Supporting Information

Toward High Permeability, Selectivity and Controllability of Water Desalination with FePc Nanopores

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1. The initial and final configurations (t = 0, 250 ns) of sysD1

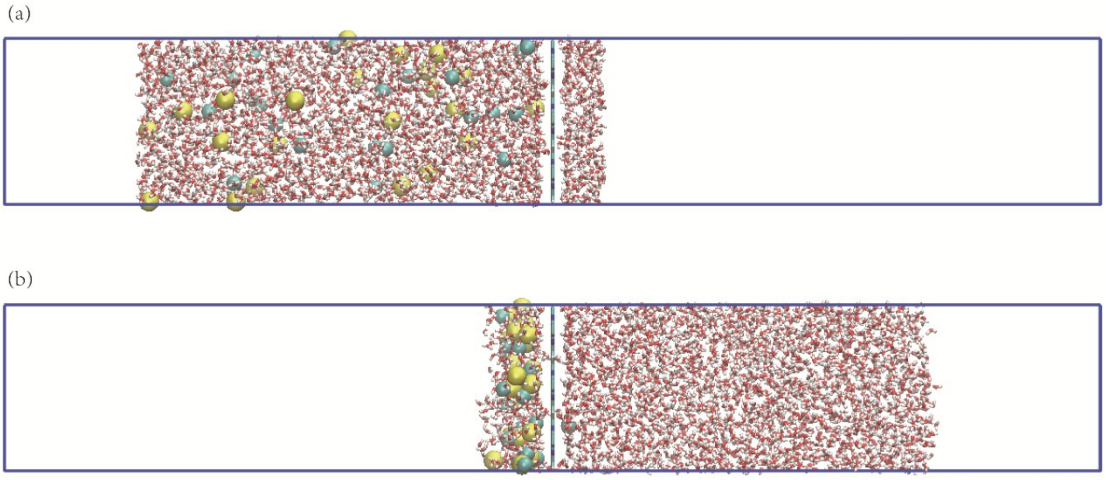


Figure S1. Side view of the initial and final configurations of sysD1 (a, t = 0 ns; b, t = 70 ns). The boundary of simulation periodic box is depicted as the blue rectangle. The FePc membrane is placed in the central plane (z = 0) of the simulation periodic box. The Na^+ and Cl^- ions are depicted as yellow and cyan spheres.

2. The calculation of partial charge distribution of FePc membrane

We utilize density function theory (DFT) method to optimize the geometry structures and calculate the partial charge distributions of FePc in various protonation states. The solvent effect is considered using the continuum model COSMO with the dielectric constant of water $\epsilon = 78.54$[1] in Dmol3 package. Spin-unrestricted computations are employed through an all-electron method within a local density approximation with Perdew-Wang correlation (PWC) for the exchange correlation term. A double numerical-polarized basis set that includes all occupied atomic orbitals with a second set of valence atomic orbitals plus polarized d-valence orbitals is chosen and the real-space global orbital cutoff radius is set as high as 4.8 Å. The k-points samplings are 3×3×1 in the Brillouin zone. The interlayer distance is set to be 20 Å to avoid the artificial interlayer interactions. Fully relaxed geometries are obtained by optimizing all atomic positions until the energy, maximum force, maximum displacement are less than 2×10^{-5} Ha, 0.002 Ha/Å and 0.005 Å, respectively. The aqueous phase results of Mulliken charge are implemented to the CHARMM force field.[2] The charge distributions of sysG0, sysG1, sysG2p, sysG2o, sysG3 and sysG4 are shown in figure S1 separately.

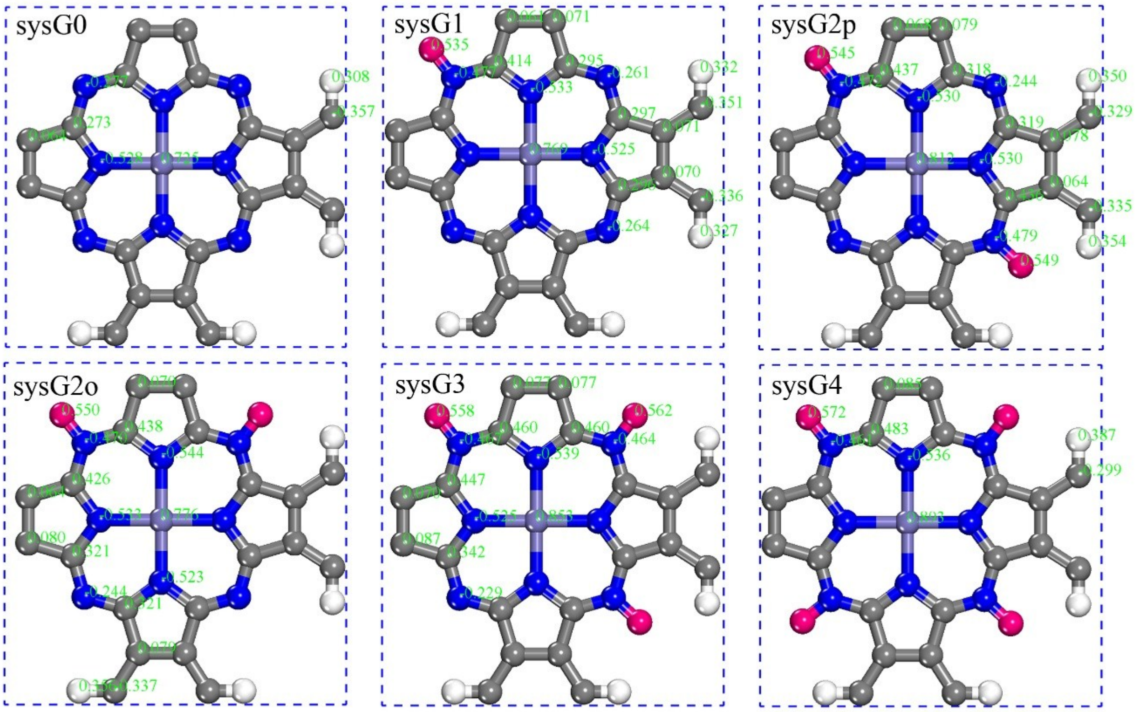


Figure S2. The Mulliken partial charge distribution in aqueous phase results for sysG0, sysG1, sysG2p, sysG2o, sysG3 and sysG4 respectively.

3. The electrostatic potential distribution of FePc membrane in sysD

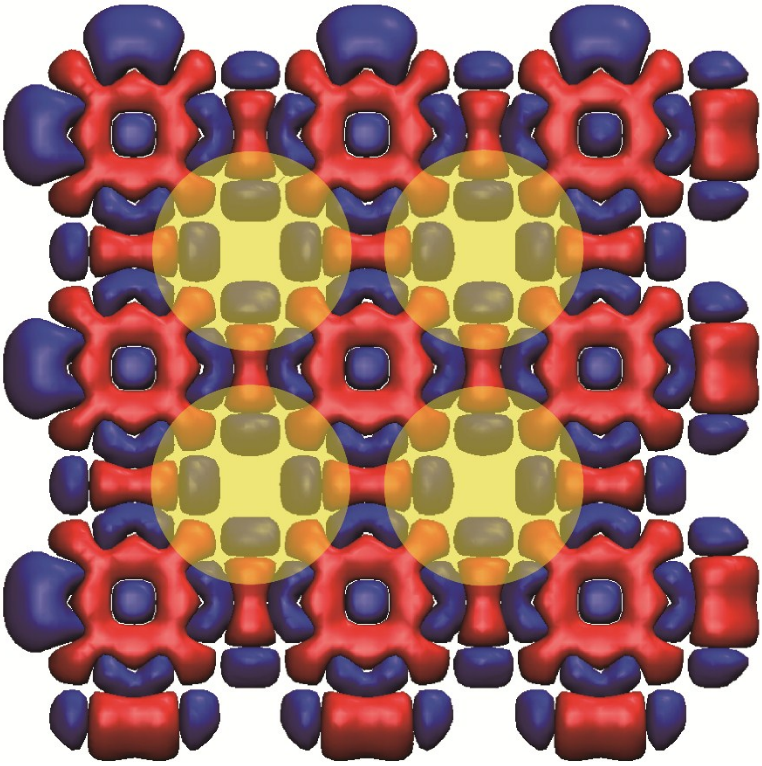


Figure S3. The electrostatic potential distribution of FePc membrane in sysD. The positive and negative electrostatic potentials are depicted in blue and red respectively. The yellow circles highlight the FePc nanopores.

4. The residence time of trapped Cl^- ion in sysD

Once the Cl^- ions get into FePc pore, the ions are trapped within nanopore by the attractive interaction with positively charged nanopore. Hence, we calculate the residence time distribution of the trapped Cl^- ion within nanopore based on the trajectory of sysD. In all cases, the residence time is larger than 0.1 ns, and the average residence time is 0.5 ns.

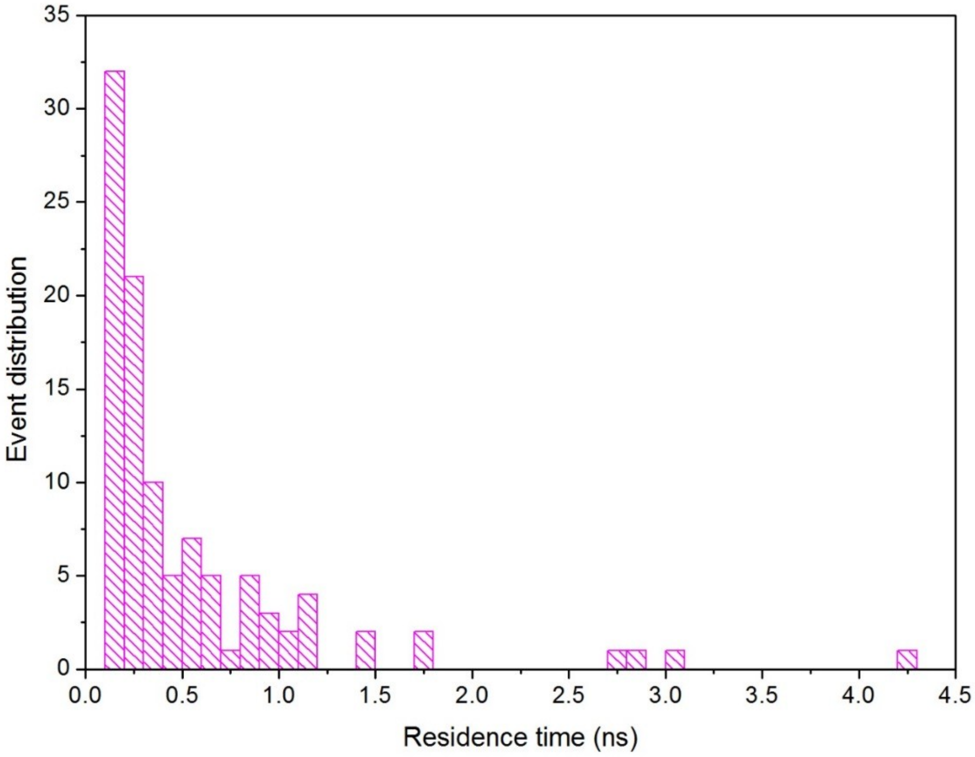


Figure S4. The residence time distribution for trapped Cl^- ions within nanopore of sysD.

5. Water transportation through charged graphene nanopore

We design a model system of charged nanopore based on graphene. The diameter of graphene nanopore is 8.46 Å, similar to FePc nanopore. There is a charge distribution around nanopore where the partial charge of the atoms are $+q$ (blue), $-q$ (red) and $-q/2$ (pink), separately. In addition, the atomic partial charges are further adjusted with $q = 0.3, 0.4, 0.6, 0.8$ e.

The graphene sheet also divides the water slab into two reservoirs, i.e. a saline reservoir and a pure water reservoir. The size of reservoirs and ion concentration are similar to sysD1. And the transportation of both water and ions under hydrostatic pressure are calculated based on 100-ns trajectory of each system. When $q = 0.3\ e$, both Na^+ and Cl^- ions can permeate through graphene nanopore. There are 4 ions (2 Na^+ ions and 2 Cl^- ions) passing through the nanopore during the simulation. When the atomic partial charge further increase to $q = 0.4\ e$, the transportation of both cation and anions are effectively blocked. While the water molecules can still quickly transport through graphene nanopore. Similar desalination phenomena can be observed in the systems with even larger atomic partial charge, i.e. $q = 0.6$ and $0.8\ e$, which still permit fast water transportation.

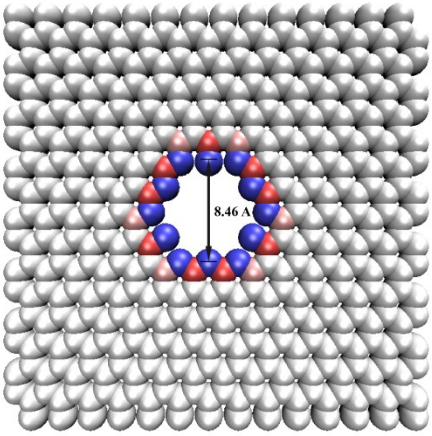


Figure S5. Graphene nanopore with the diameter of 8.46 Å, the atoms with the partial charge of +*q*, –*q* and –*q*/2 are colored in blue, red and pink respectively.

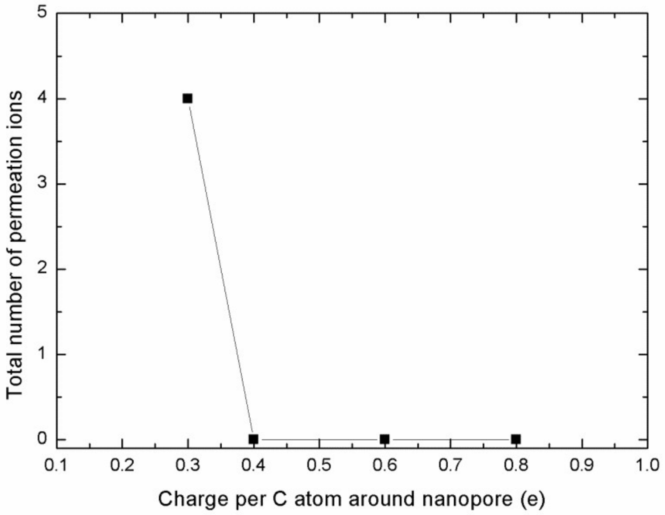
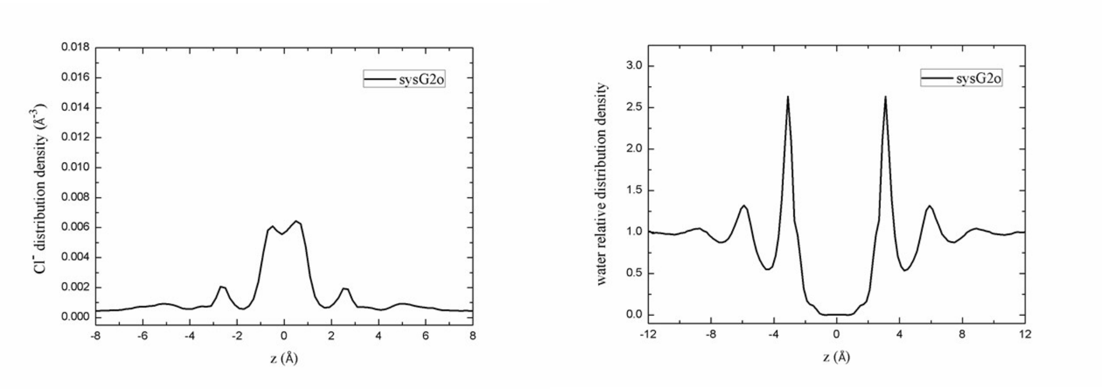


Figure S6. The number of ion permeation through charged graphene nanopore with $q = 0.3$, 0.4, 0.6, 0.8 *e*.

6. The density distributions of Cl^- ion and water molecule in sysG2o

The Cl^- density distribution of sysG2o is different from that of sysG2p (shown in figure 5 A). The ions tend to distribute in the region of -1.7 Å $< z < 1.7$ Å. As for the distribution of water molecules, there are even less water molecules in the region of -2 Å $< z < 2$ Å in sysG2o.

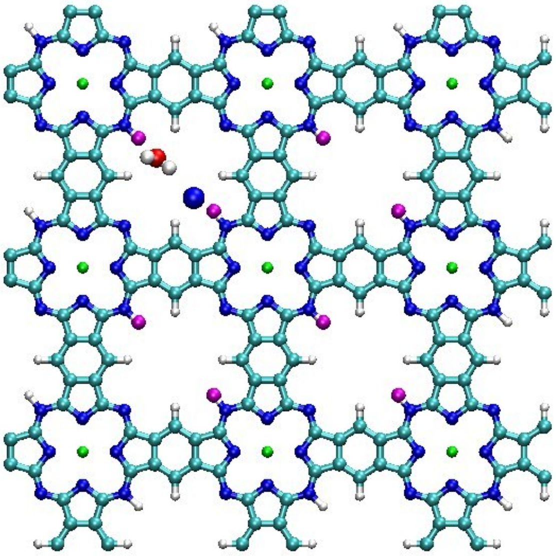


(A) (B)

Figure S7. The density distribution of Cl$^-$ ion (A) and water molecule (B) in the cylinder region corresponding to FePc nanopore in sysG2o. The scales are set as the same as figure 5 (A) and (B) respectively.

7. Relative positions of water molecule and Cl$^-$ ion within nanopore in sysG2p

In general, water conductivity decreases as the degree of protonation increase, while we noticed there is a small bump in such relationship at sysG2p, i.e., the water conductivity is relatively larger than the sysG2o. We found the water and ion can form special patterns within nanopore where the ion does not locate at the central plane, it locates 2 Å below or above the central plane instead. Hence the FePc can accommodate both water and ion in such specific pattern and the blockage of trapped ion is less efficient in sysG2p.



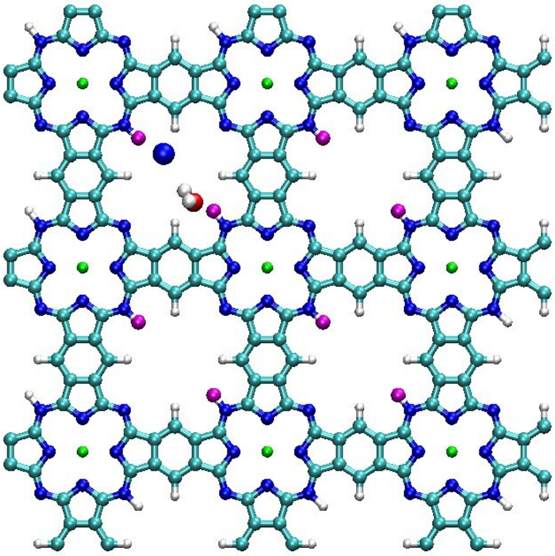


Figure S8. The relative positions of water molecule and Cl^- ion within nanopore of sysG2p.

(1) PAVELITES, J. J.; GAO, J.; BASH, P. A.; ALEXANDER D. MACKERELL, J. *Journal of Computational Chemistry* **1997**, *18*, 221.

(2) AUTENRIETH, F.; TAJKHORSHID, E.; BAUDRY, J.; LUTHEY-SCHULTEN, Z. *Journal of Computational Chemistry* **2004**, *25*, 1613.