

Supporting information

## **Solvent-Association Regulated Electrolyte Enables High-Rate**

### **Lithium Metal Batteries at Low-Temperature**

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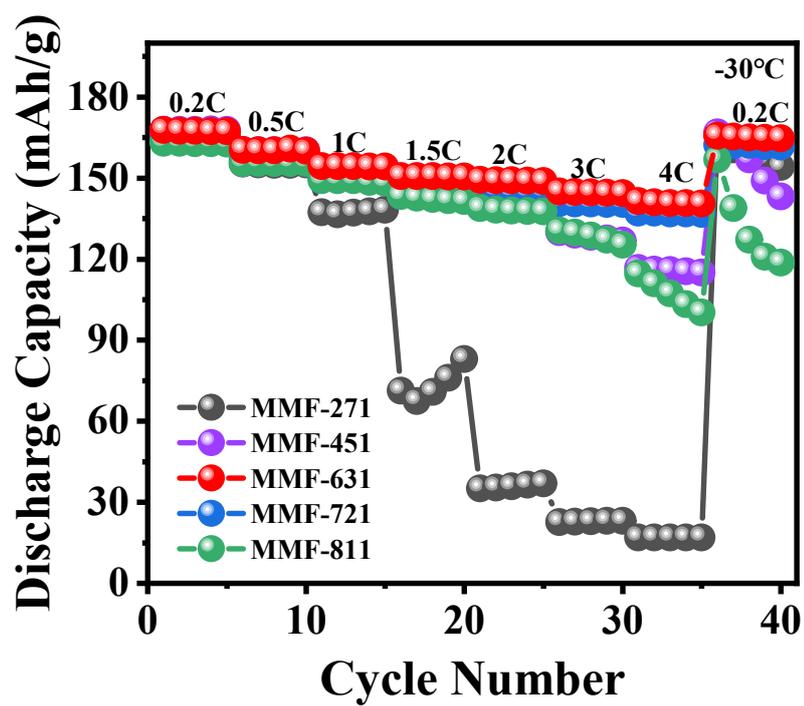


Fig. S1 Comparison of the low-temperature discharge capacities of different proportions of MTFA.

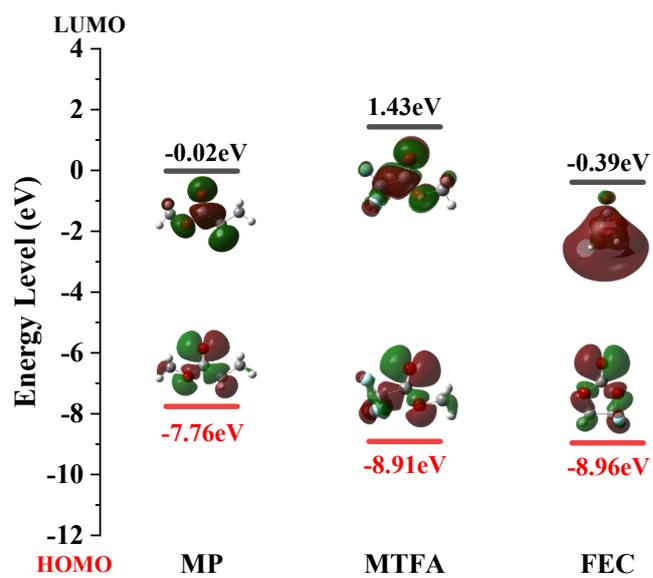
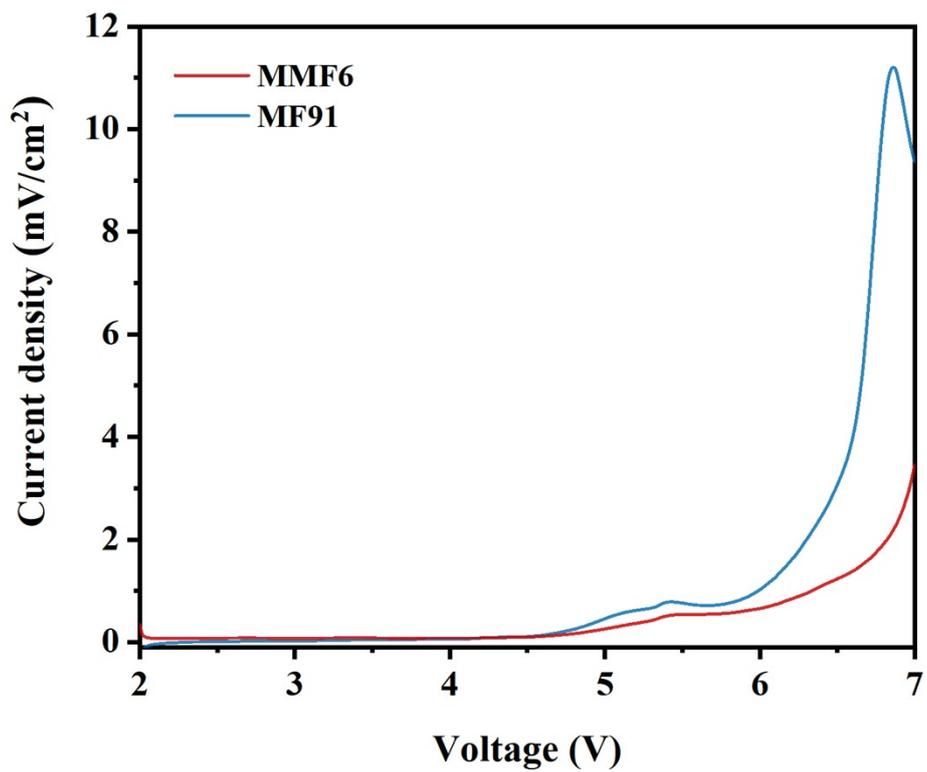
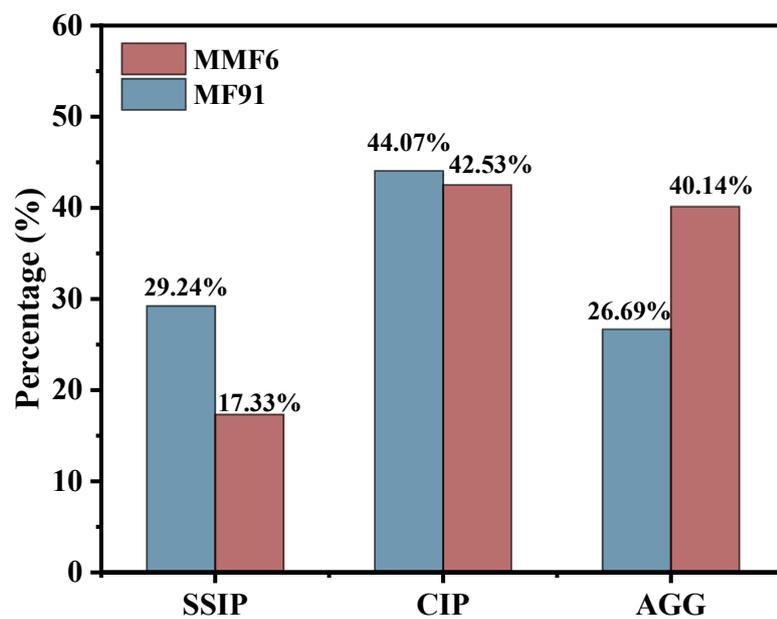


Fig. S2 HOMO and LUMO energy levels of different solvent molecules.



**Fig. S3** Linear sweep voltammetry (LSV) curves of different electrolytes.



**Fig. S4** Ratios of coordination structures for MF91 and MMF6 through Raman spectra.

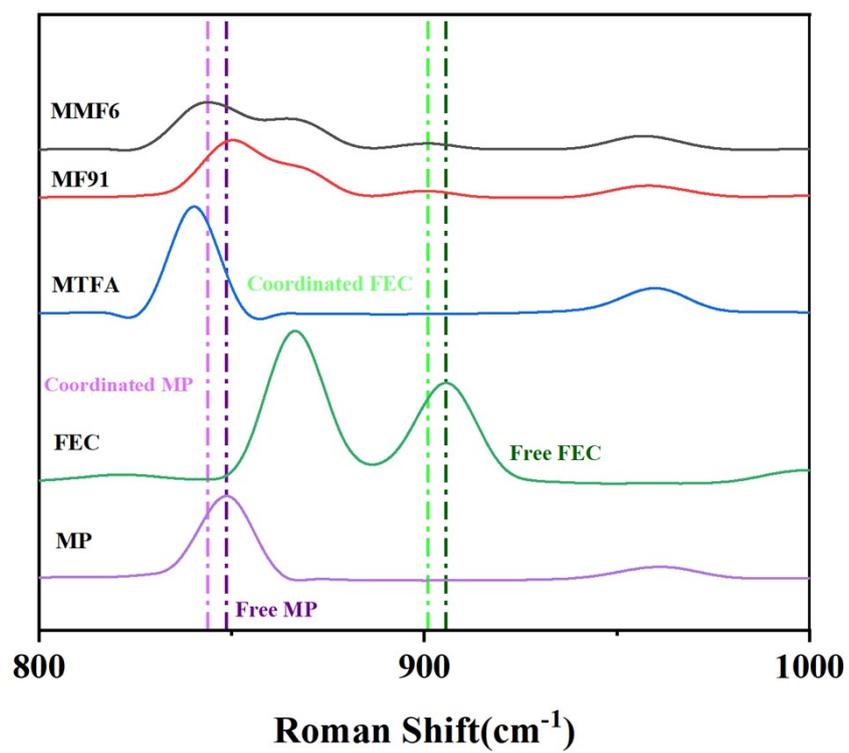
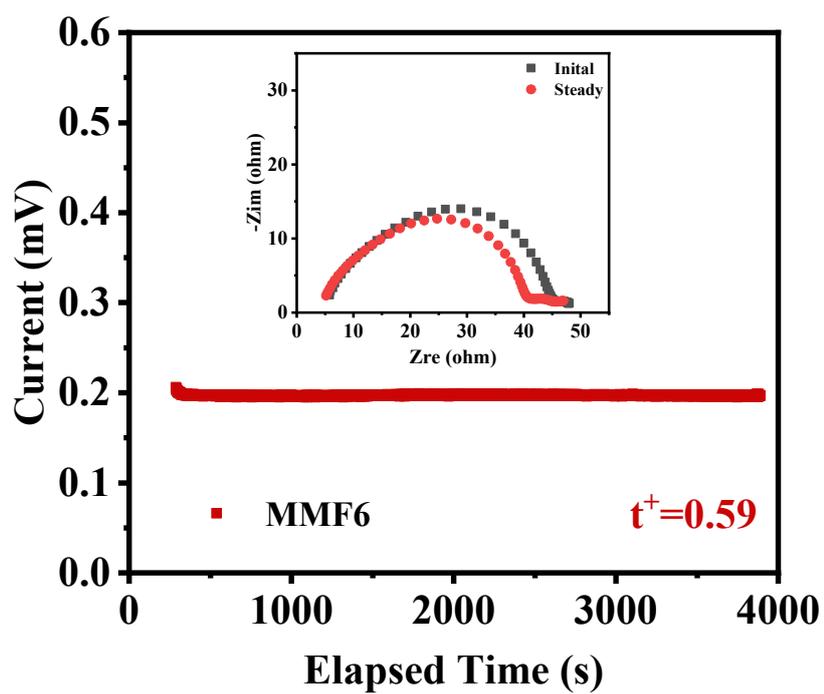


Fig. S5 Raman spectra of different electrolytes and solvents.

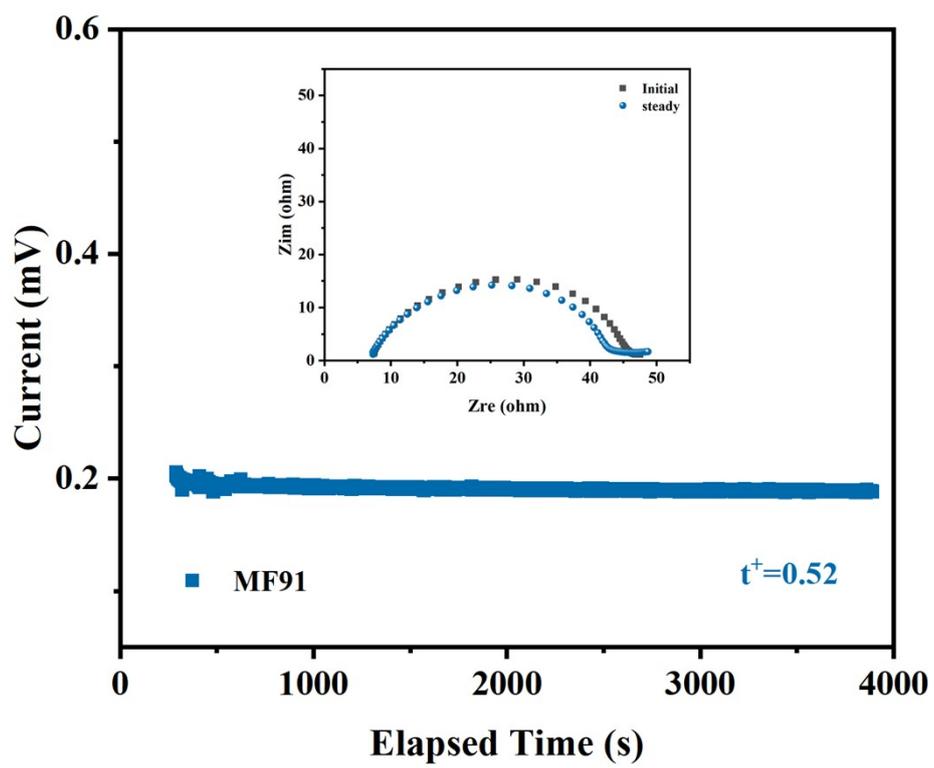
Fig. S6 Snapshots of Li<sup>+</sup> solvation structures in different electrolytes.

**Fig. S7** Impedance spectra of symmetric cells with different electrolytes before cycling at various temperatures.

**Fig. S8** Impedance spectra of symmetric cells with different electrolytes after cycling at various temperatures.



**Fig. S9** transference number of  $\text{Li}^+$  in MMF6.



**Fig. S10** transference number of Li<sup>+</sup> in MF91.

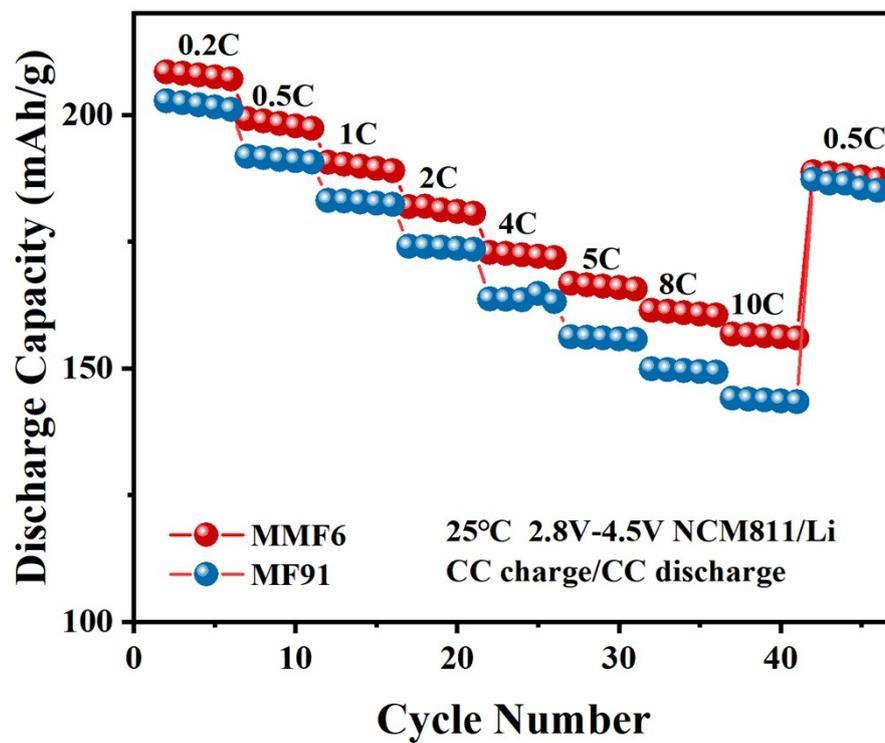


Fig. S11 The corresponding charge-discharge curves or capacity values at rates from 0.2 C to 10 C.

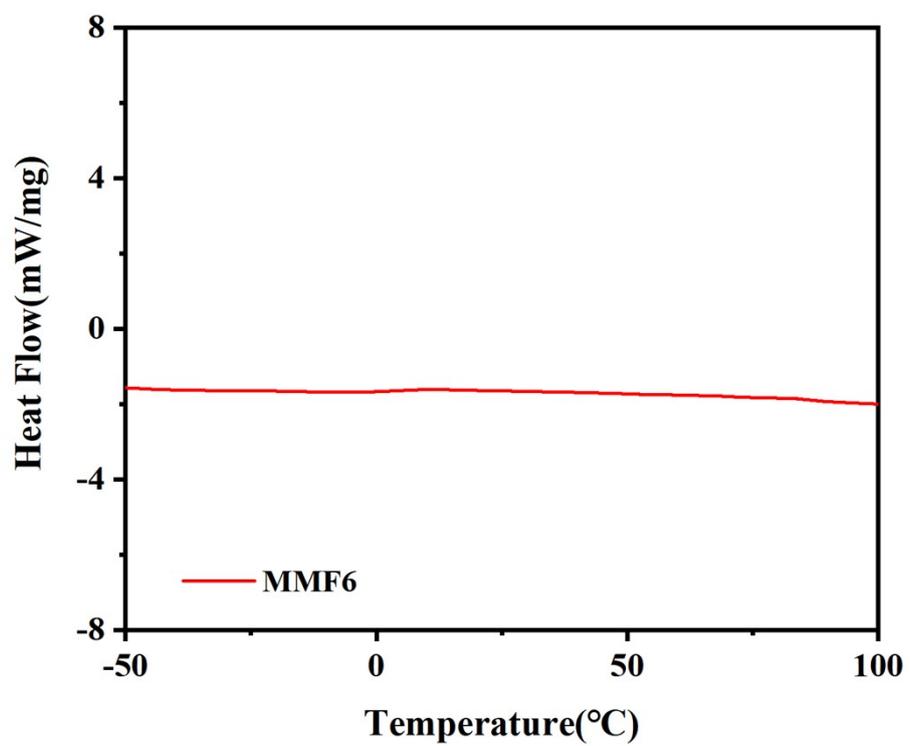


Fig. S12 Differential scanning calorimetry (DSC) curve of MMF6.

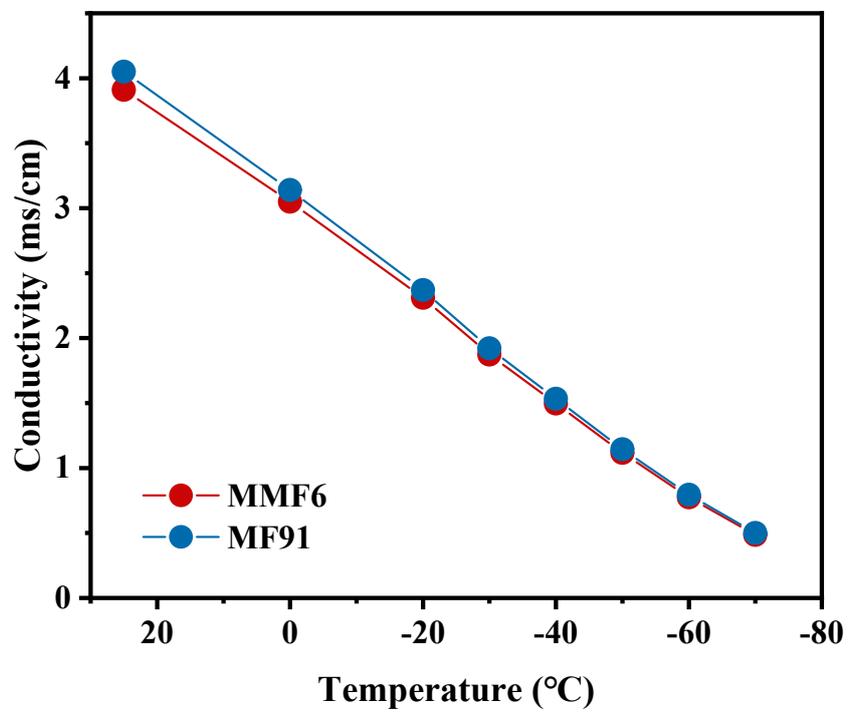
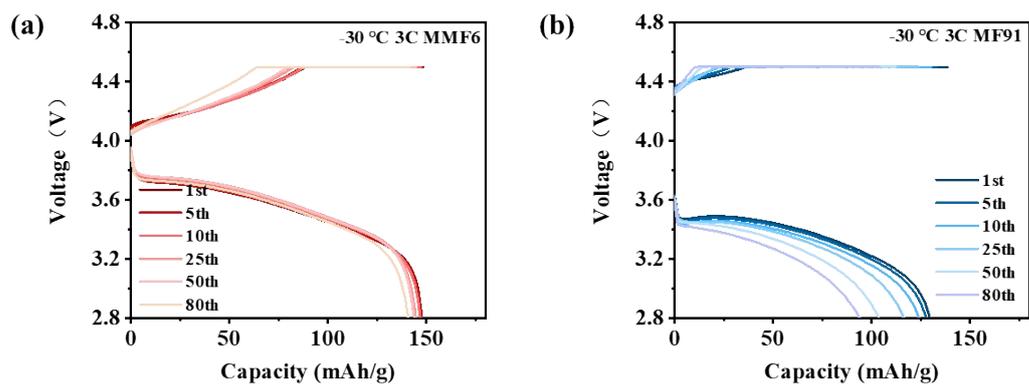
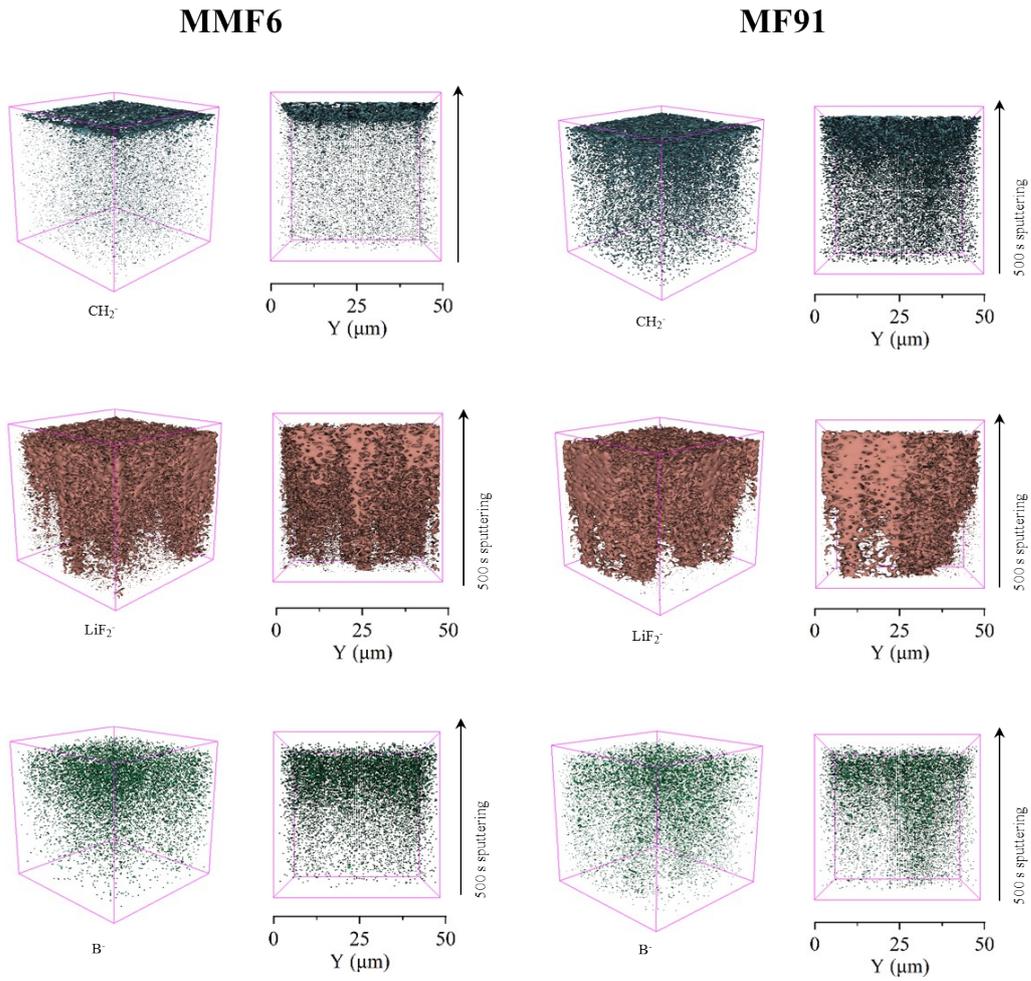


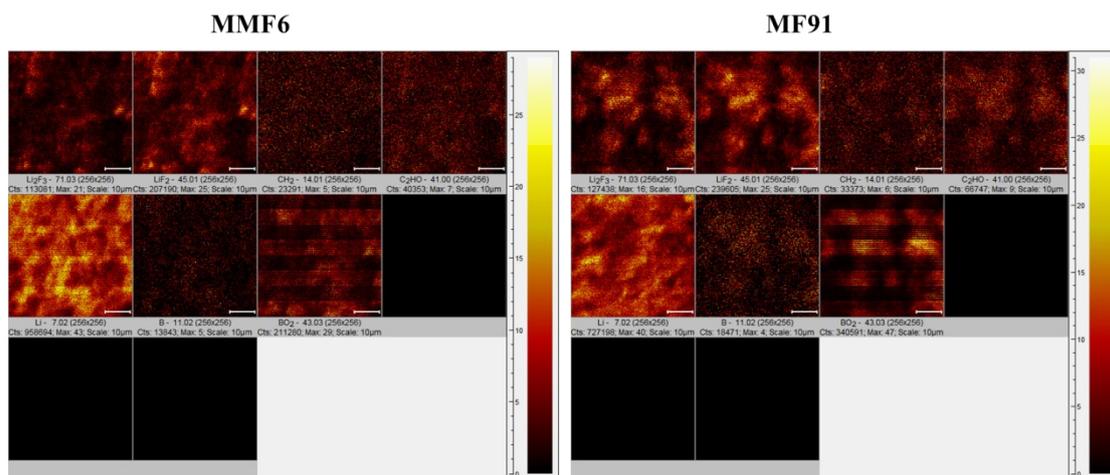
Fig. S13 Ionic conductivities of different electrolytes at various temperatures.



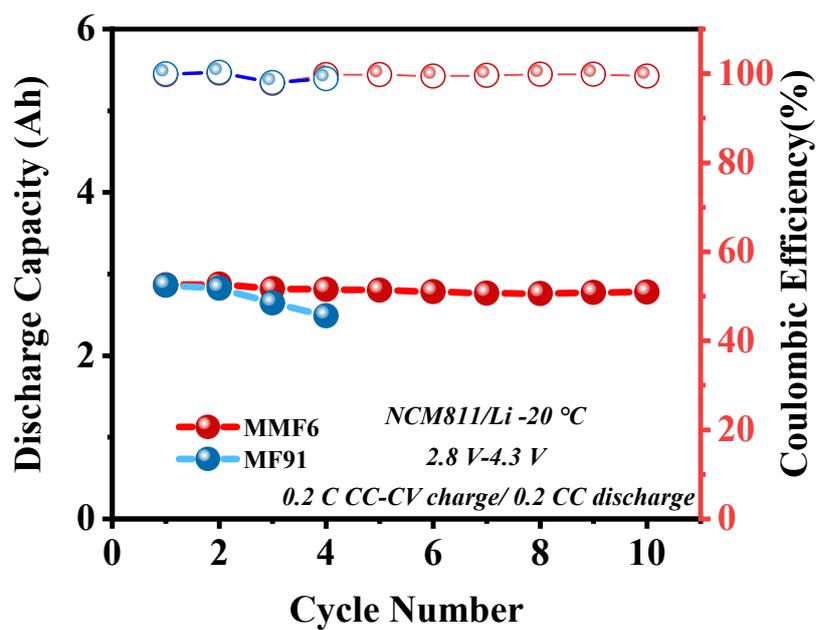
**Fig. S14** (a) Charge/discharge curves of NCM811||Li cell with MMF6 at -30 °C and 3 C (b) Charge/discharge curves of NCM811||Li cell with MF91 at -30 °C and 3 C.



**Fig. S15** TOF-SIMS 3D ion fragment distributions of Li anodes



**Fig. S16** Schematic of the SEI in MMF6 and MF91, showing the 2D distribution of different ionic fragments



**Fig. S17** Charge/discharge profiles of NCM811||Li pouch batteries with different electrolytes at  $-20\text{ }^{\circ}\text{C}$  (0.2 C charge and 0.2 C discharge).