Supporting information for

Are there stable ion-pairs in room-temperature ionic liquids? Molecular dynamics simulations of 1-*n*-butyl 3-methylimidazolium hexafluorophosphate [bmim][PF_6]

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Content

1. Absolute energies and optimized geometries of [bmim] cation and $[PF_6]$ anion

Atom type	X (Å)	Y(Å)	Z(Å)
P	0.000000	0.000000	0.000000
F	0.000000	0.000000	1.655703
F	1.655712	0.000000	0.000000
F	0.000000	1.655712	0.000000
F	-1.655712	0.000000	0.000000
F	0.000000	-1.655712	0.000000
F	0.000000	0.000000	-1.655703

Table 1: Optimized geometry of $[PF_6]$. Total energy is -940.9613816828 Hartree.

Atom type	X (Å)	Y(Å)	Z(Å)
C	0.656534	-0.111342	-0.663949
N	-0.611510	-0.277193	-0.249029
C	-0.607509	-0.436133	1.128964
C	0.697406	-0.369842	1.540768
N	1.471599	-0.165107	0.406951
C	-1.823375	-0.217942	-1.109682
C	-2.574512	1.111951	-0.953907
C	2.943949	-0.043011	0.380549
H	0.970048	0.036366	-1.687815
H	-1.520594	-0.583114	1.688003
H	1.137104	-0.453270	2.524800
H	3.263113	0.139282	-0.649358
H	3.246227	0.796085	1.015852
H	3.390112	-0.972834	0.748528
H	-1.489868	-0.365455	-2.143012
H	-2.458276	-1.066345	-0.829944
C	-3.825356	1.145420	-1.852899
H	-2.868120	1.245571	0.097631
H	-1.902346	1.942288	-1.214019
C	-4.594185	2.471000	-1.711786
H	-3.521476	0.999045	-2.900283
H	-4.480798	0.301920	-1.590937
H	-5.478491	2.479407	-2.360132
H	-4.929327	2.619408	-0.676217
H	-3.958216	3.322341	-1.990301

Table 2: Optimized geometry of [bmim]. Total energy is -423.1564494543 Hartree.

2. Supporting figures(Figure S1-S3)

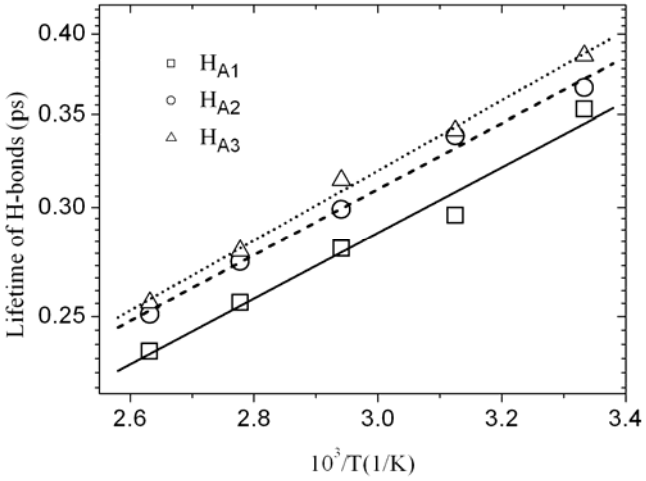

Figure S1. Lifetimes of different hydrogen bonds are shown as a function of temperature. In order to estimate the accuracy of the calculations, ten individual trajectories were analyzed to form a data set, of which the standard deviations were found to be within the range 5-16 % (for clearness, they are not shown). The straight lines show the Arrhenius fits (solid: HA1; dashed: HA2; dotted: HA3)

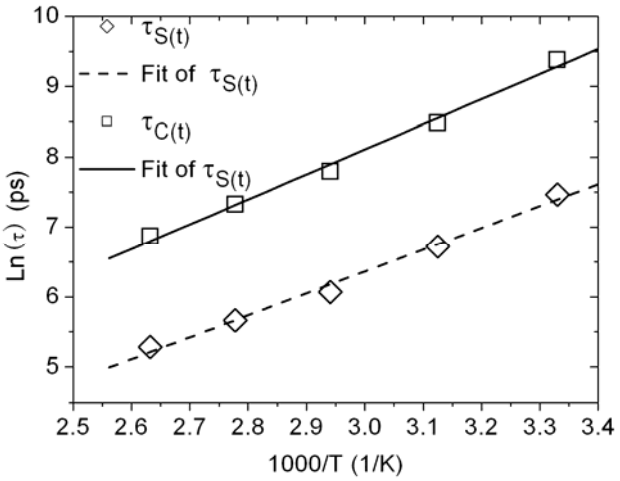

Figure S2. Temperature dependence of structural relaxation time and the lifetime of ion-pairs for the temperature range 300-380 K. The two lines are fits to Arrhenius' law. Error bars are smaller than the size of the symbols.

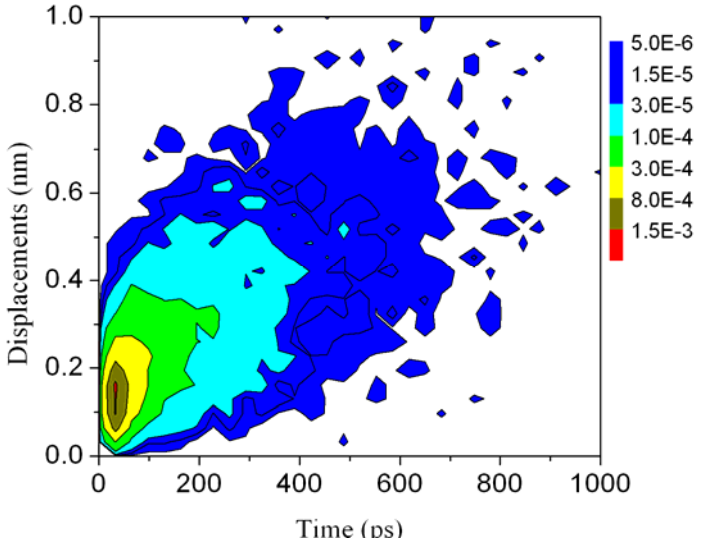

Figure S3. Occurrence density of ion-pair as functions of their lifetimes and displacements. The density is accumulated over 30 ns at 380 K. The plot unit (color code) is the number of occurrence of ion association per (0.004 nm × 8 ps).