Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information for:

Surface Charge-Driven Sodium-Ion Migration and Secondary Desolvation in MXene Nanoconfinement

Lei Li,[a] Huihong Wang,[b] and Zhu Liu*[ab]

[a]Zhejiang Key Laboratory of Intelligent Manufacturing for Functional Chemicals, ZJU-Hangzhou Global Scientific and Technological Innovation Center, Zhejiang University, Hangzhou 311215, China

[b]College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310012, China

***Corresponding author**

E-mail addresses: liuzhu@zju.edu.cn

Table S1 Lennard-Jones components and point charge parameters for $Ti_3C_2(OH)_2$

Atom	**L-J and point charge parameters**			
	ε (kcal/mol)	σ (Å)	Charge-Anode (e)	Charge-Cathode (e)
Ti-inner	0.6087	1.9565	1.04350	1.0435
Ti-outer	0.6087	1.9565	1.30535	1.30535
C	0.0660	3.5000	-1.30920 (0e) -1.33420 (40e) -1.35920 (80e) -1.38420 (120e) -1.40920 (160e) -1.43420 (200e) -1.45920 (240e)	-1.30920 (0e) -1.28420 (40e) -1.25950 (80e) -1.23420 (120e) -1.20920 (160e) -1.18420 (200e) -1.15920 (240e)
O	0.1554	3.1656	-0.9579	-0.9579
H	0.1554	1.5000	0.44000	0.44000

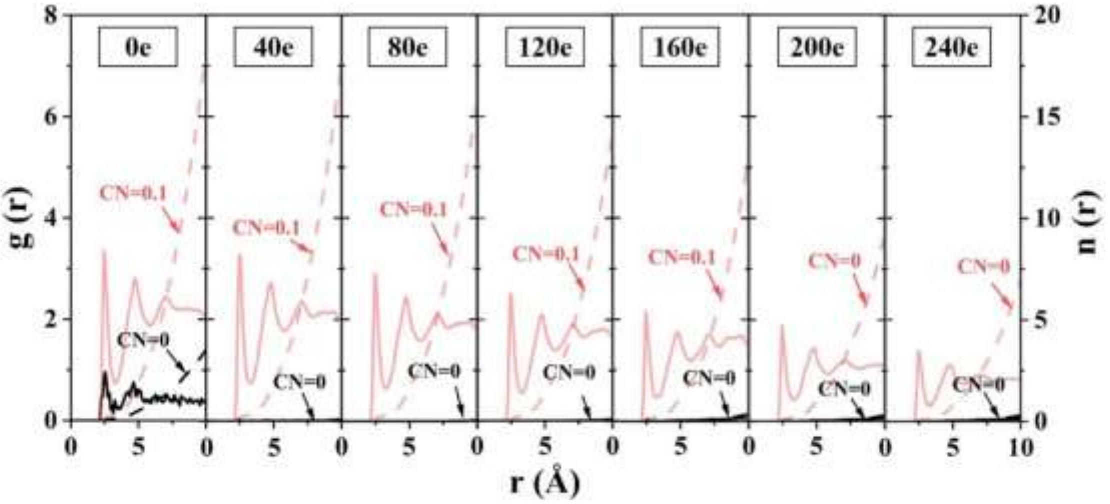

Figure S1 Radial distribution function g(r) and coordination number plots n(r) of ClO4^{-} and Na^{+}, where the black and red lines represent the MXene interlayer and the bulk phase, respectively.

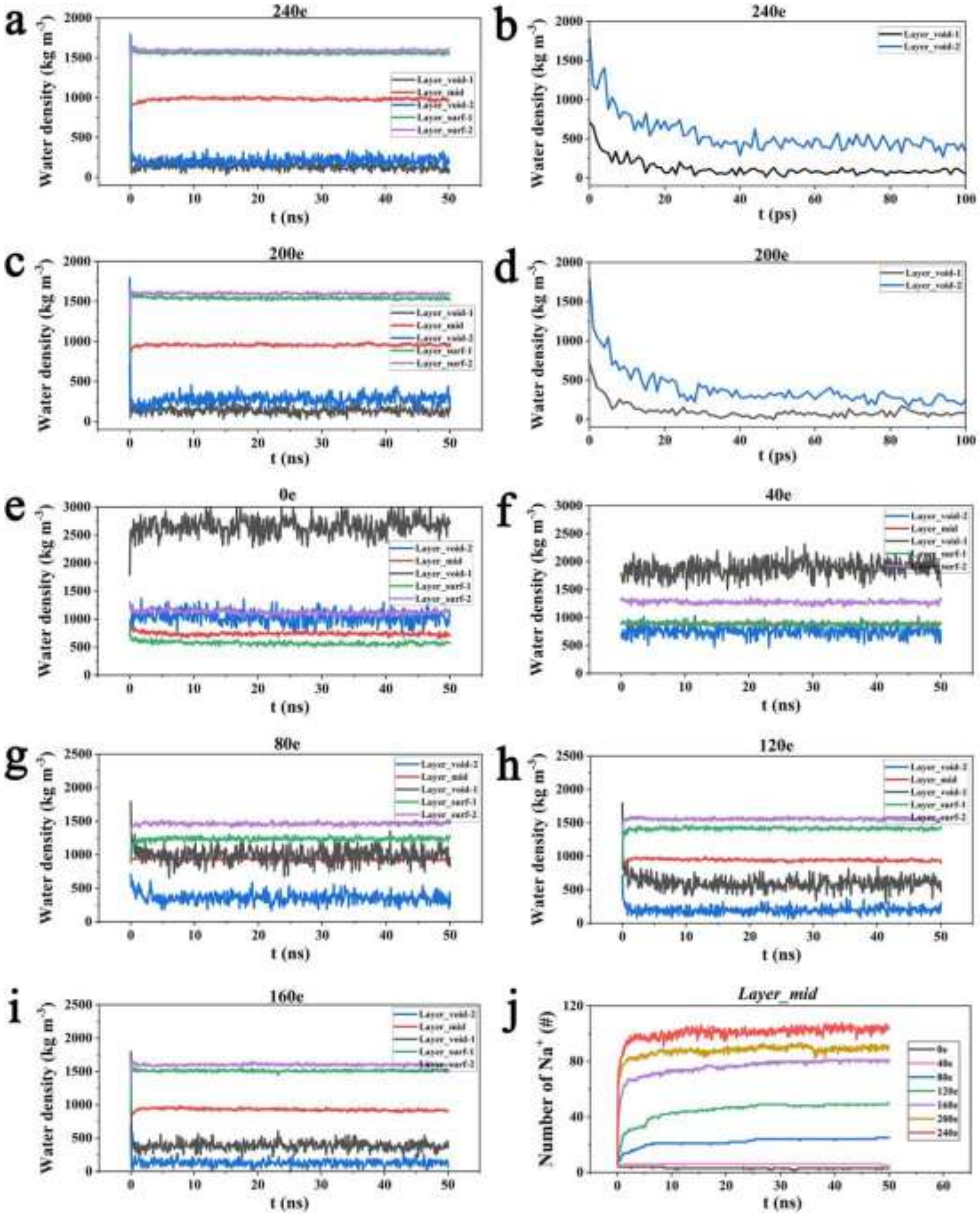

Figure S2 (a)-(i) Variation of water density in Layer_void with time for different charge cases. (j) Variation of Na$^+$ number in Layer_mid with time for different charge cases.

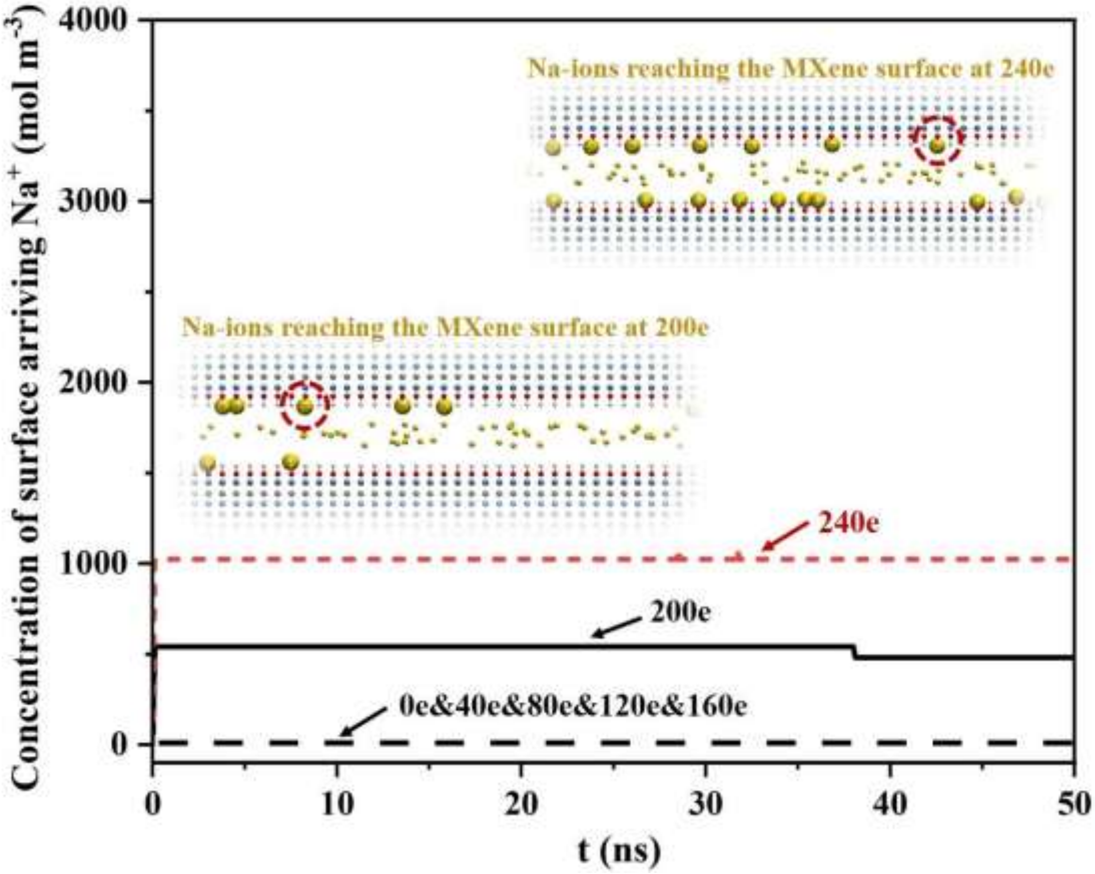

Figure S3 Variation of surface arriving Na-ions concentration with time for different charged cases. The insert image shows the Na-ions absorbed on the MXene surface at 50 ns for 200e/240e cases. Note that in order to distinguish them with the interlayer Na-ions, these surface-arriving Na-ions (marked by red circles) are intentionally drawn larger. The confined water molecules are also hidden.

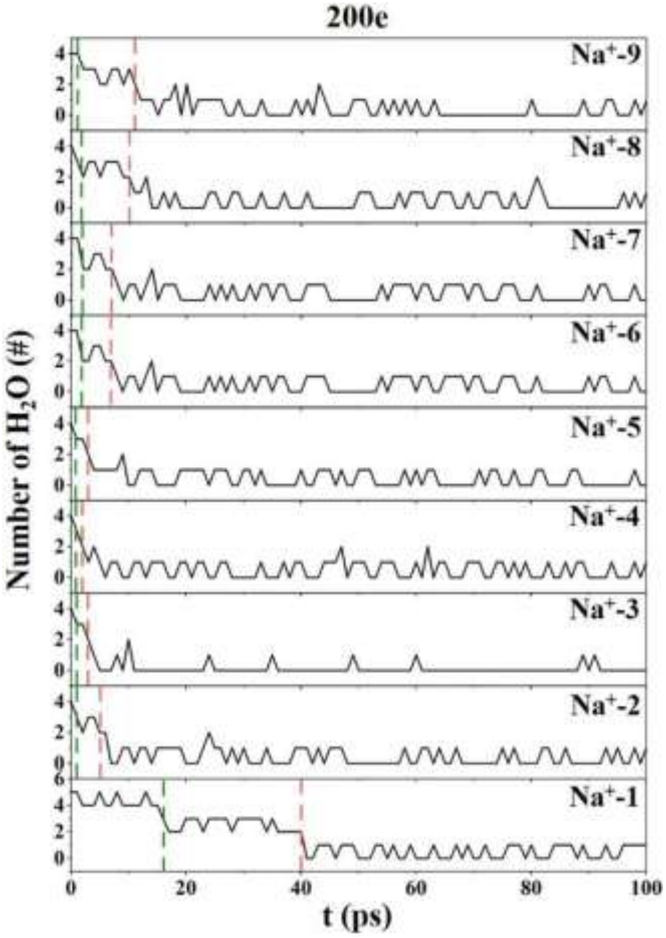

Figure S4 The change of the water molecules number around the surface-arriving Na ions over time at 200e.

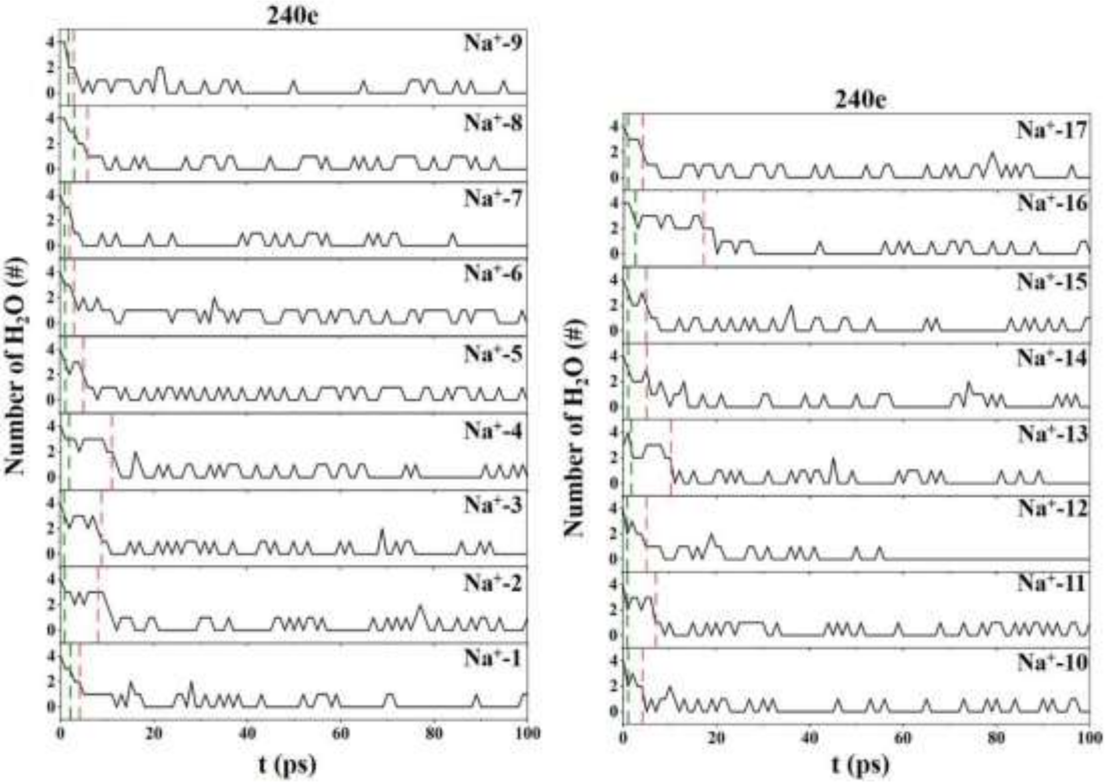

Figure S5 The change of the water molecules number around the surface-arriving Na ions over time at 240e.

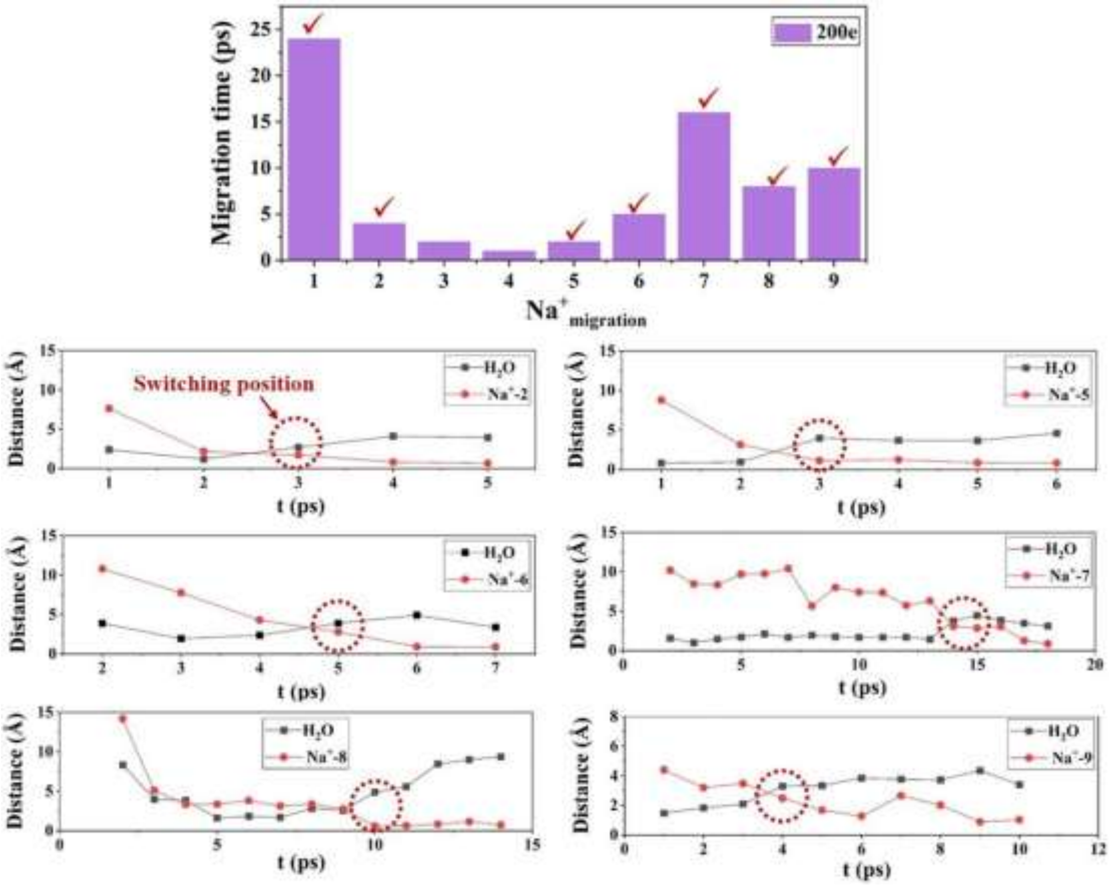

Figure S6 In the case of 200e, all surface-arriving Na ions that have switched positions with water molecules were counted. This figure shows the distance variation between surface-arriving Na ions/“blocking” water and H-COM over time. Note that Na$^+$-1 (named Na$^+$-mark in the manuscript) are present in Fig. 5d.

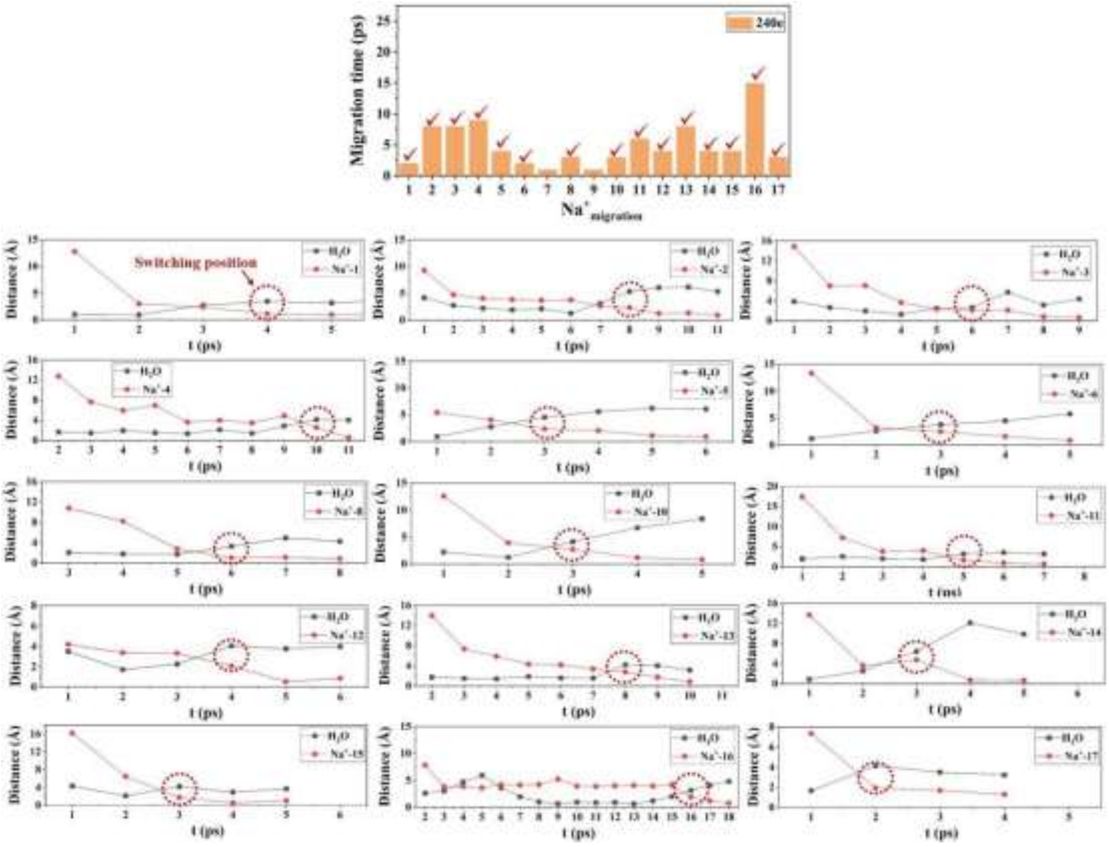

Figure S7 In the case of 240e, all surface-arriving Na ions that have switched positions with water molecules were counted. This figure shows the distance variation between surface-arriving Na ions/“blocking” water and H-COM over time.

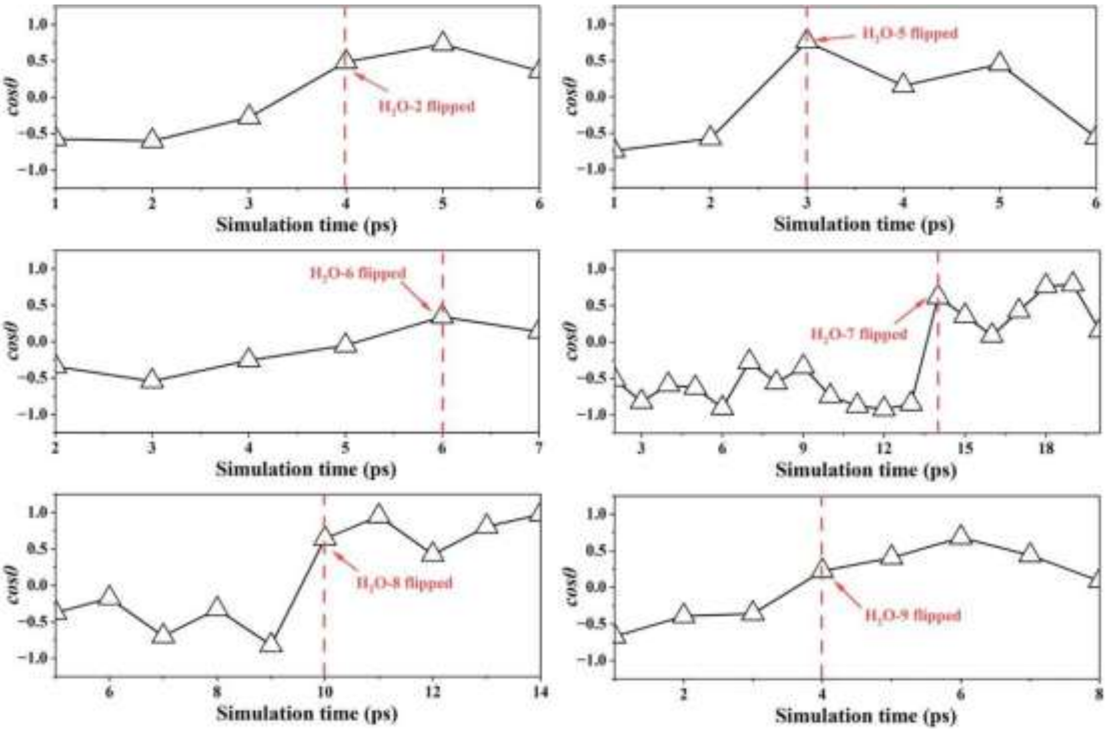

Figure S8 In the case of 200e, the orientation of the water molecule as a function of simulation time. θ is the angle between the dipole moment of the water molecule and the y-axis of the simulation box.

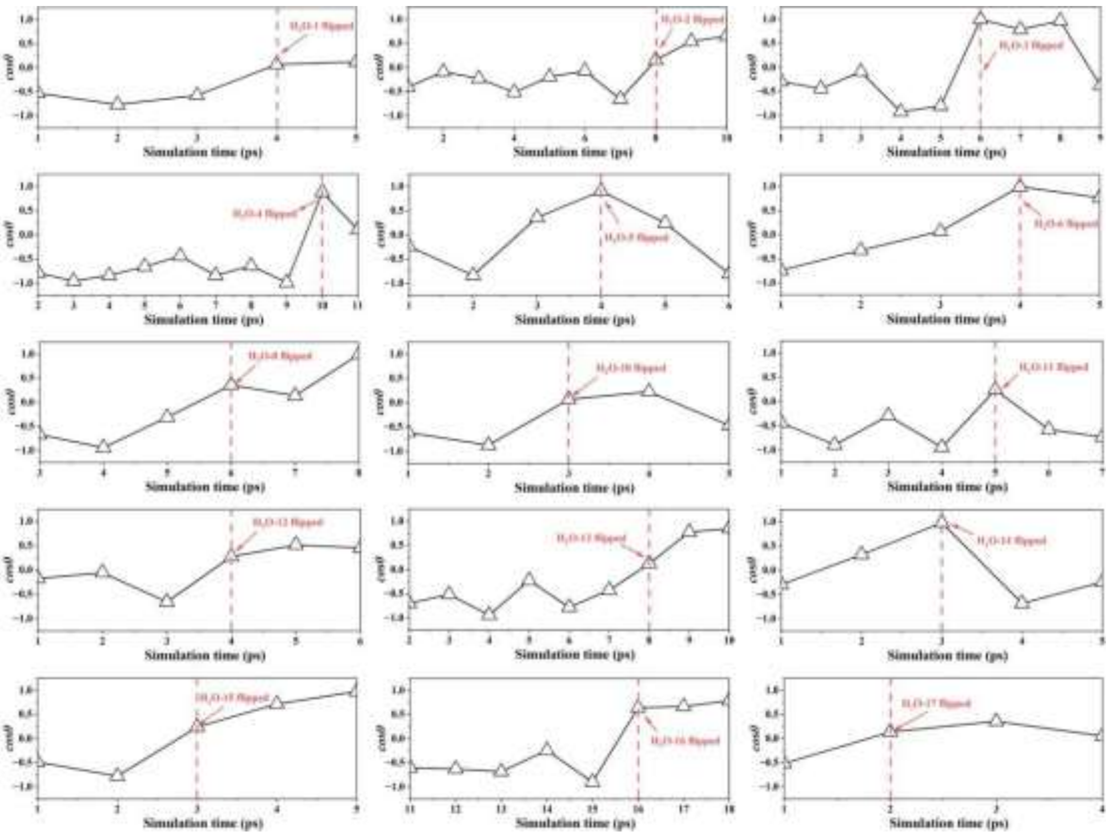

Figure S9 In the case of 240e, the orientation of the water molecule as a function of simulation time. θ is the angle between the dipole moment of the water molecule and the y-axis of the simulation box.