

# Efficient Capture and Release of the Rare-Earth Element Neodymium in Aqueous Solution by Recyclable Covalent Organic Frameworks

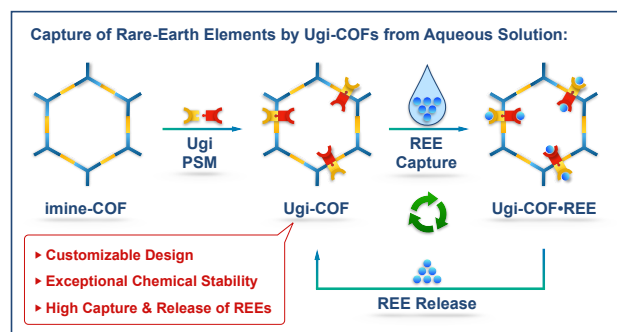
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*Rare-Earth Elements, Neodymium, Covalent Organic Frameworks*

**ABSTRACT:** Rare-earth elements (REEs) are present in a broad range of critical materials. The development of solid adsorbents for REE capture could enable the cost-effective recycling of REE-containing magnets and electronics. In this context, covalent organic frameworks (COFs) are promising candidates for REE adsorption due to their exceptionally high surface area. Despite having attractive physical properties, COFs are heavily underutilized for REE capture applications due to their limited lifecycle in aqueous acidic environments, as well as synthetic challenges associated with the incorporation of ligands suitable for REE capture. Here, we show how the Ugi multicomponent reaction can be leveraged to post-synthetically modify imine-based COFs for the introduction of diglycolic acid (DGA) moiety, a promising scaffold for REE capture. The adsorption capacity of the DGA-functionalized COF was found to be more than 40 times higher than that of the pristine imine COF precursor and more than three times higher than that of the next-best reported DGA-functionalized solid support. This rationally designed COF has appealing characteristics of high adsorption capacity, fast and efficient capture and release of the REE ions, and reliable recyclability, making it one of the most promising adsorbents for solid-liquid REE ion extractions reported to date.

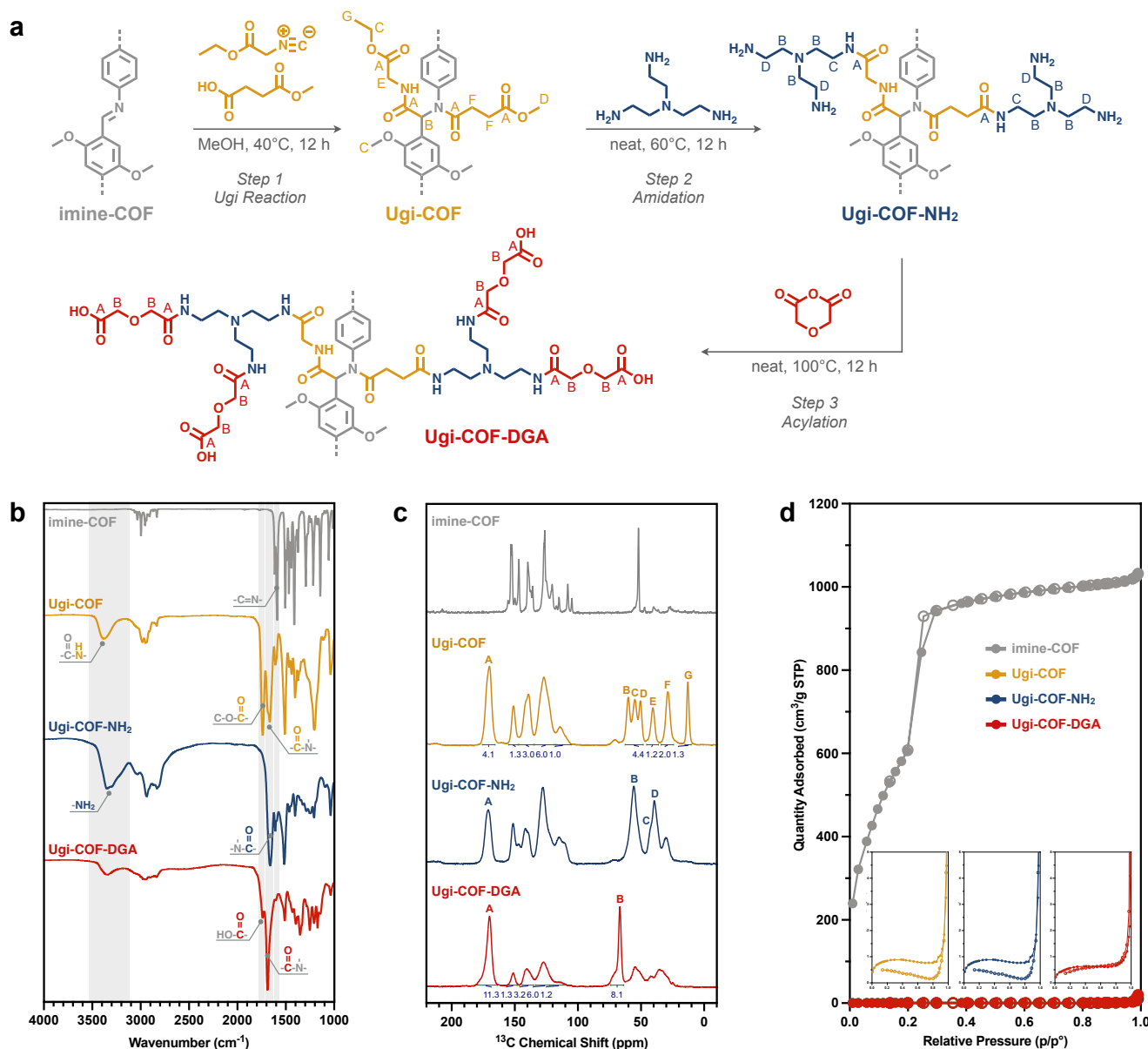


## INTRODUCTION

Rare-earth elements (REEs) are essential components in the manufacturing of semiconductors and permanent magnets. Important applications of REEs include consumer electronics, transportation, defense, power generation, health care, and petroleum refinement refining.<sup>1</sup> While the global demand for REEs is increasing, the supply is still limited.<sup>2</sup> Tremendous experimental and theoretical efforts have been invested in the last two decades to develop soluble ligands for binding REE ions using liquid-liquid extraction.<sup>3,4</sup> However, liquid-liquid extractions generate significant chemical waste, while the homogeneous ligands are difficult to recycle, dramatically increasing extraction costs.<sup>5</sup> More sustainable protocols and materials for the extraction and recycling of REEs are crucial to ensure their continuous supply. In solid-liquid extractions, on the other hand, a solid adsorbent is utilized to capture REE ions from the solution.<sup>6</sup> Because the solid adsorbent is easily separated from the liquid phase by filtration, it can potentially be recycled multiple times and eliminate the use of organic solvents, reducing the overall cost of extraction. Many solid adsorbents have been explored for REE capture, including silica,<sup>7-10</sup> zeolites,<sup>11-14</sup> metal-oxides,<sup>15,16</sup> organic polymers,<sup>17-20</sup> metal-organic frameworks,<sup>21-24</sup> and graphene oxides.<sup>25-28</sup> However, the existing materials tend to lack either the required efficiency or customizable molecular functionality and, oftentimes, cannot be

easily recycled. New solid adsorbent materials must be explored to effectively address these challenges. Next-generation REE adsorbents must possess tunable molecular structures and robust chemical backbones to achieve efficient REE capture and high stability for multiple extraction cycles.

One class of material with the requisite properties for solid-liquid extraction of REEs is covalent organic frameworks (COFs). Connected entirely through covalent bonds, COFs are assembled from customizable building blocks into porous organic solids with a defined crystal lattice and high surface area.<sup>29</sup> Despite coming in a variety of topological designs and reticular dimensions, COFs have been underexplored for REE recovery, with only a few promising reports on Sc,<sup>30</sup> La,<sup>31,32</sup> U,<sup>33-35</sup> and Th<sup>36-38</sup> extraction. The two main challenges associated with the streamlined production of COFs tailored to efficient REE extraction are the (1) limited molecular diversity of the building blocks suitable for the introduction of REE-binding scaffolds and (2) chemical lability of the COF linkages in the context of aqueous and low-pH conditions used in REE extraction applications. To overcome these challenges, we recently developed a novel and general post-synthetic modification (PSM) strategy that utilizes a facile Ugi multi-component reaction to introduce a number of useful functional groups into any imine-based COFs while retaining their structural integrity and improving chemical stability.<sup>39</sup> In this



**Figure 1.** (a) Synthetic route, (b) FT-IR spectra, (c) <sup>13</sup>C CPMAS SSNMR spectra, and (d) N<sub>2</sub> adsorption isotherms (closed and open circles represent adsorption and desorption points, respectively) of as-synthesized imine-COF (grey), Ugi-COF (gold), Ugi-COF-NH<sub>2</sub> (blue), and Ugi-COF-DGA (red).

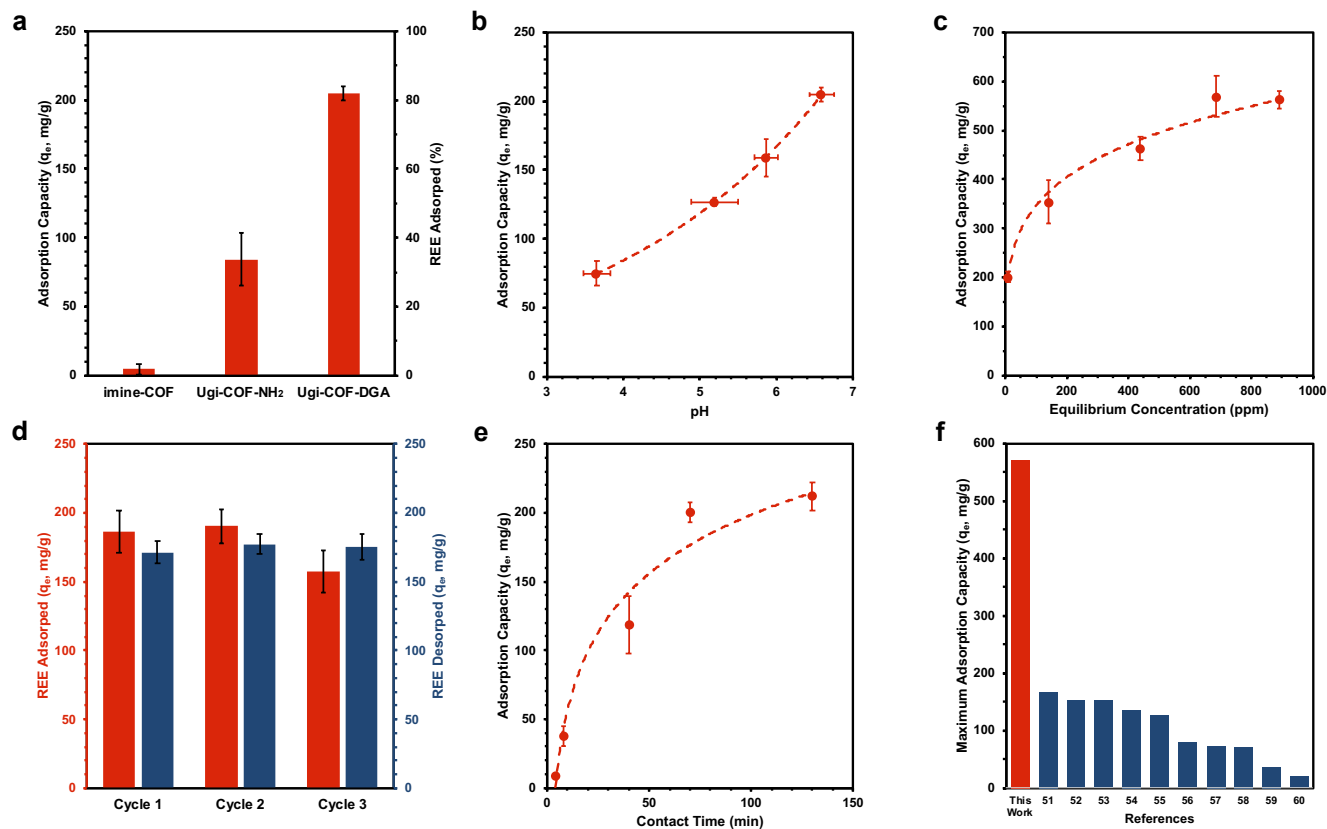
work, we demonstrate that the Ugi PSM strategy can be leveraged to rapidly tailor molecular functionality and improve the chemical integrity of an imine-based COF, both essential for producing recyclable material for efficient capture and release of REE ions.

## RESULTS AND DISCUSSION

**Design and Characterization of COFs.** The diglycolic acid (DGA) moiety is known to be an efficient chelating ligand for metal ions, including REE ions.<sup>40-42</sup> To incorporate the DGA motif for the first time in a COF, we selected a chemically robust and highly crystalline COF (imine-COF) produced by the condensation of 1,3,5-tris(4-aminophenyl)benzene with 2,5-dimethoxyterephthalaldehyde via the single-crystalline synthetic protocol.<sup>43</sup> To obtain the best material for REE adsorption, a series of post-synthetically modified COFs were rationally designed and tested, ultimately leading to the production of the Ugi-COF-DGA (Figure S1). During the first step of the PSM, the imine-COF was treated with ethyl

isocyanacetate and mono-methyl succinate in methanol at 40°C for 12 h to install ester functional groups, yielding the Ugi-COF (Figure 1a). Full conversion of the imine bonds to the corresponding Ugi bis-amide was critical to ensure the chemical stability of the material toward hydrolysis in extreme pH conditions, as well as the purity of the following synthetic transformations. During the second step, the ester groups of the Ugi-COF were amidated via the neat reaction with tris(2-aminoethyl)amine at 60°C for 12 h, providing the Ugi-COF-NH<sub>2</sub> with free amine groups. In the final step, Ugi-COF-NH<sub>2</sub> was reacted with neat diglycolic anhydride at 100 °C for 12 h to afford Ugi-COF-DGA via the ring-opening acylation of the amines.

The successful synthetic transformation at each step was confirmed by Fourier-transform infrared (FT-IR) spectroscopy and <sup>13</sup>C cross-polarization magic angle spinning (CPMAS) solid-state nuclear magnetic resonance (SSNMR) spectroscopy. For the Ugi-COF, the FT-IR spectrum revealed new amide frequencies at 1671



**Figure 2.** (a) The Nd adsorption capacity of as-synthesized imine-COF, Ugi-COF-NH<sub>2</sub>, and Ugi-COF-DGA. (b) pH-dependent study of the Nd adsorption capacity of the Ugi-COF-DGA. (c) Isotherm plot of the adsorption capacity of the Ugi-COF-DGA at different initial Nd concentrations. (d) Adsorption and desorption performance of the Ugi-COF-DGA over three recycles. (e) Time-dependent study of the adsorption performance of the Ugi-COF-DGA. (f) Comparison of the maximum adsorption capacities for the Ugi-COF-DGA and other DGA-functionalized solid supports. Unless otherwise stated, adsorption capacities of as-synthesized materials were tested using 10 mg of adsorbent in 50 mL of 50 ppm Nd solution at 25°C for 20 h. Desorption was carried out by suspending Nd-adsorbed material in 10 mL of 2.0 M HNO<sub>3</sub> at 25°C for 20 h.

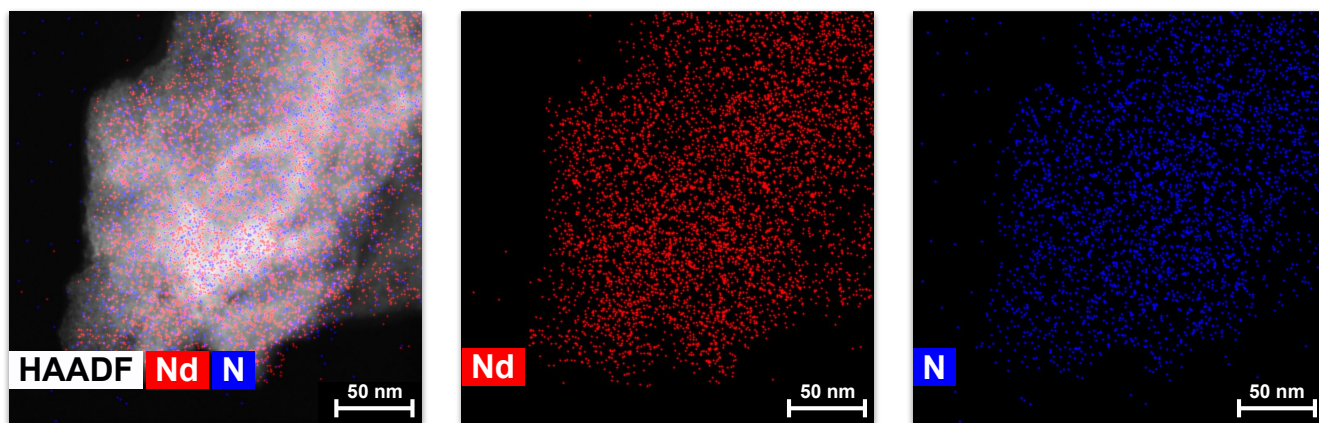
cm<sup>-1</sup> (C=O) and 3407 cm<sup>-1</sup> (N-H), as well as the ester frequency at 1743 cm<sup>-1</sup> (C=O) (Figure 1b, gold). In addition, all of the Ugi-COFs show an absence of the imine frequency (C=N) that was observed at 1592 cm<sup>-1</sup> in the imine-COF precursor (Figure 1b, grey). <sup>13</sup>C CPMAS SSNMR exhibited a new intense carbonyl carbon signal at 170.1 ppm (A, 4C), corresponding to the amide and ester functional groups, along with new aliphatic carbon signals at 60.4 ppm (B, 1C), 50.9 ppm (C, 1C), 40.9 ppm (D, 1C), 29.0 ppm (E, 1C), and 13.3 ppm (F, 2C) (Figure 1c, gold, 1C). The integration of the Ugi bisamide signals with respect to the aromatic signals of the COF backbone (aromatic carbon signals were utilized as an internal standard since no new aromatic groups were introduced in any of the PSM steps) provided a close match to the proposed structure of the Ugi-COF.

The FT-IR spectrum of the Ugi-COF-NH<sub>2</sub> displayed an intense amide frequency at 1670 cm<sup>-1</sup> (C=O), as well as a full disappearance of the ester frequency (C=O) (Figure 1b, blue). Furthermore, an intense broad frequency of the free amine groups at 3363 cm<sup>-1</sup> (N-H) was recorded. <sup>13</sup>C CPMAS SS NMR revealed new aliphatic carbon signals at 55.7 ppm (B), 41.8 ppm (C), and 39.7 ppm (D), corroborating the successful incorporation of the amine functionalities (Figure 1c, blue). Carbon signals corresponding to the ester methoxy and ethoxy groups were not observed, suggesting the amidation reaction was highly efficient.

In the case of the Ugi-COF-DGA, further amplification of the amide frequency at 1692 cm<sup>-1</sup> (C=O) was observed, as well as

significant attenuation of the aliphatic amine frequency (N-H). A new frequency appeared at 1745 cm<sup>-1</sup> (C=O), corresponding to the DGA carboxylic acid functional group (Figure 1b, red). As for the <sup>13</sup>C CPMAS SSNMR spectrum, two major peaks at 170.1 ppm (A, 12C) and 67.1 ppm (B, 8C) corresponding to the DGA functionality were detected (Figure 1c, red). The integration of the DGA signals A and B, with respect to the COF backbone aromatic signals, suggests near-quantitative conversion at each step, resulting in the loading of the DGA functional groups of ca. 3.62 mmol/g.

A complete loss of porosity of the Ugi-COFs in dry form was observed after the initial Ugi reaction on the imine-COF. In particular, the Brunauer–Emmett–Teller (BET) surface area of 2383 m<sup>2</sup>/g was recorded for the imine-COF, while only 3 m<sup>2</sup>/g was measured for the Ugi-COF and the Ugi-COF-NH<sub>2</sub>, and 2 m<sup>2</sup>/g for the Ugi-COF-DGA (Figure 1d). To account for such a dramatic loss in porosity, powder X-ray diffraction (PXRD) patterns of all four materials in dry form were collected. Through the Ugi modification, crystalline imine-COF was converted to amorphous Ugi-COF, which led to other materials produced in subsequent steps being amorphous as well (Figure S2). This behavior is well documented in other two-dimensional (2D) COFs that were utilized in post-synthetic modifications on the imine linkage, where initially rigid, C=N-linked crystalline frameworks were effectively converted to flexible, C–N-linked materials, causing disruptions of the delicate π-π stacking of the 2D COFs and, as a result, low BET surface areas and PXRD-silent profiles.<sup>44-48</sup> This challenge was previously overcome in 3D COFs, where



**Figure 3.** EDS mapping of Nd@Ugi-COF-DGA: N and Nd EDS maps overlapped with STEM image (left); Nd EDS image (center); N EDS image (right).

analogous post-synthetic transformations were shown to preserve the physical properties of the reticular structures, including high porosity and crystallinity.<sup>49-51</sup> Different structural responses of the 2D and 3D systems to the increased degrees of rotational freedom may suggest an exfoliation mechanism of the 2D COFs induced by the formation of flexible linkages.<sup>52</sup> The exfoliated COF layers in an aqueous solution would eliminate the need for diffusion of the REE ions inside the COF pores, which could be beneficial for applications in REE adsorption. Therefore, despite the non-porous nature of materials (in dry form) generated in this study, Ugi-COFs possess improved chemical stability due to robust Ugi bis-amide linkages, as well as molecular functionality of the DGA groups for REE capture in aqueous solution. Furthermore, Ugi-COF derivatives exhibited thermal stability up to 200 °C by thermogravimetric analysis (Figure S3), making these materials suitable for a wide range of REE extraction conditions.

**REE Adsorption Studies of COFs.** The performance of the COF materials for the REE adsorption was evaluated by mixing 10 mg of the adsorbent in 50 mL of 50 ppm solution of neodymium(III) nitrate ( $\text{Nd}(\text{NO}_3)_3$ ) at a pH of ca. 6.4 with stirring at 25 °C for 20 h. A preliminary assessment of the imine-COF revealed a minimal Nd adsorption capacity ( $q_e$ ) of ca. 5 mg of Nd per gram of COF (mg/g) despite the high porosity and crystallinity of the material (Figure 2a). On the other hand, Ugi-COF-NH<sub>2</sub> showed a significant improvement in the  $q_e$  value to ca. 84 mg/g, primarily due to the strong coordination ability of the aliphatic primary amine groups.<sup>53-55</sup> The addition of the DGA moiety into the Ugi-COF-DGA design provided the highest  $q_e$  value of ca. 205 mg/g. Since the latter material design proved to be the most efficient for Nd capture, we performed further mechanistic studies of adsorption behavior on the Ugi-COF-DGA.

Favorable ionic interactions between negatively charged carboxylates of the DGA moiety and positively charged metal ions should bolster the adsorption capacity of the Ugi-COF-DGA. To verify this hypothesis, we conducted a pH-dependent Nd adsorption study for the Ugi-COF-DGA material. As expected, the adsorption capacity of the Ugi-COF-DGA improved from ca. 75 to 205 mg/g as the pH increased from ca. 3.7 to 6.4. Despite the observed enhancement of the  $q_e$  value with a higher pH, a further increase in the pH was deemed unsuitable for adsorption testing due to the reaction of the REE ions with hydroxides and subsequent precipitation from the strongly alkaline solution. Hence, an optimal pH of ca.  $6.4 \pm 0.2$  was chosen for

all other studies to ensure the best performance of the Ugi-COF-DGA.

One of the critical properties distinguishing a promising adsorbent for REE capture is the material's ability to amplify the uptake of metal ions in a more concentrated solution of REEs. To evaluate the  $q_e$  response of the Ugi-COF-DGA to higher REE concentrations, an isotherm plot was generated using Nd solutions of 50 mL with initial concentrations ranging from 50 to 1000 ppm, while keeping the amount of adsorbent constant at 10 mg. Ugi-COF-DGA demonstrated an increase in the  $q_e$  value with a higher concentration of the Nd ions, varying from ca. 205 mg/g for the 50 ppm solution to ca. 570 mg/g for the 1000 ppm solution (Figure 2c). Note that the  $q_e$  value of 570 mg/g for Nd corresponds to ca. 3.95 mmol/g, which closely correlates to the maximum theoretical loading of the DGA groups in the Ugi-COF-DGA of 3.62 mmol/g. The adsorption isotherm had a good fit to the Langmuir model ( $R^2 = 0.98$ , Figure S4), suggesting a monolayer adsorption mode, and the maximum predicted adsorption capacity  $q_{\text{max}}$  of ca. 588 mg/g, which corresponds to the experimentally obtained value of ca. 570 mg/g for the Ugi-COF-DGA.

Consistently high performance and chemical stability of the material over multiple adsorption/desorption cycles are important factors for sustainable REE recovery. Hence, the recyclability of the Ugi-COF-DGA was evaluated over three adsorption/desorption cycles, and each data point was repeated thrice. Adsorption experiments were performed using 10 mg of the Ugi-COF-DGA in 50 mL of 50 ppm solution of Nd. After adsorption, Nd-loaded Ugi-COF-DGA (Nd@Ugi-COF-DGA) was isolated by filtration and suspended in 10 mL of 2.0 M nitric acid ( $\text{HNO}_3$ ) at 25 °C for 20 h with stirring, to ensure equilibrium was reached. Under these conditions, there was a near complete release of the adsorbed Nd (Figure 2d). No significant deterioration of the adsorption-desorption capacity was detected for the Ugi-COF-DGA over multiple capture and release cycles, suggesting the COF adsorbent is chemically robust. Such high molecular integrity and excellent recycling performance of the Ugi-COF-DGA in acidic aqueous conditions would not have been possible without converting hydrolyzable imine linkages of the imine-COF to stable bis-amide adducts. To the best of our knowledge, Ugi-COF-DGA is one of the most efficient, recyclable solid adsorbents for Nd capture reported to date (Table S1).

Fast adsorption kinetics is another attractive feature of a solid adsorbent for practical applications. Adsorption kinetics of the Ugi-COF-DGA were assessed by varying the contact time of 10 mg of



COF material with 50 mL of 50 ppm solution of Nd. Ugi-COF-DGA reached its best  $q_e$  value in a little over an hour (Figure 2e). The experimental data was fitted to the pseudo-first-order model ( $R^2 = 0.96$ , Figure S5), suggesting that the binding sites were present in excess of the REE ions at this concentration, which is likely the reason for such fast adsorption kinetics. Furthermore, we studied the Nd desorption kinetics of Ugi-COF-DGA. Samples of the Nd@Ugi-COF-DGA were thoroughly washed with deionized water to remove excess REEs, dried in vacuo, and subjected to time-dependent desorption studies in 2.0 M  $\text{HNO}_3$ . The release of the REE ions by Nd@Ugi-COF-DGA was almost immediate (Figure S6). Such fast and efficient adsorption and desorption performance of the Ugi-COF-DGA makes it a promising material for application in flow separation.

To assess the effect of the COF architecture as a solid support for the DGA ligand, we compared the highest  $q_e$  value of the Ugi-COF-DGA with the maximum adsorption capacities reported for other DGA-functionalized solid materials.<sup>56-65</sup> The newly developed Ugi-COF-DGA possesses the highest adsorption capacity among the best-reported DGA-modified supports (Figure 2f). Furthermore, it exhibits one of the highest reported  $q_e$  values for Nd adsorption to date (Table S1).

To verify the presence of Nd on the solid adsorbent, the Nd@Ugi-COF-DGA sample was recovered from the 1000 ppm Nd adsorption experiment, washed thoroughly with deionized water to remove excess REEs, dried in vacuo, and characterized. The FT-IR spectrum of the Nd@Ugi-COF-DGA exhibited apparent shifts of the carboxylic acid and amide carbonyl stretches to a lower frequency at  $1500\text{ cm}^{-1}$ , suggesting the weakening of the C=O bonds due to coordination to Nd (Figure S7). Nd 4d X-ray photoelectron spectroscopy (XPS) analysis of the Nd@Ugi-COF-DGA showed the presence of the Nd peak at 122 eV, which appeared at a lower binding energy than the  $\text{Nd}(\text{NO}_3)_3$  salt peak at 123 eV (Figure S8). This negative shift of ca. 1 eV in the Nd XPS suggests the coordination interaction between the electron-donating DGA groups and the electron-accepting Nd ions, which is also congruent with FT-IR observations. Importantly, energy dispersive X-ray spectroscopy (EDS) mapping of the Nd@Ugi-COF-DGA revealed a homogeneous distribution of the N and Nd atoms in the sample without apparent clustering of the metal ions, suggesting their successful adsorption by the COF material rather than precipitation from the solution (Figure 3, Figure S9).

## CONCLUSIONS

In conclusion, we demonstrated that the Ugi PSM strategy could be used to transform an imine-based COF into a readily customizable platform for efficient and recyclable adsorption of REEs. The novel Ugi-COF-DGA displays the highest adsorption capacity among other DGA-functionalized solid supports, can be recycled at least three times without compromising the performance of the material, and has fast adsorption and desorption kinetics. Future studies will be focused on optimizing the Ugi-COFs reticular and molecular design to achieve selective REE capture and integrating these materials into devices for capture or separation of REE ions from solution. This work could serve as a general strategy for the expansion of the functional diversity in imine-based COFs and inspire further exploration of these materials as promising adsorbents for efficient and recyclable capture of the REEs.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details, synthetic procedures, and structural characterizations (PDF).

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The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

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