

Supporting information

The Role of Coordination Strength in Solid Polymer Electrolytes: Compositional Dependence of Transference Numbers in the Poly(ϵ - Caprolactone)–Poly(Trimethylene Carbonate) System

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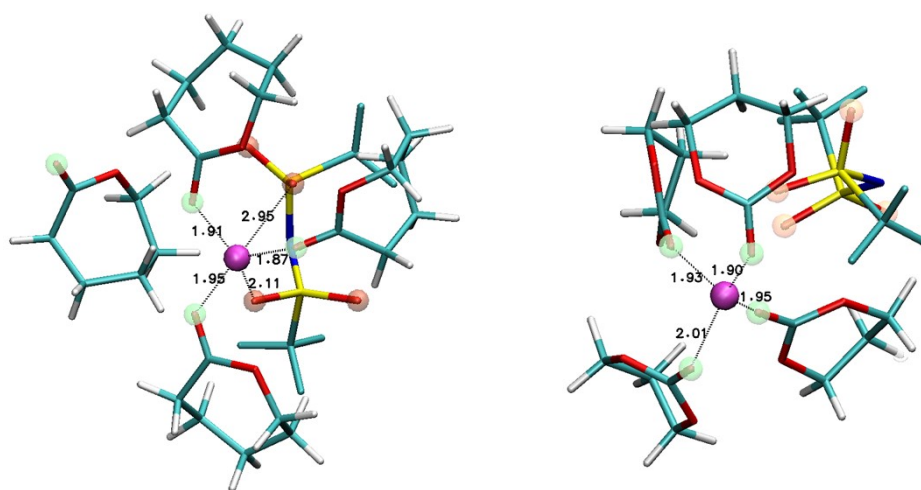


Figure S1: LiTFSI + 4 monomer complexes of CL on the left and TMC on the right (colour coding: Li – pink, O – red, C – turquoise, S – yellow, N – blue, H – white). Physical bonding between oxygens atom and Li⁺ at distances <3 Å are indicated by the black dotted lines. Carbonyl oxygens and sulfonyl oxygens (from the TFSI anion) are highlighted by green and orange spheres, respectively.

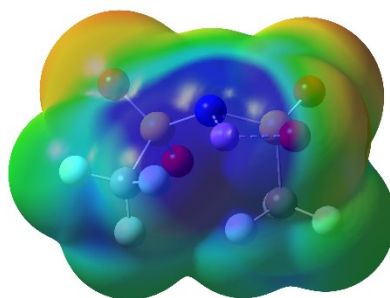


Figure S2: Charge distribution of electrostatic potential of the TFSI anion. Blue color indicates more positive charge and red more negative.

Coulomb's law (Equation S1) was used to calculate the electrostatic force ($F_{Col.}^{Li^+ - CO}$), where q_O , q_C and q_{Li^+} are the partial charges for the carbonyl oxygen, carbonyl carbon and lithium ion, k_e is the Coulomb constant, and r_{O-Li^+} and r_{CO} are the bond length between the lithium ion and the carbonyl oxygen and that of the carbonyl group.

$$F_{Col.}^{Li^+ - CO} = k_e \left[\frac{|q_O| |q_{Li^+}|}{r_{O-Li^+}^2} + \frac{|q_C| |q_{Li^+}|}{(r_{C=O} + r_{O-Li^+})^2} \right] \quad (S1)$$

Table S1: Values taken from DFT calculations using 1 monomer and 1 LiTFSI for the calculation of the electrostatic force, as well as the resulting force for the CL and TMC system when using Equation S1.

	1 CL and 1 LiTFSI	1 TMC and 1 LiTFSI
q_O (e)	-0.68	-0.78
q_{Li^+} (e)	0.87	0.84
q_C (e)	0.79	1.22
r_{O-Li^+} (Å)	1.89	1.92
$r_{C=O}$ (Å)	1.25	1.24
Calculated $F_{Col.}^{Li^+ - CO}$ (nN)	2.22	1.77

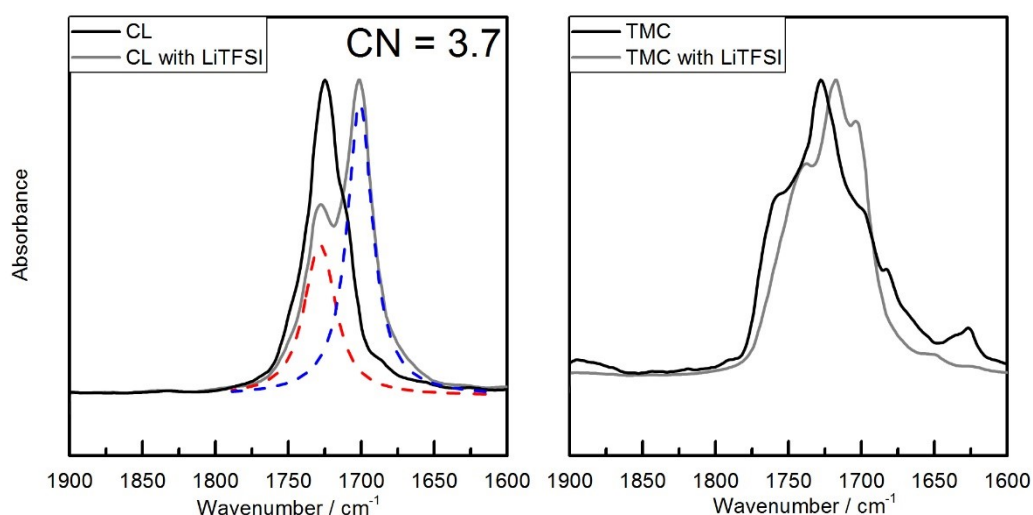


Figure S3: FT-IR spectra for CL and TMC with and without LiTFSI salt. The red dashed peak at higher wavenumbers corresponds to the uncoordinated carbonyl while the blue dashed peak at lower wavenumbers corresponds to the lithium-coordinating carbonyl peak. The calculated coordination number for CL is 3.7.

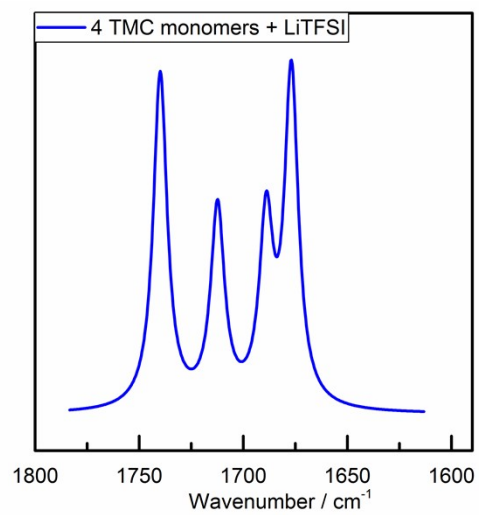


Figure S4: Computed FT-IR spectra from DFT calculations done of four TMC monomers with one LiTFSI, showing several carbonyl stretching peaks as the monomers coordinate the lithium ion.