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# Size-Selective Crystallization of Homochiral Camphorate Metal–Organic Frameworks for Lanthanide Separation

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Supporting Information

**ABSTRACT:** Lanthanides (Ln) are a group of important elements usually found in nature as mixtures. Their separation is essential for technological applications but is made challenging by their subtly different properties. Here we report that crystallization of homochiral camphorate metal–organic frameworks (MOFs) is highly sensitive to ionic radii of lanthanides and can be used to selectively crystallize a lanthanide element into predesigned MOFs. Two series of camphorate MOFs were synthesized with acetate (Type 1 with early lanthanides La–Dy) or formate (Type 2 with late lanthanides Tb–Lu and Y) as the auxiliary ligand, respectively. The Ln coordination environment in each type exhibits selectivity for $Ln^{3+}$ of different sizes, which could form the basis for a new cost-effective method for Ln separation.

Because of unique optical and magnetic properties, lanthanides are essential elements in modern technology and are widely used in applications ranging from electronics and lasers to powerful magnets. Due to chemical similarity, their minerals usually coexist in nature. As a result, the development of efficient separation methods is the first step to achieve cost-effective applications of lanthanides. The early separation used fractional crystallization, which was tedious, not because of the method itself, but because of the small solubility difference among various salts such as carbonates or oxalates, which necessitates many cycles of recrystallization. Currently, solvent extraction and ion chromatography, based on the difference in formation constant ($K_f$) of lanthanide molecular complexes, have been established as the methods of choice for the separation of lanthanides. Still, newer, more environmentally friendly and cost-effective methods are desirable.[1]

With the recent advance in solid-state coordination chemistry,[2] especially metal–organic frameworks (MOFs),[3] an opportunity has risen to integrate the above two different concepts (difference in solubility products, $K_{sp}$, for fractional crystallization, and difference in the formation constant of metal complexes, $K_f$, in solvent extraction or chromatography) into a unified MOF-based separation strategy capable of efficient separation of lanthanides. Because MOFs are polymers of metal complexes, it is hypothesized that the effect of a small difference in $K_f$ for a molecular $Ln^{3+}$ complex might be amplified during the MOF crystallization, leading to greater difference in the ability of each $Ln^{3+}$ to form a given MOF. This method, based on selective crystallization of $Ln^{3+}$ ions into MOFs could be made superior to the traditional fractional crystallization based on inorganic salts for which there is a very limited selection in counteranions.

MOFs have been widely studied for their various properties (e.g., porosity, catalytic and optical properties, and chirality[4−6]) and in particular for applications in separation processes such as the separation of small gas molecules, hydrocarbon compounds, inorganic anions, or even bulky organic ions.[7] However, there have been few studies targeted at separating metal ions through selective crystallization,[8] not to mention the separation of lanthanide mixtures, which is challenging for any separation method.

In this work, a low-cost homochiral MOF platform based on inexpensive D-camphoric and formic acids has been developed, which can be used to selectively crystallize or enrich specific lanthanide ions in predesigned MOFs. We show that the concentration of $Ln^{3+}$ ions in a MOF is dependent on the MOF structure type as well as the size of $Ln^{3+}$ ions. Specifically, we found here that larger early Ln ions only crystallize with the larger acetate ligand (as well as D-camphorate) into a MOF structure denoted as Type 1, while smaller late Ln ions only crystallizes with the smaller formate into a MOF structure denoted as Type 2 (Figure 1). Even when two Ln ions (two early $Ln^{3+}$ ions or two late $Ln^{3+}$ ions) can both form the same structure type (alloy-like Type 1 or Type 2 phases), we found that their molar ratio in the MOF is dependent on the ionic radii.

The synthesized 17 Ln–MOFs (plus many alloy-like Ln1 and Ln2 MOFs) fall into two isoreticular structure types,[9] denoted here as **1-Ln** (also called CPM-25 or Type 1, **Ln** = **La**, **Ce**, **Pr**, **Nd**, **Sm**, **Eu**, **Gd**, **Tb**, **Dy**) and **2-Ln** (also called CPM-29 or Type 2, **Ln** = **Tb**, **Dy**, **Ho**, **Er**, **Tm**, **Yb**, **Lu**, **Y**) (Figure 1). From reactions with acetic and D-camphoric acids, the early Ln elements (from **La** to **Gd**) only give Type **1**. With the use of formic and D-camphoric acids, the late Ln elements (from **Ho** to **Lu**) and yttrium only lead to Type 2. Two $Ln^{3+}$ ions that do crystallize into both types with acetate or formate are middle ones, **Tb** and **Dy**, whose ionic radii border those of early and late Ln ions.

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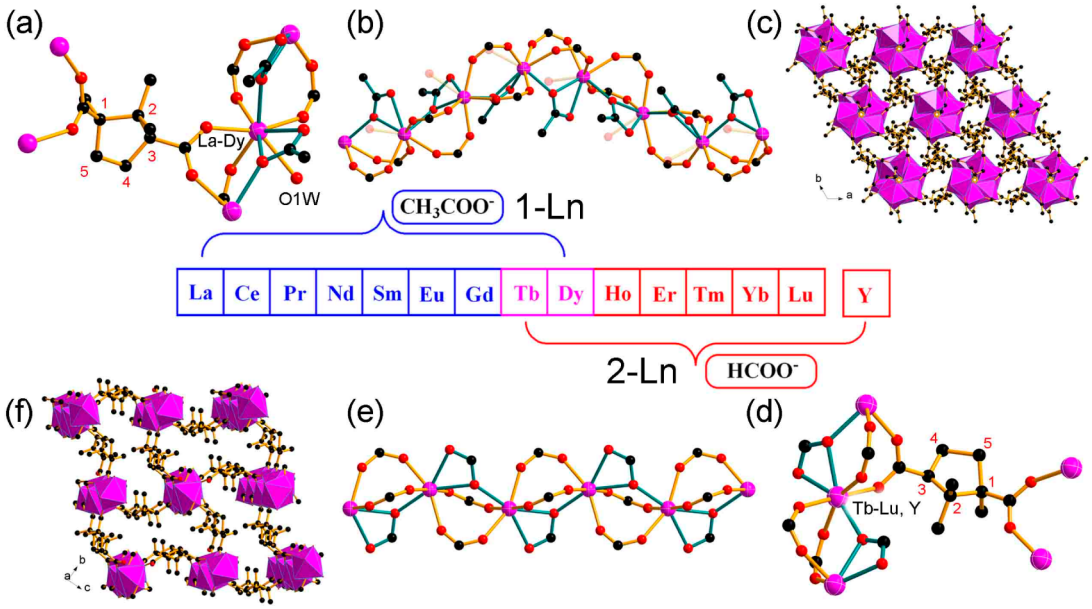


**Figure 1.** Comparison between 1-Ln and 2-Ln. (a) Local coordination environment in **1-Ln**; (b) the inorganic chain in **1-Ln** (water molecules are shown as faded); (c) 3D-framework of **1-Ln** through linkage between chains; (d) local coordination environment in **2-Ln**; (e) the inorganic chain in **2-Ln**; (f) 3D-framework of **2-Ln** through linkage between inorganic chains; (purple: Ln, red: O, black: C, purple polyhedra was defined using Ln as central atom and O as ligand atom.).

Despite many attempts, cross crystallizations (i.e., Type 1 for late $Ln^{3+}$ or Type 2 for early $Ln^{3+}$) have not been achieved, suggesting the intrinsic phase selectivity of this MOF platform (i.e., Type 1 for early $Ln^{3+}$ and Type 2 for late $Ln^{3+}$). Especially interesting is the observation that **Ho** is incapable of crystallizing in **1-Ln**, and yet its neighboring element **Dy** can readily crystallize in **1-Ln**. Similar observation was also found for **Gd** and **Tb**, whose ionic radii differ by only 0.01 Å (Figure S1), which is <0.5% of their Ln-O bond distances, suggesting high sensitivity of a particular MOF structure type to the size of ionic radii.

Typically **1-Ln** were prepared from lanthanide nitrate, D-camphoric acid, and acetic acid in a mixed solvent system containing equal amounts of N,N′-dimethylacetamide (DMA) and water. **2-Ln** were synthesized under similar conditions but with formic acid and N,N′-dimethylformamide (DMF). Although DMA and DMF are known to undergo decomposition to generate acetate and formate, respectively, we were unable to obtain **1-Ln** or **2-Ln** without formic or acetic acid. It is worth noting that the crystallization of **2-Ln** MOFs is fast and occurs within 4 h and that a high recovery yield can be obtained in <6 h. The rate of crystallization is clearly an important factor in separations.

All crystals were suitable for single crystal X-ray diffraction. A summary of crystallographic data is shown in Tables S1 and S2. **1-Ln** crystallize in the chiral space group $P6_5$ with the general formula of $[Ln(D\text{-cam})(CH_3COO)(H_2O)]$ (D-cam = D-camphorate), and **2-Ln** crystallize in chiral space group $P2_12_12_1$ with the formula of $[Ln(D\text{-cam})(HCOO)]$. One notable difference between **1-Ln** and **2-Ln** is that $Ln^{3+}$ ions have different coordination numbers. Each $Ln^{3+}$ in **1-Ln** has one pendant $H_2O$, making it 8-coordinated. In contrast, without $H_2O$, each $Ln^{3+}$ in **2-Ln** is only 7-coordinated (Figure 1a,d). This difference in coordination number correlates with ionic radii with the smaller ions adopting a lower coordination number.

Both structures can be understood as 3D frameworks assembled from parallel inorganic chains with camphorate as the bridging ligands (Figure 1c,f and Figures S2 and S3). Although the chains in **1-Ln** and **2-Ln** have different compositions and configurations, they exhibit similar features. The most notable one is that two adjacent $Ln^{3+}$ ions are bridged by two −COO groups from two camphorate ligands and a monodentate ligand, which is acetate for **1-Ln** and formate for **2-Ln** (Figure 1b,e). This monodentate carboxylate is always chelating to one metal and at the same time with one of its oxygens bridging to the other metal in a $\mu_2$-O manner. Thus, a M—O—M infinite chain is formed by the monodentate ligand. Besides their roles in reinforcing the connection of $Ln^{3+}$ ions already linked together by D-cam ligands, they also serve to render the overall framework neutral, suggesting a key role of acetate or formate in the crystallization process.

Given the above observation that early and late $Ln^{3+}$ ions show clear preference in crystallization with D-cam and acetate or D-cam and formate, respectively, we designed a series of experiments to explore whether such preference for a particular MOF structure type by $Ln^{3+}$ could be utilized for the separation of $Ln^{3+}$ ions. Thus, a mixture of two lanthanide ions (**M1** and **M2**) in 1:1 molar ratio was used to grow MOFs under conditions that could only produce **2-Ln**. M1 is chosen from the early lanthanide metals (La−Gd) that cannot lead to structure **2-Ln** by itself, while M2 is chosen from late lanthanide ions (Tb−Lu and Y) that are known to give structure **2-Ln**. With the addition of camphoric and formic acids, similar hydrothermal method was used for the synthesis. As expected, a number of these combinations lead to **2-Ln** whose purity was confirmed by powder X-ray diffraction (Figure S6).

In the above experiments starting with a mixture of M1 and M2, we were aware of the possibility for M1 to be incorporated into **2-Ln** phase, even though we had repeatedly found that when used alone, M1 could not form the **Ln-2** phase. In fact,

the observation of M1 being incorporated into **Ln-2** phase suggests that the size selective crystallization (into Type 1 or Type 2 when a single $Ln^{3+}$ source is used) may occur at the very first step of the nucleation and that M1 ions are simply unable to form nuclei of the Type 2 phase.

For the purpose of $Ln^{3+}$ separation, it is critical to know to what extent M1 would be incorporated into the **2-Ln** phase. Semiquantitative elemental analysis by energy dispersive X-ray spectroscopy (EDS) was performed on six **2-Ln** samples made from different M1-M2 combinations (Figure S7). The results, given in Figure 2, together with the ionic radius data for the relevant $Ln^{3+}$ ions, show that starting with about equal 1:1 molar ratio of two lanthanides in the mixture, the M1/M2 ratio in the crystalline phase shows large variations with the fraction of M2 in the crystals ranging from 70.5% to 98.0%. In the case of the Nd−Yb combination, a high selectivity for Yb during the crystallization was observed with only the trace amount of Nd observed in the **2-Ln** phase. As a result, a one-step separation of Yb and Nd could be realized by crystallization. This unique and simple separation process for lanthanides shows a great promise for practical applications. When the ionic radius difference between two ions becomes smaller, the selectivity for M2 decreases. Nevertheless, there is in general a clear preference for M2 in the crystals, which can serve as the basis for fractional crystallization.

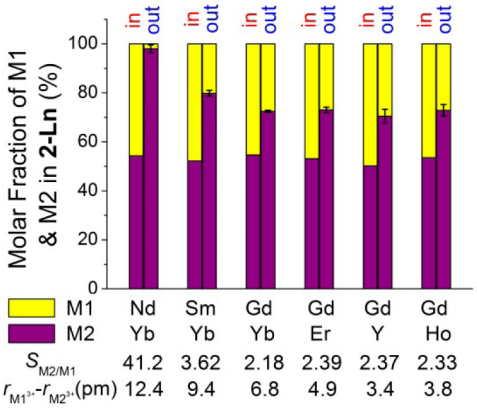


**Figure 2.** Selective crystallization of **2-Ln** (Type 2) from six combinations of an early lanthanide M1 and a late lanthanide M2. "In" and "out" indicate the lanthanide ratio in the original mixed solution and the produced crystals.

In the study discussed above, our separation strategy is based on our recognition that M1 and M2 ions prefer different MOF structures (Type 1 and Type 2, respectively) and that if we design synthetic conditions favoring one structure type (e.g., Type 2), it would result in the selective crystallization of $Ln^{3+}$ ions. Following this discovery, a new question arises: if two $Ln^{3+}$ ions (two different M1 ions, M1 and M1′ or two different M2 ions, M2 and M2′) are known to form the same structure type when used individually, how can they be separated through the MOF crystallization? Our studies described below demonstrate that even if M2 and M2′ show the same preference for a MOF structure when used alone, they are not preferred to the same extent by this MOF when the crystallization occurs from a mixture of $Ln^{3+}$ ions. Specifically in this work, we found that the smaller $Ln^{3+}$ ion is preferred for a given MOF. We attribute this preference to the stronger binding constant between smaller $Ln^{3+}$ and camphorate/formate, which is consistent with the knowledge that smaller $Ln^{3+}$ tends to form more stable metal complexes in the solution phase. It appears that the Ln separation principle used for solvent extraction and ion chromatography is directly transferable to selective MOF crystallization reported here.

Such preference by the MOF structure for smaller $Ln^{3+}$ is shown by EDS results on various combinations of late lanthanides (from Tb to Yb and Y). Nine out of the 15 combinations show a separation factor higher than 1.25 (in other words, with an equimolar M2-M2′ mixture, their distribution in the final crystal can reach about 55%−45% in molar fraction) and four of them can reach over 1.5 (60%−40% in molar fraction) (Figure 3a). Note that the selectivity between two M2 ions is lower compared to that between M1 and M2. This is due to the fact that two M2 ions are even more similar in ionic radii than M1 and M2 ions and are thus much more difficult to separate with any separation method.

Given the observation that the selectivity is strongly dependent on the ionic radius difference between two $Ln^{3+}$ ions, all 22 lanthanide combinations in this study are plotted with their selectivity versus ionic radius difference (Figure 3b). An approximately linear fit can be used to describe the trend of their selective distribution in the crystallization process.

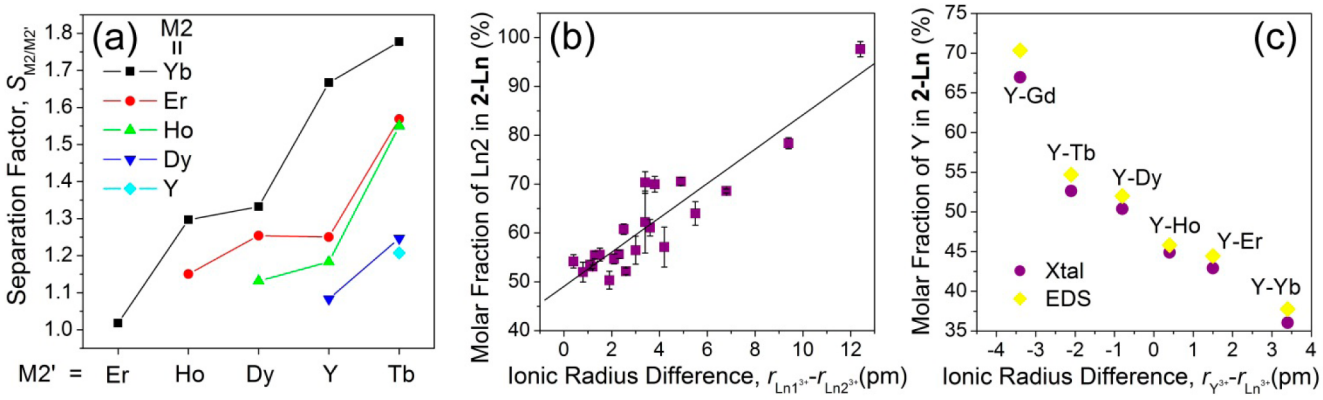


**Figure 3.** (a) Selective crystallization of **2-Ln** (Type 2) upon 15 combinations of two late lanthanides M2 and M2′ ($r_{M2'} > r_{M2}$). (b) Dependence of the molar fraction of Ln2 in **2-Ln** (Type 2) on the ionic radius difference between two different lanthanides Ln1 and Ln2 ($r_{Ln2} > r_{Ln1}$). (c) Comparison of metal distributions obtained from single crystal X-ray crystallography refinements (Xtal) and EDS measurements in six Y−Ln combinations.

All of the above EDS elemental analyses were obtained based on data from randomly selected areas from multiple samples to eliminate any possible fluctuation in sample heterogeneity and errors in EDS measurements. The similar separation factor data were obtained from separate repeat experiments. To further prove such observed selectivity of $Ln^{3+}$ ions, single crystal X-ray studies were also used to refine the molar ratio between two $Ln^{3+}$ ions. Especially, the incorporation of yttrium into **2-Ln** made it possible to verify the reliability of our method. In contrast to the combination of two lanthanides that are close to each other in both ionic radius and electron density, the combination of yttrium and a lanthanide is similar to each other only in ionic radius but very different in electron density, making it a perfect platform for reliable crystallographic refinement on the occupancy of metals. As is shown in Figure 3c, the metal distributions in six Y−Ln combinations obtained from EDS measurements and crystallographic refinements are consistent with each other, with <3% difference.

Given the selectivity for smaller $Ln^{3+}$ ions by **2-Ln** phase, we wonder whether such selectivity also occurs in other MOF platforms. To address this question, the separation of two early Ln ions (La and Pr) with **1-Ln** platform was performed. The single crystal X-ray data show that when synthesized with equimolar mixture of their nitrate salts, their molar fraction in the resulting **1-Ln** crystal is 25.9% La versus 74.1% Pr. This result indicates that the size-selective crystallization-based separation strategy reported here can be extended to more MOF platforms.

In conclusion, by systematic synthetic and structural studies of crystallization of a large series of homochiral rare-earth camphorates, we have demonstrated that crystallization processes by $Ln^{3+}$ ions are very sensitive to ionic radii and that the ionic radius difference between two $Ln^{3+}$ ions dictates the unequal concentrations of $Ln^{3+}$ in Ln−MOF crystals. For some $Ln^{3+}$ combinations, the selectivity for a particular $Ln^{3+}$ is nearly exclusive, which permits one-step separation of two $Ln^{3+}$ elements. This preference by a predesigned MOFs for specific $Ln^{3+}$ ion can serve as the basis for the industrial separation of lanthanides. The strategy demonstrated here is general and versatile in that every Ln−MOF can potentially serve as the platform for selective crystallization of $Ln^{3+}$, albeit with different selectivity factor. In fact, the method reported here shows the great potential for developing MOF platforms for other crystallization-based separations beyond just lanthanide mixtures.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details, additional figures, and cif file. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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