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Nanoconfined Interfaces for Highly Selective Separation of Critical Rare Earth Elements

Anastasia G. Ilgen, Dorina F. Sava Gallis, Kevin Leung, Jacob A. Harvey, James D. Kubicki, Eric Borguet, R. Eric Sikma, Boyoung Song, and Heath D. Watts

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ABSTRACT

Industrial demand for rare earth elements (REEs) has surged over the past three decades due to their unique properties that support sustainable energy and new technologies. Separating individual REEs is challenging and hazardous, typically done through liquid-liquid extraction. There is an urgent need for environmentally friendly and efficient separation technologies for REEs. Porous materials offer promising advances for sustainable REE separation via ion-selective capture. We hypothesize that REE separation can be efficiently achieved in reactive nanopores, such as Zr(IV) and Cr(III) metal-organic frameworks (MOFs), through surface functionalization. By integrating material synthesis, interfacial chemistry experiments, theory, computation, and machine learning, we gained insights into the chemical factors controlling REE speciation and their competitive adsorption on MOFs. Our findings show that these materials' selectivity can be tuned by surface functionalization. The machine learning component addressed ion-specific diffusion based on MOF topology and chemistry.

ACKNOWLEDGEMENTS

This work was supported by the Sandia National Laboratories Laboratory Directed Research and Development program, Project No. 225932. We acknowledge Jacob Deneff, initially postdoctoral fellow on this project, who took a staff scientist position at Sandia. We also acknowledge undergraduate students Kadie M.M. Sanchez, Jacob G. Smith, Raphael Reyes, Emily T. Nguyen, Luke M. Lucero, Keith J. Fritzsching, Caith McKeown, and Madeline I. Steinberg, who contributed to this work at Sandia.

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ACRONYMS AND TERMS

Acronym/Term	Definition
AIMD	Ab Initio Molecular Dynamics
ATR	Attenuated total reflectance
DFT	Density functional theory
FMC	Flow microcalorimeter
FTIR	Fourier transform infrared
GCMC	Grand Canonical Monte Carlo
ICP-MS	Inductively coupled plasma mass spectrometry
LCD	Largest Cavity Diameter
MD	Molecular dynamics
ML	Machine learning
MOF	Metal-organic framework
PLD	Pore limiting diameter
REE	Rare earth element
SA	Surface Area
SFG	Sum frequency generation
SUPN	Sandia University Partnership Network
VF	Void Fraction
XAFS	X-ray absorption fine structure
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy

1. INTRODUCTION

The demand for rare earth elements (REEs) has been rising steeply over the past three decades due to their critical role in sustainable energy and new technologies. Although REEs are not rare in the environment, they seldom form concentrated deposits and often co-occur, necessitating extensive separations before industrial use. Currently, separating individual REEs is achieved through liquid-liquid extractions, a challenging and hazardous process.[1] To address this, we are exploring porous materials[2-9] that offer promising advances for sustainable REE separation via ion-selective capture.

We examine the chemical factors that control how REEs partition into reactive pores within water-stable zirconium (Zr(IV)) and chromium (Cr(III))-based metal-organic frameworks (MOFs). By appending the base MOF structures through surface functionalization, we design pore chemistry and investigate molecular-scale interactions between REEs and MOF pores using molecular simulation and spectroscopic techniques.[10] To understand the chemical factors controlling REE diffusion within MOF pores—a key process defining ion adsorption—we employ machine learning and Grand Canonical Monte Carlo (GCMC) simulations.

We developed procedures to synthesize and functionalize Zr(IV)-based MOFs. Several tunable MOFs were synthesized for selective metal ion capture from complex streams,[10] and a comprehensive pipeline was developed to assess MOF stability and performance under various conditions. We selected MOFs with highly stable Zr(IV) building units for systematic functionalization with targeted metal binding groups, both via linker functionalization and at the metal oxo-cluster. Previous studies are limited, but there is some indication in the literature that by functionalizing MOF surfaces with reactive groups, their affinity for REEs may vary.[3, 7, 11, 12] The Zr(IV)-based MOFs included UiO-66, UiO-68, and MOF-808. Competitive adsorption studies revealed that ion uptake and selectivity for REE ions are directly tunable with surface functional groups and by altering the defect character of the MOFs.[10] Specifically, unfunctionalized Zr(IV) clusters are highly selective for REEs over divalent transition metals. We found that defect character significantly impacts adsorption behavior, with more defective MOFs showing high removal percentages for REE ions. This agrees

with previous studies indicating that increased defect density leads to indiscriminate metal ion adsorption.[13, 14] To pursue ion-selective adsorption, we appended Zr(IV)-based MOFs with targeted metal binding groups. Functionalization of reactive pores increased the uptake of transition metal ions but reduced selectivity for REEs.[10]

To determine the mode of adsorption (chemi- vs. physisorption) of REEs and their exact chemical arrangement within MOF pores, we performed synchrotron-based interfacial chemistry experiments using Zr(IV)-based MOFs synthesized at Sandia and commercially available Cr(III)-based MOFs (Cr-MIL-101). Synchrotron-based X-ray absorption spectroscopy (XAS) provided the first investigation of REE speciation in MOFs.[15] We demonstrated that selected REEs form chemisorbed complexes at Zr(IV) and Cr(III) metal oxo-clusters. Importantly, the addition of a phosphonoacetic acid moiety within MOFs resulted in direct coordination of REEs to this site. This finding was corroborated by density functional theory (DFT) simulations, which predicted that the free energy of adsorption for REEs onto the phosphonate group is more favorable than for the Zr-O site at the metal oxo-cluster.[15]

In our pursuit of selectivity, we discovered that pyrazole functional group appended within MOF-808 leads to the selective adsorption of nickel (Ni^{2+}) over cobalt (Co^{2+}). Using batch adsorption, along with in-house Fourier transform infrared (FTIR) and X-ray photoelectron (XPS) spectroscopies, we identified that the binding between Ni^{2+} and pyrazole molecule is more favorable and explains this selective adsorption.[16] This finding could lead to new applications in critical metal separations during recycling of lithium-ion batteries.

To understand the nature of REE interactions with various functional groups in solution and when these groups are attached to surfaces (simple oxide surface and UiO-66 surface), we used ab initio molecular dynamics simulations (AIMD) and DFT to predict differential binding energies between different lanthanides and functional groups within MOFs, on silica surfaces, and in aqueous solutions.[17] These simulations show that with increasing negative charge of the functional group, it becomes more selective towards the heavier REEs.[17] Therefore, to design surface sites that may preferentially select lighter REEs within MOF pores, a combination of negatively- and positively-charged surface groups may be employed, which requires further research.

In addition to the targeted approaches listed above, we also explored a broader range of MOF structures. To do so we ran molecular dynamics (MD) simulations of REE ions in ~845 hydrated MOF structures. We focused on diffusion coefficients as proxy for adsorption (i.e., stronger adsorption leads to slower diffusion). A Bayesian optimization procedure was utilized to direct future simulations, to rapidly converge the accuracy of the model, and thus to reduce the overall number of MD simulations required. Lastly, we developed a machine learning (ML) model on the final dataset and identified the MOF structural features that were most predictive of the diffusion coefficient. Our model shows that pore limiting diameter (PLD) is one of the main factors influencing the diffusion coefficient prediction. While potentially intuitive, it is interesting to note that all the PLDs examined in this study were significantly larger than the ion size itself, ruling out steric effects. It is possible that diffusion of the ions through MOF structures is a more collective process involving the diffusion of the ion itself, the surrounding liquid, and counterions (e.g., nitrate).

We utilized project resources to engage with three universities. Two of them were realized via small sub-contracts, and one was awarded a Sandia University Partnership Network (SUPN) award. The SUPN award with the University of Texas at El Paso was used to support two publications on DFT simulations of REE coordination to propionate and other organic functional groups, that are currently being finalized and prepared for submission (as of 09/10/2024). Two smaller sub-awards with the Georgia State University (GSU) and Temple University were used to conduct preliminary experiments: measure enthalpies of adsorption of Ni^{2+} and Co^{2+} on selected MOFs (GSU) and to develop new methodology for vibrational sum frequency generation (vSFG) measurements to characterize the chemistry of MOF surfaces (Temple). Summary findings for these research efforts accomplished by three universities are included in the last section of this report.

The employed innovative combination of theoretical and experimental approaches (summarized in four published and four prepared for submission papers) advances our understanding of ion-selective capture in MOFs. Our findings show that these materials' selectivity can be designed by surface functionalization. For the first time we show that REEs form chemisorbed surface species at the oxo-clusters for both

Zr(IV) and Cr(III)-based MOFs, and that REEs can also bind to specific functional groups, if the free energy of adsorption onto these group is more favorable compared to the metal oxo-cluster site. This new knowledge lays the foundation for material design with ion-selective properties, that can separate critical materials from ionic mixtures, including REEs, and even individual REEs from one another.

2. PUBLISHED PAPER: TUNING THE PORE CHEMISTRY OF ZR-MOFS FOR EFFICIENT METAL ION CAPTURE FROM COMPLEX STREAMS

Citation: Sikma, R. E.; Song, B.; Deneff, J. I.; Smith, J. G.; Sanchez, K. M.; Reyes, R. A.; Lucero, L.; Fritzsching, K.; Ilgen, A. G.; Sava Gallis, D. F. Tuning the pore chemistry of Zr-MOFs for efficient metal ion capture from complex streams. *Chemical Communications* **2024**, 60, 5808-5811. DOI: 10.1039/D4CC00320A.

Abstract: Metal-organic frameworks (MOFs) have shown promise for adsorptive separations of metal ions. Herein, MOFs based on highly stable Zr(IV) building units were systematically functionalized with targeted metal binding groups. Through competitive adsorption studies, it was shown that the selectivity for different metal ions was directly tunable through functional group chemistry.

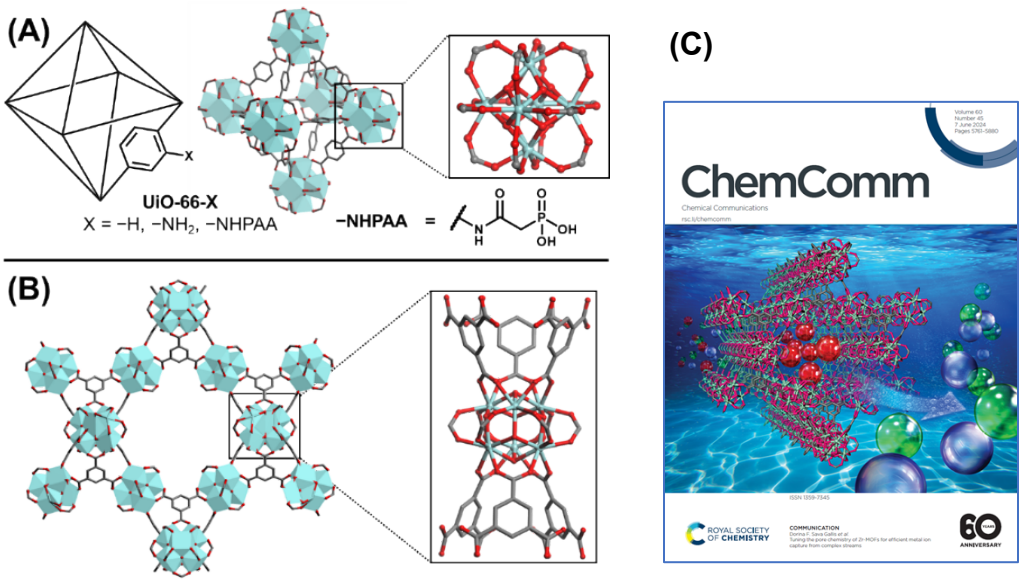


Figure 1. Representations of pore cavities and Zr6 building units of (A) UiO-66 and (B) MOF-808 from crystal structure data; (A) highlights functional groups installed in UiO-66 in this work; C = gray, O = red, Zr = teal; H atoms omitted for clarity; (C) This manuscript is highlighted on the journal's cover (Sikma et al., 2024)

3. PUBLISHED PAPER: MODELING SEPARATION OF LANTHANIDES VIA HETEROGENEOUS LIGAND BINDING

Citation: Leung K. and Ilgen A.G. Modeling Separation of Lanthanides via Heterogeneous Ligand Binding. *Physical Chemistry Chemical Physics* **2024**, 26, 20427 – 20439

Abstract: Individual lanthanide elements have physical/electronic/magnetic properties that make each useful for specific applications. Several of the lanthanide cations (Ln^{3+}) naturally occur together in the same ores. They are notoriously difficult to separate from each other due to their "chemical similarity." Predicting the Ln^{3+} differential binding energies ($\Delta\Delta E$) or free energies ($\Delta\Delta G$) at different binding sites will help design of materials with lanthanide selectivity. We apply ab initio molecular dynamics (AIMD) simulations and Density Functional Theory (DFT) to calculate $\Delta\Delta G$ for Ln^{3+} coordinated to ligands in water and embedded in metal-organic frameworks (MOFs), and $\Delta\Delta E$ for Ln^{3+} bonded to silica surfaces. Perturbative AIMD simulations of water-inundated simulation cells are applied to examine the selectivity of ligands towards adjacent Ln^{3+} in the periodic table. Static DFT calculations with a full Ln^{3+} first coordination shell, while less rigorous, show that all ligands examined with net negative charges are more selective towards the heavier lanthanides than a charge-neutral coordination shell made up of water molecules. Amine groups are predicted to be poor ligands for lanthanide-binding. We also address cooperative ion binding, i.e., using different ligands in concert to enhance lanthanide selectivity.

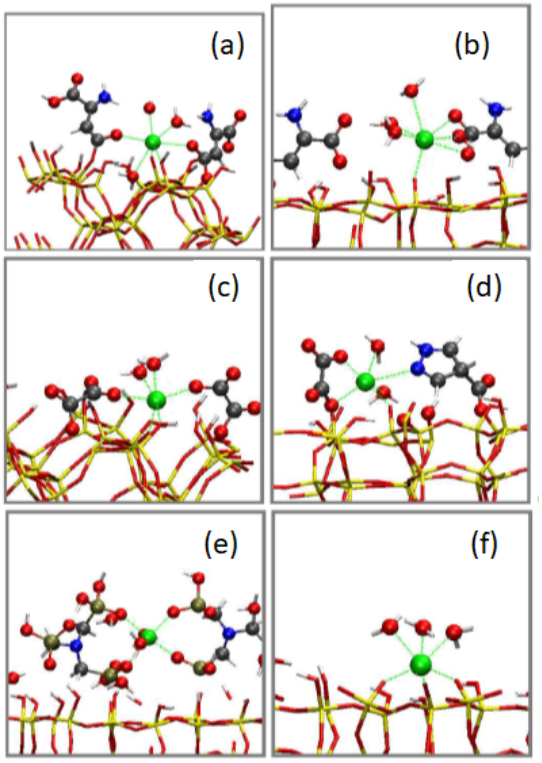
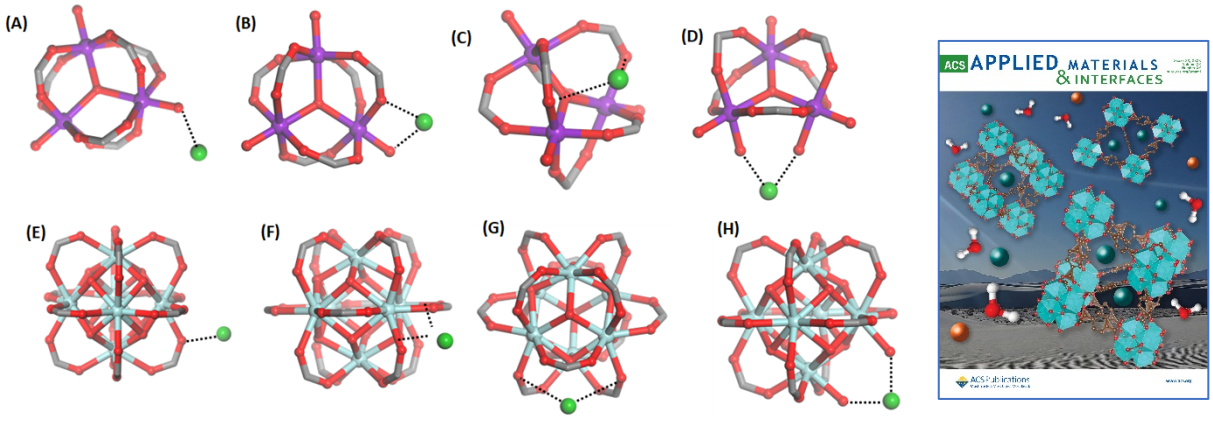


Figure 2. Lu^{3+} bound to ligands tethered to cristobalite surfaces. (a)-(b) 2 aspartates at two different distances; (c) 2 oxalates, (d) oxalate plus pyrazole; (e) 2 aminotri-(methylenephosphonic acid; (f) bare cristobalite with three deprotonated SiOH groups. Grey=C, red=O, blue=N, white=H, yellow=Si, and green= Ln^{3+}.

4. PUBLISHED PAPER: LOCAL COORDINATION ENVIRONMENT OF LANTHANIDES ADSORBED ONTO CR- AND ZR-BASED METAL-ORGANIC FRAMEWORKS

Citation: Ilgen, A. G.; Sikma, R. E.; Sava Gallis, D. F.; Leung, K.; Sun, C.; Song, B.; Sanchez, K. M.; Smith, J. G. Local Coordination Environment of Lanthanides Adsorbed onto Cr-and Zr-based Metal–Organic Frameworks. *ACS Applied Materials & Interfaces* **2024**. DOI: 10.1021/acsami.4c09445

Abstract: Separating individual lanthanide (Ln) elements in aqueous mixtures is challenging. Ion-selective capture by porous materials, such as metal-organic frameworks (MOFs), is a promising approach. To design ion-selective MOFs, molecular details of Ln adsorption complexes within MOFs must be understood. We determine the local coordination environment of lanthanides Nd^{3+}, Gd^{3+}, and Lu^{3+} adsorbed onto Cr(III)-based terephthalate MOF (Cr-MIL-101) and Zr(IV)-based Universitetet i Oslo MOFs (UiO-66, UiO-68) and their derivatives. In the Cr(III)- and Zr(IV)-based MOFs Ln adsorb as inner-sphere complexes at the metal oxo-clusters, regardless of whether the organic linkers are decorated with amino groups. Missing linkers result in favorable Ln binding sites at oxo-clusters; however, Ln can



coordinate to metal sites even with linkers in place. MOF functionalization with phosphonate groups led to Ln chemisorption onto these groups, which out-compete metal cluster sites. Ln form mono- and bi-dentate mono- and bi-nuclear surface complexes. We conclude that MOFs for ion-selective Ln capture can be designed by

a combination of: (1) maximizing metal-lanthanide interactions via shared O atoms at the metal oxo-cluster sites, where mixed oxo-clusters can lead to ion-selective Ln adsorption; and (2) functionalizing MOFs with Ln-selective groups capable of out-completing the metal oxo-cluster sites.

Figure 3. REE adsorption on Cr-MIL-101, UiO-66 MOFs and their derivatives. (A) Lu forms mono-dentate complexes at the Cr-OH sites or at the bridging oxygen between Cr and BDC linker; (B) Lu also forms bi-dentate edge- and (C, D) corner-sharing surface complexes at the Cr metal oxo-clusters by either sharing oxygen sites with the BDC linkers (as in C) or adsorbing at the defect sites where linkers are missing (as in D). Zr(IV) oxo-cluster within UiO-66 and UiO-68 MOF with proposed REE surface complexes shown: (E) mono-dentate complex; (F) bi-dentate edge-sharing complex; (G) bi-dentate corner-sharing complex with Zr-O pointing away from one another; (H) bi-dentate corner-sharing complex with Zr-O pointing towards one another. Green – Nd, or Gd, or Lu; teal – Zr, red – O, grey – C, purple – Cr. This manuscript is highlighted on the journal's cover (Ilgen et al., 2024).

5. PUBLISHED PAPER: THE SELECTIVE ADSORPTION OF Ni^{2+} OVER CO^{2+} FROM AQUEOUS SOLUTIONS IN SURFACE FUNCTIONALIZED METAL-ORGANIC FRAMEWORKS.

Citation: Song B., E. Sikma, M. Meyerson, DF. Sava Gallis, K. Leung, K. Sanchez, J. Smith, and Ilgen A. G. The selective adsorption of Ni^{2+} over Co^{2+} from aqueous solutions in surface functionalized metal-organic frameworks. *Separation and Purification Technology*. **2024** DOI: 10.1016/j.seppur.2024.129379

Abstract: In this study, two metal organic frameworks (MOFs), zirconium (IV)-based MOF-808 and chromium (III)-based MIL-101 were investigated for the selective adsorption of nickel (Ni^{2+}) over cobalt (Co^{2+}) and the role of the nitrogen (N)-containing functional groups was evaluated using pyrazole (PyC) and amine ($–NH_2$). Selective adsorption and adsorption rates were quantified using batch adsorption experiments. The post-reaction MOFs after Co^{2+} and Ni^{2+} adsorption was characterized with attenuated total reflectance Fourier transform infrared (ATR-FTIR) and X-ray photoelectron (XPS) spectroscopies to identify the active sorption sites and to infer the adsorption mechanism. The overall adsorption of Co^{2+} and Ni^{2+} by MOF-808 and MIL-101 increased after their surface functionalization with PyC and $–NH_2$. However, selective Ni^{2+} adsorption was only observed with MOF-808-PyC. The pseudo-second-order model fit to the kinetic adsorption data suggests chemically driven adsorption of Co^{2+} and Ni^{2+} onto all examined MOFs. The ATR-FTIR and XPS analyses of MOFs with adsorbed Co^{2+} and Ni^{2+} indicate that the N sites in PyC and $–NH_2$ are the reactive sites. ATR-FTIR analyses of aqueous PyC solutions with metal cations show a greater shift in the N–H vibrational band of PyC when interacting with Ni^{2+} compared to Co^{2+}, which is linked to a stronger interaction between Ni^{2+} and PyC, resulting in the Ni^{2+} selectivity by PyC-functionalized MOF-808. We propose that PyC, as a π-acceptor ligand, exhibits greater affinity for Ni^{2+} compared to Co^{2+} due to i) the greater electronegativity of Ni^{2+} and ii) the greater stability of Ni^{2+}complex with PyC ligand based on the Irving-Williams series and ligand field stabilization energy based on the electron configuration differences between Co^{2+} ($3d^7$) and Ni2+ ($3d^8$). [16]

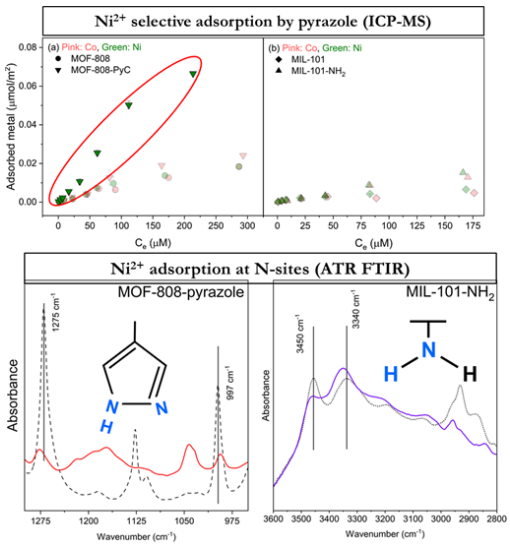


Figure 4. Enhanced adsorption of Ni^{2+} over Co^{2+} in MOF-808 functionalized with pyrazole groups. This behavior is explained by direct Ni^{2+} binding to pyrazole, shown with infrared and X-ray photoelectron spectroscopies (Song et al., 2024)

6. MANUSCRIPT IN PREPARATION: THE ROLE OF HALIDE FUNCTIONAL GROUPS IN THE SELECTIVE ADSORPTION OF LANTHANIDES WITHIN ZR-BASED METAL-ORGANIC FRAMEWORKS

Abstract: We investigated the selective adsorption of trivalent REEs by water-stable UiO-66 MOFs functionalized with halide surface groups. Both pristine and halogenated UiO-66 exhibited the greater affinity to Lu^{3+} (heavy REE) over light REEs, resulting in the selectivity of REEs from their mixture. The selective adsorption behavior of UiO-66 series can be explained by the charge densities of REEs and increasing electronegativity of halide groups, where the combination of larger charge density of Lu^{3+} and smaller electronegativity of iodide group prompted the selective adsorption. Our preliminary conclusions are that in UiO-66 system, the REE adsorption can occur at both Zr-O metal oxo-cluster sites and at halide functional groups, supported by the spectroscopic analysis. While the selective adsorption mechanism cannot be determined due to the limited information, our investigation demonstrates that selectivity of adsorption varies based on the chemical nature of appended functional group in UiO-66. Further spectroscopic investigations should be performed to elucidate the molecular scale environments of REE adsorbed in halogenated UiO-66 materials. These findings are important in different fields that rely on ion-selective capture, such as in chemical separations

and in wastewater treatment. Our study lays the foundation for this future research and development activities.

Prepared for submission to: *Environmental Science and Technology Letters*

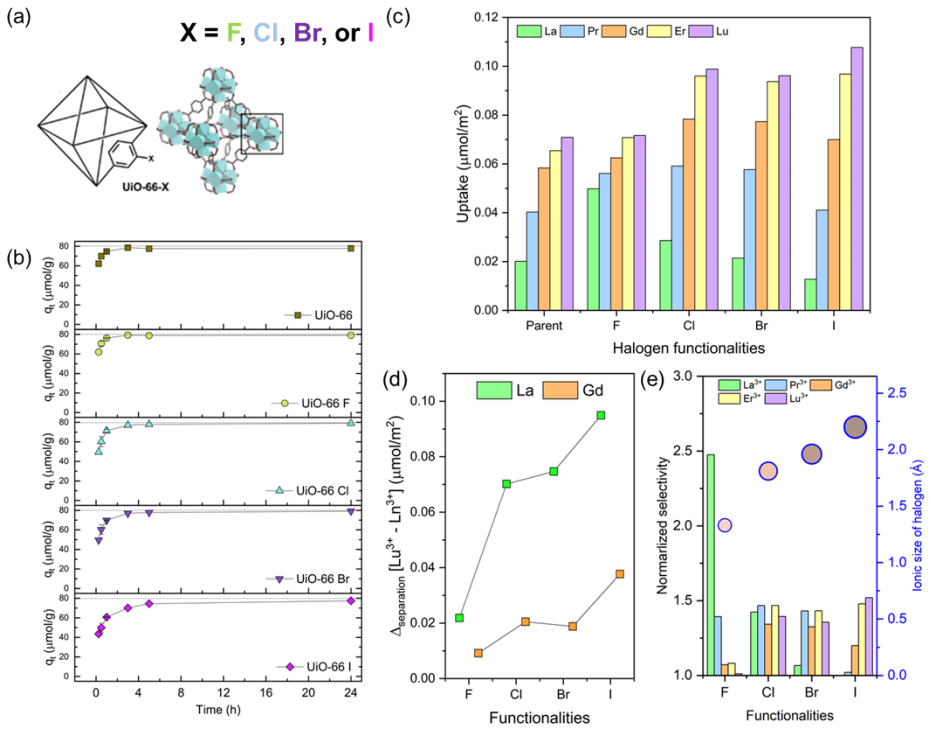


Figure 5. (a) Diagram of UiO-66 structure to show the location of halide functional groups; (b) Gd^{3+} kinetic adsorption by UiO-66 (dark green), UiO-66-F (light green), UiO-66-Cl (blue), UiO-66-Br (purple), and UiO-66-I (magenta); (c) REEs uptake in competitive systems by halogenated UiO-66; (d) separation of La^{3+} and Gd^{3+} from Lu^{3+} during adsorption; (e) calculated normalized selectivity by REEs uptake by parent UiO-66 to show the selectivity and ionic size of halogen elements in corresponding to UiO-66.

7. MANUSCRIPT IN PREPARATION: DIFFUSION OF LANTHANIDES IN METAL-ORGANIC FRAMEWORKS ASSESSED WITH MACHINE LEARNING

Abstract: Herein we used ML to identify the MOF structural features that would have the largest effect on the adsorption of REE ions. We used diffusion coefficients as a proxy for adsorption energy which was calculated from MD simulations. We developed a probabilistic prediction model for the prediction of MD-calculated diffusion coefficients of REE ions in a set of MOF structures. Using the probabilistic model, a Bayesian optimization protocol was developed which helped rapidly converge the model accuracy while focusing new simulations on those where the model was least certain in the predictions and where the model was predicting the highest diffusion coefficients. We also developed a ML model on the final dataset using a Random Forest algorithm. Using this final ML model, we identified the MOF features that were most predictive of the ion diffusion.

Prepared for submission to: *Journal of Physical Chemistry C*

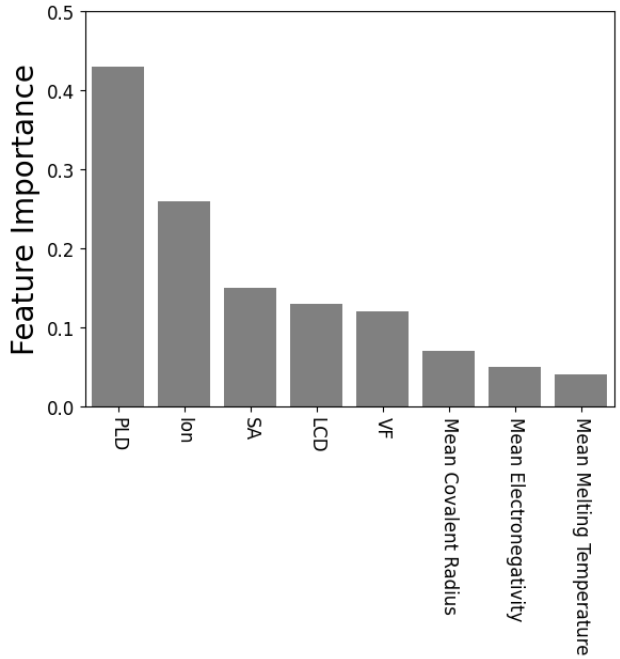


Figure 6. Calculated feature importance from the ML model to predict diffusion coefficients of RE ions in MOF structures (PLD – Pore limiting diameter, SA – Surface Area, LCD – Largest cavity diameter, VF – Void Fraction)

8. COLLABORATION WITH THE UNIVERSITY OF TEXAS AT EL PASO

8.1. Manuscript in preparation: Exploring the Potential for Propionate Pockets to Separate Y, La, Eu, and Lu Trivalent Cations: A DFT and FTIR Study

Abstract: The reactive portion of the lanmodulin protein (LanM) structure binding to rare earth elements (REEs) was modeled with propionate anions. Models were based on carboxylate group binding sites on LanM structures obtained from nuclear magnetic resonance measurements. Density functional theory calculations were performed to determine propionate Ca^{2+}/REE exchange energies and geometries (REE-O bond distances) of Y, La, Eu, and Lu. The results were compared with X-ray diffraction data. In addition, we report calculated infrared (IR) frequencies for La and Lu and compared those results to experimental FTIR data. The goal was to determine chemical interactions within the binding pockets that lead to REE separation from aqueous solution and individual lanthanides from one another.

Prepared for submission to: *The Journal of the American Chemical Society*

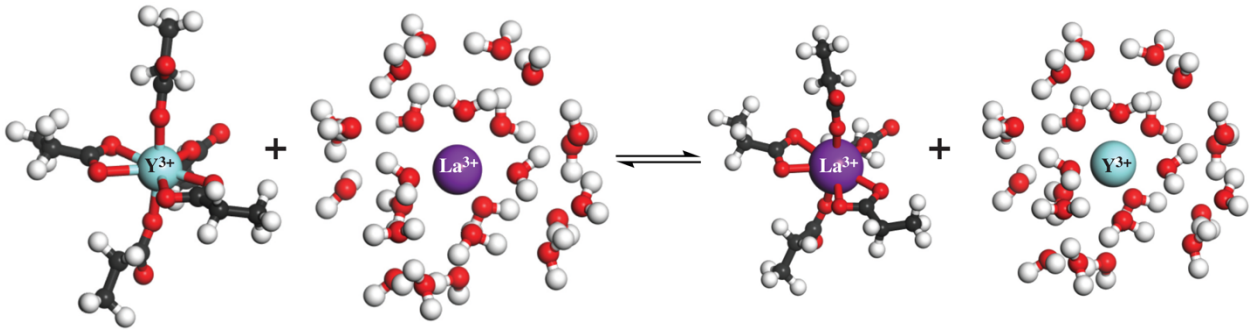


Figure 7. Example of an exchange reaction between Y^{3+} and La^{3+} in the REE $(CH_3CH_2CO_2)_5^{2-}$.

8.2. Manuscript in preparation: A study of the lanthanide-accumulating metallophore methylolanthanin and its potential to separate lanthanides: DFT NMR, vibrational frequency, structures, and thermodynamics

Abstract: The recently discovered lanthanide-accumulating metallophore methylolanthanin has a high affinity and selectivity for lanthanides and can be biologically upregulated. This chemistry could inspire a new technology of extracting and potentially separating individual lanthanides from waste materials, so that they can be recycled and reused. Here we used density functional theory calculations to explore fundamental chemistry of lanthanide-methylolanthanin complexes by calculating optimized structures and their corresponding Nuclear Magnetic Resonance chemical shifts, vibrational frequencies, geometries, and thermodynamics of formation. These results could be used to guide experiments and explain the existing experimental data obtained from lanthanide-methylolanthanin complexes.

Prepared for submission to: TBD

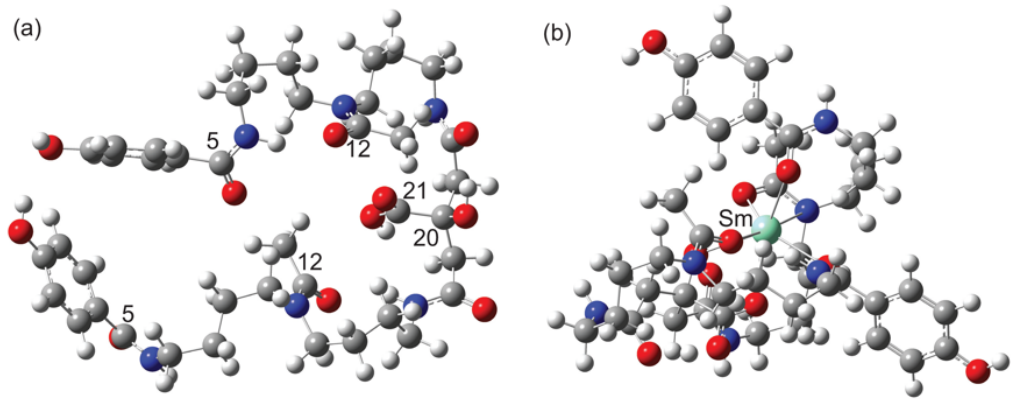


Figure 8. (a) Energy minimized methylolanthanin (MLL) model with C atoms labeled that take part in Ln^{3+}-O-C bonds and (b) energy-minimized Sm^{3+}-MLL with a coordination number of seven. In both models, H atoms are white, C atoms are gray, N atoms are blue, and O atoms are red. In (b), Sm^{3+} is labeled to the left of the light green Sm^{3+} ion.

9. COLLABORATION WITH GEORGIA STATE UNIVERSITY AND WITH TEMPLE UNIVERSITY

9.1. Preliminary studies on the energetics of ion interactions with MOFs

Summary: Work completed by Nadine Kabengi at the Department of Chemistry, Georgia State University, Atlanta, GA 30302, USA

The thermodynamics of the interactions of Nickel (Ni) and Cobalt (Co) with the four functionalized metal organic frameworks (MOF) samples were probed using in situ flow microcalorimetry. In addition to the heats, Qrxn in mJ/mg MOF, of adsorption, the mass of Ni and Co was quantified by conducting a mass-balance analysis to eventually calculate the molar enthalpies of reactions ΔHads in kJ/mol. The experiment was divided in two phases: The first phase is to inject each cation separately as single element solution and quantify the enthalpies of adsorption, and the second is to inject them together in equimolar Ni/Co mixtures to gauge their adsorption competitiveness. The target injection mass for all cations was fixed at 1 umole to match the maximum adsorption obtained from the sorption isotherms. Preliminary results indicate that reactions are endothermic for MOF-808 materials for both Ni and Co, and become exothermic for Cr-MIL-101 for Ni, and for Cr-MIL-101-NH_2 for Co.

Experimental Details: The flow microcalorimeter (FMC) used was custom-designed and fabricated in the Kabengi laboratory at Georgia State University. Information about the instrumentation and basic operational procedures have been published elsewhere. A MOF sample of known mass (10.0 mg ± 0.5 mg) was homogeneously packed into the FMC's microcolumn and equilibrated with 0.1 M HEPES solution adjusted at a pH of 6.5 ± 0.2 to obtain thermal equilibrium. Then, the input solution was changed to a solution containing the cation of interest at 1 x 10^{-4} M in a background of HEPES, adjusted to the same pH. When the thermal signal returned to the initial baseline, indicating that the reaction between the MOF surface and the cation has come to completion, the input solution was reverted to 0.1 M HEPES. During all experiments, effluent samples were collected for analysis. The mass of

cations retained at the surface was determined by a mass balance calculation between the total mass injected and the mass recovered from effluent samples.

9.2. UiO-66 MOFs: Ion Adsorption and External Surfaces

Summary: Work completed by Robert Castillo, Maxime Zitouni, Ziyad Thekkayil, Souvik Pramanick and Eric Borguet at the Department of Chemistry, Temple University, Philadelphia PA 19122, USA

Detecting and sequestering metal ions is a key challenge due to their harmful impact on the environment and human health. MOFs are potential solutions because of their high internal surface area which play a crucial role in adsorption. Understanding the chemistry of MOF is essential, as it can be tuned to enhance solvent and solute adsorption properties. To get a detailed understanding of adsorption mechanism, we are investigating the surface and capturing chemistry of a well-known MOF UiO-66 and its derivative UiO-66-NH_2.

The MOFs were immersed in ionic solutions of various concentrations and compositions. A thin layer of the MOF, separated from the solution by centrifugation, was deposited on a glass slide and investigated after drying in air. This project addresses three major issues (1) Adsorption of Co and Ni ions my MOFs (Fig. 9A); (2) Impact of solvents and salts on vibrational properties of MOFs (Fig. 9B); and (3) Developing vibrational sum frequency generation (vSFG) method to explore the chemical composition of the MOF external surface (Fig. 9C).

Raman spectroscopy was performed to explore the impacts of solvents and salts on MOFs. The Raman spectrum of solid MOF was recorded as baseline for reference. Mono-, di- and trivalent salts were dissolved in various solvents (e.g. dimethylformamide - DMF, water) and the spectra were compared with neat solvent spectra. Successful data reproducibility was demonstrated by collecting spectra at multiple regions on the MOF sample. MOFs incubated in aqueous ionic solutions, as opposed to neat water, showed stronger peaks in the O-H stretching region (~ 3400 cm^{-1}), suggesting enhancement of solvent retention inside the MOF by the trapped ions.

vSFG has revealed the signature of water adsorption by non-centrosymmetric MOFs.[18] As vSFG is forbidden in centrosymmetric environments, such as UiO-66 (space group, $Fm\bar{3}m$), there should be no bulk UiO-66 contribution to the vSFG spectra. Hence, the vSFG response from the solid UiO-66 extracted from water (Fig. 9C) is likely from the external surface. The peak above 3000 cm^{-1} is attributed to the aromatic C-H bond of the MOF linker (terephthalic acid). An unexpected peak was observed in the C-H stretch region below 3000 cm^{-1}. Such aliphatic C-H species could arise from DMF, used when synthesizing UiO-66, coordinated at the UiO-66 external surface.

Taken together, these preliminary results provide evidence for the impact of ions on solvent and suggest that the external surfaces of MOFs can be investigated with these methods.

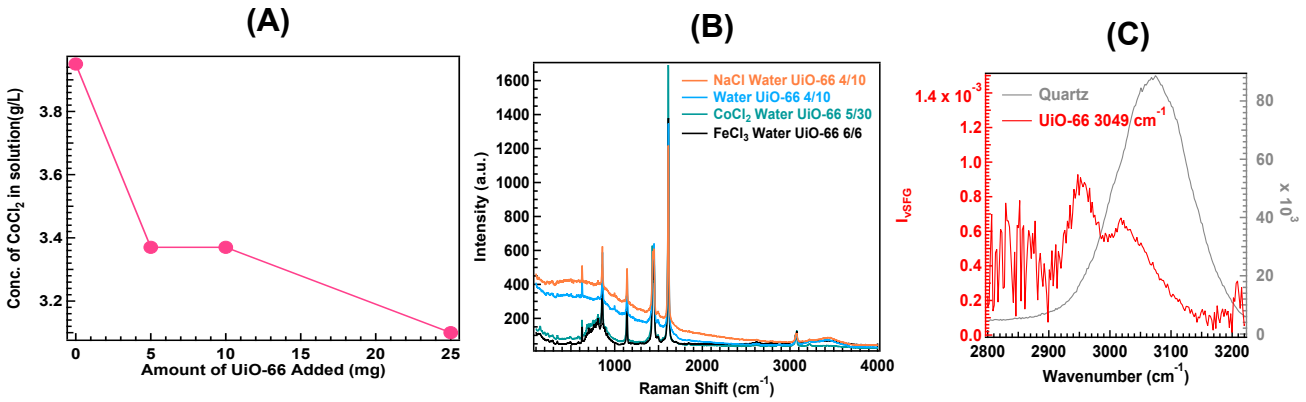


Figure 9. Adsorption of Co^{2+} and Ni^{2+} on UiO-66. (A) UV-Vis spectroscopy revealed that the concentration of $CoCl_2$ decreases with increasing amount of MOF, confirming ion capture; (B) Raman spectra of UiO-66 in various ionic solutions in water; and (C) Vibrational sum frequency spectrum of UiO-66 extracted from H_2O.

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