Supporting Information

A rare potassium-rich zirconium fluorophosphonate with high Eu^{3+} adsorption capacities from acidic solutions

Jiarong Zhang,‡[a,b,c] Long Chen,‡[c], Lanhua Chen,[c] Lei Chen,[c] Yugang Zhang,[c] Changlun Chen*[a,b], Zhifang Chai[c] and Shuao Wang*[c]

[a]*Institute of Plasma Physics, HFIPS, Chinese Academy of Sciences, P.O. Box 1126, Hefei 230031, P. R. China. E-mail: clchen@ipp.ac.cn.*

[b]*University of Science and Technology of China, Hefei 230026, P. R. China.*

[c]*State Key Laboratory of Radiation Medicine and Protection, School for Radiological and Interdisciplinary Sciences (RAD-X) and Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Soochow University, Suzhou 215123, China. E-mail: shuaowang@suda.edu.cn.*

‡ These authors contributed equally to this work.

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S1. Experimental section

*Synthesis of **SZ-8**:* The mixture of $ZrOCl_2 \cdot 8H_2O$ (64.4 mg, 0.2 mmol), methylenediphosphates (35.2 mg, 0.2 mmol), HNO_3 (70 μL), HF (20 μL), 50 mg KNO_3 and 2.5 mL mixed solvent (V_{DMA} : V_{H2O} (mL) = 4 : 1) was added into a 10 mL stainless steel PTFE vial. Then, the vial was heated to 200 ^oC for 3 days and cooled to room temperature at a rate of 5 ^oC/h. After being washed with ethanol and deionized water, colorless crystals were finally obtained as a pure phase.

X-ray Crystallography Studies: Single-crystal X-ray diffraction data collections of **SZ-8** were performed on a Bruker D8-Venture diffractometer with a Turbo X-ray Source (Mo–Kα radiation, λ = 0.71073 Å) adopting the direct-drive rotating anode technique and a CMOS detector under 298 K. The data of **SZ-8** was collected using the program APEX3 and then processed using SAINT routine in APEX3. The structure of **SZ-8** was solved by direct methods and refined by the full-matrix least-squares on F^2 using the SHELXTL.

Characterizations and Methods

Instrumentations: All the Powder X-ray diffraction (PXRD) patterns were collected from 5° to 50° with a step of 0.02° on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ=1.54056 Å) and a Lynxeye one-dimensional detector. The FT-IR spectra of **SZ-8** with KBr were recorded in the range of 4000-500 cm^{-1} on a Thermo Nicolet iS50 spectrometer.

Thermogravimetric analyses were carried out on a NETZSCH STA449F3 instrument in the range of 30-900 °C under a nitrogen flow at a heating rate of 10 K/min for the dried samples of **SZ-8**. Scanning electron microscopy images and energy-dispersive spectroscopy data (SEM/EDS) were recorded on an FEI Quanta 200FEG Scanning Electron Microscope with the energy of the electron beam being 30 keV. **SZ-8** samples were directly mounted on the carbon conductive tape and then coated with Au. The concentration of nonradioactive cations in the adsorption experiments was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Thermo Fisher Scientific iCAP 7000) or inductively coupled plasma-mass spectrometry (ICP-MS, Thermo Finnigan high-resolution magnetic sector Element 2).

Hydrolytic Stability Measurements: Hydrolytic stability measurements for **SZ-8** were studied by stirring the samples in HNO_3 solutions with different pH values of 1 to 3 for 1 d. The solids were re-collected and dried for PXRD patterns analysis.

γ Radiation Resistance Measurements: γ irradiation experiment was carried out using a ^{60}Co irradiation source (2.22×10^{15} Bq). **SZ-8** was irradiated at a dose rate of 1.2 kGy/h for 200 kGy in a dry and submerged statement, respectively. **SZ-8** was then collected for the PXRD patterns analysis.

Sr^{2+} Sorption Experiments: All the experiments were carried out at room temperature using the batch method. The solid/liquid ratio in all batch experiments was 1 g/L. In a typical ion-exchange experiment of **SZ-8**, 10 mg **SZ-8** was added into a 10 mL aqueous solution containing a certain cation (Eu^{3+}, Sr^{2+}, or Cs^{+}). The mixture was kept stirring for 18 h. The concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS) and/or inductively coupled plasma-atomic emission spectrometry (ICP-AES). The solids were separated by centrifugation or filtration. The distribution coefficient K_d is given by the equation:

$$K_d = (V[(C_0 - C_e)/C_e])/m$$

The adsorption capacity was calculated by

$$q = V(C_0 - C_e)/m$$

where q is the adsorption capacity, V is the volume (mL or L) of the testing solution, C_0 and C_e are the initial and equilibrium concentration of cations in the solution (ppm), and m is the amount of the **SZ-8** samples (g) used in the experiment.

Kinetic Studies: 40 mg of **SZ-8** material was added into a 40 mL solution containing target cations of Sr^{2+} (~ 5 ppm) and Eu^{3+} (~ 13 ppm) in pH 3. The mixture was stirred by a magnetic bar for the desired contact time. The concentrations as a function of time were obtained to determine the exchange kinetics line.

pH-Dependent adsorption: The pH-dependent adsorptions were conducted with Cs^{+} concentration of ~ 90 ppm, Sr^{2+} concentration of ~ 90 ppm, and Eu^{3+} concentration of ~ 220 ppm in the pH range of 1−6.

SZ-8 dissolution: SZ-8 material (15 mg) was added into pH 1 solution (15 mL). The mixture was stirred by a magnetic bar for the desired contact time and then the phosphorus concentrations were determined by ICP-OES to calculate the leaching ratio.

Selectivity experiments: SZ-8 (10 mg) was added into pH 2 solution (10 mL) containing Eu^{3+}, Sr^{2+} and Cs^{+}, which are at the initial molar rate of 1:1:1. The mixture was stirred for 12 h followed by measured the concentrations of the three cations.

S2. X-ray crystallography

Table S1. Crystallographic data for SZ-8.

CCDC No.	2168018
Formula	$K_2Zr[CH_2(PO_3)_2]F_2$
*M*r[g mol^{-1}]	377.37
Crystal system	monoclinic
Space group	*C*2/*c*
a(Å)	13.167(4)
b(Å)	4.7846(14)
c(Å)	14.094(4)
α(°)	90.00
β(°)	91.147(16)
γ(°)	90.00
V(Å^3)	887.8(5)
Z	2
ρ_{calcd} (g cm-3)	2.823
M (mm^{-1})	2.568
F(000)	720
T(K)	296(2)
R1, [a] wR2[b] (I>2σ(I))	0.0583, 0.1321
R1, [a] wR2[b] (all data)	0.1095, 0.1661

aR1 = Σ||Fo| - |Fc||/Σ|Fo|. bwR2 = [Σw(Fo2 - Fc2)2/Σw(Fo2)2]1/2

Table S2. Selected bond distances (Å) of SZ-8

Zr1-O2	2.092(5)	P1-O1	1.490(6)
Zr1-O3	2.092(6)	P1-O2	1.535(6)
Zr1-F1	1.991(6)	P1-O3	1.542(6)

S3. Bond Valence Sum (BVS) calculations

The bond valence of a bond length d_{ij} is calculated by the most commonly adopted empirical expression:

$$v_{ij} = \exp[(R_{ij}-d_{ij})/b].$$

Here b is equal to 0.37 Å, d_{ij} is the bond length in crystals.[1]

Table S3. BVS data of O atoms.

Atom	BVS value
O1	2 (P=O)
O2	1.8628
O3	1.8402

S4. Comparison of Eu(III) sorption capacities of SZ-8 and other adsorbents

Table S4. Comparison of Eu(III) sorption capacities of SZ-8 and other adsorbents.

Materials	Conditions	*q* (mmol/g)	References
HMS	pH = 4.0, T = 298 K	0.17	2
MWCNTs	pH = 4.3, T = 298 K	0.0073	3
CNFs	pH = 6.5, T = 298 K	0.599	4
GOs	pH = 4.5, T = 298 K	1.05	5
PA/TNTs	pH = 5.5, T = 298 K	0.96	6
GO@TiP	pH = 5.5, T = 293 K	0.42	7
FJSM-SnS-3	pH ~ 5, T = 298 K	0.41	8
KMS-5	pH = 2, T = 298 K	0.57	9
SZ-8	**pH = 2, T = 298 K**	**0.73**	**This work**

S5. FT-IR spectrum

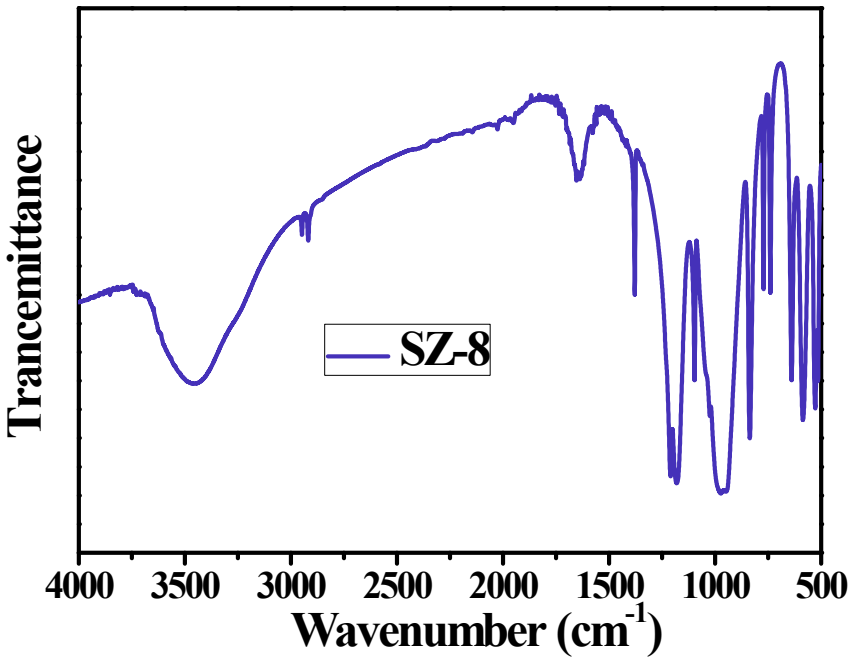

Figure S1. FT-IR spectrum of **SZ-8**.

S6. Powder X-ray diffraction (PXRD) for SZ-8 after treatment with pH 1 solution

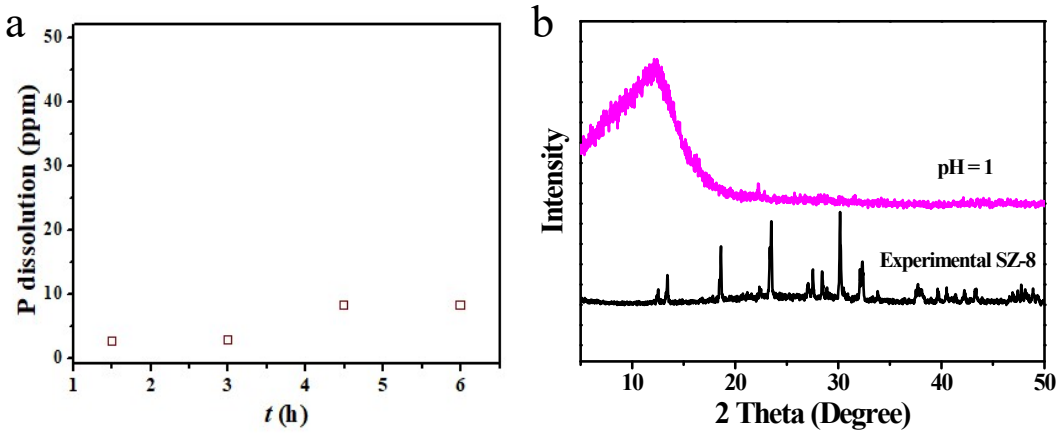

Figure S2. (a) The leaching phosphorus concentration in pH 1 solution under various contact time. (b) The PXRD pattern for **SZ-8** after treatment with pH 1 solution.

S7. Kinetics fitting results

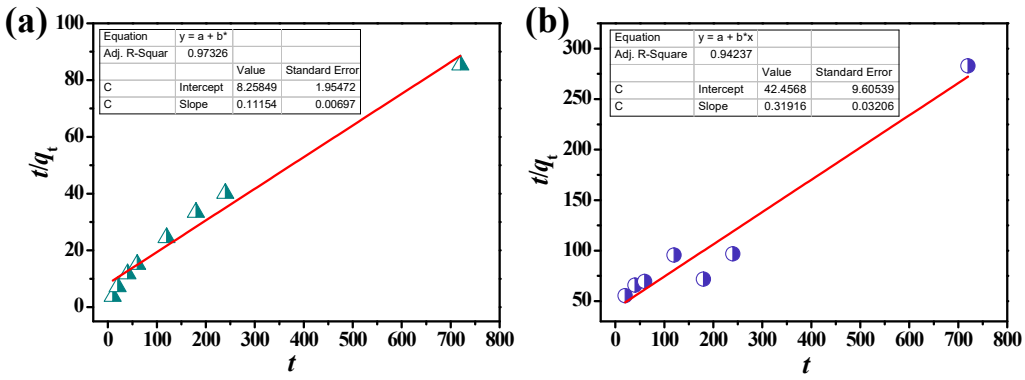

Figure S3. Kinetics fitting results of Eu^{3+} (a) and Sr^{2+} (b) adsorbed by **SZ-8**.

S8. SEM-EDS mapping analysis

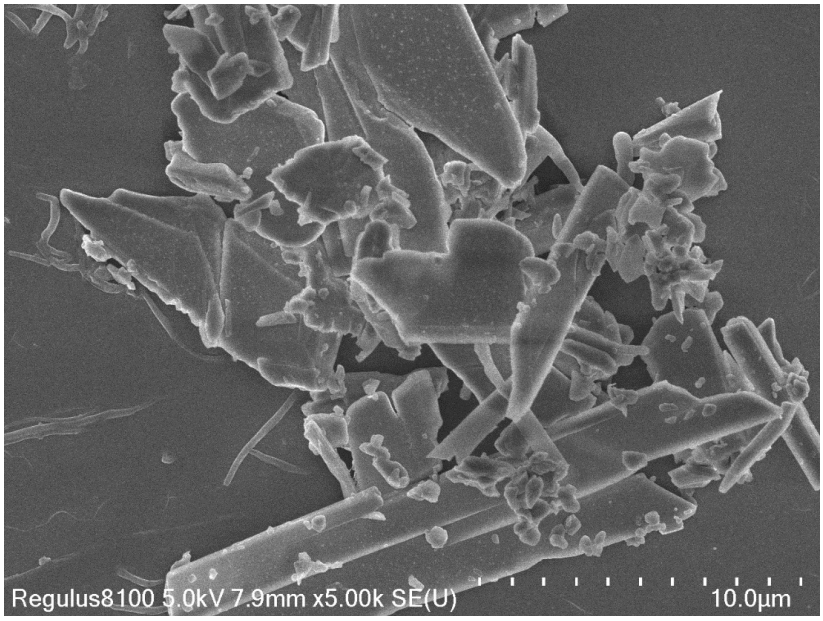

Figure S4. SEM image of **SZ-8.**

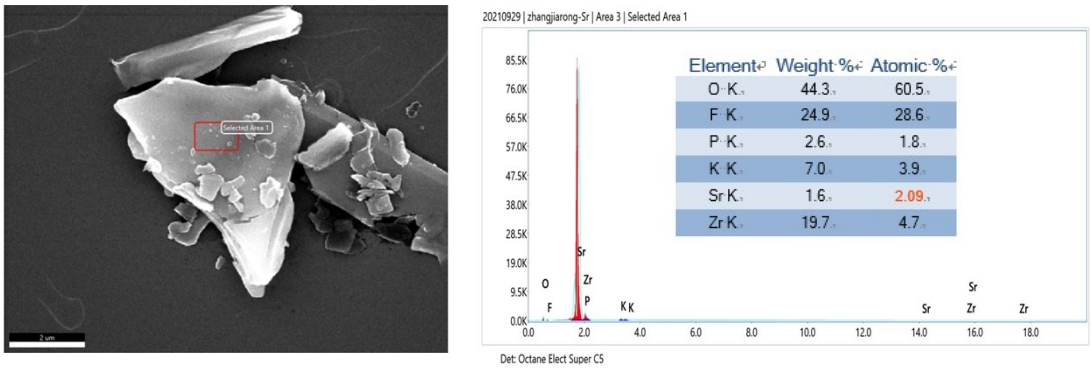

Figure S5. SEM image and EDS data of **SZ-8** after Sr^{2+} adsorption.

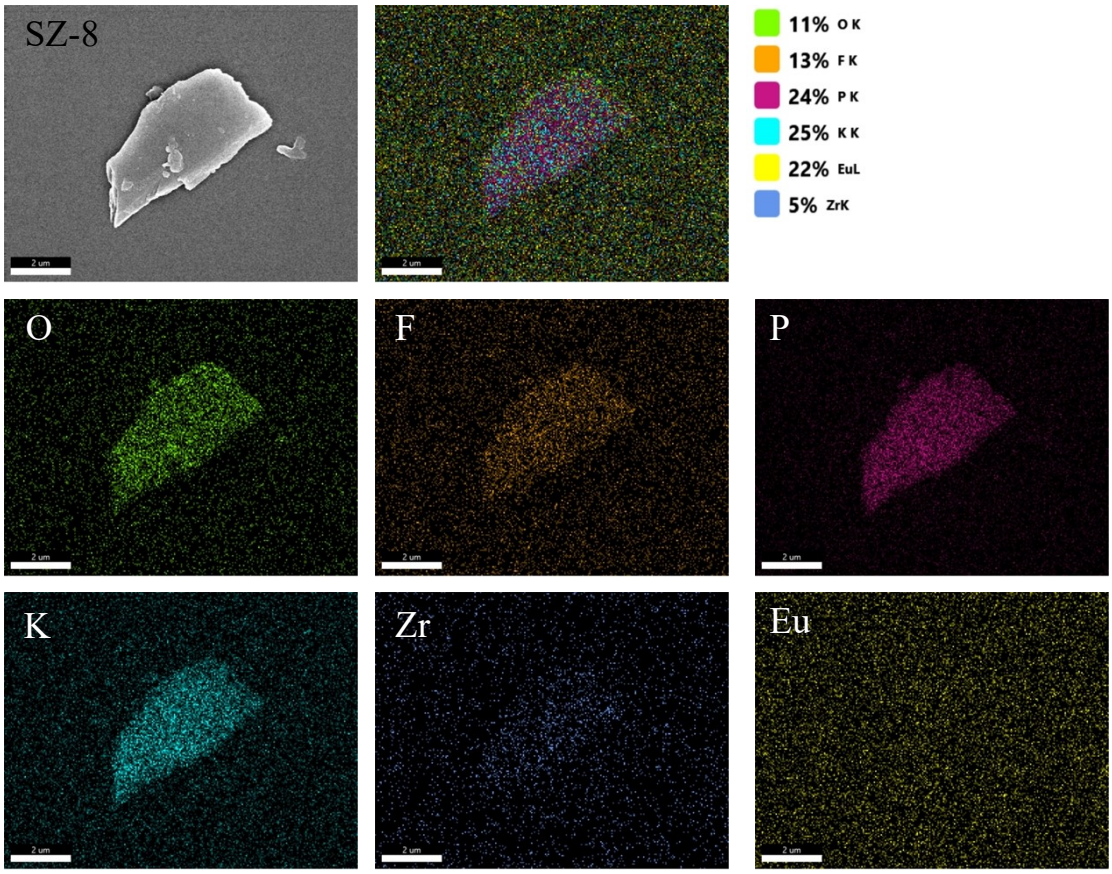

Figure S6. SEM analysis of **SZ-8** after Eu^{3+} adsorption.

S9. Powder X-ray diffraction (PXRD) after Eu^{3+} and Sr^{2+} adsorption

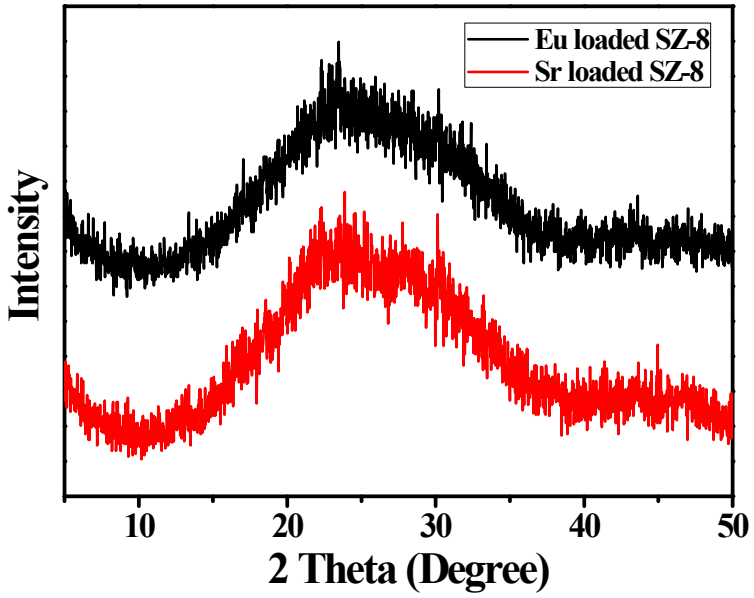

Figure S7. The PXRD patterns after Eu^{3+} and Sr^{2+} adsorption.

References:

[1] N. E. Brese and M. O'Keeffe, *Acta Cryst.* 1991, B47, 192-197.

[2] M. Hamed, M. Holiel and I. Ahmed, *Radiochim. Acta,* 2016, **12**, 873–890.

[3] Q. Fan, D. Shao, J. Hu, C. Chen, W. Wu and W. Wang, *Radiochim. Acta***,** 2009, **97**, 141-148.

[4] Y. Sun, Z. Wu, X. Wang, C. Ding, W. Cheng, S. Yu and X. Wang, *Environ. Sci. Technol.*, 2016, **50**, 4459-4467.

[5] Y. Sun, Q. Wang, C. Chen, X. Tan and X. Wang, *Environ. Sci. Technol.*, 2012, **46**, 6020-6027.

[6] C. Wu, Y. Cai, L. Xu, J. Xie, Z. Liu, S. Yang and S. Wang, *J. Mol. Liq.*, 2018, **258**, 66-73.

[7] C. Li, Y. Huang and Z. Li, *J. Mater. Chem. A,* 2014, **2**, 14979-14985.

[8] W. Li, J. Li, B. Zhang, H. -Y. Sun, J. Jin, X. Huang and M. Feng, *ACS Appl. Mater. Interfaces*, 2021, **13**(8), 10191-10201.

[9] C. Xiao, Z. H. Fard, D. Sarma, T. B. Song, C. Xu and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2017, **139**(46), 16494-16497.