Speciation of the proton in water-in-salt electrolytes

Kateryna Goloviznina,[1,2,a] Alessandra Serva,[1,2] and Mathieu Salanne[1,2,3]

[1] *Sorbonne Université, CNRS, Physicochimie des Électrolytes et Nanosystèmes Interfaciaux, F-75005 Paris, France*

[2] *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, 80039 Amiens Cedex, France*

[3] *Institut Universitaire de France (IUF), 75231 Paris, France*

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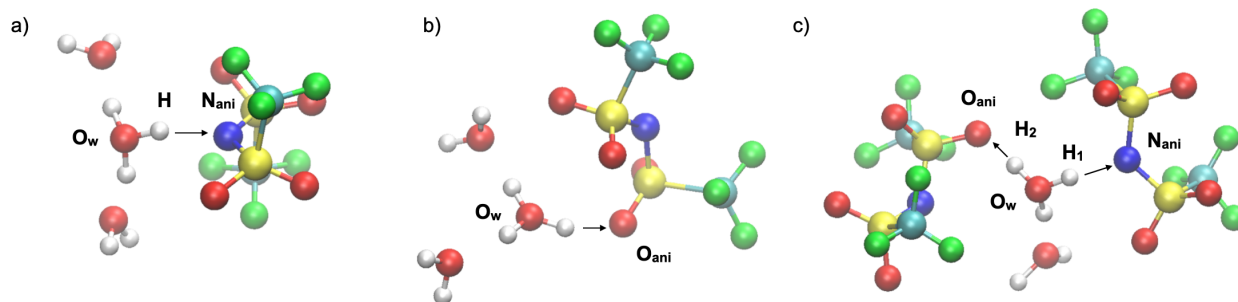[a] Electronic mail: kateryna.goloviznina@sorbonne-universite.fr

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Figure S1. Initial configuration extracted from AIMD run (S-II) used to compute free energy profiles of proton transfer. The configurations represented in subfigures (a) and (c) were used to investigate the proton transfer from H_3O^+ to the N atom of the $TFSI^-$ anion, while subfigures (b) and (c) to the O atom of the anion.
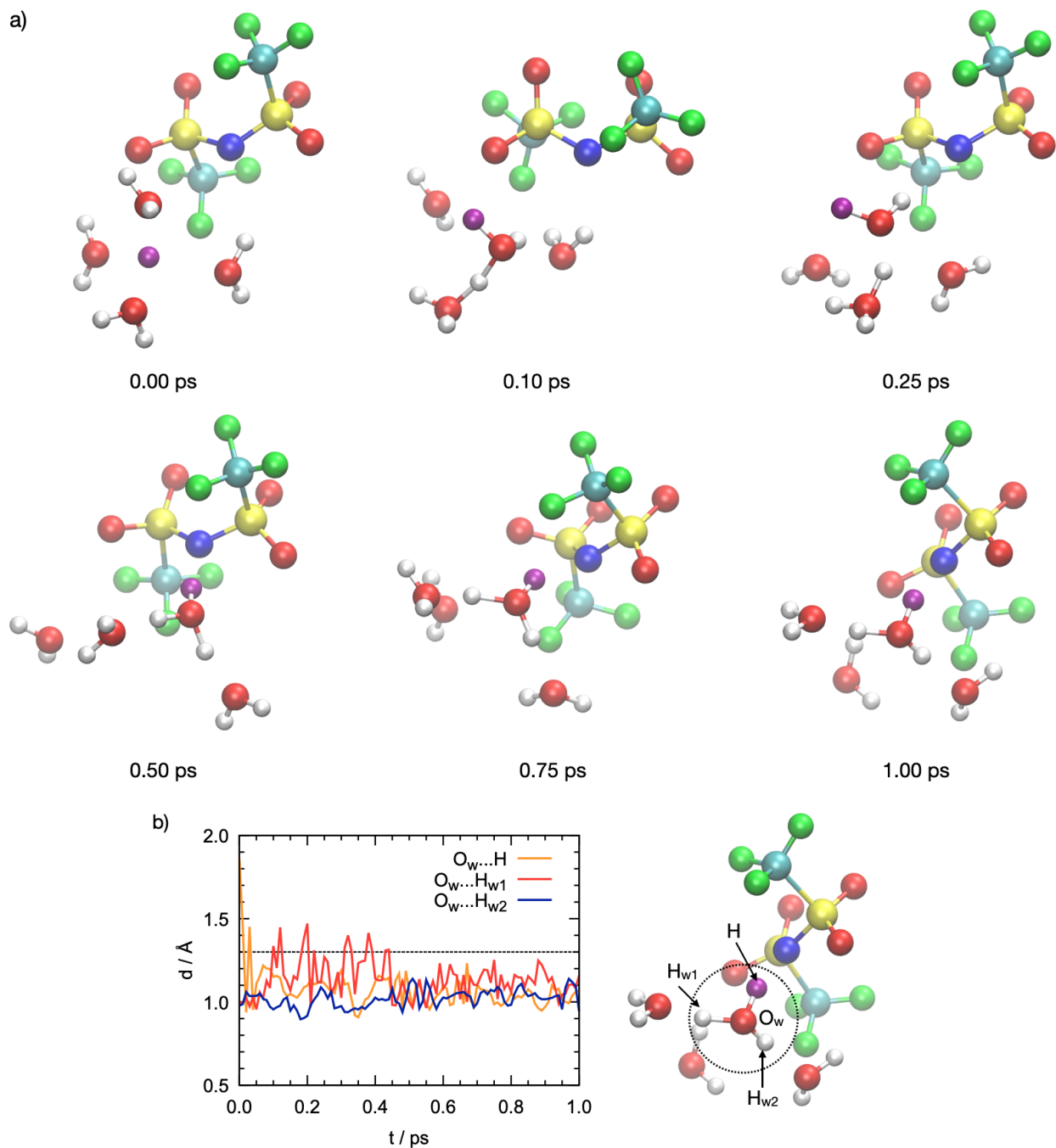
Figure S2. Equilibration of the S-II system: (a) Simulation snapshots revealing the environment of the proton (represented by a small purple sphere) as a function of time. (b) Time evolution of hydrogen–oxygen distances in the H_3O^+ cation. The horizontal dashed line corresponds to the value of $1.3\,\text{Å}$ used for the proton speciation definition. Here, the equilibration time reaches $0.45\,\text{ps}$ when a stable H_3O^+ cation is formed.
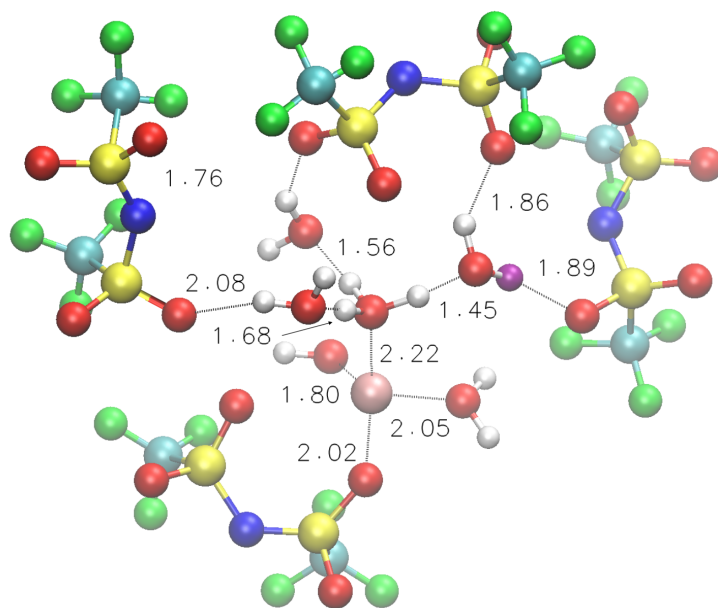
Figure S3. Simulation snapshot (S-V) revealing the local environment of the $H_9O_4{}^+$ Eigen cation, which includes the local environment of lithium cation not shown in Figure 2b (4.1 ps frame).
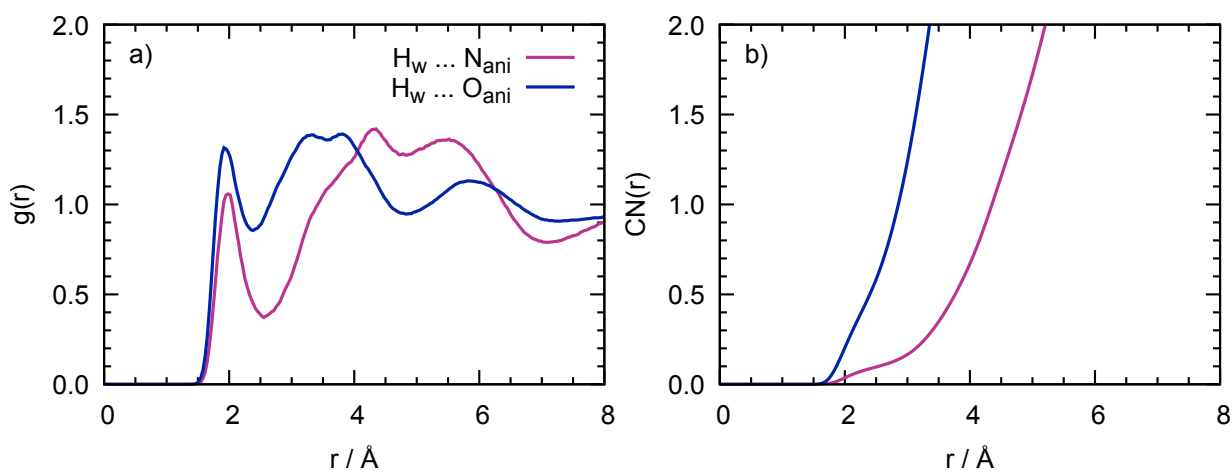

Figure S4. Radial distribution functions ($g(r)$) and running coordination numbers (CN) of O and N atoms of the TFSI$^-$ anion around H_w atoms of water molecules, obtained from the previously reported 70 ps AIMD trajectory of 21 m LiTFSI WiS.
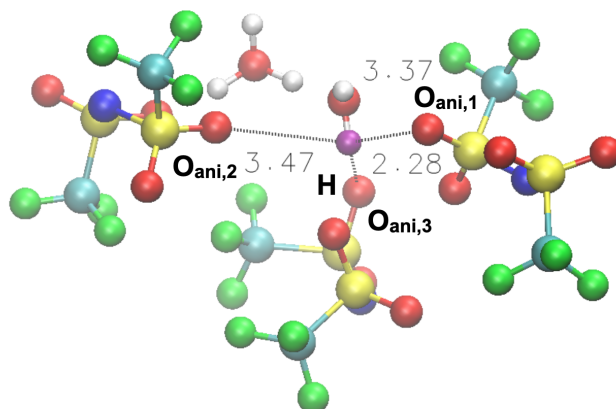
Figure S5. Simulation snapshot (at 5.1 ps, S-IV) illustrating the formation of a hydrogen bond between a water molecule and an oxygen atom of a third TFSI$^-$ anion, after moving away from the first and second anions, as shown in Figure 3c.
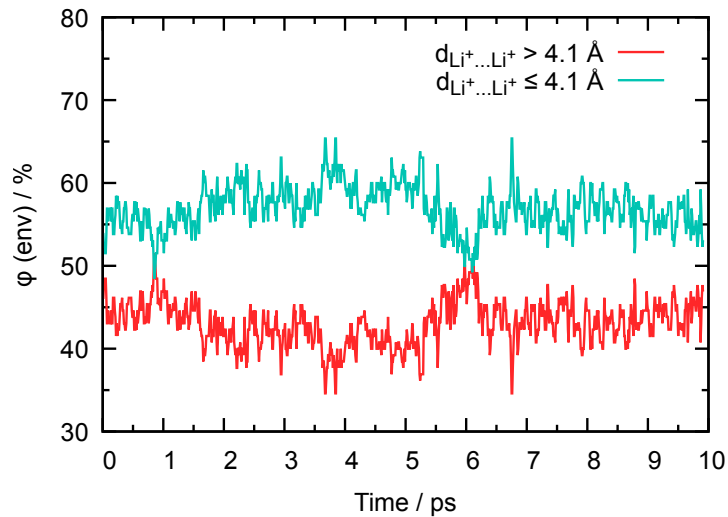

Figure S6. Time evolution of the fraction of the lithium cations ($\phi(t)$) with a Li$^+$ ... Li$^+$ distance smaller or greater than 4.1 Å in system S-V with a single Li$^+$ ion in a nanochain substituted by a H$^+$.
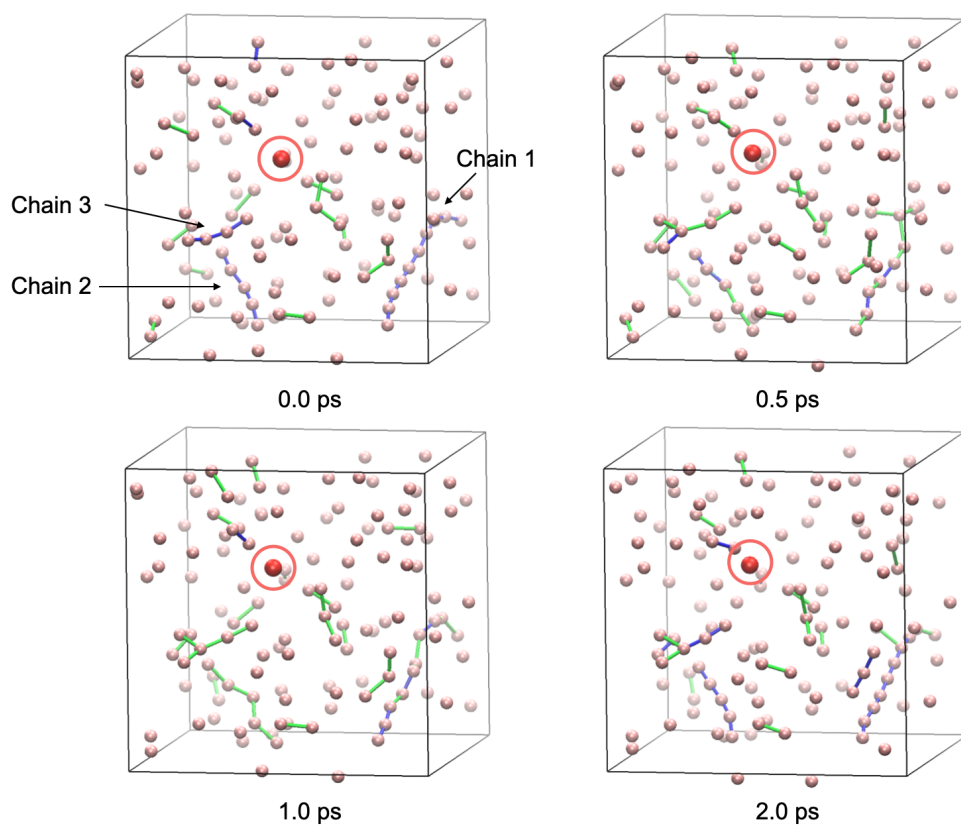
Figure S7. Simulation snapshots (S-III) revealing the evolution of lithium nanochains when a single Li^+ cation is replaced by a proton (represented by a big red sphere in a red circle). The subfigure at $0.0\,ps$ shows the starting configuration obtained from a previous $70\,ps$ *ab initio* MD run with a replaced cation. Blue lines correspond to the $Li^+ \ldots Li^+$ distances smaller than $3.0\,\text{Å}$, green lines to those larger than $3.0\,\text{Å}$ and smaller than $4.1\,\text{Å}$, which are the first and second minima of the $Li^+ \ldots Li^+$ radial distribution function (Figure 6, red curve).