

## **Supporting Information**

### **Origin of Ion Selectivity at the Air/Water Interface**

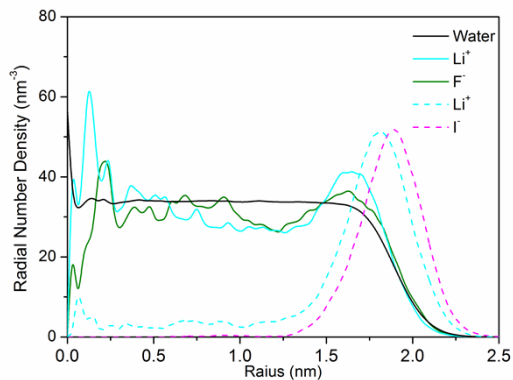
Lu Sun, Xin Li, Yaoquan Tu, and Hans Ågren\*

Division of Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology, S-10691 Stockholm, Sweden

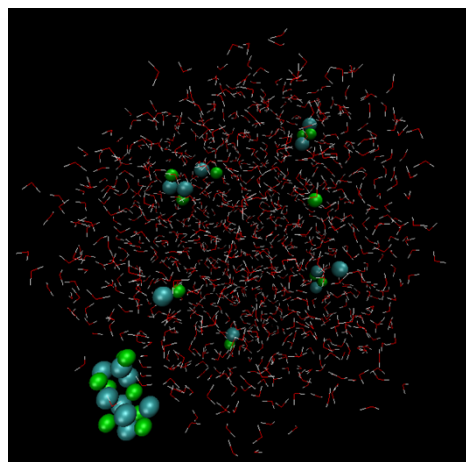
**Table S1 Ionic Properties**

	$R_{hy1}$ (nm)	$R_{hy2}$ (nm)	$N_{hb\_11}$		$L_{hb}$ (Å)		$L_{cen}$ (Å)		D (Debye)		$\tau_{w\_w}$ (ps)
			Bulk	Interface	Bulk	Interface	Bulk	Interface	Bulk	Interface	
Water	0.328	0.574	0.33	0.17	1.91	1.97			2.56	2.35	3.36
F <sup>-</sup>	0.328	0.567	0.3	0.21	1.82	1.78	0.55	0.90	1.36	1.76	3.59
Cl <sup>-</sup>	0.365	0.604	0.4	0.21	2.29	2.25	0.87	1.39	2.06	2.56	3.42
Br <sup>-</sup>	0.378	0.616	0.4	0.22	2.42	2.39	1.02	1.58	2.67	3.12	3.41
I <sup>-</sup>	0.396	0.635	0.5	0.21	2.64	2.62	1.15	1.85	3.24	3.75	3.36
Na <sup>+</sup>	0.316	0.53	0.3	0.44			0.31	0.37	0.03	0.03	3.70
K <sup>+</sup>	0.356	0.562	1.5	1.70			0.40	0.49	0.12	0.13	3.59
Rb <sup>+</sup>	0.374	0.584	2.5	2.72			0.44	0.59	0.18	0.20	3.59
Cs <sup>+</sup>	0.416	0.596	4.9	4.95			0.49	0.69	0.27	0.32	3.65

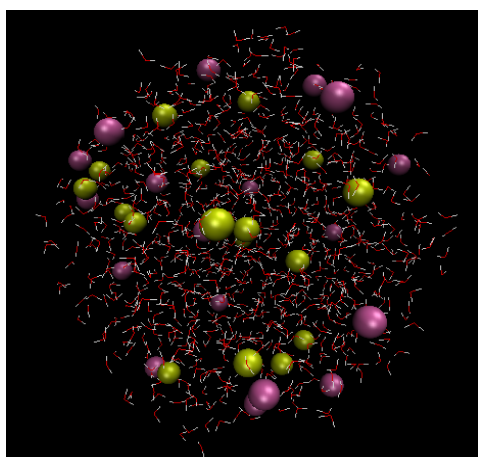
$R_{hy1}$  and  $R_{hy2}$  are the places where first and second solvation shell end.  $N_{hb\_11}$  is the number of hydrogen bonds formed between water in first hydration shell.  $L_{hb}$  is the hydrogen bond length.  $L_{cen}$  is the distance from ion to the mass center of first solvation shell water. D is the dipole moment.  $\tau_{w\_w}$  denotes the average lifetime of water-water hydrogen bond. A hydrogen-bond is formed if the water is in the first solvation shell and the O-H-A(A denotes the hydrogen acceptor) angle is over 130°.



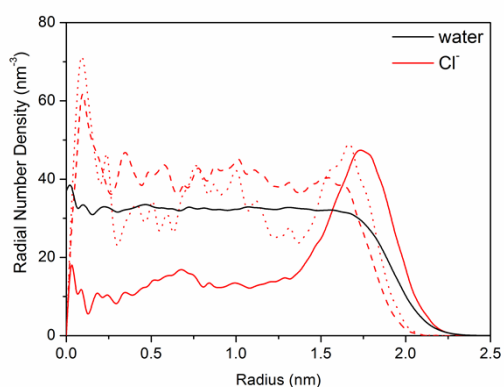
(a)



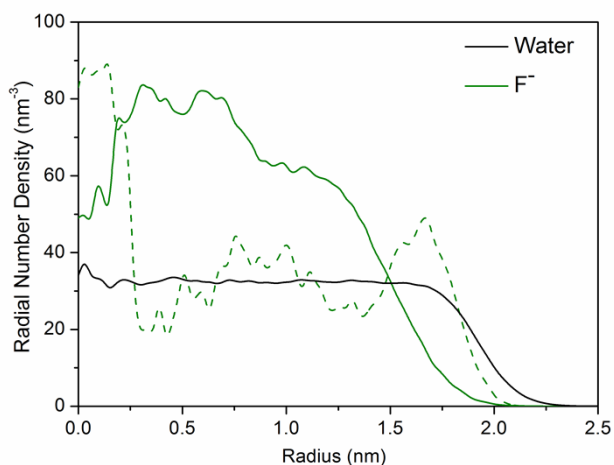
(b)



(c)

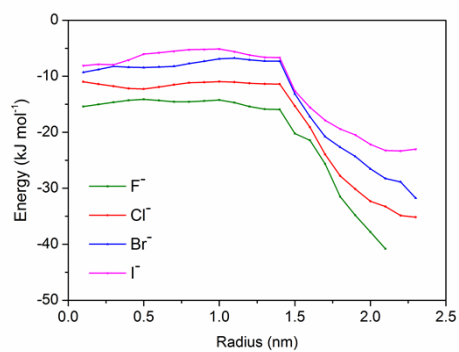


(d)

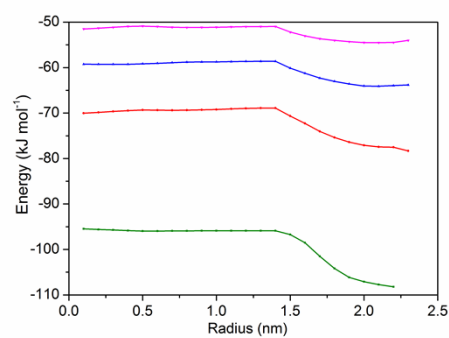


(e)

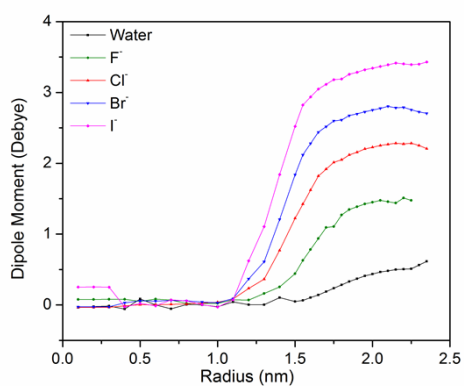
Figure S1. (a) The strong electrostatic attraction and weak Pauli repulsion make the smallest cation  $\text{Li}^+$  hard to dissociate. (b) Snapshot of  $\text{LiF}$  in the water cluster with  $\text{Li}^+$  and  $\text{F}^-$  denoted as cyan and green balls. (c) Snapshot of  $\text{KF}$  in the water cluster with  $\text{K}^+$  and  $\text{I}^-$  denoted as yellow and purple balls. (d) Polarization influences the distribution of  $\text{Cl}^-$ . The solid, dashed, and dotted lines represent the number densities of  $\text{Cl}^-$  with the polarizability of  $0.003969 \text{ nm}^{-3}$ ,  $0.001786 \text{ nm}^{-3}$ , and  $0.0 \text{ nm}^{-3}$ , respectively. (e) With the polarizability of  $\text{F}^-$  increased from  $0.001786 \text{ nm}^{-3}$  (solid line) to  $0.003969 \text{ nm}^{-3}$  (dashed line),  $\text{F}^-$  ions get much closer to the interface.



(a)



(b)



(c)

Figure S2. Interaction energies of anions with (a) non-hydrogen-bonded and (b) hydrogen-bonded water in the first hydration shell of anions.(c) The normal component of dipole moment of anions. Here  $K^+$  is the cation.

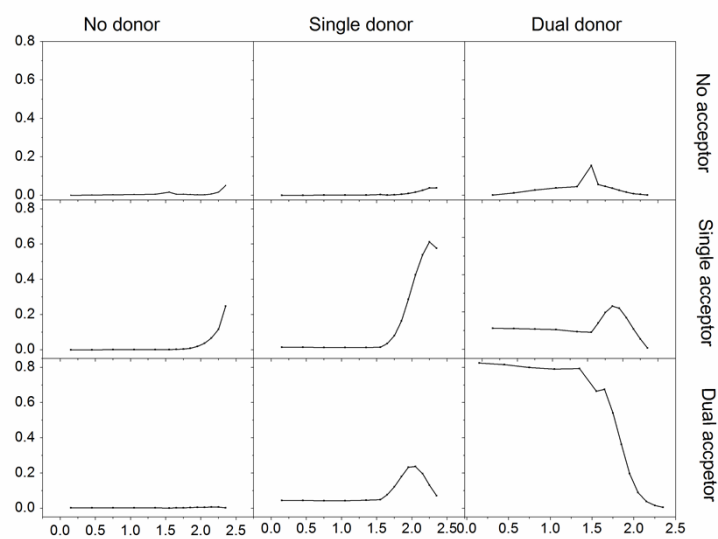
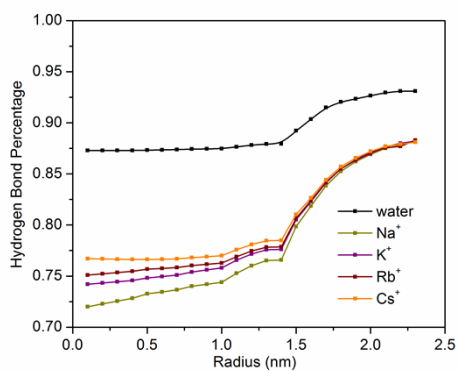
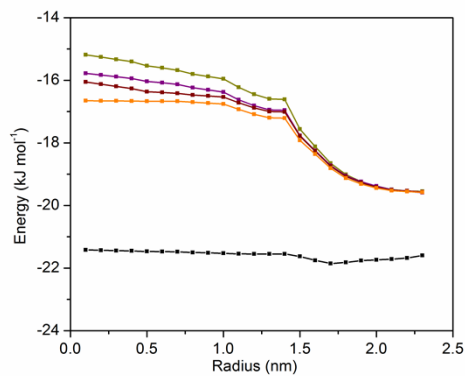


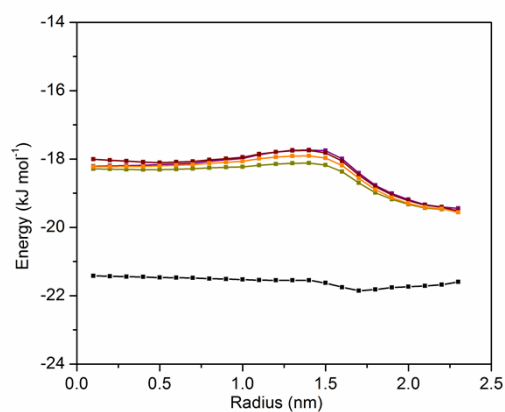
Figure S3. Hydrogen bonds formation among water. Most of water in the bulk is fully bonded. It's interesting that dual-donor no-acceptor water increase most prompt to react to the breaking of water-water hydrogen bonds, resulting water donating a little more than it accepts somewhat beneath the interface.



(a)



(b)



(c)

Figure S4. Water structure affected by cations. (a) The decreasing water-water hydrogen bond percentage with F<sup>-</sup> as anions. Average interaction energy between a water molecule and its solvation shell, with the counterion as (b) F<sup>-</sup> or (c) I<sup>-</sup>. The cations also follow the rule the smaller the more influential. But the influence is not as significant as anions.