Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

A new cluster-based chalcogenide zeolite analogue with large inter-cluster bridging angle†

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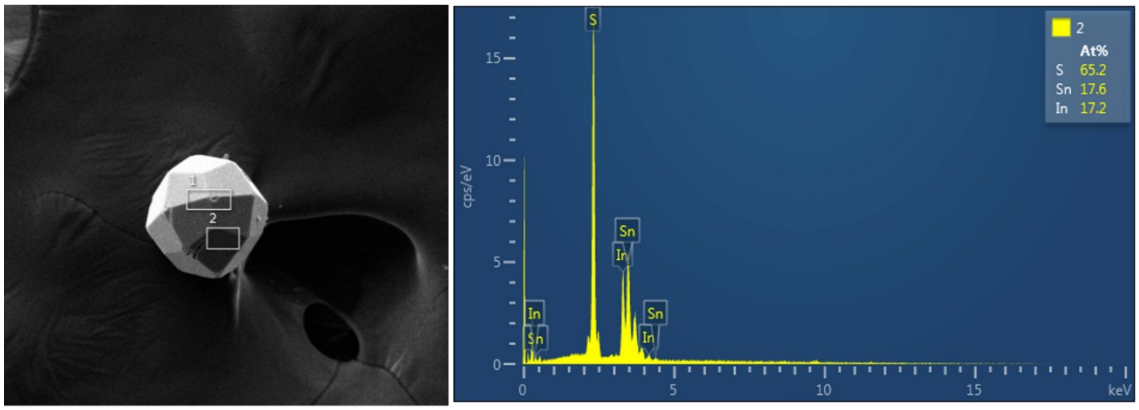

Figure S1. SEM image and the corresponding EDX element analysis of **SOF-20**.

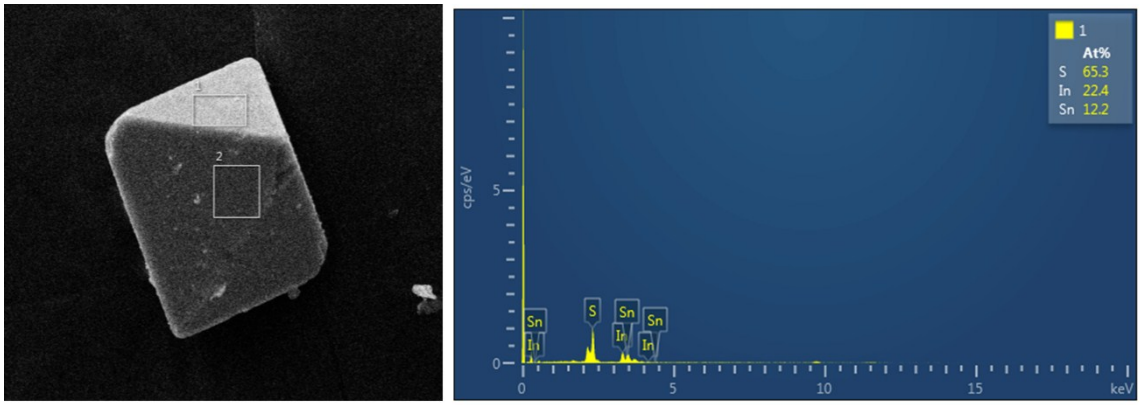

Figure S2. SEM image and the corresponding EDX element analysis of **SOF-21**.

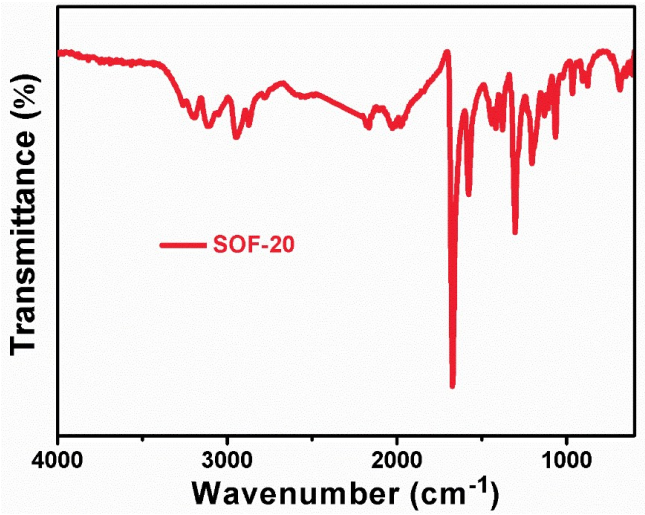

Figure S3. FT-IR spectrum of **SOF-20**.

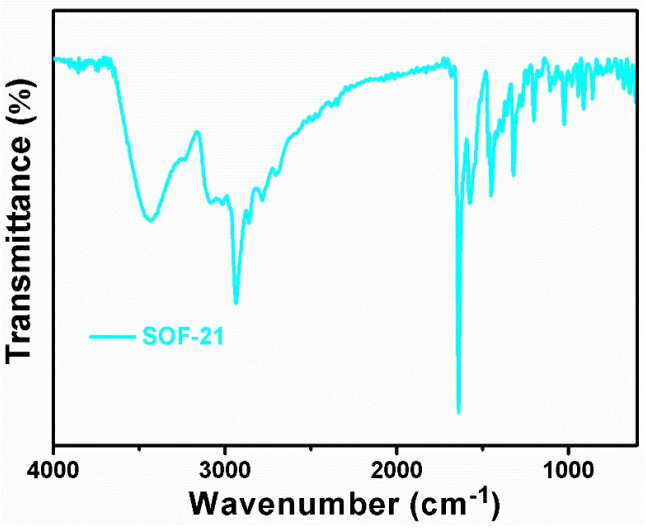

Figure S4. FT-IR spectrum of **SOF-21**.

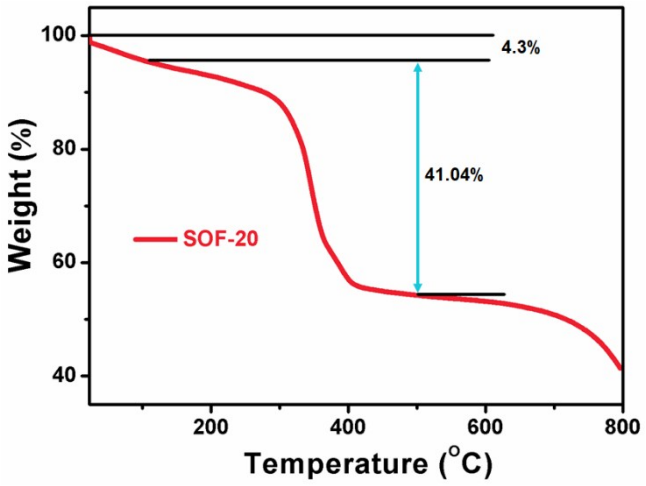

Figure S5. TG curve of **SOF-20**.

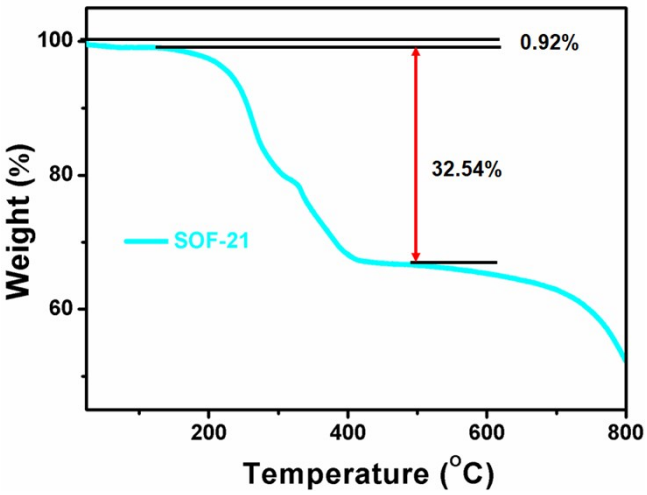

Figure S6. TG curve of **SOF-21**.

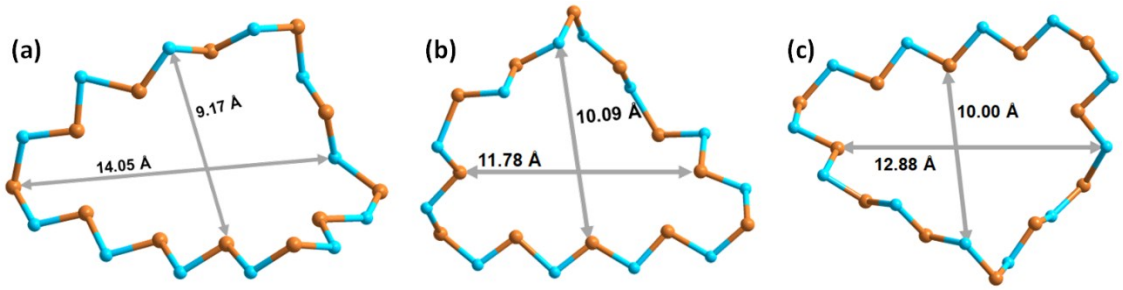

Figure S7. Three kinds of 24-MR windows observed in **SOF-20**: (a) window A; (b) window B; (c) window C.

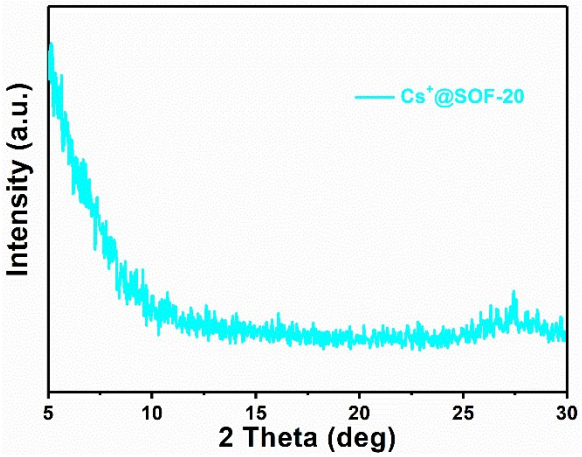

Figure S8. The PXRD patterns of Cs^+@**SOF-20** sample.

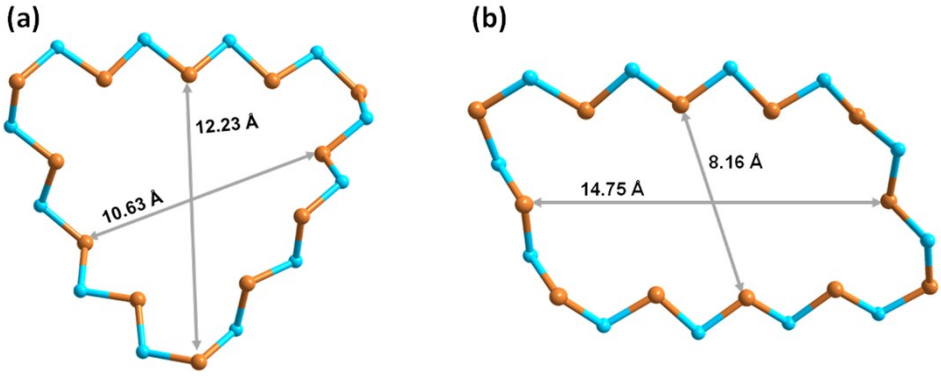

Figure S9. Two kinds of 24-MR windows observed in **SOF-21**: (a) window D; (b) window E.

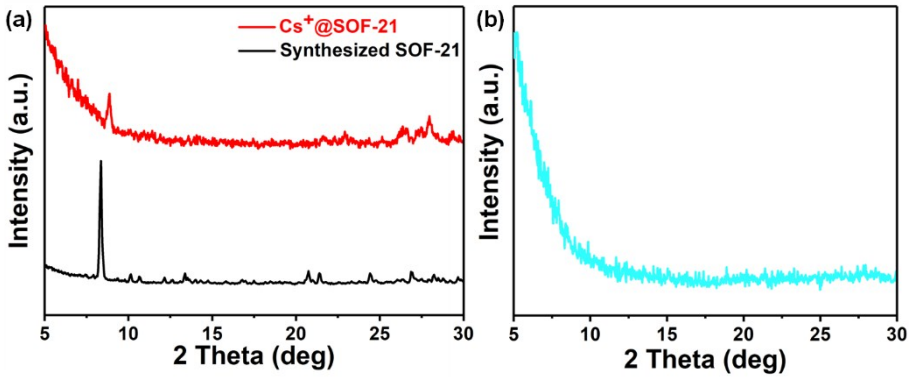

Figure S10. PXRD patterns of (a) Cs^+@**SOF-21**; (b) Cs^+@**SOF-21** after degassing process.

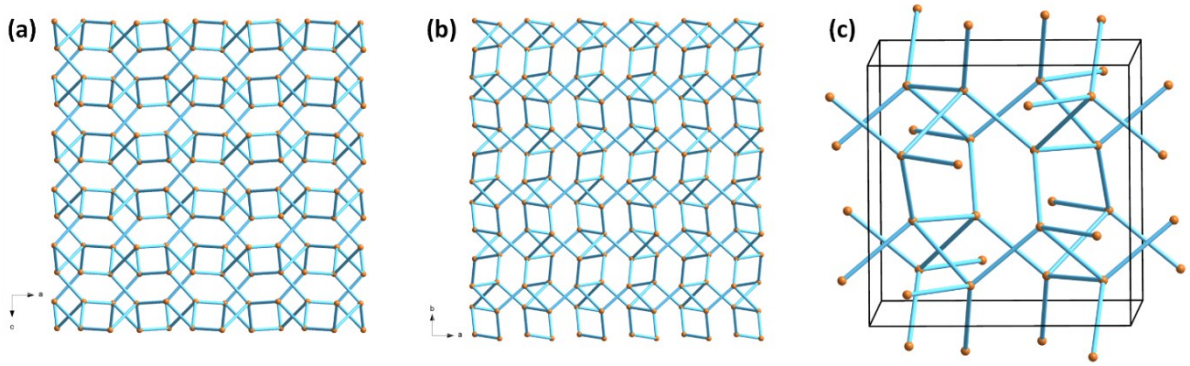

Figure S11. Topological diagrams of **SOF-20** along *b* axis (a), *c* axis (b), and obtained in a single unit cell (c).

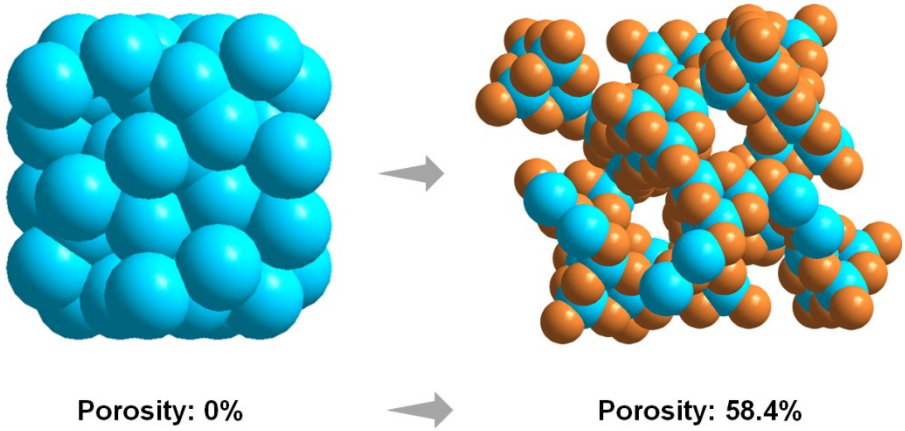

Figure S12. Comparison of the porosity between Si-based (or Ge-based) *gsi* structure and T2-cluster-based *gsi* framework.

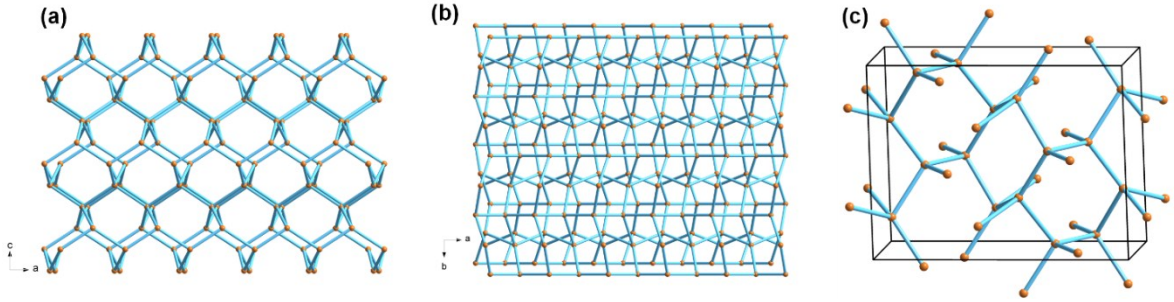

Figure S13. Topological diagrams of **SOF-21** along *b* axis (a), along *c* axis (b), obtained in a single unit cell (c).

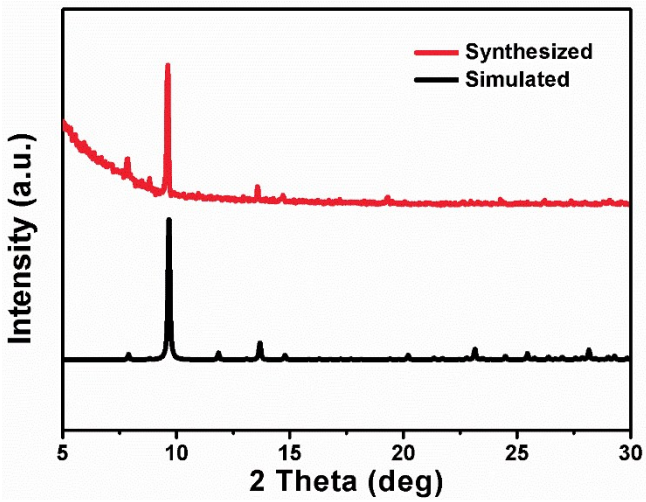

Figure S14. PXRD patterns of as-synthesized **SOF-20** and its simulated one.

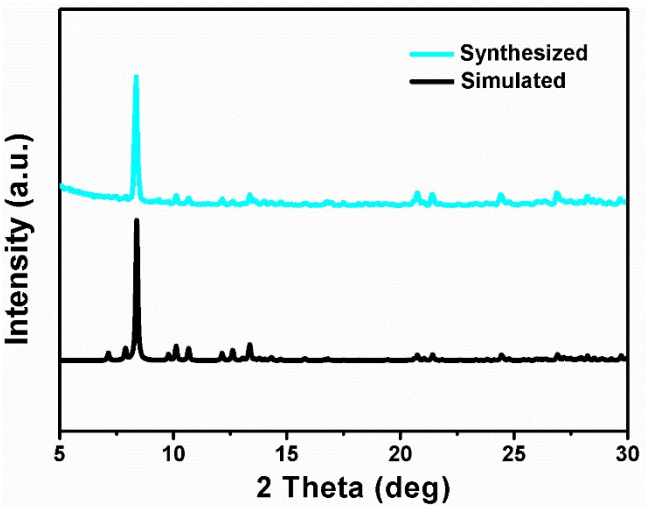

Figure S15. PXRD patterns of as-synthesized **SOF-21** and its simulated one.

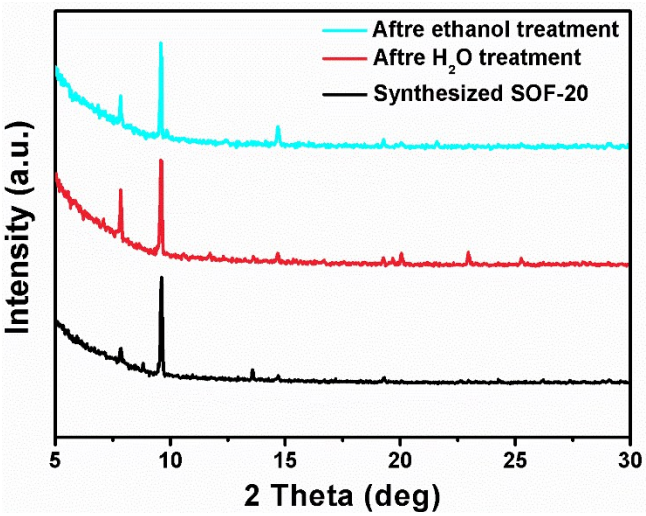

Figure S16. PXRD patterns of as-synthesized **SOF-20** and ones after the treatment of H_2O and ethanol.

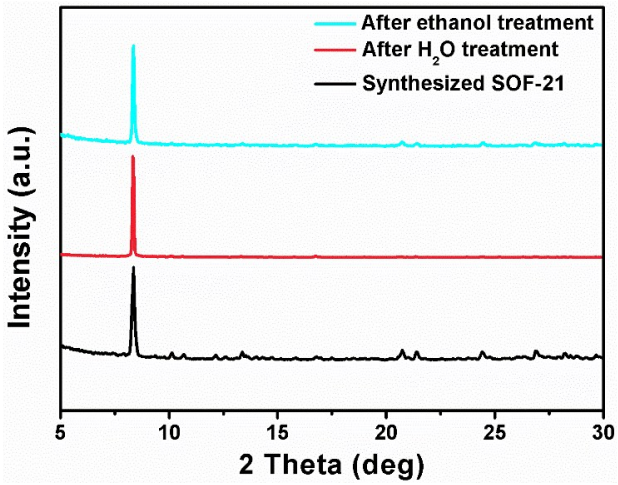

Figure S17. PXRD patterns of as-synthesized **SOF-21** and ones after the treatment of H_2O and ethanol.

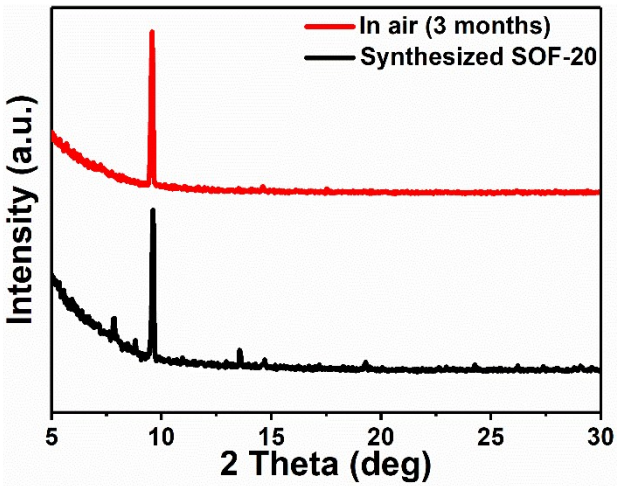

Figure S18. PXRD patterns of as-synthesized **SOF-20** and ones after exposed in air for three months.

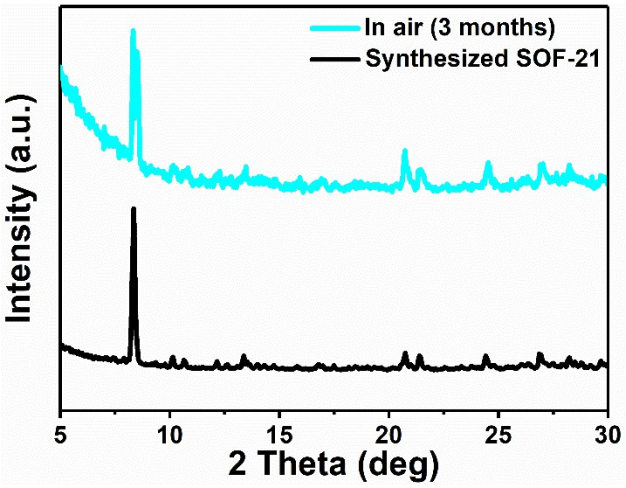

Figure S19. PXRD patterns of as-synthesized **SOF-21** and ones after exposed in air for three months.

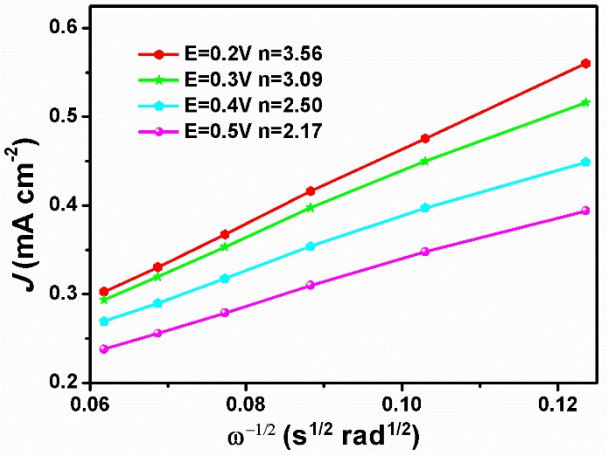

Figure S20. Corresponding K–L plots at different potentials of **SOF-20/CB**.

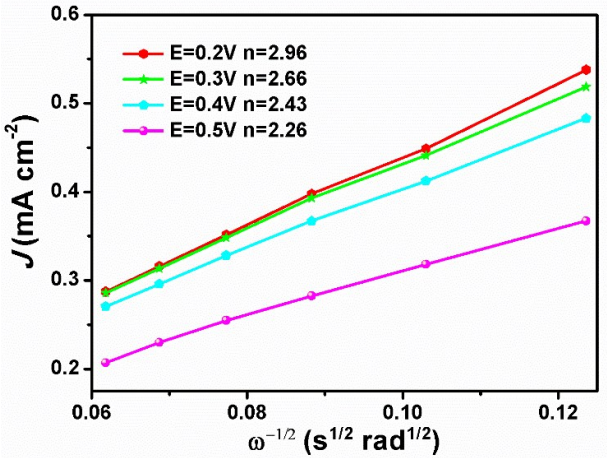

Figure S21. Corresponding K–L plots at different potentials of **SOF-21/CB**.

Table S1. Crystal data and refinement results of **SOF-20** and **SOF-21**.

Compounds	**SOF-20**	**SOF-21**
Framework formula	$[In_2Sn_2S_8]^{2-}$	$[In_{2.6}Sn_{1.4}S_8]^{2.6-}$
Formula weight	723.54	722.41
Crystal system	orthorhombic	orthorhombic
Z	8	8
Space group	*Pbca*	*Pbca*
***a* (Å)**	22.3820 (0)	13.213(10)
***b* (Å)**	22.3816 (10)	26.483 (2)
***c* (Å)**	22.3922 (11)	34.861 (3)
***α* (°)**	90	90
***β* (°)**	90	90
***γ* (°)**	90	90
***V*(Å^3)**	11217.3 (7)	12197.9 (18)
***T*(K)**	120 (2)	120 (2)
***F*(000)**	5184.0	12288.0
***D*(g/cm^{-3})**	1.695	3.811
Collected reflections	147369	44556
Independent reflections	10259	6390
GOF on F^2	1.134	1.047
***R*$_1$[a], *w*R_2[b](*I*>2σ(*I*))**	0.0595,0.1715	0.0482,0.1187
***R*$_1$, *w*[c]R_2(all data)**	0.0659,0.1792	0.0833,0.1331

[a]$R_1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b]$wR_2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$.

[c]$w = 1/[\sigma^2(Fo^2) + (xP^d)^2 + yP]$. [d]$P = (Fo^2 + 2Fc^2)/3$.

Table S2. The selected bond lengths (Å) for **SOF-20**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
In3	S9	2.421(5)	In2	S5	2.421(5)
In3	S5	2.408(4)	In7	S11	2.403(5)
In3	S6	2.413(6)	In7	S15	2.387(5)
In3	S10	2.427(7)	In7	S14	2.380(5)
In8	S1[1]	2.428(5)	In7	S9	2.416(5)
In8	S16	2.421(6)	S13	In5[4]	2.408(7)
In8	S15	2.445(6)	S13	In6	2.373(7)
In8	S8[2]	2.419(5)	In5	S13[5]	2.409(7)
In1	S4	2.410(5)	In5	S2[3]	2.443(6)
In1	S3	2.405(5)	In5	S7	2.449(7)
In1	S1	2.421(5)	In5	S16[6]	2.406(7)
In1	S2	2.410(5)	In6	S12	2.406(8)

In4	S3[3]	2.410(5)	In6	S14	2.420(5)
In4	S7	2.399(6)	In6	S10	2.394(9)
In4	S8	2.393(6)	S3	In4[7]	2.411(5)
In4	S6	2.418(5)	S1	In8[8]	2.428(5)
In2	S4	2.424(5)	S2	In5[7]	2.443(6)
In2	S11	2.436(5)	S16	In5[2]	2.406(7)
In2	S12	2.433(6)	S8	In8[6]	2.419(5)

Symmetry: 1,1/2-X,1-Y,-1/2+Z; 2,1-X,1/2+Y,1/2-Z; 3,1/2+X,1/2-Y,1-Z; 4,-1/2+X,+Y,1/2-Z; 5,1/2+X,+Y,1/2-Z; 6,1-X,-1/2+Y,1/2-Z; 7,-1/2+X,1/2-Y,1-Z; 8,1/2-X,1-Y,1/2+Z.

Table S3. The selected bond lengths (Å) for **SOF-21**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
In6	S13	2.429(3)	In4	S7	2.414(3)
In6	S12	2.424(3)	In4	S9	2.427(4)
In6	S11	2.410(4)	In4	S8	2.408(4)
In6	S14	2.416(3)	In4	S6	2.413(5)
In3	S10[1]	2.422(4)	In1	S13[4]	2.444(4)
In3	S7[1]	2.434(3)	In1	S1	2.431(4)
In3	S4[1]	2.417(4)	In1	S2	2.418(4)
In3	S8	2.404(4)	In1	S3	2.406(4)
In5	S10	2.421(4)	In2	S4	2.428(4)
In5	S11	2.399(4)	In2	S5	2.422(4)
In5	S9	2.421(4)	In2	S6	2.435(4)
In5	S5	2.442(4)	In2	S3	2.408(5)
In8	S15	2.458(3)	S13	In1[2]	2.444(4)
In8	S1[2]	2.447(4)	S10	In3[5]	2.422(4)
In8	S14	2.391(5)	S7	In3[5]	2.434(3)
In8	S16	2.386(4)	S1	In8[4]	2.447(4)
In7	S15	2.416(3)	S4	In3[5]	2.417(4)
In7	S12	2.426(4)	S2	In7[4]	2.449(4)
In7	S2[2]	2.450(4)	S16	In7[6]	2.404(4)
In7	S16[3]	2.404(4)			

Symmetry: 1,-1/2+X,+Y,3/2-Z; 2,3/2-X,-1/2+Y,+Z; 3,-1/2+X,1/2-Y,1-Z; 4,3/2-X,1/2+Y,+Z; 5,1/2+X,+Y,3/2-Z; 6,1/2+X,1/2-Y,1-Z.

Table S4. Elemental analysis results of **SOF-20** and **SOF-21**.

	Elements (*wt.*)	**N (%)**	**C (%)**	**H (%)**
SOF-20	Calculated	6.128	18.27	3.177
	Experimental	6.194	18.28	3.114
SOF-21	Calculated	4.777	16.51	3.354
	Experimental	4.769	17.37	3.587