Physical Chemistry Chemical Physics
SUPPORTING INFORMATION

Molecular Dynamics Simulation of Geminal Dicationic Ionic Liquids $[C_n(mim)_2][NTf_2]_2$ - Structural and Dynamical Properties

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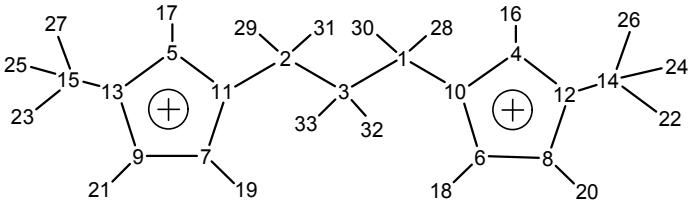
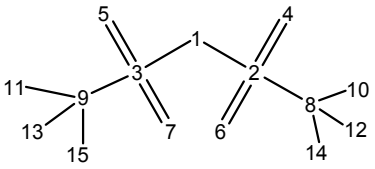
Table S1 Electrostatic charges for the atoms of $[C_3(mim)_2][NTF_2]_2$ GDIL obtained at B3LYP/6-31++G(d,p) level of theory by CHELPG method (each ionic liquid has two anions: anion a and anion b)

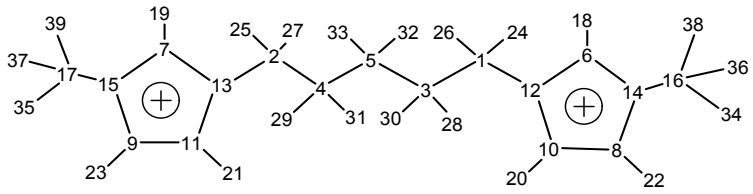


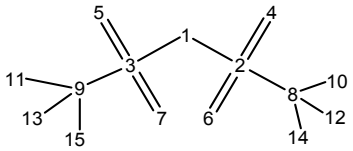


$[C_3(mim)_2]^{2+}$		
Number	Atom	q/e
1	C	0.376
2	C	0.329
3	C	-0.054
4	C	0.051
5	C	0.170
6	C	-0.005
7	C	-0.096
8	C	-0.169
9	C	-0.237
10	N	-0.040
11	N	-0.112
12	N	0.150
13	N	0.106
14	C	-0.096
15	C	-0.135
16	H	0.082
17	H	0.051
18	H	0.155
19	H	0.182
20	H	0.194
21	H	0.198
22	H	-0.011
23	H	-0.055
24	H	-0.105
25	H	0.008
26	H	0.005
27	H	-0.005
28	H	0.072
29	H	0.123
30	H	0.091
31	H	0.118
32	H	0.123
33	H	0.088
	Total	1.55

$[NTF_2]^-$		
Number	Atom	q/e
1a	Na	-0.468
2a	Sa	0.831
3a	Sa	0.898
4a	Oa	-0.460
5a	Oa	-0.484
6a	Oa	-0.504
7a	Oa	-0.515
8a	Ca	0.564
9a	Ca	0.464
10a	Fa	-0.187
11a	Fa	-0.174
12a	Fa	-0.242
13a	Fa	-0.194
14a	Fa	-0.151
15a	Fa	-0.127
1b	Nb	-0.574
2b	Sb	0.953
3b	Sb	0.812
4b	Ob	-0.479
5b	Ob	-0.473
6b	Ob	-0.531
7b	Ob	-0.468
8b	Cb	0.488
9b	Cb	0.591
10b	Fb	-0.176
11b	Fb	-0.220
12b	Fb	-0.200
13b	Fb	-0.236
14b	Fb	-0.134
15b	Fb	-0.154
	Total	-1.55

Table S2 Electrostatic charges for the atoms of $[C_5(mim)_2][NTF_2]_2$ GDIL obtained at B3LYP/6-31++G(d,p) level of theory by CHELPG method (each ionic liquid has two anions: anion a and anion b)





$[C_5(mim)_2]^{2+}$		
Number	Atom	q/e
1	C	-0.092
2	C	-0.090
3	C	0.009
4	C	-0.067
5	C	0.133
6	C	-0.072
7	C	-0.037
8	C	-0.169
9	C	-0.226
10	C	-0.114
11	C	-0.150
12	N	0.124
13	N	0.189
14	N	0.123
15	N	0.141
16	C	-0.147
17	C	-0.168
18	H	0.163
19	H	0.190
20	H	0.211
21	H	0.185
22	H	0.193
23	H	0.174
24	H	0.072
25	H	0.124
26	H	0.090
27	H	0.086
28	H	-0.004
29	H	0.005
30	H	0.015
31	H	0.110
32	H	-0.005
33	H	-0.020
34	H	0.112
35	H	0.078
36	H	0.140
37	H	0.086
38	H	0.153
39	H	0.098
	Total	1.65

$[NTF_2]^-$		
Number	Atom	q/e
1a	Na	-0.564
2a	Sa	0.971
3a	Sa	0.948
4a	Oa	-0.500
5a	Oa	-0.496
6a	Oa	-0.546
7a	Oa	-0.575
8a	Ca	0.496
9a	Ca	0.486
10a	Fa	-0.182
11a	Fa	-0.172
12a	Fa	-0.189
13a	Fa	-0.187
14a	Fa	-0.156
15a	Fa	-0.150
1b	Nb	-0.548
2b	Sb	0.930
3b	Sb	0.901
4b	Ob	-0.494
5b	Ob	-0.480
6b	Ob	-0.543
7b	Ob	-0.544
8b	Cb	0.523
9b	Cb	0.498
10b	Fb	-0.191
11b	Fb	-0.166
12b	Fb	-0.197
13b	Fb	-0.196
14b	Fb	-0.163
15b	Fb	-0.160
	Total	-1.65

Table S3 Comparison between the simulated densities (in g.cm^{-3}) of the studied GDILs with experimental values[28] at different temperatures and 1 atm

T/K	$[C_3(mim)_2][NTf_2]_2$			$[C_5(mim)_2][NTf_2]_2$		
	Exp.	Simu.	% Dev.	Exp.	Simu.	% Dev.
298.15	1.6197	1.6699	-3.09	1.5695	1.5180	3.28
318.15	1.6016	1.6545	-3.30	1.5529	1.5062	3.01
333.15	1.5880	1.6433	-3.48	1.5405	1.4919	3.15
353.15	1.5801	1.6302	-3.19	1.5239	1.4813	2.79

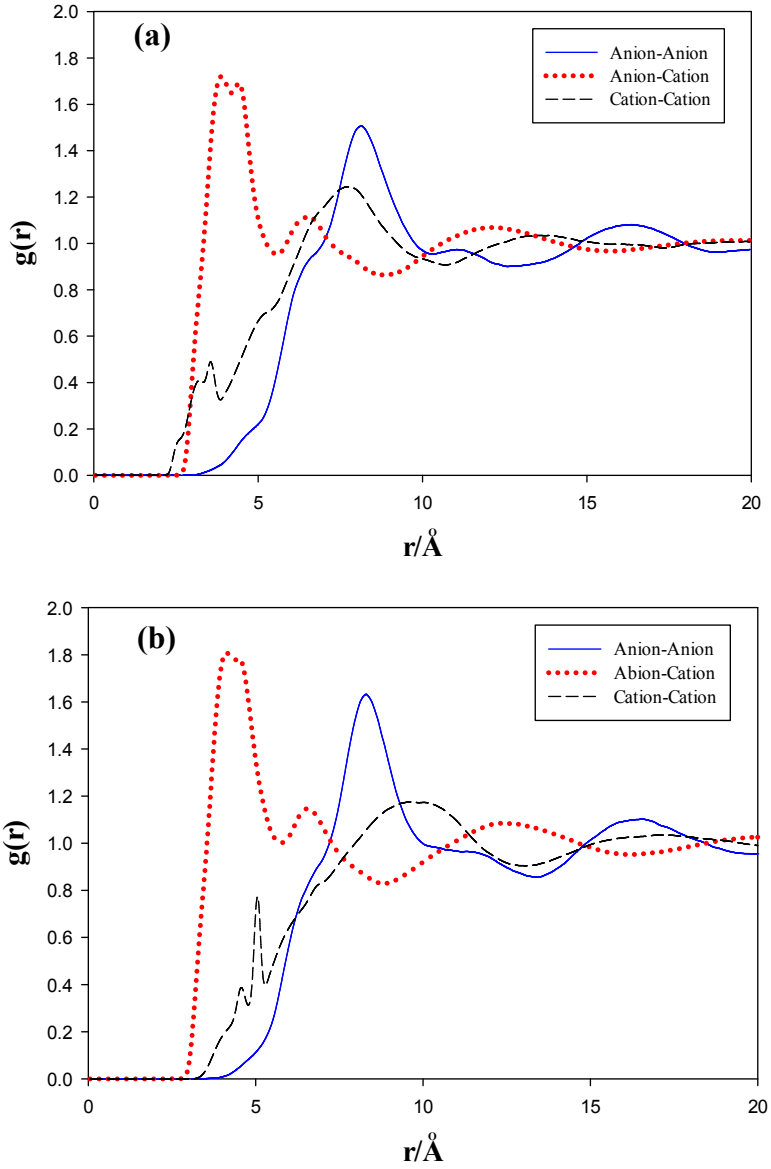


Fig. S1 Calculated radial distribution functions of cation-cation, anion-anion, and cation-anion for (a) $[C_3(mim)_2][NTf_2]_2$ and (b) $[C_5(mim)_2][NTf_2]_2$ at 333.15 K and 1 atm.

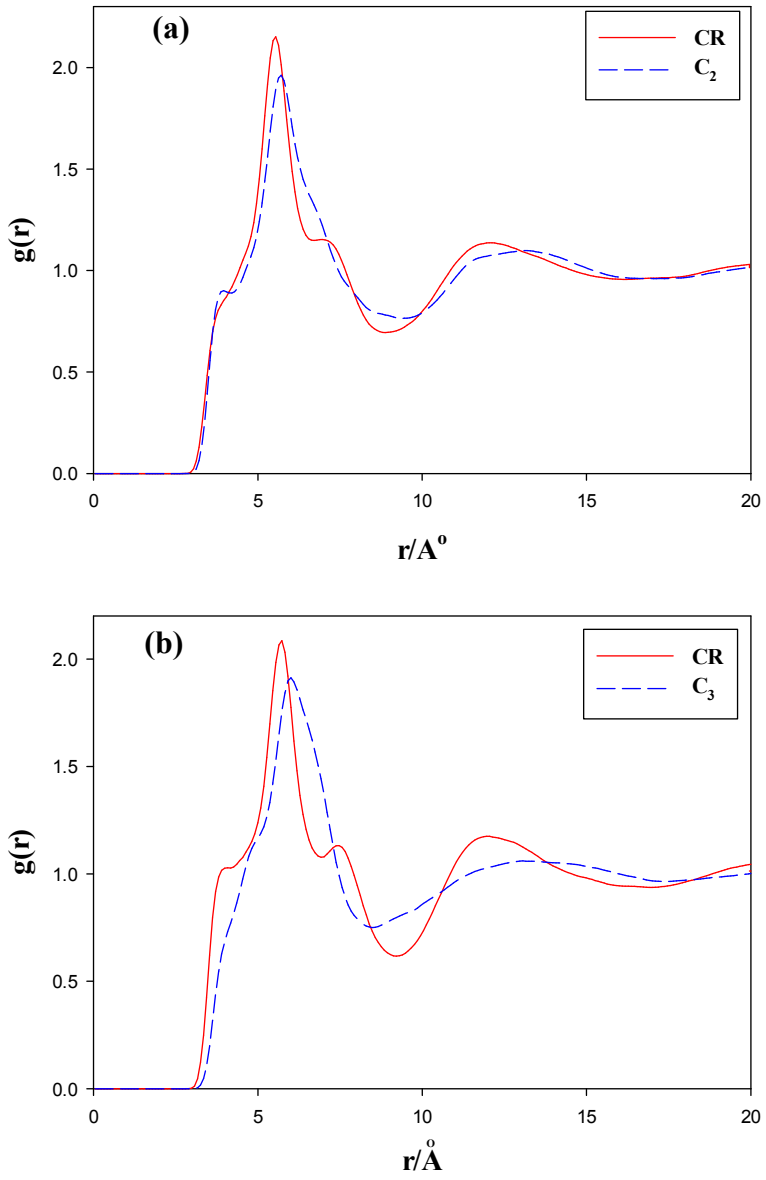


Fig. S2 Radial distribution functions of anion $[NTf_2]^-$ around the CR carbon atom of the rings and also the carbon atom in the middle of the alkyl chain for (a) $[C_3(mim)_2][NTf_2]_2$ and (b) $[C_5(mim)_2][NTf_2]_2$ at 333.15 K and 1 atm. The labels are defined according to Figure 1.

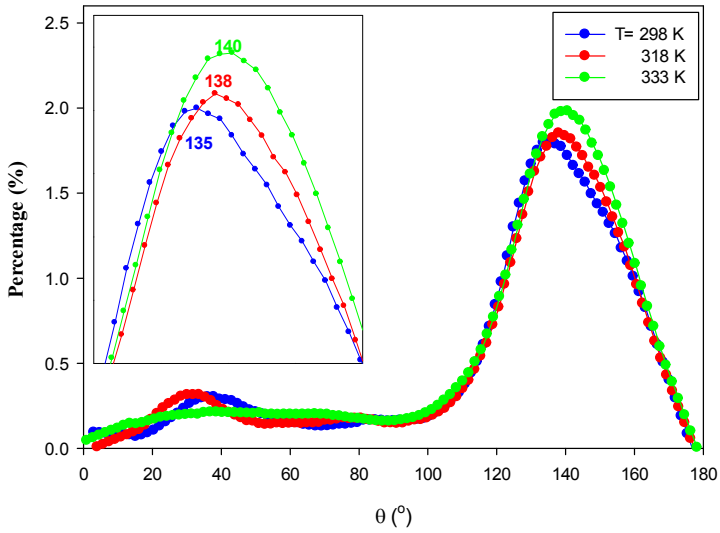


Fig. S3 Distribution of the angles formed by two vectors pointing from the rings towards the center atom of linkage chain for $[C_5(mim)_2][NTf_2]_2$ at different temperatures.

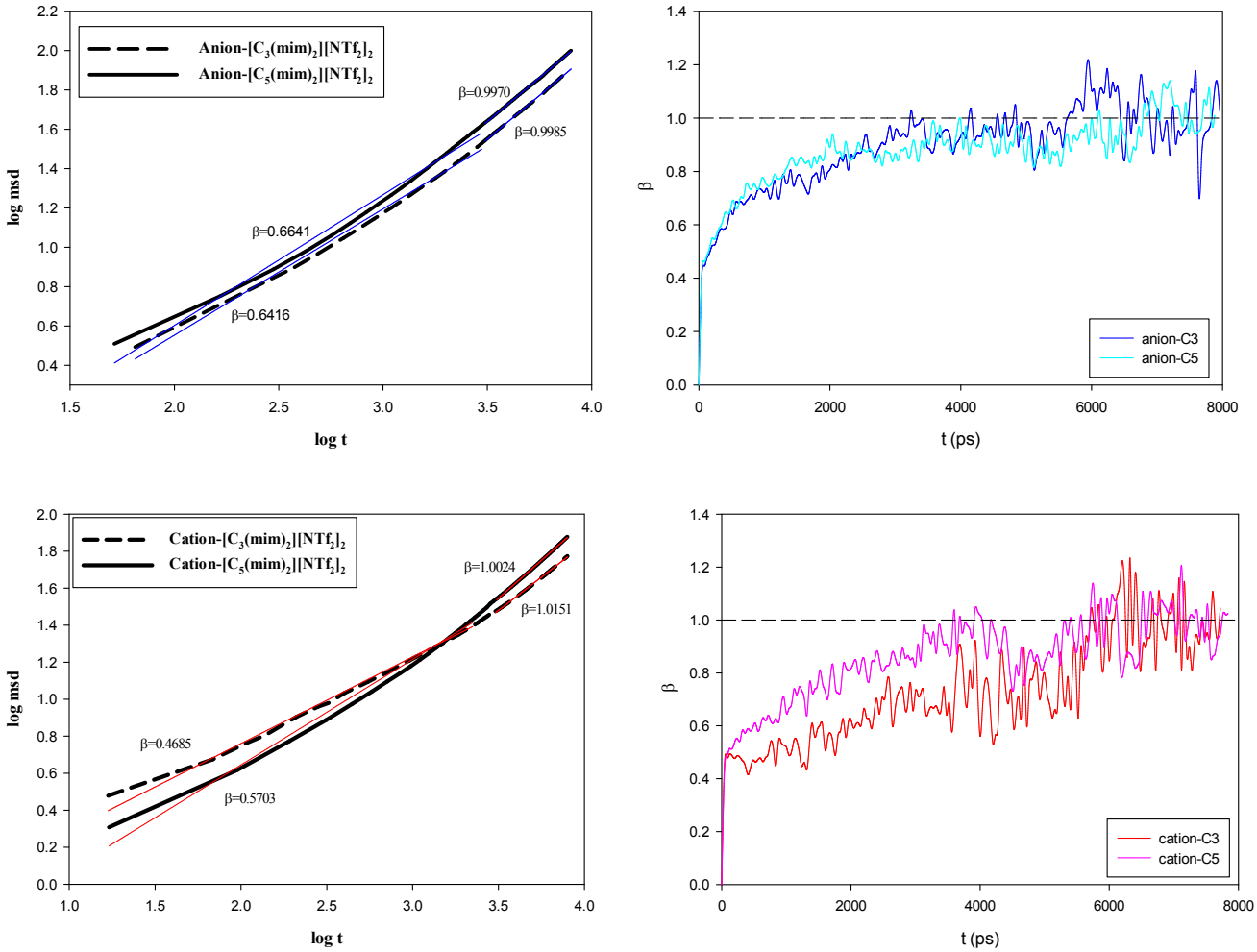


Fig. S4 The log(MSD) versus log t and also β versus t plots for the cations and anions of the $[C_3(mim)_2][NTf_2]_2$ and $[C_5(mim)_2][NTf_2]_2$.

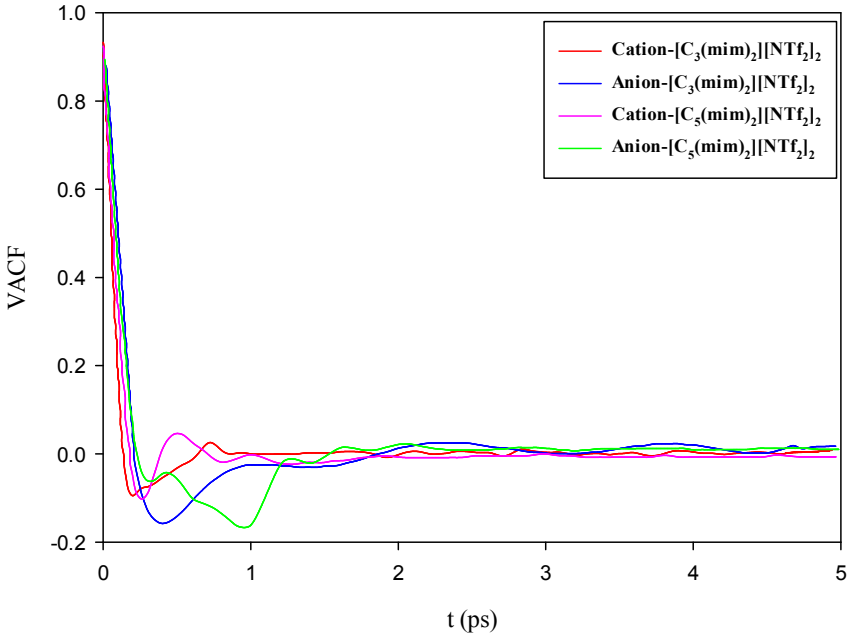


Fig. S5 The VACF plots for the cations and anions of the studied GDILs at 333.15 and 1 atm.

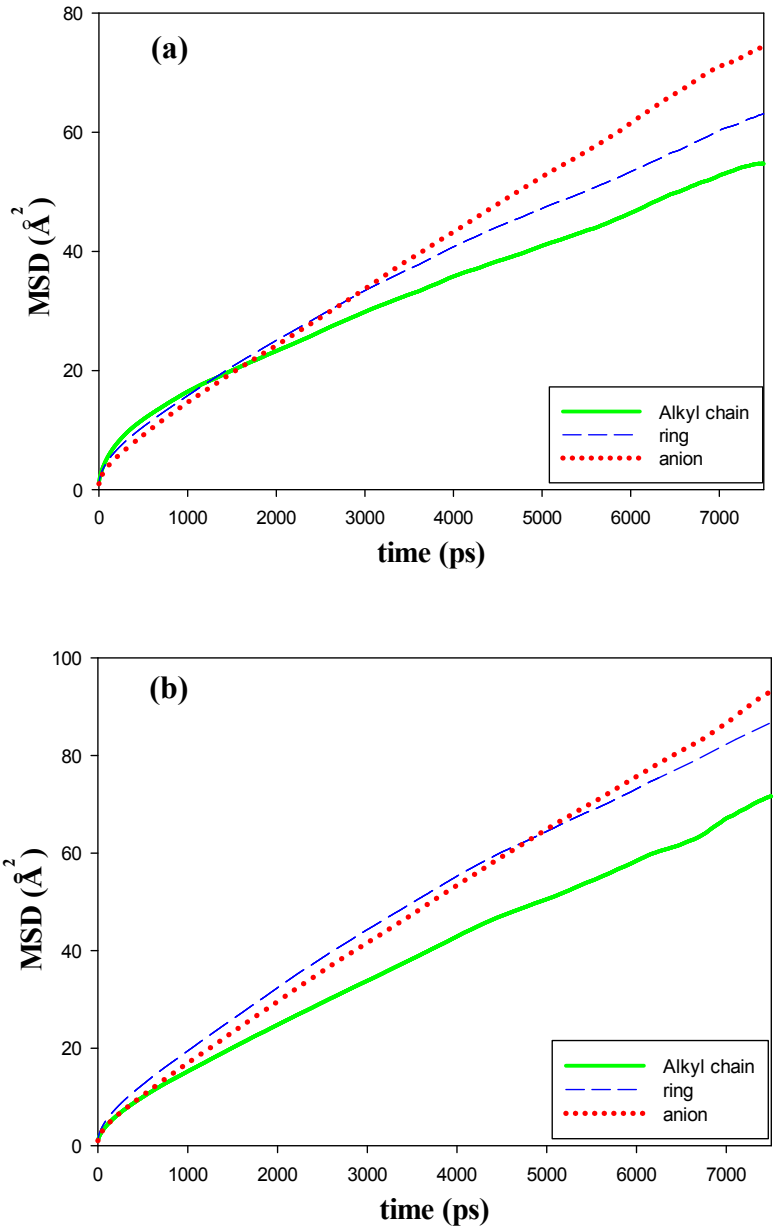


Fig. S6 Comparion among MSDs of the ring (the CR atom in the imidazolium cation), alkyl chain (the carbon atom in the middle of the alkyl chain), and anion (the nitrogen atom of the $[NTf_2]^-$), for (a) $[C_3(mim)_2][NTf_2]_2$ and (b) $[C_5(mim)_2][NTf_2]_2$ at 333.15 K and 1 atm.

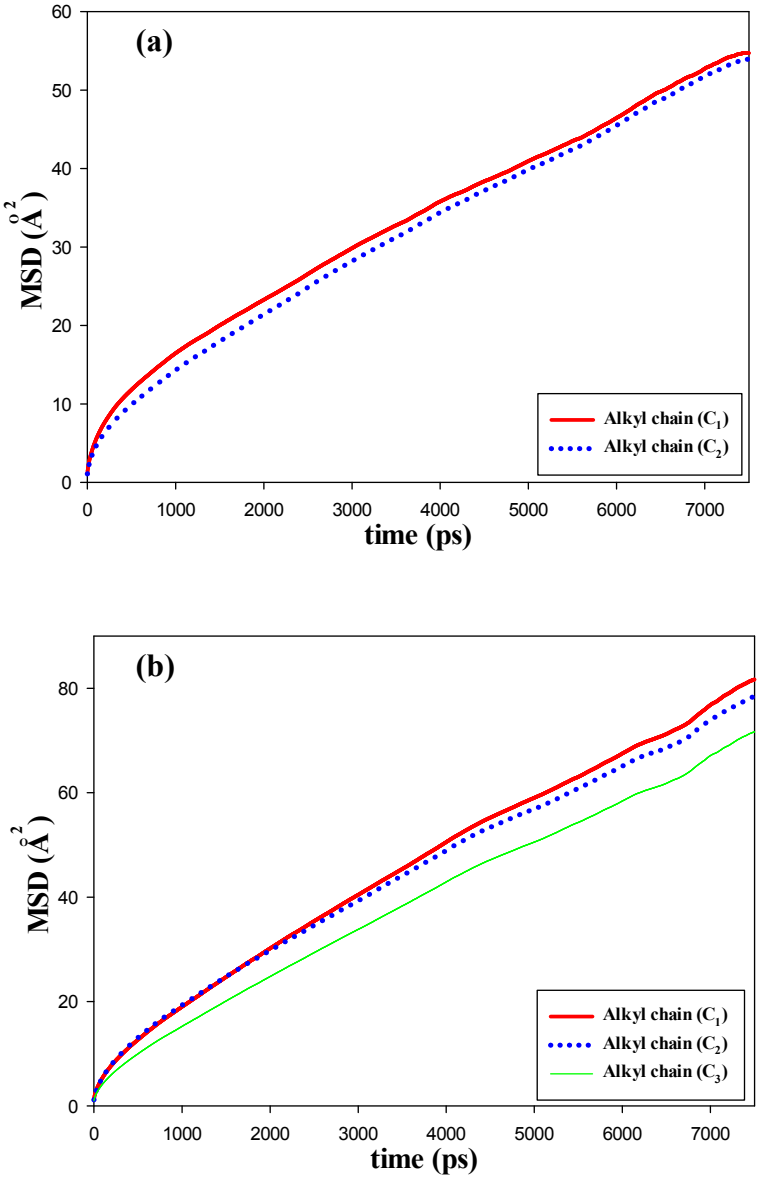


Fig. S7 Mean square displacements (MSDs) of the carbon atoms of the alkyl chain in (a) $[C_3(mim)_2][NTf_2]_2$ and (b) $[C_5(mim)_2][NTf_2]_2$ at 333.15 K and 1 atm.

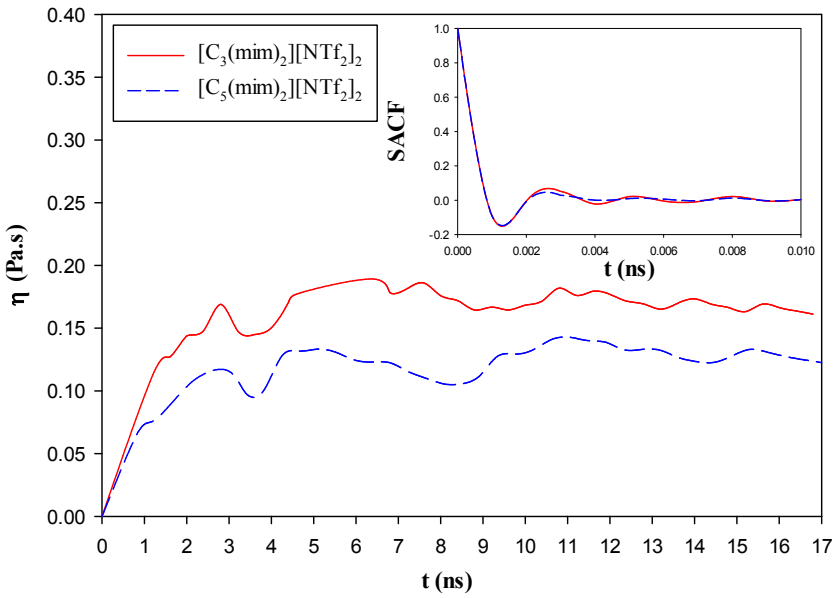


Fig. S8 Calculated viscosities for the studied GDILs as a function of simulation time at 333.15 K and 1 atm using Green-Kubo method. The plots of stress autocorrelation functions (SACFs) have been also shown.