Electronic Supplementary Information (ESI)

Ionic transport in highly concentrated lithium bis(fluorosulfonyl)amide electrolytes with keto ester solvents: Structural implications for ion hopping conduction in liquid electrolytes

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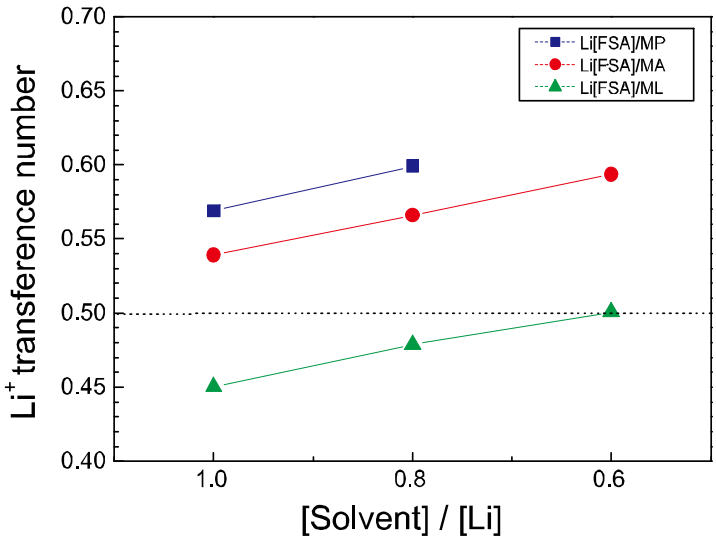
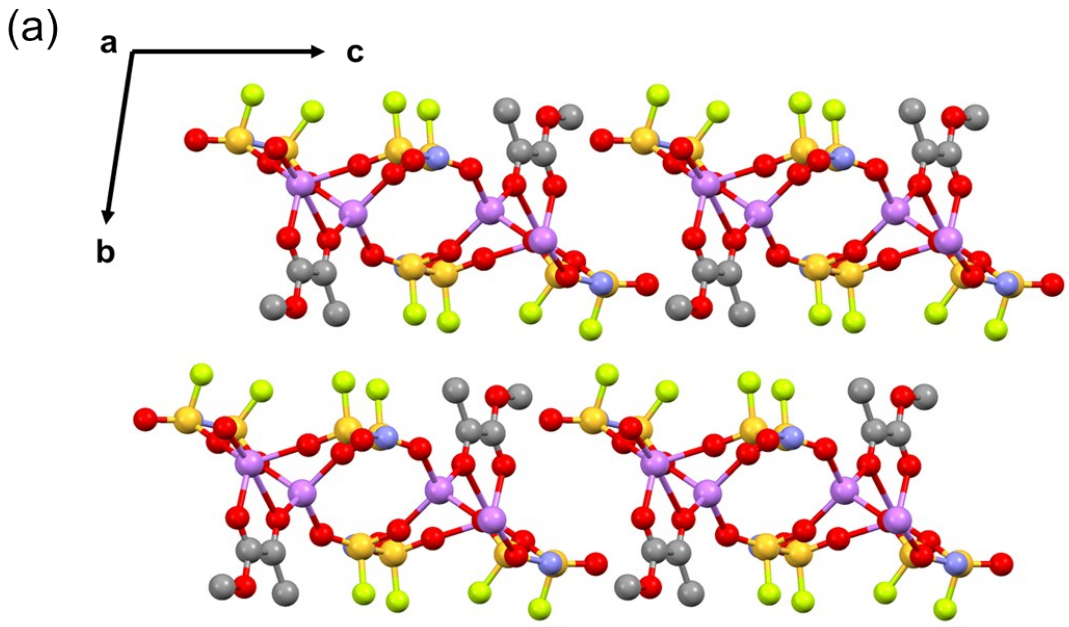


Figure S1. Li^+ transference number calculated from $t_{Li} = D_{Li}/(D_{Li} + D_{FSA})$ in the keto ester-based concentrated electrolytes at 30 °C.



(b)

	Li[FSA]:MP=1:0.5
Chemical formula	$C_8H_{12}F_8Li_4N_4O_{22}S_8$
Formula weight	317.49
Crystal system	Triclinic
Space group	P-1
a / Å	7.3617(6)
b / Å	9.6029(8)
c / Å	13.0788(10)
α / °	76.512(7)
β / °	76.556(7)
γ / °	71.936(7)
V / Å^3	841.85(12)
Z	3
D_{calc} / g cm^{-3}	1.879
μ / mm^{-1}	0.662
Temp. / K	223
Reflections collected	12731
Independent reflection, R_{int}	3657, 0.0325
R_1 [I > 2σ(I)]	0.0561
wR_2 (all data)	0.1800
Goodness of fit	1.092
Largest residual density / eÅ^{-3}	0.87, −0.47

Figure S2. Packing diagram of Li[FSA]:MP=1:0.5. Hydrogen atoms are omitted for clarity. Purple, Li; red, O; gray, C; yellow, S; light green, F; light blue, N. (b) Crystallographic data of Li[FSA]:MP=1:0.5.

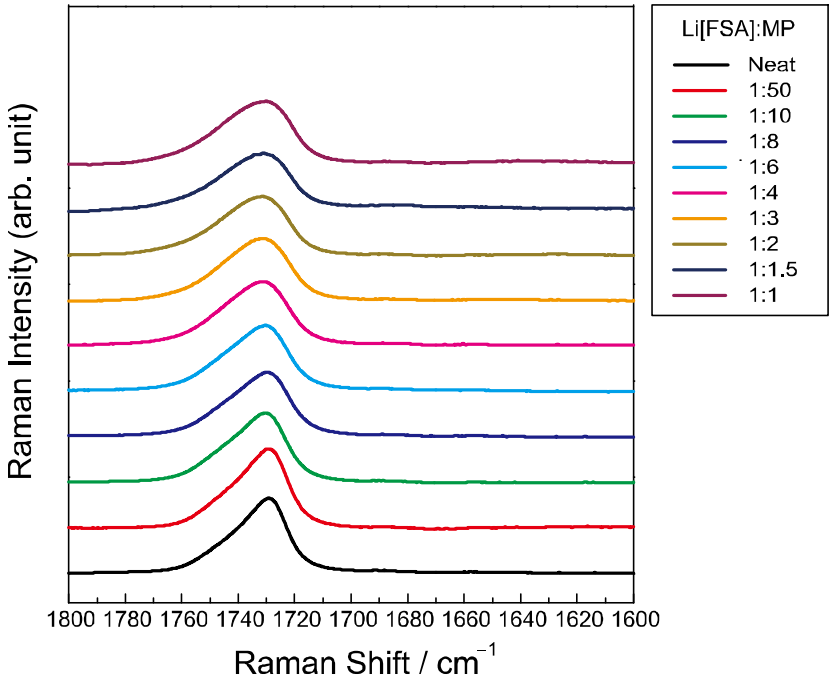


Figure S3. Raman spectra of MP-based electrolytes at various Li[FSA]:MP ratios. The peaks in the range of 1710-1770 cm^{-1} involve C=O symmetric and antisymmetric stretching vibrations at 1741 and 1737 cm^{-1} for *trans* and 1762 and 1733 cm^{-1} for *cis* form, respectively and these bands largely overlapped even with Li ion coordination.[39]

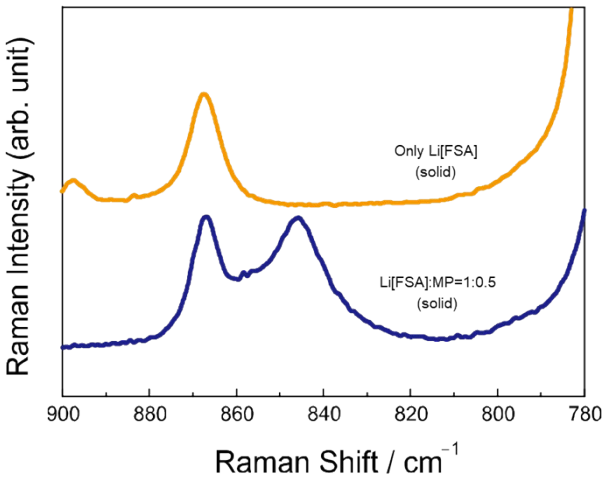


Figure S4. Raman spectra of solid Li[FSA] and MP-based electrolytes ([MP]/[Li] = 0.5).

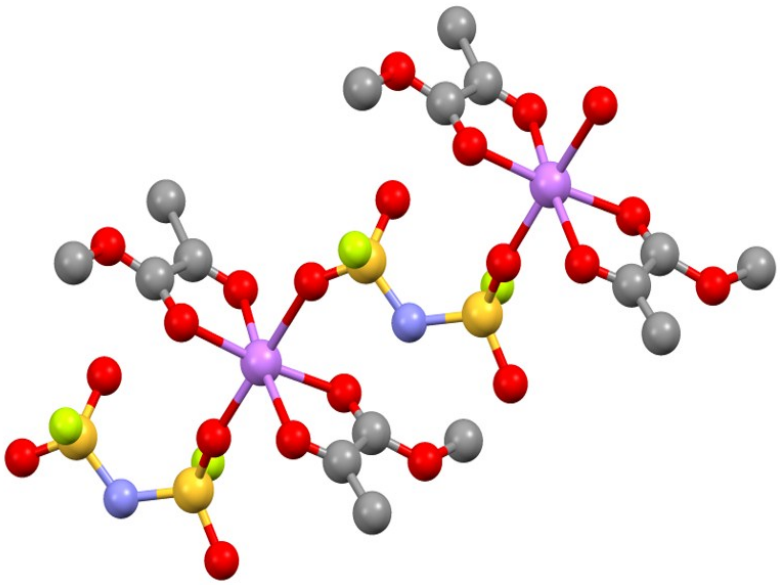


Figure S5. Local Li ion coordination structure of crystalline solvate at [MP]/[Li] = 2, suggested by the roughly refined crystallographic model. Hydrogen atoms are omitted for clarity. Purple, Li; red, O; gray, C; yellow, S; light green, F; light blue, N.

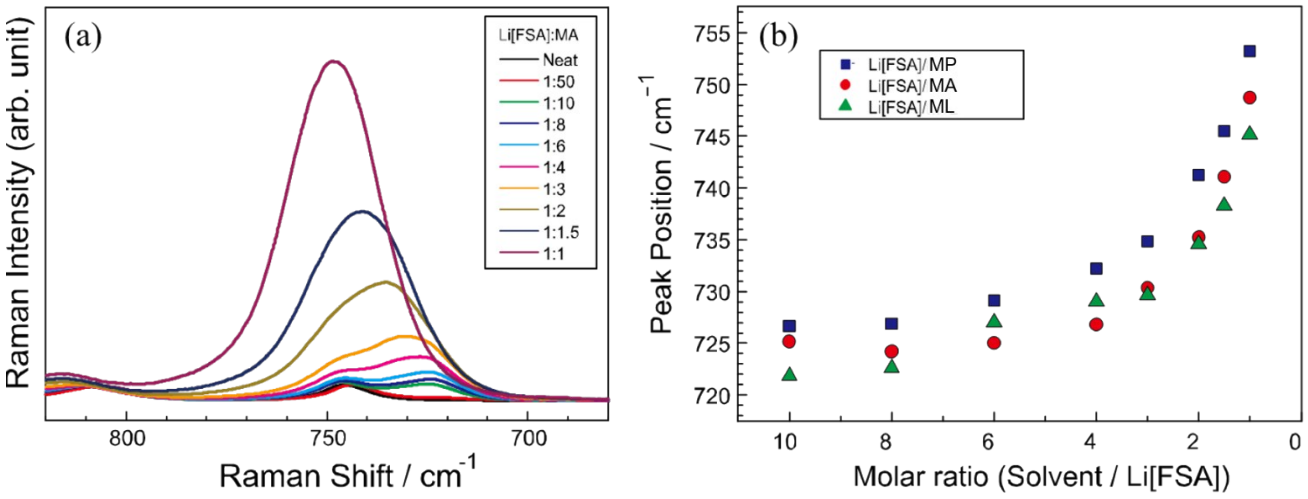


Figure S6. Raman spectra in the range of 720-760 cm^{-1} corresponding to symmetric stretching vibration of S-N-S skeleton of FSA anions with different salt concentrations; (a) MA-based at various Li[FSA]:MA ratios. (c) The peak maximum position at 720-760 cm^{-1} as a function of [solvent]/[Li] ratio.

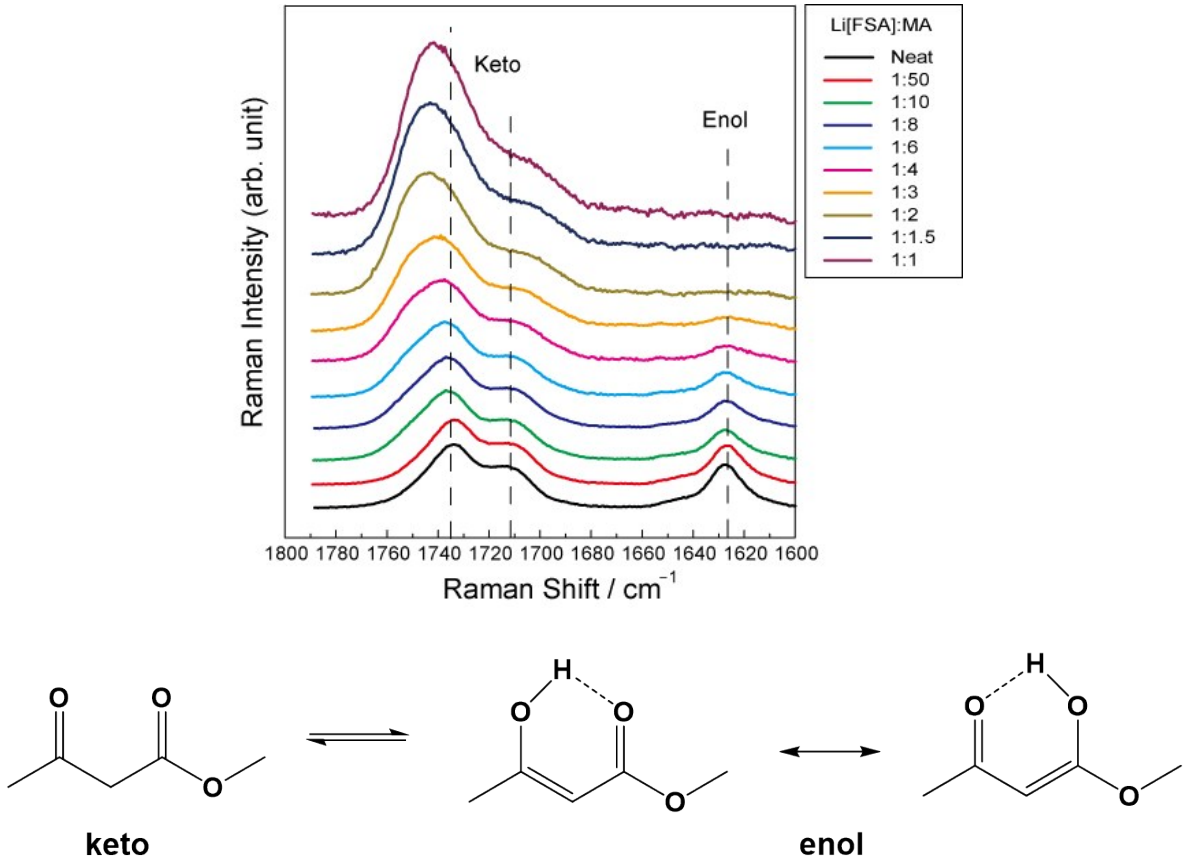
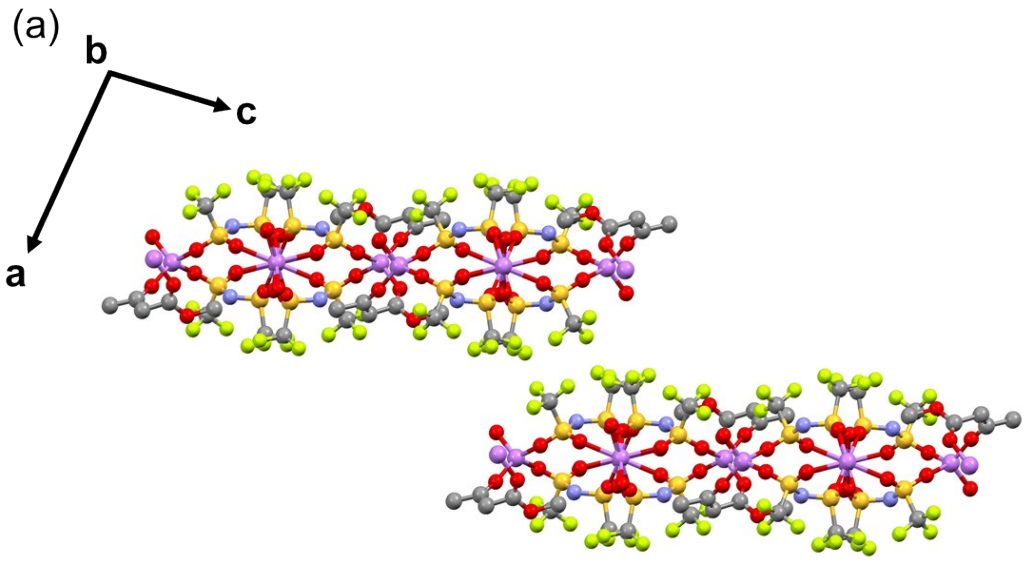


Figure S7. Raman spectra of MA-based electrolytes at various Li[FSA]:MA ratios. The peak at 1627 cm^{-1} and the peaks at 1736 cm^{-1} and 1716 cm^{-1} are C=O stretching vibrations of enol and keto structure in MA, respectively.



(b)

	Li[TFSA]:MA=1:0.5
Chemical formula	$C_9H_8F_{12}Li_2N_2O_{11}S_4$
Formula weight	690.30
Crystal system	Monoclinic
Space group	$P2_1/n$
a / Å	11.1850(5)
b / Å	10.4660(5)
c / Å	20.4745(9)
α / °	90
β / °	90.679
γ / °	90
V / Å^3	2396.62(19)
Z	4
D_{calc} / g cm^{-3}	1.913
μ / mm^{-1}	0.543
Temp. / K	223
Reflections collected	16128
Independent reflection, R_{int}	4885, 0.0326
R_1 [I > 2σ(I)]	0.0621
wR_2 (all data)	0.1837
Goodness of fit	1.061
Largest residual density / eÅ^{-3}	1.63, −0.64

Figure S8. Packing diagram of Li[TFSA]:MA=1:0.5. Hydrogen atoms are omitted for clarity. Purple, Li; red, O; gray, C; yellow, S; light green, F; light blue, N. (b) Crystallographic data of Li[TFSA]:MA=1:0.5.

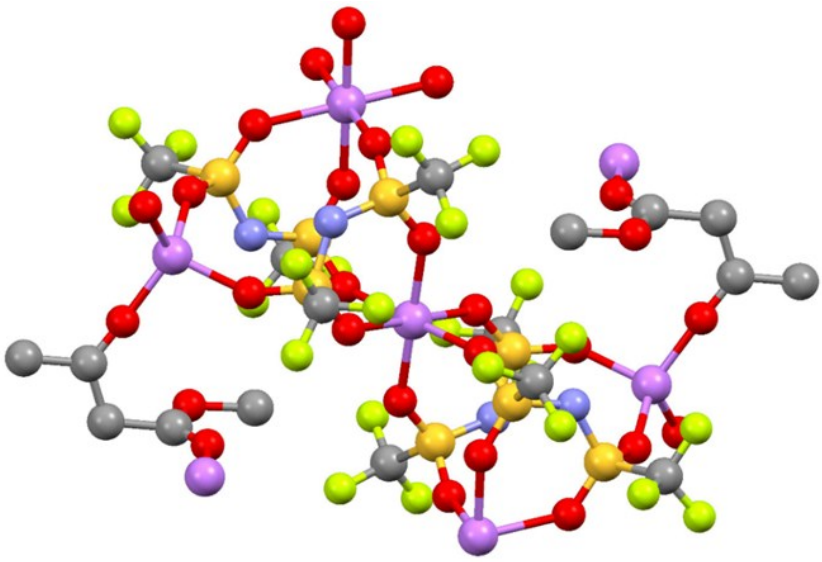


Figure S9. Ball and stick models for single crystal of MA-Li[FSA] solvate at [MA]/[Li] = 0.5., suggested by the roughly refined crystallographic model. Hydrogen atoms are omitted for clarity. Purple, Li; red, O; gray, C; yellow, S; light green, F; light blue, N.

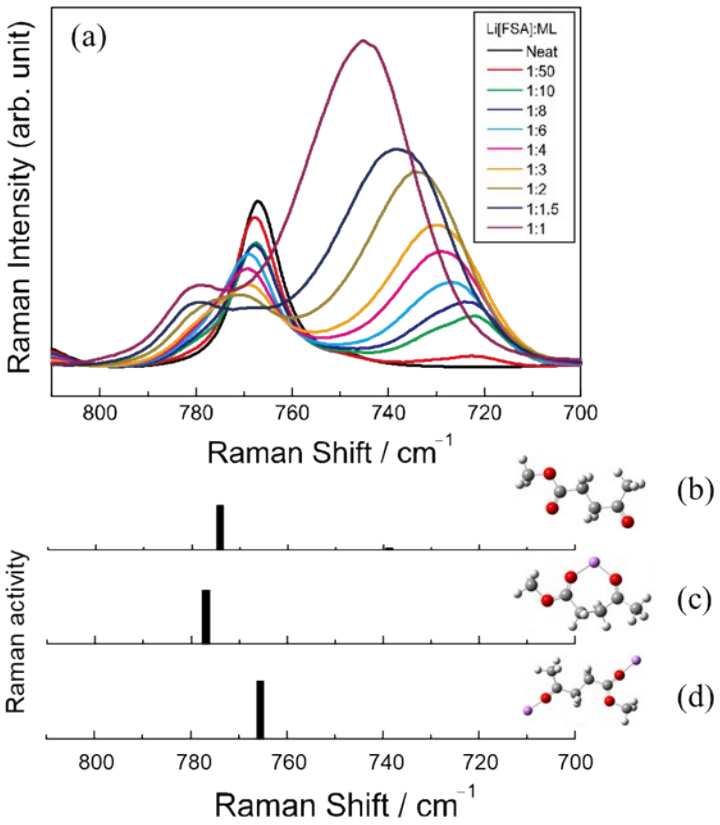


Figure S10. (a) Raman spectra of ML-based electrolytes at various Li[FSA]/MP ratios and theoretical Raman bands of optimized structures for (b) neat ML, (c) bidentate Li^+-ML (1:1) complex, and (d) Li^+-ML (2:1) complex, in the range of 700-810 cm^{-1} corresponding to symmetric stretching vibration of S-N-S skeleton of FSA anions (710-760 cm^{-1}) and C-C stretching vibration of the ketone group in ML (760-780 cm^{-1}).