

# Supporting Information

## Internally Referenced DOSY-NMR: A Novel Analytical Method in Revealing the Solution Structure of Lithium-ion Battery Electrolytes

Chi-Cheung Su<sup>a</sup>, Meinan He<sup>a</sup>, Rachid Amine<sup>b</sup>, Zonghai Chen<sup>a</sup> and Khalil Amine<sup>a,c,d\*</sup>

<sup>a</sup> Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA

<sup>b</sup> Materials Science Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA

<sup>c</sup> IRMC, Imam Abdulrahman Bin Faisal University (IAU), Dammam 34212, Saudi Arabia

<sup>d</sup> Material Science and Engineering, Stanford University, Stanford, CA 94305, USA

E-mail: amine@anl.gov

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## Experimental Section

The electrolyte components EC, PC, EMC, DMC, and LiPF<sub>6</sub> (BASF, battery grade) were used as-received. Toluene and benzene-*d*<sub>6</sub> (Sigma-Aldrich, anhydrous) were also used as-received. All samples were prepared in an argon atmosphere glovebox (<1 ppm of O<sub>2</sub> and H<sub>2</sub>O) by mixing the suitable molar ratio of each solvent, or by adding an appropriate molar ratio of each solvent to the LiPF<sub>6</sub> salt in a vial with stirring until a homogeneous solution is obtained.

Fourier transform infrared (FTIR) studies were conducted on a PerkinElmer Spectrum 100 FT-IT Spectrometer. The FTIR spectra were acquired in the attenuated total reflection (ATR) mode with 2 cm<sup>-1</sup> resolution with 1 scan to avoid evaporation of the volatile solvents, such as DMC and EMC. Raman measurements were carried out on a Renishaw inVia Raman Microscope with an exciting laser of 633 nm.

NMR analyses were carried out on a 300 MHz NMR spectrometer. Deuterated benzene was placed in an external coaxial insert and placed in the NMR tube with the samples. <sup>1</sup>H chemical shifts were referenced to benzene-*d*<sub>6</sub> at 7.16 ppm, and <sup>13</sup>C chemical shifts were referenced to benzene-*d*<sub>6</sub> at 128.39 ppm. All NMR experiments were performed on a 300 MHz spectrometer equipped with a z-axis gradient amplifier and an ATMA BBO probe with a z-axis gradient coil. The maximum gradient strength was 0.214 T/m. <sup>1</sup>H-DOSY and <sup>7</sup>Li-DOSY were performed by using the standard dstebpgp3s program, employing a double stimulated echo sequence, bipolar gradient pulses for diffusion, and 3 spoil gradients. The diffusion time was 200 ms, and the rectangular gradient pulse duration was 1200 μs. Gradient recovery delays were 200 μs. Individual rows of the quasi-2-D diffusion databases were phased and baseline corrected. Actual diffusion coefficients used for the D-α analysis were obtained with commercial software using the T1/T2 analysis module. As representative examples, the <sup>1</sup>H-DOSY attenuation curves for

toluene and EMC in pure EMC and 1:4 LiPF<sub>6</sub>:EMC electrolyte, as well as the <sup>7</sup>Li-DOSY attenuation curve for lithium in 1:4 LiPF<sub>6</sub>:EMC electrolyte are shown in Figures S7-S9.

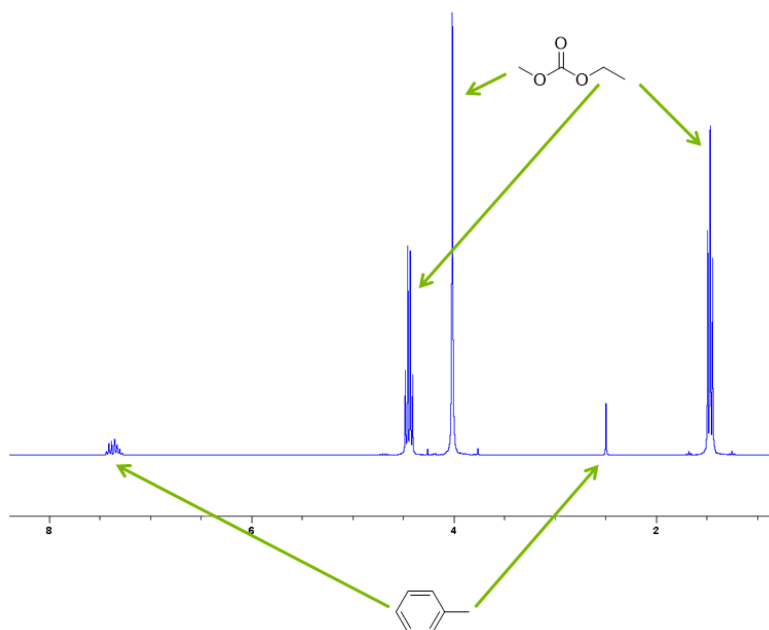


Figure S1. <sup>1</sup>H NMR spectrum of EMC with toluene added as internal reference.

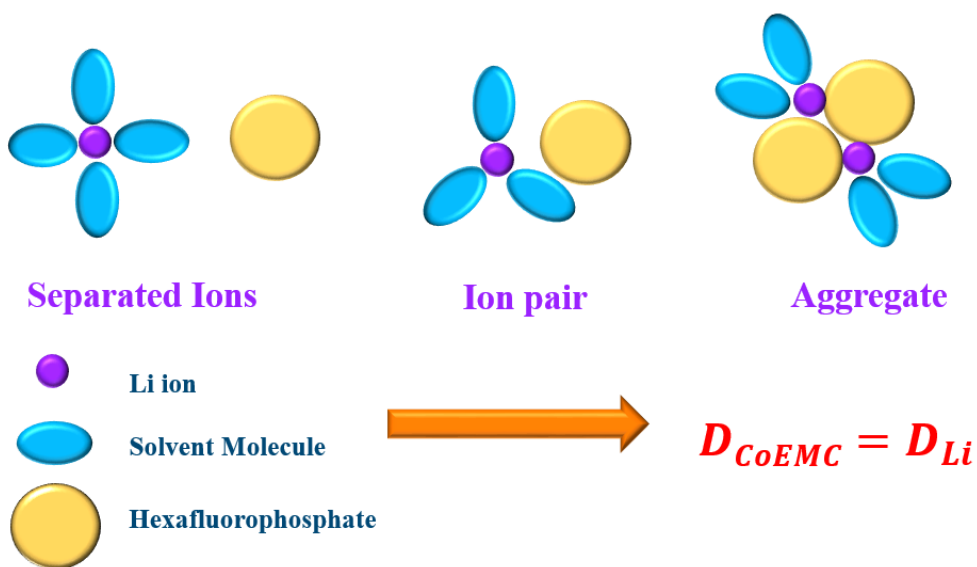


Figure S2. An illustration of lithium cations solvated by solvent molecules in separated ion, ion pair, and aggregate.

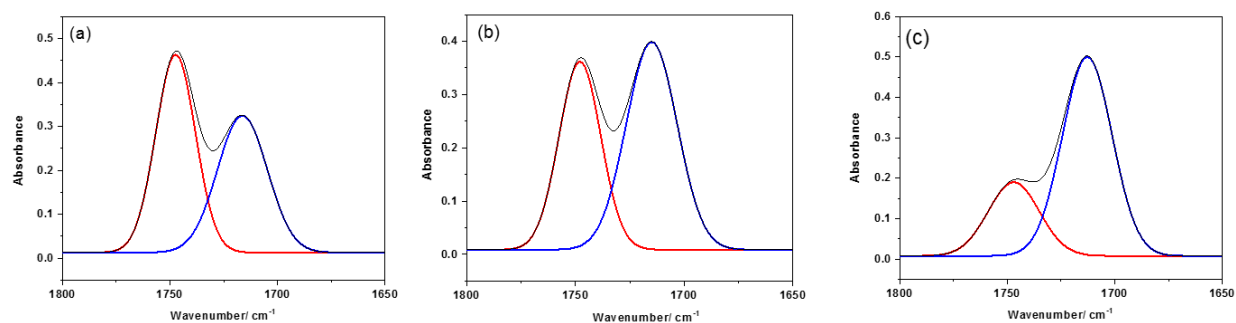


Figure S3. Deconvoluted FTIR spectra of carbonyl group in (a) 1:12 LiPF<sub>6</sub>:EMC, (b) 1:8 LiPF<sub>6</sub>:EMC, and (c) 1:4 LiPF<sub>6</sub>:EMC.

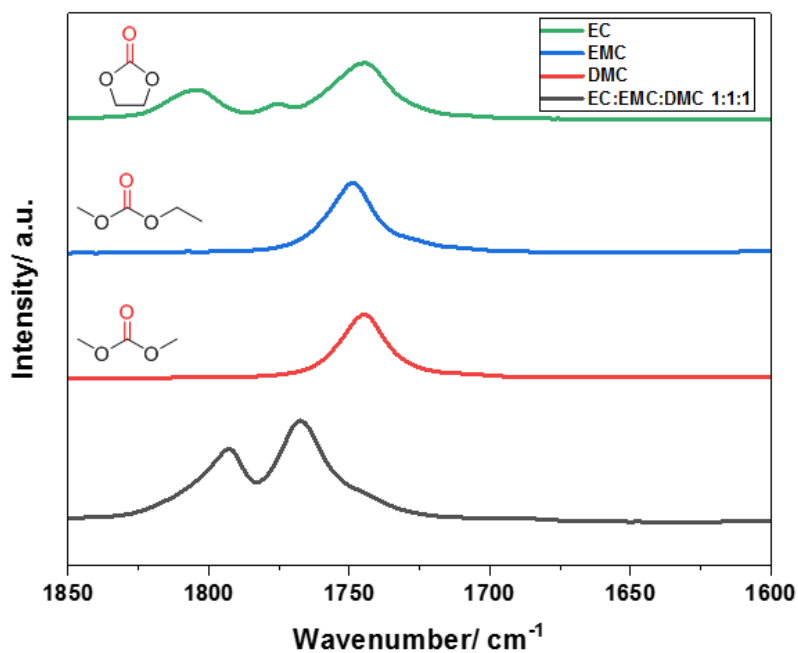


Figure S4. FTIR spectra of carbonyl group in EC, EMC, DMC, and 1:1:1 EC:EMC:DMC solution.

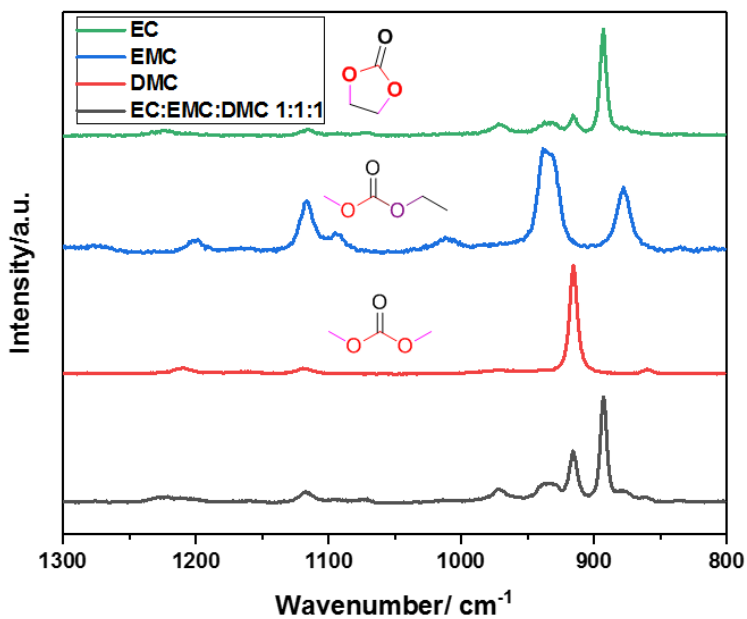


Figure S5. Raman spectra of C-O groups in EC, EMC, DMC, and 1:1:1 EC:EMC:DMC solution.

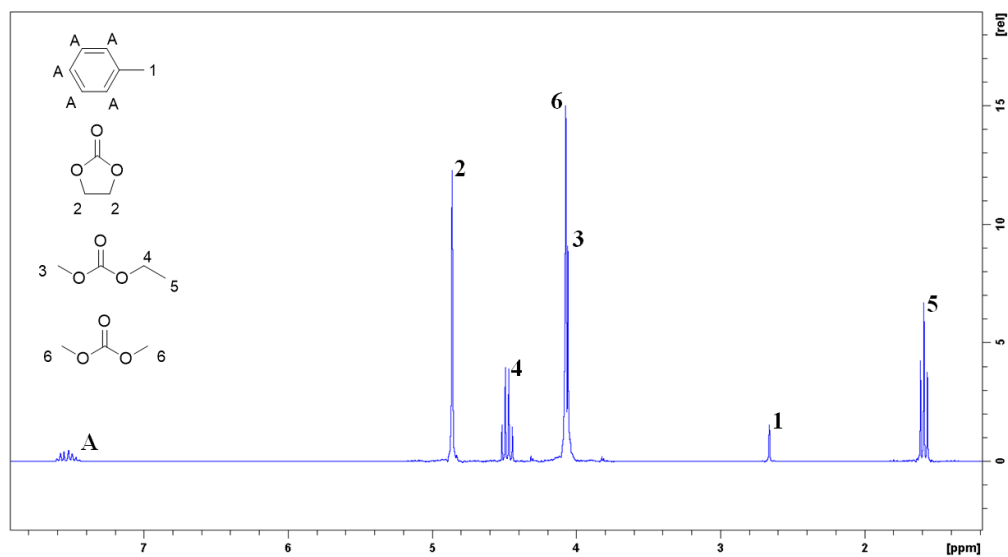


Figure S6. <sup>1</sup>H NMR spectrum of 1:1:1 EC:EMC:DMC solution with toluene added as internal reference.

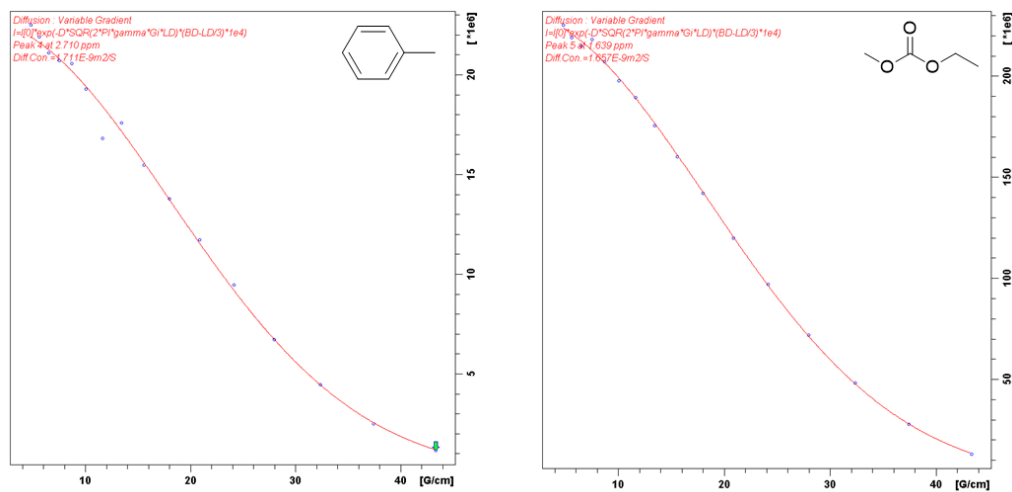


Figure S7.  $^1\text{H}$  DOSY attenuation curves for toluene and EMC in pure EMC.

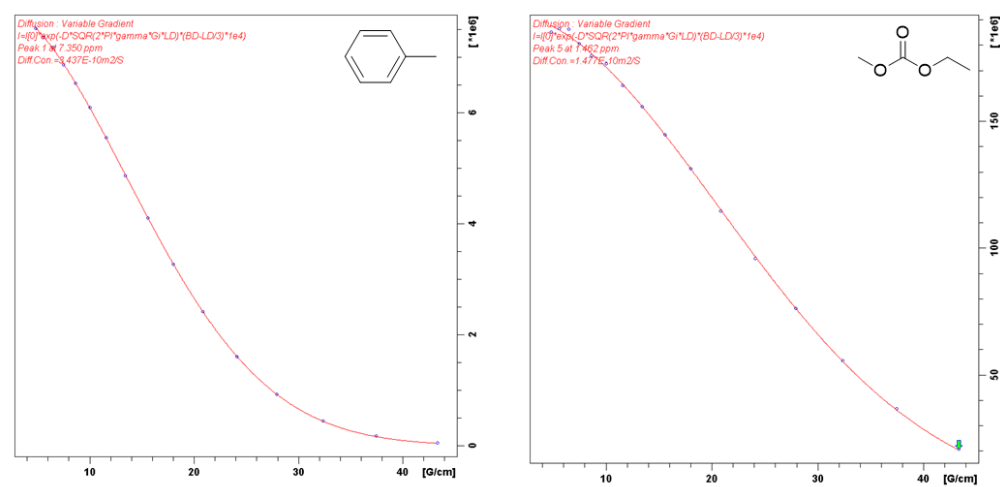


Figure S8.  $^1\text{H}$  DOSY attenuation curves for toluene and EMC in 1:4  $\text{LiPF}_6$ :EMC electrolyte.

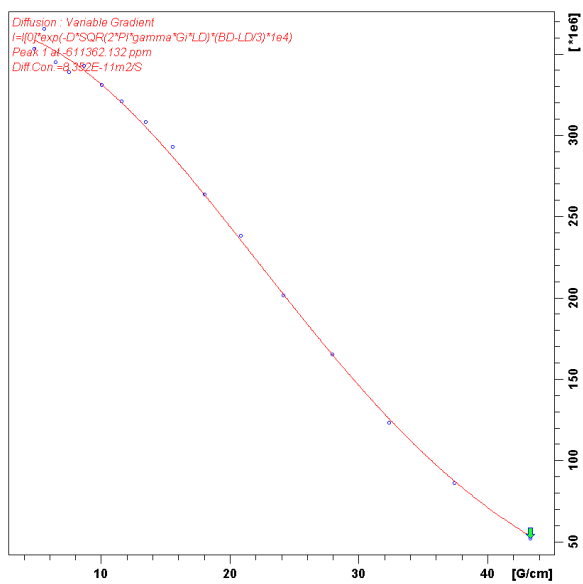


Figure S9.  $^7\text{Li}$  DOSY attenuation curves for lithium in 1:4  $\text{LiPF}_6$ :EMC electrolyte.

Table S1. The ratio of diffusion coefficients of toluene, EC, EMC, and DMC before and after the addition of  $\text{LiPF}_6$ .

Solution	$D_{\text{unsalted}}/D_{\text{salted}}$
Toluene	2.22
EC	3.79
EMC	2.96
DMC	3.14