Supporting Information for

Pseudo Single Lithium-Ion Conductors Enabled by Metal-Organic Framework with Biomimetic Lithium -Ion Chains for Lithium Metal Batteries

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Supplementary Index

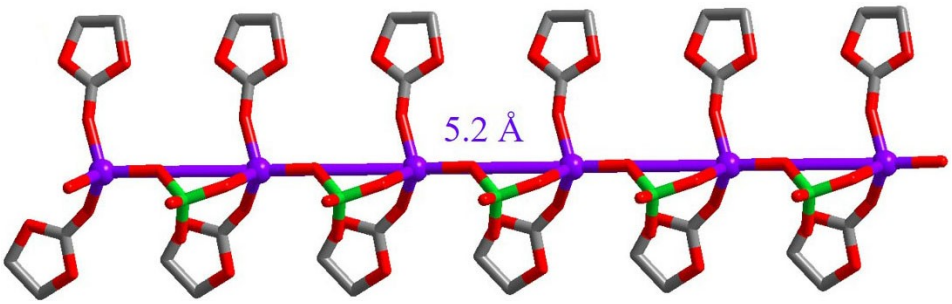

Figure S1. Structures and lithium ion chains of $LiClO_4 \cdot 2EC$.

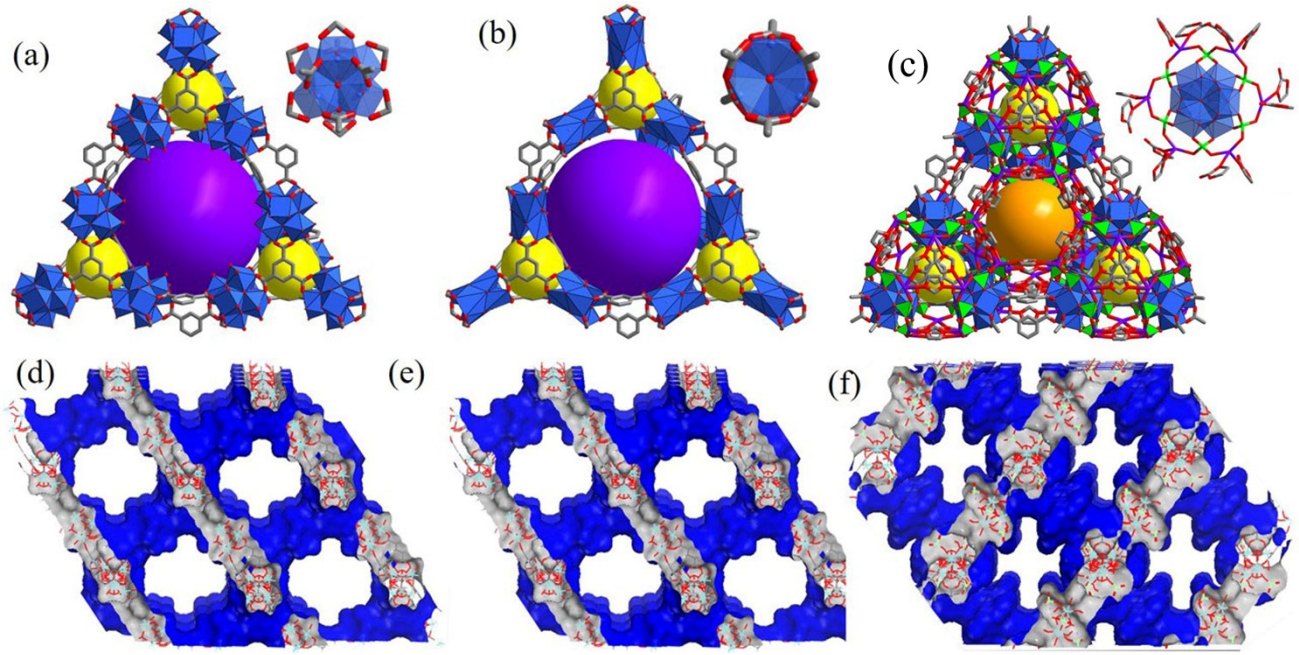

Figure S2. The polyhedral structure of (a) **808**, (b) **808-O** and (c) **808-LCE**; the pore structure of (d)

808, (e) **808-O** and (f) **808-LCE**.

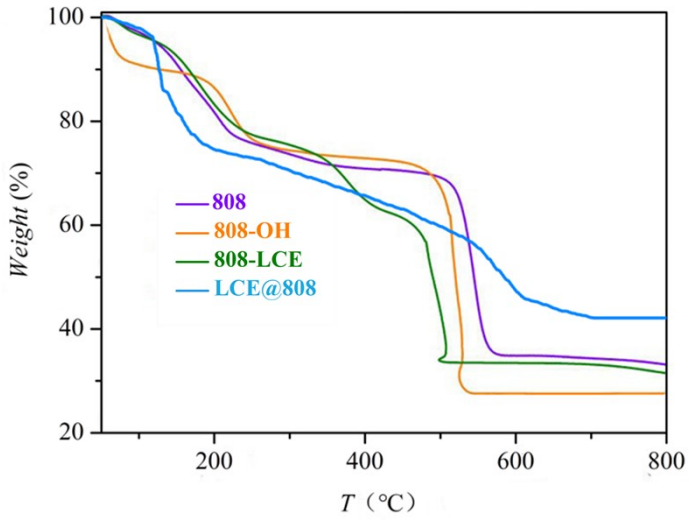

Figure S3. TG curves of **808**, **808-OH**, **808-LCE** and **LCE@808**.

The TG curve of **808-LCE** indicated that **LCE** can be removed above 480°C, the content of LCE is 43.72%, close to 44.69% in theory. The TG curve of **LCE@808** indicated that **LCE** can be removed above 400°C, the content of LCE is 35.72%, close to 34.41% in theory.

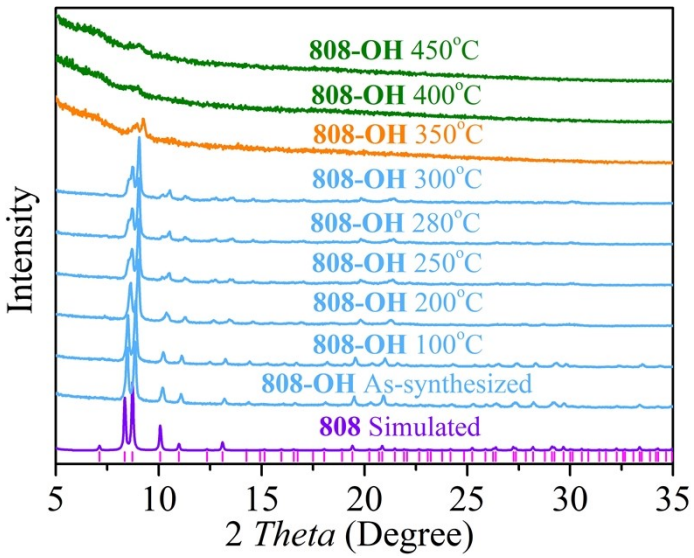

Figure S4. PXRD patterns of **808-OH** after heated at different temperatures under N_2 for 30 min.

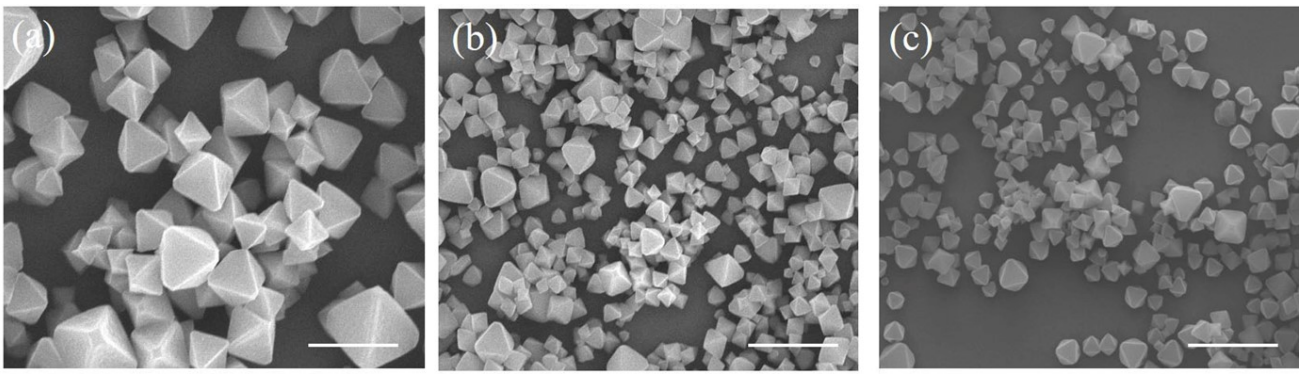

Figure S5. SEM images of (a) **808**, (b) **808-O** and (c) **LCE@808** (scale bar 2 um).

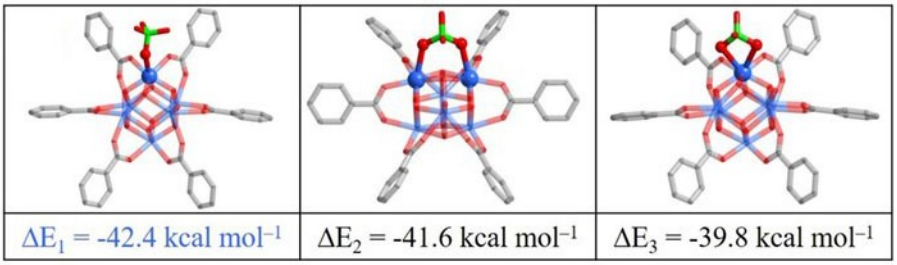

Figure S6. The calculated results of coordination modes of **808-LCE**.

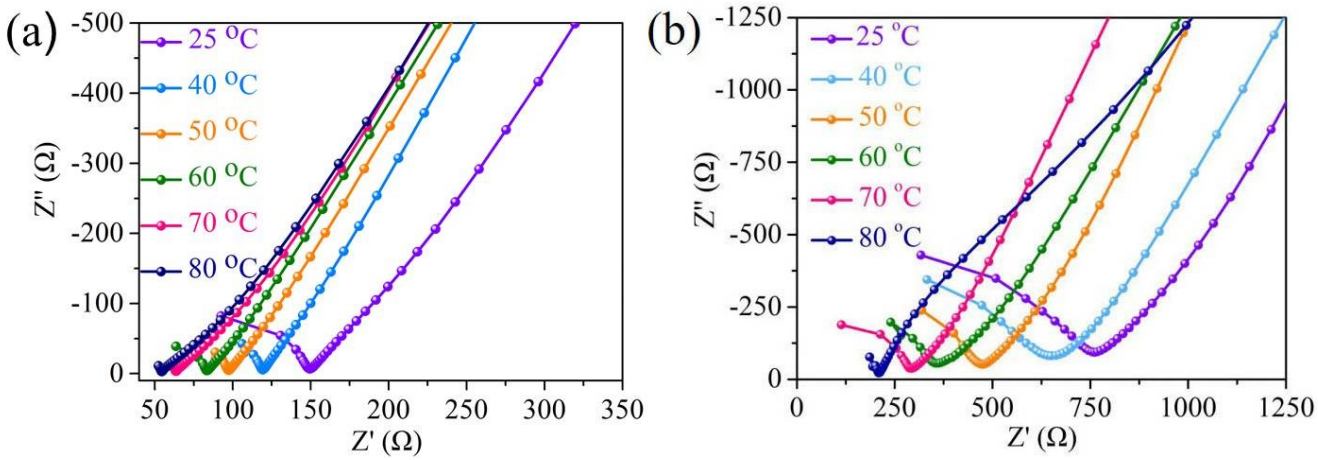

Figure S7. Nyquist plot of (a) **808-LCE** and (b) **LCE@808** at 25 °C to 80 °C.

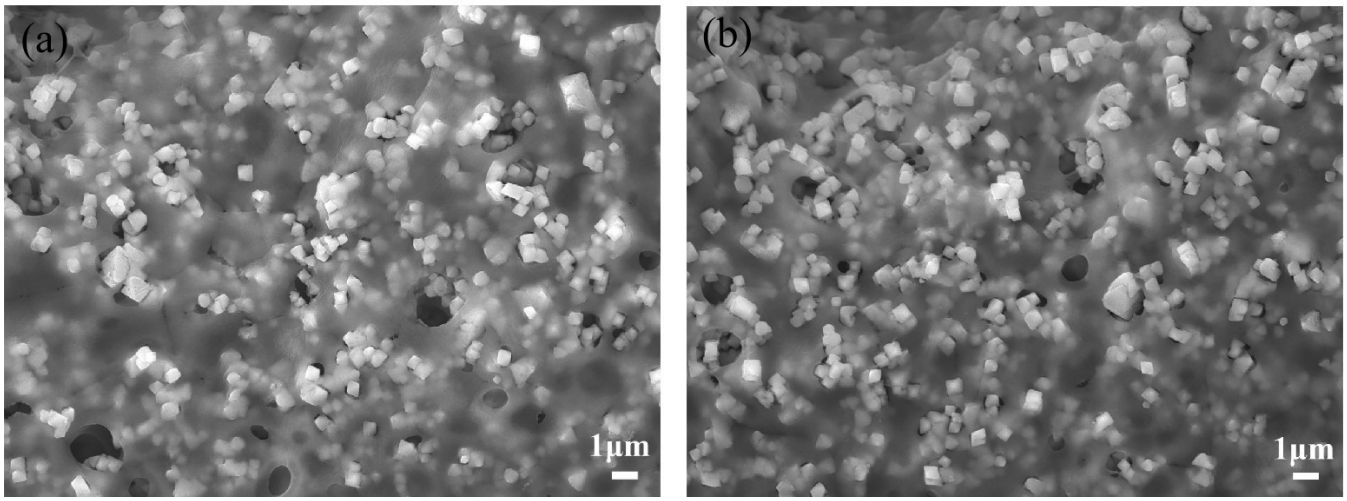

Figure S8. SEM images (a) **808-LCE** film and (b) **LCE@808** film.

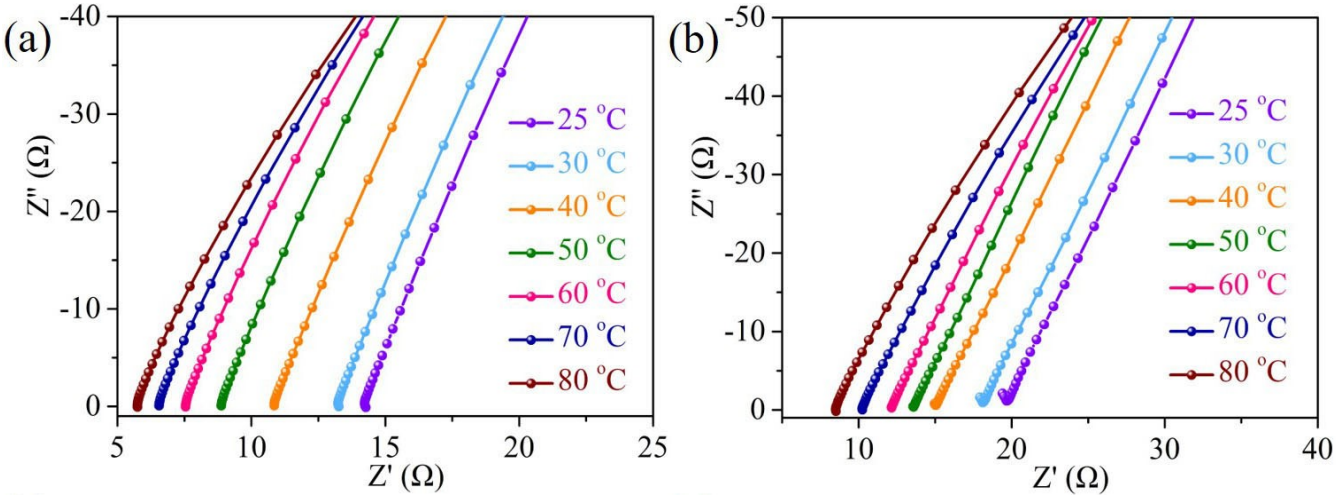

Figure S9. Nyquist plot of (a) **808-LCE** film and (b) **LCE@808** film between 25 °C to 80 °C.

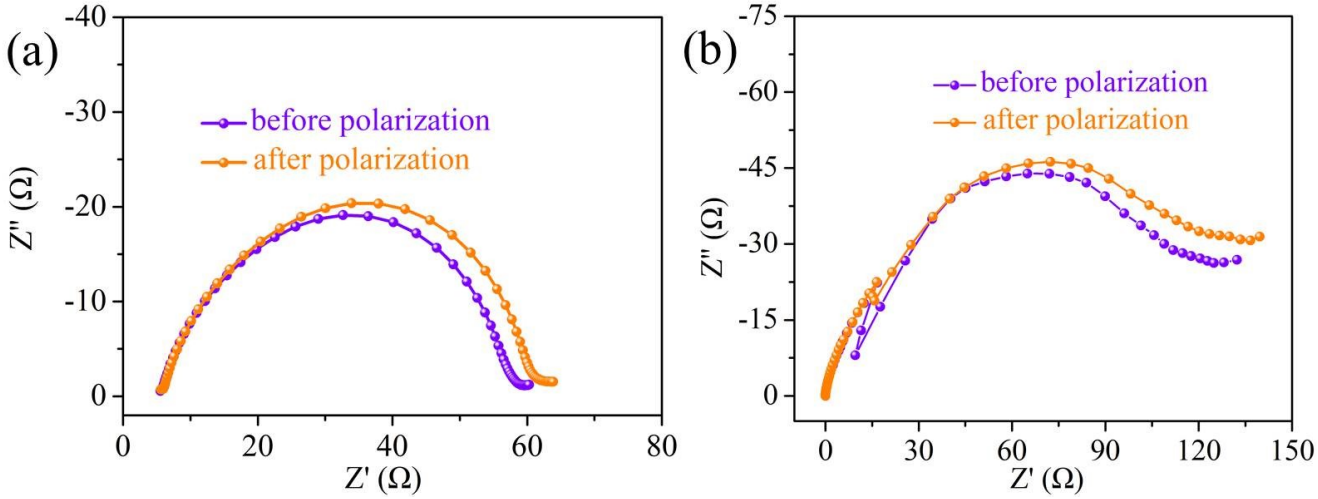

Figure S10 Impedance spectra at initial and steady states of (a) **808-LCE** and (b) **LCE@808** for Li|MOF-SEs|Li cell at 20 mV of polarization.

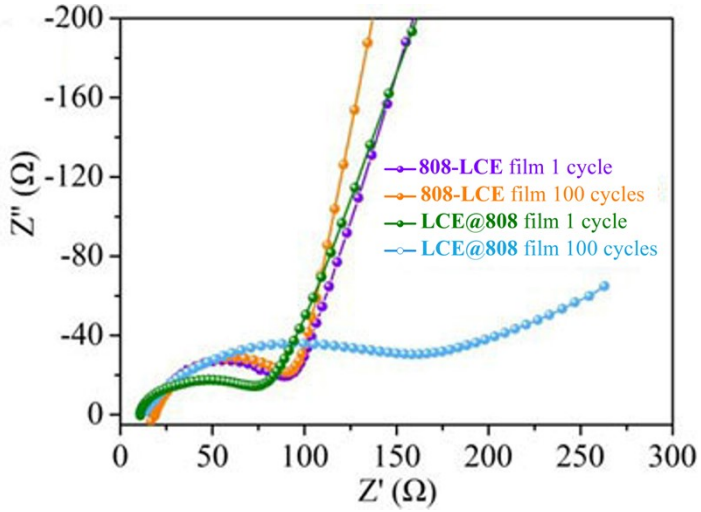

Figure S11. Electrochemical impedance spectroscopy (EIS) of $LiFePO_4$|Li cells for **808-LCE** film and **LCE@808** film after 1 cycle and100 cycles.

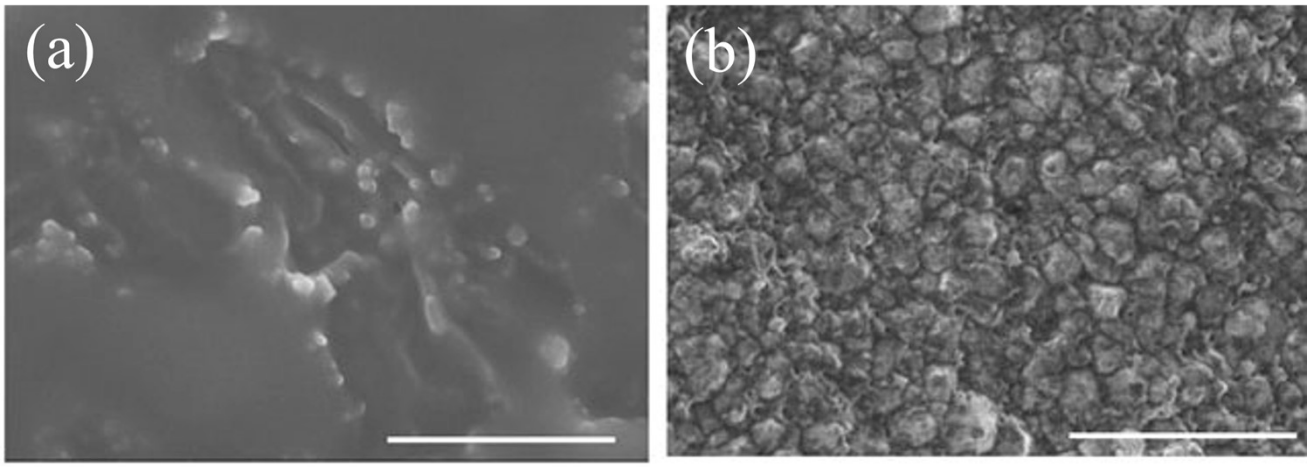

Figure S12. SEM images of solid electrolyte interface (SEI) on lithium metal of $LiFePO_4$|Li cells for **808-LCE** film and **LCE@808** film after 100 cycles.

Table S1. ICP-AES results.

Sample	W_{Zr} (mg L^{-1})	W_{Li} (mg L^{-1})	n_{Zr} (μmol L^{-1})	n_{Li} (μmol L^{-1})	Zr:Li
808-LCE	1.50	0.113	16.42	16.29	1.0:0.99
LCE@808	1.67	0.131	18.31	18.97	1.00:1.04
blank	<0.01	<0.01	<0.01	<0.01	/

Table S2. Comparison of the ionic conductivities and Li^+ conductivities for various MOF-based solid electrolytes. The parameters better than that of **808-LCE** were highlighted in blue.

Compound	Mobile ion	Guests	σ (mS cm^{-1})	T (°C)	t^+	σ_{Li+} (mS cm^{-1})	E_a (eV)	Ref.
808-LCE	Li^+	EC/DMC	0.55	25	0.64	0.35	0.19	**This Work**
LCE@808	Li^+, ClO_4^-	EC/DMC	0.48	25	0.27	0.13	0.23	
MIT-20-$LiBF_4$	Li^+, BF_4^-	PC	0.48	25	/	/	0.16	*J. Am. Chem. Soc.* **2017**, *139*, 13260.
MIT-20-LiCl	Li^+	PC	0.013	25	0.66	0.01	0.32	
Li-CON-TFSI	Li^+, $TFSI^-$	EtOH	0.057	30	/	/	0.34	*J. Am. Chem. Soc.* **2018**, *140*, 896.
$LiPF_6$@CD-COF-Li	Li^+, PF_6^-	EC DMC	2.7	30	/	/	0.26	*Angew. Chem. Int. Ed.* **2017**, *56*, 16313.
IL@MOF-525(Cu)	Li^+, $TFSI^-$	[EMIM][TFSI]	3.0	25	0.36	/	/	*Adv. Mater.* **2018**, 30, 1704436.
$LiClO_4$@COF-5	Li^+, ClO_4^-	THF	0.26		/	/	0.037	*J. Am. Chem. Soc.* **2016**, *138*, 9767.
ICOF-2	Li^+	PC	0.031	25	0.80	0.025	0.24	*Angew. Chem. Int. Ed.* **2016**, *55*, 1737.
EHU1(Sc,Li)·($LiBF_4$)	Li^+, BF_4^-	/	0.042	25	/	/	/	*Chem. Mater.* **2016**, *28*, 2519.
IL@ZIF-8	Li^+, $TFSA^-$	[EMIM][TFSI]	/	/	/	/	/	*Chem. Mater.* **2015**, *27*, 7355.
Mg_2(dobdc)·0.06LiO^iPr	Li^+	EC/DEC	0.012	25	/	/	0.15	*J. Am. Chem. Soc.* **2011**, *133*, 14522.
Mg_2(dobdc)·0.35LiO^iPr·0.25$LiBF_4$	Li^+, BF_4^-	EC/DEC	0.31	25	/	/	0.15	

Table S3. Comparison of the ionic conductivities and Li^+ conductivities for various single lithium-ion conductors.

Compound	Type of electrlytes	Mobile ion	Guests	σ (mS cm^{-1})	T (°C)	t^+	σ_{Li+} (mS cm^{-1})	E_a (eV)	Ref.
808-LCE	MOF	Li^+	EC/DMC	0.55	25	0.64	0.35	0.19	**This Work**
MIT-20-LiCl	MOF	Li^+	PC	0.013	25	0.66	0.01	0.32	*J. Am. Chem. Soc.* **2017**, *139*, 13260.
ICOF-2	MOF	Li^+	PC	0.031	25	0.80	0.025	0.24	*Angew. Chem. Int. Ed.* **2016**, *55*, 1737.
$[Mg_2(dobdc)]\cdot 0.06LiO^iPr$	MOF	Li^+	EC/DEC	0.012	25	/	/	0.15	*J. Am. Chem. Soc.* **2011**, *133*, 14522.
$–COCF(CF_3)O(CF_2)_2SO_2N^{(–)}–$	Blend polymer	Li^+	NA	*Ca.* 0.01	30	0.71 (25 °C)	0.007	/	*Electrochim. Acta,* **2013**, *93*, 254.
$–SO_2N^{(–)}SO_2CF_3$	Blend polymer	Li^+	NA	*Ca.* 10^{-3}	60	0.92	9.2×10^{-3}	/	*Electrochim. Acta*, **2001**, *46*, 1487.
$–SO_2N^{(–)}SO_2CF_3$	Random copolymer	Li^+	NA	0.1	60	0.93	0.093	/	
$–SO_2N^{(–)}SO(=NSO_2CF_3)CF_3$	Blend polymer	Li^+	NA	0.01	60	0.91	0.009	/	*Angew. Chem. Int. Ed.* **2016**, *55*, 2521.
$–SO_2N^{(–)}SO_2CF_3$	Blend polymer	Li^+	NA	0.01	60	0.90	0.009	/	*RSC Adv.* **2016**, *6*, 32454.
$–SO_2N^{(–)}SO_2CF_3$	Triblock polymer	Li^+	NA	0.013	60	0.85 (90 °C)	0.011	/	*Nat. Mater.* **2013**, *12*, 452.
$–SO_2N^{(–)}SO_2CF_3$	Block polymer	Li^+	NA	0.01	70	0.83	8.3×10^{-3}	/	*ACS Appl. Mater. Interfaces* **2016**, *8*, 10350.