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Failure-experiment-supported optimization of poorly reproducible synthetic conditions for novel lanthanide metal-organic frameworks with two-dimensional secondary building units

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The determination of synthetic conditions for obtaining novel crystalline reticular materials, such as metal–organic frameworks (MOFs) and covalent organic frameworks (COFs), has frequently been based on trial-and-error methods rather than precise reaction design. While a machine learning technique seems promising to optimize synthetic conditions for novel reticular materials, no previous research has been carried out using machine learning methods to explore conditions for the preparation of undiscovered MOFs and COFs. In this work, a series of novel MOFs containing lanthanide double-layer-based secondary building units (KGF-3) was synthesized with the assistance of machine learning. In the initial screening experiments, it was difficult to isolate pure KGF-3, and the reproducibility of the synthesis was problematic because impurity phases were frequently obtained under the same synthetic conditions. Thus, the synthetic conditions were successfully optimized by extracting the dominant factors for the synthesis of KGF-3 using two machine-learning techniques. Cluster analysis was used to classify the obtained PXRD patterns of the products and to decide automatically whether the experiments were successful or had failed. Decision tree analysis was used to visualize the experimental results, with the factors that mainly affected the synthetic reproducibility being extracted. This study is the first example of applying machine learning to the search for synthetic conditions for novel MOFs. Water adsorption isotherms revealed that KGF-3 possesses unique hydrophilic pores, while impedance measurements demonstrated good proton conductivities ($\sigma = 5.2 \times 10^{-4} \text{ S cm}^{-1}$ for KGF-3(Y)) at a high temperature (363 K) and high relative humidity (95% RH).

Introduction

Crystalline reticular materials, such as metal–organic frameworks (MOFs) and covalent organic frameworks (COFs), have been widely studied as promising environmental energy materials.^{1–5} Crystallization of these materials has been mainly achieved by solvothermal or hydrothermal synthesis in sealed reaction vessels.^{3, 6} Unfortunately, the discovery of new materials by such synthetic methods often requires patient trial and error rather than precise reaction design. It is therefore desirable to understand the crystallization mechanism of reticular materials under solvothermal conditions and thereby develop a rational approach for selective crystallization of target compounds.^{7–10} Although many in situ measurements have been carried out to understand the crystallization process in a sealed reaction vessel, it remains a challenge to identify the relationship between the reaction parameters and outcome of a reaction. Facile and reliable techniques to understand and control the target reaction – which can be applicable during the screening of a synthetic process – are therefore necessary to efficiently discover novel crystalline reticular materials.

Machine learning has recently attracted attention as an efficient exploration tool, especially in the area of materials synthesis.^{11–13} In particular, several attempts using machine

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Electronic Supplementary Information (ESI) available: General information; Table S1; Cluster analysis; Figure S1; Decision tree analysis; Figure S2; Evaluation of the lanthanide nitrate salts purchased from various companies; Figures S3 and S4; Tables S2 and S3; Optimized synthetic conditions using various lanthanide metals; Figure S5; Elemental analysis; Table S4; Figures S6–S9; Proton conductivity measurements; Figures S10 and S11; ESI References.

learning to search for crystallization conditions of materials have been reported, and it is now beginning to be regarded as a powerful method.^{14–21} While the application of machine learning techniques to predict crystallization conditions for nanoporous materials seems promising, its application in the exploration of novel materials remains limited, and no studies thus far have introduced machine learning as a tool for the preparation of unknown MOFs. This is partially due to a lack of training data; open databases for the exploration of unknown MOFs are limited and the generation of such training data is expensive.²⁰ In addition, during the exploration of novel MOFs by screening syntheses, the compounds obtained in failure experiments are generally present as complex mixtures. Therefore, facile techniques to describe such crude mixtures in a format suitable for analysis by machine learning is necessary. In this work, we focus on lanthanide-based MOFs (Ln-MOFs) in which lanthanide ions or clusters are linked by organic linkers. Ln-MOFs are promising materials for a wide range of applications, such as proton conductors and various porous, luminescent, and magnetic materials.^{22–26} Furthermore, lanthanides have been previously reported to form giant clusters under solvothermal synthetic conditions,^{27–31} and so multiple or novel properties are expected to arise due to synergism when such large clusters or more highly dimensional infinite structures are incorporated as secondary building units (SBUs) in the skeletons of MOFs.^{1, 3, 32, 33} However, since the formation of lanthanide clusters is easily affected by the reaction conditions, the rational design and syntheses of MOFs containing Ln-cluster-based giant or infinite SBUs remains a challenge. In addition, Ln-MOFs are known to exhibit crystal polymorphism due to their flexible coordination nature. It is therefore difficult to selectively synthesize crystal polymorphs, and the preparation of Ln-MOFs frequently suffers from poor reproducibility. A facile and intuitive means to evaluate the factors that predominantly influence reaction outcomes is therefore needed.

We herein report the synthesis of a novel Ln-MOF containing lanthanide-double-layer-based SBUs (KGF-3) assisted by machine learning. This is the first example of applying machine learning to solvothermal synthesis for the exploration of unknown MOFs. The synthetic results are evaluated using both cluster analysis and decision tree analysis. These analyses enable us to determine the optimal conditions for the reproducible synthesis of KGF-3. Figure 1 shows the flow process used to optimize the synthetic conditions using machine-learning techniques. Water adsorption experiments and impedance measurements are also used to analyze the pores and the proton conductivity of the prepared KGF-3.

Experimental

General characterization and analytical methods

See the Supplementary Information for further details.

Figure 1. Schematic representation of the research flow process used to optimize the synthetic conditions by incorporating machine-learning methods.

Synthetic Conditions 1 (Exploratory experiments)

$\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}$, 0.008–0.8 mmol) was dissolved in distilled water (2–200 mM), and 2-hydroxyterephthalic acid (H_2BDC ; 0.008–0.8 mmol) was separately dissolved in *N,N*-dimethylformamide (DMF; 2–200 mM). These two solutions were mixed in a Teflon-lined stainless-steel container (4, 8, 16, 30, or 100 mL) and heated at 145 or 150 °C for 24–80 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was either 5 or 12 h, and the cooling time was either rapid (10 min) or slow (12–80 h).

Synthetic Conditions 2 (Carbonate ion-added synthesis)

Three separate solutions were prepared: $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}, \text{Gd}, \text{Tb}$) was dissolved in distilled water (0.08 mmol, 2.4 mL), H_2BDC was dissolved in DMF (0.08 mmol, 1.6 mL), and Na_2CO_3 was dissolved in distilled water (0–0.036 mmol, 2.0 mL). These three solutions were then mixed in an 8 mL Teflon-lined stainless-steel container and heated at 150 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h.

Synthetic Conditions 3 (Optimized Synthetic Conditions A: Stoichiometric synthesis)

$\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}, \text{or Y}$) was dissolved in distilled water (0.16 mmol, 4.8 mL) and H_2BDC was separately dissolved in DMF (0.048 mmol, 3.2 mL). These two solutions were mixed in a 16 mL Teflon-lined stainless-steel container and heated at 150 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h. The obtained residue was washed with DMF and MeOH (×3 for each solvent).

Synthetic Conditions 4 (Optimized Synthetic Conditions B: Preparation using excess H₂BDC)

$\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}, \text{or Y}$) was dissolved in distilled water (0.16 mmol, 4.8 mL) and H₂BDC was separately dissolved in DMF (0.16 mmol, 3.2 mL). These two solutions were mixed and separated by centrifugation, and the supernatant was placed in a 16 mL Teflon-lined stainless-steel container and heated at 150 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h. The obtained residue was washed with DMF and MeOH (×3 for each solvent).

Synthetic Conditions 5 (Optimized synthetic conditions for KGF-3(Eu, Gd))

Three separate solutions were prepared: $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}, \text{Gd}$) was dissolved in distilled water (0.08 mmol, 2.4 mL), H₂BDC was dissolved in DMF (0.024 mmol, 1.6 mL), and Na₂CO₃ was dissolved in distilled water (0.04 mmol, 2.0 mL). These three solutions were then mixed in an 8 mL Teflon-lined stainless-steel container and heated at 150 °C for 6 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h. The residue was washed with DMF and MeOH (×3 for each solvent).

Synthetic Conditions 6 (Optimized synthetic conditions for KGF-3(Tb))

$\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in distilled water (0.08 mmol, 2.4 mL) and H₂BDC was separately dissolved in DMF (0.024 mmol, 1.6 mL). These two solutions were mixed in an 8 mL Teflon-lined stainless-steel container and heated at 150 °C for 48 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h. The obtained residue was washed with DMF and MeOH (×3 for each solvent).

Preparation of a single crystal of KGF-3(Gd)

Three solutions were prepared separately: $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in distilled water (0.08 mmol, 2.4 mL), H₂BDC was dissolved in DMF (0.024 mmol, 1.6 mL), and Na₂CO₃ was dissolved in distilled water (0.04 mmol, 2.0 mL). These three solutions were then mixed in an 8 mL Teflon-lined stainless-steel container and heated at 150 °C for 6 h. At the end of the heating process, the container was cooled to 30 °C. The heating time was 5 h, and the cooling time was 12 h.

Machine-learning analysis

Cluster analysis was carried out using PDXL 2.8 (Rigaku). Decision tree analysis (Partition) was performed using JMP® Pro14.3, and random forest analysis (Bootstrap Forest) was carried out using JMP® Pro 15.2.1 (SAS Institute Inc., Cary, NC, USA).

Results and discussion

Screening synthesis

Solvothermal synthesis was performed using nitrate hexahydrate salts of lanthanide metal ions ($\text{Ln}^{3+} = \text{Sm}, \text{Eu}, \text{Gd}, \text{and Tb}$) in the presence of terephthalic acid (H₂BDC) in H₂O/DMF. A total of 108 experiments were carried out, with variables including the lanthanide metal ion, the concentration of the metal ion and/or ligand solution, the reaction temperature and time, the cooling time, and the type of reaction vessel (see Synthetic Conditions 1 in the Experimental section). Solid powders were obtained under all conditions, and were characterized by powder X-ray diffractometry (PXRD), where, in some cases, novel phases were observed.

The novel $[\text{Ln}_{10}(\text{BDC})_3(\text{HCOO})_4(\mu_3\text{-OH})_{12}(\mu_5\text{-CO}_3)_4(\text{H}_2\text{O})_2]$ phase, which we refer to as “KGF-3”, was obtained in the presence of various lanthanide ions, although single crystals suitable for crystal structure analysis were obtained only when Gd³⁺ was used as the metal source. Based on the single-crystal X-ray data, KGF-3(Gd) was found to contain five types of non-equivalent Gd³⁺ ions with coordination numbers of eight or nine. Four complexes share ridges with each other to form a chain, which is then connected by another lanthanide ion to form a porous layer (Figure 2a). The two layers are cross-linked by carbonate ions (the origin of the carbonates will be discussed later) to form a double layer, and BDC bridges the layers as pillar molecules, resulting in a three-dimensional pillar-layered structure (Figures 2b–2c). The $\mu_5\text{-CO}_3^{2-}$ coordination mode is common in giant cluster synthesis but is unusual in MOFs (Figure 2d). Moreover, we found that formic acid generated by the decomposition of DMF was also coordinated. Many $\mu\text{-OH}$ groups are aligned on the KGF-3 pore surfaces, and disordered guest molecules (most likely water) are incorporated in the pores, suggesting that the pores are highly hydrophilic in nature.

Figure 2. Crystal structure of KGF-3(Gd). (a) Monolayer with 10 spread-out lanthanide clusters. (b) Double layer connected by carbonate ions. (c) View along the a-axis. (d) Pentagonal pockets showing the connections imparted by carbonate ions. H atoms are omitted for clarity.

Figure 3. Using cluster analysis to classify the acquired PXRD patterns.

Analysis by machine learning techniques

KGF-3 was difficult to isolate, and its preparation suffered from poor reproducibility, with different phases frequently being obtained even under the same synthetic conditions. In addition, a pure KGF-3 phase was not obtained after 108 experimental trials. To optimize the synthetic conditions, we extracted the dominant factors of the reaction using machine-learning techniques. To predict the conditions under which KGF-3 can be obtained more consistently, it was necessary to determine whether or not the reaction was successful using PXRD. However, the products are complex mixtures of different

phases in many cases; hence, assigning each PXRD pattern to an appropriate phase is challenging. A simple method that excluded arbitrariness was therefore required; hence, we classified the obtained patterns using cluster analysis.³⁴ All diffraction patterns were automatically analyzed and successfully classified into six categories, in which the main products were KGF-3 (cluster 1), four reported phases (clusters 2,³⁵ 3,³⁶ 4,³⁷ and 5³⁸), and another unknown phase (cluster 6), as shown in Figures 3 and S1. By examining these results, we revealed that automated classification was consistent with “researcher intuition”, with the exception of only two data points in 108 patterns (see the Cluster Analysis section in the SI).

Figure 4. (a) Visualization of the relationships between the experimental conditions and the products based on decision tree analysis. Ovals represent decision nodes, the pie charts show the product ratios, and the number of experiments is shown in the center of each pie chart; (1), (2), and (3) are branches related to the concentration conditions, the reagent company, and the lanthanide metal, respectively. Branches that are not discussed in the main text have been omitted. The complete version of the decision tree is given in Figure S2. The percentage of each parameter that contributes to the branch is shown. (b) Decision tree analysis. (c) Random forest analysis.

We next turned our attention to extracting the dominant factors responsible for poor reproducibility by employing decision tree analysis, which is considered to be one of the most interpretable machine-learning techniques.^{14, 19, 21} Initially, the experimental data and cluster analysis results were linked together in a text file, after which the data file was analyzed using the decision tree technique, whereby the objective variables were the crystal phases assigned by cluster analysis of the PXRD patterns, and the explanatory variables were the synthetic parameters (see the Decision Tree Analysis section in the SI). The results presented in Figure 4a suggest that the most suitable synthetic conditions for the preparation of KGF-3 are as follows: Ligand solution concentration, 18–22 mM; cooling time, >12 h; and metal salt source, company A. The parameters appearing at the branches in the decision tree were also identified from random forest analysis (Figure 4b–4c). Thus, visualization of the experimental data by decision tree analysis allowed us to understand the synthetic conditions at a glance. The information extracted from the decision tree is summarized as follows. Firstly, it is likely that when the ligand concentration is <18 mM, a product is formed with bridging carbonate ligands (cluster 5) (Figure 4a-(1)), suggesting that carbonate is generated by the decomposition of DMF or through capture from the air.^{39, 40} Secondly, the success or failure of the KGF-3 synthesis was determined by the reagent company employed, with the nitrate provided by company A being most suitable (Figure 4a-(2)). Finally, as shown in Figure 4a-(3), the success rate was 17% on the left branch (Eu) and 45% on the right branch (Gd and Tb), suggesting that the metal ion affects the synthetic process. To determine the synthetic conditions that maximize reproducibility, the extracted dominant factors were verified as follows.

Exploration of the optimized synthetic conditions

In terms of the supply company for the lanthanide nitrate salt, the reagents purchased from company A were superior (Figure S3), exhibiting higher purity (99.95%) compared to those obtained from companies B (99.9%) and C (99.5%). The purities guaranteed by the reagent companies were evaluated based only on the metal ion concentration. To estimate the influence of the purity of the metal source, Tb(NO₃)₃·6H₂O with the highest purity (99.999%), i.e., from company D, was also used, which gave an improved success rate compared to that obtained using Tb(NO₃)₃·6H₂O from company A; the success rate was 20% (7 out of 34 trials) using the Tb source from company A while the success rate increased to 95% using the Tb source from company D (19 out of 20 trials), as shown in Figure S4. The different purities were evaluated by inductively coupled plasma-mass spectrometry, which revealed that the Tb(NO₃)₃·6H₂O obtained from company A contained slightly higher levels of Eu than that from company D (Table S2). Therefore, the preparation of KGF-3 was carried out using lanthanide salts purchased from company D in all of the following experiments.

The results from decision tree analysis also showed that under low concentration conditions, carbonate ions are

captured within the structure (cluster 5). Generally, carbonate ions play important roles as anion templates during the formation of polynuclear lanthanide clusters.^{31, 41–43} In many cases, carbonate ions are generated by decomposition of the precursor and/or uptake of carbon dioxide from the air. Therefore, in the crystal structure of KGF-3, it is likely that the molecules coordinating to five metal ions in a pentagonal pocket (Figure 2d) are carbonate ions. To estimate the effect of these carbonate ions, KGF-3 was synthesized with the addition of sodium carbonate (Synthetic Conditions 2). For Gd and Tb, the formation of the Ln₂(BDC)₃(H₂O)₄ impurity (cluster 2) was suppressed with the addition of carbonate ions. In the case of Eu, Ln₂(BDC)₃(H₂O)₄ (cluster 2) was preferentially synthesized, regardless of whether carbonate ions were added or not (Figure 5). These results suggest that the effect imparted by the carbonate ions depends on the lanthanide metal ion.

Figure 5. PXRD patterns obtained in the presence of sodium carbonate. (a) After the addition of various concentrations of sodium carbonate to Gd. (b) Comparisons with and without the addition of sodium carbonate for Eu, Tb, and Dy.

Conclusions

In summary, we successfully synthesized a series of novel pillar-layered Ln-MOFs (metal-organic frameworks) containing lanthanide double-layer-based secondary building units that we refer to as “KGF-3.” Although it was difficult to isolate KGF-3 in our initial screening experiments due to poor synthetic reproducibility, we successfully extracted the dominant factors for KGF-3 synthesis by evaluating both failure and success using machine-learning techniques. The extracted chemical insight suggests that the lanthanide ion affects the synthetic results, and systematic synthetic experiments demonstrated the effect of the ionic radius of the metal ion. This method is a useful tool for preparing new MOFs and related compounds, such as coordination polymers and covalent organic frameworks that suffer from poor synthetic reproducibility. Through the application of this method, the exploration of novel MOFs and coordination polymers, for which it is challenging to obtain highly crystalline samples, is currently underway, and the results will be presented in due course.

Author Contributions

Y. Kitamura and E. T. carried out the syntheses. D. T. conceived the experiments and supervised the project. Z. Z. and H. Y. measured the proton conductivities and H. Y. carried out the H₂O adsorption experiments. T. I. and H. U. acquired the Raman data and M. T. acquired the ICP-MS data. Y. Kamakura performed the single crystal X-ray diffraction analysis. A. I. discussed the machine-learning method.

Conflicts of interest

There are no conflicts to declare.

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