

Intercalation route-dependent orientation of a Tb³⁺-encapsulated Preyssler-type polyoxometalate in layered double hydroxides

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ABSTRACT: In this study, a Tb³⁺-encapsulated Preyssler-type polyoxometalate (TbPOM) was intercalated into layered double hydroxides (LDHs) through four different routes: ion exchange (IE), exfoliation–restacking (ER), layer-by-layer assembly (LbL), and reconstruction via the memory effect (Re). Structural analyses based on powder X-ray diffraction and previously reported orientation models revealed that the orientation of TbPOM depends on the intercalation pathway. The IE and Re methods predominantly produced the Form-1 structure, in which the fivefold symmetry (*C*₅) axis of TbPOM is oriented perpendicular to the LDH layers, whereas the ER method yielded a coexistence of Form-1 and Form-2 structures, corresponding to perpendicular and parallel orientations of the *C*₅ axis, respectively. In contrast, the LbL method selectively generated the Form-2 structure. Thermal annealing of the ER product caused a gradual decrease of the Form-2 phase accompanied by the development of highly ordered Form-1 reflections and contraction of the interlayer spacing. These observations suggest that Form-2 is preferentially stabilized under hydrated conditions, whereas Form-1 becomes dominant upon dehydration. The results suggest that the orientation of TbPOM is influenced not only by the composition of the host LDHs but also by the intercalation process, which affects the hydration state of the interlayer galleries and thereby influences the preferred orientation of TbPOM. This study provides a new strategy for controlling POM orientation in layered materials and highlights the importance of the intercalation pathway as a key parameter influencing orientation formation in POM–LDH hybrid systems.

KEYWORDS: polyoxometalate, layered double hydroxides (LDHs), molecular orientation, intercalation

1 Introduction

Polyoxometalates (POMs) are molecular metal-oxide clusters composed of early transition-metal ions such as tungsten (W), molybdenum (Mo), and vanadium (V) bridged by oxygen atoms [1–3]. Owing to their remarkable structural diversity and multi-electron redox properties, POMs have attracted considerable attention in a wide range of fields, including catalysis [4–6], molecular magnetism [7,8], electronic materials [9,10], and energy conversion and storage [11,12]. Among them, Preyssler-type POMs, represented by the general formula [Zⁿ⁺@P₅W₃₀O₁₁₀]^{(15–n)–}, possess a characteristic cage-like structure with fivefold symmetry (*C*₅) and contain a well-defined internal cavity that serves as a stable encapsulation ion site for metal ions. The encapsulated ion can be readily substituted with a variety of cations, and the structures and functionalities of Preyssler-type POMs containing alkali-metal ions [13–16] or lanthanide ions [17–21] have been extensively investigated.

Recently, Nishihara and co-workers reported that a Tb³⁺-encapsulated Preyssler-type polyoxometalate (TbPOM)

exhibits giant polarization-switching behavior above room temperature and proposed the concept of a “single-molecule electret (SME)”, in which an individual molecule functions as a nonvolatile memory element analogous to a ferroelectric material [20,22]. In TbPOM, molecular polarization arises from the position of the encapsulated Tb³⁺ ion within the internal cavity, and polarization reversal is achieved through the intramolecular migration of the Tb³⁺ ion in response to an external electric field. Notably, the ion-migration pathway is oriented parallel to the *C*₅ axis of the Preyssler framework, resulting in a strong correlation between the molecular orientation and the direction of macroscopic polarization. Consequently, the dielectric and polarization properties of TbPOM assemblies are expected to be highly dependent on the orientation of the constituent molecules. Therefore, to fully exploit the unique molecular functionality of TbPOM, it is essential not only to assemble the molecules into solid-state architectures but also to construct higher-order structures in which their orientations are precisely controlled. When molecular dipoles are randomly oriented, their individual contributions are canceled at the macroscopic level. In

contrast, controlling the orientation of TbPOM can enhance polarization and induce anisotropic physical properties. Therefore, molecular orientation is a key design parameter in the development of molecular-based ferroelectric-like materials. From this perspective, precise control of the orientation of TbPOM molecules is expected to be essential for maximizing their intrinsic functionality and realizing orientation-dependent polarization behavior in solid-state assemblies.

Layered double hydroxides (LDHs), represented by the general formula $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2]_x^+[A^{n-}]_{x/n} \cdot mH_2O$ ($M^{2+} = Mg^{2+}, Zn^{2+}, Ni^{2+}$, etc.; $M^{3+} = Al^{3+}, Co^{3+}, Fe^{3+}$, etc.; $x = M^{3+}/(M^{2+} + M^{3+})$), are anionic clay minerals composed of positively charged brucite-like layers and exchangeable interlayer anions [23]. Owing to their anion-exchange capability and well-defined layered structures, LDHs have been widely employed as host materials for the immobilization and organization of functional anionic species. Furthermore, exfoliated LDH nanosheets have attracted considerable interest as two-dimensional building blocks for the controlled assembly of molecules and polymers in confined spaces [24–28]. In this context, LDH-based layered architectures are expected to offer a promising platform for controlling the orientation of TbPOM molecules and translating their molecular-scale dielectric functionality into macroscopic materials. POM-intercalated LDHs have emerged as an important class of host–guest hybrid materials owing to the synergistic combination of the physicochemical properties of POMs and the tunable interlayer environment of LDHs. Following the pioneering demonstration of Keggin-type POM intercalation into LDHs by Pinnavaia and co-workers [29], these materials have been extensively explored for catalytic, optical, environmental, and electrochemical applications [30–38]. Among various POM–LDH systems, Preyssler-type POMs are particularly attractive because their anisotropic molecular shape allows orientation-dependent host–guest structures to be formed within the LDH galleries [33,34]. Hu and co-workers reported that distinct molecular orientations can be obtained depending on the composition of the precursor LDHs. Specifically, ion-exchange reactions using Mg_2Al -LDHs and Zn_2Al -LDHs yielded different orientations of the Preyssler-type POM within the interlayer galleries. In the Mg_2Al -LDH-derived composite, the fivefold symmetry axis (C_5 axis) of the POM was aligned perpendicular to the hydroxide layers, whereas in the Zn_2Al -LDH-derived composite it adopted an orientation approximately parallel to the layers. These configurations, which give rise to distinct basal spacings, are referred to herein as Form-1 and Form-2, respectively (Fig. 1).

Previous studies have demonstrated that the orientation of guest species within LDH interlayers is influenced by factors such as layer charge density and hydration state [39]. In terephthalate-intercalated LDHs, for example, changes in hydration and layer charge density induce transitions between horizontal and vertical molecular arrangements, highlighting the importance of host–guest and water-mediated interactions in determining the interlayer structure [40]. Likewise, studies on POM-intercalated LDHs have shown that different orientations of Keggin-, Dawson-, and Finke-type polyoxometalates can be stabilized depending on the interaction between the guest anions and the hydroxide layers [41]. However, these studies have primarily focused on the influence of host composition, layer charge density, and guest structure. Although differences in orientation have occasionally been observed

among materials prepared by different synthetic approaches, the role of the intercalation route itself has not been systematically examined. Despite these observations, it remains unclear to what extent the final orientation of intercalated POMs is governed by intrinsic host–guest interactions or influenced by the pathway through which the host–guest architecture is constructed. Establishing such route-dependent orientation control would provide a new strategy for translating the unique polarization-switching functionality of single molecules into functional materials.

In this study, TbPOMs, which have attracted interest as molecular ferroelectric-like units, were introduced into LDHs through four different intercalation routes, namely ion exchange (IE), exfoliation–restacking (ER), layer-by-layer assembly (LbL), and reconstruction via the memory effect (Re). Structural analyses were performed based on the Form-1 and Form-2 orientation models defined from the molecular dimensions of the Preyssler-type POM and previously reported structural models [33].

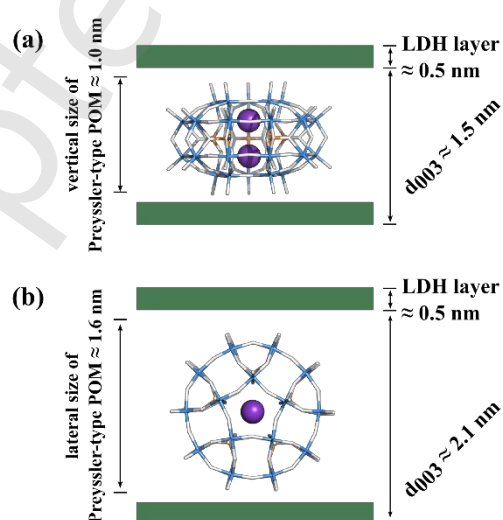


Fig. 1 Structural models of Preyssler-type POMs intercalated in LDHs. Dark green blocks represent hydroxide layers. W, O, P, and the encapsulated metal ion are shown in blue, white, orange, and purple, respectively. (a) Form-1 orientation (C_5 axis perpendicular to the hydroxide layer). (b) Form-2 orientation (C_5 axis parallel to the hydroxide layer). The dimensions of the Preyssler-type POM, the thickness of the LDH layer, and the basal spacing (d_{003}) are indicated.

By systematically comparing the structures obtained through these different intercalation routes, the relationship between the intercalation process and the orientation of TbPOM within LDH interlayers was investigated. The results demonstrate dependence of TbPOM orientation on the intercalation route, providing new insights into the structural control of single-molecule-based materials.

2 Experimental

2.1. Reagents

All chemicals were purchased from commercial suppliers and used without further purification. Deionized water was used throughout this study. For the preparation of nitrate-containing LDHs and exfoliated nanosheets, the water was boiled for 30 min and purged with N_2 for 30 min prior to use.

2.2. Synthesis of Preyssler-type POMs

$K_{12.5}Na_{1.5}[Na^+@P_5W_{30}O_{110}] \cdot nH_2O$ was synthesized according to the procedure reported by Pope et al [17]. TbPOM ($K_{12}[Tb^{3+}@P_5W_{30}O_{110}] \cdot nH_2O$) was prepared by hydrothermal ion exchange of the encapsulated Na^+ ion with Tb^{3+} using a previously reported method [17,20]. The formation and purity of TbPOM were confirmed by ^{31}P -NMR spectroscopy, as shown in Fig. S1. Detailed synthetic procedures and characterization data are provided in the Supporting Information.

2.3. Synthesis of LDHs

2.3.1. Synthesis of $CO_3^{2-}@Mg_2Al$ -LDHs

$CO_3^{2-}@Mg_2Al$ -LDHs were synthesized by the urea hydrolysis method according to a previously reported procedure [26,27]. $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and urea were dissolved in deionized water and hydrothermally treated at 140 °C for 24 h. The resulting precipitate was collected, washed with water, and dried.

2.3.2. Synthesis of $NO_3^-@Mg_2Al$ -LDHs

$NO_3^-@Mg_2Al$ -LDHs were prepared by nitrate exchange of $CO_3^{2-}@Mg_2Al$ -LDHs following a reported method [26,27]. $CO_3^{2-}@Mg_2Al$ -LDHs were treated with $NaNO_3$ solution under acidic and deoxygenated conditions, followed by filtration, washing, and drying.

2.3.3. Synthesis of $TA@Mg_2Al$ -LDHs

$TA@Mg_2Al$ -LDHs were synthesized by coprecipitation according to the literature [33,42]. $Mg(NO_3)_2 \cdot 6H_2O$ (12.83 g) and $Al(NO_3)_3 \cdot 9H_2O$ (9.38 g) were dissolved in water (35 mL) to prepare a metal nitrate solution ($Mg/Al = 2$). Terephthalic acid (4.15 g) was dispersed in water (50 mL), followed by the addition of NaOH (1.0 g). The resulting solution was heated to 75 °C under N_2 atmosphere. The metal nitrate solution was added dropwise while maintaining the pH at 10.0 by addition of 2 M NaOH. After complete addition, the suspension was stirred at 75 °C for 36 h and aged at 75 °C for an additional 18 h. The resulting slurry was used directly for subsequent intercalation experiments. A portion of the product was isolated by filtration, washed with water, and dried.

2.3.4. Synthesis of $CO_3^{2-}@Zn_3Al$ -LDHs[43]

$CO_3^{2-}@ZnAl$ -LDHs were synthesized by coprecipitation. $Zn(NO_3)_2 \cdot 6H_2O$ (17.85 g) and $Al(NO_3)_3 \cdot 9H_2O$ (7.50 g) were dissolved in water (100 mL) to prepare a metal nitrate solution ($Zn/Al = 3$). The metal nitrate solution was added dropwise to a basic solution containing 2 M NaOH and 1 M Na_2CO_3 while maintaining the pH at 10.0. After complete addition, the suspension was stirred for 1 h and aged at 70 °C for 18 h. The precipitate was collected, washed with water and ethanol, and dried.

2.4. Preparation of TbPOM/LDH Composites

For the exfoliation–restacking, layer-by-layer assembly, and reconstruction methods, no pH adjustment was performed, and the solutions were used as prepared.

2.4.1. Ion-exchange (IE) method

$TA@Mg_2Al$ -LDHs were used as precursors for the preparation of TbPOM/LDH composites by ion exchange. For $TA@Mg_2Al$ -LDHs, TbPOM (3.0 g) was dissolved in water (50 mL). A 4 wt% suspension of $TA@Mg_2Al$ -LDHs was adjusted to pH 5 with 1 M HNO_3 , followed by addition of methanol (15 mL). The TbPOM solution was added and stirred at 70 °C for 6 h under N_2 atmosphere. The resulting solid was collected, washed with water, and dried.

2.4.2. Exfoliation–restacking (ER) method

$NO_3^-@Mg_2Al$ -LDHs (0.20 g) were dispersed in degassed formamide (200 mL) and stirred at room temperature for 48 h. The exfoliated nanosheet dispersion was purified by centrifugation. TbPOM (0.50 g) was dissolved in water (60 mL) and added dropwise to the nanosheet dispersion. The mixture was stirred for 24 h to induce restacking. The resulting solid was collected by filtration, washed thoroughly with water, and dried.

2.4.3. Preparation of Layer-by-Layer Films (LbL) [27,44]

Exfoliated Mg_2Al -LDH nanosheet dispersions and aqueous TbPOM solutions were used for LbL assembly on Si substrates. One deposition cycle consisted of immersion in the LDH nanosheet dispersion for 20 min, rinsing with water for 5 min, immersion in the TbPOM solution for 10 min, and rinsing with water for 5 min. This cycle was repeated 100 times.

2.4.4. Reconstruction (Re) method [45,46]

$CO_3^{2-}@Zn_3Al$ -LDHs were calcined at 500 °C to obtain layered double oxides (LDOs). The resulting LDO powder was dispersed in an aqueous TbPOM solution and stirred under ambient conditions to induce reconstruction of the LDH structure. The resulting solid was collected by filtration, washed with water, and dried.

2.5. Characterization

Powder X-ray diffraction (PXRD) patterns were recorded using a MiniFlex 600 diffractometer (Rigaku Corp., Japan) with $Cu K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). FT-IR spectra were collected using an Avatar 370 FT-IR spectrometer (Thermo Fisher Scientific, USA) in the range of 4000–400 cm^{-1} . Thermogravimetric and differential thermal analyses (TG-DTA) were performed using a Thermo Plus EVO TG8120 thermal analyzer (Rigaku Corp., Japan) under an Ar atmosphere at a heating rate of 10 K min^{-1} . Optical microscope images were acquired using an Olympus BX53M

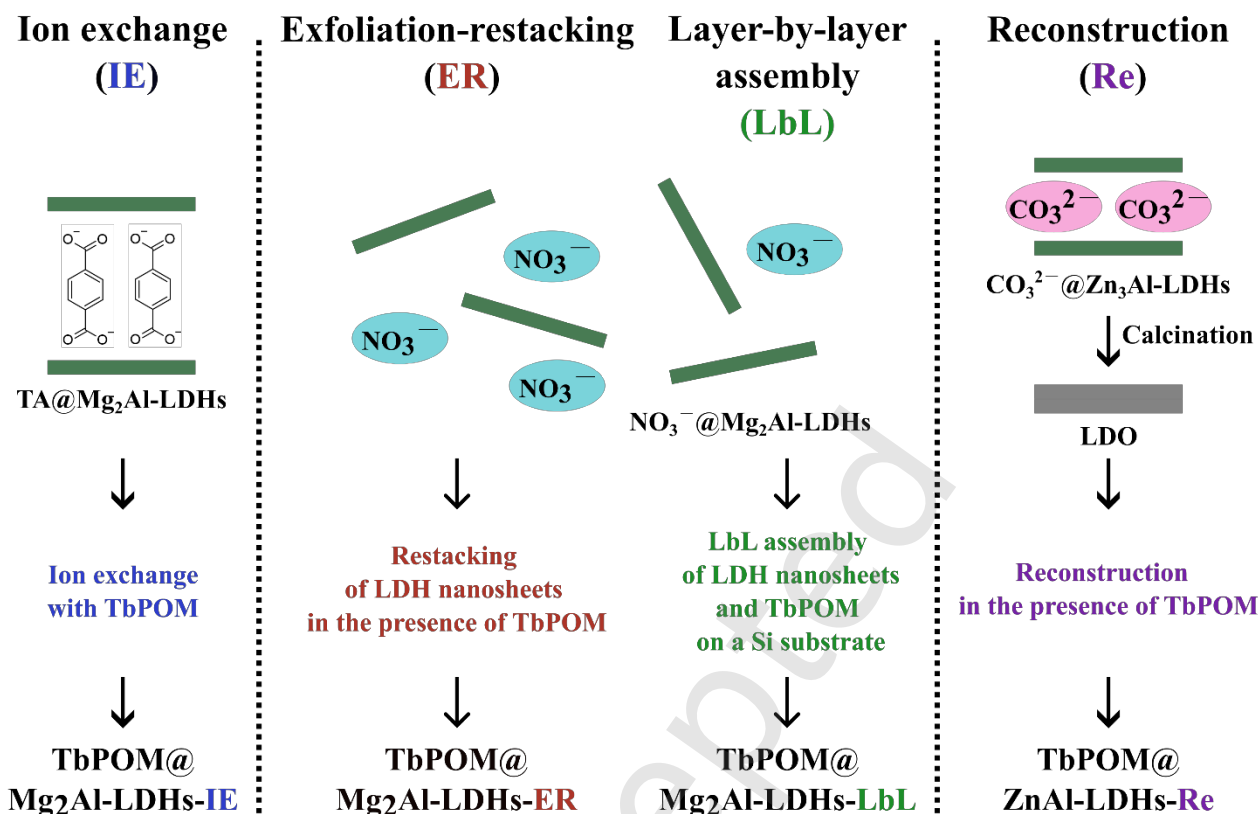


Fig. 2 Schematic illustration of the four preparation routes employed for the intercalation of TbPOM into LDHs: ion exchange (IE), exfoliation–restacking (ER), layer-by-layer assembly (LbL), and reconstruction via the memory effect (Re).

optical microscope (Olympus Corp., Japan). ³¹P-NMR spectra were recorded on a BRUKER SPECTROSPIN AVANCE 400S spectrometer (400 MHz, Bruker BioSpin GmbH, Germany) using D₂O as the solvent.

3. Results and Discussion

3.1. Ion-exchange (IE) method

TbPOM@Mg₂Al-LDHs-IE was prepared by an ion-exchange reaction using TA@Mg₂Al-LDHs as the precursor (Fig. 2). To verify the incorporation of TbPOM, FT-IR measurements were first performed (Fig. S3). The FT-IR spectrum of TbPOM@Mg₂Al-LDHs-IE exhibited characteristic absorption bands attributable to the P–O and W–O vibrations of the TbPOM framework, confirming the presence of TbPOM in the composite. At the same time, absorption bands assigned to terephthalate species were also observed, indicating that the ion-exchange process was incomplete and that a portion of the TA species remained in the sample.

The P-XRD pattern of TbPOM@Mg₂Al-LDHs-IE exhibited basal reflections at $2\theta = 6.07$ and 12.18° , characteristic of a layered structure (Fig. S2). Analysis of these reflections based on Bragg's law yielded an interlayer spacing of 1.45 nm, which is consistent with the value predicted for the Form-1 orientation of TbPOM within the LDH interlayers [33]. However, the diffraction pattern showed only minor changes compared with that of the TA@Mg₂Al-LDH precursor. Combined with the residual TA species detected by FT-IR, this makes it difficult to determine the detailed interlayer structure solely from the P-XRD data. In addition,

the absence of diffraction peaks characteristic of pristine TbPOM (Fig. S2) in the TbPOM@Mg₂Al-LDHs-IE sample indicates that detectable amounts of crystalline TbPOM were not present on the external surface of the LDHs. Although these results are consistent with the partial incorporation of TbPOM into the LDH interlayers, the presence of a minor fraction of surface-adsorbed TbPOM cannot be completely excluded. Nevertheless, the observed basal spacing is consistent with the previously proposed Form-1 structural model and differs from the larger interlayer spacing reported for Form-2 structures [33], suggesting that TbPOM was preferentially incorporated into an arrangement corresponding to the Form-1 phase.

3.2. Exfoliation-restacking (ER) method

Next, the structure of TbPOM@Mg₂Al-LDHs-ER, obtained by exfoliating NO₃⁻@Mg₂Al-LDHs into nanosheets using formamide followed by restacking in the presence of TbPOM, was investigated (Fig. 3). The P-XRD patterns of the precursor NO₃⁻@Mg₂Al-LDHs and the resulting TbPOM@Mg₂Al-LDHs-ER are shown in Fig. 3a. Upon exfoliation and restacking, the original basal reflections characteristic of NO₃⁻@Mg₂Al-LDHs disappeared, and new diffraction peaks emerged at $2\theta = 4.20, 5.40, 8.13, 12.26, 16.41, 20.62,$ and 24.79° . Analysis of these reflections based on Bragg's law revealed two distinct interlayer spacings of 2.16 and 1.64 nm (Fig. 3b). These values correspond well to the interlayer distances expected for the Form-2 and Form-1 orientations of TbPOM within the LDH galleries, respectively, indicating the coexistence of two intercalation configurations corresponding to the Form-1 and Form-2 orientations. Notably, the diffraction series assigned to the

Form-2 phase exhibited well-defined higher-order reflections, whereas only limited higher-order reflections were observed for the Form-1 phase. This result suggests that the Form-1 phase possesses a lower degree of stacking order or crystallinity than the Form-2 phase. In addition, a broad diffuse halo in the 20–35° region suggests the presence of a minor fraction of poorly restacked, low-crystalline LDH domains resulting from the exfoliation–restacking process. The FT-IR spectrum of TbPOM@Mg₂Al-LDHs-ER exhibited characteristic absorption bands at 1160 and 1022 cm⁻¹, attributable to P–O stretching vibrations, together with bands at 939, 914, and 795 cm⁻¹ assigned to W=O and W–O–W vibrations (Fig. S4)[17]. These observations confirm that the TbPOM framework was retained after the exfoliation–restacking process. In addition, absorption bands at 1387 and 1353 cm⁻¹, characteristic of nitrate species, were also detected, suggesting that a portion of the nitrate ions remained in the sample. However, no basal reflections attributable to NO₃⁻@Mg₂Al-LDHs were observed in the P-XRD pattern, indicating that the residual nitrate species do not contribute significantly to the formation of the predominant layered structure. To clarify the origin of the coexistence of the Form-1 and Form-2 structures, the thermal evolution of TbPOM@Mg₂Al-LDHs-ER was investigated by annealing treatment. The TG–DTA profiles are shown in Fig. 3c and Fig.

S6. TbPOM@Mg₂Al-LDHs-ER exhibited a two-step weight loss upon heating. The first weight-loss process is attributed to the removal of interlayer water molecules, whereas the second corresponds to the collapse of the LDH layered structure accompanied by thermal decomposition. In particular, a gradual weight loss was observed below approximately 400 K, indicating that dehydration of the interlayer galleries was the dominant process in this temperature range. To examine the influence of interlayer water on the orientation of TbPOM, the sample was annealed at 353, 363, and 393 K for one week, and the resulting structural changes were monitored by P-XRD. The evolution of the diffraction patterns during annealing is shown in Fig. 3d. As the annealing treatment progressed, the diffraction peak at 2θ = 4.20°, assigned to the Form-2 phase, gradually decreased in intensity while exhibiting almost no change in peak position. In contrast, the reflections corresponding to the Form-1 phase showed a marked increase in intensity. Notably, higher-order reflections of the Form-1 phase, which were barely discernible in the as-prepared sample, became clearly visible after annealing. These results indicate that thermal treatment significantly improves the stacking order and crystallinity of the Form-1 phase (Fig. 3b,d). Furthermore, the diffraction peaks assigned to the Form-1 phase

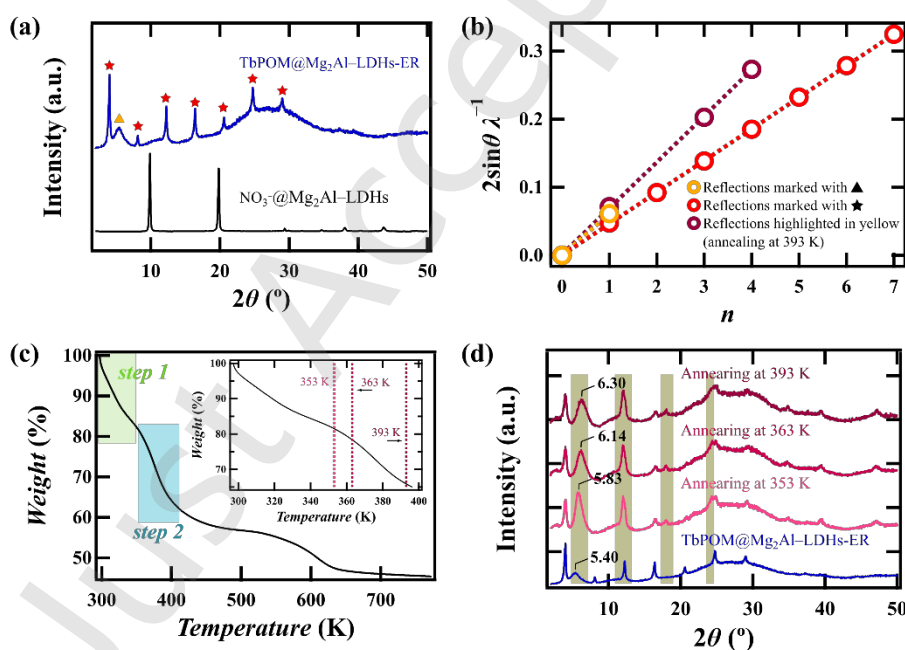


Fig. 3 Structural characterization and thermal evolution of TbPOM@Mg₂Al-LDHs-ER. (a) P-XRD patterns of NO₃⁻@Mg₂Al-LDHs and TbPOM@Mg₂Al-LDHs-ER. (b) Bragg plots of the reflections marked with ▲ and ★ in (a), and of the annealed Form-1 phase highlighted as yellow in (d). The corresponding interlayer spacings were 1.64, 2.16, and 1.48 nm, respectively. The second-order reflection of the annealed Form-1 phase was excluded from the fitting because of overlap with the second-order reflection of Form-2. Nevertheless, the remaining first-, third-, and fourth-order reflections showed excellent linearity ($R^2 > 0.999$), supporting the reliability of the derived interlayer spacing of 1.48 nm. (c) TG curve of TbPOM@Mg₂Al-LDHs-ER, showing two distinct weight-loss steps (Steps 1 and 2) in the low-temperature region. Vertical dashed lines indicate the annealing temperatures (353, 363, and 393 K). (d) P-XRD patterns after annealing at 353, 363, and 393 K for one week. Reflections highlighted in yellow correspond to the annealed Form-1 phase.

continuously shifted toward higher diffraction angles with increasing annealing temperature, reaching $2\theta = 6.30^\circ$ after annealing at 393 K. The corresponding interlayer spacing decreased to 1.48 nm, indicating contraction of the interlayer galleries upon dehydration. Such gallery contraction is expected to enhance the interaction between the intercalated TbPOM clusters and the positively charged LDH host layers. Notably, the Form-2 reflection exhibited little change in peak position throughout the annealing process and decreased only in intensity. This behavior suggests that the Form-2 structure does not undergo continuous contraction during dehydration but instead becomes progressively destabilized. The orientation and stability of guest species intercalated within LDH interlayers are known to depend strongly on both the amount of interlayer water and the nature of host-guest interactions, and several studies have reported changes in guest orientation induced by thermal dehydration [40,47]. Kooli and co-workers investigated the intercalation of benzoate and terephthalate anions into Mg-Al LDHs with various layer charge densities ($\text{Al/Mg} = 1\text{--}5$) and demonstrated that both the layer charge density of the host LDHs and the water content within the interlayer galleries significantly influence the orientation of the guest molecules [40]. In particular, high water content was found to favor a vertical orientation of terephthalate anions relative to the hydroxide layers. Furthermore, thermal annealing induced a structural transformation from the vertical orientation to a parallel orientation as a result of dehydration. Similar dehydration-induced orientation changes have also been reported for Dawson-type polyoxometalates intercalated into LDHs. Yun and Pinnavaia observed that thermal dehydration reduced the interlayer spacing of Dawson-POM/LDH hybrids and proposed a reorientation of the Dawson anions from an end-on arrangement to a more horizontal configuration within the interlayer galleries [41].

Based on these findings, the Form-2 structure generated by the exfoliation-restacking process is likely a metastable phase stabilized by interlayer water molecules. The disappearance of Form-2 upon annealing suggests that the hydration environment plays a critical role in maintaining this orientation state. In contrast, the Form-1 phase became dominant after annealing, indicating that direct electrostatic interactions between TbPOM and the LDH host layers become increasingly important under dehydrated conditions. Based on the structural model shown in Fig. 1, the Form-1 orientation is expected to provide a larger contact area between the TbPOM cluster and the hydroxide layers than the Form-2 orientation. Consequently, stronger host-guest interactions may be achieved in the Form-1 arrangement, rendering this structure apparently more stable after dehydration. This interpretation is consistent with previous studies demonstrating that the arrangement of interlayer guests is governed by a balance between hydration effects and host-guest interactions [24]. These results suggest that the orientation of TbPOM within LDH interlayers is influenced not only by the intercalation process itself but also by the presence of interlayer water. Interlayer water therefore acts as a key factor governing the relative stability of the Form-1 and Form-2 structures and plays a crucial role in controlling the molecular orientation of TbPOM in LDH hosts.

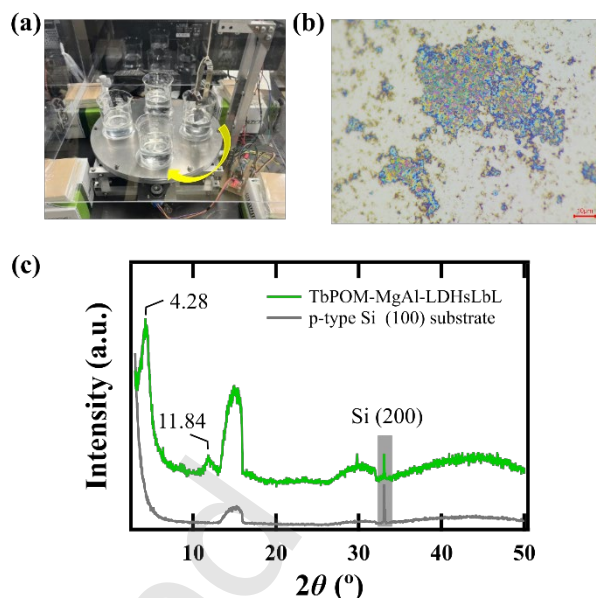


Fig. 4 Fabrication and characterization of TbPOM@Mg₂Al-LDHs-LbL thin films prepared by the layer-by-layer (LbL) method. (a) Photograph of the homemade automated LbL deposition system used for the alternate immersion of the substrate into an LDH nanosheet dispersion and a TbPOM aqueous solution. (b) Optical microscope image of the resulting TbPOM@Mg₂Al-LDHs-LbL film deposited on a p-Si (100) substrate. Scale bar = 10 μm . (c) P-XRD patterns of TbPOM@Mg₂Al-LDHs-LbL and the p-Si (100) substrate.

3.3. Layer-by-layer (LbL) method

Next, TbPOM@Mg₂Al-LDHs-LbL thin films were fabricated by the layer-by-layer (LbL) method using a dispersion of exfoliated Mg₂Al-LDH nanosheets in formamide and an aqueous solution of TbPOM. One deposition cycle consisted of immersion of the substrate in the LDH nanosheet dispersion (20 min), rinsing with deionized water (5 min), immersion in the TbPOM solution (10 min), and rinsing with deionized water (5 min). This cycle was repeated 100 times (Fig. 4a). The surface morphology of the resulting film is shown in Fig. 4b. TbPOM@Mg₂Al-LDHs-LbL did not form a continuous film uniformly covering the Si substrate surface but was observed as partially deposited island-like domains. In addition, several hexagonal plate-like particles were observed, indicating local aggregation and deposition of LDH nanosheets. Because the LbL sample was obtained as a thin film with a relatively small amount of deposited material on the Si substrate, conventional FT-IR characterization comparable to that performed for the powder samples was not feasible. The P-XRD pattern of TbPOM@Mg₂Al-LDHs-LbL is shown in Fig. 4c. In addition to the diffraction peak originating from the p-Si (100) substrate, a broad diffraction peak was observed at approximately $2\theta = 4.28^\circ$. Analysis based on Bragg's law yielded an interlayer spacing of 2.06 nm, which agrees with the value expected for the Form-2 orientation of TbPOM within the LDH interlayer galleries [33]. A weak diffraction peak was also observed at approximately $2\theta = 11.84^\circ$. This diffraction angle is close to the basal reflection characteristic of carbonate-intercalated Mg₂Al-LDHs. Because the LbL process involves repeated immersion and rinsing steps in aqueous media over an extended period, carbonate species originating from atmospheric CO₂ may have been partially incorporated into the LDH interlayers.

Therefore, the film is considered to consist predominantly of the Form-2 TbPOM-intercalated phase together with a minor carbonate-containing LDH phase.

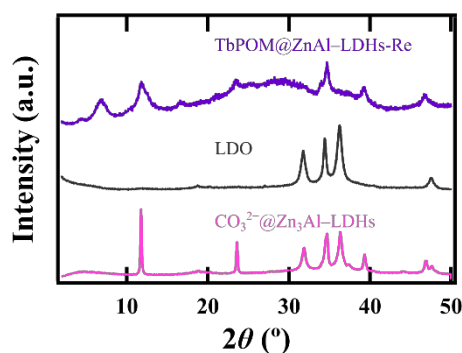


Fig. 5 P-XRD patterns of $\text{CO}_3^{2-}@Zn_3Al$ -LDHs, layered double oxide (LDO), and TbPOM@ZnAl-LDHs-Re prepared by the reconstruction method.

Interestingly, whereas both Form-1 and Form-2 structures were observed for TbPOM@Mg₂Al-LDHs-ER prepared by the exfoliation–restacking method, only the diffraction peak corresponding to the Form-2 structure was detected for TbPOM@Mg₂Al-LDHs-LbL. This result suggests that the structural environment generated during the LbL process favors the formation of the Form-2 structure. Because assembly proceeds sequentially between LDH nanosheets immobilized on the substrate surface, the host–guest assembly pathway differs substantially from that of the exfoliation–restacking method, which may contribute to the observed orientation selectivity. As discussed in the previous section, the Form-2 structure generated by the exfoliation–restacking method gradually disappeared upon annealing, whereas the Form-1 structure became dominant. These observations suggest that the relative stability of the Form-1 and Form-2 structures is strongly influenced by the hydration state of the interlayer galleries, with Form-2 being preferentially stabilized under hydrated conditions. Indeed, the orientation and stability of guest species intercalated within LDH interlayers have been reported to depend strongly on both the amount of interlayer water and the host–guest interactions, and dehydration can induce

substantial changes in guest orientation [40,41,47]. In contrast, although the IE process is also conducted in an aqueous medium, TbPOM is incorporated into a pre-existing LDH interlayer through ion exchange, suggesting that the hydration state and structural environment of the interlayer during guest incorporation, rather than the aqueous reaction medium itself, are important for determining the TbPOM orientation. Because the LbL process involves the sequential assembly of single LDH nanosheets in aqueous solution over an extended period, a relatively hydrated interlayer environment is expected during film formation. Under such conditions, stabilization by interlayer water molecules is expected to favor the selective formation of the Form-2 structure. In contrast, considering the annealing-induced transition from Form-2 to Form-1, the Form-2 phase likely becomes destabilized upon dehydration and transforms into the Form-1 structure, which can establish stronger host–guest interactions with the LDH layers. These results demonstrate that the orientation of TbPOM within LDH interlayers is governed not only by the composition of the host LDHs but also by the intercalation process and hydration environment. The LbL method therefore represents a promising strategy for selectively generating the Form-2 orientation and controlling the molecular arrangement of TbPOM within LDH-based architectures.

3.4. Reconstruction (Re) method

Finally, the intercalation of TbPOM into LDHs via the reconstruction method (memory effect) was investigated. $\text{CO}_3^{2-}@Zn_3Al$ -LDHs was employed as the precursor and calcined at 500 °C to obtain ZnAl layered double oxide (ZnAl-LDO). Subsequently, reconstruction was carried out in an aqueous solution containing TbPOM in an attempt to restore the LDH structure while simultaneously intercalating TbPOM into the interlayer galleries. The P-XRD patterns are shown in Fig. 5. For the precursor $\text{CO}_3^{2-}@Zn_3Al$ -LDHs, a basal reflection attributable to interlayer carbonate ions was observed at $2\theta = 11.76^\circ$. After calcination, this reflection disappeared and was replaced by broad diffraction features in the range of $2\theta = 30\text{--}40^\circ$, characteristic of mixed metal oxide phases. These results indicate that the layered structure of the LDHs collapsed during calcination and was transformed into an oxide phase.

Table 1 Summary of TbPOM orientations obtained by various intercalation methods.

Method	Host LDHs	Orientation	d-spacing / nm	Remarks
IE	Mg ₂ Al	Form-1	1.45	partial ion exchange
ER	Mg ₂ Al	Form-1 + Form-2	1.64, 2.16	coexistence of Form-1 and Form-2
ER + annealing	Mg ₂ Al	Predominantly Form-1	1.48	enhanced Form-1 crystallinity after dehydration
LbL	Mg ₂ Al	Form-2	2.06	thin film on Si substrate
Re	Zn ₃ Al	Predominantly Form-1	-	minor Form-2 and LDO residue

For the sample reconstructed in the presence of TbPOM, several relatively broad diffraction features were observed in the low-angle region, including those at approximately $2\theta = 6.77, 11.79$, and 16.59° . Because of the relatively low crystallinity of the reconstructed sample, these reflections

cannot be unambiguously indexed as a single basal-reflection series. In particular, the reflection at 11.79° is very close to the basal reflection of the $\text{CO}_3^{2-}@Zn_3Al$ -LDH precursor (11.76°), and therefore a contribution from a carbonate-containing LDH phase cannot be excluded.

Nevertheless, the overall diffraction pattern is consistent with the predominant formation of the Form-1 structure. A weak reflection that may be attributed to the Form-2 structure was also observed in the low-angle region, suggesting the possible coexistence of a minor Form-2 component. In addition, characteristic absorption bands originating from TbPOM were observed in the FT-IR spectrum, further confirming the presence of TbPOM in the reconstructed sample (Fig. S5). On the other hand, diffraction peaks attributable to the mixed metal oxide phase remained at $2\theta = 34.66$ and 39.13° , suggesting that a portion of the ZnAl-LDO phase remained unreacted even after the reconstruction process. Thus, although the limited crystallinity of the reconstructed sample prevents an unambiguous structural assignment based solely on the P-XRD pattern, the present results are consistent with the predominant formation of the Form-1 structure, together with minor secondary phases. In contrast to the previous report by Hu et al. [33], the reconstruction method employed in the present study predominantly yielded the Form-1 structure rather than the Form-2 structure, despite both studies utilizing ZnAl-based LDH systems. Although direct comparison is complicated by differences in the Zn/Al ratio and, consequently, the layer charge density of the host LDHs, the present results suggest that the orientation of TbPOM cannot be attributed solely to the metal composition or layer charge characteristics of the host layers. Instead, additional factors associated with the intercalation pathway and local interlayer environment may also contribute to determining the preferred orientation.

As discussed above, the ion-exchange method and the annealed exfoliation–restacking product preferentially produced the Form-1 structure, whereas the reconstruction product exhibited a diffraction pattern consistent with predominantly Form-1. In contrast, Form-2 structure was mainly observed in the as-prepared ER and LbL samples, both of which were generated under conditions expected to provide a highly hydrated interlayer environment. Based on these observations, it is suggested that, during the reconstruction process, direct host–guest interactions between TbPOM and the LDH layers become dominant as the layered structure is regenerated from the LDO precursor, leading to the preferential formation of the Form-1 structure. Taken together, these results suggest that the orientation of TbPOM cannot be fully explained by the composition of the host LDHs alone and may be influenced by both the intercalation process and the interlayer environment. The preferred structures obtained by the different intercalation routes are summarized in Table 1, highlighting the intercalation route as a key parameter controlling the orientation of TbPOM in LDH hosts.

4. Conclusion

In this study, four different intercalation methods, namely ion exchange (IE), exfoliation–restacking (ER), layer-by-layer assembly (LbL), and reconstruction (Re), were investigated to control the orientation of a TbPOM within LDH interlayers. The IE method predominantly yielded a structure corresponding to the Form-1 model in MgAl-LDHs. In contrast, both Form-1 and Form-2 structures were observed in the ER product, indicating that multiple orientation states can be generated depending on the intercalation route. Annealing experiments further revealed that the Form-2 structure gradually disappeared

upon dehydration, whereas the Form-1 structure became dominant. These observations suggest that the relative stability of the Form-1 and Form-2 structures is strongly influenced by the hydration state of the interlayer galleries. Notably, the LbL method selectively produced the Form-2 structure, whereas the reconstruction method using a ZnAl-based host predominantly yielded the Form-1 structure. Although direct comparison with previous studies is complicated by differences in host composition and layer charge density, these results suggest that the orientation of TbPOM cannot be explained solely by the composition of the host LDHs and may also be influenced by the intercalation pathway and local interlayer environment.

Taken together, the present results demonstrate that the intercalation route is an important parameter influencing the orientation of TbPOM within LDH hosts. However, because different LDH host compositions and precursor interlayer anions were used for the four intercalation methods, the effects of the intercalation route cannot be completely separated from those of the host composition and precursor structure. The ER and LbL results further suggest that interlayer water plays a significant role in determining the relative stability of the Form-1 and Form-2 structures. The insights gained in this study provide a useful framework for understanding orientation formation in POM-LDH hybrid systems and offer a new strategy for controlling the arrangement of polyoxometalates in layered materials. This route-dependent orientation control may contribute to the rational design of molecular-based functional materials that exploit the unique polarization-switching functionality of single-molecule dielectrics.

Electronic Supplementary Material: Supplementary material (additional ^{31}P -NMR, XRD patterns, FT-IR spectra, and TG analyses) is available in the online version of this article at <https://doi.org/10.26599/POM.2026.9140160>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work. Author Ryo Tsunashima is the editorial board member of this journal, but he is not involved in the peer-review or decision of this article.

Author contribution statement

Masaru Fujibayashi: Conceptualization, Methodology, Formal analysis, Supervision, Project administration, Writing – original draft, Writing – review & editing. Yuta Kawamura: Investigation, Data curation, Formal analysis. Sadafumi Nishihara: Conceptualization, Validation, Writing – review & editing. Chang-Gen Lin: Conceptualization, Validation, Writing – review & editing. Yu-Fei Song: Conceptualization, Validation, Writing – review & editing.

Ryo Tsunashima: Conceptualization, Supervision, Funding acquisition, Writing – review & editing. All authors have read and agreed to the published version of the manuscript.

Use of AI statement

During the preparation of this manuscript, the authors used ChatGPT (OpenAI) for English language editing and improvement of readability. The authors reviewed and edited all AI-generated content and take full responsibility for the final manuscript.

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Author biography



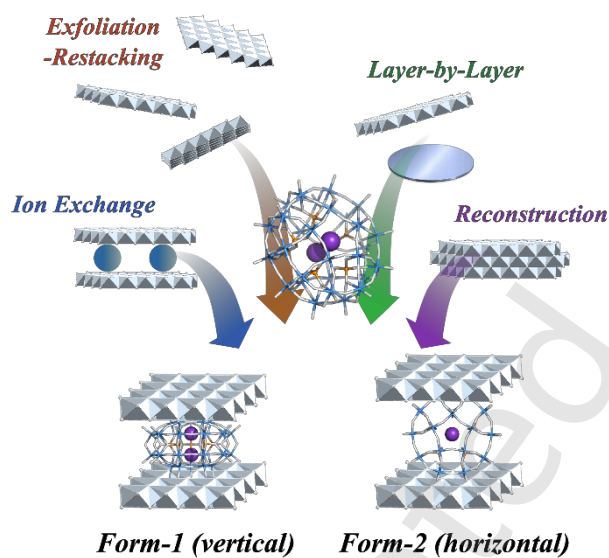
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Just Accepted

Graphical abstract



Intercalation route governs molecular orientation, while interlayer dehydration drives the transition from Form-2 to Form-1 in TbPOM-LDH hybrids.

Electronic Supplementary Material

Intercalation route-dependent orientation of a Tb³⁺-encapsulated Preyssler-type polyoxometalate in layered double hydroxides

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5. Thermogravimetric and differential thermal analysis (TG-DTA)

Just Accepted

1. Synthesis of Preyssler-type Polyoxometalates

1.1. Synthesis of $K_{12.5}Na_{1.5}[Na^+@P_5W_{30}O_{110}]\cdot nH_2O$

$K_{12.5}Na_{1.5}[Na^+@P_5W_{30}O_{110}]\cdot nH_2O$ was synthesized according to the previously reported method [1].

Sodium tungstate (33 g) was dissolved in water (30 mL), followed by the addition of phosphoric acid (26.5 mL). The resulting solution was transferred into a Teflon-lined autoclave and heated at 120 °C for 24 h. After cooling to room temperature, saturated KCl solution (15 mL) was added to precipitate the product. The precipitate was collected, washed with 2 M potassium acetate solution and methanol, and recrystallized from hot water.

1.2. Synthesis of $K_{12}[Tb^{3+}@P_5W_{30}O_{110}]\cdot nH_2O$

$K_{12}[Tb^{3+}@P_5W_{30}O_{110}]\cdot nH_2O$ was synthesized according to a previously reported procedure [1,2]. $K_{12.5}Na_{1.5}[Na^+@P_5W_{30}O_{110}]\cdot nH_2O$ (1.0 g) was dissolved in water (12 mL). $Tb(NO_3)_3$ (110 mg) dissolved in water (3 mL) was added dropwise while maintaining the nitric acid concentration at 1 M. The solution was sealed in a Teflon-lined autoclave and heated at 180 °C for 72 h. After cooling, KCl (0.4 g) was added to remove impurities. The filtrate was subsequently treated with KCl (3.6 g) to precipitate. The resulting precipitate was washed with methanol and recrystallized from water.

2. ^{31}P -NMR spectra of Preyssler-type POMs

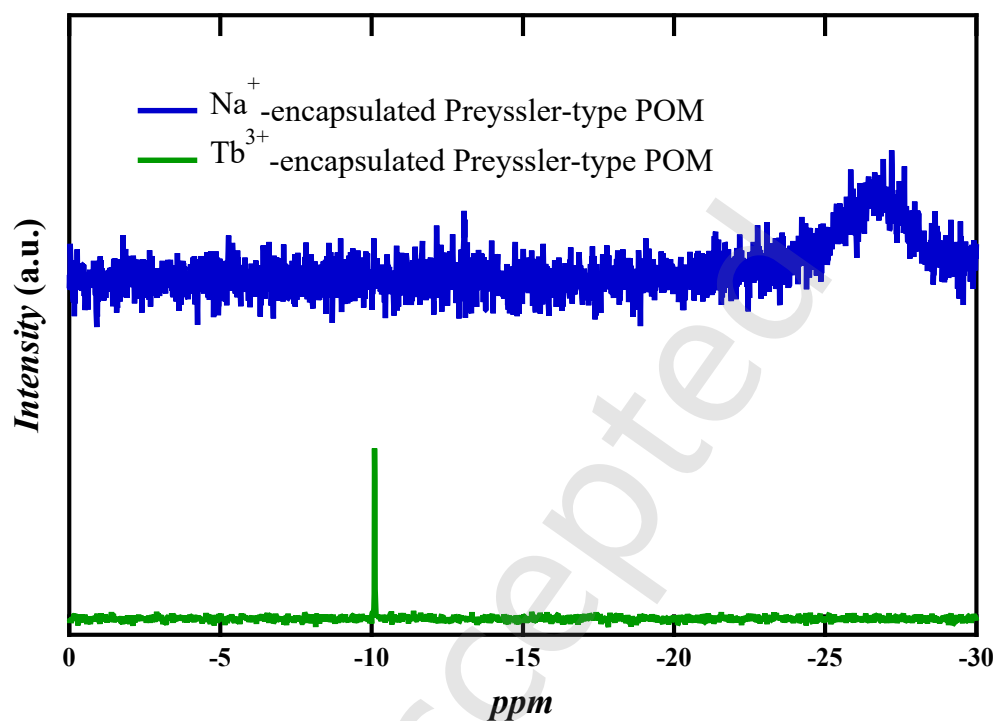


Fig. S1 ^{31}P -NMR spectra of Preyssler-type POMs.

3. Powder XRD pattern of POM@LDHs prepared by ion-exchange method

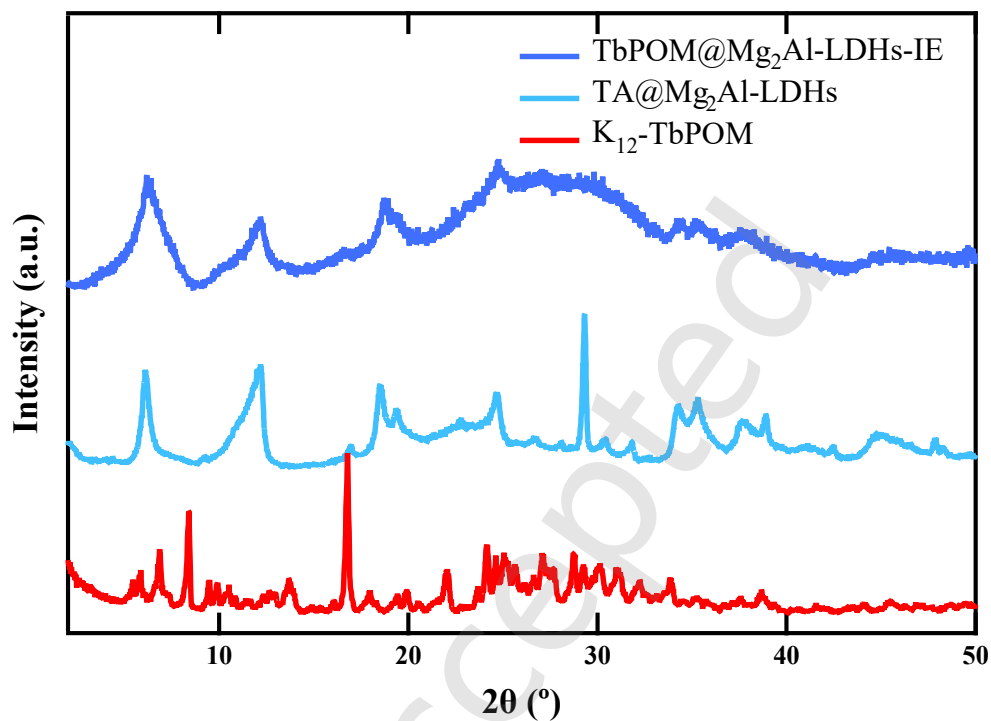


Fig. S2 Powder XRD patterns of samples prepared by ion-exchange method.

4. IR spectra of TbPOM@LDHs sample

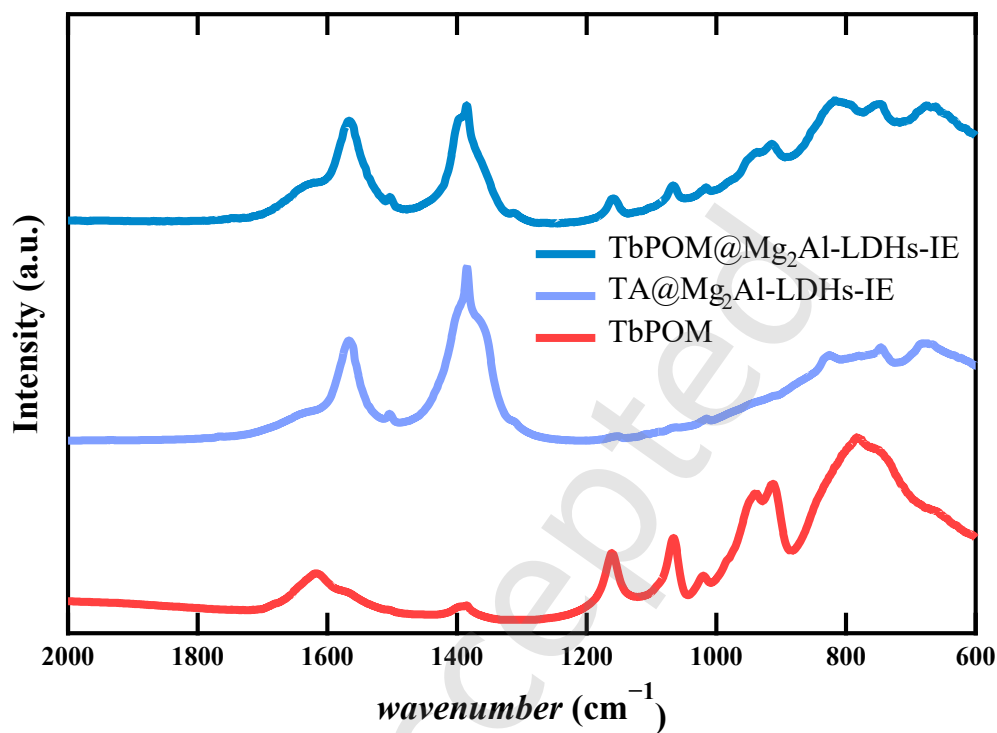


Fig. S3 FT-IR spectra of samples prepared by ion-exchange method.

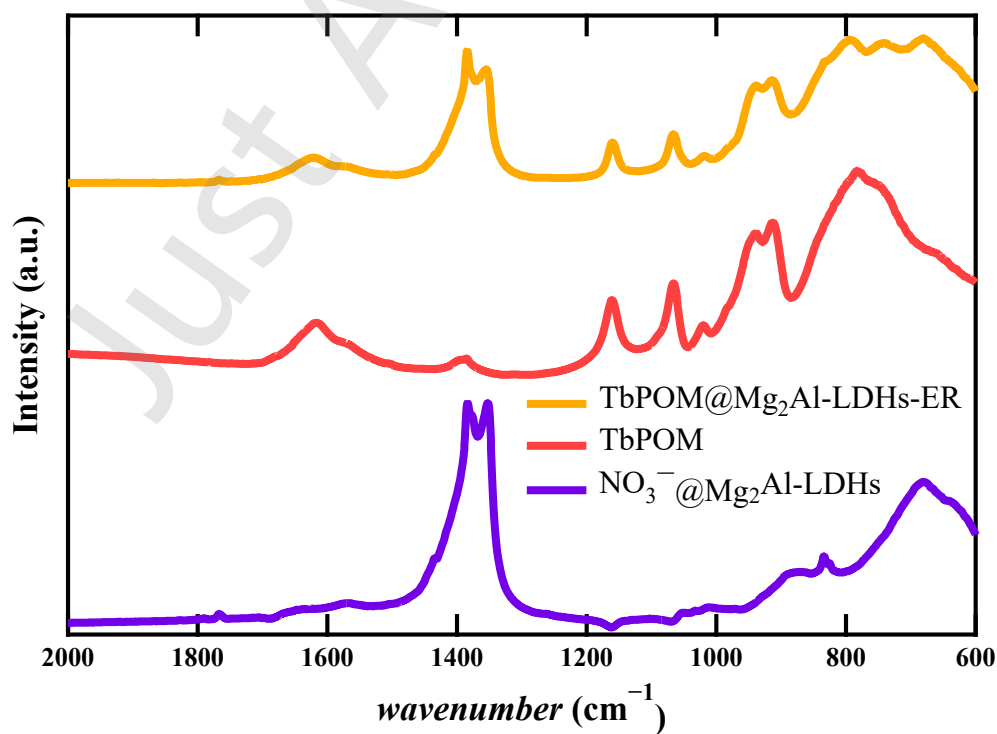


Fig. S4 FT-IR spectra of samples prepared by exfoliation-restacking method.

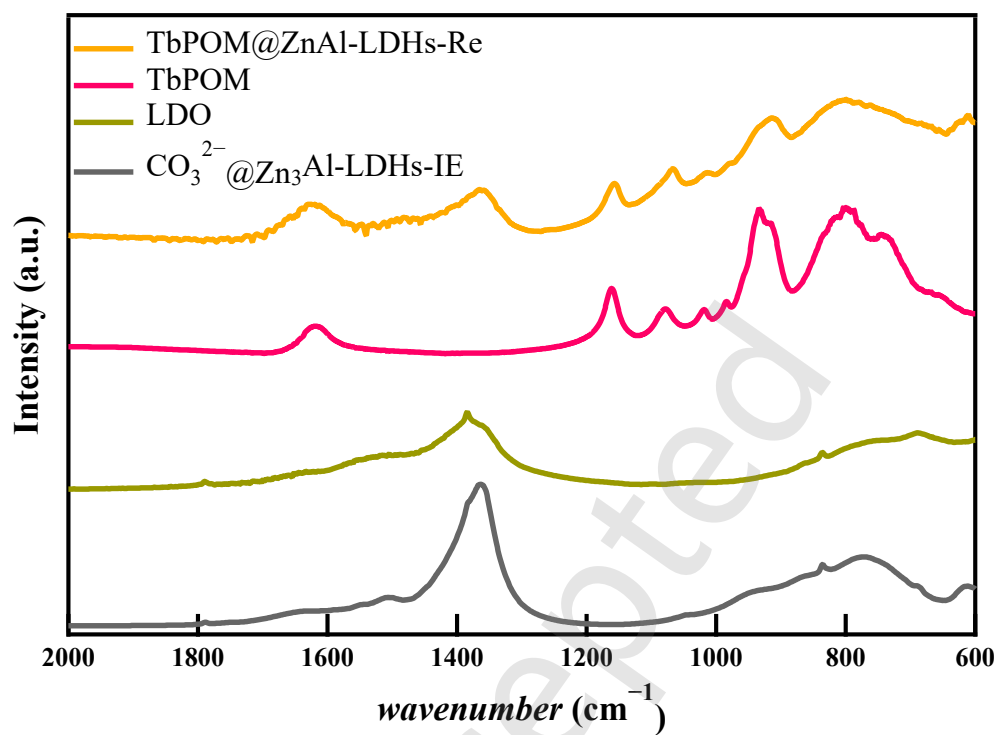


Fig. S5 FT-IR spectra of samples prepared by reconstruction method.

5. Thermogravimetric and differential thermal analysis (TG-DTA)

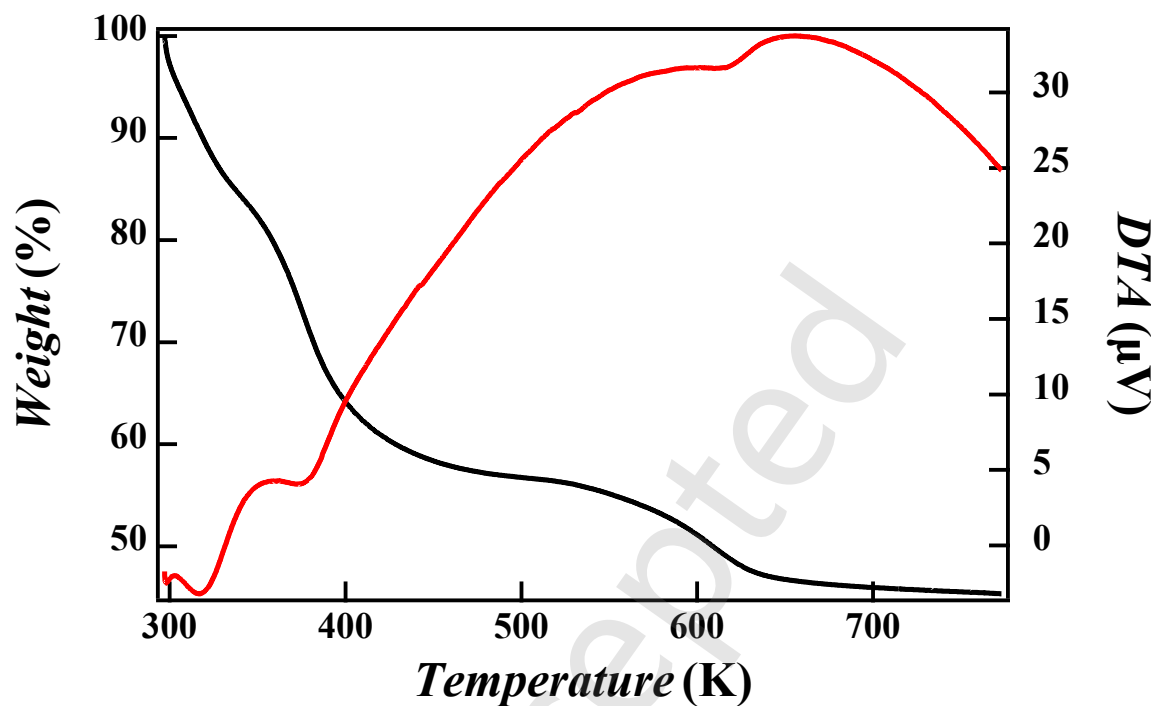


Fig. S6 TG-DTA plots of samples prepared by exfoliation-restacking method.

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