

# Collectivity in ionic liquids: A temperature dependent, polarizable molecular dynamics study

## Supplementary Information

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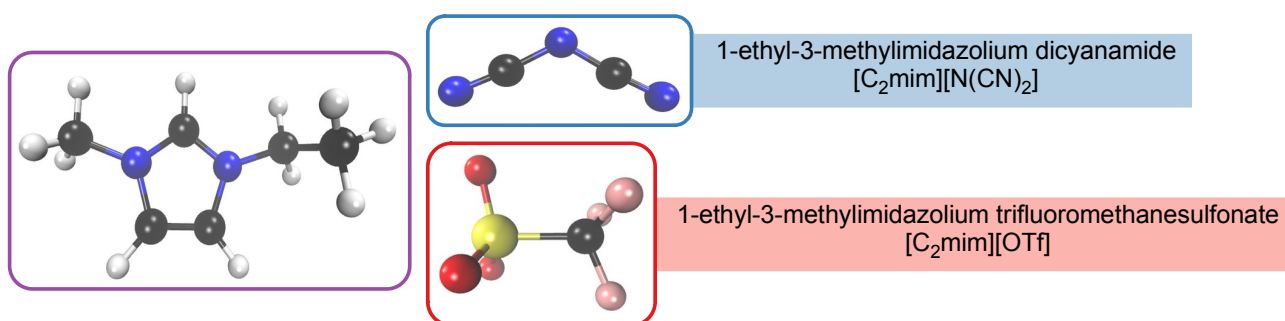


Figure S1: The two ionic liquids investigated in the frame of this study,  $[C_2mim]N(CN)_2$  and  $[C_2mim]OTf$ , modelled fully atomistically and polarizable.

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# 1 Structural features

Voronoi tessellation constructs space-filling polyhedra around each molecule in the simulation box at each timestep. For example, an exemplary polyhedron around a  $\text{N}(\text{CN})_2^-$ -anion is shown in Fig. S2. Each molecule sharing a surface with the red polyhedron is a first neighbor of the central molecule and belongs to the first shell  $s = 1$ . The outer surface of all these molecules is depicted as a turquoise area in Fig. S3 and is a picture of the ion cage around the central  $\text{N}(\text{CN})_2^-$ -anion. In addition to the nice pictures, Voronoi analysis provides much more information on the system as discussed below.

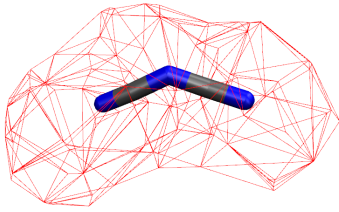


Figure S2: Voronoi surface (wire-frame) of a  $\text{N}(\text{CN})_2^-$  ion (nearest neighbors not shown)

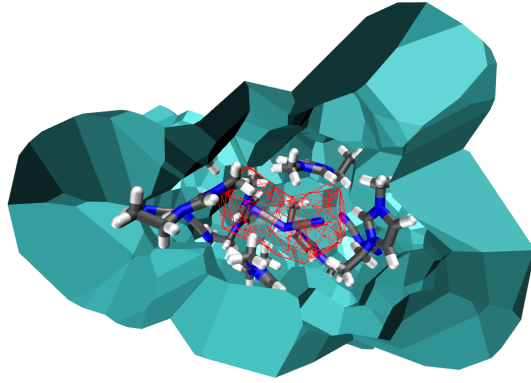


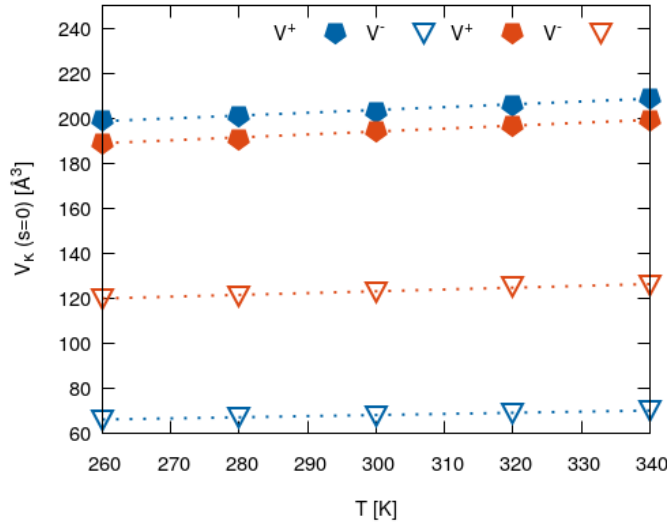
Figure S3: Voronoi surface of the first contact shell (blue) of a central  $\text{N}(\text{CN})_2^-$  ion

## 1.1 Temperature dependence of the Voronoi volumes

The molecular volumes obtained from the Voronoi polyhedra in Table S1 show a linear dependence on temperature as depicted in Fig. S4.

Table S1: Average Voronoi volume of the zeroth and first shells

	T / K	$V^\oplus(s=0) / \text{\AA}^3$	$V^\ominus(s=0) / \text{\AA}^3$	$V^\oplus(s=1) / \text{\AA}^3$	$V^\ominus(s=1) / \text{\AA}^3$
[C <sub>2</sub> mim]N(CN) <sub>2</sub>	260	199	66	2830	1696
	280	201	67	2866	1718
	300	203	68	2905	1740
	320	206	69	2954	1768
	340	209	70	2996	1793
[C <sub>2</sub> mim]OTf	260	189	120	2797	2100
	280	191	121	2832	2128
	300	194	123	2872	2160
	320	197	125	2917	2195
	340	199	126	2965	2231



system	ion $\kappa$	$V_{\kappa}^0$ [ $\text{\AA}^3$ ]	$\Delta V_{\kappa}$ [ $\text{\AA}^3/\text{K}$ ]
[C <sub>2</sub> mim] N(CN) <sub>2</sub>	C <sub>2</sub> mim <sup>+</sup>	166.1	0.125
	N(CN) <sub>2</sub> <sup>-</sup>	53.0	0.050
[C <sub>2</sub> mim] OTf	C <sub>2</sub> mim <sup>+</sup>	155.0	0.130
	OTf <sup>-</sup>	99.0	0.080

Figure S4: Temperature dependence of the molecular volume of the cations and anions in the [C<sub>2</sub>mim]N(CN)<sub>2</sub> system (blue) and [C<sub>2</sub>mim]OTf system (orange). The dotted lines correspond to the fit in Eq. (1).

Using the linear fit for the molecular volume  $V_{\kappa}(s=0, T)$

$$V_{\kappa}(s=0, T) = V_{\kappa}^0 + \Delta V_{\kappa} \cdot T \quad (1)$$

one can determine the "free-space" stemming from the thermal expansion of the liquid, *i.e.*  $\Delta V_{\kappa} \cdot T$ . The extrapolation to zero temperature yields the temperature-independent "crystal volume"  $V_{\kappa}^0$ . As shown in the table of Fig. S4 the expansion is quite small compared to the crystal volume  $V_{\kappa}^0$ . Hence, the molecular volume increases by roughly 5% in our temperature interval.

Doolittle defined relative free-space as ratio  $V_f/V_0 = (V - V_0)/V_0$ .<sup>1</sup> Applying Eq. (1) for the ionic liquid pair yields

$$\frac{V_f(T)}{V_0} = \frac{(\sum_{\kappa} V_{\kappa}^0 + \sum_{\kappa} \Delta V_{\kappa} \cdot T) - \sum_{\kappa} V_{\kappa}^0}{\sum_{\kappa} V_{\kappa}^0} = \frac{\sum_{\kappa} \Delta V_{\kappa}}{\sum_{\kappa} V_{\kappa}^0} \cdot T \quad (2)$$

In his model, the viscosity of the system depends on that ratio:

$$\eta(T) = A e^{\frac{B}{V_f(T)/V_0}} = A e^{\frac{B}{T \sum_{\kappa} \Delta V_{\kappa} / \sum_{\kappa} V_{\kappa}^0}} \quad (3)$$

Comparing this result to a classical Arrhenius behavior  $\eta = A \exp(E_A/(k_B N_A T))$  leads to a temperature independent activation energy  $E_A$

$$\frac{B}{\sum_{\kappa} \Delta V_{\kappa} / \sum_{\kappa} V_{\kappa}^0} = \frac{E_A}{k_B N_A} \quad (4)$$

$$E_A = B \frac{k_B N_A}{\sum_{\kappa} \Delta V_{\kappa} / \sum_{\kappa} V_{\kappa}^0} \quad (5)$$

which is in accordance with our results for the dynamics of the system. Therefore, we do not need a Vogel-Fulcher-Tammann equation or a compensated Arrhenius-approach<sup>2,3</sup> as our temperature regime is limited and far away from the glass transition temperature.

Interestingly, the ratio  $\sum_{\kappa} \Delta V_{\kappa} / \sum_{\kappa} V_{\kappa}^0$  is 0.0008 for both ionic liquid systems. Consequently, the different activation energies for [C<sub>2</sub>mim]N(CN)<sub>2</sub> and [C<sub>2</sub>mim]OTf arise from the different  $B$  constants.

## 1.2 Coordination numbers and potential of mean force

The decomposition of the entire simulation box into molecular Voronoi-polyhedra allows for

- determining the coordination numbers  $N_{\kappa\lambda}$  by counting shared surfaces. The mean value of the obtained numbers are the very same as using

$$N_{\kappa\lambda} = c_\lambda \int_0^\infty g_{\kappa\lambda}(r, s = 1) \cdot 4\pi r^2 dr \quad (6)$$

using the concentration  $c_\lambda = N_\lambda/V$ .

- evaluating the molecular volume ( $s = 0$  for each species and the volume of the first solvation shell  $s = 1$ ). Of course, the following equations should hold for all temperatures (except for rounding errors):

$$V = N \cdot (V_\oplus(s = 0) + V_\ominus(s = 0)) \quad (7)$$

$$V_\oplus(s = 1) = N_{\oplus\oplus} V_\oplus(s = 0) + N_{\oplus\ominus} V_\ominus(s = 0) \quad (8)$$

$$V_\ominus(s = 1) = N_{\oplus\ominus} V_\oplus(s = 0) + N_{\ominus\ominus} V_\ominus(s = 0) \quad (9)$$

The first condition is enforced by the space-filling of the Voronoi-tessellation. The second and third equation results from the definition of the solvation shell. The corresponding volumes are given in Table S1.

Table S2: Coordination numbers obtained by integration of the radial distribution functions of the first shell of [C<sub>2</sub>mim]N(CN)<sub>2</sub> (top) and [C<sub>2</sub>mim]OTf (bottom), as well as boxlengths and volumes.

	$T / \text{K}$	$N$	$N_{\oplus\ominus}$	$N_{\oplus\oplus}$	$N_{\ominus\ominus}$	Boxlength / $\text{\AA}$	$V / \text{\AA}^3$
[C <sub>2</sub> mim]N(CN) <sub>2</sub>	260	1000	7.898	11.597	1.989	64.27	265476
	280	1000	7.872	11.618	2.042	64.51	268461
	300	1000	7.840	11.644	2.089	64.76	271594
	320	1000	7.846	11.677	2.132	65.07	275513
	340	1000	7.848	11.703	2.174	65.34	278957
[C <sub>2</sub> mim]OTf	260	1000	8.035	9.689	4.802	67.61	309053
	280	1000	8.040	9.693	4.809	67.87	312632
	300	1000	8.056	9.704	4.827	68.16	316657
	320	1000	8.045	9.715	4.835	68.48	321138
	340	1000	8.097	9.719	4.840	68.81	325803

As the volume of the simulation box increases with temperature, the corresponding concentrations  $c_\lambda$  decrease. This trend also applies to the first solvation shell except for dicyanamides around dicyanamides.

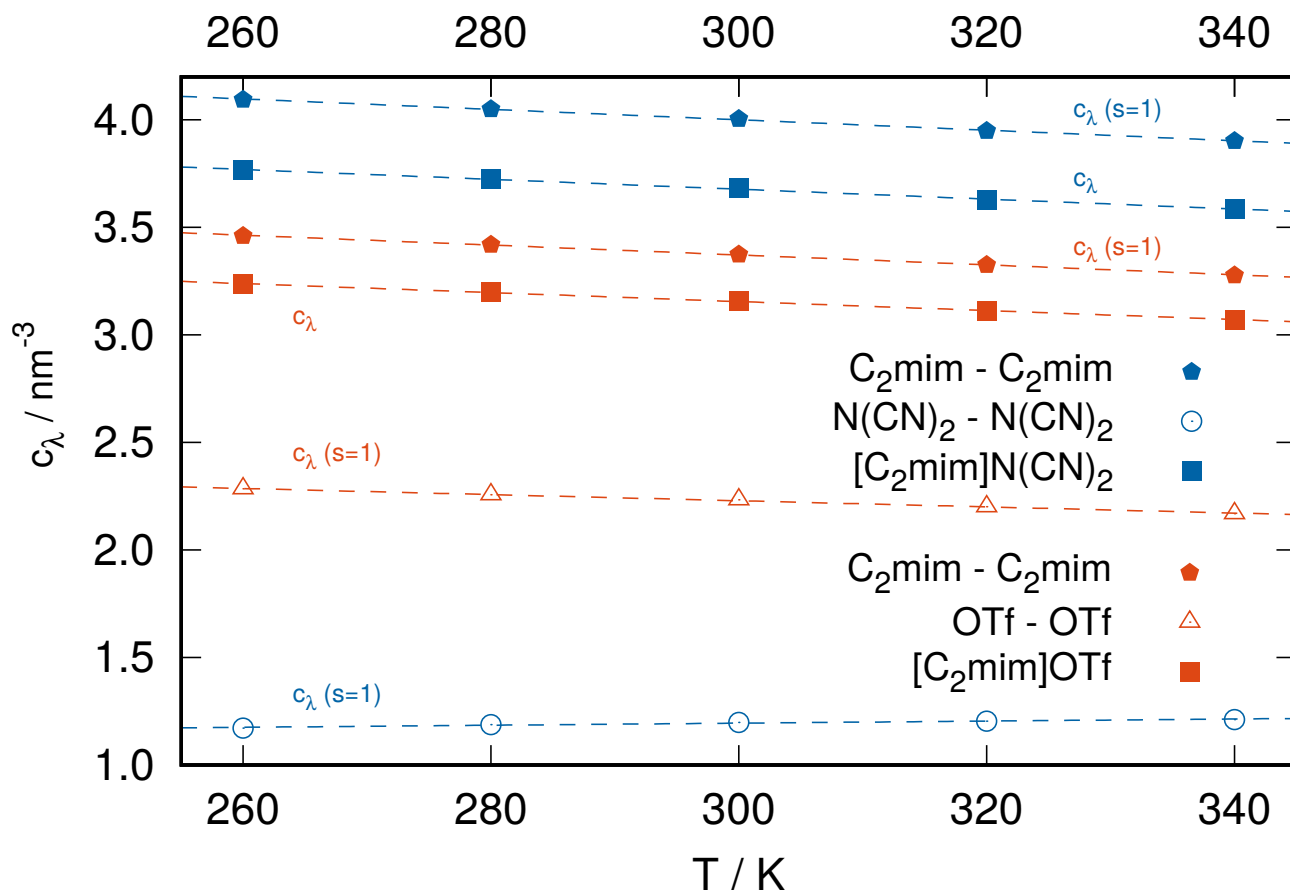


Figure S5: Concentrations (number densities) of the ionic liquids [C<sub>2</sub>mim]N(CN)<sub>2</sub> and [C<sub>2</sub>mim]OTf.  $c_\lambda(s = 1)$  is the number density of the Voronoi contact shell, as given in the main article,  $c_\lambda$  is the global number density. Note how local density is higher for cation-cation data but lower for anion-anion data, explaining why the *PMF* is negative for the former but positive for the latter.

The positive linear trend of the  $PMF_{\kappa\lambda}$  for the anions (open symbols) is shown in the bottom panel of Fig. 2 of the main article. Although the coordination number  $N_{\kappa\lambda}$  increases for  $\kappa = \lambda = \{N(CN)_2^-, OTf^-\}$  with temperature, the shell volume  $V(s = 1)$  increases more rapidly. As a result,  $c_\lambda(s = 1)/c_\lambda$  decreases for anions around anions with increasing temperature in contrast to the situation of the cations (see Fig. S5 of the ESI). Consequently, the *PMF* for the anions shows a positive trend, whereas it is negative for the cations.

## 2 Dynamics

### 2.1 Transport properties

One of the primary challenges of experimentally determining such properties arises due to sample impurity. As reported elsewhere,<sup>4</sup> water content and other impurities can have a profound effect on the viscosity (and, to a lesser extent, density). This, in turn, can negatively influence the reproducibility of other measurements, making a comparison with existing literature difficult. Please note that these coefficients do not include mutual pair diffusion and are thus not the same as the sample diffusion coefficient  $D$  obtained by some experiments, which is linked to the dynamic viscosity  $\eta$ .

Table S3: Viscosities of [C<sub>2</sub>mim]N(CN)<sub>2</sub> (top) and [C<sub>2</sub>mim]OTf (bottom). The values were determined by applying a cosine-shaped acceleration profile of 0.005, 0.01, 0.02, 0.03, 0.04 and 0.05 nm ps<sup>-2</sup> and extrapolating the resulting values to zero.

	T [K]	$\eta$ [Pa s]	T [K]	${}^a\eta$ [Pa s]
[C <sub>2</sub> mim]N(CN) <sub>2</sub>	260	0.22	258.15	0.075
	280	0.076	278.15	0.029
	300	0.036	298.15	0.015
	320	0.018	323.15	0.0078
	340	0.011	343.15	0.0054
[C <sub>2</sub> mim]OTf	260	0.57	268.15	0.17
	280	0.26	278.15	0.10
	300	0.095	298.15	0.043
	320	0.044	323.15	0.020
	340	0.023	343.15	0.012

<sup>a</sup>: Experimental values for [C<sub>2</sub>mim]N(CN)<sub>2</sub> taken from Ref. 5, for [C<sub>2</sub>mim]OTf from Ref. 6

Table S4: Diffusion coefficients of the cations ( $D_{\oplus}$ ) and the anions ( $D_{\ominus}$ ), calculated from the slopes of the mean squared displacement of the center of mass at the specified temperatures of [C<sub>2</sub>mim]N(CN)<sub>2</sub> (top) and [C<sub>2</sub>mim]OTf (bottom). The second value includes the correction due to the periodic boundary conditions in Eq. (10)

	T [K]	$D_{\oplus}$ [10 <sup>-11</sup> m <sup>2</sup> s <sup>-1</sup> ]	$D_{\ominus}$ [10 <sup>-11</sup> m <sup>2</sup> s <sup>-1</sup> ]	$\sigma_{NE}$ [S m <sup>-1</sup> ]	T [K]	${}^aD_{\oplus}$ [10 <sup>-11</sup> m <sup>2</sup> s <sup>-1</sup> ]	T [K]	${}^aD_{\ominus}$ [10 <sup>-11</sup> m <sup>2</sup> s <sup>-1</sup> ]
[C <sub>2</sub> mim]N(CN) <sub>2</sub>	260	0.48 / 0.52	0.60 / 0.64	0.31	260	0.75		
	280	1.6 / 1.7	2.1 / 2.2	0.97	280	2.64		
	300	4.0 / 4.3	5.2 / 5.5	2.2	300	5.15		
	320	7.7 / 8.3	10.0 / 10.6	4.0	320	8.70		
	340	13. / 14.	18. / 19.	6.5	340	14.8		
[C <sub>2</sub> mim]OTf	260	0.18 / 0.19	0.087 / 0.10	0.068	268.2	1.12	273.2	0.822
	280	0.70 / 0.73	0.36 / 0.39	0.24	278.5	1.87	278.3	1.04
	300	2.0 / 2.1	1.1 / 1.2	0.64	298.2	4.36	298.4	2.47
	320	4.7 / 4.9	2.3 / 2.5	1.4	322.9	9.45	322.9	5.68
	340	8.7 / 9.1	5.4 / 5.8	2.5	343.1	15.6	343.2	9.11

<sup>a</sup>: Experimental values for [C<sub>2</sub>mim]N(CN)<sub>2</sub> taken from Ref. 7, for [C<sub>2</sub>mim]OTf from Ref. 6

$$D^{\infty} = D^L + \frac{\xi k_B T}{6\pi\eta L} \quad (10)$$

Based on the Nernst-Einstein equation

$$\sigma_{NE} = \frac{1}{k_B T} \sum_{\kappa} |q_{\kappa}|^2 \rho_{\kappa} D_{\kappa} \quad (11)$$

the static conductivity can be approximated. However, due to the neglect of collective interactions, this estimate exceeds significantly the dc conductivity  $\sigma$ . The total conductivity was calculated from  $\langle \Delta M_J^2(t) \rangle$ ,  $\sigma_{\oplus\oplus}$  from  $\langle (\Delta M_J^{\oplus}(t))^2 \rangle$ ,  $\sigma_{\oplus\ominus}$  from  $\langle (\Delta M_J^{\oplus}(t) \Delta M_J^{\ominus}(t)) \rangle$  and  $\sigma_{\ominus\ominus}$  from  $\langle (\Delta M_J^{\ominus}(t))^2 \rangle$ .  $\sigma_{\oplus}$  and  $\sigma_{\ominus}$  were obtained by adding the terms containing a cation or anion term, respectively.

Table S5: Conductivities  $\sigma$  calculated from the slopes of the mean squared displacement of the electric dipole moment. The top part presents data for [C<sub>2</sub>mim]N(CN)<sub>2</sub>, the bottom part for [C<sub>2</sub>mim]OTf.

	T [K]	$\sigma$ [S m <sup>-1</sup> ]	$\sigma_{\oplus\oplus}$ [S m <sup>-1</sup> ]	$\sigma_{\oplus\ominus}$ [S m <sup>-1</sup> ]	$\sigma_{\ominus\ominus}$ [S m <sup>-1</sup> ]	$\sigma_{\oplus}$ [S m <sup>-1</sup> ]	$\sigma_{\ominus}$ [S m <sup>-1</sup> ]	T [K]	<sup>a</sup> $\sigma_{exp}$ [S m <sup>-1</sup> ]
[C <sub>2</sub> mim]N(CN) <sub>2</sub>	260	0.278	0.038	0.064	0.111	0.102	0.176	258.15	0.63
	280	0.715	0.101	0.167	0.280	0.268	0.447	278.15	1.6
	300	1.231	0.168	0.286	0.490	0.455	0.777	298.15	2.9
	320	2.568	0.356	0.600	1.013	0.956	1.613	323.15	5.2
	340	3.363	0.462	0.785	1.329	1.249	2.114	343.15	7.3
[C <sub>2</sub> mim]OTf	260	0.0466	0.0197	0.0069	0.0129	0.0268	0.020	273.15	0.35
	280	0.178	0.064	0.041	0.032	0.105	0.074	278.15	0.43
	300	0.515	0.172	0.125	0.094	0.297	0.218	298.15	0.92
	320	0.996	0.330	0.243	0.181	0.573	0.424	323.15	1.8
	340	1.607	0.525	0.392	0.297	0.917	0.690	343.15	2.8

<sup>a</sup>: Experimental values for [C<sub>2</sub>mim]N(CN)<sub>2</sub> taken from Ref. 5, [C<sub>2</sub>mim]OTf from Ref. 6

## 2.2 Molecular rotational relaxation

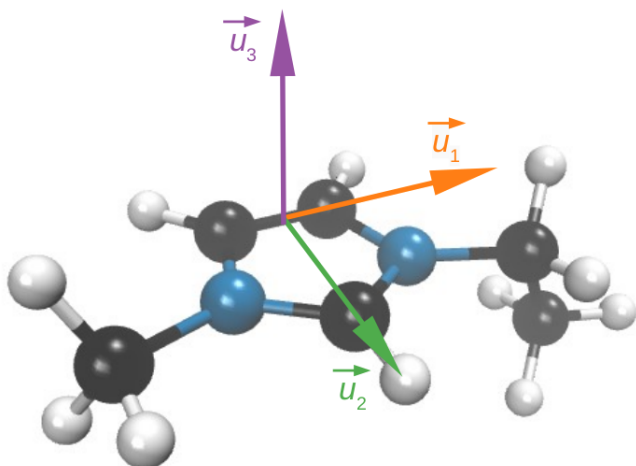


Figure S6: The three body-fixed axes used in the rotational anisotropy study. Please note that the axes do not describe rotationally inert axes, but oriented vectors whose rotational movement is tracked.

- $\vec{u}_1$  is located in the imidazolium plane and is defined as the vector joining  $C_4$  and  $C_5$ .
- $\vec{u}_2$  is also in the imidazolium plane and connects the bond between  $C_4$ - $C_5$  with  $C_2$ .
- $\vec{u}_3$  is defined as the cross product of  $\vec{u}_1$  and  $\vec{u}_2$  and represents the out-of-plane dimension.

Table S6: Relaxation times for  $[\text{C}_2\text{mim}]\text{N}(\text{CN})_2$  (top part) and  $[\text{C}_2\text{mim}]\text{OTf}$  (bottom part).  $\tau_{\oplus}^{\mu}$  symbolizes the relaxation time of the  $\text{C}_2\text{mim}$  dipole,  $\tau_{\ominus}^{\mu}$  the relaxation time of the anion dipole whereas  $\tau^{u1}$ ,  $\tau^{u2}$  and  $\tau^{u3}$  refer to the relaxation times of the three body-fixed axes.

	T [K]	$\langle \mu_{\ominus}(0) \cdot \mu_{\ominus}(0) \rangle$ [ $e^2 \text{Å}^2$ ]	$\tau_{\ominus}^{\mu}$ [ps]	$\langle \mu_{\oplus}(0) \cdot \mu_{\oplus}(0) \rangle$ [ $e^2 \text{Å}^2$ ]	$\tau_{\oplus}^{\mu}$ [ps]	$\tau^{u1}$ [ps]	$\tau^{u2}$ [ps]	$\tau^{u3}$ [ps]
[ $\text{C}_2\text{mim}$ ] $\text{N}(\text{CN})_2$	260	0.976	137.0	5.52	2132	2779	1021	1271
	280	0.985	35.32	5.51	698.8	888.7	318.2	397.1
	300	0.997	14.75	5.48	298.3	384.4	143.0	178.7
	320	1.01	7.267	5.48	152.6	196.6	73.93	91.31
	340	1.02	4.549	5.47	93.63	120.5	45.19	55.94
[ $\text{C}_2\text{mim}$ ] $\text{OTf}$	260	33.5	4824	6.53	7208	8343	3215	3227
	280	33.3	1246	6.44	2138	2554	831.3	899.3
	300	33.2	441.6	6.33	778.4	946.0	316.1	346.4
	320	33.1	196.7	6.27	364.0	445.9	150.4	164.7
	340	33.0	104.4	6.20	194.5	236.9	82.21	91.81



## 2.3 Collective rotational relaxation

### 2.3.1 Contributions to the dielectric spectrum

The dielectric spectrum is computed on the level of collective rotational correlation functions.

$$\vec{M}_D(t) = \vec{M}_D^\oplus(t) + \vec{M}_D^\ominus(t) \quad (12)$$

$$= \sum_{i \in \oplus} \vec{\mu}_i(t) + \sum_{i \in \ominus} \vec{\mu}_i(t) \quad (13)$$

$$\langle \vec{M}_D(0) \cdot \vec{M}_D(t) \rangle = \langle \vec{M}_D^\oplus(0) \cdot \vec{M}_D^\oplus(t) \rangle + 2\langle \vec{M}_D^\oplus(0) \cdot \vec{M}_D^\ominus(t) \rangle + \langle \vec{M}_D^\ominus(0) \cdot \vec{M}_D^\ominus(t) \rangle \quad (14)$$

The numerical correlation functions are typically noisy since only one sample dipole is recorded instead of  $N_\kappa$  molecular ones. Consequently, we cannot integrate the correlation functions directly but use triexponential functions

$$\Phi(t) = A_1 \exp[-t/\tau_1] + A_2 \exp[-t/\tau_2] + A_3 \exp[-t/\tau_3] \quad (15)$$

to fit the correlation functions instead. This is in accordance with a recent dielectric study on these systems.<sup>8</sup>

Table S7: Fitted relaxation times of the collective rotational dipole moments of each ion interaction of [C<sub>2</sub>mim]N(CN)<sub>2</sub> (top rows) and [C<sub>2</sub>mim]OTf (bottom rows).  $\tau_1$ ,  $\tau_2$  and  $\tau_3$  denote exponential relaxation times.  $\bar{\tau}$  is the average relaxation time weighted by the corresponding amplitudes

T [K]	$\langle M_D^\oplus(0)M_D^\oplus(t) \rangle$					$\langle M_D^\oplus(0)M_D^\ominus(t) \rangle$					$\langle M_D^\ominus(0)M_D^\ominus(t) \rangle$					
	$A_{\oplus\oplus}$ [D <sup>2</sup> ]	$\tau_1$ [ps]	$\tau_2$ [ps]	$\tau_3$ [ps]	$\bar{\tau}$ [ps]	$A_{\oplus\ominus}$ [D <sup>2</sup> ]	$\tau_1$ [ps]	$\tau_2$ [ps]	$\tau_3$ [ps]	$\bar{\tau}$ [ps]	$A_{\ominus\ominus}$ [D <sup>2</sup> ]	$\tau_1$ [ps]	$\tau_2$ [ps]	$\tau_3$ [ps]	$\bar{\tau}$ [ps]	
[C <sub>2</sub> mim]N(CN) <sub>2</sub>	260	4060	2070	60.5	0.0731	1400	238	1600	7.65	0.0337	722	780	369	9.78	0.0596	97.0
	280	4090	668	7.42	0.0713	580	171	654	55.4	0.0353	32.7	780	122	1.67	0.0550	28.0
	300	3980	505	39.7	0.167	327	190	401	8.43	0.0357	108	800	50.9	0.955	0.0512	10.1
	320	4280	196	7.82	0.0787	163	199	233	8.94	0.0369	66.0	800	32.2	0.802	0.0511	5.11
	340	4180	124	8.67	0.123	100	197	122	9.13	0.0383	35.1	820	26.1	0.723	0.0514	3.28
[C <sub>2</sub> mim]OTf	260	2660	1860	17.1	0.113	1390	1670	5610	19.3	0.216	3600	12500	703	25.1	0.587	452
	280	3980	1330	8.81	0.114	1130	1690	345	8.63	0.230	266	14600	377	22.3	0.649	225
	300	3640	530	22.1	0.165	393	2120	363	28.7	0.352	217	14800	225	13.8	0.591	128
	320	4510	539	47.0	0.159	348	2370	330	9.27	0.260	249	16000	91.6	8.17	0.557	57.3
	340	4640	187	6.42	0.130	158	2300	137	8.67	0.269	94.1	15800	50.5	6.60	0.578	30.4

The amplitude  $A$  is the first value of the corresponding correlation function  $\langle M_D^k(0) \cdot M_D^k(t) \rangle$ . It is close to the sum of the amplitudes  $A_a$  of the fitted exponential processes:

$$A = \sum_a A_a \quad (16)$$

The average time constant  $\bar{\tau}$  is the amplitude weighted average of the exponential relaxation constants  $\tau$ :

$$\bar{\tau} = \frac{\sum_a A_a \cdot \tau_a}{\sum_a A_a} \quad (17)$$

### 2.3.2 Alternative decomposition of the collective rotational correlation function

The correlation functions in Table S7 directly contribute to the frequency-dependent dielectric spectrum. However, for the discussion of collectivity we compared the collective rotational correlation function  $\langle \vec{M}_D(0) \cdot \vec{M}_D(t) \rangle$  to the single-particle rotational correlation function  $\langle \vec{\mu}_i(0) \cdot \vec{\mu}_i(t) \rangle$ . According to Eq. (27) of the main article, the cross-correlations can be obtained from the difference of collective and single-particle rotation:

$$\sum_i \sum_{j \neq i} \langle \vec{\mu}_i(0) \cdot \vec{\mu}_j(t) \rangle = \langle \vec{M}_D(0) \cdot \vec{M}_D(t) \rangle - \sum_{i \in \oplus} \langle \vec{\mu}_i(0) \cdot \vec{\mu}_i(t) \rangle - \sum_{j \in \ominus} \langle \vec{\mu}_j(0) \cdot \vec{\mu}_j(t) \rangle \quad (18)$$

This cross-correlation is displayed in Fig. S7 for both ionic liquids. The amplitude in case of [C<sub>2</sub>mim]OTf is stronger and show a clear decreasing trend with increasing temperature. Interestingly, these cross-correlation functions do not start at zero. This finding indicates that some single-particle dipole moments  $\mu_i$  are always coupled.

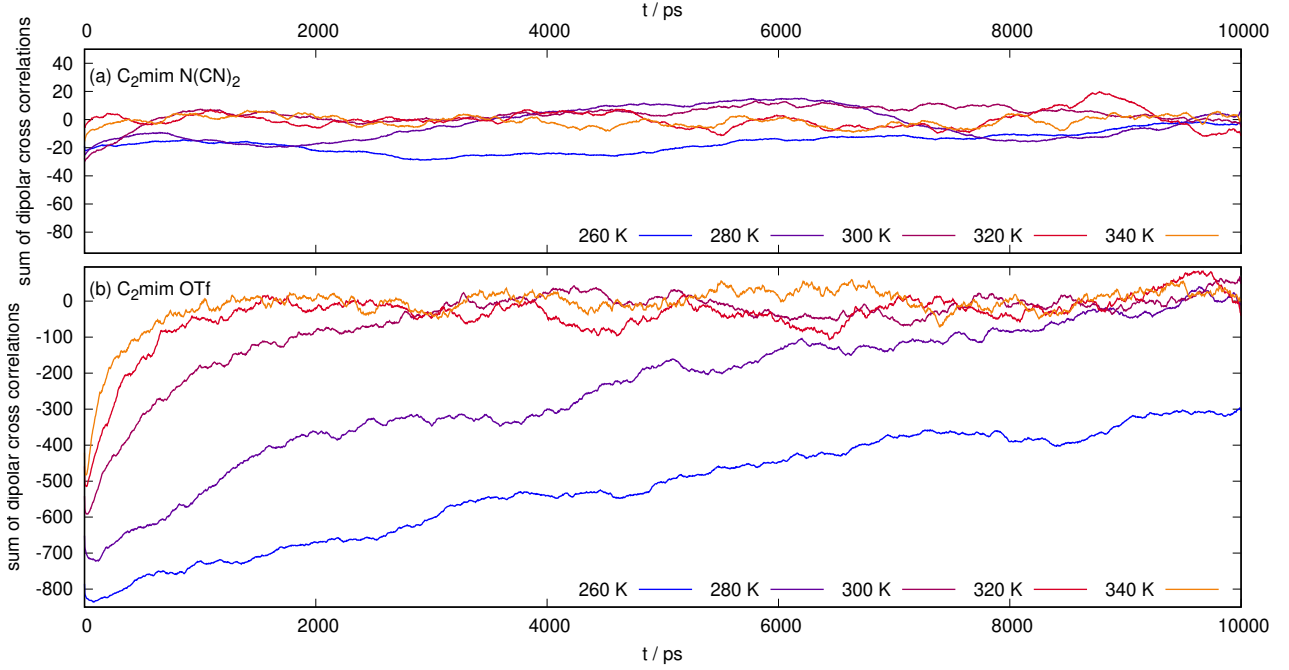


Figure S7: Dipolar cross correlations  $\sum_i \sum_{j \neq i} \langle \vec{\mu}_i(0) \cdot \vec{\mu}_j(t) \rangle$ .

Please note that this decomposition is an alternative approach compared to the previous section. Consequently, the decomposing contributions are not directly related to each other:

$$\sum_{i \in \oplus} \langle \vec{\mu}_i(0) \cdot \vec{\mu}_i(t) \rangle \neq \langle \vec{M}_D^{\oplus}(0) \cdot \vec{M}_D^{\oplus}(t) \rangle \quad (19)$$

$$\sum_{i \in \ominus} \langle \vec{\mu}_i(0) \cdot \vec{\mu}_i(t) \rangle \neq \langle \vec{M}_D^{\ominus}(0) \cdot \vec{M}_D^{\ominus}(t) \rangle \quad (20)$$

$$\langle \vec{M}_D^{\oplus}(0) \cdot \vec{M}_D^{\ominus}(t) \rangle \neq \sum_i \sum_{j \neq i} \langle \vec{\mu}_i(0) \cdot \vec{\mu}_j(t) \rangle \quad (21)$$

since cations also interact with other cations for example which is neglected on the left hand sides of Eq. (19) and (21) but included on the corresponding right hand sides.

## 2.4 Arrhenius prefactors

Table S8: Pre-exponential factors for diffusion, conductivity, single-particle and collective rotation.

		[C <sub>2</sub> mim]N(CN) <sub>2</sub>	[C <sub>2</sub> mim]OTf
Diffusion [m <sup>2</sup> s <sup>-1</sup> ]	D <sup>⊕</sup>	6.74 × 10 <sup>-6</sup>	2.95 × 10 <sup>-5</sup>
	D <sup>⊖</sup>	1.09 × 10 <sup>-5</sup>	3.15 × 10 <sup>-5</sup>
Conductivity [S m <sup>-1</sup> ]	σ	1.40 × 10 <sup>4</sup>	2.09 × 10 <sup>4</sup>
	σ <sup>⊕</sup>	5.31 × 10 <sup>3</sup>	1.15 × 10 <sup>5</sup>
	σ <sup>⊖</sup>	8.68 × 10 <sup>3</sup>	9.53 × 10 <sup>5</sup>
	σ <sup>⊕⊕</sup>	1.94 × 10 <sup>3</sup>	2.90 × 10 <sup>4</sup>
	σ <sup>⊕⊖</sup>	3.37 × 10 <sup>3</sup>	2.43 × 10 <sup>5</sup>
	σ <sup>⊖⊖</sup>	8.68 × 10 <sup>3</sup>	1.14 × 10 <sup>4</sup>
Single-particle rotation [ps <sup>-1</sup> ]	τ <sub>⊖</sub> <sup>μμ</sup>	1.64 × 10 <sup>4</sup>	2.78 × 10 <sup>3</sup>
	τ <sub>⊕</sub> <sup>μμ</sup>	3.17 × 10 <sup>2</sup>	7.29 × 10 <sup>2</sup>
	τ <sup>u1</sup>	2.52 × 10 <sup>2</sup>	4.99 × 10 <sup>2</sup>
	τ <sup>u2</sup>	5.97 × 10 <sup>2</sup>	1.94 × 10 <sup>3</sup>
	τ <sup>u3</sup>	4.96 × 10 <sup>2</sup>	1.27 × 10 <sup>3</sup>
Collective rotation [ps <sup>-1</sup> ]	τ <sub>⊕⊕</sub> <sup>MM</sup>	6.22 × 10 <sup>1</sup>	4.99 × 10 <sup>0</sup>
	τ <sub>⊖⊖</sub> <sup>MM</sup>	3.19 × 10 <sup>2</sup>	9.90 × 10 <sup>1</sup>
	τ <sub>⊕⊖</sub> <sup>MM</sup>	2.39 × 10 <sup>1</sup>	1.90 × 10 <sup>2</sup>

### 3 Input scripts

Below is a list of CHARMM topology and parameter files, as well as the dynamics input for [C<sub>2</sub>mim]N(CN)<sub>2</sub> at 260 K.

#### 3.1 Topology

\* TOPOLOGY FILE .

\*

```
  99  1
MASS  1 h1      1.008000
MASS  2 h4      1.008000
MASS  3 h5      1.008000
MASS  4 hc      1.008000
MASS  6 c3     12.010000
MASS  7 cc     12.010000
MASS  8 cd     12.010000
MASS  9 cg     12.010000
MASS 10 o      16.000000
MASS 13 n1     14.010000
MASS 14 na     14.010000
MASS 15 ne     14.010000
MASS 16 f      19.000000
MASS 18 s6     32.060000
MASS 19 c      12.010000
MASS 20 oa     16.000000
MASS 51 ODW    15.999400  ! water oxygen
MASS 52 HDW    1.008000  ! water hydrogen
MASS 60 LP     0.000000  ! general lone pair
MASS 61 DRUD   0.000000  ! drude particle
```

AUTOGENERATE DRUDE !note use of DRUDE

---

---

!EMIM

---

---

RESI EMIM 1.000

GROUP

```
ATOM C    C3      0.045  ALPHA -2.025  THOLE 1.135
ATOM H    H1      0.053
ATOM H1   H1      0.053
ATOM H2   H1      0.053
ATOM N    NA      0.102  ALPHA -0.901  THOLE 1.138
ATOM C1   CC      0.003  ALPHA -1.533  THOLE 1.409
ATOM N1   NA      0.102  ALPHA -0.901  THOLE 1.138
ATOM C2   CC     -0.076  ALPHA -1.563  THOLE 1.324
ATOM C3   CD     -0.076  ALPHA -1.563  THOLE 1.324
ATOM H3   H5      0.183
ATOM H4   H4      0.168
ATOM H5   H4      0.168
ATOM C4   C3     -0.005  ALPHA -1.675  THOLE 1.109
ATOM H6   H1      0.075
ATOM H7   H1      0.075
ATOM C5   C3      0.008  ALPHA -2.049  THOLE 1.125
ATOM H8   HC      0.023
ATOM H9   HC      0.023
ATOM H10  HC      0.023
```

```
BOND C    H          ! DIST      1.0796
BOND C    H1         ! DIST      1.0785
```

BOND C	H2	!	DIST	1.0794
BOND C	N1	!	DIST	1.4658
BOND N	C1	!	DIST	1.3138
BOND N	C3	!	DIST	1.3781
BOND N	C4	!	DIST	1.4777
BOND C1	N1	!	DIST	1.3157
BOND C1	H3	!	DIST	1.0692
BOND N1	C2	!	DIST	1.3785
BOND C2	C3	!	DIST	1.3416
BOND C2	H4	!	DIST	1.0679
BOND C3	H5	!	DIST	1.0688
BOND C4	H6	!	DIST	1.0814
BOND C4	H7	!	DIST	1.0798
BOND C4	C5	!	DIST	1.5218
BOND C5	H8	!	DIST	1.0835
BOND C5	H9	!	DIST	1.0834
BOND C5	H10	!	DIST	1.0837

ANGL C	N1	C1	!	ANGLE	126.4111
ANGL C	N1	C2	!	ANGLE	125.6300
ANGL H	C	H1	!	ANGLE	109.5510
ANGL H	C	H2	!	ANGLE	110.2559
ANGL H	C	N1	!	ANGLE	109.2611
ANGL H1	C	H2	!	ANGLE	109.5172
ANGL H1	C	N1	!	ANGLE	108.8792
ANGL H2	C	N1	!	ANGLE	109.3538
ANGL N	C1	N1	!	ANGLE	109.8941
ANGL N	C1	H3	!	ANGLE	125.1030
ANGL N	C3	C2	!	ANGLE	107.1959
ANGL N	C3	H5	!	ANGLE	122.1025
ANGL N	C4	H6	!	ANGLE	106.7043
ANGL N	C4	H7	!	ANGLE	106.9082
ANGL N	C4	C5	!	ANGLE	112.0836
ANGL C1	N	C3	!	ANGLE	107.9285
ANGL C1	N	C4	!	ANGLE	126.1921
ANGL C1	N1	C2	!	ANGLE	107.9577
ANGL N1	C1	H3	!	ANGLE	125.0025
ANGL N1	C2	C3	!	ANGLE	107.0236
ANGL N1	C2	H4	!	ANGLE	122.0406
ANGL C2	C3	H5	!	ANGLE	130.7003
ANGL C3	N	C4	!	ANGLE	125.8669
ANGL C3	C2	H4	!	ANGLE	130.9352
ANGL C4	C5	H8	!	ANGLE	111.2780
ANGL C4	C5	H9	!	ANGLE	111.5813
ANGL C4	C5	H10	!	ANGLE	109.0336
ANGL H6	C4	H7	!	ANGLE	107.7086
ANGL H6	C4	C5	!	ANGLE	111.3594
ANGL H7	C4	C5	!	ANGLE	111.7864
ANGL H8	C5	H9	!	ANGLE	108.5717
ANGL H8	C5	H10	!	ANGLE	108.3168
ANGL H9	C5	H10	!	ANGLE	107.9497

DIHE H	C	N1	C1	!	DIHE	-120.0991
DIHE H1	C	N1	C1	!	DIHE	-0.4861
DIHE H2	C	N1	C1	!	DIHE	119.1407
DIHE H	C	N1	C2	!	DIHE	60.3500
DIHE H1	C	N1	C2	!	DIHE	179.9630
DIHE H2	C	N1	C2	!	DIHE	-60.4102
DIHE C3	N	C1	N1	!	DIHE	-0.0723
DIHE C4	N	C1	N1	!	DIHE	-178.8479
DIHE C3	N	C1	H3	!	DIHE	-179.8641

DIHE C4	N	C1	H3	!	DIHE	1.3603
DIHE C1	N	C3	C2	!	DIHE	0.1214
DIHE C4	N	C3	C2	!	DIHE	178.9021
DIHE C1	N	C3	H5	!	DIHE	179.7449
DIHE C4	N	C3	H5	!	DIHE	-1.4744
DIHE C1	N	C4	H6	!	DIHE	-17.3257
DIHE C3	N	C4	H6	!	DIHE	164.1119
DIHE C1	N	C4	H7	!	DIHE	-132.3592
DIHE C3	N	C4	H7	!	DIHE	49.0783
DIHE C1	N	C4	C5	!	DIHE	104.8236
DIHE C3	N	C4	C5	!	DIHE	-73.7389
DIHE N	C1	N1	C	!	DIHE	-179.6202
DIHE H3	C1	N1	C	!	DIHE	0.1719
DIHE N	C1	N1	C2	!	DIHE	-0.0039
DIHE H3	C1	N1	C2	!	DIHE	179.7882
DIHE C	N1	C2	C3	!	DIHE	179.7003
DIHE C1	N1	C2	C3	!	DIHE	0.0802
DIHE C	N1	C2	H4	!	DIHE	-0.0517
DIHE C1	N1	C2	H4	!	DIHE	-179.6718
DIHE N1	C2	C3	N	!	DIHE	-0.1217
DIHE H4	C2	C3	N	!	DIHE	179.6001
DIHE N1	C2	C3	H5	!	DIHE	-179.7009
DIHE H4	C2	C3	H5	!	DIHE	0.0208
DIHE N	C4	C5	H8	!	DIHE	-60.5075
DIHE H6	C4	C5	H8	!	DIHE	58.9472
DIHE H7	C4	C5	H8	!	DIHE	179.4809
DIHE N	C4	C5	H9	!	DIHE	60.9322
DIHE H6	C4	C5	H9	!	DIHE	-179.6130
DIHE H7	C4	C5	H9	!	DIHE	-59.0794
DIHE N	C4	C5	H10	!	DIHE	-179.9216
DIHE H6	C4	C5	H10	!	DIHE	-60.4668
DIHE H7	C4	C5	H10	!	DIHE	60.0669
IMPH C4	C1	N	C3			
IMPH H3	N1	C1	N			
IMPH C	C1	N1	C2			
IMPH C3	H4	C2	N1			
IMPH C2	H5	C3	N			

---



---

! TRIF

---



---

RESI TRIF -1.000

GROUP

ATOM C	C3	0.366	ALPHA	-1.227	THOLE	1.068
ATOM F	F	-0.190	ALPHA	-0.028	THOLE	1.450
ATOM F1	F	-0.190	ALPHA	-0.028	THOLE	1.450
ATOM F2	F	-0.190	ALPHA	-0.028	THOLE	1.450
ATOM S	S6	0.998	ALPHA	-2.658	THOLE	1.128
ATOM O	O	-0.353	ALPHA	-0.271	THOLE	1.471
ATOM LPAO	LP	-0.145				
ATOM LPBO	LP	-0.100				
ATOM O1	O	-0.353	ALPHA	-0.271	THOLE	1.471
ATOM LPAO1	LP	-0.145				
ATOM LPBO1	LP	-0.100				
ATOM O2	O	-0.353	ALPHA	-0.271	THOLE	1.471
ATOM LPAO2	LP	-0.145				
ATOM LPBO2	LP	-0.100				

BOND C	F		!	DIST	1.3239
BOND C	F1		!	DIST	1.3237

```

BOND C      F2                ! DIST      1.3237
BOND C      S                 ! DIST      1.8184
BOND S      O                 ! DIST      1.4431
BOND S      O1                ! DIST      1.4425
BOND S      O2                ! DIST      1.4425
BOND        O      LPAO        O      LPBO
BOND        O1     LPAO1       O1     LPBO1
BOND        O2     LPAO2       O2     LPBO2

LONEPAIR relative LPAO  O      S      C      distance 0.35 angle 110.00 dihe
0.00
LONEPAIR relative LPBO  O      S      C      distance 0.35 angle 110.00 dihe 180.00
ANISOTROPY      O      S      LPAO      LPBO  A11  0.56750 A22  0.37401
LONEPAIR relative LPAO1 O1     S      C      distance 0.35 angle 110.00 dihe
0.00
LONEPAIR relative LPBO1 O1     S      C      distance 0.35 angle 110.00 dihe 180.00
ANISOTROPY      O1     S      LPAO1     LPBO1  A11  0.56750 A22  0.37401
LONEPAIR relative LPAO2 O2     S      C      distance 0.35 angle 110.00 dihe
0.00
LONEPAIR relative LPBO2 O2     S      C      distance 0.35 angle 110.00 dihe 180.00
ANISOTROPY      O2     S      LPAO2     LPBO2  A11  0.56750 A22  0.37401

ANGL C      S      O                ! ANGLE     102.6274
ANGL C      S      O1               ! ANGLE     102.6487
ANGL C      S      O2               ! ANGLE     102.6487
ANGL F      C      F1               ! ANGLE     107.1013
ANGL F      C      F2               ! ANGLE     107.1013
ANGL F      C      S                 ! ANGLE     111.7239
ANGL F1     C      F2               ! ANGLE     107.1326
ANGL F1     C      S                 ! ANGLE     111.7459
ANGL F2     C      S                 ! ANGLE     111.7459
ANGL O      S      O1               ! ANGLE     115.3458
ANGL O      S      O2               ! ANGLE     115.3458
ANGL O1     S      O2               ! ANGLE     115.3600

DIHE F      C      S      O        ! DIHE      -180.0000
DIHE F1     C      S      O        ! DIHE      -60.0184
DIHE F2     C      S      O        ! DIHE       60.0184
DIHE F      C      S      O1       ! DIHE      -60.0079
DIHE F1     C      S      O1       ! DIHE       59.9737
DIHE F2     C      S      O1       ! DIHE     -179.9895
DIHE F      C      S      O2       ! DIHE       60.0079
DIHE F1     C      S      O2       ! DIHE     179.9895
DIHE F2     C      S      O2       ! DIHE     -59.9737

=====
!DCA
=====
RESI DCA  -1.000
GROUP
ATOM N      N1      -0.611  ALPHA  -0.405  THOLE  1.211
ATOM C      CG       0.419  ALPHA  -1.042  THOLE  1.298
ATOM N1     NE      -0.616  ALPHA  -0.983  THOLE  1.337
ATOM C1     CG       0.419  ALPHA  -1.042  THOLE  1.298
ATOM N2     N1      -0.611  ALPHA  -0.405  THOLE  1.211

BOND N      C                ! DIST      1.1508
BOND C      N1               ! DIST      1.3125
BOND N1     C1               ! DIST      1.3125
BOND C1     N2               ! DIST      1.1508

```

ANGL N	C	N1		! ANGLE	175.1727
ANGL C	N1	C1		! ANGLE	118.5067
ANGL N1	C1	N2		! ANGLE	175.1727
DIHE N	C	N1	C1	! DIHE	-180.0000
DIHE C	N1	C1	N2	! DIHE	-179.9999

---



---

!OAC

---



---

RESI OAC -1.000

GROUP

ATOM C	C3	-0.426	ALPHA	-1.837	THOLE	1.104
ATOM H	HC	0.058				
ATOM H1	HC	0.058				
ATOM H2	HC	0.058				
ATOM C1	C	0.438	ALPHA	-1.243	THOLE	0.979
ATOM O	OA	-0.317	ALPHA	-0.322	THOLE	1.020
ATOM LPAO	LP	-0.110				
ATOM LPBO	LP	-0.148				
ATOM O1	OA	-0.317	ALPHA	-0.322	THOLE	1.020
ATOM LPAO1	LP	-0.100				
ATOM LPBO1	LP	-0.194				

BOND C	H		! DIST	1.0885
BOND C	H1		! DIST	1.0890
BOND C	H2		! DIST	1.0858
BOND C	C1		! DIST	1.5538
BOND C1	O		! DIST	1.2333
BOND C1	O1		! DIST	1.2354
BOND	O	LPAO	O	LPBO
BOND	O1	LPAO1	O1	LPBO1

LONEPAIR	relative	LPAO	O	C1	C	distance	0.35	angle	110.00	dihe	
											0.00
LONEPAIR	relative	LPBO	O	C1	C	distance	0.35	angle	110.00	dihe	180.00
ANISOTROPY		O	C1	LPAO	LPBO	A11	0.62676	A22	1.00186		
LONEPAIR	relative	LPAO1	O1	C1	C	distance	0.35	angle	110.00	dihe	
											0.00
LONEPAIR	relative	LPBO1	O1	C1	C	distance	0.35	angle	110.00	dihe	180.00
ANISOTROPY		O1	C1	LPAO1	LPBO1	A11	0.62676	A22	1.00186		

ANGL C	C1	O		! ANGLE	116.0140
ANGL C	C1	O1		! ANGLE	114.5436
ANGL H	C	H1		! ANGLE	106.6972
ANGL H	C	H2		! ANGLE	109.2573
ANGL H	C	C1		! ANGLE	109.6829
ANGL H1	C	H2		! ANGLE	109.2436
ANGL H1	C	C1		! ANGLE	109.7254
ANGL H2	C	C1		! ANGLE	112.0849
ANGL O	C1	O1		! ANGLE	129.4425

DIHE H	C	C1	O	! DIHE	-121.4873
DIHE H1	C	C1	O	! DIHE	121.6133
DIHE H2	C	C1	O	! DIHE	0.0569
DIHE H	C	C1	O1	! DIHE	58.5127
DIHE H1	C	C1	O1	! DIHE	-58.3867
DIHE H2	C	C1	O1	! DIHE	-179.9431

IMPH C	O	C1	O1		
--------	---	----	----	--	--



```

=====
!WATER
=====
RESI SWM4          0.000
GROUP
ATOM   OH2   ODW      0.00000 ALPHA -0.97825258 THOLE 1.3
ATOM   OM    LP       -1.11466
ATOM   H1    HDW      0.55733
ATOM   H2    HDW      0.55733

BOND   OH2   H1
BOND   OH2   H2
BOND   OH2   OM
BOND   H1    H2 ! for SHAKE

ANGLE  H1     OH2 H2

LONEPAIR bisector OM OH2 H1 H2 distance 0.24034492 angle 0.0 dihe 0.0
IC   H1  OH2  H2  H1  0.9572 104.52  0.00  37.74  1.5139
IC   H1  OM   *OH2 H2  0.9572  52.26 180.00  52.26  0.9572
IC   H2  H1   OH2  OM  1.5139  37.74  0.01  52.26  0.24034492
END

```

### 3.2 Parameters

\* FORCE FIELD PARAMETER FILE .

\*

```

=====
ATOMS
=====
MASS   1 h1      1.008000
MASS   2 h4      1.008000
MASS   3 h5      1.008000
MASS   4 hc      1.008000
MASS   6 c3     12.010000
MASS   7 cc     12.010000
MASS   8 cd     12.010000
MASS   9 cg     12.010000
MASS  10 o      16.000000
MASS  13 n1     14.010000
MASS  14 na     14.010000
MASS  15 ne     14.010000
MASS  16 f      19.000000
MASS  18 s6     32.060000
MASS  19 c      12.010000
MASS  20 oa     16.000000
MASS  51 ODW    15.999400 ! water oxygen
MASS  52 HDW    1.008000 ! water hydrogen
MASS  60 LP     0.000000 ! general lone pair
MASS  61 DRUD   0.000000 ! drude particle

```

```

=====
BONDS
=====
!
! EMIM
!
C3 H1   335.90  1.093

```

C3 NA	334.70	1.456		
CC NA	438.80	1.371		
CD NA	438.80	1.371		
CC H5	356.00	1.079		
CC CD	504.00	1.371		
CC H4	350.10	1.083		
CD H4	350.10	1.083		
C3 C3	303.10	1.535		
C3 HC	337.30	1.092		
!				
! TRIF				
!				
C3 F	363.80	1.344		
C3 S6	254.00	1.774		
O S6	541.10	1.436		
O LP	0.00	0.000		
!				
! DCA				
!				
CG NE	509.50	1.326		
CG N1	994.70	1.143		
!				
! OAc				
!				
!C3 HC	337.30	1.092	!already defined by emim	
C C3	328.30	1.508		
C OA	648.00	1.214		
OA LP	0.00	0.000		
!				
! Drudes				
!				
C DRUD	500.00	0.000		
C3 DRUD	500.00	0.000		
CC DRUD	500.00	0.000		
CD DRUD	500.00	0.000		
CG DRUD	500.00	0.000		
O DRUD	500.00	0.000		
OA DRUD	500.00	0.000		
ODW DRUD	500.00	0.000		
NA DRUD	500.00	0.000		
N1 DRUD	500.00	0.000		
NE DRUD	500.00	0.000		
F DRUD	500.00	0.000		
S6 DRUD	500.00	0.000		
!				
! WATER				
!				
ODW HDW	450.00	0.9572	! SWM4, SWM4-NDP water , Guillaume 2005	
ODW LP	0.00	0.24034492	! SWM4, SWM4-NDP water , Guillaume 2005	
HDW HDW	0.00	1.5139	! SWM4, SWM4-NDP water , Guillaume 2005	

---



---

ANGLES

---



---

!

!EMIM

!

C3 NA CC	62.560	125.090		
H1 C3 H1	39.180	109.550		
H1 C3 NA	49.900	109.450		
NA CC NA	73.650	109.330	! SAME AS NA C2 NA	

NA CC H5	49.760	122.100
NA CD CC	72.910	109.420
NA CD H4	50.220	119.660
NA C3 C3	65.730	112.810
CC NA CD	63.880	128.010
CC NA CC	68.940	109.900
NA CC CD	72.910	109.420
NA CC H4	50.220	119.660
CC CD H4	47.190	129.110
CD NA C3	62.560	125.090
CD CC H4	47.190	129.110
C3 C3 HC	46.370	110.050
H1 C3 C3	46.360	110.070
HC C3 HC	39.430	108.350

!

! TRIF

!

C3 S6 O	41.660	108.320
F C3 F	71.260	107.160
F C3 S6	81.220	109.670
O S6 O	46.660	119.730

!

! DCA

!

CG NE CG	66.000	140.000
NE CG N1	65.040	174.070

!

! OAc

!

C3 C OA	68.030	123.110
!HC C3 HC	39.430	108.350
HC C3 C	47.200	109.680
OA C OA	78.170	130.380

already defined by emim

!

! H2O

!

HDW ODW HDW	0.00	104.52
LP ODW HDW	0.00	000.00
ODW HDW HDW	0.00	000.00

---



---

## DIHEDRALS

---



---

!

!EMIM

!

X C3 NA X	0.000	2	0.0
X CC NA X	1.700	2	180.0
X CD NA X	1.700	2	180.0
X CC CD X	4.000	2	180.0
X C3 C3 X	0.156	3	0.0
CC NA C3 C3	0.027	1	0.0
CC NA C3 C3	0.232	2	180.0
CC NA C3 C3	0.314	3	180.0
CC NA C3 C3	0.033	4	180.0

```

CC NA C C3      0.0255      6      0.0

!
! TRIF
!
F C3 S6 O      0.144      3      0.0

!
! DCA
!
X CG NE X      0.000      2      180.0
CG NE CG N1    0.000      2      180.0      ! SAME AS X C1 NE X

!
! OAc
!
X C C3 X      0.000      2      180.0
HC C3 C OA    0.800      1      0.0
HC C3 C OA    0.080      3      180.0

```

---



---

IMPROPERS

---



---

```

!
!EMIM
!
C3 CC NA CD    1.100      2      180.0      ! USING DEFAULT VALUE
H5 NA CC NA    1.100      2      180.0      ! USING DEFAULT VALUE
C3 CC NA CC    1.100      2      180.0      ! USING DEFAULT VALUE
CD H4 CC NA    1.100      2      180.0      ! USING DEFAULT VALUE
CC H4 CD NA    1.100      2      180.0      ! USING DEFAULT VALUE

!
! TRIF
!
!
! DCA
!
!
! OAc
!
X OA C OA      1.100      2      180.0

```

---



---

NONBONDED

---



---

```

!
!          EMIN      RMIN/2          EMIN/2      RMIN (FOR 1-4'S)
!          (KCAL/MOL)      (A)
!
!old values (unscaled):
!
!C3      0.00      -0.1094      1.9080      0.00      -0.0547      1.9080
!H1      0.00      -0.0157      1.3870      0.00      -0.00775     1.3870
!NA      0.00      -0.1700      1.8240      0.00      -0.0850      1.8240
!CC      0.00      -0.0860      1.9080      0.00      -0.0430      1.9080
!CD      0.00      -0.0860      1.9080      0.00      -0.0430      1.9080
!H5      0.00      -0.0150      1.3590      0.00      -0.0075      1.3590
!H4      0.00      -0.0150      1.4090      0.00      -0.0075      1.4090

```

```

!HC      0.00  -0.0157  1.4870      0.00  -0.00775  1.4870
!
!new values , scaled via lambda=0.4
C3      0.00  -0.0741  1.9080      0.00  -0.0371  1.9080
NA      0.00  -0.1427  1.8240      0.00  -0.0713  1.8240
CC      0.00  -0.0602  1.9080      0.00  -0.0301  1.9080
CD      0.00  -0.0600  1.9080      0.00  -0.0300  1.9080
H1      0.00  -0.0157  1.3870      0.00  -0.00775  1.3870
H5      0.00  -0.0150  1.3590      0.00  -0.0075  1.3590
H4      0.00  -0.0150  1.4090      0.00  -0.0075  1.4090
HC      0.00  -0.0157  1.4870      0.00  -0.00775  1.4870

!
! TRIF
!
!old values (unscaled):
!
!S6      0.00  -0.2500  2.0000      0.00  -0.1250  2.00
!F      0.00  -0.0610  1.7500      0.00  -0.0305  1.7500
!O      0.00  -0.2100  1.6612      0.00  -0.1050  1.6612
!
!new values , scaled via lambda=0.4
S6      0.00  -0.1000  2.0000      0.00  -0.0500  2.00
F      0.00  -0.0607  1.7500      0.00  -0.0304  1.7500
O      0.00  -0.2005  1.6612      0.00  -0.1003  1.6612

!
! dca
!
!old values (unscaled):
!
!N1      0.00  -0.1700  1.8240      0.00  -0.0850  1.8240
!NE      0.00  -0.1700  1.8240      0.00  -0.0850  1.8240
!CG      0.00  -0.2100  1.9080      0.00  -0.1050  1.9080
!
!new values , scaled via lambda=0.4
N1      0.00  -0.1584  1.8240      0.00  -0.0792  1.8240
NE      0.00  -0.1399  1.8240      0.00  -0.0699  1.8240
CG      0.00  -0.1703  1.9080      0.00  -0.0851  1.9080

!
! OAc
!
C      0.00  -0.0860  1.9080      0.00  -0.0430  1.9080
OA     0.00  -0.2100  1.6612      0.00  -0.1050  1.6612
!
! Wildcard for Drudes and dummy atom
!
DRUD   0.0  -0.0000  0.0000      0.00  -0.00  0.00
LP     0.0  -0.0000  0.0000      0.00  -0.00  0.00
!
! WATER
!
! SWM4, SWM4-NDP water , GL, 2005
HDW    0.0  -0.0000  0.0000      0.00  -0.0000  0.00

```

```
! SWM4, SWM4-NDP water, GL, 2005
ODW      0.0   -0.2109   1.7869      0.00   -0.10545   1.7869
```

END

### 3.3 Dynamics

```
* emim_trif_1000 polarizable
*
```

---

---

```
! Topology and parameters
```

---

---

```
open read card unit 10 name ./il_pol.rtf
read  rtf card unit 10
close unit 10
```

```
open read card unit 20 name ./il_pol_04.prm
read  para card unit 20
close unit 20
```

---

---

```
! sequence, coordinates and simulation box
```

---

---

```
read SEQUENCE EMIM 1000
generate EMIM SETUP WARN DRUDE DMASS 0.2
```

```
read SEQUENCE DCA 1000
generate DCA SETUP WARN DRUDE DMASS 0.2
```

```
open read unit 10 card name structures/npt_04.crd
read  coor unit 10 card
close unit 10
```

```
set xtl = 64.27
calc xtl2 = @xtl/2
set grid = 72
```

```
crystal DEFINE cubic @xtl @xtl @xtl 90.0 90.0 90.0
crystal BUILD CUTOFF @xtl2 noperations 0
image BYRESIDUE SELECT ALL END
```

```
energy  bycb atom vatom cdiel ewal pmew vswitch -
        ctonnb          10  -
        ctofnb          11  -
        cutnb           14  -
        cutim           14  -
        kappa            0.41 -
        fftx             @grid -
        ffty             @grid -
        fftz             @grid -
        spli order       6  -
        qcor             0  -
        wmin             1.5 -
        inbfrq           -1  -
        imgfrq           -1
```

```
shake BONH PARAM TOL 1.0e-9 NOFAST -
```

```
SELECT ( .not. TYPE D* ) END -  
SELECT ( .not. TYPE D* ) END
```

---

---

```
! Temperature control - - - N V T - - -
```

---

---

```
if @?temp EQ 0 SET temp = 260.
```

```
tpcontrol N THER 2 NSTEP 20 -  
  THER 1 TAU 0.1 TREF @temp SELECT .NOT. TYPE D* END -  
  THER 2 TAU 0.005 TREF 1.00 SELECT TYPE D* END -
```

---

---

```
! Dynamics
```

---

---

```
if @?nstep EQ 0 set nstep = 200000  
if @?dt EQ 0 set dt = 0.0005 ! in ps
```

```
if @?index EQ 0 set index = 1
```

```
if @index EQ 1 then  
  set starter = START  
  set iunrea = -1
```

```
else  
  set starter = RESTART  
  set iunrea = 10
```

```
  calc prev = @index - 1  
  open unit 10 form name traj_04/emim_dca_pol_@prev.rst  
endif
```

```
! current restart file  
open unit 15 form name traj_04/emim_dca_pol_@index.rst
```

```
! current trajectory file  
open unit 20 file name traj_04/emim_dca_pol_@index.dcd
```

```
! GPU support  
cuda init  
cuda use  
energy
```

```
! trajectory production  
dyna VV2 @starter -  
  ISEED 43 36 783 28 -  
  NSTEP @nstep -  
  TIMESTEP @dt -  
  IPRFRQ 1000 -  
  IMGFRQ -1 -  
  INBFRQ -1 -  
  NTRFRQ 5000 -  
  NPRINT 100 -  
  NSAVC 50 -  
  NSAVV -1 -  
  IUNREA @iunrea -  
  IUNWRI 15 -  
  IUNCRD 20 -  
  IUNVEL -1 -  
  FIRSTT @temp
```

stop



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