Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
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Supplementary information:

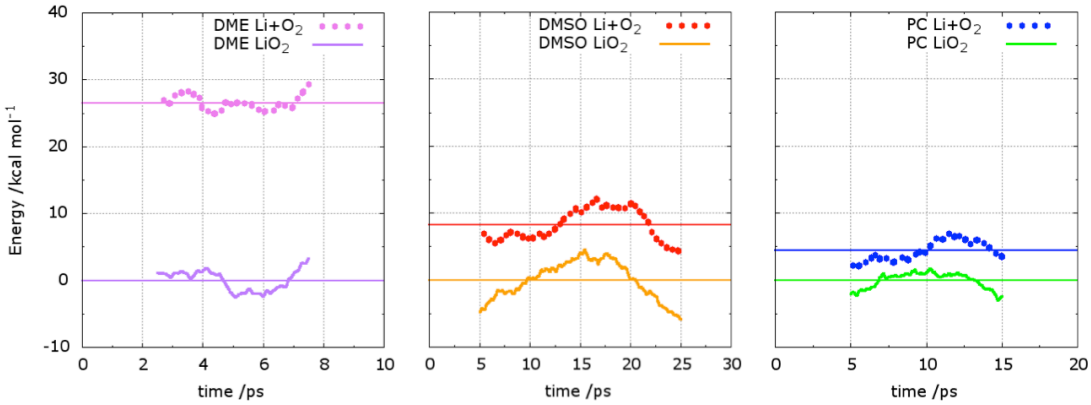

Figure S1 Energy trajectories from DFT-MD simulations of DME (total 10 ps, running average 5 ps), DMSO (total 30 ps, running average 10 ps), and PC electrolytes (total 20 ps, running average 10 ps).

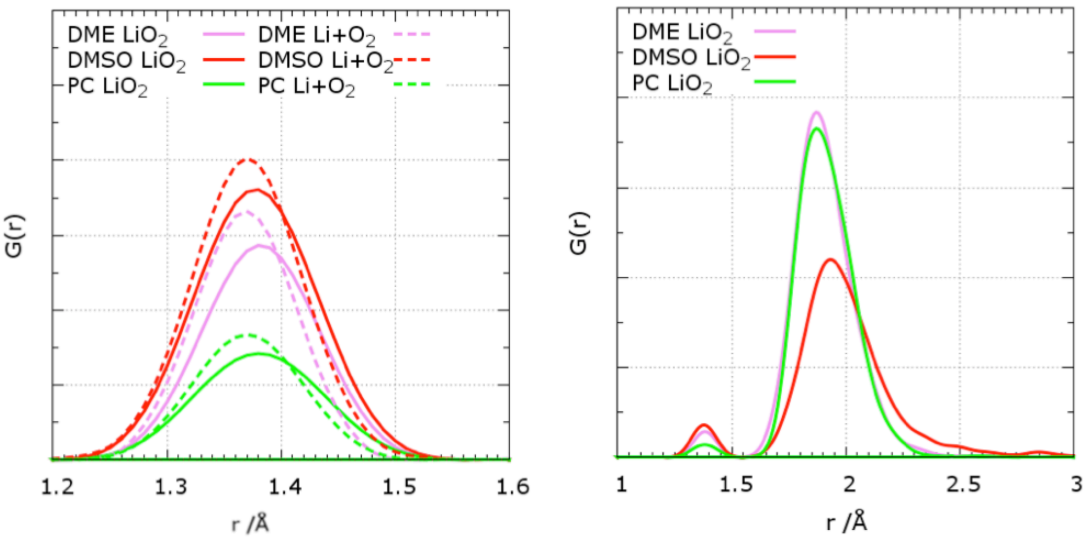

Figure S2 Radial distribution function of DME, DMSO, and PC electrolytes from DFT-MD simulations, T=353K, t=10 ps.

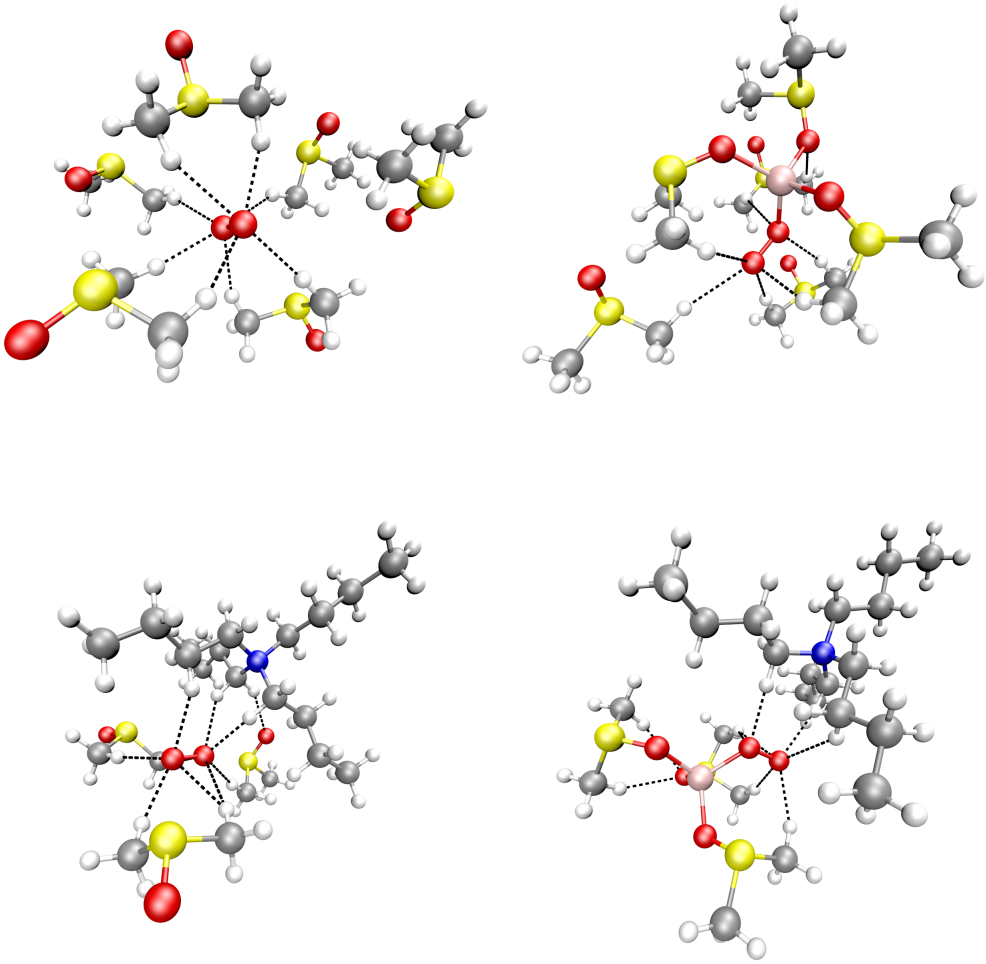

Figure S5 Cluster models of O_2^{*-} and LiO_2* with six explicit DMSO molecules each, and $[TBA]^+[O_2]^{*-}$ and $[TBA]^+[LiO_2]^*$ with three DMSO. All structures were optimized also in the presence of a continuum DMSO solvent model (PCM).

Table S1 rOO and rOLi bond distances in solvent-ion clusters. B3LYP/6-31G(d).

	Original clusters		Ionized clusters (IP)		Reduced clusters (EA)	
Solvent	rOO	rOLi	rOO	rOLi	rOO	rOLi
DME_{O2}	1.344	–	1.215	–	1.527	–
DME_{LiO2}	1.348	1.923	1.215	3.234	1.532	1.796
DME_{TBAO2}	1.342	–	1.215	–	1.515	–
$DME_{TBAO2Li}$	1.347	1.939	1.215	3.227	1.530	1.804
$DMSO_{O2}$	1.342	–	1.215	–	1.505	–
$DMSO_{LiO2}$	1.343	1.980	1.214	3.288	1.505	1.887
$DMSO_{TBAO2}$	1.342	–	1.215	–	1.510	–
$DMSO_{TBAO2Li}$	1.341	1.974	1.215	3.230	1.502	1.849
$DMSO_{O2}$	1.342	–	1.215	–	1.505	–
PC_{O2}	1.343	–	1.215	–	1.496	–
PC_{LiO2}	1.348	1.915	1.21X	3.25X	1.532	1.808
PC_{TBAO2}	1.343	–	1.214	–	1.521	–
$PC_{TBAO2Li}$	1.347	1.909	1.220	3.520	1.538	1.788

Table S2 Functional dependence of the rOO bond distances. The B3LYP and PBEPBE functionals, together with the 6-31G(d) basis set, have been used to calculate rOO of a single O_2^{*-} molecule in different continuum solvents using Gaussian.

	B3LYP	PBEPBE	DFT-MD (PBE)
rOO (O_2^{*-})	1.353 (VAC)	1.368 (VAC)	–
	1.350 (DEE)	1.364 (DEE)	–
	1.350 (DME)	1.364 (DME)	1.369 (DME)
	1.349 (DMSO)	1.364 (DMSO)	1.370 (DMSO)
	1.349 (PC)	1.364 (PC)	1.372 (PC)

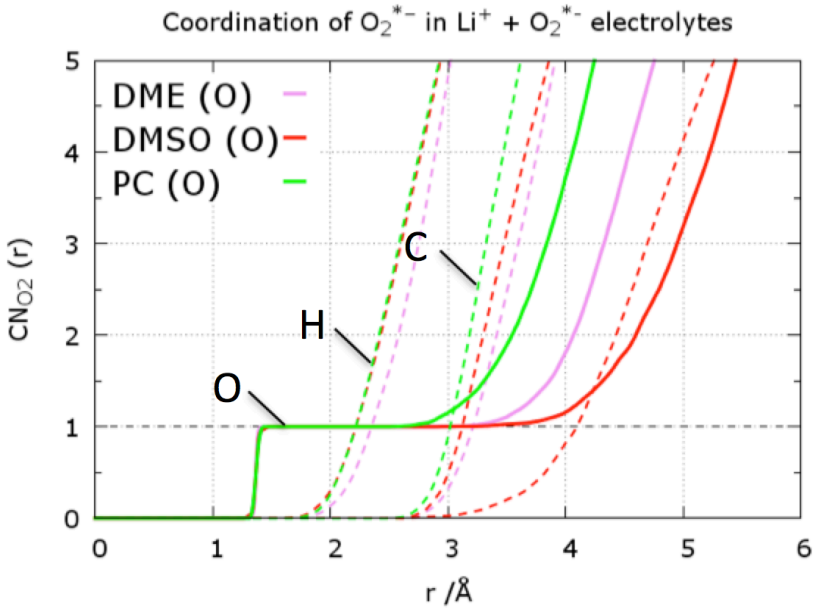

Figure S4 The average coordination number of the oxygen atoms of O_2^{*-} in DME, DMSO, and PC SSIP electrolytes.

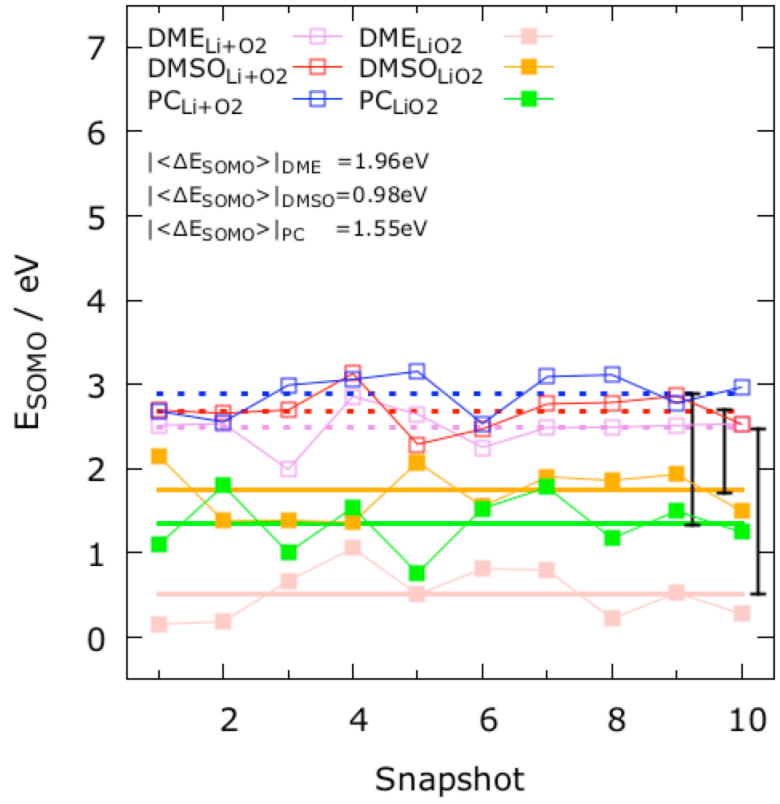

Figure S5 Calculated SOMO levels in DME, DMSO, and PC CIP and SSIP based on 10 snapshots from DFT-MD simulations.

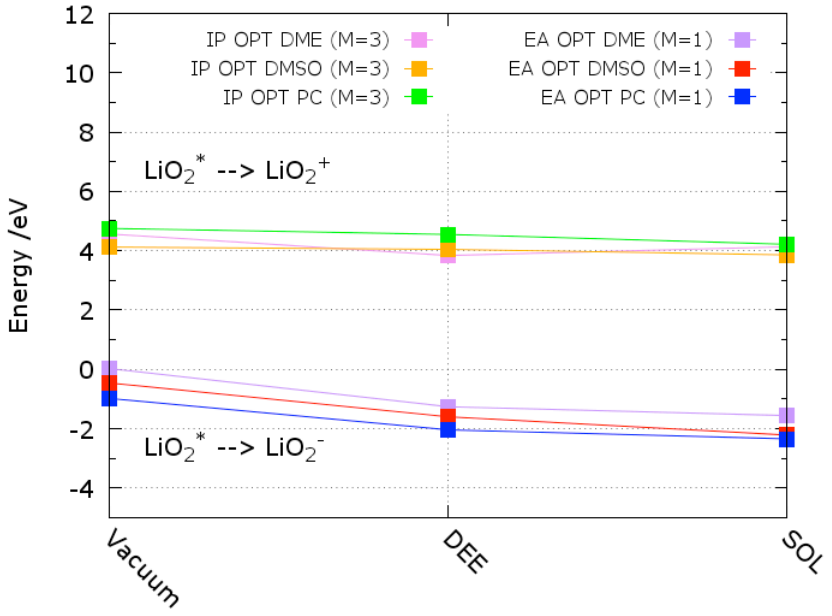

Figure S6 Ionization potentials (IP) and Electron affinities (EA) of LiO_2^* explicitly solvated by six DME, DMSO, or PC molecules and an additional PCM continuum (vacuum, DEE, or SOL=DME, DMSO, or PC). All data are based on optimized energies of the oxidation/reduction products. B3LYP/6-31G(d).

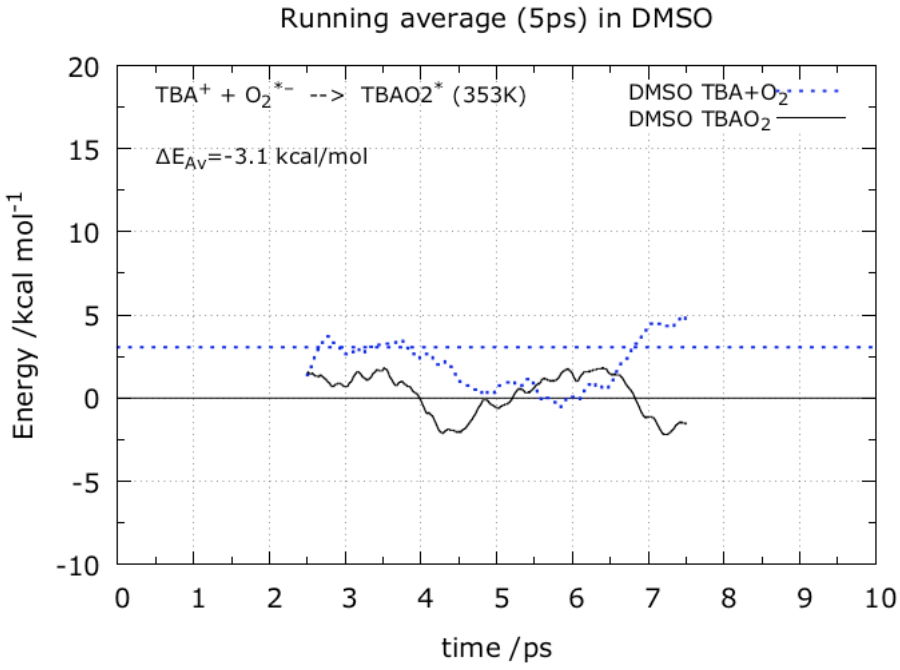

Figure S7 Running averages (5 ps) and total energy averages (10 ps) of $TBAO_2^*$ (solid) or $TBA^+ + O_2^{*-}$ (dotted) trajectories from DFT-MD simulations of DMSO. CIP formation is slightly exothermic. Absolute energies have been shifted to ease comparison. T=353K, t=10 ps.

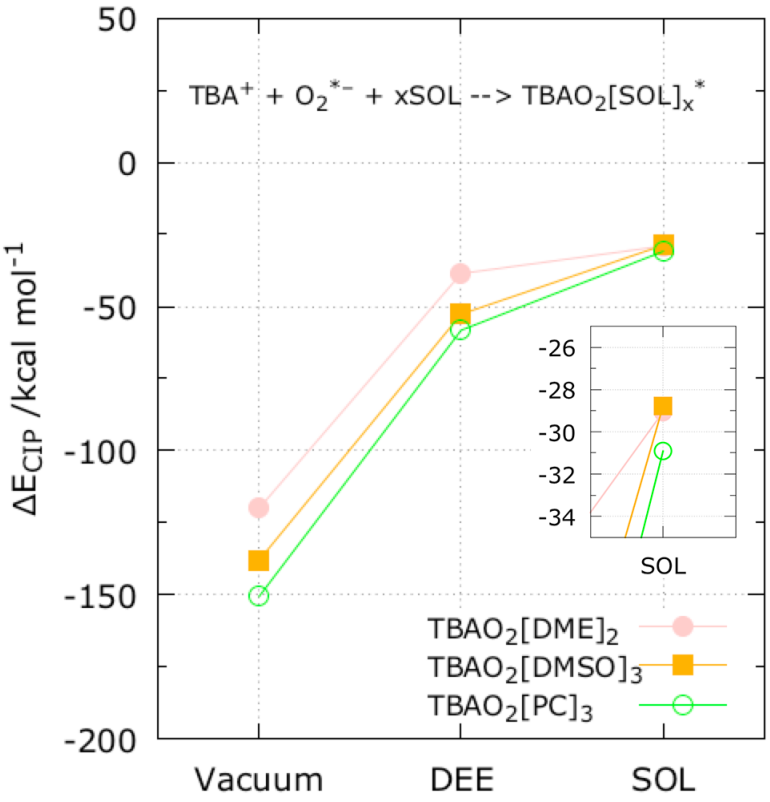

Figure S8 Formation energy of $TBAO_2^*$ CIP explicitly solvated by two or three molecules of DME, DMSO, or PC, as a function of additional implicit PCM solvation. B3LYP/6-31G(d).

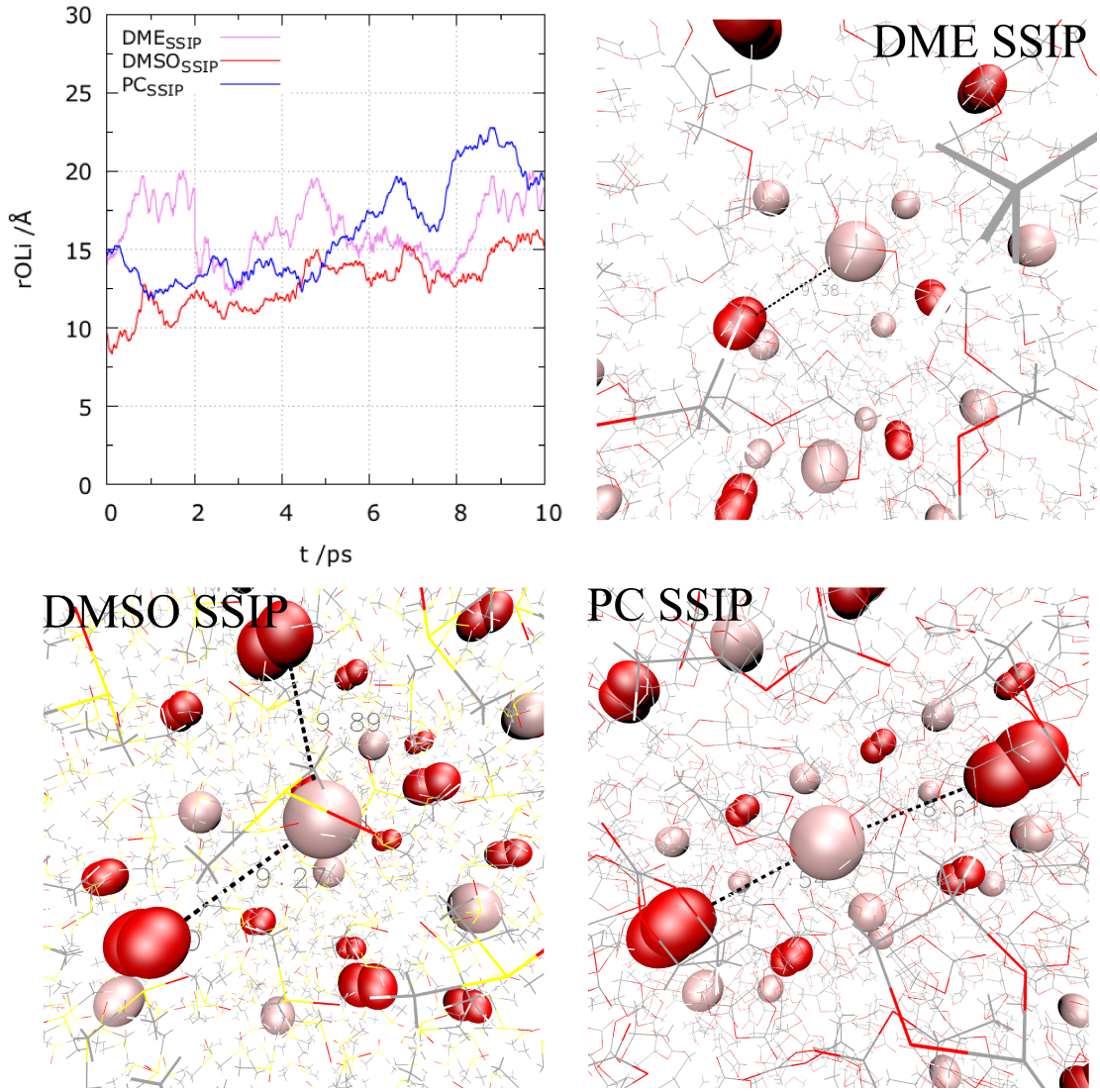

Figure S9 rOLi distance during 10ps of DFT-MD simulations of solvent-separated ion pairs (SSIP) and highlights of the final ion distributions including the nearest periodic image of each box. The final rOLi distances in each box are: 9.38Å (DME), 9.27Å (DMSO), and 7.54Å (PC). CPMD; T=350K.