Electronic Supporting Information

Nanostructuration of Ionic Liquids: impact on the cation mobility.
A multi-scale study.

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1 Rotation of the whole cation around its center-of-mass:

In the framework of the Sears approximation, \( I(Q,t)^R \), the self (incoherent) intermediate scattering function of an isotropic rotation over a sphere of radius \( b \) writes:

\[
I(Q,t)^R = j_0^2(Qb) + \sum_{l=1}^{\infty} (2l+1) j_l^2(Qb) F_l(t)
\]

(S1)

The time-dependent term \( F_l(t) \) is the first order rotational auto-correlation function:

\[
F_l(t) = \langle P_l(\cos \alpha(t)) \rangle
\]

(S2)

where \( \alpha(t) \) is the angle between \( \vec{u}(t) \), accounting for the particle orientation at time \( t = 0 \) and its orientation at time \( t \) later. \( P_l \) is the Legendre polynomial of degree \( l \). For times longer than few ps, \( F_1(t) \) and \( F_2(t) \) Eq.(S2) simplifies by just considering two correlation times \( 3\tau_1 \) and \( \tau_1 \) :

\[
I(Q,t)^R = j_0(Qb)^2 + 3 j_1(Qb)^2 e^{-t/3\tau_1} + 5 j_2(Qb)^2 e^{-t/\tau_1} + \ldots
\]

(S3)

The dynamics of bulk BMIM-TFSI has recently been investigated by Nuclear Magnetic Resonance Relaxation Dispersion (NMRD) and PFG-NMR over a wide range of temperatures. At 298 K, Seyedlar et al. measure the room temperature rotational correlation times: \( \tau_R^{BMIM} = 400 \) ps.

To our knowledge, up-to-date, no molecular rotational correlation times have been reported for OMIM-BF\(_4\). In order to estimate the contribution of the tumbling motion of the OMIM cation around the molecular center-of-mass, we rescale the BMIM-TFSI NMR derived correlation time according to Stokes-Einstein-Debye's law:

\[
\tau_R^{OMIM} = \frac{\eta_{OMIM-BF_4}}{\eta_{BMIM-TFSI}} \left( \frac{R_{OMIM}}{R_{BMIM}} \right)^3 \tau_R^{BMIM}
\]

(S4)

Following Tokuda et al.', the viscosities are \( \eta_{BMIM-TFSI} = 50 \) mPa.s, \( \eta_{OMIM-BF_4} = 92 \) mPa.s and the radius of the cations (equivalent sphere matching the 3D structure of the cations as deduced from ab-initio calculations) \( R_{OMIM} = 3.3 \) Å and \( R_{BMIM} = 3.73 \) Å. A rough numerical estimate of the isotropic rotational correlation time of OMIM at \( T = 298 \) K is \( \tau_R^{OMIM} = 1062 \) ps.

Even at the highest ToF QENS energy resolution used in this study (13 µeV), the maximum correlation accessible time is of the order of few hundred of ps. A correlation time of \( \tau_R \) in the ns range is therefore not detectable. As shown on Fig.S1 this contribution is not detectable in NSE neither. The total dynamical structure factor of OMIM then reduces to Eq.S6.

2 Derivation of the total dynamical structure factor:

As we have shown in the SI section 1 above that in the present study the molecular tumbling motion can be neglected, three contributions describe the dynamics of the IL cation: side-chain motions, local diffusion within aggregates and long-range diffusion. As they occur in different time windows, we suppose that they are independent. \( S(Q,\omega)^T \), the total dynamical structure factor, is therefore a convolution of the dynamical structure factor Eq.4, 5 and 8 related to these individual modes:

\[
S(Q,\omega)^T = S(Q,\omega)^{CF} \otimes S(Q,\omega)^{loc} \otimes S(Q,\omega)^{lr}
\]

\[
= I_A(Q)L_{lr}(Q,\omega) + I_B(Q)L_{lr+Loc}(Q,\omega)
\]

\[
+ I_C(Q)L_{lr+Loc}^{sc}(Q,\omega)
\]

\[
+ I_D(Q)L_{lr+Loc+sc}(Q,\omega)
\]

(S6)
**Figure S1** OMIM long-range translational diffusion NSE contribution, $I(Q,t)_{\text{inc}}^{\text{cation}}$ (Eq. 17) at $Q = 1.07 \, \text{Å}^{-1}$ and 298 K. The dotted red line is the estimated (see SI 1 section) contribution $Eq.S3$ of the isotropic rotation, with a radius $b = R_{\text{OMIM}} = 3.73 \, \text{Å}$, of the OMIM molecule around its center-of-mass with a correlation time $\tau_c = 1062 \, \text{ps}$ (Eq.S4). The full blue and red lines are respectively the total intermediate scattering function of OMIM if the tumbling motion of the molecule is neglected or taken into account.

Where $L_{x+y}(Q, \omega)$ is a Lorentzian line of HWHM $\Gamma_{x+y} = \Gamma_x + \Gamma_y$ and

\begin{align}
I_A(Q) &= pA_{\text{loc}}(Q)A_{\text{sc}}(Q) + (1-p)A_{\text{loc}}(Q) \\
I_B(Q) &= pA_{\text{sc}}(Q)(1-A_{\text{loc}}(Q)) + (1-p)(1-A_{\text{loc}}(Q)) \\
I_C(Q) &= pA_{\text{loc}}(Q)(1-A_{\text{sc}}(Q)) \\
I_D(Q) &= p(1-A_{\text{sc}}(Q))(1-A_{\text{loc}}(Q))
\end{align}

(S7) (S8) (S9) (S10)

The three dynamical contributions of equation S6 take place on different time ranges. The side-chain reorientational and dihedral motions are faster than the local diffusion which is itself expected to be faster than the long range one so that $\Gamma_{x} \gg \Gamma_{\text{loc}} \gg \Gamma_{\text{lr}}$. Equation S6 can then be simplified:

\[ S(Q, \omega)_{\text{inc}}^{\text{cation}} \approx I_1(Q)L_{\text{lr}}(Q, \omega) + I_2(Q)L_{\text{loc}}(Q, \omega) + I_3(Q)L_{\text{sc}}(Q, \omega) \]  

(S11)

with:

\begin{align}
I_1(Q) &= pA_{\text{loc}}(Q)A_{\text{sc}}(Q) + (1-p)A_{\text{loc}}(Q) \\
I_2(Q) &= pA_{\text{sc}}(Q)(1-A_{\text{loc}}(Q)) + (1-p)(1-A_{\text{loc}}(Q)) \\
I_3(Q) &= p(1-A_{\text{sc}}(Q))
\end{align}

(S12) (S13) (S14)

In conclusion the dynamical structure factor proposed by this model is composed by three Lorentzian relaxations whose each HWHM are linked to a unique dynamical mode while the intensities are combination of the different EISF.

### 3 Implementation of the Gaussian model:

To determine $D_{\text{loc}}$, $\sigma_{\text{loc}}$ and $\tau$, $L_{\text{loc}}(Q, \omega)$ is fitted with the Gaussian model in the time domain.

The intermediate scattering function of the Gaussian model is:

\[ I(Q,t)_{\text{inc}}^{\text{loc}} = \exp \left( -Q^2 \sigma_{\text{loc}}^2 \right) \left( 1 - \exp \left( \frac{-D_{\text{loc}}t}{\sigma_{\text{loc}}^2 (1 + 2D_{\text{loc}}Q^2 \tau)} \right) \right) \]  

(S15)

and the intermediate scattering function corresponding to the diffusion within the aggregates is:

\[ L(Q,t)_{\text{inc}}^{\text{loc}} = \exp \left( -\frac{t}{\tau_{\text{loc}}} \right) \]  

(S16)
where $\tau_{loc} = \hbar / T_{loc}$. 

$(1 - A_{loc}(Q))L(Q,t)_{loc}^{inc}$ is then fitted with $I(Q,t)_{loc}^{inc} - A_{loc}(Q)$ to obtain the Gaussian parameters $D_{loc}$, $\sigma_{loc}$ and $\tau$.

**Figure S2** Selected QENS spectra (LET, ISIS, Chilton-Didcot, UK) of bulk OMIM-BF$_4$ at 298 K as measured on LET at three energy resolutions 81, 22 and 13 $\mu$eV from top to bottom. The red thick line is the fit Eq.10 and the three dynamical contributions are shown: side-chains (Eq.4, thin red line), local diffusion within an aggregate (Eq.5, green line) and long-range diffusion of the whole cation (Eq.8, blue line).
Figure S3 Typical NSE spectrum of bulk OMIM-BF$_4$ at 298 K ($Q = 0.96 \text{ Å}^{-1}$). The total fit according to Eq.4 is shown as the thick red line. The individual dynamical contributions are shown with the same color code as in Fig.3B on an extended time range to highlight their short time behavior.

Figure S4 Line width (HWHM) of the QENS side-chains contribution Eq.3 fitted on the ToF data measured at the lower energy resolution (81 µeV). The fairly $Q$ independence of $\Gamma_{sc}$ indicates the reorientational nature of this contribution.

Figure S5 Gaussian fit of the low $Q$ range of the EISF deduced from the fit of the ToF data at the three energy resolution shown on Fig.4. The full line is the fit with a jump on three equivalent sites placed on a circle of radius $r = 1.5$ Å(Eq.15). The dotted line is the fit with a simple Guinier-like Gaussian function of the form of Eq.7. The later fit leads to a characteristic distance of the cation side-chain motion $<u_{sc}^2> = 1.2$ Å.
Figure S6 (A) Same figure as Fig.6. The fits of the experimental data with a single exponential (full red line) and with a stretched exponential (dotted line) are shown. (B) Same as (A) but on a log-log scale for a better clarity of the short time part of the curve.

References


