Supporting Information: Solvation Behavior of Carbonate-Based Electrolytes in Sodium Ion Batteries

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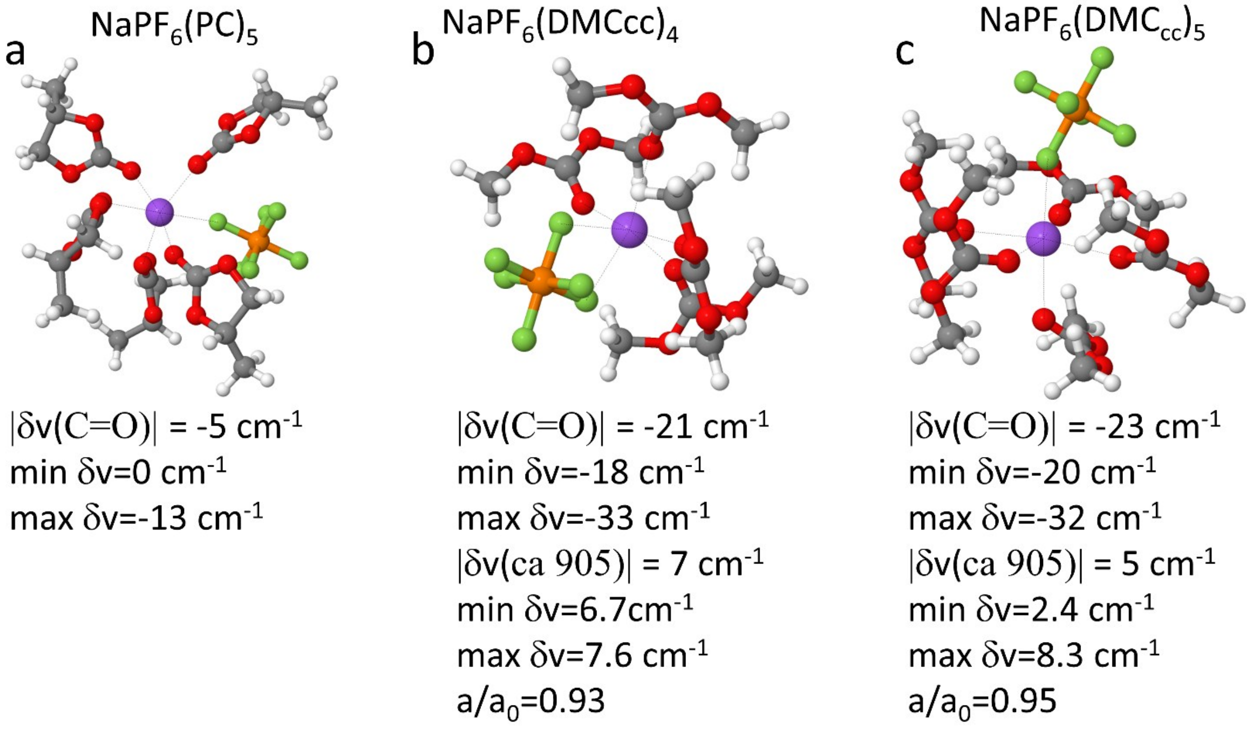

Figure S1. Optimized $NaPF_6$ solvates from PBE/6-31+G(d,p) DFT with SMD(PC) (a) and SMD(ether) solvation model (b-c). Shifts for the C=O vibrational mode and Raman activity a/a_0 upon Na^+ complexation are also shown in (b-c).

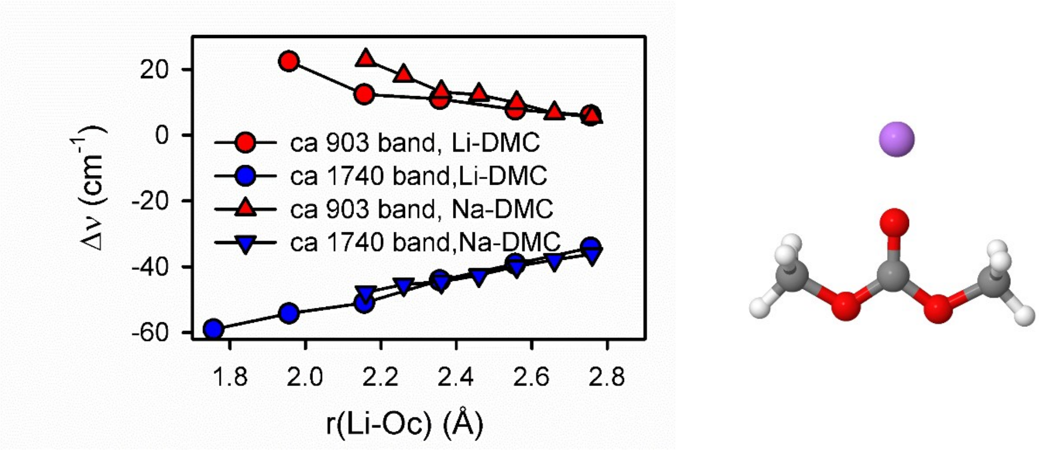

Figure S2: Band shifting due to metal coordination to DMC as a function of the distance between the metal cation and DMC carbonyl oxygen. The metal was moved along the C=O bond. The frequency shifts were calculated using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional with 6-31+G(d,p) basis set. SMD solvation model[1] developed by Truhlar group was used to implicitly account for the surrounding solvent as implemented in Gaussian g09 package[2] revision c. A built-in parameter set for dibutylether (ε=3.0473) was used in the SMD solvation model to approximate dielectric response of the low diectric constant environment of DMC.

Note that the shifts of both vibrational bands examined in this work for the Li-DMC complexes are similar to the shifts observed for the Na-DMC complexes for the metal – oxygen distances greater than 2.4 Å. This result indicates the Raman shifts are responding primarily to the ion-carbonyl interaction length and bond length the same way for both Li^+ and Na^+ and the smaller shifts observed for the Na-DMC complexes compared to the Li-DMC complexes are primarily due to the larger equilibrium Na-O(DMC) distances compared to the Li-O(DMC) distances in electrolytes.

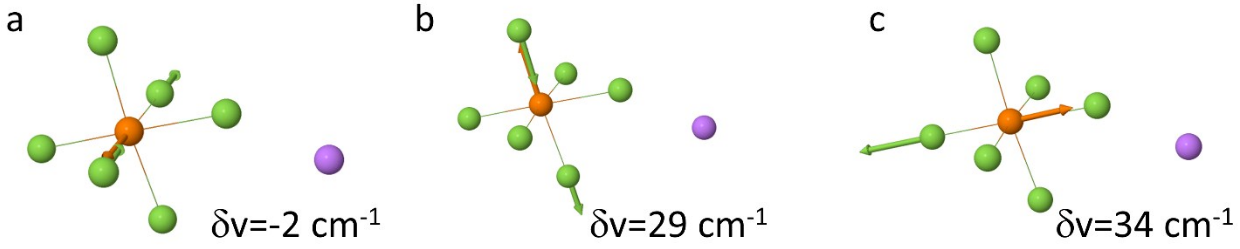

Figure S3. Shifts of the PF_6^- P-F stretch upon Li^+ monodentate binding to PF_6^- from M05-2X/aug-cc-pvTz DFT calculations with SMD(ether) solvation model. The P-F…Li^+ angle was constrained to 141°, while Li^+…F distance was constrained to 1.99 Å that is consistent with the distance found in condensed phase from MD simulations[3, 4] and neutron diffraction experiments for DMC-$LiPF_6$.[5]

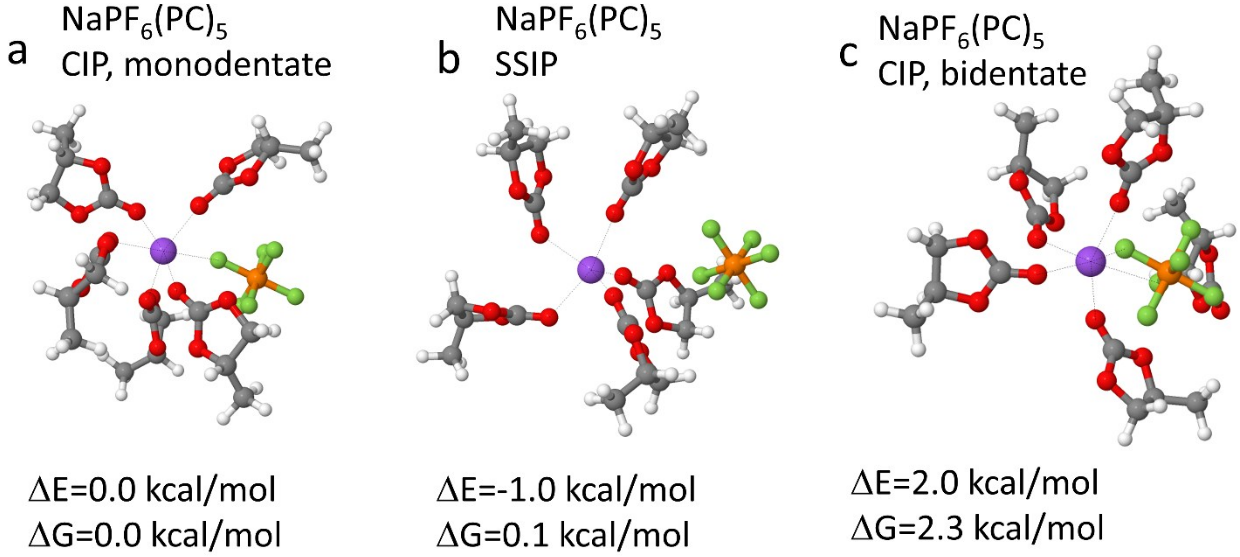

Figure S4. Relative free energies (ΔG) and energies (ΔE) for the $NaPF_6(PC)_5$ solvates surrounded by SMD(PC) implicit solvent model. The monodentate CIP (a), SSIP (b) and bidentate CIP (c) are shown. The bidendate configuration was obtained by constraining the Na…P distance to 3.3 Å to achieve bidentate binding.

References

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