

Supplementary Information

A pillar-layered chalcogenide framework assembled by [Mn₅S₁₂N₁₂]_n layers and [Sb₂S₅] inorganic pillars

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Experimental Section

Chemicals and Materials. Manganese powder (Mn, 99.99%), antimony sulfide (Sb_2S_3 , 98%), sulfur powder (S, 99.9%), ethylenediamine (en, 60%), N, N-dimethylformamide (DMF, 99.8%) and hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 80% aqueous solution) were obtained from commercial sources. All starting reagents were used as received without any additional treated.

Synthesis of $[\text{Mn}_5\text{Sb}_6\text{S}_{15}(\text{N}_2\text{H}_4)_6] \cdot (\text{H}_2\text{en}) \cdot \text{DMF} \cdot 0.5\text{N}_2\text{H}_4$ (1). Mn (0.18 mmol, 10 mg), Sb_2S_3 (0.11 mmol, 38 mg), and S (0.41 mmol, 13 mg) were added into the mixed solvents of DMF (1.0 mL), en (0.25 mL), N_2H_4 (1.0 mL) in a 18 mL glass tube and sonicated with a power output of 240 W for 15 min. The glass tube was sealed and heated at 75 °C for 8 days. Then the resulting mixture was cooled to room temperature. Orange, rod-shaped crystals were obtained and washed with ethanol several times (yield: ~ 37% based on Mn). Elemental analysis of C, N, and H calculated (wt%) for $[\text{Mn}_5\text{Sb}_6\text{S}_{15}(\text{N}_2\text{H}_4)_6] \cdot (\text{H}_2\text{en}) \cdot \text{DMF} \cdot 0.5\text{N}_2\text{H}_4$: C, 3.28; N, 12.25; H, 2.37%; found: C, 3.52; N, 12.34; H, 2.63%.

It is well known that hydrazine is a basic solvent and a good ligand with less steric hindrance. Hydrazine could dissolve the metal chalcogenide species and was useful in the growth of crystalline chalcogenides.

Single Crystal X-ray Diffraction (SCXRD). The intensity data sets of single crystal sample **MAC** were obtained on a Photon II CPAD diffractometer and irradiated with graphite-monochromated Mo- $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) irradiation at 120 K. The data sets were reduced with the APEX3 program. The structure was solved and refined against all reflections using the SHELXS-2014. The protonated amine molecules and solvent molecules located in the void space of the framework cannot be identified owing to their serious disorder. The SQUEEZR subroutine in PLATON was used to treat the data.

Powder X-ray Diffraction (PXRD). PXRD pattern was recorded on D2 PHASER desktop diffractometer, operated at 30 kV and 10 mA, with Cu $K\alpha$ ($\lambda = 1.54184 \text{ \AA}$)

radiation and in the range of $2\theta = 4\text{--}40^\circ$ with $0.03^\circ/\text{step}$.

Elemental Analysis. Elemental analyses (C, H, and N) were achieved using an Elementar VARIDEL III elemental analyzer. The energy-dispersive X-ray spectroscopy (EDS) was used to determine the elements of Mn, Sb, S using scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) detector.

Thermogravimetry analysis (TG). TG was made on a Shimadzu TGA-50 thermal analyzer in flowing N_2 atmosphere, and the operating temperature from 22°C to 800°C with a heating rate of $10^\circ\text{C}/\text{min}$.

Fourier-transform infrared absorption (FT-IR). The FT-IR spectral was recorded on a Thermo Nicolet Avatar 6700 FT-IR spectrometer in $4000\text{--}600\text{ cm}^{-1}$ region with cesium iodide optics.

X-ray photoelectron spectroscopy (XPS). The chemical compositions and oxidation states of the related elements analysis was investigated by XPS on an SSI S-Probe XPS system equipped with a monochromatic $\text{Al K}\alpha$ X-ray source and a concentric hemispherical analyzer. All XPS spectra are calibrated by the position of the C 1s peak.

UV-Vis Absorption. Solid-state UV–vis reflection spectroscopy was measured on a Shimadzu UV-3600 UV-vis-NIR spectrophotometer using BaSO_4 powder background in a quartz plate. The UV absorption spectra was calculated by using the Kubelka-Munk function: $F(R)=\alpha/S=(1-R)^2/2R$, where R , α , and S are the reflection, absorption and scattering coefficient, respectively.

Ion Exchange Experiments. 5 mg of as-synthesized sample was immersed in 5 mL 10 mL MCl ($\text{M} = \text{Li}, \text{K}, \text{Cs}$) solution ($0.1\text{ mol}\cdot\text{L}^{-1}$). The mixture was stood for 48 h at room temperature (or 65°C oven). The orange samples became darker. And then, the final products were isolated by filtration and washed by deionized water and ethanol for several times. After dried at room temperature for about 24 hours, the resulting samples of M@1 were collected for measurement of PXRD and EA.

Electrical conductivity measurement. The electrical characteristic of the sample **1** was measured by a 2-contact probe method. Firstly, both ends of the crystal were covered by silver paint the single-crystal electrodes were made using conductive silver paint and connected with gold wires (diameter is 50 micrometers). The I-V curve measurements for the single crystal electrode with a direct current two terminal method were on semiconductor analysis system (4200SCS, Keithley). The plurality of crystals was selected for measurements and each measurement performed on independent single crystals, and took an average value. The length of the crystals was about 150~500 μm .

Photoelectric Response. The **1**/ITO electrode was fabricated by electrophoretic deposition: 5.0 mg of ground **1** powder was dispersed in 10 mL isopropanol with the presence of 1.0 mg of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The sealed mixture suspension was continuously stirred for one day, and then was ultrasonically vibrated for 30 mins before electrophoretic deposition. The catalyst colloid was added to 1 cm^2 indium-tin-oxide (ITO) conductive glass substrate by electro-deposition with a working voltage of 30 V. The obtained ITO electrode decorated with **1** film on its surface was finally washed with ethanol and dried in air. The photocurrent experiment was carried out on a CHI760E electrochemistry workstation in standard three-electrode configuration, with the sample coated ITO glass as working electrode, a Pt plate electrode as auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode. A 150 W high-pressure xenon lamp was used as the light source, which was located 20 cm away from the surface of the ITO electrode. Sodium sulfate aqueous solution (0.5 M, 100 mL) was used as the supporting electrolyte.

Electrochemical measurements. The electrochemical data were collected on a CHI 760E electrochemical workstation. Using a three-electrode system consisting of rotating disk electrode (RDE) with a glass carbon disk (4 mm diameter) as working electrode, a carbon rod as counter electrode and an Ag/AgCl as reference electrode. The detailed preparation of the working electrode was described as follows. At first, 10 mg of the crystalline **1** and 10 mg carbon black (CB) were mixed and thoroughly ground. Then, 10 mg of the mixture was dispersed in 40 μL Nafion solution (5.0 % w/w in water

and 1-propanol ethanol) 210 μL anhydrous ethanol and 750 μL DI water, which was denoted as 1/CB. The mixture was sonicated for one hour to make a homogeneous ink. After that, 7 μL of the prepared ink was pipetted onto the pre-treated RDE (4 mm diameter) and then fully dried. The working electrode with catalyst ink was cycled between -1.0 and 0.2 V at a sweeping rate of $50 \text{ mV}\cdot\text{s}^{-1}$ in a nitrogen saturated and oxygen saturated KOH solution (0.1 M), respectively, at room temperature producible cyclic voltammetry (CV) testing results obtained. The linearly sweeping voltammetry (LSV) tests in the oxygen saturated were conducted from -1.0 V to 0.2 V at different rotation speeds (from 600 to 2025 rpm) with the sweeping rate of 0.005 V/s.

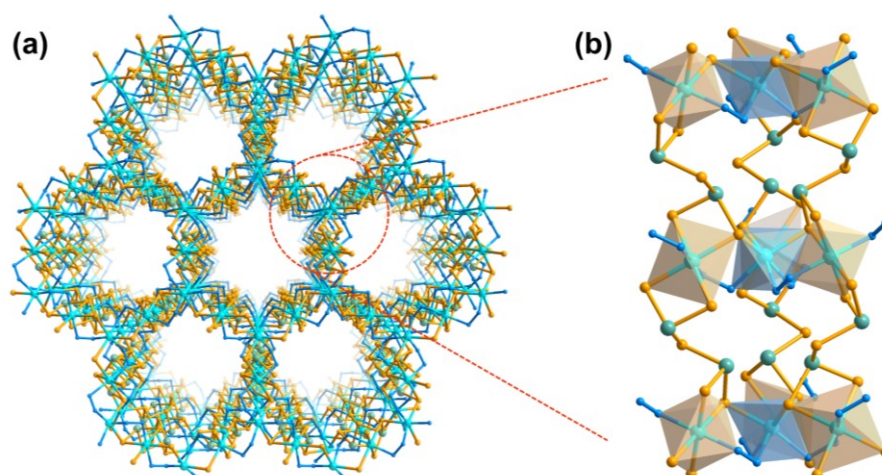


Figure S1. (a) The framework of **1** viewed along the *c*-axis, composed of edge-sharing hexagonal channels. (b) The connection mode of the Mn1, Mn2 PBU and Sb₂S₅ linker in **1**. Hydrogen atoms are omitted for clarity.

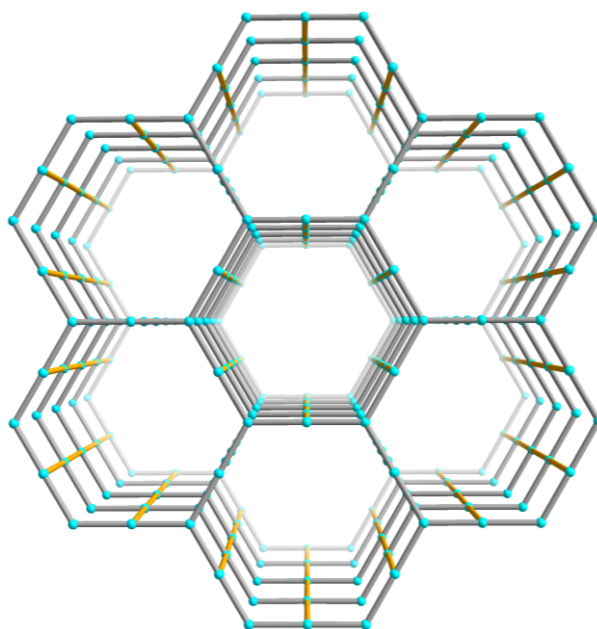


Figure S2. The tfz topology with non-interpenetrated 3D (3,4)-connected in **1** when Mn(1/2) ions are treated as nodes (N₂H₄ ligands and Sb₂S₅ units as linkers).

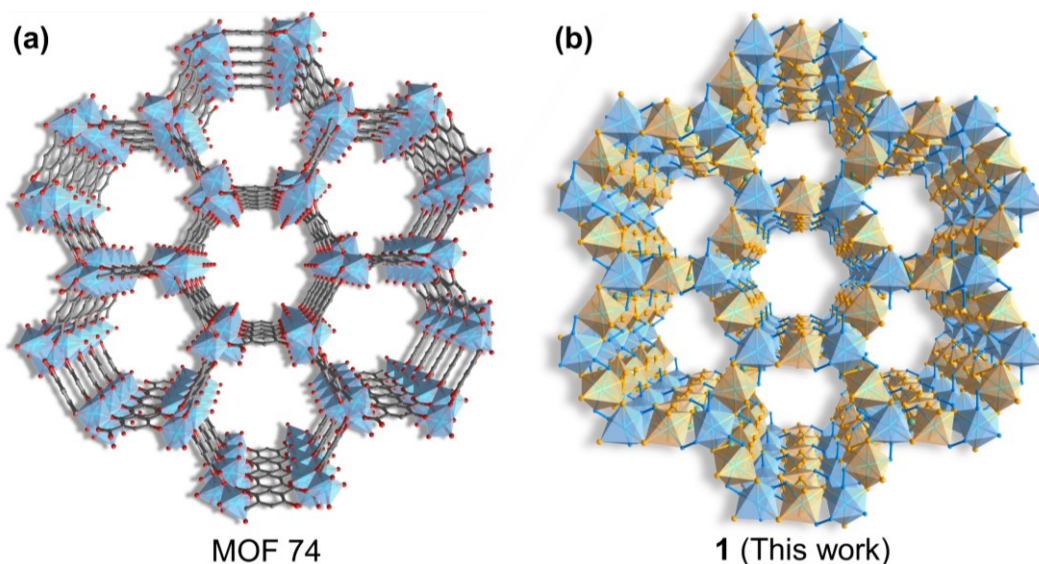


Figure S3. The 3D framework of MOF-74 (a) and **1** (b) viewed along the *c*-axis.

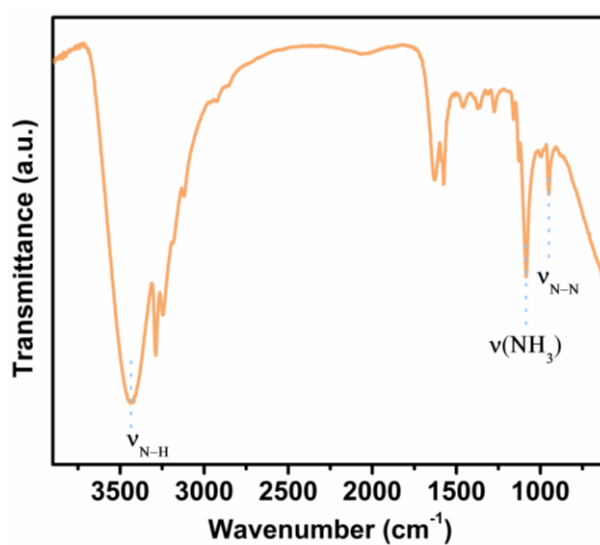


Figure S4. Fourier-transform infrared (FT-IR) spectrum of **1**. The bands at 3431 and 1083 cm⁻¹ can be assigned to the -NH stretching vibration and rocking vibrations of the NH₃ groups, respectively. The band at 950 cm⁻¹ can be assigned to the N-N vibrations.¹ These further confirm the existence of a protonated H₂en²⁺ cation and N₂H₄ molecules.

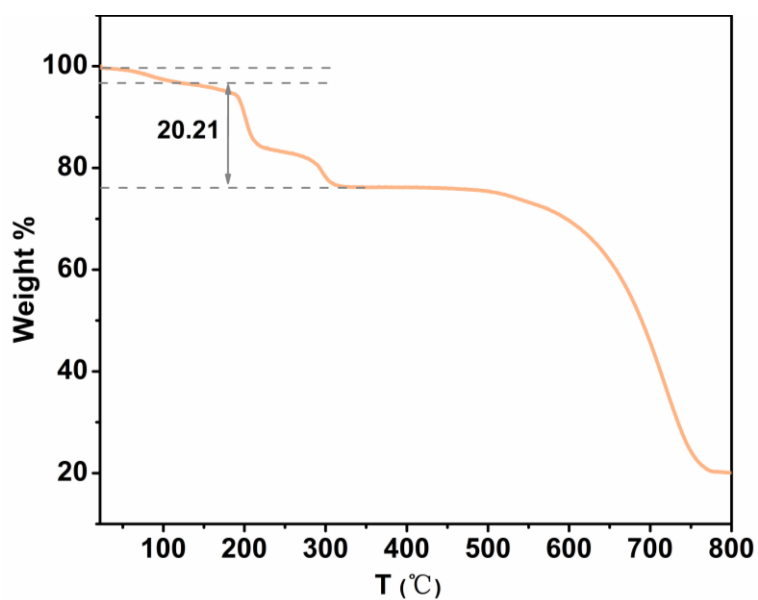


Figure S5. Thermogravimetric analysis (TGA) curves of **1** under N₂ atmosphere. The initial gradual weight loss of 2.03 % between 22–220 °C could be attributed to loss of moisture and solvent molecules adsorbed of sample. The second step weight loss of 20.21 % between 220–314 °C could be attributed to loss of en, DMF and N₂H₄ molecules, similar to the theoretical value of 18.78 %.

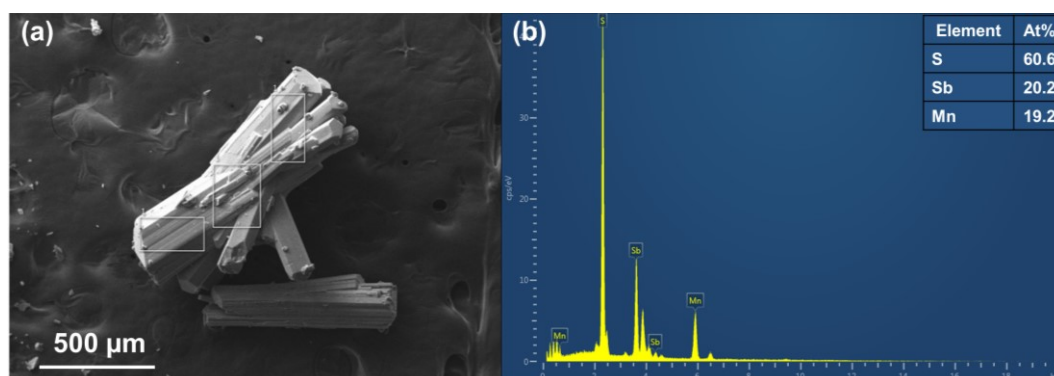


Figure S6. SEM image, and energy dispersive spectroscopy (EDS) of as-synthesized **1**.

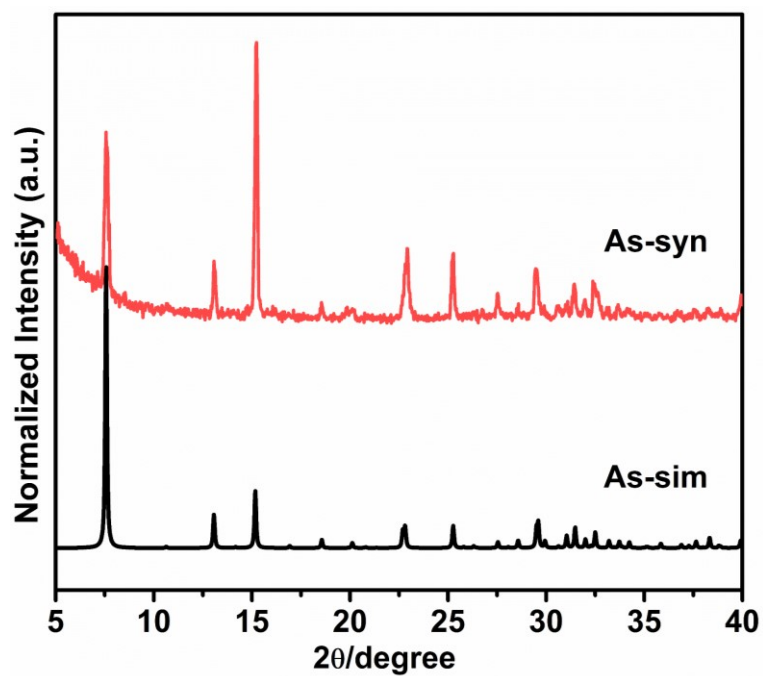


Figure S7. The powder X-ray diffraction (PXRD) pattern of **1**.

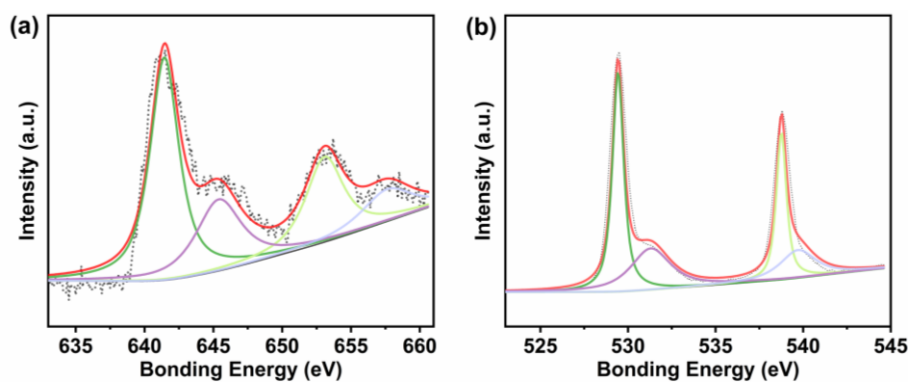


Figure S8. XPS spectra of the Mn 2p (a) and Sb 3d (b) of **1**.

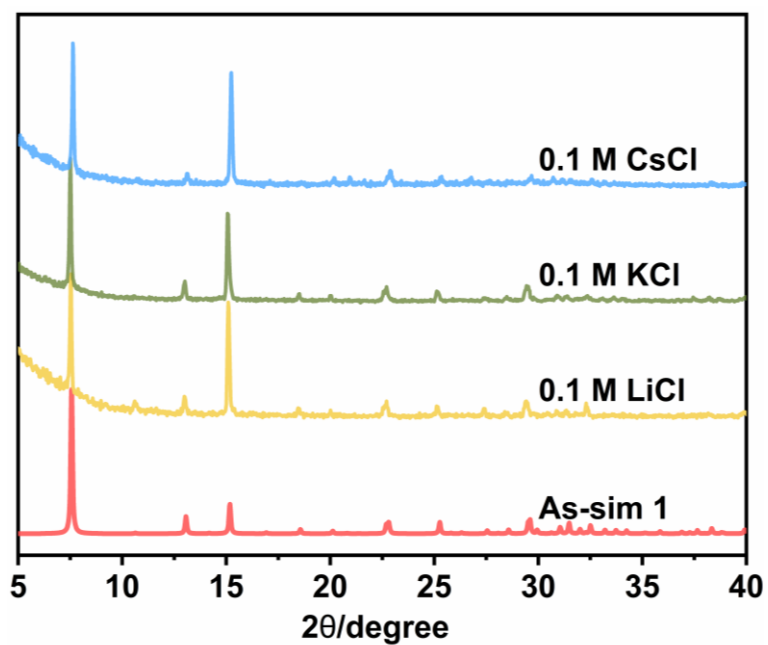


Figure S9. The PXR D patterns of **1** after immersed in MCl (M = Li, K, Cs) aqueous solution (0.1 M) for 24 hours at room temperature.

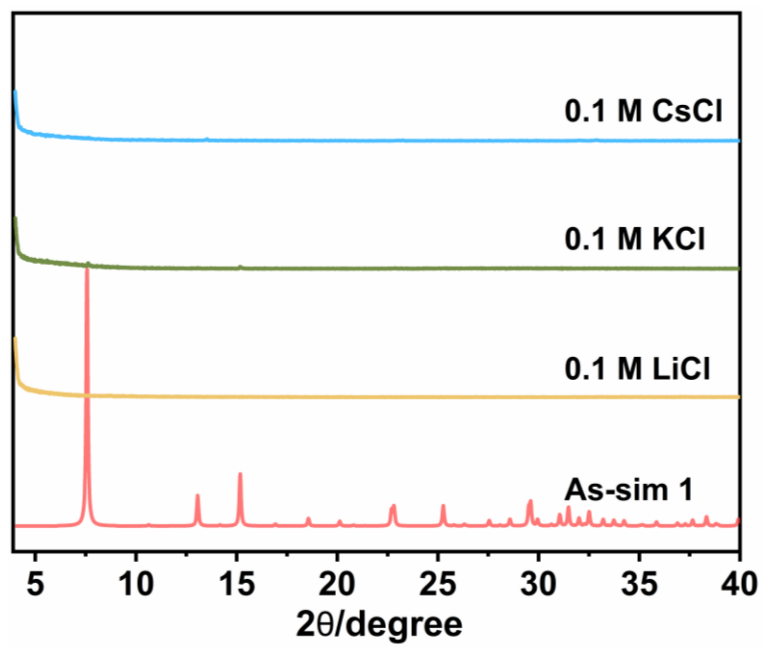


Figure S10. The PXR D patterns of **1** after immersed in MCl (M = Li, K, Cs) aqueous solution (0.1 M) for 24 hours at 65 °C.

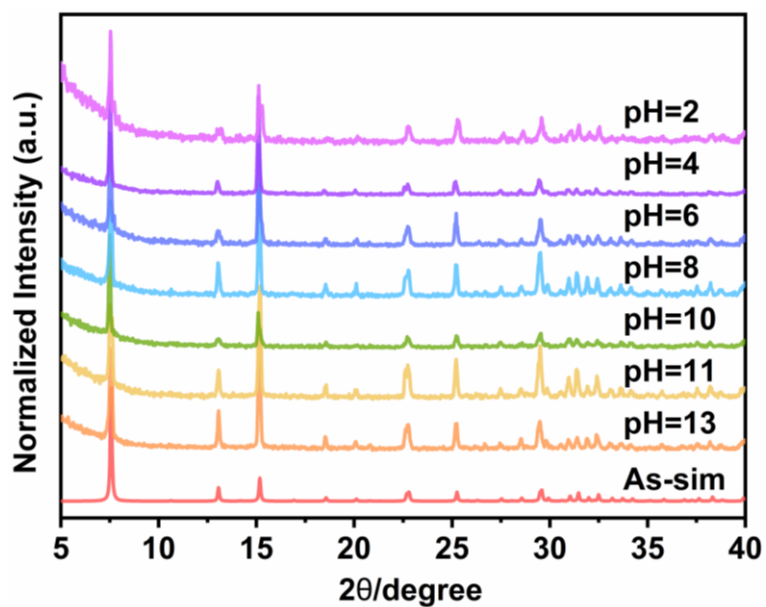


Figure S11. PXRD patterns of **1** collected after exposure to aqueous conditions with different pH values for 4 days.

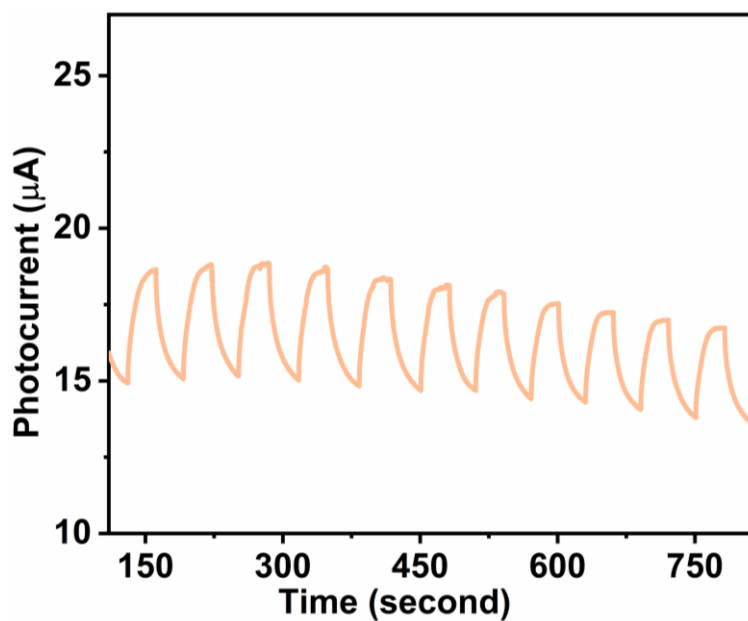


Figure S12. Photocurrent responses of **1** on ITO photo electrode under pulsed illumination at 0.4 V potential.

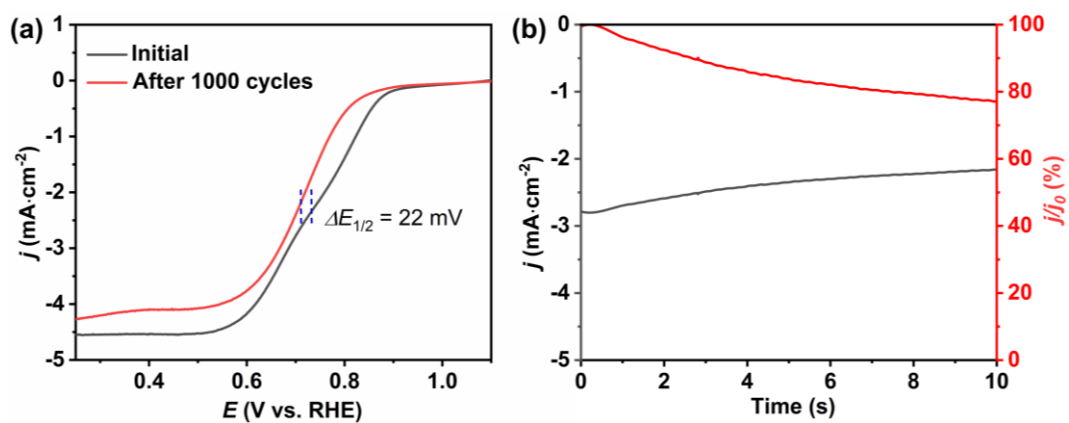


Figure S13. (a) LSV curves of **1**/CB initial (black) and after 1000 CV cycles (red) in O_2 -saturated 0.1 M KOH solution at the rotation speed of 1600 rpm with a scan rate of 5 mV/s; (b) Chronoamperometric (CA) curve of **1**/CB at 0.5 V vs. RHE with the rotation speed of 1600 rpm in O_2 -saturated 0.1 M KOH solution.

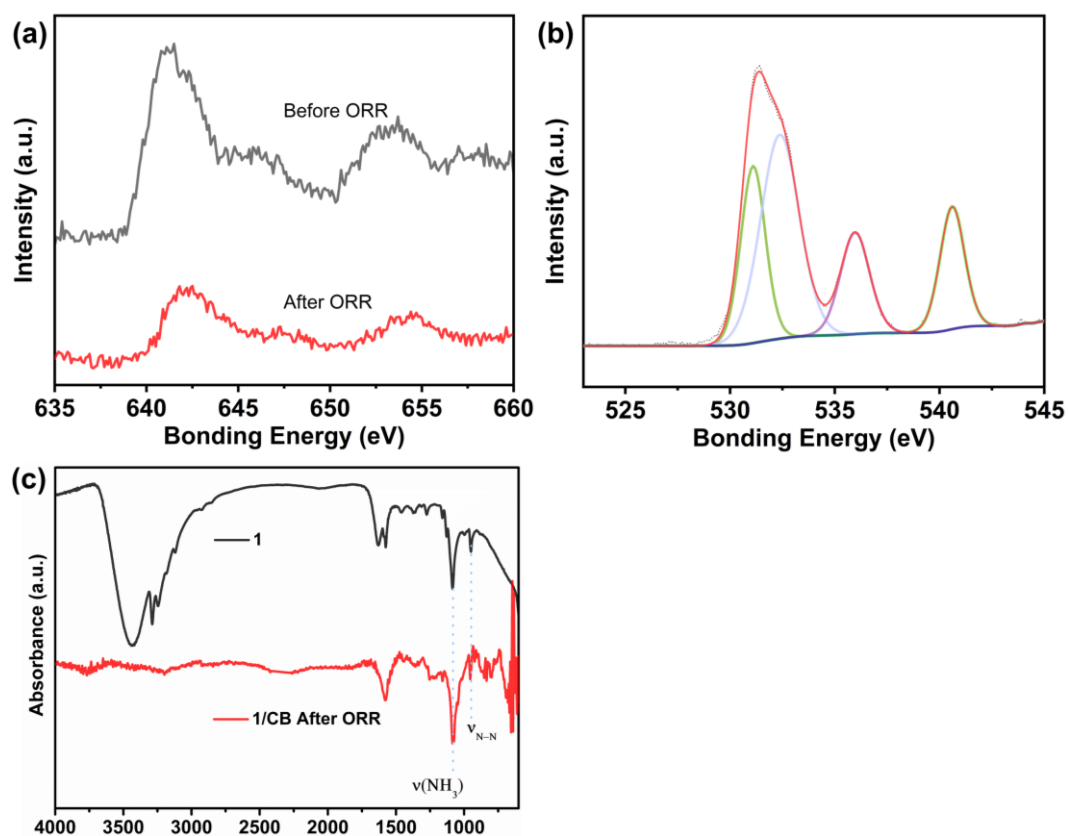


Figure S14. XPS of Mn 2p (a) and Sb 3d (b) and FT-IR (b) of **1**/CB after ORR testing. The XPS results of the oxidation state of Mn 2p reflected the good stability of **1** after the ORR. It is evident from the shape of Sb 3d_{5/2} transitions that the binding energy values of these and O 1s peaks are very close. The Sb 3d_{5/2} and Sb 3d_{3/2} peaks at 531.1

eV and 540.6 eV, indicating the oxidation of Sb(III) of **1**/CB after ORR testing to higher valence on the surface. The O1s(II) contribution appears at 532.4 eV and 536 eV assigned to the oxygen directly bounded to antimony.² The XPS results reflected the poor stability of **1** after ORR tests. According to the FT-IR curve for **1**/CB after ORR testing, the band at 950 cm⁻¹ can be assigned to the N–N vibrations,¹ which confirms the existence of N₂H₄.

Table S1. Elemental analysis of C, N, and H found (*wt %*) for $[\text{Mn}_5\text{Sb}_6\text{S}_{15}(\text{N}_2\text{H}_4)_6] \cdot (\text{H}_2\text{en}) \cdot \text{DMF} \cdot 0.5\text{N}_2\text{H}_4$ (**1**) after immersed in 0.1 mol/L MCl (M = Li, K, Cs) aqueous solution.

Element (%)	N	C	H
1 (calcd)	12.25	3.28	2.37
1 (found)	12.34	3.52	2.63
LiCl	12.09	3.54	2.54
KCl	12.29	3.59	2.54
CsCl	12.51	3.52	2.62

Table S2. Conductivity values of **1**.

Sample	Average conductivity	Conductivity ($\text{S} \cdot \text{cm}^{-1}$)		
		Sample 1	Sample 2	Sample 3
1	2.3×10^{-8}	1.28×10^{-8}	1.49×10^{-8}	4.01×10^{-8}

Table S3. Crystallographic data and structure refinement parameters for **1**.

Empirical formula	$\text{Mn}_5\text{Sb}_6\text{S}_{15}\text{N}_{16}\text{H}_{43}\text{C}_5\text{O}$
Formula weight	1829.7274
Temperature/K	120.03
Crystal system	trigonal
Space group	$P\bar{3}c1$
$a / \text{\AA}$	13.4726(8)
$b / \text{\AA}$	13.4726(8)
$c / \text{\AA}$	16.6266(12)
$\alpha / ^\circ$	90
$\beta / ^\circ$	90
$\gamma / ^\circ$	120

Volume / Å ³	2613.6(4)
Z	2
ρ_{calc} g / cm ³	2.133
μ / mm ⁻¹	4.825
F(000)	1558.0
Crystal size / mm ³	0.11 × 0.11 × 0.5
Radiation	MoK α ($\lambda = 0.71073$)
Index ranges	$-14 \leq h \leq 15, -16 \leq k \leq 16, -20 \leq l \leq 16$
Reflections collected	12653
Independent reflections	1559 [$R_{\text{int}} = 0.1114, R_{\text{sigma}} = 0.0612$]
Data/restraints/parameters	1589/0/60
Goodness-of-fit on F ²	1.025
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0479, wR_2 = 0.1131$
Final R indexes [all data]	$R_1 = 0.0668, wR_2 = 0.1255$
Largest diff. peak/hole / e Å ⁻³	1.75 / -1.27

Table S4. Selected bond distances for complex **1**.

Atom-Atom	Length/Å	Atom-Atom	Length/Å
Sb1-S2	2.423(2)	Mn1-S2 ³	2.612(2)
Sb1-S3	2.494(2)	Mn1-S1 ³	2.612(2)
Sb1-S1	2.391(2)	Mn1-S1 ²	2.612(2)
Mn2-S2 ¹	2.565(2)	Mn1-N1 ⁴	2.274(8)
Mn2-S2 ²	2.565(2)	Mn1-N1	2.274(8)
Mn2-S2	2.565(2)	S2-Mn1 ¹	2.612(2)
Mn2-N2 ²	2.324(8)	S3-Sb1 ⁵	2.494(2)
Mn2-N2	2.324(8)	S1-Mn1 ¹	2.612(2)
Mn2-N2 ¹	2.324(8)	N2-N1	1.455(10)

Mn1-S2² 2.612(2)

Symmetry codes: ¹+Y-X, 1-X, +Z; ²1-Y, 1+X-Y, +Z; ³+Y, -X+Y, 1-Z; ⁴1-X, 1-Y, 1-Z; ⁵-X, -X+Y, 1/2-Z.

Table S5. Summary of ORR catalysts based on metal chalcogenide open frameworks.

Catalysts	$E_{1/2}$ (V)	J (mA·cm ⁻²)	n	Reference
1/CB	0.73	4.5	3.3	This work
CSZ-5-InSe/CB	0.68	2.8	2.2	<i>Angew. Chem. Int. Ed.</i> , 2015 , <i>54</i> , 5103–5107
SOF-20/CB	0.70	4.0	2.5	<i>Inorg. Chem. Front.</i> , 2019 , <i>6</i> , 3063–3069
SOF-21/CB	0.69	3.6	2.6	
SOF-27/CB	0.70	2.8	2.8	<i>Inorg. Chem.</i> , 2018, 57 , 921–925
SOF-25/CB	0.67	2.86	2.2	<i>Inorg. Chem.</i> , 2019 , <i>58</i> , 31–34
SOF-28/CB	0.67	3.52	2.6	
NCF-4/CB	0.76	3.8	3.7	<i>Dalton Trans.</i> , 2018 , <i>47</i> , 3227–3230

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- 2 C. D. Wagner, *Anal. Chem.* 1980, **52**, 1445–1451.