

Supporting Information

Electronic Polarization Effect of the Water Environment in Charge-Separated Donor-Acceptor Systems: An Effective Fragment Potential Model Study

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S1. Classification of the absolute value of POL energy

In the 7 Å and 13 Å models, we discussed on how the POL energies were generated. One possibility is that a little number of polarizability points produces dominant POL energy. Another possibility is that numerous polarizability points with tiny POL energy produce dominant POL energy. To figure out the origin, the polarizability points were classified with respect to the absolute values of the POL energy as shown in Figure S1. The red and blue lines denote cumulative polarization energy and cumulative number of polarizability points, respectively. Both values were accumulated from 0.000 eV to 0.005 eV.

In the 7 Å and 13 Å models, the energy class was set to (i) 0.000 ~ 0.005 eV, (ii) 0.005 ~ 0.010 eV, (iii) 0.010 ~ 0.022 eV, and (iv) 0.022 eV ~, because the variation of the cumulative polarization energies changes at around 0.005 eV, 0.010 eV, and 0.022 eV.

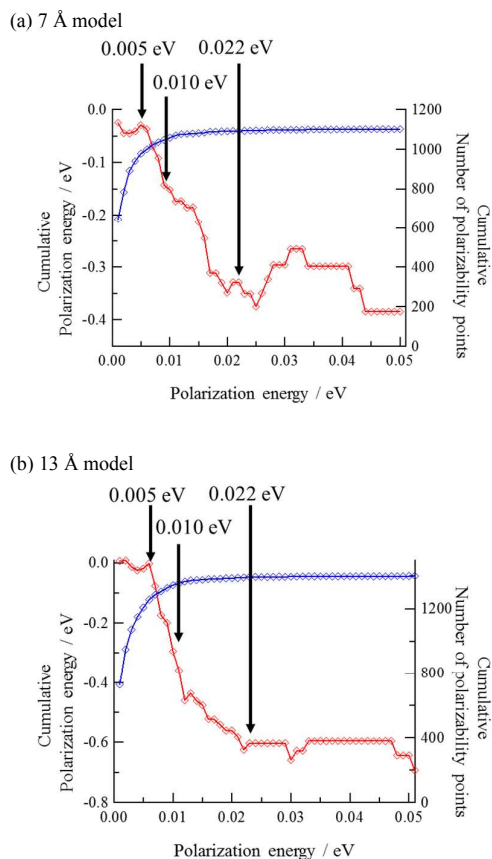


Figure S1. Cumulative polarization energy and number of polarizability points with respect to the absolute value of polarization energy. The results of (a) 7 Å model and (b)

13 Å model were shown.

S2. Molecular orbitals

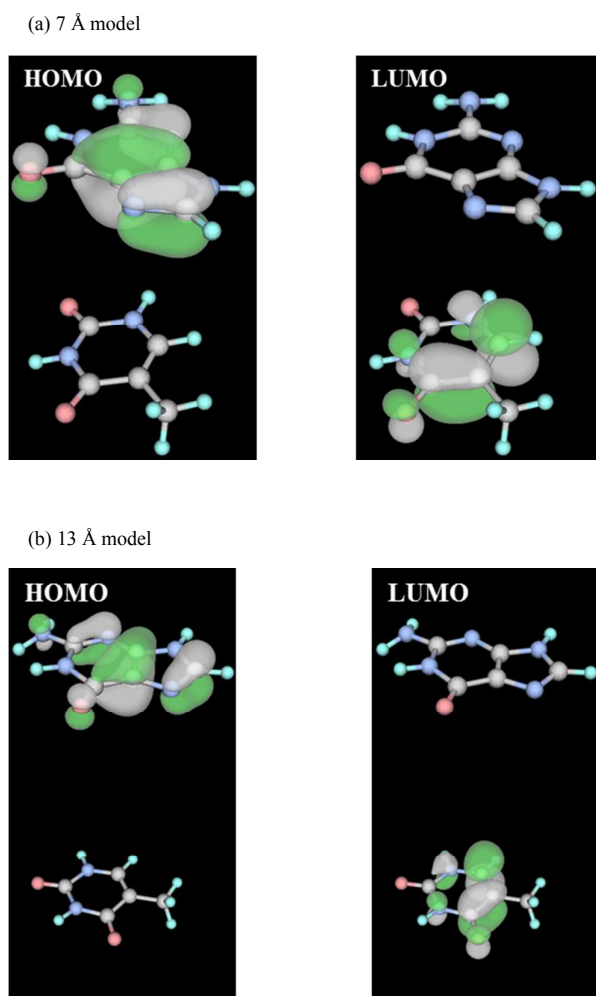


Figure S2. HOMO and LUMO of (a) 7 Å model and (b) 13 Å model.

S3. Hydration structures in the snapshots

In a previous study, Choi, Sugita, and co-workers performed EFP calculations. They analyzed the interionic hydration structure of $\text{Na}^+\text{-Cl}^-$ in aqueous solution and found ring and bridge structures.¹ The snapshots in the present analysis also involved so-called “full-bridge” structure as shown below. However, the snapshots were taken from molecular dynamics trajectory with a classical non-polarizable force field. Therefore, the electric field is not essential to form the bridged hydration structure.

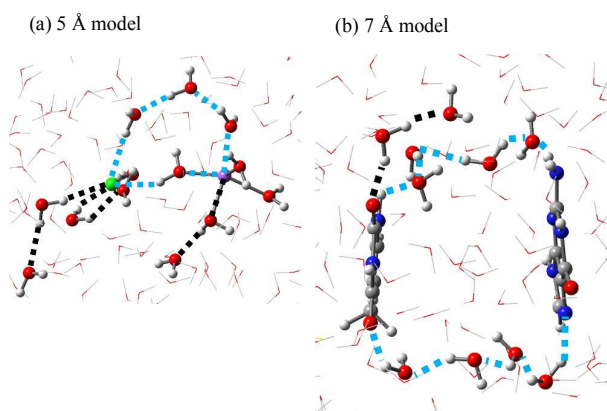


Figure S3. “Bridged” hydration structures in (a) 5 Å $\text{Na}^+ \text{Cl}^-$ model and (b) 7 Å guanine-thymine model. The hydrogen bonds along hydrogen bond networks are shown by dotted blue lines.

Reference

1. Ghosh, M. K.; Re, S.; Feig, M.; Sugita, Y.; Choi, C. H., Interionic hydration structures of NaCl in aqueous solution: a combined study of quantum mechanical cluster calculations and QM/EFP-MD simulations. *J. Phys. Chem. B* **2013**, *117*, 289-95.