**Support information**

**Trimethoxyboroxine as an electrolyte additive to enhance the 4.5 V cycling performance of Ni-rich layered oxide cathode**

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**Fig. S1.** The solvation structure of (a) blank electrolyte and (b) TMOBX-containing electrolyte.



**Fig. S2.** The Nyquist plots of Li‖NCM811 cells with blank electrolyte and TMOBX-containing electrolyte after activation at 0.2C for 3 cycles (a), and after cycling at 0.5C for 30 cycles (b)



**Fig. S3.** The time-voltage profiles of Li‖Li symmetric cells with and without 1.0 wt.% TMOBX addition at a current density of 3 mA cm-2.



**Fig. S4.** Optimized geometries of F- trapped TMOBX, EC, DMC and EMC molecules with corresponding binding energy.



**Fig. S5.** Comparison of the XRD spectra of the pristine NCM811 and the NCM811 after 200 cycles using different electrolytes.