Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Confinement of ionic liquids aqueous mixtures between amorphous TiO_2 slit nanopores: electrostatic field induction

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Table S1. The obtained partial atomic charges of $[C_4mim]BF_4$.

atom	q/e B3LYP NBO	atom	q/e B3LYP NBO
N_1	-0.357	B	1.331
C_2	0.606	F_1	-0.539
N_3	-0.355	F_2	-0.579
C_4	0.207	F_3	-0.587
C_5	0.210	F_4	-0.587
C_6	0.317		
C_7	0.276		
C_8	0.025		
C_9	0.002		
C_{10}	0.029		

Table S2. The obtained partial atomic charges of [C_4mim]Cl.

atom	q/e B3LYP NBO	atom	q/e B3LYP NBO
N_1	-0.365	Cl	-0.850
C_2	0.571		
N_3	-0.375		
C_4	0.187		
C_5	0.206		
C_6	0.303		
C_7	0.281		
C_8	0.010		
C_9	0.008		
C_{10}	0.024		

Table S3. The obtained partial atomic charges of [C_4mim]PF_6.[1]

atom	q/e CPMD ESP	atom	q/e CPMD ESP
N_1	-0.357	P	2.554
C_2	0.604	F_1	-0.567
N_3	-0.355	F_2	-0.569
C_4	0.210	F_3	-0.608
C_5	0.213	F_4	-0.600
C_6	0.318	F_5	-0.607
C_7	0.275	F_6	-0.572
C_8	0.025		
C_9	0.003		
C_{10}	0.032		

Table S4. Details of annealing rates to produce amorphous slabs with different surface charges.

TiO_2_(1)		**TiO_2_(2)**	
temperature (^{0}K)	**Time (ps)**	**temperature (^{0}K)**	**Time (ps)**
5000	100	5000	100
3000	100	3000	100
2500	100	2500	100
2000	100	2000	100
1500	100	1500	100
1000	100	1000	100
900	100	500	100
800	100	400	100
700	100	300	100
600	100		
500	100		
400	100		
380	100		
360	100		
340	100		
320	100		
300	100		

Table S5. Comparison of density and viscosity of simulated aqeous solution of IL (3 M aqeous solution of [C_4mim]Cl) with our experimental data

[C_4mim]-Cl	Experiment.	Simulation
Density (gcm^{-3})	1.037	1.056
Viscosity (cP)	2.246	1.762

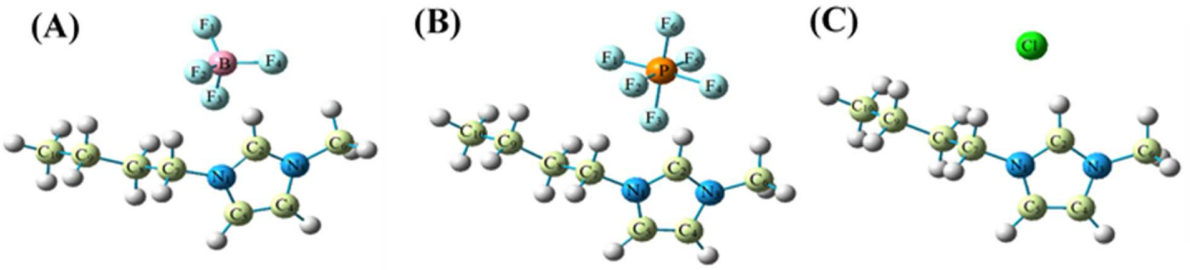

Fig. S1 Optimized molecular structures of ionic liquids (A) [C_4mim][BF_4], (B) [C_4mim][PF_6]and (C) [C_4mim][Cl] including the atoms' label. ([C_4mim]:1-buthyle-3-methyle-imidazolium)

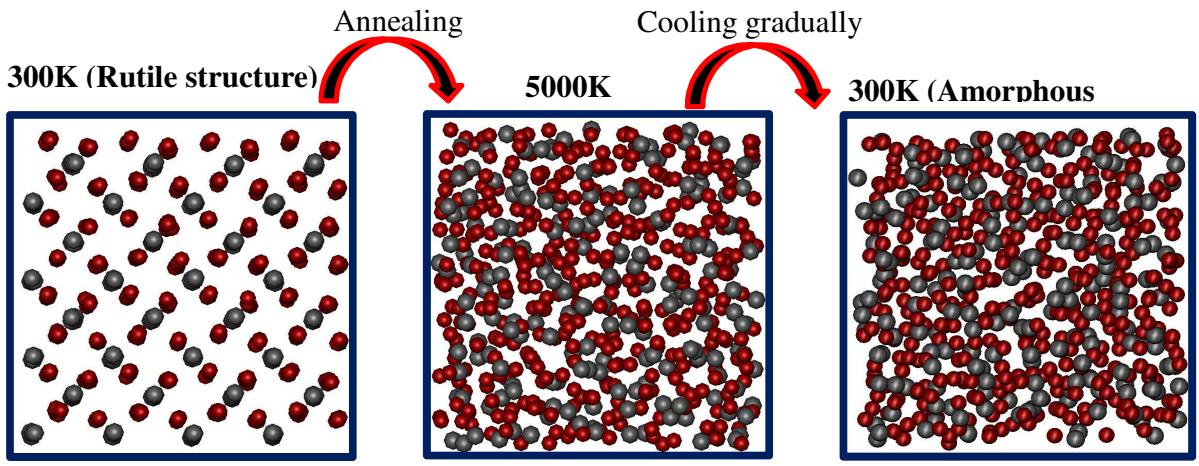

Fig. S2 Snapshots of melting a crystal and formation of amorphous TiO_2 structure.

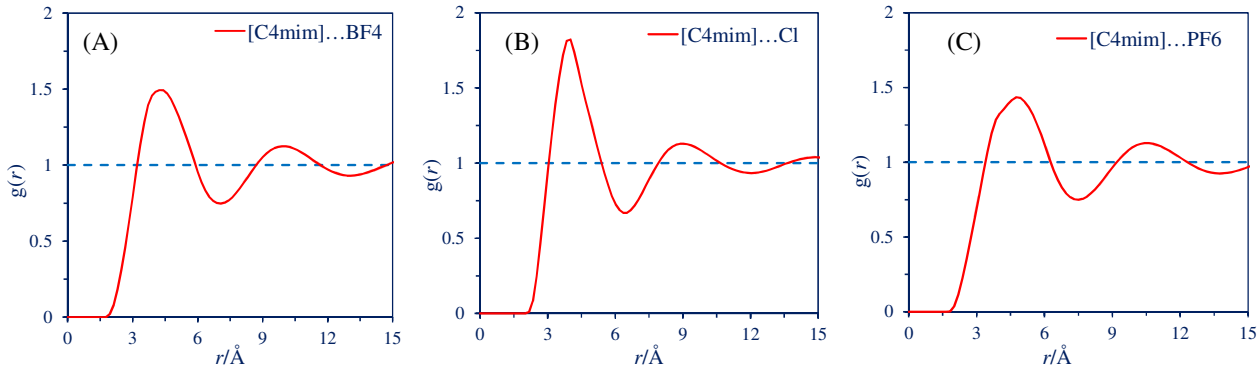

Fig. S3 Radial distribution functions between anion and cation centers of masses of the bulk IL systems (A) $[C_4mim][BF_4]$, (B) $[C_4mim][Cl]$ and (C) $[C_4mim][PF_6]$.

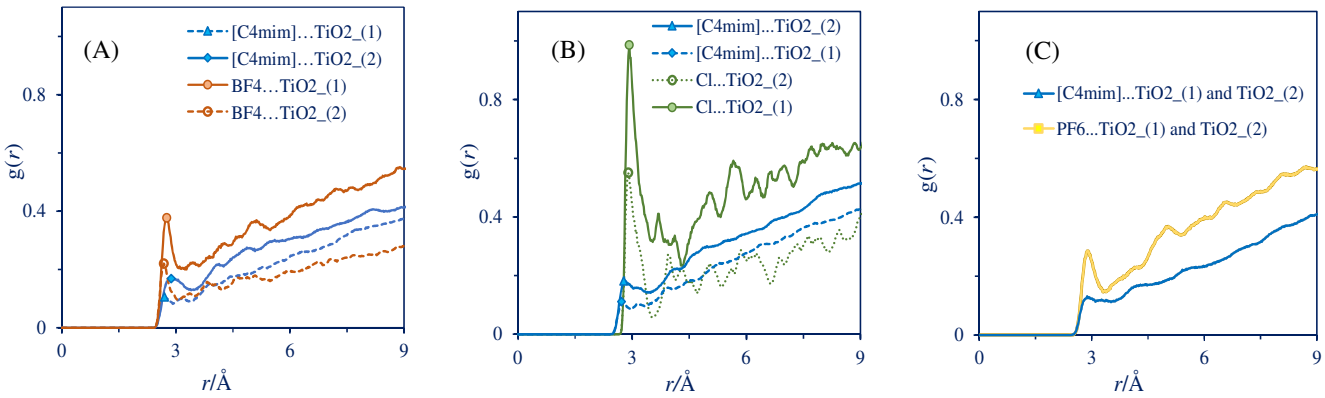

Fig. S4 Pair correlation functions $g(r)$ of cation-TiO_2 walls and anion-TiO_2 walls of bulk phase of the ILs confined inside two amorphous TiO_2 walls with pore size of 10 nm, for (A) [C_4mim][BF_4], (B) [C_4mim][Cl] and (C) [C_4mim][PF_6]. See Figure 2 for TiO_2 (1) and (2) labels.

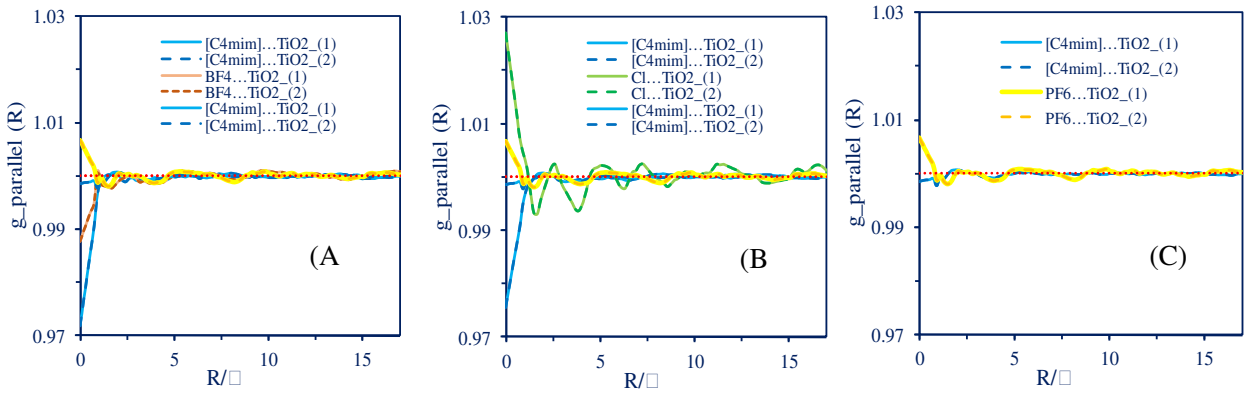

Fig. S5 Two-dimensional pair correlation functions, g_parallel(R), of cation-TiO_2 walls and anion-TiO_2 walls in the plane parallel to the slabs of bulk phase of the ILs confined inside two amorphous TiO_2 walls with pore size of 10 nm, for (A) [C_4mim][BF_4], (B) [C_4mim][Cl] and (C) [C_4mim][PF_6]. See Figure 2 for TiO_2 (1) and (2) labels.

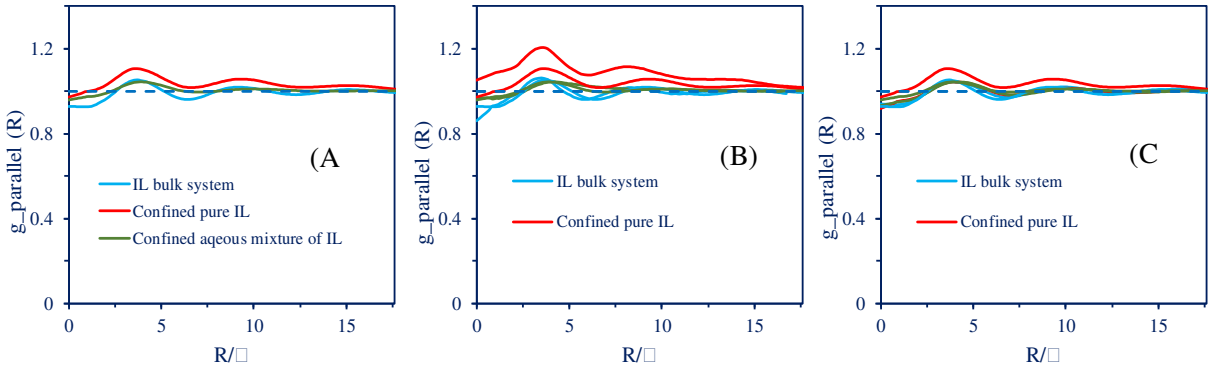

Fig. S6 Two-dimensional radial distribution functions, g_parallel(R), of cation-anions for confined pure IL, confined aqueous mixture of IL, and IL bulk systems. (A) [C_4mim][BF_4], (B) [C_4mim][Cl] (C) [C_4mim][PF_6].

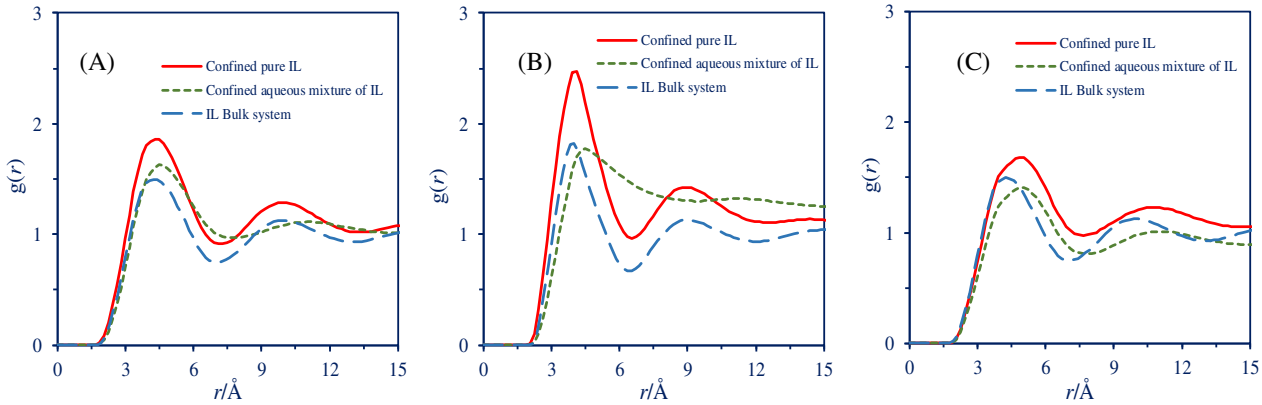

Fig. S7 Radial distribution functions of cation-anions for confined pure IL, confined aqueous mixture of IL, and IL bulk systems. (A) [C_4mim][BF_4], (B) [C_4mim][Cl] and (C) [C_4mim][PF_6]. In all cases, the correction was done based on the excluded volume effect.

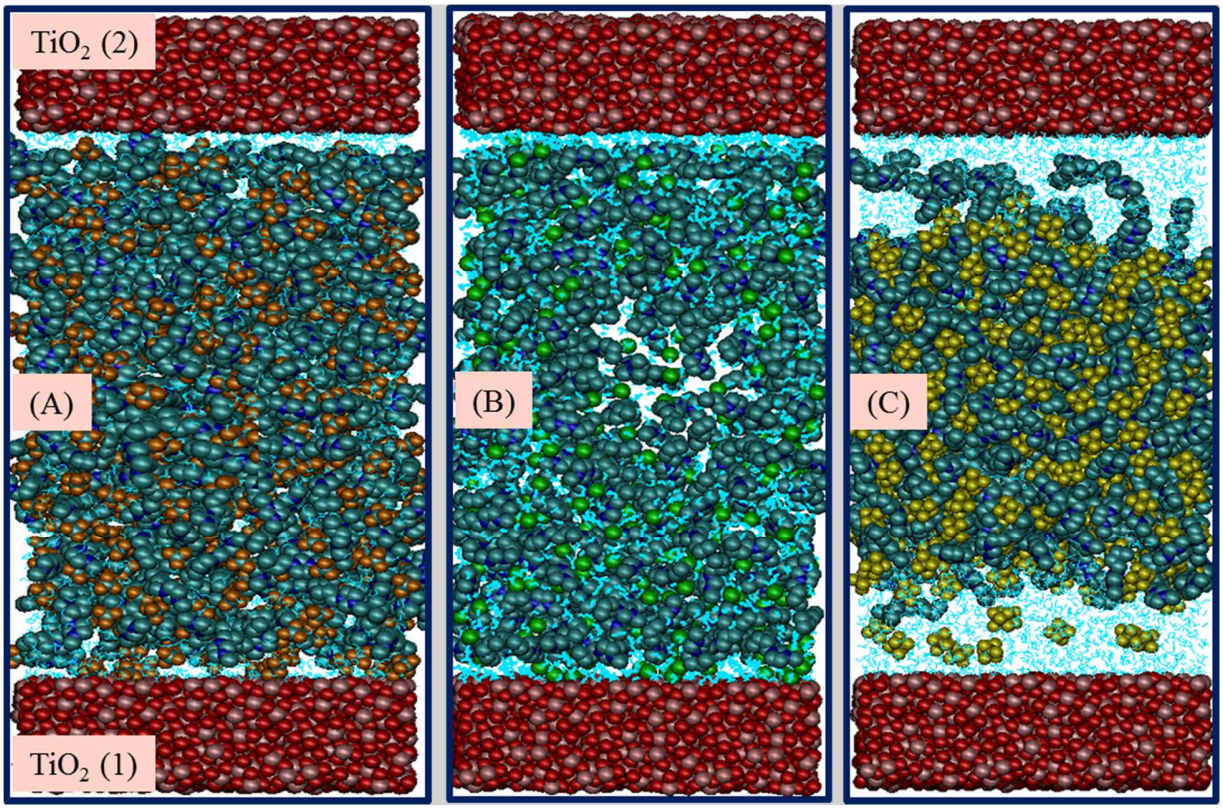

Fig. S8 Snapshots of aqueous mixtures of 360 molecule of ILs confined inside two amorphous TiO_2 walls with a 10 nm pore size, (A) [C_4mim][BF_4], (B) [C_4mim][Cl] and (C) [C_4mim][PF_6]. Number of water molecules is 3289, 3782 and 2933 for (A), (B) and (C) systems, respectively. Ti, O, Cl, N and C atoms are depicted in pink, red, green, blue and cyan, respectively. F atoms of BF_4 and PF_6 anions are depicted in orange and yellow, respectively.

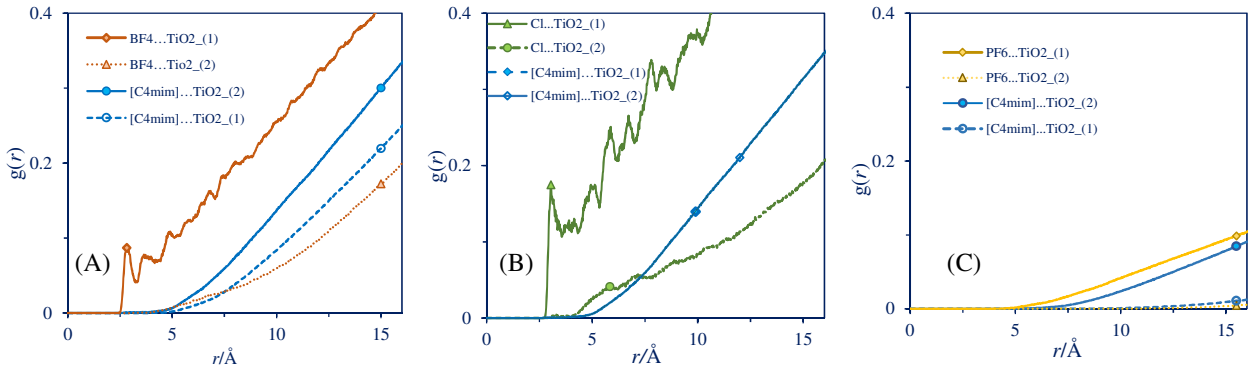

Fig. S9 Radial distribution functions $g(r)$ of cation-pore wall and anion-pore wall of aqueous mixture of 360 ILs confined inside pores with two amorphous TiO_2 walls; (A) $[C_4mim][BF_4]$, (B) $[C_4mim][Cl]$ and (C) $[C_4mim][PF_6]$. See Figure 2 for TiO_2 (1) and (2) labels.

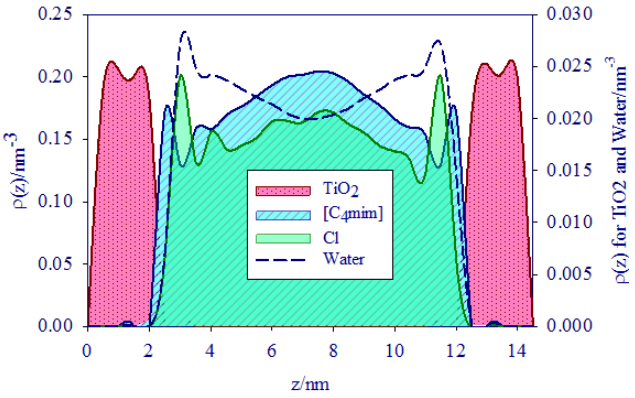

Fig. S10 Number density profiles of aqueous mixture of $[C_4mim][Cl]$ IL confined inside pore, while the potential applied to keep the two amorphous TiO_2 walls at the same potential.

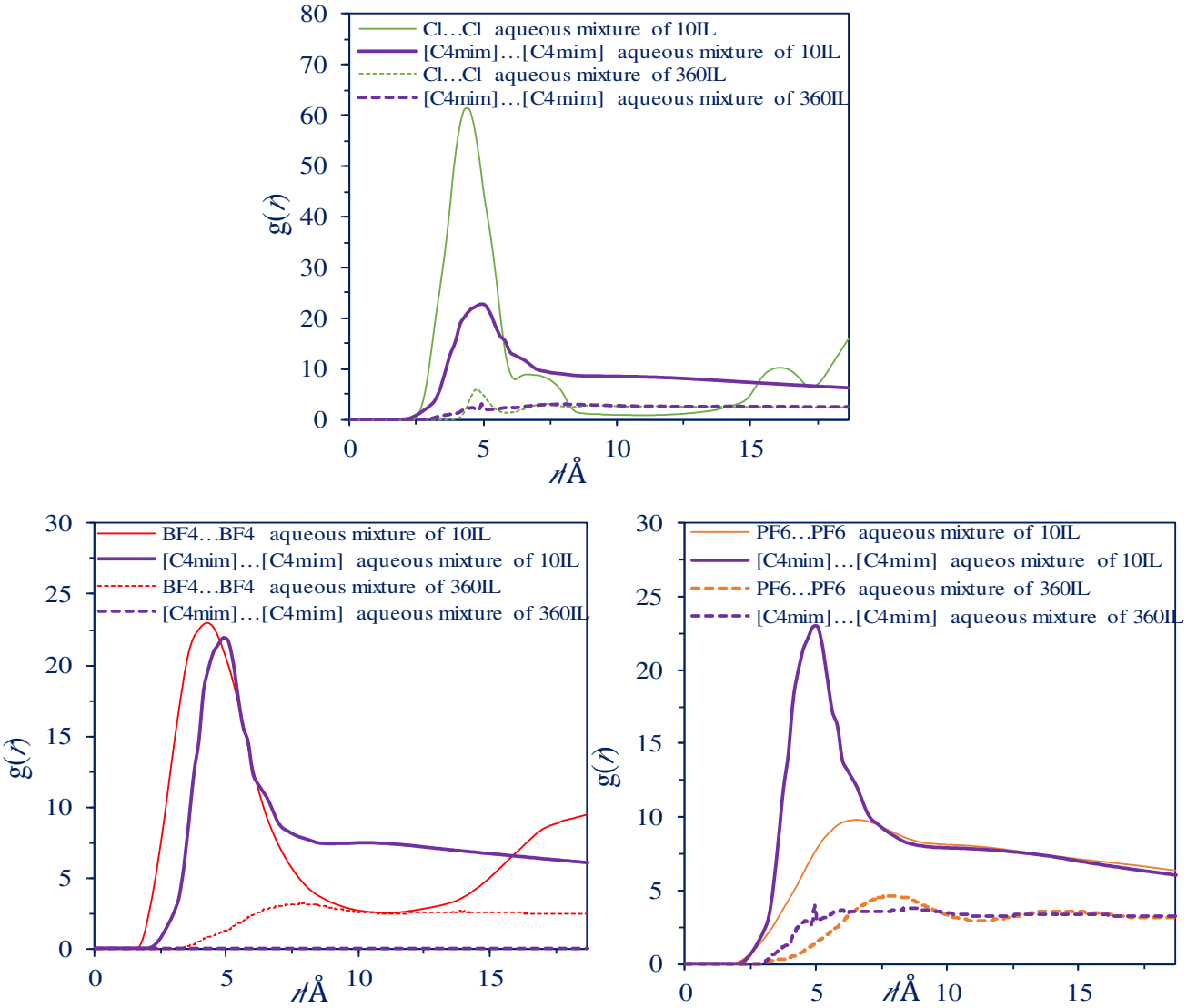

Fig. S11 The cation-cation and anion-anion radial distribution function for confined [C_4mim]Cl, [C_4mim]BF_4, and [C_4mim]PF_6 aqueous systems at two different concentrations.

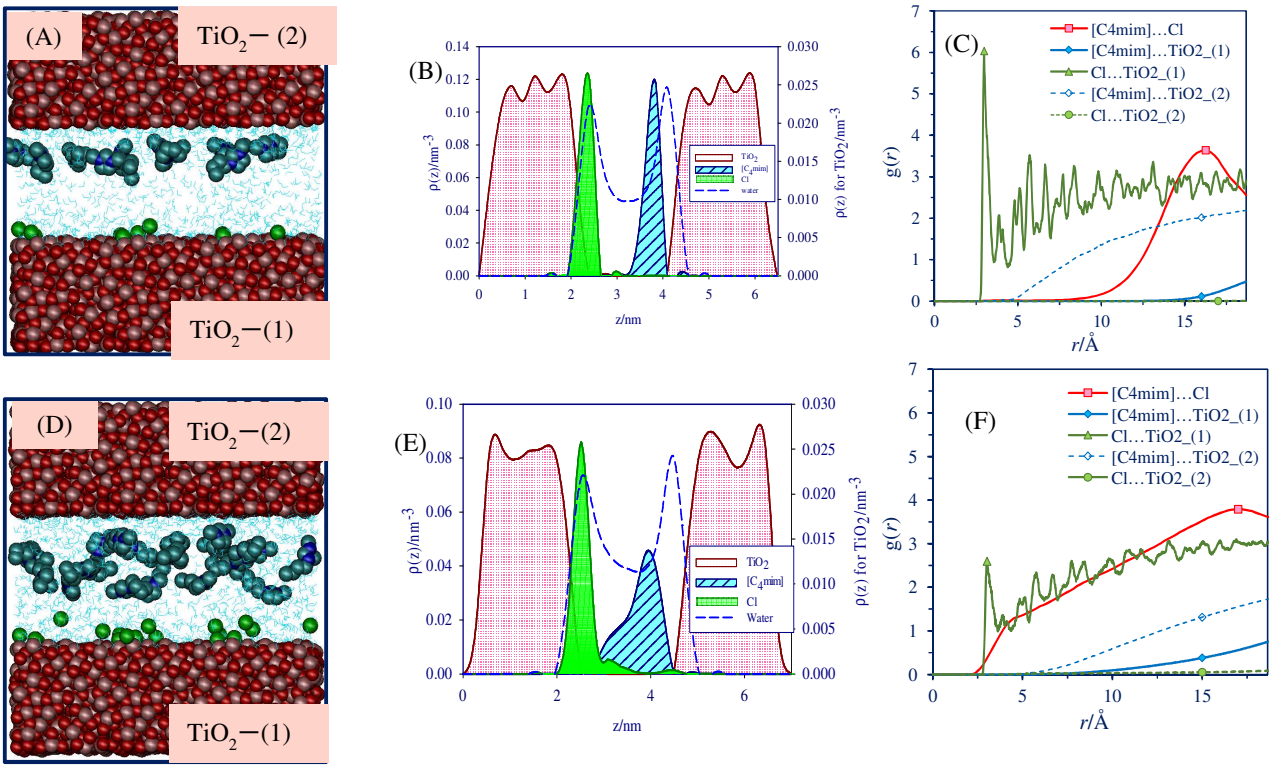

Fig. S12 Snapshots (A and D), number density profiles (B and E), and radial distribution functions (C and F) of dilute mixtures of [C_4mim][Cl] confined inside pores with two amorphous TiO_2 walls with width of 2.5 nm. (Top panel: 10 molecules of [C_4mim][Cl] and bottom panel 20 molecules of [C_4mim][Cl]). See snapshots (A and D) for TiO_2 (1) and (2) labels. Number of water molecules is 1188 and 1469 in (A) and (B) respectively.

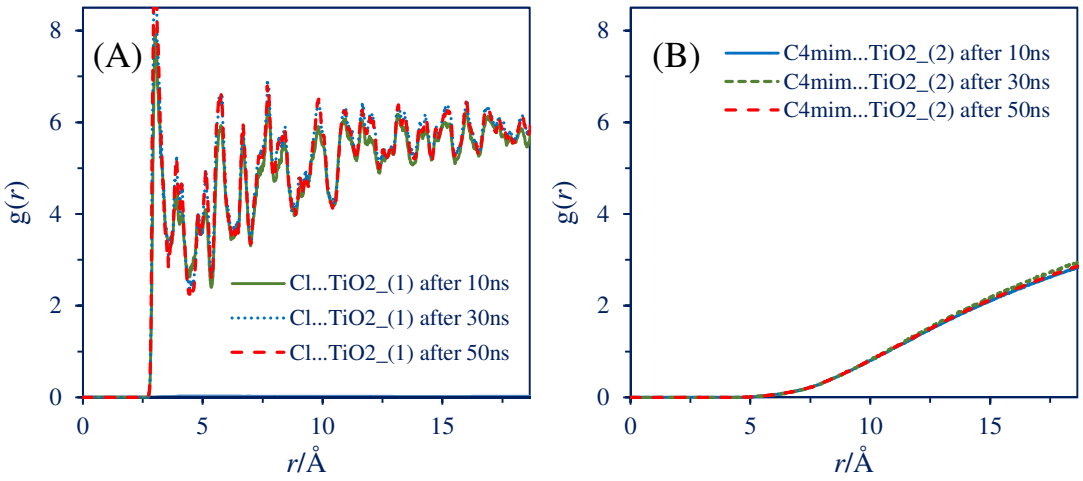

Fig. S13 Radial distribution functions of (A) Cl…TiO_2 walls and (B) [C_4mim]…TiO_2 walls of dilute mixture of [C_4mim][Cl] confined inside pores with two amorphous TiO_2 walls at different simulation times.

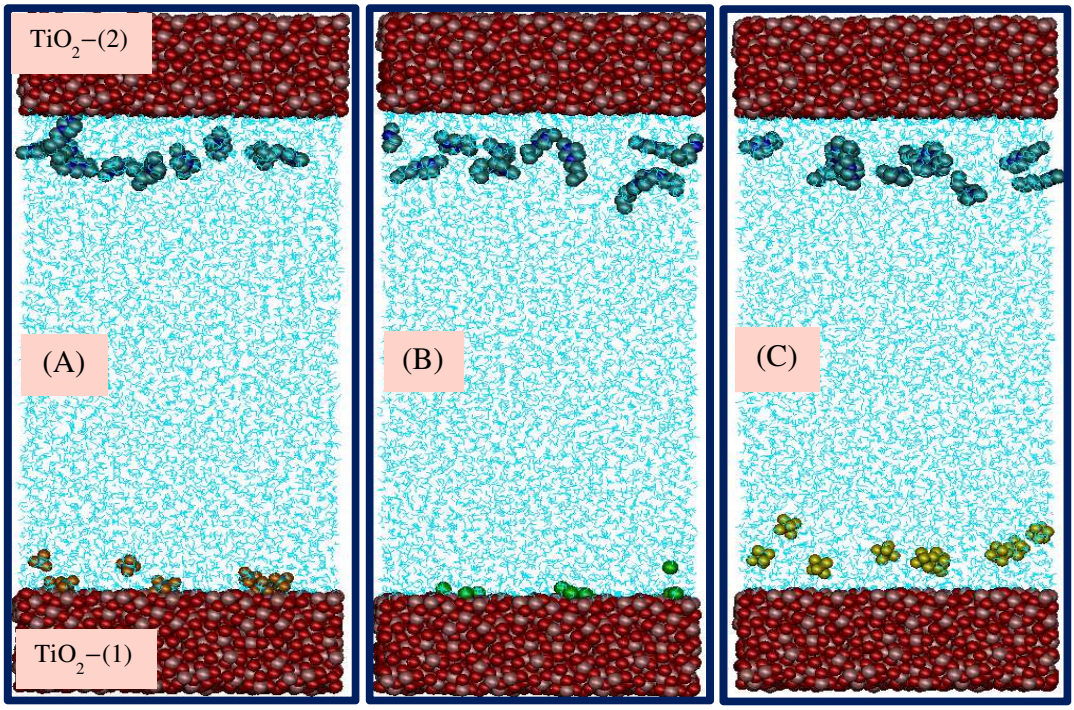

Fig. S14 Snapshots of dilute mixture of ILs confined inside pores with two amorphous TiO_2 walls, (A) [C_4mim][BF_4], (B) [C_4mim][Cl] and (C) [C_4mim][PF_6]. Number of water molecules is 6789, 6811 and 6794 in (A), (B) and (C) respectively.

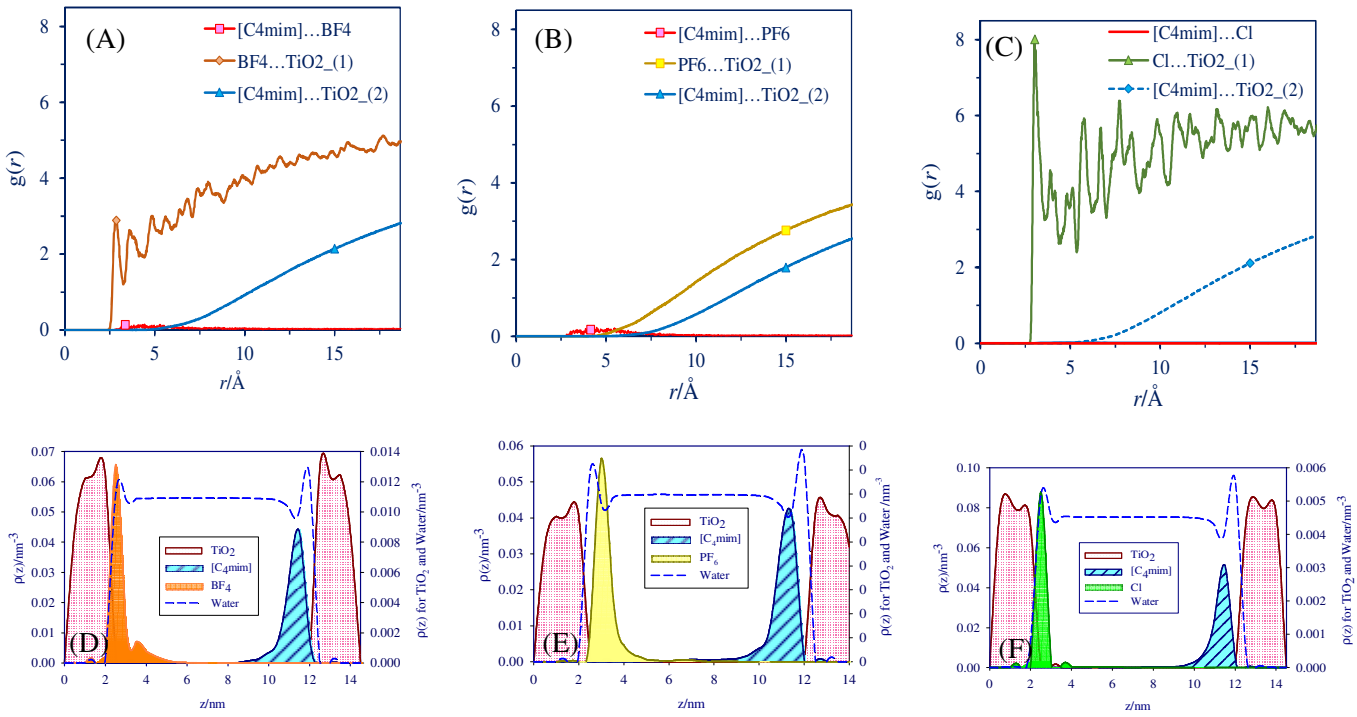

Fig. S15 (Top panel) Radial distribution functions $g(r)$ of cation-anion, cation-pore walls and anion-pore walls of dilute mixture of ILs confined inside pores with two amorphous TiO_2 walls; (Bottom panel) Number density profiles of dilute mixture of ILs confined inside pores with two amorphous TiO_2 walls along the z-direction; (A and D) [C_4mim][BF_4], (B and E) [C_4mim][PF_6] and (C and F) [C_4mim][Cl]. See Figure 2 for TiO_2 (1) and (2) labels.

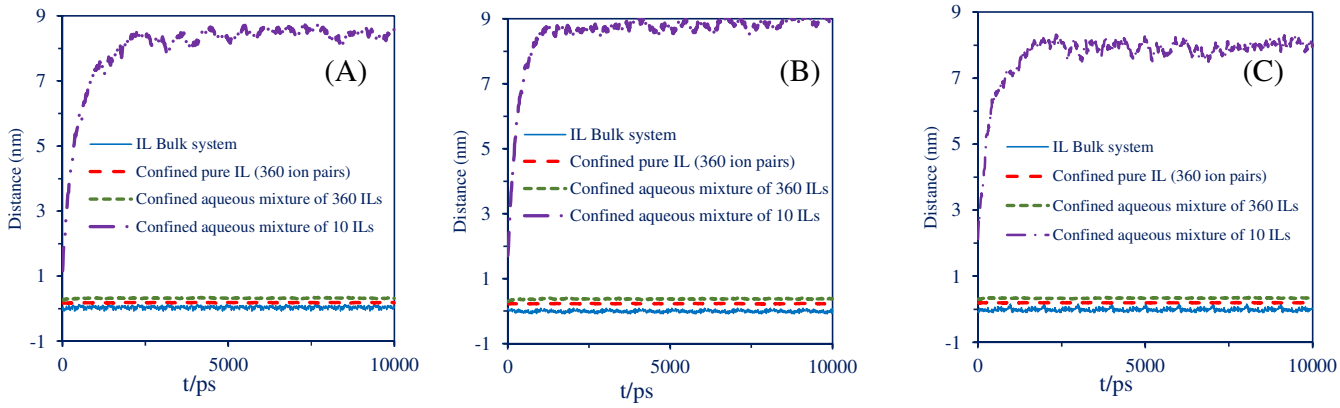

Fig. S16 Temporal development of distance between cations and anions in different systems of (A) [C_4mim][BF_4], (B) [C_4mim][Cl] and (C) [C_4mim][PF_6].

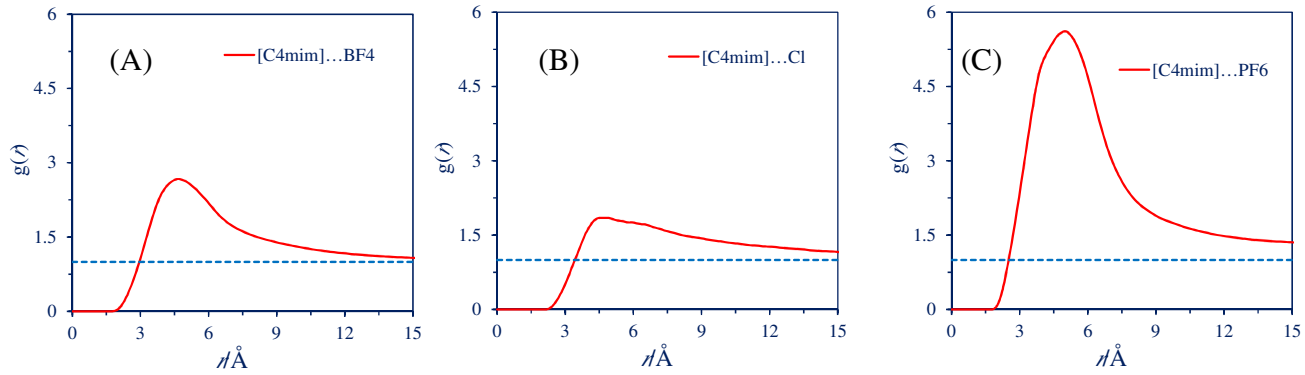

Fig. S17 Radial distribution functions between anion and cation centers of masses of the bulk dilute electrolytes consist of 10 ion pairs of (A) [C_4mim][BF_4], (B) [C_4mim][Cl] and (C) [C_4mim][PF_6].

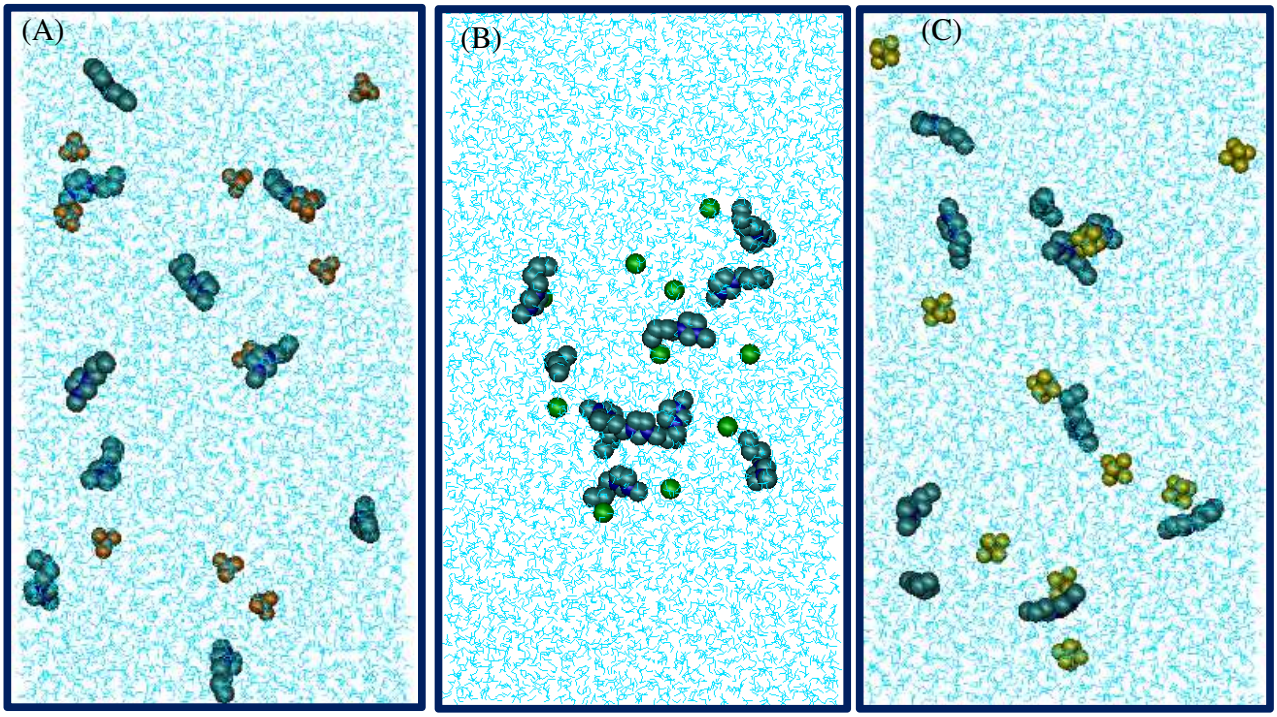

Fig. S18 Snapshots of the dilute (not confined) electrolytes consist of 10 ion pairs of (A) [C_4mim][BF_4], (B) [C_4mim][Cl] and (C) [C_4mim][PF_6]. Number of water molecules is 6789, 6811 and 6794 in (A), (B) and (C), respectively.

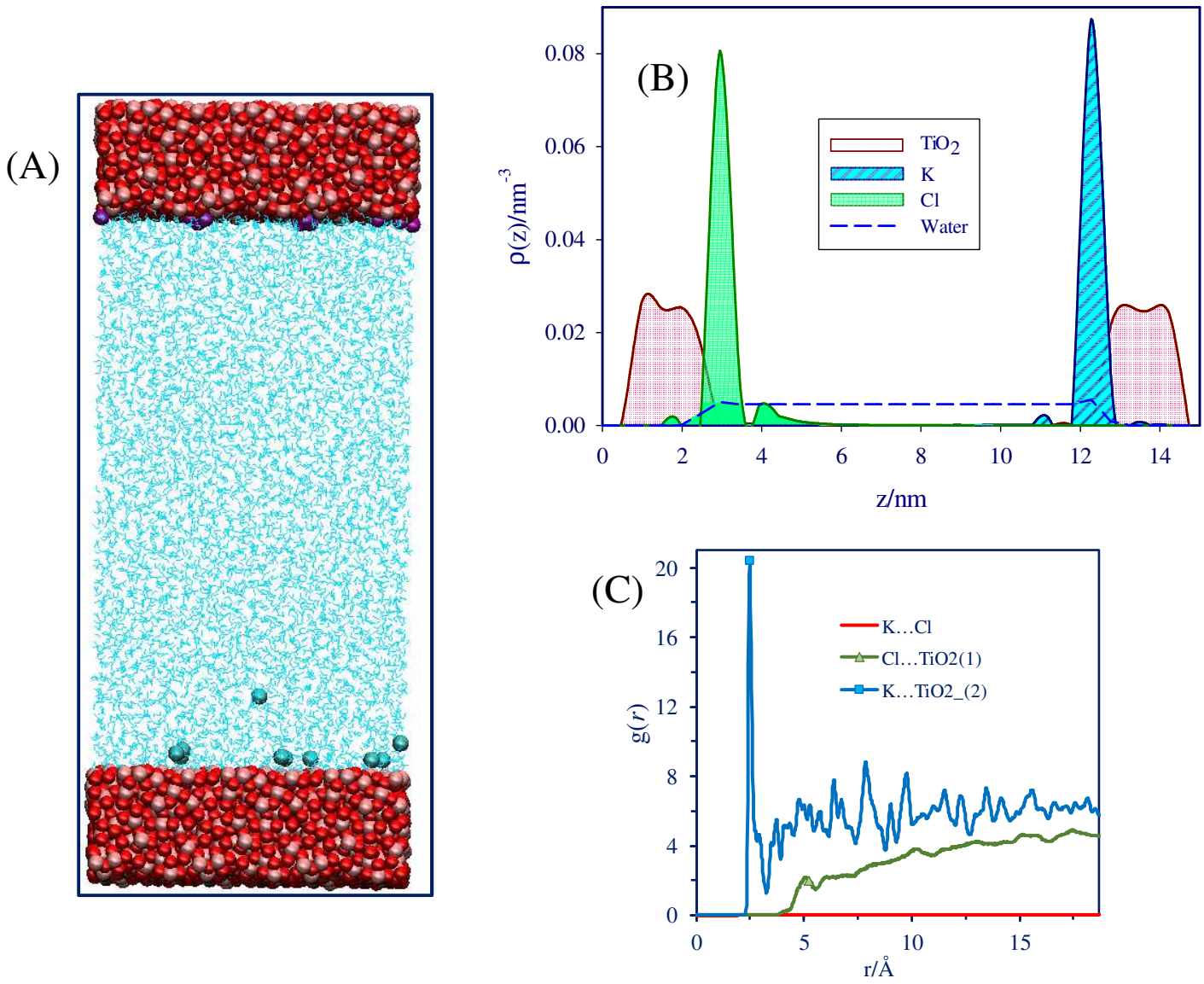

Fig. S19 Snapshot (A), number density profiles (B) and radial distribution functions (C) of dilute mixtures of KCl confined inside pores with two amorphous TiO_2 walls with width of 10 nm. Number of water molecules is 6800. Ti, O, K, Cl, N and C atoms are depicted in pink, red, purple, green, blue and cyan, respectively.

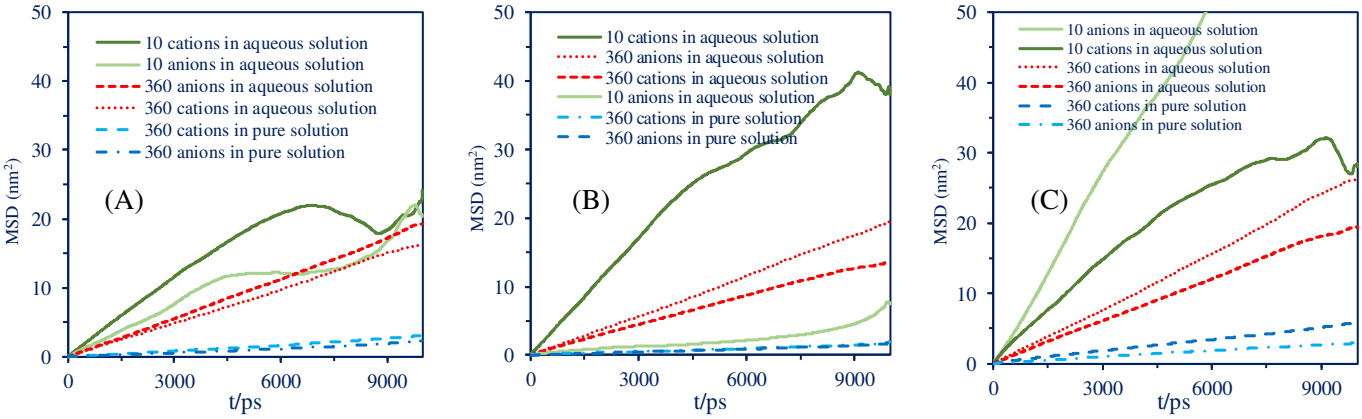

Fig. S20 Mean-squared displacement of geometrical center of IL ions in mixtures confined between two amorphous TiO_2 walls with a 10 nm size pore, (A) [C_4mim][BF_4], (B) [C_4mim][Cl] and (C) [C_4mim][PF_6].

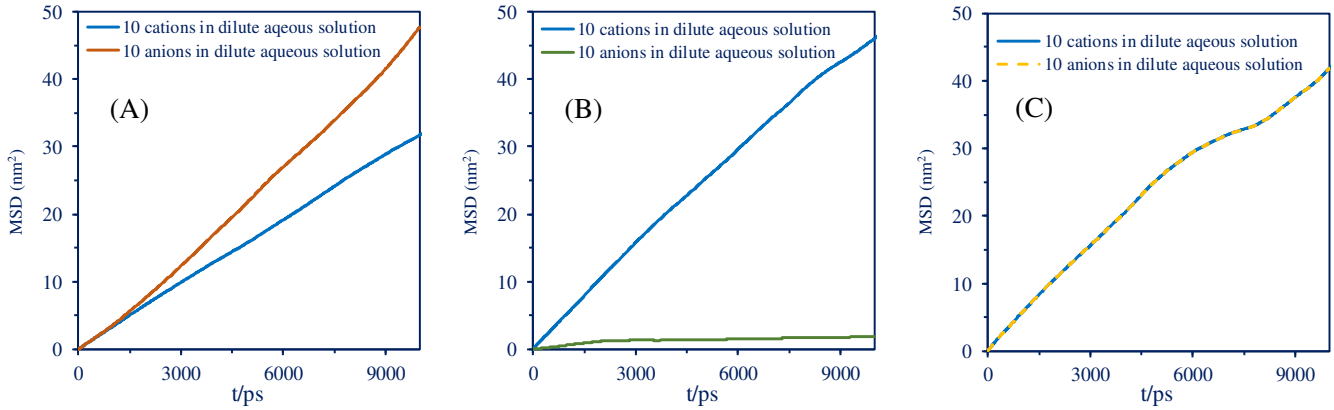

Fig. S21 Mean-squared displacement of geometrical center of IL ions in dilute mixtures confined between two amorphous TiO_2 walls with a 10 nm size pore, (A) [C_4mim][BF_4], (B) [C_4mim][Cl] and (C) [C_4mim][PF_6]. The MSDs reported here are in the *xy*-direction parallel to the amorphous walls.

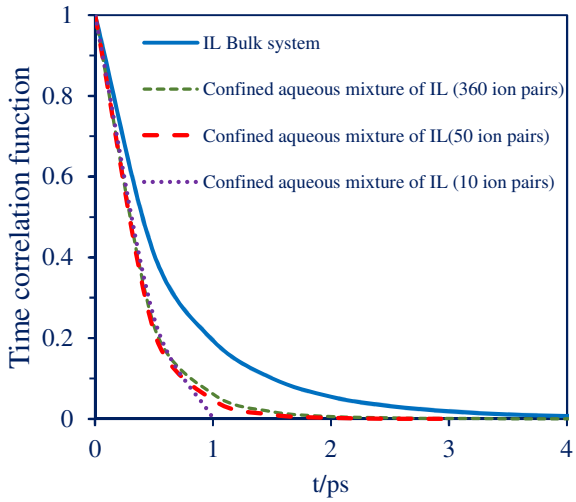

Fig. S22 Time correlation functions between C_2 atom of imidazolium ring and Cl anion for bulk system and aqueous mixtures of [C_4mim][Cl] with 360, 50 and 10 ion pairs confined inside two amorphous TiO_2 walls with pore size of 10 nm.

References:

1 M.H. Ghatee and A.R. Zolghadr, *J. Phys. Chem. C*., 2013, **117,** 2066–2077.