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Supplementary Information

Extraction of Rare Earth Elements using Magnetite@MOF Composites

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S1. Syntheses

Experimental:

All reagents and chemicals were used as purchased with no further purification required before use. The synthesis of magnetite, magnetite-PSS, and magnetite@MIL-101-SO_3 has been previously described.[1]

Synthesis of magnetite core:

Fe_3O_4 was synthesized using a modified procedure.[2] Typically 5.4 g $FeCl_3 \cdot 9H_2O$ and 100 mL ethylene glycol was stirred for 30 min then 11.5 g of sodium acetate was added to the resulting dark yellow solution and stirred for another 1 h. The resulting brown solution transferred to Teflon lined Parr autoclaves, 50 mL in each, and heated for 18 h at 200 ºC. The resulting magnetic black solid magnetite was washed with water and methanol and collected by the help of magnet. The phase purity was confirmed by powder XRD.

Synthesis of magnetite-PSS

The functionalization of the magnetite surface with poly(sodium 4-styrenesulfonate) was performed using modified procedure.[3] 1.0 g of magnetite was sonicated for 2 h in a 400 mL solution of 0.3% PSS, then washed with water and collected with help of magnet. The phase purity was confirmed by powder XRD.

Synthesis of MIL-101-SO_3

The synthesis was performed using a reported procedure.[4] In a typical synthesis, 3.5 gram of 2-sulfoterephthalic acid, 1.25 grams of CrO_3 and conc. aqueous hydrochloric acid (1 mL) was dissolved in 25 mL water and then transferred to a Teflon lined stainless steel autoclave. The solution was heated at 180 ºC for six days. The reaction product was collected by centrifugation and washed with D.I. water (3x time, 50 mL) and methanol (3x times, 100 mL), followed by air drying. The phase purity of the powder was characterized by powder XRD and BET surface area.

Synthesis of DETA-In-MOF

The synthesis was performed using a modified reported procedure.[5] Typically in a 20 mL glass vial, 0.1 g of $In(NO_3)_3 \cdot 2H_2O$ was added to 6 mL mixed solvent (4 mL DMF/ 2 mL acetonitrile). The resultant mixture was sonicated for 30 minutes, followed by addition of 0.08 g 4,5-imidazoledicarboxylic acid, 0.8 mL imidazole (1.5 M in DMF) and 1.2 m: of HNO_3 (3.5 M in DMF). The overall mixture was then heated at 85ºC for 18 hour and then at 105ºC for 48 hours. The white crystalline powder (In-MOF) so obtained was characterized by powder XRD and BET surface area analysis.

Diethylene triamine (DETA) was grafted in In-MOF by stirring 0.4 g of In-MOF with 0.8 mmol DETA in 25 mL methanol for 24 h. The product was collected by centrifugation and dried in a vacuum oven at 85ºC. The phase purity was confirmed by powder XRD and BET surface area analysis.

Synthesis of magnetite@MIL-101-SO_3

MIL101-SO_3 was prepared by the previously reported procedure, but we found that in order to grow MIL-101-SO_3 on the surface of the PSS grafted magnetic core, it is better to sonicate the CrO_3 with the magnetite-PSS for 1 h before the linker is added. This process affords uniform growth of the MOF on the core surface. magnetite@MIL-101-SO_3 was synthesized by the following procedure: typically, 0.14 g of CrO_3 was mixed with 0.5 g of Fe_3O_4-PSS in 25 mL water and sonicated for 1 hours then 3.35 g of monosodium 2-sulfoterephthalic acid and 0.8 mL concentrated aqueous hydrochloric acid were added to the mixture and then transferred to a Teflon autoclave and heated for about 6 days at 180 °C. The reaction product was harvested and washed with water and methanol. The magnetic brown solid of magnetite@MIL-101-SO_3 was separated from the medium by the help of magnet. The phase purity was confirmed by powder XRD.

Synthesis of magnetite@In-MOF

In-MOF was prepared using a previously reported procedure, but we found that in order to grow the In-MOF on the surface of magnetite-PSS, excess amount of Indium salt is first sonicated with magnetite-PSS. Typically, in 20 mL glass vial 0.1 g of $In(NO_3)_3 \cdot 2H_2O$ mixed with 0.5 g of magnetite-PSS in 8 mL solution of 4 mL DMF and 2 mL acetonitrile then the mixture was sonicated for 30 min then 0.08 g of 4,5-Imidazoledicarboxylic acid, 0.8 mL of imidazole (1.5 M in DMF) and 1.2 mL of HNO_3 (3.5 M in DMF) were added then the mixture was heated at 85 °C for 18 h then at 105 °C for another 2 days. The reaction product was harvested by help of magnet and washed with methanol. The phase purity was confirmed by powder XRD.

Synthesis of magnetite@DETA-In-MOF

Grafting of diethylene triamine (DETA) in the pores of the magnetite@In-MOF was performed by stirring 0.4 g of magnetite@In-MOF with 0.8 mmol DETA in 25 mL methanol for 24 h then the product was collected by magnet and dried in oven at 85 °C. The phase purity was confirmed by powder XRD.

S2. Powder X-Ray Diffraction Data

A Rigaku Mini Flex II benchtop X-ray diffractometer using a Cu-Ka radiation of 0.154056 nm (30 kV and 15 mA) was used to obtain diffractograms. The samples were place in a powder sample holder and scanned with a step size of 2°/min under ambient conditions.

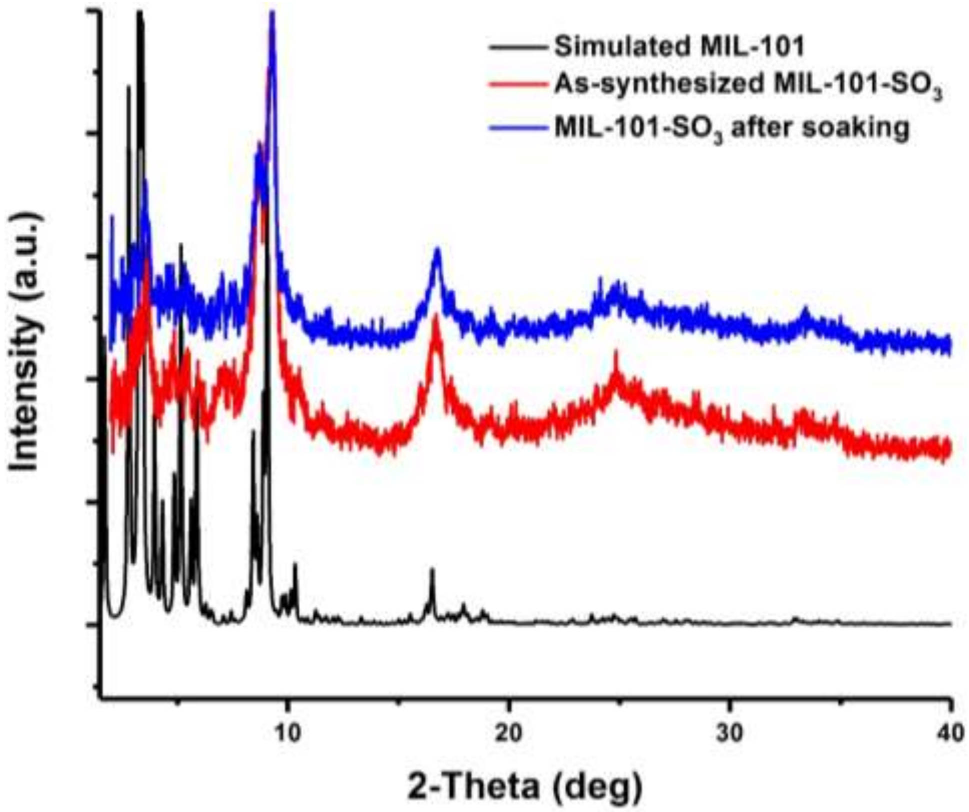

Figure S1. Powder X-ray diffraction patterns for MIL-101-SO$_3$ before and after soaking in the solution of REE ions.

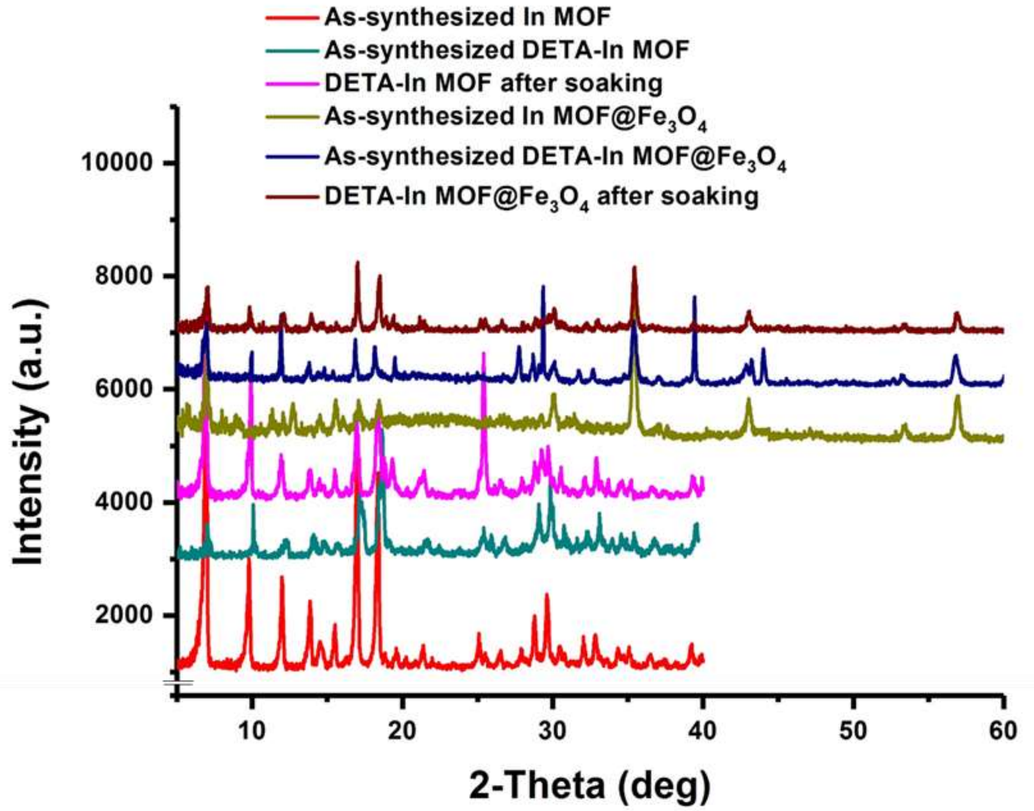

Figure S2. Powder X-ray diffraction patterns for In-MOF, DETA-In-MOF, magnetite@In-MOF, magnetite@DETA-In-MOF, before and after soaking in the solution of REE ions.

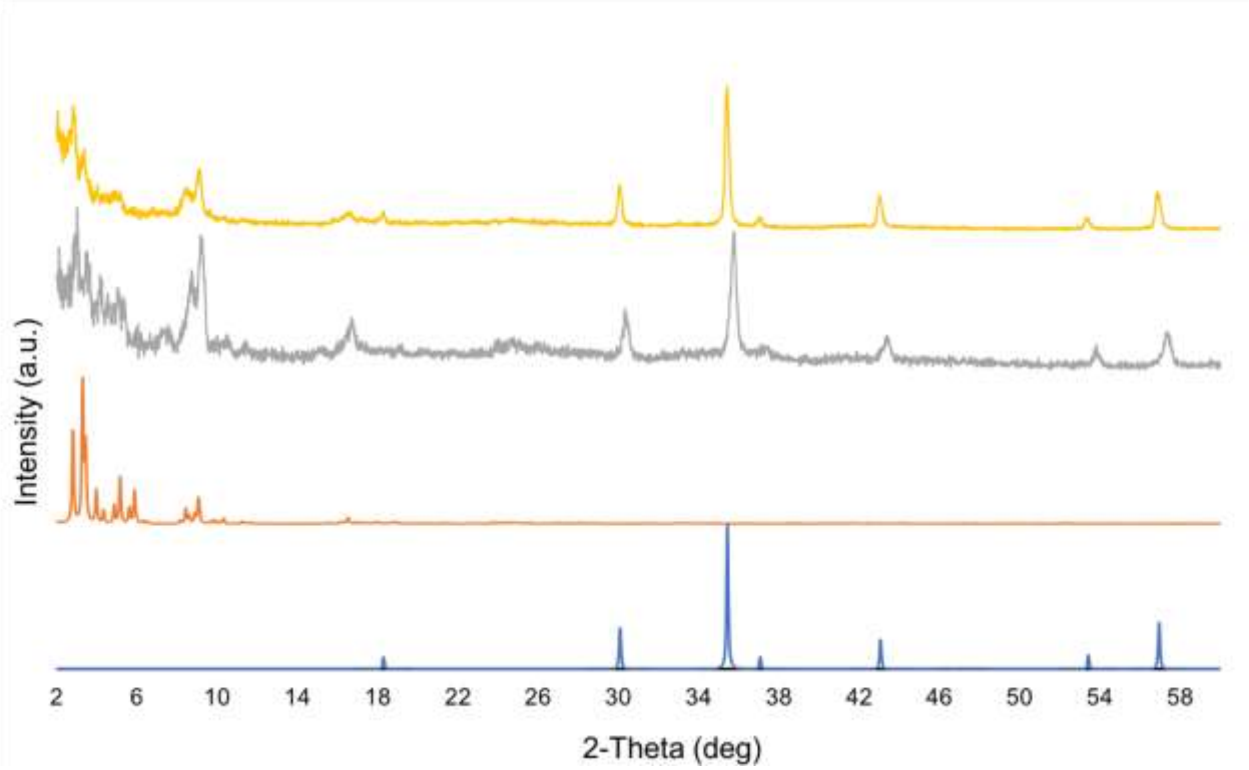

Figure S3. Powder X-ray diffraction patterns (bottom to top) of magnetite (simulated), MIL-101-SO_3 (simulated), magnetite@MIL-101-SO_3 before and after REE extraction. The magnetite peak has been normalized to highlight differences in the relative intensity of the MIL-101-SO_3 peaks.

S3. Powder X-Ray Diffraction Data

The Fourier transform infrared spectra were obtained at ambient temperature, and samples were prepared as 1% KBr pellets.

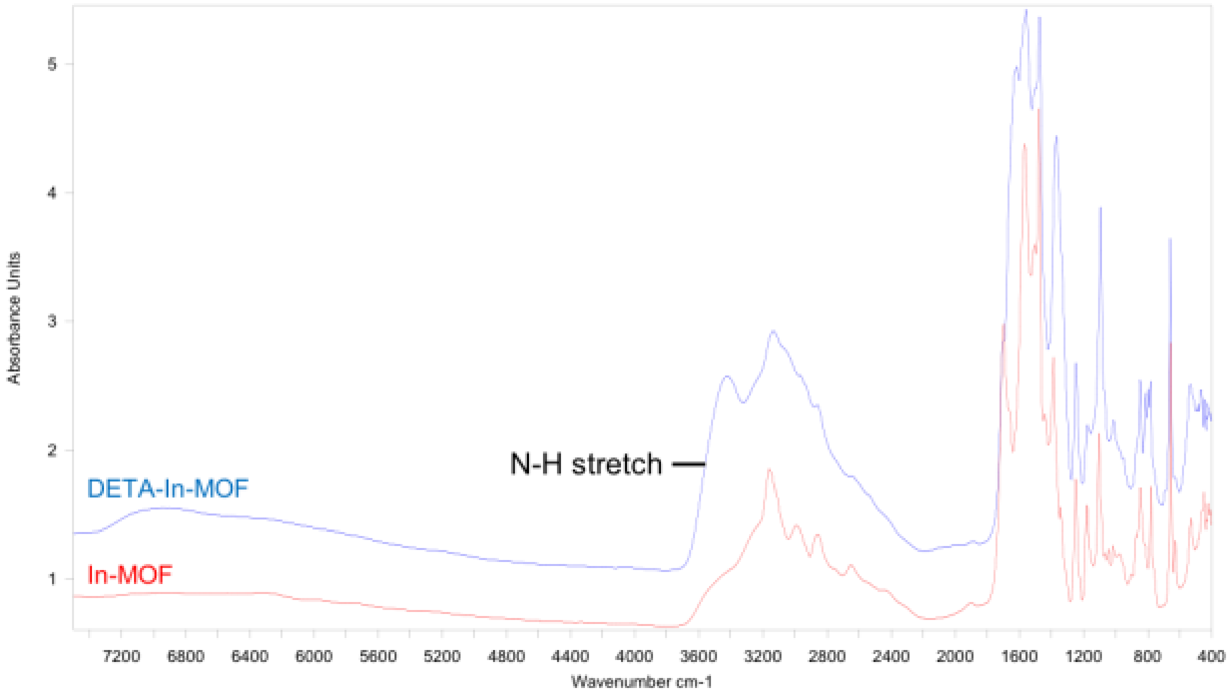

Figure S4. FT-IR spectra of In-MOF and DETA-In-MOF, highlighting N-H stretch of DETA.

S3. Brunauer-Emmett-Teller (BET) Surface Area Analysis

N2 adsorption at 77K was performed on an Autosorb iQ2 Quantachrome automated gas sorption analyzer to calculate the surface area of all samples. The samples were activated prior to measurement by heating to 200° C and maintaining this temperature for 12 h under vacuum. The apparent surface area was determined using the BET method by the Quantachrome suite.

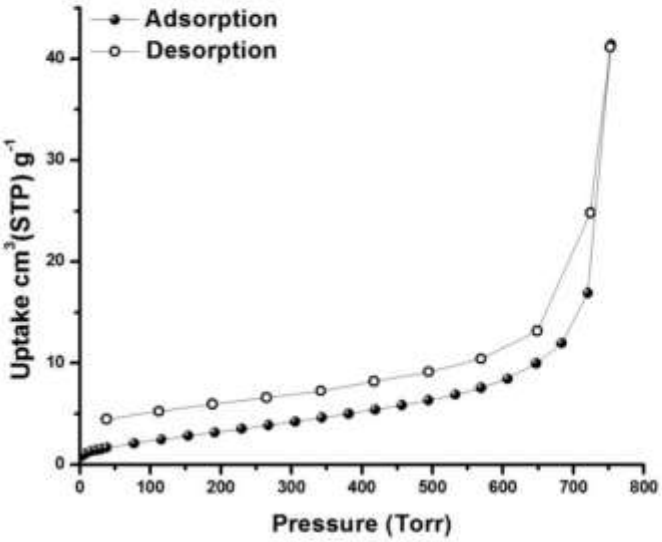

Figure S5. N_2 Sorption Isotherm of magnetite microsphere collected at 77 K (BET Surface Area = 6 m^2 g^{-1}).

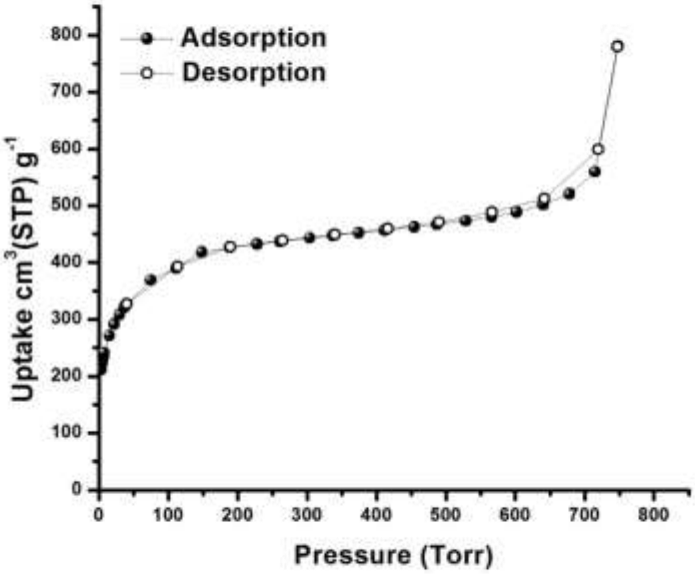

Figure S6. N_2 Sorption Isotherm of MIL-101-SO_3 collected at 77 K (BET Surface Area = 1368 m^2 g^{-1}).

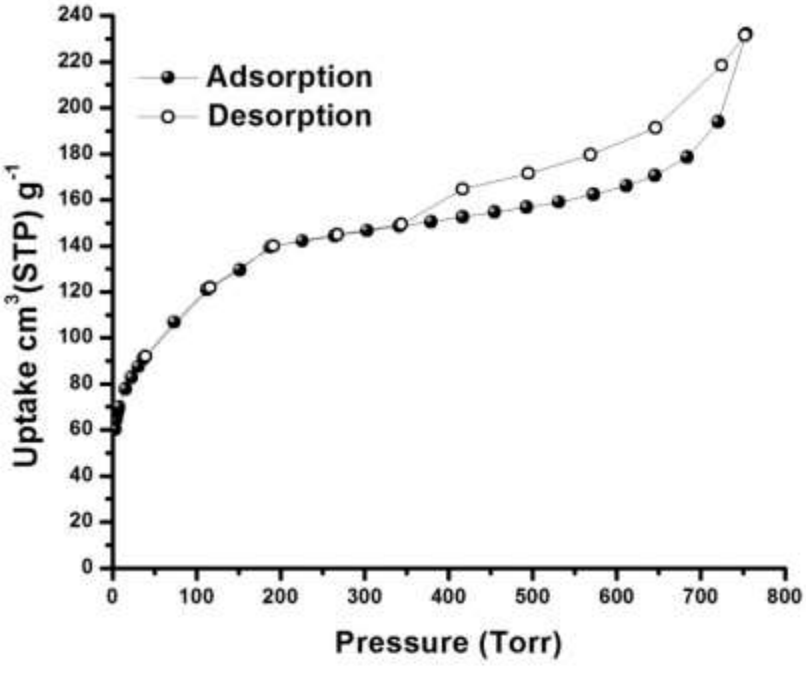

Figure S7. N_2 Sorption Isotherm of Fe_3O_4@MIL-101-SO_3 collected at 77 K (BET Surface Area = 376 m^2 g^{-1}).

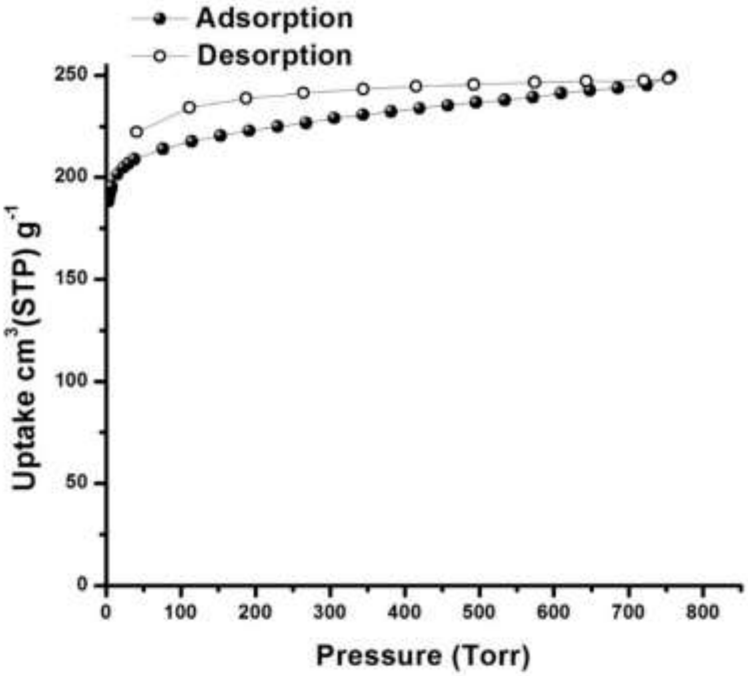

Figure S8. N_2 Sorption Isotherm of In-MOF collected at 77 K (BET Surface Area = 874 m^2 g^{-1}).

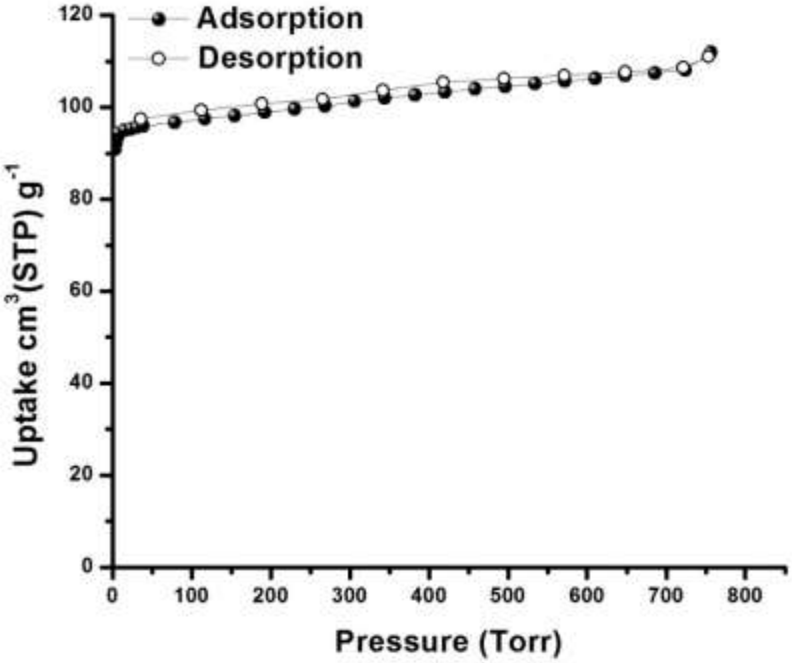

Figure S9. N_2 Sorption Isotherm of DETA-In-MOF collected at 77 K (BET Surface Area = 383 m^2 g^{-1}).

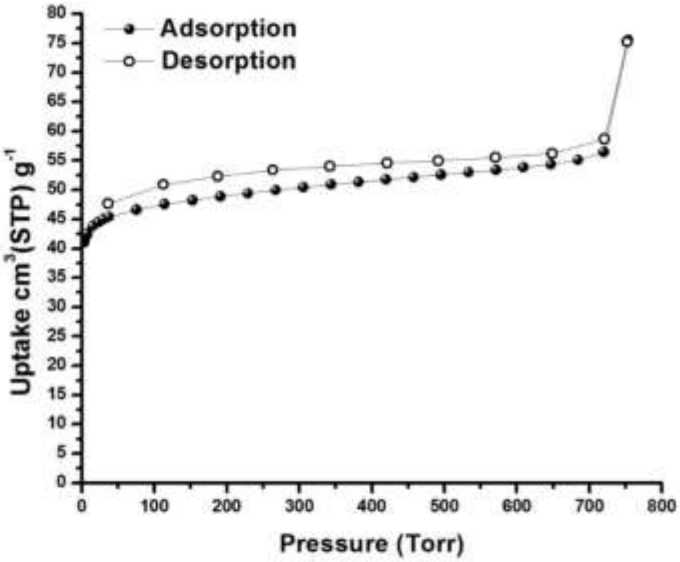

Figure S10. N_2 Sorption Isotherm of magnetite@DETA-In-MOF collected at 77 K (BET Surface Area = 190 m^2 g^{-1}).

S4. SEM Micrographs

SEM was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility.

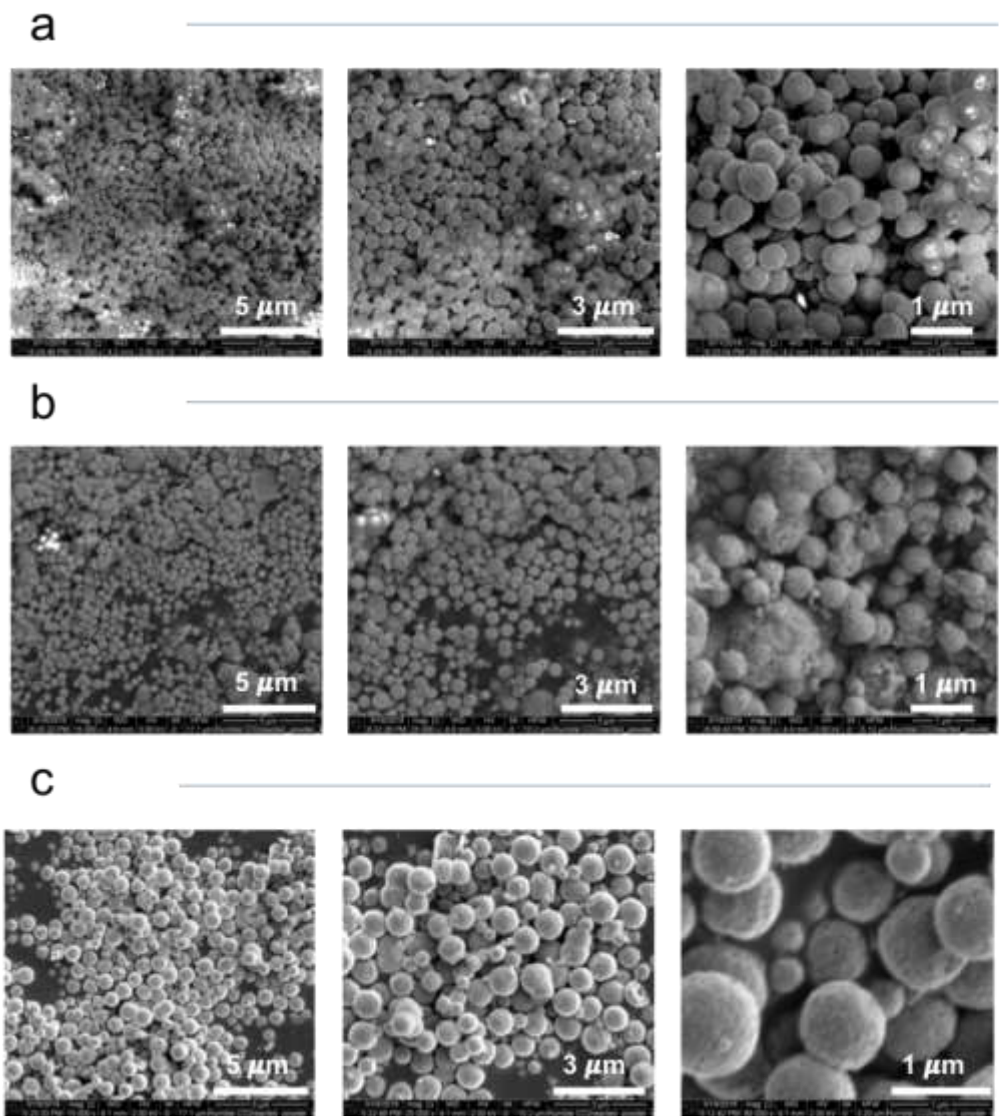

Figure S11. SEM images of (a) magnetite, (b) magnetite-PSS, and (c) magnetite@DETA-In-MOF.

S5. Ion-exchange studies

Batch experiments were performed by introducing activated functionalized MOFs and magnetite@MOF particles in a known concentration of REE solution. For unbound MOFs, initial ion-exchange studies were carried out by immersing activated MOFs (MIL-101-SO_3, In-MOF or DETA-In-MOF) into a 5 mL standard solution of individual (or mixed) RE cations in water in 1:2 molar ratio (typically 5-8 mg of MOF powder into ~0.0005M RE cation solution).For ion-exchange involving core-shell magnetic microspheres, similar experimental approach was taken, except no molar ratio calculation were carried out. In a typical ion-exchange process, ~5-8 mg of core-shell magnetic microsphere is added to a 5 mL standard RE cation solution The solution pH was ~4-5. REE uptake was determined by comparing ICP-OES analysis of blank reference solution samples where no sorbent was present with solution samples extracted after 5 min exposure to functionalized MOFs and magnetite@MOFs core particles. The extraction capacity q_e (mg g^{-1}), % REE extraction and distribution coefficient, K_d (mL/g) for functionalized MOFs and magnetite@MOFs were calculated using the equation below.

$$\%\, extraction \ = \frac{(c_0 - c_a) \times 100}{c_0}$$

$$q_e = \frac{(c_0 - c_a) \times V}{m}$$

$$K_d = \frac{(c_0 - c_a)V}{c_e \times m}$$

Where c_0 and c_a are respectively the initial and equilibrium concentration of metal ions (mg L^{-1}). V denotes the volume of the solution (mL) and m corresponds to the quantity of material used (g).

Experiments with commercially available resin (DOWEX-50W-X8, sulphonated polystyrene, Sigma-Aldrich) were performed at 0.0005 M to mimic the actual brine solution. At this concentration, the % extraction is more important than the total capacity. DOWEX-50W-X8 is found to have 70- 90% extraction efficiency with distribution coefficient of ~20,000 mL/g (Nd). This was explained by the presence of high density of chelating groups ($-SO_3^-$) on the polystyrene bead. MIL-101-SO_3, a reported MOF with high density of $-SO_3$ group was synthesized and tested under identical conditions including concentration (0.0005 M) and equilibrium time (5 min). The ICP OES data shows the MIL-101-SO_3 has over 90% of extraction efficiency with distribution coefficient reaching up to 40,000 mL/g (Dy). The high extraction efficiency and distribution coefficient (K_d) value suggest very fast kinetics by ion-exchange process for MIL-101-SO_3.

Further literature review shows that multidentate amines (such as ethylene diamine) can form stable complexes with lanthanide and actinides ions.{Eggert, 2011 #4} A functionalized MOF with free multidentate amine group is thus expected to be a good adsorbent for such ions. For example, recent report on MIL-101-SO_3 grafted with Ethylene diamine, and Diethylene triamine (DETA) suggest a superior performance for the extraction of UO_2 from aqueous solution.{Humphries, 2013 #5} The capacity of these MOFs towards U(VI) follows the order of MIL-101-DETA > MIL-101-ED > MIL-101-NH_2 > MIL-101, in which MIL-101-DETA possesses the highest capacity of 350 mg/g at pH 5.5. However, the disadvantage of this method is leaching of EDTA over a period of time. Therefore, we covalently attached DETA by reacting with free carboxyl groups present on the periphery of In-MOF with DETA. Experiments were conducted on DETA-In-MOF under identical conditions as MIL-101-SO_3 and DOWEX-50W-X8. The batch experiments suggest among all the MOFs tested including DOWEX-50W-X8 and MIL-101-SO_3, DETA-In-MOF is a superior material in terms of % extraction (99%), distribution coefficient (23×10^6 mL/g, Nd). Ion-exchange experiments were carried out using both MIL-101-SO_3 and magnetite@DETA-

In-MOF under similar experimental conditions, which shows both MIL-101-SO_3 and DETA-In-MOF coated magnetic core (e.g. magnetite@MOFs) keep their % extraction capacity. Further characterization experiments were conducted on magnetite@MIL-101-SO_3 because of the ease of synthesis and higher thermochemical stability.

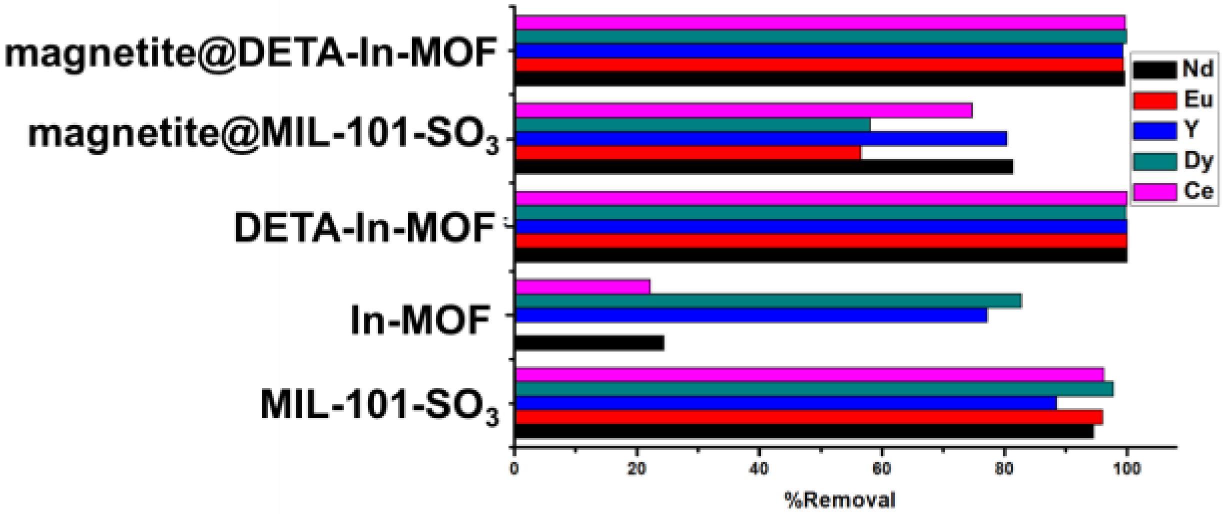

Figure S12. Percent of REEs (Nd, Eu, Y, Dy and Ce) extraction from aqueous solution by In-MOF, DETA-In-MOF, magnetite@DETA-In-MOF, MIL-101-SO_3, and magnetite@MIL-101-SO_3 after 5 min.

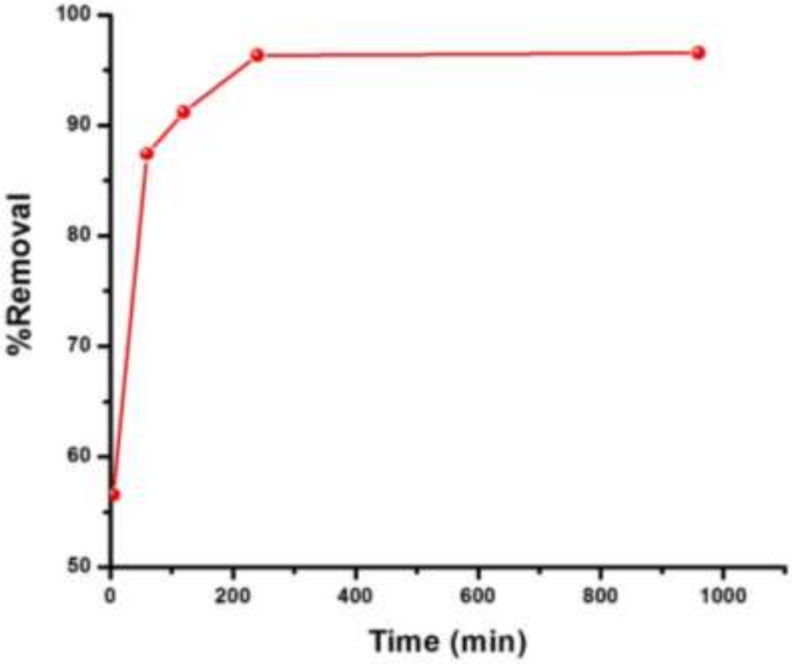

Figure S13. % extraction of Eu^{3+} as a function of contact time for magnetite@MIL-101-SO_3

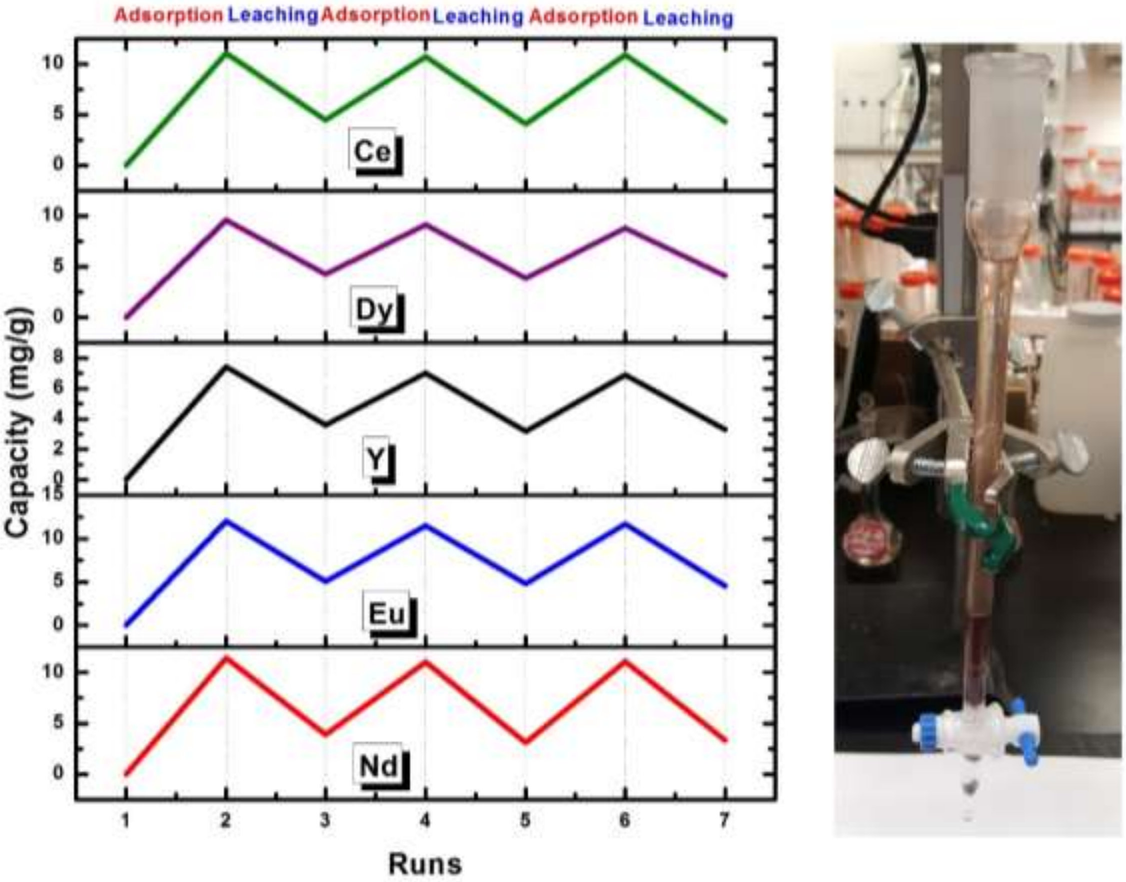

Figure S14. Cycle experiments with mixed REEs solution by magnetite@MIL-101-SO_3. 2M HNO_3 solution was used to remove REEs from the packed bed.

Table S1. Comparison of extraction capacities of REE cations (in ppm) using pristine MIL-101-SO_3, In-MOF, DETA-In-MOF and magnetite@MOFs

	Nd			**Eu**			**Y**			**Dy**			**Ce**		
Adsorbents	**Before**	**After**	**%R**	**Before**	**After**	**%R**	**Before**	**After**	**%R**	**Before**	**After**	**%R**	**Before**	**After**	**%R**
MIL-101-SO_3	91	4.9	94.50	82.6	3.1	95.99	32.86	3.76	88.50	73.86	1.66	97.70	45.59	1.71	96.20
In-MOF	99.16	64.05	24.40	65.83	13.28	81.14	50.77	21.98	77.20	72.77	12.54	82.80	95.71	74.34	22.20
DETA-In-MOF	99.16	0.01	99.99	65.83	0.01	99.98	50.77	0.01	99.98	72.77	0.189	99.80	95.71	0.04	99.99
magnetite@MIL-101-SO_3	63.83	11.98	81.23	61.92	26.98	56.42	42.83	8.38	80.43	82.6	34.61	58.10	64.17	16.2	74.75
magnetite@DETA-In-MOF	63.83	0.22	99.65	61.92	0.39	99.41	42.83	0.31	99.32	82.6	0.11	99.94	64.17	0.19	99.73

Table S2. Extraction of REE cations (in ppm) using commercial DOWEX-50W-X8 (Sigma-Aldrich)

REE	Before	After	% Extraction	K_d (mL/g)
Y	46.25	13.39	71.04	1520
Nd	99.16	1.57	98.4	20858
Dy	72.77	4.49	93.8	3980
Eu	65.27	10.71	83.59	1188
Ce	44.17	13.61	69.18	805

Table S3. REE Distribution coefficient (K_d)

Adsorbent	REE	K_d (mL/g)
MIL-101-SO_3	**Y**	7.72×10^3
	Nd	1.28×10^4
	Dy	3.62×10^4
	Eu	2.17×10^4
	Ce	2.1×10^4
DETA-In-MOF	**Y**	2.32×10^6
	Nd	5.75×10^6
	Dy	1.4×10^5
	Eu	5.39×10^6
	Ce	7.91×10^5

S6. References

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