Ingenious One-Dimensional Zirconium Phosphonate with Efficient Strontium Exchange Capability and Moderate Proton Conductivity

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S1. Experimental section

Materials: All chemical reagents and solvents purchased from commercial suppliers and directly used as received. ***Caution! Sr-90 used in this study is a high-energy β emitter with the daughter of radioactive Y-90. All Sr-90 experiments were performed in an authorized laboratory designed for radiological studies. Standard protections for radioactive materials should be followed.***

Synthesis of ***SZ-5****:* the mixture of $ZrOCl_2 \cdot 8H_2O$ (64.4 mg, 0.2 mmol), methylenediphosphonic acid (35.2 mg, 0.2 mmol), HNO_3 (100 μL), HF (50 μL) and 2.5 ml mixed solvent (V_{DMA} : V_{H2O} (ml) = 4 : 1) was added into a 10mL 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. Colourless crystals were finally obtained as a pure phase.

X-ray Crystallography Studies: Single crystal X-ray diffraction data collections of **SZ-5** 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-5** was collected using the program APEX3 and then processed using SAINT routine in APEX3. The structure of **SZ-5** was solved by direct methods and refined by the full-matrix least squares on F^2 using the SHELXTL.

Characterizations and Methods

Instrumentations: 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. Elemental analysis (C, N, and H) were performed with a Vario EL CHNOS elemental analyzer and the results were calculated to be N, 5.701%; C, 13.5%; H, 4.266%. The FT-IR spectra of **SZ-5** without KBr were recorded in the range of 4000-400 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-5**. Scanning electron microscopy images and energy-dispersive spectroscopy data (SEM/EDS) were recorded on a FEI Quanta 200FEG Scanning Electron Microscope with the energy of the electron beam being 30 keV. **SZ-5** samples were directly mounted on the carbon conductive tape, and then coated with Au. The concentration of nonradioactive Sr^{2+} 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) depending on the specific concentration, meanwhile the radioactive Sr^{2+} in solution were measured using a liquid scintillation counting system (LCS).

Hydrolytic Stability Measurements: Hydrolytic stability measurements for **SZ-5** was studied by stiring the samples in HNO_3 or NaOH solutions with different pH of 4 to 11 for 1 d. The solids were re-collected and dried for PXRD patterns analysis.

β and γ Radiation Resistance Measurements: β irradiation experiment was implemented using electron beams (1.2 MeV) provided by an electron accelerator. **SZ-5** was irradiated for two different doses (100 and 200 kGy), respectively, at a dose rate of 20 kGy/h. γ irradiation experiment was carried out using a ^{60}Co irradiation source (2.22×10^{15} Bq). **SZ-5** was irradiated at a dose rate of 1.2 kGy/h for 100 kGy and 200 kGy, respectively. **SZ-5** exhibits excellent radiation resistance as the PXRD patterns for the irradiated **SZ-5** match well with the originated samples.

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-5**, 10 mg **SZ-5** was added into 10 mL aqueous solution containing certain Sr^{2+}. The mixture was kept stirring for 12 h. The concentration of Sr^{2+} in solution was 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:

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

where V is the volume (ml) of the testing solution, C_0 and C_e are the initial and equilibrium concentration of Sr^{2+} (ppm), and m is the amount of the **SZ-5** samples (g) used in the experiment.

30 mg of **SZ-5** material was added into a 30 mL solution containing 10 ppm Sr^{2+}. The mixture was stirred by a magnetic bar for a desired contact time. The concentration of Sr^{2+} as a function of time was obtained to determine the exchange kinetics line. The Sr^{2+} removal from solutions of various concentrations was investigated by the batch experiment at the solid/liquid of 1 g/L at 12 h contact and room temperature. The data were used for the determination of Sr^{2+} adsorption isotherm. Competitive ion-exchange experiments of **SZ-5** were also performed with the batch method at the solid/liquid of 1 g/L at the contact time of 12 h and room temperature

The Real Seawater Decontamination Experiment: The **SZ-5** samples was added to 3 mL seawater containing radioactive $^{90}Sr^{2+}$ with a total β activity of 2516 cpm and the solid/liquid ratios of 10:1 and 20:1, respectively. The mixture was then shaking for the contact time of 1 d and 7 d at room temperature. The ^{90}Sr activity was determined by liquid

scintillation counting (LSC), which was used to calculate the ^{90}Sr removal percentage.

XAFS Data Collection: Sr-sorbed **SZ-5** samples for XAFS analysis were prepared by batch experiments. The Sr K_{III}-edge XAFS spectra at 6777 eV were recorded at BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China)

Proton Conductivity Measurements: Proton conductivity measurement was carried out by alternating-current (ac) impedance spectroscopy used schistose sample in the controlled thickness range of 1 to 2 mm. Alternating current impedance of the **SZ-5** was conducted on a Solartron SI1260 Impedance/Gain-Phase Analyzer with applied ac voltage amplitude over a frequency range from 4 MHz to 1 Hz with an input voltage amplitude of 500 mV. The conductivity of **SZ-5** was calculated by the equation of:

$$\sigma = L/RS$$

Where S and L are the cross-sectional area and thickness of the pellet, respectively, and R, which was obtained from the impedance plots, is the value of resistance.

S2. X-ray crystallography

Table S1. Crystallographic data for SZ-5.

Formula	$[(CH_3)_2NH_2]_2[Zr(CH_2(HPO_3)(PO_3))_2]$

*M*r[g mol-1]	507.18
Crystal system	triclinic
Space group	$P\ \bar{1}$
a(Å)	5.4161(5)
b(Å)	8.4820(9)
c(Å)	10.2407(10)
α(°)	98.482(5)
β(°)	91.994(5)
γ(°)	102.790(5)
V(Å^3)	452.65(8)
Z	1
ρ_{calcd} (g cm-3)	1.861
M (mm^{-1})	1.018
F(000)	246
T(K)	298
R1, [a] wR2[b] (I>2σ(I))	0.0395, 0.1321
R1, [a] wR2[b] (all data)	0.0519, 0.1464

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

Table S2. Selected bond distances (Å) of SZ-5

Zr1-O3	2.067(3)	P1-O1	1.555(3)

Zr1-O5	2.060(3)	P1-O2	1.501(3)
Zr1-O6	2.073(3)	P1-O3	1.539(3)
		P2-O4	1.498(3)
		P2-O5	1.548(3)
		P2-O6	1.538(3)

Table S3. Hydrogen bond distances (Å) in SZ-5

N1···O4	2.835
O1···O2	2.467/2.544
O1···O4	3.35

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 lengths in crystals.[1]

Table S4. BVS data of O atoms.

Atom	BVS value
O1	1.1416
O2	1.3210

O3	0.7037
O4	1.3317
O5	0.7172
O6	0.6924

S4. Powder X-ray diffraction (PXRD)

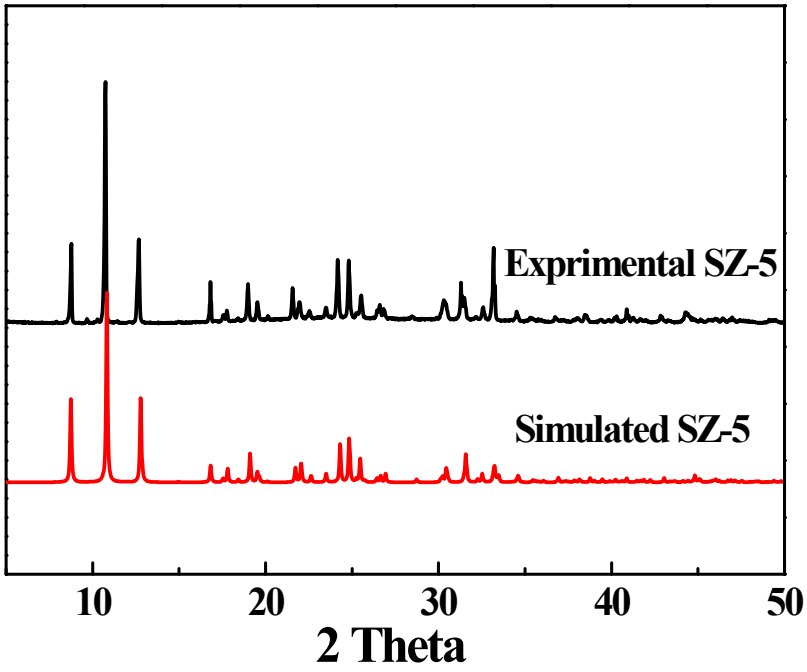


Figure S1. The powder X-ray diffraction (PXRD) for **SZ-5**

S5. FT-IR spectrum

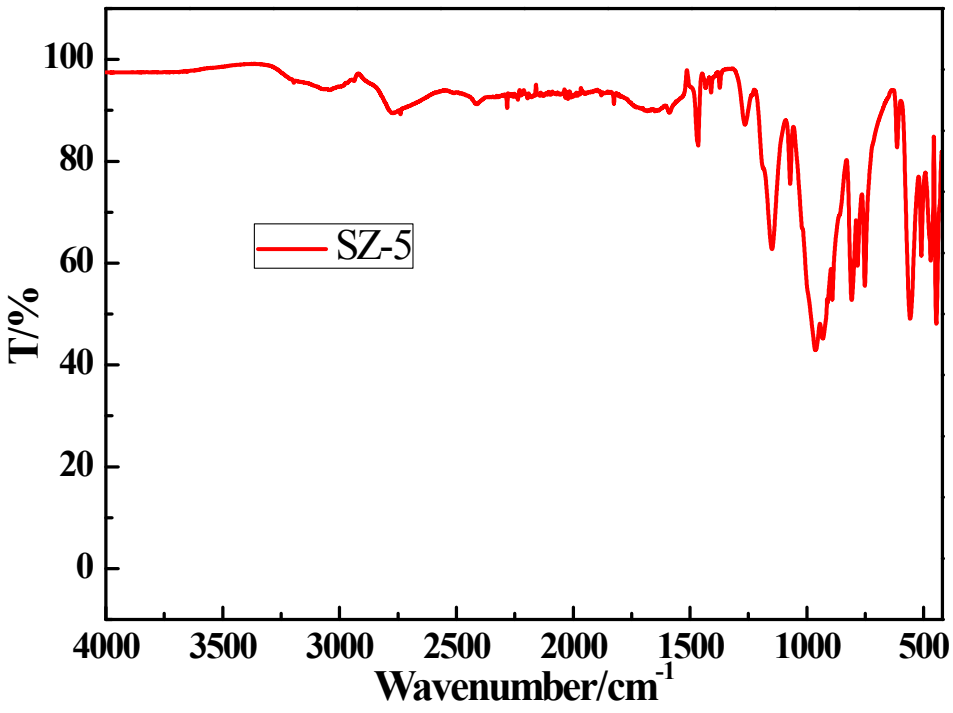
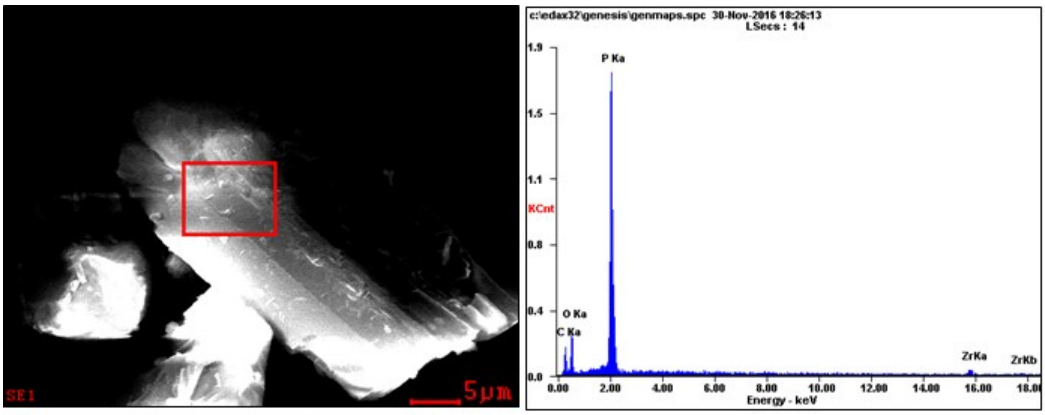


Figure S2. FT-IR spectrum of **SZ-5**.

S6. SEM-EDS analysis



Element	Wt%	At%
CK	36.22	58.36
OK	21.80	26.37
PK	18.56	11.60
AuM	11.36	01.12
ZrK	12.07	02.56
Matrix	Correction	ZAF

Figure S3. SEM images and EDS data of **SZ-5** before ion-exchange.

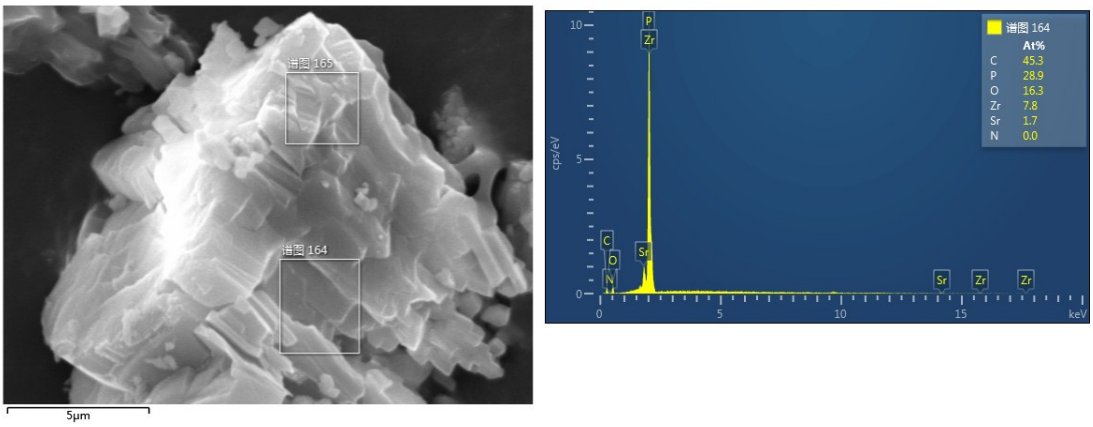


Figure S4. SEM images and EDS data of **SZ-5** after ion-exchange.

S7. XAFS Fit results for Sr-sorbed SZ-5 samples.

Table S5. The structural parameters from the XAFS analysis

Sample	Shell	interaction	CN	R (Å)
Sr-sorbed SZ-5	1	Sr-O	7.24	2.36

CN = coordination numbers

S8. Crystal structure of $Sr_3(PO_4)_2$

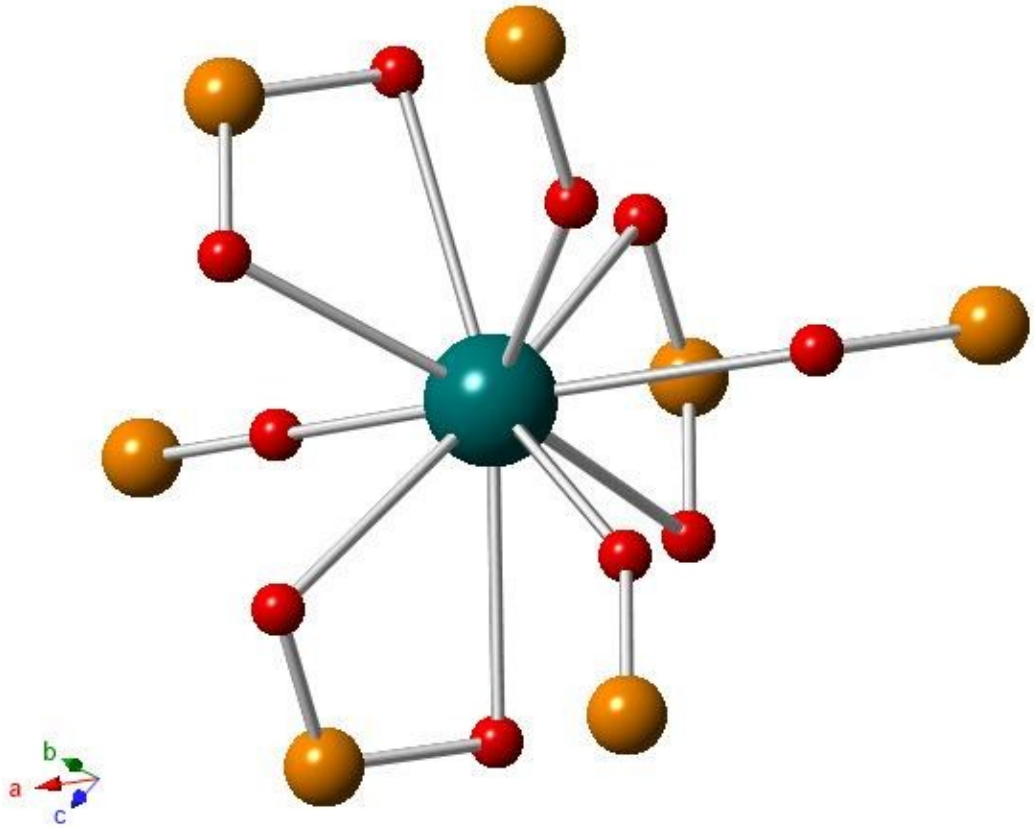


Figure S5. Crystallographic data of $Sr_3(PO_3)_2$ showing 10-coordinate Sr^{2+}.

Atom color codes: Sr = cyan, P = orange, O = red.

S9. Proton conductivity of SZ-5

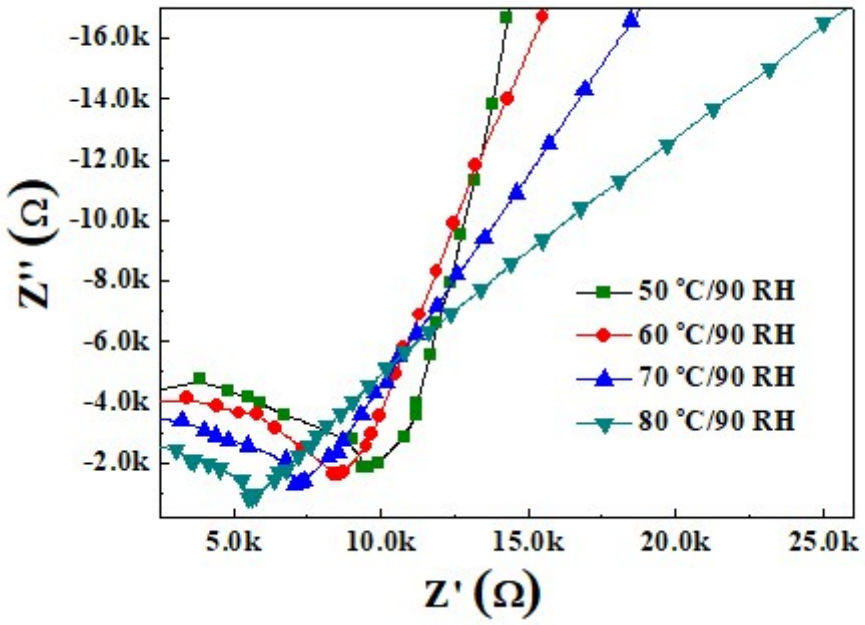


Figure S6. Impedance plots of **SZ-5** at different temperatures of 40-80 °C under 90% RH.

Reference:

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