Supporting Information

Gd^{3+} adsorption over carboxylic- and amino-group dual-functionalized UiO-66

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SI-1. Synthesis of UiO-66:

Briefly, 1.172 g of $ZrCl_4$, 0.924 g of TPA, 1.012 g of HCl, and 29.42 ml of DMF were mixed in a Teflon-lined stainless steel autoclave in a molar ratio of 1:1:2:76. The mixture was then heated at 180 °C for 24 h. The as-synthesized MOF was filtered, washed with DMF and water, and dried in a vacuum oven overnight. Before conducting adsorption runs, the MOF was further purified by mixing it with DMF (1 g of MOF to 50 ml of DMF), and the mixture was heated at 150 °C for 5 h in a Teflon-lined autoclave. After cooling, the material was filtered, washed, and dried as described previously.

SI-2. Adsorption experiments:

A stock solution was prepared by dissolving $Gd(NO_3)_3$ in water at a standard concentration of 1000 ppm Gd^{3+}. Solutions with lower concentrations were prepared by successive dilution of this stock solution. Most of the adsorption experiments were carried out using 100 ppm Gd^{3+} solutions, including those of adsorption kinetics, the effect of pH, and reusability of the material. To obtain

the equilibrium adsorption isotherms, different Gd^{3+} solutions with concentrations from 10 to 150 ppm were used. Except for the study of temperature effect on adsorption, all other adsorption experiments were carried out at 25 ^{o}C. Before adsorption, the adsorbent materials were dried in an oven to remove moisture and then accurately weighed. For each adsorption run, 15 mg of adsorbent and 15 ml of solution were placed in a glass vial and stirred magnetically for a given time. After each adsorption experiment, the adsorbents were separated from the solution using a 0.45 μm PET syringe filter, and the metal ion concentrations of the initial and filtered solutions were measured by ICP-OES. The adsorption kinetics measurement was carried out with contact times from 10 to 240 min at pH of 6.0.

Effect of pH. The effect of pH on the adsorption equilibrium was examined using 100 mg/L Gd^{3+} solution over the pH range of 2.0−7.0 at 25 °C. The pH of the solution was adjusted using either 0.1 mol/L HCl or NaOH solution. To avoid the formation of $Gd(OH)_3$, alkaline solution was not tested for the adsorption.[1]

Effect of temperature. The effect of temperature on the adsorption equilibrium was examined in the temperature range of 25 to 45 ^{o}C using Gd^{3+} ions in 100 ppm concentration.

Adsorption selectivity. To investigate the adsorption selectivity for Gd^{3+}, 15 mL of mixed solution containing Gd^{3+} and other metal ions (Na^{+}, Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+}) at a concentration of 40 ppm each was tested over 15 mg of UiO-66-COOH(25)-ED for 6 h at pH 6.0. A different set of selectivity test was also conducted under the same experimental conditions using La^{3+}, Nd^{3+} and Yb^{3+} along with the Gd^{3+} ions to investigate the adsorption selectivity among the REE ions.

Reusability tests. Reusability runs were conducted by initially saturating the adsorbent UiO-66-COOH(25)-ED with a 100 ppm Gd^{3+} solution at pH 6.0. After adsorption equilibrium was attained,

the adsorbent was separated from the suspension by filtration, and Gd^{3+} concentration of the filtrate was measured. After drying under vacuum, the adsorbent was regenerated by shaking it in 0.1 mol/L HCl for 2 h. After recovery and thorough washing, the adsorbent was dried and reused for Gd^{3+} adsorption.

SI-3. Adsorption equilibrium and kinetics measurement:

The adsorption equilibrium capacities (q_e, mg/g) were estimated using the following equation:

$q_e = (C_i - C_e) \times V/m$ ---------- (S1)

where C_i and C_e are the initial and equilibrium metal ion concentration (mg/L) in the solution, respectively, V is the volume of the solution (L), and m is the mass of the adsorbent (g). The absorption kinetics measurement for Gd^{3+} was carried out using 15 mL of 100 ppm Gd^{3+} solution over 15 mg of adsorbent with contact times of 10−240 min at pH 6.0.

SI-4. Adsorption data fitting by kinetic models

Both pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models were used to fit the experimental kinetics data.

The PFO model equation is given by[2]:

$\log (q_e - q) = \log (q_e) - (k_1/2.303)t$ ……(S2)

and the PSO model, which assumes the chemical surface reaction as the rate-limiting step, is given by[1]:

$t/q = (1/k_2 q_e^2) + t/q_e$……. (S3)

where q_e and q are the amount of Gd^{3+} adsorbed on the adsorbent (mg/g) at equilibrium and time t, respectively, and k_1 (min^{-1}) and k_2 (g/mg.min) are the PFO and PSO rate constants, respectively. The slope and intercept of log (q_e-q) vs t and t/q vs t, respectively, were used to determine the rate constants.

SI-5. Langmuir and Freundlich plot and the calculation of the maximum adsorption capacity:

The Langmuir isotherm model, which assumes that adsorption takes place homogeneously over the surface of a given adsorbent, is given by the following equation[3]:

$$C_e/q_e = 1/(Q_o b)+(C_e/Q_o) \quad \text{.....(S4)}$$

where C_e is the equilibrium concentration of the Gd^{3+} in the solution (mg/L), q_e describes the amount of Gd^{3+} adsorbed on the adsorbent at the adsorption equilibrium concentration (mg/g), Q_o represents the maximum adsorption capacity of the Gd^{3+}, and b represents a Langmuir constant related to the binding energy of adsorption (L/mg). The data was fitted to the Langmuir model by plotting c_e/q_e against c_e, and the values of Q_o and b were calculated from the slope and intercept, respectively (Figure S2).

Linear form of Freundlich isotherm equation can be expressed as[4]

$$\mathrm{Ln}q_e = \ln K_F + (1/n)\ln C_e \quad \text{..... (S5)}$$

Where C_e is the equilibrium concentration of adsorbate (mg/L), q_e is the amount adsorbed at equilibrium (mg/g), and K_F, n are constants for a given adsorbate and adsorbent at a particular temperature.

SI-6. Determination of adsorption selectivity: The affinities of the adsorbents towards a given metal ion were estimated by the distribution coefficient value (K_d, mL/g) calculated using the following equation[2]:

$K_d = ((C_i - C_f)/C_f) \times V/m$ ---------- (S6)

where C_i is the initial metal ion concentration in the aqueous solution (mg/L), C_f is the final metal ion concentration in the aqueous solution (mg/L), V is the volume of the solution (mL), and m is the mass of the adsorbent (g).

Table S1. Kinetics parameters of Gd^{3+} adsorption on UiO-66-COOH(25) and UiO-66-COOH(25)-ED

Material	Pseudo-first-order kinetics model		Pseudo-second-order kinetics model	
	k_1 (min^{-1})	R^2	k_2 (g/mg.min)	R^2
UiO-66-COOH(25)	5.77×10^{-3}	0.971	1.85×10^{-4}	0.994
UiO-66-COOH(25)-ED	4.90×10^{-3}	0.817	1.44×10^{-4}	0.965

Table S2. Adsorption Equilibrium parameters for the Adsorption of REEs over the studied materials.

Adsorbent	**Langmuir isotherm equation**			**Freundlich isotherm equation**		
	Q_0 **(mg/g)**	b **(L/mg)**	R^2	**n**	K_f	R^2
UiO-66	16	0.230	0.999	4.34	5.69	0.824
UiO-66-COOH(10)	46	0.101	0.997	2.38	7.00	0.931
UiO-66-COOH(25)	56	0.151	0.999	2.51	10.1	0.959
UiO-66-COOH(10)-ED	74	0.095	0.998	1.94	8.40	0.926
UiO-66-COOH(25)-ED	79	0.143	0.998	2.17	11.8	0.959

Table S3. Performances by different adsorbents for Gd^{3+} adsorption

Adsorbent	Functional group[a]	Maximum adsorption capacity (mg/g)	Reference
UiO-66-COOH-ED(25)	-COOH and $–NH_2$	79	This work
MIL-101-PMIDA	PMIDA	90.0	4
Mesoporous silica	MAH	85.4	5
Fe3O4-TMS-EDTA	TMS-EDTA	113	6
Metal oxide-ATMP	ATMP	8.0	7
Ionic imprinted resins	EDTA and DTPA derivatives	24.5	8
Fe_3O_4-Cys	Cys	98	9
mIIP-CS/CNT	Cys	88	10
Bacillus subtilis	-	55	11
Mycobacterium smegmatis	-	17.3	11
Silica gel-DGA	DGA	21.4	12

a. PMIDA: N-(phosphonomethyl)iminodiacetic acid hydrate; MAH: maleic anhydride; TMS-DETA: N-[(3-trimethoxysilyl)propyl]-ethylenediaminetetraacetic acid; ATMP: Tris-methylenephosphonic acid; Cys: L-cysteine; mIIP-CS/CNT: magnetically retrievable ion imprinted polymer−chitosan/carbon nanotube; EDTA: ethylenediaminetetraacetic acid; DTPA: diethylenetriaminepentaacetic acid; DGA: Diglycol amic acid.

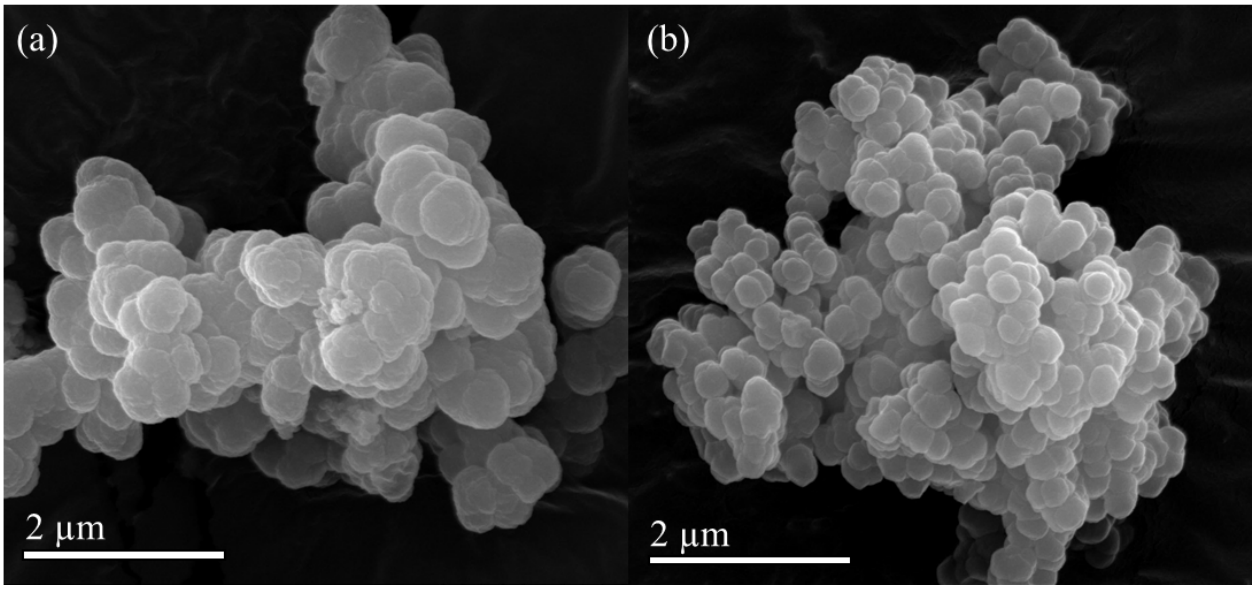

Figure S1. SEM images for (a) UiO-66 and (b) UiO-66-COOH(25)-ED.

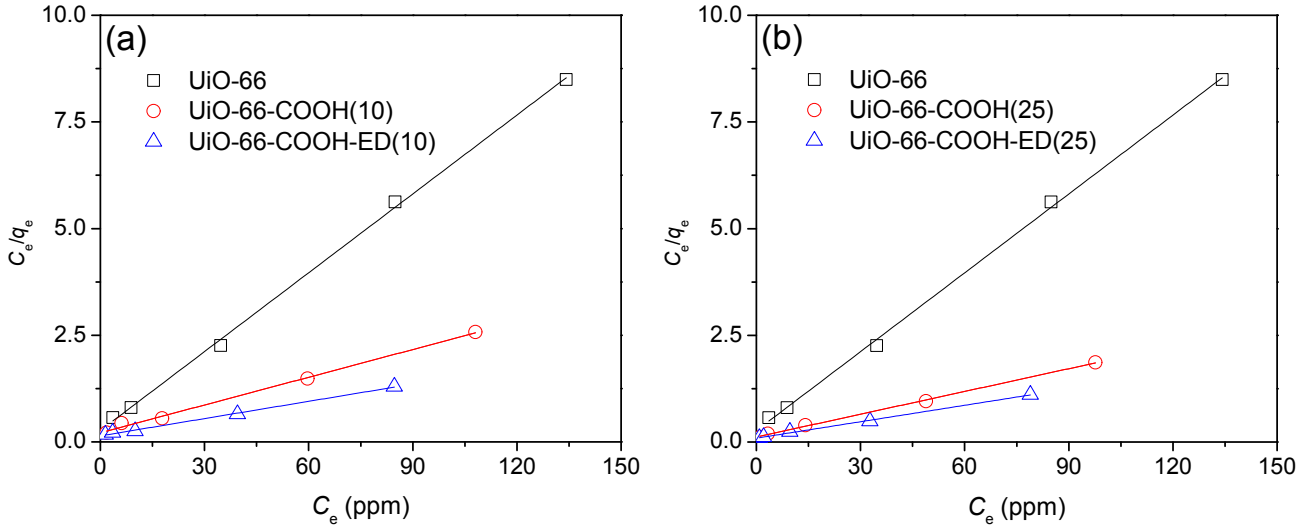

Figure S2. Langmuir isotherm plots for the adsorption of Gd^{3+} over the functionalized UiO-66 adsorbents.

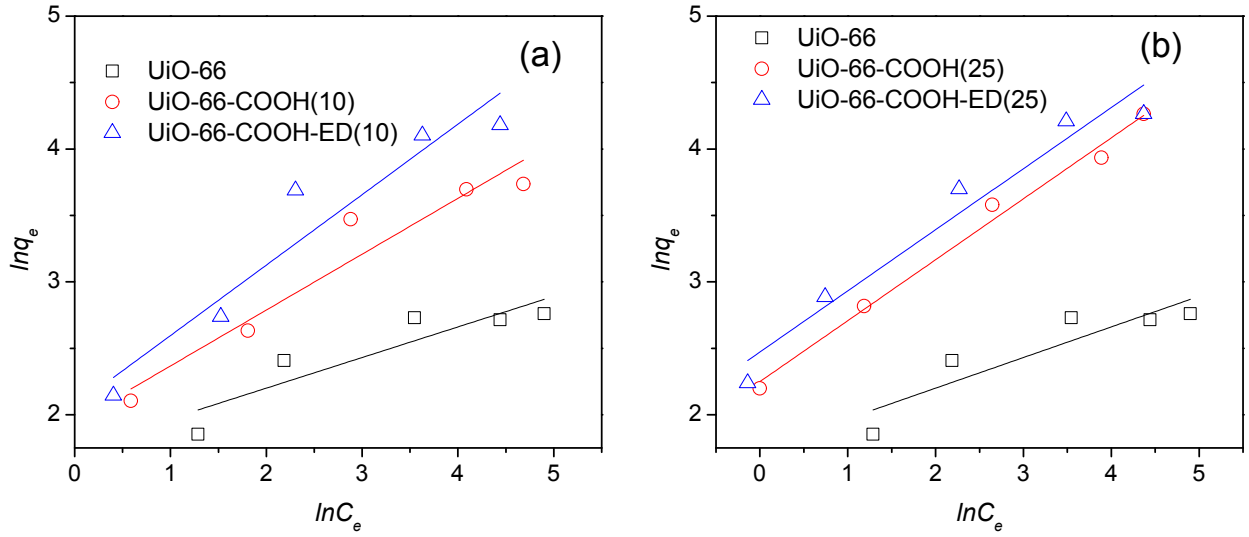

Figure S3. Freundlich isotherm plots for the adsorption of Gd^{3+} over the functionalized UiO-66 adsorbents.

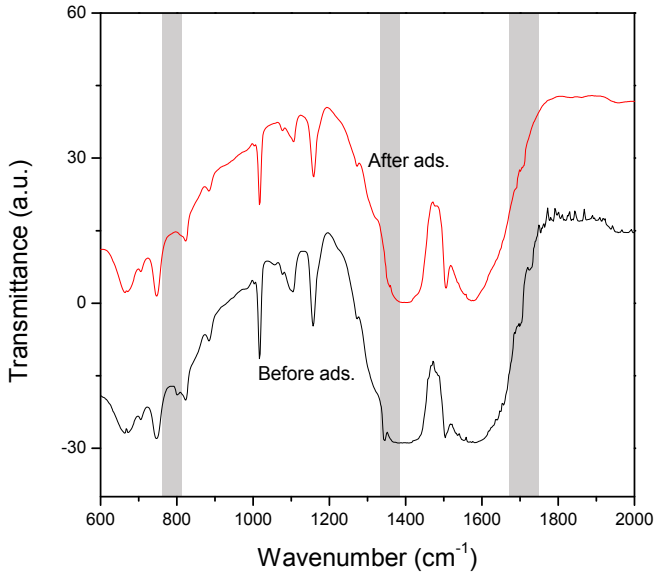

Figure S4. FT-IR spectra of UiO-66-COOH(25)-ED before and after the Gd^{3+} adsorption.

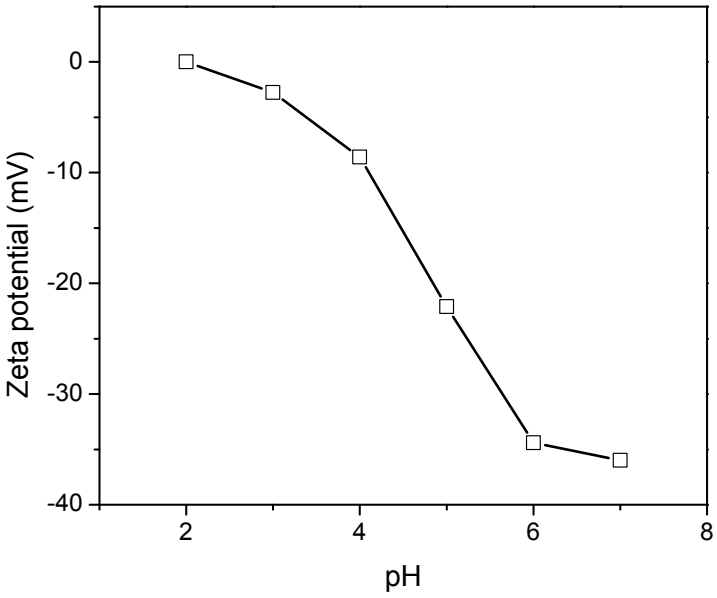

Figure S5. Zeta potential values of UiO-66-COOH(25)-ED at different pH.

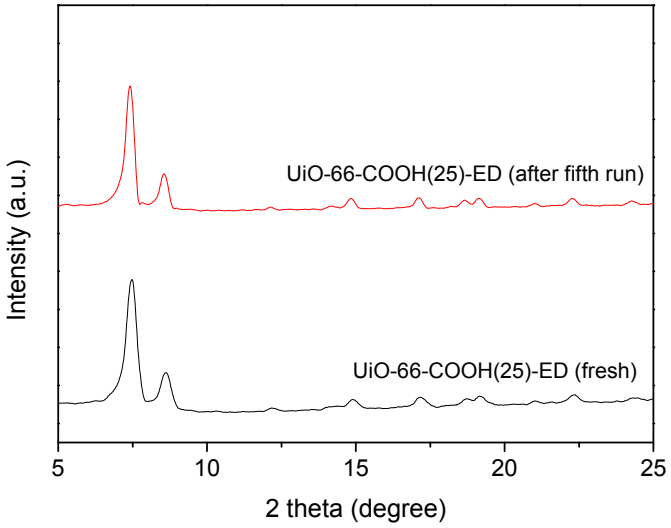

Figure S6. XRD patterns of UiO-66-COOH(25)-ED: fresh and after the fifth run in recycle.

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