# ESI for:

# Combining EXAFS spectroscopy and Molecular Dynamics simulations to understand the structural and dynamic properties of an Imidazolium Iodide Ionic Liquid

Valentina Migliorati,<sup>\*a</sup>, Alessandra Serva<sup>a</sup>, Giuliana Aquilanti,<sup>b</sup> Luca Olivi<sup>b</sup>, Sakura Pascarelli,<sup>c</sup> Olivier Mathon<sup>c</sup> and Paola D'Angelo<sup>\*a</sup>.
<sup>a</sup> Dipartimento di Chimica, Università di Roma "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy.
<sup>b</sup> Elettra-Sincrotrone Trieste S.C.p.A s.s. 14, km 163.5, I-34149 Basovizza, Trieste, Italy.
<sup>c</sup> European Synchrotron Radiation Facility, BP 220 38043, Grenoble Cedex, France.
\* valentina.migliorati@uniroma1.it, p.dangelo@uniroma1.it

## **Online Supplementary Information**

## 1 Details on Dynamic properties analysis

The ion diffusion coefficients D have been determined from the mean square displacement (MSD) using the Einstein relation:

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{\langle ||\mathbf{r}(t) - \mathbf{r}(0)||^2 \rangle}{t}$$
(1)

where  $\mathbf{r}(0)$  is the initial position of a given species and  $\mathbf{r}(t)$  is its position at time t. The standard GROMACS tool g\_msd has been used to calculate the diffusion coefficients.<sup>1</sup>

A detailed view of the dynamics of the imidazolium cation has been obtained using the reorientational correlation function, defined as:

$$C_l^{\alpha}(t) = \langle P_l(\mathbf{u}^{\alpha}(t) \cdot \mathbf{u}^{\alpha}(0)) \rangle \tag{2}$$

where  $P_l$  is the  $l^{th}$  rank Legendre polynomial, and  $\mathbf{u}^{\alpha}(t)$  is a unit vector in a certain direction  $\alpha$  at time t. The reorientational relaxation time  $\tau_{\alpha}$ , defined as the rotation time of the  $\mathbf{u}^{\alpha}$  vector, is given by the time integral:

$$\tau_{\alpha} = \int_{0}^{\infty} C_{l}^{\alpha}(t) dt \tag{3}$$

For our analyses we used l = 1 and the normal vector to the ring plane spanned by the carbon atoms CR and CWs. The reorientational correlation functions have been computed using the TRAVIS software.<sup>2</sup>

The ion-pair and ion-cage dynamics have been analyzed using two continuous time correlation functions  $C_C^{cage}(t)$  and  $C_C^{pair}(t)$  defined as:

$$C_C^{cage/pair}(t) = N \langle \sum_{t_0=0}^{T-t} \beta_{i,j}(t_0+t) \beta_{i,j}(t_0) \rangle_{i,j}$$

$$\tag{4}$$

where N is a normalization constant, T is the total simulation time, and the function  $\beta_{ij}$  has the value 1 as long as the criteria which define an aggregate species are fulfilled, and switches to 0 as soon as the criteria fail for the first time. The angle brackets mean the average over all ion pairs while the summation indicates the average over all starting times. The criterion for the ion-cage dynamics is that a certain distance has to be smaller than or

equal to the first minimum of the corresponding radial distribution function. On the contrary, in the ion-pair dynamics analysis the cation-anion distance is calculated and the nearest neighbors are taken into account according to this distance definition. In this case the  $\beta_{ij}$  function goes to zero when the neighborhood relations change, i.e. if the formely first neighbor is no longer the first neighbor. In contrast to continuous time correlation functions, also intermittent functions,  $C_I^{cage}(t)$ , can be calculated. The definition of this functions is almost the same, with the difference that interruptions of the criteria fulfillment are now allowed up to a specific duration. In other words, dissociation and recombination of the aggregates is allowed up, as long as the duration of this process does not exceed a given time threshold. The ion-pair and ion-cage dynamics has been analyzed using the TRAVIS software.<sup>2</sup> Note that in all of the analyses which use cutoff values for distances involving the imidazolium cation, the imidazolium ring geometrical center has been taken into account in the calculations.

## References

- H. J. C. Berendsen, D. van der Spoel and R. van Drunen, Comput. Phys. Commun., 1995, 91, 43–56.
- [2] M. Brehm and B. Kirchner, J. Chem. Inf. Model., 2011, 51, 2007–2023.
- [3] M. Nakakoshi, M. Shiro, T. Fujimoto, T. Machinami, H. Seki, M. Tashiro and K. Nishikawa, *Chem. Lett.*, 2006, **35**, 1400–1401.
- [4] J. N. Canongia Lopes, J. Deschamps and A. A. H. Pádua, J. Phys. Chem. B, 2004, 108, 2038–2047.
- [5] W. L. Jorgensen, J. P. Ulmschneider and J. Tirado-Rives, J. Phys. Chem. B, 2004, 108, 16264–16270.



Figure S1. Crystal structure of  $[C_4mim]I$ . Iodine atoms are in red, carbon in brown, nitrogen in cyan and hydrogen in white.



Figure S2. Instantaneous cation-anion coordination number (n) distribution calculated from the MD simulation of liquid  $[C_4mim]I$ .



Figure S3. Comparison between the EXAFS total theoretical signal calculated from the MD simulations of solid (blue line) and liquid (red line)  $[C_4 \text{mim}]I$ .



Figure S4. Definition of the  $\omega_{HCR}$  and  $\theta_{HCR}$  angles. (A)  $\omega_{HCR}$  is the angle formed by the CR-HCR and the CR-I vectors. (B)  $\theta_{HCR}$  is the angle between the normal vector to the ring plane and the ring geometrical center-I vector.



Figure S5. Spatial distribution functions (SDFs) of the anions (magenta) and cations (blue) around the cation, calculated from the MD simulation of liquid  $[C_4 mim]I$ .



Figure S6. Cation-Anion radial distribution functions, g(r)'s, calculated from the MD simulation of liquid  $[C_4 mim]$ I in six different time slices of 0.5 ns and from the entire MD trajectory (black line).



Figure S7. Cation-Anion radial distribution functions, g(r)'s, calculated from the MD simulation of liquid [C<sub>4</sub>mim]I carried out starting from a random initial configuration (black line) and from the crystallographic structure (red line).



Figure S8. Cation-Anion radial distribution functions, g(r)'s, calculated from the two MD simulations of liquid  $[C_4mim]I$  carried out at 300 K (red line) and at 400 K (black line).



Figure S9. Convergence analysis of the dynamic properties. (A) Correlation function of ion-pair dynamics,  $C_C^{Pair}(t)$ , calculated from the MD simulation at 300 K in three different time slices of 0.3 ns and from the entire MD trajectory (blue line). (B) Correlation function of ion-pair dynamics,  $C_C^{Pair}(t)$ , calculated from the MD simulation at 400 K in three different time slices of 0.1 ns and from the entire MD trajectory (blue line). (C) Correlation function of ion-cage dynamics,  $C_C^{Cage}(t)$ , calculated from the MD simulation at 300 K in two different time slices of 5 ns and from the entire MD trajectory (blue line). (D) Correlation function of ion-cage dynamics,  $C_C^{Cage}(t)$ , calculated from the MD simulation at 400 K in three different time slices of 3 ns and from the entire MD trajectory (blue line).

Atoms	R (Å)
1 H	2.98
2 H	3.05
1 H	3.11
2 H	3.30
1 H	3.34
2 H	3.42
1 H	3.51
1 H	3.55
1 H	3.58
1 C	3.60
1 H	3.64
1 H	3.67
1 C	3.68
1 N	3.72
1 H	3.89
$2 \mathrm{C}$	3.94
1 C	3.98
2 C	3.99

Table S1. I-H, I-C and I-N distances (R) as derived from the crystallographic structure of  $[C_4mim]I$  within a cut-off range of 4 Å.<sup>3</sup>

Atom type	q (e)	$\sigma$ (Å)	$\epsilon ~({\rm kJ}~{\rm mol}^{-1})$
Ν	+0.15	3.25	0.71128
$\operatorname{CR}$	-0.11	3.55	0.29288
CW	-0.13	3.55	0.29288
C1	-0.17	3.50	0.27614
C2	+0.01	3.50	0.27614
$\mathbf{CS}$	-0.12	3.50	0.27614
$\operatorname{CT}$	-0.18	3.50	0.27614
HCR	+0.21	2.42	0.12552
HCW	+0.21	2.42	0.12552
H1	+0.13	2.50	0.12552
$\mathrm{HC}$	+0.06	2.50	0.12552
Ι-	-1.00	5.40	0.29308

Table S2. Partial atomic charges and Lennard-Jones paramaters for each atom type of the imidazolium cation and I<sup>-</sup> ion used in this work. The force field parameters for the  $[C_4 mim]^+$  cation are taken from the Lopes and Padua force field,<sup>4</sup> and for the anion from OPLS.<sup>5</sup> The atom labeling is shown in Figure 1 and, as far as the hydrogen atoms are concerned, the hydrogen atoms bonded to CR, CW and C1 are labeled HCR, HCW and H1, while all of the other hydrogen atoms are named HC.