Supporting Information
The Relevance of Lithium Salt Solvate Crystals in Superconcentrated Electrolytes in Lithium Batteries

Lattice Parameters	LiMPSA-MeCN	LiTFSI-MeCN	LiDFOB-MeCN	LiBOB-MeCN
space group	monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	orthorhombic, Pnma	monoclinic, $P2_1/n$
a, b, c (Å)	10.65,20.46,10.03	10.84,11.02,19.12	8.02,6.37,24.64	7.75,22.37,15.01
α, β, γ (^{0})	90.0,96.0,90.0	90.0,91.3,90.0	90.0,90.1,90.0	90.0,92.2,90.0
V (Å^3)	2173.0	2284.4	1259.1	2600.2
density (g/cm^3)	1.51	1.91	1.41	1.51

Table S1: DFT optimized lattice parameters for salt-MeCN solvate crystals in this study.

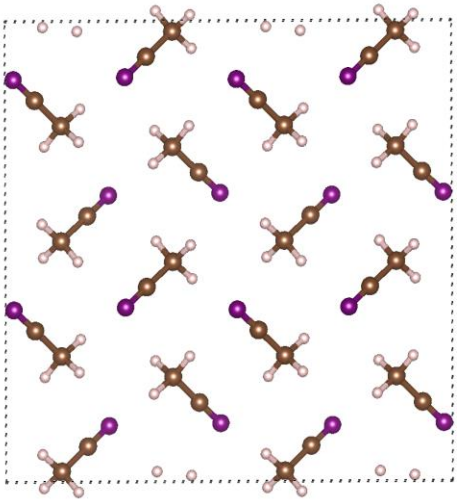

Figure S1: The crystal structure of MeCN solvent. From DFT calculation, the binding energy (E_b) of this MeCN molecular solid is ~ 0.45 eV/MeCN. Color of atom: N (purple), C (brown), H (white).

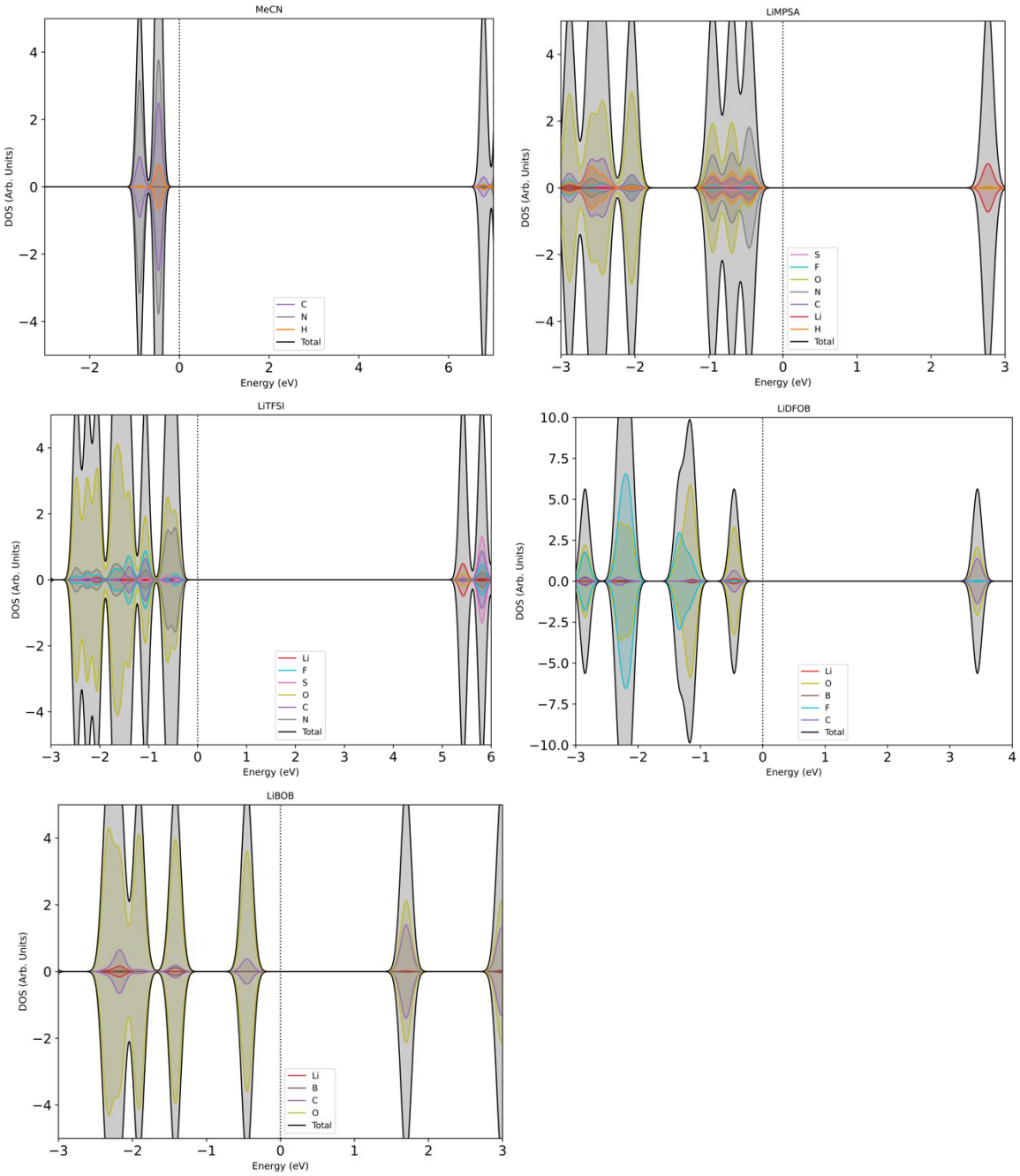

Figure S2: Site projected electron density of states (e-DOS) of pristine MeCN, LiMPSA, LiTFSI, LiDFOB, and LiBOB molecule. All these molecules are found to have large HOMO-LUMO gap. The Fermi level, E_f is represented by dotted vertical line and referenced as zero in energy level.

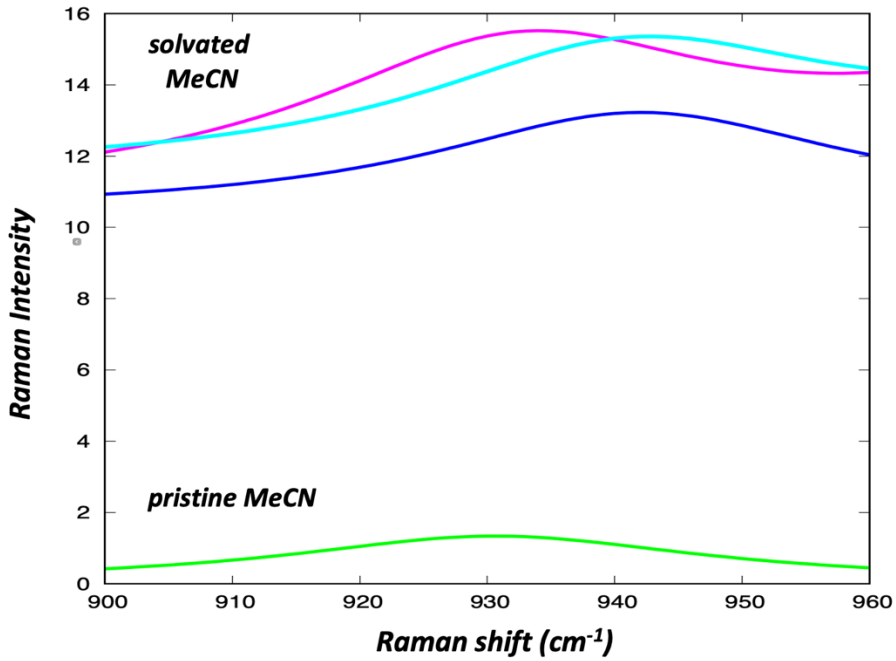

Figure S3: Quantum chemical method simulated Raman spectra that highlight the difference between a pristine MeCN solvent molecule and Li^+ coordinated MeCN in LiTFSI-$(MeCN)_2$ (neutral/anionic/cationic) solvate molecule regarding to C-C stretching mode ($\upsilon \sim 930\ cm^{-1}$) of MeCN molecule. The neutral, anion and cation MeCN-solvate species is represented by line in blue, pink, and light blue, respectively. Compared to Fig. 6 (i.e. C≡N stretching of MeCN) in the main text, a systematic upshift is not found in C-C stretching mode. Therefore, we suggest that the Raman signature of C≡N stretching of MeCN is more suitable to probe of charged species of salt-MeCN solvate molecules.