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Peer Review File

Covalent organic framework membranes for selective ion separation

Corresponding Author: Professor Tongwen Xu

This file contains all editorial decision letters in order by version, followed by all author rebuttals in order by version.

Version 0:

Decision Letter:

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Dear Professor Xu,

Thank you for submitting your manuscript, "Covalent organic framework membranes for selective ion separation", to Communications Materials. It has now been seen by 3 referees, whose comments are appended below. You will see that while they find your work of potential interest, they have raised substantial concerns that should be considered and addressed. In light of these comments, we cannot accept the manuscript for publication, but we are interested in considering a revised version that addresses these serious concerns.

In addition to the detailed description of the COF-based membranes, it would be beneficial to provide a more critical view of the selected literature reports, highlighting the pros and cons, as well as putting more emphasis on future perspectives, addressing the current challenges in this field. In addition to the critical insightful highlights, it would be beneficial to simplify the presented illustrative content. Maybe divide the presented complex figures into several simpler ones.

We hope you will find the referees' comments useful as you decide how to proceed. Should further experimental data or analysis allow you to address these criticisms, we would be happy to look at a substantially revised manuscript. However, please bear in mind that we will be reluctant to approach the referees again in the absence of major revisions. If the revision process takes significantly longer than twelve weeks, we will be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

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Please do not hesitate to contact me if you have any questions or would like to discuss the required revisions further. Thank you for the opportunity to review your work.

Best regards,

Natalia Shustova, Prof.
Editorial Board Member
Communications Materials
orcid.org/0000-0003-3952-1949

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

This article introduces the research progress of COF membranes, including structural design, manufacturing technology, and ion separation applications. It also elaborated on the research progress, challenges, and prospects of COF as an ion selective precise separation membrane material. The logical and content structure of the manuscript is good, and the content is comprehensive. After making modifications to the following issues, it can be considered for publication in Communications Materials.
1. A table should be added in Section 2.1 to classify and compare the skeleton structures, and this section should be discussed more comprehensively. In addition, this section will also discuss the role of different skeleton structures in ion separation to align with the theme of this article.
2. Pores are the key to ion-selective separation. Therefore, in Section 2.2, a more detailed and comprehensive discussion should be conducted on how to precisely regulate COFs pores, at least introducing some strategies for regulating pores.
3. A table should be added to the preparation section of COF membrane to compare the characteristics of different synthesis methods, so that readers can have a clearer understanding of different methods.
4. In order to achieve ion selective separation, different strategies have been reported for the design and modification of COF based membranes. In Section 4 of ion separation, the design ideas and modification strategies, as well as their impact on the separation efficiency of COF, should be discussed in more detail, rather than merely listing the separation performance of COF membranes.
5. As stated in the abstract of this article, there is a trade-off between permeability and selectivity in ion separation. Therefore, should the article discuss how the relevant studies reported in the design of COF membranes for ion separation coordinate such trade-off limitations.

Reviewer #2 (Remarks to the Author):

This invited review provides description of COF membranes, including structural design, fabrication techniques, and ion separation applications. This review unfortunately does not provide any new insights, which would help the future research directions in COF membranes. In fact, this review is a summary of the majority of the literature that has already been covered in previous reviews (e.g., Nat. Rev. Mater. 2016, 1 (10), 16068; Adv. Sci. 2019, 6 (2), 1801410; Small Structures 2021, 2 (10), 2100061; Chem. Soc. Rev. 2019, 48 (14), 3811– 3841). This reviewer expected expert opinion and insights from Professor Xu and team.

1. It is a common claim that the regular pore structures of the COFs are also expected in COF membranes. This statement is misleading and will lead the MS and PhD students into an incorrect direction. Similar to current study, this claim has been the selling point or novel aspect of research on COF membranes. For instance, Fig. 1D is a theoretical expectation and has not been proved through experimental data. Although it is ok in the case of COF crystals, it is strongly asked from the authors to remove this claim of regular pore structure in the case of COF membranes throughout this manuscript. This reviewer urges the authors to consult the following to works: 10.1021/jacs.0c11159, and 10.1021/jacs.3c10832.

2. The writing style in this manuscript requires significant polishing. For instance, in figure 1, COFs membranes should be COF membrane; PIMs membrane should be PIM membrane; traditional polymer membranes to traditional polymer membrane; and 2D materials- GO membrane to GO membrane (everyone knows GO is 2D material). Similarly, the interlayer nanochannels in GO membranes are also irregular similar to PIM membrane – so basically it does not make sense. Additionally, the term ion channels appear to imply that these channels consist of ions – please revised to ion-selective channels.

3. The section 3 describes the preparation of COF membranes, which have been reviewed in several recent review papers. How this study is different? This reviewer expects that the authors would focus on the implications of the membrane preparation methods on their ion-selective behaviour. Otherwise, the title should be revised to make it in-line with the contents of this work.

4. It is important to explain and derive the relationship between COF properties vs. selectivity. Currently, each section just

describes the summary of the studies consulted. There exists no real effort to provide opinions and insights. For instance, are all the COF membranes crystalline? Are COF membrane better than polymeric/MOF/commercial membranes based on data comparison? What are mechanisms?

5. What is the 'concentration' as the driving force? Do you mean osmotic pressure difference? Did you see any trend in the performance of COF membrane vs. driving force?
6. Please add a schematic diagram showing a relationship between COF membranes vs. ion-selectivity. This reviewer has read Section 5 but has not been able to reach any conclusion. Basically, you need to come up with a trend.

7. 'the benefit from the regular and atomic-level tunable pore structures, COF membranes have unique advantages in the application of ion separation and is expected to achieve high-efficient, intelligent and precise separation of ions.' The research on COF membranes does not support this conclusion because (i) COF membrane is not fully crystalline, especially using the current membrane development methods; (ii) ion separation by COF membranes with typical pore size from 1-5 nm is not expected to separate ion and their performance (except osmotic driven) is generally not better than other membranes. What do you mean by intelligent separation?

Reviewer #3 (Remarks to the Author):

Li, Xu, and coworkers provide a comprehensive summary of covalent organic framework (COF) membranes for ion separation, highlighting their potential for efficient ion transport due to their regular pore structures and customizable functionality. The paper systematically examines various strategies for fabricating COF membranes, emphasizing both their advantages, such as high ion selectivity and tunability, and the challenges associated with scalability and stability under real-world conditions. While the review offers valuable insights for researchers in the field, it mainly summarizes existing studies and presents limited critical analysis. The authors do provide a forward-looking perspective, emphasizing the need for scalable fabrication methods and bioinspired designs, which will guide future research. However, the paper could benefit from expanding on specific challenges related to ion selectivity and membrane stability, while also reducing redundancy in the discussion of fabrication techniques. Figures and tables effectively support the paper's key points, making complex information more accessible and enhancing understanding. The review serves as a valuable resource for researchers, but could be enhanced by a more in-depth critical evaluation of existing methods and more focused discussions on key issues. Thus, I recommended its publication in Communications Materials after revisions as stated below:

1. I recommend that the authors consider separating the figures, particularly Figures 2, 3, 6, 7, 8, and 9, which are currently quite densely packed. This would improve clarity and allow each figure's details to be more easily interpreted, enhancing the overall presentation of the paper.
2. I recommend that the authors provide a more critical discussion of the previous work cited in the paper. While the review offers a thorough summary of existing research, it lacks a detailed evaluation of the strengths and weaknesses of the methodologies and findings presented. A more critical analysis of the limitations, inconsistencies, and gaps in the current literature would significantly strengthen the paper, offering readers a clearer understanding of the challenges and opportunities for future research in this field. A closely related review article should be cited in the introduction (e.g., Covalent organic frameworks for membrane separation. Adv. Sci. 2025, 12, 2412600).
3. I recommend that the authors provide a more detailed analysis of the challenges associated with the scalable production of COF membranes. While the paper briefly mentions these challenges, a deeper exploration of the current obstacles and proposed solutions would significantly enhance the practical relevance of the work. This would offer valuable insights into how these challenges might be addressed, making the paper more impactful for researchers working on the commercialization and large-scale application of COF membranes.
4. I suggest that the authors provide a clearer definition of the section on ion transport mechanisms. While the paper introduces this topic, it does not fully explain the underlying processes, nor does it offer sufficient details on how the structural characteristics of COF membranes influence ion selectivity. A more focused and detailed discussion of the ion transport mechanisms would enhance this section, providing readers with a deeper understanding of the factors driving ion selectivity and transport within COF membranes. This would significantly strengthen the overall content and clarity of the paper.
5. I recommend that the authors provide a more comprehensive discussion on the long-term stability and reusability of COF membranes in real-world applications, as these factors are crucial for practical deployment. A deeper exploration of aspects such as degradation mechanisms, as well as how membrane performance maintains stability over time under operational conditions, would significantly enhance the paper's practical relevance. Addressing these issues would provide valuable insights into the durability of COF membranes and their potential for sustainable, long-term use in ion separation processes.
6. While the paper briefly mentions bioinspired design, I suggest that the authors provide a more detailed exploration of how ion transport mechanisms from biological systems could be more directly integrated into COF membrane design. A deeper discussion on this topic would offer valuable insights into how biological principles could inform and enhance the design of COF membranes, potentially improving ion selectivity and transport efficiency. This could significantly strengthen the novelty and applicability of the paper's findings.

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Version 1:

Decision Letter:

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Dear Professor Xu,

Thank you once again for submitting your manuscript, "Covalent organic framework membranes for selective ion separation," to Communications Materials. It has now been seen again by the referees, whose comments are appended below. The concerns of our reviewers have now been addressed, but there are some amendments needed before we can accept your paper.

We ask that you edit your manuscript according to the attached table. **Please read this document carefully as we will be unable to further assess your revised paper until these important points are addressed.**

Please outline all revisions made in the right-hand column and return the completed table with your updated manuscript files as a Related Manuscript file.

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When resubmitting, please provide a marked-up manuscript with all changes highlighted, as well as a clean version of your paper.

We hope to receive this updated version of your paper within 1 week, but please let us know if you find that you need more time.

Best regards,

Natalia Shustova, PhD
Editorial Board Member
Communications Materials
orcid.org/0000-0003-3952-1949

Reviewers' comments:
Reviewer #1 (Remarks to the Author):

The revision has been completed and it can be published.

Reviewer #2 (Remarks to the Author):

This revision is adequate. The manuscript may be accepted for publication.

Reviewer #3 (Remarks to the Author):

My concerns have been fully addressed. The quality of this article has been greatly improved. I recommend accepting this

article for publication in the journal as it is.

Version 2:

Decision Letter:

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Dear Professor Xu,

Thank you once again for submitting your manuscript, “Covalent organic framework membranes for selective ion separation," to Communications Materials. The concerns of our reviewers have been addressed, but there are some amendments needed before we can accept your paper.

We ask that you edit your manuscript according to the attached table. **Please read this document carefully as we will be unable to further assess your revised paper until these important points are addressed.**

Please outline all revisions made in the right-hand column and return the completed table with your updated manuscript files as a Related Manuscript file.

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When resubmitting, please provide a marked-up manuscript with all changes highlighted, as well as a clean version of your paper.

We hope to receive this updated version of your paper within 1 week, but please let us know if you find that you need more time.

Best regards,

Natalia Shustova, PhD
Editorial Board Member
Communications Materials
orcid.org/0000-0003-3952-1949

Version 3:

Decision Letter:

Dear Professor Xu,

We are delighted to accept your manuscript titled "Covalent organic framework membranes for selective ion separation" for publication in Communications Materials. Thank you for choosing to publish your interesting work with us.

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Best regards,

Natalia Shustova, PhD
Editorial Board Member
Communications Materials
orcid.org/0000-0003-3952-1949

***As a new journal, we would greatly appreciate any comments you have about your experience at Communications Materials. I hope that we have been able to meet your expectations and look forward to working with you again in the future.

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Reviewer #1 (Remarks to the Author):
This article introduces the research progress of COF membranes, including structural design, manufacturing technology, and ion separation applications. It also elaborated on the research progress, challenges, and prospects of COF as an ion selective precise separation membrane material. The logical and content structure of the manuscript is good, and the content is comprehensive. After making modifications to the following issues, it can be considered for publication in *Communications Materials*.

Response: We greatly appreciate your thoughtful comments and constructive suggestions on our manuscript. We have carefully considered all the points raised and revised the manuscript accordingly. The detailed comments are as follows:

Comment 1: A table should be added in Section 2.1 to classify and compare the skeleton structures, and this section should be discussed more comprehensively. In addition, this section will also discuss the role of different skeleton structures in ion separation to align with the theme of this article.

Response 1: We thank the reviewer for this valuable suggestion. Following your advice, we have added a new table (Table 1) in Section 2.1 that systematically classifies COF skeleton structures and compares the characteristics of those reported for ion separation. Additionally, we have also substantially expanded the discussion in this section to clarify the rationale behind the selection of different skeleton structures and their influence on ion separation performance. This revision aligns the section with the ion separation theme of our review.

"Although a considerable number of COF linked skeleton structures developed, only a few of these structures have been prepared into membranes, given considerations such as their stability and synthesis conditions. Currently, the most widely reported COF skeletons for ion separation are based on imine linkages formed *via* Schiff-base reactions, owing to their favorable crystallization under mild conditions and robust framework stability. For example, Dey et al.[59] developed an interfacial crystallization strategy to prepare a series of imine-linked COF membranes under ambient conditions. Owing to the abundant electronegative C=N bonds in imine-linked COF skeletons, they exhibit a distinct responsiveness to environmental pH. For instance, Cao et al.[60] further introduced phenolic hydroxyl groups into the monomers, synthesizing an oriented COF-DT membrane with high ion flux and stimuli-responsive behavior, enabling precise modulation of ion transport through pH-triggered changes in both imine and phenolic moieties (**Fig. 2a**). Beyond conventional imine linkages, azine-linked COFs can be synthesized using hydrazine hydrate and aldehyde monomers. The small molecular size of hydrazine hydrate (HZ) enables the construction of COF membranes with sub-nanometer pores. Yin et al.[61] prepared a hydrazone-linked TbHZ membrane with vertically aligned sub-nanometer channels, exhibiting high precision ion separation for ions differing in size at 2 Å (**Fig. 2b**). In addition, the reaction between hydrazide monomers and aldehyde monomers was utilized to synthesize COFs with hydrazone linkages. Meng et al.[62] reported a series of hydrazone-linked COF membranes with different lengths of the oligoether segments, systematically regulating

pore solvation environments and elucidating how solvating segments influence ion partitioning, diffusion, and selectivity (**Fig. 2c**). To enhance the chemical stability of COFs under harsh acidic or basic conditions, Kandambeth et al.[52] (2012) introduced the 1,3,5-triformylphloroglucinol (Tp) monomer, which first forms an imine-linked framework *via* a reversible Schiff-base reaction, followed by an irreversible enol–keto tautomerization to yield a more stable β-ketoenamine-linked structure while maintaining a crystallinity. This advancement significantly broadened the application scope of COFs. In our group, we constructed a 20 nm ultrathin β-ketoenamine-linked COF membrane on an anodic aluminum oxide (AAO) substrate and demonstrated that abundant hydrogen bonding sites in the channels can form hydrogen bonding interaction with water (**Fig. 2d**)[63]. We reveal that the hydrogen bonding interaction between hydrated cations and channel walls govern the ion selectivity, with divalent cations experiencing higher energy barriers for transport compared to monovalent ions. We also developed freestanding β-ketoenamine-linked COF membranes and demonstrated their utility in acid and alkali recovery[64]. In addition, Zhu et al.[65] prepared a dioxin linkage oxygen-rich COF and showed its potential in efficient removal of Cd(II) and Pb(II) from water (**Fig. 2e**). Since the direct synthesis of triazine-linked COFs typically requires harsh conditions, Meng et al.[66] developed an alternative strategy by reacting a triazine-functionalized amine monomer with Tp under mild conditions (**Fig. 2f**). This approach yielded a triazine-linked COF membrane capable of high-resolution Li^+/Mg^{2+} separation. The hydrophilic channel environment promotes Li^+ dissociation from sulfonate groups, facilitating hopping transport along sulfonate-functionalized side chains and shortening the Li^+ diffusion path.

Table 1. COFs with different skeletons constructed *via* various organic reactions

Non-conjugated skeleton	Partially conjugated skeleton	Fully conjugated skeleton
Boroxine linkage	Imine linkage	β-ketoenamine linkage
Boronate ester linkage	Azine linkage	Phenazine linkage
Imide linkage	Hydrazone linkage	C=C linkage
Amide linkage	Triazine linkage	
Dioxin linkage	Benzoxazole linkage	
Borazine linkage	Squaraine linkage	
Spiroborate linkage	Azodioxy linkage	
Borosilicate linkage	Viologen linkage	

”

Comment 2: Pores are the key to ion-selective separation. Therefore, in Section 2.2, a more detailed and comprehensive discussion should be conducted on how to precisely regulate COFs pores, at least introducing some strategies for regulating pores.

Response 2: We fully agree with the reviewer that precise pore regulation is crucial for ion-selective separation. We have substantially expanded Section 2.2 by providing a comprehensive discussion of pore engineering strategies. We introduced four key approaches—topology control, monomer design, synthetic conditions, and post-synthetic functionalization, illustrated with representative examples from recent literature to demonstrate how these methods facilitate the atomic-level control over pore architecture.

"Atomic-level pore engineering is achievable through four main strategies including topology control, monomer design, synthetic condition, and post-synthetic functionalization[29-31]. Firstly, monomer geometry and topology dictate COF pore shapes (hexagonal/quadrilateral/triangular)[46,67-71], while the chemical structure of monomer enable dual-pore systems with co-existing geometries or dimensionally varied hexagons (**Fig. 3a**). For example, Meng et al.[72] utilized benzene-1,3,5-tricarbohydrazide as the core building block to react with aldehydes owing different reaction sites and synthesized 0.78 nm and 1.58 nm COF membranes with similar chemistry by [2+3] and [3+3] topology configuration. Li et al.[73] adjusted the chemical structure of aldehyde monomer to regulate the pore size of COF membranes from >1 nm to sub-1-nm scale by changing the stacking mode of COF layers from AA to AB stacking. Chen et al.[71] introduced PyTTA (4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl) tetraaniline) monomer to synthesize quadrilateral single-pore COF, while Zhou et al.[74] used the similar symmetric amine monomer but different chemical structure and synthesized a dual-pore COF, which possesses both micropores and mesopore. Furthermore, Zhao et al.[75,76] designed asymmetric monomer to create COFs with tri- and tetra-pore systems.

Apart from topology control, monomer design offers precise control over pore dimensions. While most COFs exhibit pore sizes in the range of 1~3 nm[77], judicious monomer elongation allows tuning from the sub-nanometer scale to expanded mesopores. As illustrated in **Fig. 3b**, monomer elongation can precisely modulate the pore size of COF. Sun et al.[78] utilized HZ monomer and synthesized COF membrane with pore size of 0.73 nm, while Mu et al.[79] employed elongated linear linkers to synthesize mesoporous COFs with pores up to 10 nm. In addition, the channel chemistry of COFs is programmable through functional monomers, yielding positive (cationic/quaternary ammonium salts)[68,80,81], negative (sulfonic/carboxylic acids)[82,83], hydrophobic (fluorine-containing)[84], and other functionalized channels (**Fig. 3c**)[67]. Synthetic condition is another important factor defining COF pore structure. Yin et al.[61] introduced a solvent vapor annealing approach that weakens π-π interactions between COF layers, promoting reorientation from random stacking to a face-on configuration with vertically aligned pores. Similarly, Sun et al.[78] achieved partial regulation of the pore orientation of COF membranes by using different organic solvent in interfacial polymerization. Post-synthetic functionalization strategy is also widely used to modulate the pore structure of COFs. Meng et al.[7] incorporated olefin units into COF frameworks and conducted post-functionalization to manipulate the pore charge density by the thiol-ene click reaction. Ren et al.[85] constructed biomimetic smart COF

membranes with charged and switchable sub-nanochannels through grafting photo-responsive azobenzene derivatives onto channel wall *via* the sulfur(VI) fluoride exchange (SuFEx) click reaction. Our group has also reported negatively and positively charged COF membranes through post-modification with propanesulfonate and iodomethane, respectively[64]. Finally, hybridization with other materials provides an additional route to tailor pore structure of COF membranes. Yang et al.[86] adapted the sheltering effect of 1D cellulose nanofibers (CNFs) to regulate the pore size of COF membrane (0.45-1.0 nm) through a mixed-dimensional assembly of 2D COF nanosheets and 1D CNFs. Wang et al.[87] reported a 2D COF membrane with narrowed channels (0.7 nm × 0.4 nm) and excellent mechanical performance constructed by the staggered stacking of cationic and anionic 2D COF nanosheets."

Comment 3: A table should be added to the preparation section of COF membrane to compare the characteristics of different synthesis methods, so that readers can have a clearer understanding of different methods.

Response 3: Thank you for your constructive suggestion. We have included a table (Table 2) in Section 3 systematically comparing the main fabrication methods for COF membranes, where the procedure, efficiency, quality, scalability, and sustainability are evaluated to clearly outline the advantages and limitations of each method. This tabular overview also offers different fabrication strategies and their applicability across various scenarios.

"As shown in Table 2, an analysis based on five criteria (i.e., procedure, efficiency, quality, scalability, sustainability) highlights the respective advantages and disadvantages of these major methods."

Comment 4: In order to achieve ion selective separation, different strategies have been reported for the design and modification of COF based membranes. In Section 4 of ion separation, the design ideas and modification strategies, as well as their impact on the separation efficiency of COF, should be discussed in more detail, rather than merely listing the separation performance of COF membranes.

Response 4: We thank the reviewer for this important comment. We have completely restructured Section 4 to focus on the fundamental design principles and modification strategies. The revised section is based on the ion separation mechanisms enabled by precise design and modulation of COF membranes, focusing on pore architecture and wall functionality. Specific mechanisms discussed include size-sieving, electrostatic interactions, hydrogen bonding interactions, ion-dipole interactions, and synergistic effects arising from multiple ion-membrane interactions. Moreover, we discuss current challenges and outlines future directions, focusing on bioinspired designs and the integration of artificial intelligence (AI) and the Materials Genome Initiative (MGI) for developing next-generation ion-selective COF membranes.

"Conventional polymer membranes face a long-standing trade-off between ion permeability and selectivity. This limitation arises from their ill-defined ion-conduction pathways and poor dimensional stability, which leads to significant swelling in solvents

and consequent degradation of selectivity. In contrast, COF-based membranes have emerged as promising candidates for high-efficiency ion separation, owing to their well-defined pore structures and tailored functionalities[22]. The ordered channels promote fast ion transport and thus the increase of permeance, and the enhanced interactions between the ions and functionalized channel wall contribute to selective ion transport and the rising of selectivity.....”

“Cations and anions can be effectively separated by traditional ion-exchange membranes (IEMs), which leverage differences in electrostatic interactions between the fixed charges in the membrane matrix and co-ions/counter-ions[5]. However, conventional IEMs typically form hydrophilic ion transport channels through hydrophilic-hydrophobic phase separation. These channels are prone to significant swelling in aqueous environment, which is markedly exacerbated with increasing ion-exchange capacity (IEC) and consequently compromises cation/anion selectivity.....; Wang et al.[130] reported an ionic COF membrane with superhigh IEC of 4.6 mmol g^{-1} by introducing 4,4’-diaminobiphenyl-3,3’-disulfonic acid, while maintaining a low swelling ratio of ~21% at 25 °C and a prominent proton conductivity of 0.66 S cm^{-1}. Peng et al.[82] synthesized NUS-10 COF with a higher theoretical IEC of ~5.4 $mmolg^{-1}$ by utilizing highly charged 2,5-diaminobenzene1,4-disulfonic acid monomer, holding great promise in high-efficient cation/anion separation applications. Beyond conventional charged COF membranes, Lai et al.[131] engineered COF membranes with aligned benzothiadiazole dipoles (**Fig. 7d**), enabling dynamic modulation of ion permselectivity across cation-selective, ambipolar, and anion-selective states by exploiting ion-dipolar interactions. When interacting with multivalent anions, the channels exhibited strong cation conductivity and permselectivity (t_+= 0.9) even under a 1000-fold concentration gradient. Yin et al.[132] modulated ion-membrane interactions through linkage chemistry (**Fig. 7e**), showing that charge-neutral β-ketoenamine-linked COF membranes achieved record cation permselectivity under high-salinity conditions.....; Despite substantial progress in developing architecturally diverse COF membranes with exceptional cation/anion permselectivity by electrostatic, ion-dipolar, and ion-membrane interactions.....”

“Monovalent and multivalent ions carry the same charge polarity but differ in charge number, leading to marked differences in hydrated ion size and hydration energy. For instance, the hydrated diameters of Li^+ and Mg^{2+} are approximately 7.64 Å and 8.56 Å, respectively[63], while their hydration energies are about -475 kJ mol^{-1} and -1830 kJ mol^{-1}. These differences provide a basis for efficient separation through precise design of pore size and channel-wall chemistry. For example, Yin et al.[61] employed solvent vapor annealing to reorient COF channels from anisotropic to perpendicular alignment. The resultant TbHZ membrane with 9.8 Å perpendicular-aligned subnanochannels achieved 2 Å-level ion differentiation and a SO_4^{2-}/PTS^{4-} selectivity of 16.8 (**Fig. 8a**). In 2021, our group prepared an ultrathin (~20 nm) $TpBDMe_2$ COF membrane with sub-2 nm channels and abundant hydrogen-bonding sites *via* a counter-diffusion approach[63]. The membrane exhibited high monovalent cation permeation rates (K^+: ~0.2 mol m^{-2} h^{-1}) and outstanding mono-/multivalent cation selectivity through channel-cation

hydrogen bonding interactions (K^+/Mg^{2+}: 765, Na^+/Mg^{2+}: 680, Li^+/Mg^{2+}: 217), breaking the permeability-selectivity trade-off for conventional ion-separation membranes (**Fig. 8b**)[63]. Furthermore, the difference in charge number between mono- and multivalent ions also enables their separation by introducing electrostatic interactions in charged nanochannels. In 2024, Liu et al.[8] introduced positively charged aldehyde monomer and synthesized an asymmetric-structured HBAB-TAPA-COF membrane on HPAN *via* counter-diffusion. The membrane consisted of vertically aligned nanorods that enhanced water/ion contact and an ultrathin dense layer that enabled both high permeability (Cs^+: 0.33 mol m^{-2} h^{-1}) and selectivity (Cs^+/La^{3+}: 75.9) (**Fig. 8c**) .....; In addition, Meng et al.[134] improved ion-π interactions with multivalent ions through optimizing the face-to-face orientation of building blocks during the assembly of COF membranes to achieve both mono-/multivalent cations and anions separation (**Fig. 8e**). The prepared COF-170/PAN membrane show high selectivity of 214 for K^+/Al^{3+}, 62 for Cl^-/SO_4^{2-}, and 451 for NO_3^-/PO_4^{3-}.....”

“.....Biological ion-selective channels exhibit exceptional efficiency, intelligence, and precision in ion transport. For example, K^+ channels achieve specificity through funnel-shaped architectures and coordination with carbonyl oxygens, whereas Na^+ channels utilize four carboxyl groups to confer Na^+ selectivity[3,146]. Inspired by these natural paradigms, the construction of artificial nanochannels has emerged as a vibrant research frontier. COFs offer unique advantages in this regard, owing to their structural controllability and chemical tailorability, making them ideal platforms for developing bioinspired membranes for precision ion separation. Consequently, developing COF-based biomimetic membranes for precision ion separation represents a promising research direction with transformative implications. Moreover, through the precise construction of bioinspired COF membranes, it is possible to investigate the mechanisms underlying highly selective ion transport, establish clear structure-property relationships between the microscopic structural parameters of COF nanochannels and their ion separation performance, and build comprehensive databases correlating structure with ion transport behavior. Notably, with the rapid advancement of artificial intelligence (AI) and the Materials Genome Initiative (MGI) has accelerated the exploration of advanced materials. By developing computational tools that predict structure-property relationships and employing materials genomics strategies, we can analyze the COF structural database and perform computational screening to enable the high-efficiency design of high-performance COF structures.”

Comment 5: As stated in the abstract of this article, there is a trade-off between permeability and selectivity in ion separation. Therefore, should the article discuss how the relevant studies reported in the design of COF membranes for ion separation coordinate such trade-off limitations.

Response 5: Thank you for your insightful suggestion. We added a discussion on the the design of COF membranes for ion separation coordinate such trade-off limitations.

“Conventional polymer membranes face a long-standing trade-off between ion permeability and selectivity. This limitation arises from their ill-defined ion-conduction

pathways and poor dimensional stability, which leads to significant swelling in solvents and consequent degradation of selectivity. In contrast, COF-based membranes have emerged as promising candidates for high-efficiency ion separation, owing to their well-defined pore structures and tailored functionalities[22]. The ordered channels promote fast ion transport and thus the increase of permeance, and the enhanced interactions between the ions and functionalized channel wall contribute to selective ion transport and the rising of selectivity. Consequently, a growing number of COF membranes have been reported for ion separations breaking the trade-off limitations, including cation/anion, mono-/multivalent ion, and mono-/monovalent ion separation.....; In 2021, our group prepared an ultrathin (~20 nm) TpBDMe$_2$ COF membrane with sub-2 nm channels and abundant hydrogen-bonding sites *via* a counter-diffusion approach[63]. The membrane exhibited high monovalent cation permeation rates (K^+: ~0.2 mol m^{-2} h^{-1}) and outstanding mono-/multivalent cation selectivity through channel-cation hydrogen bonding interactions (K^+/Mg^{2+}: 765, Na^+/Mg^{2+}: 680, Li^+/Mg^{2+}: 217), breaking the permeability-selectivity trade-off for conventional ion-separation membranes (**Fig. 8b**)[63].....; In 2025, Meng et al.[7] prepared COF-300-V membranes using counter-diffusion, followed undergoing a post-modification by a click reaction to obtain COF-300-CH$_{0.6}$ membrane. The prepared membrane exhibited a Li^+/Mg^{2+} selectivity of 321 and a Li^+ flux of 0.53 mol m^{-2} h^{-1} in electrodialysis surpassing the reported PIM, COF, MOF GO, and MXene membranes, with electric-field-assisted decoupling revealing membrane charge density-cation transport correlations (**Fig. 8d**).....; In addition, Meng et al.[134] improved ion-π interactions with multivalent ions through optimizing the face-to-face orientation of building blocks during the assembly of COF membranes to achieve both mono-/multivalent cations and anions separation (**Fig. 8e**). The prepared COF-170/PAN membrane show high selectivity of 214 for K^+/Al^{3+}, 62 for Cl^-/SO_4^{2-}, and 451 for NO_3^-/PO_4^{3-}, which is superior to most reported polymer, GO, COF, and MOF membranes.....; As illustrated in **Fig. 10a**, the Li^+ flux and Li^+/Mg^{2+} selectivity of various membrane materials—including conventional polymer membranes, commercial ion-exchange membranes, emerging 2D material membranes, MOF membranes, and COF membranes—are compared under both diffusion and electro-driven processes[7,62,63,72,81,105,139-142]. Among these, COF membranes demonstrate superior performance in both Li^+ flux and Li^+/Mg^{2+} selectivity. Continued advances in fabrication techniques and enhanced control over crystallinity and orientation are expected to further improve their separation performance.....”

Reviewer #2 (Remarks to the Author):
This invited review provides description of COF membranes, including structural design, fabrication techniques, and ion separation applications. This review unfortunately does not provide any new insights, which would help the future research directions in COF membranes. In fact, this review is a summary of the majority of the literature that has already been covered in previous reviews (e.g., Nat. Rev. Mater. 2016, 1 (10), 16068; Adv. Sci. 2019, 6 (2), 1801410; Small Structures 2021, 2 (10), 2100061; Chem. Soc. Rev. 2019, 48 (14), 3811– 3841). This reviewer expected expert opinion and insights from Professor Xu and team.

Response: We sincerely appreciate the reviewer's thorough evaluation and constructive criticism of our manuscript. We have implemented comprehensive revisions as detailed below.

Comment 1: It is a common claim that the regular pore structures of the COFs are also expected in COF membranes. This statement is misleading and will lead the MS and PhD students into an incorrect direction. Similar to current study, this claim has been the selling point or novel aspect of research on COF membranes. For instance, Fig. 1D is a theoretical expectation and has not been proved through experimental data. Although it is ok in the case of COF crystals, it is strongly asked from the authors to remove this claim of regular pore structure in the case of COF membranes throughout this manuscript. This reviewer urges the authors to consult the following to works: 10.1021/jacs.0c11159, and 10.1021/jacs.3c10832.

Response 1: Thank you for your comment. Regarding the regular pore structure of COF membranes, we would like to clarify the following points:

Firstly, COFs are intrinsically crystalline porous materials featured by well-defined pore structures, high surface areas, high porosity, and tunable channel walls. It is undoubtedly that these structural advantages underpin their potential for membrane separation.

Secondly, although most currently synthesized COF membranes exhibit moderate crystallinity and orientation—often comprising a mixture of crystalline and amorphous domains that hinder full exploitation of their intrinsic pores for separation—the short-range ordered pores in the crystalline regions undeniably form the structural basis governing ion or molecular transport. The application of COFs in membrane separation is still rapidly evolving, and substantial evidence has demonstrated their excellent performance in ion/molecular separation. Current challenges do not diminish the contribution of their regular pore structures. Such hurdles are common in the development of advanced materials and motivate further in-depth research. We believe that separation performance will improve significantly with advances in membrane crystallinity and orientation.

Finally, recent advances in fabrication techniques have enabled the synthesis of highly crystalline and oriented COF membranes. For instance, Sahabudeen et al. developed a surfactant-monolayer-assisted interfacial synthesis strategy (SMAIS) to prepared large-area, highly crystalline COF membranes at water-air interface (*Angew. Chem. Int. Ed. Engl.*, 2020, 132, 6084–6092). Yang et al. utilized diethylenetriamine as

a sacrificial go-between to prepared a highly strong, tough and elastic single-crystal 2D COF membranes at water-air interface *via* the sacrificial go-between guided synthesis method (*Nature*, 2024, 630, 878–883). In 2025, Cusin et al. utilized the casting method, combined with solvent evaporation and annealing processes, to achieve for the first time the fabrication of a micrometre-thick oriented 2D COF membranes by leveraging a kinetically trapped amorphous 3D covalent adaptable network intermediate (*Nat. Synth.*, 2025, 4, 632–641). These promising advances are thoroughly introduced and discussed in the revised manuscript.

Comment 2: The writing style in this manuscript requires significant polishing. For instance, in figure 1, COFs membranes should be COF membrane; PIMs membrane should be PIM membrane; traditional polymer membranes to traditional polymer membrane; and 2D materials- GO membrane to GO membrane (everyone knows GO is 2D material). Similarly, the interlayer nanochannels in GO membranes are also irregular similar to PIM membrane—so basically it does not make sense. Additionally, the term ion channels appear to imply that these channels consist of ions —please revised to ion-selective channels.

Response 2: We sincerely apologize for these oversights and have carefully revised the manuscript to ensure terminological accuracy throughout. The following corrections have been made systematically: all instances of "COFs membranes" have been changed to "COF membrane," "PIMs membrane" to "PIM membrane," and "2D materials-GO membrane" has been simplified to "GO membrane". We have also replaced the term "ion channels" with "ion-selective channels" to prevent any confusion. Regarding the distinction between PIM and GO membranes, we have refined the corresponding descriptions to more accurately reflect their structural features. While both exhibit irregular transport pathways, their underlying structures differ significantly: PIM membranes contain disordered nanoscale pores with ill-defined parameters and dead-end pores, whereas GO membranes form nanochannels through the assembly of nanosheets, enabling more precise control at the atomic level. The manuscript has undergone comprehensive language editing to ensure consistency and precision in terminology across the entire text.

Comment 3: The section 3 describes the preparation of COF membranes, which have been reviewed in several recent review papers. How this study is different? This reviewer expects that the authors would focus on the implications of the membrane preparation methods on their ion-selective behaviour. Otherwise, the title should be revised to make it in-line with the contents of this work.

Response 3: We appreciate the reviewer for this valuable suggestion. In this review, we describe the preparation of COF membranes focusing on the potential strategies for scale-up production, which is different from previous review papers. The ion-selective behaviors of COF membranes are mainly determined by the pore and chemical structure of COFs, which are discussed in the Ion Separation section, such as cation/anion, mono-/multivalent ion, and mono-/monovalent ion separation.

We have reorganized Section 3 and provided a new table (Table 2) that systematically

compares COF membrane fabrication methods using the PEQSS framework (Procedure, Efficiency, Quality, Scalability, Sustainability), clearly outlining the advantages and limitations of each approach. Additionally, we added a new subsection of 3.3 to analyze potential scale-up strategies for COF membrane production. This subsection presents a systematic analysis of technical barriers in large-area fabrication including cost, solvent consumption, and control over membrane crystallinity and orientation, alongside a discussion of potential strategies to overcome these issues.

Comment 4: It is important to explain and derive the relationship between COF properties vs. selectivity. Currently, each section just describes the summary of the studies consulted. There exists no real effort to provide opinions and insights. For instance, are all the COF membranes crystalline? Are COF membrane better than polymeric/MOF/commercial membranes based on data comparison? What are mechanisms?

Response 4: Thank you for your insightful suggestion. We have substantially revised the manuscript throughout. **Firstly**, we have expanded the discussion on COF skeleton structures and pore engineering to clarify the rationale behind selecting specific architectures and their impact on ion separation performance. **Secondly**, the Section 3 has been substantially reorganized. A new table (Table 2) now provides a systematic comparison of COF membrane fabrication methods under the PEQSS framework, clearly delineating the advantages and limitations of each. Additionally, a new subsection of 3.3 specifically addresses critical challenges—including poor crystallinity and orientation, limited membrane area in testing, high production costs, and significant solvent consumption—and explores promising scale-up strategies such as interfacial polymerization and casting methods. **Finally**, we have completely restructured Section 4 to focus on the fundamental design principles and modification strategies. The revised section is centered on the ion separation mechanisms achieved through precise design and modulation of COF membranes, probing the relationship between their pore architecture, wall functionality, and ultimate separation efficacy. In addition, reported studies have indicated that COF membranes possess superior ion separation capabilities compared to other materials, including polymer, PIM, MOF, GO, and MXene membranes. To further substantiate this, we added a new subsection of Section 4.4 to provide a systematic comparison of the Li^+ flux and Li^+/Mg^{2+} selectivity between COF membranes and these materials (see **Fig. 10a**). The results confirm that COF membranes surpass the upper-bound performance of established materials, achieving superior selectivity while maintaining high permeability. Moreover, we further discussed current challenges and outlines future directions, with a focused on bioinspired designs and the promising integration of artificial intelligence (AI) and the Materials Genome Initiative (MGI) for developing next-generation COF ion-selective membranes.

"Though significant advances in the fabrication of COF membranes and their impressive performance in separation, several critical challenges remain before their widespread practical implementation can be realized. Firstly, most current synthesis methods yield COF membranes with poor crystallinity and orientation, which hinders

the full exploitation of their intrinsic pore channels for separation—particularly in terms of oriented structures. Despite a few studies have reported oriented COF membranes, these successes remain difficult to generalize, primarily due to an insufficient understanding of the crystallization and orientation mechanisms underlying membrane formation, particularly for charged COF systems. Secondly, while several fabrication strategies show potential for scaling up, only a limited number of large-area COF membranes have been successfully demonstrated, and performance evaluations are still limited to small membrane area. Finally, achieving cost-effective and environmentally sustainable manufacturing—by minimizing both production costs and the use of organic solvents—remains a major hurdle.....; In 2025, Meng et al.[7] prepared COF-300-V membranes using counter-diffusion, followed undergoing a post-modification by a click reaction to obtain COF-300-$CH_{0.6}$ membrane. The prepared membrane exhibited a Li^+/Mg^{2+} selectivity of 321 and a Li^+ flux of 0.53 mol m^{-2} h^{-1} in electrodialysis surpassing the reported PIM, COF, MOF GO, and MXene membranes, with electric-field-assisted decoupling revealing membrane charge density-cation transport correlations (**Fig. 8d**).....; In addition, Meng et al.[134] improved ion-π interactions with multivalent ions through optimizing the face-to-face orientation of building blocks during the assembly of COF membranes to achieve both mono-/multivalent cations and anions separation (**Fig. 8e**). The prepared COF-170/PAN membrane show high selectivity of 214 for K^+/Al^{3+}, 62 for Cl^-/SO_4^{2-}, and 451 for NO_3^-/PO_4^{3-}, which is superior to most reported polymer, GO, COF, and MOF membranes.....; As illustrated in Fig. 10a, the Li^+ flux and Li^+/Mg^{2+} selectivity of various membrane materials—including conventional polymer membranes, commercial ion-exchange membranes, emerging 2D material membranes, MOF membranes, and COF membranes—are compared under both diffusion and electro-driven processes[7,62,63,72,81,105,139-142]. Among these, COF membranes demonstrate superior performance in both Li^+ flux and Li^+/Mg^{2+} selectivity.....”

Comment 5: What is the ‘concentration’ as the driving force? Do you mean osmotic pressure difference? Did you see any trend in the performance of COF membrane vs. driving force?

Response 5: Thank you for your thoughtful comment. The terms "concentration", "pressure", and "electricity" refer to separation processes driven by concentration gradients, hydraulic pressure, and electric fields, respectively. We apologize for the imprecise terminology and have revised the terms accordingly. The original table has been replaced with a new figure (**Fig. 10a**) that systematically compares the Li^+ flux and Li^+/Mg^{2+} selectivity of COF membranes against other materials—including conventional polymers, commercial ion-exchange membranes, emerging 2D materials, and MOF membranes—under both diffusion and electrodialysis processes. It should be noted that ion transport behavior varies significantly under different driving forces. To date, no direct correlation has been established between the ion separation performance of COF membranes under these distinct operational modes.

Comment 6: Please add a schematic diagram showing a relationship between COF membranes vs. ion-selectivity. This reviewer has read Section 5 but has not been able

to reach any conclusion. Basically, you need to come up with a trend.

Response 6: Thank you for your insightful suggestion. We have added a new subsection (Section 4.4) that specifically compares the Li^+ flux and Li^+/Mg^{2+} selectivity of COF membranes, as shown in Fig. 10a of the revised manuscript. This comparison is accompanied by a discussion of the structural advantages underlying the performance of COF membranes, along with an analysis of remaining challenges, particularly those related to precise control of membrane crystallinity and orientation. Finally, the section highlights recent advances and unique opportunities in the design of bioinspired nanochannels based on COFs, outlining promising directions for future development.

Comment 7: 'the benefit from the regular and atomic-level tunable pore structures, COF membranes have unique advantages in the application of ion separation and is expected to achieve high-efficient, intelligent and precise separation of ions.' The research on COF membranes does not support this conclusion because (i) COF membrane is not fully crystalline, especially using the current membrane development methods; (ii) ion separation by COF membranes with typical pore size from 1-5 nm is not expected to separate ion and their performance (except osmotic driven) is generally not better than other membranes. What do you mean by intelligent separation?

Response 7: We appreciate the reviewer for this thoughtful comment. Firstly, regarding the issue of crystallinity, we have provided a detailed explanation in our response to Comment 1. Secondly, although most COFs exhibit pore sizes in the range of 1–3 nm, which are larger than the diameters of most hydrated ions, the mechanisms enabling ion separation in COF membranes are multifaceted. These include size sieving, electrostatic interactions, hydrogen bonding, ion–dipole interactions, and synergistic effects arising from multiple ion–membrane interactions. We have extensively analyzed and discussed these mechanisms in the revised manuscript. In addition, we have substantially expanded Section 2.2 to provide a more comprehensive discussion of pore engineering strategies. The revised section now comprehensively involves four key approaches—topology control, monomer design, synthetic conditions, and post-synthetic functionalization—each illustrated with representative examples from recent literature to demonstrate how these methods facilitate atomic-level control over pore architecture. Finally, concerning the concept of "intelligence," it primarily refers to the ability of bioinspired ion channels to autonomously adjust their pore structures in response to external stimuli such as pH, light, and temperature, thereby enabling precise regulation of ion transport. In Section 4.4, we elaborate on recent advances and future prospects in the construction of bioinspired COF nanochannels for selective ion separation.

Reviewer #3 (Remarks to the Author):
Li, Xu, and coworkers provide a comprehensive summary of covalent organic framework (COF) membranes for ion separation, highlighting their potential for efficient ion transport due to their regular pore structures and customizable functionality. The paper systematically examines various strategies for fabricating COF membranes, emphasizing both their advantages, such as high ion selectivity and tunability, and the challenges associated with scalability and stability under real-world conditions. While the review offers valuable insights for researchers in the field, it mainly summarizes existing studies and presents limited critical analysis. The authors do provide a forward-looking perspective, emphasizing the need for scalable fabrication methods and bioinspired designs, which will guide future research. However, the paper could benefit from expanding on specific challenges related to ion selectivity and membrane stability, while also reducing redundancy in the discussion of fabrication techniques. Figures and tables effectively support the paper's key points, making complex information more accessible and enhancing understanding. The review serves as a valuable resource for researchers, but could be enhanced by a more in-depth critical evaluation of existing methods and more focused discussions on key issues. Thus, I recommended its publication in Communications Materials after revisions as stated below:

Response: We sincerely appreciate the reviewer's thoughtful evaluation of our manuscript and their constructive suggestions, which have significantly contributed to enhancing the overall quality of this review. We have carefully addressed all the raised points and implemented extensive revisions throughout the manuscript. All modifications have been highlighted in red for ease of reference, and our detailed responses to each comment are provided below.

Comment 1: I recommend that the authors consider separating the figures, particularly Figures 2, 3, 6, 7, 8, and 9, which are currently quite densely packed. This would improve clarity and allow each figure's details to be more easily interpreted, enhancing the overall presentation of the paper.

Response 1: We thank the reviewer for this valuable suggestion. We have reorganized and streamlined the content originally presented in Figures 2–9 into a newly structured Figures 2–10. This reorganization provides a clearer thematic overview of each section and improves visual coherence. Additionally, all figures have been systematically redesigned to enhance logical flow and graphical hierarchy. For instance, Figure 7 now illustrates strategies for cation/anion separation through tailored channel-wall charge and microenvironment design, while Figure 8 highlights mechanisms for mono-/multivalent ion discrimination—such as size sieving, electrostatic interactions, and synergistic ion–membrane effects.

Comment 2: I recommend that the authors provide a more critical discussion of the previous work cited in the paper. While the review offers a thorough summary of existing research, it lacks a detailed evaluation of the strengths and weaknesses of the methodologies and findings presented. A more critical analysis of the limitations, inconsistencies, and gaps in the current literature would significantly strengthen the

paper, offering readers a clearer understanding of the challenges and opportunities for future research in this field. A closely related review article should be cited in the introduction (e.g., Covalent organic frameworks for membrane separation. Adv. Sci. 2025, 12, 2412600).

Response 2: Thank you for your insightful suggestion. We have substantially strengthened the critical analysis throughout the manuscript in the following areas:
(1) **Structural design analysis:** We have expanded the discussion on COF skeleton structures and pore engineering to clarify the rationale behind selecting specific architectures and their impact on ion separation performance. Each strategy is illustrated with representative examples from recent literature, demonstrating pathways to achieve atomic-level control over pore architecture. Inconsistencies: the pore structure of COF crystals and the COF membranes
(2) **Preparation method evaluation:** Section 3 has been reorganized and now includes a new table (Table 2) that systematically compares COF membrane fabrication methods using the PEQSS framework (Procedure, Efficiency, Quality, Scalability, Sustainability), clearly outlining the advantages and limitations of each approach. A new subsection of 3.3 has also been added to analyze potential scale-up strategies for COF membrane production. Limitations: scale-up production
(3) **Performance comparison and outlook:** A new subsection of Section 4.4 provides a direct comparison of Li^+ flux and Li^+/Mg^{2+} selectivity between COF membranes and other materials—including conventional polymers, ion-exchange membranes, 2D materials, and MOFs—as summarized in Fig. 10a. This is accompanied by a discussion of the structural advantages of COFs, remaining challenges such as precise control over crystallinity and orientation, and emerging opportunities in bioinspired nanochannel design. GAPs: in-situ characterization of ion separation mechanisms

In addition, the suggested review (Adv. Sci. 2025, 12, 2412600) has been cited in the introduction. These additions provide readers with a more balanced and forward-looking perspective on COF membranes for ion separation.

Comment 3: I recommend that the authors provide a more detailed analysis of the challenges associated with the scalable production of COF membranes. While the paper briefly mentions these challenges, a deeper exploration of the current obstacles and proposed solutions would significantly enhance the practical relevance of the work. This would offer valuable insights into how these challenges might be addressed, making the paper more impactful for researchers working on the commercialization and large-scale application of COF membranes.

Response 3: We appreciate the reviewer for this valuable suggestion. We have added a new table (Table 2) that systematically compares COF membrane fabrication methods using the PEQSS framework (Procedure, Efficiency, Quality, Scalability, Sustainability), clearly outlining the advantages and limitations of each approach. Additionally, we reorganized Section 3 and provided a new subsection of 3.3 to analyze potential scale-up strategies for COF membrane production. This subsection presents a systematic analysis of technical barriers in large-area fabrication including monomer cost, solvent consumption, and control over membrane crystallinity and orientation,

alongside a discussion of potential strategies to overcome these issues.

We have reorganized the description in the revised manuscript as below. “

3.1 Conventional preparation methods

In the early stages, due to the poor solution processability of COF materials and the harsh synthesis conditions.....

3.2 Emerging preparation methods

A significant acceleration in COF membrane occurred in 2017, marked by the introduction of interfacial polymerization as a representative strategy.....; As shown in **Table 2**, an analysis based on five criteria (i.e., procedure, efficiency, quality, scalability, sustainability) highlights the respective advantages and disadvantages of these major methods.....

3.3 Potential strategies for scale-up preparation

Though significant advances in the fabrication of COF membranes and their impressive performance in separation, several critical challenges remain before their widespread practical implementation can be realized. Firstly, most current synthesis methods yield COF membranes with poor crystallinity and orientation, which hinders the full exploitation of their intrinsic pore channels for separation—particularly in terms of oriented structures. Despite a few studies have reported oriented COF membranes, these successes remain difficult to generalize, primarily due to an insufficient understanding of the crystallization and orientation mechanisms underlying membrane formation, particularly for charged COF systems. Secondly, while several fabrication strategies show potential for scaling up, only a limited number of large-area COF membranes have been successfully demonstrated, and performance evaluations are still limited to small membrane area. Finally, achieving cost-effective and environmentally sustainable manufacturing—by minimizing both production costs and the use of organic solvents—remains a major hurdle.....”

Comment 4: I suggest that the authors provide a clearer definition of the section on ion transport mechanisms. While the paper introduces this topic, it does not fully explain the underlying processes, nor does it offer sufficient details on how the structural characteristics of COF membranes influence ion selectivity. A more focused and detailed discussion of the ion transport mechanisms would enhance this section, providing readers with a deeper understanding of the factors driving ion selectivity and transport within COF membranes. This would significantly strengthen the overall content and clarity of the paper.

Response 4: We appreciate the reviewer for this valuable suggestion. We have completely restructured Section 4 to focus on the fundamental design principles and modification strategies. The revised section is structured around the ion separation mechanisms enabled by precise design and modulation of COF membranes, focusing on pore architecture and wall functionality. Specific mechanisms discussed include size-sieving, electrostatic interactions, hydrogen bonding interactions, ion-dipole

interactions, and synergistic effects arising from multiple ion-membrane interactions. These changes provide readers with a comprehensive framework for understanding the fundamental principles driving ion separation in COF membranes.

We have reorganized the description in the revised manuscript as below. “

Conventional polymer membranes face a long-standing trade-off between ion permeability and selectivity. This limitation arises from their ill-defined ion-conduction pathways and poor dimensional stability, which leads to significant swelling in solvents and consequent degradation of selectivity. In contrast, COF-based membranes have emerged as promising candidates for high-efficiency ion separation, owing to their well-defined pore structures and tailored functionalities[22]. The ordered channels promote fast ion transport and thus the increase of permeance, and the enhanced interactions between the ions and functionalized channel wall contribute to selective ion transport and the rising of selectivity.....

Wang et al.[130] reported an ionic COF membrane with super-high IEC of 4.6 mmol g^{-1} by introducing 4,4’-diaminobiphenyl-3,3’-disulfonic acid, while maintaining a low swelling ratio of ~21% at 25 ℃ and a prominent proton conductivity of 0.66 S cm^{-1}. Peng et al.[82] synthesized NUS-10 COF with a higher theoretical IEC of ~5.4 mmol g^{-1} by utilizing highly charged 2,5-diaminobenzene1,4-disulfonic acid monomer, holding great promise in high-efficient cation/anion separation applications. Beyond conventional charged COF membranes, Lai et al.[131] engineered COF membranes with aligned benzothiadiazole dipoles (**Fig. 7d**), enabling dynamic modulation of ion permselectivity across cation-selective, ambipolar, and anion-selective states by exploiting ion-dipolar interactions. When interacting with multivalent anions, the channels exhibited strong cation conductivity and permselectivity (t_+= 0.9) even under a 1000-fold concentration gradient. Yin et al.[132] modulated ion-membrane interactions through linkage chemistry (**Fig. 7e**), showing that charge-neutral β-ketoenamine-linked COF membranes achieved record cation permselectivity under high-salinity conditions.....; Despite substantial progress in developing architecturally diverse COF membranes with exceptional cation/anion permselectivity by electrostatic, ion-dipolar, and ion-membrane interactions, critical challenges still remain.....

Monovalent and multivalent ions carry the same charge polarity but differ in charge number, leading to marked differences in hydrated ion size and hydration energy. For instance, the hydrated diameters of Li^+ and Mg^{2+} are approximately 7.64 Å and 8.56 Å, respectively[63], while their hydration energies are about -475 kJ mol^{-1} and -1830 kJ mol^{-1}. These differences provide a basis for efficient separation through precise design of pore size and channel-wall chemistry. For example, Yin et al.[61] employed solvent vapor annealing to reorient COF channels from anisotropic to perpendicular alignment. The resultant TbHZ membrane with 9.8 Å perpendicular-aligned subnanochannels achieved 2 Å-level ion differentiation and a SO_4^{2-}/PTS^{4-} selectivity of 16.8 (**Fig. 8a**). In 2021, our group prepared an ultrathin (~20 nm) $TpBDMe_2$ COF membrane with sub-2 nm channels and abundant hydrogen-bonding sites *via* a counter-diffusion approach[63]. The membrane exhibited high monovalent cation permeation rates (K+: ~0.2 mol m^{-2}

h^{-1}) and outstanding mono-/multivalent cation selectivity through channel-cation hydrogen bonding interactions (K^+/Mg^{2+}: 765, Na^+/Mg^{2+}: 680, Li^+/Mg^{2+}: 217), breaking the permeability-selectivity trade-off for conventional ion-separation membranes (**Fig. 8b**)[63]. Furthermore, the difference in charge number between mono- and multivalent ions also enables their separation by introducing electrostatic interactions in charged nanochannels. In 2024, Liu et al.[8] introduced positively charged aldehyde monomer and synthesized an asymmetric-structured HBAB-TAPA-COF membrane on HPAN *via* counter-diffusion. The membrane consisted of vertically aligned nanorods that enhanced water/ion contact and an ultrathin dense layer that enabled both high permeability (Cs^+: 0.33 mol m^{-2} h^{-1}) and selectivity (Cs^+/La^{3+}: 75.9) (**Fig. 8c**) .....; In addition, Meng et al.[134] improved ion-π interactions with multivalent ions through optimizing the face-to-face orientation of building blocks during the assembly of COF membranes to achieve both mono-/multivalent cations and anions separation (**Fig. 8e**) .....”

Comment 5: I recommend that the authors provide a more comprehensive discussion on the long-term stability and reusability of COF membranes in real-world applications, as these factors are crucial for practical deployment. A deeper exploration of aspects such as degradation mechanisms, as well as how membrane performance maintains stability over time under operational conditions, would significantly enhance the paper's practical relevance. Addressing these issues would provide valuable insights into the durability of COF membranes and their potential for sustainable, long-term use in ion separation processes.

Response 5: We sincerely thank the reviewer for this insightful comment. We have incorporated a comprehensive discussion on the long-term stability of COF membranes, encompassing degradation mechanisms and structural design strategies based on the most employed skeleton structures, reusability and anti-fouling performance, and critical perspective on current limitations and future directions. These revisions significantly enhance the practical relevance of the review and provide readers with a comprehensive assessment of the durability and real-world potential of COF membranes for ion separation.

“Long-term stability under chemical, thermal, and mechanical stresses is essential for the practical deployment of COF membranes. Although imine-linked COFs generally exhibit good hydrolytic stability, their inherent dynamic covalent chemistry often leads to degradation under strongly acidic conditions due to the reversible nature of the imine (C=N) bond[22]. Recent efforts have focused on designing COF structures resistant to harsh environments, particularly concentrated acids. For instance, Halder et al.[118] introduced interlayer C-H···N hydrogen bonding and a hydrophobic microenvironment around the C=N bonds, providing steric protection that ensures exceptional stability even in strongly acidic (e.g., 18 M H_2SO_4, 12 M HCl) and alkaline (9 M NaOH), enabling effective sulfuric acid recovery. Ren et al.[143] utilized an intramolecular Povarov reaction to postsynthetically convert imine bonds into more stable chromenoquinoline linkages, yielding COFs with outstanding chemical resistance toward strong acids, bases, and oxidizing agents. Yang et al.[144] developed a cationic

COF membrane with gradient charge distribution, which retained its structural integrity after soaking in 1 M HCl for 15 days and maintained consistent dialysis performance over ten consecutive tests. Meng et al.[66] reported a triazine-based COF membrane capable of stable Li^+/Mg^{2+} separation for nearly 100 hours. More recently, Yu et al.[145] (2024) fabricated COF-based thin-film composite membranes within 10 minutes by coating COF oligomers onto poly(ether ether ketone) ultrafiltration supports. The resulting membranes exhibited stable operation for 150 h in cross-flow devices, along with excellent anti-fouling properties, showing negligible dye adsorption after 7 days of exposure to Direct Red 23. Despite these advances, most stability tests remain limited to laboratory-scale conditions and relatively short durations. Furthermore, studies on the mechanical properties of COF membranes are scarce. Although freestanding COF membranes have been prepared *via* methods such as interfacial polymerization, their mechanical strength remains insufficient and falls far short of industrial requirements. Therefore, further improvements in operational stability—particularly mechanical robustness under demanding conditions—are critically needed to enable real-world implementation."

Comment 6: While the paper briefly mentions bioinspired design, I suggest that the authors provide a more detailed exploration of how ion transport mechanisms from biological systems could be more directly integrated into COF membrane design. A deeper discussion on this topic would offer valuable insights into how biological principles could inform and enhance the design of COF membranes, potentially improving ion selectivity and transport efficiency. This could significantly strengthen the novelty and applicability of the paper's findings.

Response 6: Thank you for your constructive suggestion. A new subsection of 4.4 has been added to directly compare the ion separation performance of COF membranes with other materials. The section also highlights recent advances and future opportunities in bioinspired nanochannel design based on COFs. We have incorporated the latest developments in bioinspired ion separation using COF membranes, including a detailed analysis of specific biological ion channels (e.g., K^+ and Na^+ channels) and their underlying separation mechanisms. Finally, the review discusses the promising integration of artificial intelligence (AI) and the Materials Genome Initiative (MGI) in designing next-generation COF ion-selective membranes.

"In addition, significant progress has also been made in the precise construction of bioinspired COF membranes and the realization of smart, selective ion transport. For instance, Ren et al.[85] developed azobenzene-functionalized COF-Azo membranes *via* a biomimetic nanochannel modulation (BNM) strategy, forming charged and photo-switchable sub-nanochannels (**Fig. 10b**). Under specific light irradiation, these membranes exhibited high selectivity for both mono/monovalent (K^+/Li^+: 17.9) and mono/divalent (Li^+/Mg^{2+}: 24.9) ion pairs, achieved through reversible angstrom-level pore size modulation *via* photoisomerization. In 2025, Wang et al.[141] reported an artificial nanochannel system based on a phase-reversed mixed-matrix COF (PRCOF) membrane incorporating localized ion-trapping sites (**Fig. 10c**). These sites provide moderate binding affinity and supplementary repulsive interactions, enabling precise

recognition and facilitated transport of Li^+ ions. By fine-tuning the micro-environment of these traps, a high Li^+/Mg^{2+} selectivity of 190 and a Li^+ permeation rate of 0.262 mol h^{-1} m^{-2} were attained in a binary mixture. In another study, Meng et al.[66] designed a triazine-based COF membrane with a suitably hydrophilic channel environment that promotes Li^+ dissociation from negatively charged functional groups, facilitating Li^+ migration *via* a hopping mechanism along sulfonic acid chains and thus shortening the diffusion path. In contrast, partially dehydrated Mg^{2+}, with its stronger effective charge, becomes trapped in energy wells. This mechanism mimics the selectivity of biological K^+ channels, allowing rapid Li^+ permeation while nearly completely blocking Mg^{2+} (**Fig. 10d**) .....

Biological ion-selective channels exhibit exceptional efficiency, intelligence, and precision in ion transport. For example, K^+ channels achieve specificity through funnel-shaped architectures and coordination with carbonyl oxygens, whereas Na^+ channels utilize four carboxyl groups to confer Na^+ selectivity[3,146]. Inspired by these natural paradigms, the construction of artificial nanochannels has emerged as a vibrant research frontier. COFs offer unique advantages in this regard, owing to their structural controllability and chemical tailorability, making them ideal platforms for developing bioinspired membranes for precision ion separation. Consequently, developing COF-based biomimetic membranes for precision ion separation represents a promising research direction with transformative implications. Moreover, through the precise construction of bioinspired COF membranes, it is possible to investigate the mechanisms underlying highly selective ion transport, establish clear structure-property relationships between the microscopic structural parameters of COF nanochannels and their ion separation performance, and build comprehensive databases correlating structure with ion transport behavior. Notably, with the rapid advancement of artificial intelligence (AI) and the Materials Genome Initiative (MGI) has accelerated the exploration of advanced materials. By developing computational tools that predict structure-property relationships and employing materials genomics strategies, we can analyze the COF structural database and perform computational screening to enable the high-efficiency design of high-performance COF structures."