

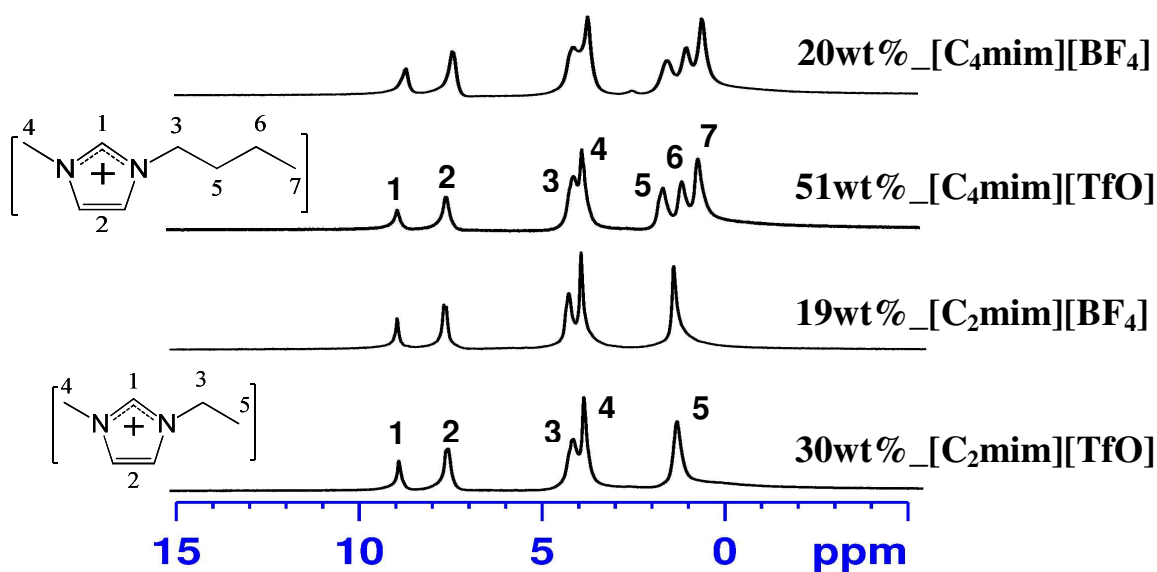
## Supporting Information

### Cation/Anion Associations in Ionic Liquids Modulated by Hydration and Ionic Medium

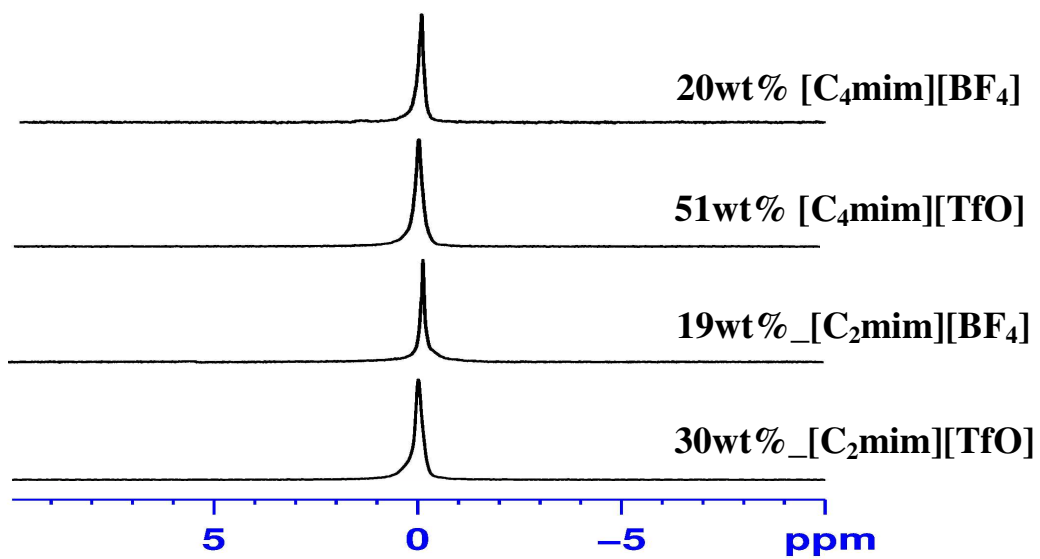
Jianbo Hou, Zhiyang Zhang, and Louis A. Madsen\*

#### Contents of supporting information

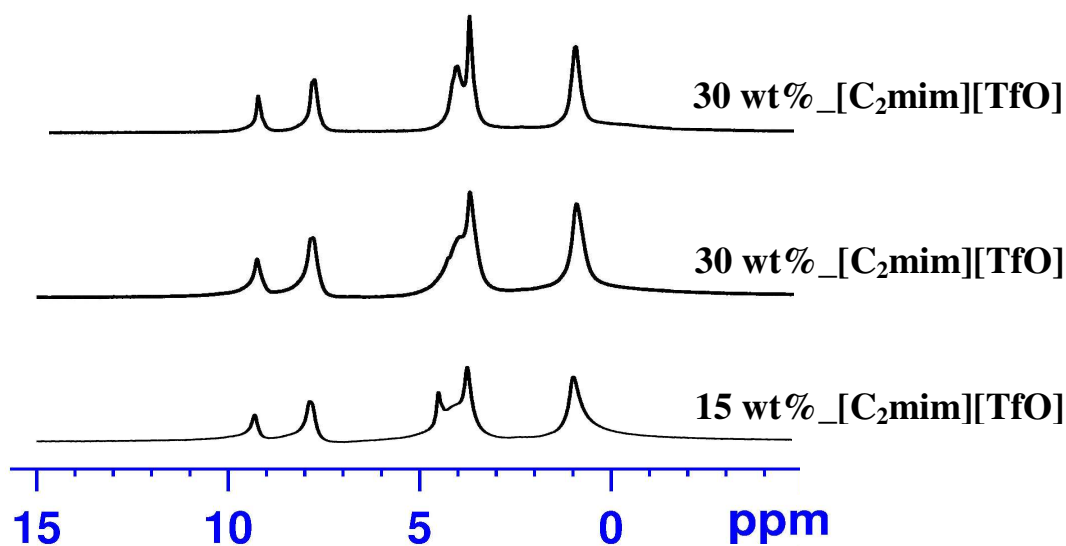
#### S.1 $^1\text{H}$ and $^{19}\text{F}$ NMR Spectra of ILs Inside Ionomers



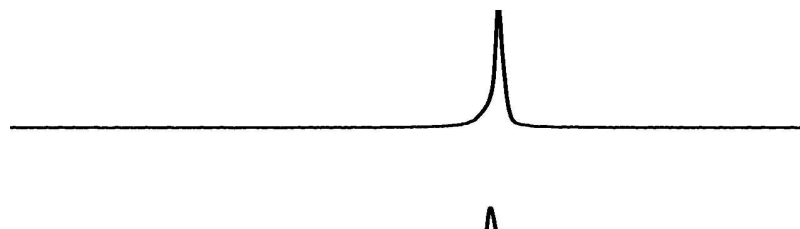
**Figure 1.** Representative  $^1\text{H}$  spectra for four  $\text{D}_2\text{O}$ -IL mixtures inside ionic polymer membranes at high uptake. Proton peaks are assigned using the numbers shown. Cation structures are shown on the left with IL uptake values listed on the right side of the spectra. Peak 3 includes residual  $^1\text{H}_2\text{O}$  signal due to slightly impure  $\text{D}_2\text{O}$ . From top to bottom, the hydration level  $\chi_{\text{water}}$  is 4.3, 2.6, 5.3, and 3.4, respectively. The linewidth varies from case to case, depending on IL uptake and hydration level.



**Figure 2.**  $^{19}\text{F}$  spectra for four  $\text{D}_2\text{O}$ -ILs mixtures inside ionic polymer membranes. Information on IL uptake and hydration level is identical to that shown in Figure 1.



**Figure 3.** Representative comparison of  $^1\text{H}$  spectra for  $[\text{C}_2\text{mim}][\text{TfO}]\text{-D}_2\text{O}$  mixtures inside ionic polymer membranes as a function of IL uptake and hydration level. IL uptakes are listed on the right side of each spectrum. From top to bottom, the hydration level  $\chi$  is 3.4, 0.7 and 1.68, respectively. The linewidth increases with the decrease in hydration level and IL uptake.



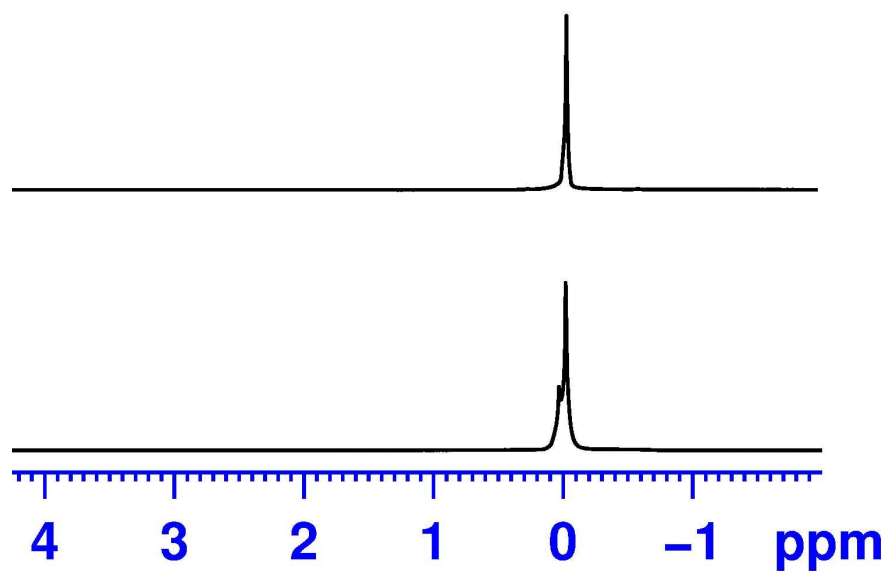
**30 wt%\_[C<sub>2</sub>mim][TfO]**

**30 wt%\_[C<sub>2</sub>mim][TfO]**

**15 wt%\_[C<sub>2</sub>mim][TfO]**

**Figure 4.** Comparison of <sup>19</sup>F spectra for [C<sub>2</sub>mim][TfO]-D<sub>2</sub>O mixture inside ionic polymer membranes as a function of IL uptake and hydration level. IL uptake and hydration level are identical to those shown in Figure 3. Similar to Figure 3, the linewidth increases with the decrease in hydration level and IL uptake.

## **S.2 <sup>19</sup>F NMR Spectra for free ILs**



**Figure 5.**  $^{19}\text{F}$  spectra for free state TfO-based (top) and  $\text{BF}_4$ -based ILs (bottom). One peak shows up for  $[\text{TfO}]^-$  and two peaks for  $[\text{BF}_4]^-$  as two boron isotopes ( $^{10}\text{B}$  and  $^{11}\text{B}$ ) are present.