

Supporting Information

One of the Distinctive Properties of Ionic Liquids over Molecular Solvents and Inorganic Salts: Enhanced Basicity Stemming from the Electrostatic Environment and “Free” Microstructure

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A Ultraviolet absorption spectrum of [Bmim]Cl:Pb²⁺

To obtain the ultraviolet absorption spectrum of [Bmim]Cl:Pb²⁺ solution, aliquots of PbCl₂ aqueous solution were added into a small vessel, and then some [Bmim]Cl was added after the fully evaporation of water to achieve a 10 ppm (molar fraction) solution of PbCl₂ in [Bmim]Cl. The obtained mixture was stirred thoroughly at 90 °C, and then was shifted to a quartz cuvette and placed in the sample cell of a Shimadzu UV-2550 UV-visible spectrophotometer. The pure [Bmim]Cl was used as reference, and the absorption spectrum was measured in the range 200-400 nm at room temperature. Scanning was repeated five times for each measurement, and the average of the maximum absorption wavelength of each record was taken as the final value. The uncertainty of the maximum absorption wavelength was ±0.5 nm.

The ultraviolet absorption spectrum of Pb²⁺ in [Bmim]Cl at room temperature is shown in Figure S1, where the wavelength of maximum absorbance was 285 nm. This wavelength was larger than that measured in NaCl (273 nm),^{1,2} implying a stronger basicity of [Bmim]Cl than NaCl. It should be pointed out that although the peak of absorbance was asymmetric, the wavelengths of the peak area in Figure S1 were generally larger than 273 nm, thus the basicity of [Bmim]Cl can still be considered stronger than that of NaCl.

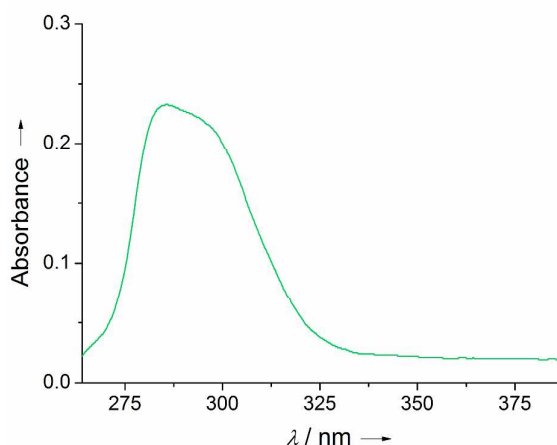


Figure S1. Ultraviolet absorption spectrum of Pb²⁺ in [Bmim]Cl at room temperature

B Calculation details of the $V_{s,m}$ and $\bar{I}_{s,m}$ of NaCl and [Bmim]Cl

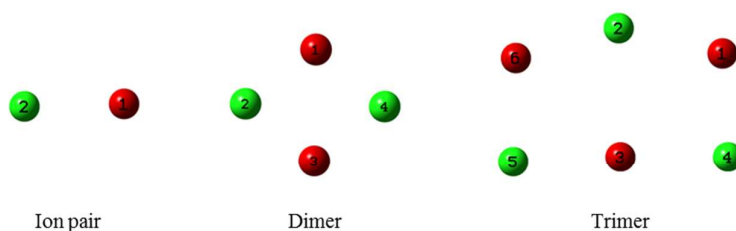


Figure S2. Optimized geometries of the ion pair, dimer, and trimer of NaCl at the B3LYP/6-311++G(d,p) level

In the NaCl dimer, the two Cl^- are identical, so the $V_{s,m}$ and $\bar{I}_{s,m}$ values of the dimer can be taken from any Cl^- . As a result, the $V_{s,m}$ and $\bar{I}_{s,m}$ are $-36.1 \text{ kcal mol}^{-1}$ and 7.68 eV , respectively, which are shown in Figure 5 of the manuscript. Similarly, in the [Bmim]Cl dimer, the two Cl^- are also almost identical, and the values of $V_{s,m}$ and $\bar{I}_{s,m}$ are $-55.9 \text{ kcal mol}^{-1}$ and 5.95 eV , respectively.

In the NaCl trimer, there are two types of Cl^- : one type is surrounded by two cations (Cl^- 4 and Cl^- 5 in Figure S2), and the other type is surrounded by three cations (Cl^- 2). The latter type of Cl^- is the Cl^- in which we are interested, as it is typical for a trimer system. Thus the $V_{s,m}$ and $\bar{I}_{s,m}$ values of the typical anion Cl^- 2 were taken for discussing the basicity of the NaCl trimer— $6.5 \text{ kcal mol}^{-1}$ and 8.36 eV , respectively, as given in Figure 5. Similarly, in the [Bmim]Cl trimer, the $V_{s,m}$ and $\bar{I}_{s,m}$ values of the typical anion (Cl^- 42 in Figure 4) were taken for discussing the basicity of the [Bmim]Cl trimer, $-37.5 \text{ kcal mol}^{-1}$ and 6.17 eV , respectively as given in Figure 5.

References

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- (2) Dryden, J. S.; Heydon, R. G. Ultraviolet A-Band Absorption in NaCl-Pb^{2+} and Clustering of Lattice-Defects. *J. Phys. C: Solid State Phys.* **1983**, *16*, 5363-5373.