

Supporting Information for

## **Size-Dependent Selective Crystallization upon an Inorganic Mixed-Oxoanion System for Lanthanide Separation**

Huangjie Lu,<sup>#,a,b</sup> Xiaojing Guo,<sup>#,a,c</sup> Yaxing Wang,<sup>d</sup> Kariem Diefenbach,<sup>‡,a</sup> Lanhua Chen,<sup>d</sup> Jian-Qiang Wang,<sup>a</sup> Jian Lin,<sup>\*,a</sup> and Shuao Wang<sup>\*,d</sup>

<sup>a</sup>Shanghai Institute of Applied Physics, Chinese Academy of Sciences, 2019 Jia Luo Road, Shanghai 201800, China

<sup>b</sup>University of Chinese Academy of Sciences, 2019 Jia Luo Road, Shanghai 201800, China

<sup>c</sup>The Education Ministry Key Laboratory of Resource Chemistry and Shanghai Key Laboratory of Rare Earth Functional Materials, Department of Chemistry and Chemical Engineering, Shanghai Normal University, 100 Guilin Road, Shanghai 200234, China

<sup>d</sup>School for Radiological and Interdisciplinary Sciences (RAD-X) and Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Soochow University, 199 Ren'ai Road, Suzhou 215123, China

<sup>#</sup>These authors contributed equally.

## **Table of contents**

**S1. Characterizations**

**S2. X-ray crystallography**

**S3. Lanthanide Separation Studies**

**S4. Powder X-ray diffraction (PXRD)**

**S5. SEM-EDS analysis**

**S6. Theoretical analysis**

**S7. Reference**

## S1. Characterizations

Single crystal X-ray diffraction measurements were performed using a Bruker D8-Venture single crystal X-ray diffractometer equipped with a digital camera. The diffraction data were collected using a Turbo X-ray Source (Mo-K $\alpha$  radiation,  $\lambda = 0.71073\text{\AA}$ ) adopting the direct-drive rotating anode technique and a CMOS detector under room temperature. The data frames were collected using the program *APEX2* and processed using the program *SAINTE* routine in *APEX2*. The structures were solved by the direct method and refined on  $F^2$  by full-matrix least-squares methods using *SHELXTL-2014* program.<sup>[1]</sup> Powder X-ray diffraction (PXRD) data were collected from 5 to 50° with a step of 0.02° and the time for data collection was 0.2-0.5 s on a Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation ( $\lambda=1.54056\text{\AA}$ ) and a Lynxeye one - Dimensional detector. Inductively coupled plasma optical emission spectrometer (ICP-AES) analysis of separation was conducted using a Thermo Scientific ICAP 7400 instrument. Scanning Electron Microscopy (SEM) images and Energy-Dispersive Spectroscopy (EDS) analysis data were collected on a Zeiss Merlin Compact LEO 1530 VP scanning electron microscope with the energy of the electron beam being 15 kV. Crystals were mounted directly on carbon conductive tape and the spectra acquisition time was 60 s.

## S2. X-ray crystallography

**Table S1.** Crystallographic data for EuIO<sub>3</sub>SeO<sub>4</sub> (**LnISO-1**) and DyIO<sub>3</sub>SO<sub>4</sub>·H<sub>2</sub>O (**LnISO-2**)

Compound	<b>LnISO-1</b>	<b>LnISO-2</b>
<i>Mass</i>	462.10	970.98
Color and habit	Colorless, block	Colorless, block
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	9.3083(3)	6.6821(17)
<i>b</i> (Å)	6.8460(3)	8.791(2)
<i>c</i> (Å)	8.2575(3)	13.632(3)
$\alpha$ (deg)	90	90
$\beta$ (deg)	104.6960(10)	90
$\gamma$ (deg)	90	90
<i>V</i> (Å <sup>3</sup> )	508.99(3)	800.7(3)
<i>Z</i>	4	2
<i>T</i> (K)	301(2)	296(2)
$\lambda$ (Å)	0.71073	0.71073
<i>Max 2<math>\theta</math></i> (deg)	54.96	55.228
$\rho_{calcd}$ (g cm <sup>-3</sup> )	5.519	4.027
$\mu$ (Mo Ka)	18.774	13.483
<i>R</i> <sub>1</sub>	0.0210	0.0238
<i>wR</i> <sub>2</sub>	0.0554	0.0598
<i>Rint</i>	0.0233	0.0520
<i>GOF</i>	1.117	0.948

### S3. Lanthanide Separation Studies

**Materials.**  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln} = \text{La}$  to  $\text{Lu}$ , except  $\text{Pm}$ ) (99.99%, Energy Chemical Reagent),  $\text{HIO}_3$  (99.99%, Alfa Aesar), and  $\text{H}_2\text{SO}_4$  (98%, Alfa Aesar) were used as received.

**Separation factor calculation.** Separation factors (SFs) were calculated using the following equation

$$SF = (n_{\text{Ln}2} / n_{\text{Ln}1})_c \times (n_{\text{Ln}1} / n_{\text{Ln}2})_m \quad (1)$$

Crystallization yield are calculated as

$$Y = 1 - (n_{\text{Ln}} / n_0)_m \quad (2)$$

where  $n_{\text{Ln}1}$ ,  $n_{\text{Ln}2}$  is the molar mass of different lanthanides,  $n_0$  is the initial molar mass of certain lanthanide charged into the autoclave.  $c$  represents the case in the solid products, and  $m$  represents the case in the mother liquid solutions. The separation factors were calculated based on a biphasic solid–liquid model.

**S3.1 Precipitation reaction under ambient conditions.**  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.1 mmol),  $\text{HIO}_3$  (0.1 mmol),  $\text{H}_2\text{SO}_4$  (0.55 mmol) were charged into a vial with 5mL volume, then dissolved using 2 mL deionized water. The early lanthanides ( $\text{La}$ – $\text{Gd}$ , except  $\text{Pm}$ ) precipitated hydrolytically from the solutions whereas the solutions of late lanthanides ( $\text{Tb}$ – $\text{Lu}$ ) retained clear.



**Fig. S1.** Precipitation reaction of lanthanide elements under ambient condition.

A binary ( $\text{Nd}/\text{Dy}$ ) lanthanide separation study was conducted by reacting equimolar  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  with  $\text{HIO}_3$  in  $\text{H}_2\text{SO}_4$  solution under ambient condition. The resulting products were filtrated and the precipitates were washed extensively with deionized water. The wash solution and filtrate were gathered in 10 mL centrifuge tubes and added to a constant volume with deionized water for further determination of the molar quantities of  $\text{Nd}$  and  $\text{Dy}$ . The precipitates were washed with ethanol, dried at room temperature, and further dissolved

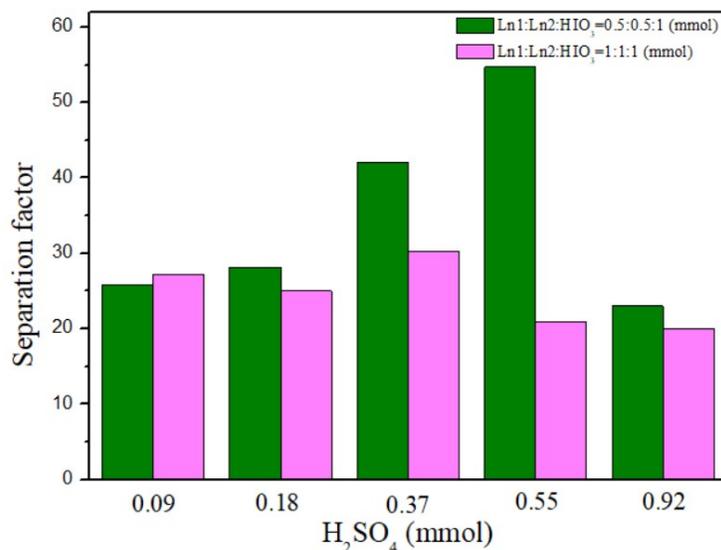
in concentrated nitric acid. The resulting solutions were diluted to 5% nitric acid solution before quantitatively analyzed using ICP-AES.

**S3.2 Selective crystalizations under hydrothermal conditions.** In unitary lanthanide reaction,  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.1 mmol),  $\text{HIO}_3$  (0.1 mmol),  $\text{H}_2\text{SO}_4$  (0.55 mmol), and 2 mL water were charged into a PTEF-lined Parr 4749 autoclave with a 15 mL internal volume. The autoclaves were sealed and heated at 180 °C for 3 days followed by slow cooling to room temperature over a period of 1 day. Prisms of **LnISO-1** (Ln = La–Gd, except Pm) and blocks of **LnISO-2** (Ln = Tb–Lu) were isolated in their corresponding reactions.

Three combinations of binary lanthanide Ln1/Ln2 (Nd/Dy, La/Lu, and Gd/Tb) crystallization experiments were performed.  $\text{Ln}(1)(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.05 mmol) (Ln1 = Nd, La, Gd),  $\text{Ln}(2)(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.05 mmol) (Ln2 = Dy, Lu, Tb),  $\text{HIO}_3$  (0.1 mmol),  $\text{H}_2\text{SO}_4$  (0.55 mmol), 2 mL of deionized water were charged into a PTEF-lined Parr 4749 autoclave. The autoclaves were sealed and heated at 180 °C for 3 days followed by slow cooling to room temperature over a period of 1 day. **LnISO-1** precipitates as crystalline products whereas **LnISO-2** cannot be identified in the solid phase.

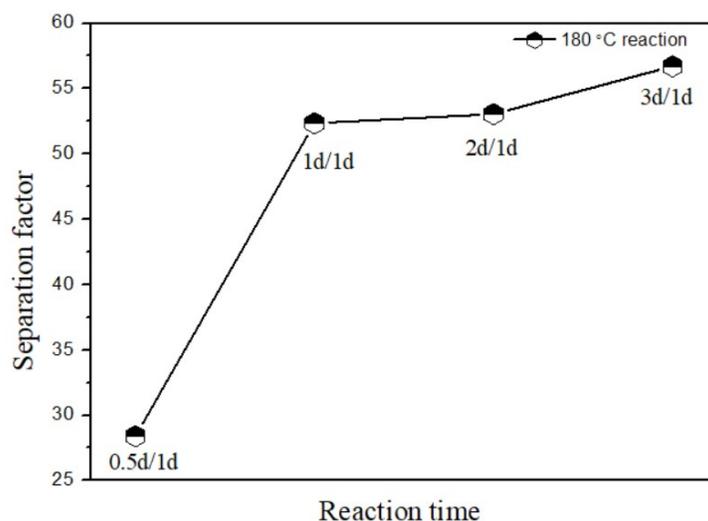
### S3.3 Separation optimization

*Effect of stoichiometry on SFs.*  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.05 or 0.1 mmol),  $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.05 or 0.1 mmol),  $\text{HIO}_3$  (0.1 mmol),  $\text{H}_2\text{SO}_4$  (0.09, 0.18, 0.37, 0.55, or 0.92 mmol) were charged into a PTEF-lined Parr 4749 autoclave with a 15 mL internal volume, then dissolved using 2 mL of deionized water. The samples were sealed and heated at 180 °C for 3 days followed by slow cooling to room temperature over 1 day. The resulting products were washed extensively with deionized water. The wash solutions were gathered in 10 mL centrifuge tubes and added to a constant volume with deionized water for further determination of the molar quantities of Nd and Dy. The products were then washed with ethanol, which dried at room temperature. In order to precisely determine the quantities of Nd and Dy in solids, the crystalline solids were further dissolved in concentrated nitric acid, and then diluted to 5% nitric acid solution before quantitatively analyzed using ICP-AES. The wash solution samples were also analyzed in order to determine the separation factor (Fig. S2).



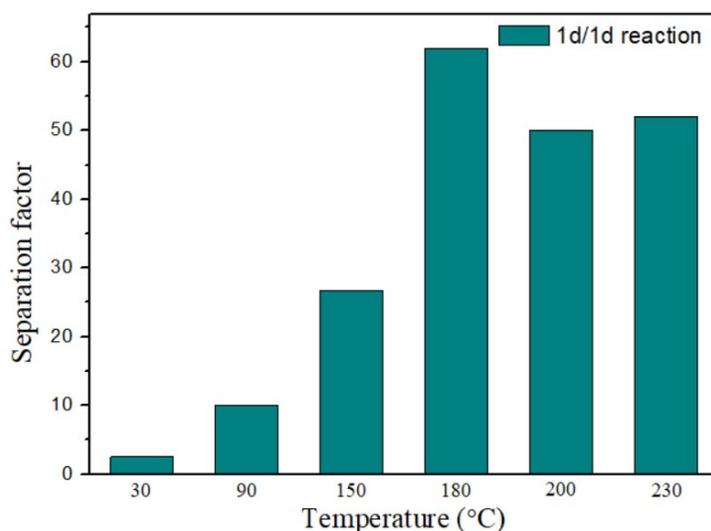
**Fig. S2.** Separation factor of Nd/Dy separation experiment with different starting material at 180 °C (Ln1 = Nd, Ln2 = Dy).

**Effect of kinetics on SFs.** Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.05 mmol), Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.05 mmol), HIO<sub>3</sub> (0.1 mmol), H<sub>2</sub>SO<sub>4</sub> (0.55 mmol) were charged into a PTEF-lined Parr 4749 autoclave with a 15 mL internal volume, then dissolved using 2 mL of deionized water. The samples were sealed and heated at 180 °C for 0.5, 1, 2, and 3d, followed by slow cooling to room temperature over 1 day. Similar procedures were followed to determine the SF of Nd/Dy (Fig. S3).



**Fig. S3.** Separation factor of Nd/Dy separation experiment with different reaction time at 180 °C (Ln1 = Nd, Ln2 = Dy).

**Effect of reaction temperature on SFs.**  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.05 mmol),  $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.05 mmol),  $\text{HIO}_3$  (0.1 mmol),  $\text{H}_2\text{SO}_4$  (0.55 mmol) were charged into a PTEF-lined Parr 4749 autoclave with a 15 mL internal volume, then dissolved using 2 mL of deionized water. The samples were sealed and heated at 30, 90, 150, 180, 200, or 230 °C for 1 days followed by slow cooling to room temperature over 1 day. Similar procedures were followed to determine the SF of Nd/Dy (Fig. S4).



**Fig. S4.** Separation factor of Nd/Dy separation experiment with different reaction temperature (Ln1 = Nd, Ln2 = Dy).

The results show that the highest SF can be achieved by reacting  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.05 mmol),  $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.05 mmol),  $\text{HIO}_3$  (0.1 mmol), and  $\text{H}_2\text{SO}_4$  (0.55 mmol) at 180 °C for 3 days. Consequently, the Nd/Dy, La/Lu, and Gd/Tb lanthanide separations were performed under the aforementioned conditions and the resulting SFs are shown in Table S2.

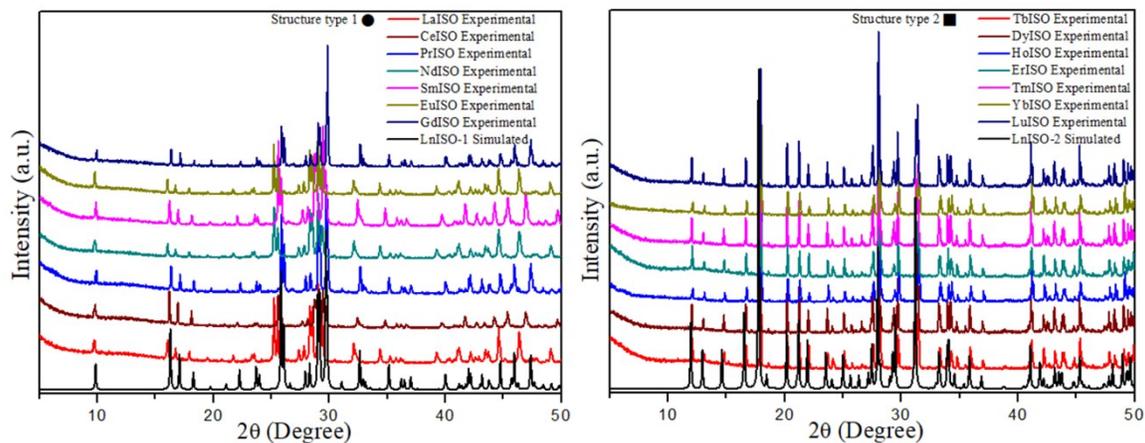
**Table S2.** Result summary of Nd/Dy, Gd/Tb La/Lu, La/Dy, and Nd/Lu separation experiment (the separation factor is calculated using the solid/aqueous model), reaction at 180 °C for 3 days followed by slow cooling to room temperature over 1 day, and Nd/Dy separation experiment at room temperature (RT).

Element	The molar mass in reactants / mmol	The molar mass in products / mmol	The molar mass in wash solutions / mmol	Crystallizat ion yield	Crystallizat ion purity	Separation factor
Nd	0.05±0.005	0.0455±0.0036	0.0042±3.8E-5	0.9144±0.0	0.9140±0.0	123.38±4.807
Dy	0.05±0.005	0.0043±0.0005	0.0492±0.0010	062	028	
La	0.05±0.005	0.0464±0.0013	0.0042±0.0002	0.9178±0.0	0.9016±0.0	100.17±2.460
Lu	0.05±0.005	0.0051±0.0005	0.0453±0.0004	057	067	
Gd	0.05±0.005	0.0249±0.0008	0.0241±0.0006	0.5079±0.0	0.6195±0.0	2.40±0.1723
Tb	0.05±0.005	0.0153±0.0005	0.0355±0.0015	037	146	
La	0.05±0.005	0.0463±0.0010	0.0043±5.5E-5	0.9142±0.00	0.9227±0.00	137.25±9.25
Dy	0.05±0.005	0.0039±0.0003	0.0498±0.0015	23	57	
Nd	0.05±0.005	0.0438±0.0014	0.0042±0.0001	0.9119±0.00	0.8916±0.00	85.43±5.979
Lu	0.05±0.005	0.0053±0.0002	0.0438±0.0009	18	29	
Nd (RT)	0.05±0.005	0.0230±0.0023	0.0294±0.0035	0.4400±0.05	0.6031±0.01	1.82±0.1887
Dy (RT)	0.05±0.005	0.0151±0.0014	0.0349±0.0017	37	25	

**Table S3.** Comparing the separation factors results with other methods.

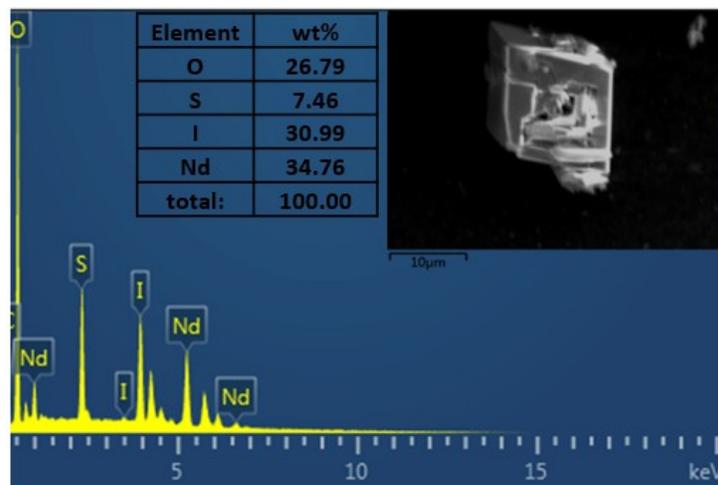
	<i>This work</i>		<i>references</i>		
Nd/Dy	123.38	986 [2]	359 [3]	302 [4]	148 [6]
La/Lu	100.17	90.9 [4]	17326 [5]	/	/
Gd/Tb	2.40	1.51 [2]	1.6 [5]	/	/
La/Dy	137.25	182 [4]	54.4 [4]	3038 [6]	/
Nd/Lu	85.43	39.6 [4]	660 [4]	/	/

#### S4. Powder X-ray diffraction (PXRD)

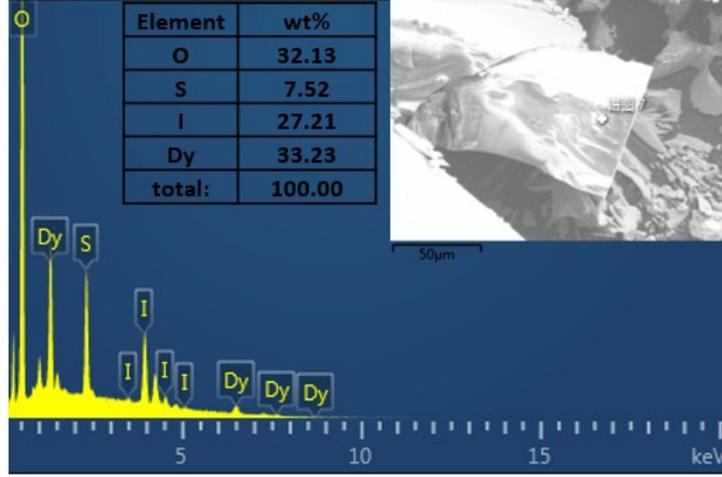


**Fig. S5.** Simulated and experimental PXRD patterns for compound **LnISO-1** (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd) and **LnISO-2** (Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu) confirming their phase-purity.

### S5. SEM-EDS analysis



**Fig. S6.** SEM-EDS analysis for compound  $\text{NdIO}_3\text{SO}_4$  confirming phase-purity.



**Fig. S7.** SEM-EDS analysis for compound  $\text{DyIO}_3\text{SO}_4(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$  confirming phase-purity.

## S6. Theoretical analysis

To evaluate the relative stability of each **LnISO-1** (Ln= La, Nd, Gd, Lu, Dy and Tb), the formation energy ( $\Delta E_f$ ) was calculated for **LnISO-1** using density functional theory (DFT) calculations with the Vienna ab-initio simulation package (VASP) [7]. A plane-wave basis set ( $E_{cut} = 400$  eV) and the generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof (PBE) functional were used for all the DFT calculations [8]. The projector augmented wave (PAW) method was used for description of the interaction between core and valence electrons [9-10]. The structure of **LnISO-1** was determined by single crystal X-ray diffraction and the single-point energy of each crystal was calculated based on the CIFs. The Monkhorst-Pack k-mesh of  $11 \times 15 \times 13$  was adopted for **LnISO-1** to guarantee the specified k-point separation within  $0.01 \text{ \AA}^{-1}$ . The spin polarization scheme was adopted during the calculations [11].

The  $\Delta E$  was determined according Eq. (3):

$$\Delta E_f = 1/n \left( E_{\text{LnISO-1}} + 3n \times E_{\text{HNO}_3} - n \times E_{\text{Ln}(\text{NO}_3)_3} - n \times E_{\text{HIO}_3} - n \times E_{\text{H}_2\text{SO}_4} \right) \quad (3)$$

where  $E_{\text{LnISO-1}}$  is the total energy of the crystal structure of **LnISO-1** (Ln= La, Nd, Gd, Lu, Dy and Tb),  $E_{\text{HNO}_3}$ ,  $E_{\text{Ln}(\text{NO}_3)_3}$ ,  $E_{\text{HIO}_3}$ , and  $E_{\text{H}_2\text{SO}_4}$  are the energies of  $\text{HNO}_3$ ,  $\text{Ln}(\text{NO}_3)_3$ ,  $\text{HIO}_3$  and  $\text{H}_2\text{SO}_4$ , and  $n$  denotes the number of Ln in each unit cell of **LnISO-1**. Each component, including  $\text{HNO}_3$ ,  $\text{Ln}(\text{NO}_3)_3$ ,  $\text{HIO}_3$ , or  $\text{H}_2\text{SO}_4$ , was placed into a  $50 \text{ \AA} \times 50 \text{ \AA} \times 50 \text{ \AA}$  periodic box, and the k-point was restricted to the gamma point for calculating  $E_{\text{component}}$ . The calculation

results are summarized in Table S3.

Table S4. Relative formation energies ( $\Delta\Delta E$ , eV) for **LnISO-1**.

Complex	$\Delta\Delta E_f^a$ (eV)
<b>LaISO-1</b>	0.00
<b>NdISO-1</b>	0.06
<b>GdISO-1</b>	0.24
<b>LnISO-1@Tb</b>	0.29
<b>LnISO-1@Dy</b>	0.34
<b>LnISO-1@Lu</b>	0.56

<sup>a</sup> $\Delta\Delta E_f$  is  $\Delta E_f$  relative to **LaISO-1**.

## S7. Reference

- [1] G. Sheldrick, *SHELXTL, P, version 6.12, an integrated system for solving, refining, and displaying crystal structures from diffraction data; Siemens Analytical X-ray Instruments: Madison, WI, 2001.*
- [2] X. Yin, Y. Wang, X. Bai, Y. Wang, L. Chen, C. Xiao, J. Diwu, S. Du, Z. Chai, T. E. Albrecht-Schmitt and S. Wang, *Nat. Commun.*, 2017, **8**, 14438.
- [3] J. A. Bogart, C. A. Lippincott, P. J. Carroll and E. J. Schelter, *Angew. Chem., Int. Ed.*, 2015, **54**, 8222–8225.
- [4] J. A. Bogart, B. E. Cole, M. A. Boreen, C. A. Lippincott, B. C. Manor, P. J. Carroll and E. J. Schelter, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, 14887–14892.
- [5] M. R. Healy, A. S. Ivanov, Y. Karslyan, V. S. Bryantsev, B. A. Moyer and S. Jansone-Popova, *Chem. Eur. J.*, 2019, **25**, 1–7.
- [6] X. Sun and K. E. Waters, *ACS Sustainable Chem. Eng.*, 2014, **2**, 2758-2764.
- [7] G. Kresse and J. Furthmuller, *Phys. Rev. B.*, 1996, **54**, 11169-11186.
- [8] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. B.*, 1996, **77**, 3865-3868.
- [9] P. E. Blöchl, *Phys. Rev. B.*, 1994, **50**, 17953-17979.
- [10] G. Kresse and D. Joubert, *Phys. Rev. B.*, 1999, **59**, 1758-1775.
- [11] M. Methfessel and A. T. PaxtonPhys, *Phys. Rev. B.*, 1989, **40**, 3616-3621.