

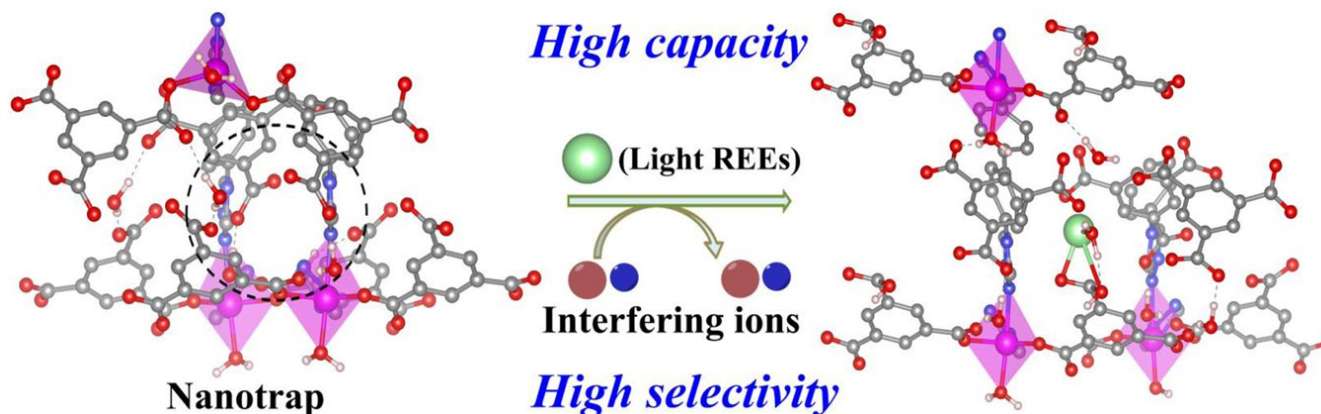
Rationally designed nanotrap structures for efficient separation of rare earth elements over a single step

Received: 15 July 2022

Accepted: 5 February 2024

Qing-Hua Hu^{1,2,3}, An-Min Song², Xin Gao², Yu-Zhen Shi², Wei Jiang²,
Ru-Ping Liang²✉ & Jian-Ding Qiu^{1,2}✉

1. State Key Laboratory of Nuclear Resources and Environment, East China University of Technology, Nanchang, China.
2. School of Chemistry and Chemical Engineering, Nanchang University, Nanchang, China.
3. School of Chemistry and Chemical Engineering, Jinggangshan University, Ji'an, China.



Sonali Seth
Oct 5, 2024

Background

Inorganic Chemistry

Cite This: *Inorg. Chem.* 2018, 57, 13895–13900

Article

pubs.acs.org/IC


Lanthanide Discrimination with Hydroxyl-Decorated Flexible Metal–Organic Frameworks

Marta Mon,[†] Rosaria Bruno,[‡] Rosangela Elliani,[‡] Antonio Tagarelli,[‡] Xiaoni Qu,^{†,§} Sanping Chen,[§] Jesús Ferrando-Soria,^{*,†} Donatella Armentano,^{*,‡} and Emilio Pardo^{*,†}

[†]Instituto de Ciencia Molecular, Universidad de Valencia, Paterna 46980, Valencia, Spain

[‡]Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Rende 87036, Cosenza, Italy

[§]College of Chemistry and Materials Science, Northwest University, Xi'an 710069, China

 Supporting Information

ACS APPLIED MATERIALS
& INTERFACES

Cite This: *ACS Appl. Mater. Interfaces* 2018, 10, 23918–23927


Research Article

www.acsami.org

Selective Adsorption of Rare Earth Elements over Functionalized Cr-MIL-101

Yu-Ri Lee, Kwangsun Yu, Seenu Ravi, and Wha-Seung Ahn^{*,†}

Department of Chemistry and Chemical Engineering, Inha University, Incheon, Republic of Korea

 Supporting Information

J | A | C | S
A | R | T | I | C | L | E | S

Published on Web 02/18/2009

Macrocyclic Receptor Exhibiting Unprecedented Selectivity for Light Lanthanides

Adrián Roca-Sabio,[†] Marta Mato-Iglesias,[†] David Esteban-Gómez,[†] Éva Tóth,[‡] Andrés de Blas,[†] Carlos Platas-Iglesias,^{*,†} and Teresa Rodríguez-Blas^{*,†}

Departamento de Química Fundamental, Universidade da Coruña, Campus da Zapateira, Alejandro de la Sota 1, 15008 A Coruña, Spain, and Centre de Biophysique Moléculaire, CNRS, rue Charles Sadron, 45071 Orléans, Cedex 2, France

Received November 4, 2008; E-mail: cplatas@udc.es (C.P.-I.); mayter@udc.es (T.R.-B.)

3.2 Å cavity size

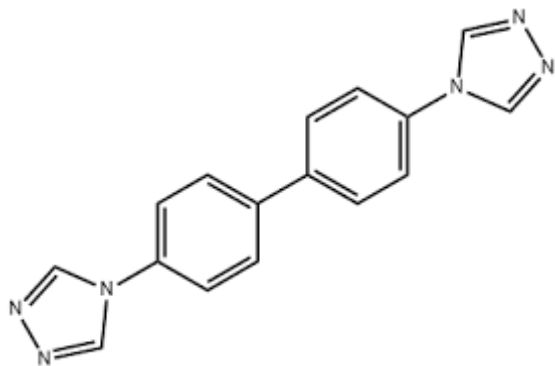
Why this paper?

Synergic effect of pore size and uncoordinated –COOH groups help in selective separation of REEs.

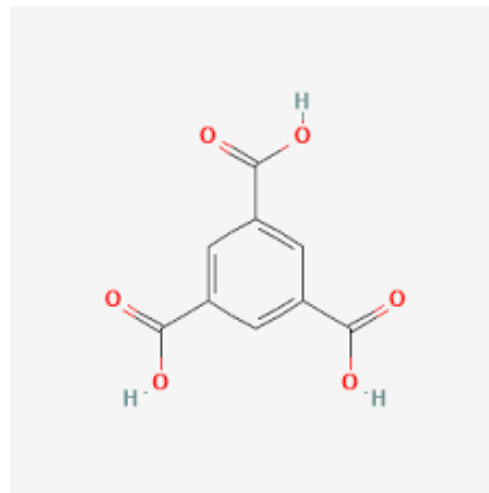
Cryo-EM studies were done to confirm the adsorption of REEs onto the nanotrap.

Separation factor is higher as compared to the existing MOFs

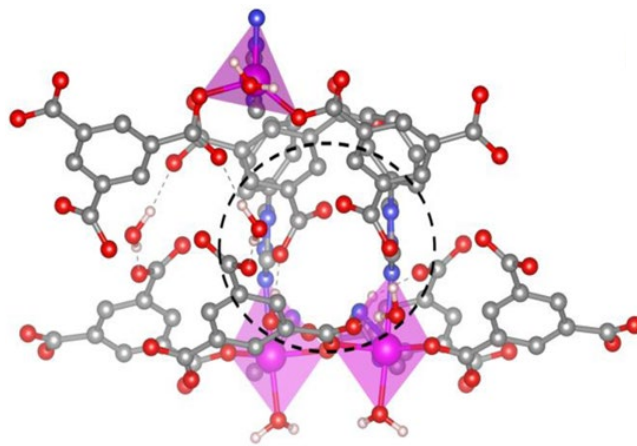
Introduction



4,4-di(4H-1,2,4-triazol-4-yl)-1,1-biphenyl
(DTB)



Trimesic acid
(BTC)



Nanotrapp

Zn-based MOF

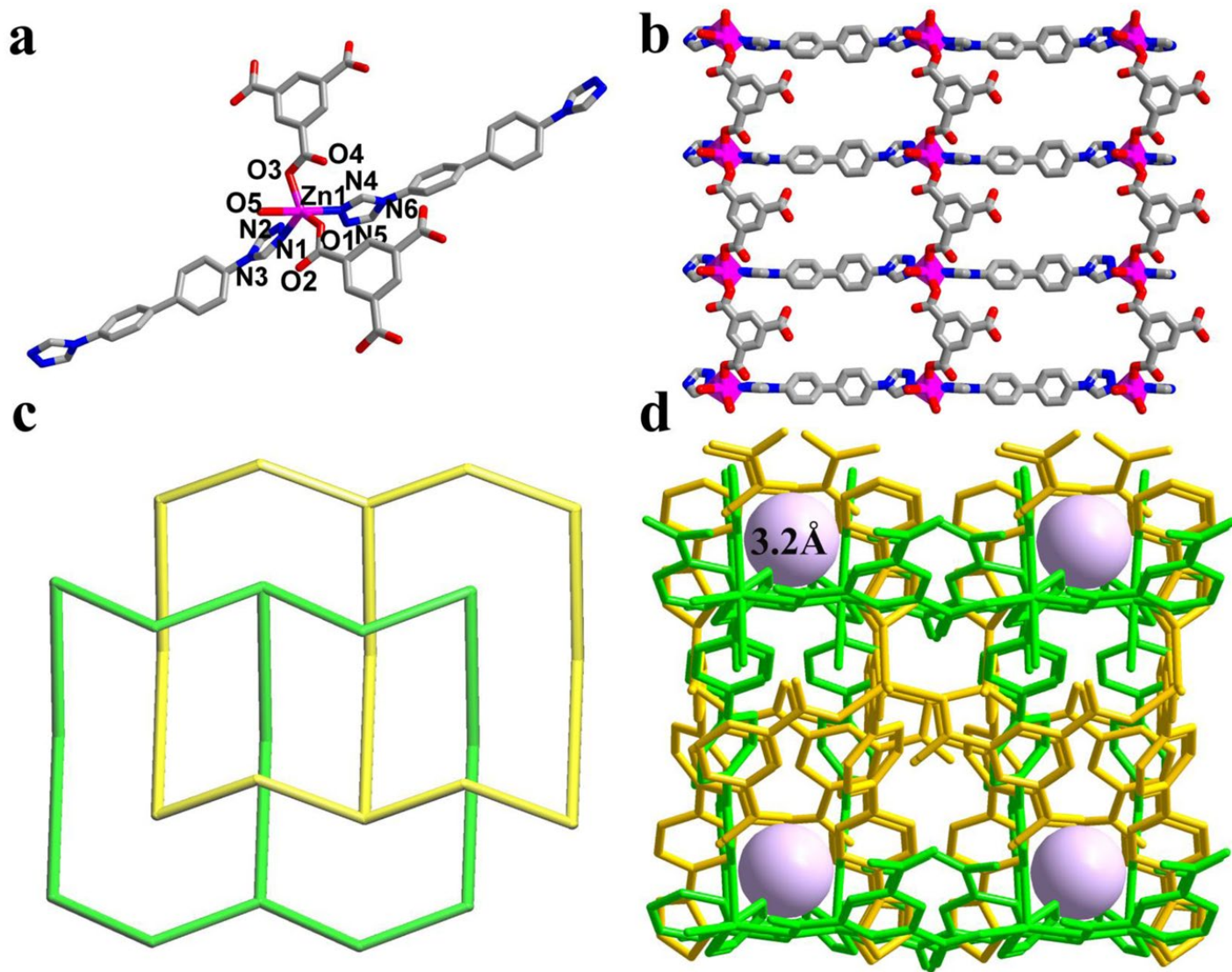
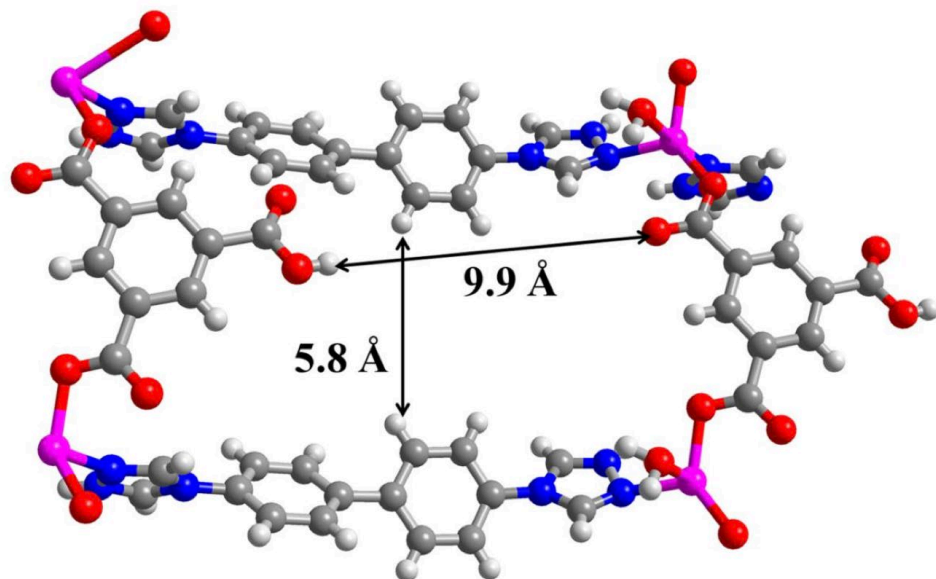
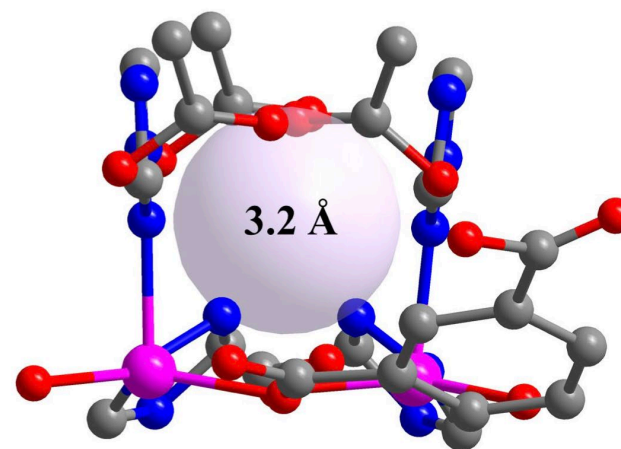


Fig. 2 Crystal structure of NCU-1. a The coordination environment of Zn^{2+} . b The 2D extended framework of NCU-1. c The simplified topological structure of 2-fold interpenetration (different colors represent different single sets of the interpenetration). d The two fold-interpenetrated structure of NCU-1 produces numerous square small pockets. (Zn, magenta; C, dark gray; N, blue; O, red).

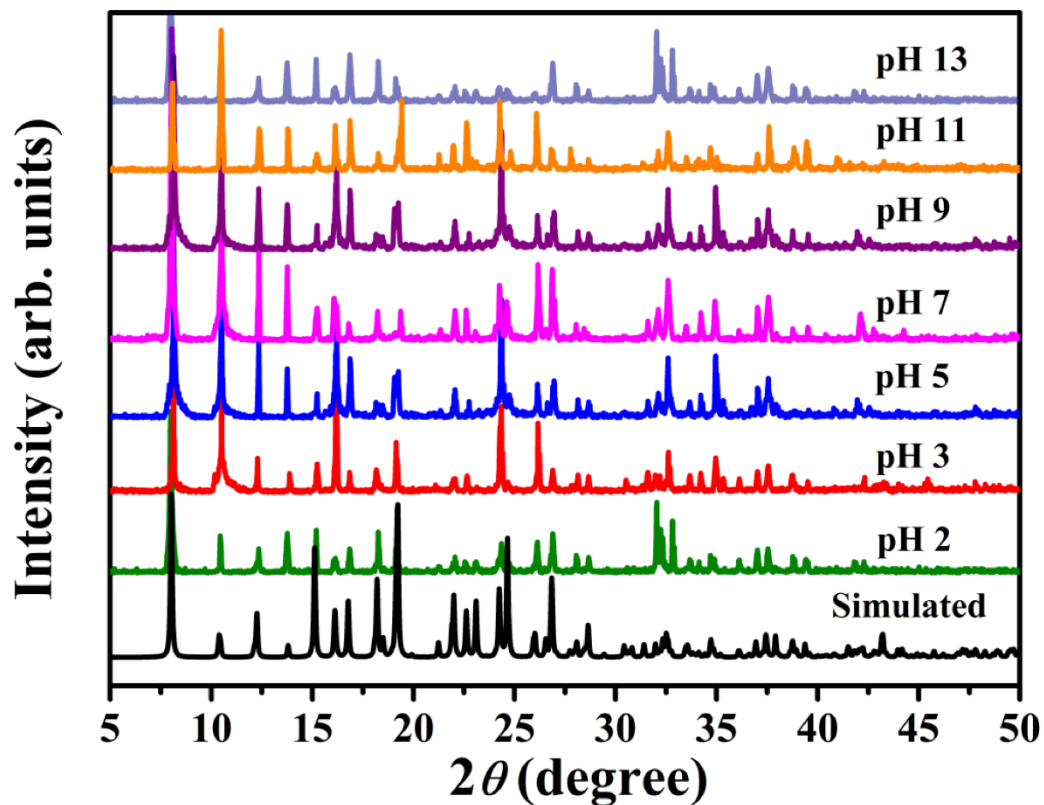


Supplementary Fig. 2 | Diagram of the square windows formed by four Zn²⁺ ions, two trimesic acids, and DTB ligands.



Supplementary Fig. 3 | Depiction of one pocket with a diameter of 3.2 Å constructed by triazole rings and carboxylate groups (Zn, magenta; C, dark gray; N, blue; O, red).

Stable in harsh conditions



Supplementary Fig. 5 | PXRD patterns of NCU-1 after immersion in aqueous solutions with different pH values ranging from 2 to 13 for 12 h.

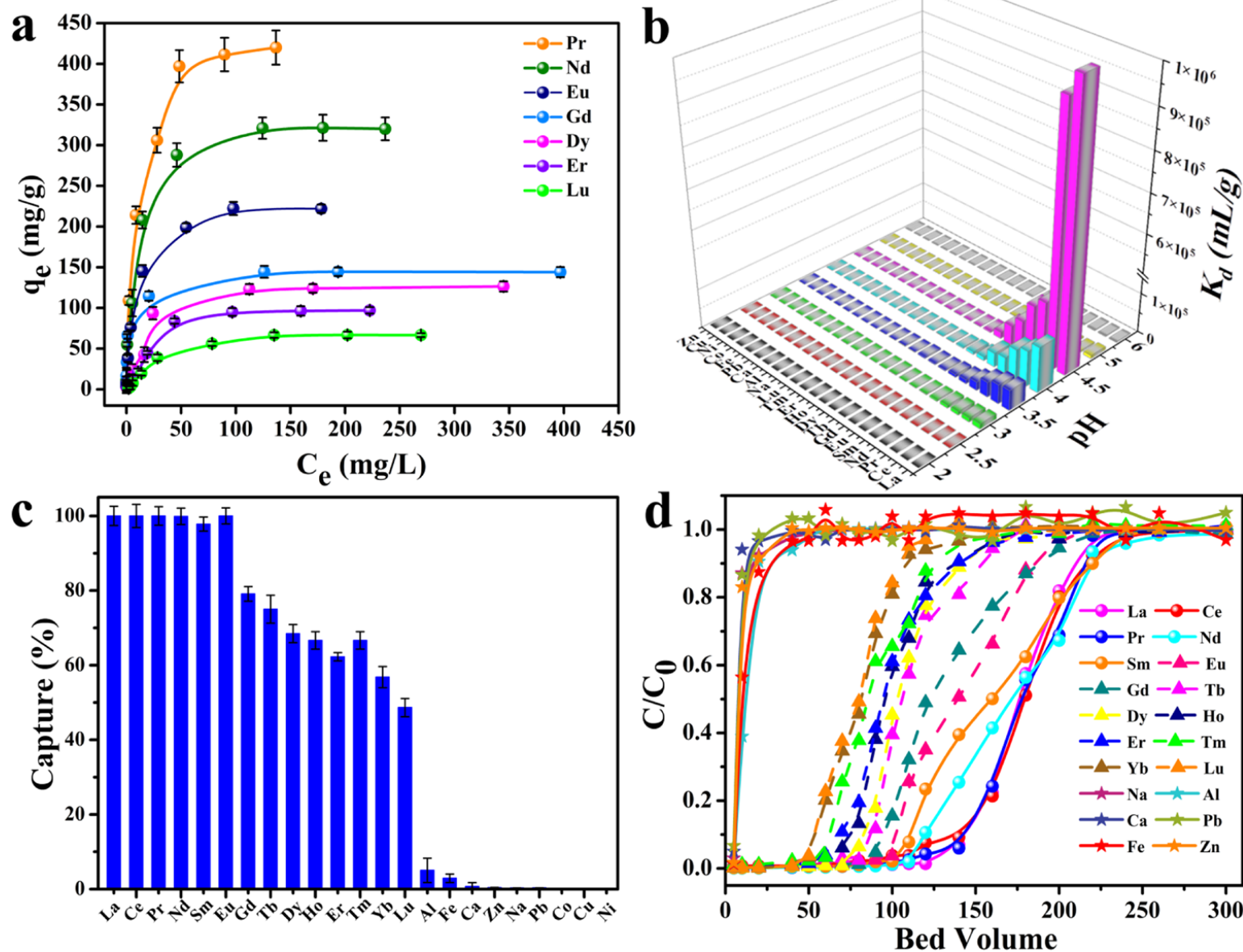


Fig. 3 Sorption experiment results of NCU-1. a Equilibrium data for Pr³⁺, Nd³⁺, Gd³⁺, and Dy³⁺ adsorption of NCU-1 and fitted with the Langmuir isotherm models. b K_d values of metal ions captured by NCU-1 at various pH values from 2.0 to 6.0. c NCU-1 capture efficiency of metal ions in mine tailings collected from Ganzhou city. d Mine tailing breakthrough curves of metal ions. Error bars represent S.D. n = 3 independent experiments.

ICP-MS data of REEs tailings

Supplementary Table 2 | Elemental composition of mineral leachates and NCU-1 capture efficiency of rare earth in tailings collected from Ganzhou city.

REE (mg/L)				Interfering ions (mg/L)			
Metal ions	C ₀ (mg/L)	C _e (mg/L)	Capture (%)	Metal ions	C ₀ (mg/L)	C _e (mg/L)	Capture (%)
La	0.25	0	100	Al ³⁺	8.15	7.74	5.03
Ce ³⁺	0.13	0	100	Fe ³⁺	1.03	1.00	2.91
Pr ³⁺	0.35	0	100	Ca ²⁺	0.56	0.55	1.79
Nd ³⁺	0.81	0.01	98.77	Na ⁺	1.86	1.85	0.54
Sm ³⁺	0.46	0.01	97.83	Zn ²⁺	0.23	0.23	0
Eu ³⁺	0.32	0	100	Co ²⁺	0.01	0.01	0
Gd ³⁺	0.67	0.14	79.10	Cu ²⁺	0.01	0.01	0
Tb ³⁺	0.16	0.04	75.00	Ni ²⁺	0.02	0.02	0
Dy ³⁺	0.92	0.29	68.48	Pb ²⁺	0.06	0.06	0
Ho ³⁺	0.18	0.06	66.67				
Er ³⁺	0.53	0.2	62.26				
Tm ³⁺	0.09	0.03	66.67				
Yb ³⁺	0.44	0.19	56.82				
Lu ³⁺	0.37	0.19	48.65				

C₀, the initial concentration of metal ions in tailings collected from Ganzhou city. C_e, the equilibrium concentration of metal ions after adsorption by 10 mg NCU-1 at a rate of 120 rpm for 6 h.

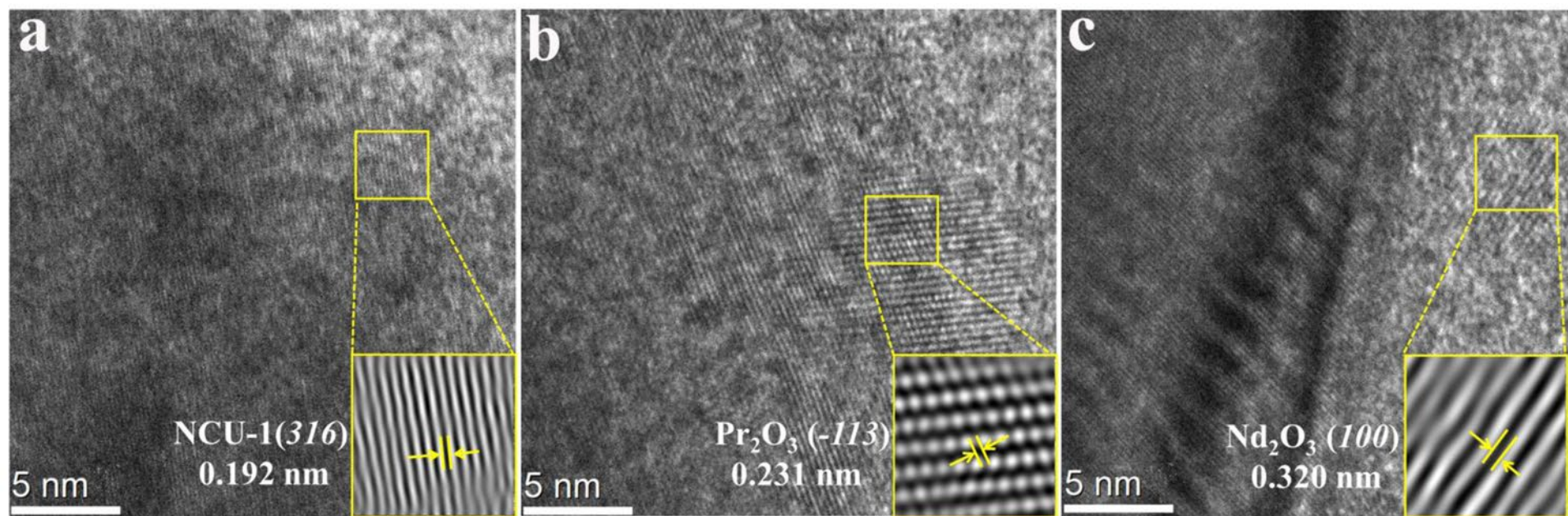


Fig. 4 Cryo-EM images of NCU-1 and after adsorption REEs. Cryo-EM images of a NCU-1, b NCU-1-Pr, and c NCU-1-Nd.

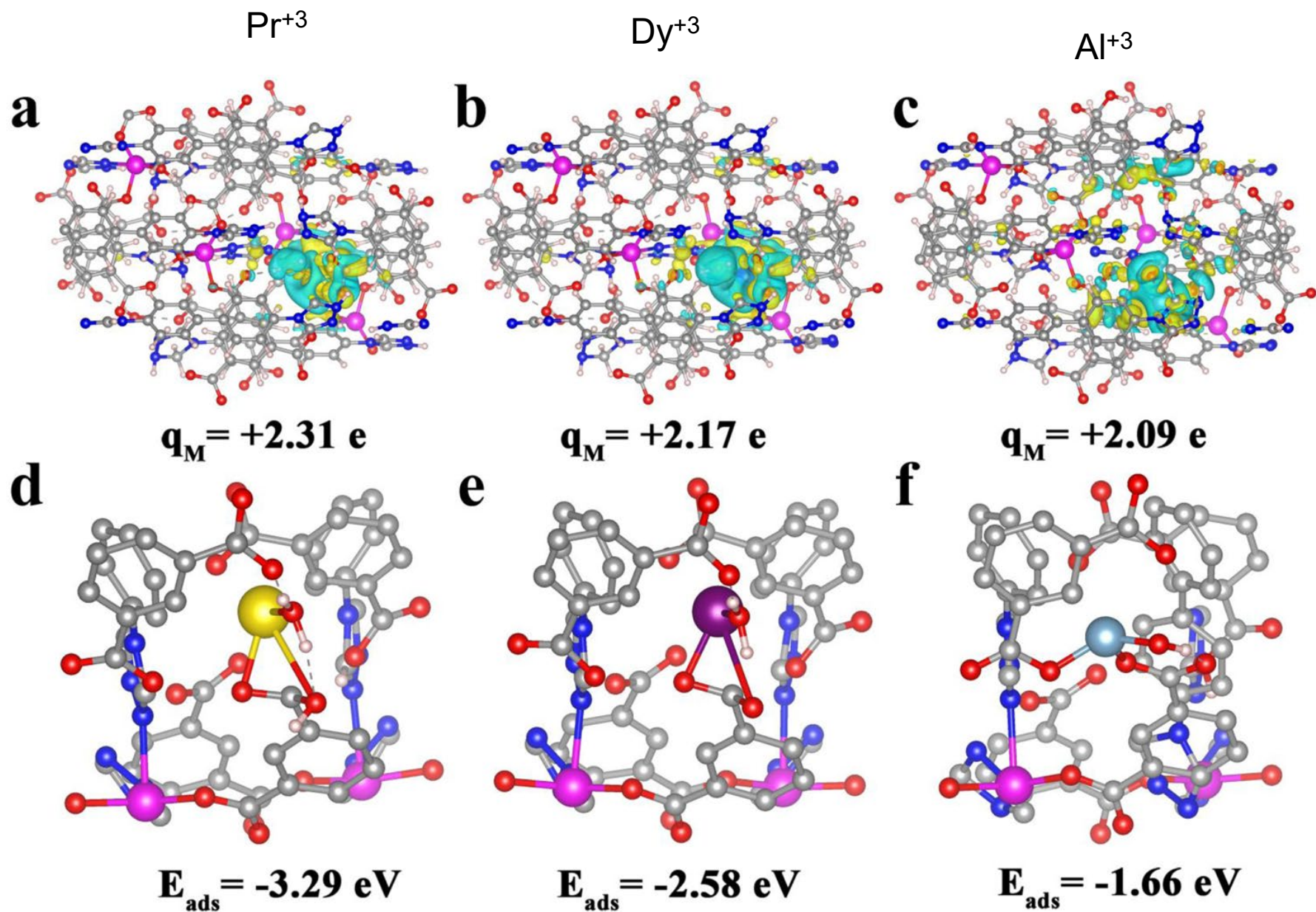


Fig. 5 Differential charge distribution of NCU-1 configuration after adsorption with **a** Pr^{3+} , **b** Dy^{3+} , and **c** Al^{3+} with the corresponding Bader charges. The Bader charge on the metal ion is defined as q_M . Optimized structures of NCU-1 and the adsorption energy of metal ions **d** Pr^{3+} , **e** Dy^{3+} , and **f** Al^{3+} (Pr^{3+} , yellow; Dy^{3+} , purple; Al^{3+} , light blue).

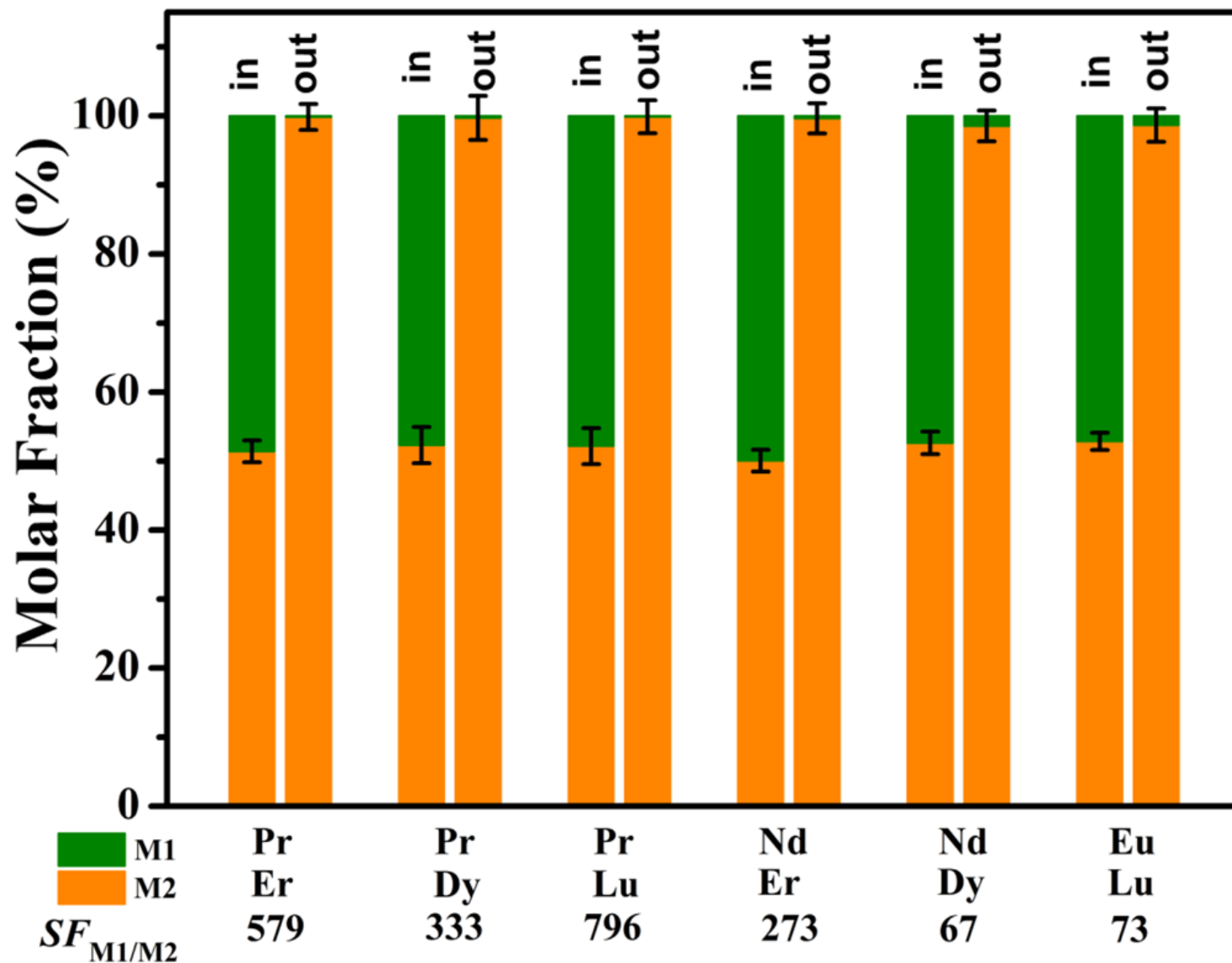
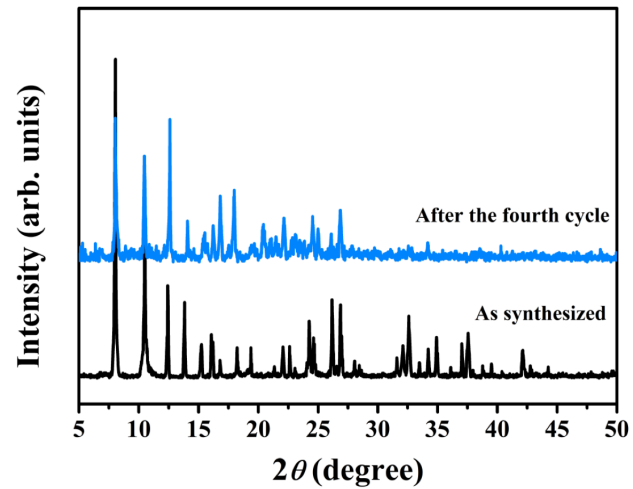
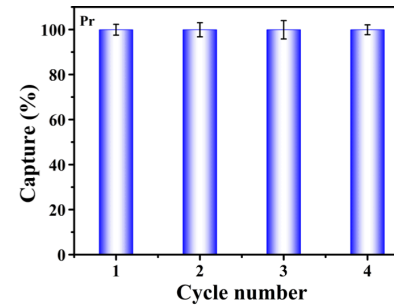


Fig. 6 Selective adsorption of NCU-1 from six combinations of a light REEs M1 and a heavy REEs M2. “In” and “out” indicate the REEs ratio in the original mixed solution and filtrates. Error bars represent S.D. $n = 3$ independent experiments.

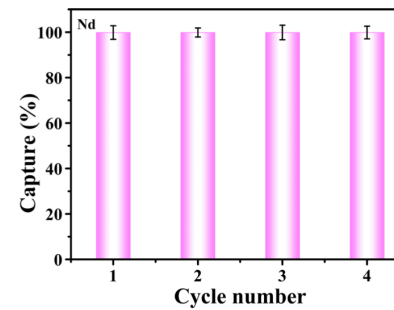
Regeneration studies



Supplementary Fig. 51 | PXRD patterns of NCU-1 after the fourth cycle.



Supplementary Fig. 47 | Reusability of NCU-1 for capturing Pr^{3+} . Error bars represent S.D. n=3 independent experiments.



Supplementary Fig. 48 | Reusability of NCU-1 for capturing Nd^{3+} . Error bars represent S.D. n=3 independent experiments.

Conclusion

- Unique REE nanotrap for selective separation of lighter REE from heavier ones.
- Real field mine tailings have been separated efficiently even in harsh pH conditions.