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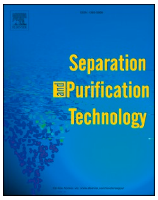

Effect of hydrophilicity on ion rejection of sub-nanometer pores

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ABSTRACT

Ion rejection by (sub)nanometer-sized pores enables membrane-based desalination. Narrowing the pore size is long considered as the primary choice to increase the ion rejection rate, which is unfortunately at much sacrifice of the water permeance. Using the uniform sub-nanometer pore channels in covalent organic frameworks (COFs) as the model system, we herein demonstrate that hydrophilicity of pore walls plays a significant role in determining ion rejections, and ion rejections can be significantly improved by enhancing hydrophilicity with less loss in water permeance. Via non-equilibrium molecular dynamics simulation, the augmented in-pore effect caused by significant pore-wall-involved hydration effect is discovered to dominate the ion rejections. Furthermore, the desalination mechanism of hydrophilic nanopores is proposed: strong hydrophilicity can make cations enter nanopores more easily than anions by compensation of ionic hydrations, but all ions are not able to transport inside nanopores due to the extreme in-pore effect; hence membranes consequently carry positive net charges after being saturated adsorption by ions and then in turn exclude cations by electrostatic repulsions. These findings and understandings on desalination mechanisms can also be applicable to other kinds of nanoporous materials and thus could provide guidelines for the experimental design of next-generation desalination membranes.

1. Introduction

Water scarcity has become an important challenge in modern society due to the rapid growth of the population and the significant acceleration of industrialization in the world [1]. Huge effort has been devoted to boost fresh water supplies from desalination and wastewater reuse [1,2]. Membrane-based techniques such as reverse osmosis and nanofiltration are considered as most promising methods for desalination and water treatment due to their low energy consumption, easy operation and environmental friendliness [3,4].

Conventional reverse osmosis or nanofiltration membranes are usually made from dense amorphous polymers such as polyamide or polyimide [4,5]. These polymers are composed with disordered “free volume” pores, which allows only water molecules to pass through membranes. However, these disordered pores make it hard to further improve water permeance due to the lack of well-defined channels. Covalent organic frameworks (COFs) [6,7], as an emerging crystalline polymeric networks, are expected to remarkably improve the water permeance of membranes because of their inherent properties of permanent porosity, uniform and well-defined pore aperture, as well as ordered channel structure [8]. In addition, their pore sizes can be tunable down to less than one nanometer, making them promising building blocks of membranes for desalination or ion separation [9,10]. Our previous work [11] has built up an equation to predict water permeances of COF membranes with sub-nanometer pores. In that work, we systemically discussed the effect of pore hydrophilicity on water permeance while its effect on ion rejection, which is another key parameter of a desalination membrane, remained untouched. In this work, we come to the next question: how is the effect of pore hydrophilicity on ion rejection? One may simply take it for granted that hydrophilicity does not show an effect on ion rejection as it is generally considered to be determined by pore size and surface charge. However, our simulations reported in this work demonstrates that pore hydrophilicity plays a vital role in influencing ion rejection when the pores are narrowed down to the sub-nanometer scale.

Actually, COF membranes have been experimentally applied for desalination [12,13]. Liu *et al.* recently reported a IISERP-COOH-COF1 membrane, which is experimentally prepared through post-synthetic modification of a two-dimensional (2D) hydroxyl-functionalized COF membrane, shows 90.6% rejection to $MgCl_2$ and 82.9% rejection to NaCl [13]. However, these rejection rates are still not comparable to the traditional polymeric membranes (>99.5%), and very few works on

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nanoporous membranes could exhibit such a superior ion rejection performance. Enhancing the selectivity is the focus of current studies on developing the next-generation desalination membranes [2], hence the strategies for improving ion rejections of state-of-the-art nanoporous membranes are emergent.

It is revealed from our previous work that ion rejection by nanopores can be enhanced from two main contributions: the pore-entrance sieving effect and the in-pore transport effect [14]. Therefore, seeking the methods to strength these two effects is essential for improving ion rejection. The pore-entrance sieving effect is commonly enhanced by narrowing the pore size, which would unfortunately sacrifice much permeability [15,16]. It is noteworthy that increasing the thickness of ultrathin membranes could also strengthen the pore-entrance effect while avoiding sacrificing pore size and thus water permeance, but this method requires membranes with atomic thickness and hydrophobic nature [17]. On the contrary, the in-pore effect is discovered to be determined by the polarity of pore wall [14]. Therefore, enhancing it could also promote the ion rejection performance without much reducing the pore size and is applicable to membranes with thicknesses from nanometer to micrometer scale. Accordingly, this method has a high possibility that ion rejections will be improved while water permeance won't decline much. In general, the polarity of nanopores is correlated with the hydrophilicities of pore-wall functional groups. The hydrophilic groups are reported to able to evidently influence the ionic hydrations and thus their transport behaviors [16,18,19]. Such influence might be attributed to the in-pore effect, but the relationship between pore hydrophilicity and ion rejection has not been systematically investigated yet.

Clarifying the effect of pore-wall hydrophilicity on ion rejection is instructive to the design of next-generation membranes for desalination. In this work, we perform non-equilibrium molecular dynamics simulations (NEMD) to gain insights into the underlying mechanisms by investigating the ion rejection performances in a series of COFs membranes. These COFs originate from a super-microporous phosphazene-based COF (MPCOF), which is synthesized from hexachlorocyclotriphosphazene (HECTP) and *p*-phenylenediamine (Pa) [20]. It possesses a good water stability and sub-nanometer pores that are close to the size of hydrated ions. Moreover, this parent COF is modified by 8 types of various functional groups to produce 8 types of modified MPCOF-R membranes, which have different hydrophilicities and thus are divided into two sets: weakly hydrophilic (WH) and strongly hydrophilic (SH). The rejections of all these membranes to NaCl and $MgCl_2$ are firstly tested. The pore-wall hydrophilicity is found to play a significant role in ion rejection while the SH membranes exhibit 100% rejections to all ions. Based on the molecular observations, the desalination mechanism of SH membranes is probed, from which the experimental observations in the literature can be easily explained. More importantly, the method proposed in this work is discovered to sacrifice less saline permeance than the method of narrowing pore size while dramatically improving the ion rejection performance.

2. Model

The CoRE COF database [21], which constructs and compiles disorder-free and solvent-free COFs structures from experimental studies, provided the atomic structure of MPCOF. According to the experimental studies [20], MPCOF was synthesized from two monomers, HECTP (knot) and Pa (linker), as shown in Fig. 1a. The monomer Pa is easy to be modified by various functional groups R, thus the resultant MPCOF-R could exhibit different degree of hydrophilicity. As demonstrated in Fig. 1b, 8 types of functional MPCOF-R were constructed from corresponding monomers.

The pressure-driven filtration method where the membrane is placed between a feed side and a permeated side is commonly employed to test the membrane performances in experiments. Due to the influence of the law of electroneutrality in its both sides, the transport of cations and anions is dependent on each other (*i.e.* once cation or anion is rejected, the other one is then also incidentally rejected). Therefore, it is difficult to separately investigate the respective effect of cations or anions on the observed rejection performances in experiments. Fortunately, NEMD provides two effective methods to test ion rejections. The first is the "piston" method (Fig. 2a), which has the same limitation as the

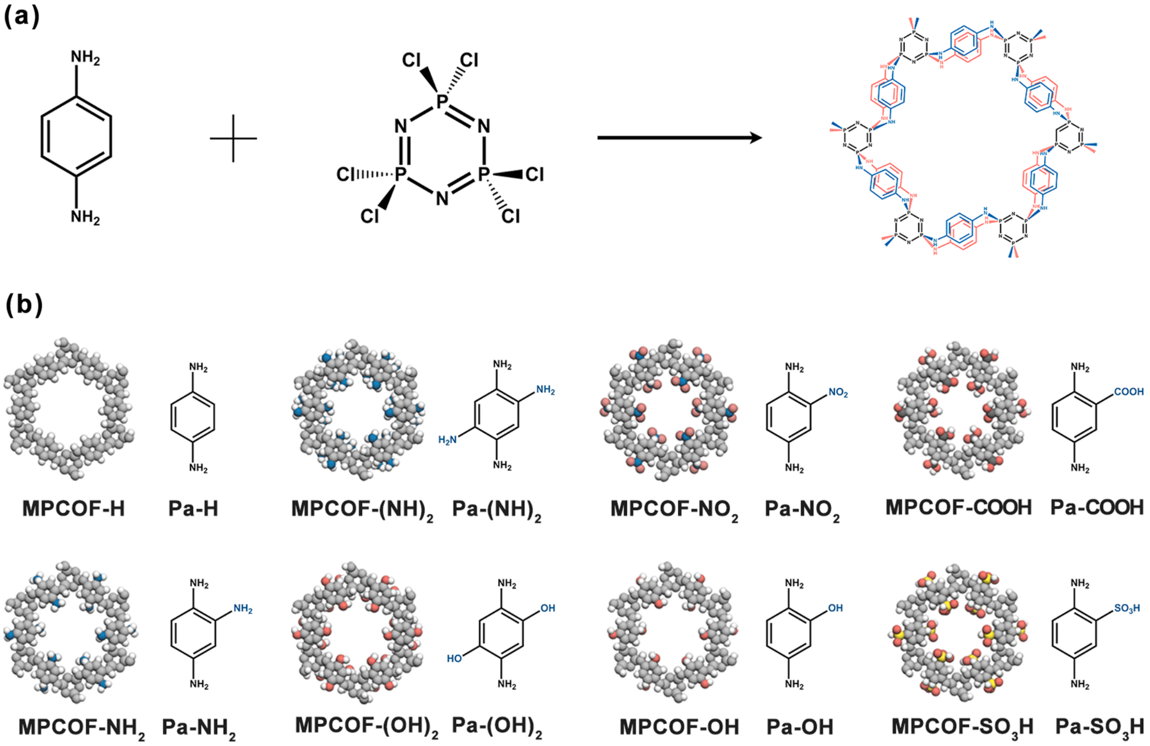

Fig. 1. (a) Schematic of the synthesis of MPCOF and (b) models of MPCOF-R series with corresponding Pa-R linkers.

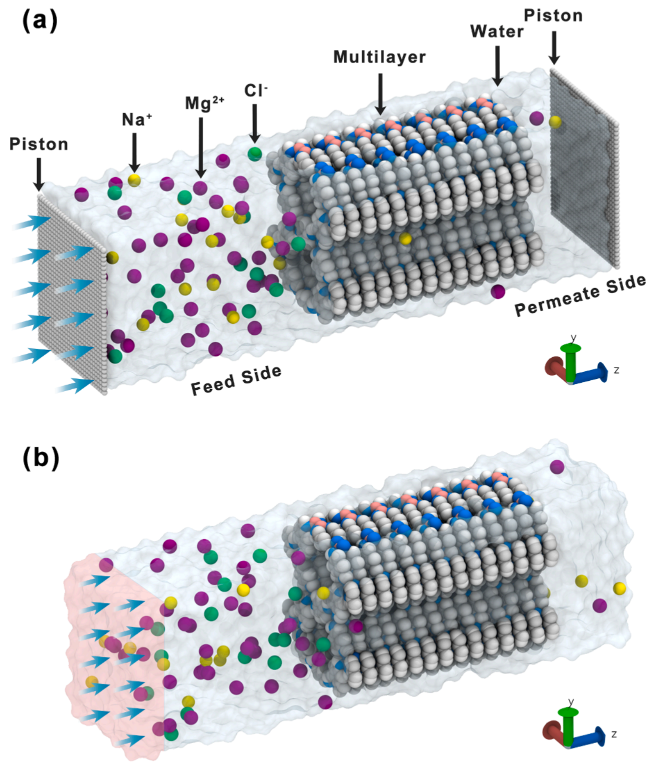

Fig. 2. Schematic simulation systems of the (a) “piston” method and (b) “pump” methods for water transport through MPCOF-R membranes. All the elements are labeled in the figure.

experiments since it is similar to the dead-end filtration and thus can be used to simulate the apparent rejection rates. The other is the “pump” method (Fig. 2b), where cations and anions can transport independently without the interference between each other. In the “pump” method, the feed and permeate sides are connected by periodic boundary conditions in the flowing direction, hence there is no need to maintain the electrical neutrality in both sides. Accordingly, the intrinsic transport ability of cation and anion through the membranes can be separately investigated. These two methods have been discussed in detail in our previous work [14]. See Supplementary Material for more simulation details.

3. Results and discussion

3.1. Ion rejection

The structural and chemical properties of all MPCOF-Rs have been calculated in our previous work [11], which are listed in Table S2. According to the previous work [11], all of them are testified to be suitable for water transport under experimentally accessible ΔPs. Moreover, their pore sizes are all smaller than one nanometer, indicating their potential for desalination. Although the contact angles of all MPCOF-Rs are less than 90°, they still differ in pore-wall hydrophilicity between each other. Therefore, we divide these MPCOF-R into two sets: weakly hydrophilic (WH, including —H, —NO_2, —NH_2, —OH, whose contact angles are larger than 45°) and strongly hydrophilic (SH, consisting of —COOH, —SO_3H, —$(NH_2)_2$, —$(OH)_2$, whose contact angles are less than 45°).

Since Cl^-, Na^+, Mg^{2+} are the most three abundant ions in seawater, they are selected as the typical solutes in this work. Moreover, the inclusion of two kinds of cations with different valence could help to understand whether influence of hydrophilicity on ion rejection is related to ion valence. The “piston” method, similar to the dead-end filtration in realistic experiments, is firstly applied to test the apparent rejections. In this method, rejections to cation and anion are identical thus maintaining respective electroneutrality in the feed and permeate side. Consequently, the apparent ion rejections are represented by the salt rejections in this method.

As shown in Fig. 3a, WH membranes show rejections of 40–60% to NaCl while 80–98% to $MgCl_2$. In contrast, the rejections to NaCl and $MgCl_2$ of the SH membranes all reach 100%. Such complete rejection indicates that the strong hydrophilicity of nanopores is favorable to improve the rejection. This finding also implies that the pore-wall hydrophilicity dramatically influence the ion rejection at the sub-nanometer scale.

Due to the limitation of electroneutrality law in both feed and permeate side, it is difficult to distinguish the respective rejections to three types of ions in the “piston” method. The “pump” method is then used, where cations and anions can transport independently without the interference between each other. Accordingly, the intrinsic transport ability of each type of ions through the membranes can be separately investigated, which has been discussed in our previous work in detail [14].

The rejection performances to each ion of all membranes are shown in Fig. 3b. For the WH membranes, all the three types of ions cannot be completely rejected. The rejections to Na^+ are less than the rejections to Cl^-, indicating that the rejection to NaCl in the “piston” method is determined by the rejection to Cl^-, as once Cl^- is rejected, the Na^+ is also incidentally rejected to maintain the electrical neutrality in experiments. Consequently, rejections to Cl^- (Fig. 3b) of different WH membranes vary in the same way with rejections to NaCl (Fig. 3a). However, the rejection to $MgCl_2$ is determined by Mg^{2+} since the rejections to Mg^{2+} is higher than the rejections to Cl^-, and rejections to Mg^{2+} and $MgCl_2$ (Fig. 3b and a) change accordingly in the same way.

For the SH membranes, the rejections to three types of ions are all 100%, hence they show complete rejection to NaCl and $MgCl_2$ in the “piston” method. To figure out the underlying mechanism, it is necessary to quantitatively clarify the cause of complete rejection. Our previous work [14] revealed that the origins of ion rejection include two parts: pore-entrance sieving effect and in-pore transport effect. Analyzing these two effects can help to understand the underlying mechanism of ion rejections.

3.2. Origins of ion rejection

According to the rejection equation [14], ion rejection origins from two contributions:

$$R = 1 - \frac{c_{in}}{c_0}\frac{v_{ion}}{v_{H_2O}} \tag{6}$$

where c_{in}/c_0 is the ratio of the in-pore ion concentration to the original concentration, which is related to the pore-entrance sieving effect. A larger value of c_{in}/c_0 will cause a lower rejection rate, and thus implies a weaker pore-entrance effect. v_{ion}/v_{H_2O} is the ratio of ion flow rate to water flow rate inside nanopores, which is recognized as the in-pore transport effect. A larger value of v_{ion}/v_{H_2O} suggests a less pronounced in-pore effect since it will result in a lower rejection rate. To intuitively exhibit these two parts, they are represented by $(1 - c_{in}/c_0)$ and $(1 - v_{ion}/v_{H_2O})$ in Fig. 4a and 4b, respectively. A larger value of $(1 - c_{in}/c_0)$ or $(1 - v_{ion}/v_{H_2O})$ implies a stronger pore-entrance or in-pore effect, respectively

For the WH membranes, the pore-entrance sieving effect to ions follows the order of $Mg^{2+} > Cl^- > Na^+$ (Fig. 4a), which is consistent with respective rejections to them in Fig. 3b. In addition, flow rates of Na^+ and Cl^- inside the WH membranes are all close to water molecules, thus they show negligible in-pore transport effects to Na^+ and Cl^- (Fig. 4b). Therefore, their rejections to NaCl are determined by pore-entrance sieving effect. However, Mg^{2+} behaves differently. First, only the $(1 - v_{Mg^{2+}}/v_{H_2O})$ of the MPCOF-H approaches zero. Second, it is unable to measure the $v_{Mg^{2+}}/v_{H_2O}$ of the MPCOF-NO_2 because Mg^{2+} is

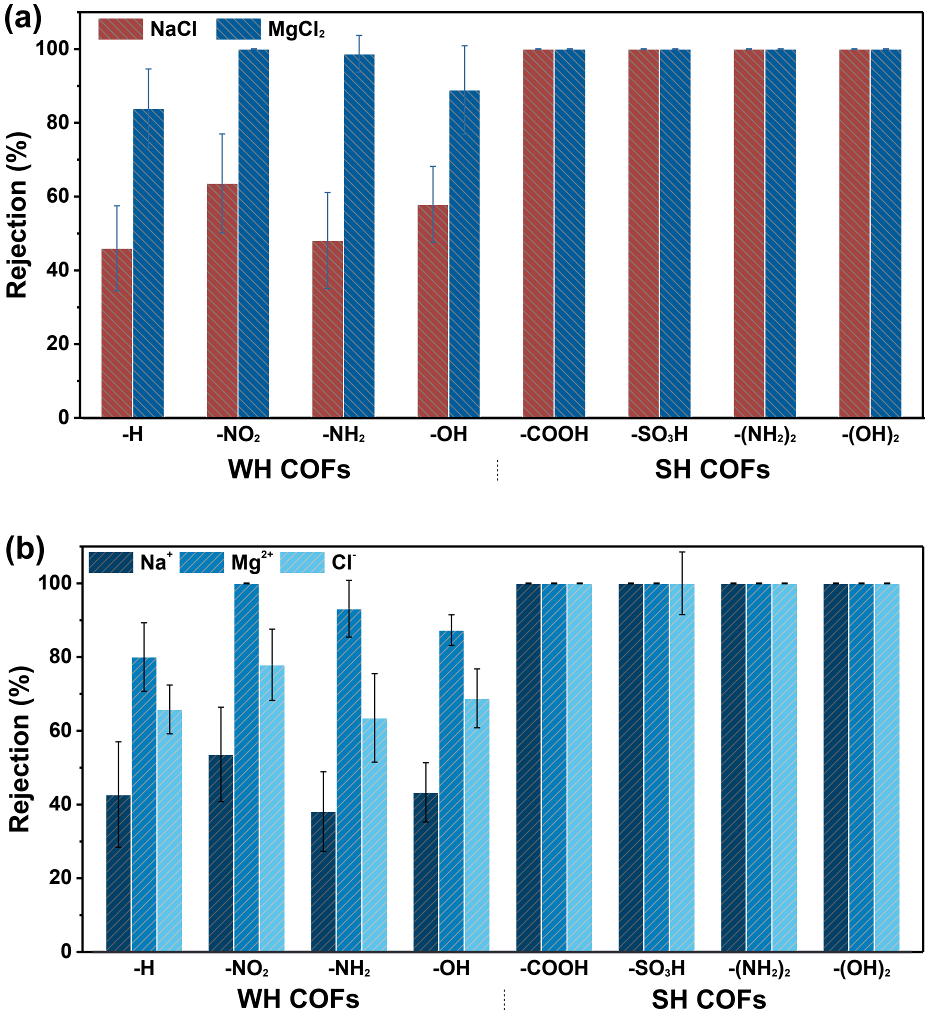

Fig. 3. (a) Apparent rejections to NaCl and $MgCl_2$ of each MPCOF-R. (b) Respective rejections to each ion of all MPCOF-Rs.

completely sieved by the pore entrance ($1 - c_{Mg^{2+}}/c_0 = 1$). This can be explained by the smaller pore diameter (7.3 Å) of MPCOF-NO_2 as shown in Table S2. Although the pore diameter is merely one angstrom smaller than other WH COFs, the exclusion effect at pore entrance enhances significantly. The reason is the size of Mg^{2+} hydration shell (9.8 Å) being close to these pore sizes, which suggests the rejection to Mg^{2+} of MPCOF-R series being sensitive to the pore size. The $1 - \nu_{Mg^{2+}}/\nu_{H_2O}$ of the other two WH membranes are found to increase dramatically, indicating that the rejections to $MgCl_2$ of MPCOF-NH_2/—OH are determined by both pore-entrance sieving effect and in-pore transport effect to Mg^{2+}.

For the SH membranes, the pore-entrance sieving effects to all ions are basically equivalent with those in the WH membranes except the MPCOF-$(OH)_2$. However, the pore-entrance effects to Na^+ and Mg^{2+} of MPCOF-$(OH)_2$ become weak and even negative, which means that cations tend to enter nanopores. This can be explained by the significant pore-wall-involved (PW-involved) hydration effect [14], which means that pore-wall atoms could compensate the cation hydration shell and consequently facilitate ions to enter nanopores. In contrast with the pore-entrance effect, all values of the $1 - \nu_{Na^+}/\nu_{H_2O}$, $1 - \nu_{Mg^{2+}}/\nu_{H_2O}$ and $1 - \nu_{Cl^-}/\nu_{H_2O}$ are equal to 1.0 (Fig. 4b), implying all ions are adsorbed to pore walls (*i.e.* extreme in-pore effects). Therefore, a strong hydrophilicity could completely enhance the in-pore effect to all ions. This observation is also related to the significant PW-involved hydration, which will be discussed in the next section.

In summary, increasing the pore-wall hydrophilicity can evidently enhance the in-pore effect, thus increasing ion rejections. Furthermore, such effect is stronger to ions with higher valence.

3.3. *Molecular analysis*

To investigate the mechanism causing the difference in ion rejections between the WH and SH membranes, PW-involved hydrations are characterized by the radial distribution functions (RDFs). RDFs of three types of ions inside nanopores with water molecules and pore-wall atoms for three typical membranes (—H, —OH, —$(OH)_2$) are shown in Fig. 5.

For MPCOF-H, no peak of RDFs between three ions and H atoms on the pore wall can be observed, indicating that no ionic hydration can be compensated by pore-wall atoms of MPCOF-H and thus all ions transport as fast as water molecules with no in-pore effect taking place.

For MPCOF-OH (WH representative), some peaks of RDF between each type of ions and oxygen atoms on the pore wall appear. The pore-wall atoms participate in the first hydration shell of Na^+ but its peak is still lower than the peak of Na^+ with oxygen atoms in water molecules. This implies that the interaction between Na^+ and MPCOF-OH is weaker than that between Na^+ and water molecules, hence $1 - \nu_{Na^+}/\nu_{H_2O}$ in Fig. 4b is still close to 0 and little in-pore effect happens. However, as the first hydration of Mg^{2+} is extremely strong, it possesses smaller size and hard to be replaced by pore-wall atoms. As a result, the pore-wall atoms enter the second hydration shell of Mg^{2+}, and hence the second hydration should be considered for Mg^{2+}. It can be seen that the peak of Mg^{2+} with oxygen atoms on the pore wall is equivalent with that of Mg^{2+} with

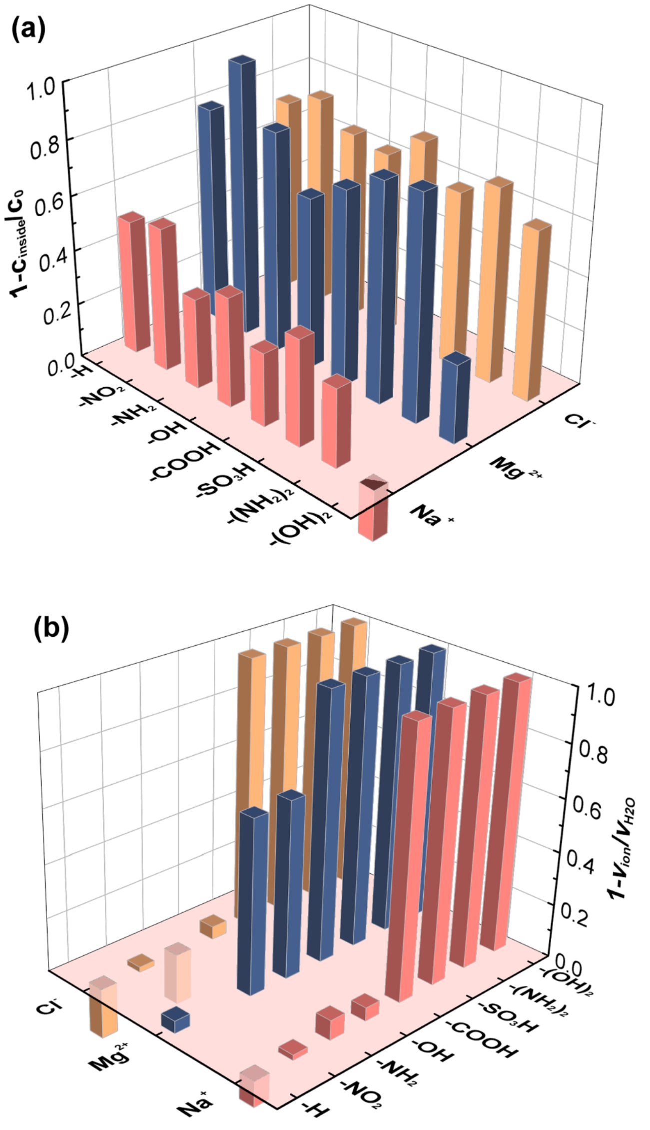

Fig. 4. Two origins, (a) $1 - c_0/c_{in}$ and (b) $1 - v_{H_2O}/v_{ion}$, of rejections to three types of ions for all modified MPCOF-Rs.

oxygen atoms in water molecules, which suggests that the interaction between Mg^{2+} and MPCOF-OH is close to the second water hydration of Mg^{2+}. This could explain the increased in-pore effect to Mg^{2+} of MPCOF-OH shown in Fig. 4b. The RDFs for Cl^- vary in the similar way with that for the Na^+, causing the little in-pore effect to Cl^- in MPCOF-OH.

In terms of MPCOF-$(OH)_2$ (SH representative), the peaks of RDF between each type of ions and oxygen atoms on the pore wall become much higher than those in the above two cases. Both peaks of Na^+ and Cl^- with pore-wall atoms are higher than their first hydrations with water, and the peak of Mg^{2+} with pore-wall atoms is higher than its second hydrations with water. Therefore, three ions all possess stronger interactions with pore-wall atoms than water, resulting in that $1 - v_{Na^+}/v_{H_2O}$, $1 - v_{Cl^-}/v_{H_2O}$ and $1 - v_{Mg^{2+}}/v_{H_2O}$ are all equal to 1.0 in the MPCOF-$(OH)_2$ as well as extreme in-pore effects to three ions.

Therefore, we can explain why membranes need strong hydrophilicities to generate significant in-pore effect to Na^+ and Cl^- while only weak hydrophilicities are required to Mg^{2+}.

3.4. Discussions on rejection mechanism

It should be noted that the pore-wall affinity of SH membranes with Na^+ is distinctly stronger than Cl^- from the RDF, resulting in that the $1 - c_{Na^+}/c_0$ is smaller than the $1 - c_{Cl^-}/c_0$ in Fig. 4a (*i.e.* the c_{Na^+}/c_0 is larger than the c_{Cl^-}/c_0). Therefore, it suggests that Na^+ has the stronger ability to enter the nanopores than Cl^- does. After entering the nanopores, both of them could be adsorbed on the pore wall due to extreme in-pore effect. Hence, the concentrations of cations are larger than that of anions inside the nanopores. Accordingly, the nanopores are speculated to be positively charged after saturated adsorption.

Fig. 6 shows the net charges that membranes carry (*i.e.* sum charges of all ions inside the nanopores) during the simulation time. The cations and anions alternately enter the WH membranes in equal quantities, causing that the net charge oscillates around zero value. Therefore, no apparent charge effect can be observed for the WH membranes during the entire filtration process. This is consistent with the above results that the weak hydrophilicities contribute little to the in-pore effect for Na^+. In contrast, the net charges of all SH membranes vary in a different way. Their net charges with simulation times are essentially larger than zero, resulting in the average values being positive. Therefore, the SH membranes carry certain positive charges during the filtration process, which confirms our speculation mentioned above.

According to these findings, the mechanism of enhancing ion rejections by strong hydrophilicity can be revealed. Cations are more prone than anions to enter the SH nanopores due to more significant affinity with pore-wall atoms. However, all ions are not able to transport inside after entering the nanopores due to the extreme in-pore effect (ions are adsorbed to pore walls), which is caused by significant pore-involved hydrations inside the nanopores. Therefore, the membranes are positively charged after being saturated by ions due to the higher concentration of cations than anions inside nanopores. Cations are in turn excluded outside the nanopores due to electrostatic repulsion by positively charged membranes and thus complete rejections are achieved.

According to the experimental work [13], the ion rejection of fabricated IISERP-COOH-COF1 membranes was attributed to that the carboxyl-modification constricts the pore aperture and reduces non-selective transport through invisible intercrystalline defects. Although post-modifications decrease the pore size, the hydrophilic groups were reported to attract ions by compensating its hydration shell [16,18,19] and thus decrease the energy barrier to facilitate ions entering nanopores [14]. Therefore, the nanopores carrying hydrophilic groups cannot exclude the ions outside even their pore sizes are smaller than the sizes of hydrated ions. Accordingly, it would be more reasonable to attribute the desalination performance to the above mechanism since the pore wall of IISERP-COOH-COF1 is rich in hydroxyl groups that are strongly-hydrophilic. Moreover, we predict that the proposed mechanism would be applicable to most SH desalination membranes made of various nanoporous materials.

3.5. Permeance comparison

Traditionally, the rejection is improved by narrowing the pore size but thus losing much water permeance. However, the above-proposed mechanism shows that the strong hydrophilicity can also effectively enhance the ion rejection of MPCOF membranes. Importantly, the pore sizes of the SH membranes change little compared to the WH membranes, which indicates that it avoids sacrificing the pore size. In this section, the saline permeances of these two methods are compared to exam their desalination efficiencies.

The saline permeances of all membranes are presented in Fig. 7. The saline permeances of WH membranes are basically larger than those of SH membranes, which indicates that the rise of rejection with the drop of permeance still obey the tradeoff effect. Among SH MPCOF-Rs, the saline permeances of MPCOF-SO_3H and MPCOF-$(OH)_2$ show declines compared with the other two. The dramatic decline of MPCOF-SO_3H permeance is due to the shrunk pore size (Table S2). All ions are most favorable to enter the MPCOF-$(OH)_2$ as demonstrated in Fig. 4a, and they all anchor to the pore wall after entry as shown in Fig. 4b.

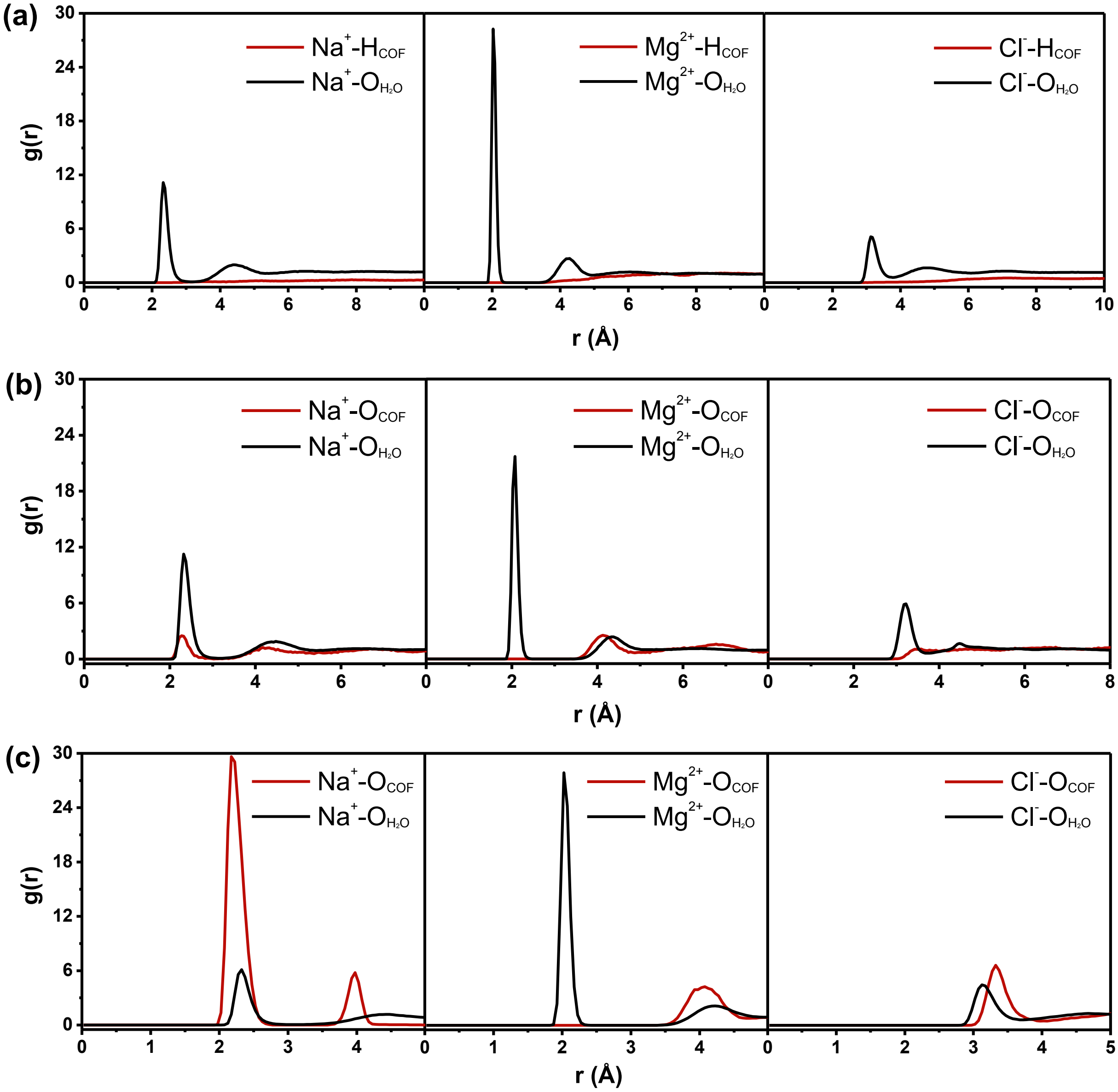

Fig. 5. RDFs of ions with water molecules and pore-wall atoms of (a) MPCOF-H, (b) MPCOF-OH, (c) MPCOF-$(OH)_2$.

Therefore, ion blockage is most evident in MPCOF-$(OH)_2$ nanopores, resulting the huge drop of saline permeance.

For comparison, a method to decrease the pore size is needed. The nanopores of MPCOF are formed by stacking MPCOF layers in the eclipsed manner. Therefore, the pore size can be narrowed by changing the stacking style, *i.e.* adjusting the offset between adjacent layers. This method can effectively change the pore size while keeping the pore-wall hydrophilicity, so as to consider the separate effect of pore size on water permeance [22]. Therefore, we displace the adjacent layers of the MPCOF-H by offset in x and y direction of 1, 2, 3 Å, denoted by offset-1 Å, offset-2 Å, offset-3 Å, respectively. The COF with a larger offset possess a smaller pore size. Since the MPCOF-H exhibits no in-pore effect to any ions, these three offset membranes only exert the pore-entrance effect to ions.

As shown in Fig. 7, the offset-3 Å is able to exclude all ions outside the nanopores and thus reject NaCl by 100% while the offset-1 Å and offset-2 Å are not capable. Therefore, the offset-3 Å can be recognized as the pore possessing the largest size that can exclude Na^+ and Cl^- outside the nanopores. It is obvious that MPCOF-COOH and MPCOF-$(NH_2)_2$ exhibit higher permeances than offset-3 Å does while keep the same 100% rejection to NaCl. Therefore, the strategy of increasing the pore-wall hydrophilicity has the potential to sacrifice less permeance than the method of decreasing the pore size. In addition, it is unrealistic to experimentally adjust the offsets between adjacent layers of COFs at the angstrom level while it is facile to introduce functional groups in COFs through predesigned synthesis or postsynthesis treatment [6,23]. Therefore, hydrophilic modifications are expected to be a promising strategy to improve the ion rejection of sub-nanometer pores.

4. Conclusion

In conclusion, 8 types of covalent-organic-frameworks (COFs) multilayers are constructed as membrane models to investigate the desalination mechanism via non-equilibrium molecular dynamics simulations. These 8 COFs are derived from a water-stable parent COF with a sub-nanometer pore size, and modified by 8 various functional groups R (—H, —NO_2, —NH_2, —OH, —COOH, —SO_3H, —$(NH_2)_2$, —$(OH)_2$) to exhibit different hydrophilicities. According to their degrees of pore-wall hydrophilicity, they are divided into two sets: weakly hydrophilic (WH: —H, —NO_2, —NH_2, —OH) and strongly hydrophilic (SH:

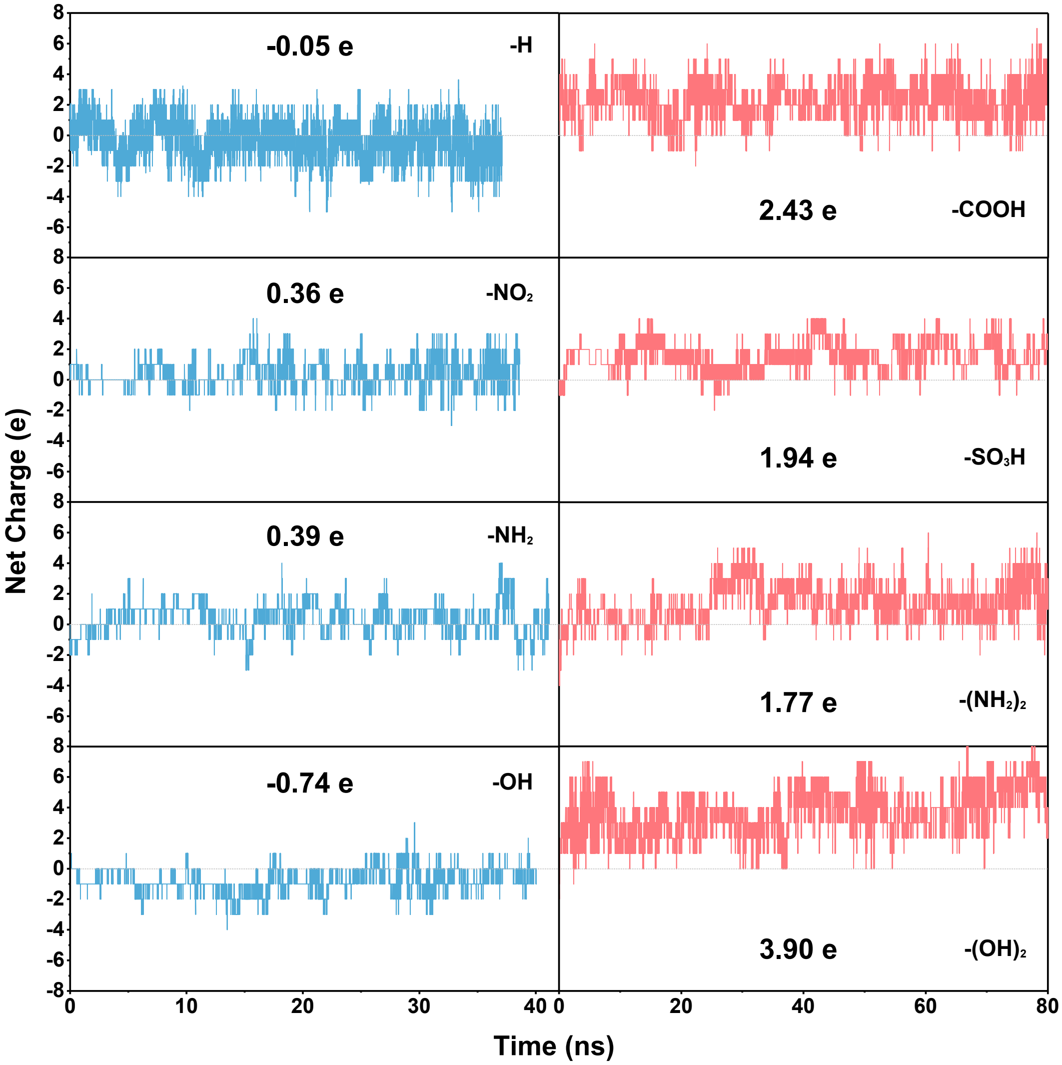

Fig. 6. Net charges that membranes carry during the simulations. The insert number represents the average value of net charges that each MPCOF-R carrys after saturated by ions; the gray dash line plots the zero value.

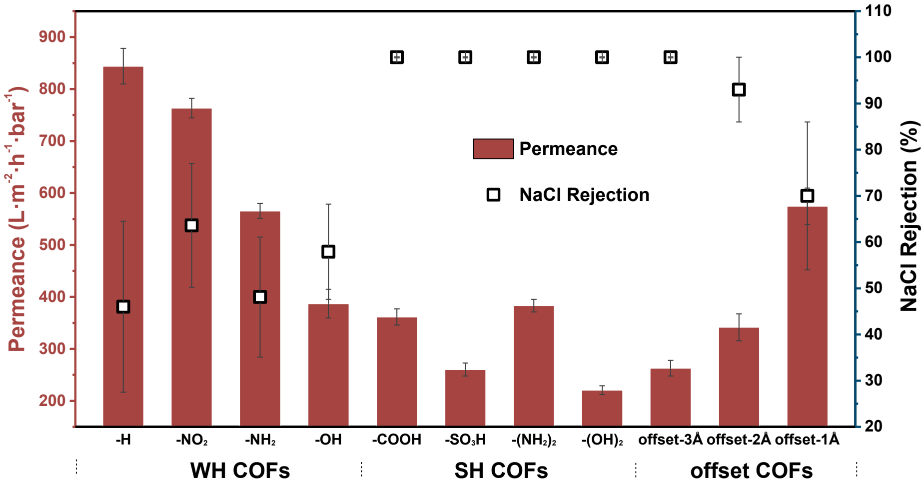

Fig. 7. Saline permeances of all MPCO-R membranes.

—COOH, —SO_3H, —$(NH_2)_2$, —$(OH)_2$). The WH membranes exhibit ~50% rejection to NaCl and ~95% to $MgCl_2$ while the SH membranes reject all ions by 100%. By analyzing the origins of ion rejection, the rejections to NaCl of the WH membranes follow the mechanism of pore-entrance sieving while its rejections to $MgCl_2$ is caused by both pore-entrance and in-pore effects. In contrast, the SH membranes show extreme in-pore effect (*i.e.* adsorption) to all ions, resulting in a complete 100% rejection. The augmented in-pore effect with rising pore-wall hydrophilicity is caused by more significant pore-wall-involved hydration of ions. In summary, the pore-wall hydrophilicity is found to dramatically influence ion rejection at the sub-nanometer scale, which is not previously recognized.

In addition, the SH membranes are found to carry positive net charges after saturated adsorption by ions due to the stronger affinity of hydrophilic membranes with cations than anions. The positive charges accordingly in turn exclude cations outside the nanopores by electrostatic repulsion and 100% rejection is thus achieved. This desalination mechanism can be used to explain the desalination performance of the current COF membranes. From the comparison of saline permeances, an appropriate hydrophilic modification is capable to improve the ion rejection to 100% but sacrifice less water permeance than the method of narrowing pore size. In addition, we believe these findings are also applicable to various desalination membranes consisting of other kinds of nanoporous materials.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2020.117937.

References

[1] M. Elimelech, W.A. Phillip, The future of seawater desalination: Energy, technology, and the environment, Science 333 (2011) 712–717.

[2] J.R. Werber, C.O. Osuji, M. Elimelech, Materials for next-generation desalination and water purification membranes, Nat. Rev. Mater. 1 (2016).

[3] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination-development to date and future potential, J. Membr. Sci. 370 (2011) 1–22.

[4] P.S. Goh, T. Matsuura, A.F. Ismail, N. Hilal, Recent trends in membranes and membrane processes for desalination, Desalination 391 (2016) 43–60.

[5] P. Vandezande, L.E.M. Gevers, I.F.J. Vankelecom, Solvent resistant nanofiltration: separating on a molecular level, Chem. Soc. Rev. 37 (2008) 365–405.

[6] D. Jiang, X. Chen, K. Geng, R. Liu, K.T. Tan, Y. Gong, Z. Li, S. Tao, Q. Jiang, Covalent organic frameworks: chemical approaches to designer structures and built-in functions, Angewandte Chemie International Edition, Accepted Author Manuscript, 2019.

[7] S. Kandambeth, K. Dey, R. Banerjee, Covalent organic frameworks: chemistry beyond the structure, J. Am. Chem. Soc. 141 (2019) 1807–1822.

[8] S.S. Yuan, X. Li, J.Y. Zhu, G. Zhang, P. Van Puyvelde, B. Van der Bruggen, Covalent organic frameworks for membrane separation, Chem. Soc. Rev. 48 (2019) 2665–2681.

[9] K. Dey, M. Pal, K.C. Rout, H.S. Kunjattu, A. Das, R. Mukherjee, U.K. Kharul, R. Banerjee, Selective molecular separation by lnterfacially crystallized covalent organic framework thin films, J. Am. Chem. Soc. 139 (2017) 13083–13091.

[10] M. Matsumoto, L. Valentino, G.M. Stiehl, H.B. Balch, A.R. Corcos, F. Wang, D. C. Ralph, B.J. Marinas, W.R. Dichtel, Lewis-acid-catalyzed interfacial polymerization of covalent organic framework films, Chem 4 (2018) 308–317.

[11] F. Xu, M. Wei, X. Zhang, Y. Wang, Effect of hydrophilicity on water transport through sub-nanometer pores, J. Membr. Sci. 611 (2020) 118297.

[12] V.A. Kuehl, J.S. Yin, P.H.H. Duong, B. Mastorovich, B. Newell, K.D. Li-Oakey, B. A. Parkinson, J.O. Hoberg, A highly ordered nanoporous, two-dimensional covalent organic framework with modifiable pores, and its application in water purification and ion sieving, J. Am. Chem. Soc. 140 (2018) 18200–18207.

[13] C.Y. Liu, Y.Z. Jiang, A. Nalaparaju, J.W. Jiang, A.S. Huang, Post-synthesis of a covalent organic framework nanofiltration membrane for highly efficient water treatment, J. Mater. Chem. A 7 (2019) 24205–24210.

[14] F. Xu, M. Wei, X. Zhang, Y. Wang, Ion rejection in covalent organic frameworks: revealing the overlooked effect of in-pore transport, ACS Appl. Mater. Interfaces 11 (2019) 45246–45255.

[15] L.C. Lin, J.W. Choi, J.C. Grossman, Two-dimensional covalent triazine framework as an ultrathin-film nanoporous membrane for desalination, Chem. Commun. 51 (2015) 14921–14924.

[16] K. Zhang, Z.J. He, K.M. Gupta, J.W. Jiang, Computational design of 2D functional covalent-organic framework membranes for water desalination, Environ. Sci.-Water Res. Technol. 3 (2017) 735–743.

[17] X. Zhang, M. Wei, F. Xu, Y. Wang, Thickness-dependent ion rejection in nanopores, J. Membr. Sci. 601 (2020) 117899.

[18] D. Cohen-Tanugi, J.C. Grossman, Water desalination across nanoporous graphene, Nano Lett. 12 (2012) 3602–3608.

[19] Y. Kang, Z.S. Zhang, H. Shi, J.Q. Zhang, L.J. Liang, Q. Wang, H. Agren, Y.Q. Tu, Na^+ and K^+ ion selectivity by size-controlled biomimetic graphene nanopores, Nanoscale 6 (2014) 10666–10672.

[20] S. Zhang, X.S. Zhao, B. Li, C.Y. Bai, Y. Li, L. Wang, R. Wen, M.C. Zhang, L.J. Ma, S. J. Li, "Stereoscopic" 2D super-microporous phosphazene-based covalent organic framework: design, synthesis and selective sorption towards uranium at high acidic condition, J. Hazard. Mater. 314 (2016) 95–104.

[21] M.M. Tong, Y.S. Lan, Q.Y. Yang, C.L. Zhong, Exploring the structure-property relationships of covalent organic frameworks for noble gas separations, Chem. Eng. Sci. 168 (2017) 456–464.

[22] W. Zhou, M.J. Wei, X. Zhang, F. Xu, Y. Wang, Fast desalination by multilayered covalent organic framework (cof) nanosheets, ACS Appl. Mater. Interfaces 11 (2019) 16847–16854.

[23] H. Ding, A. Mal, C. Wang, Tailored covalent organic frameworks by post-synthetic modification, Mater. Chem. Front. 4 (2020) 113–127.