Two carboxyl-decorated anionic metal-organic framework as solid-state electrolyte exhibiting high Li^+ and Zn^{2+} conductivity

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1. Synthesis of solid-state electrolytes:

200 mg of compound **InOF** were added in 446 mg of LiTFSI (bis(trifluoromethanesulfoneimide) lithium salt) in 10 mL of PC (propylene carbonate) solution and keeping the mixture in a shaker for 10~12 hours to adsorb Li^+ in pores. Then the obtained solid was separated by centrifugation, washed with PC solution slightly to remove the LiTFSI on surface. And finally the solid is dried at 100 °C for 2 hours to obtain **InOF**-Li. The preparation methods of **InOF**-Na, **InOF**-K and **InOF**-Zn are same as that of **InOF**-Li above, except that LiTFSI is replaced with the corresponding NaTFSI (bis(trifluoromethanesulfoneimide) sodium salt, 331.028 mg), KPF_6 (Potassium hexafluorophosphate, 201.102 mg) and $Zn(ClO_4)_2(H_2O)_6$ (Zinc perchlorate, 406.64 mg).

The powder pellets of **InOF**-Li, **InOF**-Na, **InOF**-K and **InOF**-Zn were prepared by pressing powder between two stainless steel sheets of 8 mm diameter and the pressure of 6 Mpa. The thicknesses of the pellets is approximately between 0.05 cm and 0.08 cm.

InOF-Li (400 mg) and PVDF-HFP (100 mg) were mixed in NMP. After magnetically stirring for 24 h, the mixture was casted onto cleaned petri dishes and prebaked for half an hour under infrared lamp. Then the mixture was further dried at 80 °C under vacuum for 12 h to remove the NMP solvent. The obtained flexible membranes were stored in an argon filled glove box (≤ 0.1 ppm H_2O and O_2) (MIKROUNA). The flexible membrane was immersed in liquid electrolyte (1M LiTFSI in PC) for 12 h and then was dried to remove the excess solution for the current-time curve and the ac impedance spectra before and after polarization.

2. X-ray Crystallography

The single crystal measurement of **InOF** were executed on Bruker APEX-II diffractometer coupled to CCD detector with graphite-monochromatic Mo Kα radiation (lambda = 0.71073 Å) and Atlas detector at 298 K. The unit cell parameters and data were determined and collected directly by CrysAlisPro program. The structure of **InOF** was solved by the direct methods and refined by the full matrix least square method of SHELX program package. All non-hydrogen atoms were directly located according to Fourier diffraction points and refined by anisotropy. H atoms on the ligand were added by theoretical model. The disordered solvent molecules and ions in the crystal channel were computed by PLATON software/SQUEEZE subroutine. CCDC:

1947427. Crystallographic data are summarized in Table S1.

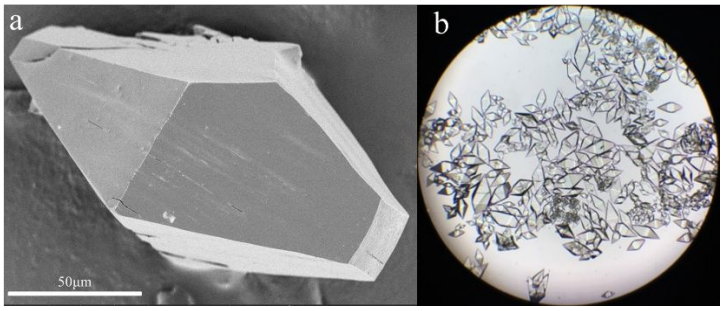

Fig. S1 SEM images of **InOF** (a) and the optical photograph (b).

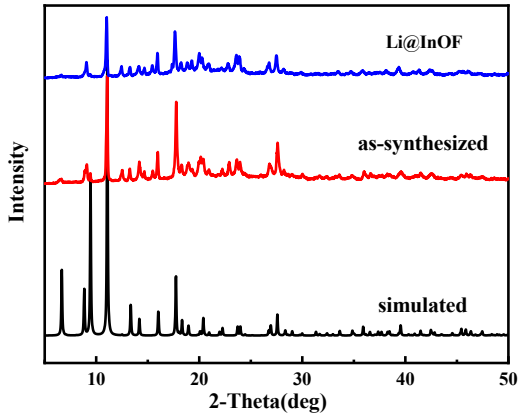

Fig. S2 PXRD patterns of as-synthesized **InOF** (red), the simulated XRD pattern from the single-crystal X-ray structure (black) and Li^+-loaded **InOF** (blue).

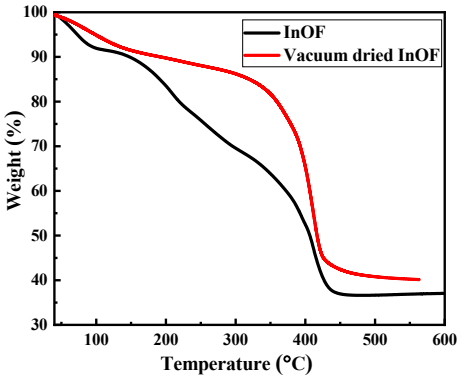

Fig. S3 TGA curves of as-synthesized **InOF** (black) and vacuum dried **InOF** (blue).

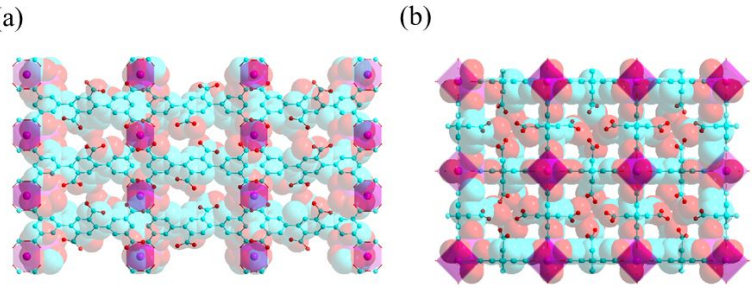

Fig. S4 Single crystal structure of **InOF** (a) the structure viewed along the a, b axis; (b) the structure viewed along the c axis.

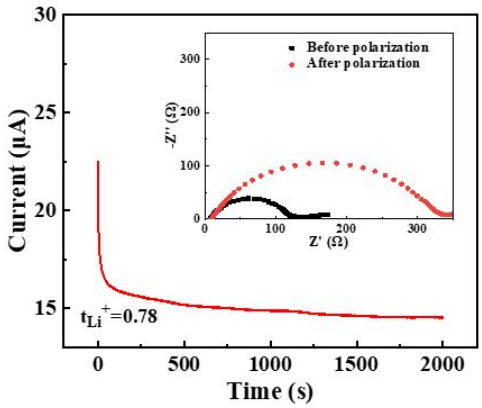

Fig. S5 Current-time curve at 10 mV of polarization; the inset is the EIS before and after polarization of Li|**InOF**-Li-based SE|Li and symmetric cell.

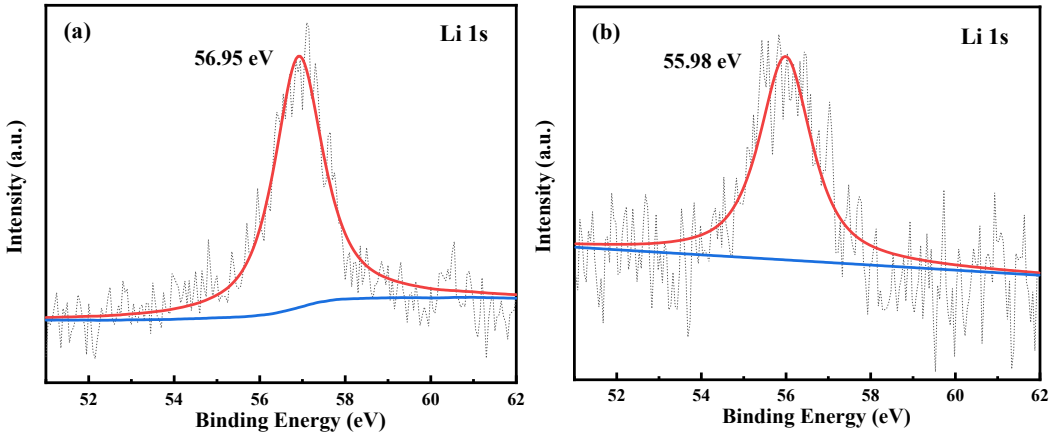

Fig S6 XPS characterization of Li 1s spectra for lithium salts and MOFs. (a) LiTFSI (56.95 eV); (b) **InOF** treated with LiTFSI (55.98 eV).

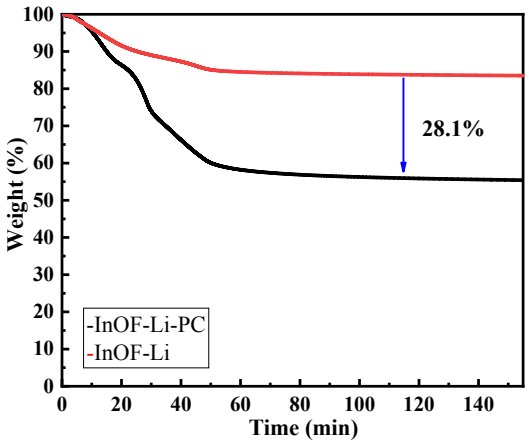

Fig. S7 TGA plots of **InOF**-Li and **InOF**-Li-PC.

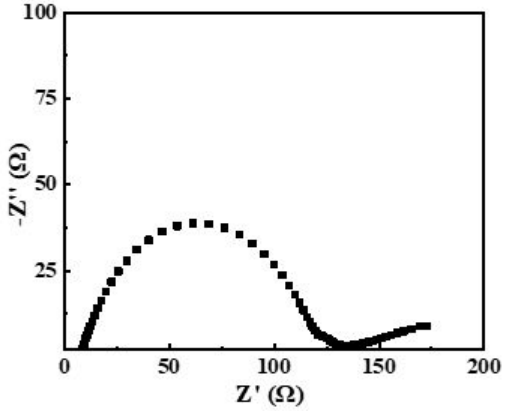

Fig. S8 the AC impedance spectra before polarization of Li|**InOF**-Li-based SE|Li and symmetric cell.

Table S1. Crystallographic Data Collection and Refinement Results for **InOF.**

	InOF
Chemical formula	$C_{48}H_{24}In_2O_{28}$
Formula weight	1278.31
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	tetragonal
Space group	P 4_2/nnm
a (Å)	14.1360(15)
b (Å)	14.1360(15)
c (Å)	26.520(3)
V (Å^3)	5299.4(9)
Z	2
Density (calculated g/cm^3)	0.801
Absorbance coefficient (mm^{-1})	0.481

$F(000)$	1268
Crystal size(mm^3)	0.13×0.07×0.05
Goodness of fit on F^2	1.051
R_1, wR_2 [$I>2\sigma(I)$]	0.0876,0.1889
R_1, wR_2 (all data)	0.1566,0.2010
Largest difference peak and hole(e/$Å^3$)	1.072,-1.012

Table S2. Comparison of the ion density of MOFs.

MOFs	framework	negative sites based on the linker	Reference
InOF	$[In_2(THBA)_2]^{6-}$	3	This work
ZJU-28	$[In_3(BTB)_4]^{3-}$	0.75	1
bio-MOF-1	$[Zn_8(Ad)_4(BPDC)_6]^{2-}$	0.2	2
NOTT-210	$[In_2(C_{22}O_8H_{10})_2]^{2-}$	1	3
SNU-100’	$[Zn_3(TCPT)_2(HCOO)]^-$	0.5	4
UiO-66-COOH	$[Zr_6O_4(OH)_4(L)_6]^{6-}$	1	5
UiO-66-2COOH	$[Zr_6O_4(OH)_4(L)_6]^{12-}$	2	5
$Cu_2THBA(H_2O)_2$	$[Cu_2THBA]^{2-}$	2	6
$Cu_2(L)(H_2O)_2$	$[Cu_2(L)]^-$	1	7
MIT-20	$[Cu_2Cl_3BTDD]^-$	1	8

Table S3. Comparison of the ion conductivity of MOFs based on lithium ion solid state electrolytes.

materials	Ionic conductivity (S/cm)	Activation energy (eV)	t_{Li^+}	ref
InOF-Li	1.49×10^{-3} (25 °C)	0.19	0.78	This work
$Mg_2(dobdc)\cdot 0.35LiOiPr\cdot 0.25LiBF_4$	3.1×10^{-4} (27 °C)	0.15		9
MIT-20-LiCl	1.3×10^{-5} (25 °C)	0.32	0.66	8
MOF-525 (Cu)	3.0×10^{-4} (25 °C)		0.36	10
HKUST-1	3.8×10^{-4} (25 °C)	0.18		11
MOF-5	1.3×10^{-4} (25 °C)	0.4		11
$Cu_2(BPY)_2(NDIDS)$	2.3×10^{-4} (RT)	0.167		12
ZIF-67	2.29×10^{-3} (30 °C)			13
D-UiO-66-NH_2	3.1×10^{-5} (25 °C)		0.72	14
MIL-100-Al	1.22×10^{-3} (25 °C)	0.21		11
MIL-100-Cr	2.3×10^{-4} (25 °C)	0.18		11
MIL-100-Fe	9.0×10^{-4} (25 °C)	0.18		11
$Cu_4(ttpm)_2(CuCl_2)_{0.6}(LiCl)_{1.8}$	2.4×10^{-5} (25 °C)	0.34	0.69	15
$Cu_4(ttpm)_2(CuCl_2)_{0.6}(LiBr)_{1.8}$	3.2×10^{-5} (25 °C)	0.3	0.42	15
$Cu_4(ttpm)_2(CuCl_2)_{0.6}(LiI)_{1.0}$	1.1×10^{-4} (25 °C)	0.24	0.34	15
MOF-688	4.6×10^{-4} (30 °C)		0.87	16

UiO-66	1.8×10^{-4} (RT)	0.21		11
UiOLiTFSI	2.07×10^{-4} (25 °C)	0.31	0.84	17
UiO-67	6.5×10^{-4} (≈25 °C)	0.12	0.65	11
MIL-101(Cr)-DET-Li	7.13×10^{-4} (30 °C)	0.2	0.87	18
SE-PMOF	1.7×10^{-3} (30 °C)	0.27	0.8	19
LCMOF-1	4.42×10^{-4} (25 °C)		0.58	5

Table S4. Ionic conductivity for **InOF**-Li for different temperature.

Material	Temperature (°C)	Body resistance (Ω)	σ (S/cm)
InOF-Li	-20	361.11	4.45×10^{-4}
	-10	226.46	7.10×10^{-4}
	0	155.06	1.04×10^{-3}
	10	111.94	1.22×10^{-3}
	20	85.85	1.49×10^{-3}
	30	69.372	7.97×10^{-3}
	40	57.105	7.69×10^{-3}
	50	48.12	1.22×10^{-3}
	60	41.29	1.22×10^{-3}

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