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

Electronic Supplementary Information

New Insight into Electrosynthesis of Ordered TiO_2 Nanotubes in EG-Based Electrolyte Solutions: Combined Experimental and Computational Assessment

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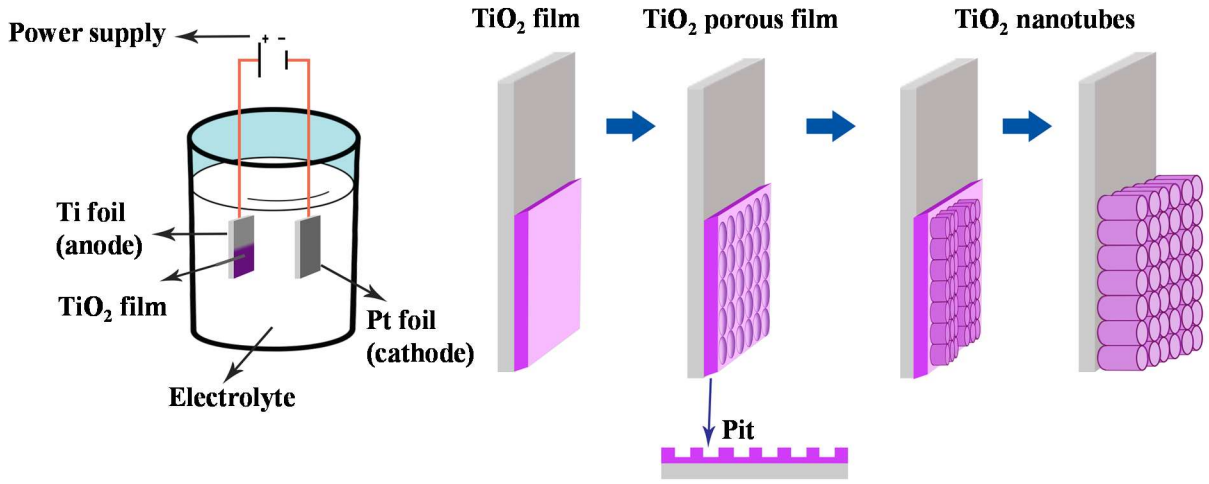


Fig. S1 The Schematic representation of TiO_2-NT formation steps.

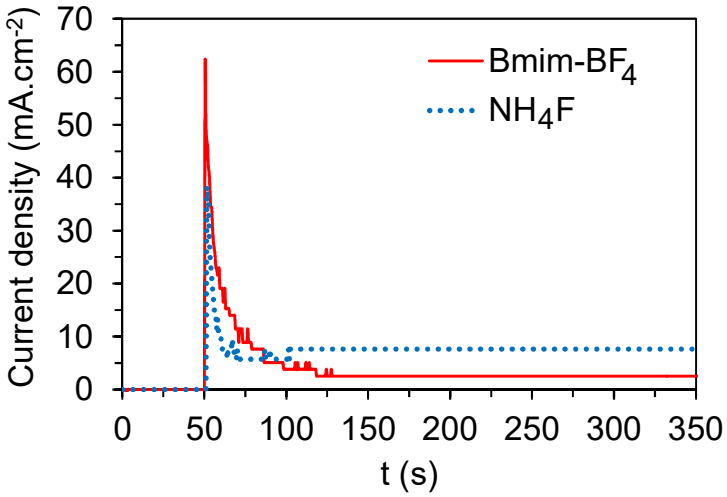


Fig. S2 Current density curves recorded during anodization at 60 V for different electrolyte solutions examined in this study.

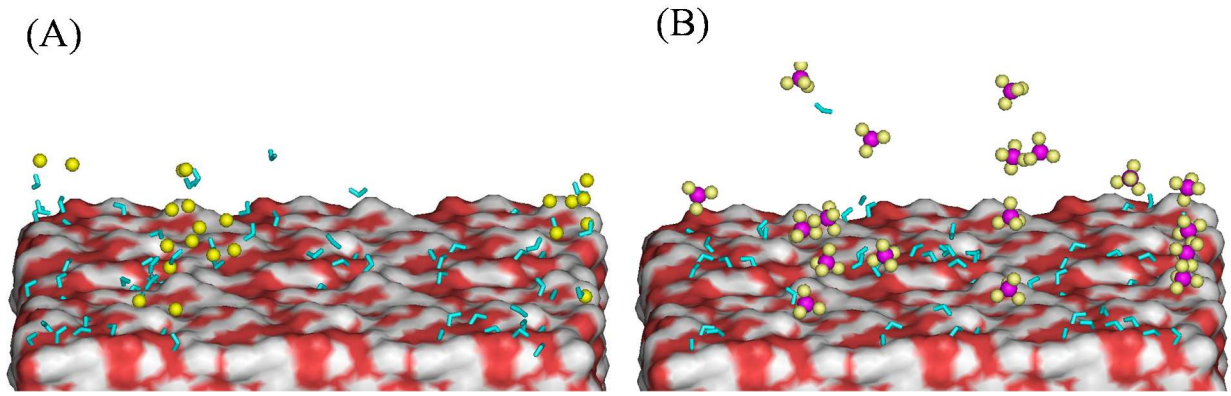


Fig. S3 Location of anions and water molecules on TiO_2 surface for (A) NH_4F and (B) Bmim-BF_4 systems.

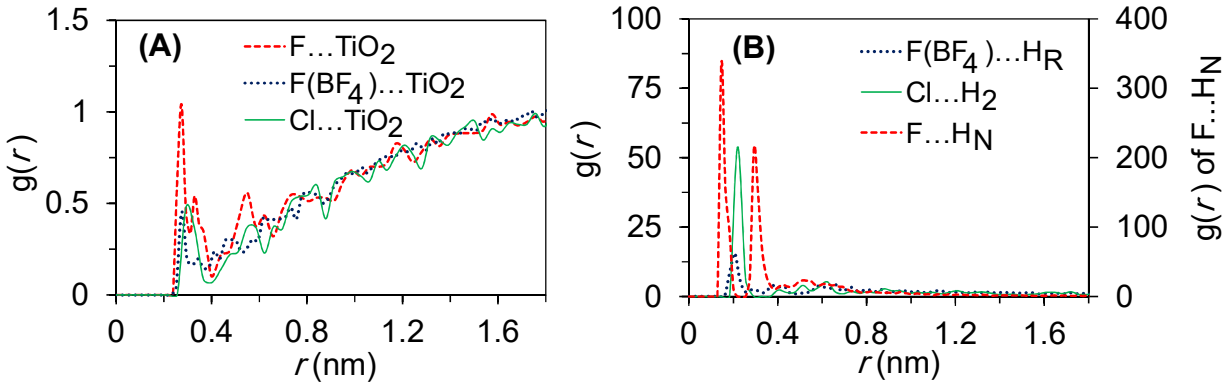


Fig. S4 Corrected radial distribution functions of anion sites with TiO_2 surface (A) and with atomic sites of cations (B). The corrections were done based on the excluded volume effect.

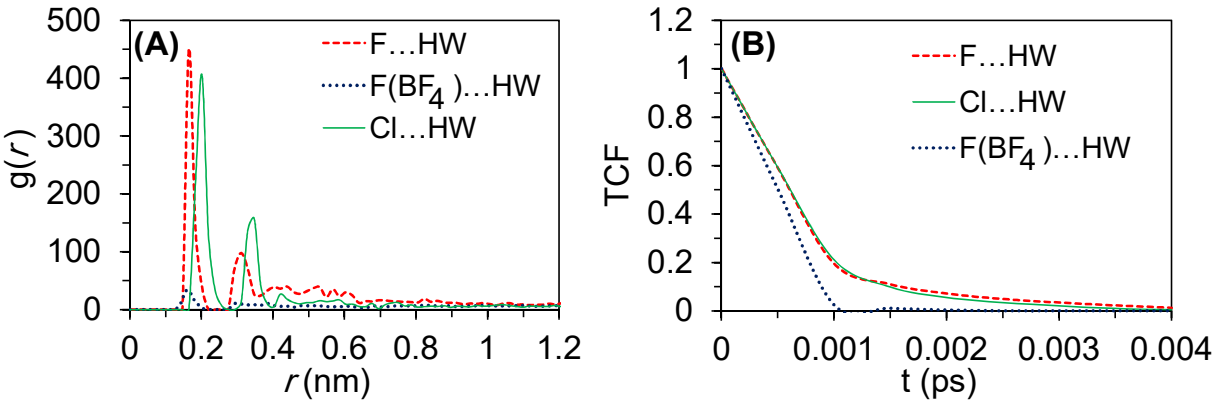


Fig. S5 (A) Radial distribution functions of anion sites with hydrogen atoms of water for all systems. (B) Time correlation functions of anion sites with hydrogen of water molecules.

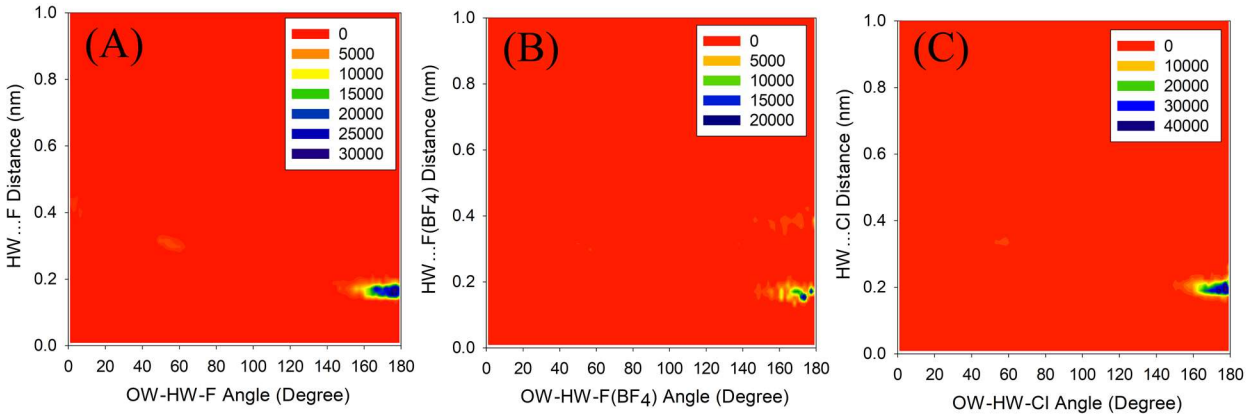


Fig. S6 Combined radial/angular distribution functions of (A) NH_4F, (B) Bmim-BF_4, and (C) Bmim-Cl systems in the case of anion…water interaction.

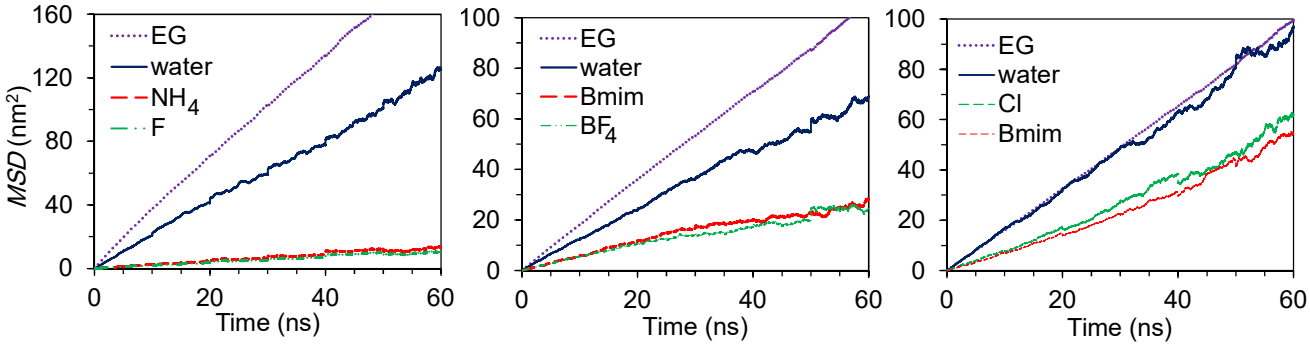


Fig. S7 Mean-square-displacement for EG, water, cations and anions of different electrolyte solutions.

Table S1. Molecular topographies of the various ion pairs. The bond critical points, ring critical points and cage critical points are represented as red, yellow and green circles, respectively.

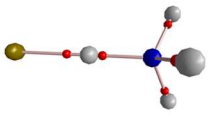
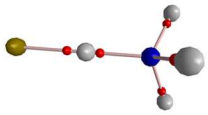
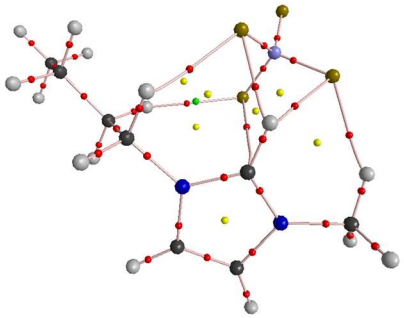
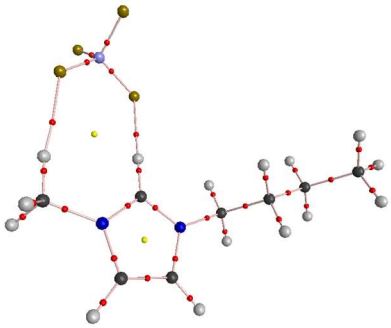
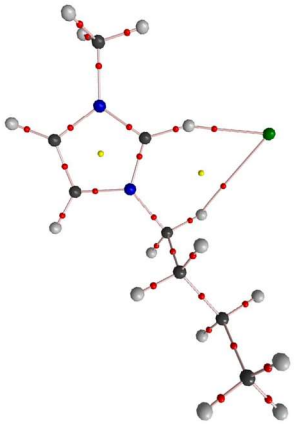
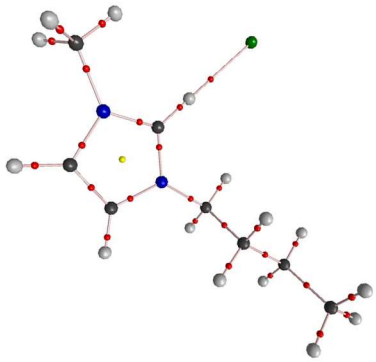
	Gas phase	EG phase
NH_4F		
Bmim-BF_4		
Bmim-Cl		

Table S2. The calculated total electron density $\sum \rho(r)$ values for different ionic specious.

Ionic specious	Gas phase	EG phase
NH_4F	0.152	0.103
Bmim-BF_4	0.073	0.029
Bmim-Cl	0.053	0.019

Table S3. Donor–acceptor NBO interactions and their second-order perturbation energies in (kcal/mol). Lewis' structures, in which two-center functions are identified with bonds (BD) and one-center functions with lone pairs (LP).

	Donor	Acceptor	Gas phase	EG phase
NH_4F	LP(1) F	BD*(1) $N–H_N$	0.52	11.41
	LP(4) F	BD*(1) $N–H_N$	9.20	126.64
Bmim-BF_4	LP(1) F(BF_4)	BD*(1) $C_M–H_M$	3.81	3.72
	LP(3) F(BF_4)	BD*(1) $C_R–H_R$	10.96	9.54
	LP(3) F(BF_4)	BD*(1) $C_R–H_R$	4.14	3.56
	LP(3) F(BF_4)	BD*(1) $C_M–H_M$	3.39	2.68
	LP(3) F(BF_4)	BD*(2) $N_Z–C_R$	4.94	3.64
Bmim-Cl	LP(1) Cl	BD*(2) $C_2–H_2$	13.51	10.67
	LP(3) Cl	BD*(2) $C_3–H_3$	8.28	7.07
	LP(4) Cl	BD*(2) $C_2–H_2$	147.32	127.03
	LP(4) Cl	BD*(2) $C_3–H_3$	1.88	1.59