Supplementary Materials for

Tuning Hydrogen Bond Network Connectivity in the Electric Double Layer with Cations

Bo Tang[a], Yeguang Fang[b], Shuang Zhu[a], Qi Bai[a], Xiaojiao Li[a], Laiyang Wei[a], Zhenyu Li[c,] * and Chongqin Zhu[a,] *

[a]Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, China. E-mail: cqzhu@bnu.edu.cn
[b]Laboratory of Theoretical and Computational Nanoscience, CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China
[c]Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui230026, P. R. China. E-mail: zyli@ustc.edu.cn

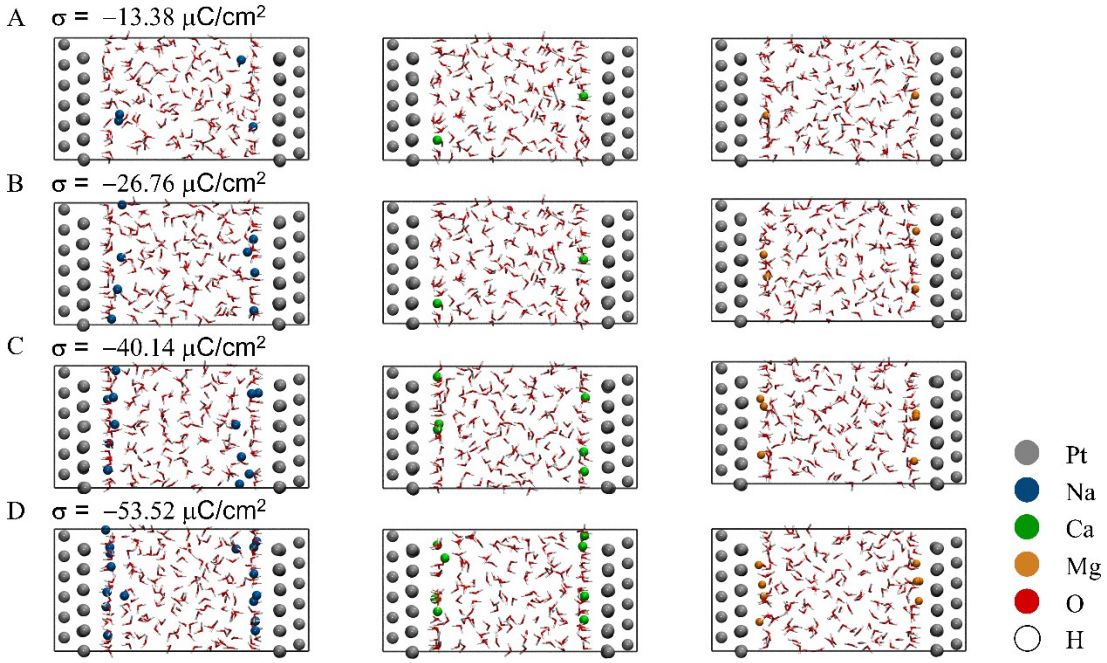

Fig. S1. AIMD models of Pt(111)/water interfaces in the presence of different counter cations. (A) σ = -13.38 μC/cm^2, (B) σ = -26.76 μC/cm^2, (C) σ = -40.14 μC/cm^2, (D) σ = -53.52 μC/cm^2. The Pt, Na, Ca, Mg, O and H atoms are colored by silver, blue, green, orange, red and white, respectively.

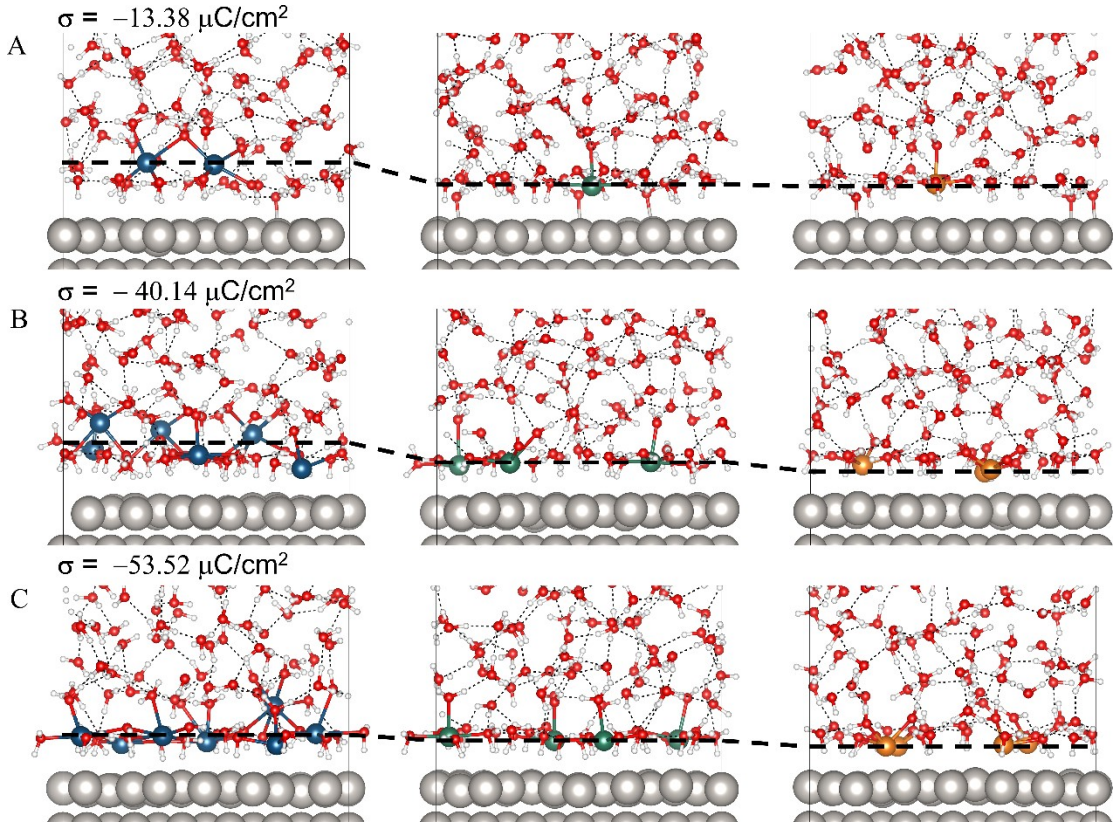

Fig. S2. Representative snapshots of the EDL structure at Pt(111)/water interfaces in the Na^{+}, Ca^{2+} and Mg^{2+}systems. (A) σ = -13.38, (B) -40.14 and (C) -53.52 μC/cm^2. The CIPs for all systems are presented by black dashed lines.

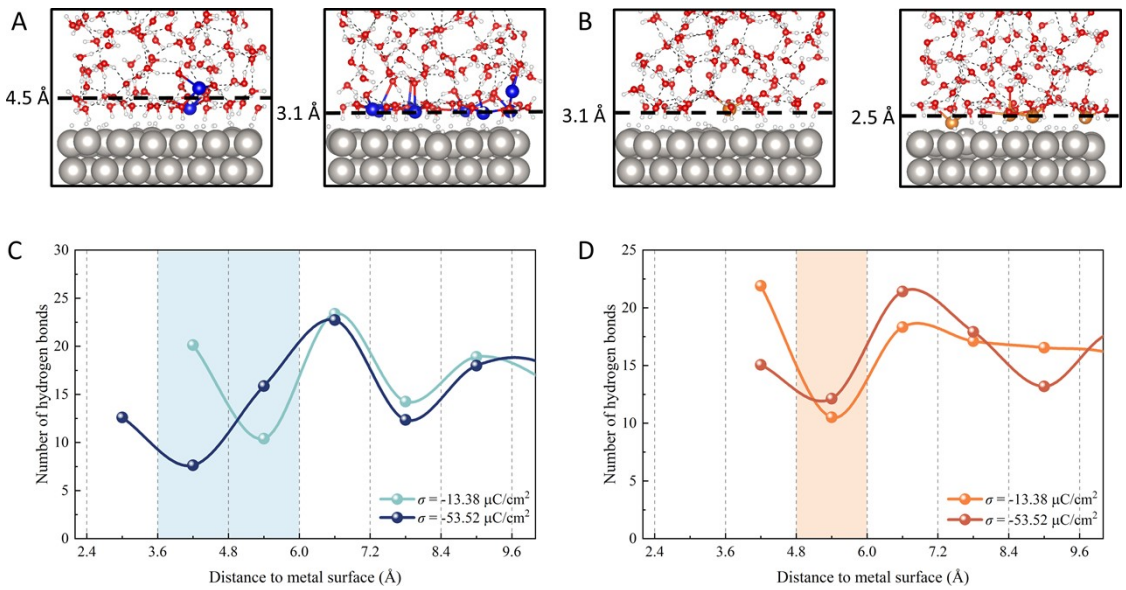

Figure S3. Representative snapshots of EDL structures at Pt(111)-H_{ad}/water interfaces (covered with 2/3 monolayer H_{ad}) for (A) Na^+ and (B) Mg^{2+} systems at σ = -13.38 μC/cm^2 and σ = -53.52 μC/cm^2. The red, white, silver, blue and orange spheres represent O, H, Pt, Na and Mg elements, respectively. Statistic distributions of the number of H-bonds along the surface normal direction in the (C) Na^+ and (D) Mg^{2+} systems at σ = -13.38 μC/cm^2 and σ = -53.52 μC/cm^2. The CIPs for all systems are presented by black dashed lines.

As shown in Figure S1, models for three systems (Na^+, Ca^{2+}, Mg^{2+}) were constructed at different charge densities by varying the number of cations. Using the developed computational standard hydrogen electrode (cSHE),[1] the electrode potential *U* at Pt/water interfaces with respect to the SHE can be calculated with

$$e_0U = -E_F^{(i)} - e_0\phi_{wat}^{(i)} + \Delta_{dp}A_{H_3O^+}^{(w)} - \mu_{H^+}^{g,\circ} - \Delta E_{zp}$$

where e_0 is the unit charge, $E_F^{(i)}$ and $\phi_{wat}^{(i)}$ are the Fermi energy and the electrostatic potential of the bulk water in the interface model, respectively. $\Delta_{dp}A_{H_3O^+}^{(w)}$ is the deprotonation free energy of $H_3O^+(aq)$ calculated in a pure water model with a recommended value of 15.35 eV. $\mu_{H^+}^{g,\circ}$ and ΔE_{zp} are the standard chemical potential of gas phase proton and a correction for the zero-point energy of O-H bond in $H_3O^+(aq)$, respectively. These two terms are known constants, 15.81 eV and 0.35 eV, respectively. By averaging over *ab initio* molecular dynamics (AIMD) trajectories of the interface models, one can easily obtain $E_F^{(i)}$ and $\phi_{wat}^{(i)}$. Figure S2 shows the time accumulative averages of $E_F^{(i)}$ and $\phi_{wat}^{(i)}$ for the three systems, both of which are averaged over configurations taken every 20 MD steps along the AIMD trajectories to check their convergence. It can be seen that both $E_F^{(i)}$ and $\phi_{wat}^{(i)}$ converge well within an uncertainty of 0.1 eV after ~10 ps AIMD runs.

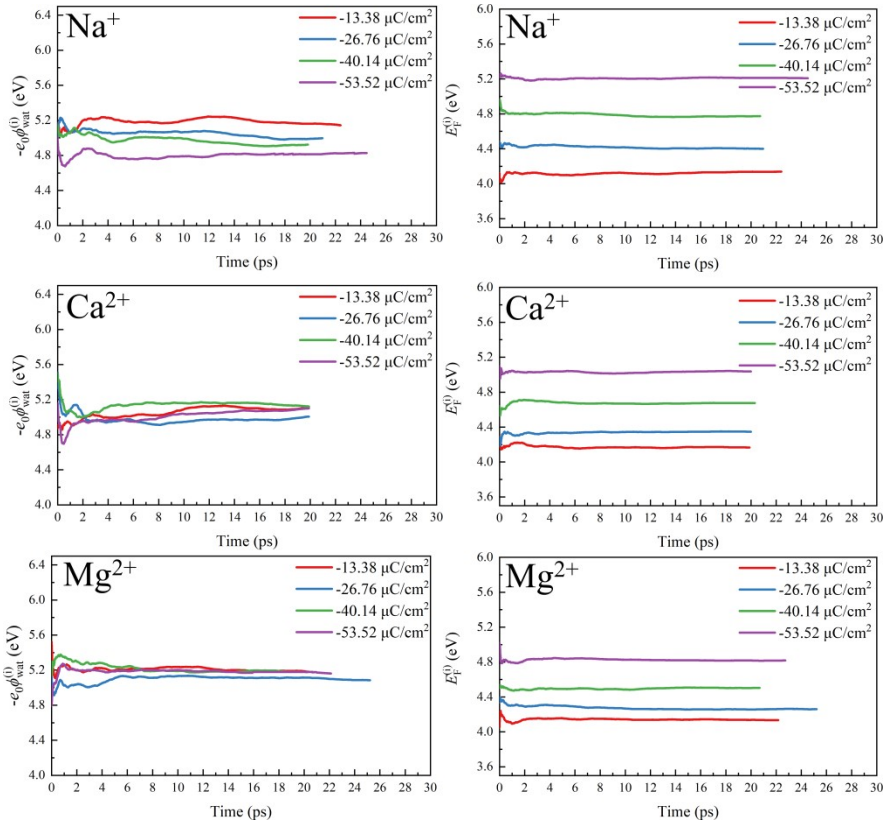

Fig. S4. Calculated $E_F^{(i)}$ and $-e_0\phi_{wat}^{(i)}$ for the three systems. Time-accumulated averages of Fermi energies ($E_F^{(i)}$) and electrostatic potential energies of bulk water ($-e_0\phi_{wat}^{(i)}$) in AIMD simulations of Na^+, Ca^{2+}, and Mg^{2+} systems at various surface charge densities.

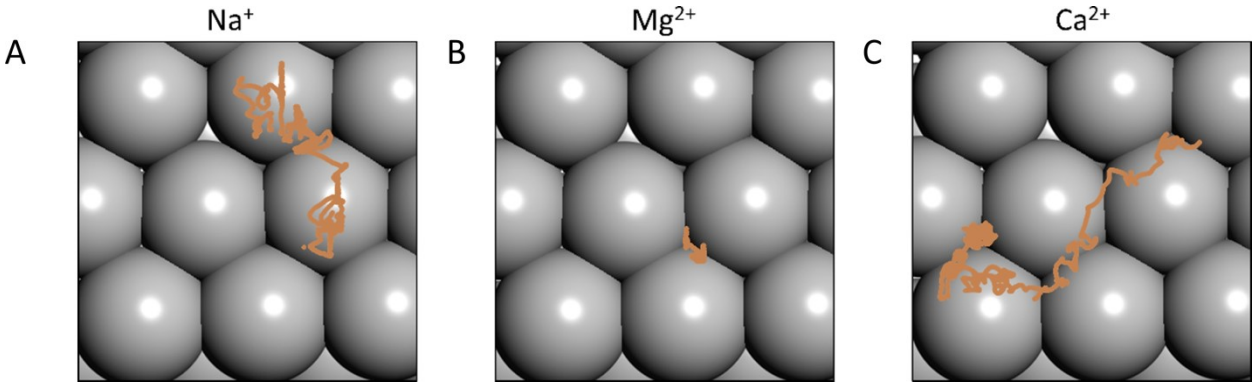

Figure S5. A ~10 ps trajectory of a (A) Na^+, (B) Mg^{2+} or (C) Ca^{2+} on the Pt(111) surface at σ = -53.52 μC/cm^2.

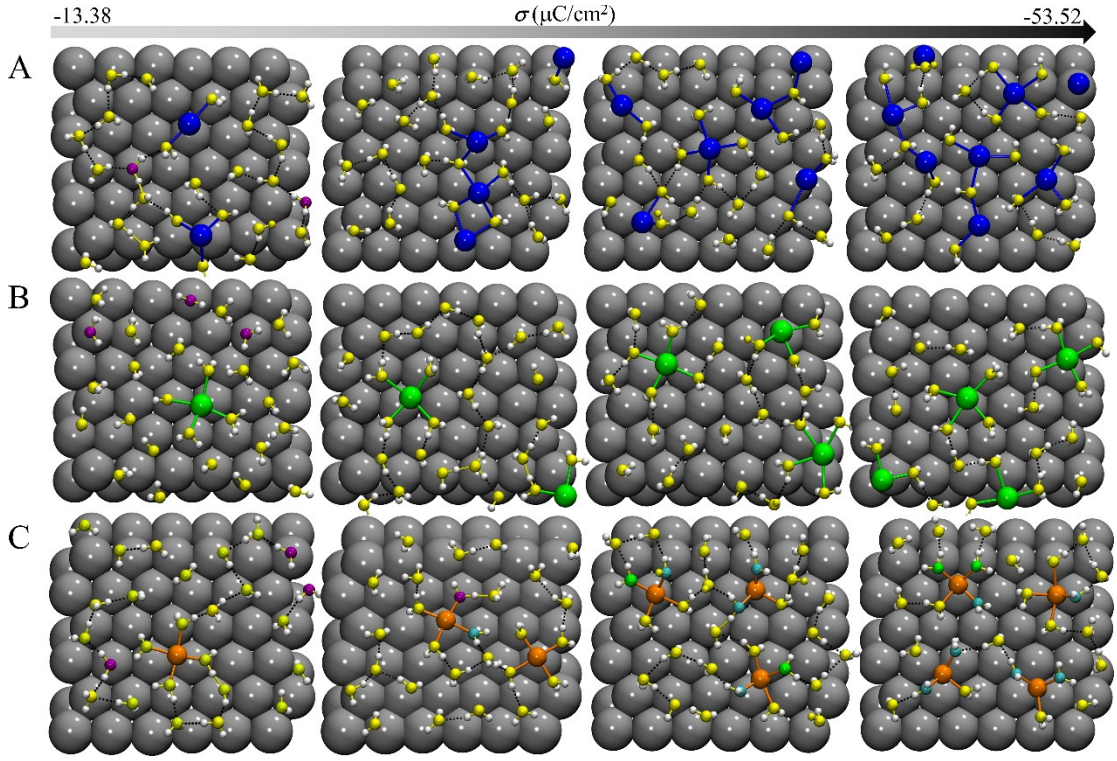

Fig. S6. Top view of representative AIMD snapshots of local structures of the (A) Na^{+}, (B) Ca^{2+}, and (C) Mg^{2+} systems.

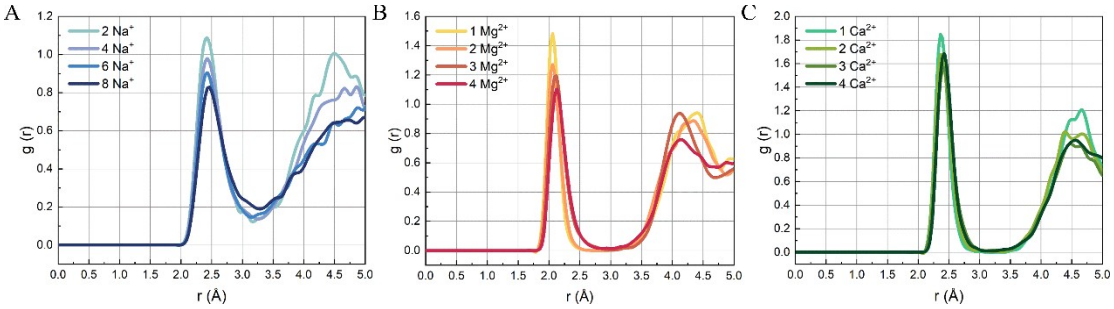

Fig. S7. Radial distribution functions for (A) Na^{+}-O_w, (B) Mg^{2+}-O_w, and (C) Ca^{2+}-O_w at the Pt-water interface for different surface charge densities.

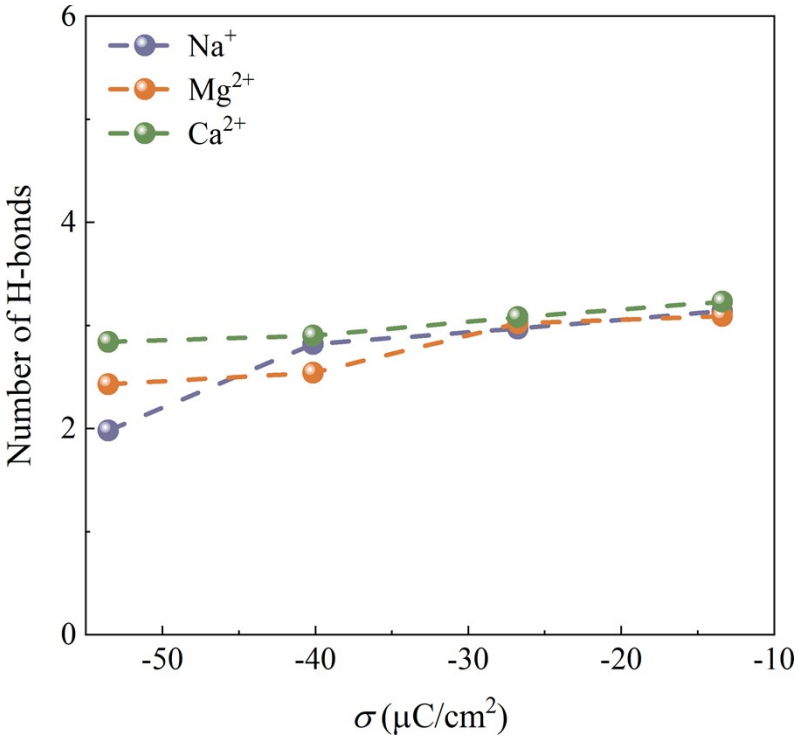

Fig. S8. The number of Hydrogen bonds per water molecule in the H-bond gap zone as a function of σ in the three systems.

REFERENCE

1. J. Le, M. Iannuzzi, A. Cuesta, J. Cheng, Determining potentials of zero charge of metal electrodes versus the standard hydrogen electrode from density-functional-theory-based molecular dynamics. *Phys. Rev. Lett.* **119**, 016801 (2017).