Supporting Information

Solvation structure and dynamics of Li and LiO_2 and their transformation in non-aqueous organic electrolyte solvents from first-principles simulations

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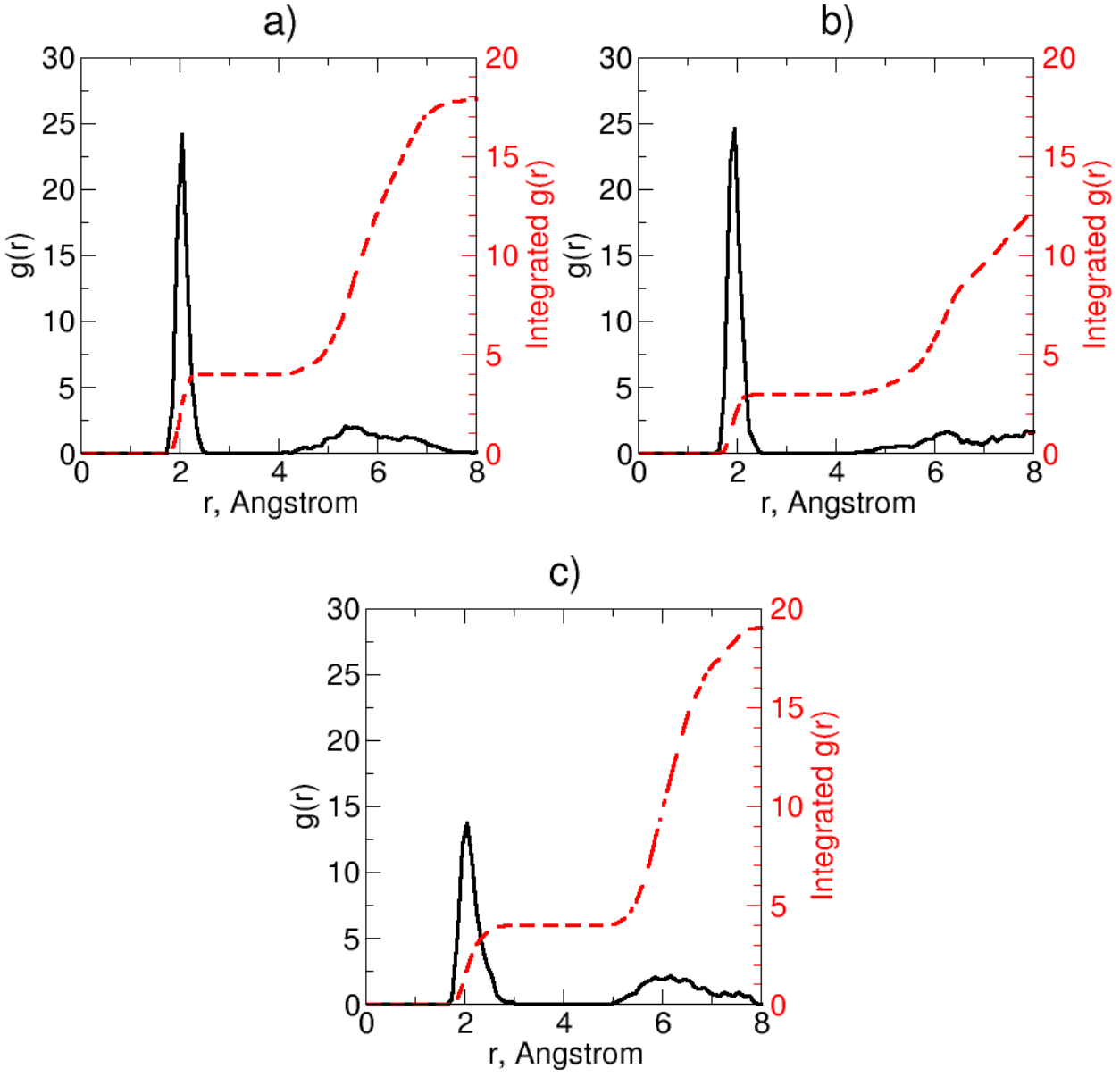

Figure S1. Integrated radial distribution function (RDF) of Li^+ solvation in the three electrolytes a) Li-N for CAN, b) Li-O for DMSO, and c) Li-O for DME. The integrated RDFs show that Li^+ in ACN, DMSO, and DME is bonded to 4, 3 and 2 electrolyte molecules, respectively, in the first solvation shell. (Note that for the DME solvent, the integrated RDF shows a coordination of 4, which corresponds to the 2 oxygen atoms of each of the 2 bonded DME molecules)

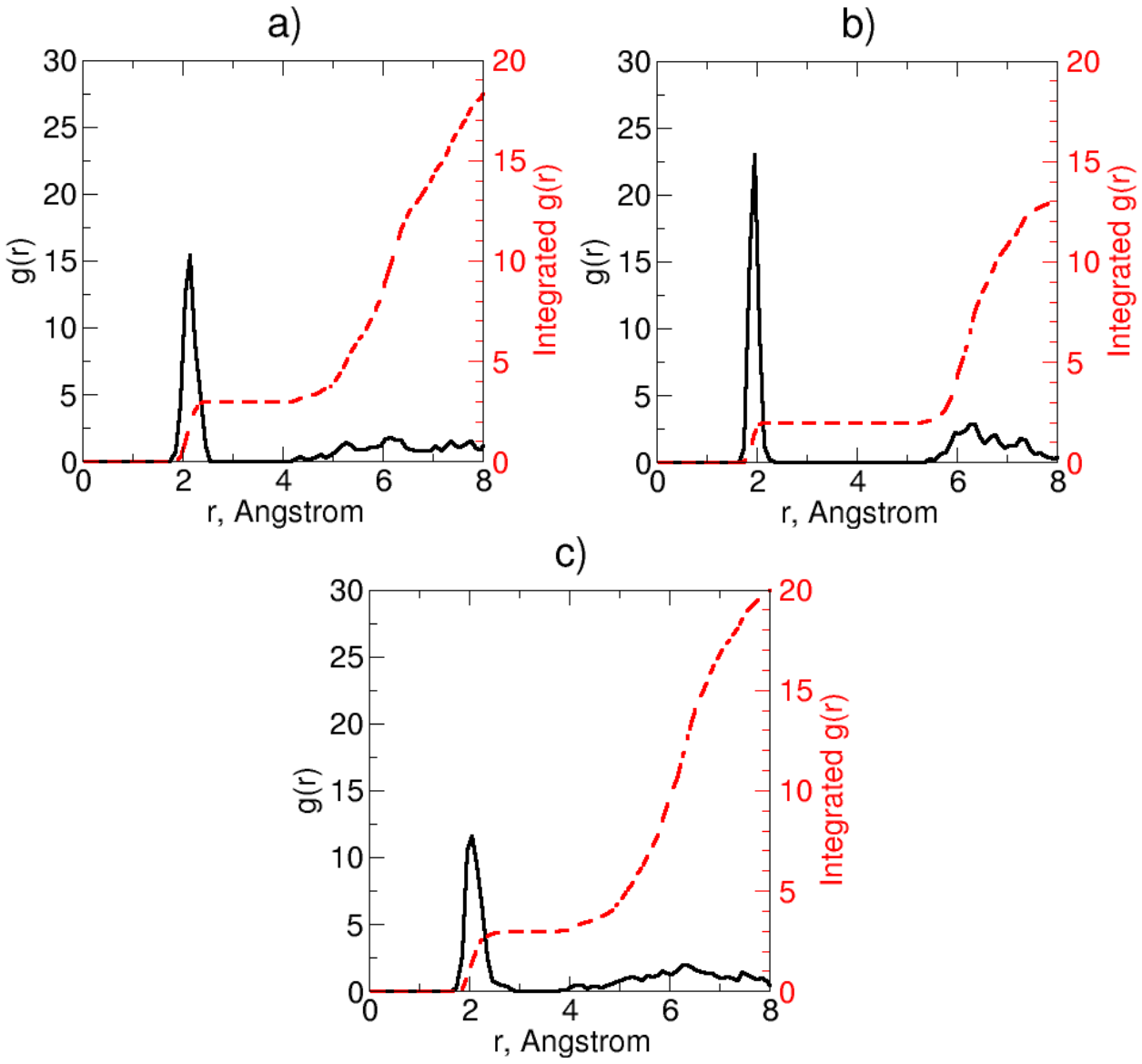

Figure S2. Integrated radial distribution function (RDF) **of LiO_2 solvation in the three electrolytes a) Li-N for ACN, b) Li-O for DMSO, and c) Li-O for DME. The integrated RDFs show that LiO_2 in ACN, DMSO, and DME is bonded to 3, 2, and 2 electrolyte molecules, respectively, in the first solvation shell. (Note that for the DME solvent, the integrated RDF shows a coordination of 3, which corresponds to 2 oxygen atoms of one DME and one oxygen atom of another DME molecule)**

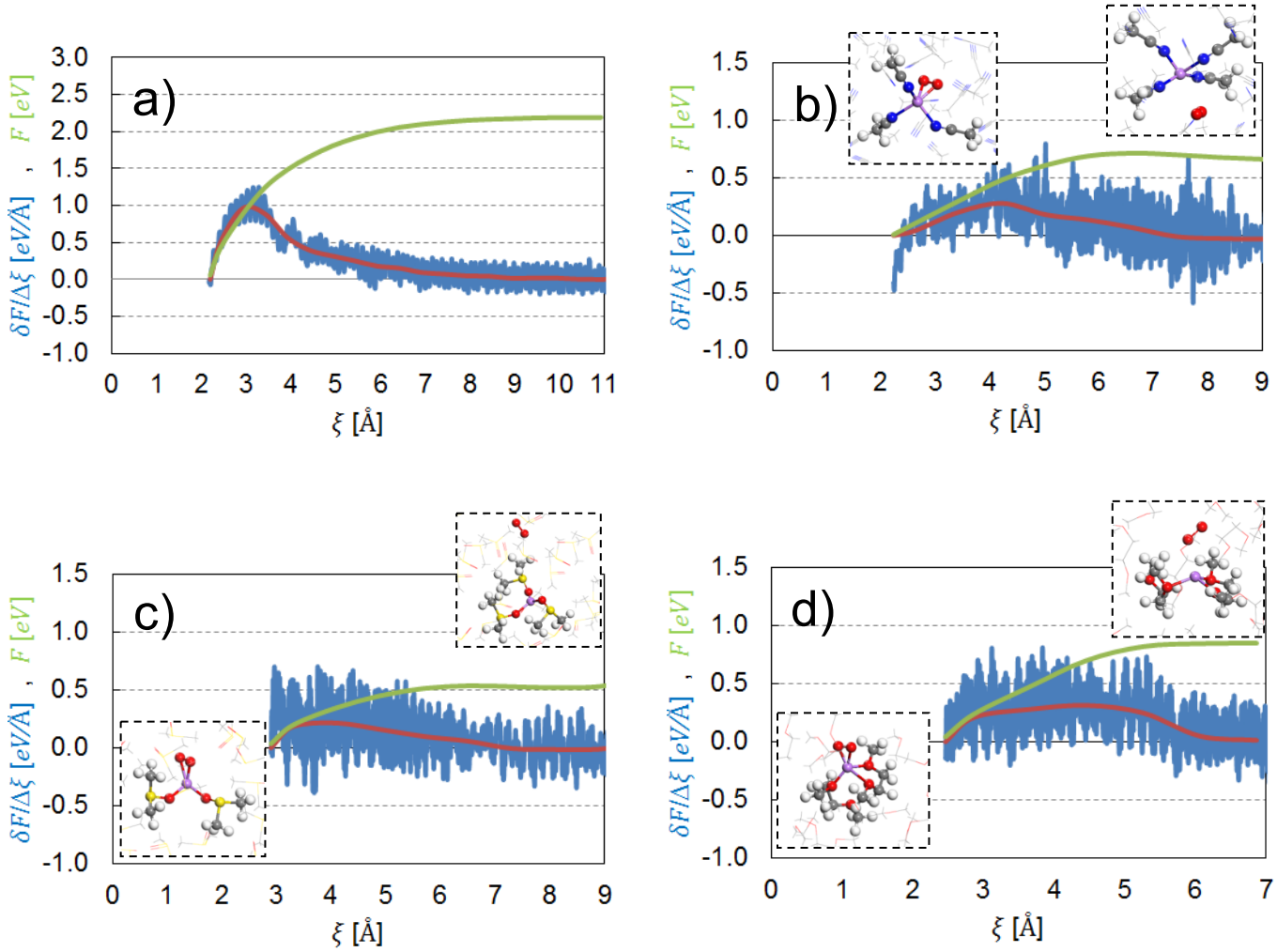

Figure S3. Free energy profiles of $LiO_2 \rightarrow Li + O_2$ reaction (dissociation) in a) vacuum, b) ACN, c) DMSO, and d) DME electrolytes resulting from Blue Moon ensemble AIMD simulations. Insets are showing intial and final configurations in each electrolyte. Blue curves correspond to the free energy gradients directly calculated by the simulations. Red curves are derived by averaging the free energy gradients. Green curves which are derived by integrating the red curves, correspond to the free energy (barrier).

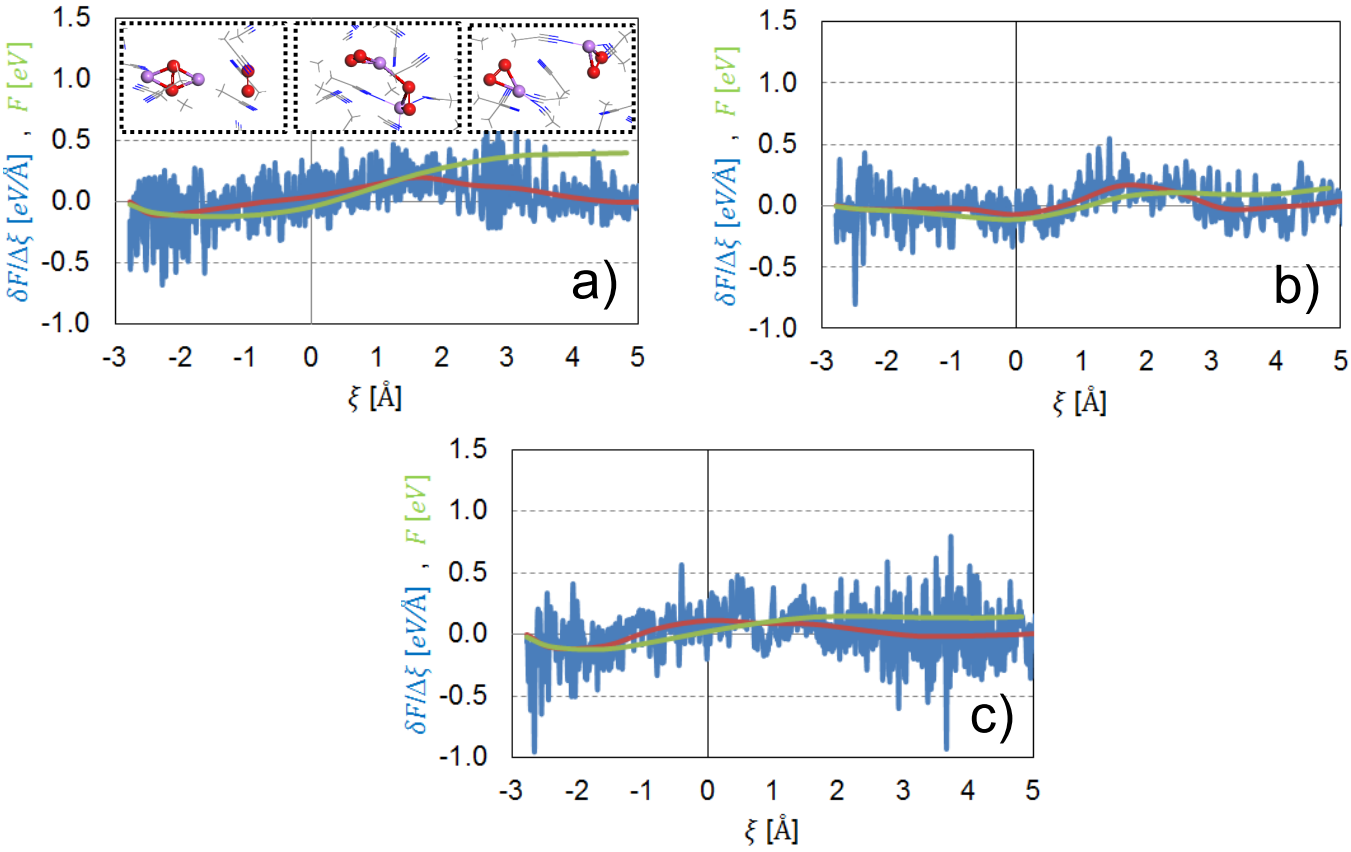

Figure S4. Free energy profiles of $Li_2O_2 + O_2 \rightarrow 2(LiO_2)$ reaction (disproportionation) in a) ACN, b) DMSO, and c) DME electrolytes resulting from Blue Moon ensemble AIMD simulations. Blue curves correspond to the free energy gradients directly calculated by the simulations. Red curves are derived by averaging the free energy gradients. Green curves which are derived by integrating the red curves, correspond to the free energy (barrier).