

Supporting information for

**A Unique Non-Interpenetrated Open-Framework
Chalcogenide with Large Cavity**

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EXPERIMENTAL SECTION

Materials. Indium powder (In, 99.99%, powder), sublimed sulfur (S, 99.9%, powder), hydrated ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99%), 4,4'-trimethylenedipiperidine (TMDP, 97%, solid), and deionized water. All analytical grade chemicals employed in this study were commercially available and used without further purification.

Synthesis. Indium powder (85 mg), sulfur powder (65 mg), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (180 mg), and TMDP (608 mg) were mixed with deionized water (4.025 g) in a 23-mL Teflon lined stainless autoclave and under vigorous stirring for 30 min. Then the vessel was sealed and heated at 190 °C for 14 days and then taken out from the oven. The autoclave was subsequently allowed to cool to room temperature and dark red triangle crystals were obtained. The crystals were washed by ethanol, and then dried in air. And the compound is stable under ambient conditions.

Single Crystal X-ray Diffraction (SCXRD). The single-crystal X-ray diffraction measurements were performed on Photon II CPAD diffractometer controlled using graphite-monochromated Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation at 296 K. The structure was solved by direct method using SHELXS-2014 and the refinements against all reflections of the compound were performed using SHELXS-2014. The protonated organic amines and water molecules located in the void space of the framework cannot be identified owing to their serious disorder. As a result, the contribution of the disordered solvent molecules was subtracted from the reflection data by the SQUEEZE method as implanted in PLATON program. The templates and solvents were assigned based on charge balance as well as EA results i.e. 4.5 protonated TMDP molecules and 6 water molecules per formula.

Powder X-ray Diffraction (PXRD). PXRD data were collected on a desktop diffractometer (D2 PHASER, Bruker, Germany) using Cu-K α ($\lambda = 1.54056 \text{ \AA}$) radiation operated at 30 kV and 10 mA. The samples were ground into fine powders for several minutes before the test.

Elemental Analysis. Energy dispersive spectroscopy (EDS) analysis was obtained on energy dispersive spectroscopy (EDS) detector. The EDS measurement indicates that

Fe : In is 7.3 : 31.1 and close to the ratio of Fe : In = 1 : 4. Elemental analysis (EA) of C, H, and N was performed on VARIDEL III elemental analyzer {Calcd. (wt%): C , 16.86; H, 3.34; N, 3.03. Found: C, 18.00; H, 3.91; N, 3.07}. The content deviation of C could be ascribed to some carbon impurities formed in the solvothermal reaction.

Thermogravimetric Analysis (TGA). TGA measurement was performed with a Shimadzu TGA-50 system under nitrogen flow. The TG curve was performed by heating the sample from 20 to 800 °C with heating rate of 10°C /min.

UV-Vis Absorption. Room-temperature solid-state UV-Vis diffuse reflectance spectra of crystal samples were measured on a SHIMADZU UV-3600 UV-Vis-NIR spectrophotometer coupled with an integrating sphere by using BaSO₄ powder as the reflectance reference. The absorption spectra were calculated from reflectance spectra by using the Kubelka-Munk function: $F(R)=\alpha/S=(1-R)^2/2R$, where R , α , and S are the reflection, the absorption and the scattering coefficient, respectively.

Fourier Transform Infrared Absorption. Fourier transform-Infrared spectral analysis was performed on a Thermo Nicolet Avatar 6700 FT-IR spectrometer with cesium iodide optics allowing the instrument to observe from 600-4000 cm⁻¹.

Ion Exchange. The sample of **OCF-89** (20 mg) was dipped in 20 mL aqueous solution of CsCl (1 M) in glass vial, which was slowly shaken by hand for several seconds, then placed at room temperature, 45 °C and 85 °C, respectively. During the treatment, the CsCl solution (1 M) was refreshed twice. After a certain time, the crystals were taken out of solution and washed with deionized water to remove residual Cs⁺ ions adsorbed on the crystal surface. The products were then characterized by EA and EDS.

Gas Adsorption. N₂ sorption measurement of Cs⁺ exchanged sample was carried out on a Micromeritics ASAP 2020 Physisorption Analyzer with the temperature controlled at 77 K by liquid N₂. Prior to the measurement, the as-synthesized sample was dried in the vacuum oven for several hours and further dried by using “degas” process of the surface area analyzer for 12 hours at 60 °C.

Table S1. Crystal data and refinement results of **OCF-89**.

	OCF-89
Formula	Fe ₈ In ₃₂ S ₆₅
Formula weight	6204.94
Crystal morphology	triangle
Crystal system	orthorhombic
Z	2
Space group	<i>Imm2</i>
T/K	296(2)
$\lambda/\text{\AA}$	0.71073
$a/\text{\AA}$	47.294(5)
$b/\text{\AA}$	15.6118(17)
$c/\text{\AA}$	22.614(3)
$\alpha/^\circ$	90.00
$\beta/^\circ$	90.00
$\gamma/^\circ$	90.00
$V(\text{\AA}^3)$	16697(3)
$F(000)$	5632
$D(\text{g cm}^{-3})$	1.234
$\mu (\text{mm}^{-1})$	2.907
Collected reflections	21410
Independent reflections	6974
GOF on F^2	1.049
$R_1, wR_2 (I > 2\sigma(I))$	0.0476, 0.0817
R_1, wR_2 (all data)	0.0856, 0.0883

Table S2. TMDP-directed Tn clusters-based COFMCs.

Name	Framework composition	Extra-framework volume (%)	Topology	Interpenetration
UCR-20 ¹	T2-GaSnS	67	sod	No
UCR-1 ²	T4-CdInS	63	UCR-1	No
OCF-6 ³	T3-GaSe	70	single dia	No
OCF-13 ³	T3-GaSe	73	CrB4	No
OCF-5 ⁴	T4-ZnGaSnSeS	56	double dia	Yes
UCR-17 ⁵	T5-CuInS	63	double dia	Yes
OCF-42 ⁶	T2-GaGeSe/T4-ZnGaSe	64.5	OCF-42	No
OCF-89 (this work)	T4-FeInS	70.5	OCF-89	No

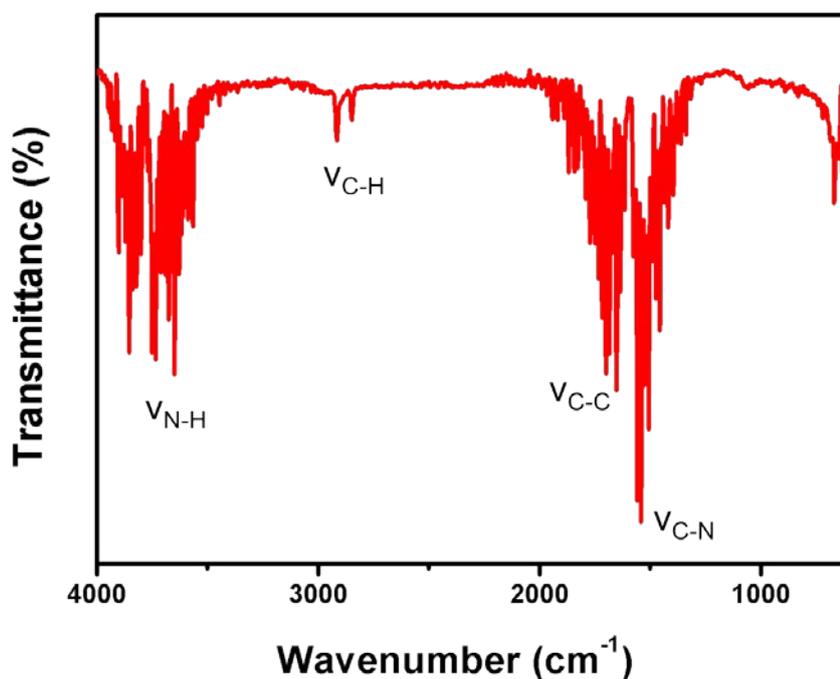


Figure S1. FTIR spectrum of **OCF-89**.

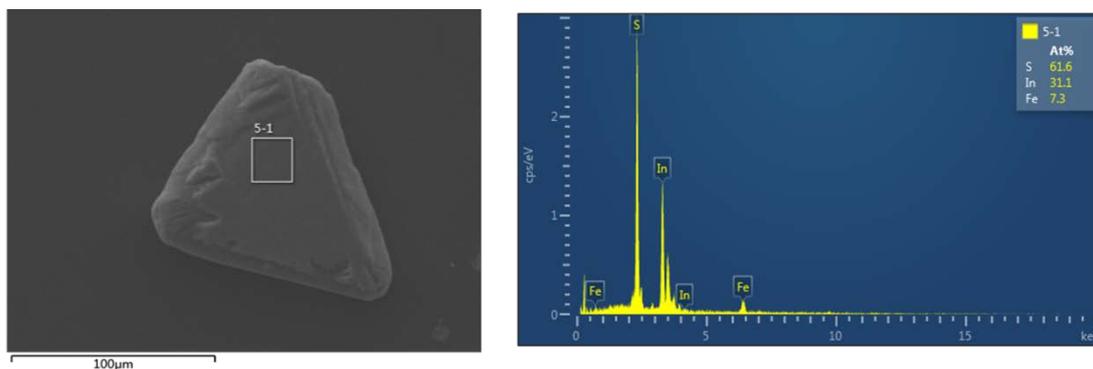


Figure S2. Left: SEM image of as-synthesized **OCF-89** crystal. Right: energy dispersive spectroscopy (EDS) of **OCF-89**.

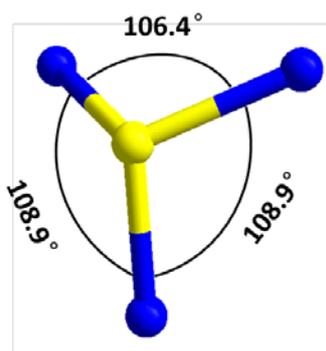


Figure S3. The In-S-In angles of tri-coordinated vertex sulfur in **OCF-89**.

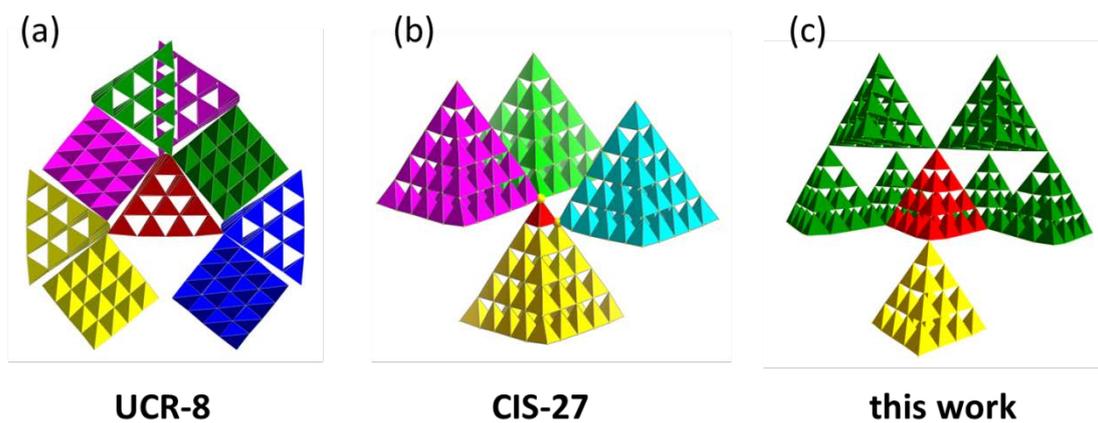


Figure S4. (a) Polyhedral mode of nine T4 clusters in UCR-8; (b) Polyhedral mode of four adjacent T5 clusters in CIS-27, and (c) Polyhedral mode of eight adjacent T4 clusters in **OCF-89**.

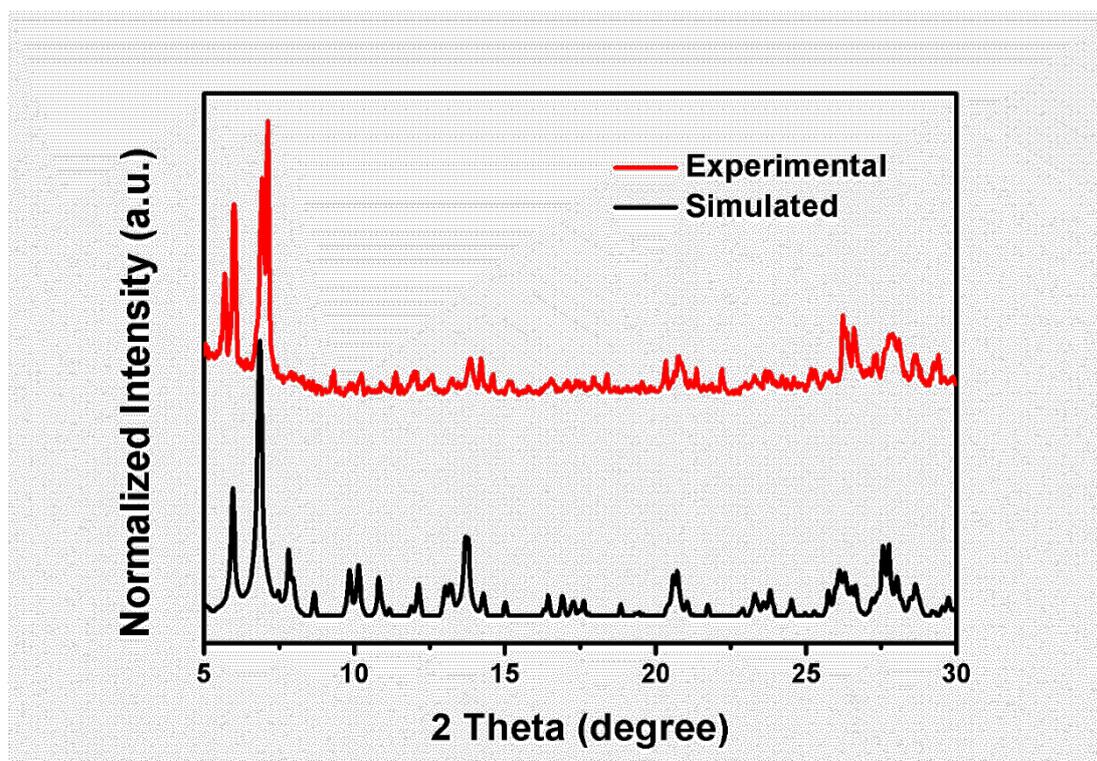


Figure S5. The simulated and experimental PXRD patterns of **OCF-89**.

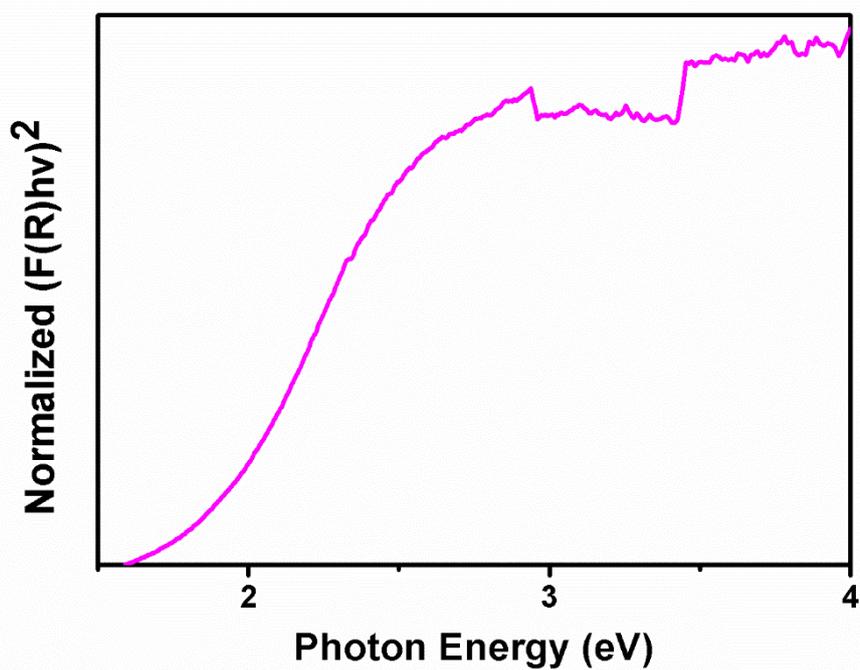


Figure S6. Tauc plots of compound **OCF-89** derived from UV/Vis DRS. The abrupt decrease between 2.9 and 3.4 eV was caused by the changing of the detector.

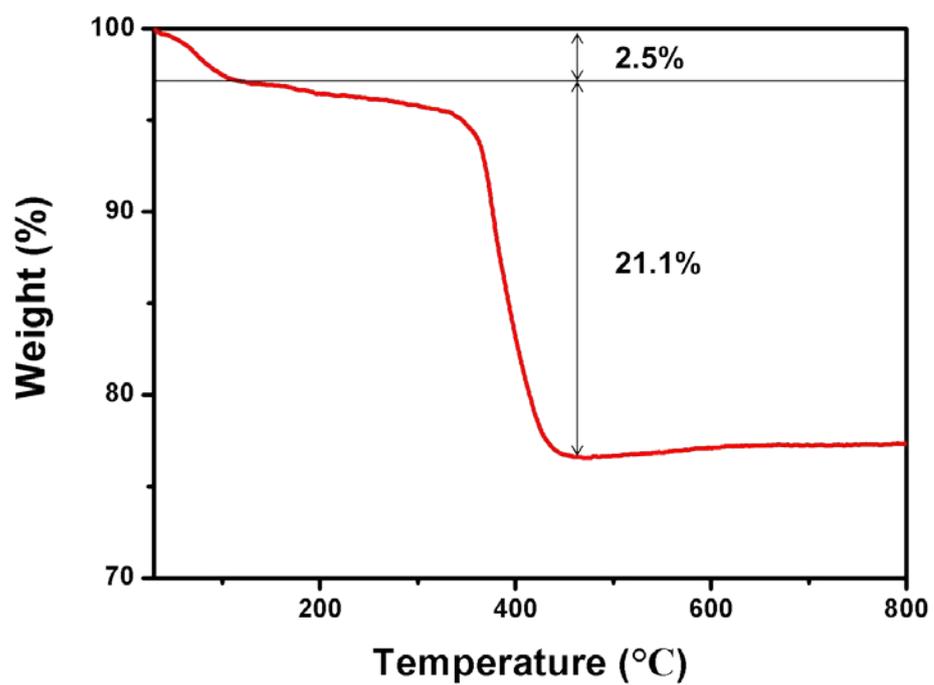


Figure S7. TGA curve of OCF-89.

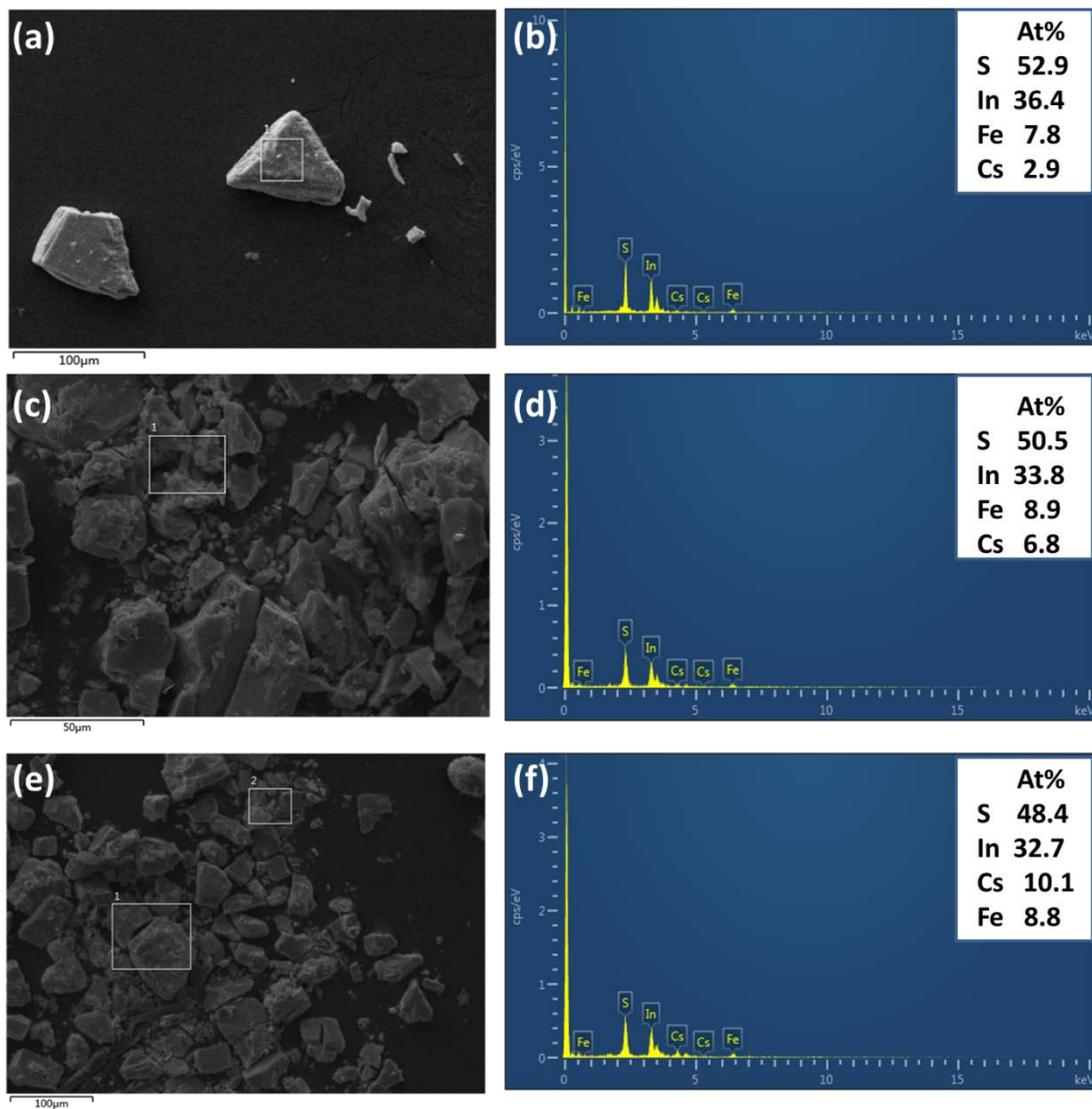


Figure S8. (a) (c) (e) SEM images of **OCF-89** after ion-exchange at room temperature, 45 °C, and 85 °C, respectively. (b) (d) (f) Energy dispersive spectroscopy (EDS) of **OCF-89** after ion-exchange at room temperature, 45 °C, and 85 °C, respectively.

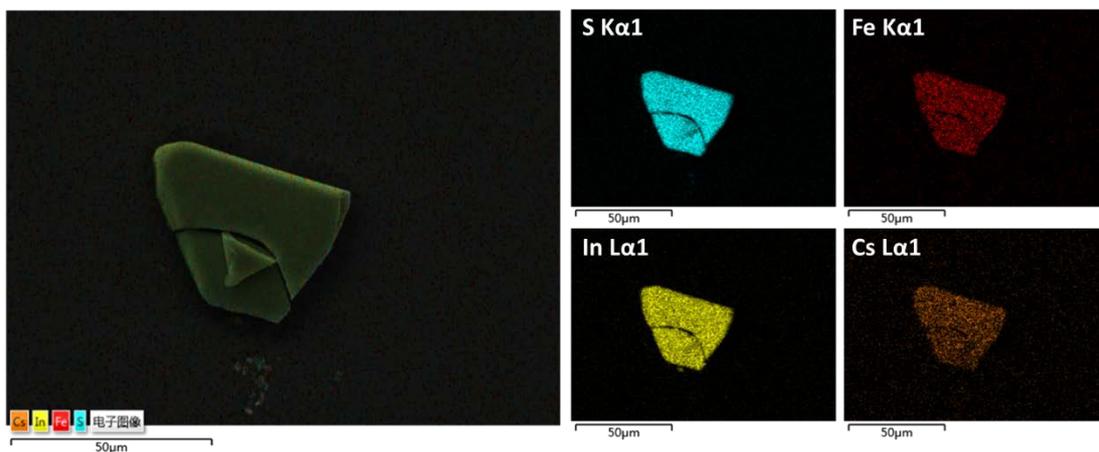


Figure S9. Elemental mapping of Cs⁺ exchanged samples at 45 °C for 48 h.

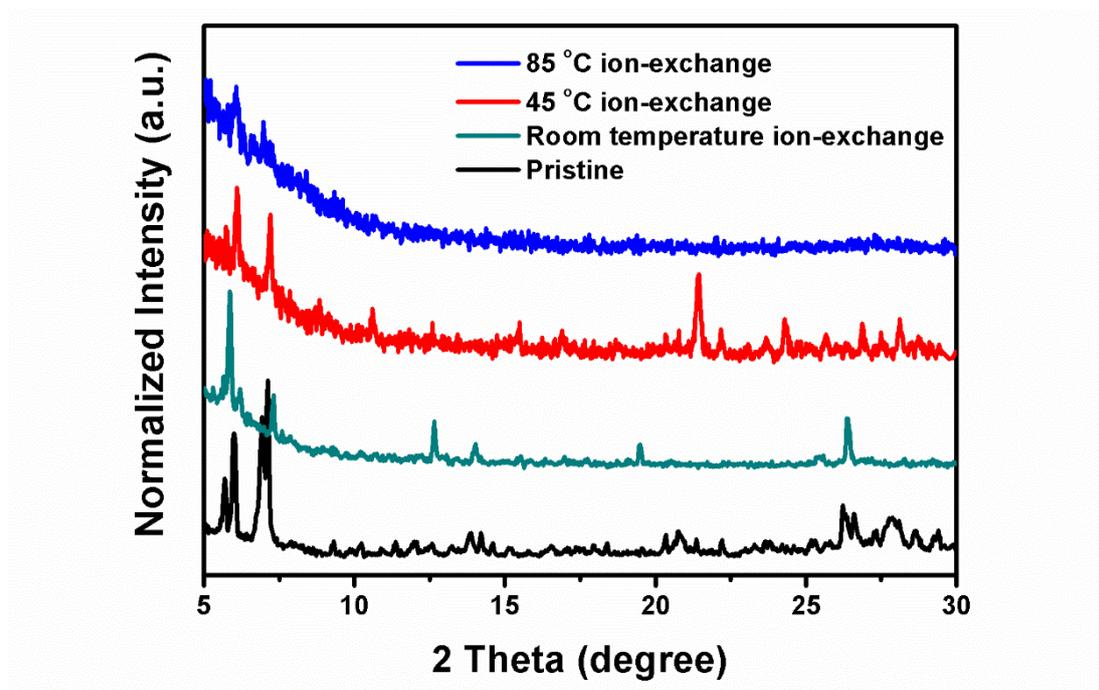


Figure S10. The PXRD patterns of pristine and ion-exchanged **OCF-89** at room temperature, 45 °C, and 85 °C, respectively.

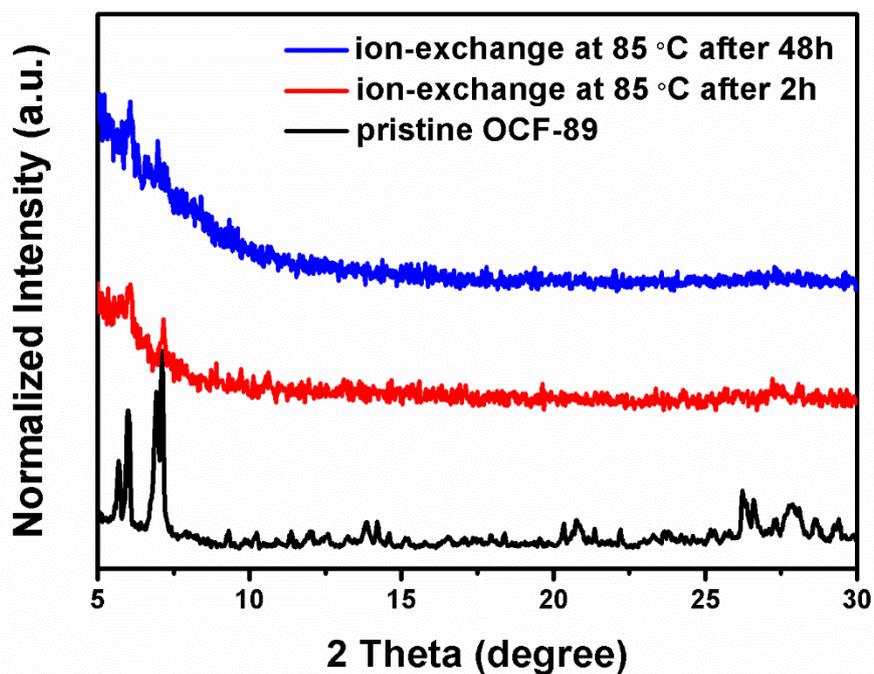


Figure S11. The PXRD patterns of pristine and ion-exchanged **OCF-89** at 85 °C with different time.

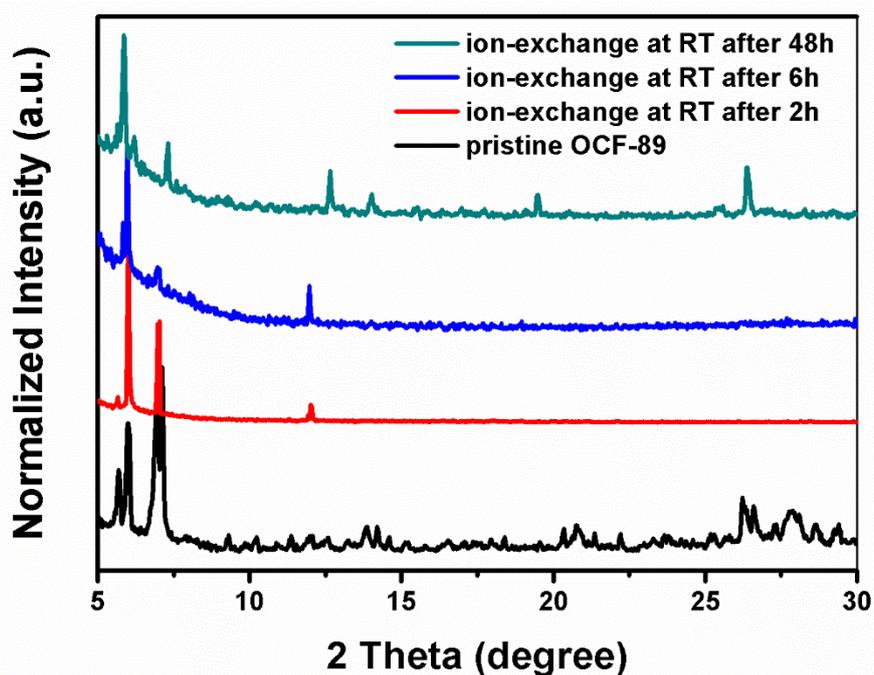


Figure S12. The PXRD patterns of pristine and ion-exchanged **OCF-89** at room temperature with different time. It should be noted that the only several peaks were shown in the PXRD pattern of the exchanged samples at 2 h and 4 h. This situation is just because the samples were not ground rather than the second phase, which can be clearly seen from Figure S18.

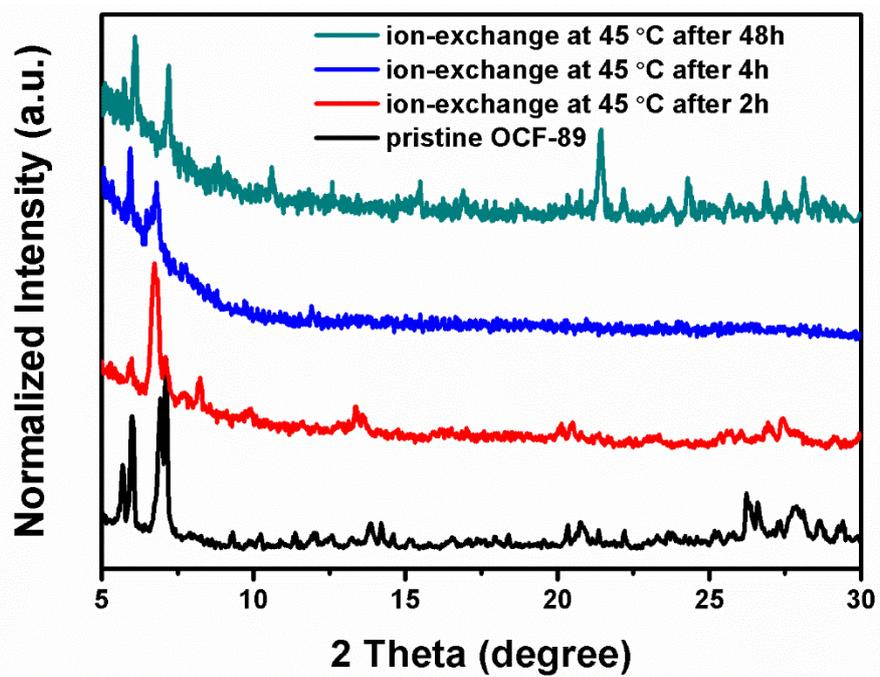


Figure S13. The PXR D patterns of pristine and ion-exchanged **OCF-89** at 45 °C with different time.

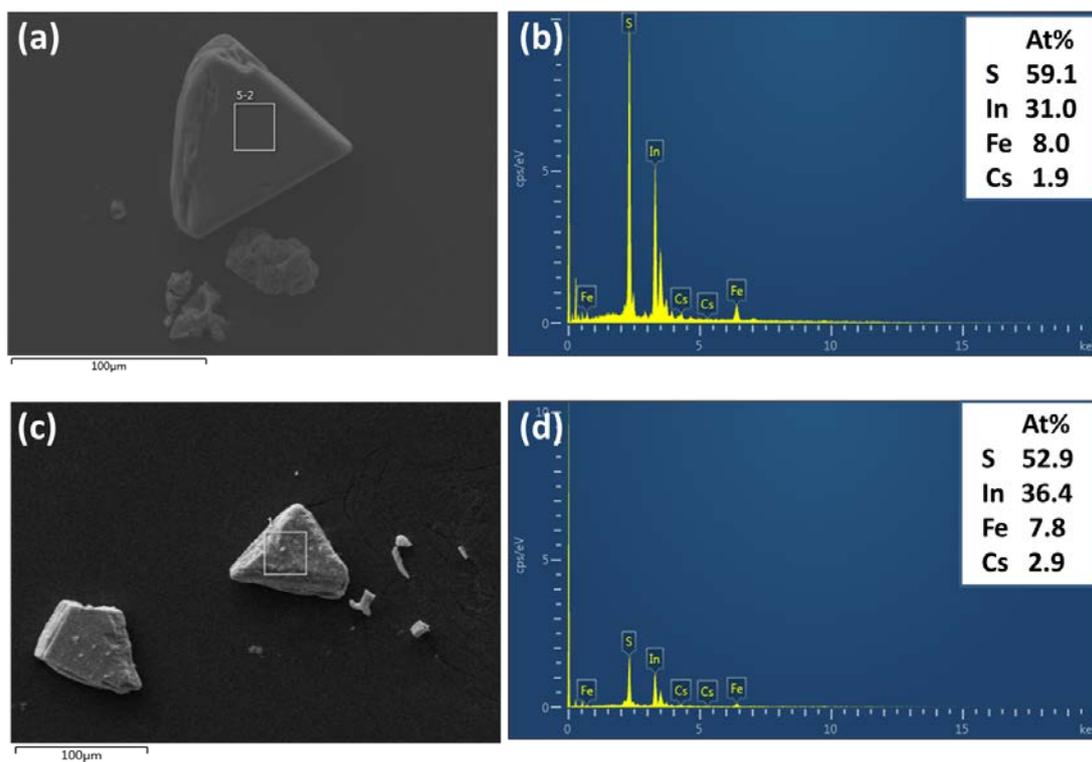


Figure S14. (a) (c) SEM images of **OCF-89** after ion-exchange at room temperature for 2h and 48h respectively. (b) (d) Energy dispersive spectroscopy (EDS) of **OCF-89** after ion-exchange at room temperature for 2h and 48h respectively.

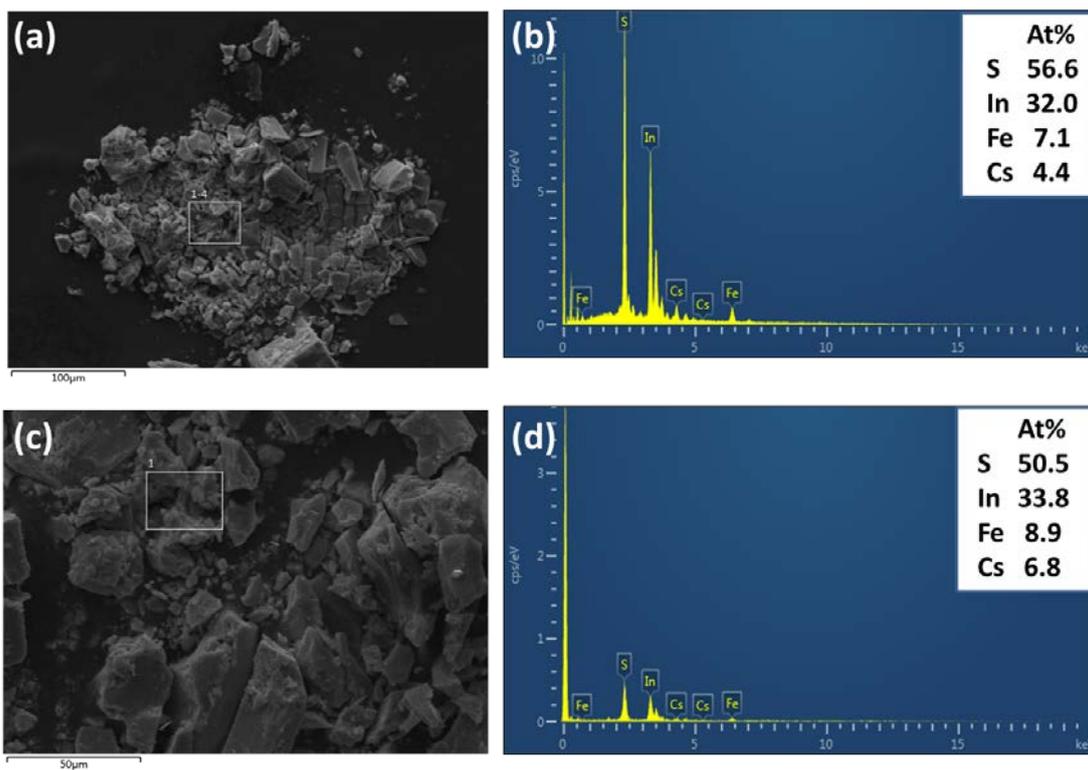


Figure S15. (a) (c) SEM images of **OCF-89** after ion-exchange at 45 °C for 2h and 48h respectively. (b) (d) Energy dispersive spectroscopy (EDS) of **OCF-89** after ion-exchange at 45 °C for 2h and 48h respectively.

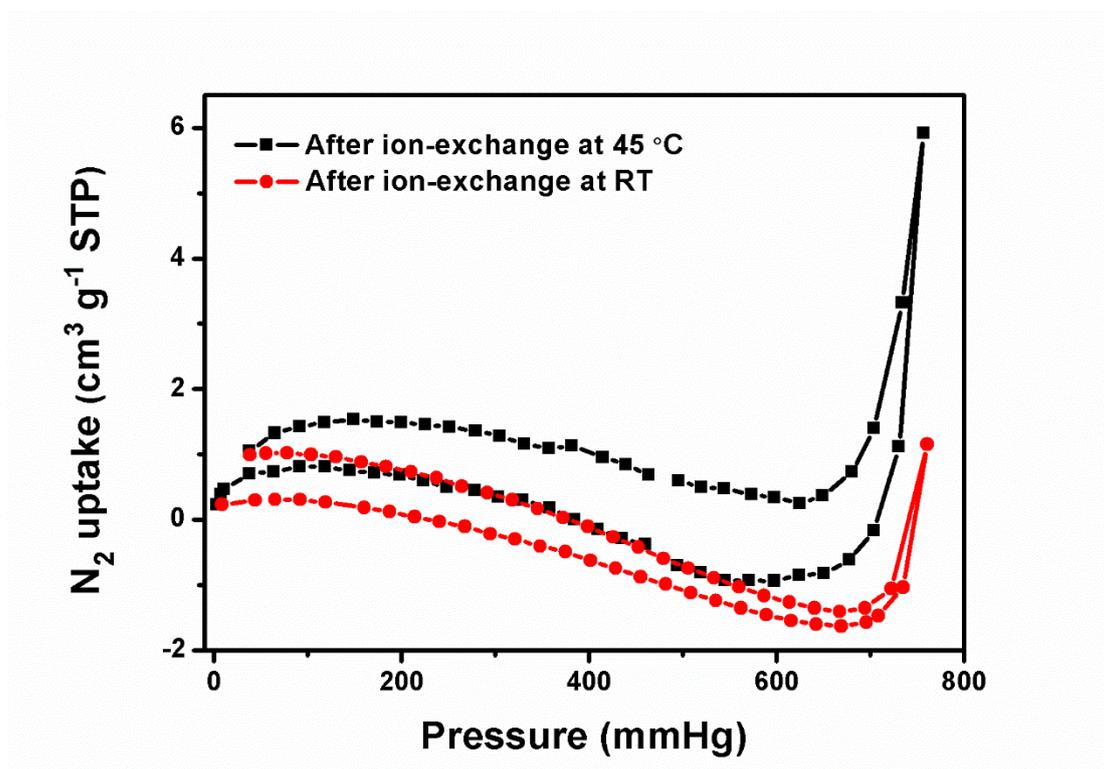


Figure S16. The N₂ adsorption isotherms at 77K on Cs⁺ exchanged **OCF-89** at RT and 45 °C.

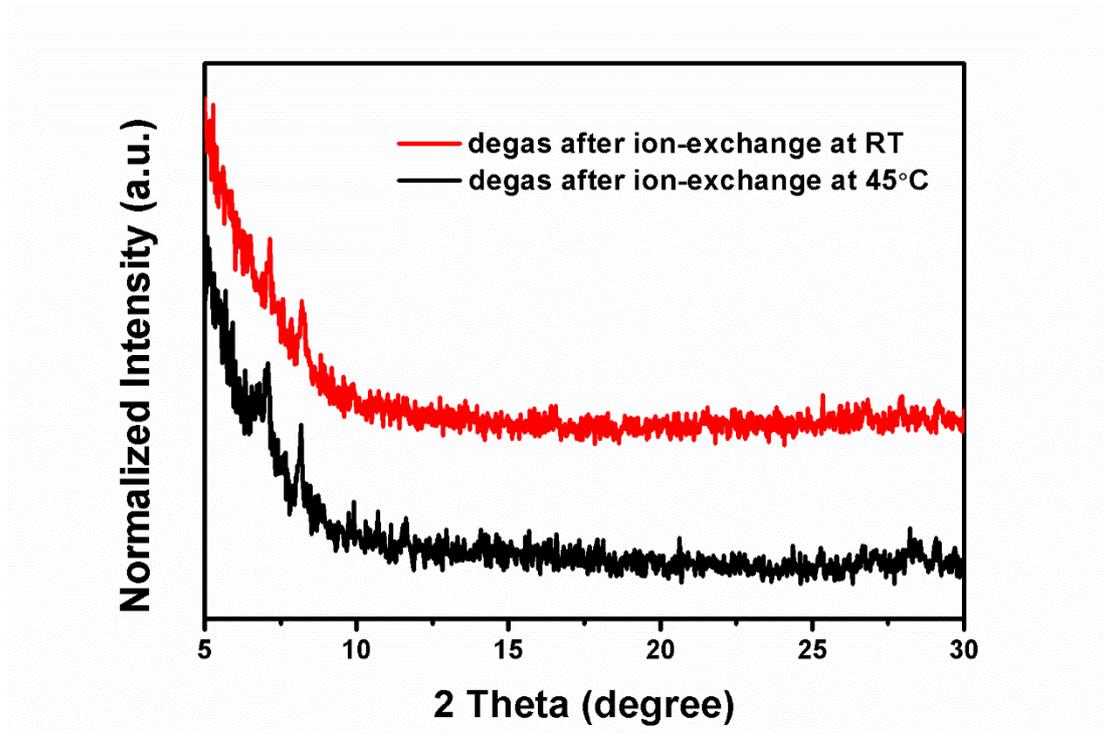


Figure S17. The PXRD pattern of Cs⁺ exchanged **OCF-89** at RT and 45 °C after degas process.

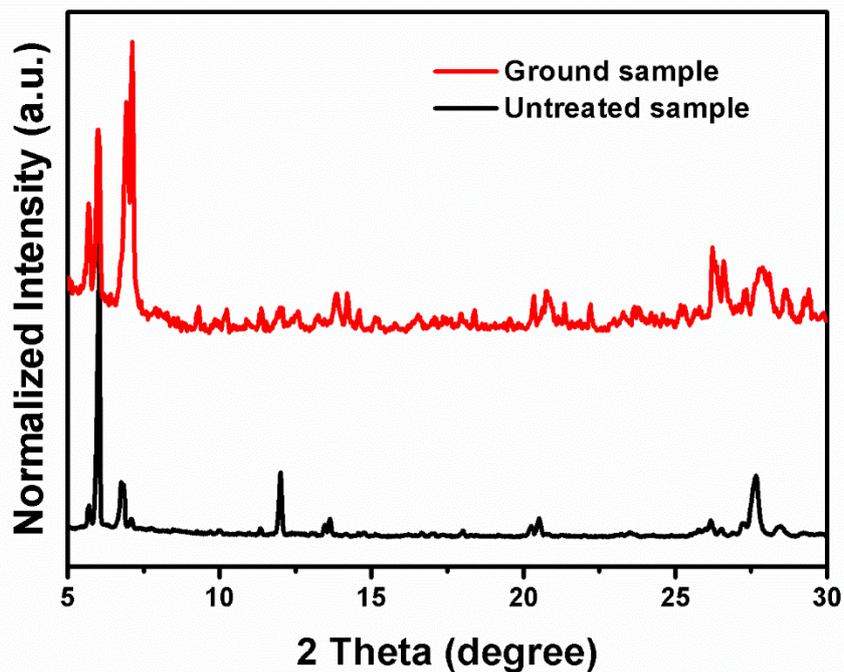


Figure S18. The PXRD patterns of different treatments of the same sample.

Reference

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- 2 C. Wang, Y. Li, X. Bu, N. Zheng, O. Zivkovic, C. S. Yang and P. Feng, *J. Am. Chem. Soc.*, 2001, **123**, 11506.
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