# Homogenous Mixing of Ionic Liquids: Molecular Dynamics Simulations

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# Supporting Information

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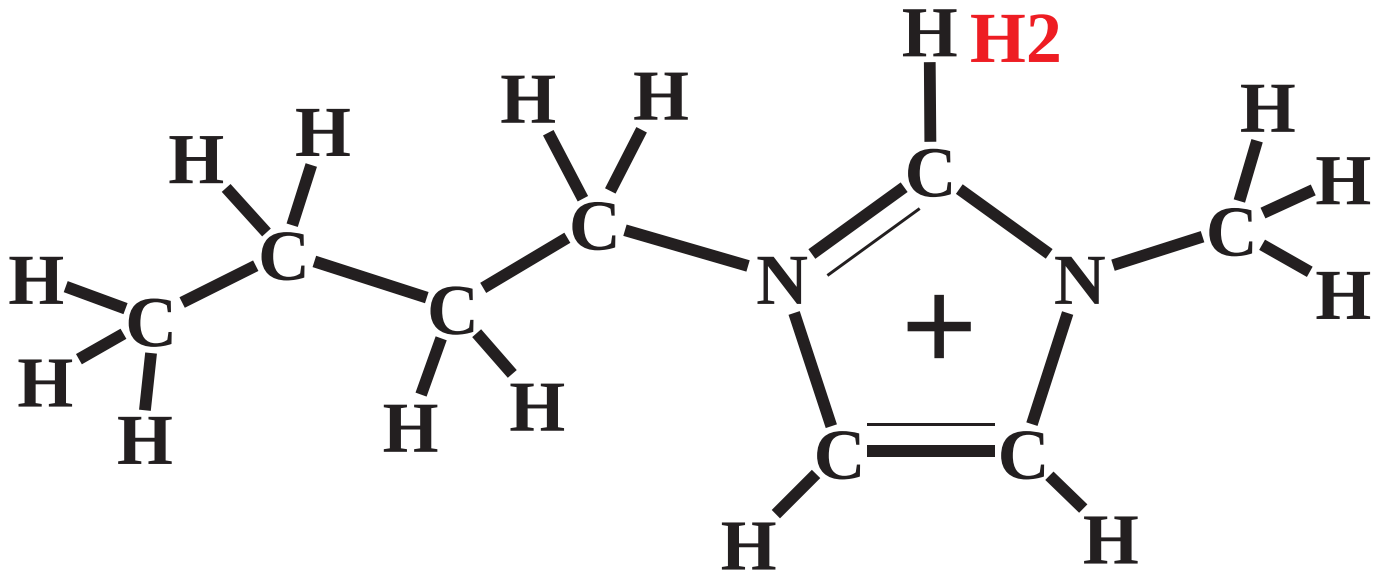



**Fig. S1** Schematic of cation.

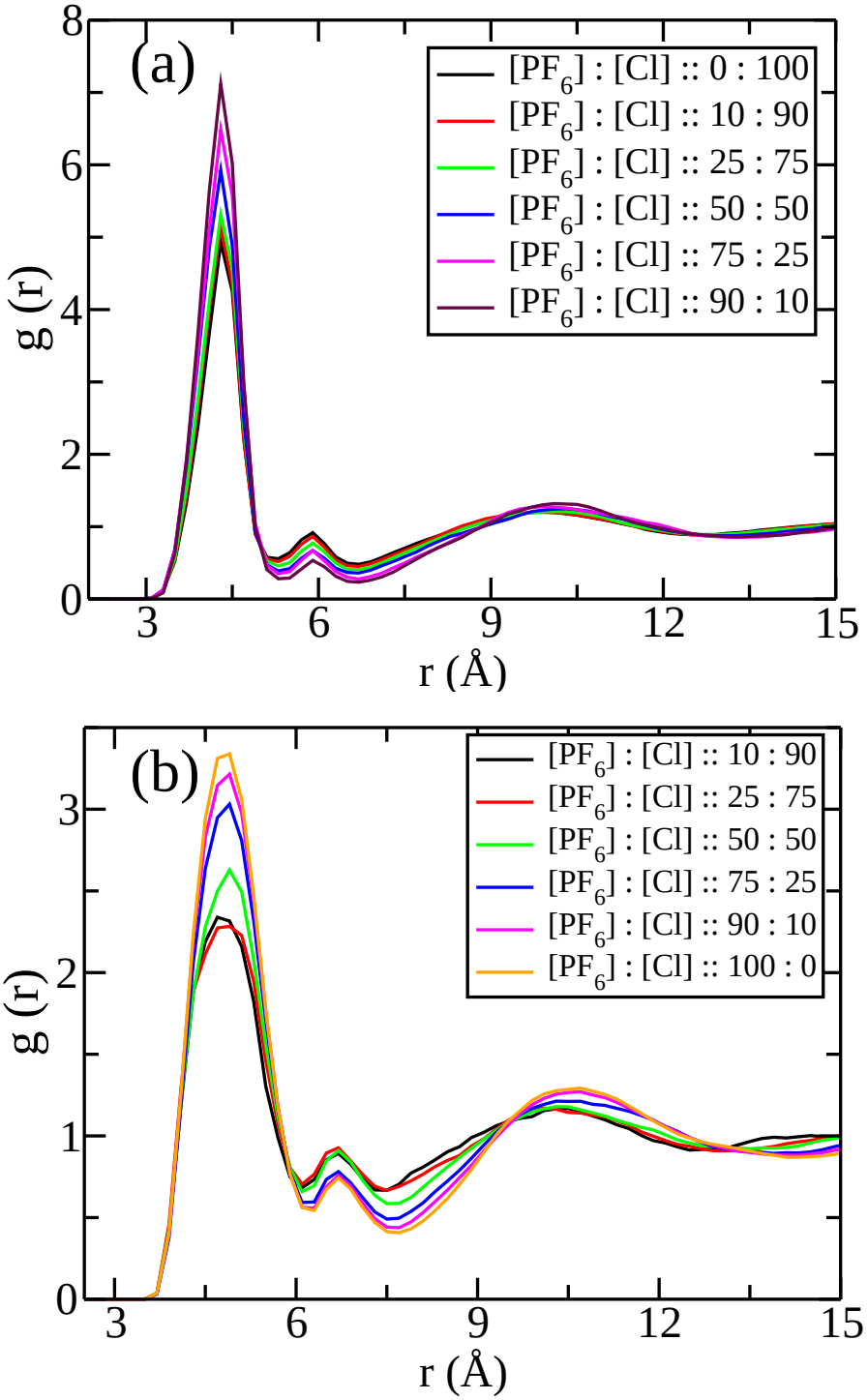



**Fig. S2** Radial distribution function between (a) Cation - Cl, (b) Cation - $PF_6$ in the $[C_4mim][PF_6]$-$[C_4mim][Cl]$ system displayed over a larger distance than what is shown in the main manuscript.

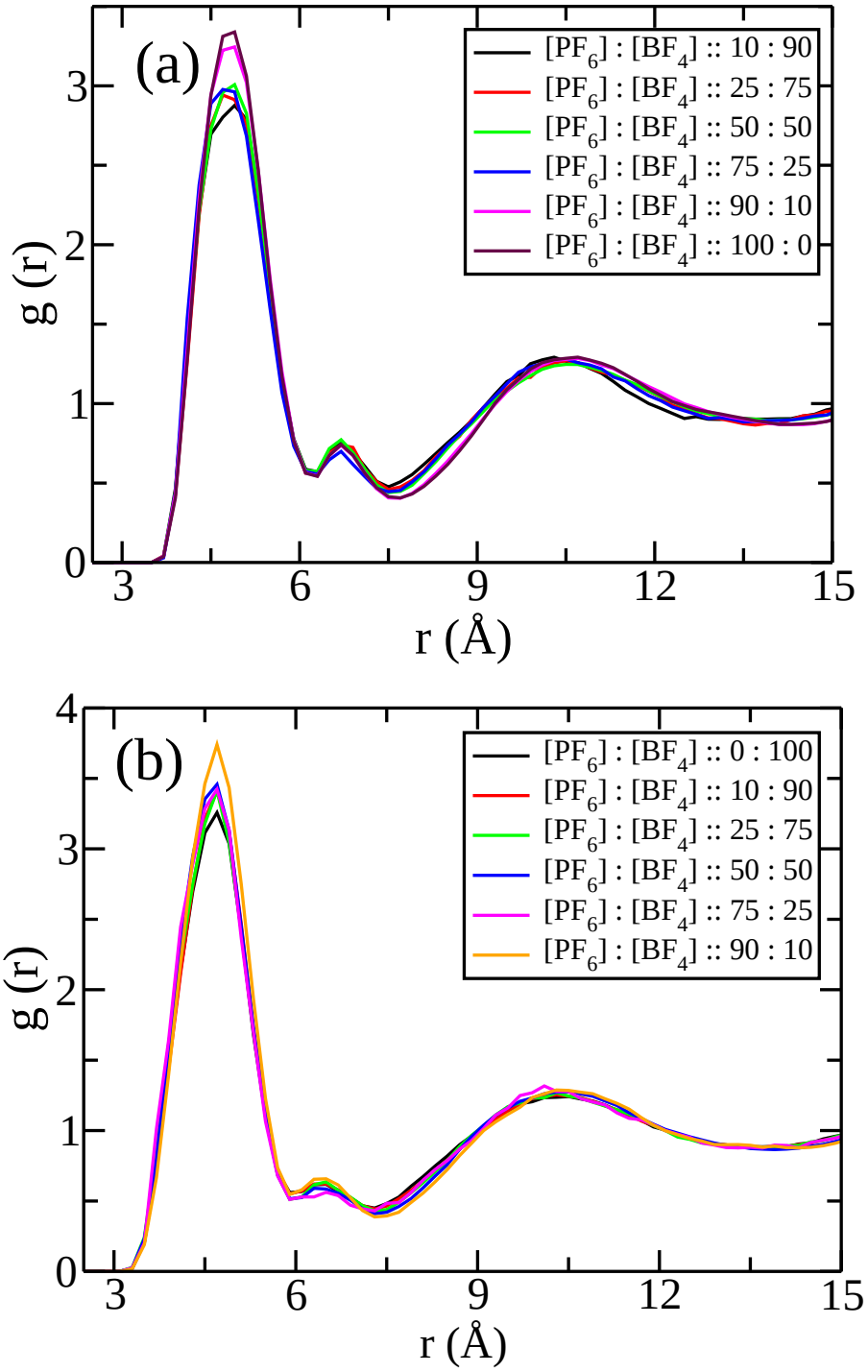



**Fig. S3** Radial distribution function between (a) Cation - $PF_6$, (b) Cation - $BF_4$ in the $[C_4mim][PF_6]$-$[C_4mim][BF_4]$ system displayed over a larger distance than what is shown in the main manuscript.

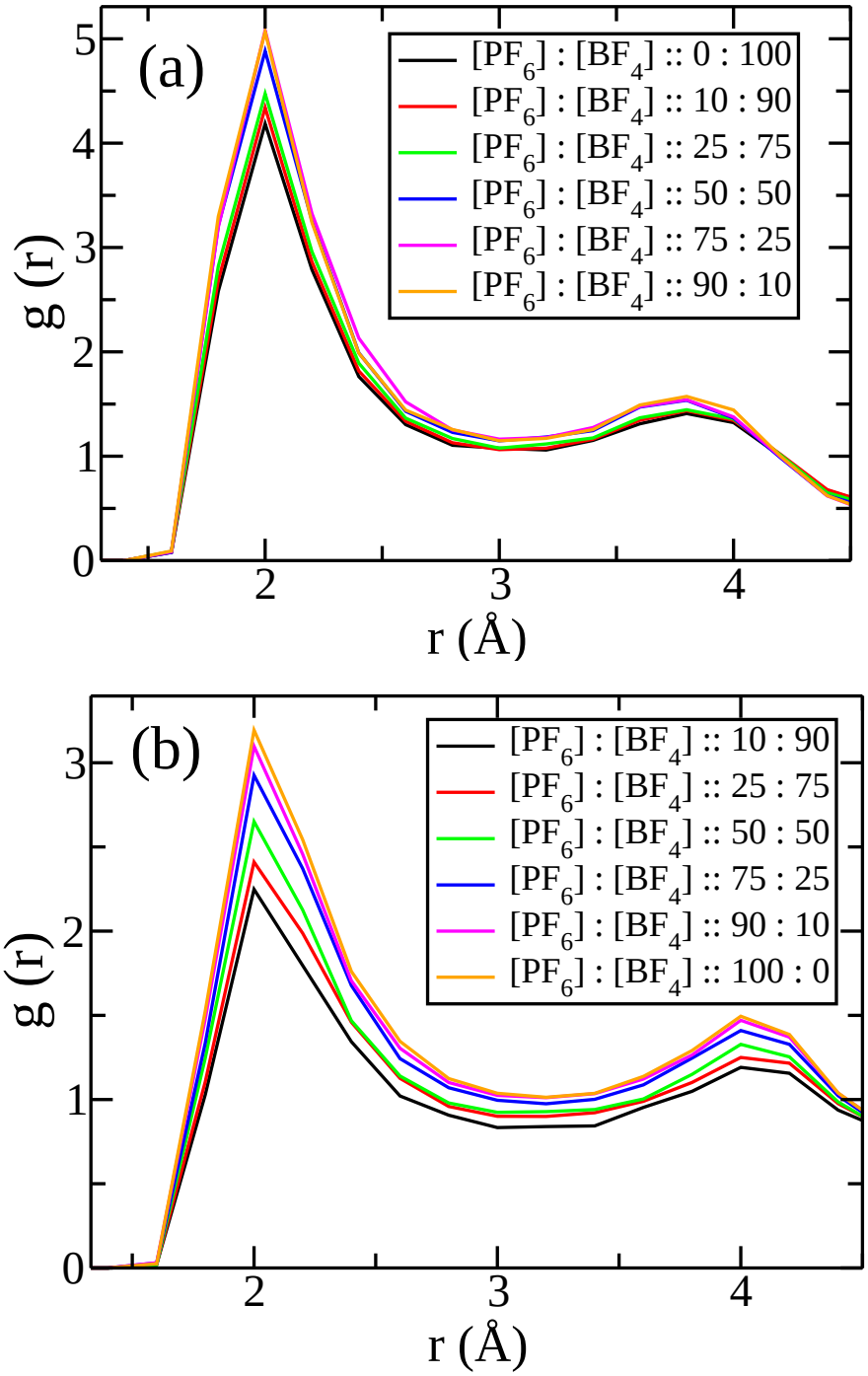
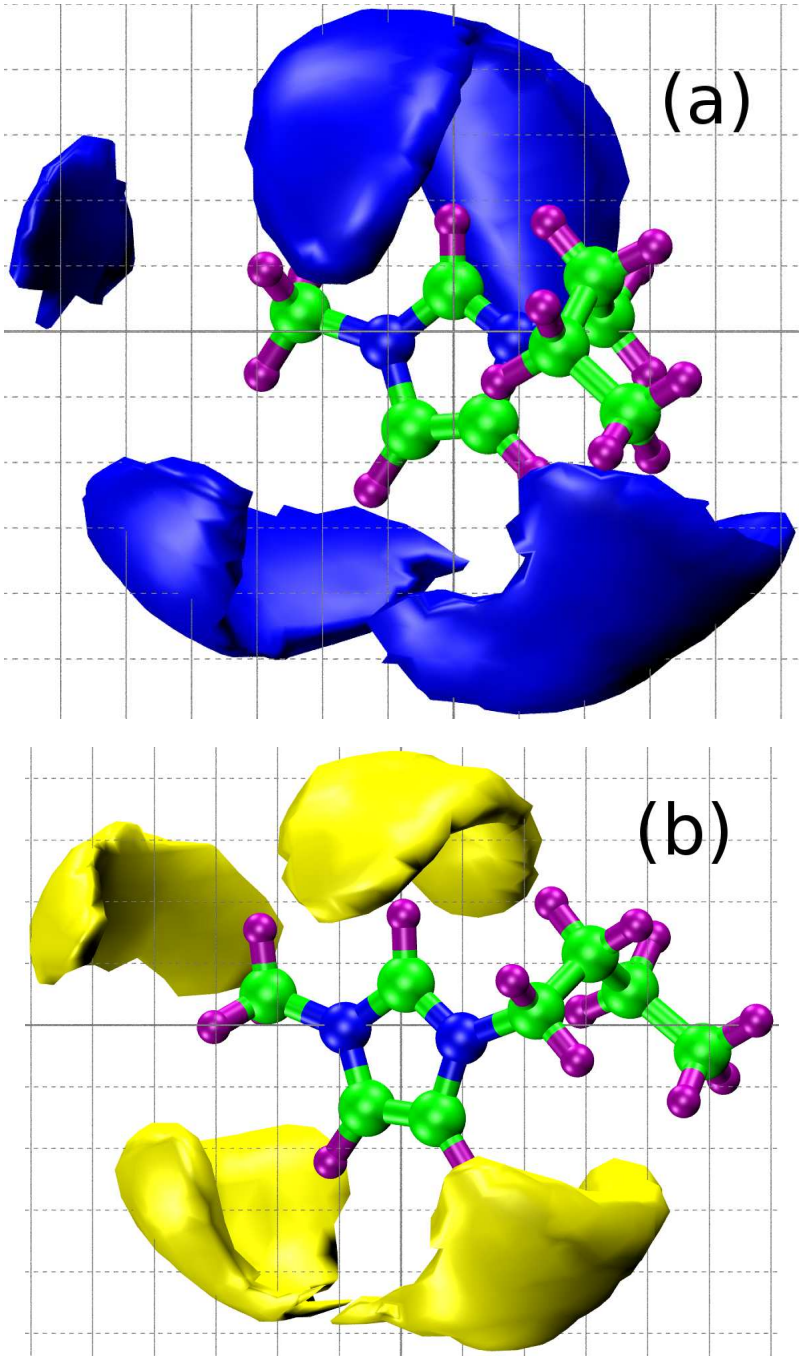



**Fig. S4** Radial distribution function between (a) H2-F ($BF_4$) and (b) H2-F ($PF_6$) in the $[C_4mim][PF_6]$-$[C_4mim][BF_4]$ system.


(a)
(b)

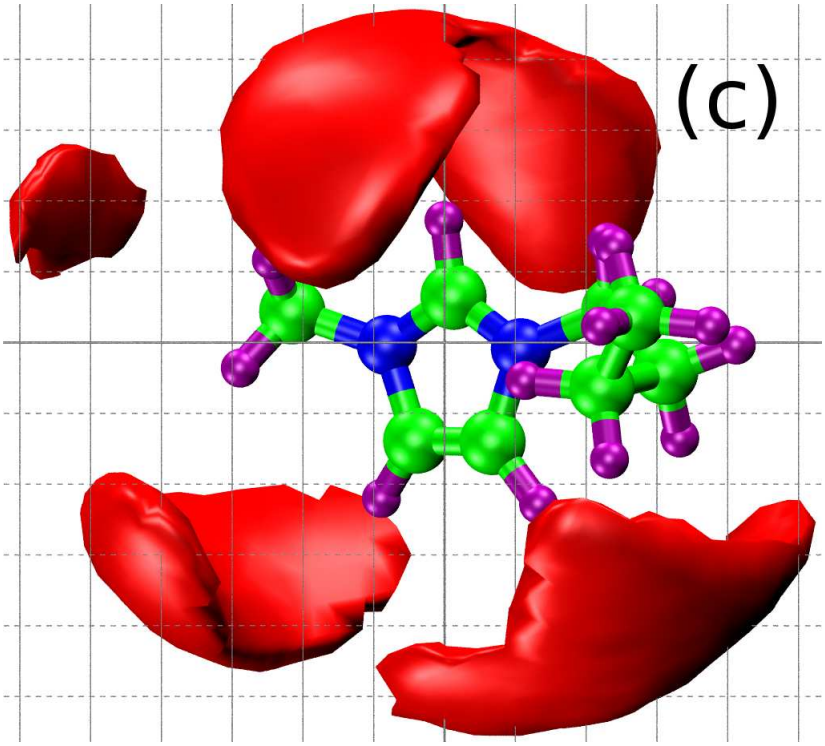
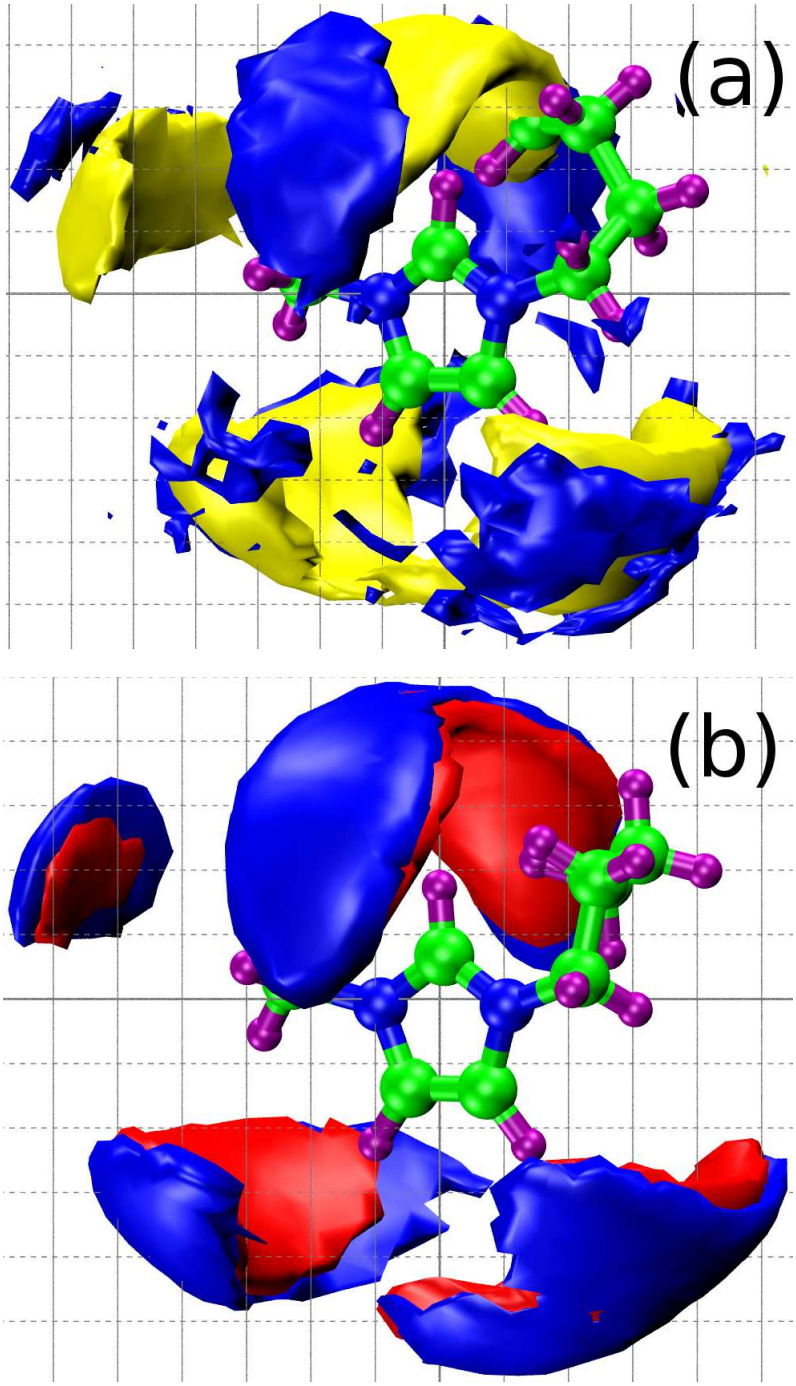



**Fig. S5** Spatial density maps of anion around cation in the three neat ionic liquids (a) $PF_6$, (b) Cl and (c) $BF_4$. Isosurfaces: $PF_6$ : Blue, Cl : Yellow, $BF_4$ : Red. Atoms: C in Green, N in Blue, H in Purple). The isosurfaces are at a density of 0.0184 $Å^{-3}$ for all the systems.


(a)
(b)

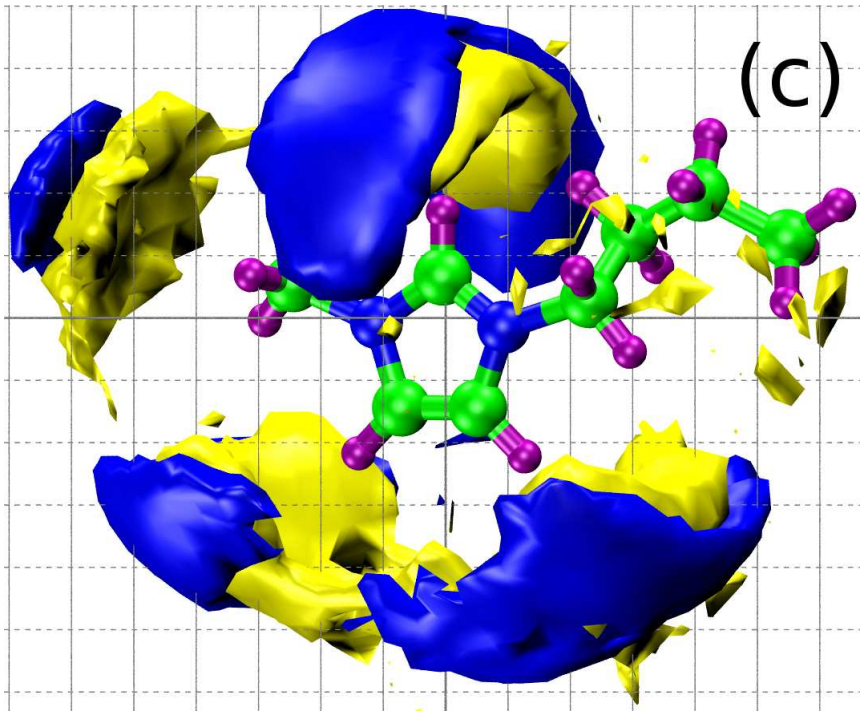
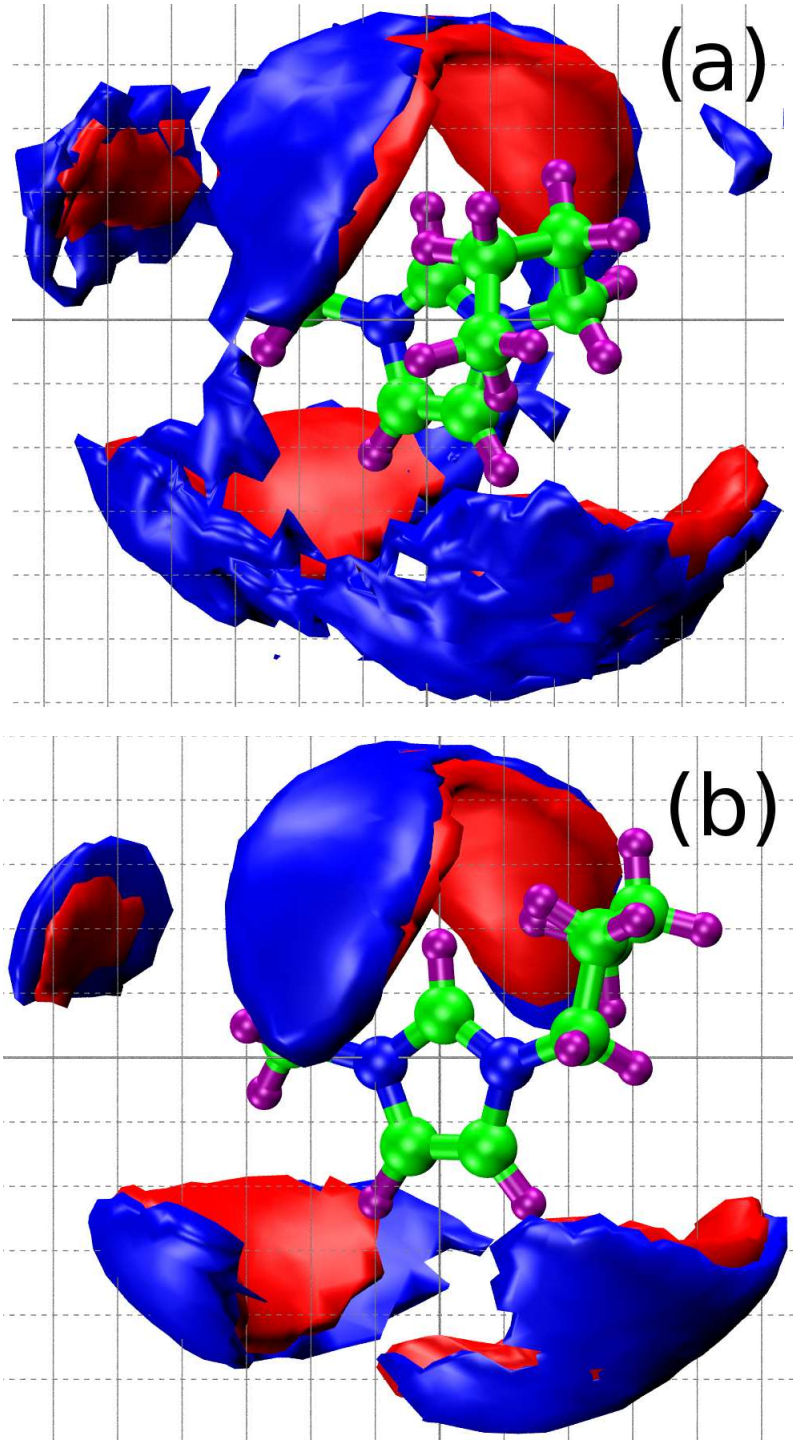



**Fig. S6** Spatial density maps of anion around cation in the $[C_4mim][PF_6]$-$[C_4mim][Cl]$ system (a) $PF_6$:Cl :: 10:90, b) $PF_6$:Cl :: 50:50 and c) $PF_6$:Cl :: 90:10. Isosurfaces and atom colour codes are the same as in Figure S2. Isosurfaces are at a density of (a) 0.00184 $Å^{-3}$ for $PF_6$ and 0.01656 $Å^{-3}$ for Cl, (b) 0.092 $Å^{-3}$ for both $PF_6$ and Cl and (c) 0.01656 $Å^{-3}$ for $PF_6$ and 0.00184 $Å^{-3}$ for Cl.


(a)
(b)

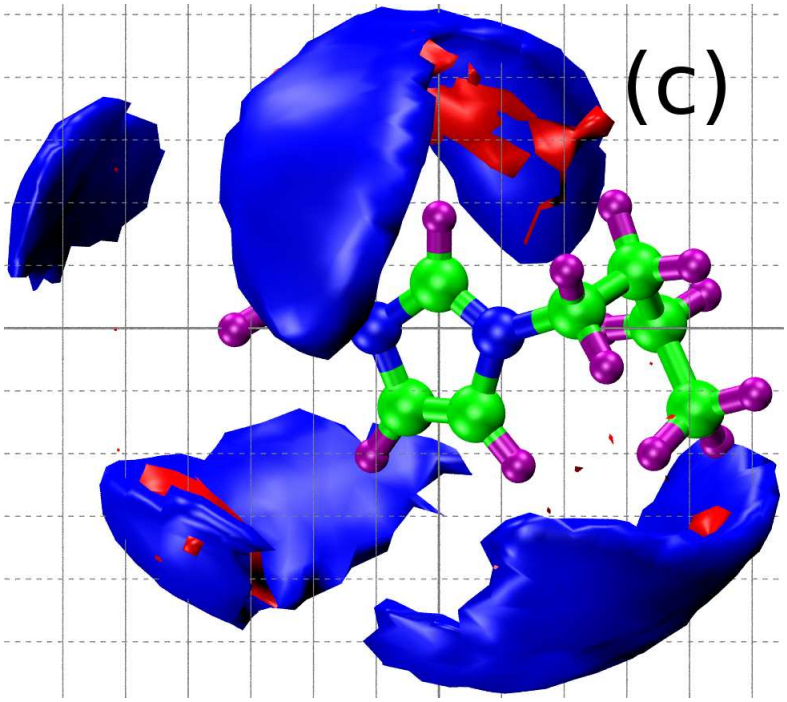



**Fig. S7** Spatial density maps of anion around cation in the $[C_4mim][PF_6]$-$[C_4mim][BF_4]$ system (a) $PF_6$:$BF_4$ :: 10:90, (b) $PF_6$:$BF_4$ :: 50:50 and (c) $PF_6$:$BF_4$ :: 90:10. Isosurfaces and atom colour codes are same as in Figure S2. Isosurfaces have density of (a) 0.00184 $Å^{-3}$ for $PF_6$ and 0.01656 $Å^{-3}$ for $BF_4$, (b) 0.092 $Å^{-3}$ for both $PF_6$ and $BF_4$ and (c) 0.01656 $Å^{-3}$ for $PF_6$ and 0.00184 $Å^{-3}$ for $BF_4$.

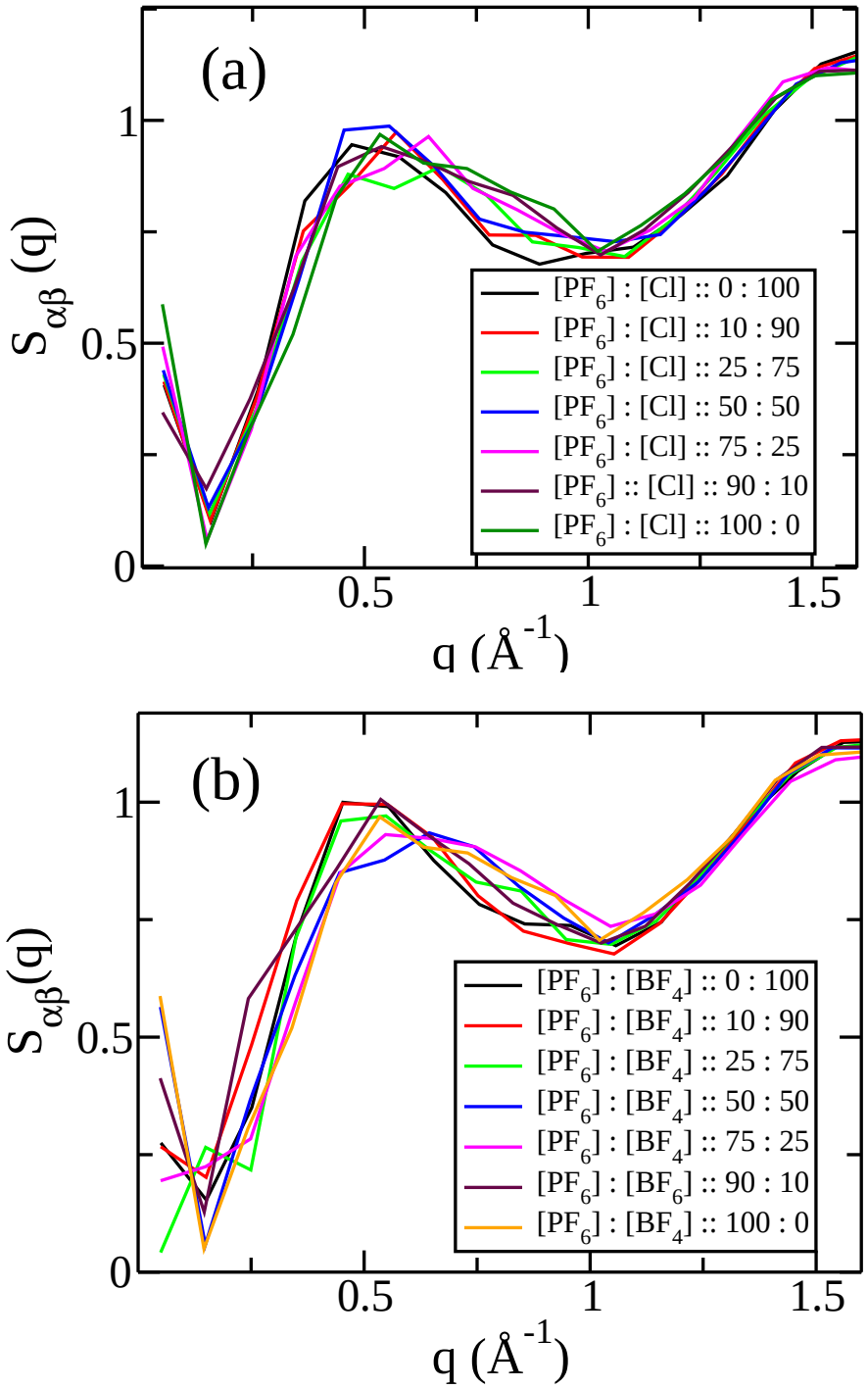



**Fig. S8** Partial structure factor between the terminal carbon atoms in the alkyl group of cations (tail-tail) for (a) [$C_4$mim][$PF_6$]-[$C_4$mim][Cl] and (b) [$C_4$mim][$PF_6$]-[$C_4$mim][$BF_4$] systems.

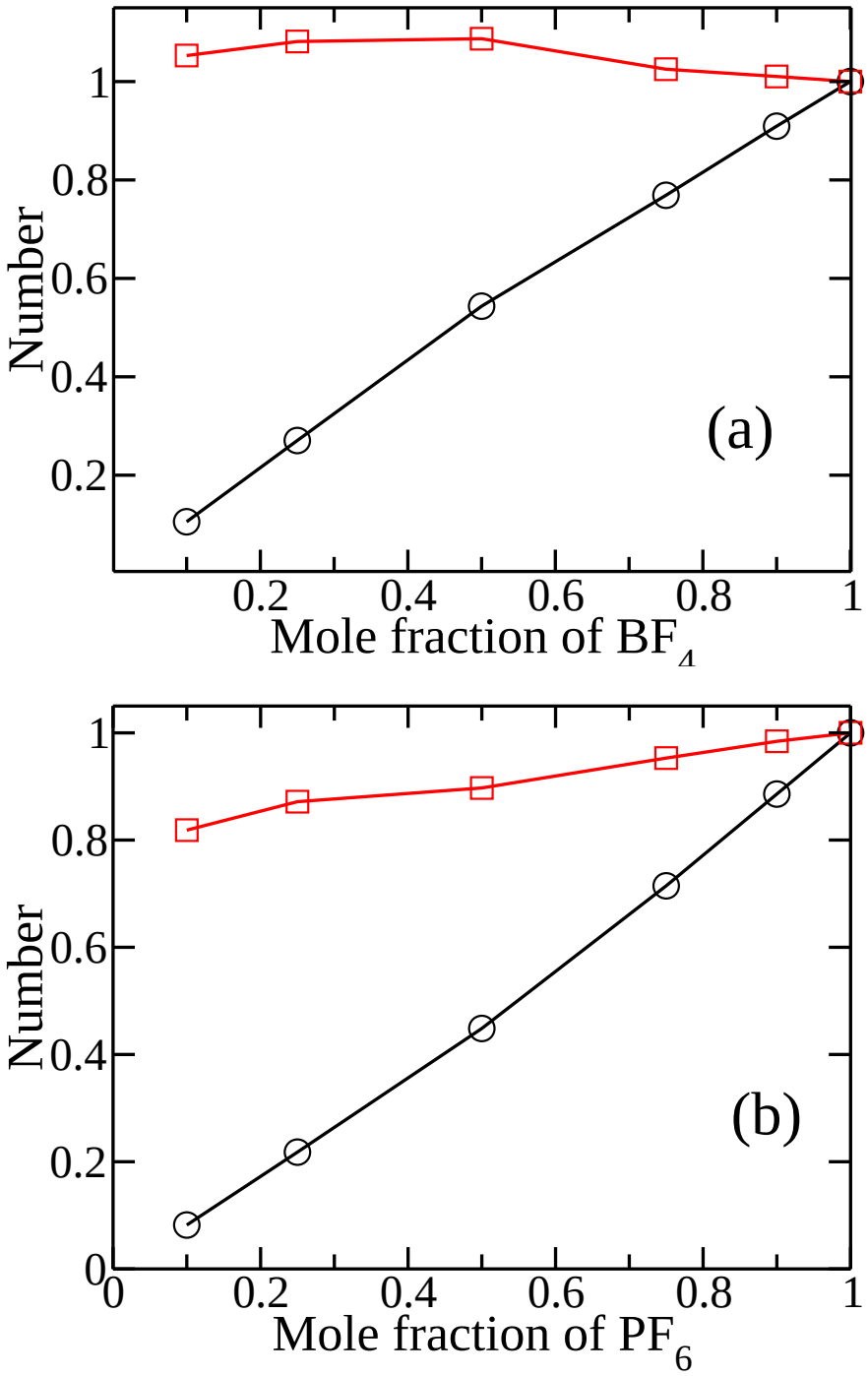



**Fig. S9** Normalized first shell coordination number as a function of mole fraction for (a) H2-F ($BF_4$) and (b) H2-F ($PF_6$) in the [$C_4$mim][$PF_6$]-[$C_4$mim][$BF_4$] system. The black line with circles is the normalized coordination number while the red curve with squares is the ratio of this quantity to the mole fraction of the anion.

Figure S10 represents the mapping scheme between all-atom (AA) and coarse grained (CG) beads. The bead-bead interaction parameters were chosen from the coarse grained model developed by us earlier[1] for $[C_4mim][PF_6]$. Correspondingly, the charge of Cl was also scaled to 0.8. Non-bonded interactions of the 9-6 type Lennard- Jones type were determined so that cation-anion pair correlation functions in neat $[C_4mim][Cl]$ obtained from the CG simulations reproduced those from the AA run, as well as the system density. The pair correlations between pairs of different bead types obtained from AA and CG MD simulations are displayed in Figure S11. These validate the interaction parameters for the CG model adopted here. A real space cutoff of 15 Å was applied for both LJ and Coulombic interactions. Table S1 displays the parameters employed in our CG simulations for $[C_4mim][Cl]$. Lorentz-Berthelot mixing rules were employed for cross interactions. Spatial density maps were created using software package VMD.[2]

**Table S1** 9-6 Lennard-Jones interaction parameters for the coarse grain model of [$C_4$mim][Cl].

| Bead pair | $\epsilon$ (kcal mol$^{-1}$) | $\sigma$ ( Å ) |
|---|---|---|
| I1 - I1 | 0.3757152 | 4.100 |
| I1 - I2 | 0.3604245 | 4.050 |
| I1 - I3 | 0.2739623 | 4.050 |
| I1 - CM | 0.3914031 | 4.340 |
| I1 - Cl | 0.0457049 | 4.570 |
| I2 - I2 | 0.3457295 | 4.100 |
| I2 - I3 | 0.2628021 | 4.050 |
| I2 - CM | 0.3754372 | 4.340 |
| I2 - Cl | 0.0557049 | 4.720 |
| I3 - I3 | 0.0997725 | 2.850 |
| I3 - CM | 0.2853807 | 3.800 |
| I3 - Cl | 0.2988648 | 3.810 |
| CM - CM | 0.4690000 | 4.585 |
| CM - Cl | 0.2651688 | 4.243 |
| Cl - Cl | 0.0155586 | 3.150 |

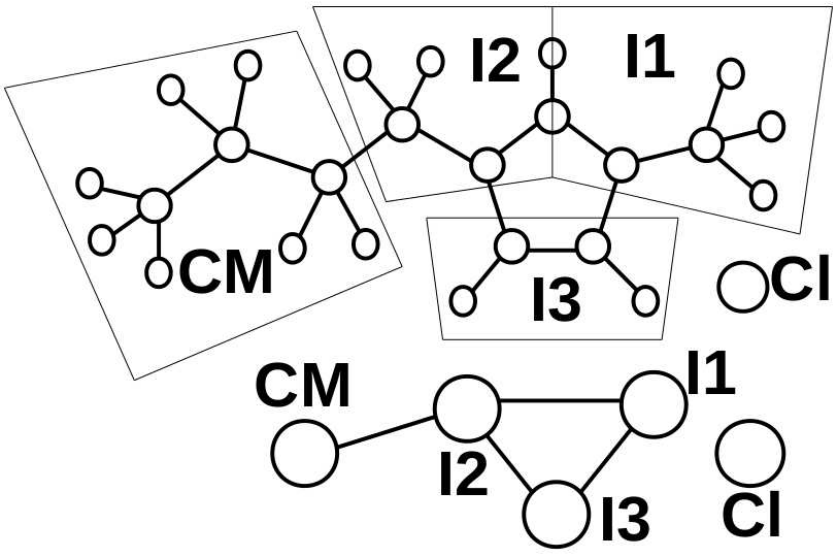
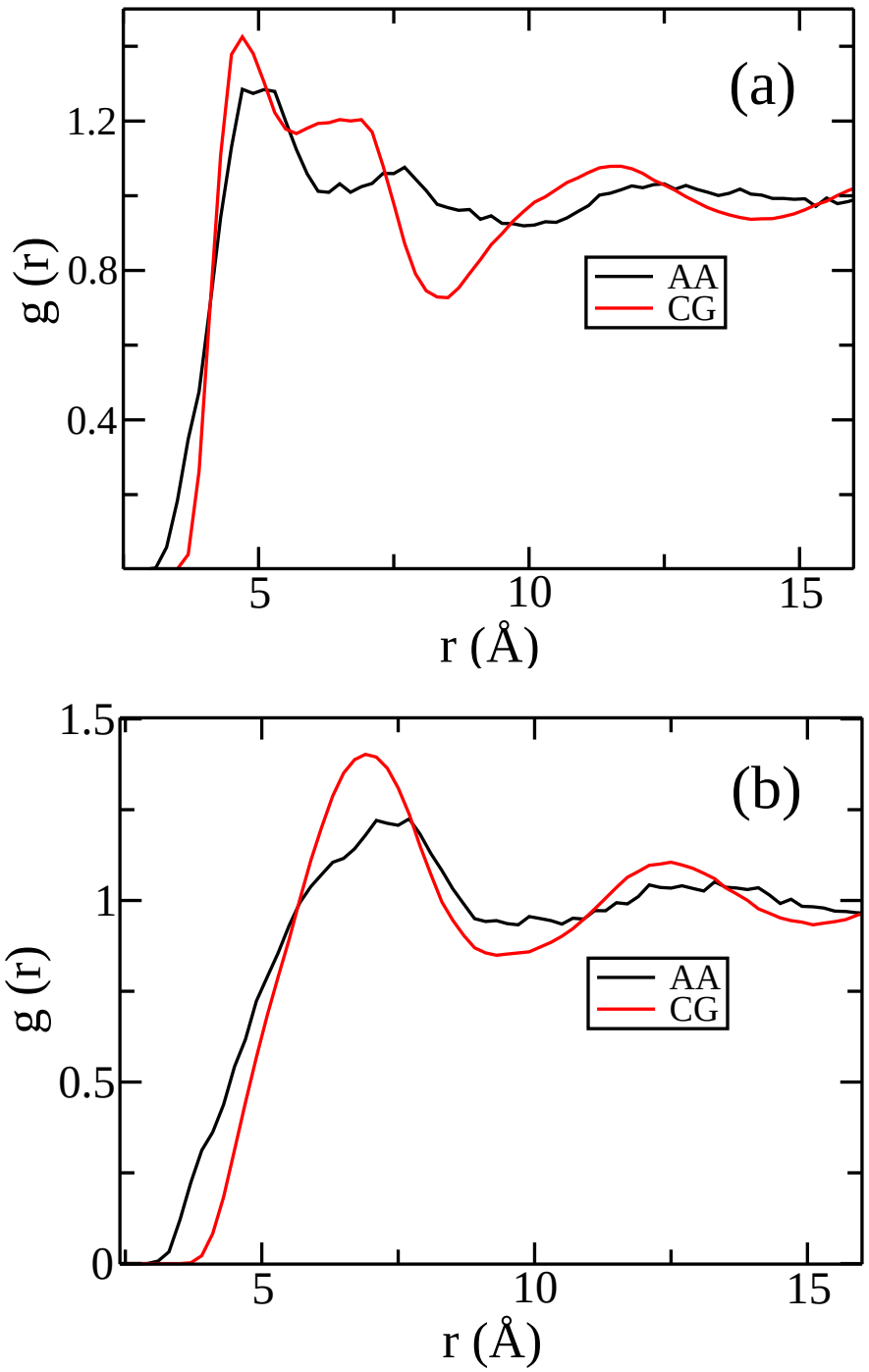
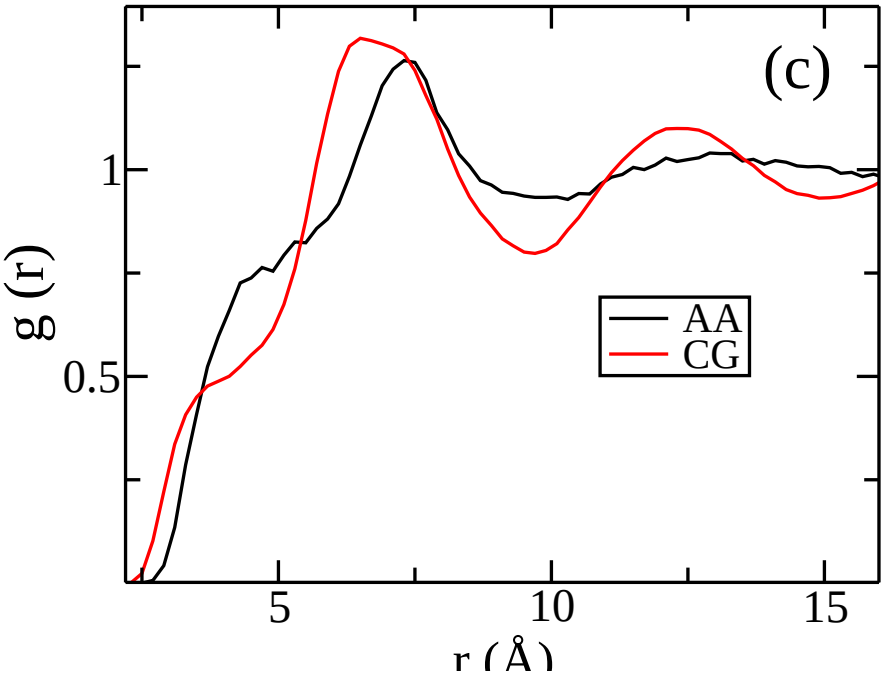
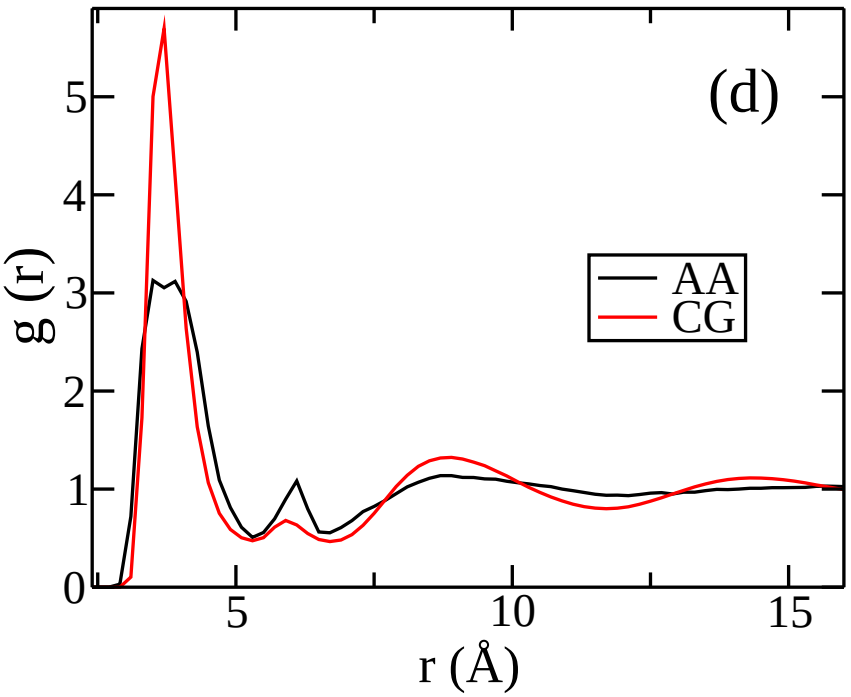
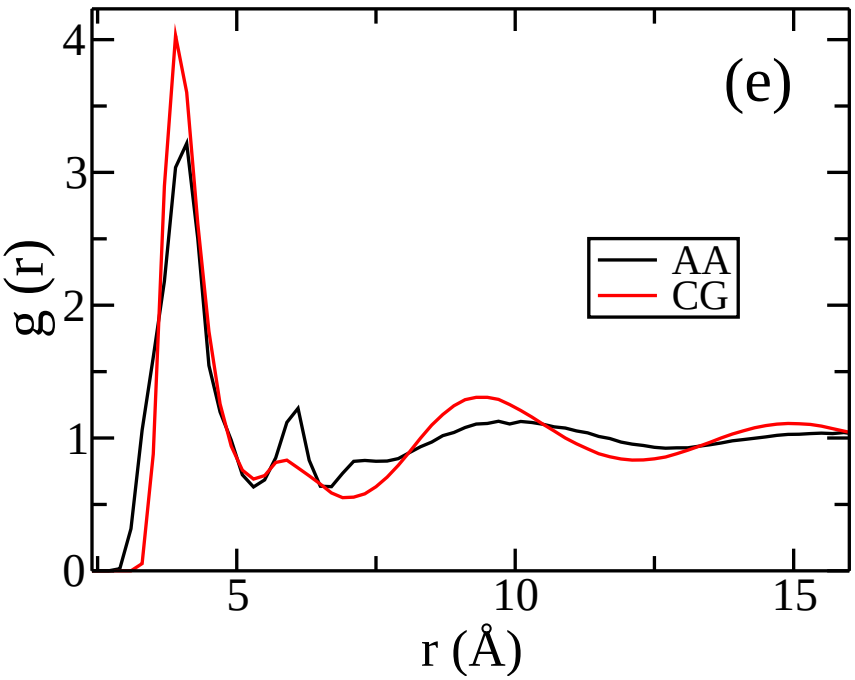


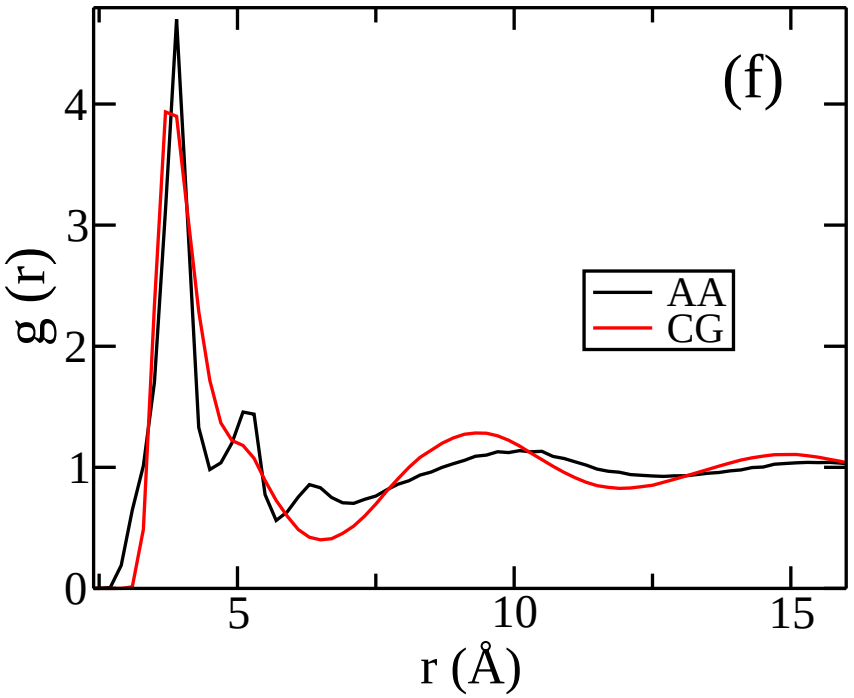

**Fig. S10** Schematic showing the mapping from all-atom to the coarse grained model in [$C_4$mim][Cl].


(a)
1.2
0.8
0.4
g (r)
AA
CG
5
10
15
r (Å)
(b)
1.5
1
0.5
0
g (r)
AA
CG
5
10
15
r (Å)


(c)
g (r)
1
0.5
5
10
15
r (Å)
AA
CG


(d)
g (r)
5
4
3
2
1
0
5
10
15
r (Å)
AA
CG


(e)
AA
CG
g (r)
r (Å)
0
1
2
3
4
5
10
15


(f)
AA
CG
g (r)
r (Å)
0
1
2
3
4
5
10
15

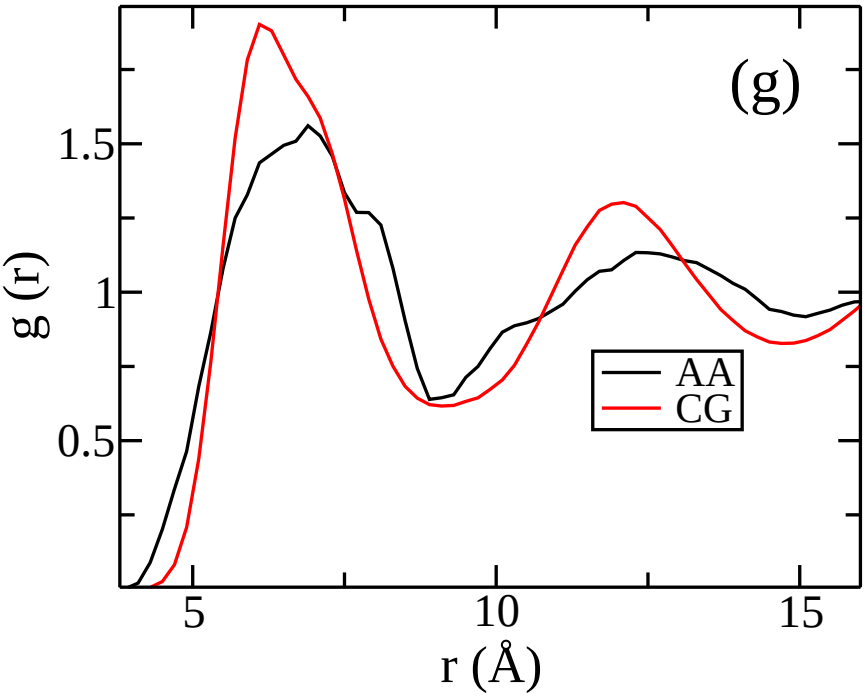
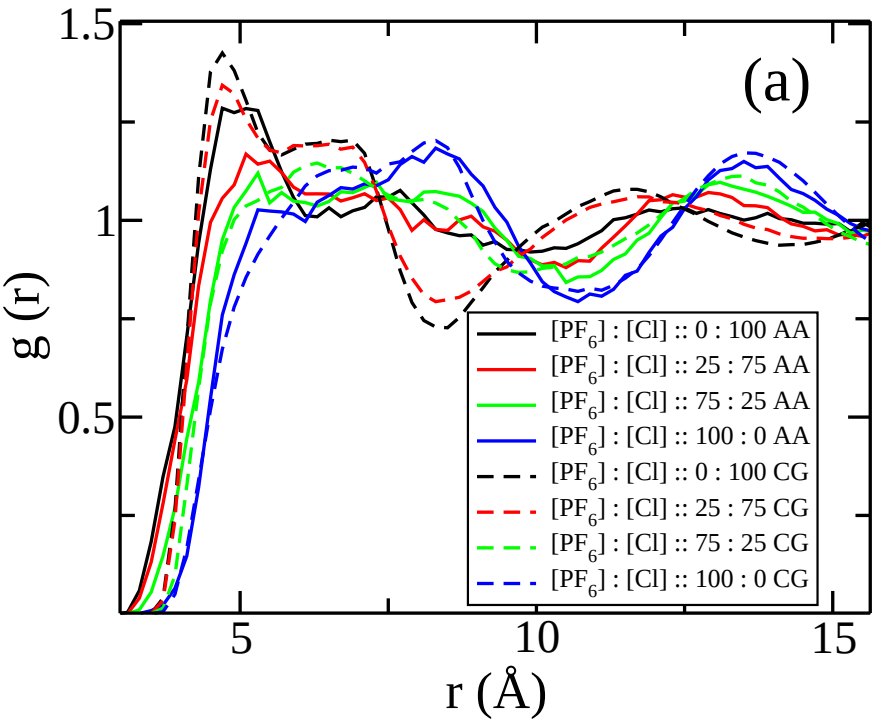
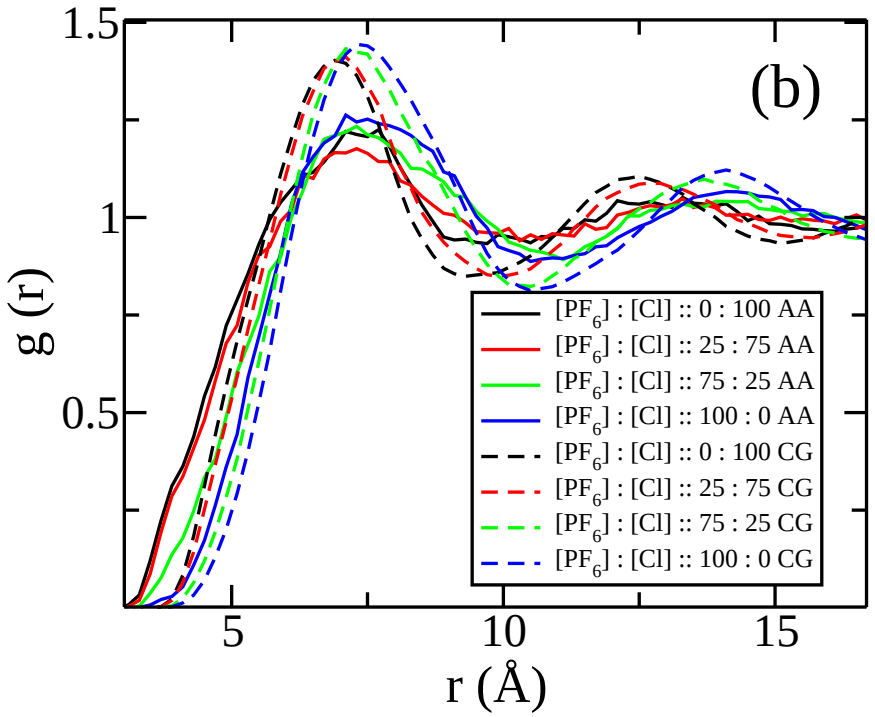


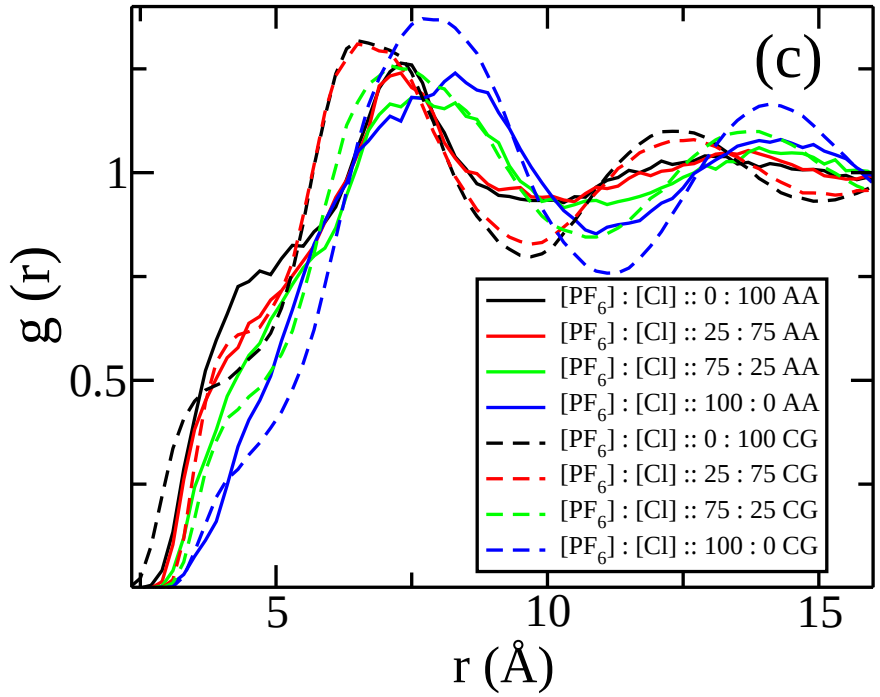

**Fig. S11** Radial distribution functions betwen (a) I1-I1, (b) I2-I2, (c) I3-I3, (d) I1-Cl, (e) I2-Cl, (f) I3-Cl and (g) Cl-Cl compared between that from AA and CG MD simulations for pure [$C_4$mim][Cl].

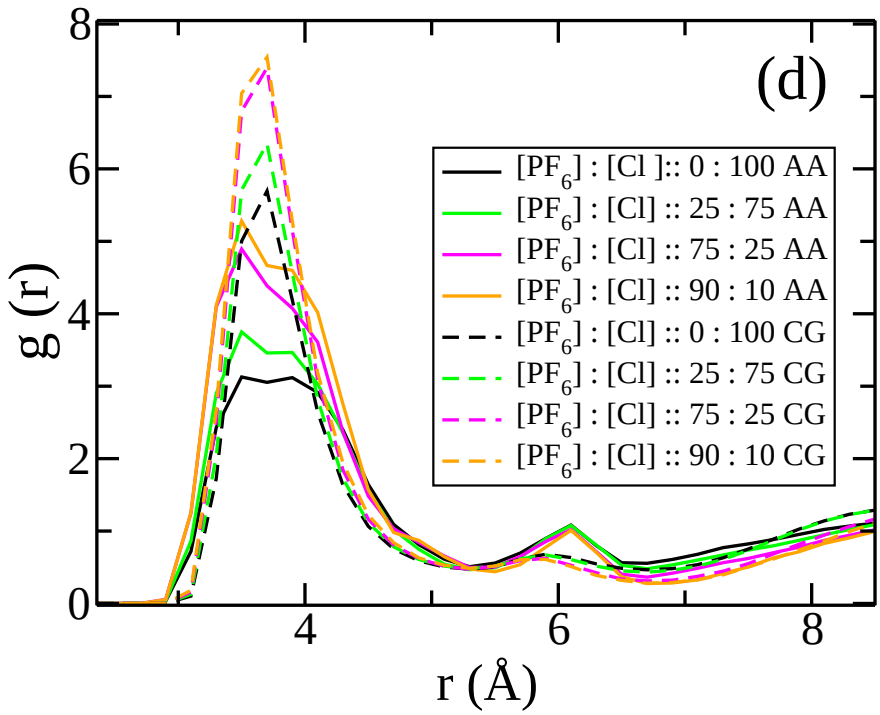
**Table S2** Box length and fraction of ion pairs for ionic liquids with [$C_4$mim] as cation. 800 and 24000 ion pairs were used in the all-atom (AA) and coarse grained (CG) MD simulations respectively.

| Anion | Fraction (%) | Box length (Å) (AA) | Box length (Å) (CG ) |
|---|---|---|---|
| $PF_6$ | 100 | 64.640 | 200.8515 |
| [Cl] | 100 | 59.940 | 186.0311 |
| $BF_4$ | 100 | 62.344 | – |
| $PF_6$ : [Cl] | 10 - 90 | 60.514 | 188.0311 |
| | 25 - 75 | 61.024 | 189.6157 |
| | 50 - 50 | 62.220 | 193.3320 |
| | 75 - 25 | 63.500 | 197.3093 |
| | 90 - 10 | 64.211 | 199.5185 |
| $PF_6$ : $BF_4$ | 10 - 90 | 62.652 | – |
| | 25 - 75 | 63.020 | – |
| | 50 - 50 | 63.400 | – |
| | 75 - 25 | 64.195 | – |
| | 90 - 10 | 64.389 | – |


(a)
g (r)
r (Å)
1.5
1
0.5
5
10
15
[PF6] : [Cl] :: 0 : 100 AA
[PF6] : [Cl] :: 25 : 75 AA
[PF6] : [Cl] :: 75 : 25 AA
[PF6] : [Cl] :: 100 : 0 AA
[PF6] : [Cl] :: 0 : 100 CG
[PF6] : [Cl] :: 25 : 75 CG
[PF6] : [Cl] :: 75 : 25 CG
[PF6] : [Cl] :: 100 : 0 CG


(b)
g (r)
r (Å)
1.5
1
0.5
5
10
15
[PF6] : [Cl] :: 0 : 100 AA
[PF6] : [Cl] :: 25 : 75 AA
[PF6] : [Cl] :: 75 : 25 AA
[PF6] : [Cl] :: 100 : 0 AA
[PF6] : [Cl] :: 0 : 100 CG
[PF6] : [Cl] :: 25 : 75 CG
[PF6] : [Cl] :: 75 : 25 CG
[PF6] : [Cl] :: 100 : 0 CG


(c)
g (r)
r (Å)
[PF6] : [Cl] :: 0 : 100 AA
[PF6] : [Cl] :: 25 : 75 AA
[PF6] : [Cl] :: 75 : 25 AA
[PF6] : [Cl] :: 100 : 0 AA
[PF6] : [Cl] :: 0 : 100 CG
[PF6] : [Cl] :: 25 : 75 CG
[PF6] : [Cl] :: 75 : 25 CG
[PF6] : [Cl] :: 100 : 0 CG


(d)
g (r)
r (Å)
[PF6] : [Cl ]:: 0 : 100 AA
[PF6] : [Cl] :: 25 : 75 AA
[PF6] : [Cl] :: 75 : 25 AA
[PF6] : [Cl] :: 90 : 10 AA
[PF6] : [Cl] :: 0 : 100 CG
[PF6] : [Cl] :: 25 : 75 CG
[PF6] : [Cl] :: 75 : 25 CG
[PF6] : [Cl] :: 90 : 10 CG

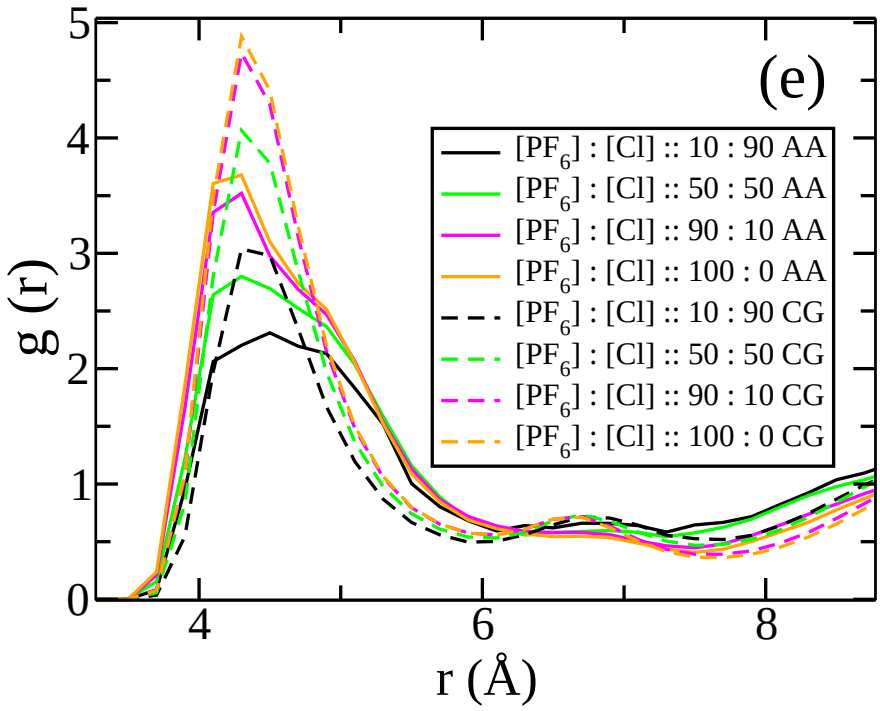



**Fig. S12** Radial distribution functions at various concentrations of anions in the $[C_4mim][PF_6]$-$[C_4mim][Cl]$ system between (a) I1-I1, (b) I2-I2, (c) I3-I3, (d) I1-Cl and (e) I1-$PF_6$, compared between AA and CG MD simulations.

## References

1 B. L. Bhargava, R. Devane, M. L. Klein and S. Balasubramanian, *Soft Matter*, 2007, **3**, 1395–1400.
2 W. Humphrey, A. Dalke and K. Schulten, *Journal of Molecular Graphics*, 1996, **14**, 33–38.