

Supplementary Information

Two-dimensional Covalent Triazine Framework as an Ultrathin-film Nanoporous Membrane for Desalination

Li-Chiang Lin^{1,2,†}, Jongwon Choi^{2,†}, Jeffrey C. Grossman^{2,*}

¹ *Department of Process and Energy, Delft University of Technology, 2628
CB Delft, the Netherlands*

² *Department of Materials Science and Engineering, Massachusetts Institute
of Technology, Cambridge, MA 02139, USA*

† These authors contributed equally to this work

*Email: jcg@mit.edu

Computational details

Desalination simulations: Classical molecular dynamics (MD) simulation techniques implemented within the LAMMPS package are used to investigate the desalination performance of CTF membranes. In this work, we assume that CTF membranes are rigid. The simulation box consists of a CTF membrane, a piston, and salt water. The dimension of the simulation box along the X-Y plane is approximately 2.9 by 2.6 nm. The salt water in the feed side has 16 Na⁺ and 16 Cl⁻ ions solvated by 900 water molecules, while 200 water molecules are initially placed in the permeate side. Periodic boundary conditions are applied on the X, Y, and Z-directions. To avoid the interaction between the feed side and the permeate side, the dimension of the simulation box along the Z-direction is set to be 12 nm, resulting in sufficiently large vacuum region in between. As mentioned in the manuscript, to describe intermolecular interactions (i.e., salt water – salt water and salt water – membrane), a Lennard-Jones (L-J) plus Columbic potential is used. We use the SPC/E¹ model for water molecules and the corresponding parameters proposed by Joung et al. for salt ions.² L-J parameters from the Dreiding force field³ are adopted for membrane atoms. For all pair-wise L-J terms, the Lorentz-Berthelot mixing rule is applied. The partial atomic charges of membrane atoms are derived using the REPEAT algorithm⁴ based on an electrostatic potential calculated from density functional theory. The applied pressure on the piston is approximately 53 MPa, substantially higher than the typical value used in a RO plant, in order to obtain better statistics within the short MD time scales (i.e., 10-20 ns).^{5,6} The simulations are performed in the NVT ensemble at 300K using a Nosé-Hoover thermostat with a damping factor of 100 time steps, i.e., 100 fs. The adopted time step, 1 fs, is found to be sufficiently small to ensure energy conservation. For each membrane, 10 independent simulations are carried out to obtain statistically representative desalination performance (i.e., the water permeability and salt rejection of each CTF membrane are calculated from averaging results of 10 independent simulations). Moreover, to ensure our simulated predictions are not biased by a finite size effect, we have also carried out 5 independent desalination simulations for the CTF-1 membrane with an enlarged simulation dimension along the X-Y plane (i.e., approximately 5.9 by 5.1 nm with a total of 3600 and 800 water molecules in the feed side and the

permeate side, respectively. A total of 64 Na⁺ and 64 Cl⁻ are placed in the feed side). The desalination performance of the CTF-1 membrane predicted from the regular, chosen simulation box and the enlarged one is found to be in excellent agreement as shown in Table S1.

Table S1 The Desalination performance of the CTF-1 membrane predicted using different simulation dimensions. The water permeability and salt rejection are calculated from averaging results of 10 and 5 independent calculations while using the regular and enlarged simulation box, respectively. The salt rejection in this study is defined as the percentage of salt ions remaining in the feed side when half of the feed water has permeated through the membrane at an applied pressure of approximately 53 MPa.

Structure	Water flux (L cm ⁻² day ⁻¹ MPa ⁻¹)	Salt rejection (%)
CTF-1 (3.0 by 2.5 nm)	64.2 ± 5.1	91 ± 3
CTF-1 (6.0 by 5.0 nm)	64.0 ± 2.9	90 ± 1

Deformation simulations: We use MD simulations implemented in the LAMMPS package to perform biaxial (i.e., for fracture stress and Young’s modulus) and uniaxial (i.e., for Poisson’s ratio) strain tests. The simulation box has a dimension of approximately 10 by 10 nm along the X-Y plane. Periodic boundary conditions are applied along the X and Y directions. A dimension of 0.34 nm (i.e., twice the van der Waals radius of carbon atoms, the assumed thickness of a single-sheet CTF layer) is used along the non-periodic Z-direction. Reactive force fields (ReaxFF) are adopted with parameters from two different sets (i.e., Budzien et al. and Strachan et al.).^{7,8} A small time step of 0.1 fs is used. Biaxial strain tests are performed in the NVT ensemble using a Nosé-Hoover thermostat at 300K with a damping factor of 100 time steps, whereas a Nosé-Hoover barostat at zero pressure is additionally applied on the non-enforced-strained boundary in the uniaxial strain tests (i.e., in the NpT ensemble) with a damping factor of 500 time steps. During the strain tests, a strain increment every 5000 steps at a rate of 5x10⁻⁷ fs⁻¹ is

enforced. The stress at a given strain value is obtained by averaging the stress value in the last 2500 steps before the next strain increment. A single calculation is performed for each test.

Structural feature calculations: To determine the pore feature of all structures studied in this work, we first project the atomic positions of these structures onto the X-Y plane. Grid points with a distance interval of 0.1 Å along each direction are created and overlapped with each structure. At each grid point, the distance to the nearest atom is computed and the value is assigned to the grid point. We note that the regions inside the van der Waals radius of each atom (i.e., 1.2 Å, 1.70 Å, 1.55 Å, and 1.75 Å for H, C, N, and Cl, respectively) are excluded. Pore features including pore area and pore radius (i.e., the largest free sphere radius) are then calculated based upon the assigned distance values of all grid points.

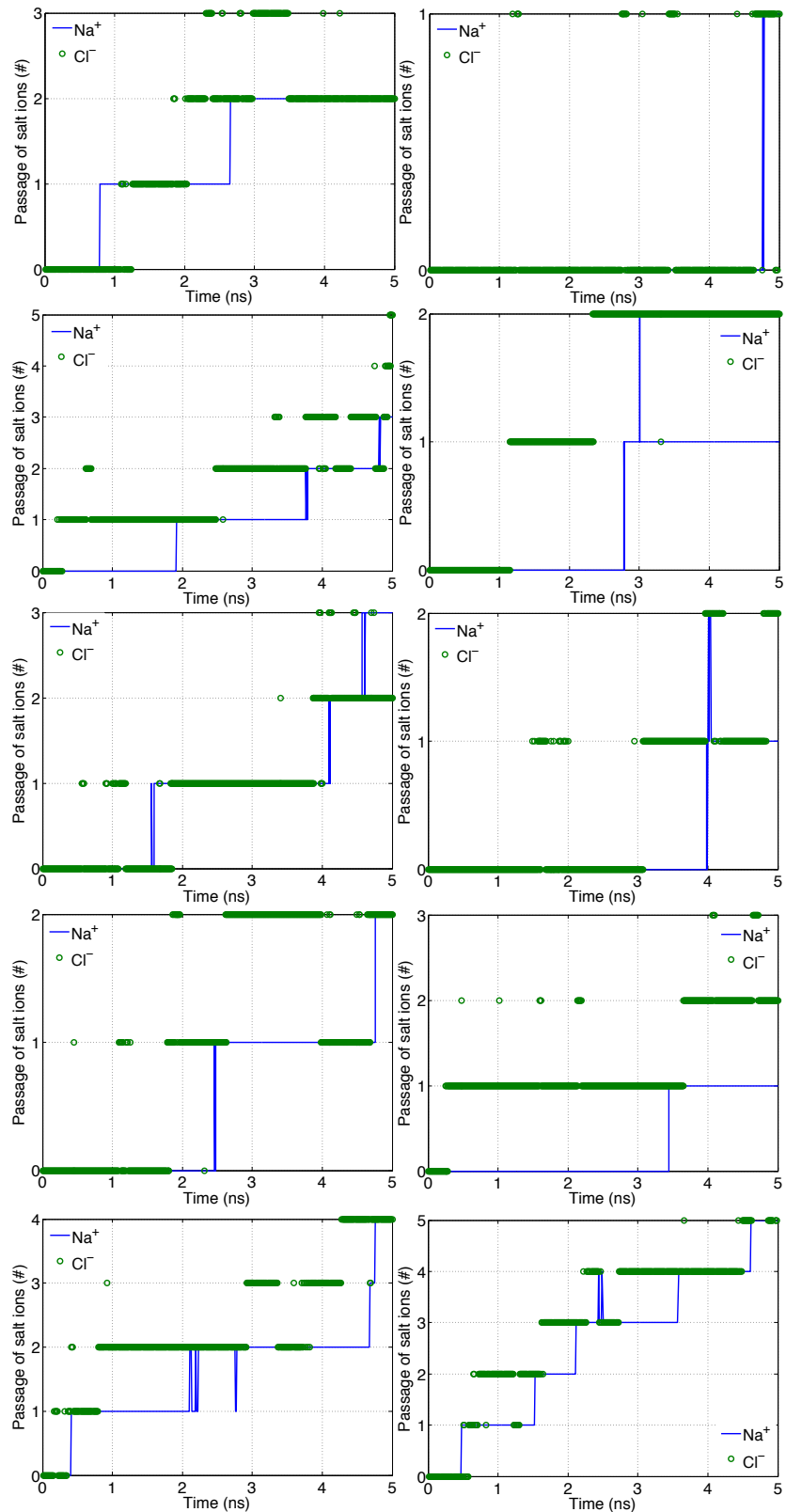


Figure S1 Salt ions permeated for the CTF-1 membrane. The number of salt ions passage as a function of simulation time for 10 different independent simulations.

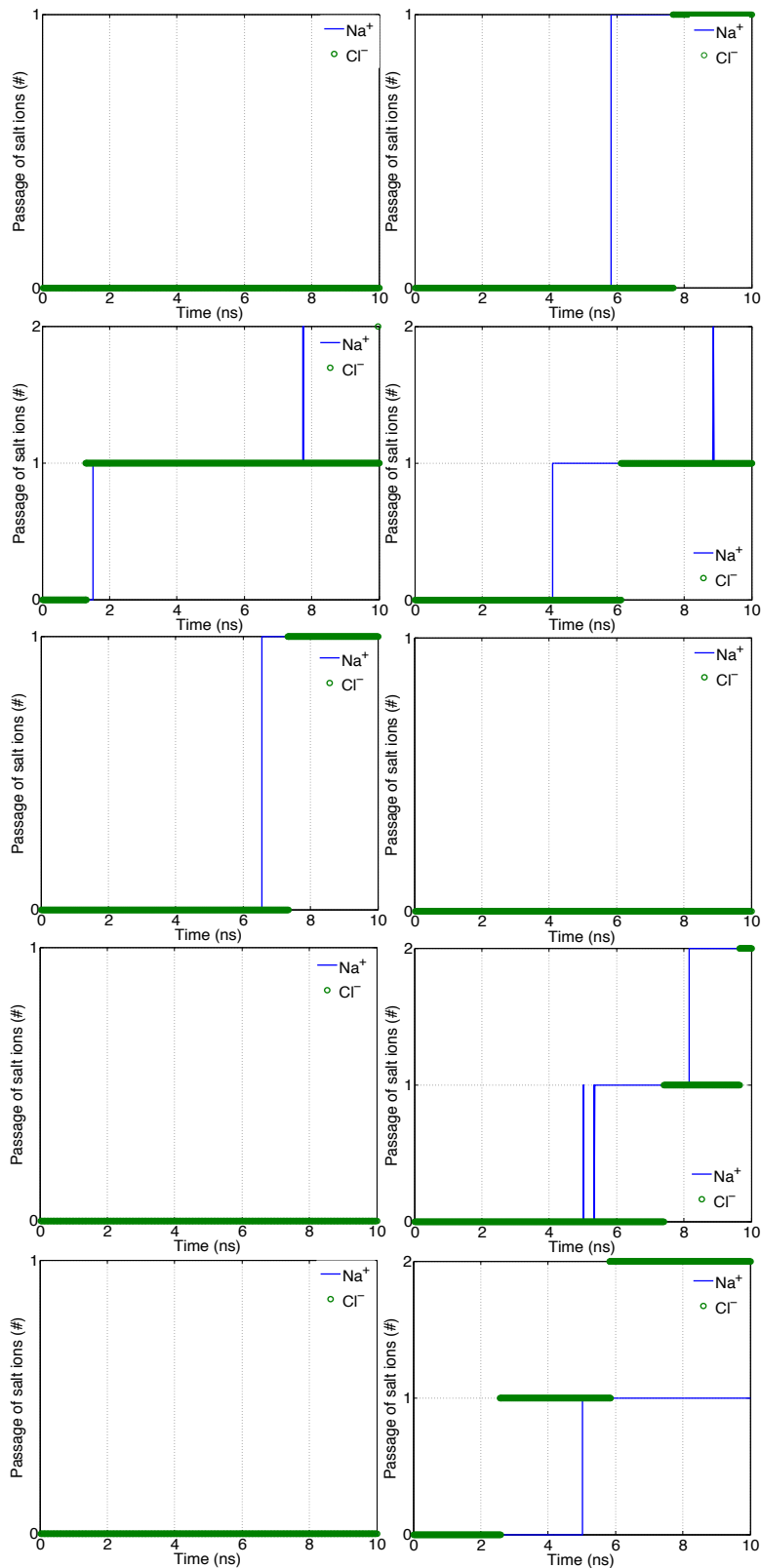


Figure S2 Salt ions permeated for the CTF-1-Cl membrane. The number of salt ions passage as a function of simulation time for 10 different independent simulations.

CTF-1 building unit

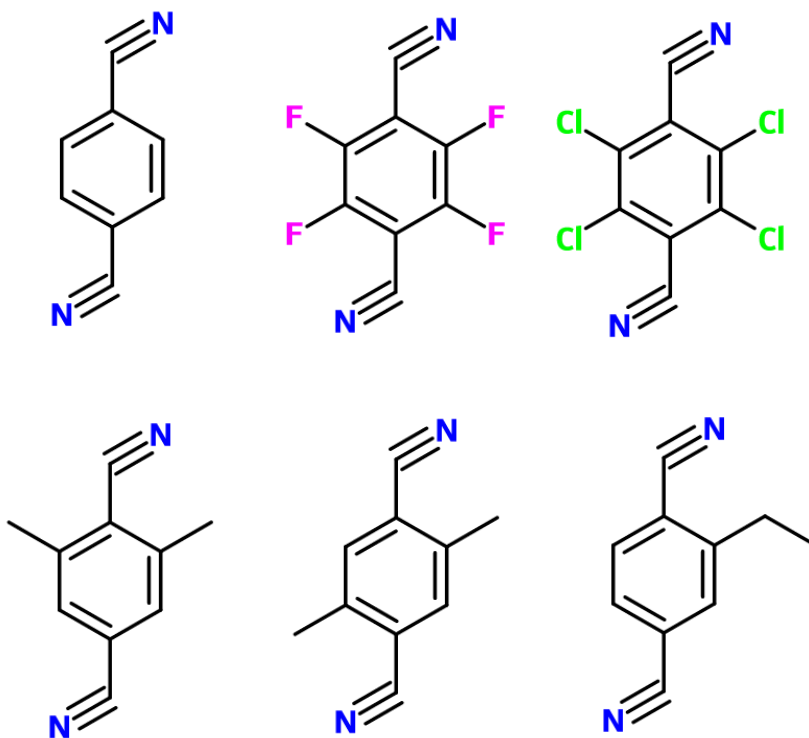


Figure S3 Commercially available building blocks. Several functionalized derivatives of the CTF-1 building block are shown in the figure. These building blocks have been synthesized and are already commercially available (from the eMolecules database⁹). It is expected that these building blocks could result in structures of smaller pore size compared to that of CTF-1. As shown in the manuscript, we have computationally demonstrated that enhanced desalination performance can be achieved by selecting building blocks to control over the pore structure and chemistry.

References

1. H. Berendsen, J. R. Grigera and T. P. Straatsma, *J. Phys. Chem.*, 1987, **91**, 6269.
2. I. Joung and T. Cheatham, *J. Phys. Chem. B*, 2008, **112**, 9020.
3. S. Mayo, B. Olafson and W. Goddard, *J. Phys. Chem.*, 1990, **94**, 8897.
4. C. Campañá, B. Mussard and T. K. Woo, *J. Chem. Theory Comput.*, 2009, **5**, 2866.
5. D. Cohen-Tanugi and J. C. Grossman, *Nano Lett.*, 2012, **12**, 3602.
6. D. Cohen-Tanugi and J. C. Grossman, *J. Chem. Phys.*, 2014, **141**, 074704.
7. J. Budzien, A. P. Thompson and S. V. Zybin, *J. Phys. Chem. B*, 2009, **113**, 13142.
8. A. Strachan, A. van Duin, D. Chakraborty, S. Dasgupta and W. A. Goddard, *Phys. Rev. Lett.*, 2003, **91**, 098301.
9. Website: <http://www.emolecules.com>.