Supporting Information

Structural, dynamical, and electronic properties of the ionic liquid 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM] [TFSI]

Kana Ishisone, Guido Ori, Mauro Boero

University of Strasbourg, Institut de Physique et Chimie des Matériaux de Strasbourg, CNRS, UMR

7504, 23 rue du Loess, F-67034 France

Table S1. Computed vibrational frequencies via normal mode analysis to complement the information of the IR spectrum for [EMIM]-cis [TFSI] dimer and their assignments: ip, in-plane; op, out-of-plane; sym, symmetric; asym, antisymmetric.



Figure S1. Variation of the main parameters controlling the simulation. (a) Temperature and classical energy (=Kohn Sham energy + Ionic kinetic energy). (b) Residual pressure. The system reaches the thermal equilibration in about 30 ps.



Figure S2. Each center of mass position of [EMIM] (orange) and [TFSI] (purple). The atoms color code adopted here and in the following is white for H, gray for C, blue for N, red for O, yellow for S and cyan for F.



Figure S3. Pair correlation function between [EMIM] and [TFSI] center of mass (COM). The conformers of [TFSI] are characterized from the colored region of C-S-S-C torsion angle in Figure 4 in the manuscript. The peak positions of the first coordination shell are different between [EMIM]-*cis* [TFSI] and [EMIM]-*trans* [TFSI].



Figure S4. Pair correlation functions of the H atoms of the cation and (a) N atoms, (b) F atoms of the anion involved in the formation of H-bonds.



Figure S5. The number of [EMIM] molecules which has H---O bonds smaller than 3.0 Å around *cis* or *trans* [TFSI]. The average number of [EMIM] molecules around *cis* [TFSI] is 4.12, and 4.23 for *trans* [TFSI].



Figure S6. Distribution of the two most relevant out-of-plane angles (θ_1 : Ceth2-Ceth1-N2 angle, θ_2 : Ceth2-Ceth1-N2-C1 torsion angle) of the [EMIM] cation as extracted from the dynamics.



Figure S7. C-S-S-C torsion angle change during the simulation time on each [TFSI] anion.



Figure S8. Trajectories of Ceth2-Ceth1-N2-C1 torsion angle of [EMIM] cation during the simulation.



Figure S9. Average Bader charges of each atom in (a) [EMIM] *cis*-[TFSI] and (b) [EMIM] *trans*-[TFSI] dimers in vacuum. We recall that a Bader analysis provides a partitioning of the electron density distribution, hence being is the most appropriate scheme in DFT-based approaches where $r(\mathbf{x})$ is the physical quantity.



Figure S10. Wannier functions centers (orange spheres) of [EMIM][TFSI].



Figure S11. (a) C-F-wannier center angle distribution of 4 wannier centers surrounding one F atom. These 4 wannier centers are labeled as its angle, from smallest (1st) to largest (4th). The distribution of C-F-wannier angle of each labeled wanier center is plotted in the same graph. (b) The distance F-wannier and C-wannier of "1st" wannier centers, which is between C and F. Most of the wannier centers are located at the distance F-wannier=0.4~0.5 Å, C-wannier=0.8~1.0 Å, which means the wannier centers are located close to F atoms.



Figure S12. Wannier functions centers distribution around N and C atoms. In [EMIM], the bond N-C is ionic bond, and the C-C bond is covalent. In [TFSI], 2 Wannier functions centers are placed between N-S bonds but the other 2 Wannier functions centers are not used in any chemical bonds, which means there are lone pair electrons around N atom.



Figure S13. Coordination number of [TFSI] around [EMIM] in the first coordination cell (COM distance is less than 9.3 Å).

Reference

[1] J. Kiefer, J. Fries and A. Leipertz, Experimental Vibrational Study of Imidazolium-Based Ionic Liquids: Raman and Infrared Spectra of 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide and 1-Ethyl 3methylimidazolium Ethylsulfate, *Appl. Spectroscopy*, 2007, **61**, 1306–1311.