Supplementary Information

Extractive Electrospray Ionization Mass Spectrometry of Ionic Liquids

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Figures and Tables

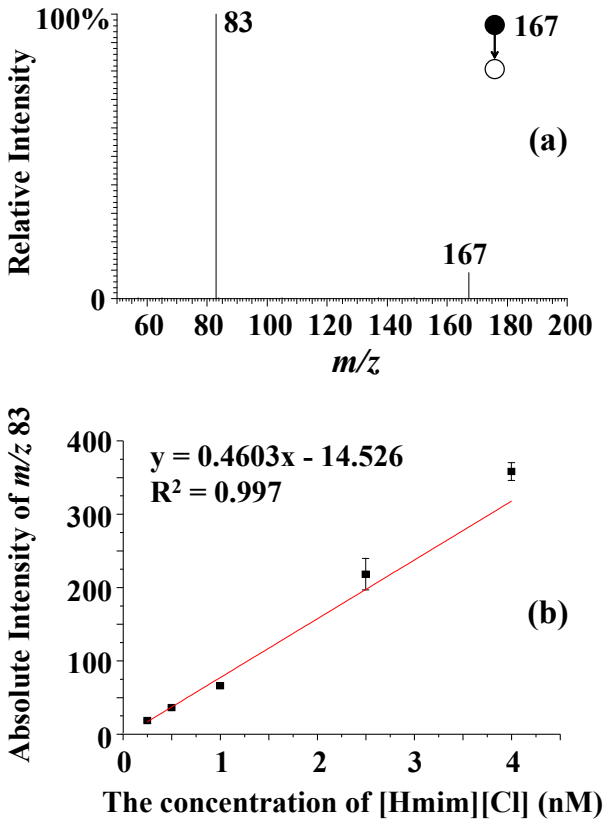

Figure S-1: (a) EESI-MS/MS analysis of isolated $Hmim^+$ cation (*m/z* 167) from [Hmim][Cl] ionic liquid; (b) signal intensity of the fragment ion at *m/z* 83 as a function of [Hmim][Cl] concentration. We did not study linearity in a broader range using the experimental configuration in Figure 1a, because sampling of high-concentration ILs resulted in chemical contamination of the instrument.

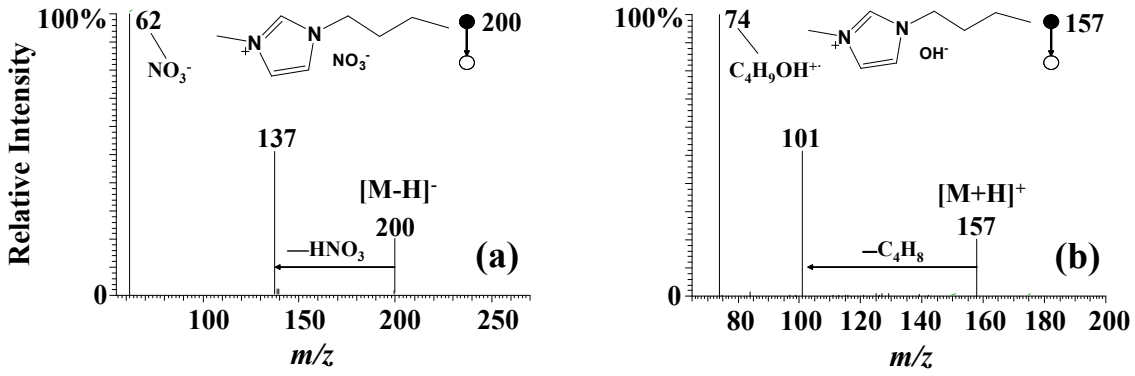

Figure S-2: (a) The precursor ions at *m/z* 200 observed in EESI(-) of [Bmim][NO_3] in methanol dissociate via the loss of NO_3 anions (*m/z* 62) as well as the neutral loss of HNO_3 (*m/z* 137). The net negative charge of [Bmim][NO_3] complex results from the deprotonation of Bmim cation, which is quite likely given its acidic nature (Cui, X., Zhang, S., Shi, F., Zhang, Q., Ma, X., Lu, L., Deng, Y.: The influence of the acidity of ionic liquids on catalysis. *ChemSusChem*. 3(9), 1043-1047, 2010). (b) MS/MS analysis of a protonated $[CA+H]^+$ complex (*m/z* 157) observed for the more basic [Bmim][OH] IL in which protonation is likely to occur at OH^- anion. The neutral loss of 56 u fragment (C_4H_8) was observed (*m/z* 101), characteristic for Bmim fragmentation. The other fragment at *m/z* 74 is tentatively assigned to $C_4H_9OH^{+\bullet}$ ions.

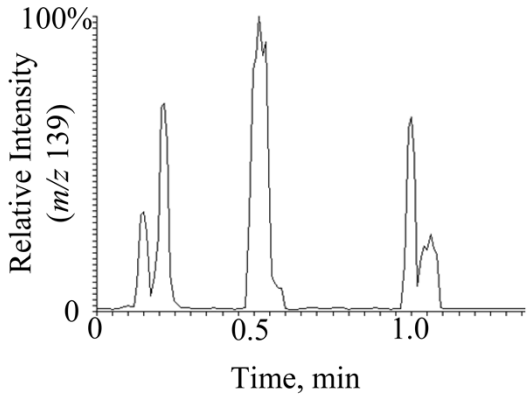

Figure S-3: Single-ion chromatogram of Bmim signal at *m/z* 139 during the EESI-MS analysis of [Bmim][BF_4] using the 'droplet' configuration (Figure 1b).Three successive samplings are shown. IL signals, e.g., C^+ or A^-, rapidly increased when the loaded pipette tip was brought in front of the neutral spray followed by the rapid signal decrease to the background level when the pipette was removed. Instability of the peak shape is attributed to hand sampling.

Table S-1: The observation of protonated and deprotonated CA complexes for different ILs by EESI-MS in correlation with their acid-base properties. CA signals are marked as **+++,** ++ or +, depending on their intensity: "+" = LTQ intensity < 10^2; "++" = LTQ intensity between 10^2-10^3; "+++" = LTQ intensity > 10^3. Non-observed signals are marked as —.

ILs	Acid-base properties	CA+H	CA-H
[Bmim][OH]	**Basic**	+++	—
[Omim][OH]	**Basic**	+++	—
[Bmim][PF_6]	**Weak basic**	+++	++
[Aemim][PF_6]	**Weak basic**	+++	+
[Bmim][Ac]	**Weak basic**	++	+
[Bmim][NO_3]	**Weak acidic**	—	+++
[Emim][HSO_4]	**Acidic**	—	—
[Bmim][HSO_4]	**Acidic**	—	—
[BuPy][BF_4]	**Acidic**	—	—
[Bmim][Cl]	**Neutral**	—	—