Supporting information

1 Computational details

The average number of neighbor atoms n within a sphere radius R, is available in terms of the integral

$$n(R) = \int_0^R 4 \cdot \pi \cdot \rho \cdot r^2 \cdot g(r) dr \tag{1}$$

in our case R is the first minimum of the corresponding radial distribution function (RDF), see table 1, ρ is the particle density, r is the distance and $g(r)$ is the RDF.

Table 1: Explicit length of the first minimum of the radial distribution function for C10 and C10. All length are given in pm.

system	R
RESP	684
NBO	684
SEN	735

To investigate the dynamical properties of the hydrogen bonds, we calculated the intermittent time correlation functions $C_I^{\mathrm{HB}}(t)$ and the continuous time correlation function $C_C^{\mathrm{HB}}(t)$. $C_I^{\mathrm{HB}}(t)$ is defined as

$$C_I^{\mathrm{HB}}(t) = \frac{\langle \delta h(0) \delta h(t) \rangle}{\langle \delta h^2 \rangle} = \frac{\langle h(0)h(t) \rangle - \langle h \rangle^2}{\langle h \rangle - \langle h \rangle^2} \approx \frac{\langle h(0)h(t) \rangle}{\langle h \rangle} \tag{2}$$

with $h(t)$ being the population variable. $h(t)$ is unity when a particular hydrogen-bromide pair is hydrogen-bonded at a particular time, and zero otherwise.

The angle brackets denote an possible average over all hydrogen donor and acceptor pairs and all starting times. The average number of hydrogen bonds is denoted as $\langle h \rangle$. By definition, $C(t)$ describes the probability that a particular tagged hydrogen bond is intact at a time t, given that it was intact at time zero. A reformation of the hydrogen bond after bond breaking is permitted.

$C_C^{\mathrm{HB}}(t)$ is defined by the following function:

$$C_C^{\mathrm{HB}}(t) = \frac{\langle \delta h(0) \delta H(t) \rangle}{\langle \delta h(0) \delta H(0) \rangle} = \frac{\langle h(0) H(t) \rangle - \langle h \rangle \langle H \rangle}{\langle h \rangle - \langle h \rangle \langle H \rangle} \approx \frac{\langle h(0) H(t) \rangle}{\langle h \rangle} \tag{3}$$

$H(t)$ is equal to one, if the tagged H-Br distance remains continuously hydrogen bonded during the time duration t, according to the definition below, and zero otherwise.

The presence of a hydrogen bond is given, if two criteria are satisfied. First, the C-H$\cdots$Br angle amounts between $150°$ and $180°$ and second, the distance between the hydrogen atom and bromide anion is less or equal than the first minimum of the corresponding radial distribution function, see table 2.

In order to determine the relaxation time τ, the $C_I(t)$ and $C_C(t)$ curves were fitted with the following formula

$$f(t) = a \cdot exp\left(-\frac{t}{b}\right) + c \cdot exp\left(-\frac{t}{d}\right) + e \cdot exp\left(-\frac{t}{f}\right) \tag{4}$$

where a, b, c, d, e, and f are the fitting parameters. The relaxation time τ is given by the time integral

$$\tau = \int_0^\infty f(t)dt. \tag{5}$$

The anion cation contact dynamics was analyzed using a time correlation function $C_I^{\text{cage}}(t)$ in analogy to equation 2 and the continuous time correlation function $C_C^{\text{cage}}(t)$ analogous to equation 3:

$$C_I^{\text{cage}}(t) = \frac{\langle \delta p(0) \delta p(t) \rangle}{\langle \delta p^2 \rangle} = \frac{\langle p(0)p(t) \rangle - \langle p \rangle^2}{\langle p \rangle - \langle p \rangle^2} \approx \frac{\langle p(0)p(t) \rangle}{\langle p \rangle} \tag{6}$$

where the population variable $p(t)$ is unity when the ions are in contact at time t, and zero otherwise. The angle brackets mean the average over all ion pairs and all starting times. The average probability of an ion pair is defined as $\langle p \rangle$. By definition, $C(t)$ describes the probability that a particular tagged ion pair is intact at time t, provided that it was intact at time zero. A reformation of an ion pair is permitted.

$$C_C^{\text{cage}}(t) = \frac{\langle \delta p(0) \delta P(t) \rangle}{\langle \delta p(0) \delta P(0) \rangle} = \frac{\langle p(0)P(t) \rangle - \langle p \rangle \langle P \rangle}{\langle p \rangle - \langle p \rangle \langle P \rangle} \approx \frac{\langle p(0)P(t) \rangle}{\langle p \rangle} \tag{7}$$

$P(t)$ is the survival index, which is one if the tagged ion pair remains intact continuously until the time t, and otherwise zero. $C_C^{\text{cage}}(t)$ provides a definition of the lifetime of a tagged ion pair. The criterion for a tagged ion pair is the distance between the centers of mass of the cation and the anion, which has to be smaller or equal than the first minimum of the corresponding radial distribution function. This is the reason why this number includes not only one particular ion pair, but one cation with all it's surrounding anions. Therefore, we chose the term ion cage dynamics.

In our analysis, it was found that $C_C^{\text{cage}}(t)$ and $C_I^{\text{cage}}(t)$ cannot be described by a single-exponential function or stretched exponential function. Therefore, we used the same fitting formula as before, see Eqn. 4 for the determination of τ.

Please note, the values in brackets in table 4 are not determined by integration of the fitting formula, because they cannot be described with the three weighted exponentials in the whole time range. To obtain the relaxation times we integrated numerically until $C_I^{\text{cage}}(t) = 0.7$. For the smaller values of $C_I^{\text{cage}}(t)$ we used the fitting formula, integrated from $C_I^{\text{cage}}(t) = 0.69$ until infinity and added the two values.

To investigate another aspect of the local dynamics we calculated next to the time correlations described above, reorientational correlation functions $C_\alpha(t)$, which describe the reorientational dynamics. $C_\alpha(t)$ is defined as

$$C_\alpha(t) = \langle P_2(\mathbf{u}(t) \cdot \mathbf{u}(0)) \rangle \tag{8}$$

with $\mathbf{u}$ being a unit vector pointing from one atom to another one. Alternatively, the vector $\mathbf{u}$ constitutes the normal vector to the plane which is spanned by the carbon atoms C2, C4 and C5. $P_2(x)$ is the second Legendre polynomial.

The reorientational relaxation time τ_α is given by the time integral

$$\tau_\alpha = \int_0^\infty C_\alpha(t)dt \tag{9}$$

The integration is performed in to steps. First $C_\alpha(t)$ is fitted by the Kohlrausch–Williams–Watts equation:[1]

$$C_\alpha(t) \approx exp\left(-\left(\frac{t}{a}\right)^b\right) \tag{10}$$

where a and b are the fitting parameters. This function is then analytically integrated.

Table 2: Explicit length of the first minimum of the radial distribution function for Br$^-$ and H2, H4, H5 and the center of mass of the cation, respectively. All length are given in pm.

system	H2	H4	H5	center of mass
RESP	483	455	455	770
NBO	438	479	471	778
SEN	567	616	596	675

2 Structural properties

2.1 Radial distribution functions
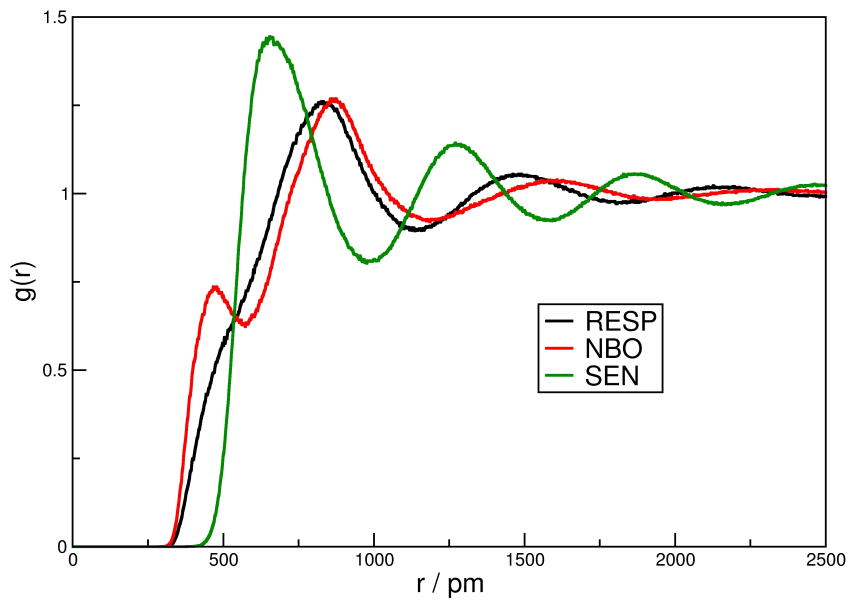
Figure 1: Radial distribution function for N1 and N1.

The RDF for the RESP system is characterized by a strong peak around 810 pm with a weak shoulder around 490 pm. The RDF for the NBO system has nearly the same features. The mean peak can be found at 860 pm. The shoulder at 470 pm is more pronounced than in the RESP system. This shoulder is due to the cation being located above or below the imidazolium ring and the main peak is caused by the cations in the ring plane. Due to the Lennard–Jones contacts, the distances between the cations can be relatively short. There are some experimental evidences that this parallel arrangement of the imidazolium rings is present in the liquid state of other ionic liquids containing the $[C_4C_1im]$ cation.[2,3] In the SEN system, Lennard–Jones contacts are absent because the areas above and below the ring plane are occupied by the anions. For this reason the RDF of the SEN system has only one main peak at 660 pm.

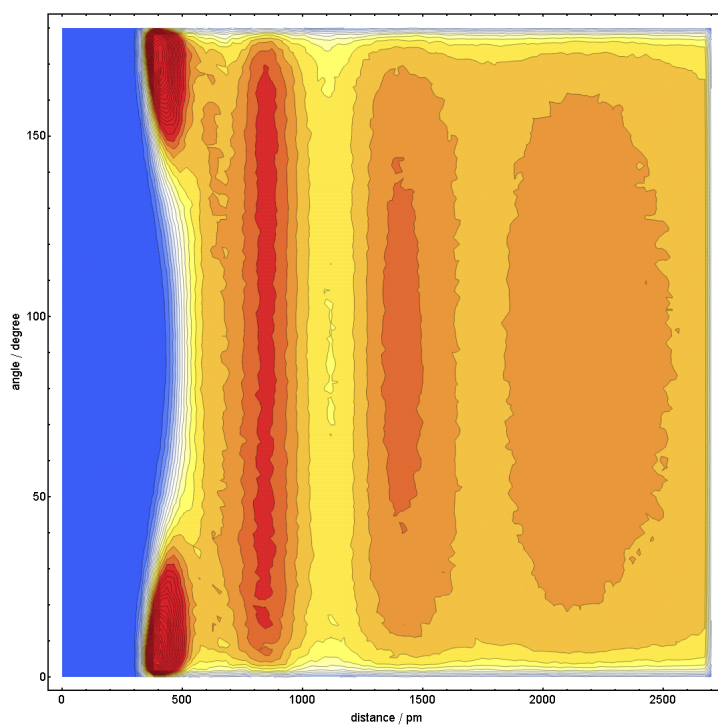## 2.1.1 Spatial distribution functions of the anions and cations

Figure 2: Radial angular distribution function for the RESP system. The angle between the normal vector of the plane, which is defined by C2, C4 and C5, of one cation and of all other is plotted against the distance between their ring centers. The color is an extent for the probability of finding a given angle in a given distance, low probabilities result in blue color, high ones in red.
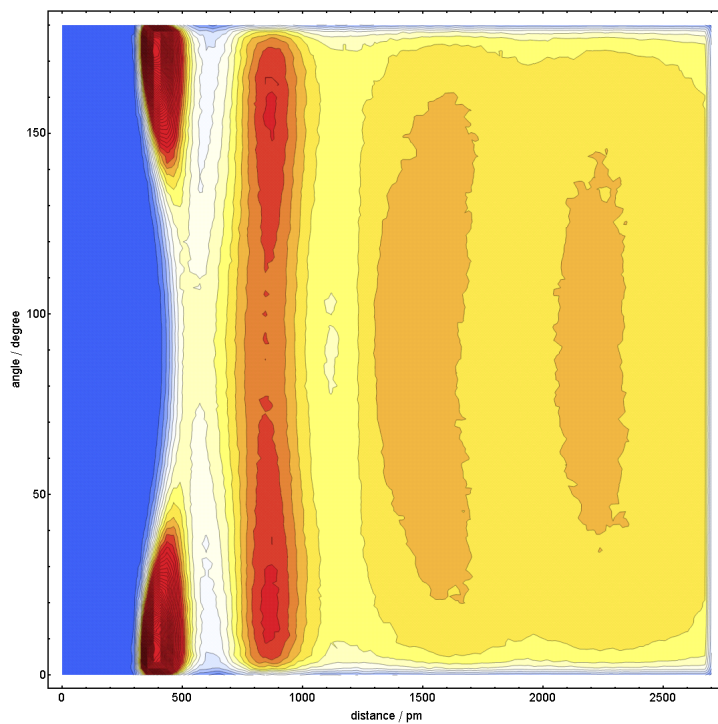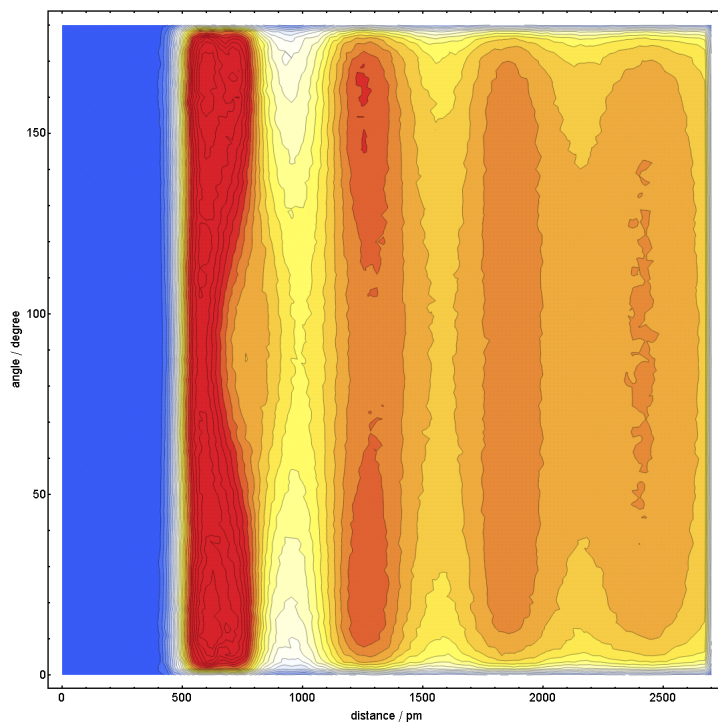
Figure 3: Radial angular distribution function for the NBO system. The angle between the normal vector of the plane, which is defined by C2, C4 and C5, of one cation and of all other is plotted against the distance between their ring centers. The color is an extent for the probability of finding a given angle in a given distance, low probabilities result in blue color, high ones in red.

Figure 4: Radial angular distribution function for the SEN system. The angle between the normal vector of the plane, which is defined by C2, C4 and C5, of one cation and of all other is plotted against the distance between their ring centers. The color is an extent for the probability of finding a given angle in a given distance, low probabilities result in blue color, high ones in red.
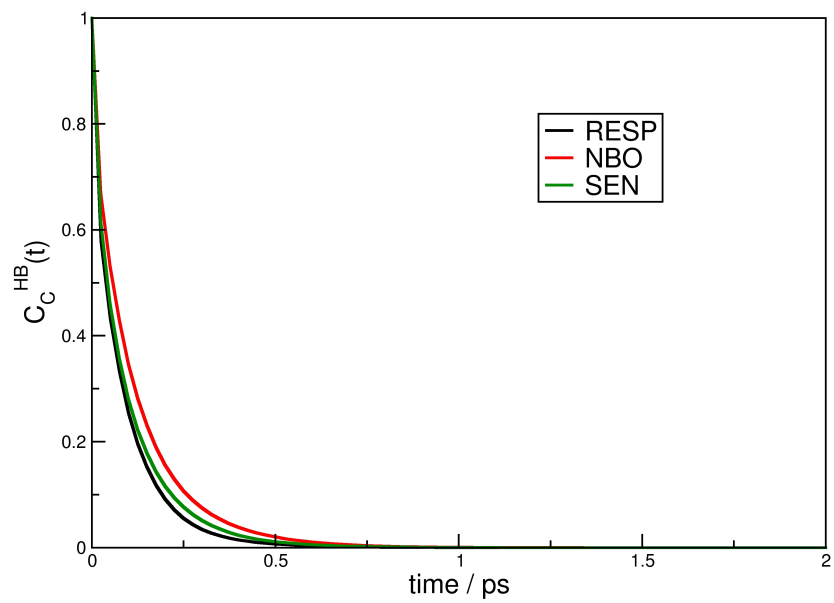
3 Dynamical properties

3.0.2 Hydrogen bond dynamics

Figure 5: $C_C^{\mathrm{HB}}(t)$ of H2 for the different systems at 373 K.
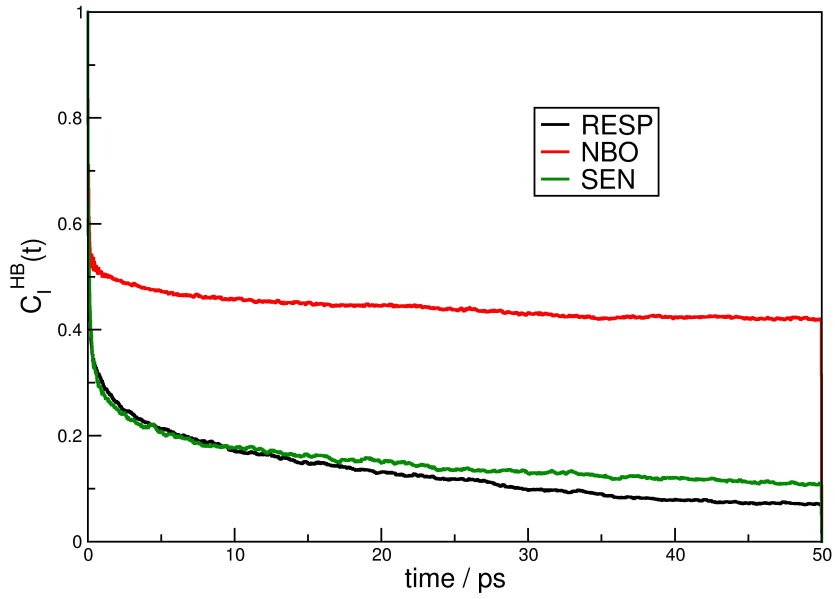
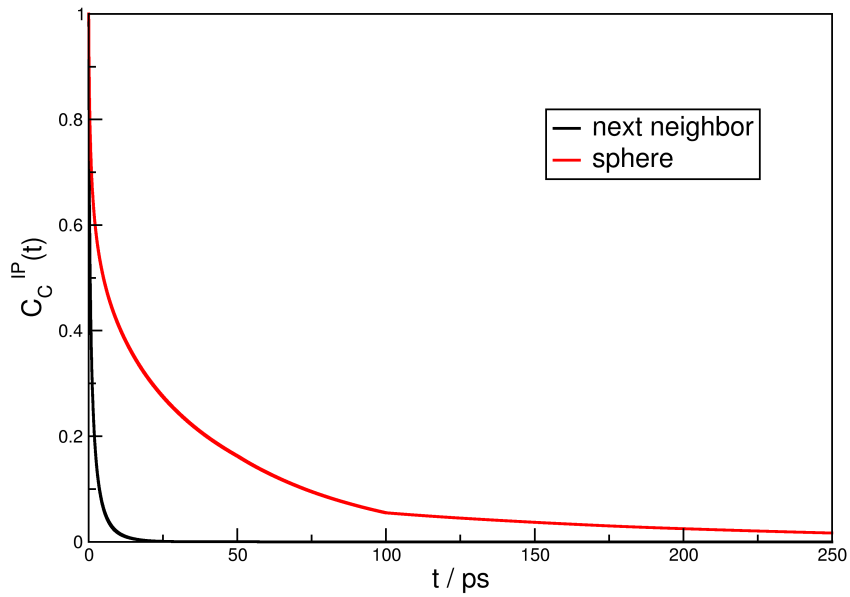Figure 6: $C_I^{\mathrm{HB}}(t)$ of H2 for the different systems at 373 K.

Figure 7: $C_C^{\mathrm{cage}}(t)$ for the ion pair dynamics in the RESP system at 373 K. The black-colored curve has been calculated for the next neighboring anion and cation only while the red-colored curve has been calculated with the before used ion pair definition.
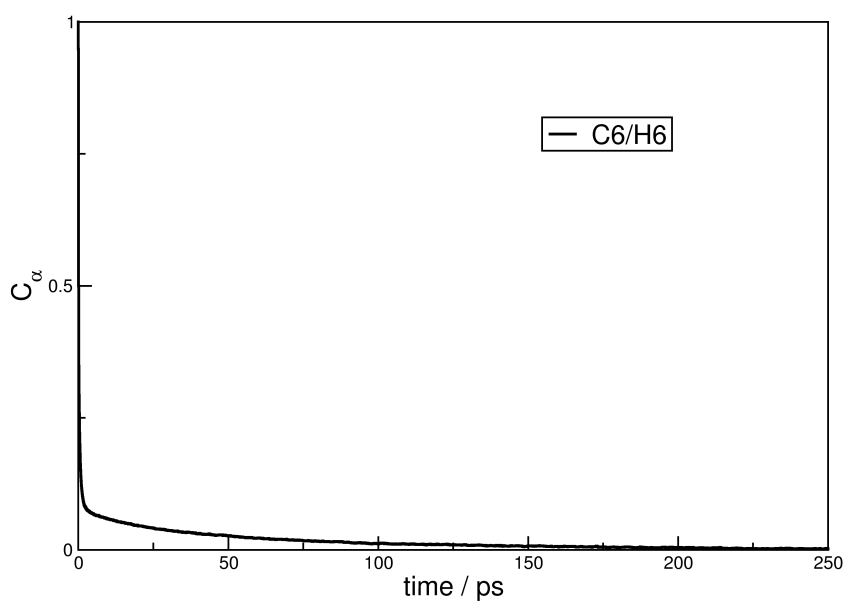
3.0.3 Reorientation

Figure 8: C_α of C6/H6 at 360 K.

References

[1] Schröder, C.; Wakai, D.; Weingärtner, H.; Steinhauser, O. *J. Chem. Phys.* **2007**, *126*, 084511.

[2] Xiao, D.; Hines, L. G.; Li, S.; Bartsch, R. A.; Quitevis, E. L. *J. Phys. Chem. B* **2009**, *113*, 6426–6433.

[3] Billard, I.; Moutiers, G.; Labet, A.; El Azzi, A.; Gaillard, C.; Mariet, C.; Lützenkirchen, K. *Inorg. Chem.* **2003**, *42*, 1726–1733.