond, MicromATR Vision, Czitek). Micro-Raman spectroscopy was performed with a JASCO NRS-7200 using a 785nm laser. Before the measurements, the Raman shift was calibrated with a silicon substrate. One-dimensional X-ray diffraction was performed in reflection mode on an X-ray diffractometer SmartLab SE equipped with a 1D detector D/teX Ultra 250 (Rigaku Corp.) using Cu K α radiation ($\lambda = 0.154$ nm), while two-dimensional XRD in transmission mode and GI-XRD was performed on an X-ray diffractometer FR-E equipped with a two-dimensional detector R-Axis IV (Rigaku Corp.) involving an imaging plate (Fujifilm Corp.) using Cu K α radiation ($\lambda = 0.154$ nm).

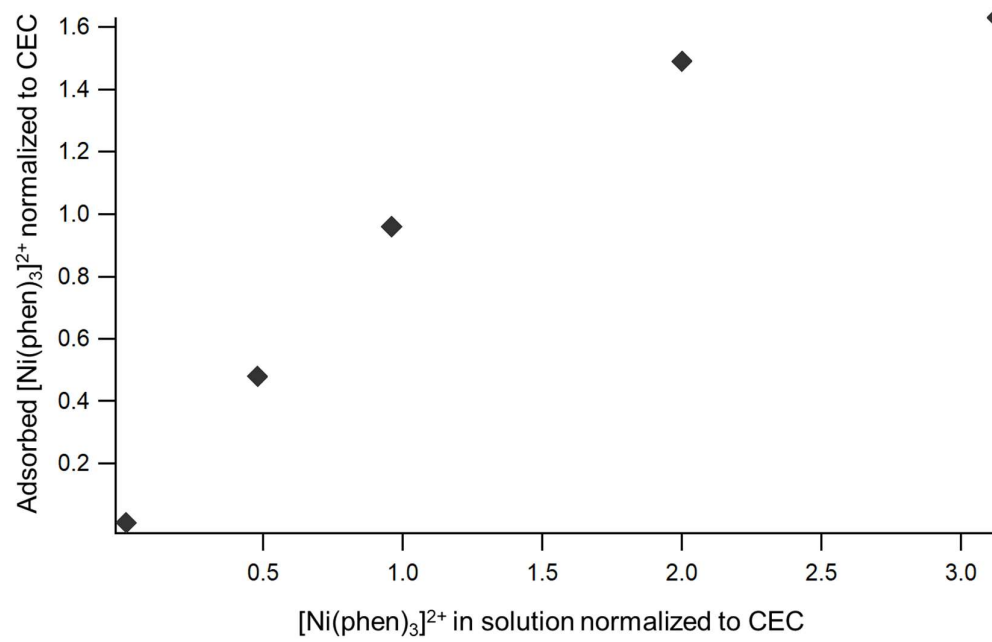


Figure S1 Adsorption isotherm of [Ni(phen)₃]Cl₂ on **Na-Mt**.

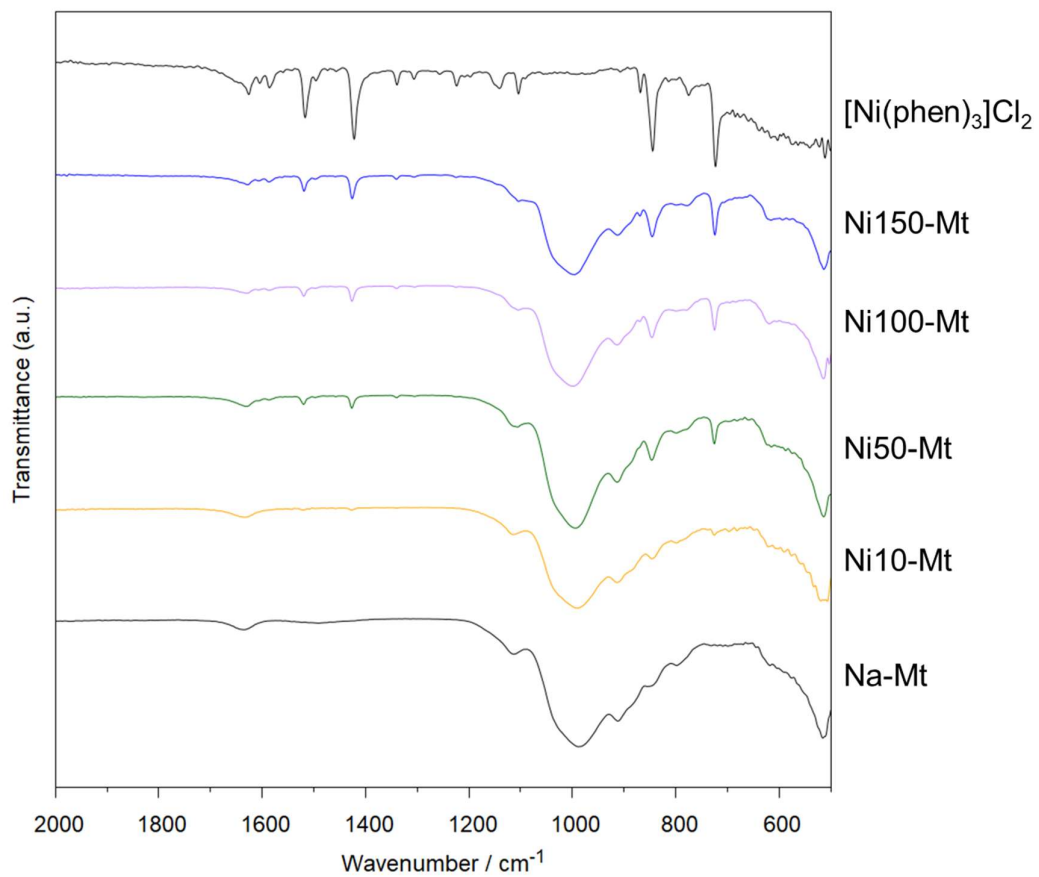


Figure S2 ATR-IR spectra of Na-Mt, Ni10-Mt, Ni50-Mt, Ni100-Mt, Ni150-Mt, and [Ni(phen)₃]Cl₂.

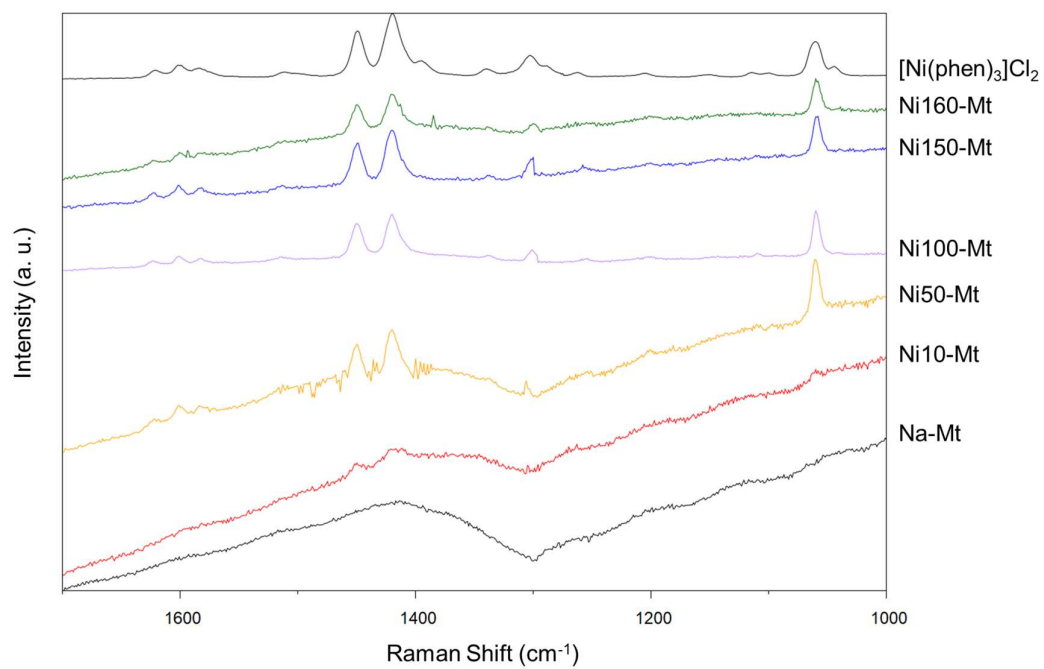


Figure S3 Raman spectra of Na-Mt, Ni10-Mt, Ni50-Mt, Ni100-Mt, Ni150-Mt, Ni160-Mt, and [Ni(phen)₃]Cl₂. The wavelength of the laser used is 785 nm.

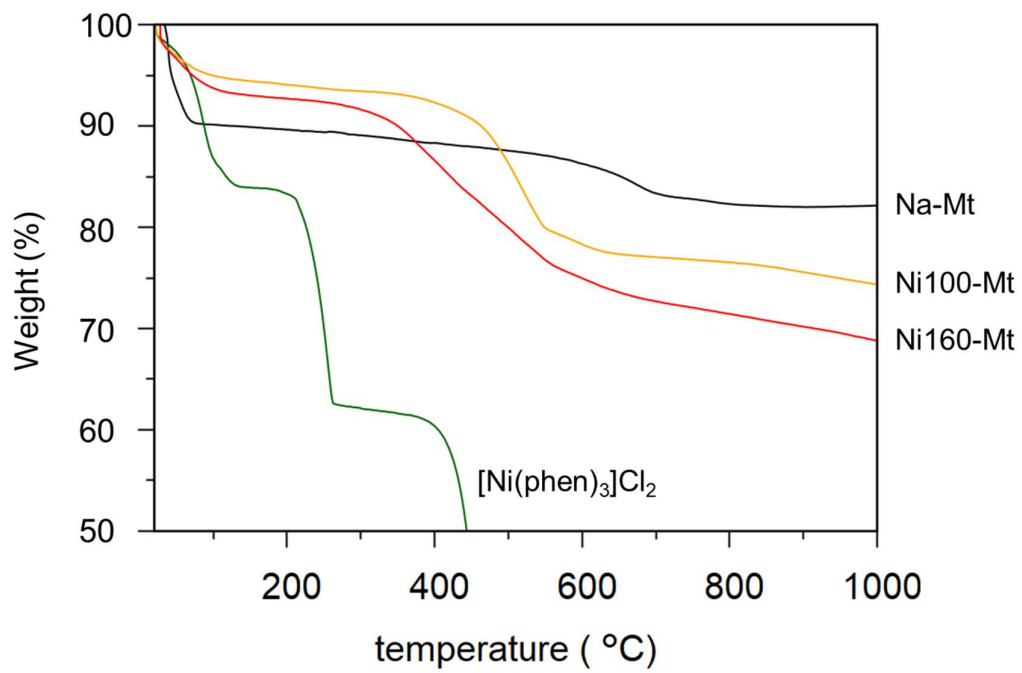


Figure S4 TG curves of Na-Mt, Ni100-Mt, Ni160-Mt, and [Ni(phen)₃]Cl₂.

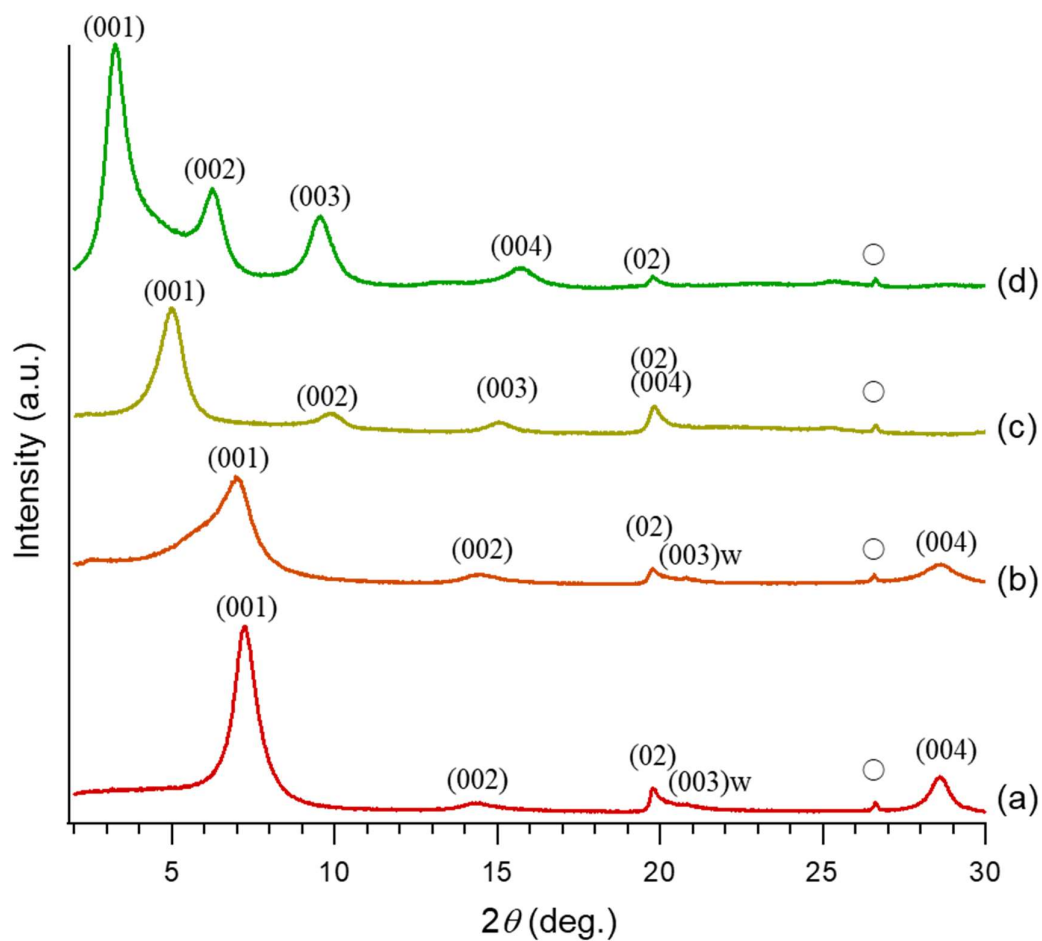


Figure S5 Powder XRD patterns of (a) **Na-Mt**, (b) **Ni10-Mt**, (c) **Ni100-Mt**, and (d) **Ni160-Mt** measured in reflection mode with samples loaded on a glass plate. The reflections marked with circles are attributed to quartz included in **Na-Mt** as an impurity.

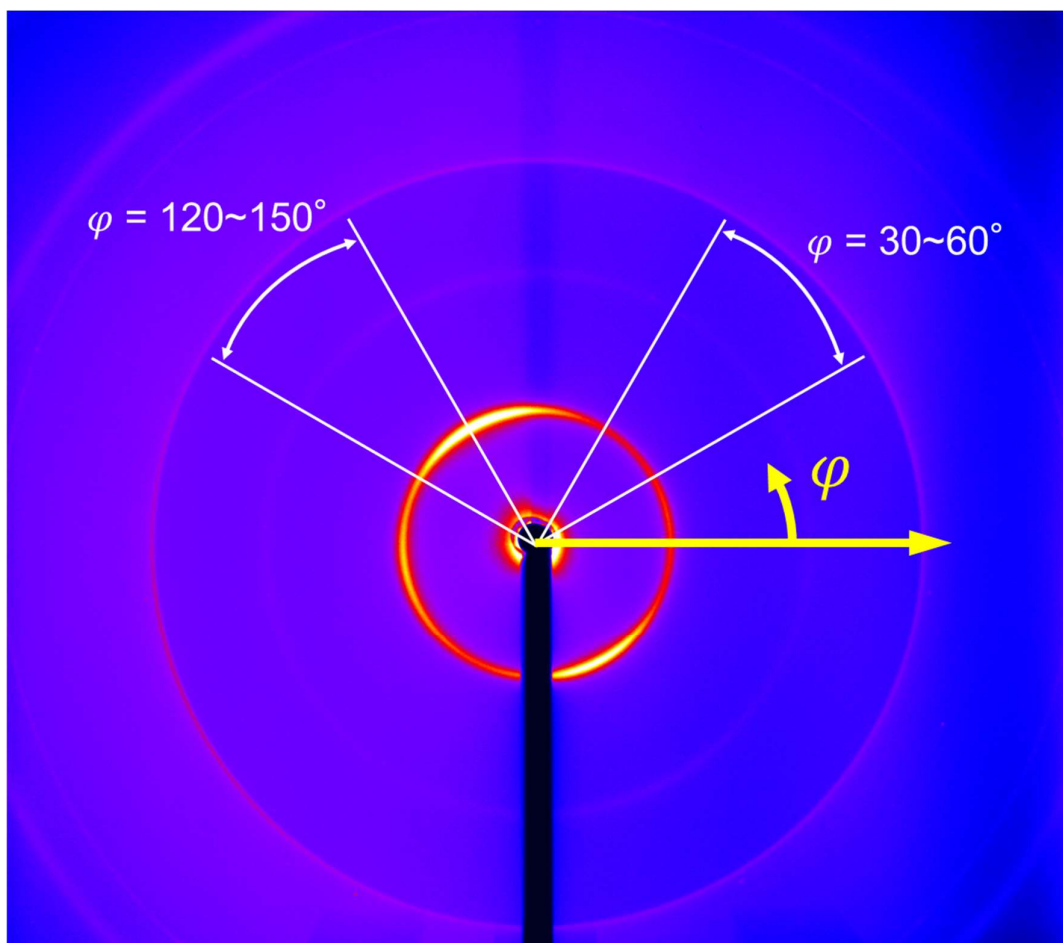


Figure S6 2D XRD image of Na-Mt measured in transmission mode.

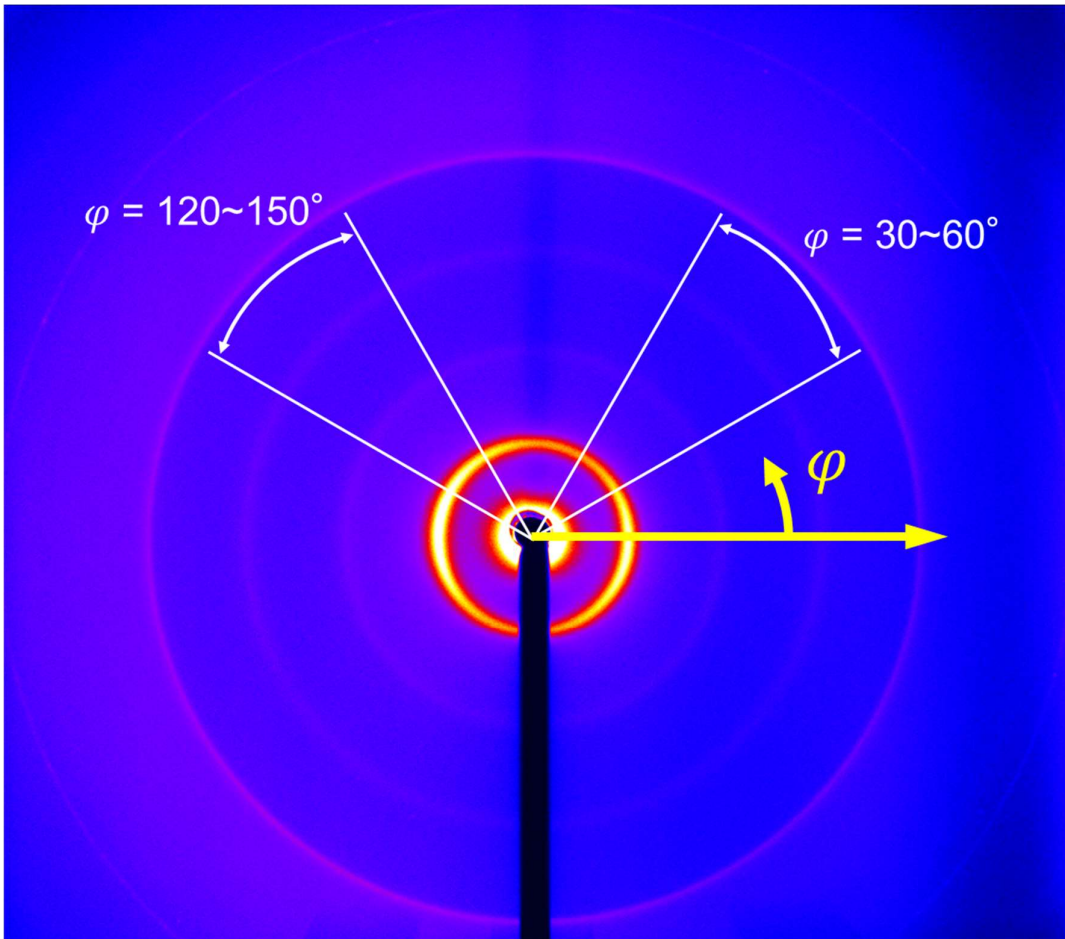


Figure S7 2D XRD image of Ni₅₀-Mt measured in transmission mode.

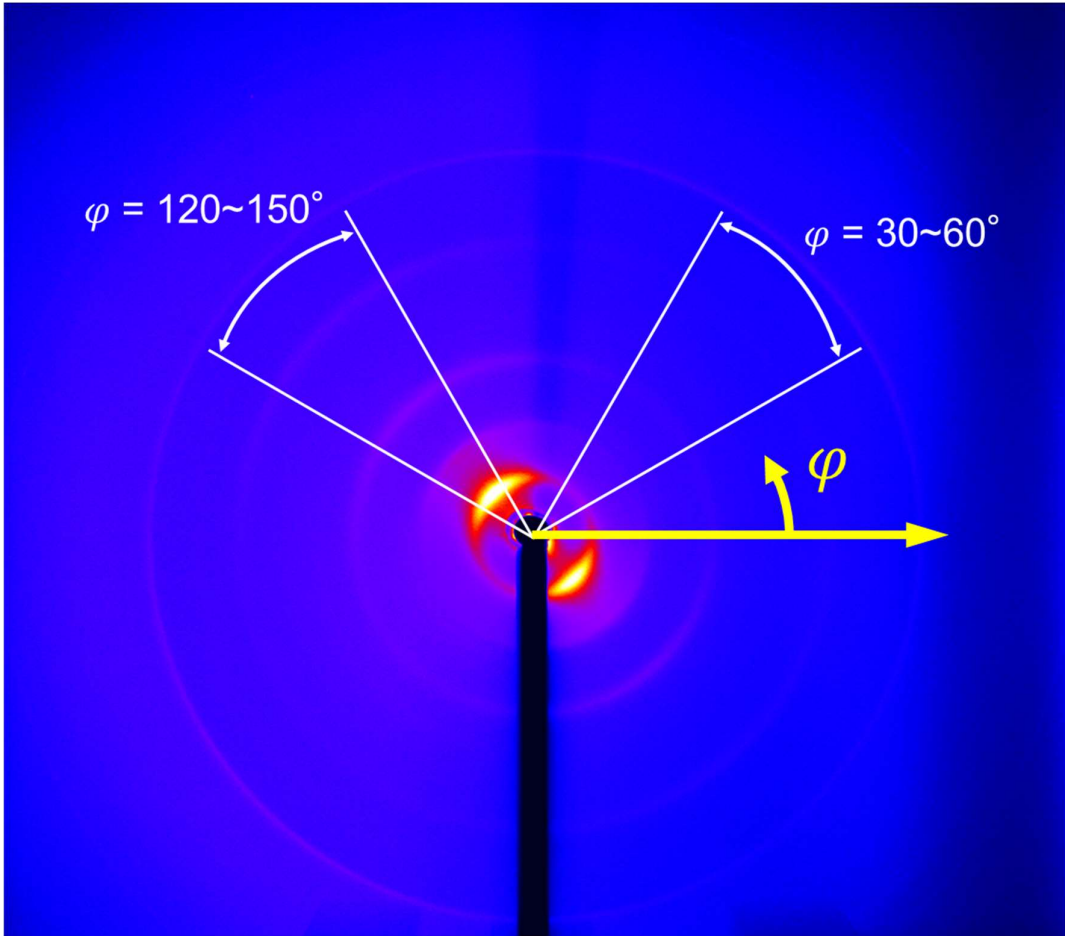


Figure S8 2D XRD image of Ni₁₅₀-Mt measured in transmission mode.

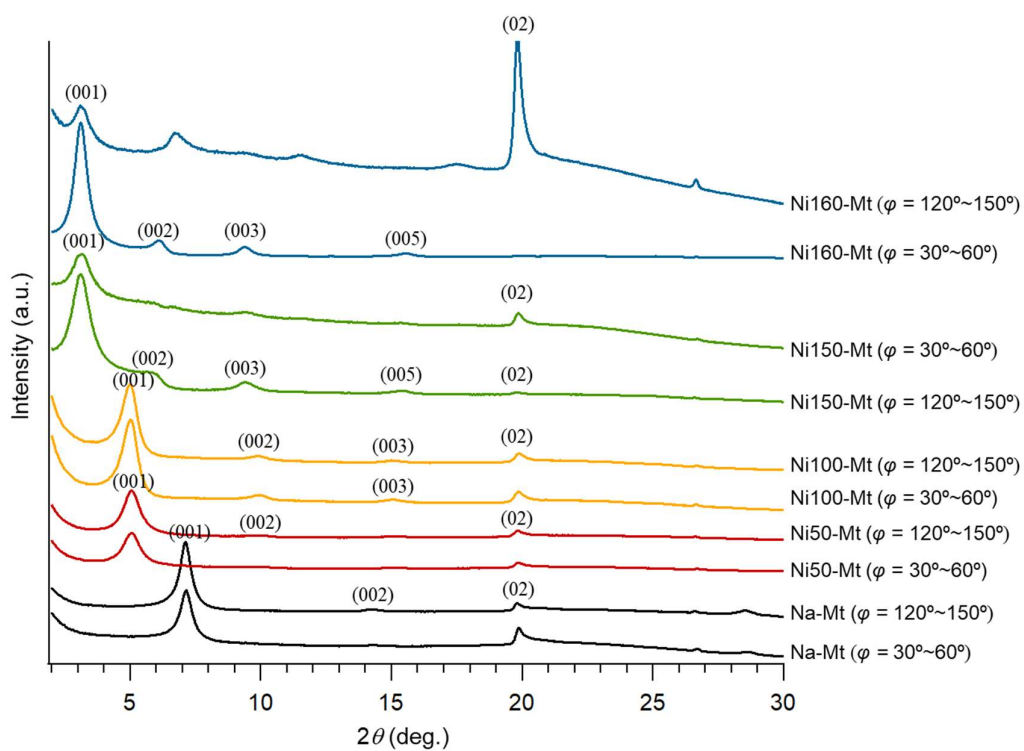


Figure S9 1D XRD patterns of **Na-Mt**, **Ni50-Mt**, **Ni100-Mt**, **Ni150-Mt**, and **Ni160-Mt**, which were deduced from the azimuthal integration of $30^\circ \sim 60^\circ$ and $120^\circ \sim 150^\circ$ regions in each 2D XRD image. Indices of the basal reflections are shown in black characters, while the reflections attributed to the (020) plane are marked with blue characters.

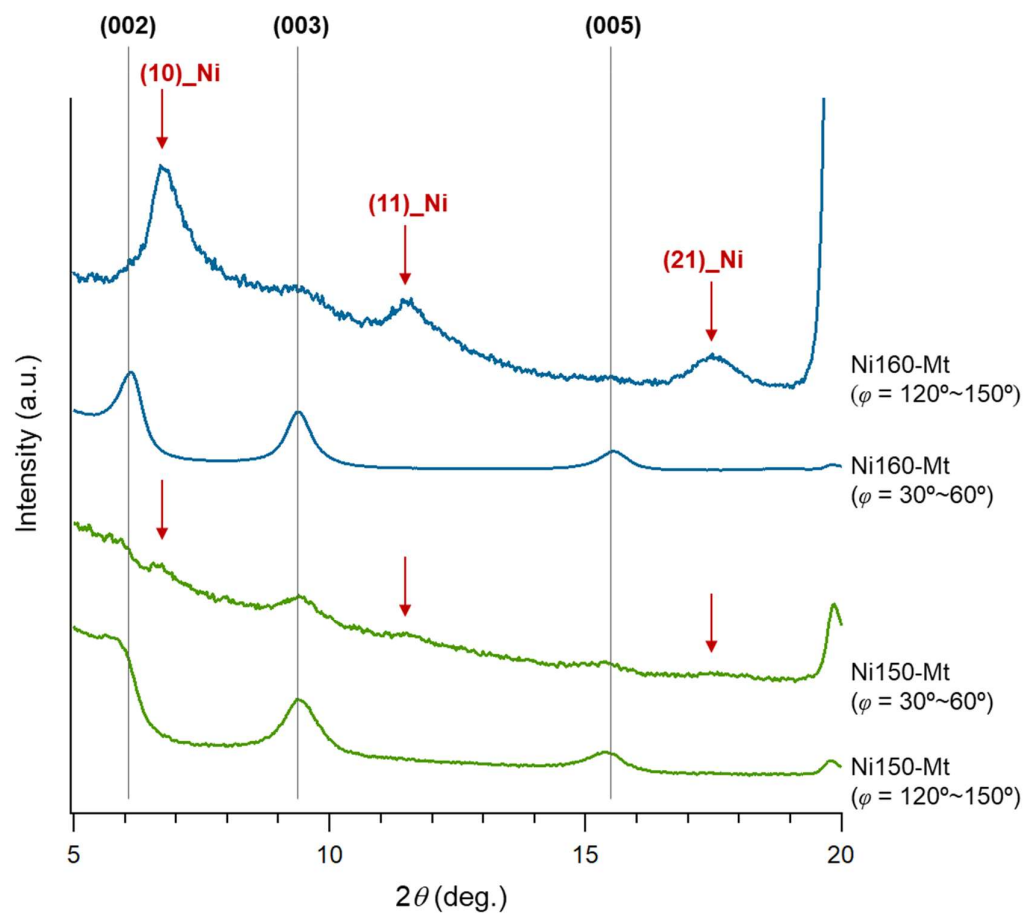


Figure S10 Enlarged view of 1D XRD patterns of Ni150-Mt and Ni160-Mt, which were deduced from the azimuthal integration of $30^\circ \sim 60^\circ$ and $120^\circ \sim 150^\circ$ regions in each 2D XRD image. Indices of the reflections attributed to the host clay are shown in black characters, whereas those attributed to two-dimensional assembly of Ni complexes are shown in red characters and arrows.

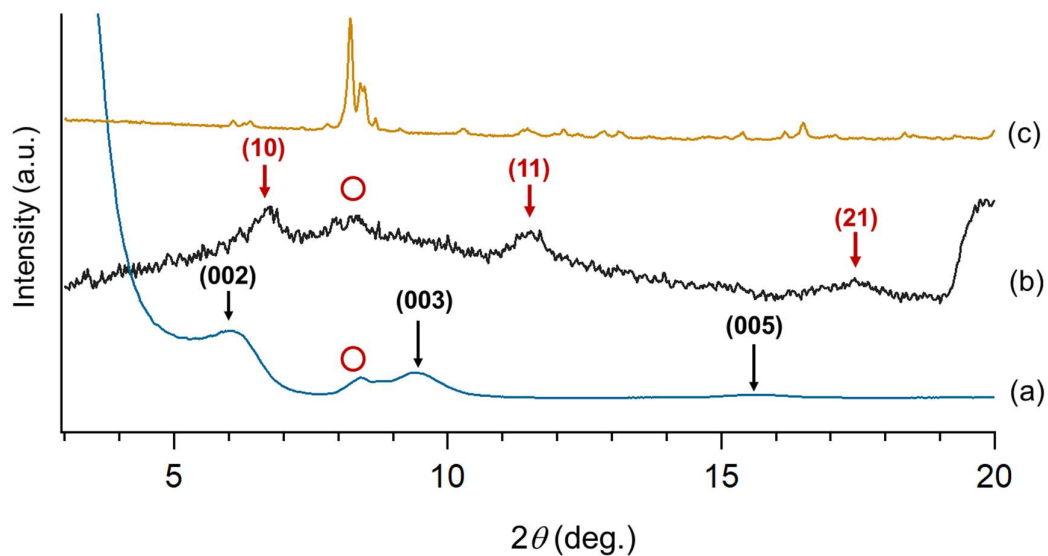


Figure S11 1D XRD patterns of **Ni160-Mt** derived from the GI-XRD image along (a) the meridional and (b) equatorial directions. (c) 1D XRD pattern of powder $[\text{Ni}(\text{phen})_3]\text{Cl}_2$. Indices of the reflections attributed to the host clay and guest Ni complexes are shown in black and red characters, respectively. The reflections attributed to $[\text{Ni}(\text{phen})_3]\text{Cl}_2$ in **Ni160-Mt** are marked with red circles.

Reference

- 1 G. B. Kauffman, L. T. Takahashi, K. H. Pearson, L. W. Sequin and S. Kirschner, *Inorg. Synth.*, 1966, 227–232.