Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Validation of PBE/6-31+G(d,p) calculations

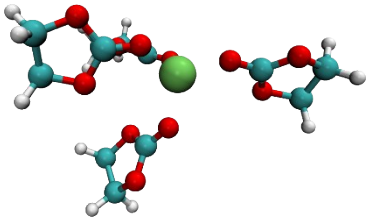
Table S1: Formation energies and free energies for Li+-solvent, Li+-anion and Li+-oligomer dimers calculated at the PBE/6-31+G(d,p) and the G4MP2 level1 using the SMD implicit solvation model.2 PBE/6-31+G(d,p) calculations including the empirical D3 dispersion correction with Becke-Johnson damping3 are also shown. For LiTFSI, a distinction between mono- and bidentate coordination4 has been made. For the PBE calculations, the mean absolute deviation (MAD) to the G4MP2 results as averaged over all dimers is also shown.

	PBE/6-31+G(d,p)		**PBE/6-31+G(d,p) + GD3BJ**		**G4MP2**	
Dimerization energies	**Δ*E*** **[kcal/mol]**	**Δ*G*** **[kcal/mol]**	**Δ*E*** **[kcal/mol]**	**Δ*G*** **[kcal/mol]**	**Δ*E*** **[kcal/mol]**	**Δ*G*** **[kcal/mol]**
Li^+-EC	-13.9	-7.2	-14.6	-8.2	-14.0	-8.1
Li^+-PC	-14.1	-8.1	-14.9	-8.1	-14.3	-8.6
Li^+-(MMA)	-14.9	-8.6	-16.3	-8.7	-14.9	-7.5
Li^+-$(MMA)_2$	-20.2	-12.2	-22.5	-14.5	-19.4	-11.0
Li^+-(TEGDME)	-46.9	-35.0	-55.1	-42.7	-51.1	-39.3
LiTFSI (monodentate)	-14.9	-9.1	-15.7	-9.2	-17.8	-10.8
LiTFSI (bidentate)	-23.8	-17.3	-25.5	-18.7	-23.7	-16.8
LiBOB	-19.9	-12.2	-20.6	-12.9	-20.0	-11.7
MAD	**1.1**	**1.3**	**1.8**	**1.7**	**-**	**-**

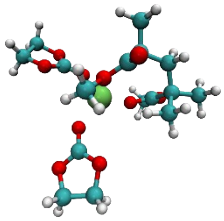
Cluster Stabilities

Table S2: Cluster formation energies ΔE and free energies ΔG relative to $[Li(EC)_4]^+$ calculated at the PBE/6-31+G(d,p) level of theory including the SMD solvation model[2]. The energies have been computed according to the formal reaction equation $[Li(EC)_4]^+ + n\ L \rightarrow [Li(L)_n(EC)_{4-n}]^+ + n\ EC$, where L is any ligand (solvent, polymer, or anion) coordinating with one or multiple coordination sites (in total n coordinating sites from one or multiple ligands replace n EC molecules). In all cases except those involving TEGDME, the total coordination number has been constrained to four, while for TEGDME also higher coordination numbers as determined from the geometry optimization (see Figure S1) have been taken into account. For clusters involving TEGDME or monodentate TFSI (involved in $[Li(TFSI)_2(MMA)_2]^-$), a correction based on the (free) energy differences between the PBE and the G4MP2 calculations has been applied (see main text).

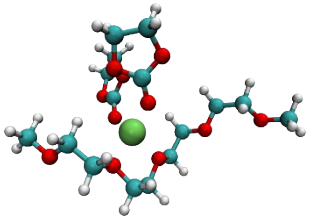
Cluster	**Δ*E* [kcal/mol]**	**Δ*G* [kcal/mol]**
$[Li(EC)_4]^+$	0.0	0.0
$[Li(MMA)_2(EC)_2]^+$	5.7	-2.2
$[Li(TEGDME)(EC)_2]^+$	-3.9	-12.4
$[Li(TEGDME)]^+$	-2.9	-29.0
$[Li(TFSI)(EC)_2]$	0.8	-8.8
$[Li(BOB)(EC)_2]$	3.8	-6.2
[Li(TFSI)(TEGDME)]	-5.7	-20.3
[Li(BOB)(TEGDME)]	-5.0	-20.2
$[Li(TFSI)(MMA)_2]$	6.4	-11.8
$[Li(BOB)(MMA)_2]$	10.0	-7.6
$[Li(TFSI)_2(MMA)_2]^-$	-1.8	-6.9
$[Li(BOB)_2(MMA)_2]^-$	4.4	-2.1



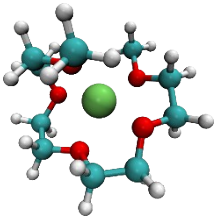
$[Li(EC)_4]^+$



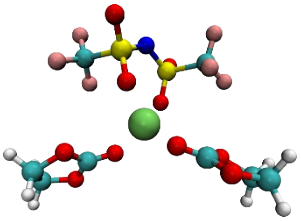
$[Li(MMA)_2(EC)_2]^+$



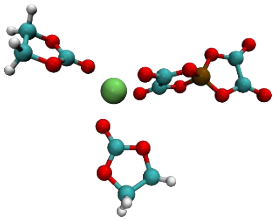
$[Li(TEGDME)(EC)_2]^+$



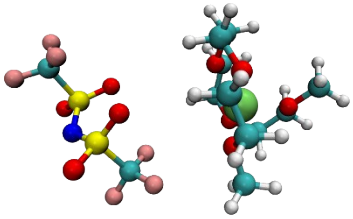
$[Li(TEGDME)]^+$



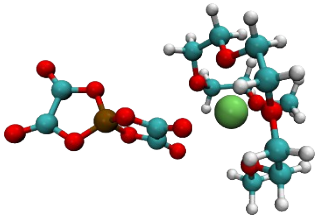
$[Li(TFSI)(EC)_2]$



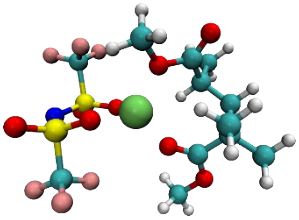
$[Li(BOB)(EC)_2]$



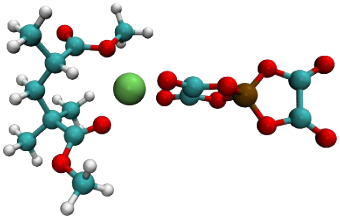
[Li(TFSI)(TEGDME)]



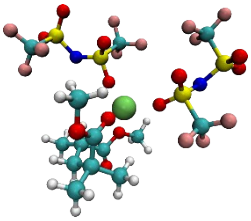
[Li(BOB)(TEGDME)]



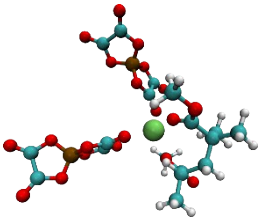
$[Li(TFSI)(MMA)_2]$



$[Li(BOB)(MMA)_2]$



$[Li(TFSI)_2(MMA)_2]^-$



$[Li(BOB)_2(MMA)_2]^-$

Fig. S1 Optimized geometries of the clusters reported in Table S2 calculated at the PBE/6-31+G(d,p) level of theory created with VMD.[5] White, H; lime, Li; ochre, B; cyan, C; blue, N; red, O; pink, F; yellow, S.

References

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