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SUPPLEMENTARY INFORMATION

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Non-flammable electrolytes with high salt-to-solvent ratios for Li-ion and Li-metal batteries

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Improving compatibility of nonflammable electrolytes with high salt-to-solvent ratios in Li-ion and Li-metal batteries

Ziqi Zeng[1], Vijayakumar Murugesan[3], Kee Sung Han[3], Xiaoyu Jiang[1], Yuliang Cao[1*], Lifen Xiao[2*], Xinping Ai[1], Hanxi Yang[1], Ji-Guang Zhang[3], Maria L. Sushko[3], Jun Liu[3*]

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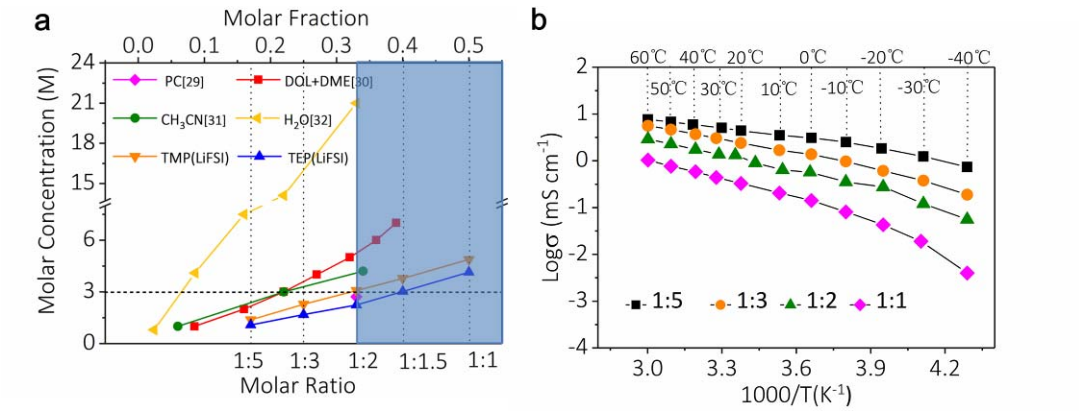
Supplementary Table

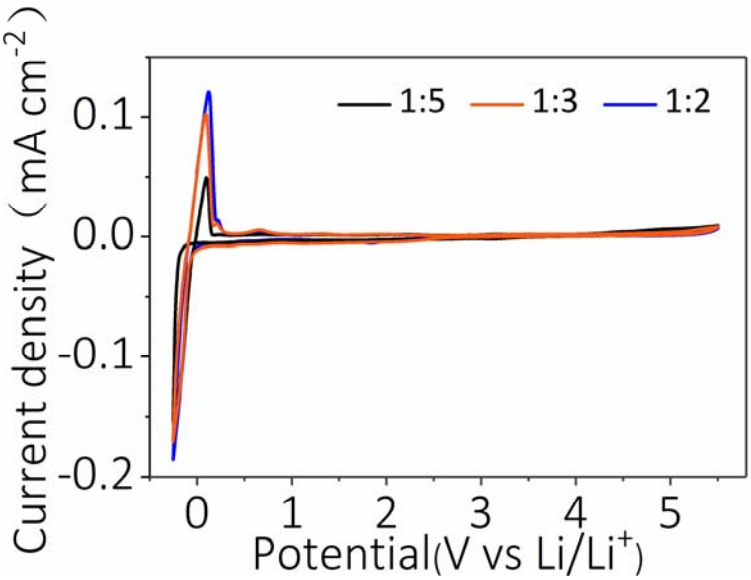
Supplementary Table 1 XPS element analysis of the surface products on the cycled graphite anodes in different MR electrolytes

Element content (%)	C	O	P	S	F
1:5 LiFSI-TEP	57.02	36.98	2.01	1.17	2.82
1:2 LiFSI-TEP	52.83	38.08	1.19	2.13	5.59

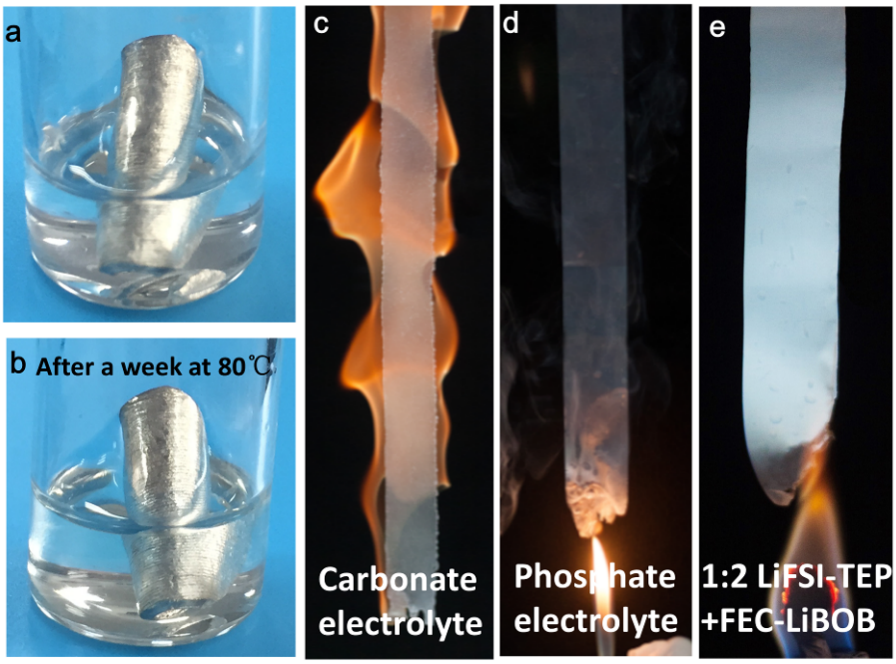
Supplementary Figures:



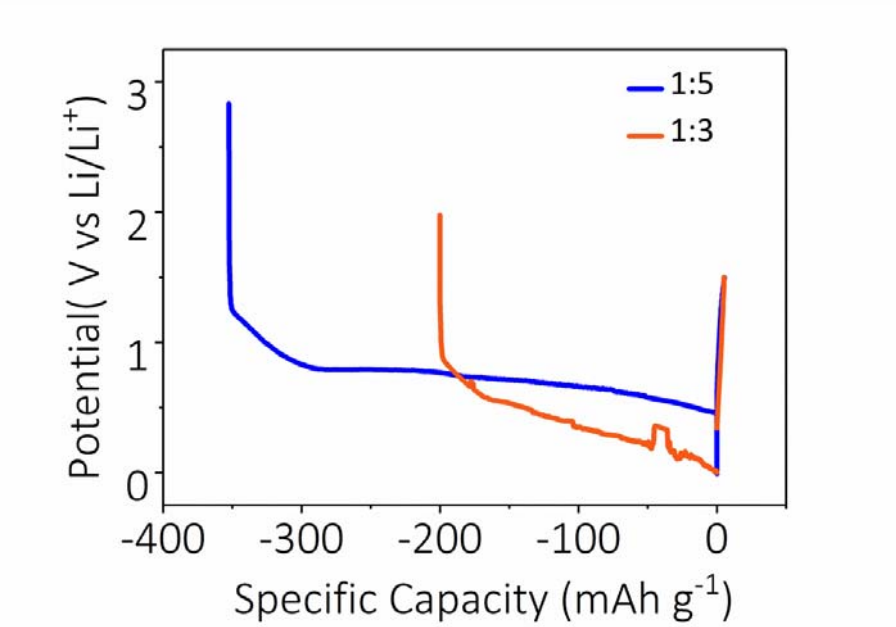
Supplementary Figure 1 | **a,** Correlation of molar concentration and different MRs of salts in various solvents. The shaded area is the stability region of electrolyte. **b,** Ionic conductivities of LiFSI-TEP electrolytes with various MRs under different temperatures.



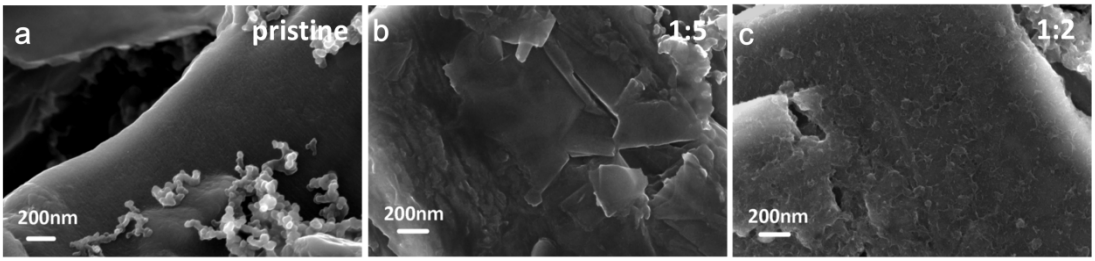
Supplementary Figure 2 | The electrochemical stability window of LiFSI-TEP electrolytes at MRs of 1:5, 1:3, and 1:2 as measured on a Pt microelectrode at a scanning rate of 50 mV s^{-1}.



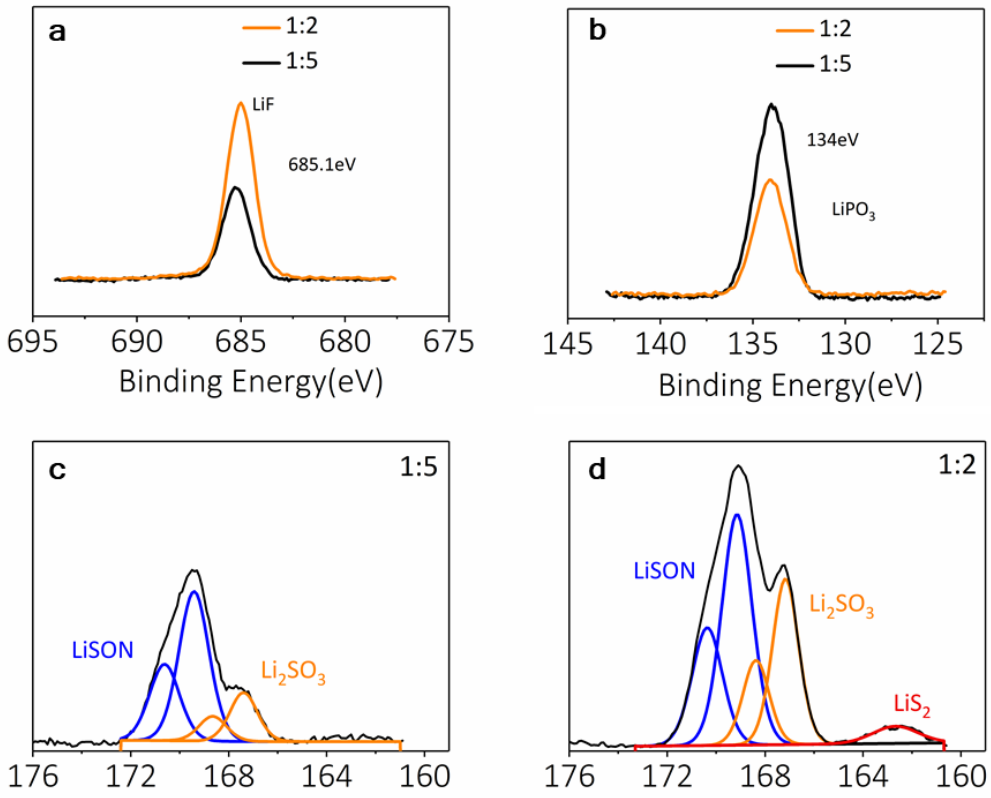
Supplementary Figure 3 | **a,b,** Optical images of Li foil in 1:2 LiFSI-TEP electrolyte stored at 80 °C before **(a)** and after **(b)** a week. **c-e,** Flame tests of 1.0 M $LiPF_6$/EC:DEC:EMC (1:1:1 by vol) electrolyte **(c),** 1:2 LiFSI-TEP electrolyte **(d)** and 1:2 LiFSI-TEP + FEC-LiBOB electrolyte **(e).** ("FEC-LiBOB" refers to 5 vol% FEC and 0.05 M LiBOB)



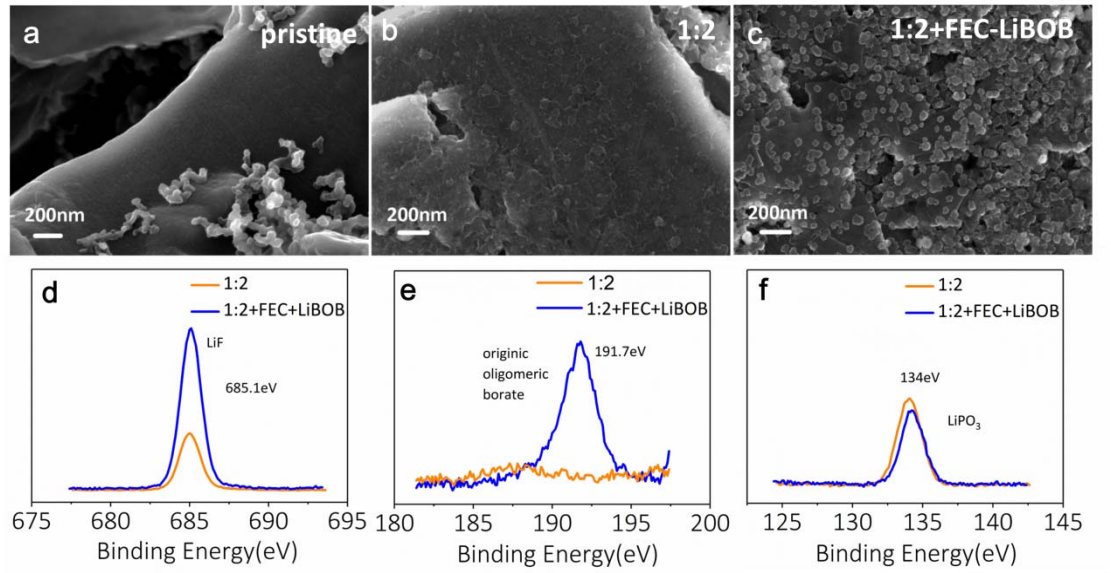
Supplementary Figure 4 | The initial charge-discharge curves of graphite electrodes cycled in LiFSI-TEP electrolytes with different MRs at a specific current of 20 mA g^{-1}.



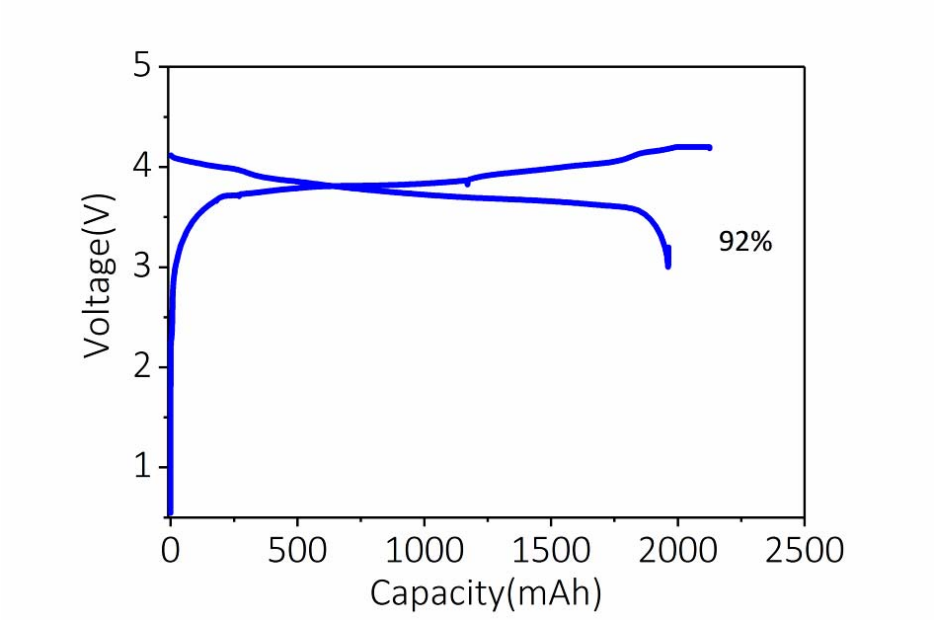
Supplementary Figure 5 | SEM images of the pristine and cycled graphite anodes in different MR electrolytes after 10 cycles. **a,** pristine, **b,** in 1:5 LiFSI-TEP, **c,** in 1:2 LiFSI-TEP.



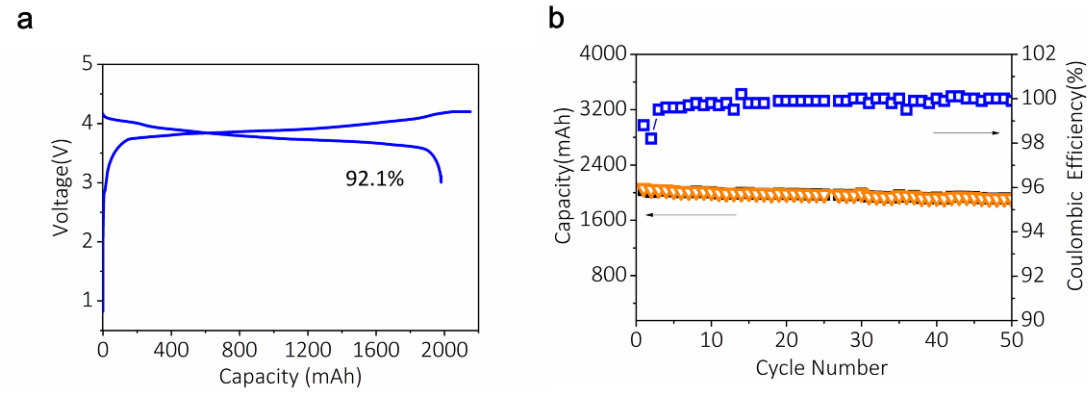
Supplementary Figure 6 | XPS spectra of the graphite anodes in different MR electrolytes after 10 cycle. **a**, F1s. **b**, P2p. **c, d,** S2p.



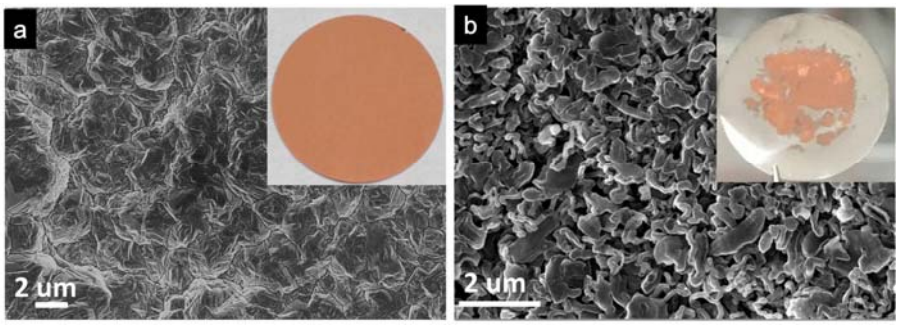
Supplementary Figure 7 | a,b,c SEM images of the pristine and cycled graphite anodes in different electrolytes for 10 cycles. a, pristine electrode. **b,** in 1:2 LiFSI-TEP. **c,** in1:2 LiFSI-TEP+FEC-LiBOB. d,e.f XPS spectra of cycled graphite anodes in electrolytes with or without additives for 10 cycles. **d,** F1s. **e,** B1s. **f,** P2p.



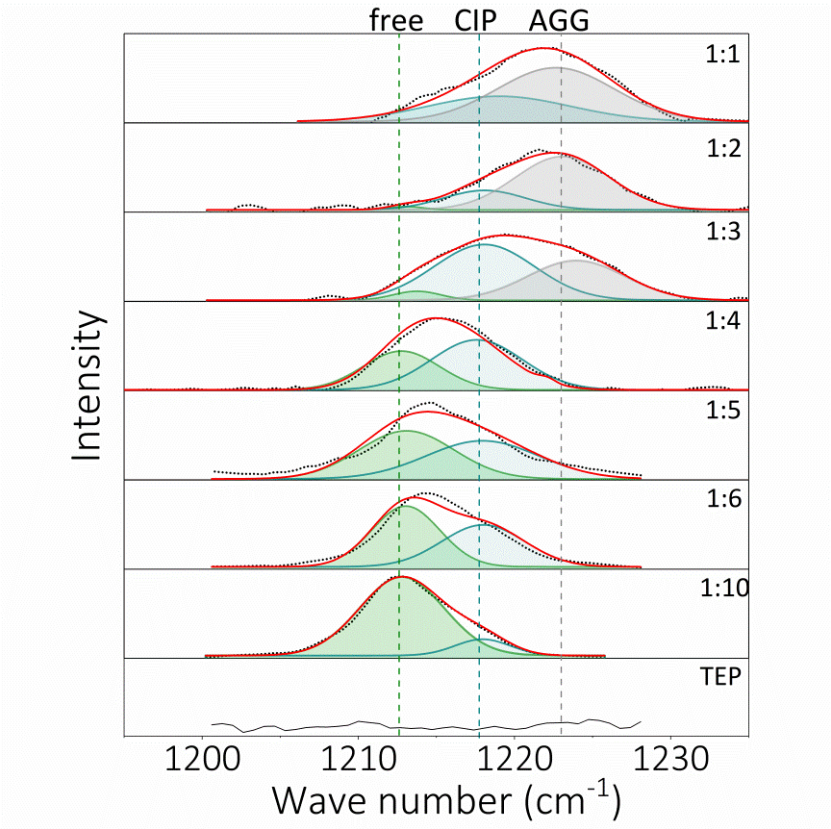
Supplementary Figure 8 | The initial charging-discharging curves of the 18650 cell using carbonate electrolyte (1M $LiPF_6$ EC:DEC:EMC=1:1:1 by volume) between 3.0 V and 4.2 V at a current rate of 0.05 C. 1 C=2000 mA. After constant current charge, a constant voltage step was carried out at 4.2 V with a cut-off current of 40 mA. The initial CE of 18650 cell in the carbonate electrolyte is 92%.



Supplementary Figure 9 | The initial charge-discharge curve **(a)** and cycling performance **(b)** of the 18650 cell using 1:2 LiFSI-TMP electrolyte with FEC-LiBOB. ("FEC-LiBOB" refers to 5 vol% FEC and 0.05 M LiBOB) between 3.0 V and 4.2 V at a current rate of 0.05 C. 1 C=2000 mA. After constant current charge, a constant voltage step was carried out at 4.2 V with a cut-off current of 40 mA. The initial CEs of 18650 cell in 1:2 LiFSI-TMP electrolyte with FEC-LiBOB is 92.1%.



Supplementary Figure 10 | **a,b,** SEM and optical images (inset) of the bare Cu substrate **(a)** and Li metal plating on a Cu substrate in 1:3 electrolytes **(b)**. The diameter of the Cu substrate shown in the insert of **(a,b)** was 1.68 cm.



Supplementary Figure 11 | Raman spectra of LiFSI-TEP electrolytes at the range of 1200 to 1230 cm^{-1} (S=O stretching mode of FSI^-). Black dots and solid lines represent the original spectra and fitted results, respectively. The band at 1213 cm^{-1} (left vertical–dashed line) is attributed to free FSI^-. The peak at 1218 cm^{-1} (middle vertical–dashed line) is attributed to FSI^- coordinating to one Li^+. The peak at 1223 cm^{-1} (right vertical–dashed line) is attributed to FSI^- coordinating to two or more Li^+. Curve fitting was performed with a Gaussian–Lorentz function. Shaded region corresponds to fitting peak profile.

Supplementary discussion

The coordination of Li^+ with FSI^- was also studied with by Raman vibrational modes in the range of 1200-1230 cm^{-1}. The original data and fitted curves are presented in Supplementary Fig. 11. It shows that the pure TEP has no band in this region.[1] With the addition of LiFSI, a new band appears at 1213 cm^{-1} associated with the S=O stretching vibrations of FSI^-.[2] A remarkable upshift of the FSI^- band (1213 cm^{-1}) was observed as MR increases from 1:10 to 1:1, indicating a simultaneous formation of contact ion pairs (CIPs, FSI^- coordinating to one Li^+) and aggregates

(AGGs, FSI^- coordinating to two or more Li^+). The Raman spectra are deconvoluted by using Gaussian–Lorentzian function into three bands at around 1213 cm^{-1} (free), 1218 cm^{-1} (CIPs) and 1223 cm^{-1} (AGGs). As MR increases from 1:10 to 1:4, FSI^- exist as free anions and CIPs. With further increasing MR, the free FSI^- anions decrease significantly due to the coordination with Li^+ cations to form contact ion pairs (CIPs) and aggregates (AGGs).

Supplementary References

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